Supporting Information

Cross-Dehydrogenative Couplings between Indoles and *β*-Keto Esters: Ligand-Assisted Ligand Tautomerization and Dehydrogenation via a Proton-Assisted Electron Transfer to Pd(II)

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1 General Information

All reactions were carried out under air in oven-dried glassware, unless otherwise noted. When needed, nonaqueous reagents were transferred under argon *via* syringe or cannula and dried prior to use. Toluene, THF, Et_2O and CH_2Cl_2 were obtained by passing deoxygenated solvents through activated alumina columns (MBraun SPS-800 Series solvent purification system). Other solvents and reagents were used as obtained from supplier, unless otherwise noted. Analytical TLC was performed using Merck silica gel F254 (230-400 mesh) plates and analyzed by UV light or by staining upon heating with anisaldehyde solution (2.8 mL anisaldehyde, 2 mL conc. H_2SO_4, 1.2 mL conc. CH_3COOH, 100 mL EtOH), vanillin solution (6 g vanillin, 5 mL conc. H_2SO_4, 3 mL glacial acetic acid, 250 mL EtOH) or $KMnO_4$ solution (1 g $KMnO_4$, 6.7 g K_2CO_3, 1.7 mL 1M NaOH, 100 mL H_2O). For silica gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230-400 mesh) and p.a. grade solvents unless otherwise noted.

The ^{1}H NMR and ^{13}C NMR spectra were recorded in either acetone-d6, $CDCl_3$, CD_3CN or C_6D_6 on Bruker Avance 500, 400, 300 or 250 spectrometers. The chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.26), CHD_2CN (δ 1.94), 1,4-Dioxane-D_8 (δ 3.53) or C_6D_5H (7.16) for ^{1}H NMR. For the ^{13}C NMR spectra, the residual acetone-d6 (δ 29.84), $CDCl_3$ (δ 77.16), CD_3CN (δ 118.26) or C_6D_6 (128.06) were used as the internal standards. Melting points (mp) were determined in open capillaries using melting point apparatus. IR spectra were recorded on a FT-IR spectrometer. Optical rotations were obtained with a polarimeter. High resolution mass spectrometric data were measured using MicroMass LCT Premier Spectrometer. Slow addition of the reagents was controlled by a syringe pump. Microwave irradiation was done at microwave reactor.

2 Experimental Details

2.1 Coupling Products

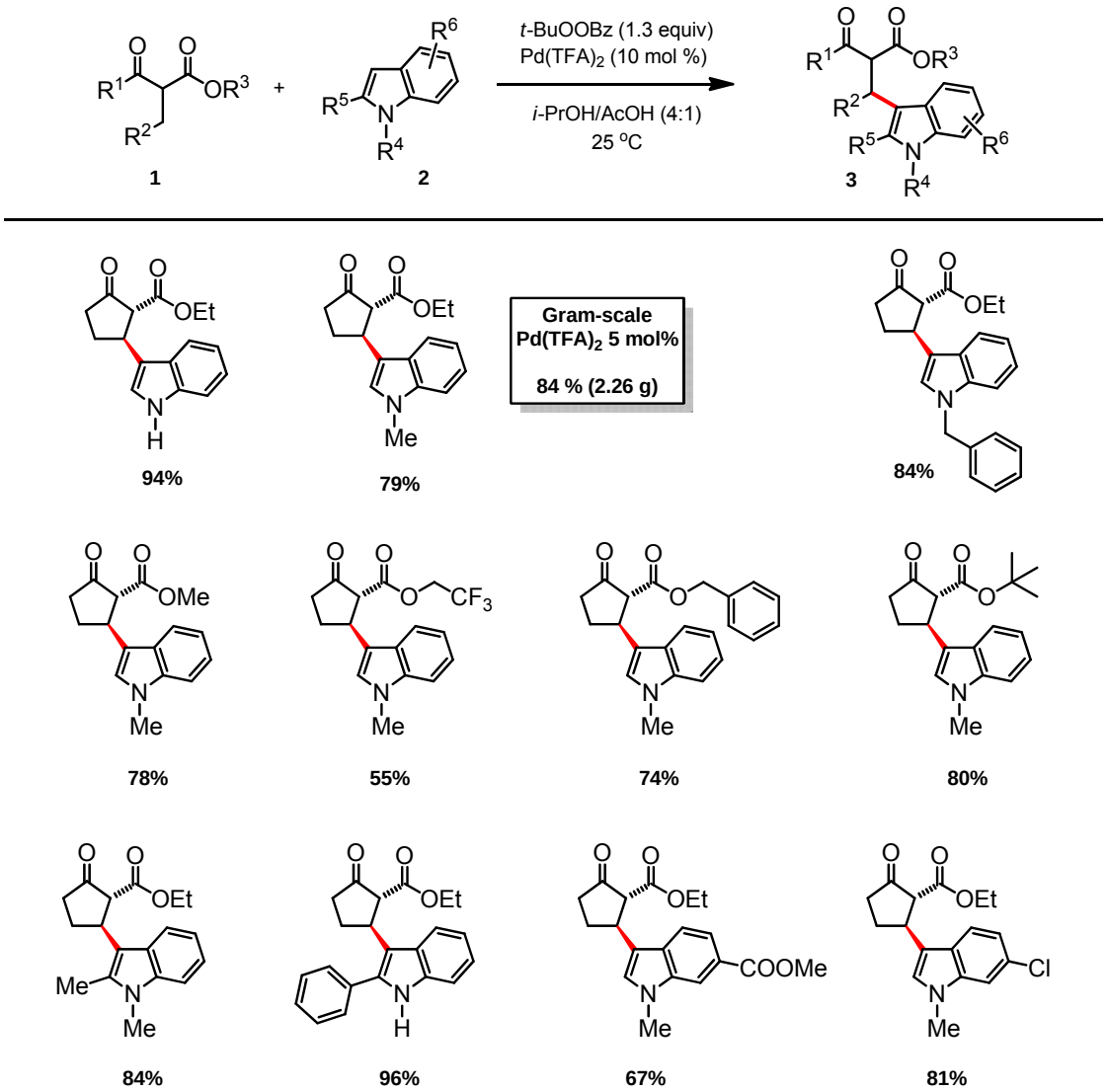
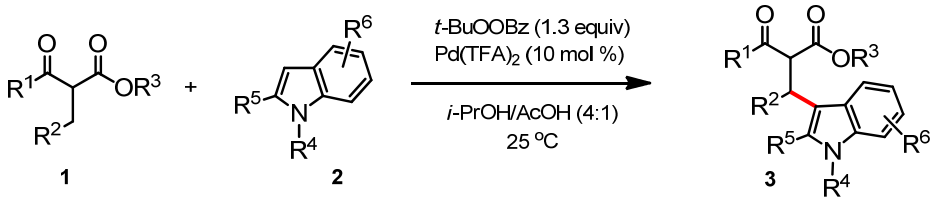


Chart S1. Full scope of the coupling reaction: indole component.



1 2 3

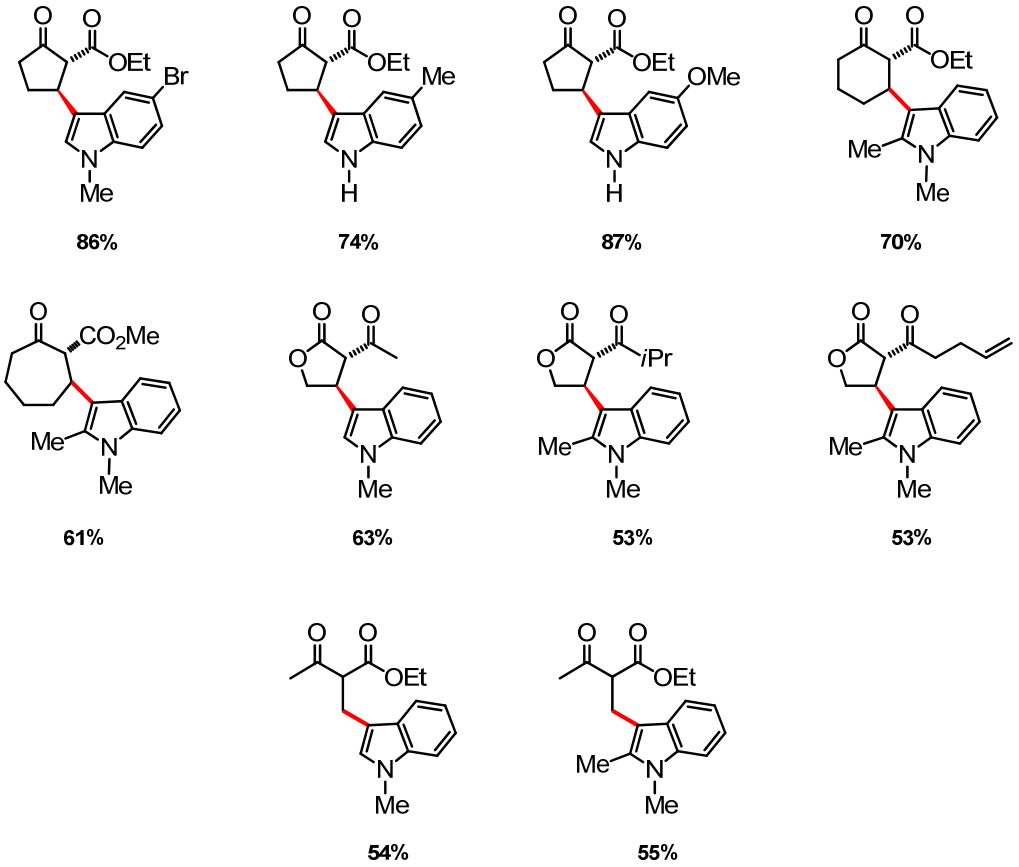
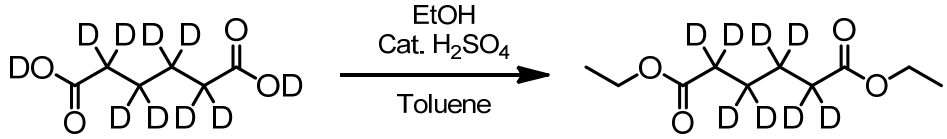


Chart S2. Full scope of the coupling: β-keto ester component.

2.2 Synthesis of Deuterated Starting Materials

2.2.1 Diethyl Adipate-D_8

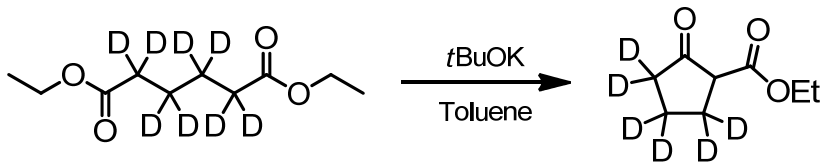


D_{10}-adipic acid **7**

The reaction flask was equipped with Dean-Stark trap. To a solution of D_{10}-adipic acid (1.00 g, 6.40 mmol, 100 mol-%) and EtOH (2.00 ml, 33.34 mmol, 521 mol-%) in 20 mL toluene at rt was added 3 drops of H_2SO_4 (cat.). The reaction mixture was refluxed under argon. After 30 min and 3h, respectively, 1 mL of atzeotrope was taken out from the Dean-Stark trap and EtOH (2.00 mL, 33.34 mmol, 521 mol-%) was added to the reaction mixture. The reaction mixture was refluxed 18h and allowed to cool to rt. After the completion of the reaction, 50 mL EtOAc was added to the reaction mixture and was washed with saturated Na_2CO_3 solution (3x20 mL) and with saturated brine solution (50 mL). The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude product was used directly in next step without any purification. Yield: 1.45 g (quant.) as a clear, colorless oil.

R_f (20% EtOAc/hexanes) = 0.53, IR (film, cm^{-1}): 2982, 1727, 1366, 1254, 1145, 1083, 1029; ^1H NMR (400 MHz, $CDCl_3$): δ 4.08 (q, 4H, J = 7.2 Hz), 1.21 (t, 6H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 60.3, 33.2 (qn, J = 19.5 Hz), 23.4 (qn, J = 19.5 Hz), 14.3; HRMS (ESI^+): m/z [M+Na] calcd for [$C_{10}D_8H_{10}O_4Na$] 233.1605, found 233.1607.

2.2.2 Ethyl 2-oxocyclopentanecarboxylate-D_6

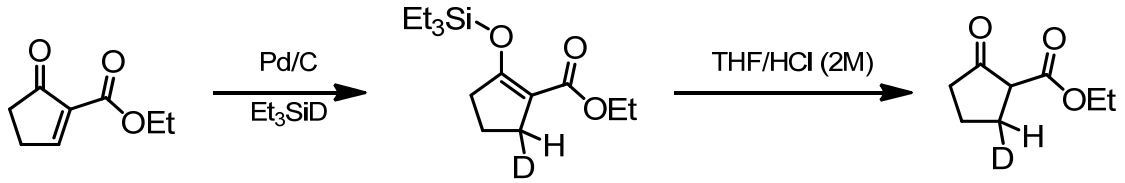


7 **D_6-1a**

Diethyl adipate-D_8 was dried by azeotropic distillation with toluene prior to use. To a solution of diethyl adipate-D_8 (1.35 g, 6.90 mmol, 100 mol-%) in 20 mL toluene at rt was added potassium *tert*-butoxide (1.55 g, 13.79 mmol, 200 mol-%). The reaction mixture was refluxed for 3 h. After the completion of the reaction, 50 mL ice was added, the pH of the aqueous layer was adjusted to 0 with 20% HCl and the mixture was extracted with EtOAc (3x20 mL). The combined organic layers were washed with saturated $NaHCO_3$ (25 mL) and brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography to afford pure deuterated product **D_6-1a**. Yield 740 mg (66%) as a clear, colorless oil.

R_f (20% EtOAc/hexanes) = 0.41; IR (film, cm^{-1}): 2984, 1751, 1719, 1369, 1323, 1253, 1195, 1148, 1118, 1028, ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (q, 2H, J = 7.1 Hz), 3.11 (br s, 1H), 1.26 (t, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.7, 169.5, 61.4, 54.7, 37.5 (m), 26.6 (m), 20.0 (m), 14.3; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol > 25:1, ^{1}H NMR: δ 10.39 (br s, 0.04H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for $[C_8D_6H_6O_3Na]$ 185.1061, found 185.1066.

2.2.3 Ethyl 2-oxocyclopentanecarboxylate-D_1



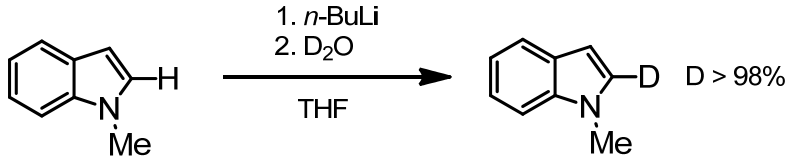
4a **D_1-1a**

D_1-1a was prepared using a Pd-catalyzed hydrosilylation method previously developed by us.[1] A slightly modified method which employed commercial Pd/C was used.[2]

R_f (20% EtOAc/hexanes) = 0.41;^{1}H NMR (400 MHz, $CDCl_3$): δ 4.18 (qd, J = 7.1, 0.6 Hz, 2H), 3.18 – 3.08 (m, 1H), 2.35 – 2.20 (m, 3H), 2.19 – 2.05 (m, 1H), 1.94 – 1.77 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.5, 169.5, 61.5, 54.8, 38.2, 21.0, 20.0, 14.3, 6.3 (d, J = 77,2 Hz); in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol > 25:1, ^{1}H NMR: δ 10.40 (br s, 0.03H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for $[C_8H_{11}DO_3Na]$ 180.07414, found 180.0735.

[1] Benehould, M.; Tuokko, S.; Pihko, P. M. *Chem. Eur. J.* **2011**, *17*, 8404.
[2] Tuokko, S.; Pihko, P. M.; Honkala, K. *Manuscript in preparation*.

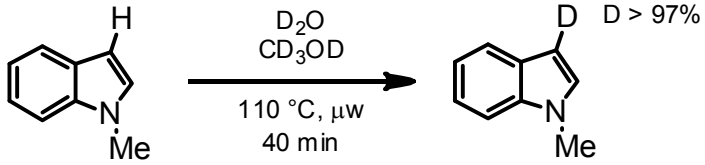
2.2.4 2-D-1-Methylindole



2a **D-2a**

D-2a was prepared using a previously published method. [3,4]

2.2.5 3-D-1-Methylindole



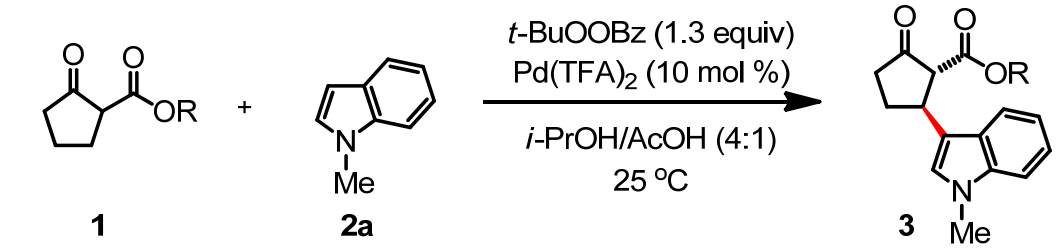
2a **3-D-2a**

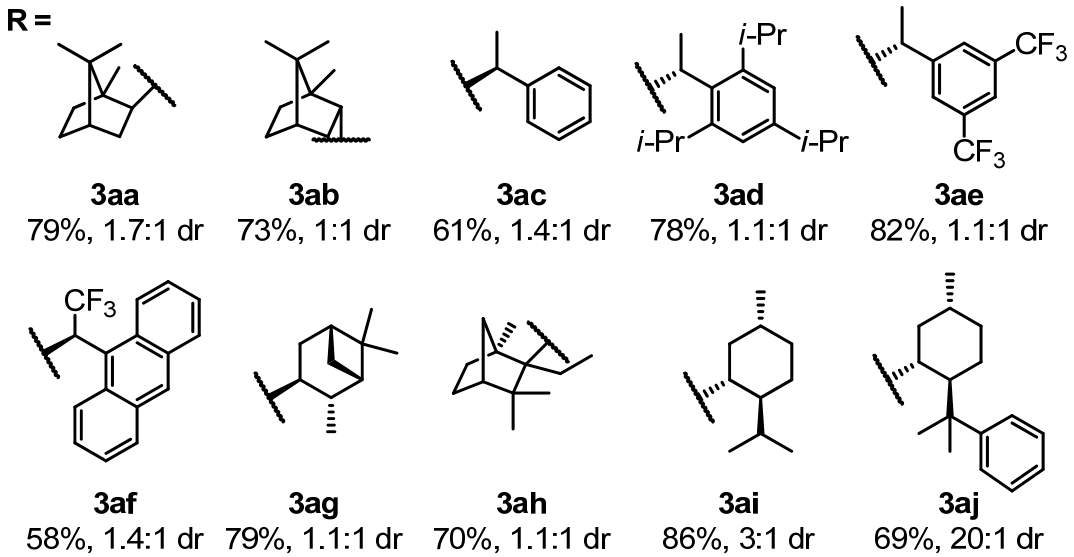
A solution of 1-methylindole (**2a**) (1.00 g, 0.95 mL, 7.62 mmol) in mixture of CD_3OD (5 mL) and D_2O (5 mL) was heated to 110 ˚C with microwave irradiation (300W) for 40 min. The reaction mixture was extracted with toluene (3x10 mL) and dried over Na_2SO_4. The combined organic layers were concentrated in vacuo. The product **3-D-2a** (3-D > 97%) was used without a further purification. Yield: 0.94 g (93%) as a clear oil. The characterization data corresponded a previously published data.4[5]

[3] Sundberg, R. J.; Russell, H. F., *J. Org. Chem.* **1973**, *38*, 3324.
[4] Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050.
[5] Daunis, J.; Soufiaoui, M.; Laude, B., *Org. Mass Spec.* **1979**, *14*, 121.

2.3 Screening of Chiral β-Keto Esters

Scheme S1. Exploration of the Diastereoselective Dehydrogenative Coupling with Different Chiral β-Keto Esters[a]



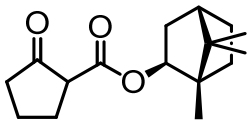


[a] Isolated yields of pure products are reported. Conditions: **1** (1.5 equiv), **2a** (0.4 mmol, 1.0 equiv), *t*-BuOOBz (1.3 equiv), $Pd(TFA)_2$ (0.1 equiv), *i*-PrOH/AcOH (4:1, 0.5 mL) at rt. **Note**: the absolute stereochemistry of the newly generated stereocenters in the product is not known except for **3aj** (see section 2.6.12 below) and it is shown arbitrarily here as (*1R,2S*). The stereochemistry of the cyclopentanone unit of product **3aj** is (*1S,2R*) (see section 2.6.12).

2.4 General Synthesis of Chiral β-Keto Esters

A solution of ethyl 2-oxocyclopentanecarboxylate (100 mol%), chiral alcohol (150 mol%) and a catalytic amount of PPh_3 (10 mol%) in toluene (typically 0.2 M) was refluxed under argon. After the completion of the reaction, the reaction mixture was concentrated in vacuo and the crude product was purified by flash column chromatography to afford pure chiral *β*-keto esters.

2.4.1 (*1S,2S,4S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 2-oxocyclopentanecarboxylate **1aa**

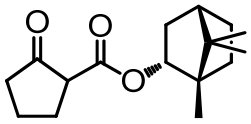


1aa

Compound **1aa**: Prepared according to the general procedure using β-keto ester **1a** (3.80 mL, 25.61 mmol 100 mol-%), isoborneol (5.98 g, 38.79 mmol, 150 mo-%), PPh_3 (0.68 g, 2.58 mmol, 10 mol%) and toluene (120 ml). Reaction time 22 h. Yield: 5.41 g (80%) as pink oil.

R_f (10% Et_2O/toluene) = 0.44; IR (film, cm^{-1}): 2953, 2874, 1754, 1720, 1454, 1247, 1182, 1107, 1051; ^1H NMR (250 MHz, $CDCl_3$): δ 4.67 (obs. t, 0.5 x 1H, J = 3.6 Hz), 4.64 (obs. t, 0,5 x 1H, J = 4.5 Hz), 3.08 (obs. t, 0.5 x 1H, J = 8.8 Hz), 3.07 (obs. t, 0.5 x 1H, J = 8.7 Hz), 2.38-2.20 (m, 4H), 2.19-2.01 (m, 1H), 1.95-1.65 (m, 5H), 1.65-1.42 (m, 1H), 1.18-0.99 (m, 2H), 0.97 (s, 0.5 x 3H), 0.93 (s, 0.5 x 3H), 0.85 (s, 0.25 x 6H), 0.81 (s, 0.75 x 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): 212.3, 212.2, 169.1, 168.9, 82.1, 82.0, 55.2, 54.8, 48.9, 48.8, 47.0, 45.1, 38.9, 38.8 38.2, 38.1, 33.80, 33.77, 27.6, 27.5, 27.1, 21.13, 21.07, 20.2, 19.91, 19.88, 11.5, 11.4; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 12:1, ^1H NMR: δ 10.36 (s, 0.08 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{16}H_{24}O_3Na$] 287.1623, found 287.1630.

2.4.2 (*1S,2R,4S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 2-oxocyclopentanecarboxylate **1ab**



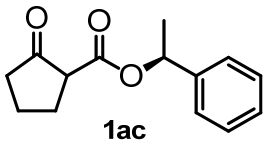
1ab

Compound **1ab**: Prepared according to the general procedure using β-keto ester **1a** (3.80 mL, 25.61 mmol 100 mol-%), (-)-borneol (5.96 g, 38.64 mmol, 150 mo-%), PPh_3 (0.68 g, 2.58 mmol, 10 mol%) and toluene (120 ml). Reaction time 21 h. Yield: 6.45 g (95%) as pink oil.

R_f (10% EtOAc/hexanes) = 0.33; IR (film, cm^{-1}): 2953, 2872, 1754, 1721, 1453, 1253, 1188, 1109, 1019; ^1H NMR (250 MHz, $CDCl_3$): δ 4.96-4.84 (m, 1H), 3.13 (t, 1H, J = 8.8

Hz), 2.39-2.19 (m, 5H), 2.18-2.02 (m, 1H), 2.00-1.61 (m, 4H), 1.35-1.10 (m, 2H), 0.97 (ddd, 1H, J = 13.8, 7.8, 3.5 Hz), 0.86 (s, 3H), 0.83 (s, 3H), 0.82 (s, 0.5 x 3H), 0.79 (s, 0.5 x 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 212.3, 212.2, 169.8, 169.7, 80.9, 80.8, 55.1, 54.9, 49.0, 48.9, 47.9, 44.9, 38.09, 38.06, 36.8, 36.6, 28.04, 28.01, 27.52, 27.47, 27.2, 27.1, 21.1, 19.7, 18.9, 13.5, 13.4; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 19:1, ^{1}H NMR: δ 10.38 (s, 0.05 x 1H, enol O-H); HRMS (ESI$^+$): m/z [M+Na] calcd for [$C_{16}H_{24}O_3Na$] 287.1623, found 287.1630.

2.4.3 (*S*)-1-Phenylethyl 2-oxocyclopentanecarboxylate **1ac**

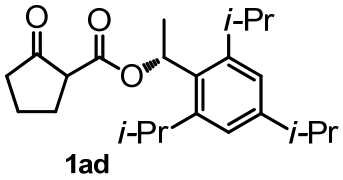


1ac

Compound **1ac**: Prepared according to the general procedure using β-keto ester **1a** (950 µL, 6.4 mmol 100 mol-%), (*S*)-(-)-1-phenylethanol (850 µL, 7.04 mmol, 150 mo-%), PPh_3 (168 mg, 0.64 mmol, 10 mol%) and toluene (30 mL). Reaction time 7 h. Yield: 905 mg (61%) as a yellowish oil.

R_f (10% Et_2O/toluene) = 0.47; IR (film, cm^{-1}): 3033, 2980, 2933, 2883, 1754, 1720, 1452, 1252, 1188, 1107, 1061, 761, 698; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.33 (m, 4H), 7.32-7.23 (m, 1H), 5.92 (obs. q, 0.5 x 1H, J = 6.6 Hz), 5.90 (obs. q, 0.5 x 1H, J = 6.6 Hz), 3.18 (obs. t, 0.5 x 1H, J = 8.8 Hz), 3.17 (obs. t, 0.5 x 1H, J = 8.9 Hz), 2.33-2.21 (m, 4H), 2.17-2.03 (m, 1H), 1.92-1.75 (m, 1H), 1.58 (d, 0.5 x 3H, J = 6.6 Hz), 1.55 (d, 0.5 x 3H, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.2, 212.0, 168.8, 168.5, 141.4, 141.3, 128.53, 128.48, 128.0, 127.8, 126.1, 125.9, 73.40, 73.36, 54.84, 54.77, 38.08, 38.06, 27.4, 27.3, 22.3, 22.2, 20.9; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 24:1, ^{1}H NMR: δ 10.38 (s, 0.04 x 1H, enol O-H) HRMS (ESI$^+$): m/z [M+Na] calcd for [$C_{14}H_{16}O_3Na$] 255.0997, found 255.1006.

2.4.4 (*R*)-1-(2,4,6-triisopropylphenyl)ethyl 2-oxocyclopentanecarboxylate **1ad**

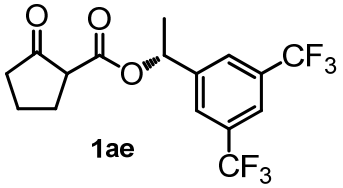


1ad

Compound **1ad**: Prepared according to the general procedure using β-keto ester **1a** (300 µL, 2.0 mmol 100 mol-%), (*R*)-(+)-1-(2,4,6-triisopropylphenyl)ethanol (500 mg, 2.0 mmol, 100 mo-%), PPh_3 (53 mg, 0.2 mmol, 10 mol%) and toluene (10 mL). Reaction time 6.5 h. Yield: 611 mg (85%) as a white crystalline solid.

R_f (10% Et_2O/toluene) = 0.50; mp. 108-110 °C; IR (film, cm^{-1}): 2956, 2868, 1752, 1716, 1460, 1187, 1109, 1051, 908, 731; ^1H NMR (250 MHz, $CDCl_3$): δ 7.03 (s, 2H), 6.55 (q, 1H, *J* = 6.9 Hz), 3.51 (br. s, 2H), 3.13 (t, 1H, *J* = 9.1 Hz), 2.87 (septet, 1H, *J* = 6.9 Hz), 2.41-2.05 (m, 4H), 1.94-1,74 (m, 1H), 1.68 (d, 3H, *J* = 6.9 Hz), 1.33-1.20 (m, 18H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 212.2, 168.9, 148.2, 131.9, 69.7, 55.1, 38.2, 34.2, 29.4, 27.2, 24.0, 22.3, 20.9; in addition the following characteristic peaks are for the minor diastereomer: ^1H NMR: δ 6.56 (q, 0.62 x 1H, *J* = 6.9 Hz), 3.12 (t, 0.62 x 1H, *J* = 9.3 Hz), 1.63 (d, 0.62 x 3H, *J* = 6.9 Hz); ^{13}C NMR: δ 212.1, 169.1, 131.7, 69.6, 55.3, 38.1, 29.4, 24.9, 24.3, 22.2, 21.1; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 13:1, ^1H NMR: δ 10.57 (s, 0.08 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{23}H_{34}O_3Na$] 381.2406, found 381.2403.

2.4.5 (*R*)-1-(3,5-Bis(trifluoromethyl)phenyl)ethyl 2-oxocyclopentanecarboxylate **1ae**

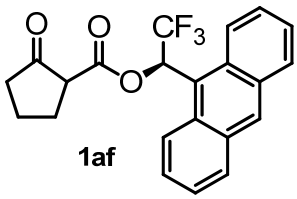


1ae

Compound **1ae**: Prepared according to the general procedure using β-keto ester **1a** (630 µL, 4.24 mmol 100 mol-%), (*R*)-1-(3,5-bis(trifluoromethyl)phenyl)ehanol (1.10 g, 4.26 mmol, 100 mo-%), PPh_3 (0.11 g, 0.43 mmol, 10 mol%) and toluene (20 mL). Reaction time 23 h. Yield: 1.12 g (71%) as a yellowish oil.

R_f (10% Et_2O/toluene) = 0.76; IR (film, cm^{-1}): 2986, 2888, 1758, 1729, 1384, 1276, 1169, 1125, 1073, 1017, 898, 841, 706, 682; ^1H NMR (250 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.80 (s, 2H), 5.98 (obs. q, 0.5 x 1H, J = 6.6 Hz), 5.97 (obs. q, 0.5 x 1H, J = 6.6 Hz), 3.25 (obs. t, 0.5 x 1H, J = 9.3 Hz), 3.22 (obs. t, 0.5 x 1H, J = 9.2 Hz), 2.45-2.22 (m, 4H), 2.22-2.02 (m, 1H), 1.98-1.79 (m, 1H), 1.61 (obs. d, 0.5 x 3H, J = 6.7 Hz), 1.59 (obs. d, 0.5 x 3H, J = 6.7 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 211.8, 211.6, 168.7, 168.4, 144.4, 144.2, 131.95 (q, $^2J_{C\text{-}F}$ = 33 Hz, -$\underline{C}CF_3$), 131.86 (q, $^2J_{C\text{-}F}$ = 33 Hz, -$\underline{C}CF_3$), 129.0, 128.2, 126.2, 125.3, 123.35 (q, $^1J_{C\text{-}F}$ = 273 Hz, -C$\underline{C}F_3$), 123.29 (q, $^1J_{C\text{-}F}$ = 273 Hz, -C$\underline{C}F_3$), 121.8, 71.9, 54.74, 54.72, 37.9, 27.4, 26.9, 22.3, 22.2, 20.9, 20.8; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 25:1, ^1H NMR: δ 10.26 (s, 0.04 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{16}H_{14}O_3F_6Na$] 391.0745, found 391.0737.

2.4.6 (*R*)-1-(Anthracen-9-yl)-2,2,2-trifluoroethyl 2-oxocyclopentanecarboxylate **1af**

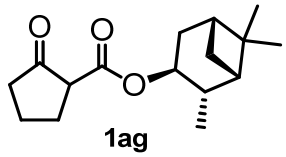


1af

Compound **1af**: Prepared according to the general procedure using β-keto ester **1a** (2.29 mL, 8.67 mmol 300 mol-%) in two batch, (*R*)-1-(anthracen-9-yl)-2,2,2-trifluoroethanol (0.80 g, 2.90 mmol, 100 mo-%), PPh_3 (76 mg, 0.29 mmol, 10 mol%) and toluene (15 mL). Reaction time 48 h. Yield: 630 mg (56%) as a yellowish oil.

R_f (10% Et_2O/toluene) = 0.64; IR (film, cm^{-1}): 3056, 2974, 2885, 1766, 1737, 1352, 1274, 1179, 1129, 1104, 1075, 732; ^1H NMR (300 MHz, $CDCl_3$): δ 8.76 (d, 1H, J = 8.5 Hz), 8.54 (s, 1H), 8.38 (d, 1H, J = 8.9 Hz), 8.01 (d, 2H, J = 8.1 Hz), 7.88 (q, 1H, J = 8.0 Hz), 7.68-7.55 (m, 2H), 7.54-7.45 (m, 2H), 3.32 (t, 1H, J = 8.9 Hz), 2.36-1.99 (m, 5H), 1.95-1.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.51, 210.48, 167.7, 131.8, 131.6, 131.5, 131.4, 131.1, 130.9, 130.6, 129.6, 129.4, 129.3, 127.9, 127.2, 126.6, 126.4, 125.1, 124.34 (q, $^1J_{C\text{-}F}$ = 283 Hz, -C$\underline{C}F_3$), 124.30 (q, $^1J_{C\text{-}F}$ = 283 Hz, -C$\underline{C}F_3$), 122.5, 120.8, 120.7, 69.70 (q, $^2J_{C\text{-}F}$ = 35 Hz, -$\underline{C}CF_3$), 69.65 (q, $^2J_{C\text{-}F}$ = 35 Hz, -$\underline{C}CF_3$), 54.3, 54.1, 38.05, 37.98, 27.5, 27.3, 20.93, 20.88; HRMS (ESI^+): m/z [M+Na] calcd for [$C_{22}H_{17}O_3F_3Na$] 409.1027, found 409.1026.

2.4.7 (*1S,2S,3S,5R*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl 2-oxocyclopentanecarboxylate **1ag**

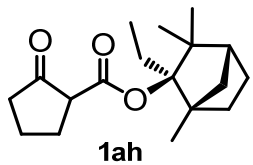


1ag

Compound **1ag**: Prepared according to the general procedure using β-keto ester **1a** (1.20 mL, 8.04 mmol 124 mol-%) in two batch, (+)-isopinocampheol (1.00 g, 6.48 mmol, 100 mo-%), PPh_3 (0.17 g, 0.65 mmol, 10 mol%) and toluene (20 mL). Reaction time 7 h. Yield: 1.62 g (95%) as a pinkish oil.

R_f (20 % EtOAc/hexanes) = 0.50; IR (film, cm^{-1}): 2909, 1754, 1719, 1251, 1189, 1152, 1107, 993; ^1H NMR (250 MHz, $CDCl_3$): δ 5.01-4.90 (m, 1H), 3.03 (t, 1H, J = 8.9 Hz), 2.53-2.34 (m, 1H), 2.32-2.12 (m, 5H), 2.12-1.94 (m, 2H), 1.88-1.68 (m, 3H), 1.58 (obs. tt, 1H, J = 7.1, 3.4 Hz), 1.11 (s, 3H), 1.01 (obs. d, 0.5 x 3H, J = 7.4 Hz), 0.99 (obs. d, 0.5 x 3H, J = 7.4 Hz), 0.84 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 212.0, 211.9, 169.2, 74.89, 74.86, 54.7, 54.6, 47.35, 47.31, 43.7, 43.4, 41.0, 38.1, 38.0, 37.84, 37.82, 35.6, 35.5, 33.23, 33.17 27.30, 27.28, 27.26, 27.24, 23.6, 20.8, 20.33, 20.30; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 26:1, ^1H NMR: δ 10.37 (s, 0.04 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{16}H_{24}O_3Na$] 287.1623, found 287.1617.

2.4.8 (*1S,2R,4R*)-2-Ethyl-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2-oxocyclopentanecarboxylate **1ah**



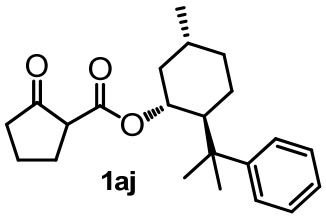
1ah

Compound **1ah**: Prepared according to the general procedure using β-keto ester **1a** (1.2 mL, 8.07 mmol 130 mol-%) in two batch, (+)-isopinocampheol (1.2 mL, 6.29 mmol, 100 mo-%), PPh_3 (0.17 g, 0.63 mmol, 10 mol%) and toluene (15 mL). Reaction time 23 h. Yield: 0.54 g (29%) as a pinkish oil.

R_f (20% EtOAc/hexanes) = 0.55; IR (film, cm^{-1}): 2937, 2877, 1752, 1721, 1466, 1252, 1191, 1113, 1096, 986, 939; ^1H NMR (250 MHz, $CDCl_3$): δ 3.08 (t, 1H, J = 8.6 Hz),

2.31-2.19 (m, 3H), 2.18-2.00 (m, 2H), 1.99-1.86 (m, 1H), 1.86-1.76 (m, 1H), 1.75-1.55 (m, 3H), 1.55-1.48 (m, 2H), 1.47-1.30 (m, 1H), 1.16 (d, 2H, J = 2.2 Hz), 1.05 (s, 3H), 1.02 (s, 1H), 0.98 (s, 1H), 0.96 (s, 1H), 0.94 (s, 0.5 x 3H), 0.92 (s, 0.5 x 3H), 0.783 (t, 0.5 x 3H, J = 7.2 Hz), 0.780 (t, 0.5 x 3H, J = 7.2 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 212.4, 168.41, 168.36, 94.8, 94.7, 55.5, 55.4, 53.9, 53.7, 50.3, 49.44, 49.41, 46.9, 46.8, 42.72, 42.67, 41.2, 38.2, 31.2, 31.1, 28.0, 27.9, 26.82, 26.80, 25.25, 25.18, 23.8, 23.5, 23.4, 21.2, 19.6, 19.5, 10.0; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 14:1, ^{1}H NMR: δ 10.53 (s, 0.07 x 1H, enol O-H); HRMS (ESI$^+$): m/z [M+Na] calcd for [$C_{18}H_{28}O_3Na$] 315.1936, found 315.1933.

2.4.9 (*1R,2S,5R*)-5-Methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-oxocyclopentanecarboxylate **1aj**



1aj

Compound **1aj**: Prepared according to the general procedure using β-keto ester **1a** (0.77 mL, 5.18 mmol 130 mol-%) in two batch, (-)-8-phenylmenthol (1.00 g, 4.30 mmol, 100 mo-%), PPh_3 (0.11 g, 0.44 mmol, 10 mol%) and toluene (15 mL). Reaction time 7 h. Yield: 1.43 g (97%) as a pinkish oil.

R_f (10 % Et_2O/toluene) = 0,55; IR (film, cm^{-1}): 2953, 2921, 2870, 1753, 1716, 1455, 1331, 1296, 1251, 1188, 1109, 1094, 992, 764, 700; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.21 (m, 4H), 7.15-7.07 (m, 1H), 4.84 (td, 1H, J = 10.7, 4.5 Hz), 2.25-2.15 (m, 2H), 2.14-2.05 (m, 2H), 2.05-1.95 (m, 2H), 1.94-1.81 (m, 2H), 1.80-1.55 (m, 4H), 1.52-1.38 (m, 1H), 1.29 (s, 3H), 1.20 (s, 3H), 1.19-0.97 (m, 2H), 0.88 (d, 3H, J = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 168.4, 151.9, 127.9, 125.5, 124.9, 75.1, 54.6, 50.3, 41.6, 39.7, 38.1, 34.61, 31.42, 28.8, 27.6, 26.87, 26.52, 24.1, 21.8, 20.7; in addition the following characteristic peaks are for the minor diastereomer: ^{1}H NMR: δ 4.82 (td, 1H, J = 10.7, 4.5 Hz), 2.67 (t, 1H, J = 8.9 Hz), 1.36 (s, 3H), 1.24 (s, 3H), 0.86 (d, 3H, J = 6.7 Hz); ^{13}C NMR: δ 212.4, 169.1, 151.5, 128.0, 125.7, 125.2, 75.9, 54.9, 50.4, 41.5, 40.0, 38.0, 34.65, 31.39, 26.93, 26.46, 21.0; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 14:1, ^{1}H NMR: δ 10.43 (s, 0.07 x 1H, enol O-H), 4.96 (td, 0.09 x 1H, J = 10.7, 4.4 Hz), 2.45 (tt, 0.1 x 1H, J = 7.8, 1.3 Hz); HRMS (ESI$^+$): m/z [M+Na] calcd for [$C_{22}H_{30}O_3Na$] 365.2093, found 365.2097.

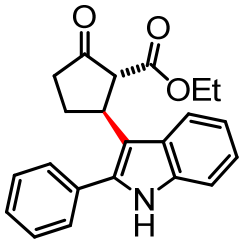
2.5 General Procedure of β-Arylations with Indoles

An oven-dried 4-mL vial with a magnetic stir bar was charged with $Pd(TFA)_2$ (13.3 mg, 0.04 mmol, 0.1 equiv) and β-ketoester (0.6 mmol, 1.5 equiv) in *i*-propanol (0.4 mL) and acetic acid (0.1 mL). After stirring for 5 minutes at room temperature, *tert*-butyl perbenzoate (100 μL, 0.525 mmol, 1.3 equiv) and indole (0.4 mmol, 1.0 equiv) were added to the mixture, respectively. The vial was sealed with a rubber-lining cap and stirred magnetically at room temperature. *The reaction can be also conducted in an open flask without dry solvents.*

After the reaction was complete, the reaction mixture was quenched with the mixture of saturated sodium bicarbonate solution (15 mL) and sodium sulfite (10%, 5 mL). The aqueous phase was extracted with ethyl acetate (3 x 10 mL), and the combined organic phases were washed with saturated brine solution (30 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flask column chromatography to afford pure coupling product.

2.6 Characterization Data for Coupling Products

2.6.1 Ethyl 2-oxo-5-(2-phenyl-1H-indol-3-yl)cyclopentanecarboxylate **3c**



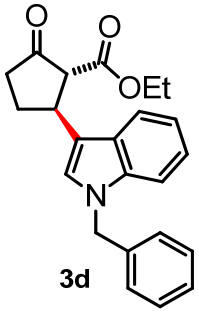
3c

Compound **3c**: Prepared according to the general procedure using β-ketoester **1c** (78 μL, 82 mg, 130 mol-%) and indole **2c** (78 mg). Yield: 133 mg (96%) as yellow gum.

R_f (20% EtOAc/hexanes) = 0.28; IR (film, cm^{-1}): 3375, 2979, 1748, 1716, 1451, 1274, 1192, 1110, 1024, 909; ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (br s, 1H), 7.65-7.57 (m, 3H), 7.52-7.46 (m, 2H), 7.45-7.38 (m, 2H), 7.23 (ddd, 1H, J = 8.1, 7.1, 1.1 Hz), 7.15 (ddd, 1H, J = 8.0, 7.0, 1.1 Hz), 4.29-4.19 (m, 1H), 4.06 (obs. ABX_3, 2H, $|J_{AB}|$ = 10.9 Hz, $|J_{AX}| = |J_{BX}|$ = 7.2 Hz, Δv = 30.5 Hz), 3.97 (obs. dd, 1H, J = 12.1, 0.9 Hz), 2.66-2.24 (m, 4H), 1.11 (t, 3H, J = 7,1 Hz);^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 169.2, 136.4, 136.3, 132.8, 129.1, 129.0, 128.4, 126.6, 122.4, 119.9, 119.7, 111.6, 111.3, 61.5, 60.5, 39.2, 38.5, 28.1, 14.1; in addition, the following characteristic peaks are for the

minor enol tautomer, keto/enol > 25:1, ^{1}H NMR: δ 10.78 (s, 0.05H, enol O-H); HRMS (ESI$^+$): m/z [M+Na] calcd for [$C_{22}H_{21}NO_3Na$] 370.1419, found 370.1418.

2.6.2 Ethyl 2-(1-benzyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3d**

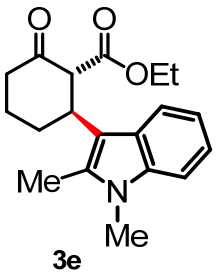


3d

Compound **3d**: Prepared according to the general procedure using β-ketoester **1d** (90 μL, 94 mg, 150 mol-%) and indole **2d** (83 mg). Yield: 121 mg (83%) as a yellow gum.

R_f (20% EtOAc/hexanes) = 0.32; IR (film, cm^{-1}): 2939, 1737, 1707, 1470, 1370, 1334, 1254, 1226, 1144, 1038, 908, 726; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dt, 1H, J = 7.9, 1.0 Hz), 7.34-7.24 (m, 5H), 7.20 (td, 1H, J = 7.6, 1.1 Hz), 7.16-7.08 (m, 3H), 6.99 (s, 1H), 5.28 (s, 2H), 4.22-4.05 (m, 3H), 3.45 (d, 1H, J = 11.1 Hz), 2.65-2.47 (m, 3H), 2.18-2.06 (m, 1H) 1.20 (t, 3H, J = 7.1 Hz);^{13}C NMR (126 MHz, $CDCl_3$): δ 211.7, 169.4, 137.4, 137.2, 128.9, 127.8, 127.2, 126.9, 124.7, 122.3, 119.6, 119.4, 116.1, 110.1, 62.2, 61.6, 50.1, 38.8, 38.7, 28.7, 14.2; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol > 25:1, ^{1}H NMR: δ 10.82 (s, 0.03H, enol O-H); HRMS (ESI$^+$): m/z [M+Na$^+$] calcd for [$C_{23}H_{23}NO_3Na^+$] 384.1570, found 384.1588.

2.6.3 Ethyl 2-(1,2-dimethyl-1H-indol-3-yl)-6-oxocyclohexanecarboxylate **3e**

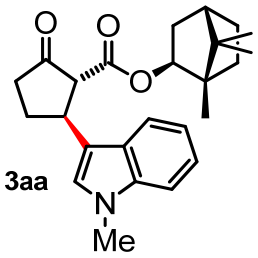


3e

Compound **3e**: Prepared according to the general procedure using β-ketoester **1e** (84 µL, 89 mg, 130 mol-%) and indole **2e** (58 mg). Yield: 87 mg (70%) as an off-white solid which turns reddish under air.

R_f (30% EtOAc/hexanes) = 0.43; mp. 95-98 °C; IR (film, cm^{-1}): 2939, 1737, 1707, 1470, 1370, 1334, 1254, 1226, 1144, 1038, 908, 726; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, 1H, J = 7,1 Hz), 7.27-7.24 (m, 1H), 7.16 (ddd, 1H, J = 8.1, 7.1, 1.1 Hz), 7.08 (ddd, 1H, J = 7.9, 7.0, 1.1 Hz), 4.12 (dd, 1H, J = 12.5, 0.7 Hz), 3.95 (ABX$_3$, 2H, $|J_{AB}|$ = 10.8 Hz, $|J_{AX}| = |J_{BX}|$ = 7.1 Hz, Δv = 27.4 Hz), 3.62 (s, 3H), 2.64-2.42 (m, 3H), 2.40 (s, 3H), 2.23-2.16 (m, 1H), 2.03-1.97 (m, 1H), 1.85 (tq, 1H, J = 13.5, 4.1 Hz), 0.98 (t, 3H, J = 7.1 Hz);^{13}C NMR (126 MHz, $CDCl_3$): δ 206.0, 169.5, 137.2, 133.6, 125.8, 120.5, 118.91, 118.86, 111.1, 109.1, 63.0, 60.6, 41.6, 40.2, 31.2, 29.7, 25.9, 14.0, 10.6 ; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol > 25:1, ^{1}H NMR: δ 12.49 (s, 0.14H, enol O-H); HRMS (ESI$^+$): m/z [M+Na] calcd for [$C_{19}H_{23}NO_3Na$] 336.1576, found 336.1571.

2.6.4 (*1R,2S*)-(1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3aa**

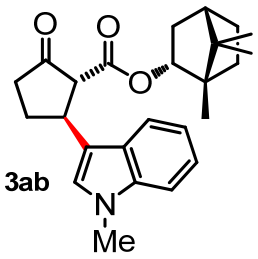


Compound **3aa**: Prepared according to the general procedure using β-keto ester **1aa** (162 mg, 150 mol-%) and indole **2a** (50 µL, 53 mg, 0.4 mmol, 100 mol%). Reaction time 17.5 h. Yield: 125 mg (79%) as off white solid. The diastereomeric ratio was 1.7:1. Only one of the diastereomers is shown.

R_f (20% EtOAc/hexanes) = 0.29; mp. 126-130 °C; IR (film, cm^{-1}): 2954, 2874, 1752, 1713, 1473, 1454, 1242, 1107, 1050, 908, 730; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (obs. dt, 1H, J = 8.0, 0.9 Hz), 7.32 (dt, 1H, J = 8.2, 0.9 Hz), 7.25 (ddd, 1H, J = 8.1, 7.0, 1.0 Hz), 7.13 (ddd, 1H, J = 7.9, 7.0, 1.0 Hz), 6.91 (s, 1H), 4.68 (obs. t, 1H, J = 5.8 Hz), 4.04 (obs. td, 1H, J = 10.8, 6.4 Hz), 3.751 (s, 3H), 3.46 (obs. d, 1H, J = 10.8 Hz), 2.66-2.58 (m, 1H), 2.57-2.44 (m, 2H), 2.12-2.00 (m, 1H), 1.83-1.79 (m, 1H), 1.78-1.62 (m, 3H), 1.58-1.47 (m, 1H), 1.17-1.00 (m, 2H), 0.96 (s, 3H), 0.81 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6, 169.0, 137.5, 126.91, 125.3, 122.0, 119.40, 119.1, 115.3, 109.5, 82.3, 61.9, 48.78, 47.00, 45.1, 39.0, 38.78, 38.7, 33.79, 32.7, 29.00, 27.1, 20.2,

19.9, 11.3; in addition, the following characteristic peaks are for the minor diastereomer: ^{1}H NMR: δ 7.63 (obs. dt, 1H, *J* = 8.0, 0.9 Hz), 4.69 (obs. t, 1H, *J* = 4.2 Hz), 4.05 (obs. td, 1H, *J* = 10.7, 6.4 Hz), 3.749 (s, 3H), 3.44 (obs. d, 1H, *J* = 10.6 Hz), 0.86 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H); ^{13}C NMR: δ 211.5, 168.9, 126.88, 119.38, 115.4, 61.2, 48.84, 46.99, 38.9, 38.80, 38.7, 33.80, 29.03, 19.8, 11.5; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 71:1, ^{1}H NMR: δ 10.95 (s, 0.011 x 1H, enol O-H), 10.91 (s, 0.014 x 1H, enol O-H); HRMS (ESI^{+}): m/z [M+Na] calcd for [$C_{25}H_{31}NO_3Na$] 416.2202, found 416.2205.

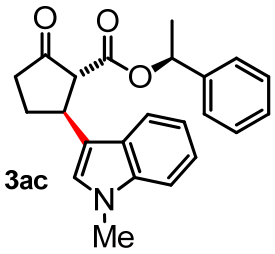
2.6.5 (*1R,2S*)-(*1S,2R,4S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3ab**



Compound **3ab**: Prepared according to the general procedure using β-keto ester **1ab** (162 mg, 150 mol-%) and indole **2a** (50 µL, 53 mg, 0.4 mmol, 100 mol%). Reaction time 18h. Yield: 115 mg (73%) as light yellow crystalize solids. The diastereomeric ratio was 1:1.

R_f (20% EtOAc/hexanes) = 0.32; mp. 139-144 °C; IR (film, cm^{-1}): 2954, 2872, 1753, 1720, 1474, 1453, 1271, 1239, 1109, 1017, 907, 739; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dt, 1H, *J* = 8.0, 0.9 Hz), 7.31 (dt, 1H, *J* = 8.3, 0.8 Hz), 7.24 (obs. ddd, 1H, *J* = 8.2, 7.0, 1.1 Hz), 7.11 (ddd, 1H, *J* = 8.0, 6.9, 1.0 Hz), 6.920 (s, 1H), 4.90 (ddd, 1H, *J* = 9.9, 3.4, 1.9 Hz), 4.057 (obs. td, 1H, *J* = 10.9, 6.1 Hz), 3.750 (s, 3H), 3.48 (dd, 1H, *J* = 11.0, 0.6 Hz), 2.66-2.46 (m, 3H), 2.38-2.23 (m, 2H), 2.16-2.04 (m, 1H), 1.92-1.82 (m, 1H), 1.73-1.63 (m, 2H), 1.28-1.22 (m, 2H), 0.86 (s, 3H), 0.837 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.6, 169.7, 137.5, 126.9, 125.4, 122.0, 119.4, 119.2, 115.3, 109.6, 81.1, 62.2, 49.0, 47.9, 45.0, 38.74, 38.73, 36.8, 32.8, 28.9, 28.0, 27.2, 19.8, 18.9, 13.4; in addition, the following characteristic peaks are for the other diastereomer: ^{1}H NMR: δ 6.924 (s, 1H), 4.95 (ddd, 1H, *J* = 10.0, 3.4, 2.2 Hz), 4.064 (obs. td, 1H, *J* = 10.9, 6.1 Hz), 3.755 (s, 3H), 0.87 (s, 3H), 0.844 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.5, 169.7, 137.5, 126.9, 125.5, 119.5, 119.2, 115.4, 81.0, 62.1, 49.1, 48.0, 44.9, 38.8, 36.6, 28.0, 27.2, 19.8, 19.0, 13.5; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 91:1, ^{1}H NMR: δ 10.87 (s, 0.011 x 1H, enol O-H), 10.85 (s, 0.007 x 1H, enol O-H, minor diastereomer); HRMS (ESI^{+}): m/z [M+Na] calcd for [$C_{25}H_{31}NO_3Na$] 416.2202, found 416.2205.

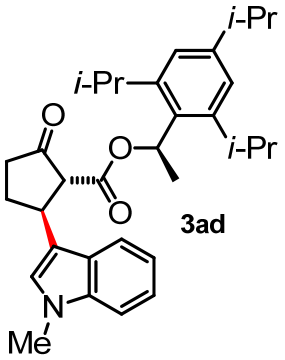
2.6.6 (*1R,2S*)-(*S*)-1-phenylethyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3ac**



Compound **3ac**: Prepared according to the general procedure using β-keto ester **1ac** (142 mg, 150 mol-%) and indole **2a** (50 µL, 53 mg, 0.4 mmol, 100 mol%). Reaction time 17.5 h. Yield: 88 mg (61%) as a brownish oil. The diastereomeric ratio was 1.4:1.

R_f (20% EtOAc/hexanes) = 0.21; IR (film, cm^{-1}): 3057, 2979, 2934, 1750, 1720, 1475, 1453, 1327, 1241, 1185, 1108, 1061, 964, 741, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, 1H, *J* = 8.0 Hz), 7.42-7.26 (m, 6H), 7.25-7.20 (m, 1H), 7.16-7.08 (m, 1H), 6.88 (s, 1H), 5.91 (obs. q, 1H, *J* = 6.9 Hz), 4.08 (obs. td, 1H, *J* = 11.0, 6.0 Hz), 3.74 (s, 3H), 3.51 (obs. d, 1H, *J* = 10.6 Hz), 2.67-2.45 (m, 3H), 2.20-2.05 (m, 1H), 1.50 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1, 168.4, 141.4, 137.5, 128.5, 127.8, 126.9, 126.0, 125.5, 122.0, 119.44, 119.15, 115.2, 109.5, 73.6, 62.3, 38.75, 38.5, 32.73, 28.6, 22.13; in addition, the following characteristic peaks are for the minor diastereomer: ^{1}H NMR: δ 6.83 (s, 1H), 5.95 (obs. q, 1H, *J* = 6.9 Hz), 4.11 (obs. td, 1H, *J* = 10.9, 5.7 Hz), 3.69 (s, 3H), 3.54 (obs. d, 1H, *J* = 9.6 Hz), 1.56 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR: δ 211.4, 168.8, 141.2, 128.4, 126.8, 126.1, 125.4, 119.42, 119.16, 115.1, 73.5, 62.1, 38.82, 38.7, 32.68, 28.8 22.09; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 42:1, ^{1}H NMR: δ 10.75 (s, 0.02 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{23}H_{23}NO_3Na$] 384.1576, found 384.1570.

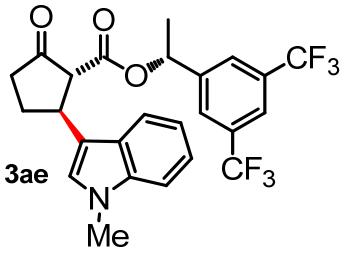
2.6.7 (*1R,2S*)- (R)-1-(2,4,6-triisopropylphenyl)ethyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3ad**



Compound **3ad**: Prepared according to the general procedure using β-keto ester **1ad** (108 mg, 150 mol-%) and indole **2a** (25 µL, 26 mg, 0.2 mmol, 100 mol%). Reaction time 17.5 h. Yield: 76 mg (78%) as a yellow oil. The diastereomeric ratio was 1.1:1.

R_f (20% EtOAc/hexanes) = 0.36 and 0.27; IR (film, cm^{-1}): 2960, 2870, 1754, 1720, 1240, 1054, 740; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, 0.5 x 1H, *J* = 8.0 Hz), 7.54 (d, 0.5 x 1H, *J* = 8.0 Hz), 7.33 (d, 0.5 x 1H, *J* = 8.2 Hz), 7.26 (obs. dt, 0.5 x 1H, *J* = 9.4, 1.0 Hz), 7.25 (obs. ddd, 0.5 x 1H, *J* = 8.2, 6.9, 1.1 Hz), 7.20 (ddd, 0.5 x 1H, *J* = 8.1, 7.0, 0.9 Hz), 7.10-6.97 (m, 3H), 6.94 (s, 0.5 x 1H), 6.81 (s, 0.5 x 1H), 6.58 (obs. q, 0.5 x 1H, *J* = 6.9 Hz), 6.56 (obs. q, 0.5 x 1H, *J* = 6.9 Hz), 4.13 (td, 0.5 x 1H, *J* = 10.9, 5.8 Hz), 4.06 (td, 0.5 x 1H, *J* = 11.3, 6.0 Hz), 3.77 (s, 0.5 x 3H), 3.64 (s, 0.5 x 3H), 3.45 (d, 0.5 x 1H, *J* = 11.0 Hz), 3.40 (d, 0.5 x 1H, *J* = 11.0 Hz), 3.38-3.27 (m, 1H), 2.94-2.81 (m, 1H), 2.66-2.47 (m, 3H), 2.20-2.06 (m, 1H), 1.68 (d, 0.5 x 3H, *J* = 6.8 Hz), 1.53 (d, 0.5 x 3H, *J* = 6.8 Hz), 1.35-1.10 (m, 19 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.45, 211.43, 169.6, 168.9. 148.24, 148.15, 137.50, 137.47, 131.8, 131.7, 129.2, 128.7, 126.9, 126.8, 125.32, 125.27, 122.1, 121.9, 119.5, 119.4, 119.2, 119.1, 115.32, 115.26, 109.5, 109.4, 69.9, 69.8, 62.7, 62.4, 39.5, 38.9, 38.8, 38.2, 34.20, 34.17, 32.8, 32.6, 29.5, 29.4, 28.7, 28.5, 26.4, 24.45, 24.41, 24.04, 24.01, 22.4, 22.1; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 60:1, ^{1}H NMR: δ 10.98 (s, 0.008 x 1H, enol O-H), 10.94 (s, 0.017 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{32}H_{41}NO_3Na$] 510.2984, found 510.2987.

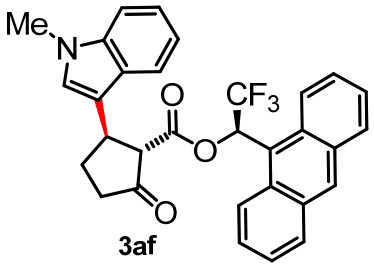
2.6.8 (*1R,2S*)-(*R*)-1-(3,5-Bis(trifluoromethyl)phenyl)ethyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3ae**



Compound **3ae**: Prepared according to the general procedure using β-keto ester **1ae** (221 mg, 150 mol-%) and indole **2a** (50 µL, 53 mg, 0.4 mmol, 100 mol%). Reaction time 17 h. Yield: 164 mg (82%) as a yellow oil. The diastereomeric ratio was 1.1:1.

R_f (20% EtOAc/hexanes) = 0.27; IR (film, cm^{-1}): 2939, 1756, 1727, 1277, 1170, 1126, 1073, 898, 741, 706, 682; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (br.s, 1H), 7.75 (br.s, 1H), 7.66 (br. s, 1H), 7.54 (dt, 1H, *J* = 8.0, 0.9 Hz), 7.27 (obs. dt, 1H, *J* = 8.4, 0.9 Hz), 7.20 (ddd, 1H, *J* = 8.2, 7.0, 1.1 Hz), 7.03 (ddd, 1H, *J* = 8.0, 7.0, 1.0 Hz), 6.87 (s, 1H), 5.96 (obs. td, 1H, *J* = 15.4, 6.7 Hz), 4.05 (obs. td, 1H, *J* = 11.4, 6.0 Hz), 3.71 (s, 3H), 3.52 (d, 1H, *J* = 11.5 Hz), 2.65-2.51 (m, 2H), 2.38-2.26 (m, 1H), 2.20-2.08 (m, 1H), 1.59 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.2, 168.8, 144.0, 137.5, 131.9 (q, ^2J = 33 Hz, -$\underline{C}CF_3$), 126.7, 126.3, 126.2, 125.1, 123.3 (q, ^1J = 273 Hz, -$C\underline{C}F_3$), 122.2, 121.9, 119.2, 119.1, 114.85, 109.67, 72.15, 62.2, 54.8, 38.8, 38.3, 32.7, 28.7, 22.38; in addition, the following characteristic peaks are for the minor diastereomer: ^{1}H NMR: δ 7.90 (br. s, 1H), 7.81 (br. s, 1H), 7.79 (br. s, 1H), 7.63 (dt, 1H, *J* = 8.0, 0.9 Hz), 7.33 (dt, 1H, *J* = 8.2, 0.8 Hz), 6.92 (s, 1H), 4.08 (obs. td, 1H, *J* = 11.4, 6.2 Hz), 3.76 (s, 3H), 3.57 (d, 1H, *J* = 11.5 Hz), 1.50 (d, 3H, *J* = 6.7 Hz); ^{13}C NMR: δ 210.7, 168.3, 144.3, 137.6, 132.0 (q, ^2J = 33 Hz, -$\underline{C}CF_3$), 126.8, 125.6, 123.4 (q, ^1J = 273 Hz, -$C\underline{C}F_3$), 119.,4, 119.3, 114.94, 109.71, 72.24, 62.1, 38.9, 38.1, 32.8, 28.6, 22.40; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 55:1, ^{1}H NMR: δ 10.62 (s, 0.018 x 1H, enol O-H), 10.57 (s, 0,012 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{25}H_{21}NO_3F_6Na$] 520.1323, found 520.1323.

2.6.9 (*1R,2S*)-(*R*)-1-(Anthracen-9-yl)-2,2,2-trifluoroethyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3af**

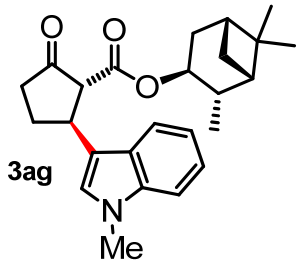


3af

Compound **3af**: Prepared according to the general procedure using β-keto ester **1af** (226 mg, 170 mol-%) and indole **2a** (50 µL, 53 mg, 0.4 mmol, 100 mol%). Reaction time 17 h. Yield: 120 mg (58%) as yellow crystalline solid. The diastereomeric ratio was 1.4:1.

R_f (20% EtOAc/hexanes) = 0.21; mp. 80-84 °C; IR (film, cm^{-1}): 3055, 2929, 1765, 1736, 1179, 1160, 1150, 1129, 1106, 1073, 734; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65-8.45 (m, 2H), 8.36 (br. d, 1H, *J* = 9.2 Hz), 8.01 (br. d, 2H, *J* = 9.3 Hz), 7.88 (obs. q, 1H, *J* = 7.9 Hz), 7.68-7.58 (m, 1H), 7.56-7.34 (m, 4H), 7.32-7.26 (m, 1H), 7.18-7.13 (m, 1H), 6.96 (ddd, 1H, *J* = 8.0, 5.6, 2.4 Hz), 6.47 (s, 1H), 4.01 (obs. td, 1H, *J* = 11.1, 5.5 Hz), 3.78 (d, 1H, *J* = 11.3 Hz), 3.33 (s, 3H), 2.70-2.48 (m, 3H), 2.18-2.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.7, 167.7, 137.4, 131.7, 131.4, 131.1, 130.6, 129.57, 129.2, 126.3, 126.23, 125.6, 125.1, 122.6, 121.9, 120.8, 119.2, 119.3, 114.1, 109.5, 69.74 (q, ^2J = 35 Hz, -CHCF$_3$), 61.2, 39.15, 38.7, 32.3, 28.77; in addition, the following characteristic peaks are for the minor diastereomer: ^{1}H NMR: δ 8.53 (s, 1H), 8.49 (br. d, 1H, *J* = 9.2 Hz), 7.98 (br. d, 2H, *J* = 9.3 Hz), 7.87 (obs. q, 1H, *J* = 8.0 Hz), 7.06 (ddd, 1H, *J* = 8.0, 5.4, 2.6 Hz), 6.63 (s, 1H), 4.10 (obs. td, 1H, *J* = 11.0, 5.9 Hz), 3.71 (d, 1H, *J* = 11.3 Hz) 3.56 (s, 3H); ^{13}C NMR: δ 209.5, 167.5, 137.6, 131.8, 131.5, 129.61, 126.5, 126.17, 125.0, 122.1, 120.7, 119.1, 114.2, 109.7, 69.66 (q, ^2J = 35 Hz, -CHCF$_3$), 39.23, 32.5, 28.84; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 7:1, ^{1}H NMR: δ 10.45 (d, 0.14 x 1H, enol O-H); HRMS (ESI$^+$): m/z [M+Na] calcd for [$C_{31}H_{24}NO_3F_3Na$] 538.1606, found 538.1600

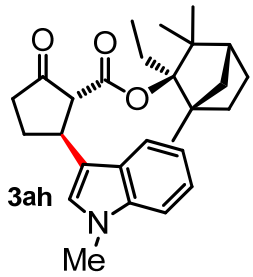
2.6.10 (*1R,2S*)-(*1S,2S,3S,5R*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl 2-(1-methyl-1*H*-indol-3-yl)-5-oxocyclopentanecarboxylate **3ag**



Compound **3ag**: Prepared according to the general procedure using β-keto ester **1ag** (163 mg, 150 mol-%) and indole **2a** (50 µL, 53 mg, 0.4 mmol, 100 mol%). Reaction time 17 h. Yield: 124 mg (79%) as yellow crystalline solid. The diastereomeric ratio was 1.1:1.

R_f (20 % EtOAc/hexanes) = 0,33; mp. 99-101 °C; IR (film, cm^{-1}): 2910, 1750, 1716, 1473, 1338, 1270, 1241, 1187, 1154, 1126, 1107, 974, 738; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.32 (dt, 1H, *J* = 8.3, 1.0 Hz), 7.25 (ddd, 1H, *J* = 8.2, 6.9, 1.1 Hz), 7.13 (ddd, 1H, *J* = 7.9, 6.7, 0.8 Hz), 6.94 (s, 1H), 5.14-5.05 (m, 1H), 4.10 (td, 1H, *J* = 10.9, 5.9 Hz), 3.76 (s, 3H), 3.44 (obs. d, 1H, *J* = 10.9 Hz), 2.67-2.47 (m, 4H), 2.35 (tdd, 1H, *J* = 11.9, 6.1, 2.3 Hz), 2.22-2.02 (m, 2H), 1.96-1.86 (m, 1H), 1.84-1.77 (m, 1H), 1.30-1.20 (m, 1H), 1.22 (s, 3H), 1.19-1.09 (m, 1H), 1.01 (d, 3H, *J* = 7.4 Hz), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 169.5, 137.5, 127.0, 125.3, 122.0, 119.5, 119.1, 115.5, 109.5, 75.5, 62.2, 47.5, 43.6, 41.3, 38.8, 38.6, 38.3, 35.9, 33.4, 32.8, 28.6, 27.5, 23.8, 20.5; in addition, the following characteristic peaks are for the minor diastereomer: ^{1}H NMR: δ 3.45 (obs. d, 1H, *J* = 10.9 Hz), 1.60 (ddd, 1H, *J* = 14.5, 4.2, 2.8 Hz), 1.11 (d, 3H, *J* = 7.4 Hz); ^{13}C NMR: δ 211.6, 169.4, 126.9, 125.4, 115.4, 75.4, 62.3, 47.6, 43.9, 41.2, 38.7, 38.5, 35.6, 28.7, 20.6; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 71:1, ^{1}H NMR: δ 10.84 (s, 0.014 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{25}H_{31}NO_3Na$] 416.2202, found 416.2206.

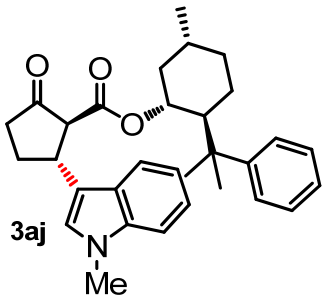
2.6.11 (*1R,2S*)-(*1S,2R,4R*)-2-Ethyl-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3ah**



Compound **3ah**: Prepared according to the general procedure using β-keto ester **1ah** (191 mg, 170 mol-%) and indole **2a** (50 µL, 53 mg, 0.4 mmol, 100 mol%). Reaction time 17 h. Yield: 118 mg (70%) as brownish viscous oil. The diastereomeric ratio was 1.1:1.

R_f (20% EtOAc/hexanes) = 0,42 and 0,33; IR (film, cm^{-1}): 2936, 2878, 1750, 1719, 1467, 1327, 1271, 1243, 1108, 972, 740; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dq, 1H, *J* = 8.0, 1.0 Hz), 7.31 (dt, 1H, *J* = 8.2, 1.0 Hz), 7.24 (obs. ddd, 1H, *J* = 8.2, 6.9, 1.1 Hz), 7.12 (ddd, 1H, *J* = 8.0, 6.9, 1.2 Hz), 6.942 (s, 0.5 x 1H), 6.936 (s, 0.5 x 1H) 4.14-4.02 (m, 1H), 3.91 (d, 1H, *J* = 8.9 Hz), 3.74 (s, 3H), 3.58-3.51 (m, 2H), 2.69-2.59 (m, 1H), 2.57-2.50 (m, 1H), 2.22-2.11 (m, 1H), 2.10-1.99 (m, 1H), 1.94-1.78 (m, 1H), 1.76-1.54 (m, 3H), 1.53-1.49 (m, 1H), 1.44-1.24 (m, 2H), 1.19 (s, 1H), 1.16 (s, 1H), 1.07 (s, 2H), 1.05 (s, 2H), 0.97 (s, 0.5 x 3H), 0.94 (s, 0.5 x 3H), 0.71 (t, 0.5 x 3H, *J* = 7.3 Hz), 0.65 (t, 0.5 x 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.00, 211.98, 168.3, 168.2, 137.63, 137.60, 126.8, 125.59, 125.57, 122.0, 119.5, 119.4, 119.1, 115.5, 115.4, 109.6, 95.33, 95.32, 62.2, 62.1, 53.77, 53.76, 49.5, 49.4, 47.0, 42.94, 42.92, 39.3, 39.0, 38.84, 38.82, 32.8, 31.3, 31.2, 29.59, 29.56, 26.89, 26.87, 25.1, 23.9, 23.8, 23.7, 23.6, 19.7, 19.6, 9.9, 9.8; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol = 40:1, ^{1}H NMR: δ 11.15 (s, 0.015 x 1H, enol O-H), 11.07 (s, 0.025 x 1H, enol O-H); HRMS (ESI^+): m/z [M+Na] calcd for [$C_{27}H_{35}NO_3Na$] 444.2515, found 444.2518

2.6.12 (*1S,2R*)-(*1R,2S,5R*)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3aj**



Compound **3aj**: Prepared according to the general procedure using β-keto ester **1aj** (239 mg, 170 mol-%) and indole **2a** (100 µL, 105 mg, 0.4 mmol, 100 mol%). Reaction time 17 h. Yield: 131 mg (69%) as an off white crystalline solid. The diastereomeric ratio was 20:1.

R_f (20 % EtOAc/hexanes) = 0.33; mp. 64-66 °C; $[\alpha]_D$ = +3.6 (*c* 1.00, CH_2Cl_2); IR (film, cm^{-1}): 3054, 2953, 2923, 1752, 1715, 1472, 1329, 1270, 1241, 1186, 1108, 741, 702; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dt, 1H, *J* = 8.0, 0.9 Hz), 7.31 (dt, 1H, *J* = 8.2, 0.9 Hz), 7.28-7.24 (m, 1H), 7.16 (ddd, 1H, *J* = 8.0, 6.9, 1.1 Hz), 7.06-6.97 (m, 5H), 6.88 (s, 1H), 4.77 (td, 1H, *J* = 10.7, 4.3 Hz), 3.95 (obs. td, 1H, *J* = 10.9, 6.1 Hz), 3.77 (s, 3H), 3.04 (d, 1H, *J* = 11.0 Hz), 2.57-2.38 (m, 3H), 2.18-2.06 (m, 1H), 1.96 (ddt, 2H, *J* = 13.9, 10.4, 2.9 Hz), 1.60-1.54 (m, 1H), 1.48 (obs. ddt, 1H, *J* = 12.9, 5.9, 3.1 Hz), 1.45-1.38 (m, 1H), 1.05-0.92 (m, 1H), 1.01 (s, 3H), 0.97 (s, 3H), 0.91-0.72 (m, 2H), 0.86 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$): δ 211.3, 168.4, 151.2, 137.5, 127.9, 127.1, 125.5, 125.4, 124.9, 122.1, 119.9, 119.2, 115.6, 109.4, 76.3, 62.9, 50.2, 41.4, 39.8, 38.7, 37.7, 34.6, 32.7, 31.4, 28.1, 27.0, 26.6, 26.0, 21.8; in addition, the following characteristic peaks are for the minor diastereomer, ^{1}H NMR: δ 3.08 (d, 0.05 x 1H, *J* = 10.7 Hz) HRMS (ESI^+): m/z [M+Na] calcd for [$C_{31}H_{37}NO_3Na$] 494.2671, found 494.2670.

For the determination of the relative stereochemistry, a single crystal of **3aj** was subjected to single-crystal X-ray analysis.

For details, please see the associated CIF file.

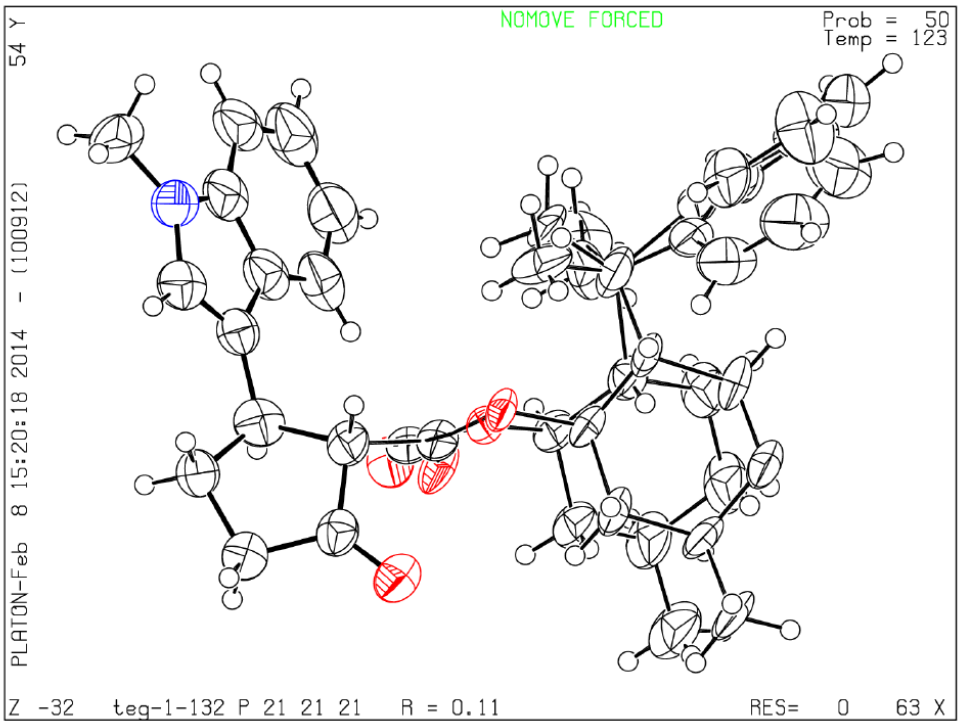
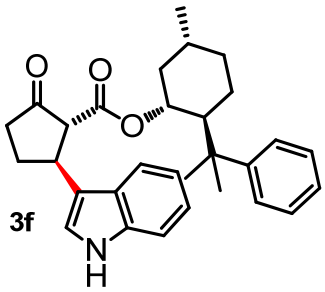


Figure S1. ORTEP plot of the crystal structure of **3aj**.

2.6.13 (1*R*,2*S*,5*R*)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3f**

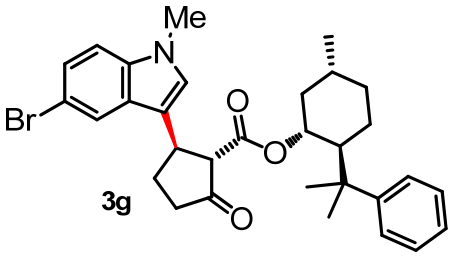


Compound **3f**: Prepared according to the general procedure using β-keto ester **1aj** (89 mg, 130 mol-%) and indole **2b** (23 mg, 0.2 mmol, 100 mol%). Reaction time 20 h. Yield: 62 mg (68%) as an off white crystalline solid. The diastereomeric ratio was 8.6:1.

R_f (30 % EtOAc/hexanes) = 0.41; mp. 69-73 °C; $[\alpha]_D$ = +1.0 (*c* 0.10, CH_2Cl_2); IR (film, cm^{-1}): 3402, 3056, 2954, 2921, 2870, 1747, 1711, 1457, 1332, 1268, 1113, 739, 702; ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (br. s, 1H), 7.69 (d, 1H, *J* = 7.9 Hz), 7.36 (dt, 1H, *J* =

8.1, 0.8 Hz), 7.22 (ddd, 1H, *J* = 8.0, 7.1, 1.0 Hz), 7.15 (ddd, 1H, *J* = 7.9, 7.1, 0.9 Hz), 7.02-6.92 (m, 5H), 4.76 (td, 1H, *J* = 10.7, 4.2 Hz), 3.92 (td, 1H, *J* = 10.8, 6.0 Hz), 2.99 (d, 1H, *J* = 10.8 Hz), 2.56-2.35 (m, 3H), 2.17-2.04 (m, 1H), 2.00-1.89 (m, 2H), 1.60-1.46 (m, 2H), 1.46-1.35 (m, 1H), 1.33-1.21 (m, 2H), 0.99 (s, 3H), 0.95 (s, 3H), 0.93-0.86 (m, 1H), 0.83 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 168.4, 151.3, 136.8, 127.9, 126.6, 125.5, 124.9, 122.5, 120.6, 119.8, 119.7, 117.2, 111.4, 76.4, 62.7, 50.2, 41.4, 39.8, 38.7, 37.6, 34.7, 31.4, 27.9, 26.9, 26.6, 26.1, 21.8; in addition, the following characteristic peaks are for the minor diastereomer, ^{1}H NMR: δ 3.06 (d, 1H, *J* = 10.0 Hz); in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol 30:1, ^{1}H NMR: δ 10.78 (s, 0.03 H, enol O-H); HRMS (ESI$^+$): m/z [M+Na]$^+$ calcd for $[C_{30}H_{35}NO_3Na]^+$ 480.2509, found 480.2516.

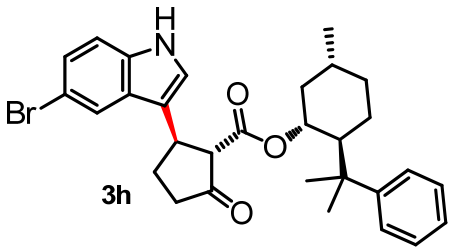
2.6.14 (1*R*,2*S*,5R)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(5-bromo-1-methyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3g**



Compound **3g**: Prepared according to the general procedure using β-keto ester **1aj** (89 mg, 130 mol-%)) and indole (42 mg). Yield: 66 mg (59%) as light yellow crystalline solid. The diastereomeric ratio was 10.4:1.

R_f (30 % EtOAc/hexanes) = 0.38; mp. 81-83 °C; $[\alpha]_D$ = +26 (*c* 0.10, CH_2Cl_2); IR (film, cm^{-1}): 3057, 2954, 2923, 1753, 1714, 1475, 1370, 1269, 1239, 1188, 1109, 792, 737, 703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, 1H, *J* = 1.5 Hz), 7.31 (dd, 1H, *J* = 8.6, 1.7, Hz), 7.15 (d, 1H, *J* = 8.6 Hz), 7.07-6.96 (m, 5H), 6.80 (s, 1H), 4.76 (td, 1H, *J* = 10.7, 4.2 Hz), 3.73 (s, 3H), 3.70 (obs. td, 1H, *J* = 11.3, 5.8 Hz), 2.89 (d, 1H, *J* = 11.2 Hz), 2.59-2.35 (m, 3H), 2.08-1.97 (m, 2H), 1.86 (dddd, 1H, *J* = 12.3, 3.7, 1.8 Hz), 1.60-1.50 (m, 2H), 1.48-1.37 (m, 1H), 1.32-1.19 (m, 3H), 1.02 (s, 3H), 0.99 (s, 3H), 0.81 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7, 168.1, 151.6, 136.1, 128.8, 127.9, 126.6, 125.6, 124.9, 122.6, 115.5, 112.7, 111.1, 76.5, 63.3, 50.1, 41.2, 39.7, 38.6, 37.1, 34.6, 33.0, 31.4, 28.0, 26.90, 26.86, 25.6, 21.8; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol 16:1, ^{1}H NMR: δ 10.64 (s, 0.06H, enol O-H); HRMS (ESI$^+$): m/z [M+Na]$^+$ calcd for $[C_{31}H_{36}BrNO_3Na]^+$ 572.1771, found 572.1747.

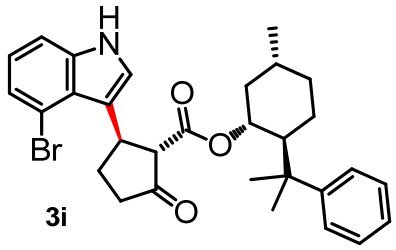
2.6.15 (1R,2S,5R)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(5-bromo-1H-indol-3-yl)-5-oxocyclopentanecarboxylate



Compound **3h**: Prepared according to the general procedure using β-keto ester **1aj** (89 mg, 130 mol-%) and 5-bromoindole (39 mg, 0.2 mmol, 100 mol%). Reaction time 21 h. Yield: 63 mg (59%) as a light brown crystalline solid. The diastereometric ratio 14.0:1.

R_f (30 % EtOAc/hexanes) = 0.24; mp. 88-90 °C; $[\alpha]_D$ = +37 (*c* 0.10, CH_2Cl_2); IR (film, cm^{-1}): 3377, 3056, 2956, 2923, 2870, 1750, 1713, 1458, 1270, 1114, 740, 703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (br. s, 1H), 7.80 (d, 1H, *J* = 1.8 Hz), 7.30 (dd, 1H, *J* = 8.6, 1.8 Hz), 7.23 (br. d, 1H, *J* = 8.6 Hz), 7.06-6.97 (m, 5H), 6.99 (s, 1H), 4.77 (td, 1H, *J* = 10.7, 4.2 Hz), 3.70 (td, 1H, *J* = 11.3, 6.0 Hz), 2.87 (dd, 1H, *J* = 11.2, 0.6 Hz), 2.56-2.35 (m, 3H), 2.09-1.98 (m, 2H), 1.88-1.81 (m, 1H), 1.61-1.54 (m, 2H), 1.47-1.36 (m, 1H), 1.32-1.19 (m, 3H), 1.02 (s, 3H), 1.00 (s, 3H), 0.80 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 168.1, 151.7, 135.3, 128.5, 127.9, 125.5, 125.4, 124.9, 122.6, 121.8, 117.1, 113.0, 112.8, 76.6, 63.1, 50.0, 41.2, 39.7, 38.6, 36.9, 34.6, 31.4, 27.7, 27.3, 26.8, 25.4, 21.8; in addition, the following characteristic peaks are for the minor diastereomer, ^{1}H NMR: δ 2.93 (d, 0.05 x 1H, *J* = 11.1 Hz); HRMS (ESI^+): m/z $[M+Na]^+$ calcd for $[C_{30}H_{34}BrNO_3Na]^+$ 558.1615, found 558.1619.

2.6.16 (1R,2S,5R)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(4-bromo-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3i**

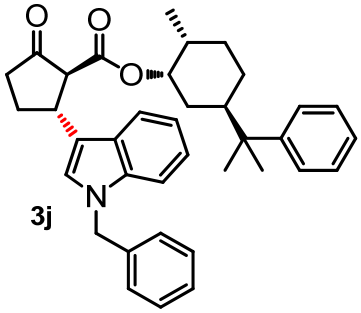


3i

Compound **3i**: Prepared according to the general procedure using β-keto ester **1aj** (89 mg, 130 mol-%) and 7-bromoindole (25 µL, 39 mg, 0.2 mmol, 100 mol%). Reaction time 24 h. Yield: 57 mg (53%) as a light brown crystalline solid. The diastereomeric ratio was 2.1:1.

R_f (20 % EtOAc/hexanes) = 0.19; mp. 80-85 °C; $[\alpha]_D$ = -1.4 (*c* 1.00, CH_2Cl_2); IR (film, cm^{-1}): 3369, 3057, 2954, 2923, 2870, 1749, 1708, 1335, 1268, 1186, 1117, 773, 739, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (br. s, 1H), 7.33 (dd, 1H, *J* = 7.5, 0.6 Hz), 7.31-7.28 (m, 1H), 7.25-7.21 (m, 2H), 7.18-7.13 (m, 2H), 7.03 (t, 1H, *J* = 7.8 Hz), 6.93 (d, 1H, *J* = 2.1 Hz), 4.80 (td, 1H, *J* = 10.7, 4.4 Hz), 4.59 (td, 1H, *J* = 8.8, 6.8 Hz), 3.23 (d, 1H, *J* = 9.2 Hz), 2.80-2.69 (m, 1H), 2.54-2.25 (m, 4H), 2.00 (ddd, 1H, *J* = 12.2, 10.6, 3.4 Hz), 1.93-1.82 (m, 2H), 1.56-1.50 (m, 1H), 1.50-1.43 (m, 1H), 1.23 (s, 3H), 1.15 (s, 3H), 1.00-0.92 (m, 2H), 0.79 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 168.0, 151.0, 138.2, 128.0, 125.7, 125.2, 124.7, 123.3, 121.7, 118.4, 114.2, 110.8, 76.4, 61.8, 50.2, 41.5, 40.1, 38.0, 37.3, 34.6, 31.6, 31.42, 27.6, 27.1, 26.0, 21.8; in addition, the following characteristic peaks are for the minor diastereomer, ^{1}H NMR: δ 4.37 (td, 1H, *J* = 10.6, 4.4 Hz), 3.53 (d, 1H, *J* = 9.0 Hz), 2.65-2.54 (m, 4H), 1.27 (s, 3H), 1.17 (s, 3H), 0.52 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR: δ 213.4, 168.9, 151.1, 137.9, 128.1, 125.8, 125.0, 124.4, 123.4, 115.3, 114.3, 110.7, 74.6, 60.3, 50.3, 39.9, 39.6, 39.0, 38.1, 34.3, 31.38, 30.8, 27.03, 27.00, 26.6, 21.6; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol 9:1, ^{1}H NMR: δ 10.89 (s, 0.12H, enol O-H); HRMS (ESI$^+$): m/z $[M+Na]^+$ calcd for $[C_{30}H_{34}BrNO_3Na]^+$ 558.1614, found 558.1641.

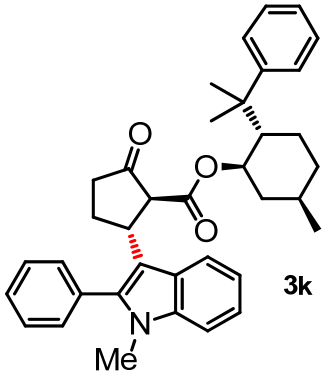
2.6.17 (1*S*,2*R*,5*R*)-2-methyl-5-(2-phenylpropan-2-yl)cyclohexyl 2-(1-benzyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3j**



Compound **3j**: Prepared according to the general procedure using β-keto ester **1aj** (89 mg, 130 mol-%) and indole **2j** (42 mg, 0.2 mmol, 100 mol%). Reaction time 23 h. Yield: 60 mg (55%) as a light brown crystalline solid. The diastereomeric ratio was 25.5:1.

R_f (20 % EtOAc/hexanes) = 0.41; mp. 66-70 °C; $[\alpha]_D$ = -7.8 (*c* 1.00, CH_2Cl_2); IR (film, cm^{-1}): 3055, 3030, 2954, 2920, 2869, 1753, 1716, 1468, 1455, 1331, 1267, 1182, 1116, 741, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (br. d, 1H, *J* = 7.6 Hz), 7.32-7.27 (m, 4H), 7.22 (dd, 1H, *J* = 7.0, 1.0 Hz), 7.18 (dd, 1H, *J* = 6.4, 1.2 Hz), 7.16-7.12 (m, 3H), 7.05-7.01 (m, 2H), 7.02-6.97 (m, 1H), 6.96-6.93 (m, 1H), 6.92 (s, 1H), 5.28 (d, 2H, *J* = 2.3 Hz), 4.78 (td, 1H, *J* = 10.7, 4.3 Hz), 3.92 (td, 1H, *J* = 10.6, 6.0 Hz), 3.00 (d, 1H, *J* = 10.6 Hz), 2.55-2.36 (m, 3H), 2.16-2.05 (m, 1H), 2.00-1.90 (m, 2H), 1.65-1.54 (m, 2H), 1.50 (ddt, 1H, *J* = 13.4, 3.3 Hz), 1.46-1.38 (m, 1H), 1.34-1.13 (m, 3H), 1.00 (s, 3H), 0.98 (s, 3H), 0.84 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.3, 168.3, 151.3, 137.5, 137.2, 128.9, 127.9, 127.8, 127.3, 127.0, 125.5, 124.9, 124.6, 122.3, 120.0, 119.4, 116.4, 109.9, 76.3, 62.6, 50.2, 50.1, 41.4, 39.8, 38.6, 37.5, 34.6, 31.4, 28.1, 26.9, 26.3, 21.8; in addition, the following characteristic peaks are for the minor diastereomer, ^{1}H NMR: δ 3.15 (d, 0.025 x 1H, *J* = 11.0 Hz); in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol 16:1, ^{1}H NMR: δ 10.83 (s, 0.06H, enol O-H); HRMS (ESI^+): m/z $[M+Na]^+$ calcd for $[C_{37}H_{41}NO_3Na]^+$ 570.2979, found 570.2962.

2.6.18 (1R,2S,5R)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(1-methyl-2-phenyl-1H-indol-3-yl)-5-oxocyclopentanecarboxylate **3k**

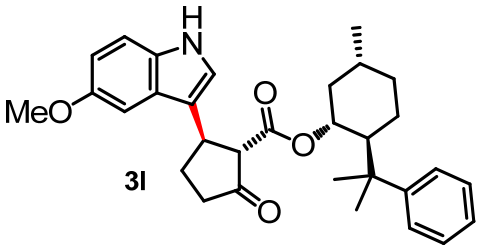


3k

Compound **3k**: Prepared according to the general procedure using β-keto ester **1aj** (89 mg, 130 mol-%) and indole **2k** (42 mg, 0.2 mmol, 100 mol%). Reaction time 20 h. Yield: 59 mg (54%) as a light yellow crystalline solid. The diastereometric ratio >25:1.

R_f (20 % EtOAc/hexanes) = 0.47; mp. 88-90 °C; $[\alpha]_D$ = +18.6 (*c* 1.00, CH_2Cl_2); IR (film, cm^{-1}): 3055, 2954, 2922, 2870, 1752, 1718, 1584, 1469, 1363, 1337, 1270, 1183, 1108, 742, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dt, 1H, *J* = 7.9, 0.8 Hz), 7.33 (dt, 1H, *J* = 8.2, 0.9 Hz), 7.24 (obs. ddd, 1H, *J* = 8.1, 7.0, 1.0 Hz), 7.15 (ddd, *J* = 7.9, 7.1, 0.9 Hz), 4.65 (td, 1H, *J* = 10.7, 4.3 Hz), 3.94 (obs. td, 1H, *J* = 11.6, 7.0 Hz), 3.75 (d, 1H, *J* = 12.3 Hz), 3.55 (s, 3H), 2.60-2.47 (m, 1H), 2.44-2.29 (m, 2H), 2.27-2.16 (m, 1H), 1.90 (dddd, 1H, *J* = 12.3, 3.8, 1.9 Hz), 1.69 (obs. ddd, 1H, *J* = 12.0, 10.7, 3.4 Hz), 1.65-1.55 (m,1H), 1.51-1.43 (m, 1H), 1.41-1.32 (m, 1H), 1.32-1.27 (m, 1H), 1.27-1.21 (m, 1H), 1.19-1.09 (m, 1H), 0.92 (s, 3H), 0.82 (d, 3H, *J* = 6.5 Hz), 0.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6, 168.4, 150.2, 138.7, 137.6, 131.7, 131.0, 128.6, 128.5, 127.7, 125.7, 125.6, 125.1, 121.8, 119.5, 119.4, 111.5, 109.9, 76.1, 61.3, 50.2, 41.4, 39.9, 39.1, 38.5, 34.5, 31.3, 30.8, 28.6, 28.0, 27.1, 24.2, 21.7; in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol 20:1, ^{1}H NMR: δ 10.47 (s, 0.05H, enol O-H); HRMS (ESI^+): m/z $[M+Na]^+$ calcd for $[C_{37}H_{41}NO_3Na]^+$ 570.2979, found 570.2987.

2.6.19 (1*R*,2*S*,5*R*)-5-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(5-methoxy-1H-indol-3-yl)-5-oxocyclopentanecarboxylate

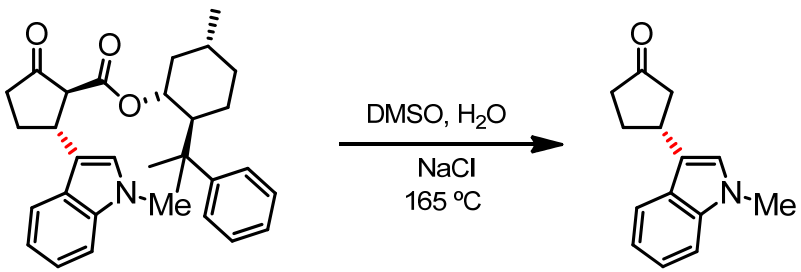


3l

Compound **3l**: Prepared according to the general procedure using β-keto ester **1aj** (89 mg, 130 mol-%) and indole **2l** (30 mg, 0.2 mmol, 100 mol%). Reaction time 17 h. Yield: 40 mg (41%) as a light brown crystalline solid. The diastereomeric ratio was 13.1:1.

R_f (20 % EtOAc/hexanes) = 0.15; mp. 59-62 °C; $[\alpha]_D$ = +18 (*c* 0.10, CH_2Cl_2); IR (film, cm^{-1}): 3398, 3055, 2954, 2922, 2852, 1749, 1714, 1486, 1456, 1442, 1279, 1215, 1114, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (br. s, 1H), 7.23 (s, 1H), 7.15 (d, 1H, *J* = 2.2 Hz), 6.96 (s, 6H), 6.88 (dd, 1H, *J* = 8.8, 2.4 Hz), 4.75 (td, 1H, *J* = 10.7, 4.2 Hz), 3.90 (s, 3H), 3.96-3.84 (m, 1H), 2.88 (d, 1H, *J* = 10.7 Hz), 2.57-2.35 (m, 3H), 2.15-2.04 (m, 1H), 2.01-1.88 (m, 2H), 1.60-1.48 (m, 2H), 1.47-1.37 (m, 1H), 1.26 (s, 3H), 0.98 (s, 3H), 0.94 (s, 3H), 0.84 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 168.6, 154.2, 151.4, 131.9, 127.8, 127.2, 125.5, 124.9, 121.3, 117.1, 112.7, 112.1, 101.8, 76.4, 62.8, 56.1, 50.2, 41.4, 39.7, 38.7, 37.5, 34.7, 31.5, 29.8, 27.6, 26.9, 26.7, 25.8, 21.8; in addition, the following characteristic peaks are for the minor diastereomer, ^{1}H NMR: δ 3.03 (d, 0.05 x 1H, *J* = 10.8 Hz) in addition, the following characteristic peaks are for the minor enol tautomer, keto/enol 31:1, ^{1}H NMR: δ 10.78 (s, 0.03H, enol O-H); HRMS (ESI^+): m/z $[M+Na]^+$ calcd for $[C_{31}H_{37}NO_4Na]^+$ 510.2615, found 510.2620.

2.7 Decarboxylation of 3aj



3aj
20:1 dr

6
62%, *er* 98:2

3aj (82 mg, 0.17 mmol, 100 mol-%) and NaCl (51 mg, 0.86 mmol, 800 mol-%) was dissolved into a mixture of DMSO (5 mL) and H_2O (0.5 mL).[6] The reaction mixture was refluxed for 3 h at 165 °C. H_2O (15 mL) was added and the mixture was extracted with toluene (3x10 mL). The combined organic layers were washed with brine (30 ml), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography to afford pure decarboxylated product **6**. Yield: 23 mg (62%, *er* 98:2) as a brownish oil.

The enantiomeric ratio (*er*) of the product was determined by GC in comparison to the corresponding racemic sample using a SUPELCO Astec CHIRALDEX B-DM Column (ø 0.25 mm × 30 m). The racemic sample was obtained from product **3a** (103 mg) in 82% yield (81%) using the same procedure.

R_f (30% EtOAc/hexanes) = 0.32; $[\alpha]_D$ = +6 (*c* = 0.42, CH_2Cl_2); IR (film, cm^{-1}): 3051, 2957, 1735, 1474, 1242, 1153, 739; ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (dt, 1H, *J* = 7.9, 0.9 Hz), 7.34 (dt, 1H, *J* = 8.2, 1.0 Hz), 7.28 (ddd, 1H, *J* = 8.0, 6.8, 1.2 Hz), 7.16 (ddd, 1H, *J* = 8.0, 6.7, 1.3 Hz), 6.86 (d, 1H, *J* = 0.7 Hz), 3.77 (s, 3H), 2.80 (dt, 0.4 x 1H, *J* = 7.7, 1.2 Hz), 2.74 (dt, 0.6 x 1H, *J* = 7.6, 1.2 Hz), 2.60-2.26 (m, 4H), 2.21-2.07 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 219.4, 137.5, 127.1, 124.9, 122.0, 119.2, 119.0, 109.5, 45.5, 38.2, 33.8, 32.7, 30.2; HRMS (ESI^+): m/z [M+Na] calcd for [$C_{14}H_{15}NONa$] 236.1051, found 236.1054.

2.8 Crystallographic Details of $[Pd_2TFA_2(3a)_2]$

Ethyl 2-oxocyclopentanecarboxylate **1a** (16 mg, 15 µL, 0.1 mmol), 1-methylindole **2a** (13 mg, 13 µL, 0.1 mmol) and $Pd(TFA)_2$ (33 mg, 0.1 mmol) were dissolved in EtOAc (1 mL) and stirred 5 min. The solution was filtered through a 0.2 µm GHP membrane to remove solids. Crystals suitable for single crystal X-ray diffraction analyses were obtained by a slow diffusion of hexane in a solution of the compounds in EtOAc at -18 °C over 1 month.

For details of the crystal structure, please see the associated CIF file.

[6] Taber, D. F.; Saleh, S. A.; Korsmeyer, R. W. *J. Org. Chem.* **1980**, *45*, 4699.

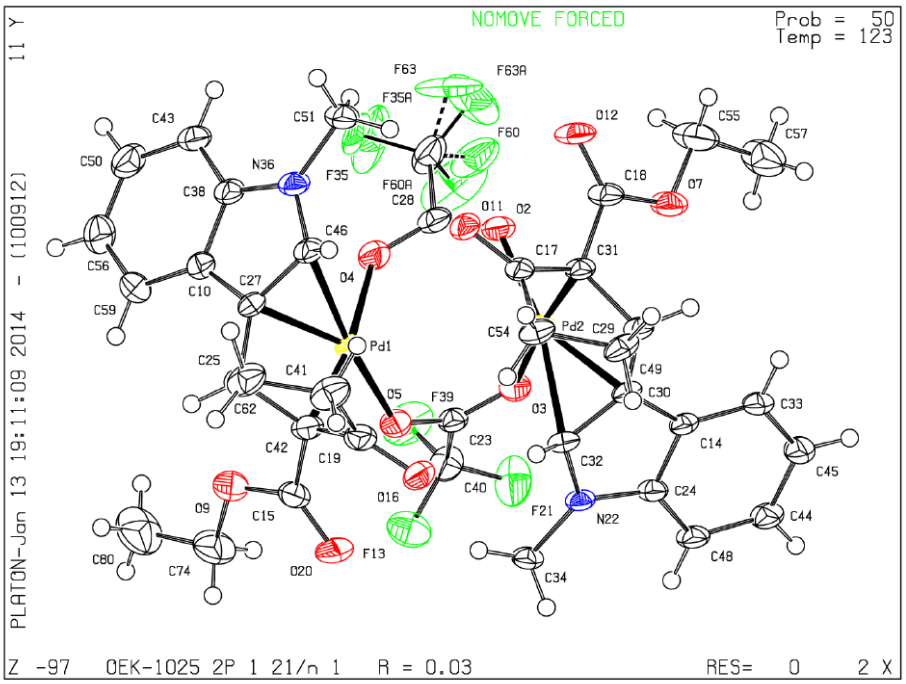


Figure S2. ORTEP plot of the crystal structure of [Pd_2TFA_2(**3a**)$_2$].

3 Details of Kinetic Experiments

General Methods: Kinetic experiments were carried out by monitoring the reaction progress with ^{1}H NMR (400 MHz or 300 MHz) with dibenzyl ether as the internal standard. The spectra were processed and integrated with MestReNova (8.0.2) and the data was processed in Microsoft Excel (2010). The graphs were plotted with OriginPro (8.6). The reported initial rates are the average of at least two independent experiments.

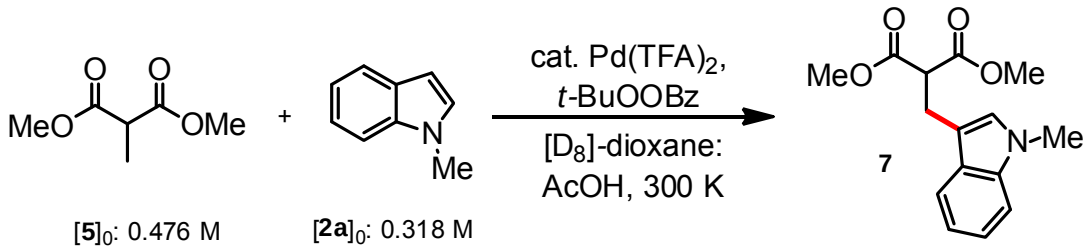
General Procedure: A 4 mL vial was charged with the reagents, dibenzyl ether (25 µL as an internal standard) and the solvents (d_8-dioxane and acetic acid 100 µL). The total volume was adjusted to 630 µL with d_8-dioxane. The mixture was stirred for 1 to 3 min at 27 °C in an aluminium heating block to stabilize the reaction temperature. The mixture was then transferred into to a standard 5 mm bore NMR tube and the reaction was monitored by ^{1}H NMR scans at 1 or 2 min intervals (400 MHz or 300 MHz). The probe temperature was set to 300 K and the spinning rate to 20 Hz.

Table S1. Characteristic ^{1}H NMR resonances used for following the concentrations of the monitored species.[7]

Species	δ
1a	3.10 (1H, t)
D_6-1a	3.08 (1H, s)
2a	3.69 (3H, s)
D-2a	3.69 (3H, s)
3a	3.64 (3H, s)
D-3a	3.64 (3H, s)
D_5-3a	3.65 (3H, s)
D_6-3a	3.65 (3H, s)
4a	8.25 (1H, t)
***t*BuOOBz**	1.33 (9H, s)
Dibenzyl ether	4.49 (4H, s)

[7] The chemical shifts are reported in ppm relative to 1,4-dioxane-D_8 (δ 3.53) for ^{1}H NMR.

3.1 Reaction with Malonate 5



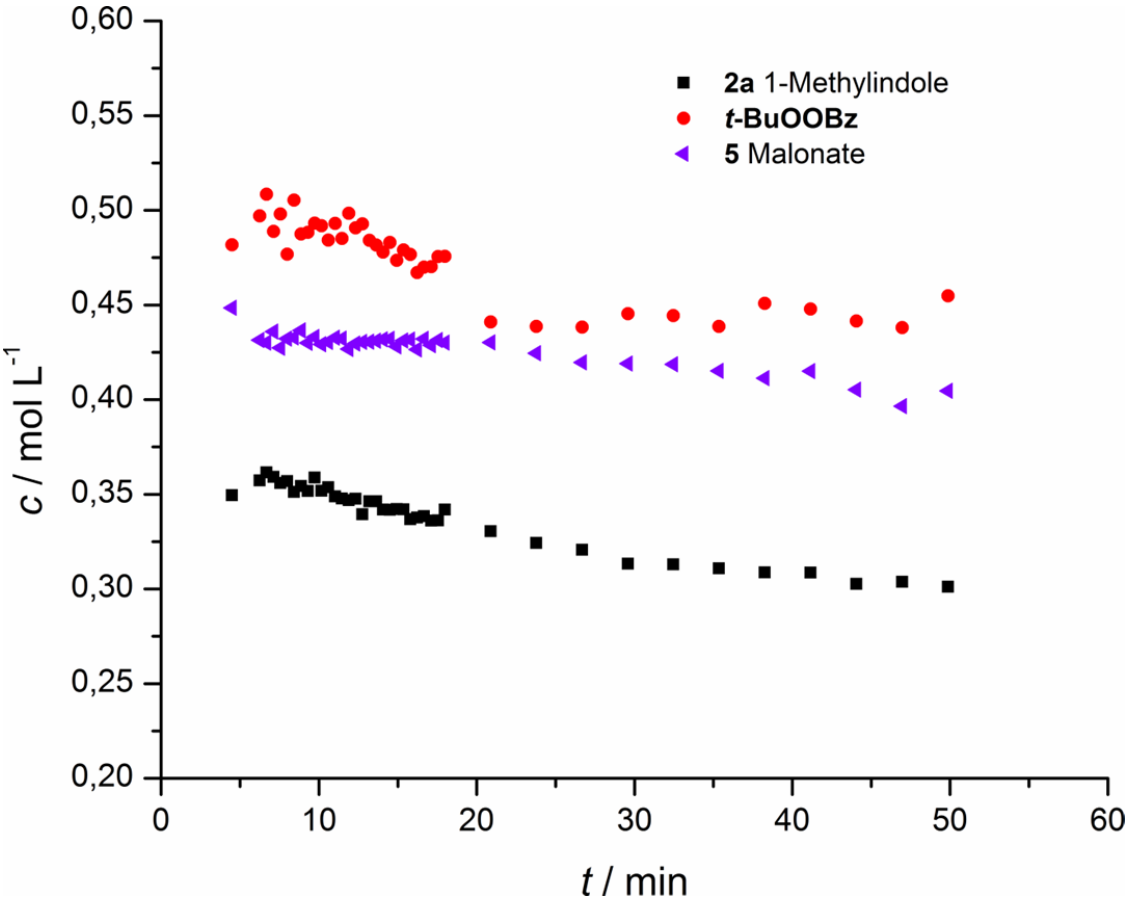


Figure S3. Monitoring of the temporal progress of the reaction with dimethyl methylmalonate **5.** Reaction conditions: $[\mathbf{5}]_0$= 0.476 M, $[\mathbf{2a}]_0$= 0.318 M, $[t\text{BuOOBz}]_0$= 0.413 M, 10 mol% $Pd(TFA)_2$, 4:1 [D8]-dioxane/AcOH, 300 K.

Neither the coupling product **7** nor the dehydrogenation product of **5** could be detected.

3.2 Kinetics with Both Deuterated Starting Materials

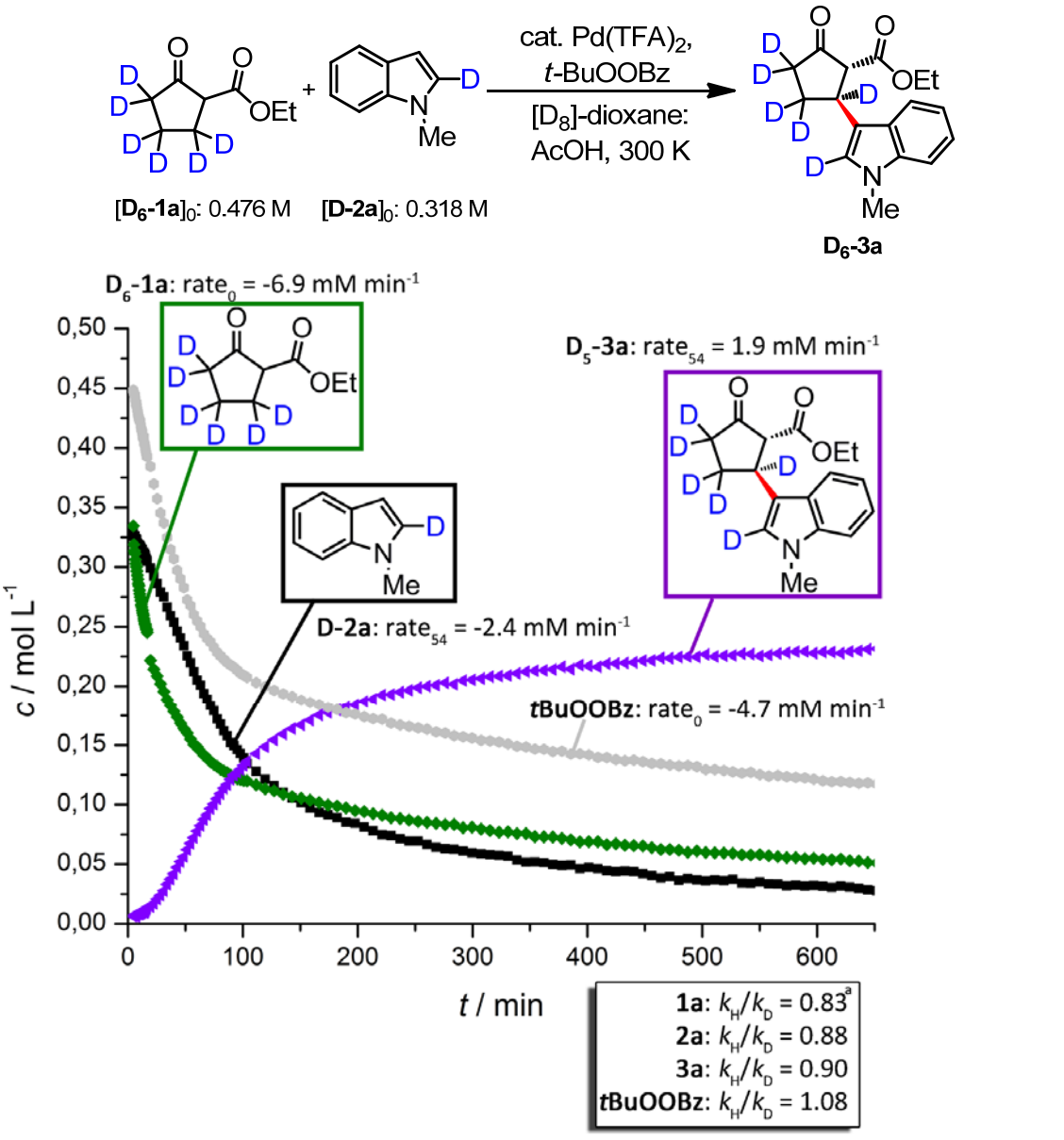
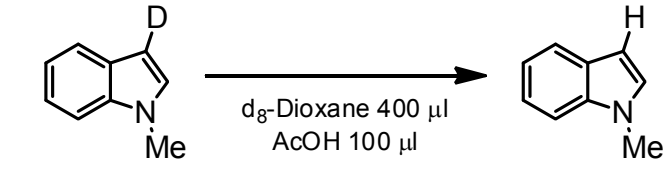


Figure S4. Monitoring of the temporal progress of the reaction with both deuterated starting materials**.** Reaction conditions: [**D6-1a**]$_0$= 0.476 M, [**D-2a**]$_0$= 0.318 M, [*t*BuOOBz]$_0$= 0.413 M, 10 mol% Pd(TFA)$_2$, 4:1 [D8]-dioxane/AcOH, 300 K. Rates are averages of two experiments. a) The dehydrogenation step produces exchangeable deuterium which may lead to isotopic scrambling at the α-proton. The background exchange may affect the observed KIE in this experiment since the integral of the α-proton of **D6-1a** is used to monitor [**D6-1a**]. Similar considerations apply to the experiment in Figure 2b in the main manuscript.

3.3 Kinetics of D/H Exchange with 3-Deuterium-1-methylindole

These experiments demonstrated that H/D exchange takes place at a rate that is comparable to the rate of the overall reaction under either acid (TFA) or $Pd(TFA)_2$ catalysis.



[**3-D-2a**]$_0$: 0.318 M

2a

Initial rate: 0.04 mM min^{-1}

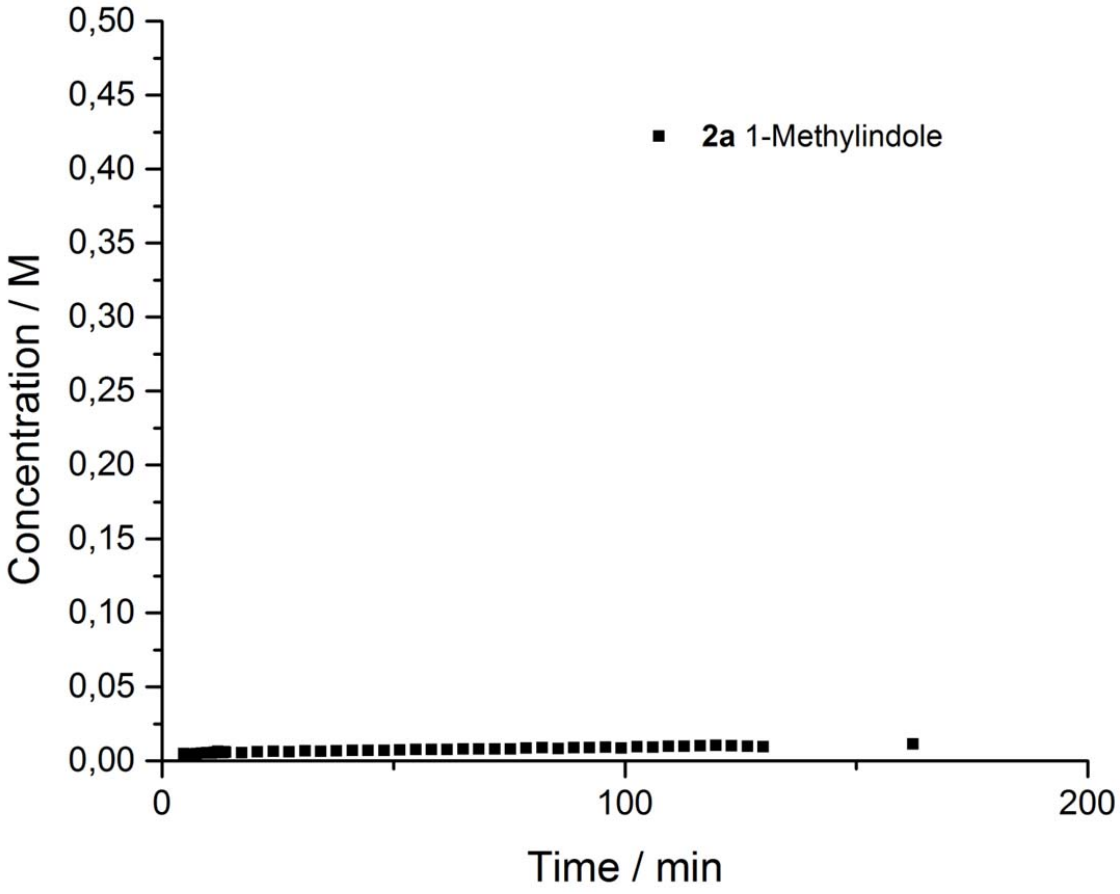


Figure S5. Monitoring of the temporal progress of H/D exchange with **3-D-2a** and the reaction solvent.

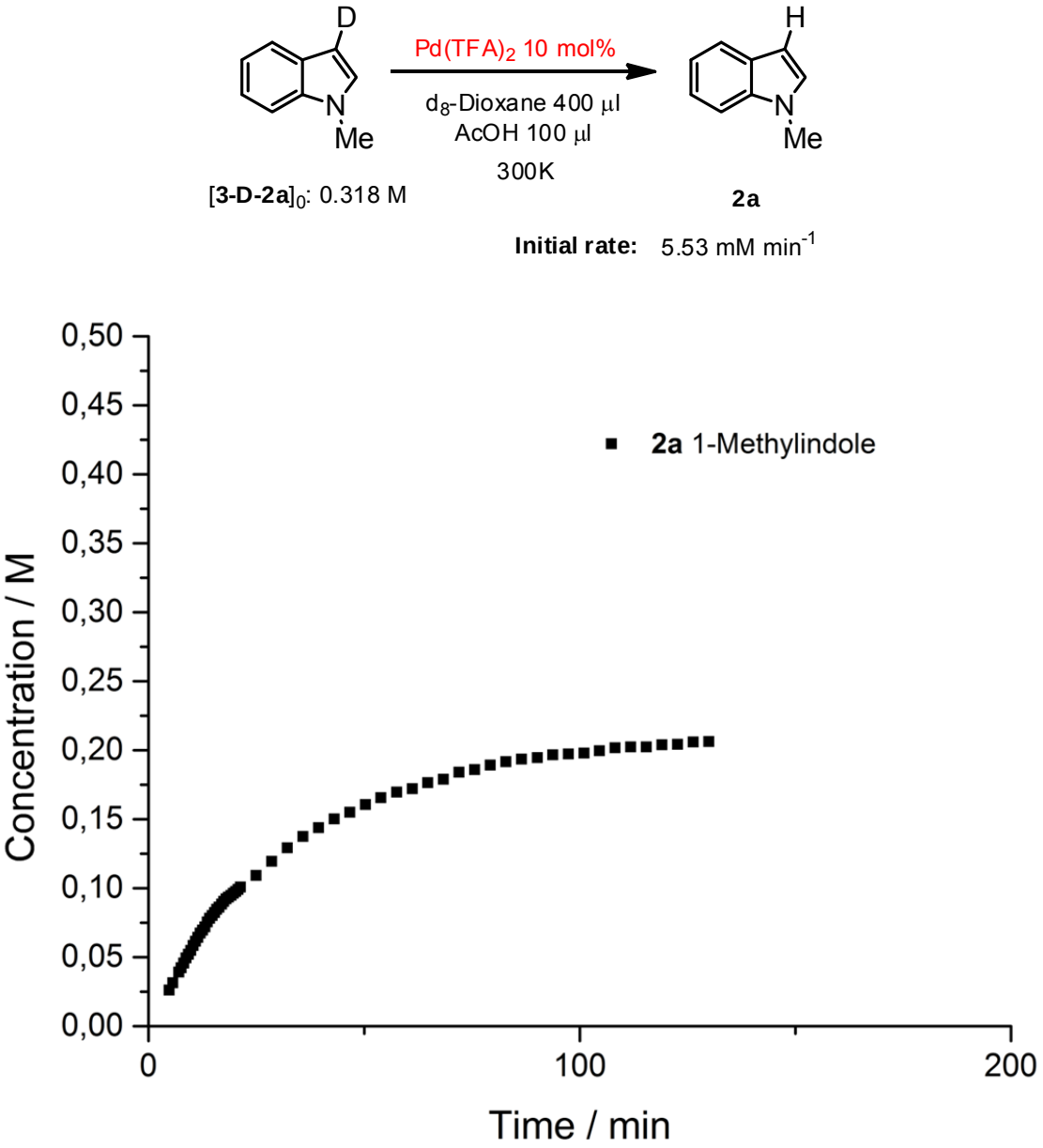


Figure S6. Monitoring of the temporal progress of H/D exchange with **3-D-2a**, with added $Pd(TFA)_2$ catalyst.

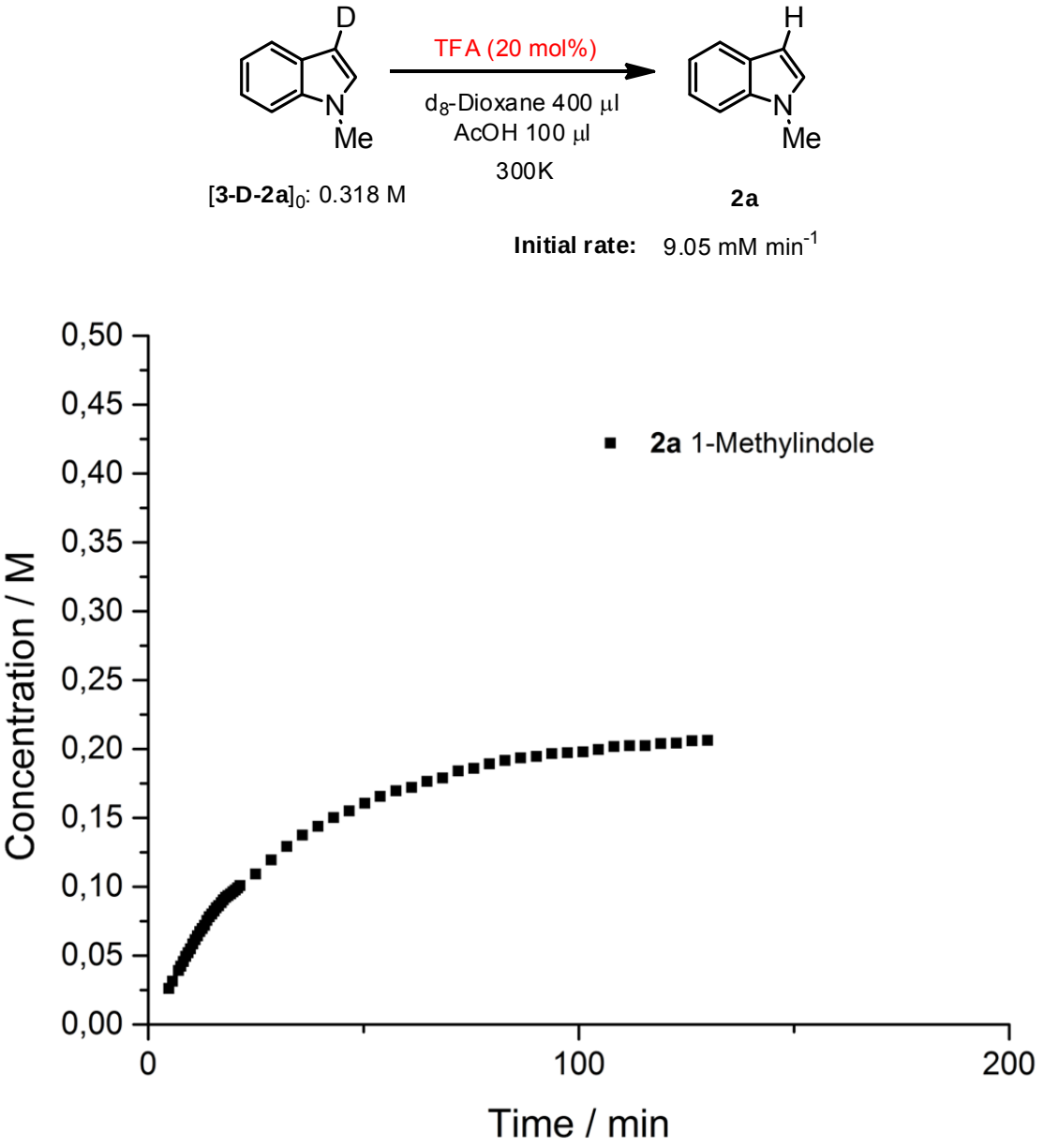


Figure S7. Monitoring of the temporal progress of H/D exchange with **3-D-2a**, with added TFA catalyst.

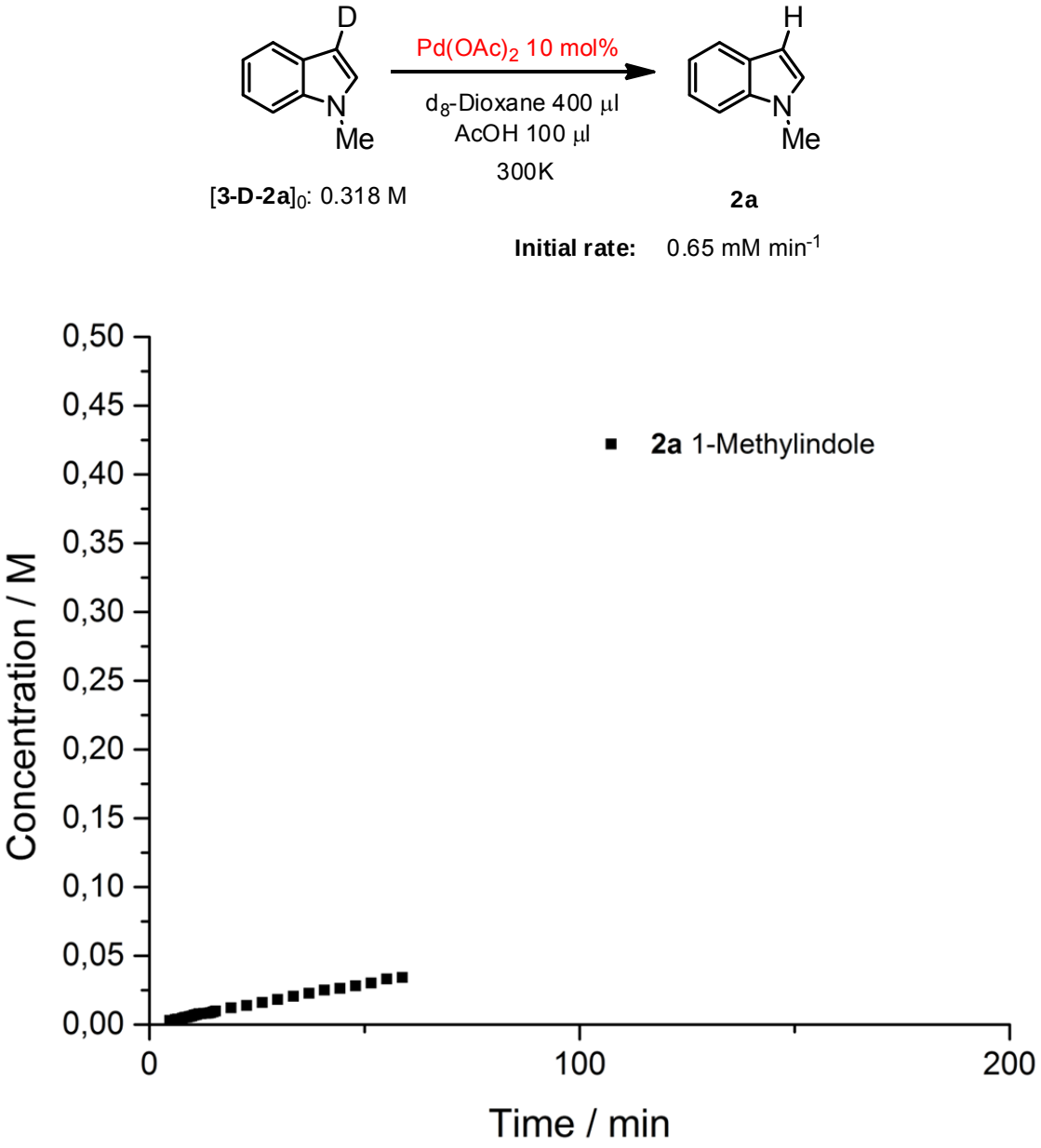
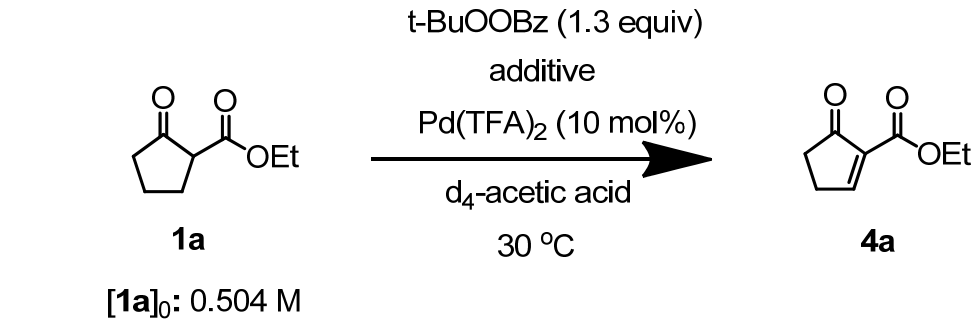


Figure S8. Monitoring of the temporal progress of H/D exchange with **3-D-2a**, with added $Pd(OAc)_2$ catalyst.

3.4 Ligand-Assisted Pd(II)-Catalyzed Dehydrogenations of β-Ketoester 1a

To an oven-dried 4-mL vial was charged with $Pd(TFA)_2$ (6.7 mg, 0.02 mmol, 10 mol%, 33.6 mM) and d_4-acetic acid (500 μL). With gentle shaking, the additive was added to the mixture. The solution was transferred to another oven-dried 4-mL vial containing **1a** (45 μL, 0.3 mmol, 1.5 equiv, 0.504 M), *t*-BuOOBz (50 μL, 0.26 mmol, 1.3 equiv, 0.437 M) and Bn_2O (25 μL, as ^1H NMR internal standard) using a disposable pipette (all Pd(II) should dissolve completely in this stage; t_0 represents the time of mixing). After mixing for approx. 30 sec., the resulting mixture was transferred to a NMR tube. Continuous ^1H NMR experiments performed in a preheated NMR probe at 30 ^oC with tube spinning (each ^1H NMR experiment consists of 16 scans). Reaction progress was monitored on a regular basis and, in most cases, beyond 50% conversion of the starting materials.

Enone **2a** was identified according to its characteristic ^1H NMR signals (250 MHz, d_4-acetic acid) at 8.50 (t, 1H, J = 2.8 Hz) and 2.75-2.69 ppm (m, 2H). [**2a**] of different time-points were determined by the comparison of its peak area integration to that of the internal standard (Bn_2O), which has a characteristic ^1H NMR signal peak at 4.58 ppm (s, 4H).



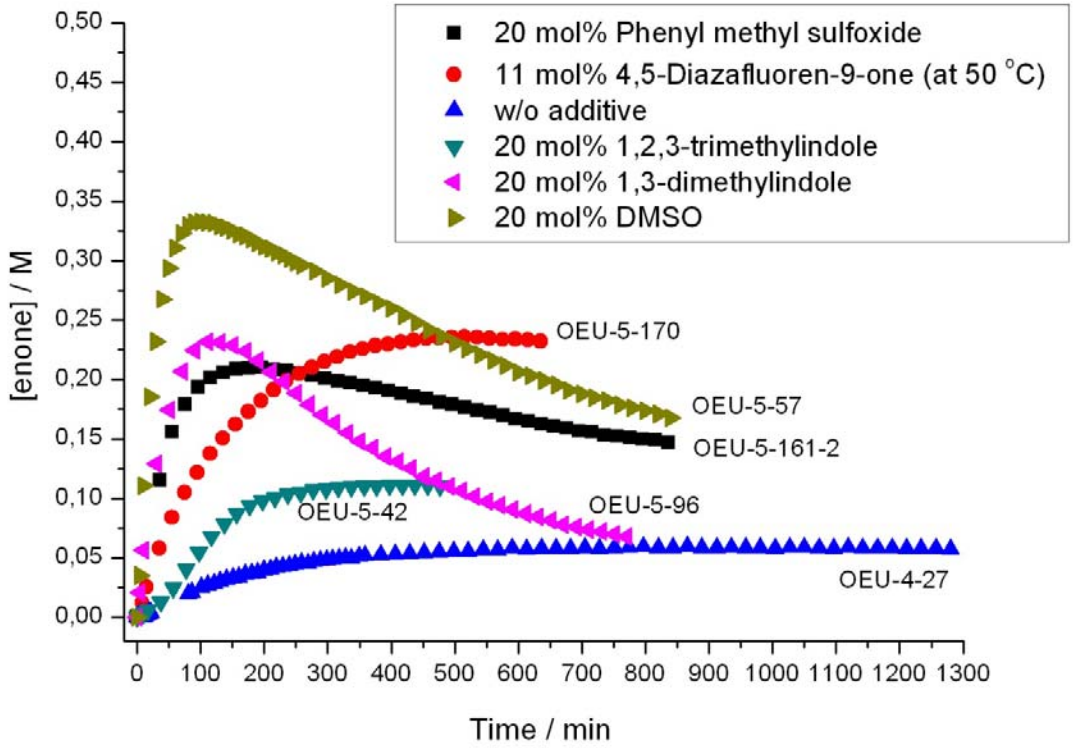


Figure S9. Monitoring of the temporal progress of the dehydrogenation reaction with **1a** using various sulfoxide, indole, and 4,5-diazafluorenone ligands.

In general, indole, sulfoxide and electron-deficient bidentate pyridine-based derivatives are three classes of additive that could accelerate Pd(II)-catalyzed dehydrogenation of β-ketoester **1a**.

4 Computational Details

In the present study, the geometries of the investigated species (reactants, products, intermediates and transition states) were optimized using density functional theory at the ωB97X-D/SDDP level, where ωB97X-D refers to the dispersion-corrected range-separated hybrid exchange-correlation functional developed by Chai and Head-Gordon,[8,9] and SDDP denotes a basis set including the Stuttgart–Dresden relativistic small core ECP basis set for Pd and the Dunning/Huzinaga double-zeta plus polarization all electron basis set for the lighter atoms.[10] For each optimized structure, additional single-point energy calculation was carried out using the same functional but with a larger basis set (additional diffuse functions on lighter atoms with exponents α_p^H = 0.036, α_d^C = 0.0438, α_d^N = 0.0639, α_d^O = 0.0845, α_d^F = 0.1076). This basis set is referred to as SDDP'.

The initial structures used in geometry optimizations were obtained from Monte Carlo conformational search using the OPLS_2005 force fields as implemented in the *MacroModel* software.[11] In these calculations, the metal-ligand bond distances were fixed at arbitrarily chosen values (no force field parameters exist for Pd atom). For some of the reaction intermediates, additional conformational screening computations were performed by scanning the ωB97X-D/SDDP potential energy surface (PES) along a particular structural parameter, or by simply considering all possible isomeric forms systematically. The initial structures for transition state (TS) calculations were determined similarly, i.e. via PES scan calculations with respect to selected internal coordinates, which were then followed by ωB97X-D/SDDP TS optimizations. For all located transition states, intrinsic reaction coordinate (IRC) calculations were performed to identify the energy minima on both reactant and product sides of the transition state.[12]

The nature of the stationary points were characterized via vibrational analysis. The harmonic frequencies were computed at the ωB97X-D/SDDP level. These data were also utilized to estimate the zero-point energies as well as the thermal and entropic

[8] Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615. (b) Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, *128*, 084106.
[9] For dispersion corrections, see: Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.
[10] (a) Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. *J. Phys. Chem.*, **1993**, *97*, 5852; (b) Dunning, T. H. Jr. *J. Chem. Phys.*, **1970**, *52*, 2823; (c) Dunning, T. H. Jr.; Hay, P. J. in *Modern Theoretical Chemistry, Vol. 3*, ed.; Schaefer III, H. F., Plenum Press: New York, 1976.
[11] *Macromodel embedded in Maestro suite (Version 9.1)*; Schrödinger, Inc.: Portland, OR, 2010.
[12] Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

contributions to the Gibbs free energies. The thermochemical data were obtained within the ideal gas – rigid rotor – harmonic oscillator approximation for T = 298.15K and c = 1 mol/dm^3 conditions. The solvent effects were also taken into account at the ωB97X-D/SDDP level by estimating the solvation free energies (solvent=1,4-dioxane) by using the integral equation formalism variant of the polarizable continuum model (IEFPCM).[13] The atomic radii and non-electrostatic terms in the IEFPCM calculations were those introduced recently by Truhlar and coworkers (SMD solvation model).[14]

The energy values reported in the paper correspond to solution phase Gibbs free energies that are based on ωB97X-D/SDDP' electronic energies and all additional terms computed at the ωB97X-D/SDDP level (see Table C1). All DFT calculations were carried out with the *Gaussian 09* software.[15]

We note that the ωB97X-D functional was found to be a very promising DFT method in recent benchmark studies[16,17] yielding reasonably accurate data for general main group thermochemistry, kinetics and noncovalent interactions as well as for structural parameters of metal-ligand systems (all relevant to our present work). It should be, however, taken into account that the mean absolute error of the wB97X-D method for predicting reaction energies is 2.5 kcal/mol.[16] Considering the empirical ingredients of the polarizable continuum solvent model and the approximations employed in the calculation of gas-phase entropic contributions, the error bar on the relative Gibbs free energies reported in the present work is expected to be even larger (about 3-4 kcal/mol). All our conclusions in this paper were drawn in the light of these uncertainties.

[13] Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Struct. (Theochem)* **1999**, *464*, 211.
[14] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B*, **2009**, *113*, 6378.
[15] *Gaussian 09, Revision A.02*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, **2009**.
[16] Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670.
[17] Minenkov, Y.; Singstad, Å.; Occhipinti, G.; Jensen, V. R. *Dalton Trans.* **2012**, *41*, 5526.

4.1 Alternative C-C bond Formation Pathways

We examined several alternative reaction pathways for the C–C bond formation between indole **2a** and enone **4a** (cycle B). Herein, we summarize our findings.

4.1.1 a) TFA-catalyzed C-C Coupling (Brønsted Acid Catalyzed Pathway).

The main steps of the acid-catalyzed C–C coupling are summarized in Figure S10. Starting from the ternary complex of **2a**, **4a** and TFAH, the transition state corresponding to the C–C bond formation (**TS$_{add}$**) could be easily located. This process is formally a Michael addition of indole **2a** (nucleophile) to enone **4a** (electrophile). TFAH acts as a Bronsted acid catalyst via H-bonding to the keto carbonyl group. Transition state **TS$_{add}$** is predicted to be 17.7 kcal/mol above the separated reactants (**2a** + **4a** + TFAH). Proton transfer to the adduct species takes place in concert with the C–C bond formation leading to **int$_{add}$**.

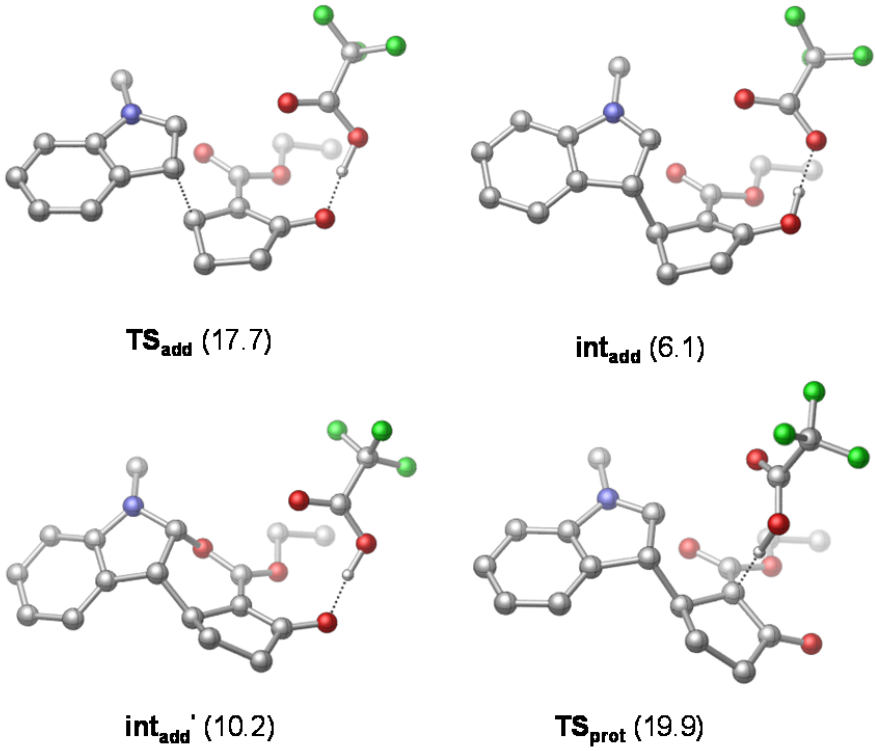


Figure S10. Key transition states and intermediates in the TFAH-catalyzed C–C coupling.

Deprotonation of **int_{add}** by the TFA anion results in a cyclic fused dihydropyran intermediate (**int_{add}'**)[18] lying slightly higher in free energy. The protonation of the dihydropyran (via transition state **TS_{prot}**) is found to be the rate-determining step of this mechanism.[19] The computed activation barrier is 19.9 kcal/mol., which is very similar to that found for the Pd(II)-catalyzed pathway discussed in the manuscript. This step also determines the relative *trans* stereochemistry of the product, although it is also possible that the *trans* stereochemistry is simply a result of thermodynamic equilibration. Finally, indole is deprotonated at C3. This process is very facile (the corresponding transition state is at 6.3 kcal/mol).

These results suggest that the acid-catalyzed C–C coupling pathway represents a feasible alternative mechanistic scenario.

4.1.2 b) Friedel-Crafts type C-C Coupling (Pd^{2+} as a Lewis Acid)

Assuming that the Pd catalyst can act as a Lewis acid in the activation of enone, the C-C bond formation may occur via a $Pd(TFA)_2$(**4a**) intermediate involving a chelating enone ligand (see Figure S11a). The located transition state and the corresponding product state of this process are depicted in Figure S11b and S11c, respectively.

The C-C coupling along this pathway takes place via a relatively small barrier (15.6 kcal/mol) and yields a zwitterionic iminium-enolate intermediate (**int_{FC}**) lying only 4.1 kcal/mol above the reference level ($Pd(TFA)_2$(**2a**) + **4a**).[20] The reaction proceeds by deprotonation of the indole moiety of the adduct species, however, the hydrogen atom involved in this step is not easily accessible by the TFA ligands in this structure (see Figure S11c). Consequently, the transition state corresponding to the direct proton-shift to one of the TFA ligands represents a fairly high barrier (26.6 kcal/mol), which is notably larger than that predicted for the mechanism discussed above (19.7 kcal/mol; see Figure S10). The deprotonation transition state is illustrated in Figure S12a.

[18] A similar structure has been characterized experimentally. See: Ziegler, R. E.; Tan, S.-J.; Kam, T.-S.; Porco, J. A., Jr. *Angew. Chem. Int. Ed.* **2012**, *51*, 9348.

[19] For an example of a rate-determining protonation in a conjugate addition, see: Sahoo, G.; Rahaman, H.; Madarász, Á.; Pápai, I.; Melarto, M.; Valkonen, A.; Pihko, P. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 13144

[20] Note that the reference level is identical to that used for the pathway discussed in the manuscript.

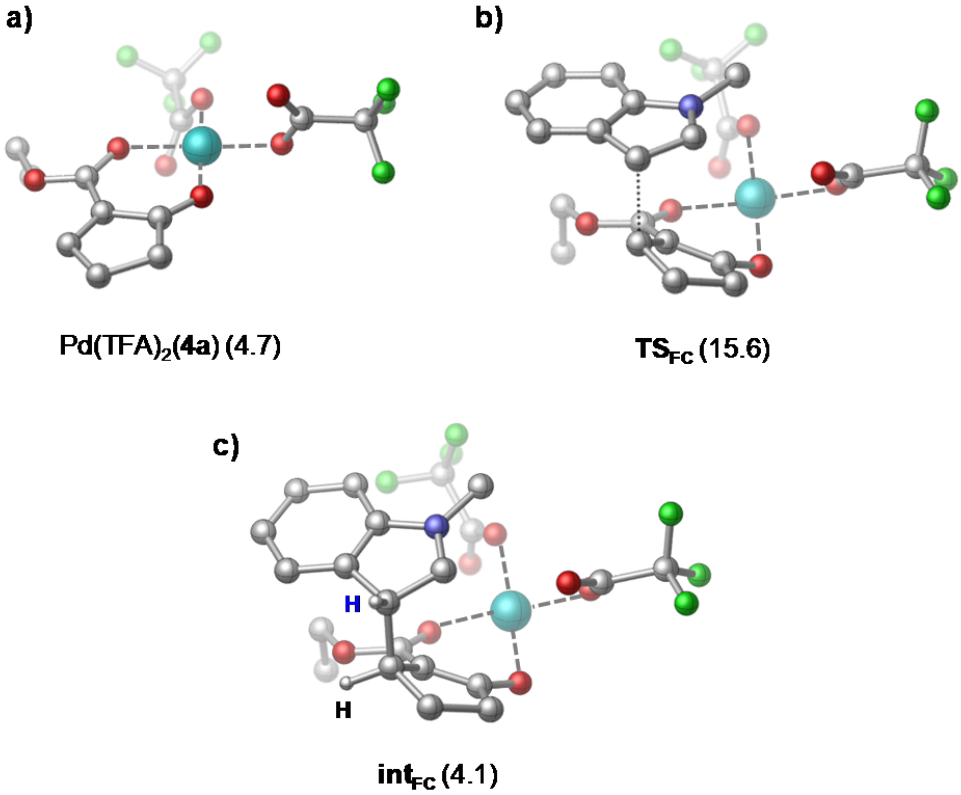


Figure S11: Stationary points identified for the Friedel-Crafts C-C bond formation pathway: a) reactant state prior to C-C bond formation, b) transition state, c) intermediate formed upon the C-C coupling. Relative Gibbs free energies (in kcal/mol, with respect to $Pd(TFA)_2$(**2a**) + **4a**) are shown in parenthesis. Metal-ligand bonds are indicated by dashed lines, whereas the evolving C-C bond is highlighted by dotted line. For clarity of figures, hydrogen atoms are omitted, except those of the new C-C bond in $\mathbf{int}_{FC}$. H atom involved in the next step is highlighted in blue.

A more favored deprotonation elementary step could be identified computationally, which corresponds to a different coordination mode of the enolate (via Pd-C bond as shown in Figure S12b); however, the ligand rearrangement to achieve this coordination mode is hindered kinetically. We find that the transition state leading to the cleavage of the Pd-O bonds in $\mathbf{int}_{FC}$ lies 27.1 kcal/mol above the reference level (for TS structure, see Figure S12c).

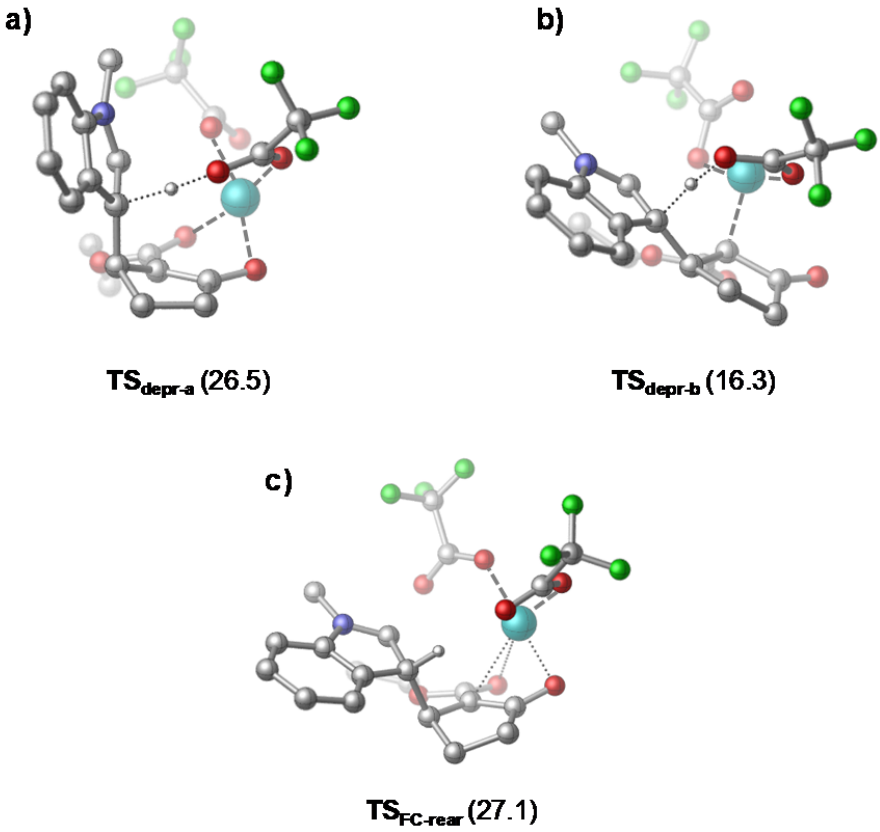
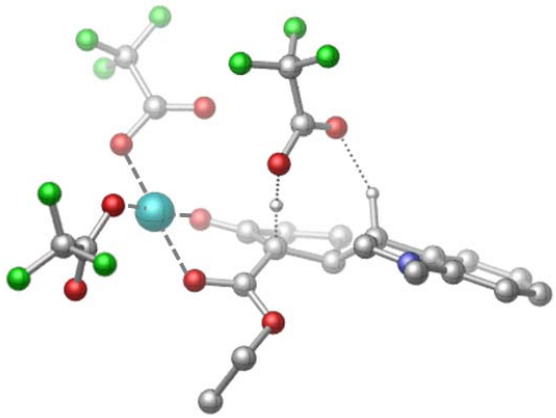


Figure S12: Indole deprotonation pathways in the Friedel-Crafts mechanism: a) direct deprotonation from **int$_{FC}$**, b) deprotonation from Pd-C bonded adduct, c) transition state of Pd-O cleavage in **int$_{FC}$**. Relative Gibbs free energies (in kcal/mol, with respect to Pd(TFA)$_2$(**2a**) + **4a**) are shown in parenthesis. Metal-ligand bonds are indicated by dashed lines, whereas the evolving/cleaved bonds are highlighted by dotted line. For clarity of figures, hydrogen atoms are omitted, except those involved in the proton-shift.

We also envisioned that the proton transfer occurring after the C-C bond formation step could be facilitated by and external (not coordinated) HTFA molecule. This scenario is consistent with the acidic conditions used for the reaction. The located transition state is depicted in Figure S13 and it represents a barrier of 22.3 kcal/mol with respect to the Pd(TFA)$_2$(**2a**) + **4a** + HTFA state.



TS_{HTFA} (22.3)

Figure S13: Transition state corresponding to the proton transfer mediated by an external HTFA molecule in the Friedel-Crafts mechanism. Relative Gibbs free energies (in kcal/mol, with respect to $Pd(TFA)_2$(**2a**) + **4a** + HTFA) are shown in parenthesis. Metal-ligand bonds are indicated by dashed lines, whereas the evolving/cleaved bonds are highlighted by dotted line. For clarity of figures, hydrogen atoms are omitted, except those involved in the proton-shift.

This transition state describes a concerted but asynchronous proton transfer process from the indole to the dicarbonyl unit of the adduct molecule. At the initial phase of this reaction, the acidic HTFA protonates the unsaturated carbon, followed by the deprotonation step. In other words, the HTFA molecule acts in a bifunctional manner. The computed barrier is only slightly higher than those calculated for the other two routes (C-palladation and Bronsted acidic pathways), however, we point out that the stoichiometry of this mechanism is different from the other two pathways (additional HTFA molecule is involved). For this reason, the computed barriers might not be directly comparable. For a more adequate comparison, an HTFA molecule should be added to the previous models as well, however, these calculations were out of scope of the present work.

Based on these results, the Friedel-Crafts pathway of Pd-catalyzed C-C bond formation between **2a** and **4a** cannot be clearly excluded from the possible mechanistic scenarios, but the *C*-palladation pathway discussed in the text was nevertheless the pathway leading to lowest overall barrier.

4.1.3 c) C-C Coupling via Double C–H Activation

In principle, C–C bond formation between two C–H activated substrates can also occur. However, the transition state corresponding to this process is computed to be at 26.1 kcal/mol with respect to the reference level (see Figure S14). Hence, the predicted activation barrier is higher than that found for the mechanism presented in the manuscript.

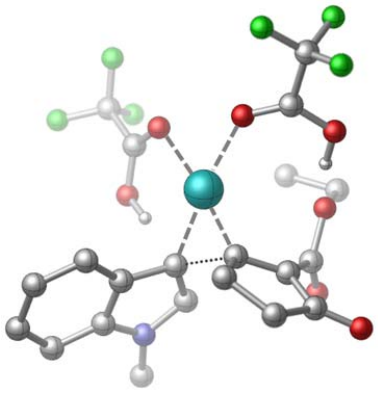
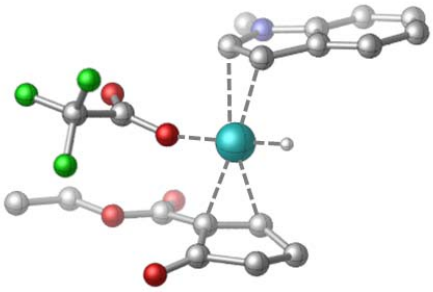


Figure S14: Transition state of C-C coupling between C-H activated substrates. Relative Gibbs free energies (in kcal/mol, with respect to Pd(TFA)$_2$(**2a**) + **4a**) are shown in parenthesis. Metal-ligand bonds are indicated by dashed lines,whereas the evolving C-C bond is highlighted by dotted line. For clarity of figures, hydrogen atoms are omitted, except those of the TFAH molecules.

4.2 Computational Search for "PdH" Intermediates

An extensive conformational search has been carried out to identify palladium-hydride species formed upon an envisioned β-hydride elimination process in cycle A. We found that in structures having a TFA ligand in *cis* position to the PdH hydride bond, the H atom shifted spontaneously to the TFA oxygen yielding a Pd^0(TFAH)(**2a**)(**4a**) complex (PCET process as described in the manuscript). Geometry optimizations carried out for structures bearing the *trans* arrangement of the TFA and hydride ligands did give a PdH species, however, this structure lies very high on the free energy scale (at 14.8 kcal/mol, which is higher than the transition state located for the PCET process). The structure of the high-lying PdH(TFA)(**2a**)(**4a**) complex is depicted in Figure S15).



PdH(TFA)(2a)(4a) (14.8)

Figure S15: Thermodynamically unstable PdH species identified computationally. Relative Gibbs free energy (in kcal/mol, with respect to $Pd(TFA)_2$(**2a**) + **4a**) is shown in parenthesis. Metal-ligand bonds are indicated by dashed lines. For clarity of figures, hydrogen atoms are omitted, except that of the PdH unit.

4.3 Population Analysis for the Species Involved in the PCET Step

To characterize the nature of the Pd-mediated hydrogen migration step identified computationally for cycle A (see Figure 5 of the manuscript), we computed the net atomic charges of the Pd center and the migrating H species in the involved stationary points (**int$_3$**, **TS$_{PCET}$** and **int$_4$**) using the NBO population analysis scheme. The results are presented in Table S2.

Table S2. Computed Pd and H atomic charges in structures related to the PCET step

	NBO charges	
	Pd	H
int$_2$	+0.43	+0.23
TS$_{PCET}$	+0.31	+0.36
int$_3$	+0.17	+0.52

The obtained NBO atomic charges point to a gradual increase of the positive charge on the migrating H species along the reaction coordinate (i.e. going from **int$_3$** to **TS$_{PCET}$** and **int$_4$**). At the same time, the electron density on the Pd center is found to increase along this series (positive charge is gradually reduced). These variations suggest that the present hydrogen migration can be viewed as a concerted proton-coupled electron transfer (PCET) process involving proton migration from the C-H bond of the

coordinated enolate to TFA and a simultaneous $2e^-$ electron transfer to the metal center. Note that in a β-hydride elimination process, the electron density is expected to increase on the H unit. Indeed, the computed atomic charge on the hydridic H in the high-lying PdH(TFA)(**2a**)(**4a**) species is +0.09.

4.4 KIE Calculations

According to the transition state theory, the KIE related to a process involving intermediate I and transition state TS can be calculated from the following equation:

$$KIE = \frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = e^{\frac{\left(G_{\mathrm{tc}}^{\mathrm{TS}}(\mathrm{D}) - G_{\mathrm{tc}}^{\mathrm{I}}(\mathrm{D})\right) - \left(G_{\mathrm{tc}}^{\mathrm{TS}}(\mathrm{H}) - G_{\mathrm{tc}}^{\mathrm{I}}(\mathrm{H})\right)}{RT}} = e^{\frac{\left(G_{\mathrm{tc}}^{\mathrm{TS}}(\mathrm{D}) - G_{\mathrm{tc}}^{\mathrm{TS}}(\mathrm{H})\right) - \left(G_{\mathrm{tc}}^{\mathrm{I}}(\mathrm{D}) - G_{\mathrm{tc}}^{\mathrm{I}}(\mathrm{H})\right)}{RT}}$$

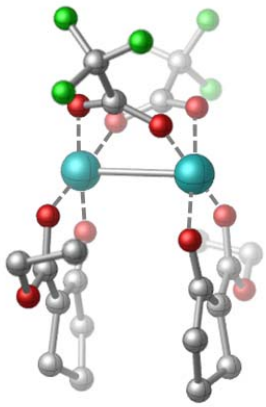
where G_{tc} denotes thermal correction to Gibbs Free Energy ($G_{\mathrm{tc}} = G^o - E_o$) for protium (H) and deuterium (D). R is the universal gas constant and T is the temperature. The reliable estimation of KIE values assumes the right choice of the transition state and the reaction intermediate.

4.4.1 Calculation of the KIE for the C_2–H vs C_2–D labeled indoles.

Our experimental observations indicated that the KIE is likely related to the dehydrogenation process, therefore we considered cycle A for KIE calculations. Based on the computed Gibbs free energy diagram (Figure 6 in the paper), the KIE determining transition state is $\mathbf{TS_{rear}}$, and $\mathbf{int_1}$ is the most stable reaction intermediate (I in the KIE formula). With this choice for TS and I, the calculated KIE is 1.00. Comparing the environments of the C-D or C-H bonds in $\mathbf{TS_{rear}}$ and in $\mathbf{int_1}$, they are basically the same, which explains the calculated KIE value of 1.00. This is, however, in contrast with the measured KIE (≈0.8, see Figure 2 of the manuscript).

In order to rationalize the experimental KIE, the most stable intermediate (the resting state of the catalyst in the cycle) should be considered, wherein the environment of the corresponding C-D/C-H bonds is different from that in TS_{rear}. The largest structural difference in this particular system would be in the case with no Pd-C bond between the metal and the indole molecule (a Pd complex representing the resting state and the separated indole). Indeed, a Pd dimer, [Pd(**1a**-enolate)(TFA)]$_2$, involving only

deprotonated **1a** (enolate of **1a**) and TFA anions (i.e. no coordinated indole molecule) was identified computationally. The relative free energy of this dimer is -6.2 kcal/mol, that is more stable than **int$_1$**. The structure of this species is depicted in Figure S16.



[Pd(**1a**-enolate)(TFA)]$_2$ (-6.2)

Figure S16: Possible resting state of the catalyst identified computationally for cycle A. Relative Gibbs free energy (in kcal/mol, with respect to Pd(TFA)$_2$(**2a**) + **4a**) is shown in parenthesis.

Because of the uncertainty of the KIE determining transition state and intermediate, we have calculated the KIE values with all combinations of the transition states and intermediates identified computationally for cycle A. The results are reported in Table S3 below.

Table S3. Calculated KIE values with different transition states (TS) and intermediates (I) for the C2-H vs C2-D-labeled indoles

I/TS	**TS$_{depr}$**	**TS$_{rear}$**	**TS$_{PCET}$**
Pd dimer + **2a**	0.81	0.85	0.86
int$_1$	0.96	1.00	1.01
int$_2$	0.96	1.01	1.01
int$_3$	0.96	1.00	1.01
int$_4$	0.93	0.98	0.99

The results indicate that significant inverse kinetic isotope effect can be obtained only with the I = Pd dimer + **2a** choice. For all other possible intermediates, the computed KIE is very close to 1.0. Considering the [Pd(**1a**-enolate)(TFA)]$_2$ complex as the resting state, all TS combinations give notable inverse KIE since indole is coordinated to Pd in these

transition states. For **TS_{rear}**, which is predicted to be the rate-determining TS of cycle A, the calculated KIE is 0.85. This value is in line with the measured KIE.

4.4.2 Calculation of the KIE for the **1a** vs **D_6-1a**.

The calculated KIE values obtained for the deuterium-labelled β-keto ester (**1a** vs **D_6-1a**) are listed in Table S4. Again, various I/TS combinations were considered.

Table S4. Calculated KIE values for **1a** vs **D_6-1a**

I/TS	**TS_{depr}**	**TS_{rear}**	**TS_{PCET}**
$Pd(TFA)_2$(**2a**) + **1a**	1.01	1.01	6.78
[Pd(**1a**-enolate)(TFA)]$_2$	1.05	1.05	7.06
int_1	0.99	0.99	6.66
int_2	1.11	1.11	7.50
int_3	0.72	0.72	4.86
int_4	0.82	0.82	5.51

As expected, large normal KIE is predicted for transition state **TS_{PCET}**, which involves an H/D shift. It is therefore quite unlikely that this step is rate-determining. For the most likely I/TS combination (i.e. [Pd(**1a**-enolate)(TFA)]$_2$/**TS_{rear}**, as judged from experimental and computational evidence), computations predict KIE = 1.05, which is consistent with the small normal KIE found experimentally.

4.5 Total Energy Data of the Calculated Structures

The energy data computed for the ωB97X-D/SDDP optimized geometries of the structures discussed in the manuscript and in the Supporting Information are listed in Tables S5-S8. The notation of the stationary points corresponds to that used in the manuscript and in the SI.

Table S5. Energy data (in atomic units) computed for ωB97X-D/SDDP optimized structures of cycle A[a]

	E_o	G^o	G_{sol}	E_o'	G
$\mathbf{TS_{depr}}$	-2121.1046	-2120.7622	-2121.1226	-2121.1354	-2120.8109
$\mathbf{int_1}$	-1594.3238	-1594.0065	-1594.3413	-1594.3452	-1594.0454
$\mathbf{TS_{rear}}$	-1594.2902	-1593.9734	-1594.3081	-1594.3119	-1594.0131
$\mathbf{int_2}$	-1594.3024	-1593.9874	-1594.3218	-1594.3244	-1594.0289
$\mathbf{int_3}$	-1594.3051	-1593.9916	-1594.3249	-1594.3284	-1594.0348
$\mathbf{TS_{PCET}}$	-1594.2891	-1593.9792	-1594.3056	-1594.3118	-1594.0185
$\mathbf{int_4}$	-1594.3040	-1593.9910	-1594.3202	-1594.3267	-1594.0298

[a] Notation: E_o and E_o' refer to electronic energies computed at ωB97X-D/SDDP and ωB97X-D/SDDP' level of DFT; G^o and G_{sol} denote gas-phase and solution-phase Gibbs free energies obtained from ωB97X-D/SDDP calculations. The last column is computed as $G = E_o' + (G^o - E_o) + (G_{sol} - E_o)$ and the relative Gibbs free energies reported in the manuscript and in the SI are obtained from these values. Note that G^o corresponds to T = 298.15 K and c = 1 mol/dm^3 conditions.

Table S6. Energy data (in atomic units) computed for ωB97X-D/SDDP optimized structures of cycle B (acid-catalyzed C-C coupling)[a]

	E_o	G^o	G_{sol}	E_o'	G
$\mathbf{TS_{add}}$	-2119.8390	-2119.5141	-2119.8555	-2119.8692	-2119.5607
$\mathbf{int_{add}}$	-2119.8556	-2119.5279	-2119.8762	-2119.8864	-2119.5792
$\mathbf{int_{add}'}$	-2119.8607	-2119.5292	-2119.8754	-2119.8894	-2119.5726
$\mathbf{TS_{prot}}$	-2119.8275	-2119.5060	-2119.8483	-2119.8580	-2119.5572

[a] See footnote of Table S5.

Table S7. Energy data (in atomic units) computed for ωB97X-D/SDDP optimized structures of cycle B (Pd^{II}-catalyzed C-C coupling)[a]

	E_o	G^o	G_{sol}	E_o'	G
$\mathbf{TS_{CH}}$	-2119.8536	-2119.5343	-2119.8753	-2119.8853	-2119.5877
$\mathbf{int_{CH}}$	-2119.8770	-2119.5550	-2119.8960	-2119.9080	-2119.6050
$\mathbf{TS_{CC}}$	-2119.8671	-2119.5437	-2119.8863	-2119.8979	-2119.5936
$\mathbf{int_{CC}}$	-2119.9229	-2119.5966	-2119.9427	-2119.9535	-2119.6470

[a] See footnote of Table S5.

Table S8. Energy data (in atomic units) computed for ωB97X-D/SDDP optimized structures discussed in the SI)[a]

	E_o	G^o	G_{sol}	E_o'	G
Pd(TFA)$_2$(**4a**)	-1716.7996	-1716.6271	-1716.8226	-1716.8235	-1716.6740
TS$_{FC}$	-2119.8696	-2119.5416	-2119.8900	-2119.9018	-2119.5943
int$_{FC}$	-2119.8909	-2119.5587	-2119.9128	-2119.9228	-2119.6125
TS$_{depr-a}$	-2119.8515	-2119.5287	-2119.8693	-2119.8820	-2119.5769
TS$_{depr-b}$	-2119.8635	-2119.5418	-2119.8842	-2119.8941	-2119.5931
TS$_{FC-rear}$	-2119.8499	-2119.5206	-2119.8731	-2119.8820	-2119.5759
TS$_{doub}$	-2119.8484	-2119.5284	-2119.8666	-2119.8794	-2119.5775
PdH(TFA)(**2a**)(**4a**)	-1594.2809	-1593.9721	-1594.3021	-1594.3041	-1594.0164

[a] See footnote of Table S5.

4.6 Cartesian Coordinates of the Calculated Structures

Cartesian coordinates of ωB97X-D/SDDP optimized geometries are given below in standard XYZ format (units are ångstroms). First line indicates total number of atoms, second line is molecule name (as defined above, see also Tables S5-S8).

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TS$_{depr}$
Pd -0.556980 -0.092780 -1.170690
C -1.773050 -2.655430 -1.582250
C -2.266360 -3.993150 -0.954730
C 0.994500 2.418070 -1.013270
C 1.375440 2.312490 0.368410
C 0.483770 1.735540 1.395950
O -1.371550 -1.845240 -0.666800
O -1.846070 -2.492720 -2.791020
O 0.314580 1.646040 -1.735380
O -0.277990 0.790840 1.248650
F -2.488490 -4.918680 -1.887580
F -3.425250 -3.782950 -0.298740
F -1.384050 -4.489070 -0.079300
O 0.641230 2.346260 2.578790
C -0.117800 1.807840 3.675270
C 1.661920 3.618450 -1.641420

C	0.271440	2.585190	4.918310
C	2.783620	3.971390	-0.656840
C	2.221960	3.539230	0.708800
H	0.103010	0.740940	3.773790
H	-1.185130	1.909340	3.452750
H	1.980070	3.411070	-2.665240
H	0.896900	4.406170	-1.673530
H	1.338060	2.469110	5.127540
H	-0.293000	2.211450	5.777310
H	0.054580	3.649830	4.795400
H	3.678260	3.386950	-0.894600
H	3.052330	5.029300	-0.687370
H	3.008700	3.309400	1.430320
H	1.598690	4.329570	1.143110
C	2.479710	-0.799890	-0.583490
C	3.565960	-1.901430	-0.754870
O	1.366920	-1.046090	-1.062000
O	2.917740	0.228350	0.019190
F	3.059600	-3.029010	-1.242140
F	4.151770	-2.171850	0.416990
F	4.511000	-1.462750	-1.603360
H	2.190650	1.197420	0.155170
C	-2.492120	2.196670	-1.004550
C	-2.269750	2.736270	-2.285510
C	-2.079410	4.102690	-2.497410
C	-2.131840	4.930930	-1.376690
C	-2.357950	4.408700	-0.088410
C	-2.538340	3.040770	0.107840
C	-2.542680	0.746290	-1.157970
C	-2.400960	0.511530	-2.552060
H	-1.893170	4.509250	-3.486720
H	-1.994290	6.001130	-1.501040
H	-2.388850	5.084830	0.760550
H	-2.693840	2.629950	1.100740
H	-3.032340	0.065830	-0.471800
H	-2.500220	-0.428210	-3.085890
N	-2.241410	1.689410	-3.206850
C	-1.806460	1.823290	-4.581840
H	-0.750740	2.111140	-4.616800
H	-1.929230	0.864460	-5.086760
H	-2.410500	2.575030	-5.096780

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int_1

Pd	-0.305600	0.018200	0.337400
C	-0.155100	-2.457000	1.720400
C	-0.041200	-4.010300	1.710100
C	0.732200	2.669600	-0.096700
C	2.052300	2.304000	0.118800
C	2.465600	0.994100	0.481900
O	-0.276400	-1.981500	0.528800
O	-0.089800	-1.870500	2.785200
O	-0.355700	1.981600	-0.050000
O	1.727700	-0.022600	0.584700
F	-0.625900	-4.549800	2.782800
F	1.258200	-4.365300	1.726500
F	-0.593000	-4.573300	0.621100
O	3.767000	0.860800	0.731300
C	4.236000	-0.439600	1.147900
C	0.648200	4.154400	-0.386600
C	4.417500	-1.386000	-0.029300
C	2.096900	4.535200	-0.736500
C	2.972300	3.500700	0.007000
H	3.538400	-0.854000	1.879700
H	5.190700	-0.229000	1.634100
H	-0.078000	4.365100	-1.175900
H	0.299900	4.656000	0.524900
H	3.456100	-1.608300	-0.496900
H	4.850300	-2.324700	0.329500
H	5.093100	-0.955100	-0.773800
H	2.247200	4.426200	-1.815200
H	2.338000	5.566300	-0.467200
H	3.263800	3.867400	0.999400
H	3.894400	3.275600	-0.535300
C	-3.082600	-0.926900	1.210300
C	-3.174700	-1.981400	0.282700
C	-3.615300	-3.256500	0.644500
C	-3.998500	-3.438600	1.969800
C	-3.935800	-2.387400	2.906600
C	-3.472500	-1.129200	2.538800
C	-2.317000	-0.233800	-0.828100
C	-2.492300	0.201200	0.506700
H	-3.639100	-4.077100	-0.064800
H	-4.339000	-4.417600	2.293500

H	-4.227200	-2.575000	3.935200
H	-3.383000	-0.331900	3.269800
H	-2.072400	0.358600	-1.701200
H	-2.564300	1.239600	0.804500
N	-2.730500	-1.525200	-0.957000
C	-2.385300	-2.402600	-2.057400
H	-1.536100	-3.033200	-1.775800
H	-3.242100	-3.029200	-2.319100
H	-2.115800	-1.799100	-2.926000

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TS_{rear}

Pd	-0.234040	-0.036980	-0.339260
C	-0.245180	-1.457210	2.073500
C	-0.299050	-2.746990	2.942310
C	0.763490	2.114630	-0.336360
C	1.811430	1.438200	0.290200
C	2.555720	0.315900	-0.304320
O	-0.283110	-1.698540	0.811960
O	-0.150560	-0.379980	2.642770
O	0.057500	1.683430	-1.341490
O	2.083290	-0.504250	-1.090560
F	-1.197550	-2.620990	3.926320
F	0.902220	-2.963590	3.507020
F	-0.616030	-3.845480	2.240560
O	3.827490	0.281420	0.097470
C	4.639330	-0.800490	-0.398170
C	0.404730	3.371180	0.431980
C	5.207860	-0.484630	-1.773310
C	1.593980	3.564500	1.388100
C	2.219250	2.159160	1.553040
H	4.039690	-1.714250	-0.420220
H	5.432570	-0.902110	0.345380
H	0.237270	4.206920	-0.252170
H	-0.534560	3.185080	0.966900
H	4.407040	-0.409410	-2.512420
H	5.888310	-1.285270	-2.079020
H	5.766600	0.455160	-1.753210
H	2.325080	4.236330	0.927550
H	1.294640	3.999840	2.343630
H	1.799010	1.636360	2.419310
H	3.303870	2.195040	1.677330

C	-3.132540	-0.548130	0.464810
C	-3.093990	-1.920230	0.148010
C	-3.617250	-2.892710	1.004490
C	-4.217240	-2.446700	2.178060
C	-4.288590	-1.075180	2.496790
C	-3.741860	-0.118330	1.649350
C	-2.010750	-0.858670	-1.507580
C	-2.407760	0.145440	-0.585430
H	-3.540390	-3.952010	0.782490
H	-4.625220	-3.174020	2.873530
H	-4.754900	-0.769800	3.428070
H	-3.762200	0.935700	1.909520
H	-1.652500	-0.733760	-2.522630
H	-2.495270	1.198070	-0.826890
N	-2.449000	-2.082250	-1.073230
C	-1.939390	-3.352260	-1.549220
H	-1.157310	-3.715610	-0.874660
H	-2.749740	-4.083850	-1.606290
H	-1.518650	-3.216490	-2.547110

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int_2

Pd	-0.365000	0.402000	-0.230400
C	-0.375800	-1.042100	2.196100
C	-0.185800	-2.334300	3.042200
C	0.634500	2.386700	-0.308000
C	1.538500	1.350900	0.128400
C	2.310200	0.478600	-0.807100
O	-0.128700	-1.232200	0.949500
O	-0.687100	-0.010500	2.771200
O	-0.170300	2.203900	-1.276800
O	2.176700	0.429900	-2.015800
F	-1.097900	-2.419000	4.014100
F	1.030800	-2.316900	3.618100
F	-0.264700	-3.459800	2.311500
O	3.192300	-0.264600	-0.120000
C	3.980800	-1.194400	-0.880700
C	0.555700	3.505800	0.707900
C	5.197500	-0.521200	-1.499100
C	1.755800	3.231500	1.631700
C	2.040300	1.712400	1.516700
H	3.352300	-1.649200	-1.651100

H	4.275400	-1.955200	-0.155000
H	0.582900	4.476200	0.205900
H	-0.403200	3.425900	1.231200
H	4.889900	0.228000	-2.232100
H	5.812100	-1.270600	-2.007500
H	5.806400	-0.041000	-0.728000
H	2.625000	3.793700	1.276000
H	1.560400	3.532100	2.662300
H	1.485000	1.156500	2.276700
H	3.098800	1.477800	1.637700
C	-3.219700	-0.651900	0.269200
C	-2.890000	-2.018300	0.164200
C	-3.308200	-2.961800	1.108400
C	-4.102000	-2.501900	2.152700
C	-4.462600	-1.141800	2.260300
C	-4.022600	-0.209700	1.329600
C	-1.880100	-0.981700	-1.542000
C	-2.542800	0.025200	-0.820300
H	-3.014000	-4.004300	1.043900
H	-4.439400	-3.202700	2.910200
H	-5.074400	-0.820700	3.097500
H	-4.271700	0.842100	1.433100
H	-1.365600	-0.906700	-2.492500
H	-2.770900	1.012300	-1.202900
N	-2.098000	-2.196300	-0.963200
C	-1.337400	-3.398700	-1.238300
H	-0.570900	-3.535900	-0.469500
H	-2.004000	-4.264900	-1.258600
H	-0.859000	-3.302000	-2.214400

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int_3

Pd	0.303900	-0.213300	0.906500
C	1.552200	-1.712900	1.454500
O	-1.348100	0.945800	0.317900
C	1.945100	-1.448800	2.891500
C	0.305600	-2.545100	1.468200
C	2.574100	-1.991400	0.398700
C	-2.394800	0.582400	0.954300
C	0.779400	-1.903400	3.766200
O	2.978700	-0.950600	3.289200
C	0.046200	-2.958500	2.931200

H	-0.602700	-1.902900	1.148400
H	0.308400	-3.351700	0.734400
O	3.581000	-1.109500	0.424400
O	2.486000	-2.889800	-0.416200
C	-3.618300	1.485000	0.629600
O	-2.514600	-0.339100	1.756800
H	0.137900	-1.028300	3.935700
H	1.139100	-2.252400	4.735200
H	-1.018800	-3.018100	3.158200
H	0.491700	-3.944300	3.095800
C	4.609000	-1.289700	-0.563100
F	-3.746300	1.675500	-0.696900
F	-3.461200	2.696700	1.195800
F	-4.762000	0.968900	1.078400
C	5.612200	-0.167500	-0.376400
H	4.154000	-1.271900	-1.559400
H	5.067700	-2.273300	-0.423600
H	5.132600	0.807800	-0.503200
H	6.410800	-0.260000	-1.117900
H	6.054100	-0.207900	0.622200
C	1.106000	2.536400	1.719900
C	0.496400	3.191300	0.633200
C	-0.317100	4.314000	0.799300
C	-0.473800	4.792100	2.096100
C	0.154700	4.167500	3.193500
C	0.942900	3.035400	3.018100
C	1.595500	1.437700	-0.219900
C	1.797400	1.374500	1.181500
H	-0.821800	4.785200	-0.037900
H	-1.101700	5.660900	2.269000
H	0.008100	4.574600	4.189300
H	1.414100	2.541700	3.863000
H	2.073500	0.847800	-0.992400
H	2.627500	0.860700	1.652700
N	0.837700	2.518300	-0.538300
C	0.187300	2.742400	-1.814400
H	0.665900	2.121700	-2.573800
H	-0.869800	2.471600	-1.738200
H	0.288000	3.792000	-2.102900

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TS_{PCET}

Pd	0.415740	-0.080560	0.646410
C	1.565400	-1.491000	1.566350
O	-1.458490	0.737910	-0.126090
C	1.943130	-0.907290	2.903260
C	0.214140	-2.017620	1.652720
C	2.557480	-2.081520	0.616290
C	-2.364060	-0.083860	0.128510
C	0.688720	-0.932840	3.776100
O	3.029520	-0.482050	3.241240
C	-0.242360	-1.961990	3.120120
H	-0.914960	-1.336920	0.994270
H	0.000930	-2.924930	1.086700
O	3.639780	-1.307020	0.472750
O	2.391530	-3.130740	0.026330
C	-3.808250	0.289490	-0.289740
O	-2.241390	-1.201260	0.698360
H	0.258150	0.076380	3.751110
H	0.952750	-1.157930	4.810850
H	-1.300630	-1.714240	3.223920
H	-0.087250	-2.950370	3.564930
C	4.653910	-1.793630	-0.420920
F	-3.860900	1.494020	-0.865440
F	-4.610820	0.306110	0.780970
F	-4.284780	-0.607770	-1.160980
C	5.730190	-0.727720	-0.503060
H	4.202470	-1.994330	-1.397660
H	5.046260	-2.737790	-0.030170
H	5.318790	0.209190	-0.890280
H	6.526510	-1.059620	-1.175450
H	6.161310	-0.537030	0.482970
C	1.455650	2.517820	1.648190
C	0.546000	3.323060	0.927370
C	-0.217050	4.318930	1.548570
C	-0.021270	4.509380	2.912430
C	0.902070	3.728580	3.642240
C	1.643910	2.729460	3.022280
C	1.411280	1.856080	-0.523510
C	2.009770	1.562900	0.706630
H	-0.933290	4.917840	0.994370
H	-0.592530	5.275530	3.428780
H	1.028280	3.912050	4.705090
H	2.346240	2.115030	3.579160

H	1.641170	1.450850	-1.501010
H	2.897880	0.960280	0.851400
N	0.563750	2.926810	-0.399420
C	-0.360400	3.398480	-1.409450
H	-0.106930	2.937800	-2.365540
H	-1.385860	3.120400	-1.151010
H	-0.279830	4.484720	-1.511520

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int$_4$

Pd	0.451200	-0.175900	0.667500
C	1.651400	-1.553800	1.647700
O	-1.518900	0.651500	-0.162900
C	2.022300	-0.875800	2.933500
C	0.312900	-2.030300	1.742600
C	2.625900	-2.124600	0.673700
C	-2.468500	-0.097200	-0.015700
C	0.770500	-0.858200	3.814700
O	3.102800	-0.415700	3.249400
C	-0.205300	-1.857900	3.172800
H	-1.482600	-1.452200	0.783000
H	0.019700	-2.908100	1.166700
O	3.707700	-1.347400	0.525200
O	2.454600	-3.164600	0.066700
C	-3.891600	0.313200	-0.464400
O	-2.434900	-1.287700	0.516600
H	0.378300	0.165400	3.799000
H	1.039400	-1.097100	4.845600
H	-1.245100	-1.522500	3.224300
H	-0.152400	-2.826000	3.684600
C	4.700600	-1.815800	-0.398200
F	-3.871000	1.520100	-1.022900
F	-4.711800	0.341900	0.589000
F	-4.365100	-0.562600	-1.353800
C	5.774500	-0.747400	-0.485000
H	4.229500	-1.999700	-1.369200
H	5.103500	-2.766800	-0.034900
H	5.354100	0.195000	-0.848600
H	6.558400	-1.067300	-1.177700
H	6.223500	-0.571000	0.495800
C	1.488500	2.517600	1.622400
C	0.520900	3.306000	0.956300

C	-0.235800	4.276800	1.626100
C	0.017500	4.456500	2.981800
C	0.994100	3.690600	3.657300
C	1.732500	2.720100	2.990100
C	1.361800	1.874400	-0.546500
C	2.025000	1.595000	0.644000
H	-0.989500	4.866800	1.112800
H	-0.547500	5.202200	3.533900
H	1.164100	3.863800	4.715900
H	2.474400	2.116400	3.506300
H	1.551700	1.483300	-1.538200
H	2.905700	0.975000	0.757300
N	0.483000	2.921800	-0.369600
C	-0.458100	3.419900	-1.346600
H	-0.263200	2.939500	-2.306800
H	-1.486500	3.192300	-1.049700
H	-0.343200	4.501800	-1.467300

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TS_{add}

C	-1.768360	-2.150480	6.227340
C	-1.801130	-3.355130	6.990420
C	-2.286170	-1.070680	6.994140
C	-1.159000	-1.911510	4.930610
C	-2.558730	-3.077600	8.285660
O	-1.281290	-4.468610	6.768900
C	-3.142610	-1.671640	8.099200
O	-0.932520	-3.028230	4.225020
O	-0.889910	-0.789060	4.505700
H	-1.837060	-3.119890	9.110280
H	-3.305830	-3.853070	8.469040
H	-3.169280	-1.076820	9.014630
H	-4.167780	-1.727490	7.717300
C	-0.276840	-2.862440	2.960870
C	-0.150300	-4.237570	2.331570
H	0.705120	-2.403660	3.124310
H	-0.864480	-2.181150	2.337140
H	0.430410	-4.901990	2.975720
H	0.357050	-4.153890	1.365780
H	-1.136970	-4.680590	2.171330
H	-2.632050	-0.172740	6.487300
C	-0.862210	-0.132380	8.029570

C	-1.427120	1.180210	8.351520
C	0.065410	0.125630	6.988740
C	-0.942510	2.079670	7.382400
C	-2.342360	1.637980	9.303980
N	-0.022460	1.390670	6.578120
C	-1.350130	3.410310	7.307460
C	-2.749270	2.971730	9.255240
H	-2.722070	0.976100	10.077080
C	0.596630	1.930880	5.383240
C	-2.265700	3.845750	8.265360
H	-0.974290	4.083630	6.543020
H	-3.452870	3.344640	9.993620
H	1.152340	2.840070	5.627990
H	-0.172390	2.150160	4.638440
H	1.273130	1.183600	4.970270
H	-2.607120	4.876350	8.248640
H	0.729580	-0.586860	6.514980
H	-0.673930	-0.910390	8.760090
O	1.434010	-2.624020	6.291770
C	1.694100	-3.697730	5.782590
H	-0.016170	-4.584550	6.038370
C	3.089350	-3.938160	5.139830
O	0.943360	-4.745880	5.661960
F	2.964060	-4.115820	3.812890
F	3.678700	-5.025590	5.649000
F	3.895670	-2.895250	5.337910

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int_{add}

C	-1.863900	-2.309300	6.458500
C	-1.689700	-3.449900	7.191700
C	-2.483000	-1.224900	7.300900
C	-1.395300	-1.976200	5.120200
C	-2.360700	-3.321400	8.542300
O	-1.010000	-4.540100	6.946800
C	-3.188600	-2.029100	8.413500
O	-1.177600	-3.024600	4.334400
O	-1.246500	-0.807300	4.757200
H	-1.583200	-3.256600	9.313900
H	-2.961600	-4.206000	8.769900
H	-3.274600	-1.481800	9.357900
H	-4.200100	-2.273400	8.077700

C	-0.535100	-2.765200	3.073800
C	-0.250900	-4.109200	2.431400
H	0.386400	-2.205300	3.260500
H	-1.195500	-2.144500	2.459200
H	0.389700	-4.707300	3.083900
H	0.261600	-3.957500	1.476900
H	-1.180400	-4.655300	2.247300
H	-3.176300	-0.604200	6.728100
C	-1.386900	-0.255200	7.881400
C	-1.771700	1.193300	8.028100
C	-0.179600	-0.157100	7.015400
C	-0.852600	1.963300	7.310000
C	-2.826400	1.820800	8.677200
N	0.110400	1.079300	6.739400
C	-0.926800	3.343800	7.204200
C	-2.928000	3.216000	8.589400
H	-3.560300	1.246800	9.235000
C	1.190400	1.489100	5.853100
C	-1.993500	3.965400	7.865000
H	-0.204500	3.920200	6.634900
H	-3.747000	3.725800	9.087400
H	1.834600	2.207400	6.365300
H	0.756500	1.943600	4.959400
H	1.757100	0.599900	5.572600
H	-2.099100	5.044300	7.808700
H	0.455000	-0.989900	6.676700
H	-1.043800	-0.681700	8.835900
O	1.591900	-2.089600	5.907000
C	1.826400	-3.249400	5.511400
H	-0.239300	-4.394700	6.293800
C	3.154300	-3.407400	4.703000
O	1.151900	-4.295600	5.612900
F	2.917800	-3.153600	3.393300
F	3.672100	-4.636900	4.783000
F	4.100100	-2.544100	5.105100

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int_{add}'

C	-1.672600	-2.308700	6.783200
C	-1.838800	-3.657000	7.232400
C	-2.122700	-1.317400	7.832800
C	-1.123100	-1.856900	5.612700

C	-2.534900	-3.600300	8.586800
O	-1.454500	-4.718100	6.709400
C	-2.209800	-2.188400	9.104600
O	-0.992800	-2.605500	4.536300
O	-0.726500	-0.595500	5.506900
H	-2.200200	-4.411600	9.235700
H	-3.611900	-3.723600	8.417300
H	-1.232300	-2.204700	9.599800
H	-2.944500	-1.815100	9.823200
C	-0.176600	-2.116400	3.448000
C	-0.100200	-3.223000	2.414000
H	0.812800	-1.857600	3.837900
H	-0.636500	-1.213700	3.036100
H	0.319700	-4.134400	2.846100
H	0.539900	-2.900100	1.588100
H	-1.092600	-3.452500	2.018100
H	-3.126800	-0.955800	7.575600
C	-1.191400	-0.091200	7.915100
C	-1.829900	1.275600	7.799500
C	-0.162400	-0.041100	6.769000
C	-1.012300	2.073900	6.986600
C	-2.982400	1.795600	8.360900
N	0.105400	1.336400	6.568900
C	-1.330100	3.399900	6.714200
C	-3.320800	3.135400	8.101300
H	-3.619700	1.179500	8.991100
C	0.940900	1.768300	5.469500
C	-2.500700	3.920200	7.289300
H	-0.704600	4.016600	6.076000
H	-4.222400	3.560600	8.531300
H	1.395700	2.735200	5.705000
H	0.381500	1.858400	4.528500
H	1.745200	1.042100	5.328500
H	-2.772000	4.953600	7.092300
H	0.736900	-0.636600	6.945400
H	-0.610600	-0.133000	8.845300
O	1.482600	-3.058200	6.232800
C	1.554800	-4.057900	5.546400
H	-0.211000	-4.800300	5.861900
C	2.861600	-4.322400	4.744500
O	0.666800	-4.987700	5.358600
F	3.242600	-3.193500	4.125600

F	2.726900	-5.270300	3.815800
F	3.842600	-4.688500	5.578400

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TS_{prot}

C	-1.236350	-2.475080	6.775000
C	-2.093770	-3.669980	6.902080
C	-1.936580	-1.315260	7.461970
C	-0.543210	-2.130930	5.559640
C	-3.209110	-3.329590	7.902150
O	-1.993240	-4.749080	6.344700
C	-2.783380	-2.006560	8.548250
O	-0.157960	-3.134170	4.782430
O	-0.269260	-0.941920	5.273040
H	-3.362410	-4.147480	8.609300
H	-4.132010	-3.212740	7.321860
H	-2.155360	-2.211100	9.423590
H	-3.632030	-1.399020	8.876890
C	0.630880	-2.799700	3.631860
C	0.970990	-4.102270	2.931550
H	1.531510	-2.269900	3.959080
H	0.056660	-2.130780	2.982290
H	1.554000	-4.751880	3.589130
H	1.558240	-3.895340	2.031530
H	0.059830	-4.632480	2.643210
H	-2.592560	-0.794250	6.751450
C	-0.980260	-0.230800	8.033090
C	-1.581240	1.151520	8.124440
C	0.228080	0.028800	7.182600
C	-0.777020	2.031250	7.396800
C	-2.735180	1.629060	8.730230
N	0.340290	1.304460	6.898770
C	-1.063220	3.378540	7.240030
C	-3.050460	2.988740	8.593670
H	-3.379790	0.969350	9.302860
C	1.389540	1.889290	6.084740
C	-2.228620	3.849320	7.858670
H	-0.424980	4.041640	6.664470
H	-3.946600	3.381340	9.064230
H	1.853180	2.724120	6.616370
H	0.961540	2.242250	5.142780
H	2.135960	1.124680	5.871600

H	-2.495300	4.897360	7.763420
H	1.058940	-0.659100	7.053160
H	-0.603880	-0.581600	9.004560
O	2.256520	-2.236140	7.238540
C	1.862710	-2.950950	8.149170
H	-0.107210	-2.928020	7.699010
C	2.886640	-3.552540	9.154810
O	0.652480	-3.275110	8.455190
F	2.721530	-2.977260	10.360770
F	4.141200	-3.330930	8.763860
F	2.718650	-4.870370	9.298280

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TS_{CH}

Pd	-0.680630	0.726510	-0.409480
C	-0.605340	-1.425890	-0.610780
O	-0.920340	2.823200	-0.235710
C	-1.961770	-1.974840	-1.053720
C	0.018000	-0.860840	-1.723320
C	0.114360	-2.027250	0.564030
C	-3.386430	0.913740	-0.156670
C	-2.106920	-1.696930	-2.545610
O	-2.724330	-2.607930	-0.366610
C	-0.852370	-0.913780	-2.964860
H	1.091500	-0.737650	-1.802890
O	-0.659310	-2.041960	1.634130
O	1.252710	-2.455060	0.499170
C	-4.880280	1.035380	-0.561630
O	-2.616630	0.745940	-1.172700
H	-3.035570	-1.151030	-2.711190
H	-2.177320	-2.663370	-3.053330
H	-1.093520	0.088740	-3.327750
H	-0.290980	-1.419890	-3.756750
C	-0.126930	-2.635280	2.832580
F	-5.089030	2.177680	-1.237300
F	-5.685580	1.029280	0.498740
F	-5.241300	0.016560	-1.362420
C	-0.296480	-4.146090	2.809990
H	-0.706850	-2.176940	3.634920
H	0.922240	-2.345960	2.939290
H	0.304860	-4.591620	2.013670
H	0.030590	-4.564880	3.766570

H	-1.345820	-4.407640	2.652990
C	1.011880	0.682460	2.042580
C	2.232910	0.165220	2.506700
C	2.501190	-0.059230	3.859160
C	1.479340	0.242050	4.756180
C	0.241180	0.748230	4.309990
C	-0.006100	0.974900	2.959960
C	1.107190	0.819110	0.583260
C	2.383130	0.299900	0.286680
H	3.454910	-0.448990	4.202210
H	1.638860	0.082490	5.818320
H	-0.535370	0.962230	5.038030
H	-0.972420	1.338570	2.619110
H	2.866520	0.211960	-0.678820
N	3.053440	-0.045800	1.394520
C	4.392140	-0.595620	1.462940
H	5.030910	0.039110	2.083180
H	4.352130	-1.602290	1.887650
H	4.811900	-0.652780	0.458160
O	-3.053920	0.982240	1.019680
H	1.286110	2.110840	0.321120
C	0.010820	3.634020	-0.054070
O	1.225950	3.382590	0.160360
C	-0.355730	5.144040	-0.098320
F	-0.001940	5.732400	1.050090
F	-1.655590	5.335620	-0.289390
F	0.312630	5.736710	-1.097940

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int_{CH}

Pd	-0.485200	0.593180	-0.458720
C	-0.759800	-1.562740	-0.523320
O	-0.245130	2.604330	0.068910
C	-2.212640	-1.864910	-0.872660
C	-0.099110	-1.196380	-1.688030
C	-0.102360	-2.209800	0.669160
C	-3.553030	1.327560	-0.847240
C	-2.338250	-1.780380	-2.391430
O	-3.081440	-2.179360	-0.095690
C	-1.004670	-1.213380	-2.904230
H	0.980130	-1.234780	-1.782330
O	-0.719780	-1.885470	1.795880

O	0.838120	-2.966690	0.559110
C	-4.842070	1.160500	-1.698780
O	-2.480020	0.985770	-1.346720
H	-3.211300	-1.192120	-2.671490
H	-2.499160	-2.802810	-2.748300
H	-1.120330	-0.217140	-3.339320
H	-0.546760	-1.849010	-3.667770
C	-0.202980	-2.470300	3.010090
F	-5.624270	2.233240	-1.603860
F	-5.520590	0.091290	-1.270740
F	-4.534580	0.974090	-2.985320
C	-0.745490	-3.875590	3.212290
H	-0.539280	-1.791230	3.794820
H	0.889380	-2.453590	2.970000
H	-0.382020	-4.548690	2.432210
H	-0.409990	-4.258110	4.181100
H	-1.838550	-3.869650	3.198500
C	1.466810	0.509930	1.824260
C	2.860440	0.359830	2.039700
C	3.431990	0.450700	3.317710
C	2.580580	0.713350	4.383650
C	1.190950	0.879230	4.186710
C	0.628880	0.774720	2.922830
C	1.258040	0.351680	0.408720
C	2.489960	0.137830	-0.153710
H	4.500300	0.327680	3.471480
H	2.991560	0.799310	5.385430
H	0.554750	1.094230	5.040220
H	-0.443140	0.885340	2.785810
H	2.771300	-0.001040	-1.189270
N	3.465150	0.137020	0.823990
C	4.881010	-0.067180	0.623930
H	5.450670	0.804730	0.962500
H	5.227020	-0.952900	1.167220
H	5.074860	-0.216620	-0.439630
O	-3.786220	1.800310	0.315000
H	-2.920890	2.070650	0.869440
C	-0.859990	3.094870	1.048320
O	-1.906630	2.693600	1.599510
C	-0.242020	4.400360	1.623580
F	-0.834720	5.457080	1.038860
F	1.067450	4.477020	1.390010

F	-0.440350	4.487670	2.939320

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TS_{cc}

Pd	-0.299740	-0.036780	-0.733890
C	-0.691140	-2.091710	-1.010940
O	0.085090	2.012790	-0.137540
C	-1.493610	-2.198640	-2.298200
C	0.676430	-2.077830	-1.344190
C	-1.128260	-2.563100	0.352420
C	-2.909040	0.394530	0.488360
C	-0.512900	-1.922520	-3.442040
O	-2.653560	-2.504940	-2.412840
C	0.867700	-2.212300	-2.840240
H	1.423920	-2.426350	-0.641980
O	-2.443970	-2.643800	0.459570
O	-0.332950	-2.832080	1.233140
C	-4.462640	0.436000	0.473940
O	-2.378420	0.282610	-0.643500
H	-0.617130	-0.868050	-3.721530
H	-0.765430	-2.531120	-4.311080
H	1.673550	-1.587350	-3.222880
H	1.148990	-3.257730	-3.017290
C	-2.966670	-3.055340	1.742340
F	-4.865840	1.704500	0.288100
F	-4.971770	0.008670	1.635250
F	-4.974950	-0.311540	-0.502620
C	-4.425520	-3.414100	1.539490
H	-2.840330	-2.219800	2.438330
H	-2.382070	-3.904050	2.107090
H	-4.523190	-4.242150	0.832890
H	-4.860990	-3.714070	2.496920
H	-4.988620	-2.561540	1.155150
C	2.506760	-0.172900	0.410960
C	3.742050	0.449010	0.101270
C	4.764370	0.586210	1.050820
C	4.525940	0.078220	2.322060
C	3.304580	-0.555360	2.644500
C	2.293100	-0.686740	1.703140
C	1.703650	-0.104140	-0.783130
C	2.470280	0.520090	-1.737500
H	5.703990	1.075120	0.810080

H	5.293510	0.171470	3.084860
H	3.156560	-0.942880	3.647870
H	1.357870	-1.183130	1.948950
H	2.221950	0.789490	-2.756090
N	3.703100	0.852410	-1.216400
C	4.748650	1.589650	-1.888510
H	4.895210	2.568540	-1.419850
H	5.692490	1.035710	-1.858720
H	4.469160	1.741510	-2.932530
O	-2.361470	0.506620	1.605550
H	-1.101080	1.178230	1.846730
C	0.281480	2.286530	1.047180
O	-0.289000	1.794590	2.084760
C	1.332520	3.377690	1.383970
F	0.706270	4.530540	1.656830
F	2.149110	3.577180	0.350520
F	2.060860	3.027790	2.441090

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int$_{cc}$

Pd	-0.060950	0.037270	-0.499640
C	-0.405790	-1.985760	-0.819290
O	0.592850	1.986550	-0.158010
C	-1.090210	-1.977820	-2.122270
C	1.064990	-2.339100	-1.053070
C	-1.021030	-2.509260	0.434870
C	-3.225260	0.504110	-0.175450
C	-0.082870	-2.274110	-3.223600
O	-2.278910	-1.743160	-2.370630
C	1.134350	-2.869190	-2.500150
H	1.424210	-3.072670	-0.330020
O	-2.356420	-2.434530	0.436100
O	-0.365120	-2.952840	1.359120
C	-4.252680	1.352710	0.622260
O	-2.035510	0.702770	0.028530
H	0.136420	-1.329710	-3.735560
H	-0.535700	-2.936560	-3.964250
H	2.084270	-2.634710	-2.987270
H	1.037990	-3.958360	-2.473260
C	-3.021820	-2.846150	1.647550
F	-4.810290	0.581010	1.570500
F	-5.223940	1.800780	-0.177010

F	-3.669000	2.387240	1.208690
C	-4.500100	-2.981260	1.337260
H	-2.831910	-2.087670	2.414060
H	-2.588400	-3.789900	1.988430
H	-4.665600	-3.748240	0.575790
H	-4.916330	-2.037900	0.976710
H	-5.035140	-3.271360	2.246060
C	2.592210	-0.677570	0.364430
C	3.309590	0.486650	0.039340
C	4.135880	1.136540	0.956770
C	4.247970	0.557540	2.218100
C	3.551680	-0.620900	2.551780
C	2.712480	-1.246350	1.636250
C	1.775440	-1.016490	-0.798620
C	2.103140	-0.031920	-1.768450
H	4.651090	2.059930	0.713930
H	4.872630	1.035660	2.966410
H	3.653150	-1.030310	3.551930
H	2.128850	-2.121770	1.906040
H	1.778570	0.039160	-2.798560
N	3.006180	0.835620	-1.280680
C	3.389000	2.089800	-1.902520
H	2.847220	2.913180	-1.431800
H	4.465960	2.238210	-1.793400
H	3.144380	2.050510	-2.965190
O	-3.797000	-0.341160	-0.957250
H	-3.140860	-0.972630	-1.447630
C	0.690150	2.227140	1.101310
O	0.462760	1.487120	2.044530
C	1.168180	3.684750	1.367600
F	0.263790	4.575450	0.930640
F	2.327880	3.943000	0.713620
F	1.385480	3.917570	2.660390

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$Pd(TFA)_2$(**4a**)

Pd	1.13849	0.40177	0.15930
C	2.06894	2.78548	-0.87522
C	3.17275	3.87238	-1.02971
C	-0.99770	1.42840	1.91086
C	-1.65071	0.10529	1.99341
C	-1.19752	-1.10576	1.27175

O	0.97453	2.94196	-1.38626
O	2.49603	1.80160	-0.15195
O	0.01953	1.73543	1.29455
O	-0.24350	-1.11613	0.49410
F	3.42086	4.45167	0.16029
F	2.79390	4.83010	-1.87709
F	4.32047	3.35058	-1.48006
O	-1.91667	-2.17272	1.51287
C	-1.50197	-3.42007	0.86541
C	-1.79160	2.40468	2.74674
C	-0.32670	-4.05362	1.58769
C	-2.91668	1.56747	3.37629
C	-2.71796	0.19143	2.81594
H	-1.26560	-3.20199	-0.17818
H	-2.40035	-4.03586	0.91986
H	-1.12944	2.87245	3.47896
H	-2.16141	3.19848	2.09208
H	0.57013	-3.43216	1.52241
H	-0.10532	-5.01134	1.10813
H	-0.57047	-4.24296	2.63663
H	-2.85929	1.53387	4.46937
H	-3.91672	1.93662	3.12782
H	-3.36736	-0.64563	3.05378
C	2.59656	-1.91743	-0.28981
C	3.20041	-2.98510	-1.24696
O	2.50480	-2.17413	0.90115
O	2.19828	-0.87483	-0.93305
F	3.80562	-2.45758	-2.31169
F	2.19794	-3.77713	-1.69095
F	4.07856	-3.76454	-0.61216

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TS_{FC}

Pd	1.377440	0.099630	0.588600
C	1.968700	2.681360	-0.369860
C	2.951480	3.781360	-0.866450
C	-0.424930	1.444910	2.172760
C	-1.411340	0.442420	1.915190
C	-1.073940	-0.942770	1.645720
O	0.775710	2.980840	-0.321270
O	2.548850	1.573160	-0.108610
O	0.823410	1.342320	2.113330

O	0.047360	-1.324780	1.251240
F	4.234380	3.481600	-0.668520
F	2.699490	4.945350	-0.249310
F	2.768440	3.971630	-2.187350
O	-2.029740	-1.815690	1.883150
C	-1.738650	-3.213680	1.618860
C	-1.103270	2.741390	2.530370
C	-0.959670	-3.844710	2.759830
C	-2.585300	2.369500	2.669130
C	-2.700140	1.004400	2.015800
H	-1.194740	-3.285360	0.674750
H	-2.726720	-3.661690	1.502820
H	-0.662310	3.187450	3.423870
H	-0.905030	3.422210	1.693730
H	0.036980	-3.405880	2.839630
H	-0.843570	-4.914040	2.561240
H	-1.489740	-3.724010	3.708690
H	-2.854460	2.242430	3.724110
H	-3.263250	3.115200	2.250330
H	-3.567650	0.382150	2.206110
C	-3.506840	1.381700	0.072040
C	-3.662480	0.005170	-0.378990
C	-2.388130	1.875160	-0.639310
C	-2.536020	-0.288130	-1.166780
C	-4.604590	-0.999590	-0.130310
N	-1.785930	0.886840	-1.305450
C	-2.287360	-1.551900	-1.704920
C	-4.387790	-2.260000	-0.681430
H	-5.490230	-0.800760	0.466630
C	-0.655960	1.006450	-2.219480
C	-3.239140	-2.535530	-1.450700
H	-1.395100	-1.762590	-2.285570
H	-5.116250	-3.048880	-0.517950
H	-1.019650	0.884120	-3.243780
H	0.087030	0.235950	-1.999320
H	-0.197790	1.984340	-2.085260
H	-3.092430	-3.532070	-1.855840
H	-1.955180	2.867840	-0.637890
H	-4.312010	2.019590	0.413500
C	2.135910	-2.187080	-0.917710
C	2.028120	-2.962370	-2.264100
O	2.552650	-2.747110	0.076460

O	1.697090	-0.980300	-1.065270
F	2.542040	-2.274030	-3.290920
F	0.719810	-3.190470	-2.548220
F	2.635120	-4.145170	-2.211110

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int_{FC}

Pd	1.374250	0.168600	0.745660
C	1.899330	2.735070	-0.329410
C	2.850710	3.871610	-0.802730
C	-0.462880	1.475200	2.272740
C	-1.405920	0.486200	1.986520
C	-1.037840	-0.879990	1.787370
O	0.690300	2.985840	-0.366040
O	2.503500	1.667470	0.001490
O	0.811330	1.402240	2.250950
O	0.112740	-1.271070	1.461360
F	4.140390	3.608300	-0.602570
F	2.558640	5.018520	-0.171410
F	2.669870	4.075780	-2.123410
O	-1.992060	-1.781310	1.979140
C	-1.678630	-3.158070	1.658190
C	-1.149070	2.787980	2.576290
C	-0.913110	-3.842550	2.777960
C	-2.652930	2.454690	2.537430
C	-2.784420	1.077350	1.837700
H	-1.115660	-3.184450	0.721280
H	-2.658660	-3.615580	1.504790
H	-0.816600	3.184020	3.538690
H	-0.832050	3.505050	1.810560
H	0.078620	-3.400890	2.890750
H	-0.789780	-4.901520	2.532490
H	-1.457140	-3.765650	3.723680
H	-3.036580	2.355350	3.555740
H	-3.241350	3.234650	2.044320
H	-3.576860	0.477430	2.294260
C	-3.144990	1.183730	0.311810
C	-3.377970	-0.158060	-0.335260
C	-1.981320	1.688460	-0.494500
C	-2.398980	-0.358320	-1.305600
C	-4.305720	-1.161170	-0.090170
N	-1.600130	0.823540	-1.380260

C	-2.253930	-1.529800	-2.034680
C	-4.203790	-2.348940	-0.823910
H	-5.076610	-1.041570	0.664820
C	-0.512860	0.966950	-2.348450
C	-3.187240	-2.536310	-1.771240
H	-1.456050	-1.670750	-2.756060
H	-4.917790	-3.147750	-0.647610
H	-0.930790	0.821010	-3.347180
H	0.246470	0.207150	-2.134050
H	-0.078390	1.958630	-2.240750
H	-3.114680	-3.478590	-2.304380
H	-1.437560	2.622670	-0.386020
H	-3.998340	1.862320	0.182680
C	1.894230	-2.172720	-0.853740
C	1.455900	-2.967260	-2.122440
O	2.409460	-2.794420	0.053730
O	1.584850	-0.924380	-0.940760
F	1.161860	-2.180970	-3.177320
F	0.326820	-3.661770	-1.837660
F	2.380140	-3.841050	-2.514570

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$TS_{deprot\text{-}a}$

Pd	-1.28744	0.39550	-1.33684
C	1.16575	1.94327	-1.11468
C	1.96890	3.27320	-1.20541
C	0.41683	-1.31278	-2.39281
C	0.12492	-2.12380	-1.29592
C	-1.20400	-2.26764	-0.79179
O	1.87375	0.97316	-0.72482
O	-0.04008	2.02470	-1.41838
O	-0.32413	-0.41245	-2.93339
O	-2.14893	-1.45574	-1.01862
F	1.26917	4.25000	-1.77083
F	3.09177	3.09342	-1.90945
F	2.31021	3.66033	0.03531
O	-1.42731	-3.33538	-0.04075
C	-2.74114	-3.48464	0.54949
C	1.85106	-1.51212	-2.82454
C	-3.73944	-4.05652	-0.44360
C	2.40059	-2.53243	-1.80860
C	1.41203	-2.51873	-0.61405

H	-3.07425	-2.51554	0.93022
H	-2.57285	-4.16837	1.38366
H	1.90094	-1.85854	-3.85995
H	2.36018	-0.54463	-2.77610
H	-3.92438	-3.34854	-1.25378
H	-4.68664	-4.24722	0.06941
H	-3.37334	-4.99892	-0.86008
H	2.39014	-3.53520	-2.24304
H	3.42814	-2.30062	-1.52594
H	1.38278	-3.49019	-0.11282
C	1.71917	-1.43101	0.43519
C	2.96186	-1.24380	1.20122
C	0.72682	-0.83026	1.25322
C	2.64638	-0.43622	2.31093
C	4.29287	-1.64701	1.02385
N	1.26948	-0.19903	2.29751
C	3.59672	0.02282	3.22458
C	5.25042	-1.21769	1.93770
H	4.58279	-2.29069	0.20074
C	0.57378	0.72374	3.18173
C	4.91092	-0.38318	3.02054
H	3.32521	0.66328	4.05791
H	6.28353	-1.52737	1.81273
H	1.03351	1.71273	3.11045
H	0.62778	0.36585	4.21277
H	-0.46770	0.79705	2.86908
H	5.68522	-0.05654	3.70776
H	-0.33511	-0.71911	1.06865
H	1.63932	-0.19022	-0.21469
C	-3.18597	1.00981	0.71829
C	-3.43434	1.06864	2.25458
O	-4.12055	0.96285	-0.05295
O	-1.91369	0.98372	0.48319
F	-2.77264	2.08751	2.83198
F	-2.97518	-0.07274	2.82959
F	-4.72019	1.18480	2.55996

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$TS_{deprot\text{-}b}$

C	-0.100590	-0.729860	1.974060
C	0.170370	0.150210	3.194730
C	-1.636910	-0.712230	1.763970

C	0.490740	-2.116640	2.133810
C	-1.158170	0.616190	3.768290
O	1.260540	0.445600	3.625620
C	-2.165190	0.460410	2.629190
O	-0.131770	-2.994910	1.318820
O	1.402410	-2.421370	2.866110
H	-1.073930	1.626840	4.170200
H	-1.395590	-0.058980	4.600110
H	-2.227830	1.384890	2.049870
H	-3.168780	0.247480	3.003210
C	0.485880	-4.283880	1.175150
C	0.039330	-4.849750	-0.160920
H	0.174740	-4.918060	2.011810
H	1.570350	-4.161620	1.217120
H	-1.052040	-4.914170	-0.217680
H	0.452440	-5.853340	-0.295820
H	0.407810	-4.217530	-0.974970
H	-2.029150	-1.640550	2.197700
C	-2.124350	-0.674260	0.315230
C	-3.538140	-0.575030	-0.099820
C	-1.528360	-1.446630	-0.716360
C	-3.639620	-1.156390	-1.376780
C	-4.676340	0.026270	0.451860
N	-2.381380	-1.675070	-1.713130
C	-4.813960	-1.167900	-2.129320
C	-5.864720	0.005010	-0.273600
H	-4.641560	0.507770	1.422140
C	-2.058190	-2.299980	-2.983500
C	-5.936050	-0.581730	-1.550660
H	-4.857430	-1.611970	-3.119030
H	-6.755320	0.459100	0.149980
H	-2.175460	-1.577880	-3.795840
H	-2.719670	-3.152740	-3.155220
H	-1.024350	-2.645950	-2.957870
H	-6.876390	-0.571490	-2.092930
H	-0.510800	-1.813000	-0.766550
H	-1.712370	0.538860	-0.144250
Pd	1.024300	0.067530	0.457420
C	-0.688450	2.409040	0.240240
C	-0.946270	3.934250	0.375900
O	-1.567190	1.780160	-0.410360
O	0.318900	1.971750	0.832600

F	-1.407140	4.446000	-0.765910
F	0.148870	4.596630	0.728740
F	-1.879920	4.119560	1.327820
C	2.366380	-1.102600	-1.297920
C	2.993490	-2.017130	-2.375030
O	2.380990	0.132730	-1.420850
O	1.783730	-1.707330	-0.340300
F	3.709870	-2.999080	-1.824300
F	3.765340	-1.343490	-3.219010
F	1.991920	-2.587280	-3.085070

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$TS_{FC\text{-}rear}$

C	-0.51888	-1.60598	1.96943
C	0.41113	-0.83860	2.69730
C	-1.84646	-0.86896	1.98155
C	-0.33154	-2.99329	1.50954
C	-0.25769	0.31481	3.40593
O	1.68321	-0.95177	2.59610
C	-1.74819	-0.01927	3.26685
O	-1.47966	-3.46841	0.98108
O	0.68923	-3.65512	1.59939
H	0.02730	1.23449	2.88173
H	0.09136	0.39183	4.43787
H	-2.38404	0.86705	3.25043
H	-2.07123	-0.63971	4.10777
C	-1.40364	-4.77065	0.37099
C	-2.59802	-4.90418	-0.55383
H	-1.41341	-5.52632	1.16258
H	-0.46310	-4.84627	-0.17766
H	-3.53928	-4.77270	-0.01163
H	-2.59828	-5.89642	-1.01344
H	-2.53126	-4.16081	-1.35342
H	-2.70304	-1.54604	2.00655
C	-1.96516	0.02486	0.69485
C	-3.24452	0.78721	0.45671
C	-1.92036	-0.85220	-0.49652
C	-3.80467	0.33349	-0.74168
C	-3.88040	1.82072	1.13756
N	-2.94306	-0.67127	-1.27512
C	-4.98025	0.82522	-1.28936
C	-5.07239	2.33644	0.61469

H	-3.46071	2.24174	2.04465
C	-3.18810	-1.37860	-2.52705
C	-5.61951	1.84414	-0.57687
H	-5.38483	0.45102	-2.22439
H	-5.57779	3.14266	1.13716
H	-3.23185	-0.65268	-3.34153
H	-4.13713	-1.91426	-2.45358
H	-2.36784	-2.07682	-2.69987
H	-6.54194	2.26789	-0.96081
H	-1.17394	-1.61143	-0.73782
H	-1.07712	0.68448	0.65965
Pd	1.54791	-1.09043	0.60084
C	0.74423	-2.00672	-2.10569
C	0.96520	-1.89952	-3.64174
O	-0.12842	-2.79808	-1.72947
O	1.44481	-1.19938	-1.42924
F	2.03432	-1.19145	-3.98412
F	-0.12299	-1.29355	-4.18169
F	1.06386	-3.11171	-4.19744
C	2.07962	1.59494	0.31053
C	2.92854	2.86844	0.02259
O	2.79096	0.53697	0.28734
O	0.87081	1.72201	0.52072
F	3.88043	3.02452	0.95609
F	2.17493	3.97285	0.02175
F	3.52966	2.78198	-1.17238

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TS_{HTFA}

C	-1.96632	-2.14678	5.96363
C	-2.95774	-3.24345	5.98755
C	-2.49866	-1.01815	6.84926
C	-1.42841	-1.83685	4.62699
C	-4.10220	-2.89155	6.89692
O	-2.89757	-4.30444	5.36101
C	-3.59966	-1.69319	7.71077
O	-1.19477	-0.55052	4.39953
O	-1.14115	-2.68267	3.77316
H	-4.39759	-3.75384	7.49674
H	-4.94649	-2.62649	6.24850
H	-3.15693	-2.05952	8.64017
H	-4.40543	-0.99757	7.95423

C	-0.56892	-0.21654	3.12468
C	-1.55988	-0.26322	1.97466
H	0.26237	-0.90541	2.95564
H	-0.18903	0.79428	3.28722
H	-1.87731	-1.28839	1.77674
H	-1.06967	0.11762	1.07429
H	-2.43127	0.36351	2.18484
H	-2.92273	-0.21254	6.24085
C	-1.39728	-0.41104	7.75941
C	-1.70730	0.85547	8.49841
C	-0.10539	-0.08247	7.12707
C	-0.64663	1.74460	8.30784
C	-2.77439	1.24270	9.30365
N	0.31141	1.10414	7.46577
C	-0.58021	3.01065	8.87504
C	-2.74172	2.51532	9.88238
H	-3.60527	0.57198	9.49383
C	1.58884	1.70594	7.10604
C	-1.66350	3.38731	9.67294
H	0.26116	3.67787	8.71733
H	-3.56354	2.83425	10.51575
H	1.40817	2.64255	6.57440
H	2.14467	1.01933	6.46828
H	2.15944	1.90419	8.01575
H	-1.66624	4.36565	10.14234
H	-1.13571	-1.24395	8.46516
O	-0.85245	-3.05629	8.98018
C	0.05485	-3.41490	8.22240
H	-0.92115	-2.62919	6.51318
C	1.13688	-4.38053	8.77655
O	0.26830	-3.00219	7.03066
F	2.09829	-3.61675	9.36089
F	1.72526	-5.10216	7.82788
F	0.65264	-5.19706	9.70606
H	0.50296	-0.75668	6.53464
Pd	-1.15278	-4.69436	4.31231
C	0.54547	-4.64448	2.10177
C	1.98423	-4.58204	1.51073
O	-0.39845	-4.33791	1.39290
O	0.56753	-4.97039	3.34835
F	1.97698	-4.71910	0.18254
F	2.80647	-5.50411	2.01658

F	2.51412	-3.36550	1.78873
C	-1.10564	-6.70361	6.22857
C	-1.08661	-8.20588	6.63729
O	-1.12817	-5.84169	7.09397
O	-1.11966	-6.57872	4.94633
F	-2.24987	-8.79333	6.29879
F	-0.92723	-8.34952	7.95437
F	-0.09790	-8.87189	6.02694

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TS_{doub}

H	0.23488	0.35191	-0.54706
C	2.30175	0.47228	-0.15233
Pd	1.63438	2.38042	0.07167
O	1.47051	4.55775	0.50752
C	1.98296	5.52280	-0.02858
O	2.64989	5.57140	-1.14382
H	2.69755	4.69097	-1.61471
C	1.86153	6.92714	0.62010
F	3.06946	7.47628	0.77362
F	1.12896	7.72329	-0.16851
F	1.27444	6.84670	1.80746
O	-0.69186	2.41287	0.16137
C	-1.28049	1.41830	-0.21579
O	-0.75412	0.28659	-0.60681
C	-2.82796	1.38746	-0.30883
F	-3.34855	2.50400	0.18185
F	-3.31732	0.34669	0.36926
F	-3.19399	1.26964	-1.59209
C	2.22290	-0.44006	0.98243
C	2.35975	-0.36582	-1.26587
C	2.12430	-0.24369	2.36974
C	2.23040	-1.75856	0.47589
H	2.50608	-0.09765	-2.30475
C	2.05331	-1.35406	3.20134
H	2.10261	0.76400	2.77764
C	2.14965	-2.88635	1.30217
C	2.06524	-2.66343	2.67177
H	1.97944	-1.21776	4.27609
H	2.15020	-3.89342	0.89544
H	2.00378	-3.51091	3.34816
N	2.31941	-1.68110	-0.90384

C	2.38262	-2.81730	-1.79860
H	3.21975	-3.46775	-1.52793
H	1.45280	-3.39341	-1.75730
H	2.53314	-2.45994	-2.81818
C	4.14759	2.25362	-1.41173
C	5.60081	2.34314	-1.27305
C	3.52559	1.90026	-0.22968
C	3.45465	2.37928	-2.70982
C	5.92803	2.01081	0.18355
O	6.41421	2.64173	-2.13288
C	4.57038	1.82965	0.87892
O	2.66490	3.50091	-2.76067
O	3.50972	1.60622	-3.63854
H	6.53935	2.80838	0.61225
H	6.52532	1.09411	0.19800
H	4.36760	2.63467	1.59466
H	4.49741	0.89055	1.43102
C	1.72567	3.61042	-3.85252
C	0.43770	2.87806	-3.50770
H	2.19237	3.20997	-4.75397
H	1.55981	4.68307	-3.97364
H	0.62957	1.80988	-3.37054
H	-0.28717	2.99725	-4.31815
H	0.00200	3.27815	-2.58681

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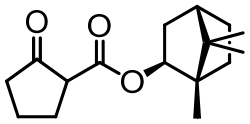
PdH(TFA)(**2a**)(**4a**)

Pd	1.36009	0.69083	0.01778
C	-0.23035	2.21367	0.05007
O	-0.02183	-0.61026	-0.92742
C	-0.75165	2.32607	-1.36929
C	0.95815	2.92802	0.14076
C	-1.00926	1.82725	1.27595
C	-0.73853	-1.38571	-0.21362
C	0.39573	2.90083	-2.20624
O	-1.86697	2.08746	-1.75951
C	1.34483	3.55169	-1.18733
H	2.46435	1.55960	0.61395
H	1.33054	3.30666	1.08597
O	-2.12085	1.18232	0.97139
O	-0.62170	2.08022	2.40211
C	-1.73055	-2.21690	-1.07886

O	-0.71448	-1.56628	1.00337
H	0.00644	3.58766	-2.95868
H	0.87328	2.06219	-2.72486
H	1.15905	4.62934	-1.10990
H	2.40284	3.41649	-1.41716
C	-2.86726	0.63541	2.07705
F	-2.53453	-2.97700	-0.32576
F	-1.05035	-3.03889	-1.90143
F	-2.50428	-1.42842	-1.83444
C	-4.05395	-0.10378	1.49281
H	-3.17212	1.45562	2.73478
H	-2.20631	-0.03726	2.63082
H	-4.66435	-0.50969	2.30487
H	-3.71718	-0.93305	0.86718
H	-4.67183	0.56547	0.88860
C	4.24462	-0.48314	0.08995
C	4.45868	-0.41557	1.48229
C	5.65393	0.05399	2.03367
C	6.66356	0.41441	1.14446
C	6.48180	0.31460	-0.24968
C	5.27621	-0.12824	-0.78671
C	2.87045	-0.93458	-0.10519
C	2.36645	-1.16590	1.19499
H	5.79857	0.13179	3.10697
H	7.61034	0.77707	1.53363
H	7.29495	0.59572	-0.91214
H	5.13354	-0.19054	-1.86166
H	2.48450	-1.41599	-0.99639
H	1.41294	-1.60436	1.47835
N	3.30532	-0.85399	2.12457
C	3.06130	-0.74774	3.54891
H	2.11501	-1.23646	3.78294
H	3.86422	-1.23984	4.10409
H	2.99881	0.30327	3.84940

5 Spectral Data and GC Chromatograms



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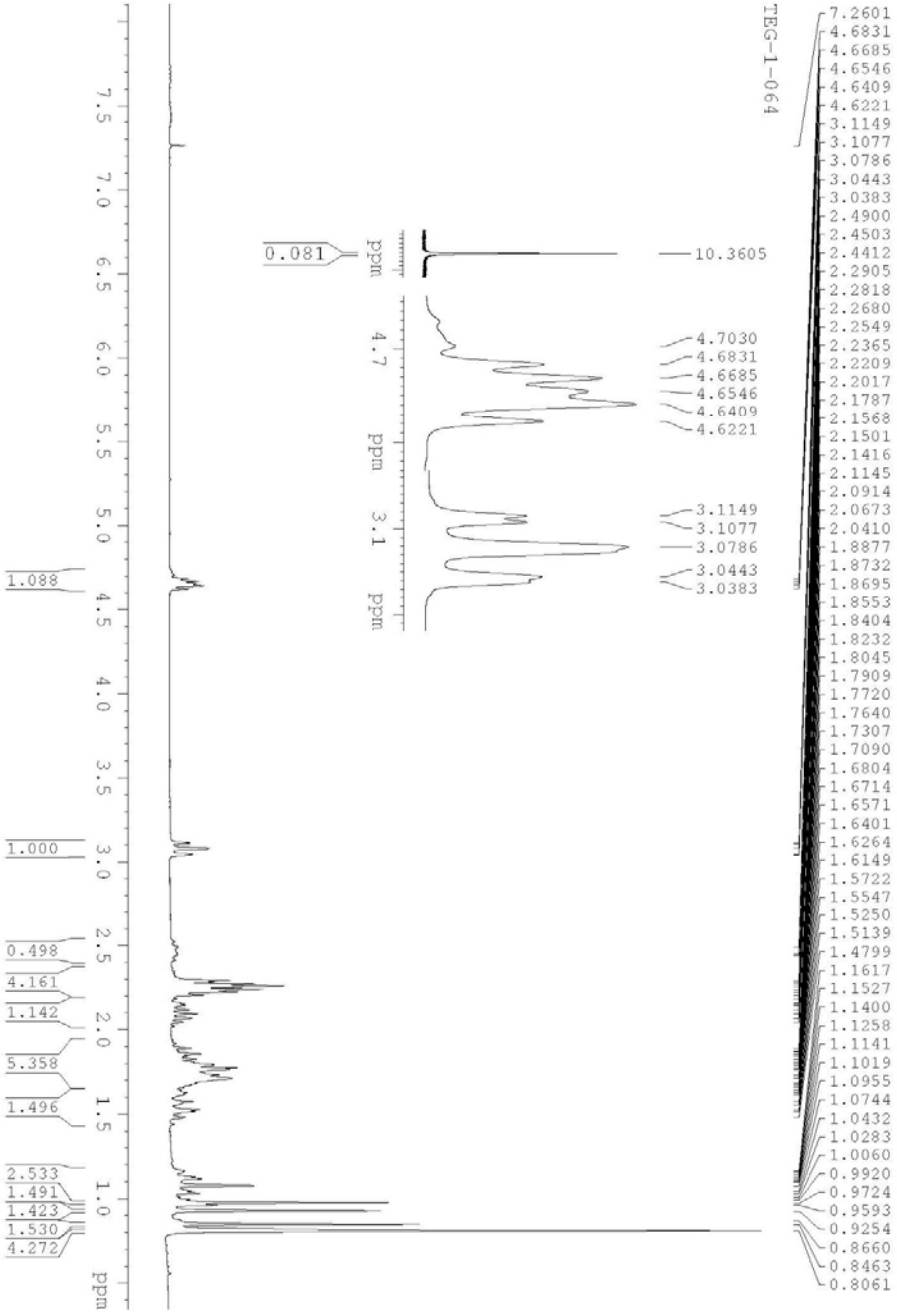
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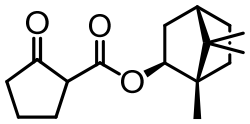

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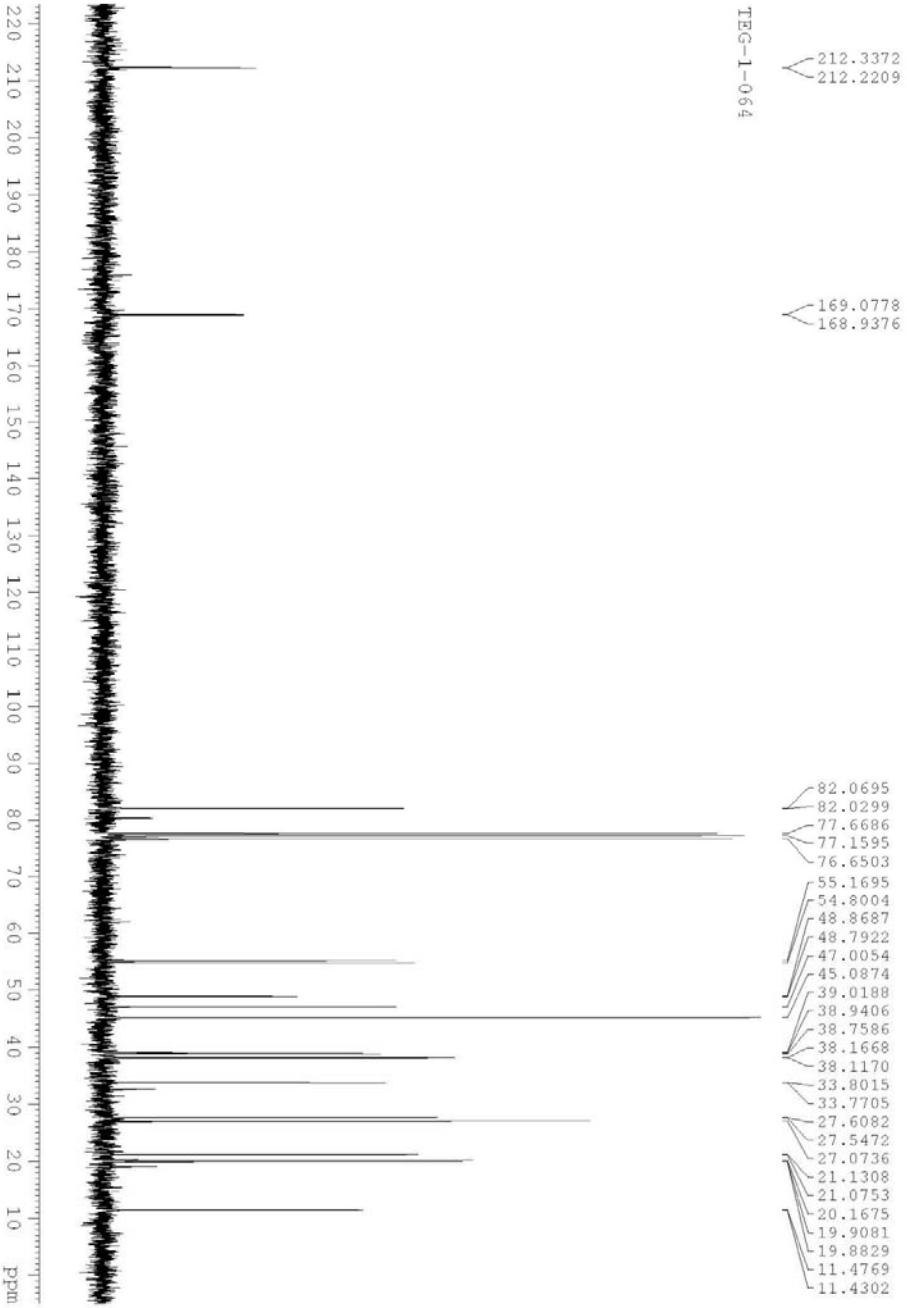
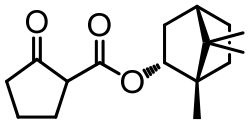

TEG-1-064
212.3372
212.2209
169.0778
168.9376
82.0695
82.0299
77.6686
77.1595
76.6503
55.1695
54.8004
48.8687
48.7922
47.0054
45.0874
39.0188
38.9406
38.7586
38.1668
38.1170
33.8015
33.7705
27.6082
27.5472
27.0736
21.1308
21.0753
20.1675
19.9081
19.8829
11.4769
11.4302
ppm



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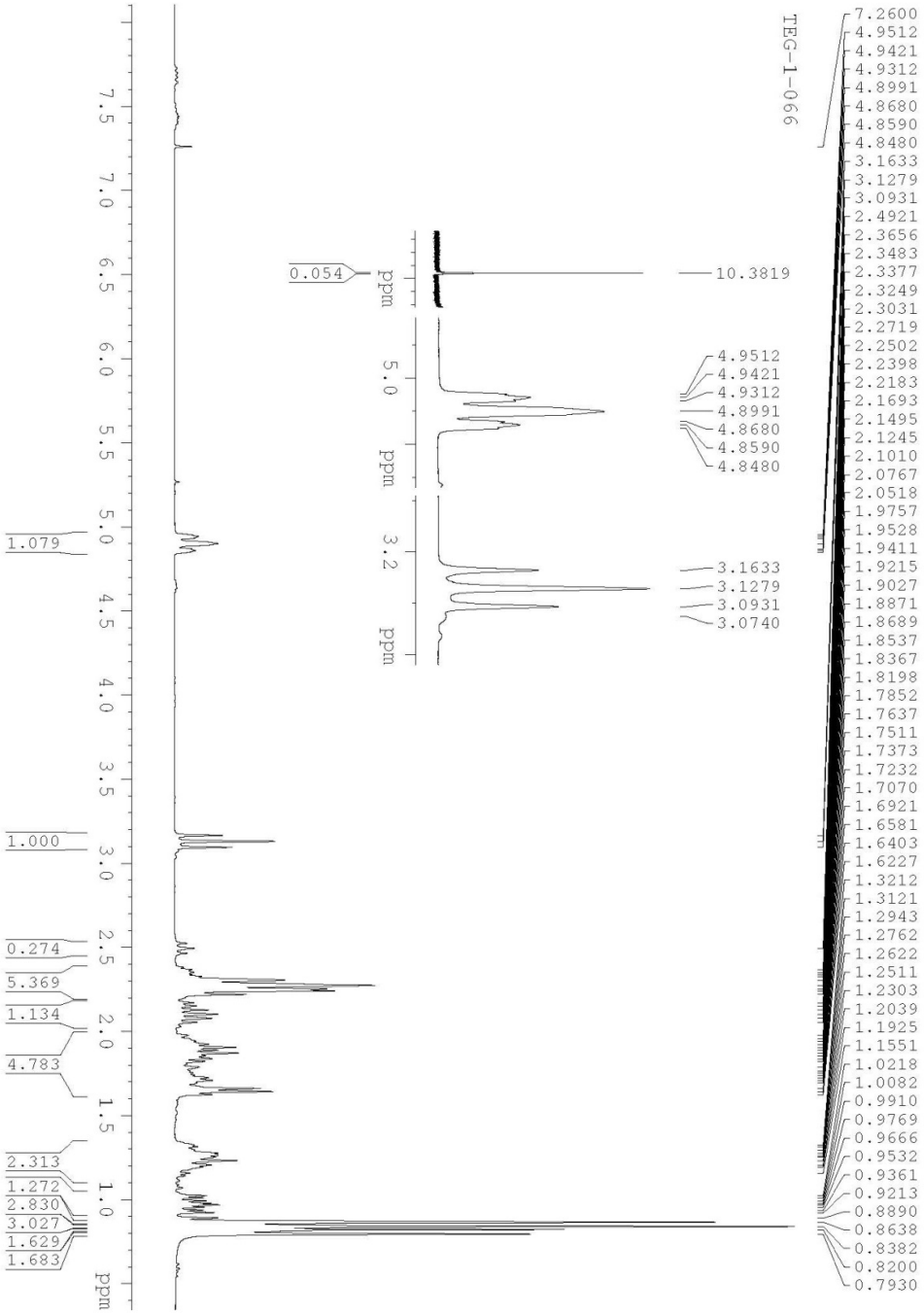
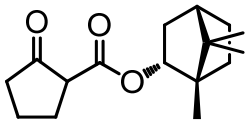

TEG-1-066
7.2600
4.9512
4.9421
4.9312
4.8991
4.8680
4.8590
4.8480
3.1633
3.1279
3.0931
2.4921
2.3656
2.3483
2.3377
2.3249
2.3031
2.2719
2.2502
2.2398
2.2183
2.1693
2.1495
2.1245
2.1010
2.0767
2.0518
1.9757
1.9528
1.9411
1.9215
1.9027
1.8871
1.8689
1.8537
1.8367
1.8198
1.7852
1.7637
1.7511
1.7373
1.7232
1.7070
1.6921
1.6581
1.6403
1.6227
1.3212
1.3121
1.2943
1.2762
1.2622
1.2511
1.2303
1.2039
1.1925
1.1551
1.0218
1.0082
0.9910
0.9769
0.9666
0.9532
0.9361
0.9213
0.8890
0.8638
0.8382
0.8200
0.7930
0.054
10.3819
4.9512
4.9421
4.9312
4.8991
4.8680
4.8590
4.8480
3.1633
3.1279
3.0931
3.0740
1.079
1.000
0.274
5.369
1.134
4.783
2.313
1.272
2.830
3.027
1.629
1.683
ppm



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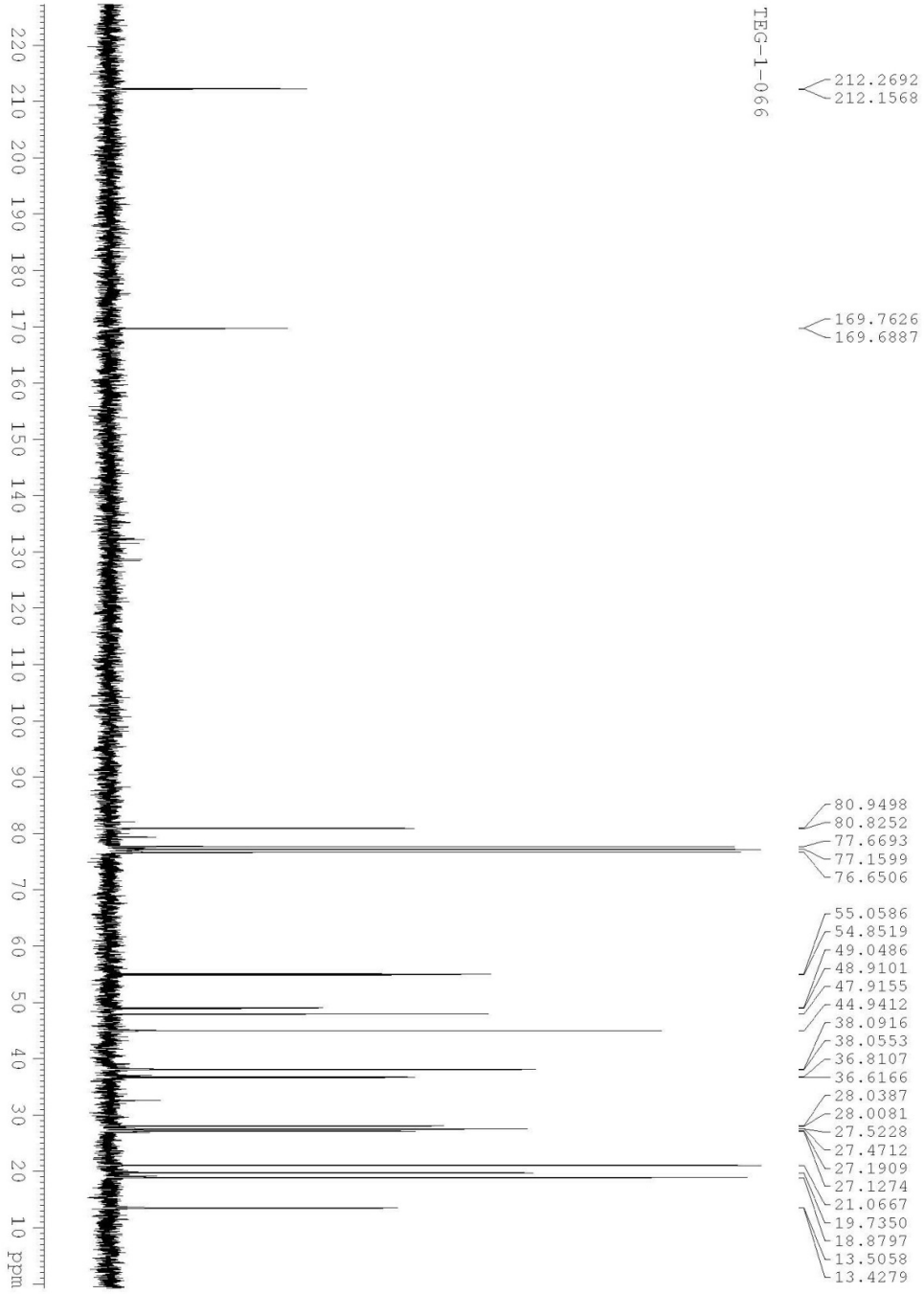
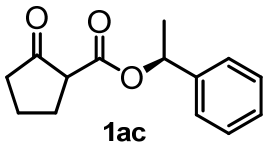

TEG-1-066
212.2692
212.1568
169.7626
169.6887
80.9498
80.8252
77.6693
77.1599
76.6506
55.0586
54.8519
49.0486
48.9101
47.9155
44.9412
38.0916
38.0553
36.8107
36.6166
28.0387
28.0081
27.5228
27.4712
27.1909
27.1274
21.0667
19.7350
18.8797
13.5058
13.4279
ppm



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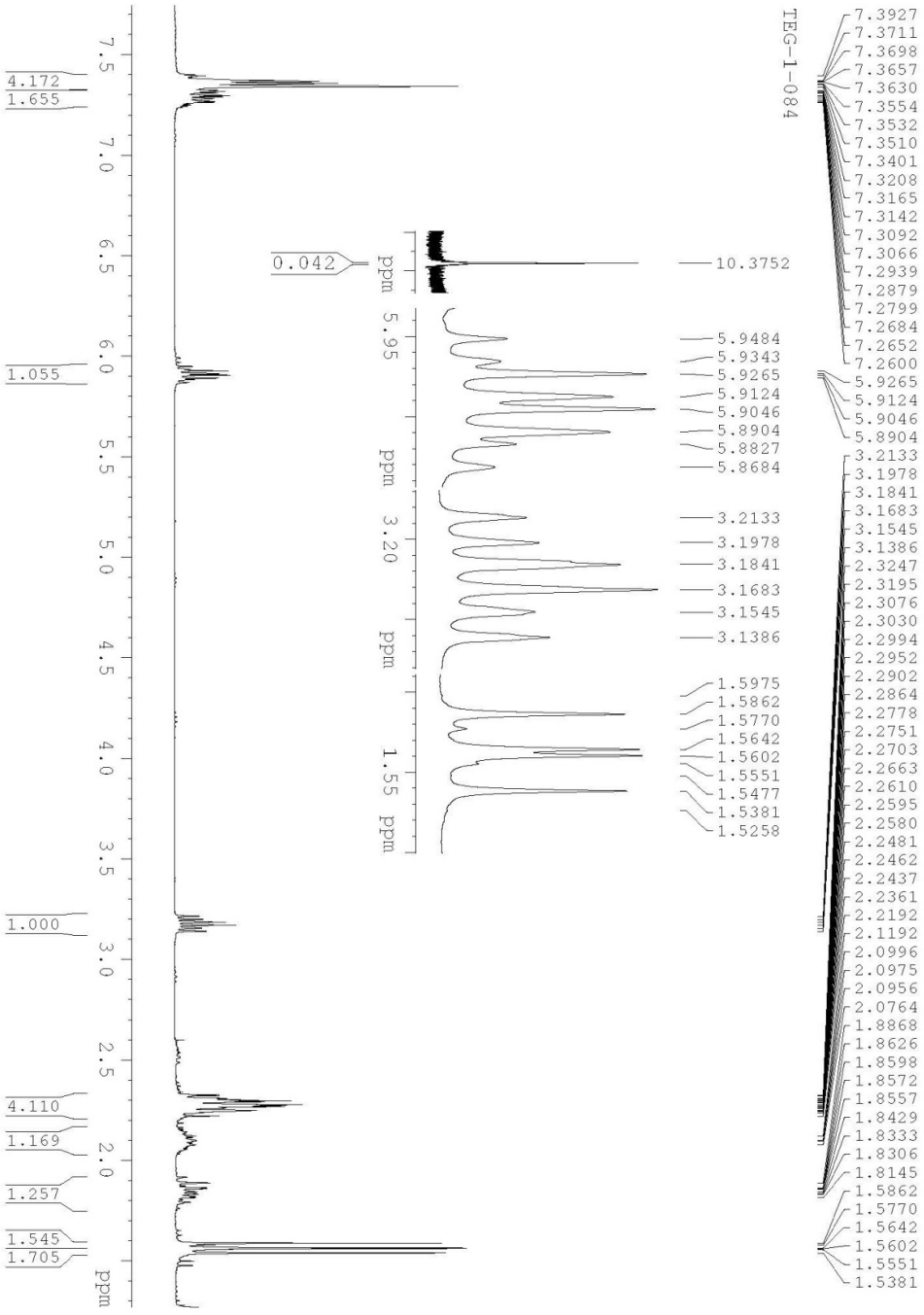
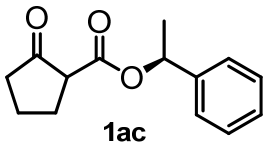

TEG-1-084
4.172
1.655
1.055
1.000
4.110
1.169
1.257
1.545
1.705
0.042
ppm
5.95
ppm
3.20
ppm
1.55
ppm
10.3752
5.9484
5.9343
5.9265
5.9124
5.9046
5.8904
5.8827
5.8684
3.2133
3.1978
3.1841
3.1683
3.1545
3.1386
1.5975
1.5862
1.5770
1.5642
1.5602
1.5551
1.5477
1.5381
1.5258
7.3927
7.3711
7.3698
7.3657
7.3630
7.3554
7.3532
7.3510
7.3401
7.3208
7.3165
7.3142
7.3092
7.3066
7.2939
7.2879
7.2799
7.2684
7.2652
7.2600
5.9265
5.9124
5.9046
5.8904
3.2133
3.1978
3.1841
3.1683
3.1545
3.1386
2.3247
2.3195
2.3076
2.3030
2.2994
2.2952
2.2902
2.2864
2.2778
2.2751
2.2703
2.2663
2.2610
2.2595
2.2580
2.2481
2.2462
2.2437
2.2361
2.2192
2.1192
2.0996
2.0975
2.0956
2.0764
1.8868
1.8626
1.8598
1.8572
1.8557
1.8429
1.8333
1.8306
1.8145
1.5862
1.5770
1.5642
1.5602
1.5551
1.5381
ppm



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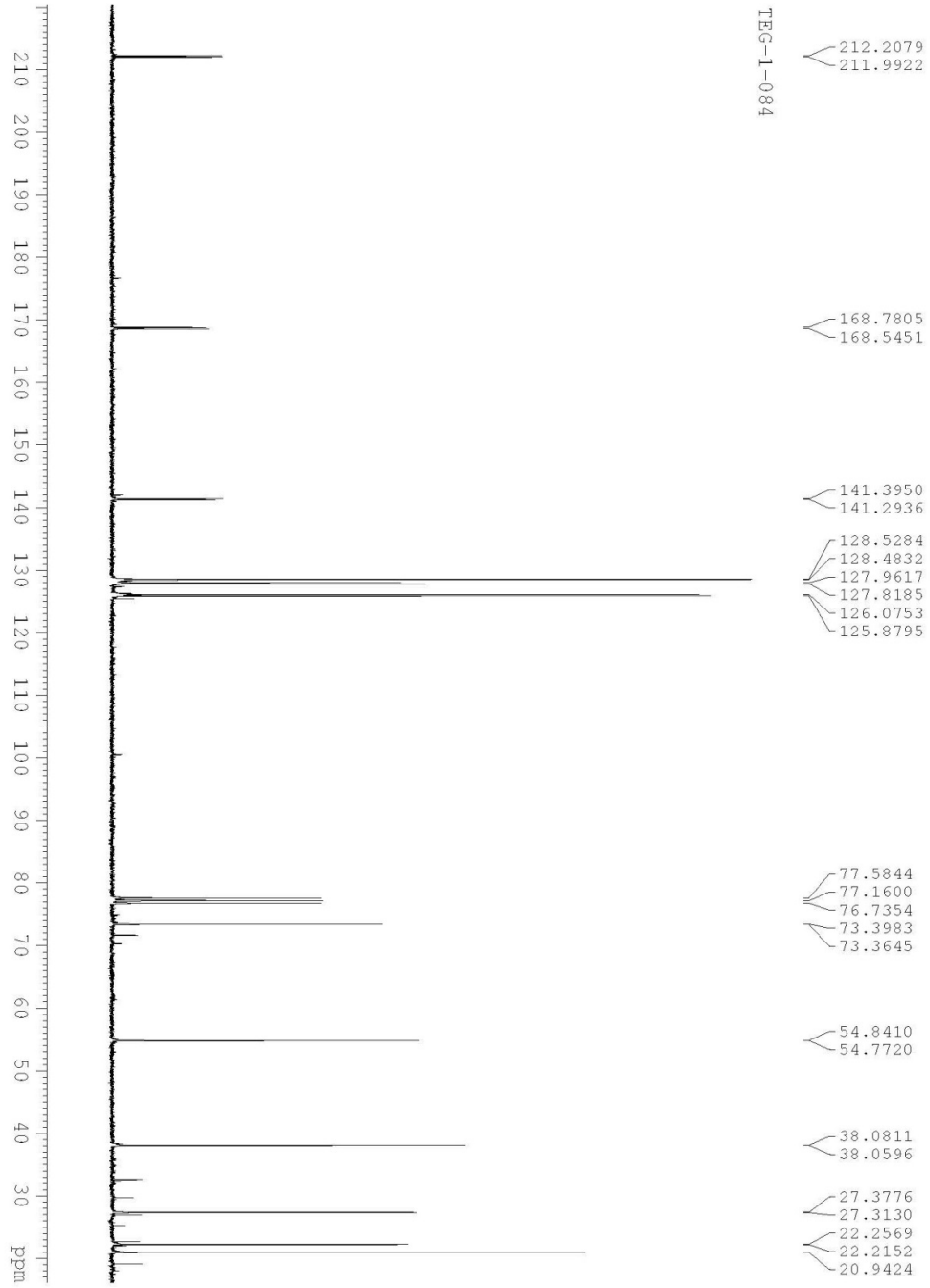
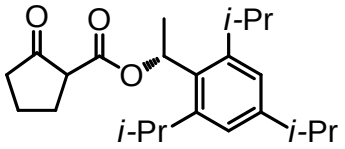
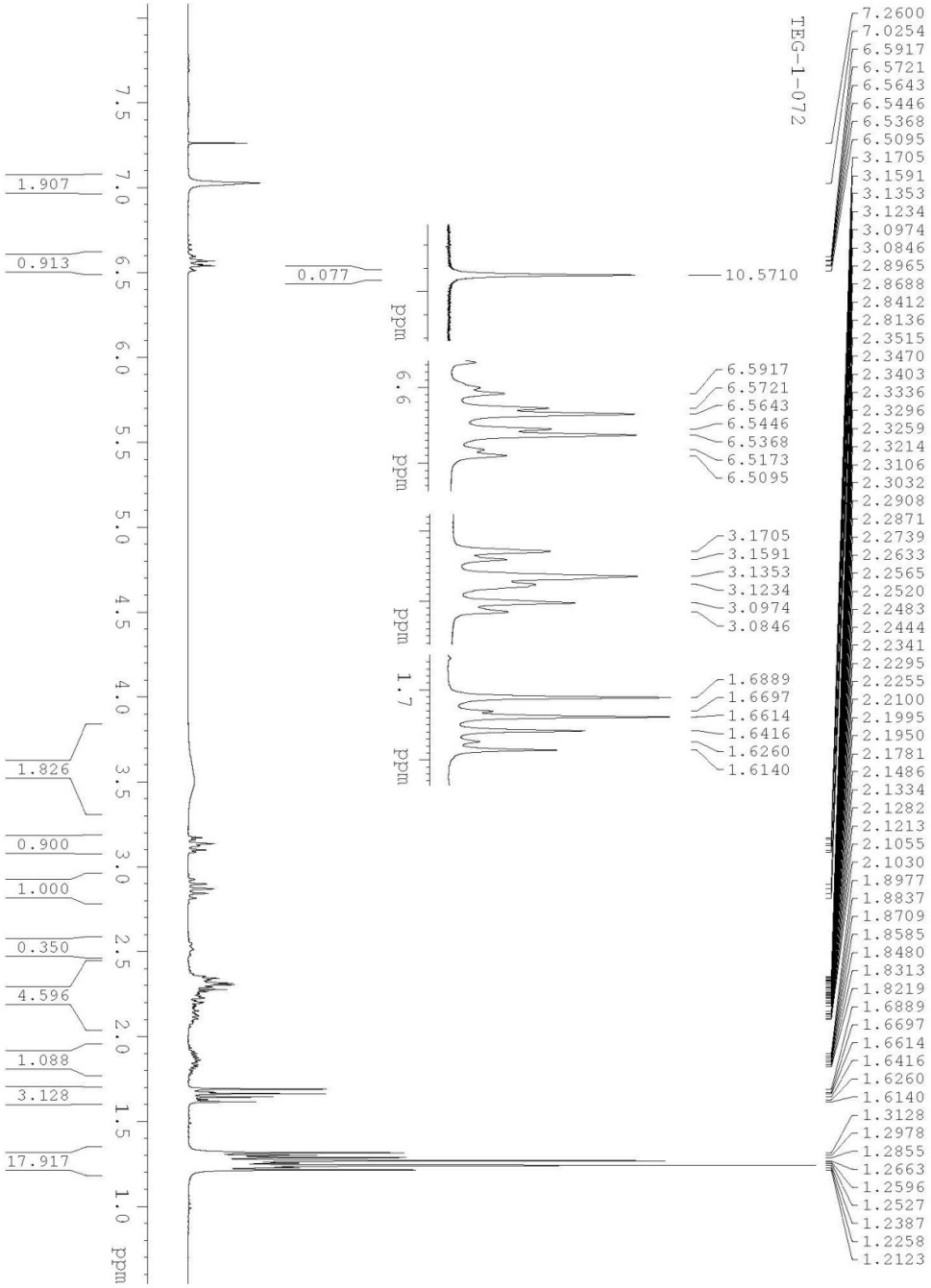
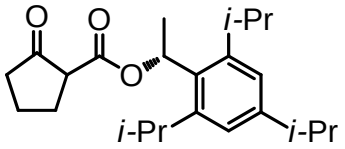

TEG-1-084
212.2079
211.9922
168.7805
168.5451
141.3950
141.2936
128.5284
128.4832
127.9617
127.8185
126.0753
125.8795
77.5844
77.1600
76.7354
73.3983
73.3645
54.8410
54.7720
38.0811
38.0596
27.3776
27.3130
22.2569
22.2152
20.9424
ppm

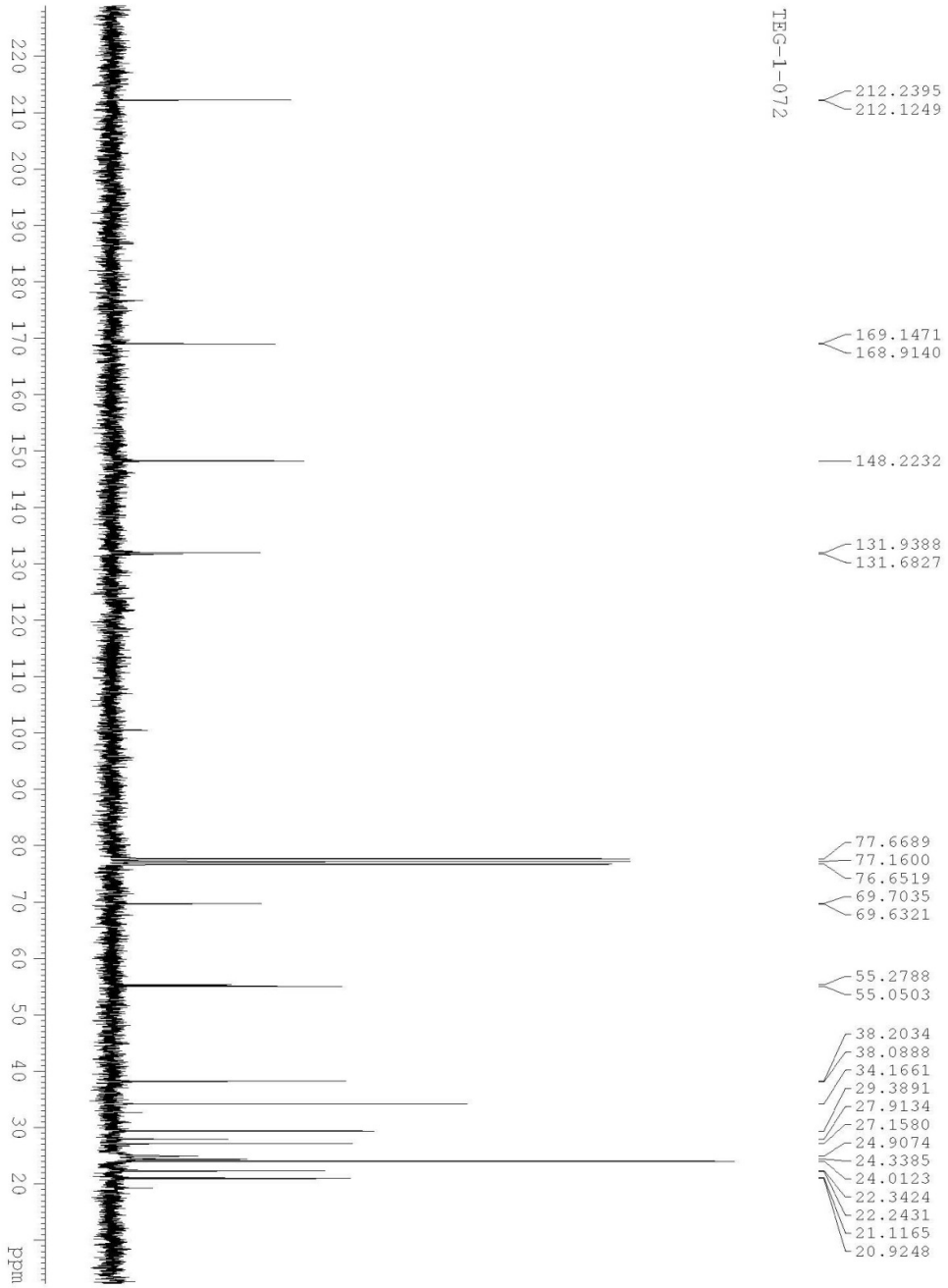

O
O
O
i-Pr
i-Pr
i-Pr

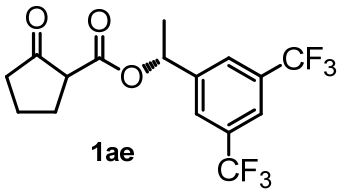
1ad


TEG-1-072
7.2600
7.0254
6.5917
6.5721
6.5643
6.5446
6.5368
6.5095
3.1705
3.1591
3.1353
3.1234
3.0974
3.0846
2.8965
2.8688
2.8412
2.8136
2.3515
2.3470
2.3403
2.3336
2.3296
2.3259
2.3214
2.3106
2.3032
2.2908
2.2871
2.2739
2.2633
2.2565
2.2520
2.2483
2.2444
2.2341
2.2295
2.2255
2.2100
2.1995
2.1950
2.1781
2.1486
2.1334
2.1282
2.1213
2.1055
2.1030
1.8977
1.8837
1.8709
1.8585
1.8480
1.8313
1.8219
1.6889
1.6697
1.6614
1.6416
1.6260
1.6140
1.3128
1.2978
1.2855
1.2663
1.2596
1.2527
1.2387
1.2258
1.2123
1.907
0.913
1.826
0.900
1.000
0.350
4.596
1.088
3.128
17.917
0.077
10.5710
6.5917
6.5721
6.5643
6.5446
6.5368
6.5173
6.5095
3.1705
3.1591
3.1353
3.1234
3.0974
3.0846
1.6889
1.6697
1.6614
1.6416
1.6260
1.6140
ppm

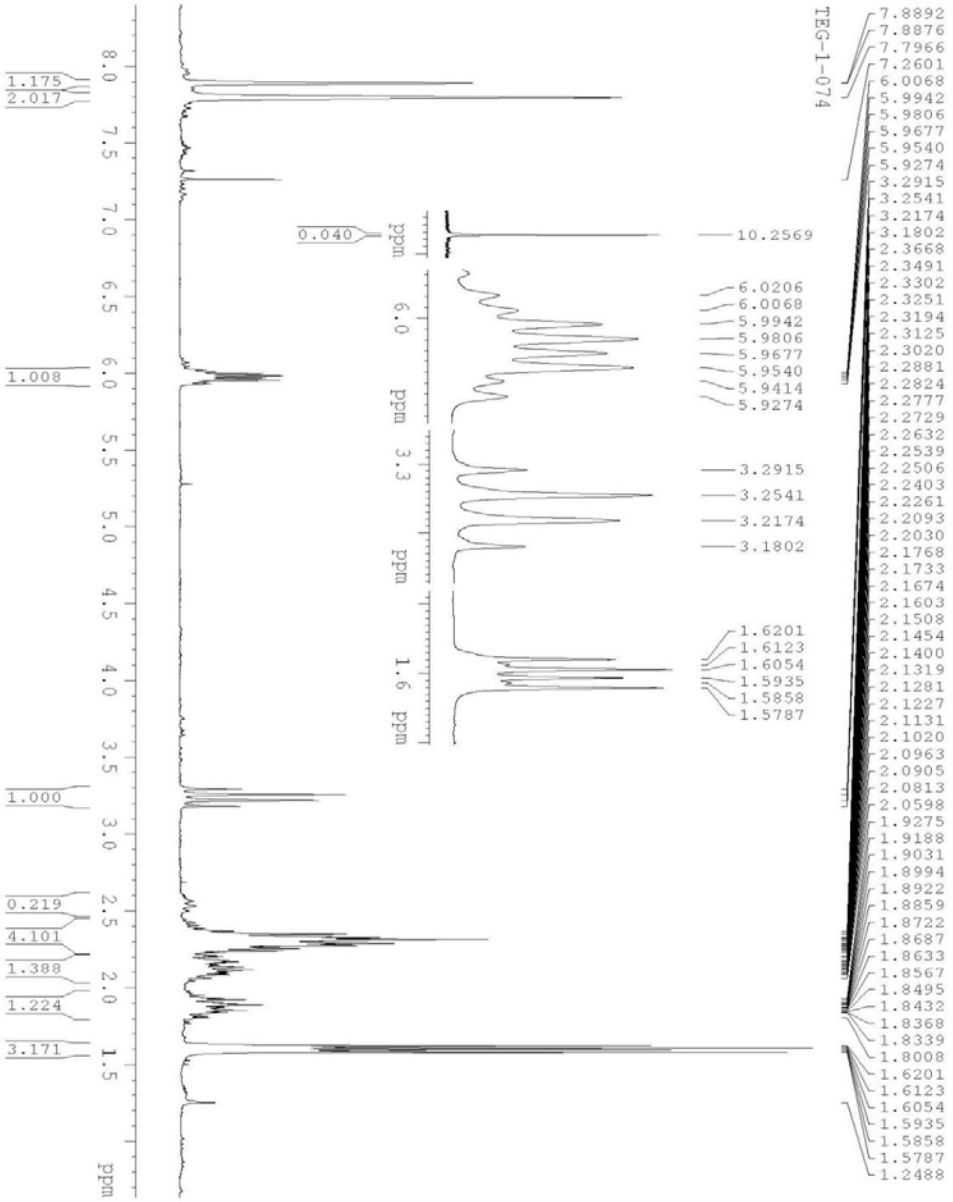

O
O
O
i-Pr
i-Pr
i-Pr

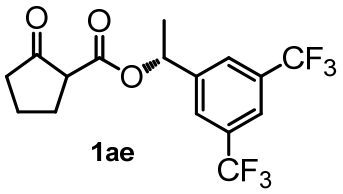
1ad


TEG-1-072
212.2395
212.1249
169.1471
168.9140
148.2232
131.9388
131.6827
77.6689
77.1600
76.6519
69.7035
69.6321
55.2788
55.0503
38.2034
38.0888
34.1661
29.3891
27.9134
27.1580
24.9074
24.3385
24.0123
22.3424
22.2431
21.1165
20.9248
ppm

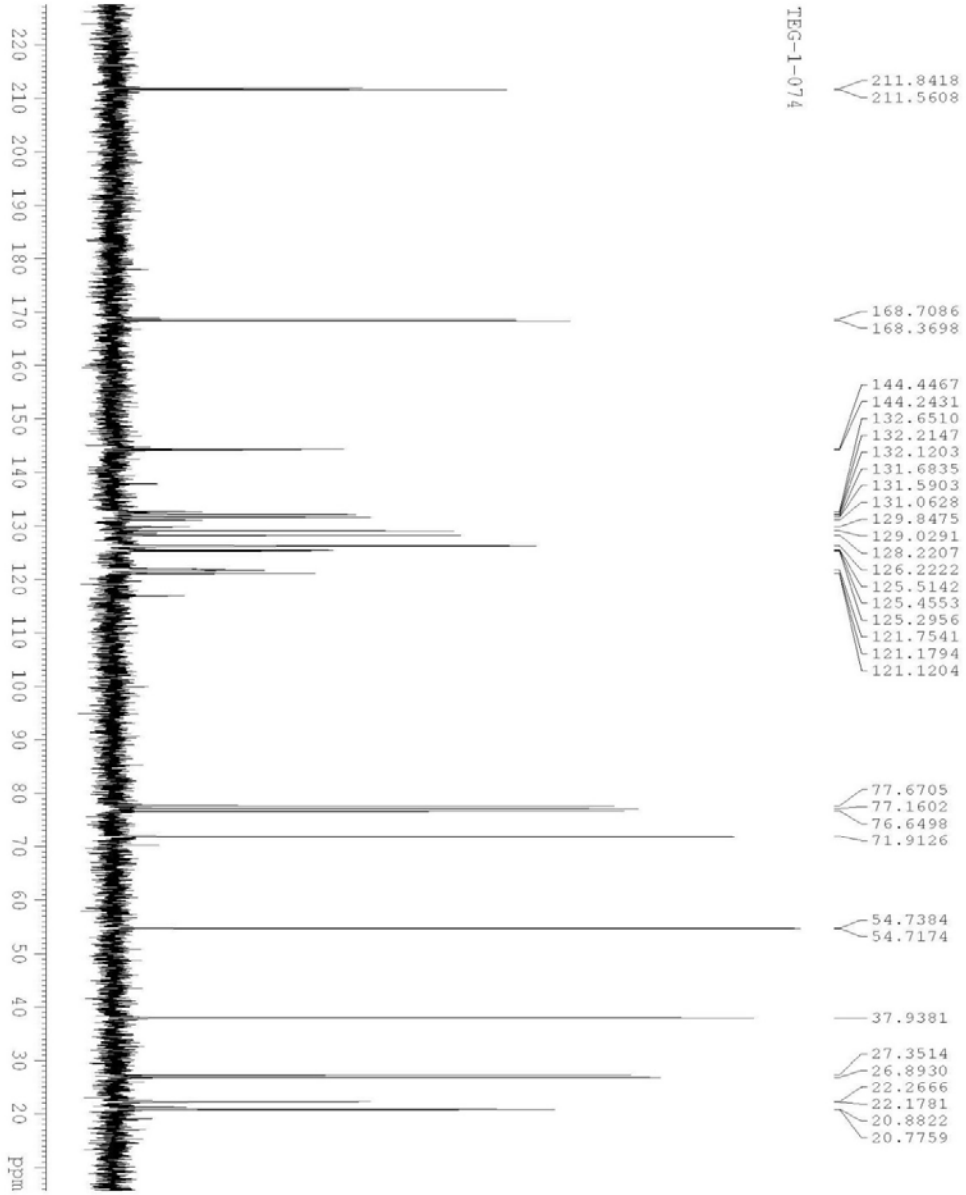

O
O
O
CF3
CF3

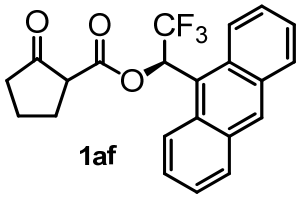
1ae


TEG-1-074
7.8892
7.8876
7.7966
7.2601
6.0068
5.9942
5.9806
5.9677
5.9540
5.9274
3.2915
3.2541
3.2174
3.1802
2.3668
2.3491
2.3302
2.3251
2.3194
2.3125
2.3020
2.2881
2.2824
2.2777
2.2729
2.2632
2.2539
2.2506
2.2403
2.2261
2.2093
2.2030
2.1768
2.1733
2.1674
2.1603
2.1508
2.1454
2.1400
2.1319
2.1281
2.1227
2.1131
2.1020
2.0963
2.0905
2.0813
2.0598
1.9275
1.9188
1.9031
1.8994
1.8922
1.8859
1.8722
1.8687
1.8633
1.8567
1.8495
1.8432
1.8368
1.8339
1.8008
1.6201
1.6123
1.6054
1.5935
1.5858
1.5787
1.2488
10.2569
6.0206
6.0068
5.9942
5.9806
5.9677
5.9540
5.9414
5.9274
3.2915
3.2541
3.2174
3.1802
1.6201
1.6123
1.6054
1.5935
1.5858
1.5787
0.040
1.175
2.017
1.008
1.000
0.219
4.101
1.388
1.224
3.171
ppm

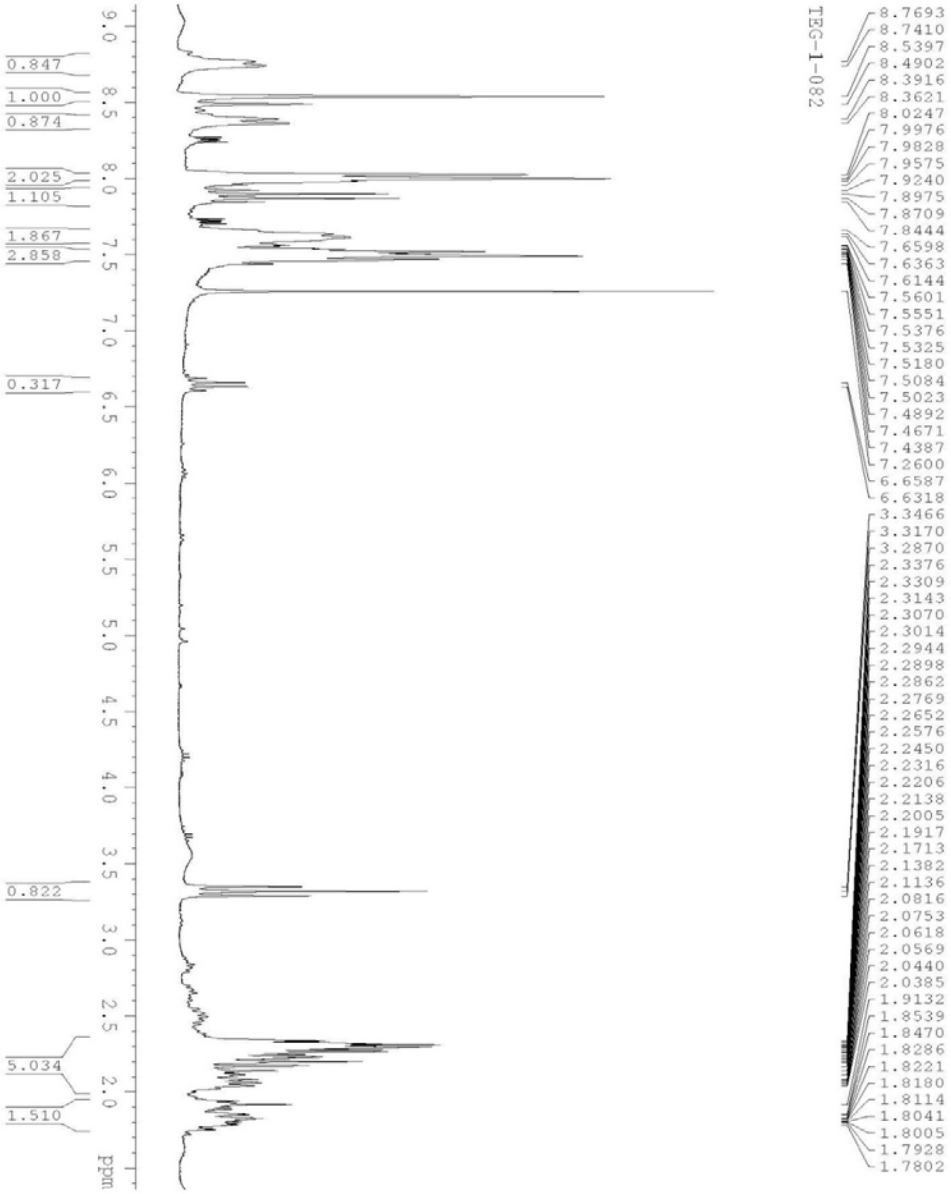

O
O
O
CF3
CF3

1ae


TES-1-074
211.8418
211.5608
168.7086
168.3698
144.4467
144.2431
132.6510
132.2147
132.1203
131.6835
131.5903
131.0628
129.8475
129.0291
128.2207
126.2222
125.5142
125.4553
125.2956
121.7541
121.1794
121.1204
77.6705
77.1602
76.6498
71.9126
54.7384
54.7174
37.9381
27.3514
26.8930
22.2666
22.1781
20.8822
20.7759
ppm


O
O
CF3
O

1af


0.847
1.000
0.874
2.025
1.105
1.867
2.858
0.317
0.822
5.034
1.510
ppm
TEG-1-082
8.7693
8.7410
8.5397
8.4902
8.3916
8.3621
8.0247
7.9976
7.9828
7.9575
7.9240
7.8975
7.8709
7.8444
7.6598
7.6363
7.6144
7.5601
7.5551
7.5376
7.5325
7.5180
7.5084
7.5023
7.4892
7.4671
7.4387
7.2600
6.6587
6.6318
3.3466
3.3170
3.2870
2.3376
2.3309
2.3143
2.3070
2.3014
2.2944
2.2898
2.2862
2.2769
2.2652
2.2576
2.2450
2.2316
2.2206
2.2138
2.2005
2.1917
2.1713
2.1382
2.1136
2.0816
2.0753
2.0618
2.0569
2.0440
2.0385
1.9132
1.8539
1.8470
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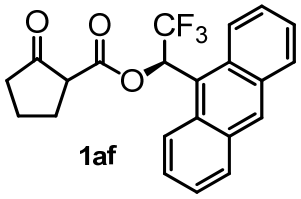
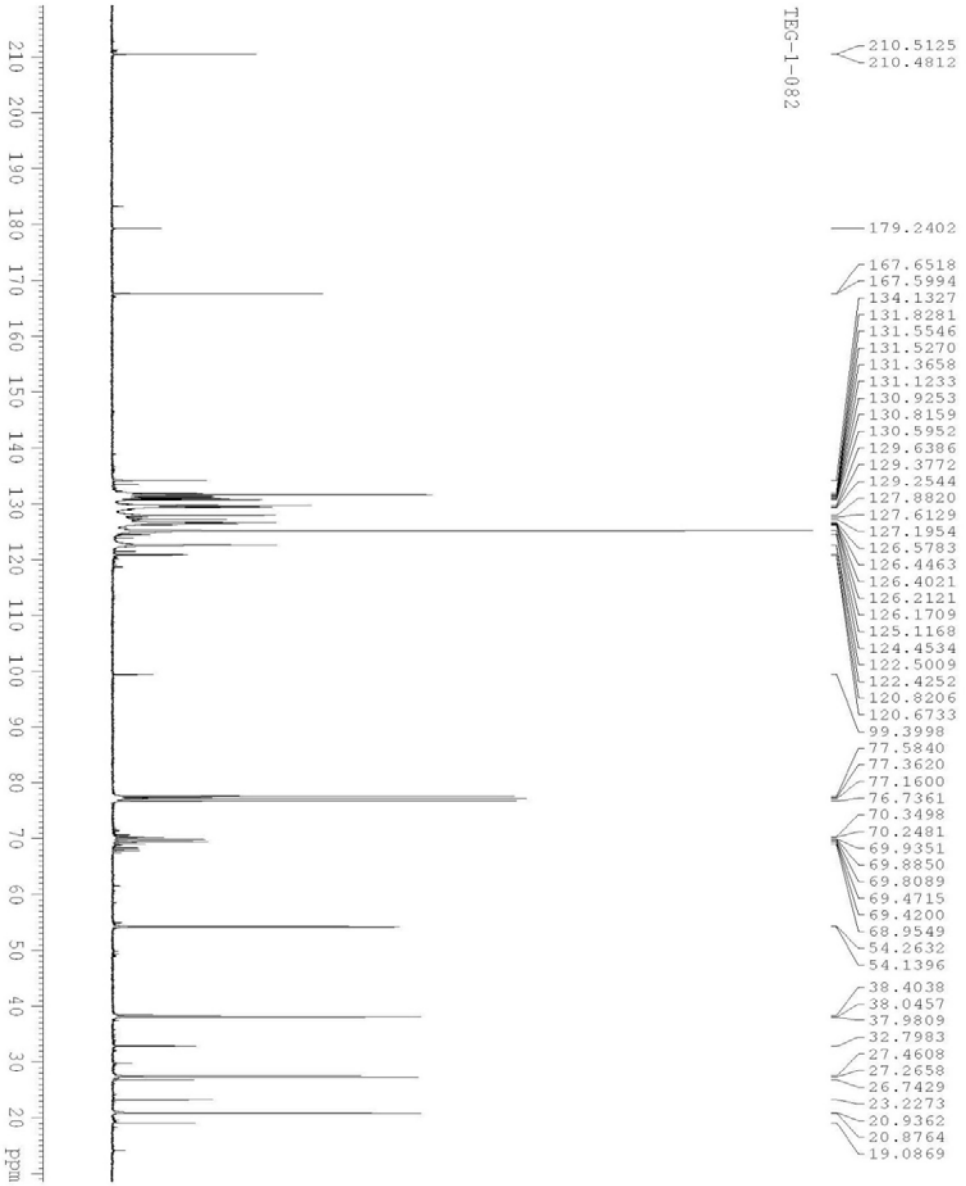
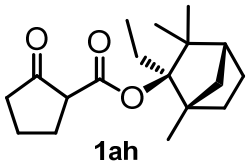
1.8114
1.8041
1.8005
1.7928
1.7802

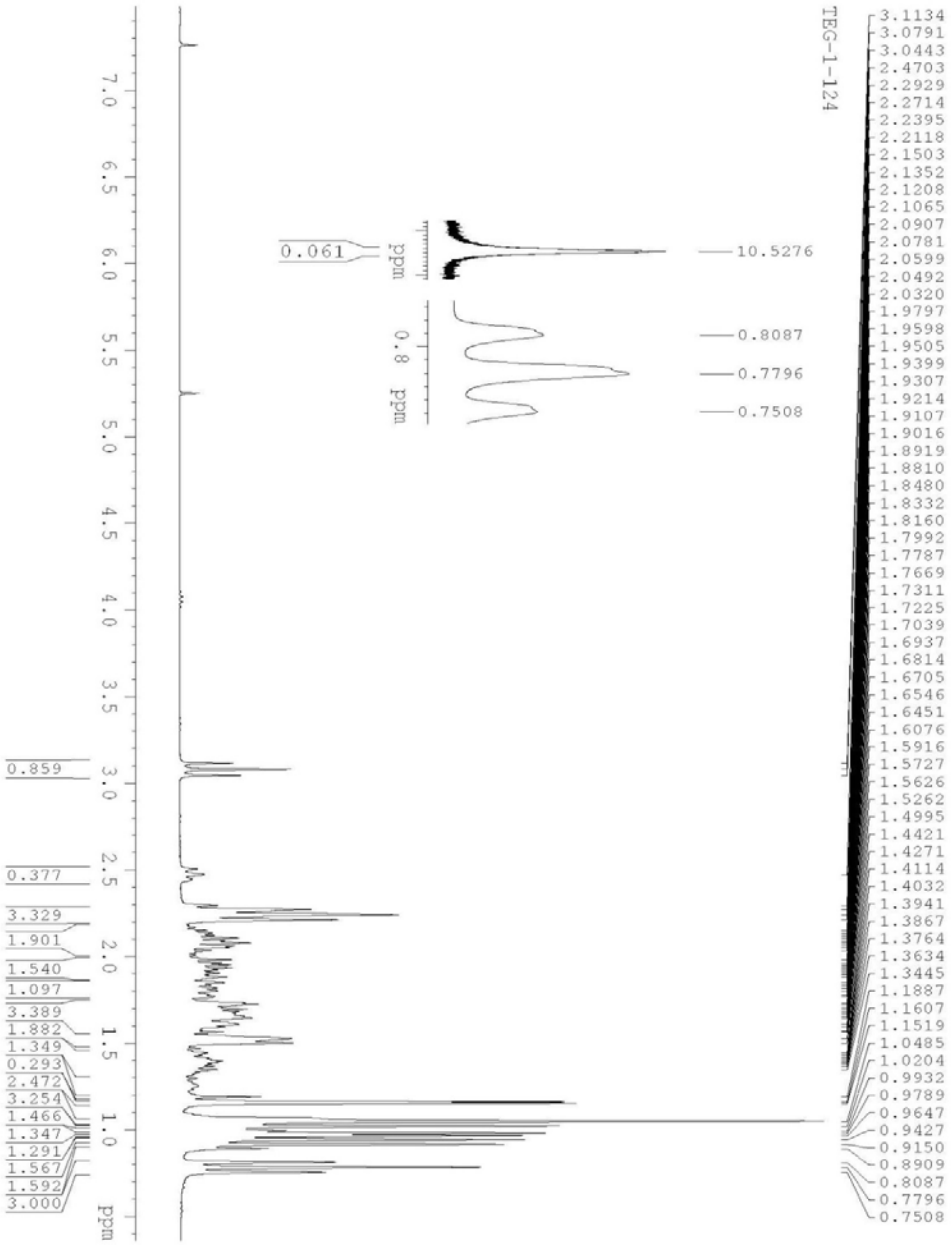

O
O
CF3
O

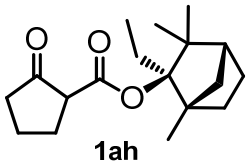
1af


TEG-1-082
210.5125
210.4812
179.2402
167.6518
167.5994
134.1327
131.8281
131.5546
131.5270
131.3658
131.1233
130.9253
130.8159
130.5952
129.6386
129.3772
129.2544
127.8820
127.6129
127.1954
126.5783
126.4463
126.4021
126.2121
126.1709
125.1168
124.4534
122.5009
122.4252
120.8206
120.6733
99.3998
77.5840
77.3620
77.1600
76.7361
70.3498
70.2481
69.9351
69.8850
69.8089
69.4715
69.4200
68.9549
54.2632
54.1396
38.4038
38.0457
37.9809
32.7983
27.4608
27.2658
26.7429
23.2273
20.9362
20.8764
19.0869
ppm

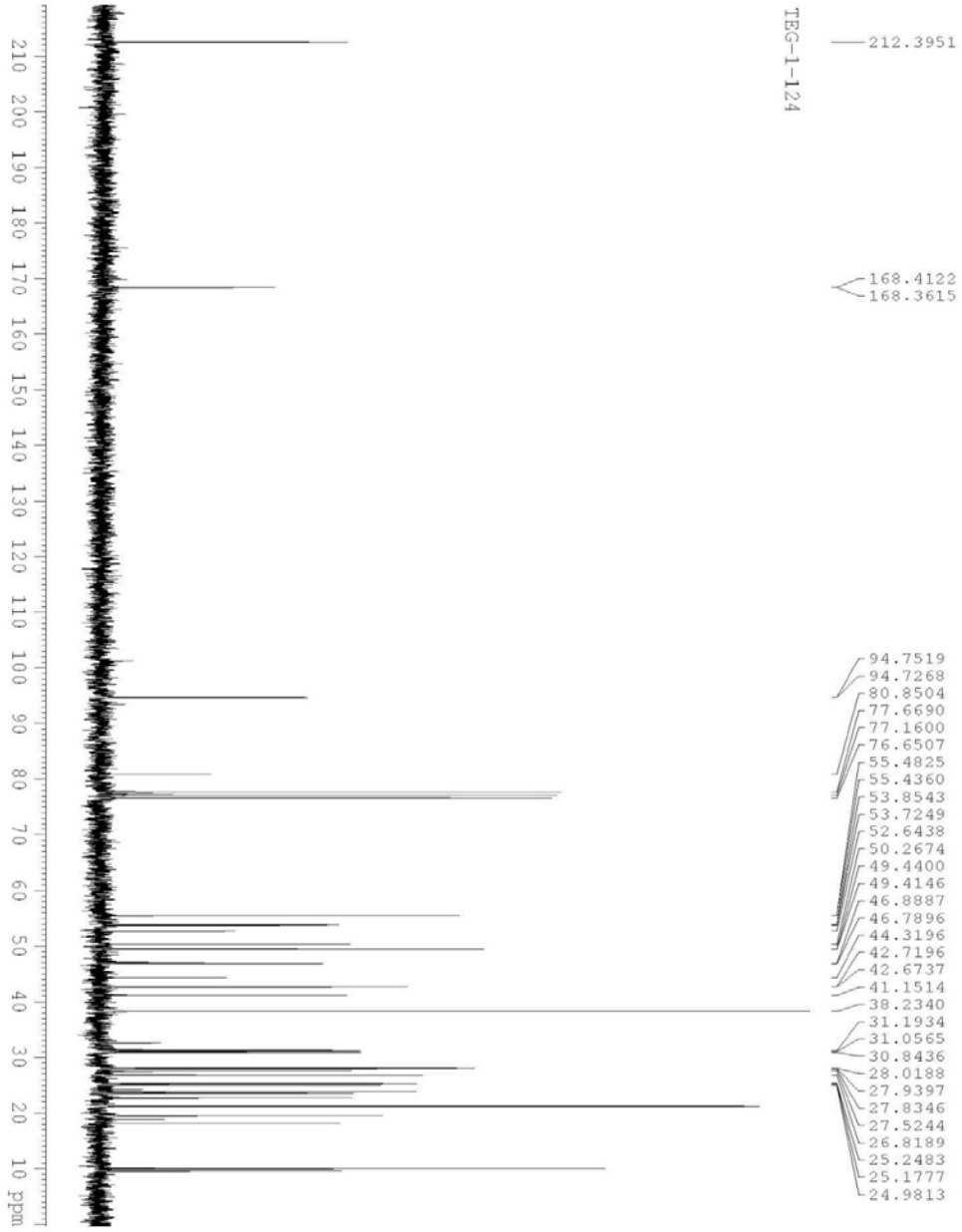


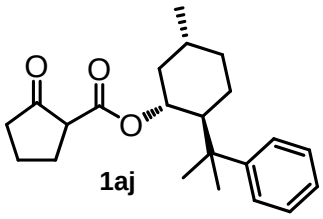
1ah


TEG-1-124
0.061
ppm
0.8 ppm
10.5276
0.8087
0.7796
0.7508
0.859
0.377
3.329
1.901
1.540
1.097
3.389
1.882
1.349
0.293
2.472
3.254
1.466
1.347
1.291
1.567
1.592
3.000
ppm



1ah


TEG-1-124
212.3951
168.4122
168.3615
94.7519
94.7268
80.8504
77.6690
77.1600
76.6507
55.4825
55.4360
53.8543
53.7249
52.6438
50.2674
49.4400
49.4146
46.8887
46.7896
44.3196
42.7196
42.6737
41.1514
38.2340
31.1934
31.0565
30.8436
28.0188
27.9397
27.8346
27.5244
26.8189
25.2483
25.1777
24.9813
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



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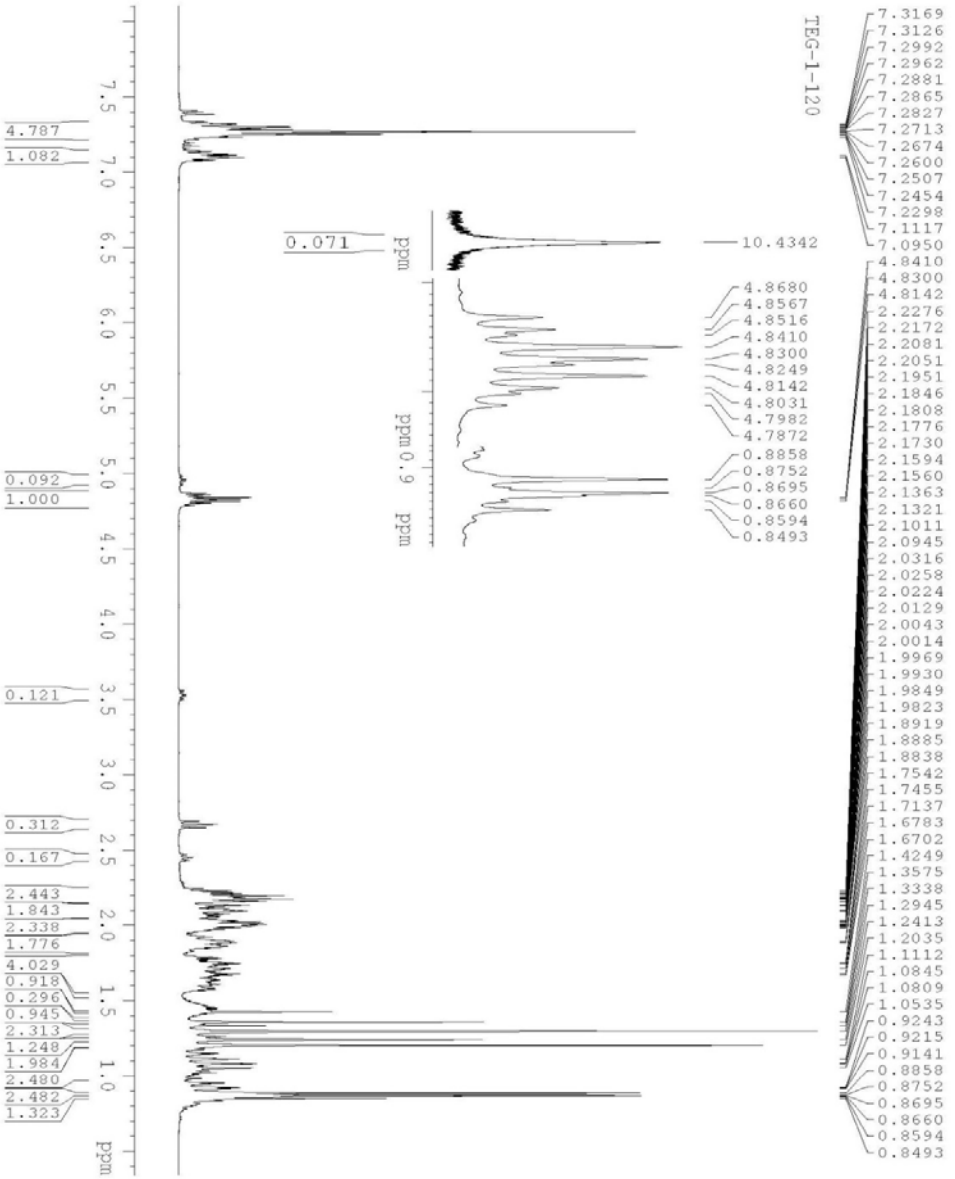
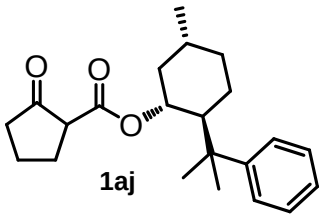
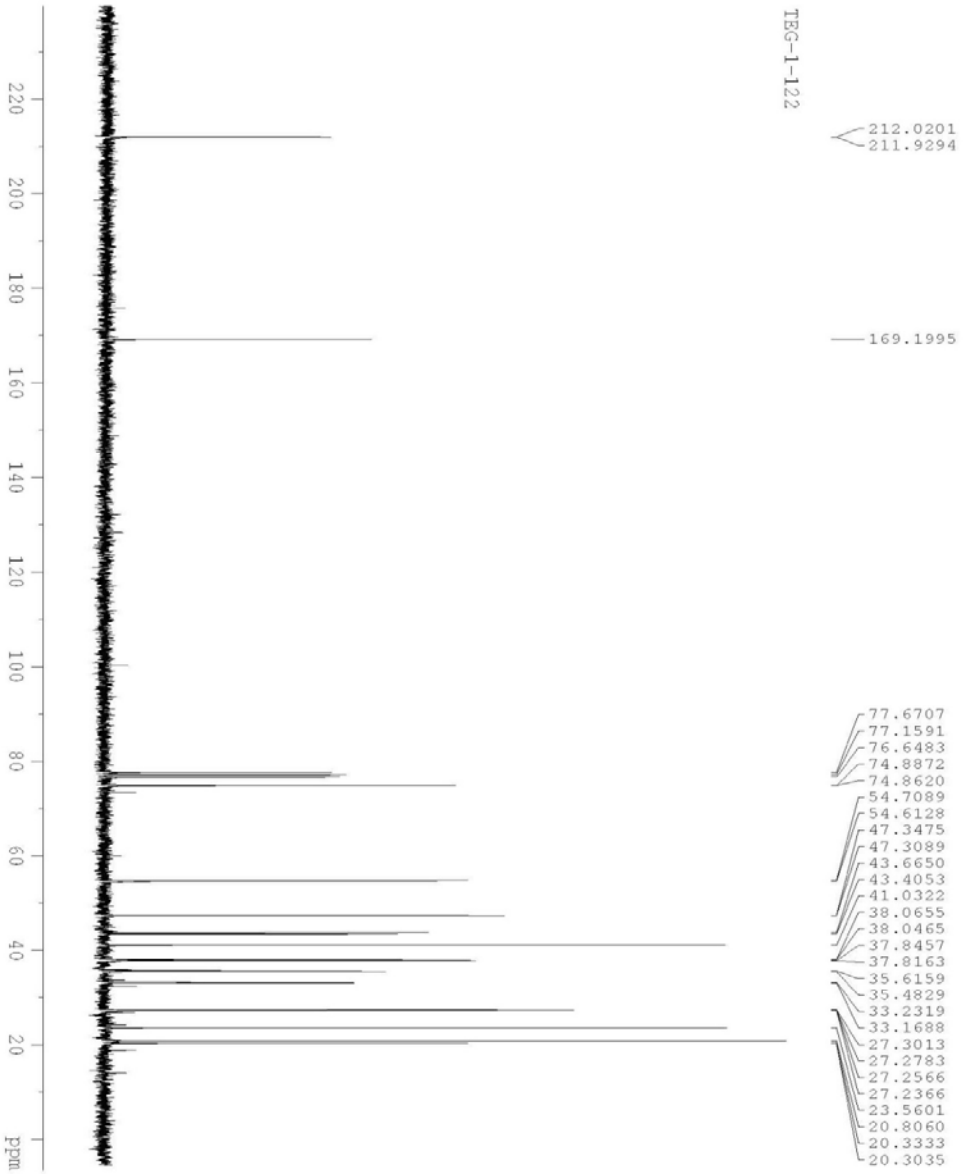

TEG-1-120
7.3169
7.3126
7.2992
7.2962
7.2881
7.2865
7.2827
7.2713
7.2674
7.2600
7.2507
7.2454
7.2298
7.1117
7.0950
4.8410
4.8300
4.8142
2.2276
2.2172
2.2081
2.2051
2.1951
2.1846
2.1808
2.1776
2.1730
2.1594
2.1560
2.1363
2.1321
2.1011
2.0945
2.0316
2.0258
2.0224
2.0129
2.0043
2.0014
1.9969
1.9930
1.9849
1.9823
1.8919
1.8885
1.8838
1.7542
1.7455
1.7137
1.6783
1.6702
1.4249
1.3575
1.3338
1.2945
1.2413
1.2035
1.1112
1.0845
1.0809
1.0535
0.9243
0.9215
0.9141
0.8858
0.8752
0.8695
0.8660
0.8594
0.8493
10.4342
4.8680
4.8567
4.8516
4.8410
4.8300
4.8249
4.8142
4.8031
4.7982
4.7872
0.8858
0.8752
0.8695
0.8660
0.8594
0.8493
0.071
ppm
0.6 ppm
4.787
1.082
0.092
1.000
0.121
0.312
0.167
2.443
1.843
2.338
1.776
4.029
0.918
0.296
0.945
2.313
1.248
1.984
2.480
2.482
1.323
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm



1aj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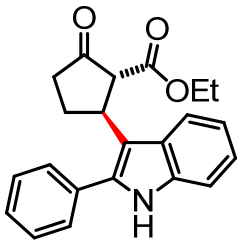
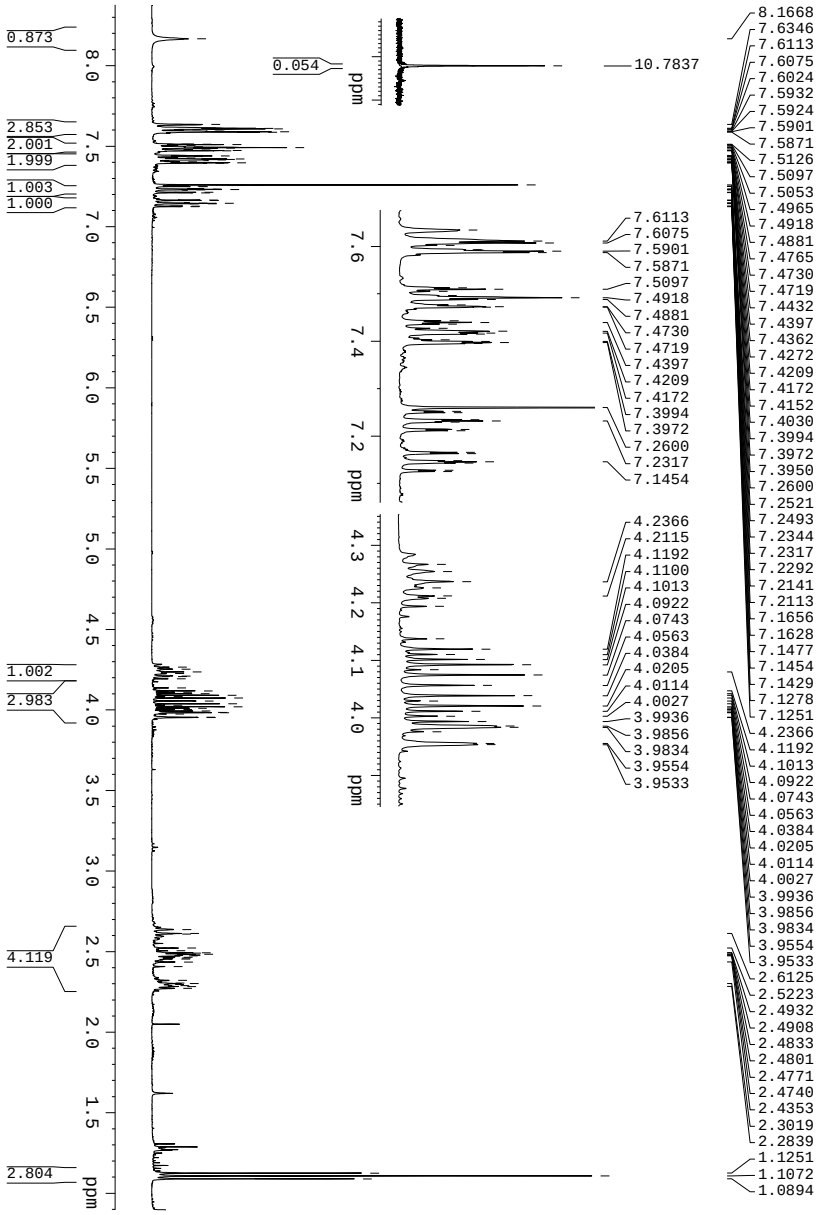
169.1995
77.6707
77.1591
76.6483
74.8872
74.8620
54.7089
54.6128
47.3475
47.3089
43.6650
43.4053
41.0322
38.0655
38.0465
37.8457
37.8163
35.6159
35.4829
33.2319
33.1688
27.3013
27.2783
27.2566
27.2366
23.5601
20.8060
20.3333
20.3035
220
200
180
160
140
120
100
80
60
40
20
ppm


O
O
OEt
N
H

3c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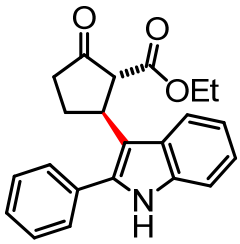
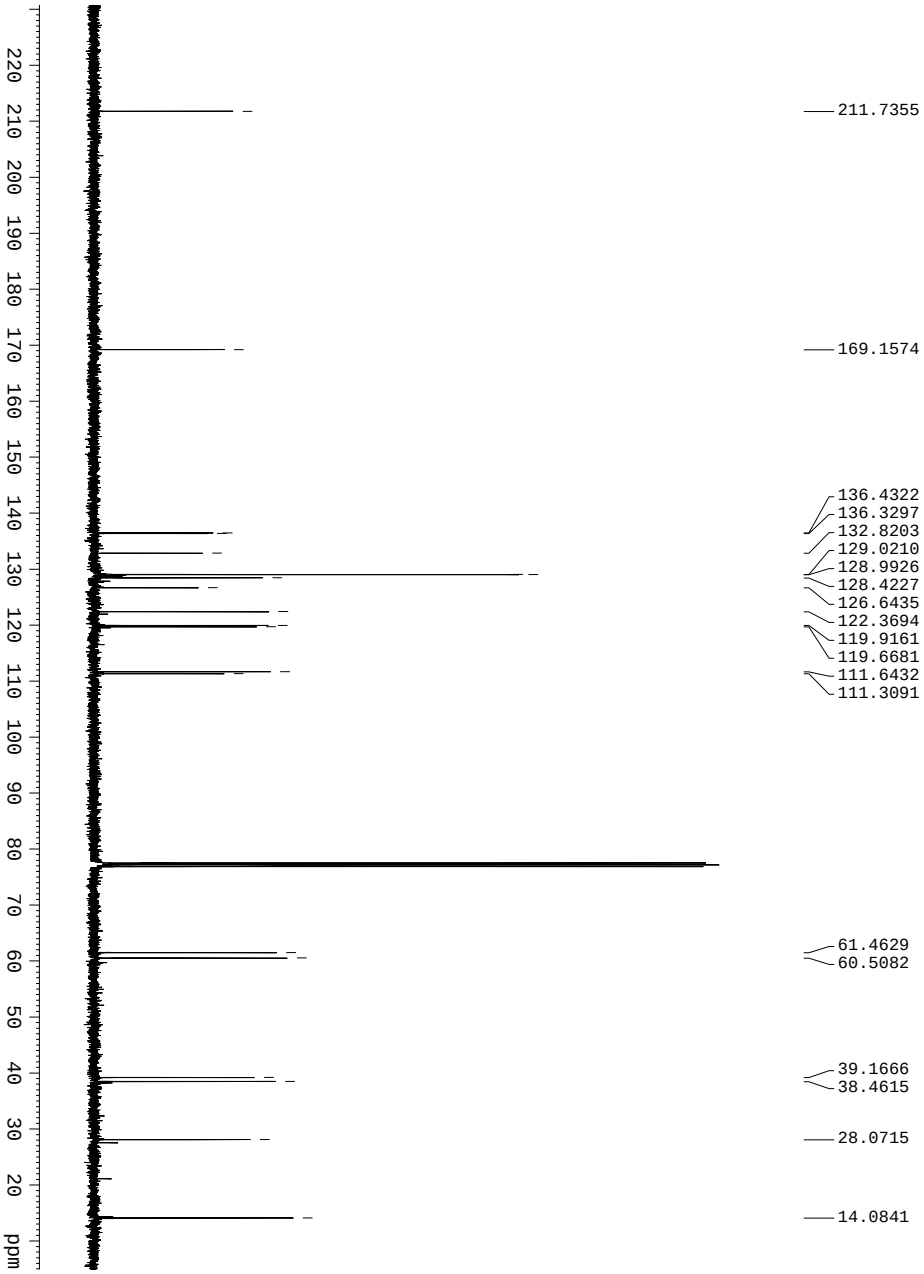
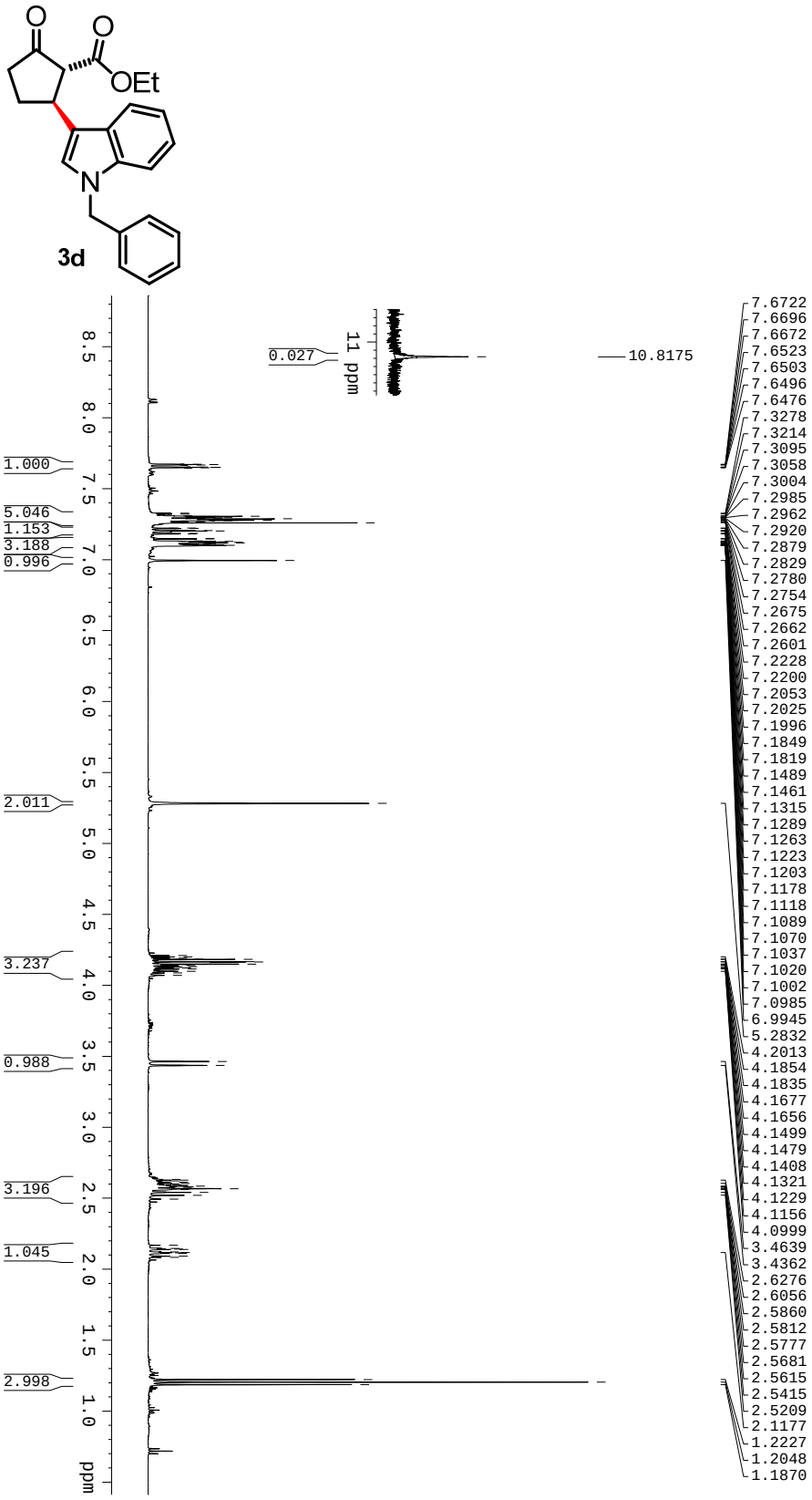
2.001
1.999
1.003
1.000
1.002
2.983
4.119
2.804
0.054
10.7837
ppm
8.1668
7.6346
7.6113
7.6075
7.6024
7.5932
7.5924
7.5901
7.5871
7.5126
7.5097
7.5053
7.4965
7.4918
7.4881
7.4765
7.4730
7.4719
7.4432
7.4397
7.4362
7.4272
7.4209
7.4172
7.4152
7.4030
7.3994
7.3972
7.3950
7.2600
7.2521
7.2493
7.2344
7.2317
7.2292
7.2141
7.2113
7.1656
7.1628
7.1477
7.1454
7.1429
7.1278
7.1251
4.2366
4.1192
4.1013
4.0922
4.0743
4.0563
4.0384
4.0205
4.0114
4.0027
3.9936
3.9856
3.9834
3.9554
3.9533
2.6125
2.5223
2.4932
2.4908
2.4833
2.4801
2.4771
2.4740
2.4353
2.3019
2.2839
1.1251
1.1072
1.0894


O
O
OEt
N
H

3c


211.7355
169.1574
136.4322
136.3297
132.8203
129.0210
128.9926
128.4227
126.6435
122.3694
119.9161
119.6681
111.6432
111.3091
61.4629
60.5082
39.1666
38.4615
28.0715
14.0841
ppm


O
O
OEt
N
3d
0.027
11 ppm
10.8175
1.000
5.046
1.153
3.188
0.996
2.011
3.237
0.988
3.196
1.045
2.998
ppm
7.6722
7.6696
7.6672
7.6523
7.6503
7.6496
7.6476
7.3278
7.3214
7.3095
7.3058
7.3004
7.2985
7.2962
7.2920
7.2879
7.2829
7.2780
7.2754
7.2675
7.2662
7.2601
7.2228
7.2200
7.2053
7.2025
7.1996
7.1849
7.1819
7.1489
7.1461
7.1315
7.1289
7.1263
7.1223
7.1203
7.1178
7.1118
7.1089
7.1070
7.1037
7.1020
7.1002
7.0985
6.9945
5.2832
4.2013
4.1854
4.1835
4.1677
4.1656
4.1499
4.1479
4.1408
4.1321
4.1229
4.1156
4.0999
3.4639
3.4362
2.6276
2.6056
2.5860
2.5812
2.5777
2.5681
2.5615
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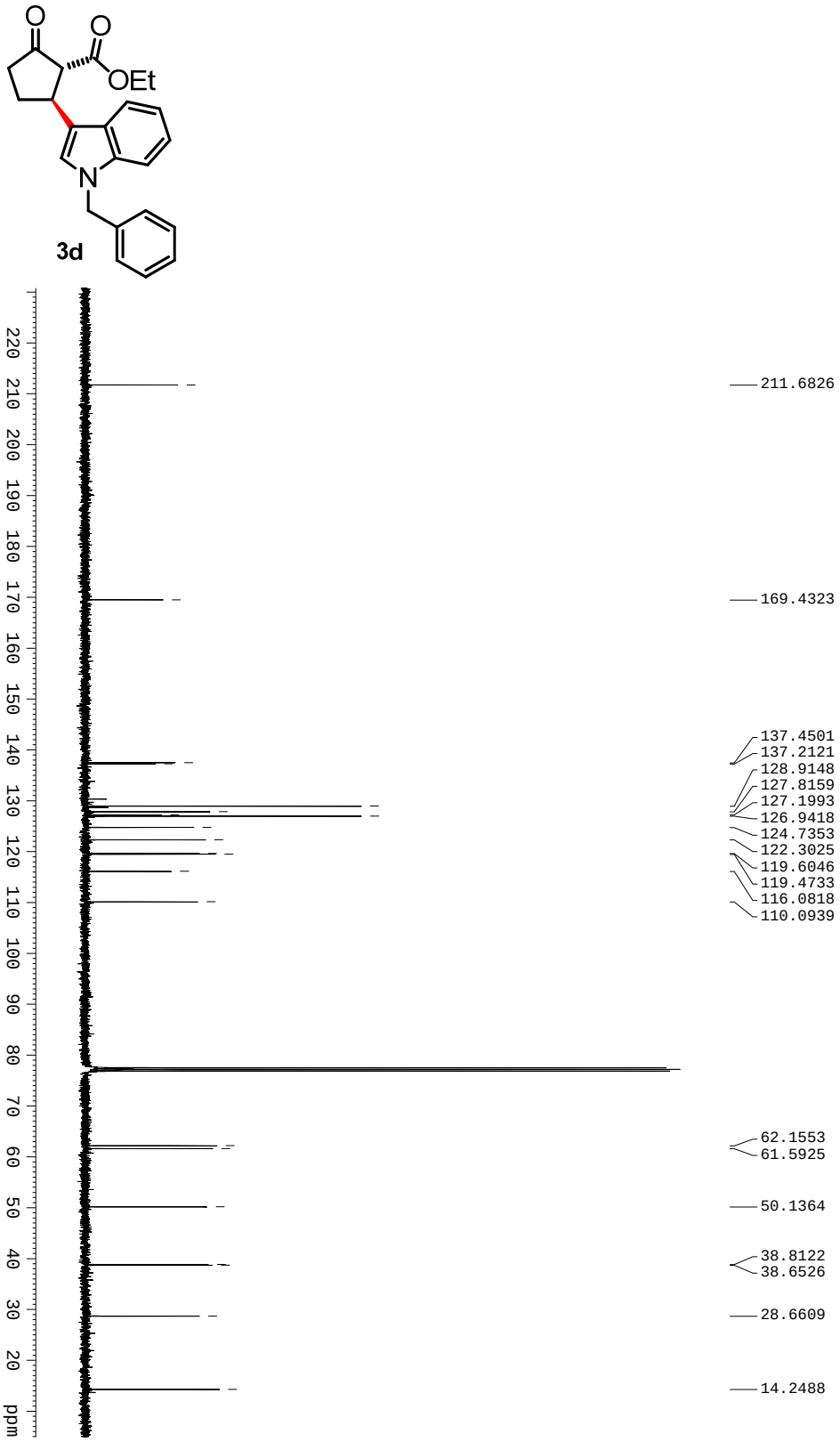
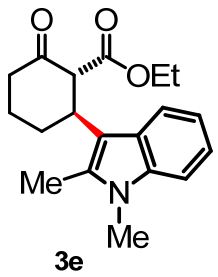
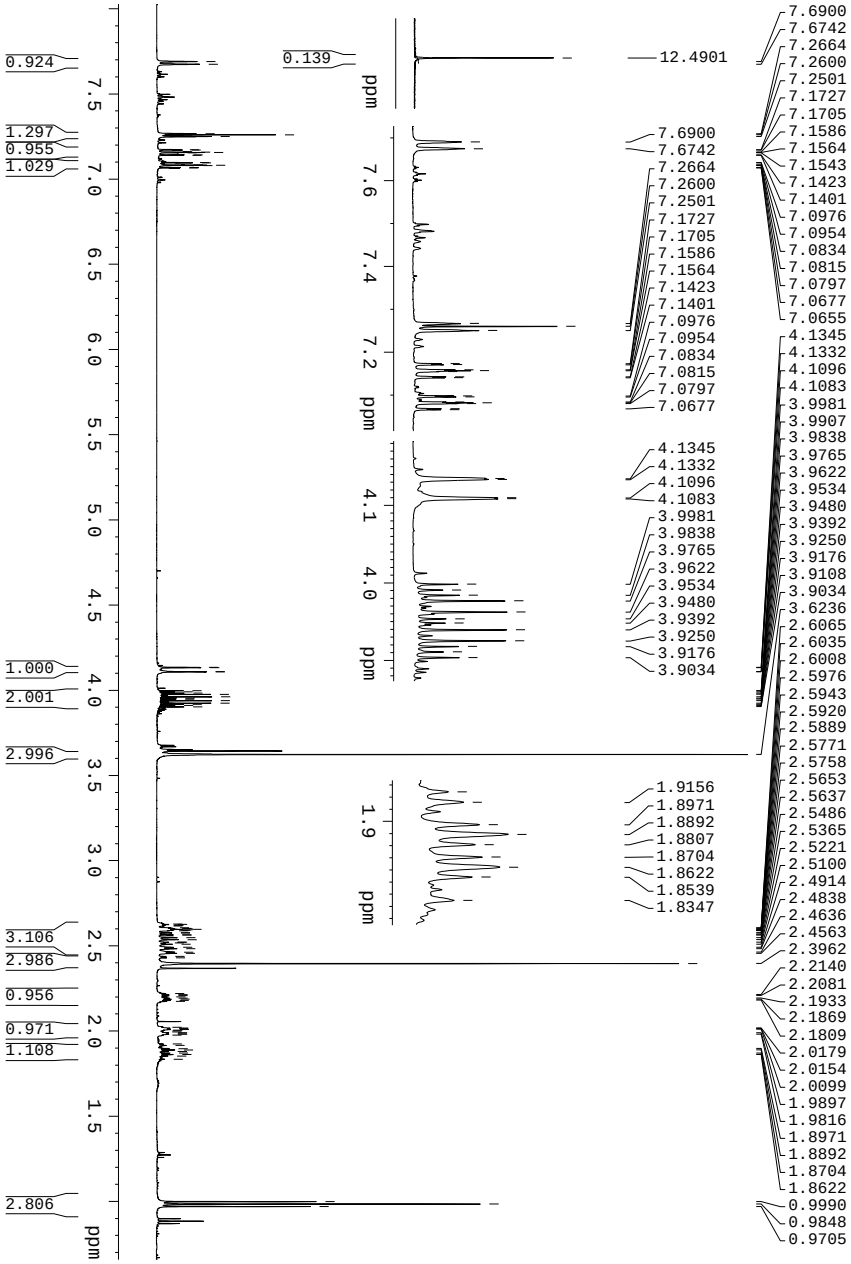
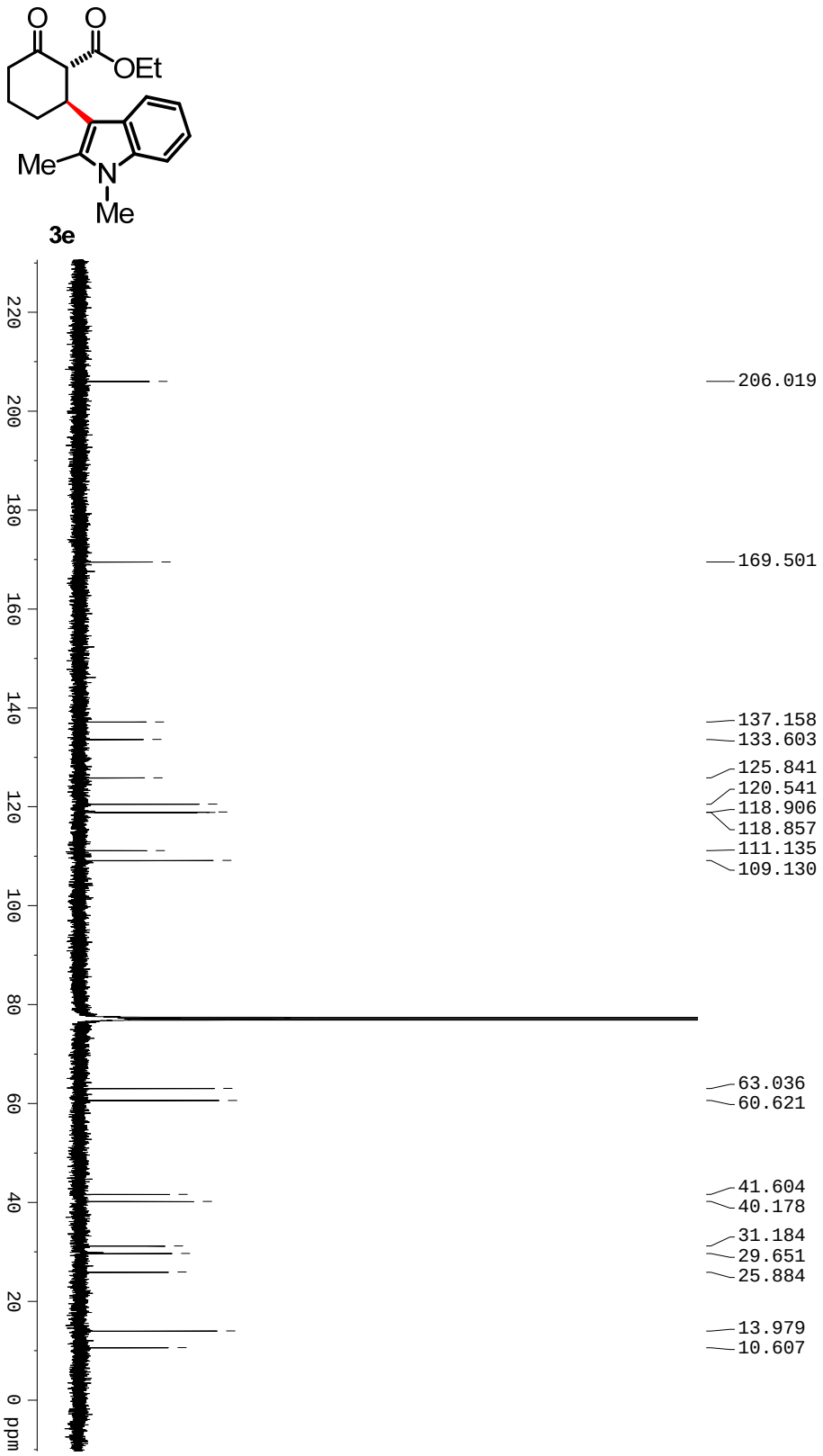
2.5209
2.1177
1.2227
1.2048
1.1870

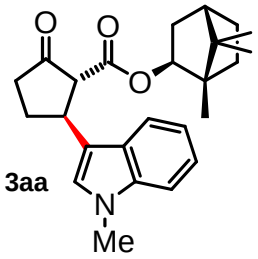

O
O
OEt
N
3d
211.6826
169.4323
137.4501
137.2121
128.9148
127.8159
127.1993
126.9418
124.7353
122.3025
119.6046
119.4733
116.0818
110.0939
62.1553
61.5925
50.1364
38.8122
38.6526
28.6609
14.2488
ppm


O
O
OEt
Me
N
Me

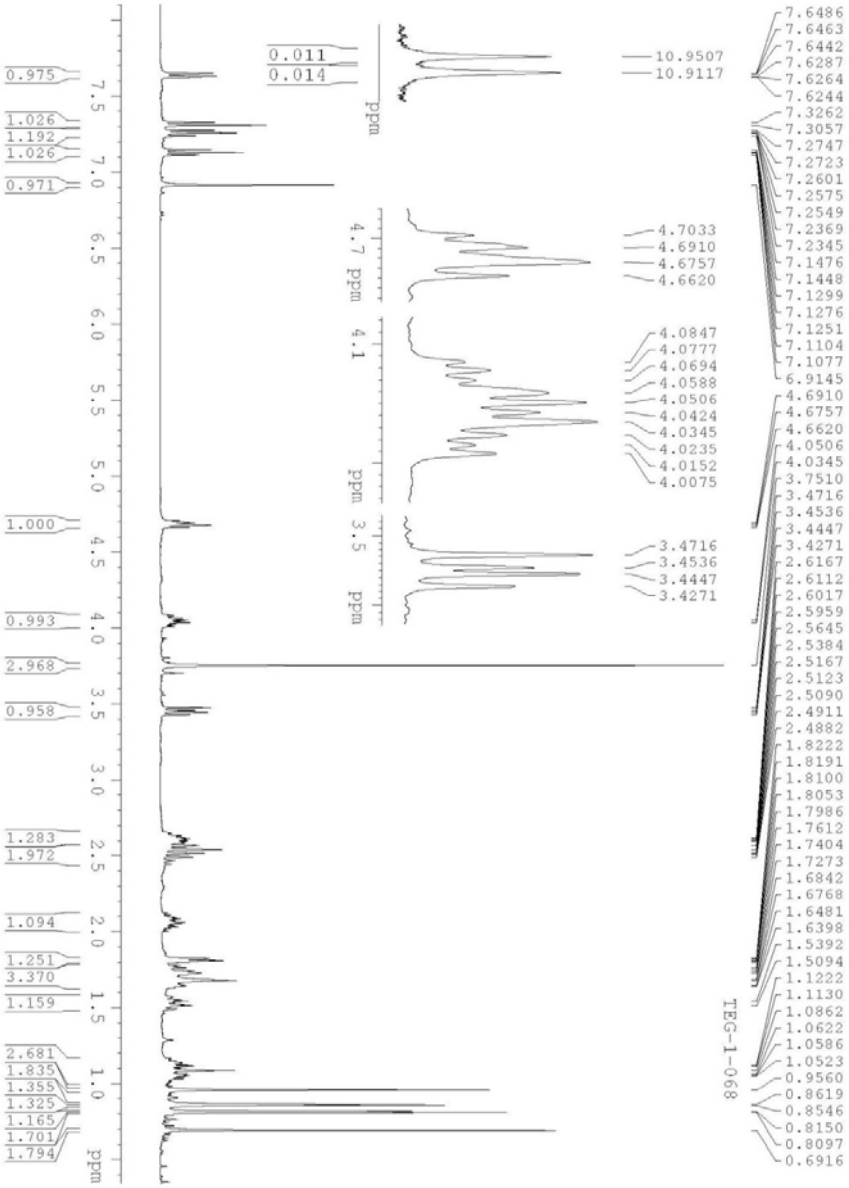
3e

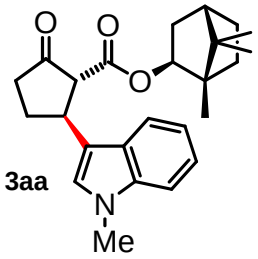

0.924
1.297
0.955
1.029
1.000
2.001
2.996
3.106
2.986
0.956
0.971
1.108
2.806
0.139
12.4901
7.6900
7.6742
7.2664
7.2600
7.2501
7.1727
7.1705
7.1586
7.1564
7.1423
7.1401
7.0976
7.0954
7.0834
7.0815
7.0797
7.0677
4.1345
4.1332
4.1096
4.1083
3.9981
3.9838
3.9765
3.9622
3.9534
3.9480
3.9392
3.9250
3.9176
3.9034
1.9156
1.8971
1.8892
1.8807
1.8704
1.8622
1.8539
1.8347
0.9990
0.9848
0.9705
ppm


3e
206.019
169.501
137.158
133.603
125.841
120.541
118.906
118.857
111.135
109.130
63.036
60.621
41.604
40.178
31.184
29.651
25.884
13.979
10.607
220
200
180
160
140
120
100
80
60
40
20
0 ppm

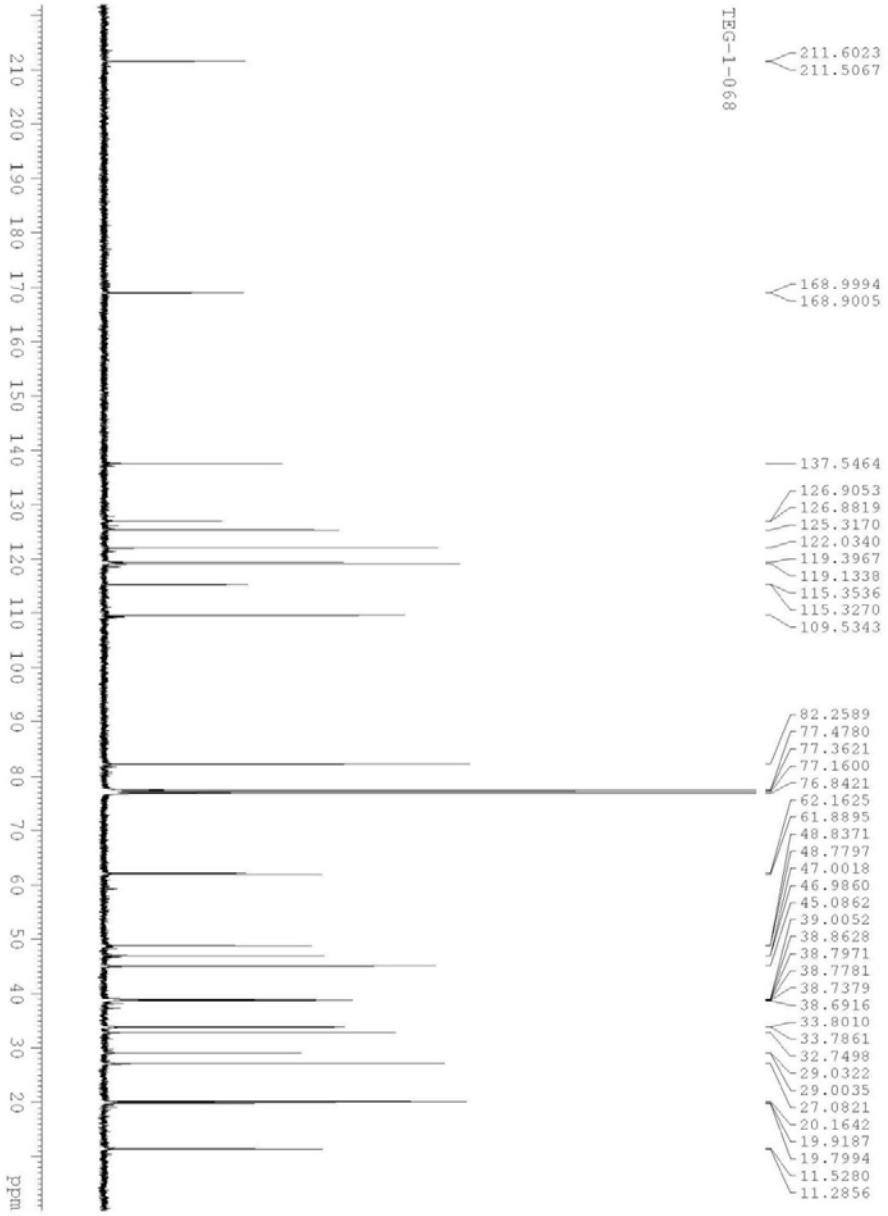

O
O
O
N
Me

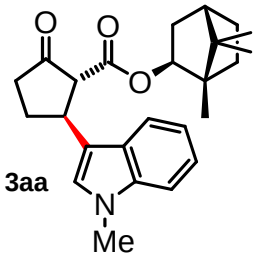
3aa


0.975
1.026
1.192
1.026
0.971
1.000
0.993
2.968
0.958
1.283
1.972
1.094
1.251
3.370
1.159
2.681
1.835
1.355
1.325
1.165
1.701
1.794
ppm
0.011
0.014
4.7 ppm
4.1
ppm
3.5
ppm
10.9507
10.9117
4.7033
4.6910
4.6757
4.6620
4.0847
4.0777
4.0694
4.0588
4.0506
4.0424
4.0345
4.0235
4.0152
4.0075
3.4716
3.4536
3.4447
3.4271
7.6486
7.6463
7.6442
7.6287
7.6264
7.6244
7.3262
7.3057
7.2747
7.2723
7.2601
7.2575
7.2549
7.2369
7.2345
7.1476
7.1448
7.1299
7.1276
7.1251
7.1104
7.1077
6.9145
4.6910
4.6757
4.6620
4.0506
4.0345
3.7510
3.4716
3.4536
3.4447
3.4271
2.6167
2.6112
2.6017
2.5959
2.5645
2.5384
2.5167
2.5123
2.5090
2.4911
2.4882
1.8222
1.8191
1.8100
1.8053
1.7986
1.7612
1.7404
1.7273
1.6842
1.6768
1.6481
1.6398
1.5392
1.5094
1.1222
1.1130
1.0862
1.0622
1.0586
1.0523
0.9560
0.8619
0.8546
0.8150
0.8097
0.6916
TEG-1-068

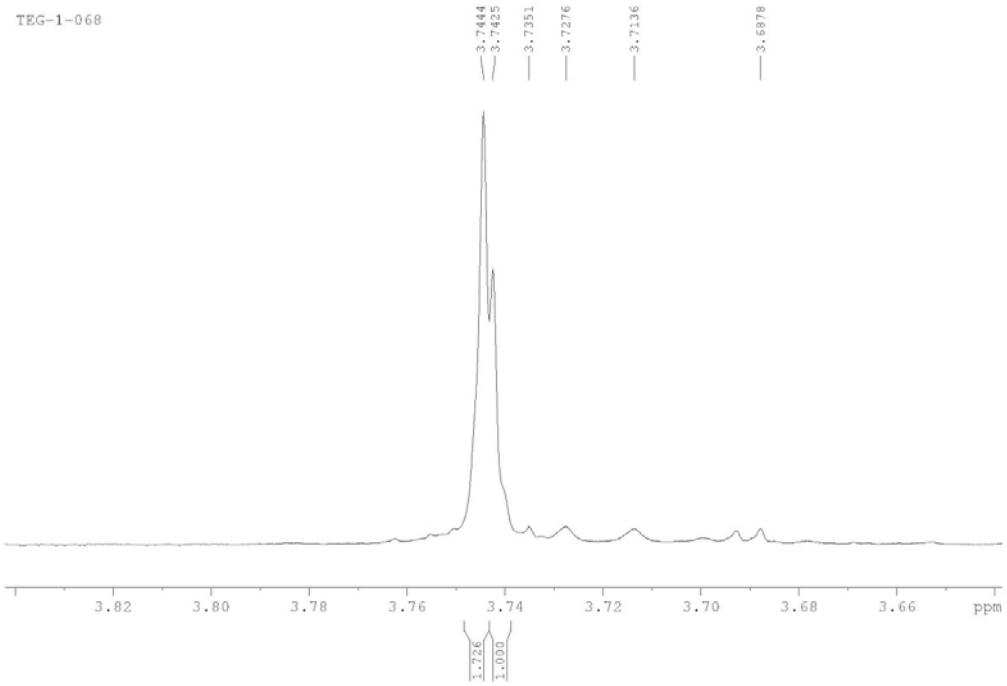

O
O
O
N
Me

3aa


TEG-1-068
211.6023
211.5067
168.9994
168.9005
137.5464
126.9053
126.8819
125.3170
122.0340
119.3967
119.1338
115.3536
115.3270
109.5343
82.2589
77.4780
77.3621
77.1600
76.8421
62.1625
61.8895
48.8371
48.7797
47.0018
46.9860
45.0862
39.0052
38.8628
38.7971
38.7781
38.7379
38.6916
33.8010
33.7861
32.7498
29.0322
29.0035
27.0821
20.1642
19.9187
19.7994
11.5280
11.2856
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm


O
O
O
N
Me

3aa


TEG-1-068
3.7444
3.7425
3.7351
3.7276
3.7136
3.6878
3.82
3.80
3.78
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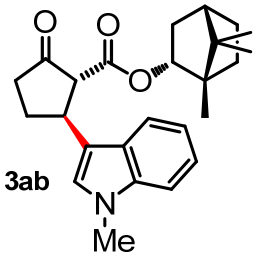
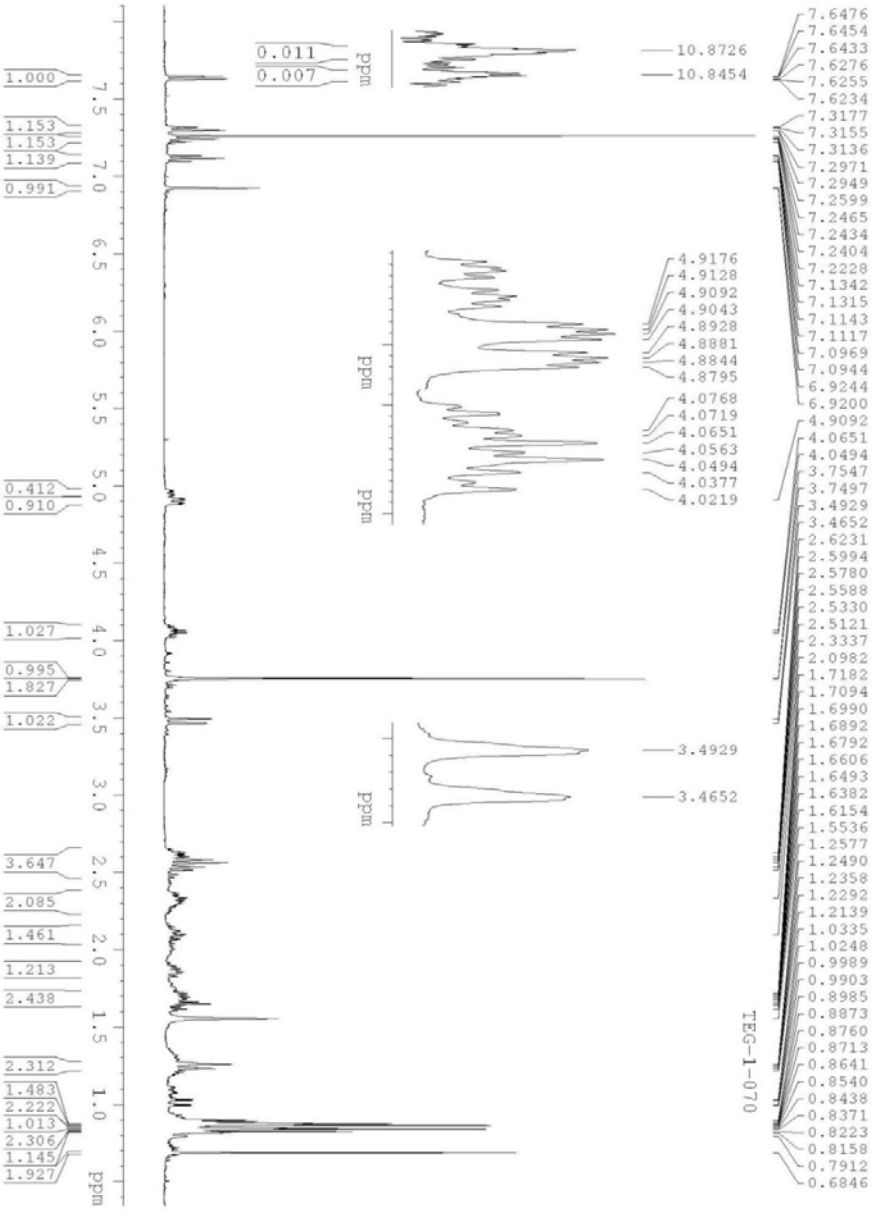
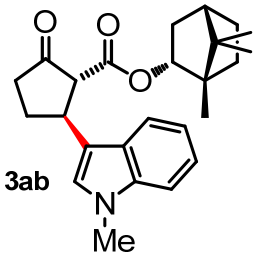
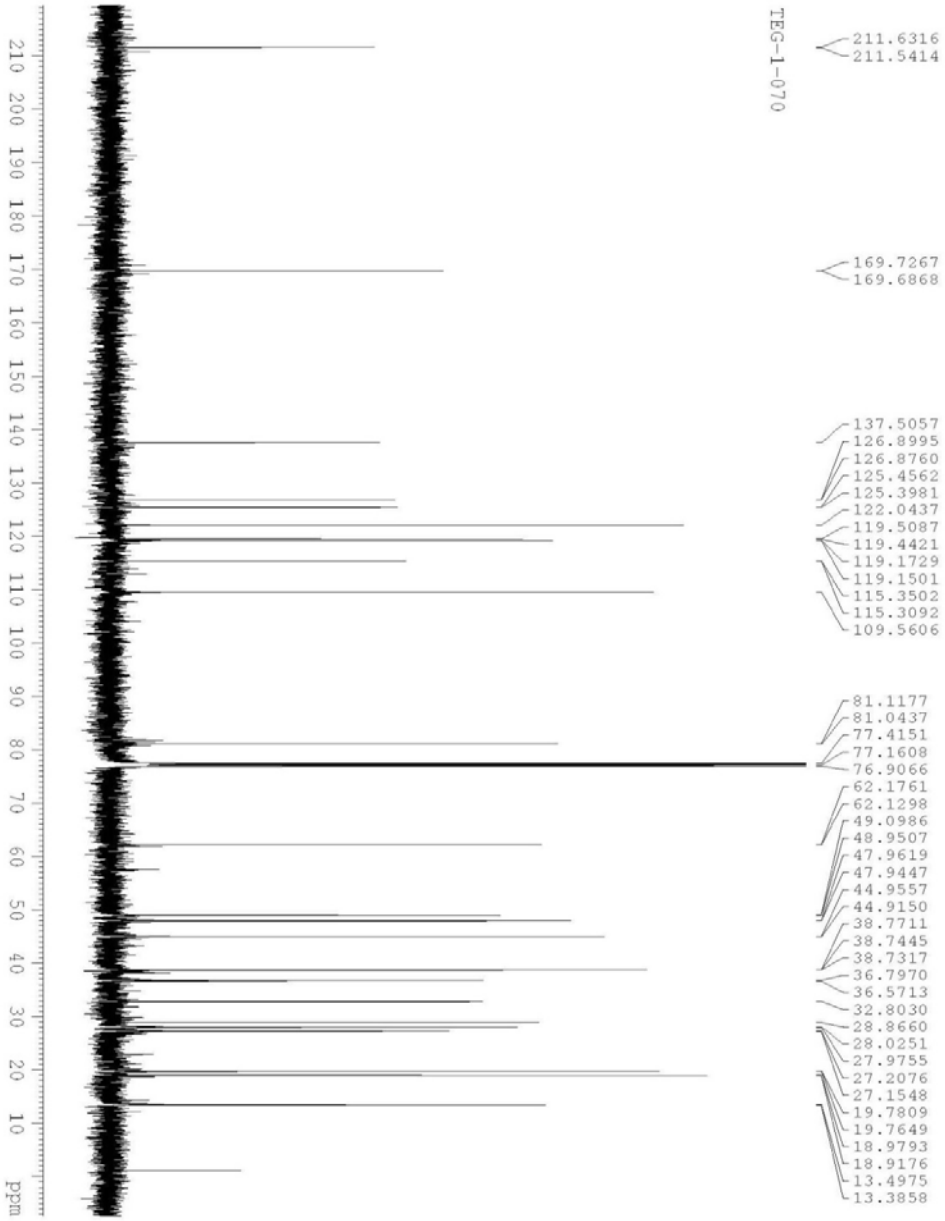
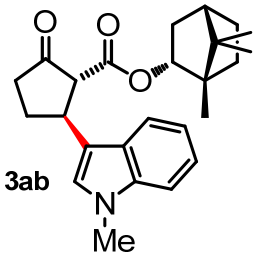
3.74
3.72
3.70
3.68
3.66
ppm
1.726
1.000

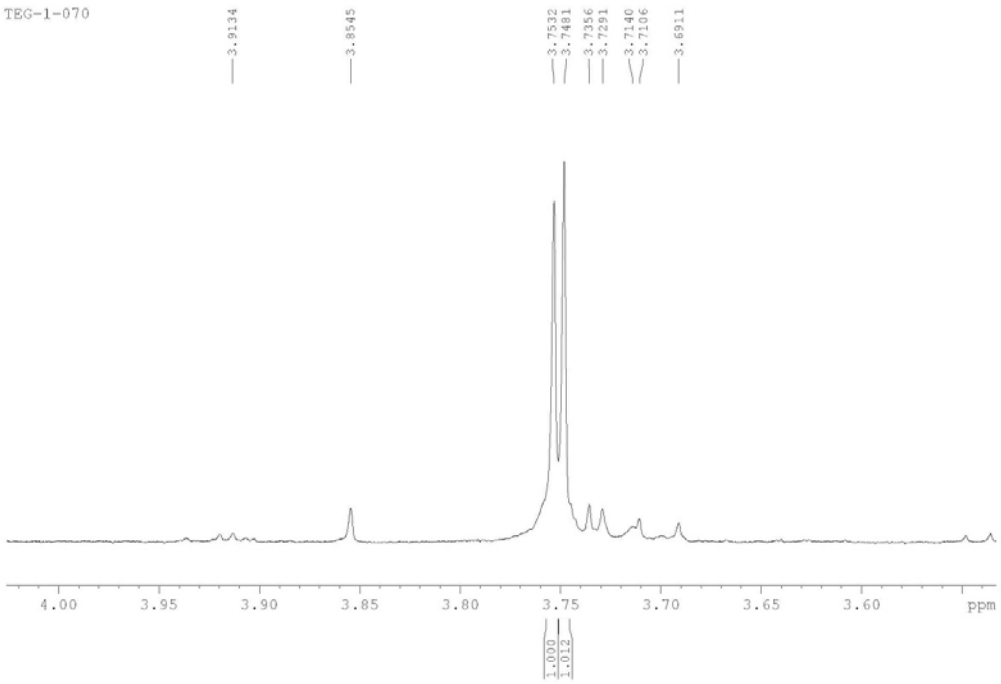

3ab
O
O
O
N
Me


1.000
1.153
1.153
1.139
0.991
0.412
0.910
1.027
0.995
1.827
1.022
3.647
2.085
1.461
1.213
2.438
2.312
1.483
2.222
1.013
2.306
1.145
1.927
0.011
0.007
ppm
10.8726
10.8454
4.9176
4.9128
4.9092
4.9043
4.8928
4.8881
4.8844
4.8795
4.0768
4.0719
4.0651
4.0563
4.0494
4.0377
4.0219
3.4929
3.4652
TEG-1-070


3ab
N
Me


TEG-1-070
211.6316
211.5414
169.7267
169.6868
137.5057
126.8995
126.8760
125.4562
125.3981
122.0437
119.5087
119.4421
119.1729
119.1501
115.3502
115.3092
109.5606
81.1177
81.0437
77.4151
77.1608
76.9066
62.1761
62.1298
49.0986
48.9507
47.9619
47.9447
44.9557
44.9150
38.7711
38.7445
38.7317
36.7970
36.5713
32.8030
28.8660
28.0251
27.9755
27.2076
27.1548
19.7809
19.7649
18.9793
18.9176
13.4975
13.3858
ppm


O
O
O
3ab
N
Me


TEG-1-070
3.9134
3.8545
3.7532
3.7481
3.7356
3.7291
3.7140
3.7106
3.6911
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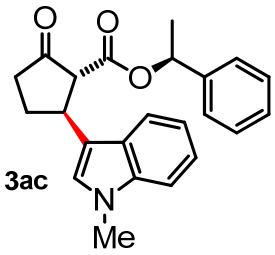
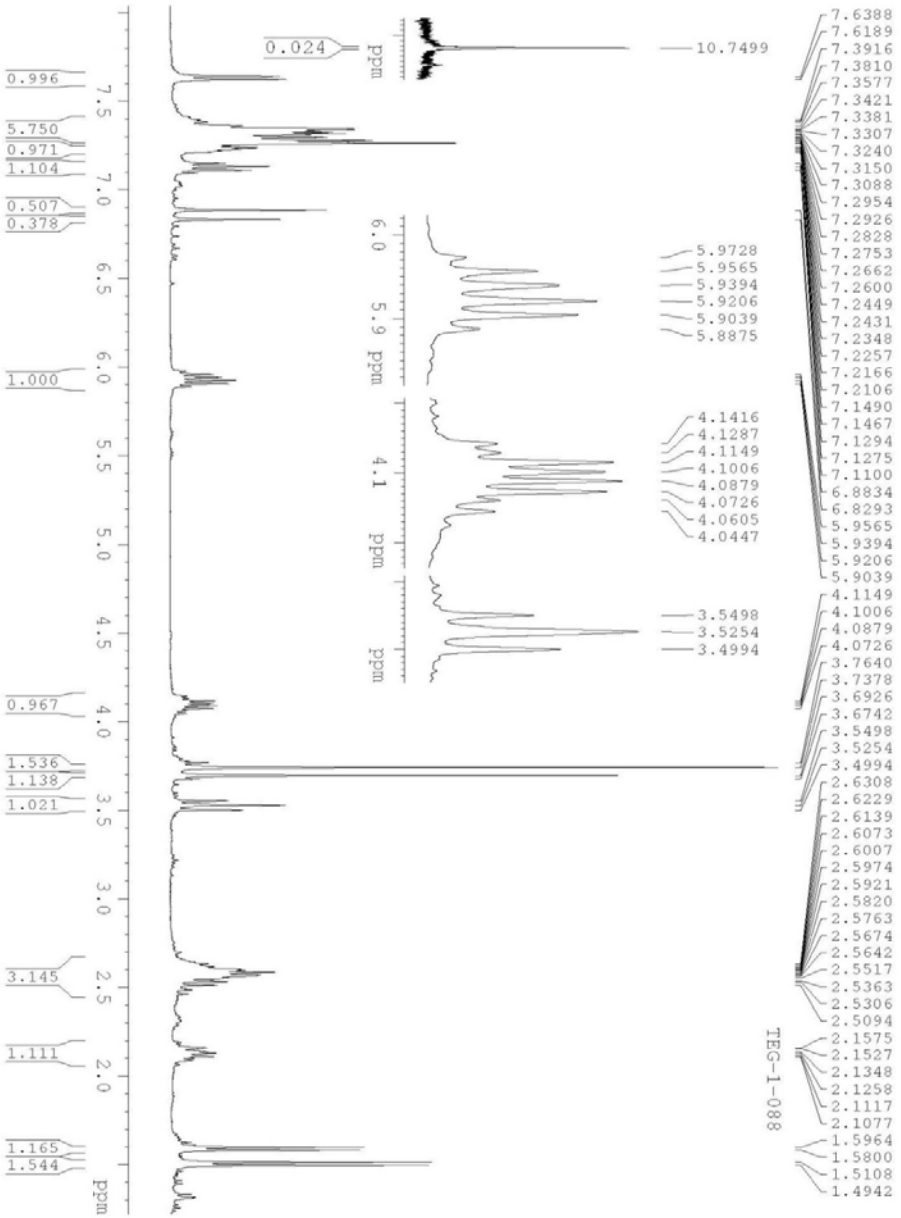
3.70
3.65
3.60
ppm
1.000
1.012


3ac
N
Me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1.111
1.165
1.544
0.024
10.7499
5.9728
5.9565
5.9394
5.9206
5.9039
5.8875
4.1416
4.1287
4.1149
4.1006
4.0879
4.0726
4.0605
4.0447
3.5498
3.5254
3.4994
7.6388
7.6189
7.3916
7.3810
7.3577
7.3421
7.3381
7.3307
7.3240
7.3150
7.3088
7.2954
7.2926
7.2828
7.2753
7.2662
7.2600
7.2449
7.2431
7.2348
7.2257
7.2166
7.2106
7.1490
7.1467
7.1294
7.1275
7.1100
6.8834
6.8293
5.9565
5.9394
5.9206
5.9039
4.1149
4.1006
4.0879
4.0726
3.7640
3.7378
3.6926
3.6742
3.5498
3.5254
3.4994
2.6308
2.6229
2.6139
2.6073
2.6007
2.5974
2.5921
2.5820
2.5763
2.5674
2.5642
2.5517
2.5363
2.5306
2.5094
2.1575
2.1527
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2.1117
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1.5108
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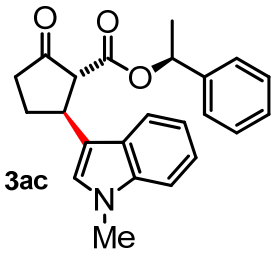
TEG-1-088
ppm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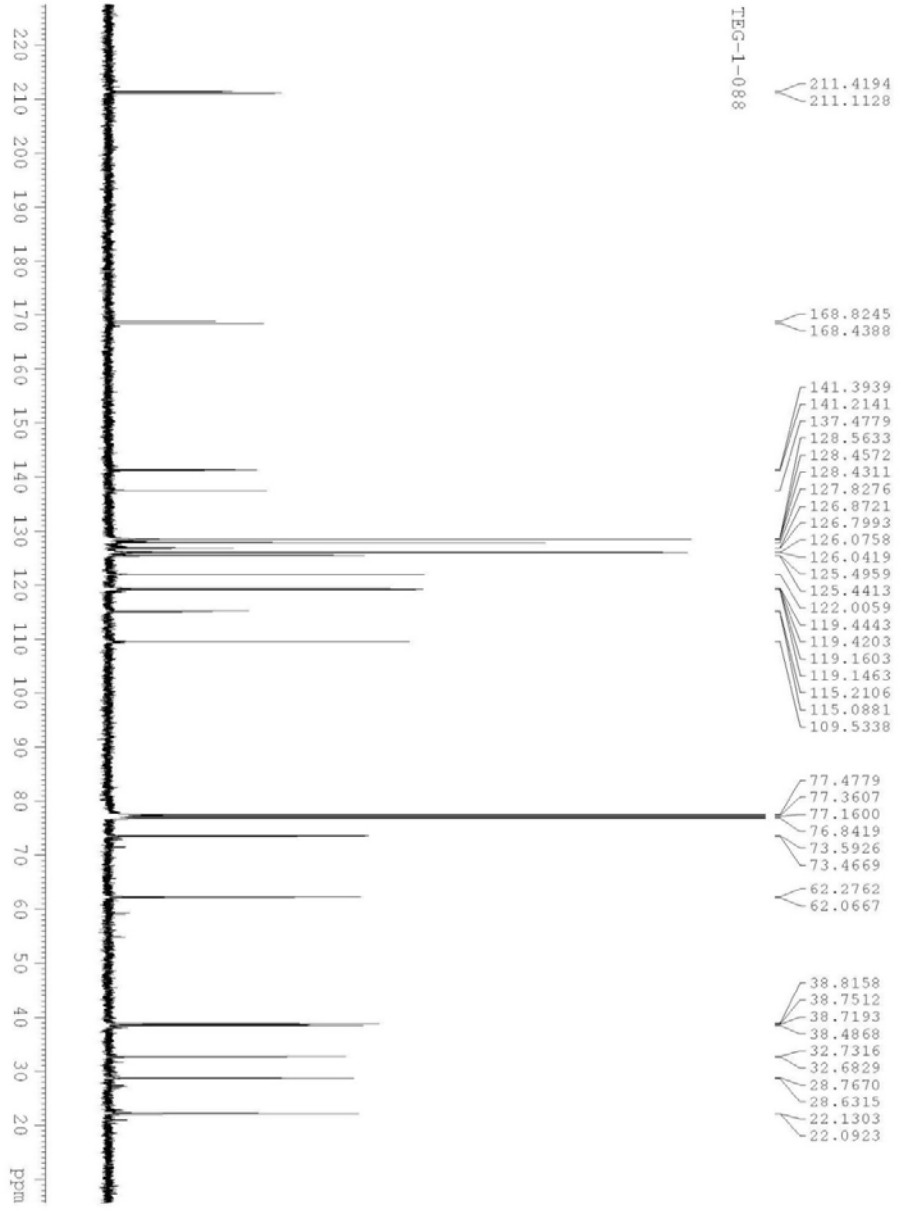
O
O
3ac
N
Me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128.4572
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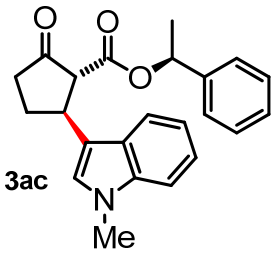
127.8276
126.8721
126.7993
126.0758
126.0419
125.4959
125.4413
122.0059
119.4443
119.4203
119.1603
119.1463
115.2106
115.0881
109.5338
77.4779
77.3607
77.1600
76.8419
73.5926
73.4669
62.2762
62.0667
38.8158
38.7512
38.7193
38.4868
32.7316
32.6829
28.7670
28.6315
22.1303
22.0923
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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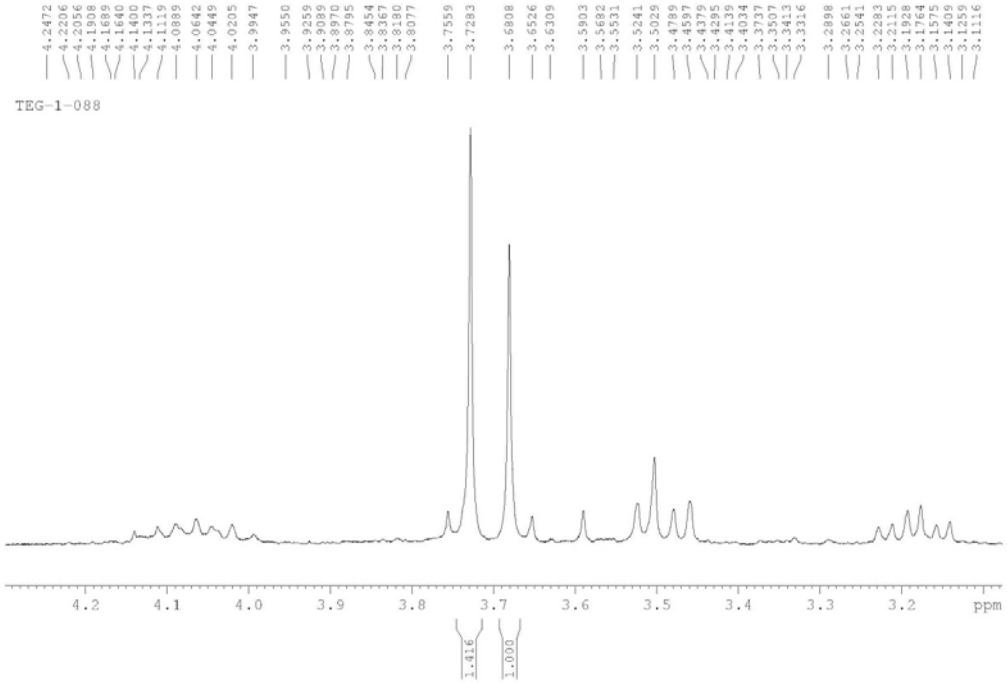
3ac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4.0642
4.0449
4.0295
3.9947
3.9550
3.9259
3.9089
3.8970
3.8795
3.8454
3.8367
3.8180
3.8077
3.7559
3.7293
3.6808
3.6526
3.6309
3.5903
3.5682
3.5531
3.5241
3.5029
3.4789
3.4597
3.4379
3.4295
3.4139
3.4034
3.3737
3.3507
3.3413
3.3316
3.2898
3.2661
3.2541
3.2283
3.2115
3.1928
3.1764
3.1575
3.1409
3.1259
3.1116
TEG-1-088
4.2
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3.8
3.7
3.6
3.5
3.4
3.3
3.2
ppm
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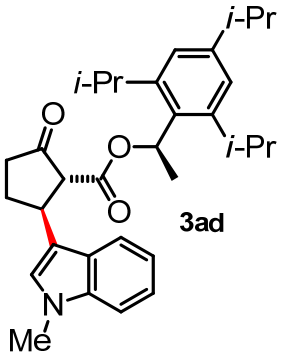
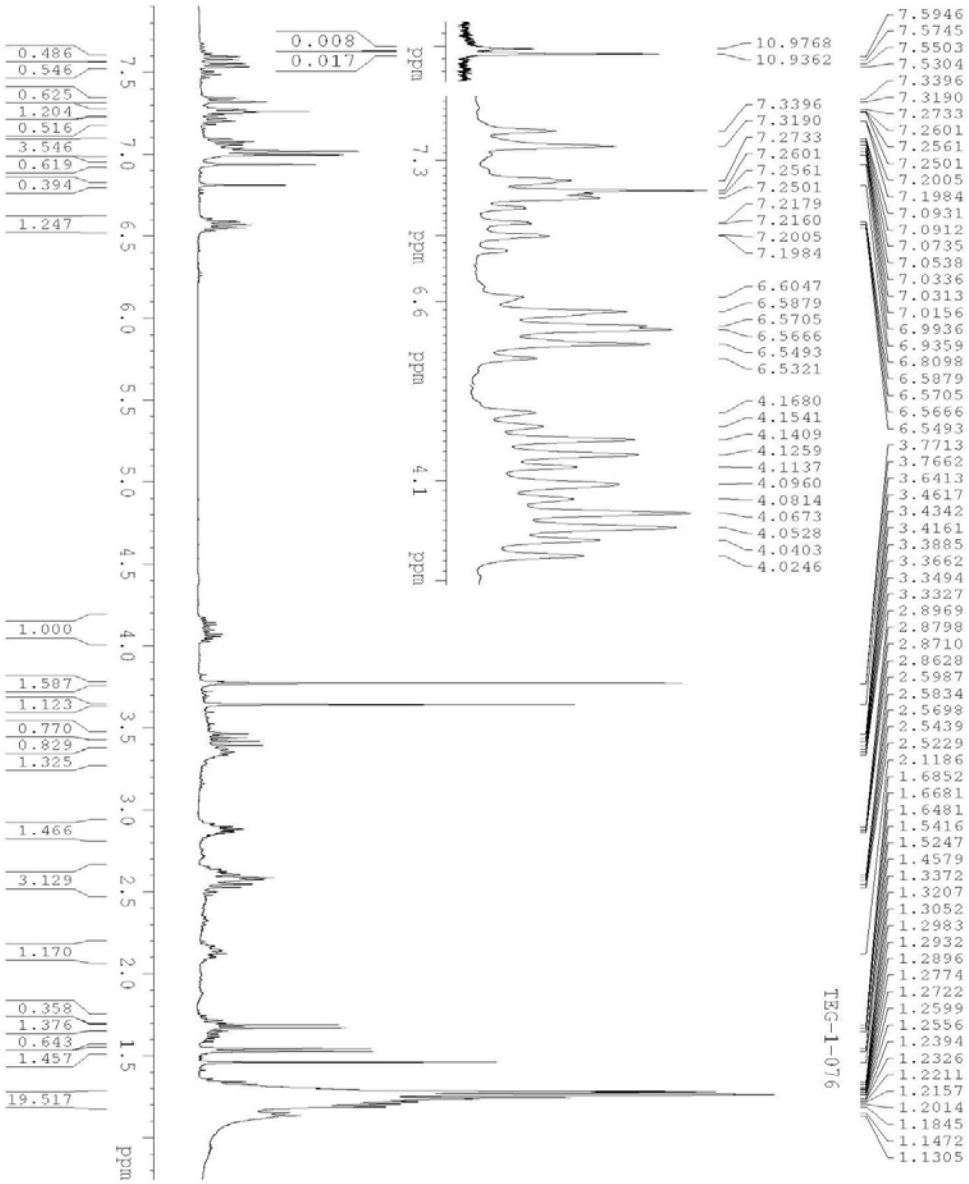
1.000


i-Pr
i-Pr
i-Pr
O
O
O
3ad
N
Me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0.516
3.546
0.619
0.394
1.247
1.000
1.587
1.123
0.770
0.829
1.325
1.466
3.129
1.170
0.358
1.376
0.643
1.457
19.517
0.008
0.017
10.9768
10.9362
7.3396
7.3190
7.2733
7.2601
7.2561
7.2501
7.2179
7.2160
7.2005
7.1984
6.6047
6.5879
6.5705
6.5666
6.5493
6.5321
4.1680
4.1541
4.1409
4.1259
4.1137
4.0960
4.0814
4.0673
4.0528
4.0403
4.0246
7.5946
7.5745
7.5503
7.5304
7.3396
7.3190
7.2733
7.2601
7.2561
7.2501
7.2005
7.1984
7.0931
7.0912
7.0735
7.0538
7.0336
7.0313
7.0156
6.9936
6.9359
6.8098
6.5879
6.5705
6.5666
6.5493
3.7713
3.7662
3.6413
3.4617
3.4342
3.4161
3.3885
3.3662
3.3494
3.3327
2.8969
2.8798
2.8710
2.8628
2.5987
2.5834
2.5698
2.5439
2.5229
2.1186
1.6852
1.6681
1.6481
1.5416
1.5247
1.4579
1.3372
1.3207
1.3052
1.2983
1.2932
1.2896
1.2774
1.2722
1.2599
1.2556
1.2394
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1.2211
1.2157
1.2014
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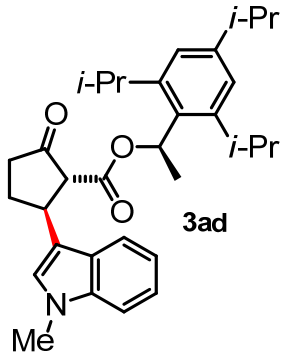
1.1472
1.1305
TEC-1-076
ppm


i-Pr
i-Pr
i-Pr
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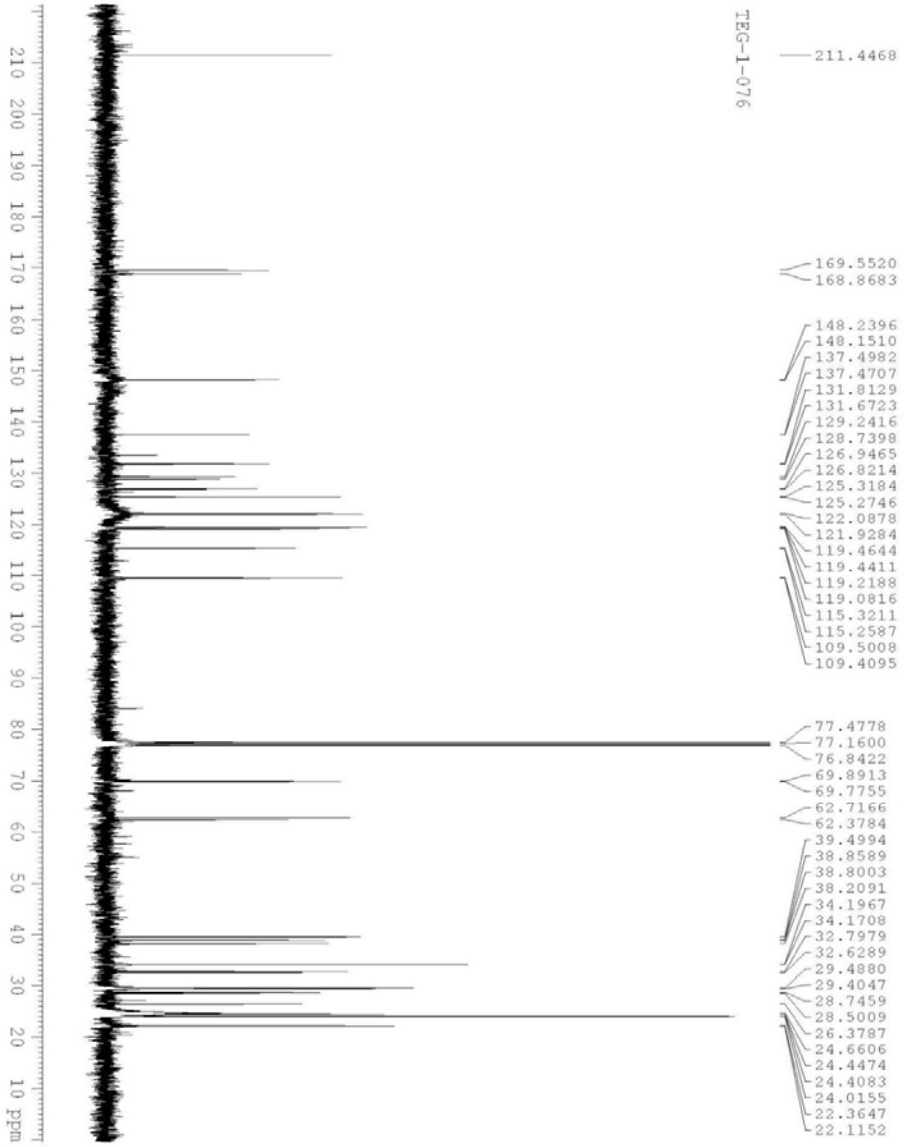
O
O
N
Me

3ad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148.1510
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137.4707
131.8129
131.6723
129.2416
128.7398
126.9465
126.8214
125.3184
125.2746
122.0878
121.9284
119.4644
119.4411
119.2188
119.0816
115.3211
115.2587
109.5008
109.4095
77.4778
77.1600
76.8422
69.8913
69.7755
62.7166
62.3784
39.4994
38.8589
38.8003
38.2091
34.1967
34.1708
32.7979
32.6289
29.4880
29.4047
28.7459
28.5009
26.3787
24.6606
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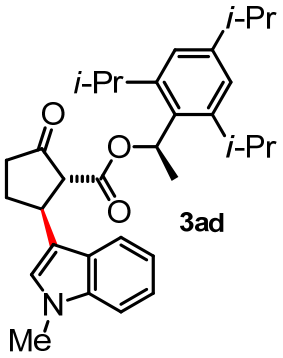
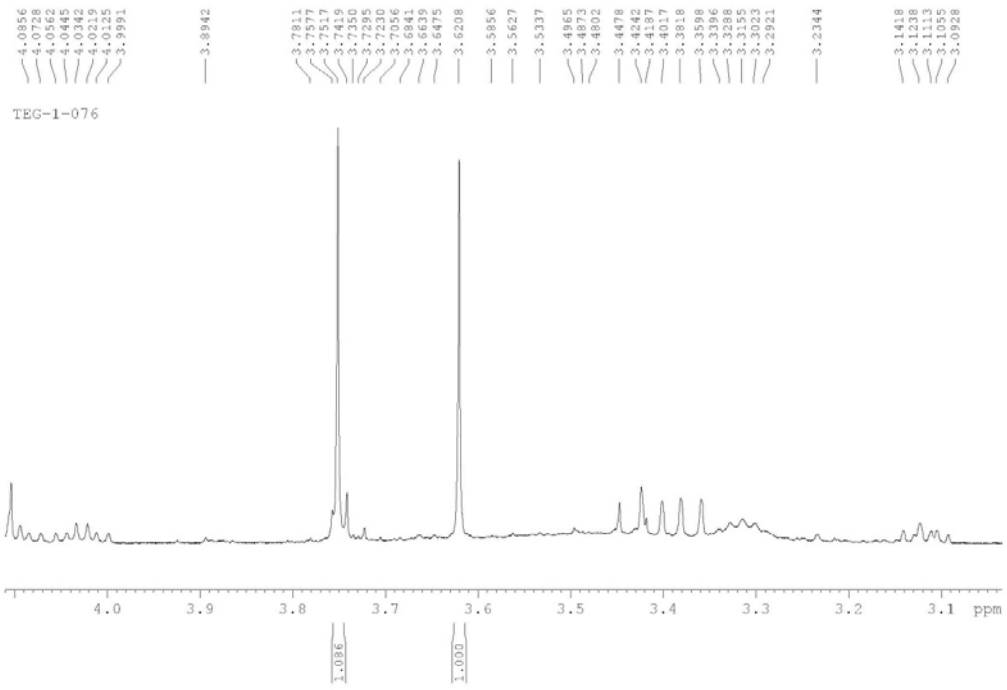
24.4083
24.0155
22.3647
22.1152
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


i-Pr
i-Pr
i-Pr
O
O
O
N
Me
3ad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4.0342
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4.0125
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3.8942
3.7811
3.7577
3.7517
3.7419
3.7350
3.7295
3.7230
3.7056
3.6841
3.6639
3.6475
3.6298
3.5856
3.5627
3.5337
3.4865
3.4873
3.4802
3.4478
3.4242
3.4187
3.4017
3.3818
3.3598
3.3396
3.3288
3.3155
3.3023
3.2921
3.2344
3.1418
3.1238
3.1113
3.1055
3.0928
TEG-1-076
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3.7
3.6
3.5
3.4
3.3
3.2
3.1
ppm
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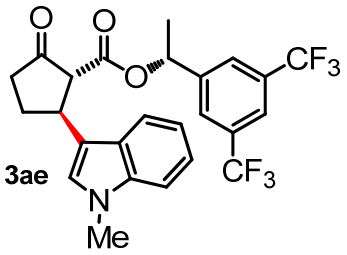
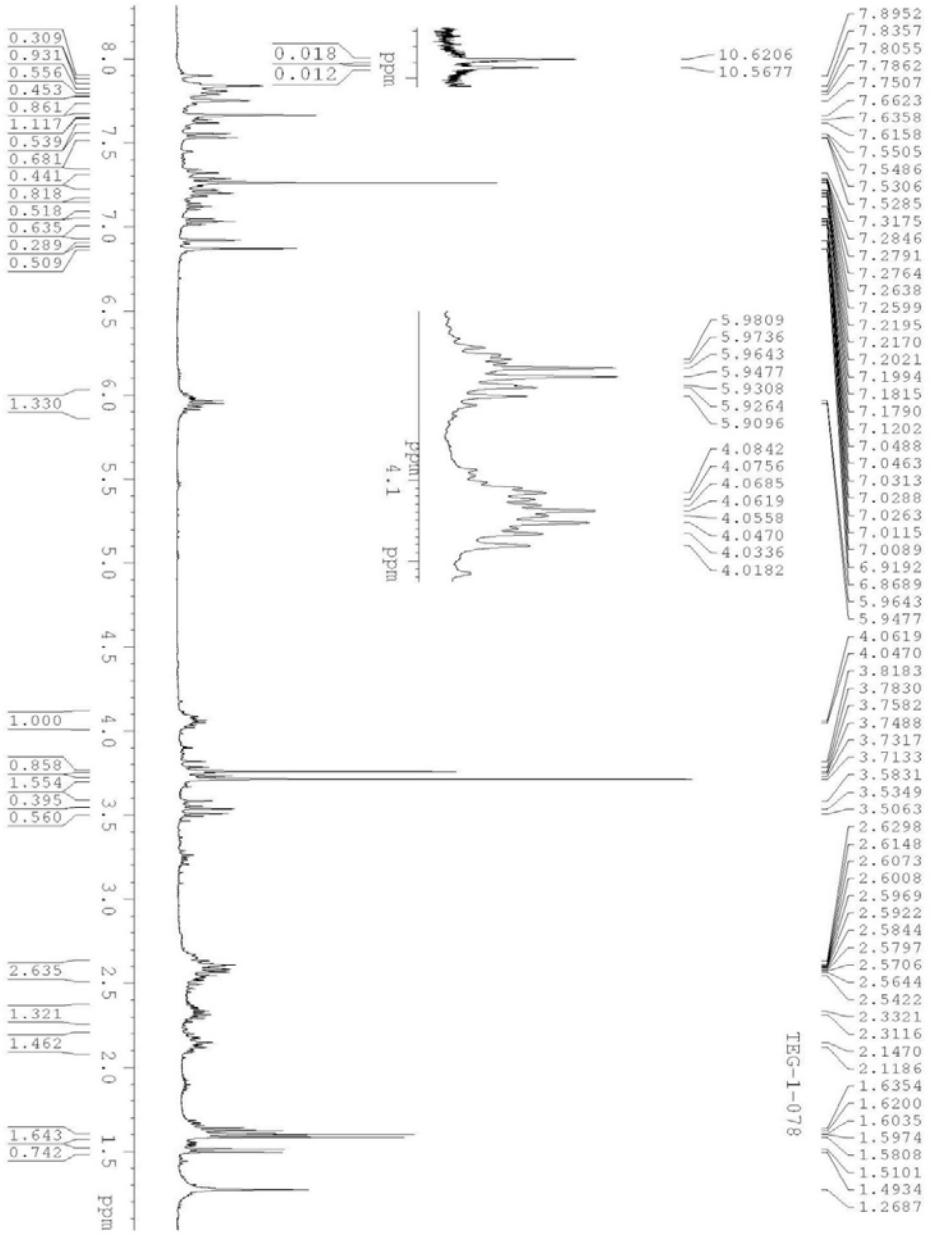
1.000


O
O
O
CF3
CF3
3ae
N
Me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0.556
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1.117
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0.681
0.441
0.818
0.518
0.635
0.289
0.509
1.330
1.000
0.858
1.554
0.395
0.560
2.635
1.321
1.462
1.643
0.742
0.018
0.012
10.6206
10.5677
5.9809
5.9736
5.9643
5.9477
5.9308
5.9264
5.9096
4.0842
4.0756
4.0685
4.0619
4.0558
4.0470
4.0336
4.0182
7.8952
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7.7862
7.7507
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7.6358
7.6158
7.5505
7.5486
7.5306
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7.3175
7.2846
7.2791
7.2764
7.2638
7.2599
7.2195
7.2170
7.2021
7.1994
7.1815
7.1790
7.1202
7.0488
7.0463
7.0313
7.0288
7.0263
7.0115
7.0089
6.9192
6.8689
5.9643
5.9477
4.0619
4.0470
3.8183
3.7830
3.7582
3.7488
3.7317
3.7133
3.5831
3.5349
3.5063
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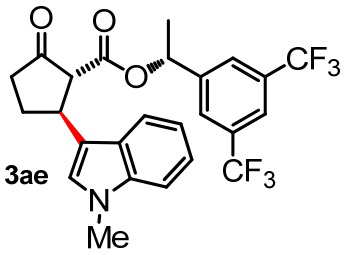
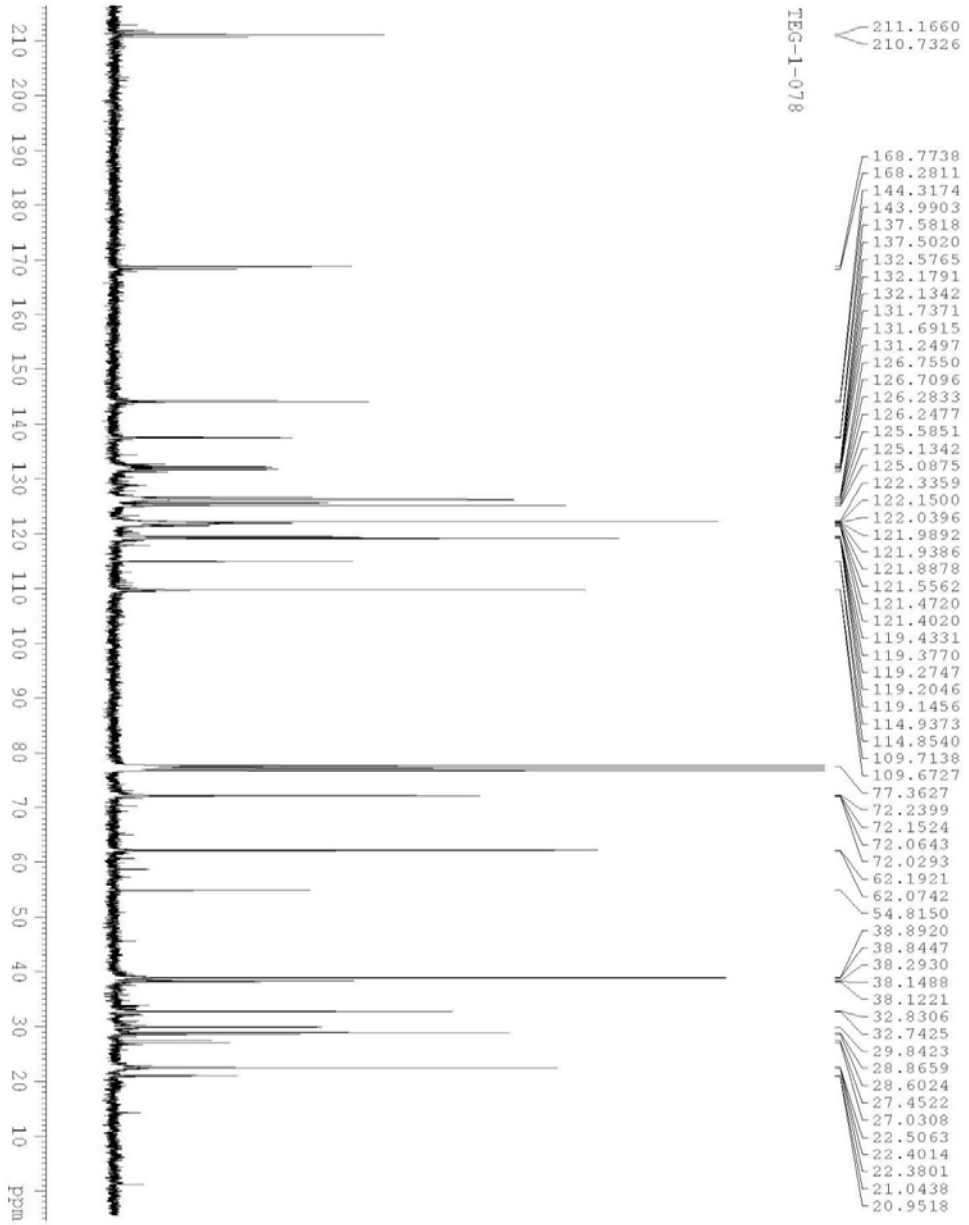
2.6148
2.6073
2.6008
2.5969
2.5922
2.5844
2.5797
2.5706
2.5644
2.5422
2.3321
2.3116
2.1470
2.1186
1.6354
1.6200
1.6035
1.5974
1.5808
1.5101
1.4934
1.2687
TEG-1-078
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
4.1
ppm


O
O
O
CF3
CF3
3ae
N
Me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137.5020
132.5765
132.1791
132.1342
131.7371
131.6915
131.2497
126.7550
126.7096
126.2833
126.2477
125.5851
125.1342
125.0875
122.3359
122.1500
122.0396
121.9892
121.9386
121.8878
121.5562
121.4720
121.4020
119.4331
119.3770
119.2747
119.2046
119.1456
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114.8540
109.7138
109.6727
77.3627
72.2399
72.1524
72.0643
72.0293
62.1921
62.0742
54.8150
38.8920
38.8447
38.2930
38.1488
38.1221
32.8306
32.7425
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27.0308
22.5063
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22.3801
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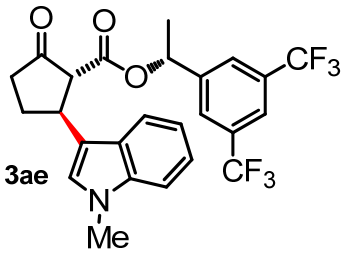
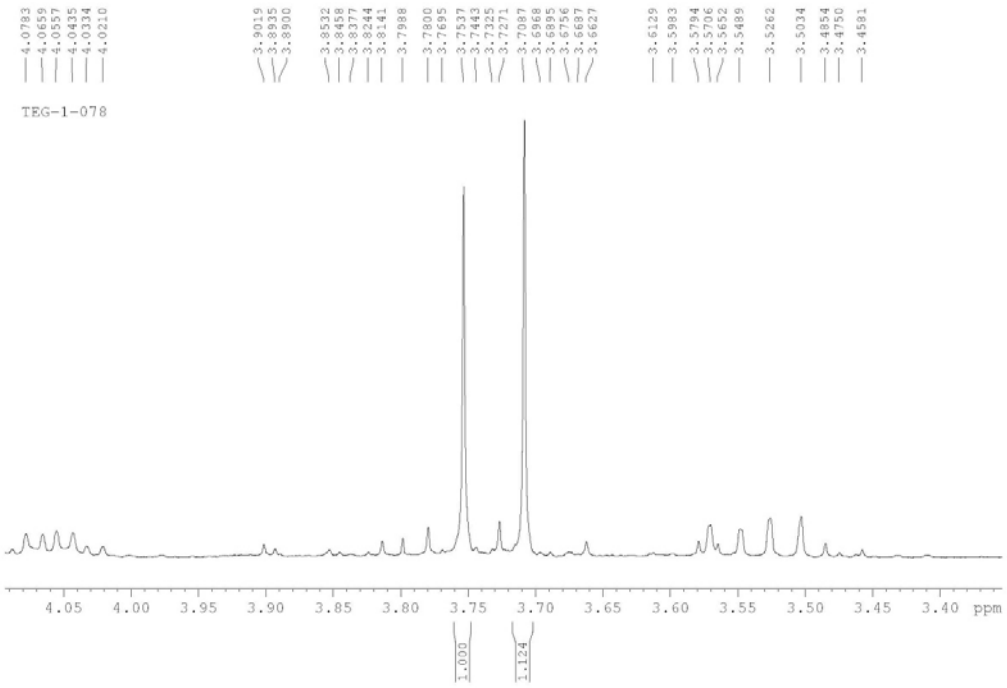
ppm


O
O
O
CF3
CF3
3ae
N
Me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4.0210
3.9019
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3.8900
3.8532
3.8458
3.8377
3.8244
3.8141
3.7988
3.7800
3.7695
3.7537
3.7443
3.7325
3.7271
3.7087
3.6968
3.6895
3.6756
3.6687
3.6627
3.6129
3.5983
3.5794
3.5706
3.5652
3.5489
3.5262
3.5034
3.4854
3.4750
3.4581
TEG-1-078
4.05
4.00
3.95
3.90
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3.70
3.65
3.60
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3.50
3.45
3.40
ppm
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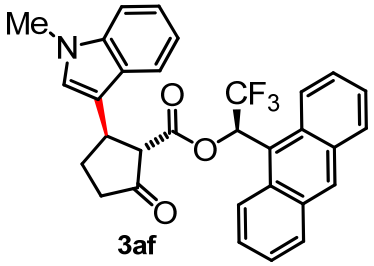
1.124


Me
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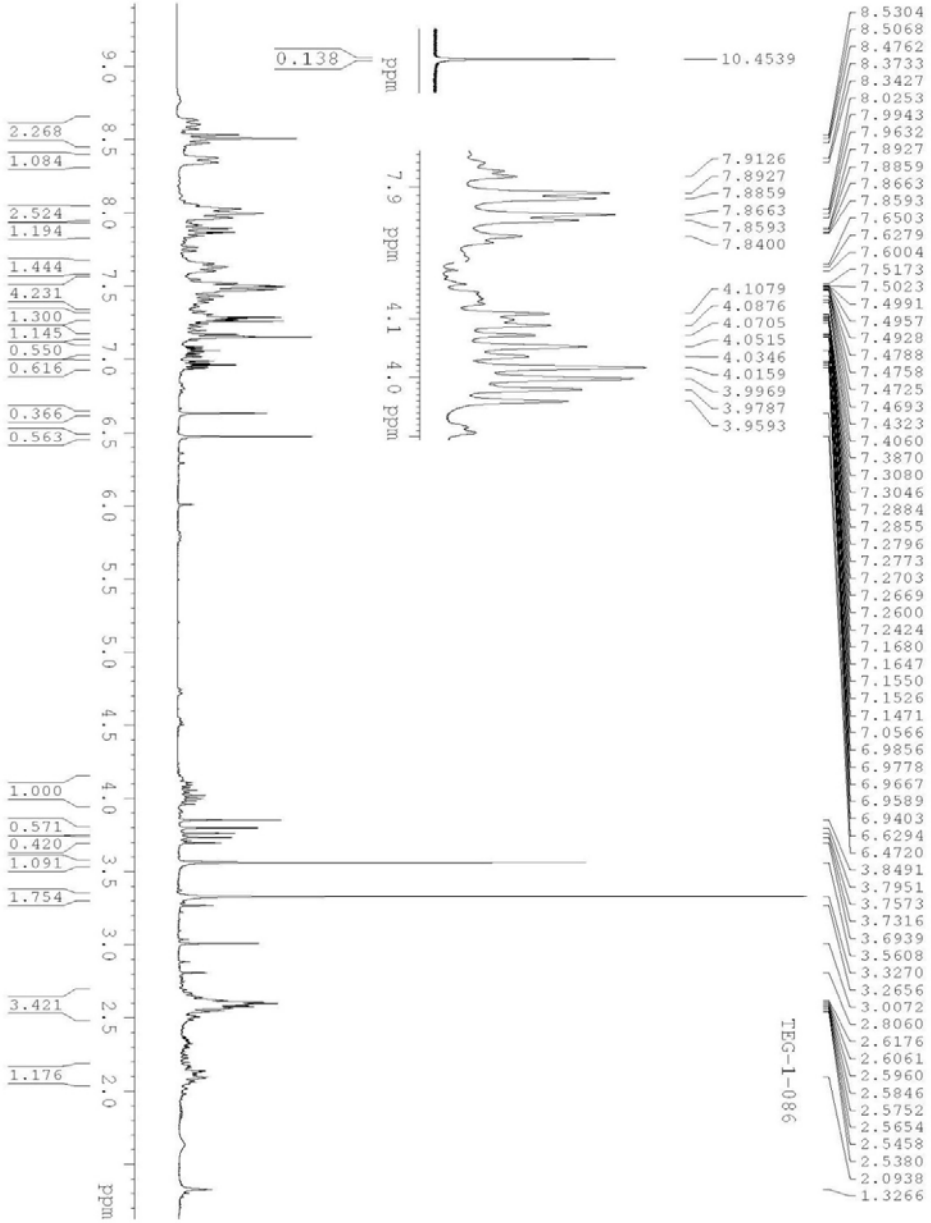
O
O
O
CF3
3af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4.0876
4.0705
4.0515
4.0346
4.0159
3.9969
3.9787
3.9593
2.268
1.084
2.524
1.194
1.444
4.231
1.300
1.145
0.550
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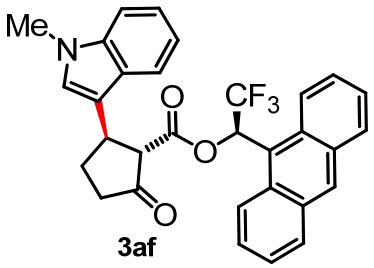
1.176
TBG-I-086
ppm


Me
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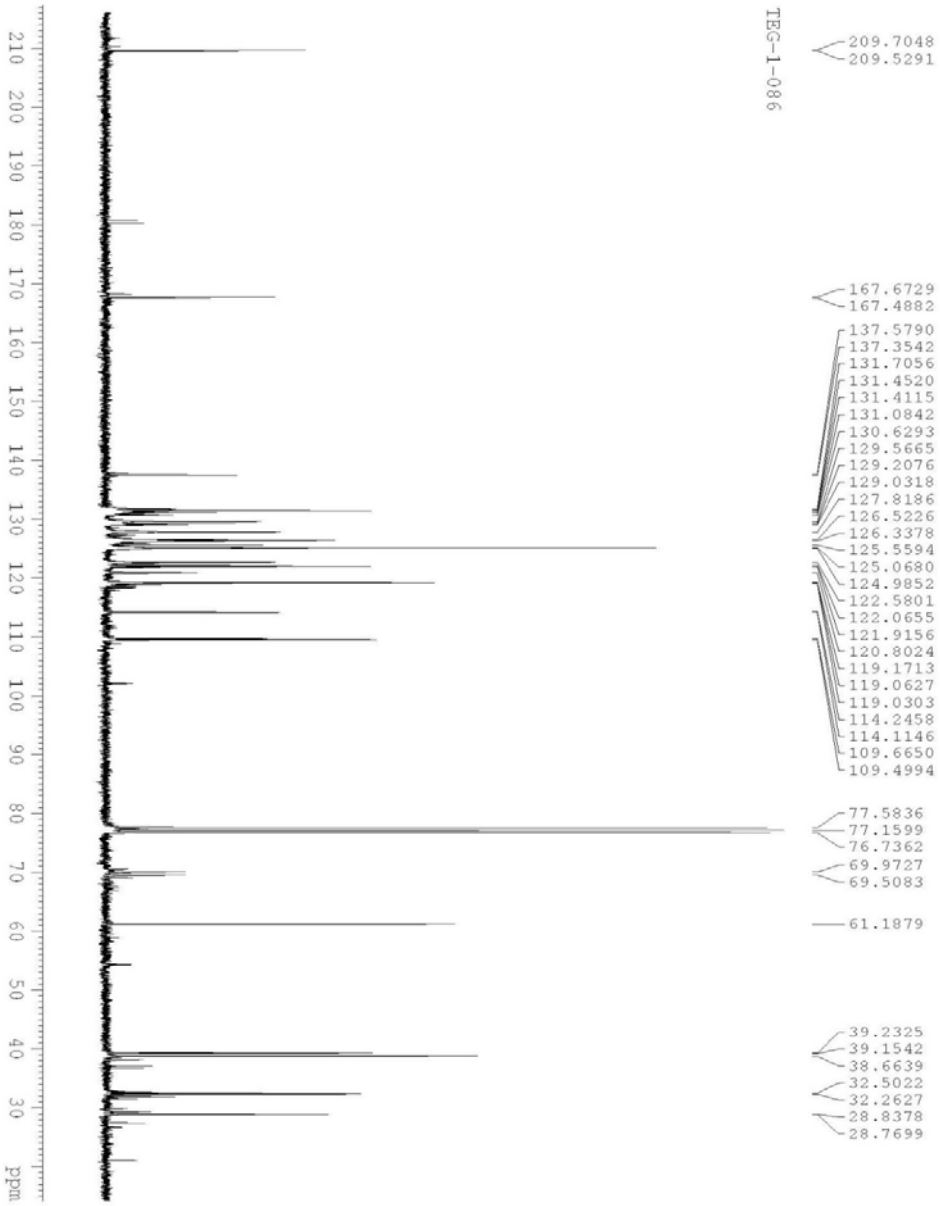
O
O
O
CF3
3af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137.3542
131.7056
131.4520
131.4115
131.0842
130.6293
129.5665
129.2076
129.0318
127.8186
126.5226
126.3378
125.5594
125.0680
124.9852
122.5801
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120.8024
119.1713
119.0627
119.0303
114.2458
114.1146
109.6650
109.4994
77.5836
77.1599
76.7362
69.9727
69.5083
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39.2325
39.1542
38.6639
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32.2627
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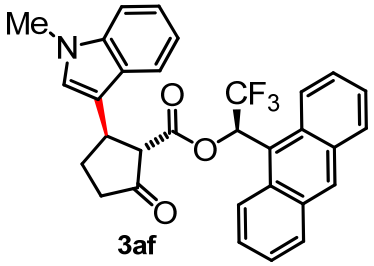
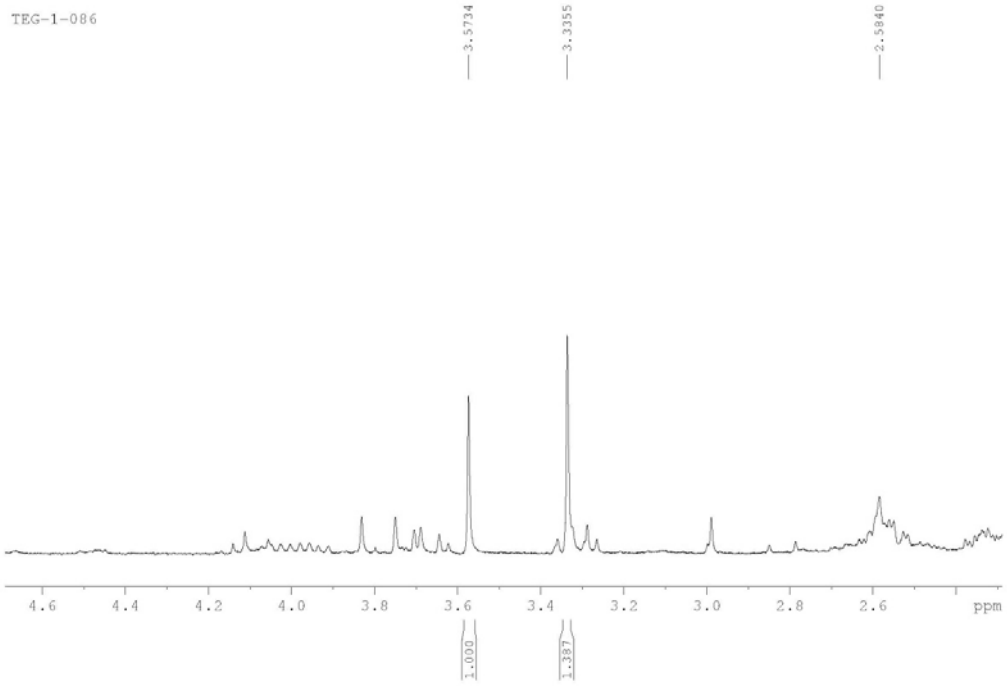
ppm


Me
N
O
O
O
CF3

3af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4.4
4.2
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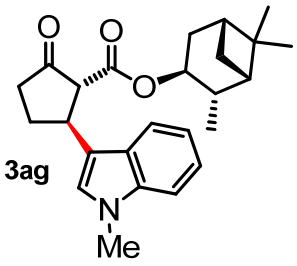
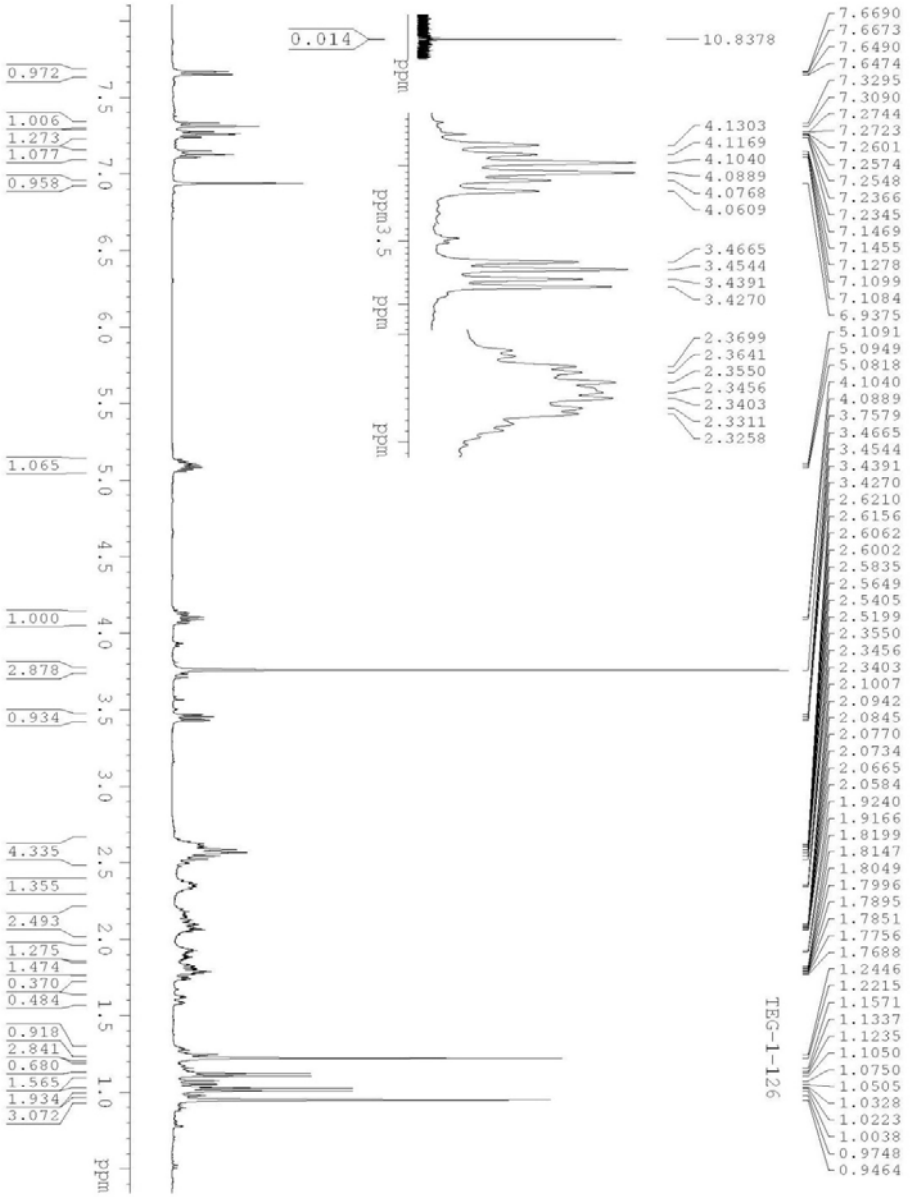
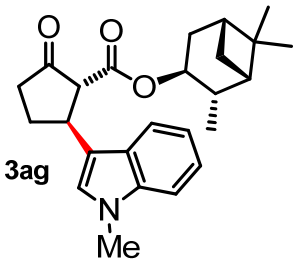
3.8
3.6
3.4
3.2
3.0
2.8
2.6
ppm
1.000
1.387


3ag
O
O
O
N
Me


0.014
10.8378
4.1303
4.1169
4.1040
4.0889
4.0768
4.0609
3.4665
3.4544
3.4391
3.4270
2.3699
2.3641
2.3550
2.3456
2.3403
2.3311
2.3258
7.6690
7.6673
7.6490
7.6474
7.3295
7.3090
7.2744
7.2723
7.2601
7.2574
7.2548
7.2366
7.2345
7.1469
7.1455
7.1278
7.1099
7.1084
6.9375
5.1091
5.0949
5.0818
4.1040
4.0889
3.7579
3.4665
3.4544
3.4391
3.4270
2.6210
2.6156
2.6062
2.6002
2.5835
2.5649
2.5405
2.5199
2.3550
2.3456
2.3403
2.1007
2.0942
2.0845
2.0770
2.0734
2.0665
2.0584
1.9240
1.9166
1.8199
1.8147
1.8049
1.7996
1.7895
1.7851
1.7756
1.7688
1.2446
1.2215
1.1571
1.1337
1.1235
1.1050
1.0750
1.0505
1.0328
1.0223
1.0038
0.9748
0.9464
0.972
1.006
1.273
1.077
0.958
1.065
1.000
2.878
0.934
4.335
1.355
2.493
1.275
1.474
0.370
0.484
0.918
2.841
0.680
1.565
1.934
3.072
TEG-1-126
ppm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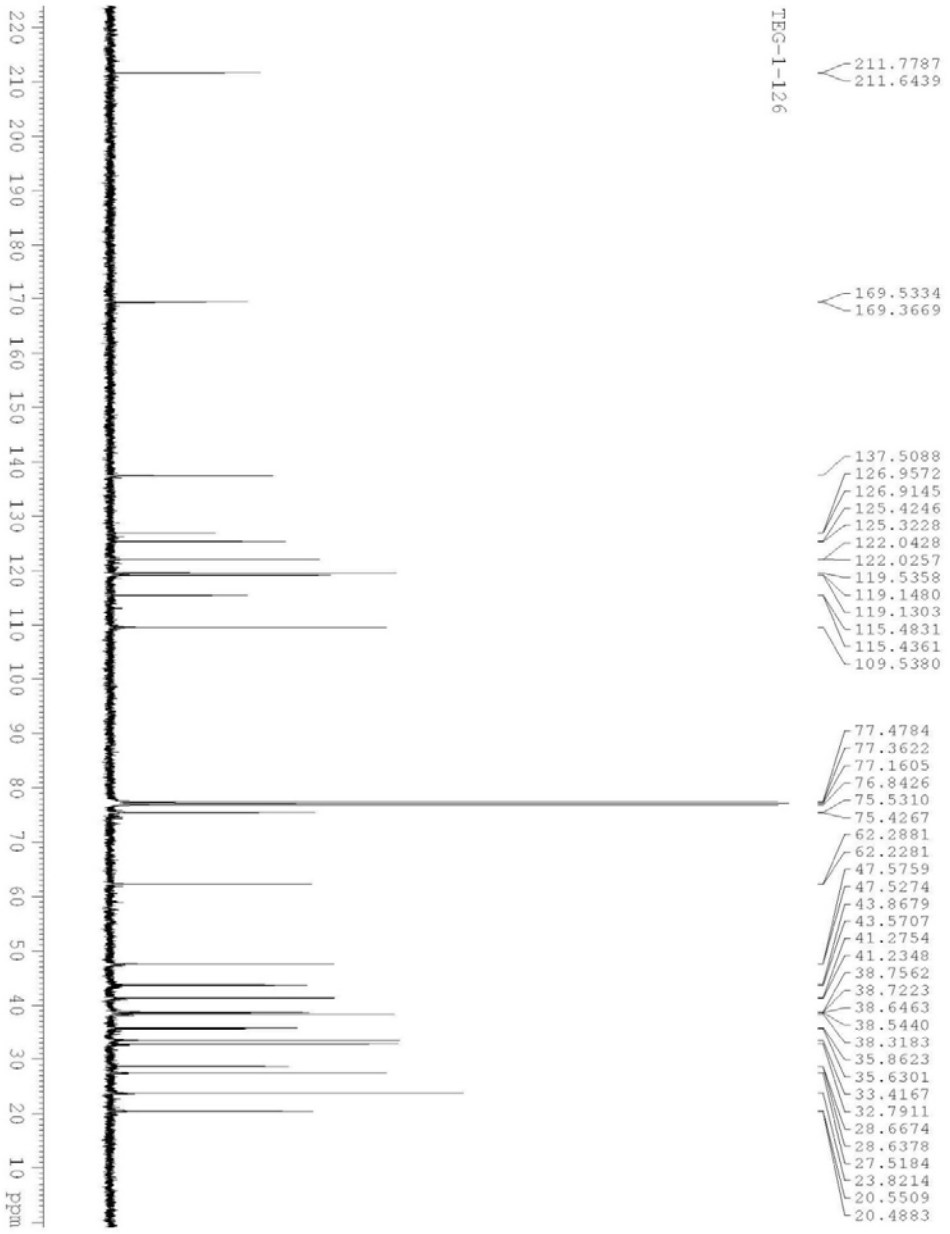
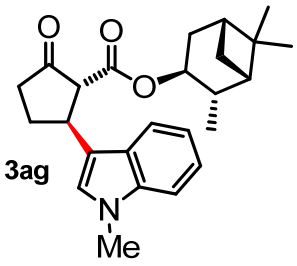
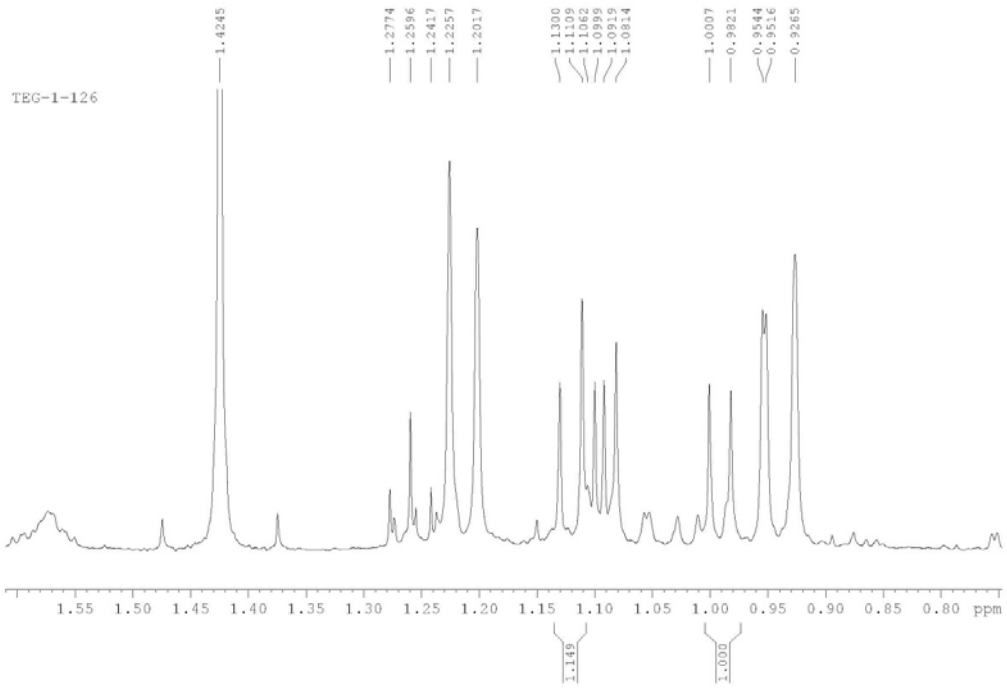
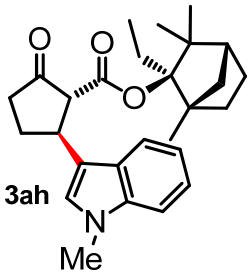
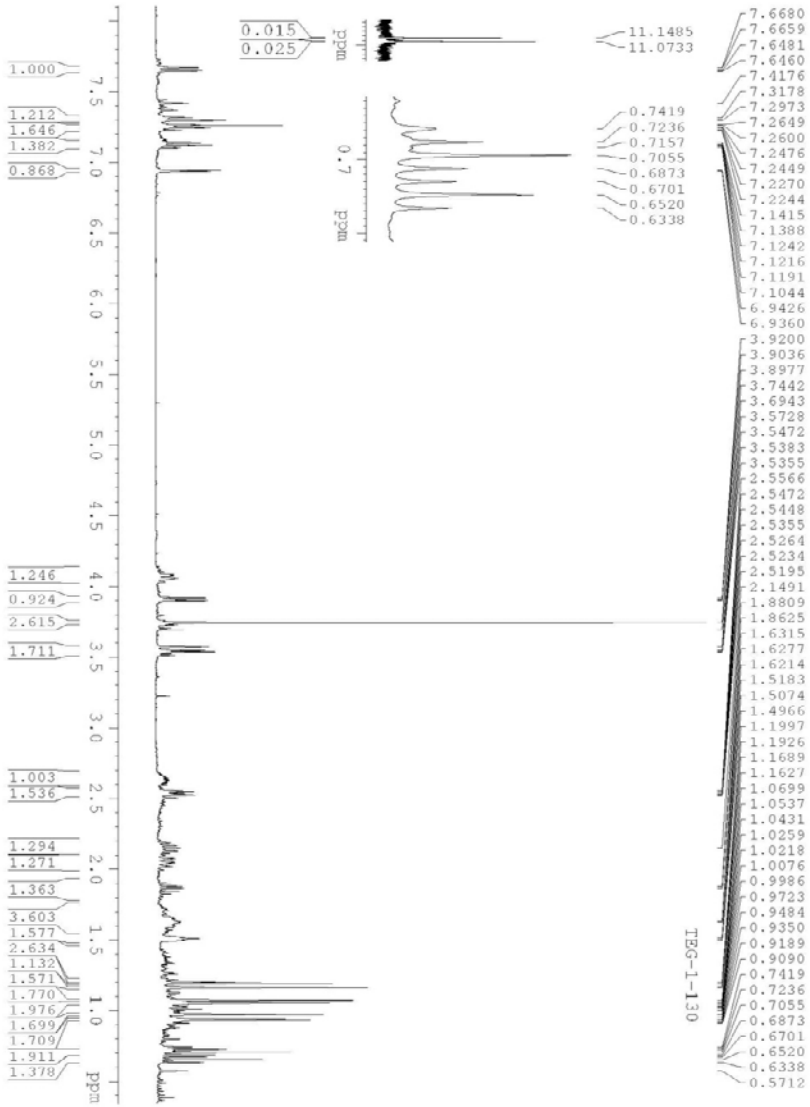
O
3ag
N
Me

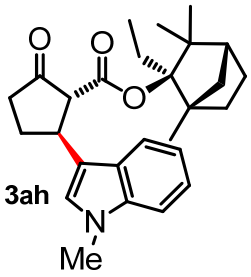

TEG-1-126
211.7787
211.6439
169.5334
169.3669
137.5088
126.9572
126.9145
125.4246
125.3228
122.0428
122.0257
119.5358
119.1480
119.1303
115.4831
115.4361
109.5380
77.4784
77.3622
77.1605
76.8426
75.5310
75.4267
62.2881
62.2281
47.5759
47.5274
43.8679
43.5707
41.2754
41.2348
38.7562
38.7223
38.6463
38.5440
38.3183
35.8623
35.6301
33.4167
32.7911
28.6674
28.6378
27.5184
23.8214
20.5509
20.4883
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

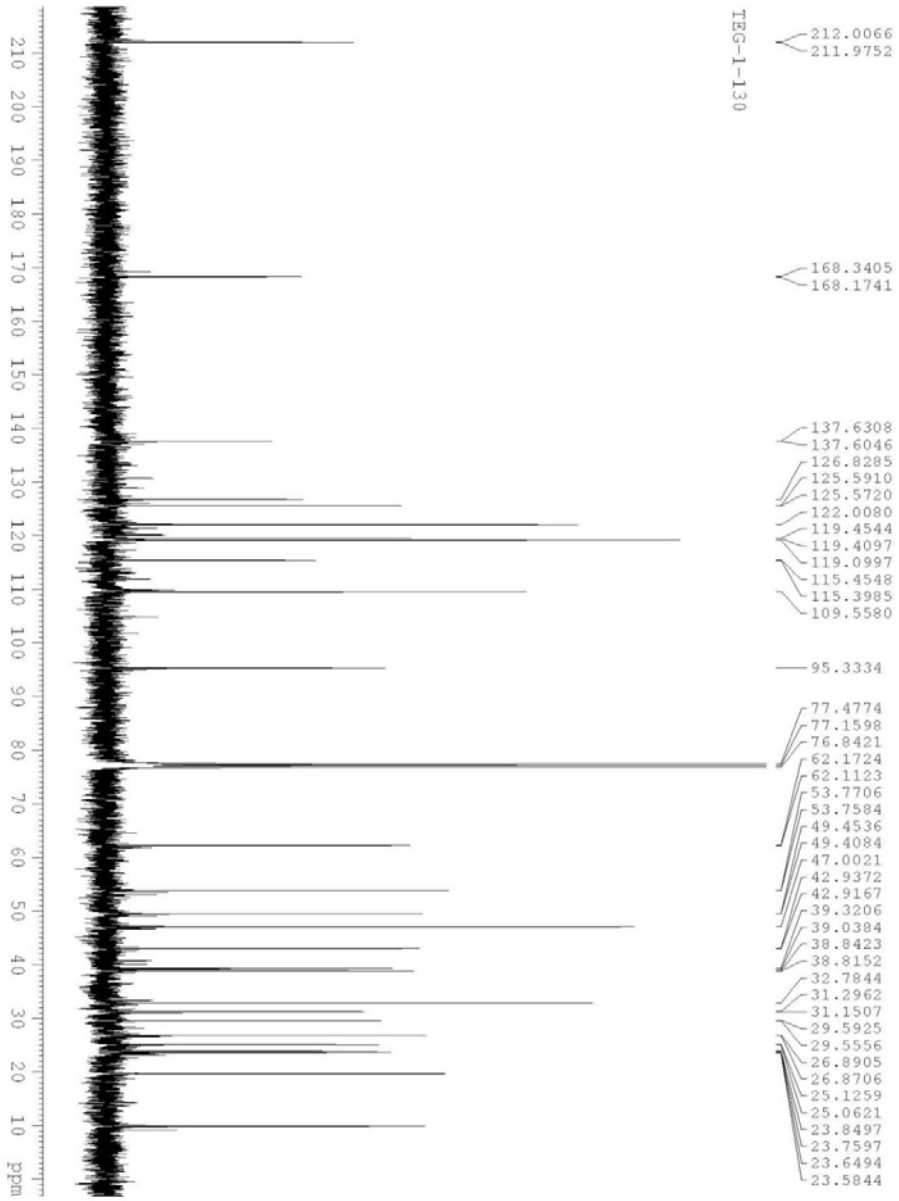

O
O
O
3ag
N
Me

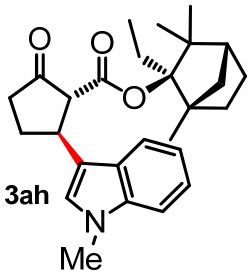

TEG-1-126
1.4245
1.2774
1.2596
1.2417
1.2257
1.2017
1.1300
1.1109
1.1062
1.0999
1.0919
1.0814
1.0007
0.9821
0.9544
0.9516
0.9265
1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 ppm
1.149
1.000

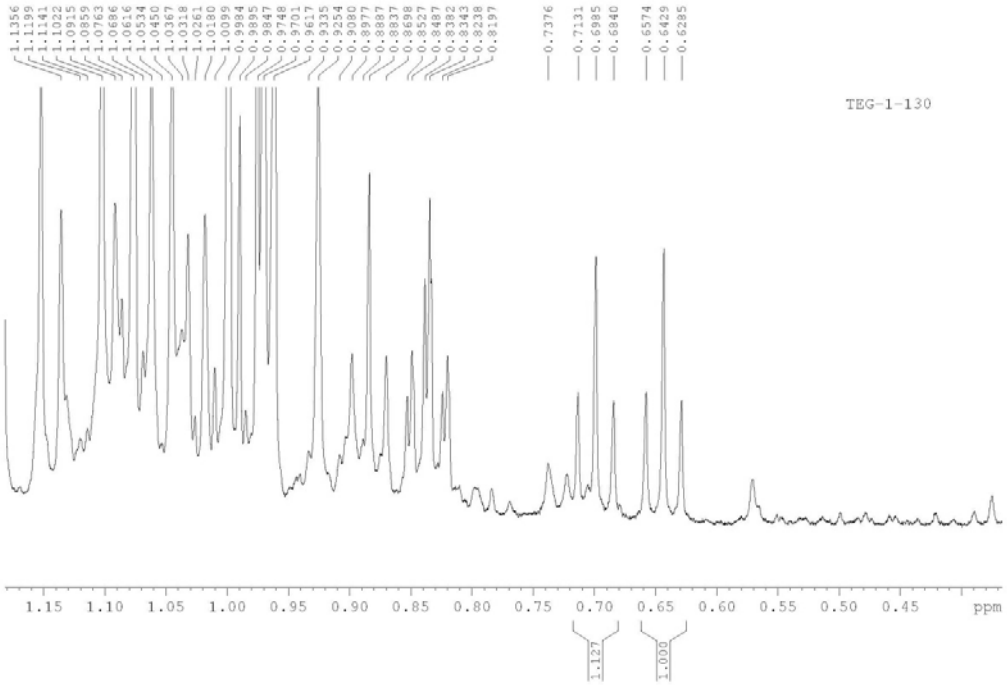

O
O
O
3ah
N
Me

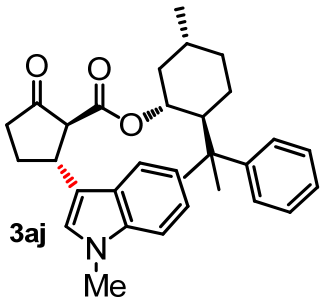

0.015
0.025
11.1485
11.0733
0.7419
0.7236
0.7157
0.7055
0.6873
0.6701
0.6520
0.6338
7.6680
7.6659
7.6481
7.6460
7.4176
7.3178
7.2973
7.2649
7.2600
7.2476
7.2449
7.2270
7.2244
7.1415
7.1388
7.1242
7.1216
7.1191
7.1044
6.9426
6.9360
3.9200
3.9036
3.8977
3.7442
3.6943
3.5728
3.5472
3.5383
3.5355
2.5566
2.5472
2.5448
2.5355
2.5264
2.5234
2.5195
2.1491
1.8809
1.8625
1.6315
1.6277
1.6214
1.5183
1.5074
1.4966
1.1997
1.1926
1.1689
1.1627
1.0699
1.0537
1.0431
1.0259
1.0218
1.0076
0.9986
0.9723
0.9484
0.9350
0.9189
0.9090
0.7419
0.7236
0.7055
0.6873
0.6701
0.6520
0.6338
0.5712
1.000
1.212
1.646
1.382
0.868
1.246
0.924
2.615
1.711
1.003
1.536
1.294
1.271
1.363
3.603
1.577
2.634
1.132
1.571
1.770
1.976
1.699
1.709
1.911
1.378
TEG-1-130
ppm

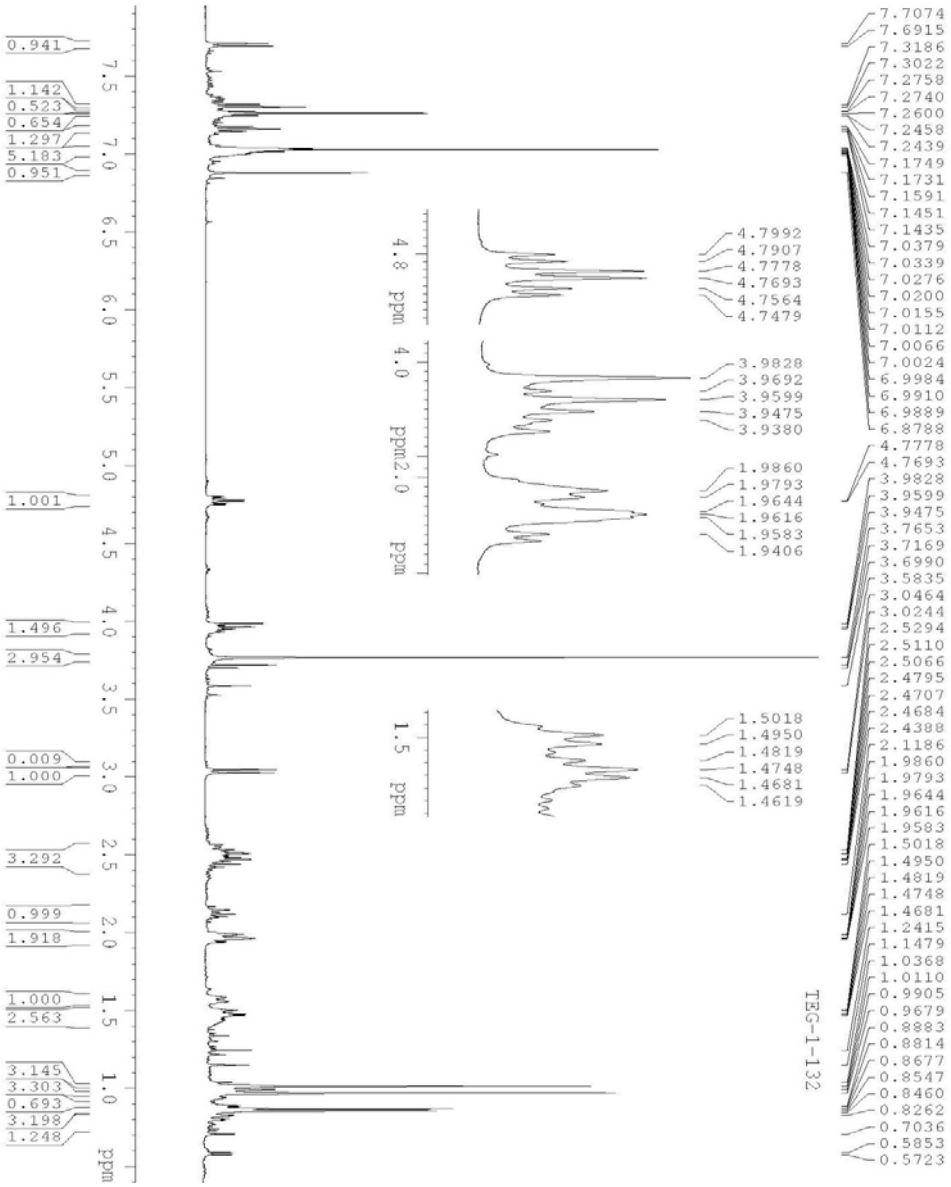

O
O
O
3ah
N
Me


TEG-1-130
212.0066
211.9752
168.3405
168.1741
137.6308
137.6046
126.8285
125.5910
125.5720
122.0080
119.4544
119.4097
119.0997
115.4548
115.3985
109.5580
95.3334
77.4774
77.1598
76.8421
62.1724
62.1123
53.7706
53.7584
49.4536
49.4084
47.0021
42.9372
42.9167
39.3206
39.0384
38.8423
38.8152
32.7844
31.2962
31.1507
29.5925
29.5556
26.8905
26.8706
25.1259
25.0621
23.8497
23.7597
23.6494
23.5844
ppm


O
O
O
3ah
N
Me


1.1356
1.1199
1.1141
1.1022
1.0915
1.0859
1.0763
1.0686
1.0616
1.0534
1.0450
1.0367
1.0318
1.0261
1.0180
1.0099
0.9984
0.9895
0.9847
0.9748
0.9701
0.9617
0.9335
0.9254
0.9080
0.8977
0.8887
0.8837
0.8698
0.8527
0.8487
0.8382
0.8343
0.8238
0.8197
0.7376
0.7131
0.6985
0.6840
0.6574
0.6429
0.6285
TEG-1-130
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
ppm
1.12
1.00


O
O
O
3aj
N
Me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1.142
0.523
0.654
1.297
5.183
0.951
1.001
1.496
2.954
0.009
1.000
3.292
0.999
1.918
1.000
2.563
3.145
3.303
0.693
3.198
1.248
ppm
4.8 ppm
4.0 ppm
2.0 ppm
1.5 ppm
4.7992
4.7907
4.7778
4.7693
4.7564
4.7479
3.9828
3.9692
3.9599
3.9475
3.9380
1.9860
1.9793
1.9644
1.9616
1.9583
1.9406
1.5018
1.4950
1.4819
1.4748
1.4681
1.4619
7.7074
7.6915
7.3186
7.3022
7.2758
7.2740
7.2600
7.2458
7.2439
7.1749
7.1731
7.1591
7.1451
7.1435
7.0379
7.0339
7.0276
7.0200
7.0155
7.0112
7.0066
7.0024
6.9984
6.9910
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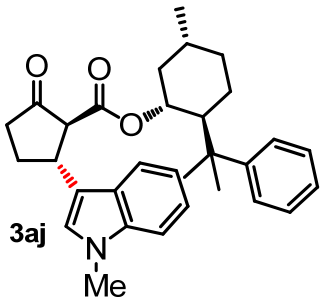
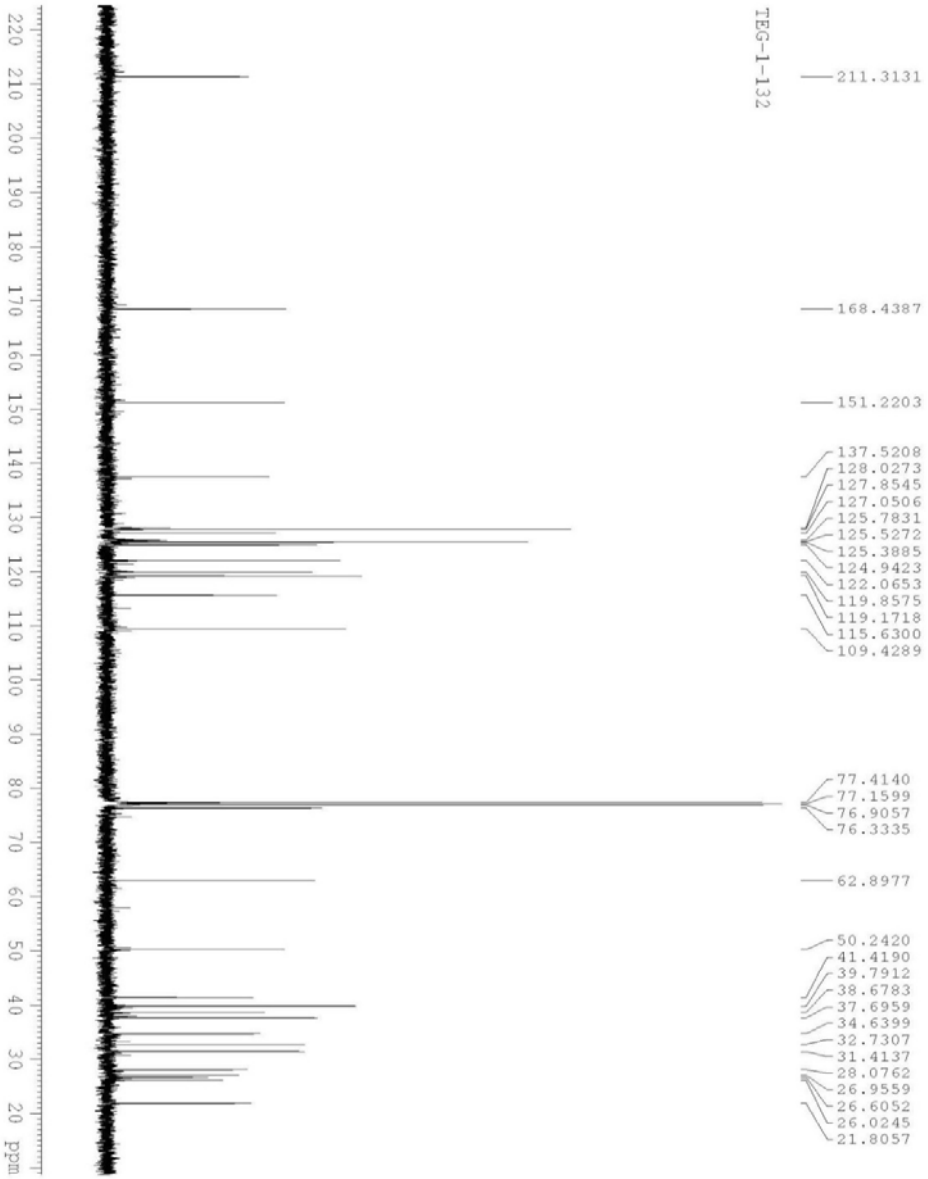
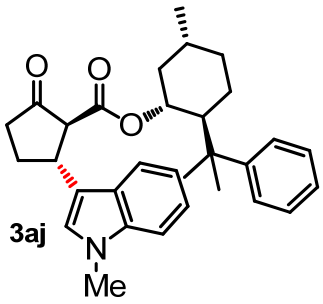
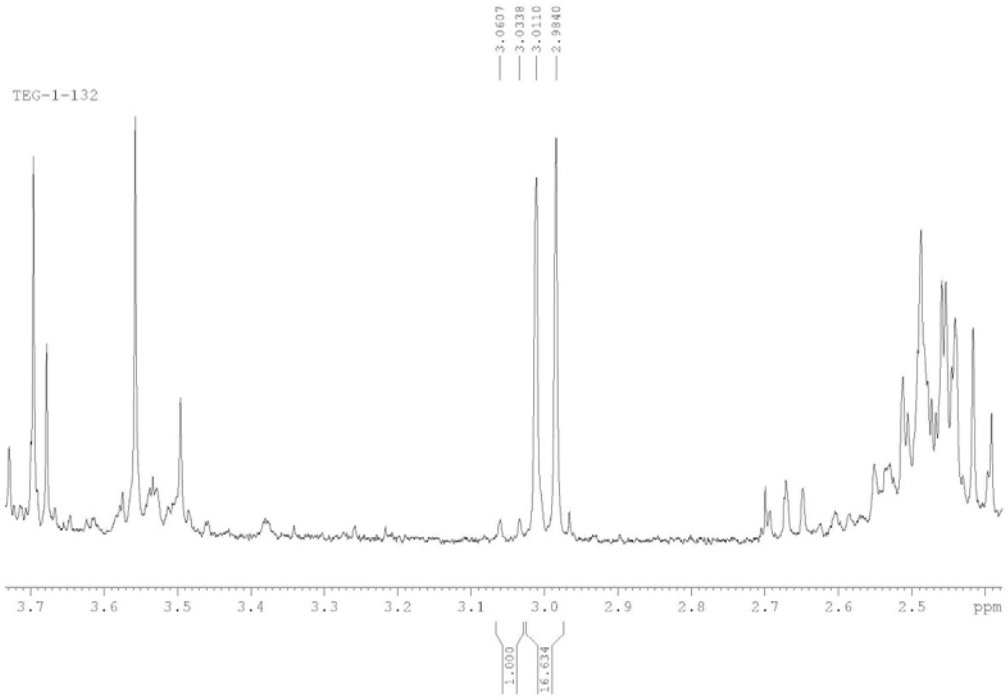
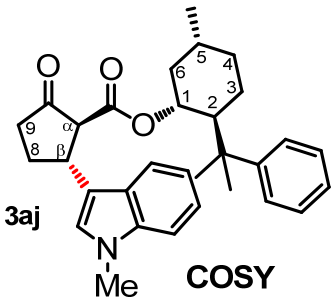
4.7778
4.7693
3.9828
3.9599
3.9475
3.7653
3.7169
3.6990
3.5835
3.0464
3.0244
2.5294
2.5110
2.5066
2.4795
2.4707
2.4684
2.4388
2.1186
1.9860
1.9793
1.9644
1.9616
1.9583
1.5018
1.4950
1.4819
1.4748
1.4681
1.2415
1.1479
1.0368
1.0110
0.9905
0.9679
0.8883
0.8814
0.8677
0.8547
0.8460
0.8262
0.7036
0.5853
0.5723
TEG-1-132

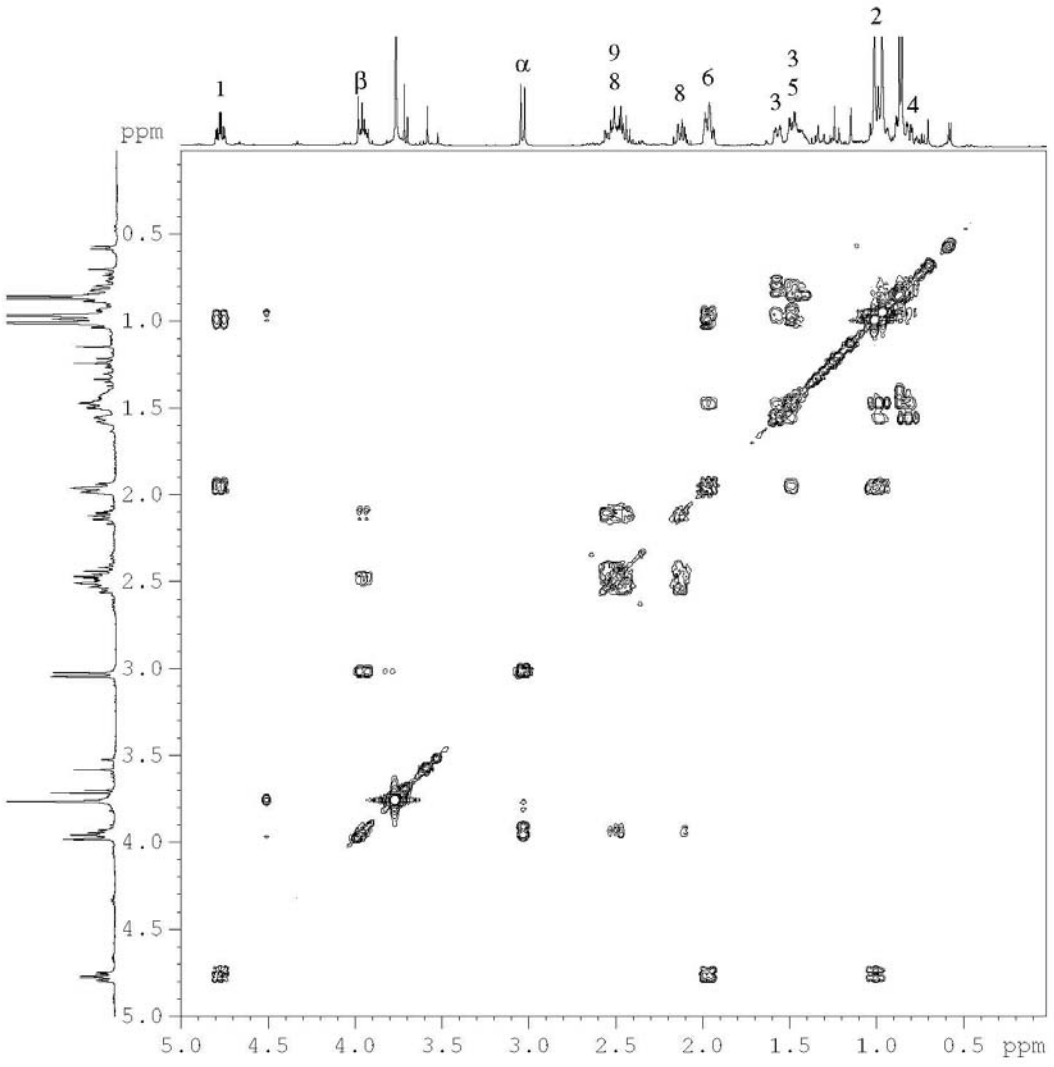

O
O
O
3aj
N
Me

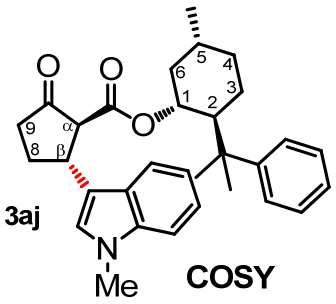

TEG-1-132
211.3131
168.4387
151.2203
137.5208
128.0273
127.8545
127.0506
125.7831
125.5272
125.3885
124.9423
122.0653
119.8575
119.1718
115.6300
109.4289
77.4140
77.1599
76.9057
76.3335
62.8977
50.2420
41.4190
39.7912
38.6783
37.6959
34.6399
32.7307
31.4137
28.0762
26.9559
26.6052
26.0245
21.8057
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


O
O
O
3aj
N
Me

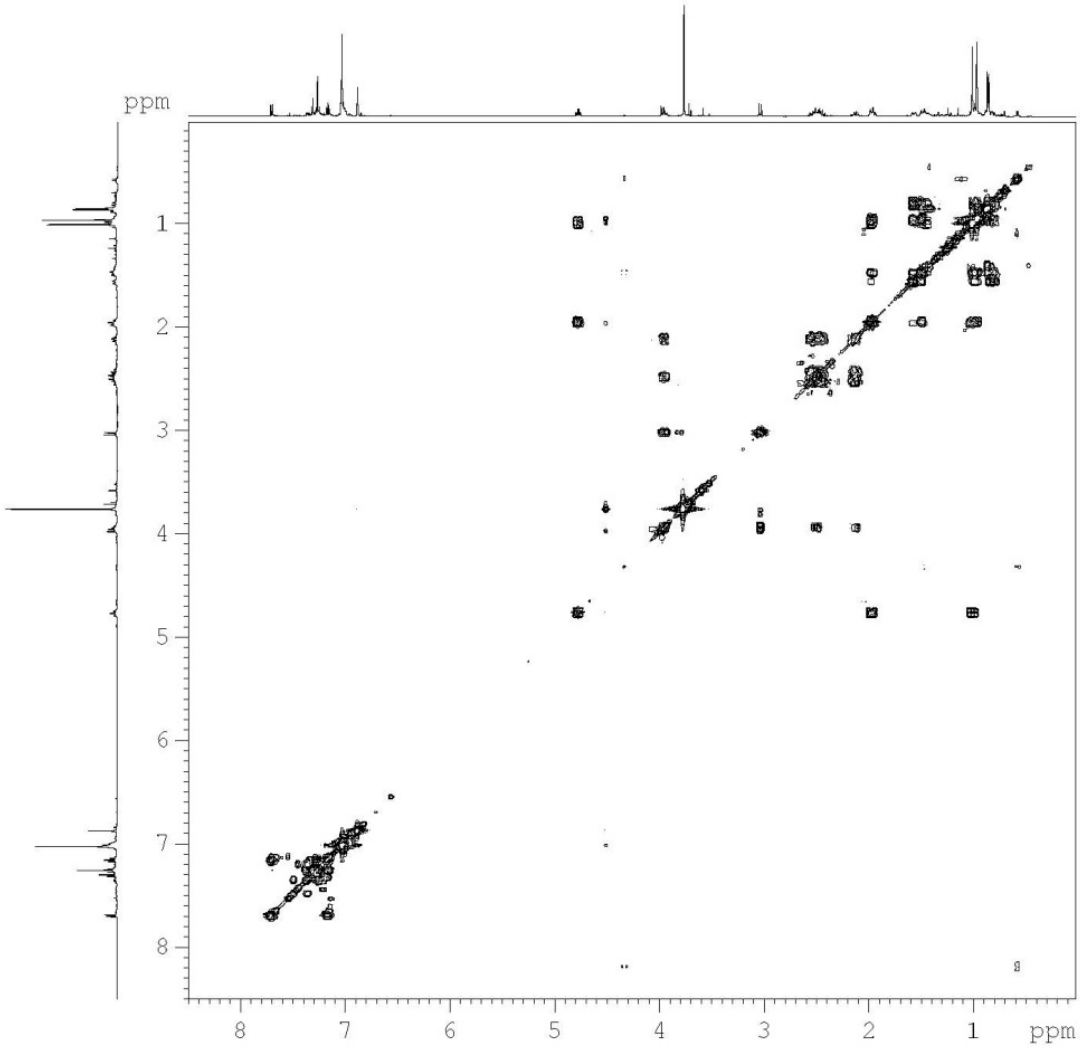

3.0697
3.0338
3.0110
2.9840
TEG-1-132
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
ppm
1.000
16.634

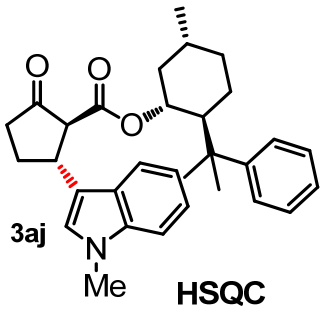

3aj
Me
COSY


1
β
α
9
8
8
6
3
3
5
3
2
4
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

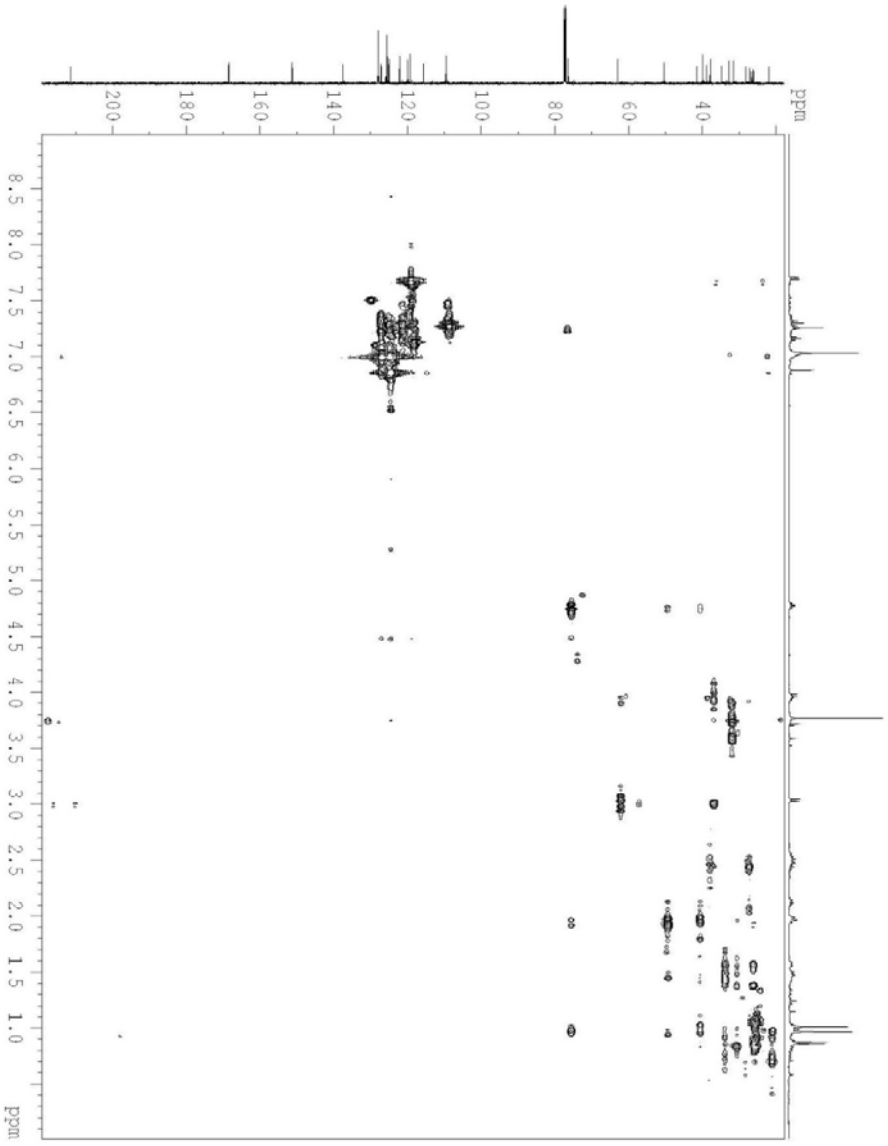


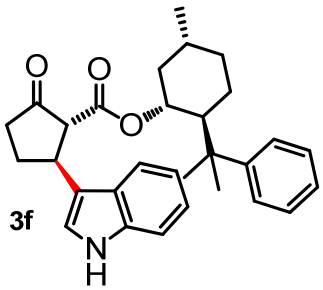
3aj **COSY**

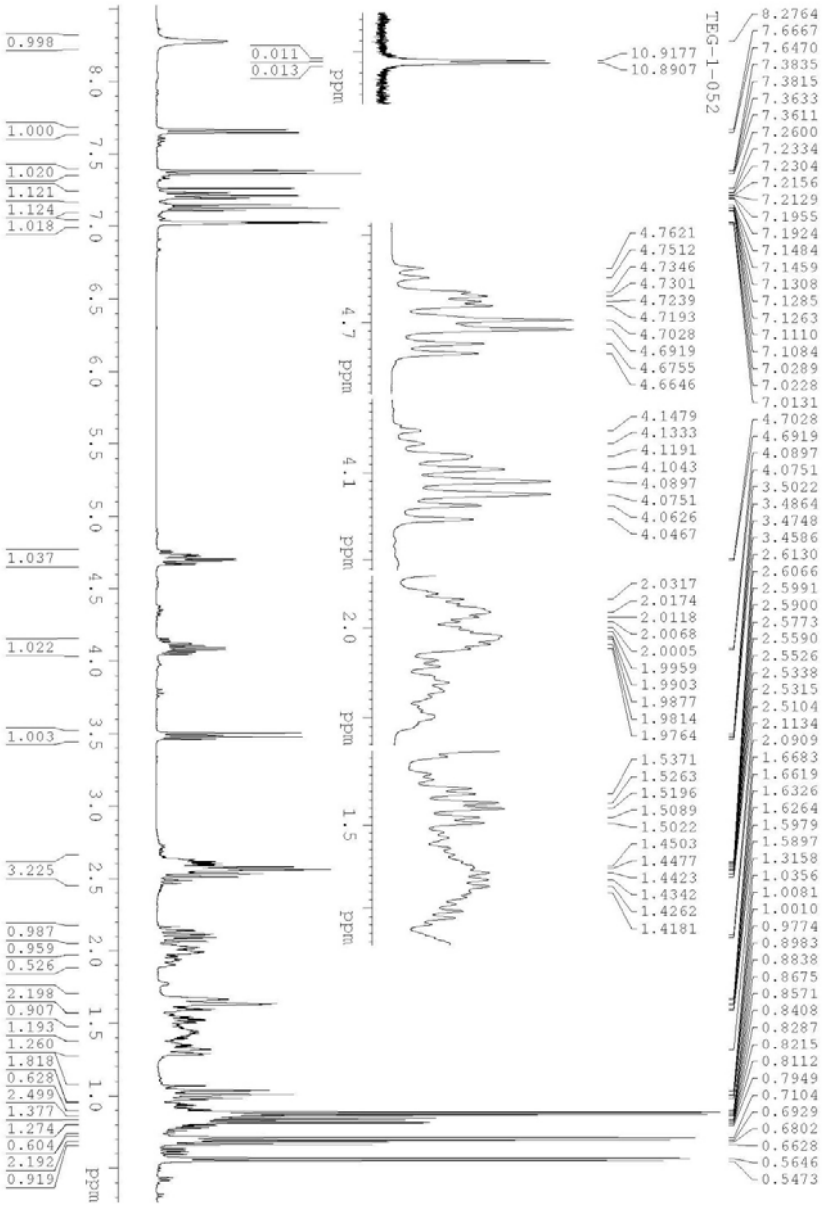



O
O
O
3aj
N
Me

HSQC


ppm
200
180
160
140
120
100
80
60
40
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


O
O
O
3f
N
H


TEG-1-052
10.9177
10.8907
8.2764
7.6667
7.6470
7.3835
7.3815
7.3633
7.3611
7.2600
7.2334
7.2304
7.2156
7.2129
7.1955
7.1924
7.1484
7.1459
7.1308
7.1285
7.1263
7.1110
7.1084
7.0289
7.0228
7.0131
4.7621
4.7512
4.7346
4.7301
4.7239
4.7193
4.7028
4.6919
4.6755
4.6646
4.1479
4.1333
4.1191
4.1043
4.0897
4.0751
4.0626
4.0467
2.0317
2.0174
2.0118
2.0068
2.0005
1.9959
1.9903
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1.9814
1.9764
1.5371
1.5263
1.5196
1.5089
1.5022
1.4503
1.4477
1.4423
1.4342
1.4262
1.4181
4.7028
4.6919
4.0897
4.0751
3.5022
3.4864
3.4748
3.4586
2.6130
2.6066
2.5991
2.5900
2.5773
2.5590
2.5526
2.5338
2.5315
2.5104
2.1134
2.0909
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1.6619
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1.6264
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1.3158
1.0356
1.0081
1.0010
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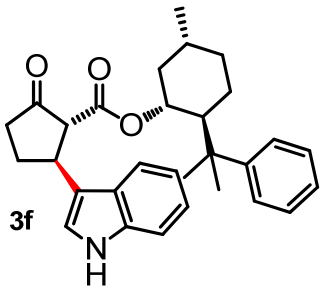
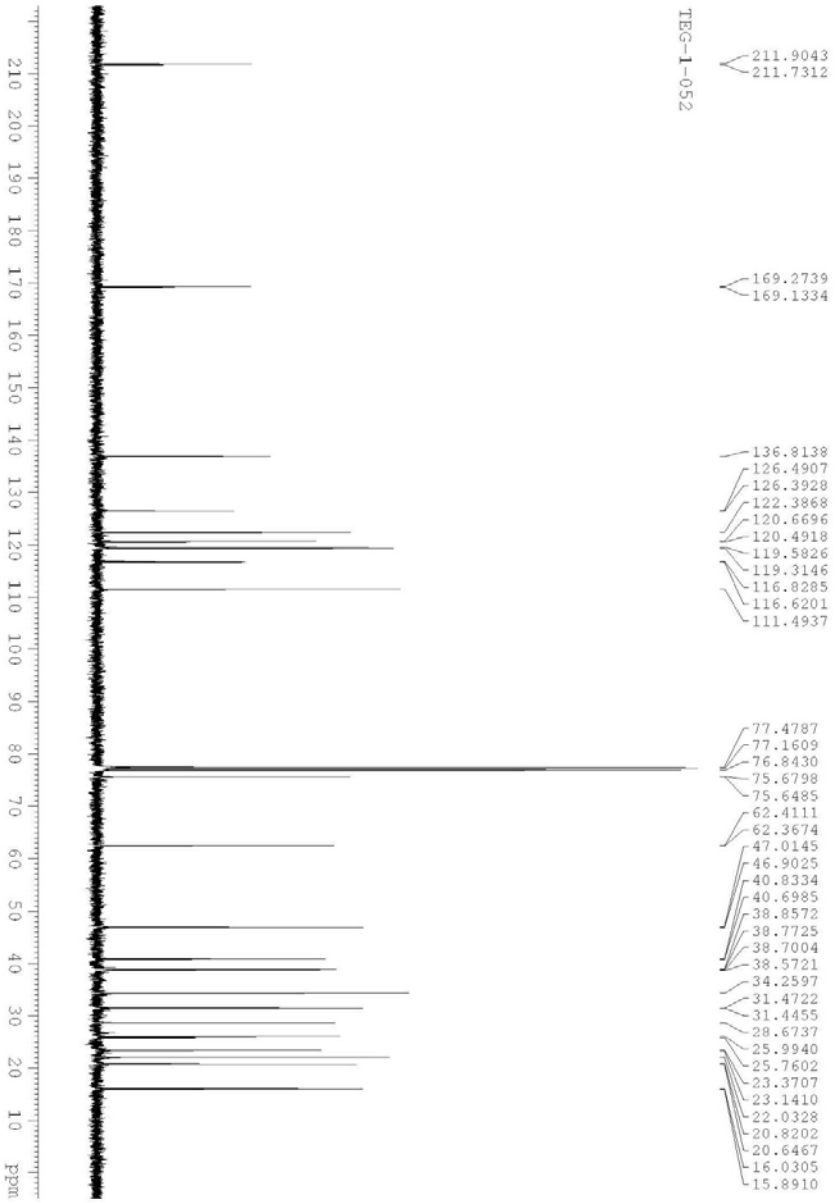
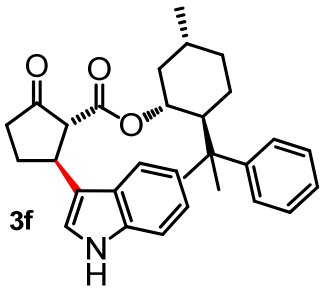
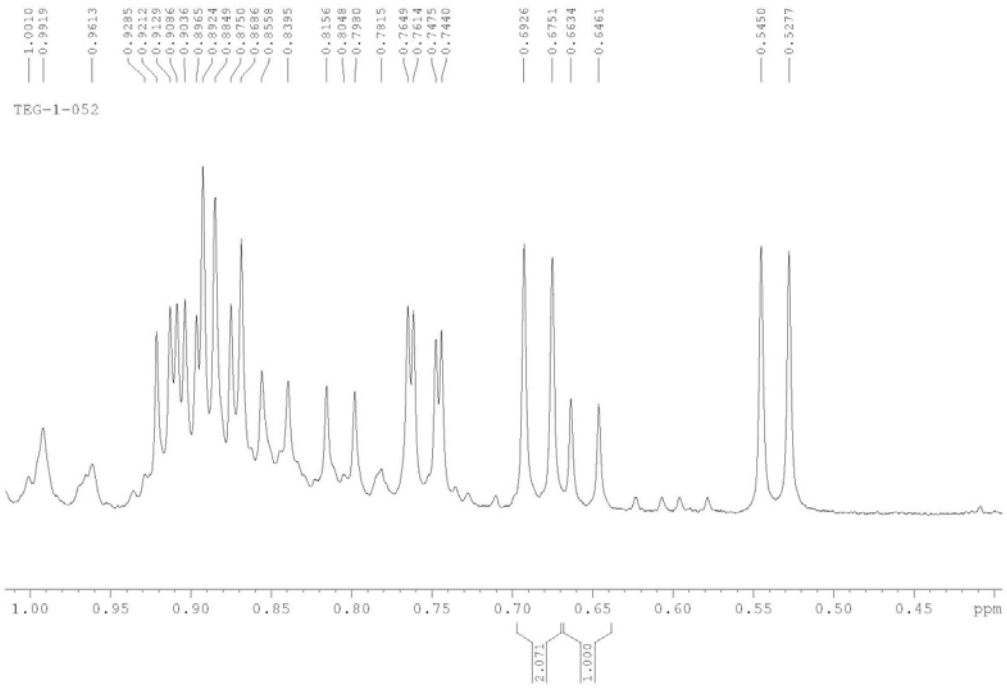
0.8983
0.8838
0.8675
0.8571
0.8408
0.8287
0.8215
0.8112
0.7949
0.7104
0.6929
0.6802
0.6628
0.5646
0.5473
0.998
1.000
1.020
1.121
1.124
1.018
1.037
1.022
1.003
3.225
0.987
0.959
0.526
2.198
0.907
1.193
1.260
1.818
0.628
2.499
1.377
1.274
0.604
2.192
0.919
0.011
0.013
ppm

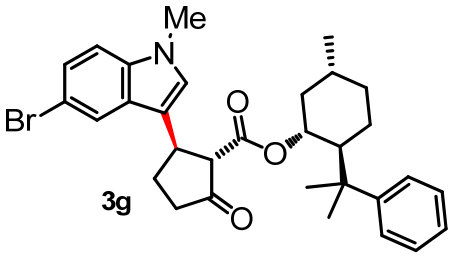

O
O
O
3f
N
H

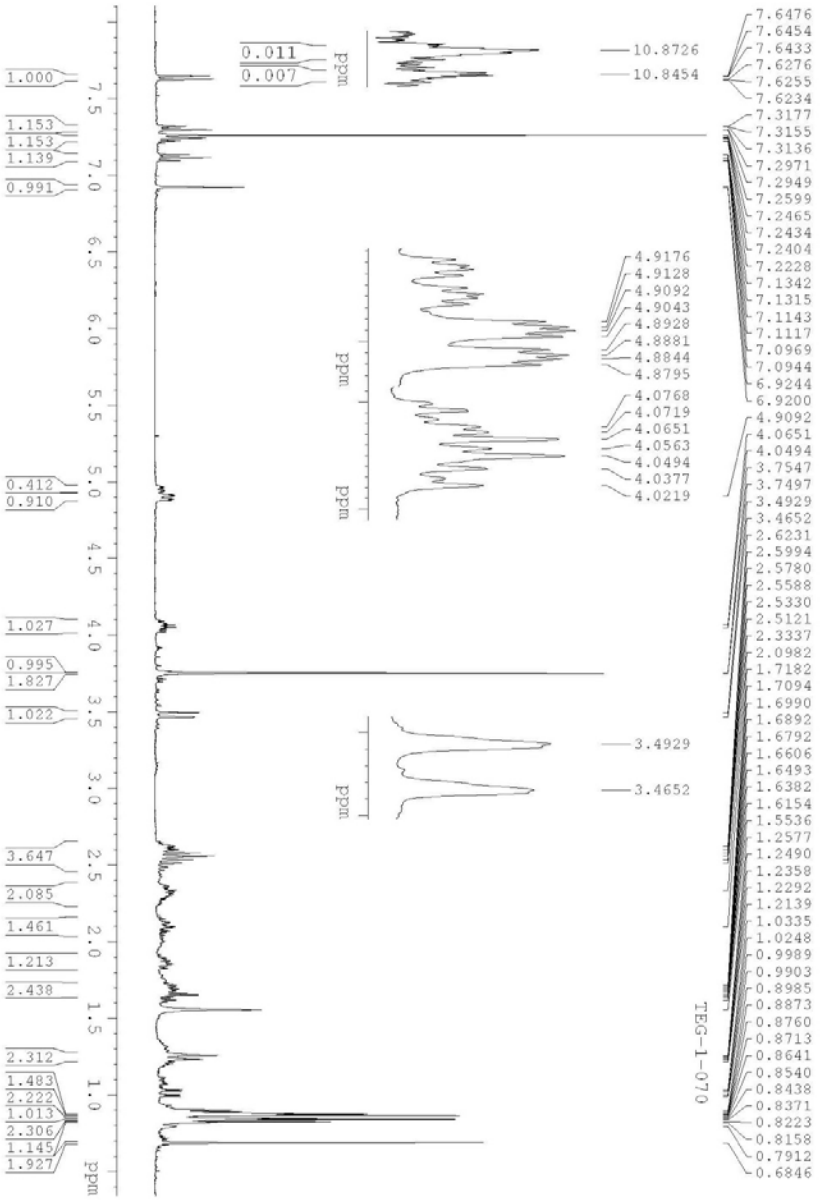

TEG-1-052
211.9043
211.7312
169.2739
169.1334
136.8138
126.4907
126.3928
122.3868
120.6696
120.4918
119.5826
119.3146
116.8285
116.6201
111.4937
77.4787
77.1609
76.8430
75.6798
75.6485
62.4111
62.3674
47.0145
46.9025
40.8334
40.6985
38.8572
38.7725
38.7004
38.5721
34.2597
31.4722
31.4455
28.6737
25.9940
25.7602
23.3707
23.1410
22.0328
20.8202
20.6467
16.0305
15.8910
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

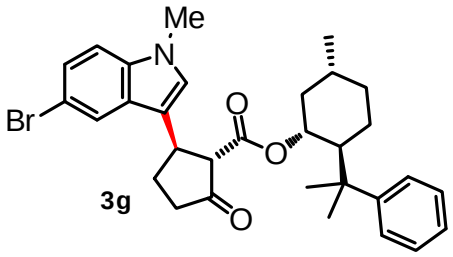

O
O
O
N
H

3f

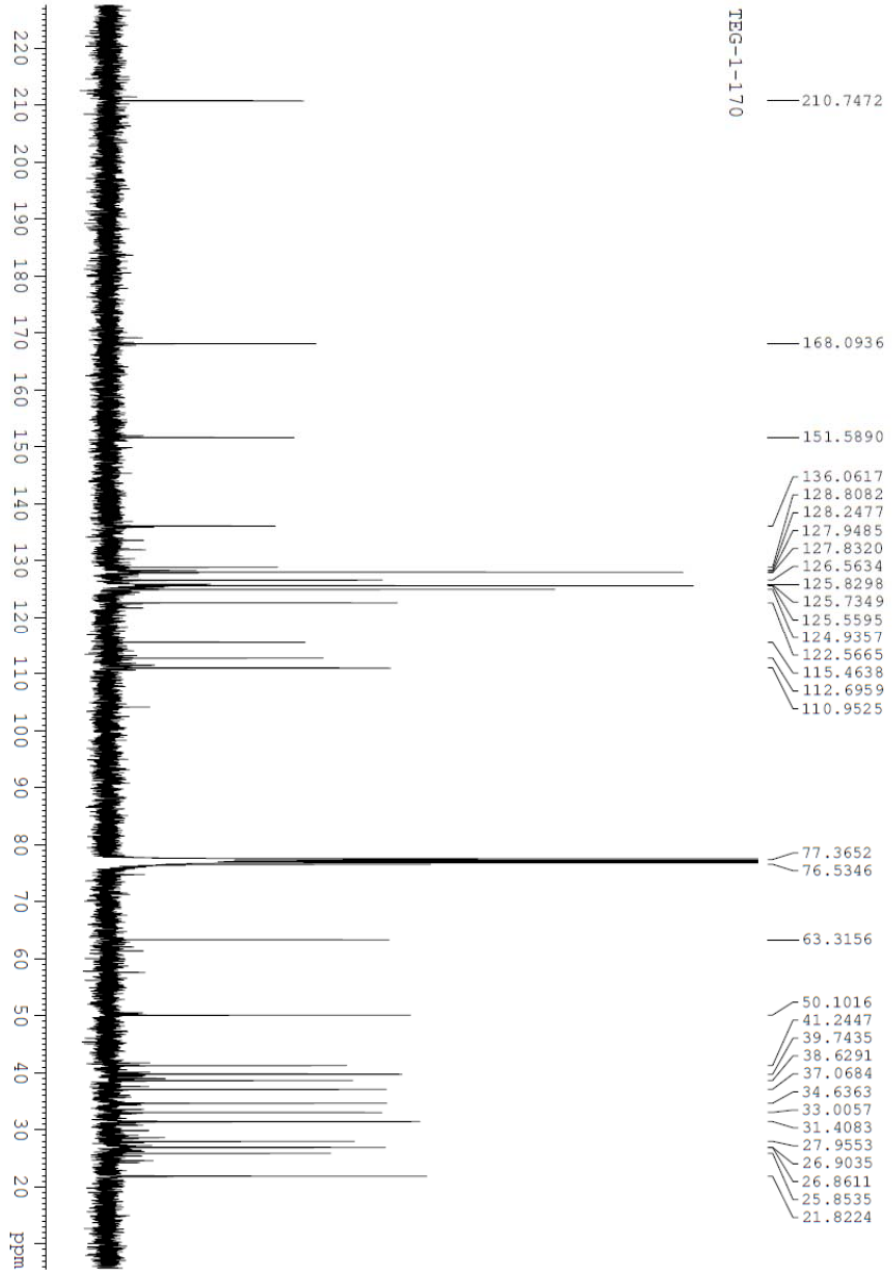

1.0010
0.9919
0.9613
0.9285
0.9212
0.9129
0.9086
0.9036
0.8965
0.8924
0.8849
0.8750
0.8686
0.8558
0.8395
0.8156
0.8048
0.7980
0.7815
0.7649
0.7614
0.7475
0.7440
0.6926
0.6751
0.6634
0.6461
0.5450
0.5277
TEG-1-052
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
ppm
2.072
1.000

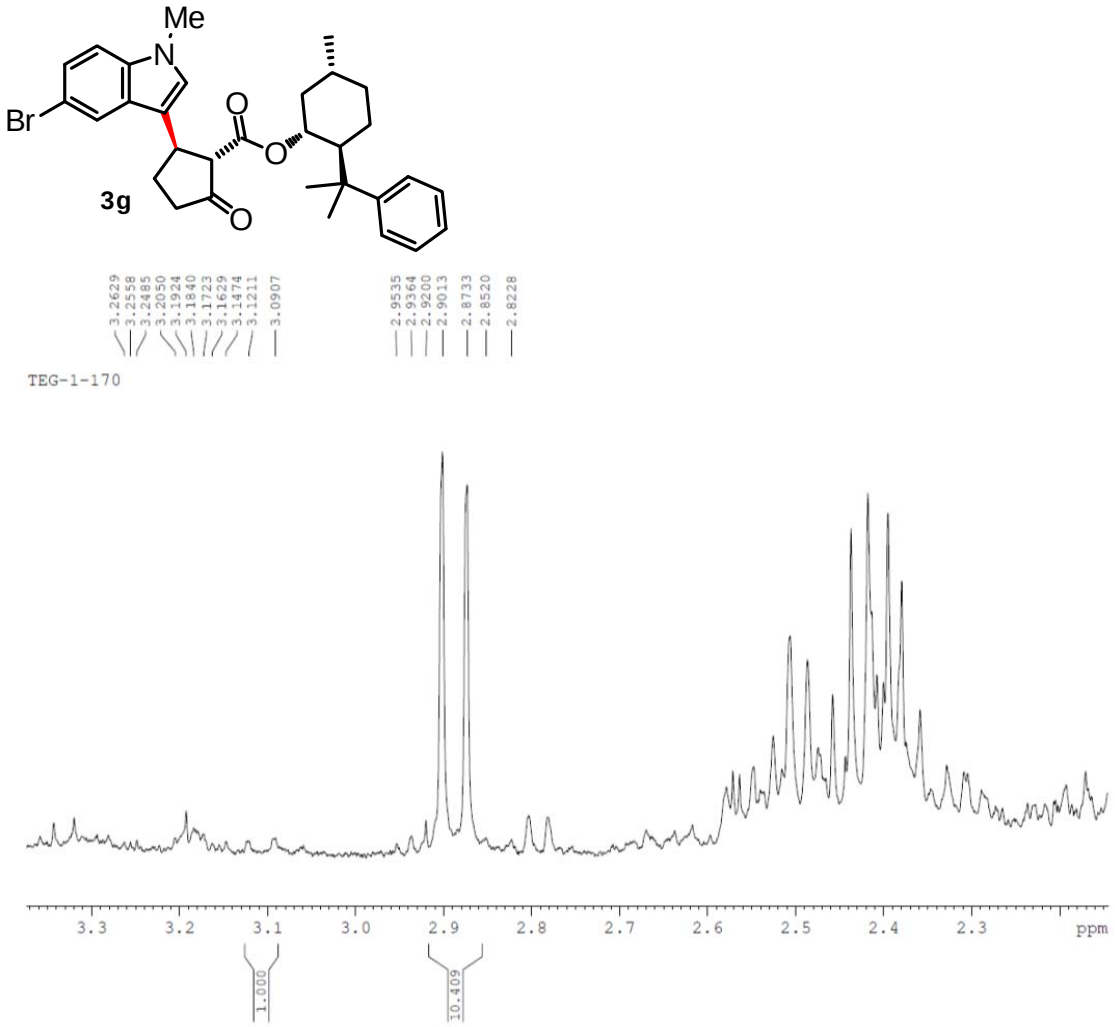

Me
N
Br
O
O
O
3g

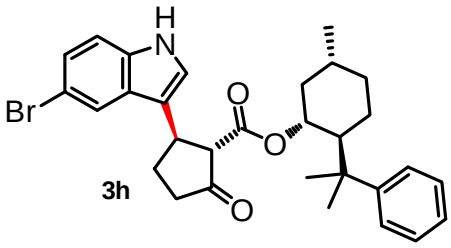

1.000
1.153
1.153
1.139
0.991
0.412
0.910
1.027
0.995
1.827
1.022
3.647
2.085
1.461
1.213
2.438
2.312
1.483
2.222
1.013
2.306
1.145
1.927
0.011
0.007
udd
udd
udd
10.8726
10.8454
4.9176
4.9128
4.9092
4.9043
4.8928
4.8881
4.8844
4.8795
4.0768
4.0719
4.0651
4.0563
4.0494
4.0377
4.0219
3.4929
3.4652
7.6476
7.6454
7.6433
7.6276
7.6255
7.6234
7.3177
7.3155
7.3136
7.2971
7.2949
7.2599
7.2465
7.2434
7.2404
7.2228
7.1342
7.1315
7.1143
7.1117
7.0969
7.0944
6.9244
6.9200
4.9092
4.0651
4.0494
3.7547
3.7497
3.4929
3.4652
2.6231
2.5994
2.5780
2.5588
2.5330
2.5121
2.3337
2.0982
1.7182
1.7094
1.6990
1.6892
1.6792
1.6606
1.6493
1.6382
1.6154
1.5536
1.2577
1.2490
1.2358
1.2292
1.2139
1.0335
1.0248
0.9989
0.9903
0.8985
0.8873
0.8760
0.8713
0.8641
0.8540
0.8438
0.8371
0.8223
0.8158
0.7912
0.6846
TEG-1-070
ppm

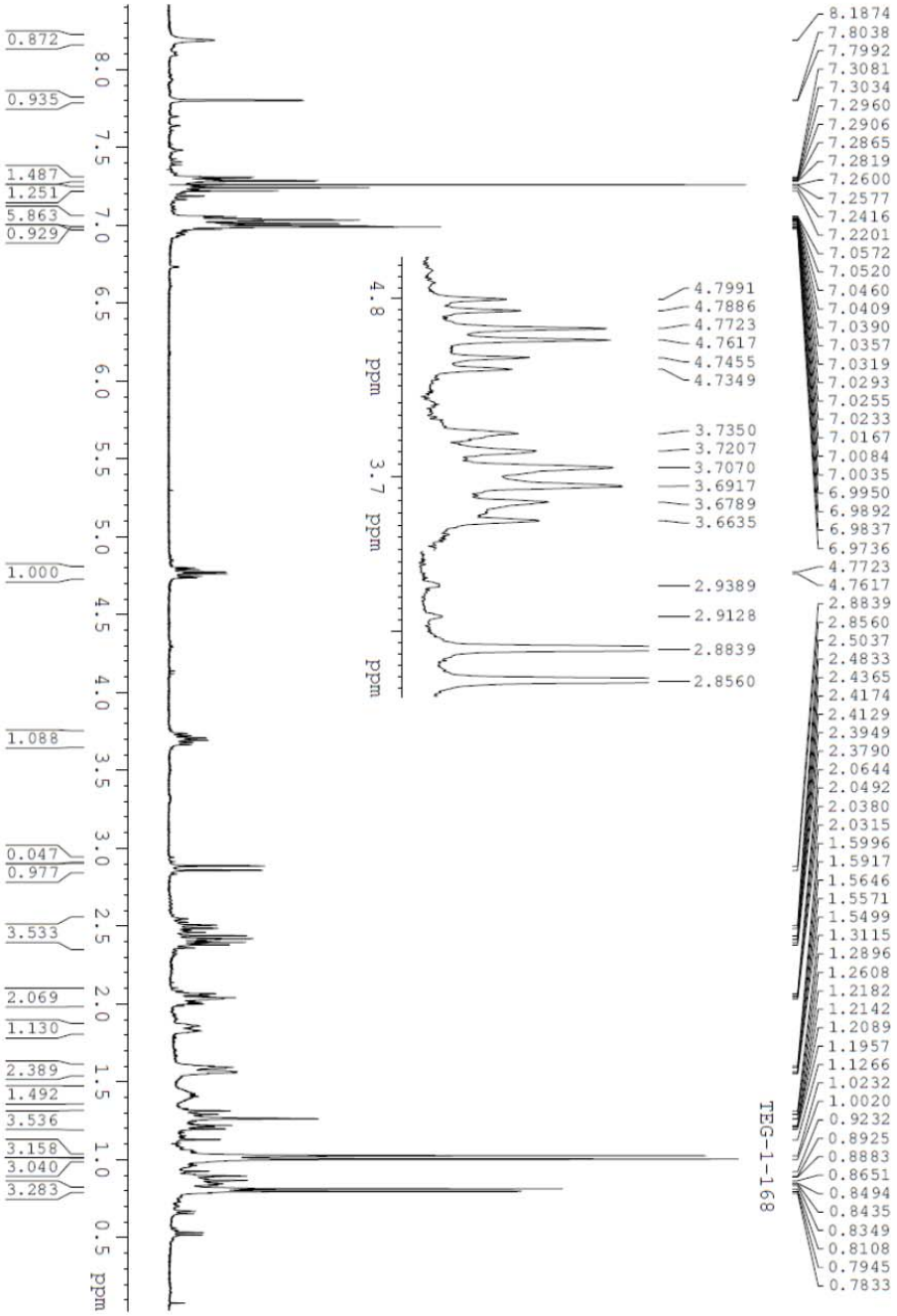

Me
N
Br
O
O
O
O

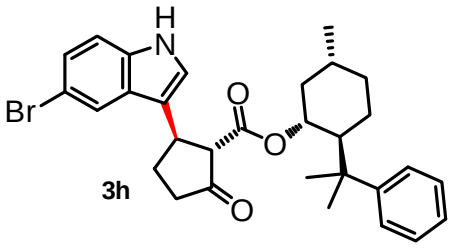
3g

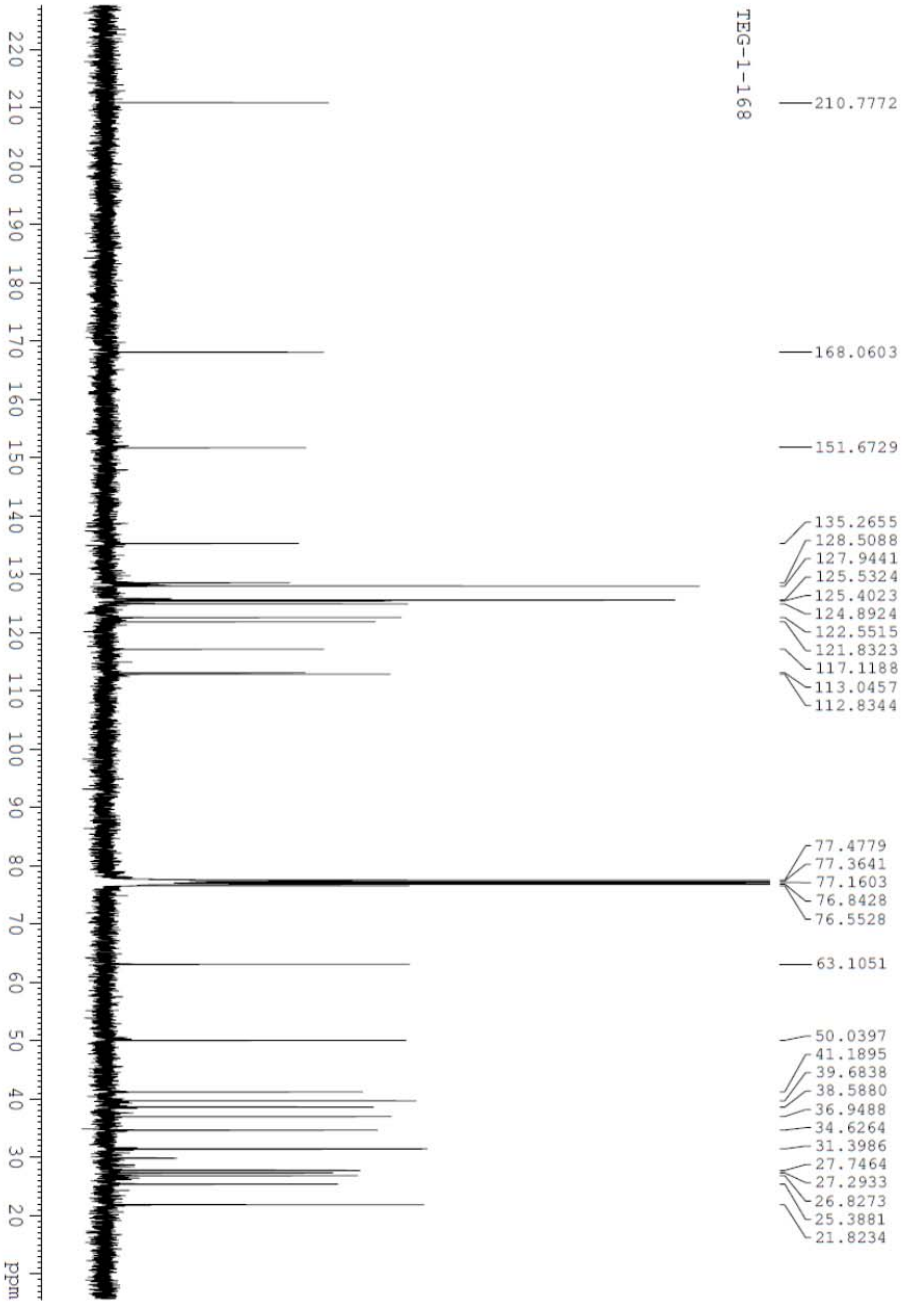

TEG-1-170
210.7472
168.0936
151.5890
136.0617
128.8082
128.2477
127.9485
127.8320
126.5634
125.8298
125.7349
125.5595
124.9357
122.5665
115.4638
112.6959
110.9525
77.3652
76.5346
63.3156
50.1016
41.2447
39.7435
38.6291
37.0684
34.6363
33.0057
31.4083
27.9553
26.9035
26.8611
25.8535
21.8224
ppm

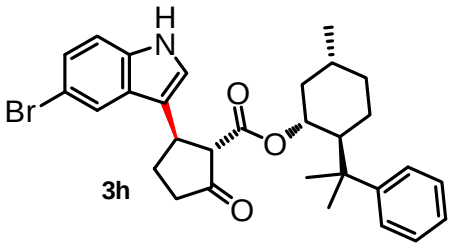

Me
N
Br
O
O
O
3g
3.2629
3.2558
3.2485
3.2050
3.1924
3.1840
3.1723
3.1629
3.1474
3.1211
3.0907
2.9535
2.9364
2.9200
2.9013
2.8733
2.8520
2.8228
TEG-1-170
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
ppm
1.000
10.409


H
N
Br
O
O
O
3h

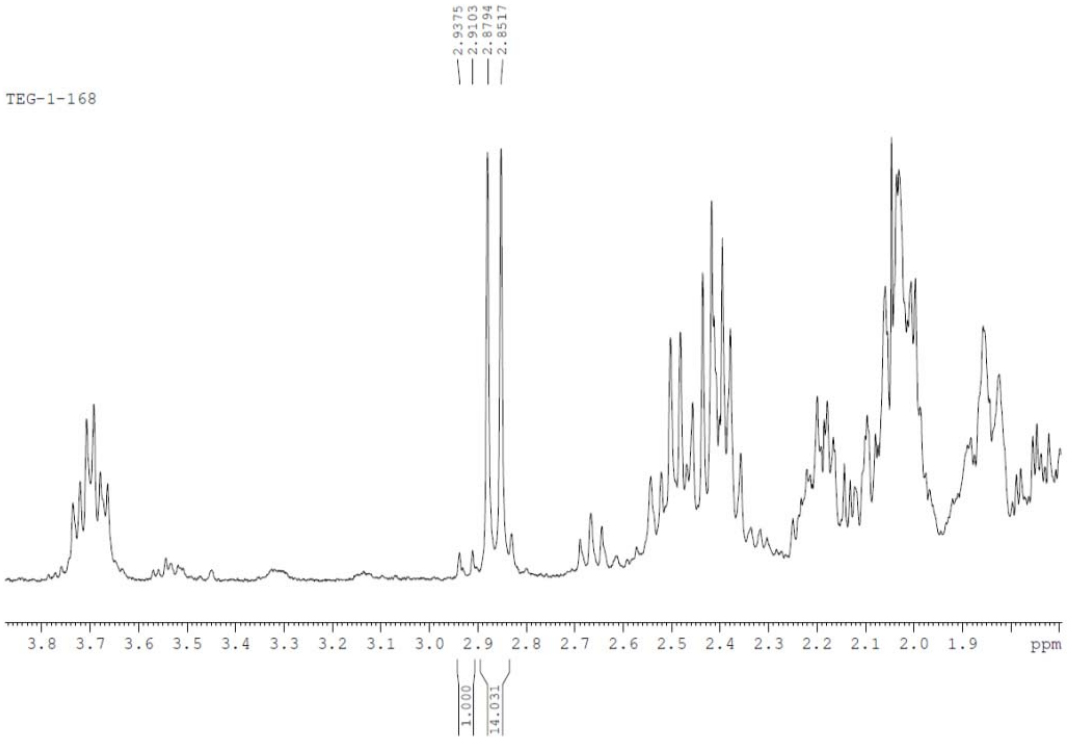

0.872
0.935
1.487
1.251
5.863
0.929
1.000
1.088
0.047
0.977
3.533
2.069
1.130
2.389
1.492
3.536
3.158
3.040
3.283
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.8 ppm
3.7 ppm
4.7991
4.7886
4.7723
4.7617
4.7455
4.7349
3.7350
3.7207
3.7070
3.6917
3.6789
3.6635
2.9389
2.9128
2.8839
2.8560
8.1874
7.8038
7.7992
7.3081
7.3034
7.2960
7.2906
7.2865
7.2819
7.2600
7.2577
7.2416
7.2201
7.0572
7.0520
7.0460
7.0409
7.0390
7.0357
7.0319
7.0293
7.0255
7.0233
7.0167
7.0084
7.0035
6.9950
6.9892
6.9837
6.9736
4.7723
4.7617
2.8839
2.8560
2.5037
2.4833
2.4365
2.4174
2.4129
2.3949
2.3790
2.0644
2.0492
2.0380
2.0315
1.5996
1.5917
1.5646
1.5571
1.5499
1.3115
1.2896
1.2608
1.2182
1.2142
1.2089
1.1957
1.1266
1.0232
1.0020
0.9232
0.8925
0.8883
0.8651
0.8494
0.8435
0.8349
0.8108
0.7945
0.7833
TEG-1-168

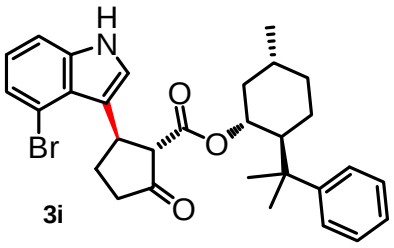

H
N
Br
O
O
O
3h


TEG-1-168
210.7772
168.0603
151.6729
135.2655
128.5088
127.9441
125.5324
125.4023
124.8924
122.5515
121.8323
117.1188
113.0457
112.8344
77.4779
77.3641
77.1603
76.8428
76.5528
63.1051
50.0397
41.1895
39.6838
38.5880
36.9488
34.6264
31.3986
27.7464
27.2933
26.8273
25.3881
21.8234
ppm

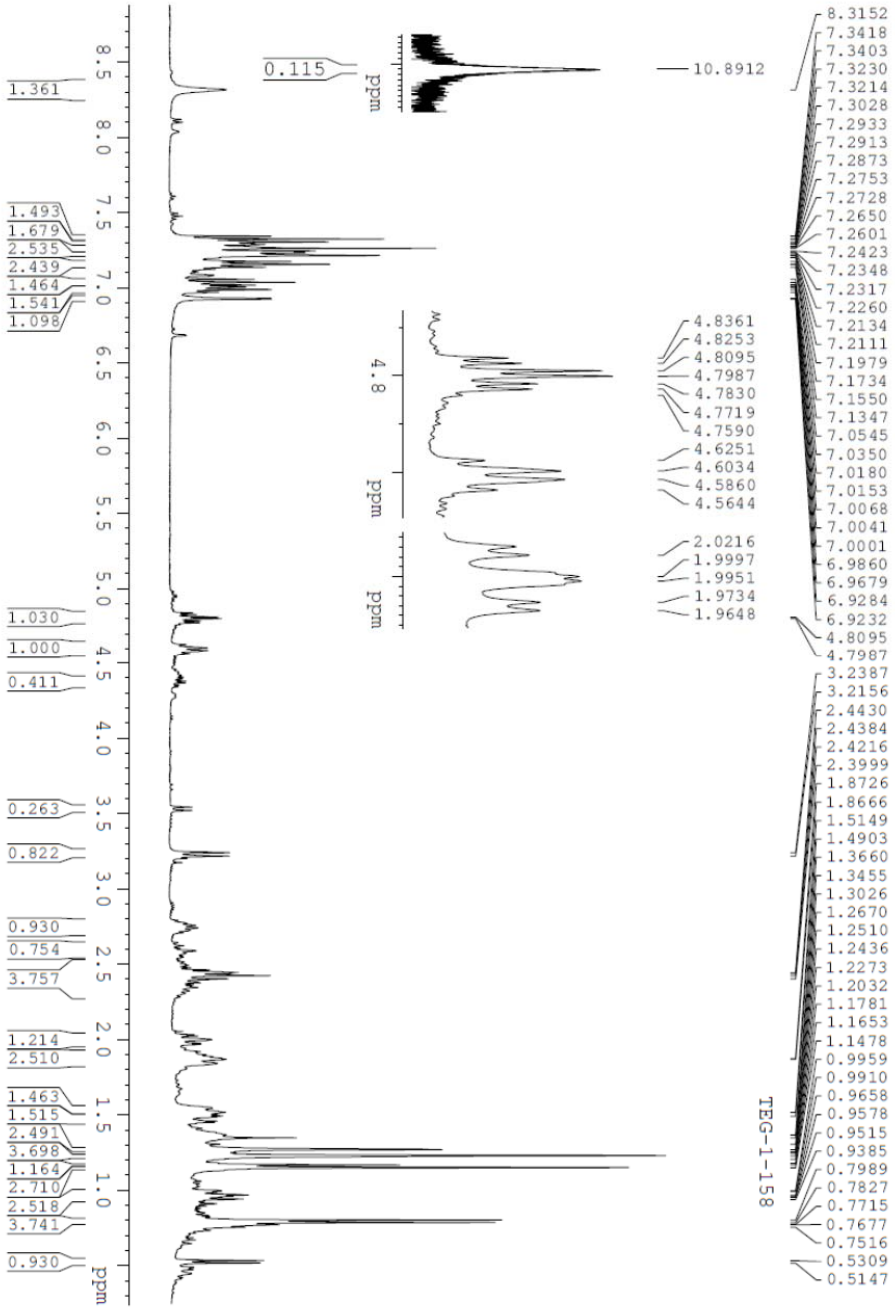

H
N
Br
O
O
O
O

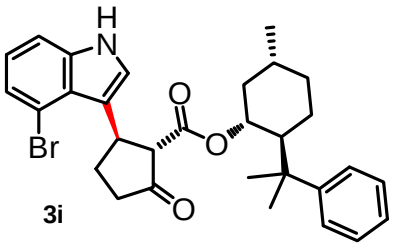
3h


2.9375
2.9103
2.8794
2.8517
TEG-1-168
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 ppm
1.000
14.031

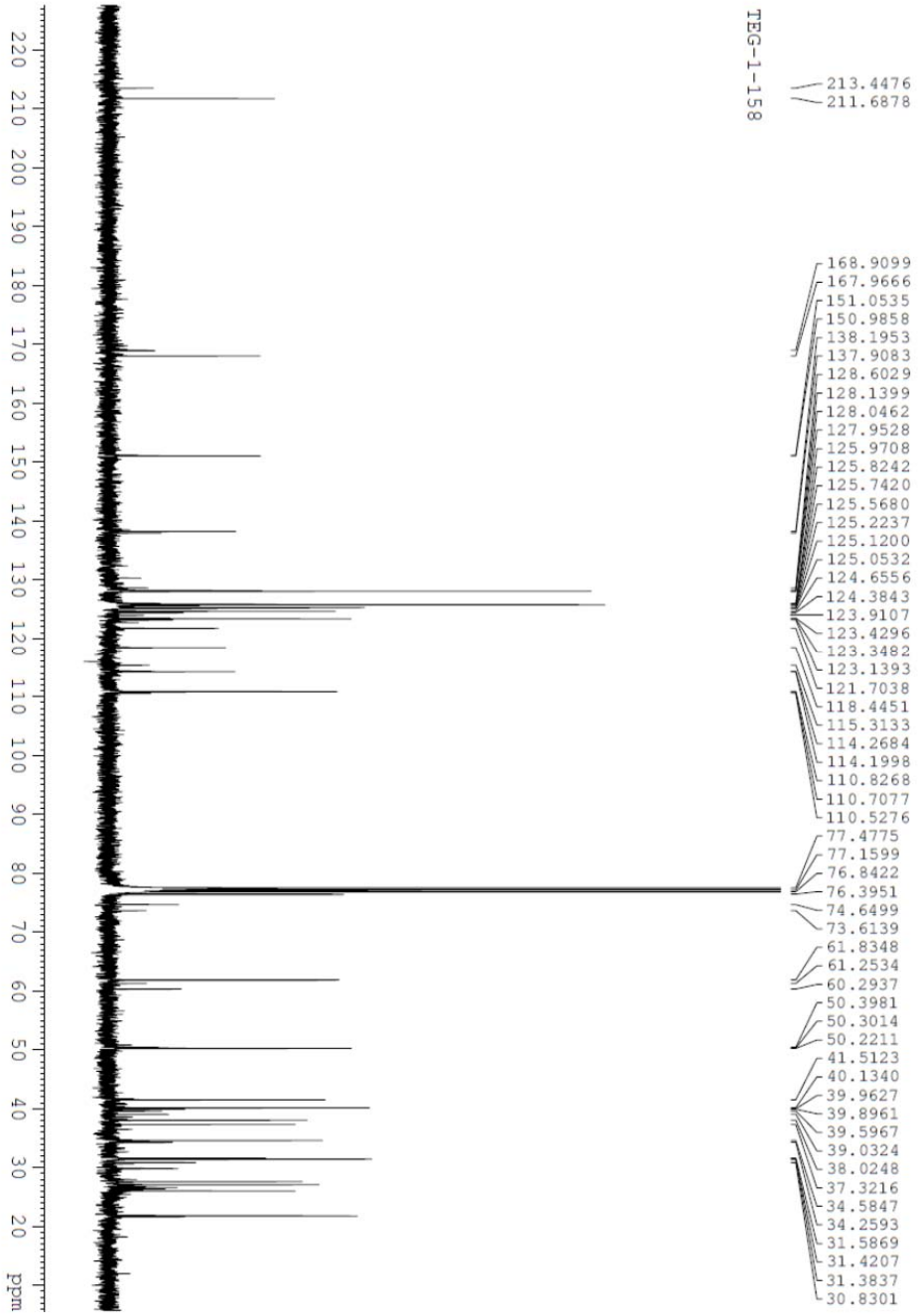

H
N
Br
O
O
O

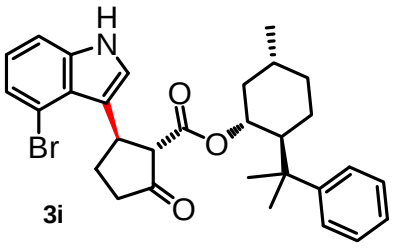
3i


1.361
1.493
1.679
2.535
2.439
1.464
1.541
1.098
1.030
1.000
0.411
0.263
0.822
0.930
0.754
3.757
1.214
2.510
1.463
1.515
2.491
3.698
1.164
2.710
2.518
3.741
0.930
0.115
4.8
10.8912
4.8361
4.8253
4.8095
4.7987
4.7830
4.7719
4.7590
4.6251
4.6034
4.5860
4.5644
2.0216
1.9997
1.9951
1.9734
1.9648
8.3152
7.3418
7.3403
7.3230
7.3214
7.3028
7.2933
7.2913
7.2873
7.2753
7.2728
7.2650
7.2601
7.2423
7.2348
7.2317
7.2260
7.2134
7.2111
7.1979
7.1734
7.1550
7.1347
7.0545
7.0350
7.0180
7.0153
7.0068
7.0041
7.0001
6.9860
6.9679
6.9284
6.9232
4.8095
4.7987
3.2387
3.2156
2.4430
2.4384
2.4216
2.3999
1.8726
1.8666
1.5149
1.4903
1.3660
1.3455
1.3026
1.2670
1.2510
1.2436
1.2273
1.2032
1.1781
1.1653
1.1478
0.9959
0.9910
0.9658
0.9578
0.9515
0.9385
0.7989
0.7827
0.7715
0.7677
0.7516
0.5309
0.5147
TEG-1-158
ppm

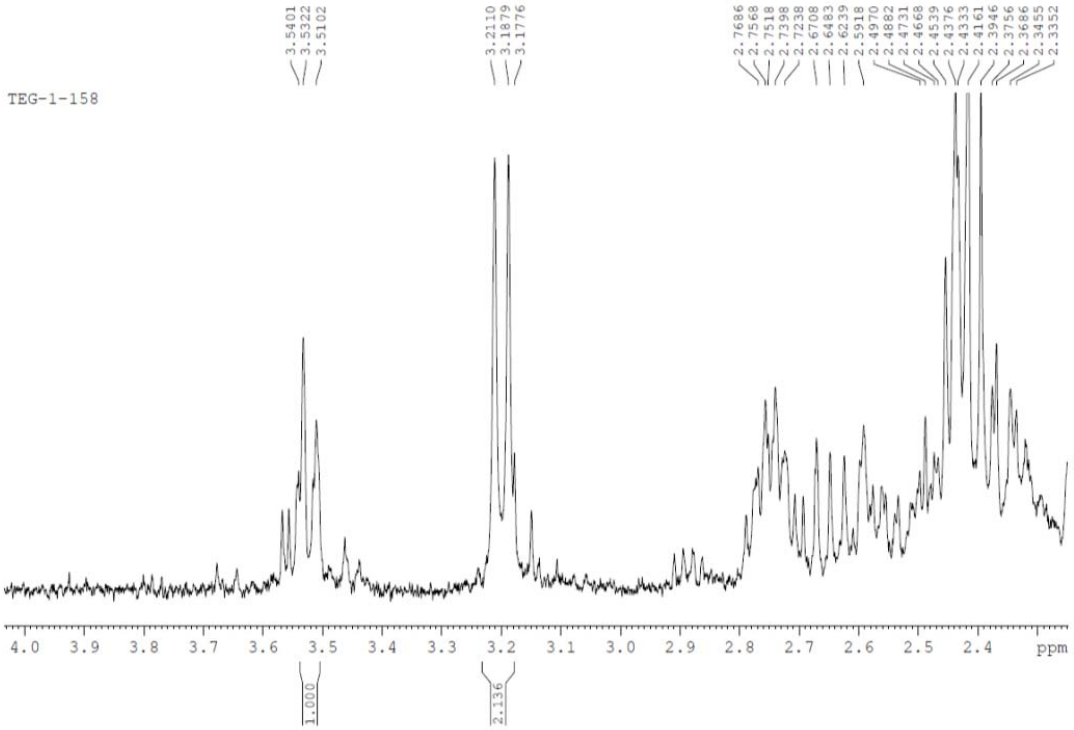

H
N
Br
O
O
O

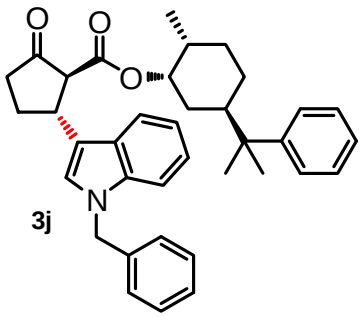
3i

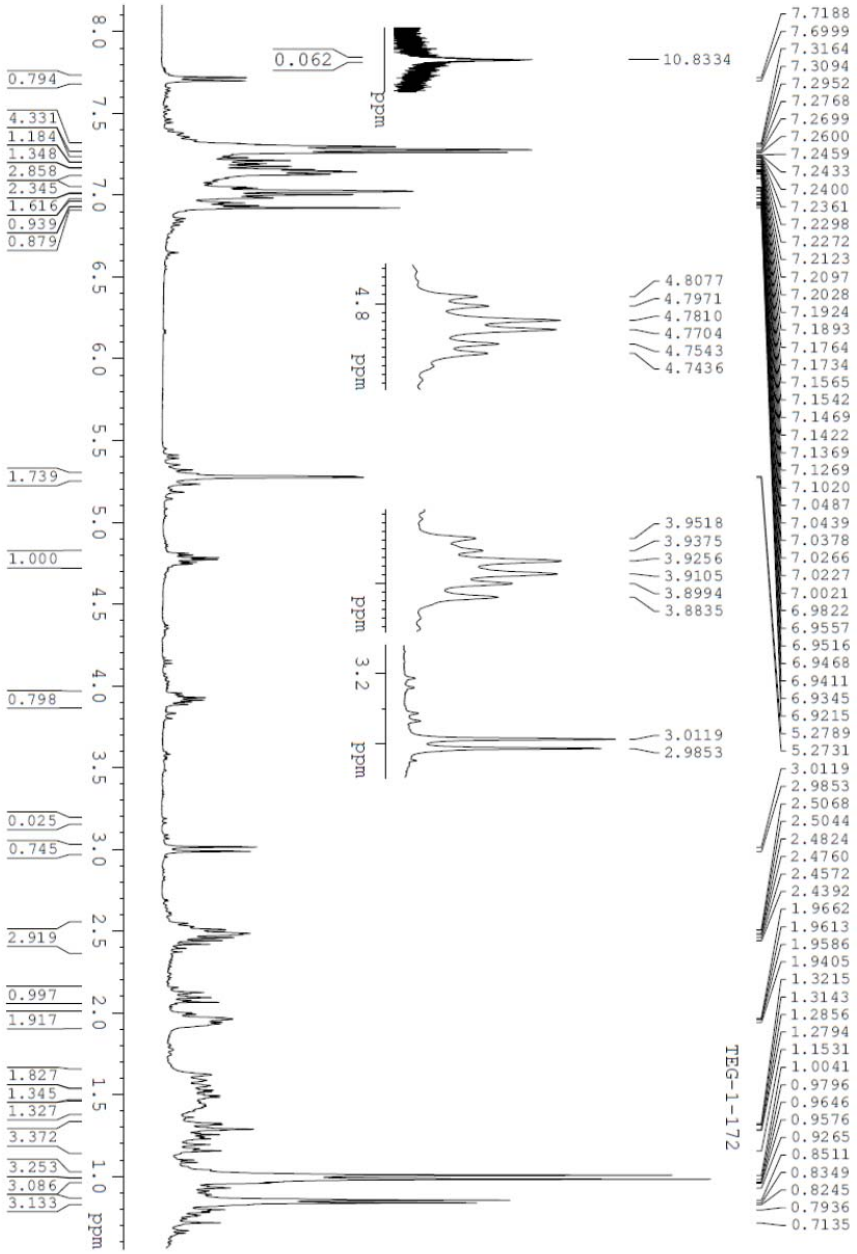

TEG-1-158
213.4476
211.6878
168.9099
167.9666
151.0535
150.9858
138.1953
137.9083
128.6029
128.1399
128.0462
127.9528
125.9708
125.8242
125.7420
125.5680
125.2237
125.1200
125.0532
124.6556
124.3843
123.9107
123.4296
123.3482
123.1393
121.7038
118.4451
115.3133
114.2684
114.1998
110.8268
110.7077
110.5276
77.4775
77.1599
76.8422
76.3951
74.6499
73.6139
61.8348
61.2534
60.2937
50.3981
50.3014
50.2211
41.5123
40.1340
39.9627
39.8961
39.5967
39.0324
38.0248
37.3216
34.5847
34.2593
31.5869
31.4207
31.3837
30.8301
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

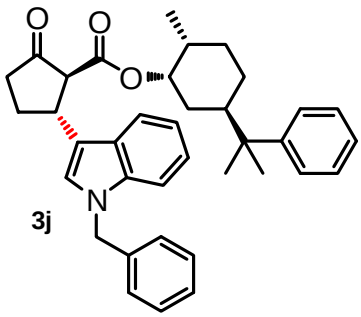

H
N
Br
O
O
O

3i

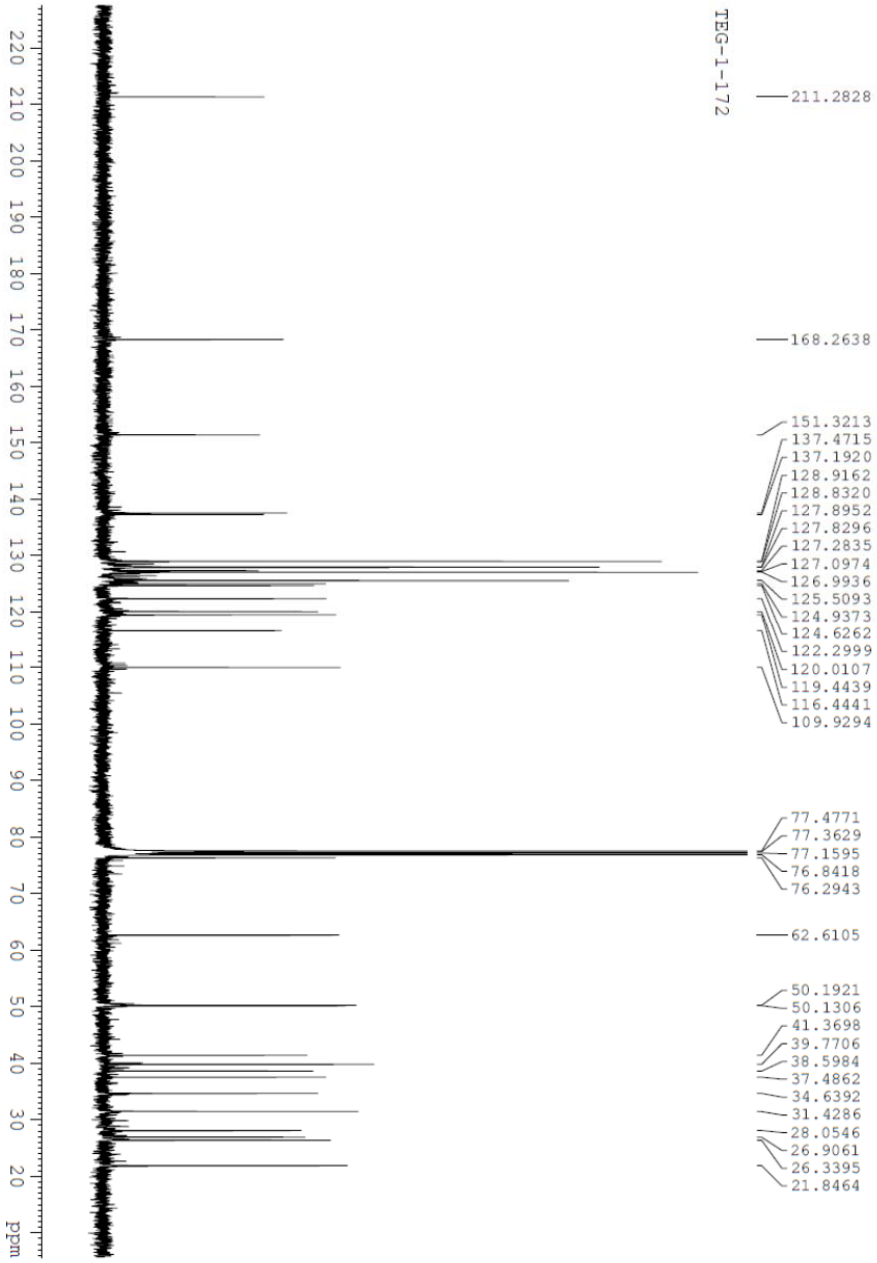

TEG-1-158
3.5401
3.5322
3.5102
3.2110
3.1879
3.1776
2.7686
2.7568
2.7518
2.7398
2.7238
2.6708
2.6483
2.6239
2.5918
2.4970
2.4882
2.4731
2.4668
2.4539
2.4376
2.4333
2.4161
2.3946
2.3756
2.3686
2.3455
2.3352
4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 ppm
1.000
2.136

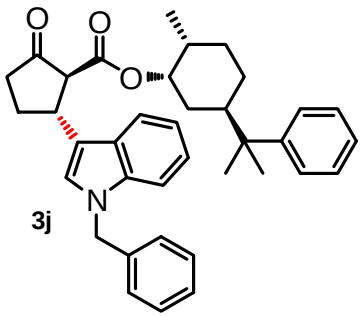

O
O
O
N
3j


0.794
4.331
1.184
1.348
2.858
2.345
1.616
0.939
0.879
1.739
1.000
0.798
0.025
0.745
2.919
0.997
1.917
1.827
1.345
1.327
3.372
3.253
3.086
3.133
0.062
10.8334
4.8077
4.7971
4.7810
4.7704
4.7543
4.7436
3.9518
3.9375
3.9256
3.9105
3.8994
3.8835
3.0119
2.9853
7.7188
7.6999
7.3164
7.3094
7.2952
7.2768
7.2699
7.2600
7.2459
7.2433
7.2400
7.2361
7.2298
7.2272
7.2123
7.2097
7.2028
7.1924
7.1893
7.1764
7.1734
7.1565
7.1542
7.1469
7.1422
7.1369
7.1269
7.1020
7.0487
7.0439
7.0378
7.0266
7.0227
7.0021
6.9822
6.9557
6.9516
6.9468
6.9411
6.9345
6.9215
5.2789
5.2731
2.5068
2.5044
2.4824
2.4760
2.4572
2.4392
1.9662
1.9613
1.9586
1.9405
1.3215
1.3143
1.2856
1.2794
1.1531
1.0041
0.9796
0.9646
0.9576
0.9265
0.8511
0.8349
0.8245
0.7936
0.7135
TEG-1-172
ppm

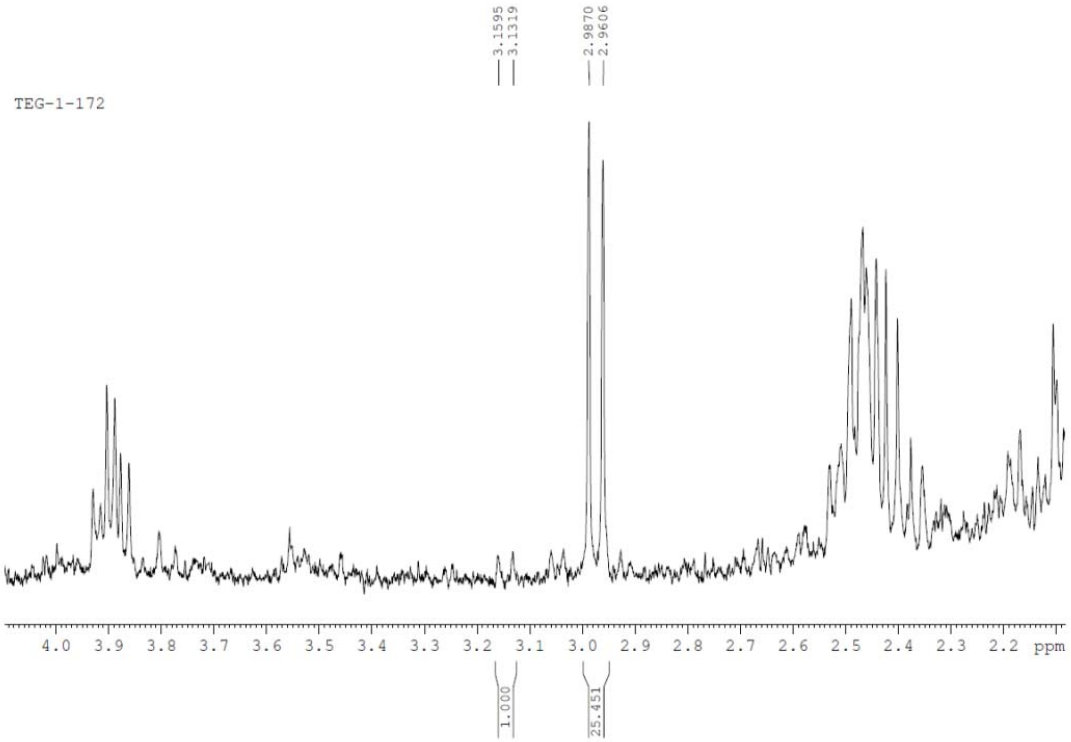

O
O
O
N

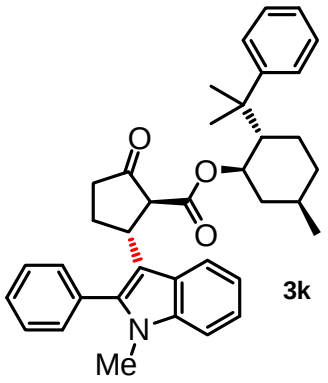
3j


TEG-1-172
211.2828
168.2638
151.3213
137.4715
137.1920
128.9162
128.8320
127.8952
127.8296
127.2835
127.0974
126.9936
125.5093
124.9373
124.6262
122.2999
120.0107
119.4439
116.4441
109.9294
77.4771
77.3629
77.1595
76.8418
76.2943
62.6105
50.1921
50.1306
41.3698
39.7706
38.5984
37.4862
34.6392
31.4286
28.0546
26.9061
26.3395
21.8464
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

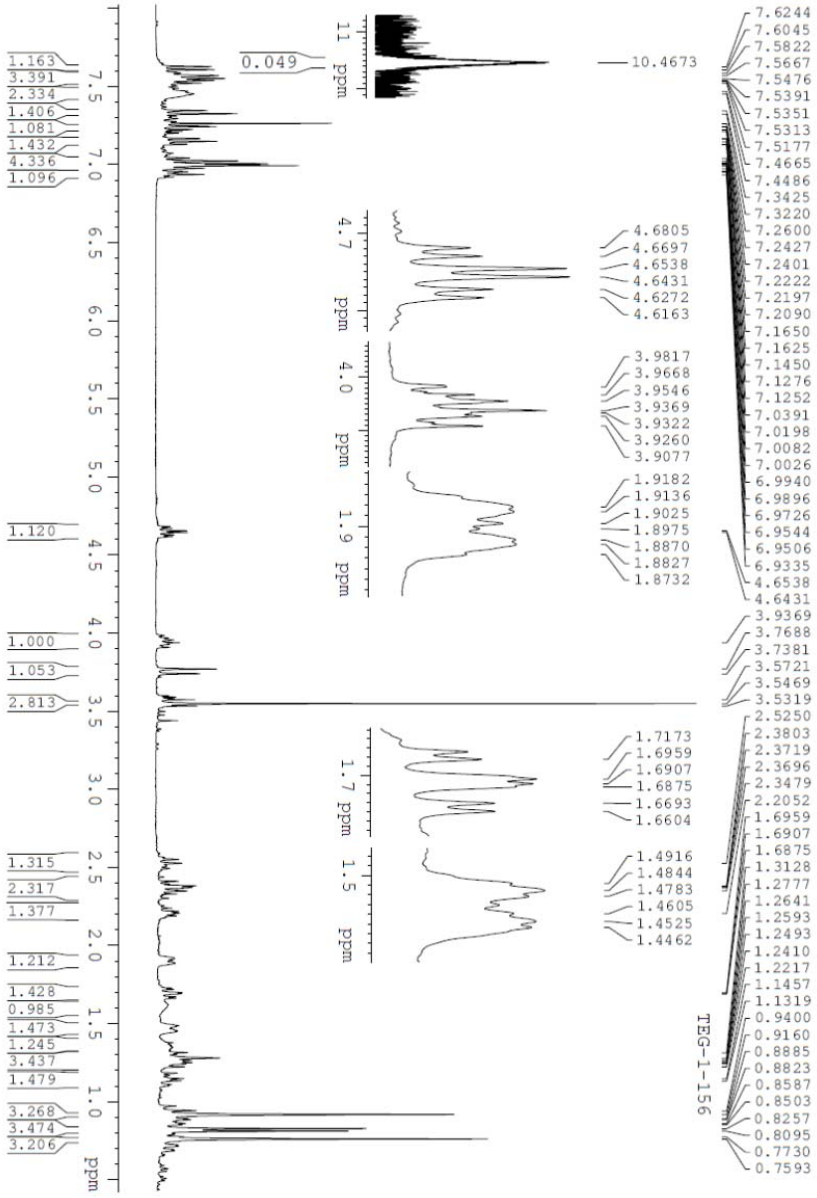

O
O
O
N

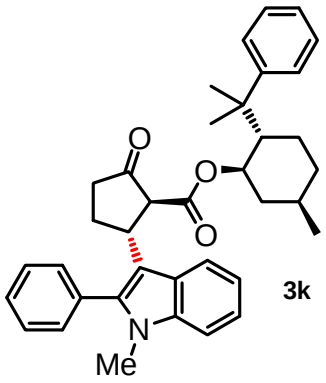
3j


3.1595
3.1319
2.9870
2.9606
TEG-1-172
4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 ppm
1.000
25.451

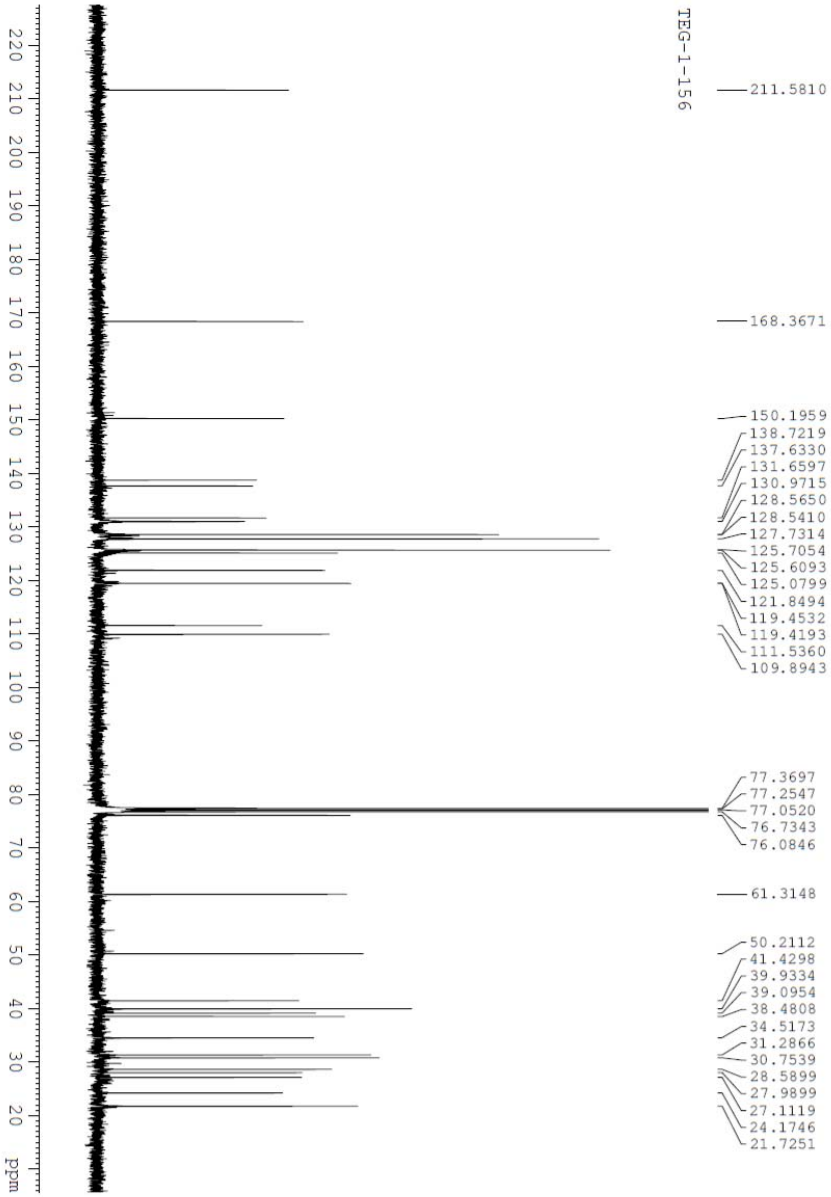

O
O
O
N
Me

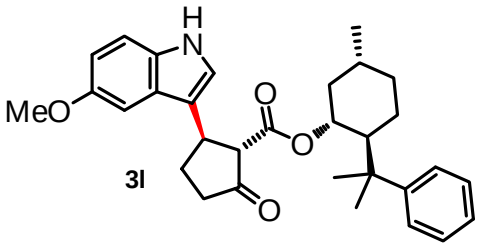
3k

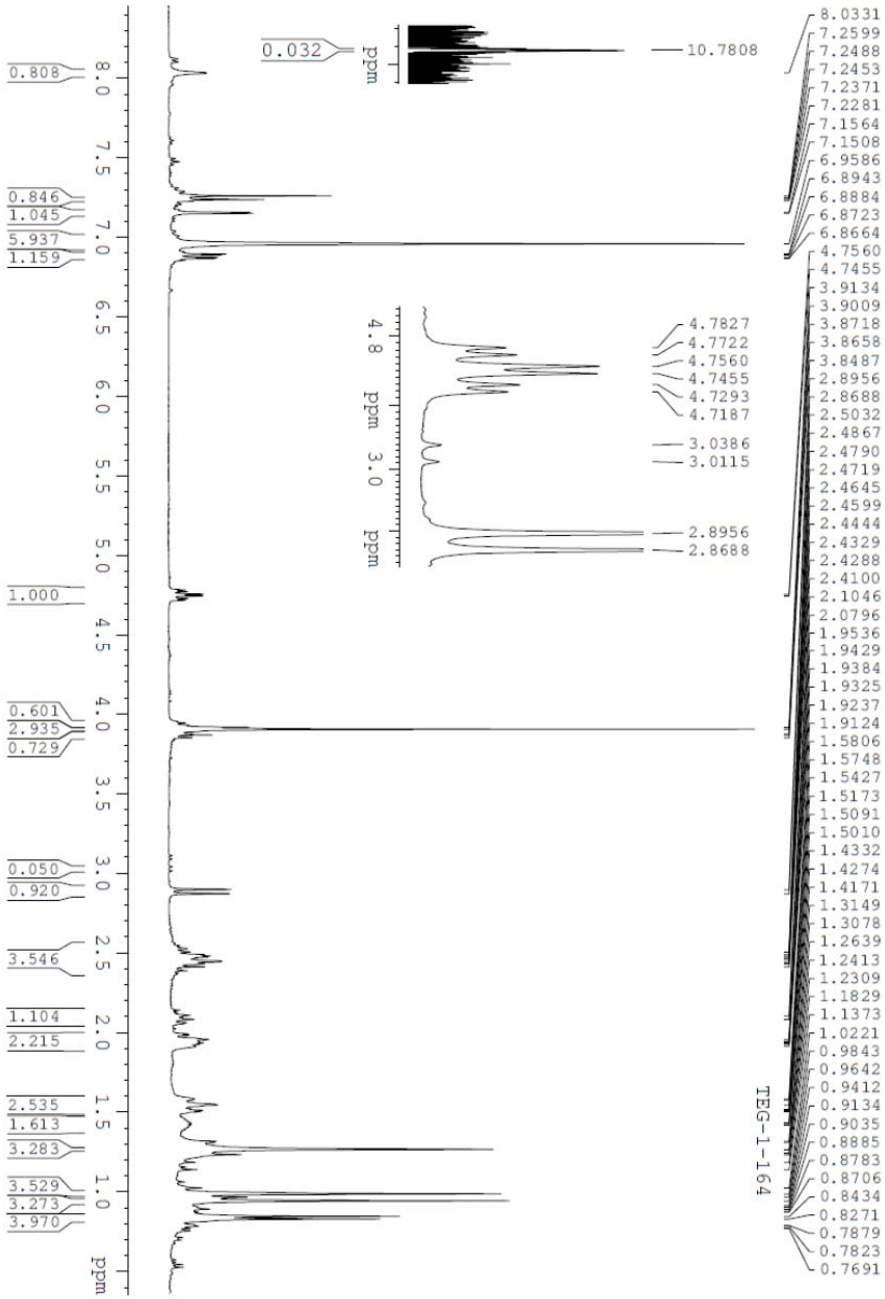

11 ppm
4.7 ppm
4.0 ppm
1.9 ppm
1.7 ppm
1.5 ppm
0.049
10.4673
TEG-1-156
ppm

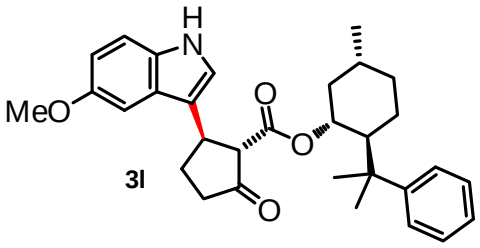

O
O
O
N
Me

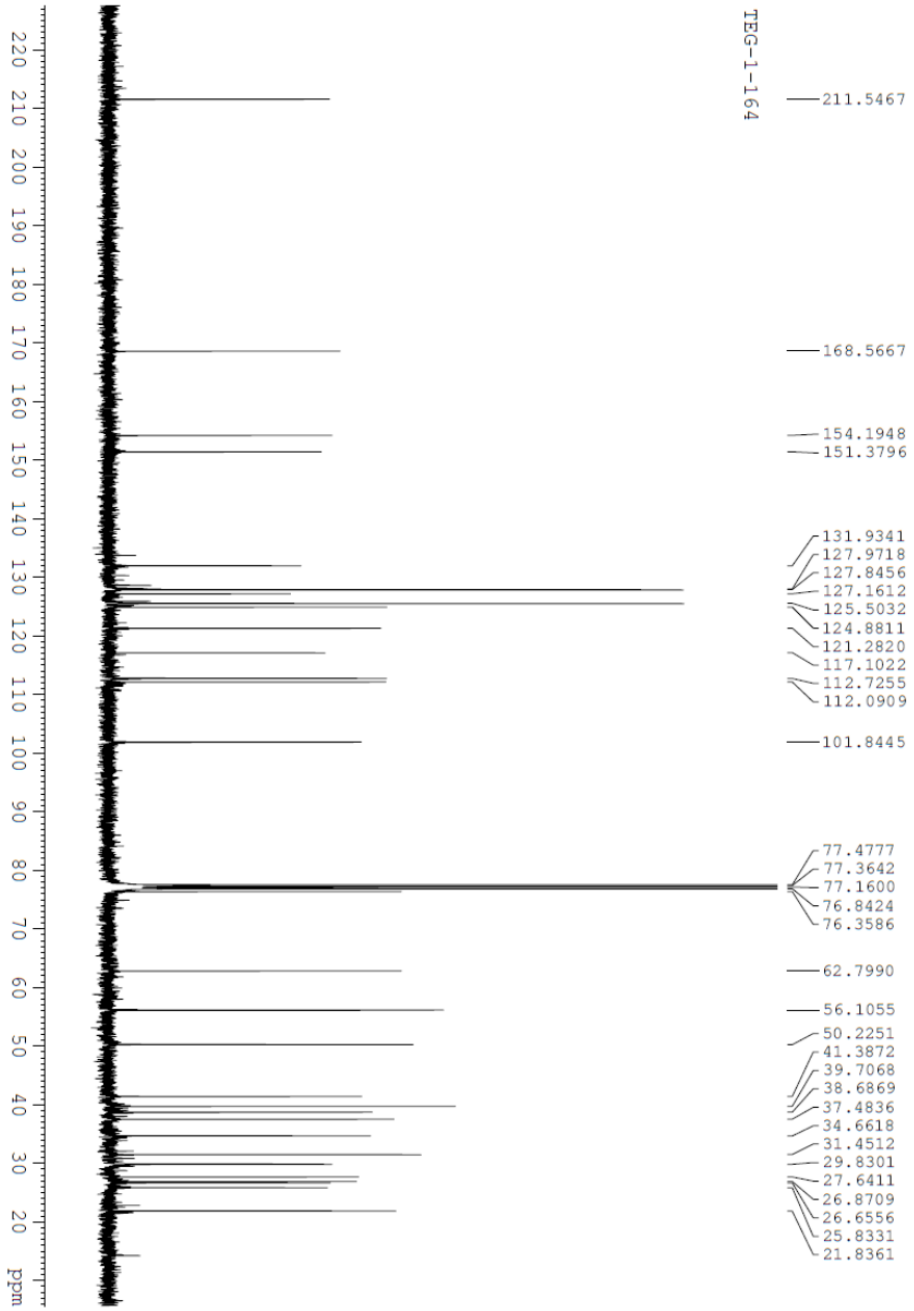
3k

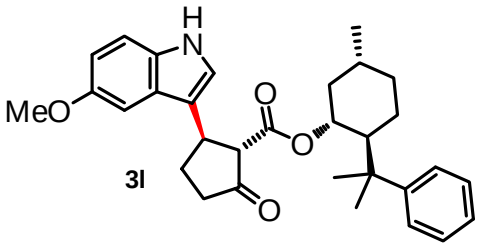

TEG-1-156
211.5810
168.3671
150.1959
138.7219
137.6330
131.6597
130.9715
128.5650
128.5410
127.7314
125.7054
125.6093
125.0799
121.8494
119.4532
119.4193
111.5360
109.8943
77.3697
77.2547
77.0520
76.7343
76.0846
61.3148
50.2112
41.4298
39.9334
39.0954
38.4808
34.5173
31.2866
30.7539
28.5899
27.9899
27.1119
24.1746
21.7251
ppm


H
N
MeO
O
O
O
3l

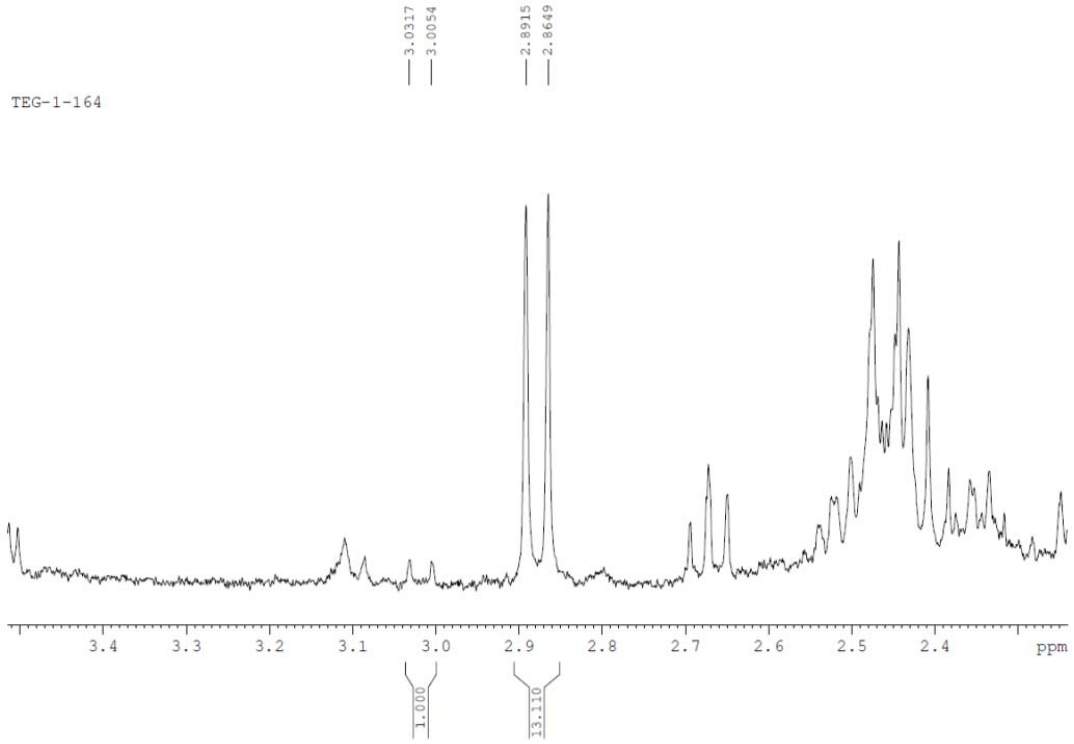

0.032
10.7808
0.808
0.846
1.045
5.937
1.159
1.000
0.601
2.935
0.729
0.050
0.920
3.546
1.104
2.215
2.535
1.613
3.283
3.529
3.273
3.970
4.7827
4.7722
4.7560
4.7455
4.7293
4.7187
3.0386
3.0115
2.8956
2.8688
TEG-1-164

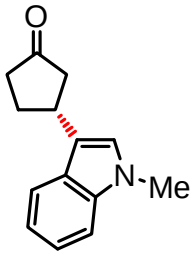

H
N
MeO
O
O
O
3l


TEG-1-164
211.5467
168.5667
154.1948
151.3796
131.9341
127.9718
127.8456
127.1612
125.5032
124.8811
121.2820
117.1022
112.7255
112.0909
101.8445
77.4777
77.3642
77.1600
76.8424
76.3586
62.7990
56.1055
50.2251
41.3872
39.7068
38.6869
37.4836
34.6618
31.4512
29.8301
27.6411
26.8709
26.6556
25.8331
21.8361
ppm

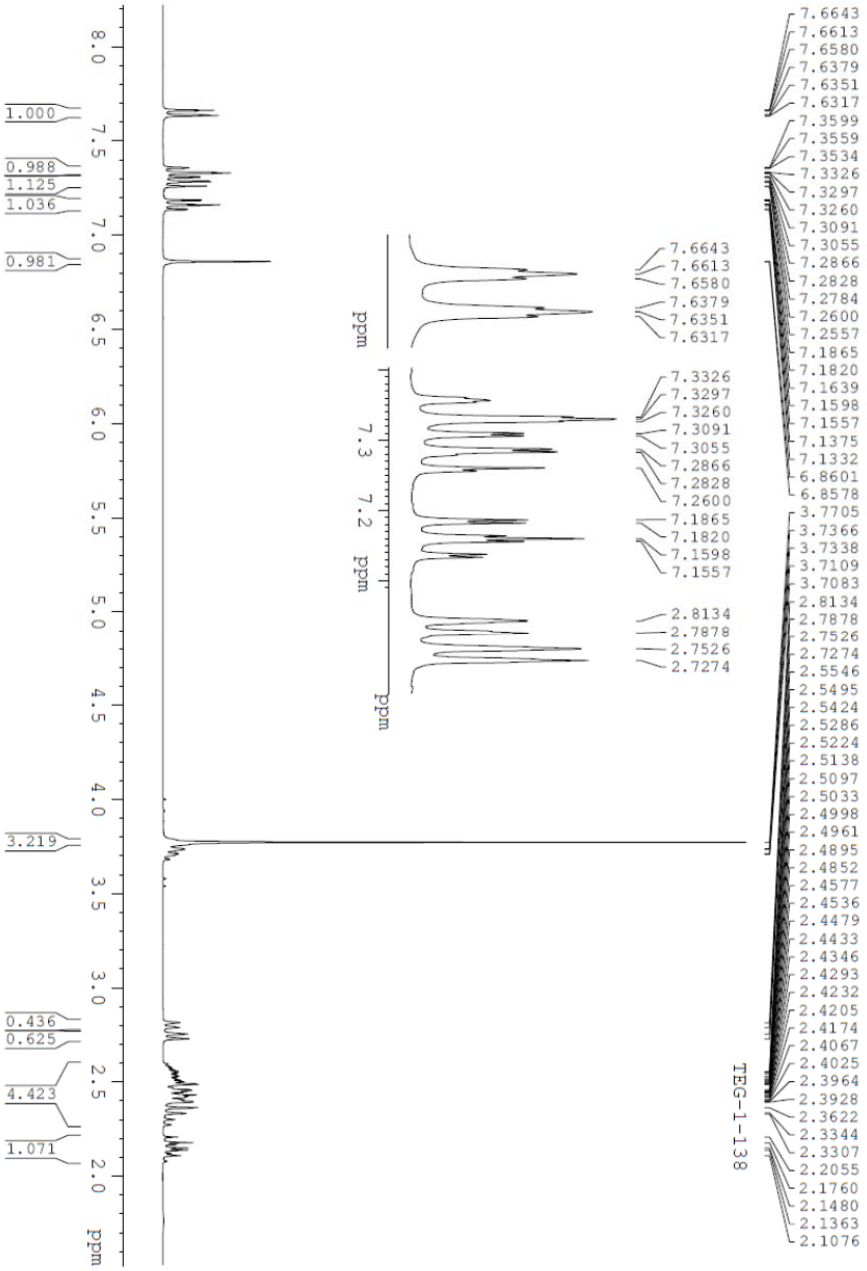

H
N
MeO
O
O
O

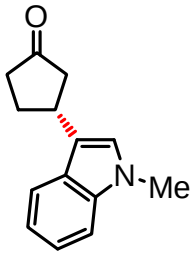
3l


3.0317
3.0054
2.8915
2.8649
TEG-1-164
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
ppm
1.000
13.110

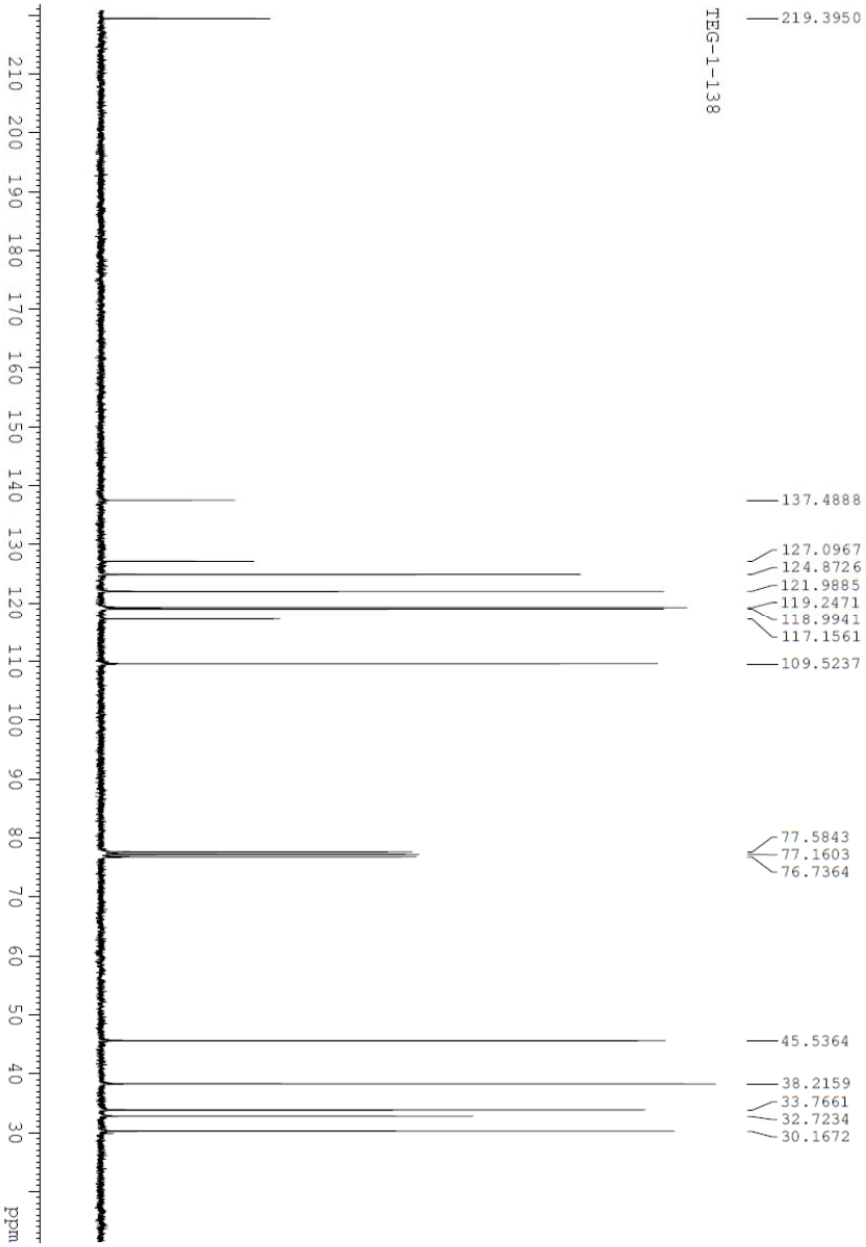

O
N
Me

6


1.000
0.988
1.125
1.036
0.981
3.219
0.436
0.625
4.423
1.071
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
7.3
7.2
ppm
7.6643
7.6613
7.6580
7.6379
7.6351
7.6317
7.3326
7.3297
7.3260
7.3091
7.3055
7.2866
7.2828
7.2600
7.1865
7.1820
7.1598
7.1557
2.8134
2.7878
2.7526
2.7274
TEG-1-138


O
N
Me

6


TEG-1-138
219.3950
137.4888
127.0967
124.8726
121.9885
119.2471
118.9941
117.1561
109.5237
77.5843
77.1603
76.7364
45.5364
38.2159
33.7661
32.7234
30.1672
ppm

GC chromatograms of decarboxylated product **6** and the corresponding racemate (±)-**6**

```
ta File C:\CHEM32\1\DATA\AINI\AINI 2012-10-09 14-12-02\201B0101.D
mple Name: TEG-1-062 Racemate

==========================================================================
Acq. Operator    : Aini                          Seq. Line :   1
Acq. Instrument : Instrument 1                    Location : Vial 201
Injection Date   : 10/9/2012 2:13:20 PM               Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method      : C:\CHEM32\1\DATA\AINI\AINI 2012-10-09 14-12-02\AINI 100C 20MIN B-DM.M
Last changed     : 10/9/2012 2:11:38 PM by Aini
Analysis Method : C:\CHEM32\1\METHODS\SARIN 150C-180C 20-6-10 36MIN B-DM.M
Last changed     : 2/17/2014 6:29:58 PM by Aurelie
                   (modified after loading)
Additional Info : Peak(s) manually integrated
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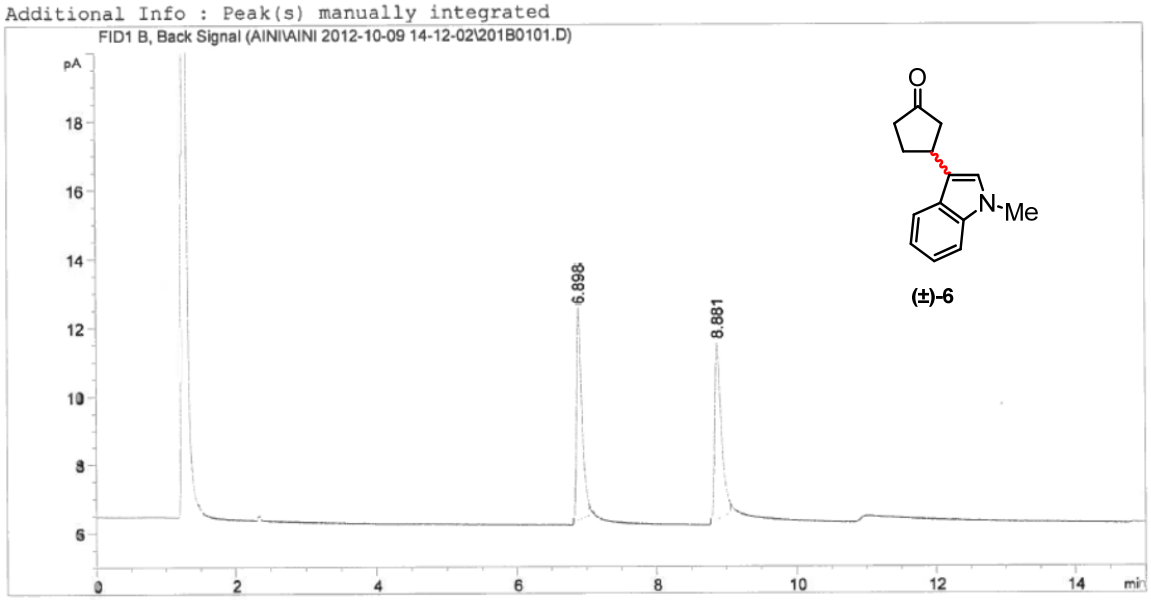


```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   6.898 BB    0.0825   33.55399    6.18123 48.97603
   2   8.881 BB    0.1015   34.95706    5.15596 51.02397

Totals :                    68.51105   11.33720

==========================================================================
                        *** End of Report ***
```

```
Acq. Operator    : Aini                                  Seq. Line :   2
Acq. Instrument  : Instrument 1                           Location : Vial 202
Injection Date   : 10/9/2012 2:34:37 PM                       Inj :   1
                                                       Inj Volume : 1 µl

Acq. Method      : C:\CHEM32\1\DATA\AINI\AINI 2012-10-09 14-12-02\AINI 100C 20MIN B-DM.M
Last changed     : 10/9/2012 2:11:38 PM by Aini
Analysis Method  : C:\CHEM32\1\METHODS\SARIN 150C-180C 20-6-10 36MIN B-DM.M
Last changed     : 2/17/2014 6:41:48 PM by Aurelie
                   (modified after loading)
Additional Info  : Peak(s) manually integrated
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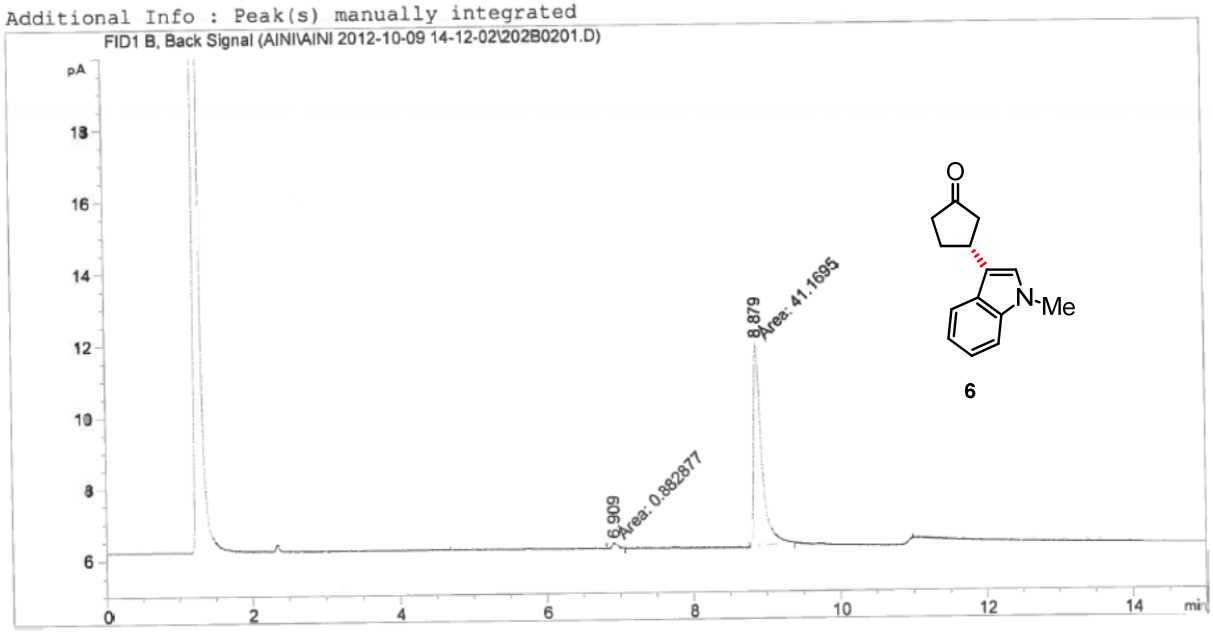


```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   6.909 MM    0.0926 8.82877e-1 1.58945e-1  2.09947
   2   8.879 MM    0.1219   41.16945    5.62970 97.90053

Totals :                    42.05233    5.78865

                        *** End of Report ***
```