New Electrophilic Addition of α-Diazoesters with Ketones for Enantioselective C-N Bond Formation

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Supporting Information

CONTENTS:

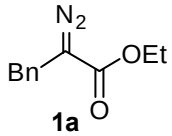
(A) General

^{1}H NMR spectra were recorded on commercial instruments (400 MHz or 600 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100 MHz or 150 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Daicel Chiralcel OD-H, AD-H, AS-H, IA and IC in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. All ketones were purchased from Alfa Aesar with further purification. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, H CP.

(B) Preparation of α-diazoacetates[1]

All α-diazoacetates were prepared according to the literatures[1].

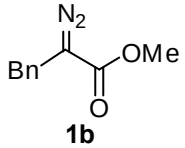
ethyl 2-diazo-3-phenylpropanoate (1a)



1a

Known compound, see: Taber, D. F.; Sheth, R. B.; Joshi, P. V. *J. Org. Chem.* **2005**, *70*, 2851.

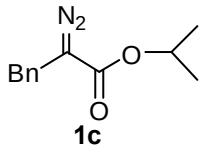
methyl 2-diazo-3-phenylpropanoate (1b)



1b

Known compound, see: Zhao, Z.; Liu, Y.; Gong, M.; Zhao, X.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 1139.

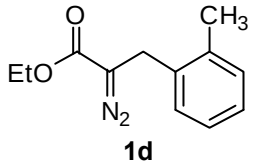
isopropyl 2-diazo-3-phenylpropanoate (1c)



1c

Known compound, see: Taber, D. F.; Sheth, R. B.; Joshi, P. V. *J. Org. Chem.* **2005**, *70*, 2851.

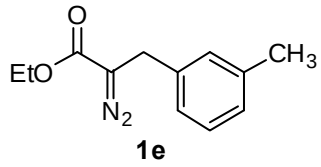
ethyl 2-diazo-3-*o*-tolylpropanoate (1d)



1d

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.10 (m, 4H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 2H), 2.32 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.38, 136.43, 134.84, 130.60, 129.22, 127.40, 126.27, 60.94, 26.88, 19.37, 14.54.

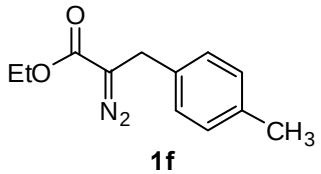
ethyl 2-diazo-3-*m*-tolylpropanoate (1e)



1e

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 6.97 (m, 4H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.59 (s, 2H), 2.34 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.37, 138.49, 137.21, 129.12, 128.68, 127.87, 125.38, 60.92, 29.22, 21.40, 14.53.

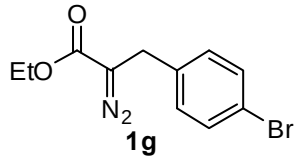
ethyl 2-diazo-3-*p*-tolylpropanoate (1f)



1f

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (s, 4H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.58 (s, 2H), 2.32 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.38, 136.73, 134.16, 129.47, 128.29, 60.90, 28.91, 21.07, 14.53.

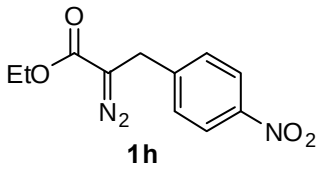
ethyl 3-(4-bromophenyl)-2-diazopropanoate (1g)



1g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.13-7.10 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.58 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02, 136.41, 131.89, 130.06, 121.02, 61.07, 28.95, 14.51.

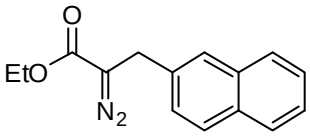
ethyl 2-diazo-3-(4-nitrophenyl)propanoate (1h)



1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.11 (m, 2H), 7.45-7.42 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 147.14, 145.23, 129.14, 124.06, 61.29, 29.48, 14.48.

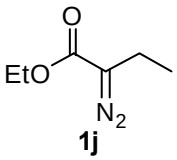
ethyl 2-diazo-3-(naphthalen-2-yl)propanoate (1i)



1i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 3H), 7.67 (s, 1H), 7.52 – 7.31 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.45, 134.74, 133.47, 132.52, 128.64, 127.68, 127.63, 126.81, 126.60, 126.27, 125.81, 61.00, 29.57, 14.53.

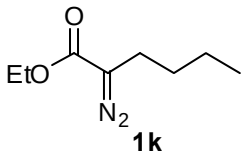
ethyl 2-diazobutanoate (1j)



1j

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (q, *J* = 7.1 Hz, 2H), 2.35 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.72, 60.66, 16.54, 14.51, 11.91.

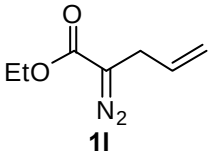
ethyl 2-diazohexanoate (1k)



1k

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (q, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 7.4 Hz 2H), 1.53-1.46 (m, 2H), 1.43-1.34 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.73, 60.66, 29.67, 22.66, 21.84, 14.50, 13.71.

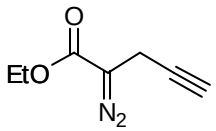
ethyl 2-diazopent-4-enoate (1l)



1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 16.6, 10.0, 6.5 Hz, 1H), 5.19-5.14 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.05 (d, *J* = 6.5 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.37, 132.52, 117.55, 60.85, 27.31, 14.51.

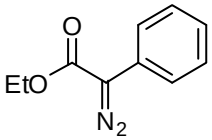
ethyl 2-diazopent-4-ynoate (1m)



1m

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (q, *J* = 7.1 Hz, 2H), 3.30 (d, *J* = 2.5 Hz, 2H), 2.17 (t, *J* = 2.6 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 77.62, 71.32, 61.14, 14.49, 13.74.

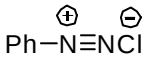
ethyl 2-diazo-2-phenylacetate (1n)[1b]



1n

Known compound, see: Maier, T. C.; Fu, G. C. *J. Am. Chem. Soc.* **2006,** *128*, 4594.

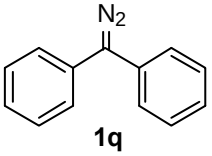
benzenediazonium chloride (1o)



1o

Known compound, see: Lyčka, A. et al. *Tetrahedron lett.* **2010**, *51*, 3149.

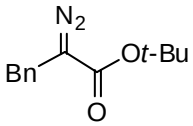
(diazomethylene)dibenzene (1p)



1q

Known compound, see: Kumar, S.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1040.

tert-butyl 2-diazo-3-phenylpropanoate (1q)



Known compound, see: Li, W.; Wang, J.; Hu, X. L.; Shen, K.; Wang, W. T.; Chu, Y. Y.; Lin, L. L.; Liu, X. H.; Feng, X. M. *J. Am. Chem. Soc.* **2010**, *132*, 8532.

(C) General procedure for chiral *N,N'*-dioxide preparation

The *N,N'*-dioxide ligands **L1**-**L4** were synthesized by the same procedure in the literatures.[2]

(D) General procedure for the catalytic asymmetric reaction

THF (50.0 μL) was added to a dry reaction tube charged with **L1** (0.005 mmol), $Sc(OTf)_3$ (0.006 mmol) and Li_2CO_3 (0.01 mmol) under N_2 atmosphere. The mixture was stirred at 20 °C for 0.5 h. After removing THF in vacuum, liquid ketone **2** (50.0 μL for **2a**, **2h**, **2i**, **2k**, and **2n**–**2q**), or other solid ketone **2** (0.2 mmol in 50.0 μL CH_2Cl_2), or cyclohexanone (0.2 mmol in 50.0 μL CH_2Cl_2) was added under N_2

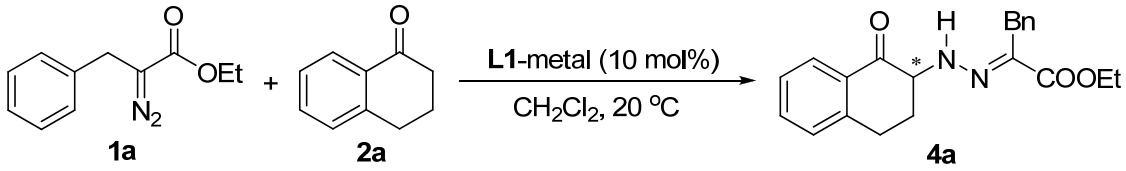
atmospher. After stirring for 5 min, α-diazoester **1** (0.1 mmol) was added, and the reaction was stirred at 20 °C for the indicated time. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4/1–1/1) at the temperature below 5 °C to afford the desired product. Caution: low temperature should be kept to avoid the racemization of the products during the seperation process of silica gel chromotograph. The products are stable in neutral and base conditions at room temperature. The enantiomeric excess was determined by high-performance liquid chromatography (HPLC) with Chiralcel AD-H, Chiralcel AS-H, Chiralcel OD-H or Chiralcel IC.

(E) General procedure for the preparation of the racemic products

The racemic prodcuts were prepared with the same procedure of the catalytic asymmetric reaction, using racemic ligand **L2** instead of chiral ligand **L1**.

(F) Optimization of the reaction conditions

Table 1. Screening of metals[a]

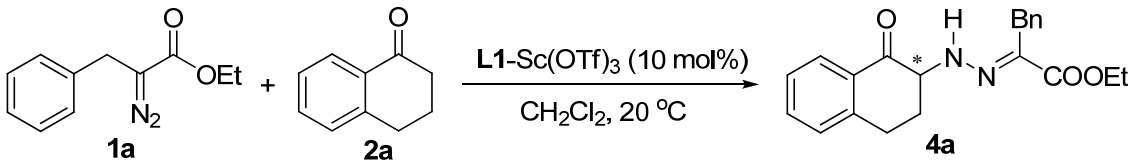


entry	ligand	metal	time (h)	yield (%)[b]	ee (%)[c]
1	**L1**	$Zn(OTf)_2$	72	0	-
2	**L1**	$Sm(OTf)_3$	72	0	-
3	**L1**	$Y(OTf)_3$	72	0	-
4	**L1**	$La(OTf)_3$	72	0	-
5	**L1**	$Yb(OTf)_3$	72	0	-
6	**L1**	$Sc(OiPr)_3$	72	0	-
7	**L1**	$Sc(OTf)_3$	72	21	95

8	-	$Sc(OTf)_3$	72	trace	-
9	**L1**	-	72	0	-

[a]The reactions were carried out with **L1**/metal (10 mol %, 1/1), **1a** (0.1 mmol), **2a** (0.2 mmol) in CH_2Cl_2 (0.2 mL) at 20 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

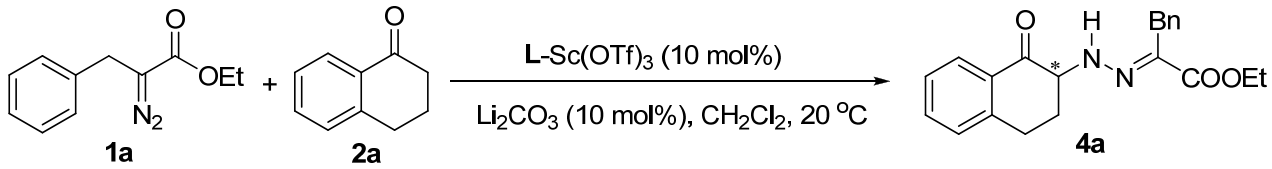
Table 2. Optimization of additives[a]



entry	additive	time (h)	yield (%)[b]	ee (%)[c]
1	Li_2CO_3	72	85	95
2	Na_2CO_3	72	68	95
3	K_2CO_3	72	33	95
4	Cs_2CO_3	72	42	94
5	Et_3N	24	trace	N.D.
6	PhCOOH	24	0	-
7	(10 mg) 3 Å MS	24	10	93

[a] The reactions were carried out with **L1**/$Sc(OTf)_3$ (10 mol %, 1/1), **1a** (0.1 mmol), **2a** (0.2 mmol), and additive (10 mol%) in CH_2Cl_2 (0.2 mL) at 20 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

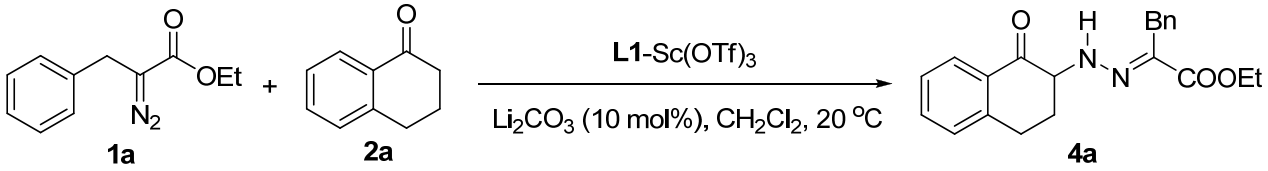
Table 3. Screening of ligands[a]



entry	ligand	time (h)	yield (%)[b]	ee (%)[c]
1	**L1**	72	85	95
2	**L2**	72	42	95
3	**L3**	72	6	80
4	**L4**	72	0	-

[a] The reactions were carried out with **L**/Sc(OTf)$_3$ (10 mol %, 1/1), **1a** (0.1 mmol), **2a** (0.2 mmol) in CH_2Cl_2 (0.2 mL) at 20 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

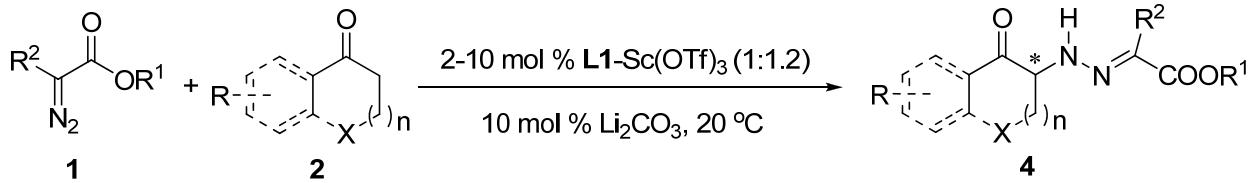
Table 4. Optimization of other conditions[a]

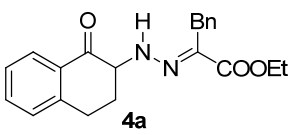


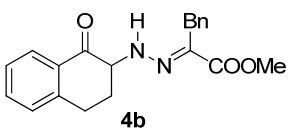
entry	**L1**:Sc(OTf)$_3$	catalyst loading (mol %)	time (h)	yield (%)[b]	ee (%)[c]
1	1.2:1	10	24	50	95
2	1:1	10	24	90	95
3	1:1.2	10	15	99	95
4	1:1.2	5	24	98	95
5	1:1.2	2	24	45	95

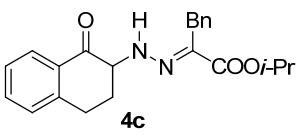
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (50.0 μL), **L1**-Sc(OTf)$_3$ (2-10 mol%), Li_2CO_3 (10 mol%) at 20 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

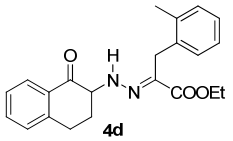
Table 5. Full list of the products[a]

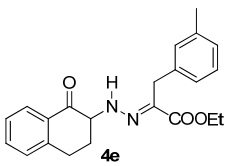


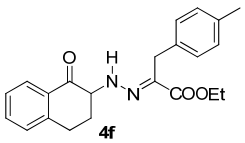


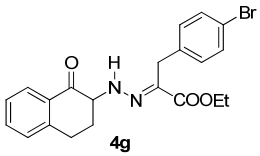


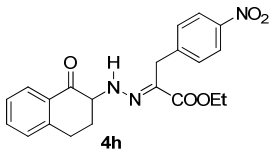


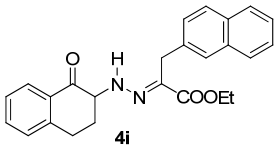


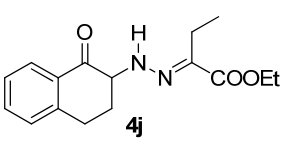


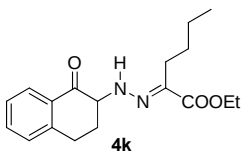


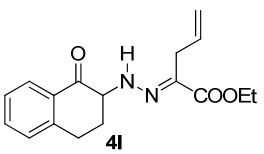


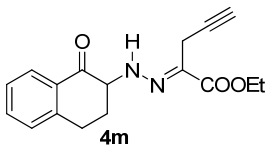




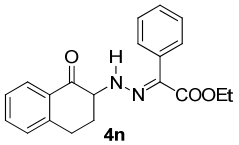




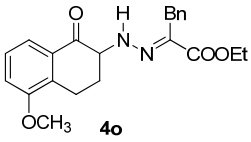




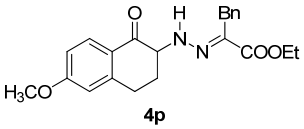
4m



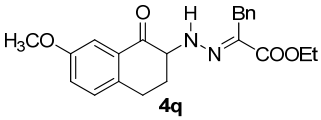
4n



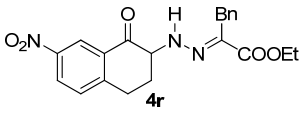
4o



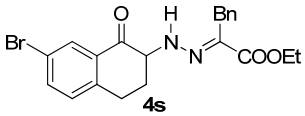
4p



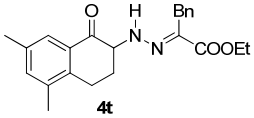
4q



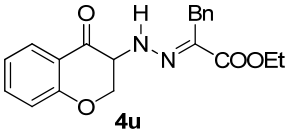
4r



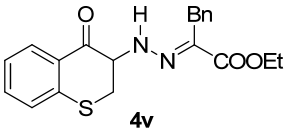
4s



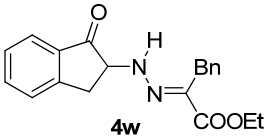
4t



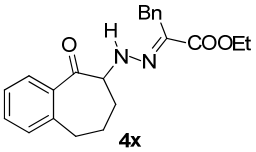
4u



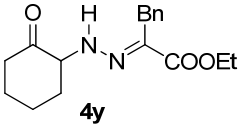
4v



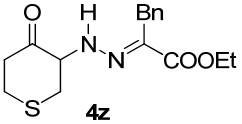
4w



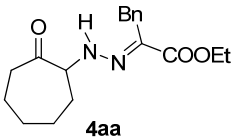
4x



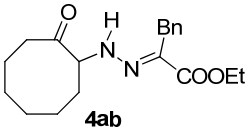
4y



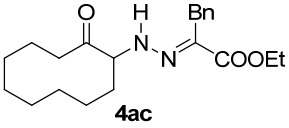
4z



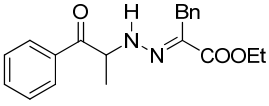
4aa



4ab



4ac



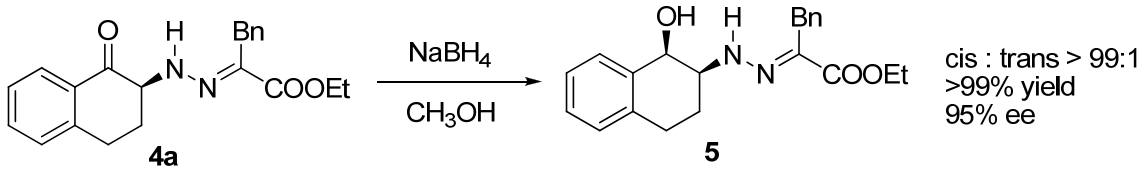
4ad

entry	**1**	**2**	catalyst loading (mol %)	time (h)	**4**	yield (%)[b]	ee (%)[c]
1	**1a**	**2a**	5	24	**4a**	98	95
2	**1b**	**2a**	5	30	**4b**	81	93
3	**1c**	**2a**	5	27	**4c**	95	93
4	**1d**	**2a**	5	24	**4d**	93	92
5	**1e**	**2a**	5	24	**4e**	95	95
6	**1f**	**2a**	5	27	**4f**	92	96
7	**1g**	**2a**	5	25	**4g**	98	97
8	**1h**	**2a**	5	26	**4h**	95	96
9	**1i**	**2a**	5	24	**4i**	92	97
10	**1j**	**2a**	5	35	**4j**	80	93

11	**1k**	**2a**	5	26	**4k**	89	93
12	**1l**	**2a**	5	20	**4l**	90	91
13	**1m**	**2a**	2	26	**4m**	92	95
14	**1n**	**2a**	5	56	**4n**	85	97
15	**1a**	**2b**	5	50	**4o**	89	95
16	**1a**	**2c**	5	72	**4p**	65	93
17	**1a**	**2d**	5	50	**4q**	93	99
18	**1a**	**2e**	5	58	**4r**	88	94
19	**1a**	**2f**	5	50	**4s**	96	99
20	**1a**	**2g**	5	50	**4t**	80	99
21	**1a**	**2h**	10	60	**4u**	75	98
22	**1a**	**2i**	5	65	**4v**	90	98
23	**1a**	**2j**	5	72	**4w**	53	89
24	**1a**	**2k**	5	40	**4x**	98	99
25	**1a**	**2l**	5	56	**4y**	83	71
26	**1a**	**2m**	5	72	**4z**	70	61
27	**1a**	**2n**	5	48	**4aa**	81	74
28	**1a**	**2o**	10	72	**4ab**	45	77
29	**1a**	**2p**	5	24	**4ac**	75	52
30	**1a**	**2q**	10	72	**4ad**	45	66

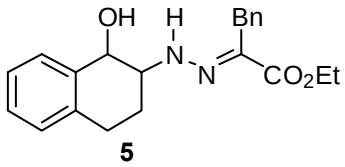
[a]Reaction conditions: **1** (0.1 mmol), **2** (50.0 μL of liquid ketone **2a**, **2h**, **2i**, **2k**, and **2n**–**2q**) or **2** (0.20 mmol in 50 μL CH_2Cl_2), **L1**-Sc(OTf)$_3$ (2-10 mol%), Li_2CO_3 (10 mol%) at 20 ^oC. [c]Isolated yield after silica gel column chromatography. [d] Determined by chiral HPLC.

(G) Synthetic transformation of the prodcut

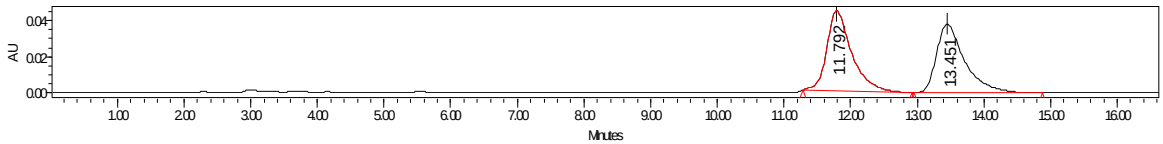


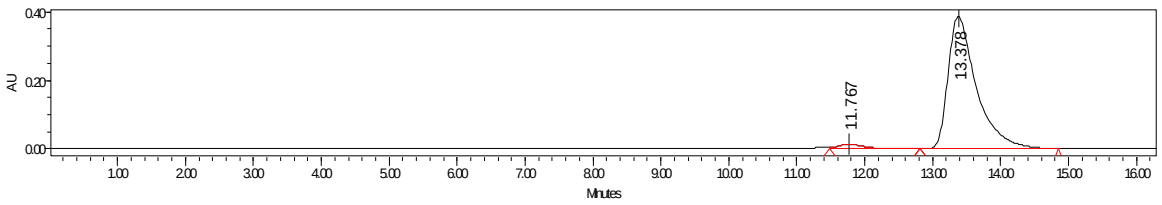
To a solution of **4a** (0.4 mmol) in CH_3OH (2.0 mL) was added $NaBH_4$ (0.4 mmol) at -78 ^oC. After stirring for 1 d at -78 ^oC, the resulting mixture was quenched with aqueous NaCl and extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, evaporated in vacuo, and was further purified by column chromatography on silica gel. The relative configuration of **5** was determined to be *cis* by NOE spectroscopy.

(E)-ethyl 2-(2-(1-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (5)



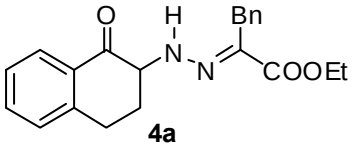
colorless oil; >99% yield, 95% ee, >99:1 dr. HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.77 min (minor), 13.38 min (major). ^1H NMR (400 MHz, DMSO) δ 7.94 (d, *J* = 4.3 Hz, 1H), 7.52 – 7.39 (m, 1H), 7.26 – 7.20 (m, 2H), 7.20 – 7.12 (m, 5H), 7.08 – 7.03 (m, 1H), 5.46 (d, *J* = 6.7 Hz, 1H), 4.63 (t, *J* = 7.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 2H), 3.50 (ddd, *J* = 14.7, 7.9, 3.7 Hz, 1H), 2.79 (qt, *J* = 17.0, 5.3 Hz, 2H), 2.05 (ddd, *J* = 13.1, 8.6, 4.9 Hz, 1H), 1.92 – 1.74 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16, 136.81, 135.14, 134.15, 129.11, 128.19, 128.05, 127.59, 127.36, 127.04, 126.52, 73.34, 61.34, 61.27, 30.92, 27.41, 25.82, 14.37. HRMS (ESI-TOF) calcd for: $C_{21}H_{24}N_2NaO_3$ ([M+Na^+]) = 375.1685, Found 375.1694.





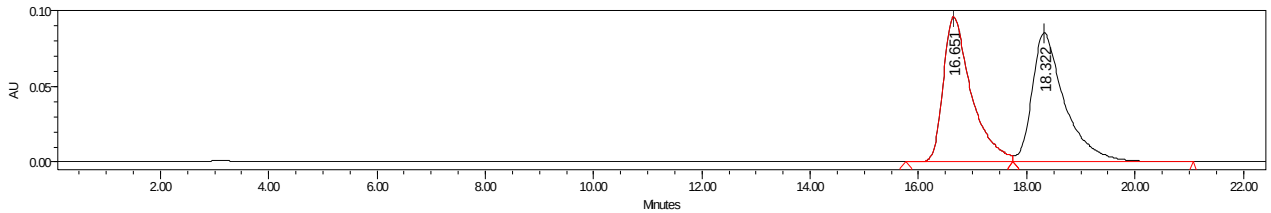
(H) The analytical and spectral characterization data of the products

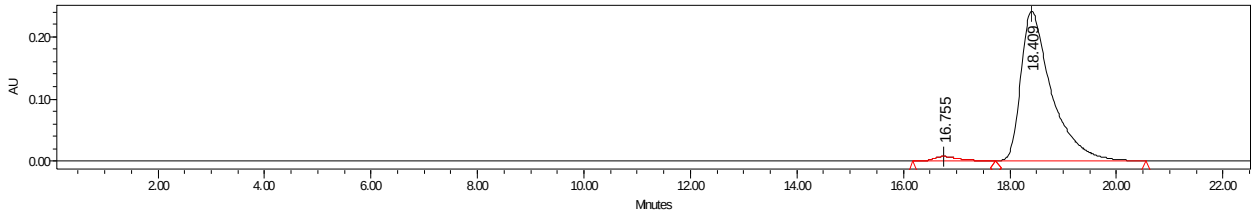
(*S*,E)-ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4a)



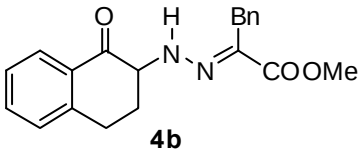
4a

yellow solid; m.p. 78-80 °C; 98% yield, 95% ee. $[\alpha]_D^{23}$ = –96.2 (c = 0.66 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.76 min (minor), 18.41min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.27 – 7.19 (m, 3H), 4.45 – 4.23 (m, 3H), 3.95 (dd, *J* = 63.2, 15.6 Hz, 2H), 3.21-3.12 (m, 1H), 3.08 – 2.94 (m, 1H), 2.89 – 2.67 (m, 1H), 2.07 – 1.85 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.80, 165.28, 143.88, 135.58, 135.37, 134.04, 131.28, 128.89, 128.42, 127.52, 126.83, 126.77, 64.12, 61.25, 31.32, 30.75, 28.05, 14.43. HRMS (ESI-TOF) calcd for $C_{21}H_{22}N_2O_3Na$ ([M+Na^+]) = 373.1528, Found 373.1518.



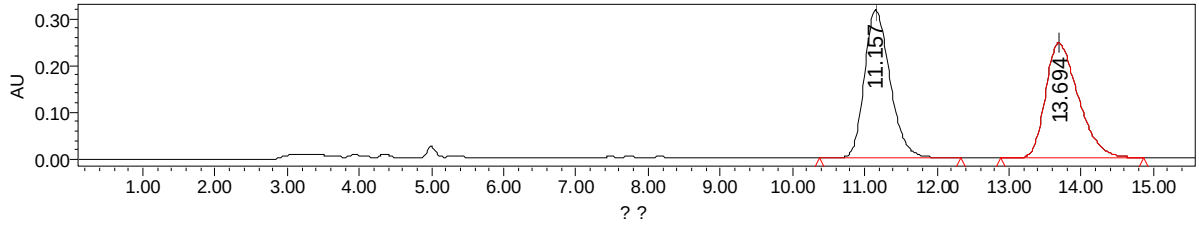


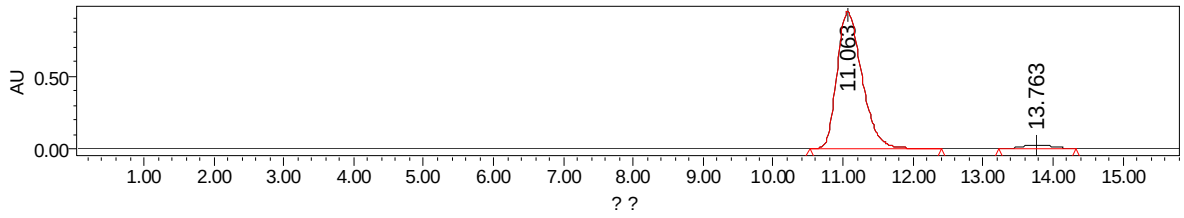
methyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4b)



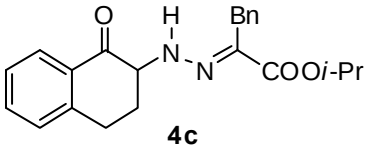
4b

yellow solid; m.p. 80-82 °C; 81% yield, 93% ee. $[\alpha]_D^{15}$ = –91.2 (c = 0.58 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OD-H, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.06 min (major), 13.76 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 1H), 7.50 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.26 – 7.20 (m, 3H), 4.36 (ddd, *J* = 13.6, 4.9, 2.8 Hz, 1H), 4.04 (d, *J* = 15.6 Hz, 1H), 3.89 (d, *J* = 16.1 Hz, 4H), 3.17 (ddd, *J* = 17.2, 13.0, 4.4 Hz, 1H), 3.09 – 2.92 (m, 1H), 2.83 – 2.70 (m, 1H), 2.03-1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.71, 165.81, 143.84, 135.26, 135.19, 134.07, 131.25, 128.92, 128.91, 128.40, 127.54, 126.85, 126.83, 64.11, 52.50, 31.30, 30.79, 28.01. HRMS (ESI-TOF) calcd for $C_{20}H_{20}N_2O_3Na$ ([M+Na$^+$]) = 359.1372, Found 359.1355.





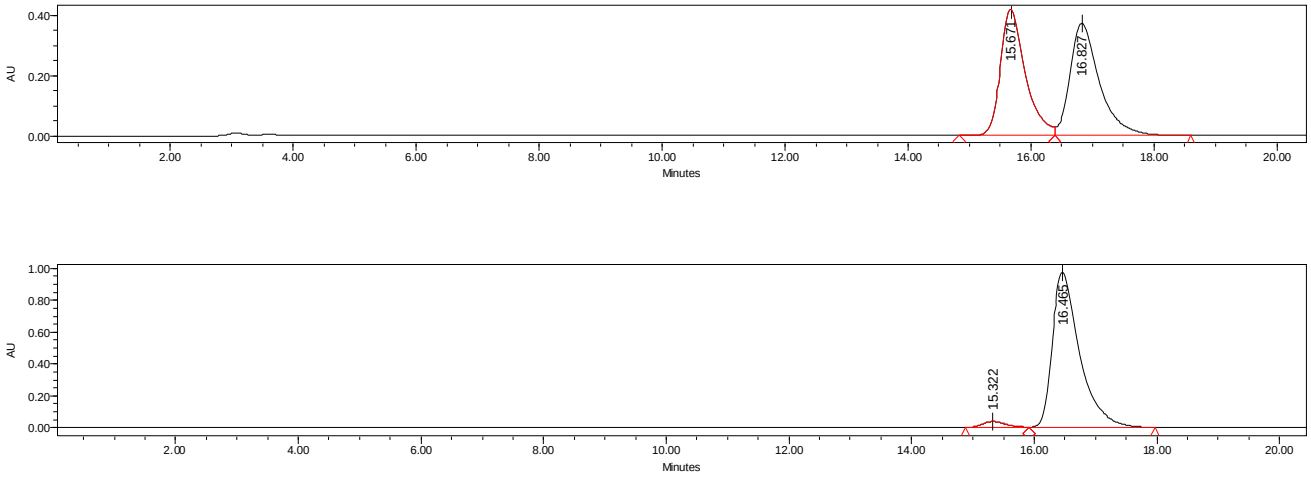
isopropyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4c)



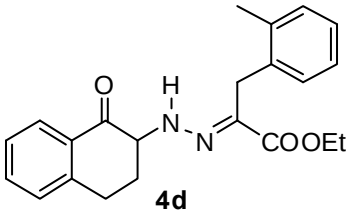
4c

yellow solid; 95% yield, 93% ee. $[\alpha]_D^{15}$ = –75.7 (c = 0.68 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.32 min (minor), 16.47 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.51-7.40 (m, 1H), 7.33 – 7.29 (m, 5H), 7.28 – 7.19 (m, 3H), 5.17 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.35 (ddd, *J* = 13.6, 4.9, 2.5 Hz, 1H), 4.00 (d, *J* = 15.6 Hz, 1H), 3.85 (d, *J*

= 15.6 Hz, 1H), 3.16 (ddd, *J* = 17.2, 13.1, 4.3 Hz, 1H), 3.03 (dd, *J* = 13.9, 3.0 Hz, 1H), 2.88 – 2.74 (m, 1H), 1.99 (qd, *J* = 13.1, 4.4 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.92, 164.63, 143.94, 135.89, 135.56, 134.01, 131.29, 128.91, 128.85, 128.43, 127.49, 126.80, 126.72, 68.58, 64.13, 31.35, 30.70, 28.07, 21.93. HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_3Na$ ([M+Na$^+$]) = 387.1685, Found 387.1677.

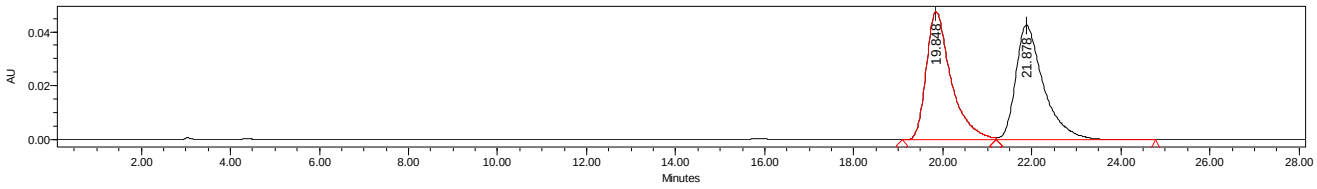


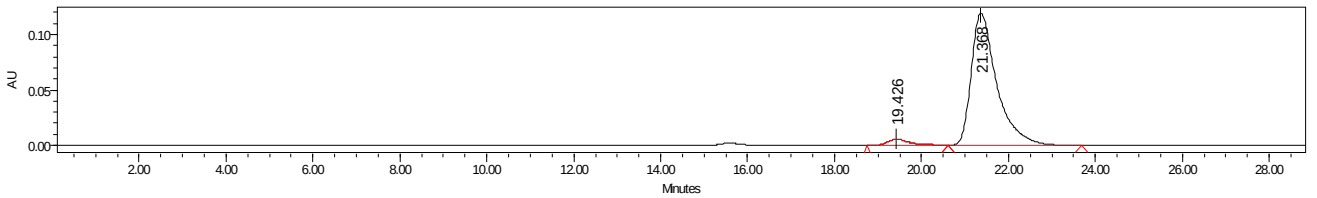
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-*o*-tolylpropanoate (4d)



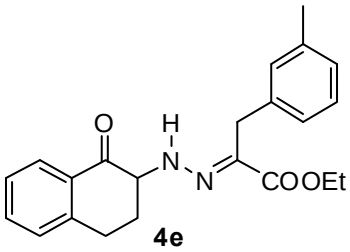
4d

yellow solid; m.p. 86-88 °C; 93% yield, 92% ee. $[\alpha]_D^{12}$ = –92.2 (c = 0.69 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.43 min (minor), 21.37 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33 – 7.09 (m, 5H), 7.07 – 6.90 (m, 2H), 4.43 – 4.23 (m, 3H), 3.90 (dd, *J* = 42.9, 16.5 Hz, 2H), 3.17 (ddd, *J* = 17.1, 12.9, 4.3 Hz, 1H), 3.09 – 2.96 (m, 1H), 2.88 – 2.72 (m, 1H), 2.41 (s, 3H), 1.99 (qd, *J* = 13.0, 4.5 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.77, 165.24, 143.82, 136.65, 135.37, 133.99, 132.81, 131.34, 130.60, 128.88, 127.52, 127.14, 126.93, 126.80, 126.41, 64.30, 61.24, 30.74, 29.17, 28.12, 19.89, 14.41. HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_3Na$ ([M+Na$^+$]) = 387.1685, Found 387.1702.



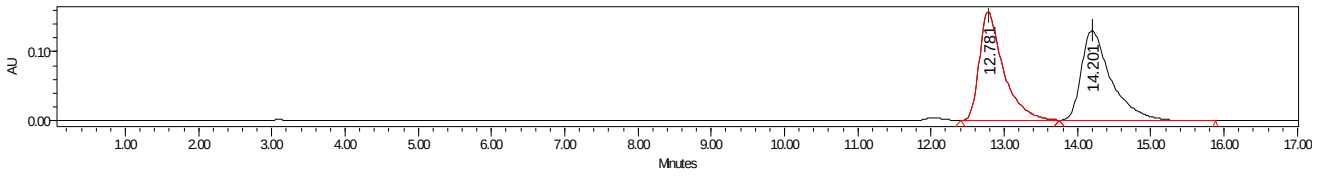


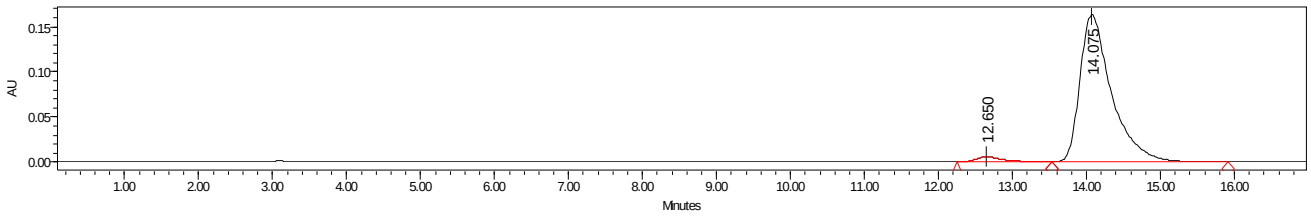
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-*m*-tolylpropanoate (4e)



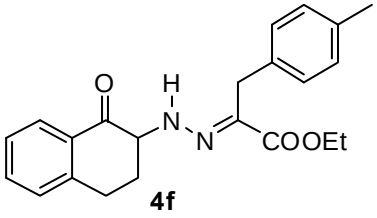
4e

yellow solid; m.p. 90-93 ^{o}C; 95% yield, 95% ee. $[\alpha]_D^{12}$ = –97.5 (c = 0.69 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.65 min (minor), 14.08 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 – 7.17 (m, 4H), 7.12-7.02 (m, 3H), 4.42 – 4.22 (m, 3H), 3.92 (dd, *J* = 68.9, 15.6 Hz, 2H), 3.17 (ddd, *J* = 17.2, 12.9, 4.4 Hz, 1H), 3.07 – 2.93 (m, 1H), 2.86 – 2.71 (m, 1H), 2.33 (s, 3H), 2.10 – 1.90 (m, 1H), 1.40 – 1.32 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.75, 165.31, 143.87, 138.56, 135.70, 135.20, 134.01, 131.32, 129.15, 128.90, 128.74, 127.53, 126.82, 125.46, 64.17, 61.24, 31.26, 30.73, 28.06, 21.44, 14.43. HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_3Na$ ([M+Na^+]) = 387.1685, Found 387.1690.



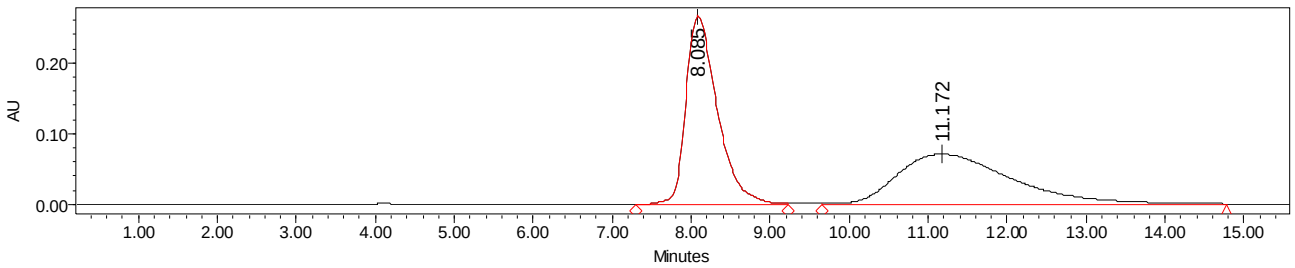


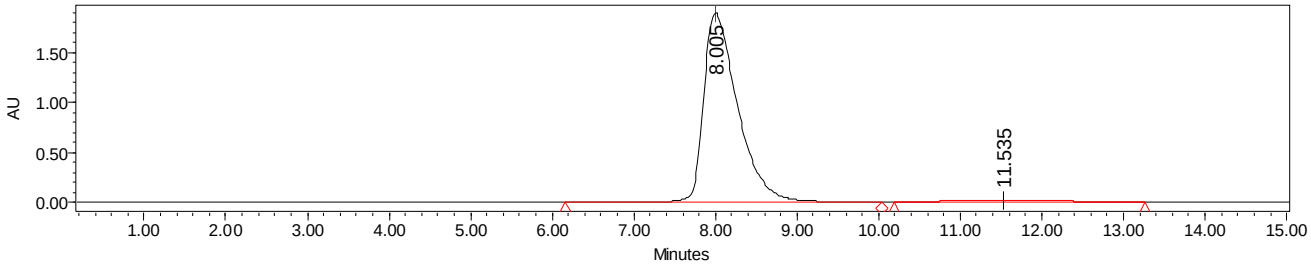
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-*p*-tolylpropanoate (4f)



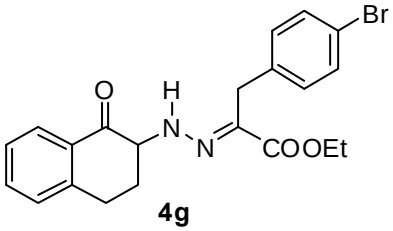
4f

yellow solid; m.p. 90-92 ^{o}C; 92% yield, 96% ee. $[\alpha]_D^{13}$ = –91.2 (c = 0.70 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.01 min (major), 11.54 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 1H), 7.49 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33-7.19 (m, 5H), 7.16 – 7.07 (m, 2H), 4.79 – 4.21 (m, 3H), 3.98 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H), 3.17 (ddd, *J* = 17.2, 12.9, 4.4 Hz, 1H), 3.10 – 2.93 (m, 1H), 2.89 – 2.71 (m, 1H), 2.30 (s, 3H), 2.10 – 1.93 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.85, 165.30, 143.90, 136.28, 135.85, 134.02, 132.16, 131.31, 129.58, 128.91, 128.28, 127.52, 126.82, 64.12, 61.23, 30.90, 30.74, 28.05, 21.09, 14.43. HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_3Na$ ([M+Na^+]) = 387.1685, Found 387.1688.



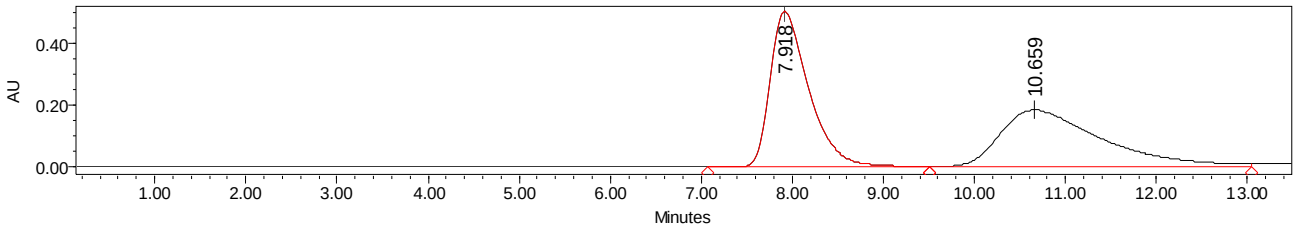


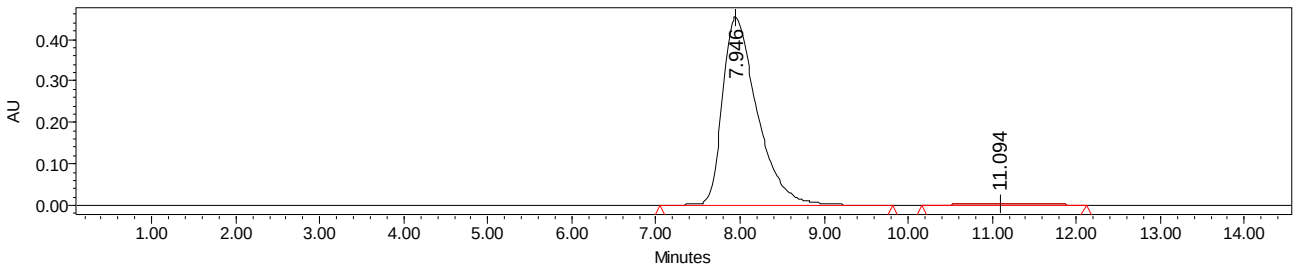
ethyl 3-(4-bromophenyl)-2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)propanoate(4g)



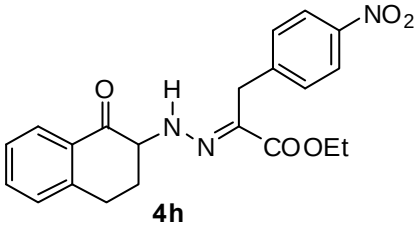
4g

yellow solid; m.p. 98-100°C; 98% yield, 97% ee. $[\alpha]_D^{13}$ = –74.9 (c = 0.70 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, *n*-hexane/2-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.95 min (major), 11.09 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.38 (m, 3H), 7.38 – 7.21 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 3H), 4.44 – 4.24 (m, 3H), 3.95 (d, *J* = 15.7 Hz, 1H), 3.83 (d, *J* = 15.7 Hz, 1H), 3.18 (ddd, *J* = 17.1, 13.0, 4.3 Hz, 1H), 3.09 – 2.96 (m, 1H), 2.90 – 2.72 (m, 1H), 2.01 (qd, *J* = 13.0, 4.5 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.85, 165.15, 143.89, 134.82, 134.39, 134.15, 131.93, 131.19, 130.15, 128.95, 127.52, 126.90, 120.60, 64.04, 61.35, 30.70, 30.57, 28.02, 14.42. HRMS (ESI-TOF) calcd for $C_{21}H_{21}BrN_2O_3Na$ ([M+Na^+]) = 451.0633, Found 451.0634.



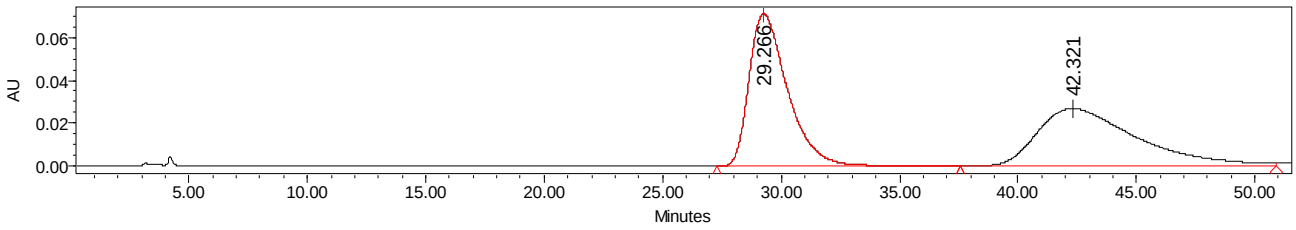


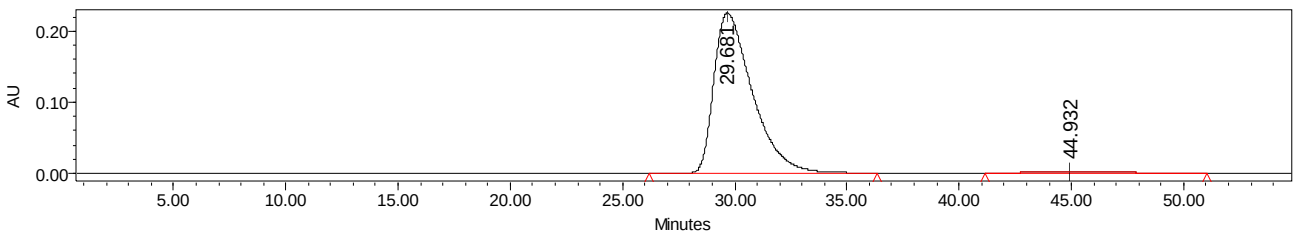
ethyl 3-(4-nitrophenyl)-2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)propanoate (4h)



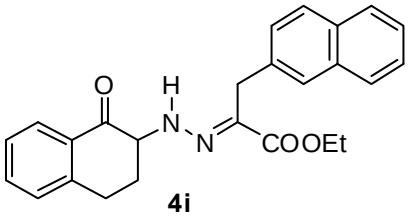
4h

yellow solid; m.p. 92-94 °C; 95% yield, 96% ee. $[\alpha]_D^{11}$ = –63.6 (c = 0.43 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 29.68 min (major), 44.93 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.14 (m, 2H), 7.98 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54-7.47 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.19 (d, *J* = 2.2 Hz, 1H), 4.46 – 4.25 (m, 3H), 4.04 (dd, *J* = 42.1, 16.0 Hz, 2H), 3.20 (ddd, *J* = 17.2, 12.9, 4.4 Hz, 1H), 3.11 – 2.96 (m, 1H), 2.91 – 2.72 (m, 1H), 2.03 (qd, *J* = 13.0, 4.5 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.87, 165.00, 146.89, 143.89, 143.29, 134.30, 133.63, 131.04, 129.31, 128.98, 127.53, 126.97, 124.11, 64.00, 61.53, 30.94, 30.67, 27.99, 14.40. HRMS (ESI-TOF) calcd for $C_{21}H_{21}N_3O_5Na$ ([M+Na$^+$]) = 418.1379, Found 418.1389.



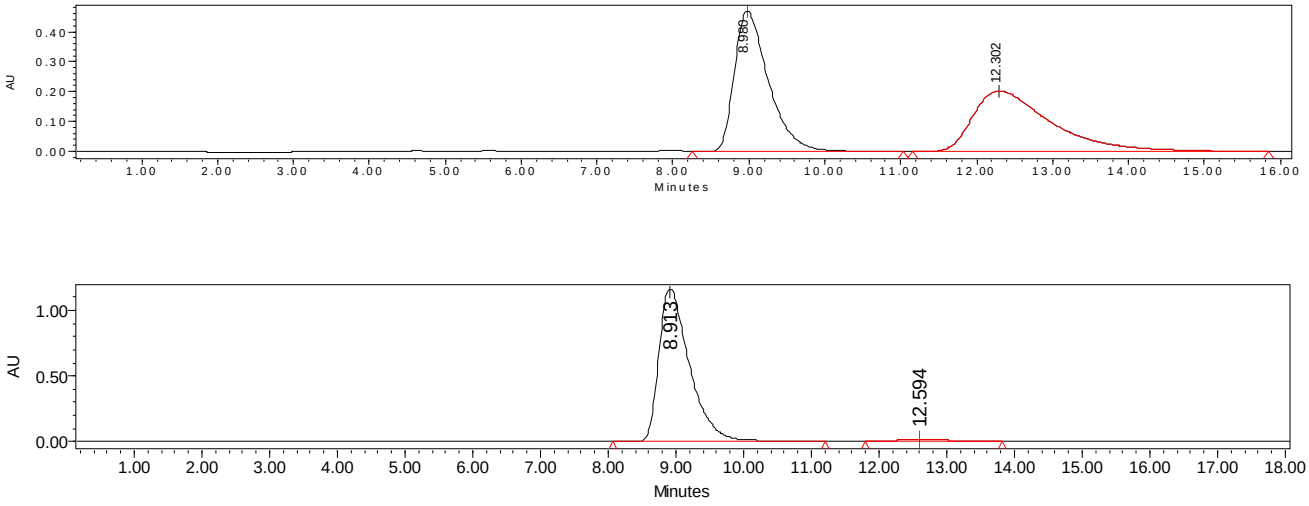


ethyl 3-(naphthalen-2-yl)-2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)propanoate(4i)

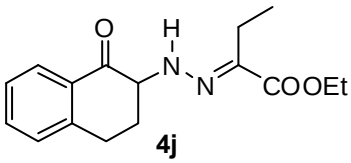


4i

yellow solid; 92% yield, 97% ee. $[\alpha]_D^{14}$ = –80.1 (c = 0.95 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, *n*-hexane/2-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.91 min (major), 12.59 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.85 – 7.71 (m, 4H), 7.51 – 7.36 (m, 4H), 7.34 – 7.18 (m, 3H), 4.49 – 4.27 (m, 3H), 4.11 (dd, *J* = 50.0, 15.8 Hz, 2H), 3.14 (ddd, *J* = 17.2, 12.9, 4.4 Hz, 1H), 3.06 – 2.92 (m, 1H), 2.86 – 2.69 (m, 1H), 2.07 – 1.87 (m, 1H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.71, 165.33, 143.81, 135.32, 133.98, 133.67, 132.77, 132.38, 131.30, 128.86, 128.64, 127.68, 127.64, 127.51, 126.84, 126.79, 126.74, 126.13, 125.59, 64.17, 61.27, 31.43, 30.64, 28.04, 14.43. HRMS (ESI-TOF) calcd for $C_{25}H_{24}N_2O_3Na$ ([M+Na$^+$]) = 423.1685, Found 423.1676.



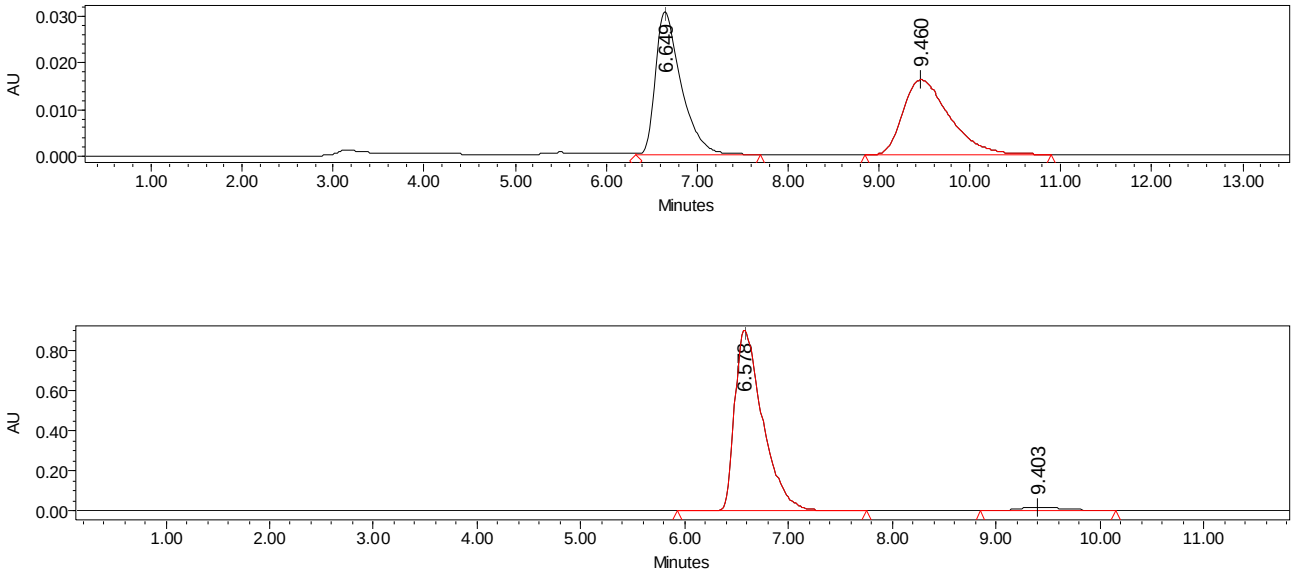
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)butanoate (4j)



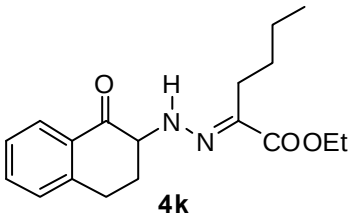
4j

yellow solid; m.p. 53-55 °C; 80% yield, 93% ee. $[\alpha]_D^{12}$ = –60.1 (c = 0.42 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.58 min

(major), 9.40 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.53 (td, *J* = 7.5, 1.3 Hz, 1H), 7.41 – 7.25 (m, 2H), 7.02 (d, *J* = 2.1 Hz, 1H), 4.43 (ddd, *J* = 13.7, 5.0, 2.7 Hz, 1H), 4.35 – 4.20 (m, 2H), 3.23 (ddd, *J* = 17.2, 13.0, 4.4 Hz, 1H), 3.10-3.05 (m, 1H), 2.85 (dtd, *J* = 12.2, 4.7, 2.6 Hz, 1H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.11 (qd, *J* = 13.0, 4.5 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.55, 164.87, 144.04, 139.36, 134.10, 131.37, 128.97, 127.51, 126.87, 64.32, 61.00, 30.88, 28.20, 18.04, 14.40, 9.07. HRMS (ESI-TOF) calcd for $C_{16}H_{20}N_2O_3Na$ ([M+Na$^+$]) = 311.1372, Found 311.1382.



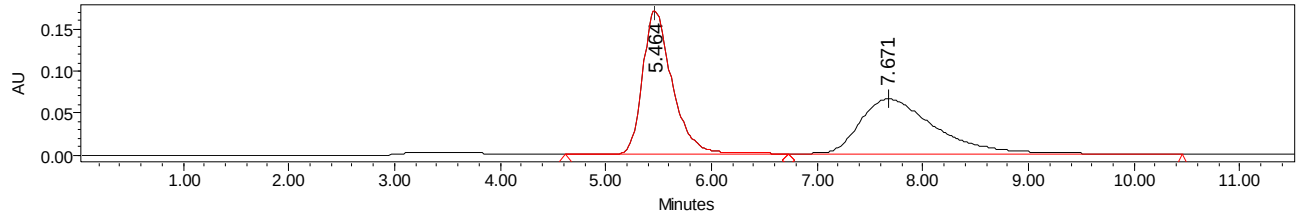
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)hexanoate (4k)

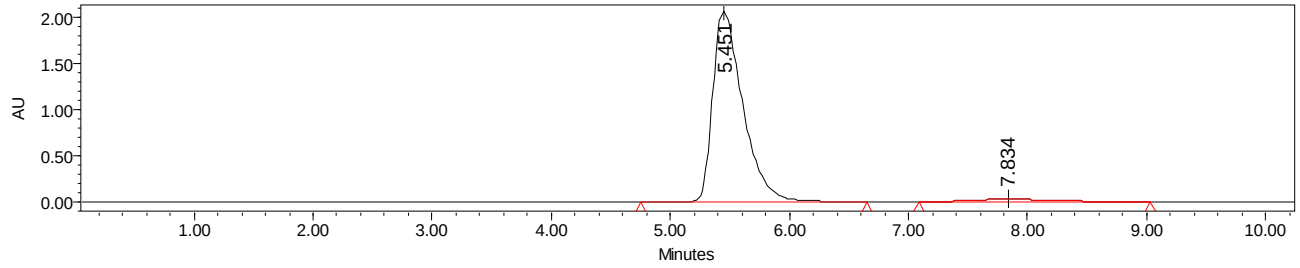


4k

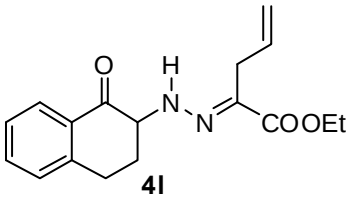
yellow solid; m.p. 56-58 °C; 89% yield, 93% ee. $[\alpha]_D^{12}$ = –61.6 (c = 0.50 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.45 min (major), 7.83 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.49 (m, 1H), 7.38 – 7.24 (m, 2H), 7.04 (s, 1H), 4.42 (ddd, *J* = 13.6, 4.9, 2.4 Hz, 1H), 4.36 – 4.19 (m, 2H), 3.22 (ddd, *J* = 17.2, 13.0, 4.4 Hz, 1H), 3.13 – 2.99 (m, 1H), 2.91 – 2.76 (m, 1H), 2.65 – 2.47 (m, 2H), 2.23 – 1.99 (m,

1H), 1.58-1.50 (m, 2H), 1.47-1.38 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.50, 165.10, 144.04, 138.52, 134.10, 131.36, 128.97, 127.49, 126.87, 64.26, 60.99, 30.87, 28.17, 26.82, 24.57, 22.98, 14.38, 13.87. HRMS (ESI-TOF) calcd for $C_{18}H_{24}N_2O_3Na$ ([M+Na^+]) = 339.1685, Found 339.1682.





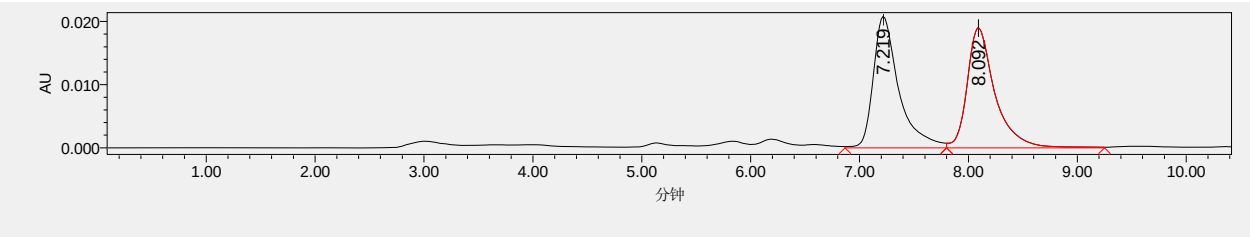
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)pent-4-enoate (4l)

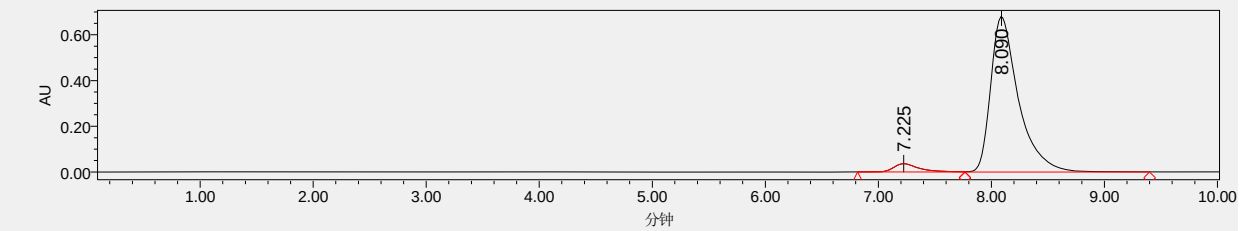


4l

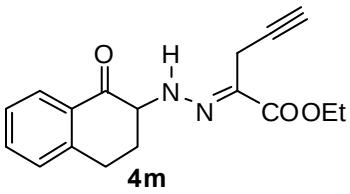
yellow oil; 90% yield, 91% ee. $[\alpha]_D^{12}$ = –120.4 (c = 0.54 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.23 min (minor), 8.09 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.9, 1.1 Hz, 1H), 7.52 (td, J = 7.5, 1.4 Hz, 1H), 7.39 – 7.19 (m, 3H), 5.80 (dddd, J = 16.8, 10.1, 6.5, 5.5 Hz, 1H), 5.30-5.20 (m, 2H), 4.43 (ddd, J = 13.6, 5.0, 2.7 Hz, 1H), 4.37-4.23 (m, 2H), 3.48 (ddt, J = 16.0, 5.3, 1.8 Hz, 1H), 3.35 – 3.15 (m, 2H), 3.07 (ddd, J = 17.1, 4.2, 2.6 Hz, 1H), 2.90 – 2.76 (m, 1H), 2.08 (qd, J = 13.0, 4.5 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.87, 164.88, 143.96, 134.55, 134.08, 131.33, 130.30, 128.94, 127.51,

126.88, 117.70, 64.26, 61.17, 30.85, 29.97, 28.11, 14.40. HRMS (ESI-TOF) calcd for $C_{17}H_{20}N_2O_3Na$ ([M+Na^+]) = 323.1372, Found 323.1366.



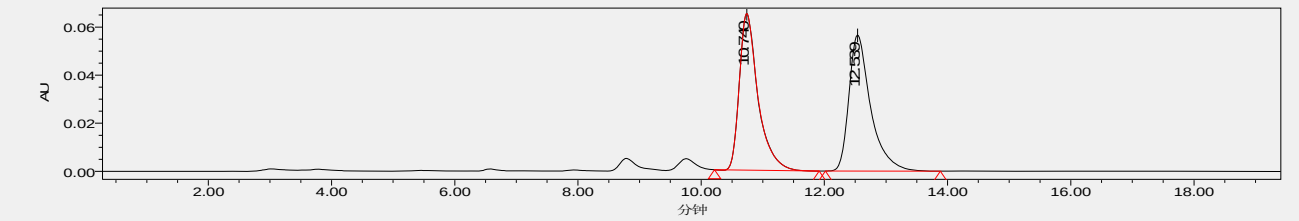


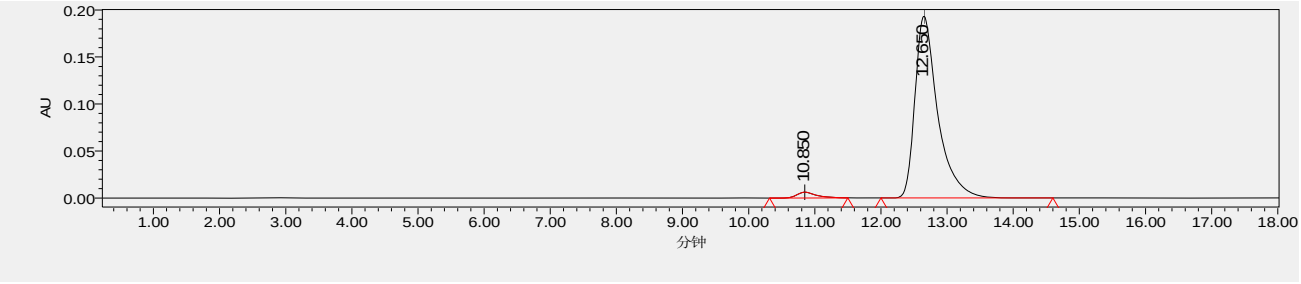
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)pent-4-ynoate (4m)



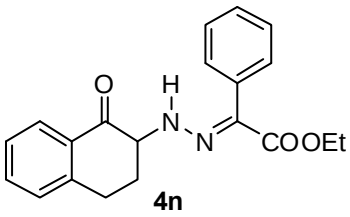
4m

yellow solid; m.p. 52-54 ^oC; 92% yield, 95% ee. $[\alpha]_D^{12}$ = –190.8 (c = 0.48 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.85 min (minor), 12.65 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 – 7.20 (m, 2H), 4.51 (ddd, *J* = 13.6, 5.0, 2.7 Hz, 1H), 4.41 – 4.21 (m, 2H), 3.68 (dd, *J* = 17.7, 2.8 Hz, 1H), 3.38 (dd, *J* = 17.7, 2.8 Hz, 1H), 3.23 (ddd, *J* = 17.2, 12.9, 4.4 Hz, 1H), 3.08 (ddd, *J* = 17.1, 4.2, 2.7 Hz, 1H), 2.90 – 2.78 (m, 1H), 2.21 (t, *J* = 2.8 Hz, 1H), 2.12 (qd, *J* = 13.0, 4.5 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.75, 164.08, 143.92, 134.12, 131.33, 129.82, 128.95, 127.58, 126.92, 76.15, 71.32, 64.56, 61.45, 30.89, 28.11, 15.08, 14.40. HRMS (ESI-TOF) calcd for $C_{17}H_{18}N_2O_3Na$ ([M+Na^+]) = 321.1215, Found 321.1217.



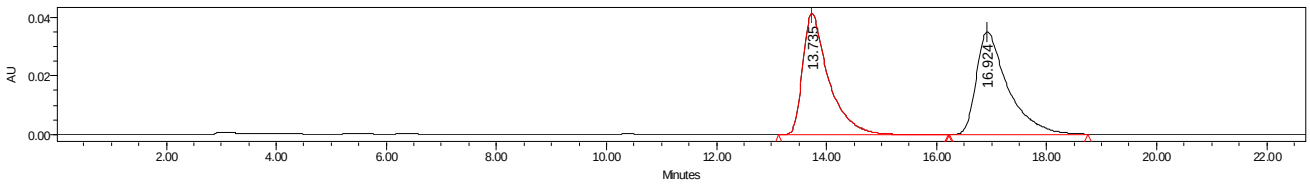


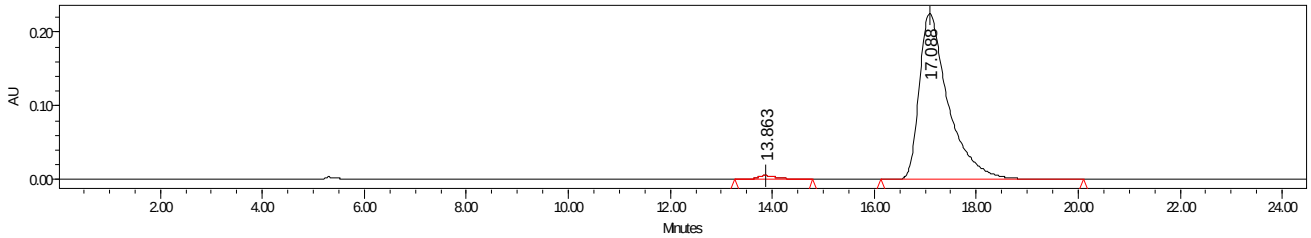
ethyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-2-phenylacetate (4n)



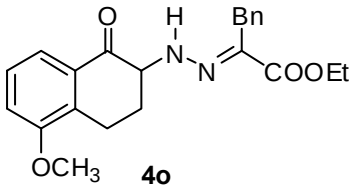
4n

yellow solid; m.p. 77-79 ^{o}C; 85% yield, 97% ee. $[\alpha]_D^{15}$ = –10.9 (c = 0.46 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.86 min (minor), 17.09 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.24 (m, 2H), 4.50 – 4.40 (m, 1H), 4.34 – 4.21 (m, 2H), 3.21 (ddd, *J* = 17.1, 13.2, 4.3 Hz, 1H), 3.09-3.04 (m, 1H), 2.88 – 2.78 (m, 1H), 2.10 (qd, *J* = 13.1, 4.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.04, 164.53, 143.81, 135.23, 134.02, 131.41, 130.66, 129.25, 129.17, 128.90, 128.88, 127.45, 126.86, 64.40, 61.06, 30.59, 28.27, 14.36. HRMS (ESI-TOF) calcd for $C_{20}H_{21}N_2O_3$ ([M+H$^+$]) = 337.1547, Found 337.1552.



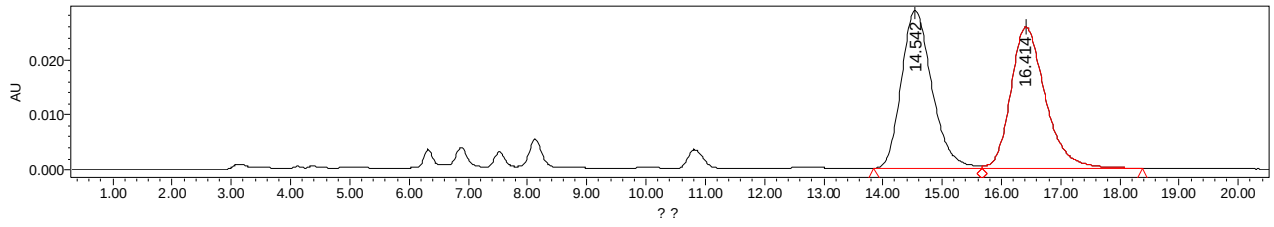


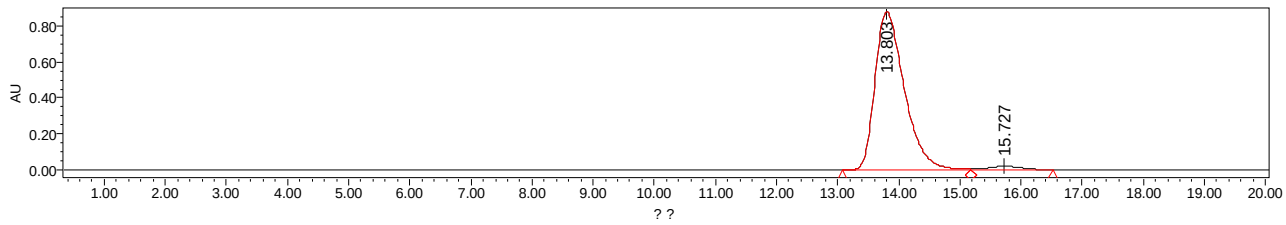
ethyl 2-(2-(5-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4o)



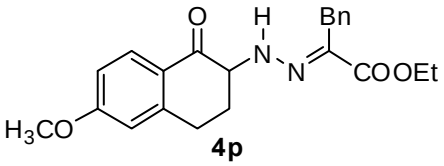
4o

yellow solid; m.p. 116-118 °C; 89% yield, 95% ee. $[\alpha]_D^{12}$ = –79.3 (c = 0.46 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.80 min (major), 15.73 min (minor). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.30 – 7.25 (m, 1H), 7.24 – 7.17 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 4.40 – 4.27 (m, 3H), 4.02 (d, *J* = 15.6 Hz, 1H), 3.90 – 3.83 (m, 4H), 3.24 – 3.14 (m, 1H), 2.84 – 2.72 (m, 2H), 1.94 – 1.82 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.12, 165.30, 156.76, 135.38, 135.33, 132.78, 132.31, 128.88, 128.41, 127.29, 126.75, 118.88, 114.74, 63.62, 61.25, 55.67, 31.28, 29.92, 21.77, 14.43. HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_4Na$ ([M+Na$^+$]) = 403.1634, Found 403.1640.



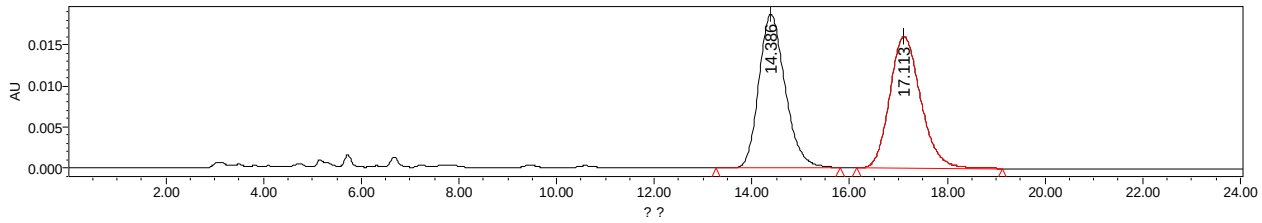


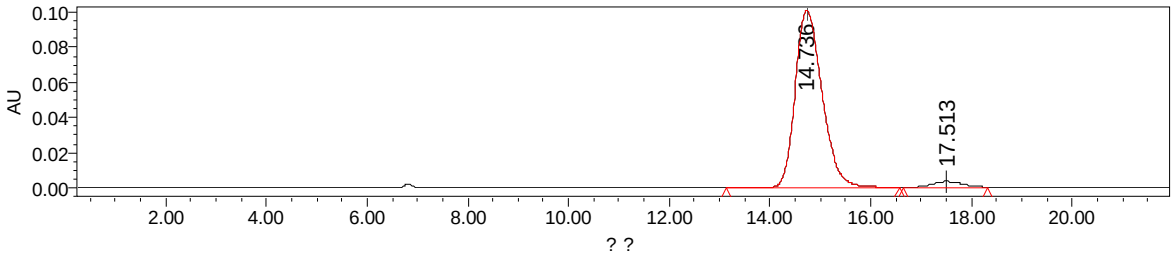
ethyl 2-(2-(6-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4p)



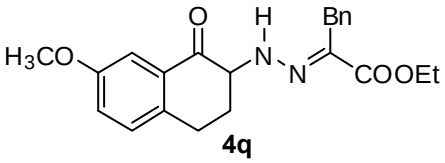
4p

yellow solid; m.p. 80-82 °C; 65% yield, 93% ee. $[\alpha]_D^{16}$ = –101.7 (c = 0.48 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OD-H, *n*-hexane/2-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.74 min (major), 17.51 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.38 – 7.15 (m, 6H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 1H), 4.42 – 4.22 (m, 3H), 4.03 (d, *J* = 15.6 Hz, 1H), 3.90 – 3.80 (m, 4H), 3.12 (ddd, *J* = 17.2, 13.0, 4.4 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.83 – 2.72 (m, 1H), 1.96 (qd, *J* = 13.0, 4.4 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.35, 165.31, 164.09, 146.47, 135.44, 135.40, 129.97, 128.86, 128.43, 126.73, 124.74, 113.52, 112.65, 63.72, 61.20, 55.51, 31.29, 30.69, 28.39, 14.42. HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_4Na$ ([M+Na$^+$]) = 403.1634, Found 403.1649.



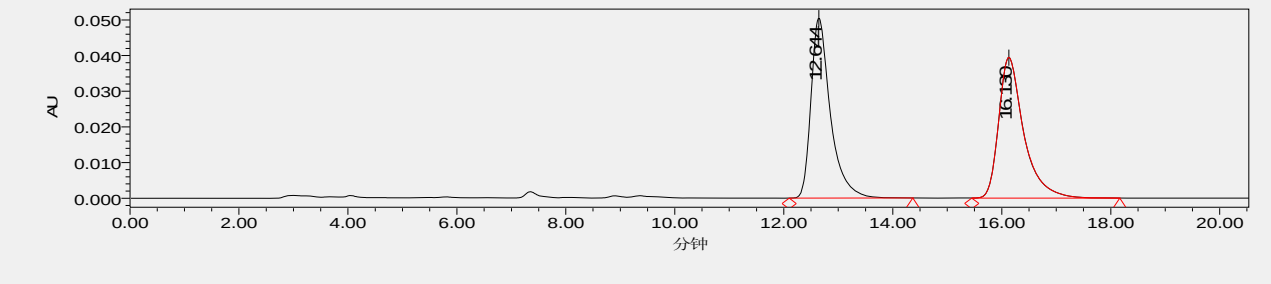


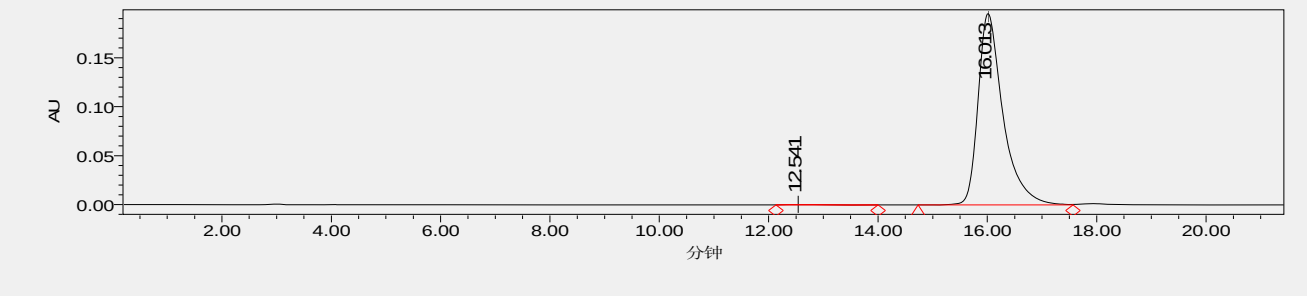
ethyl 2-(2-(7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4q)



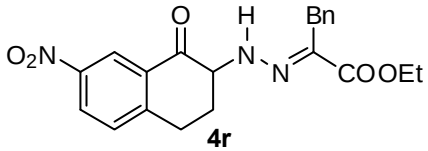
4q

yellow solid; m.p. 100-102 °C; 93% yield, 99% ee. $[\alpha]_D^{12}$ = –101.4 (c = 0.564 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.54 min (minor), 16.01 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.8 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.25-7.21 (m, 1H), 7.19-7.15 (m, 2H), 7.10 – 7.05 (m, 1H), 4.42 – 4.21 (m, 3H), 4.05 (d, *J* = 15.6 Hz, 1H), 3.86 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 3H), 3.09 (ddd, *J* = 17.0, 12.9, 4.3 Hz, 1H), 2.96 (ddd, *J* = 16.8, 4.3, 2.6 Hz, 1H), 2.83 – 2.73 (m, 1H), 1.96 (qd, *J* = 12.9, 4.6 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.83, 165.29, 158.40, 136.54, 135.57, 135.37, 132.01, 130.13, 128.90, 128.41, 126.79, 122.51, 109.23, 64.12, 61.27, 55.54, 31.35, 31.00, 27.27, 14.43. HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_4Na$ ([M+Na^+]) = 403.1634, Found 403.1639.





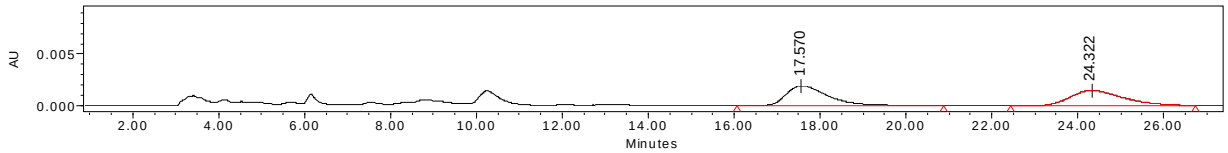
ethyl 2-(2-(7-nitro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4r)

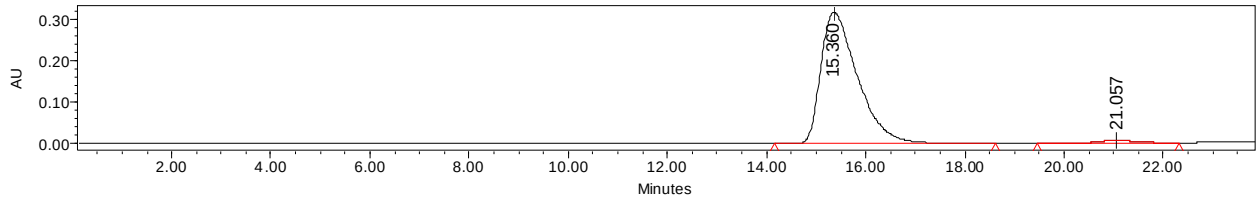


4r

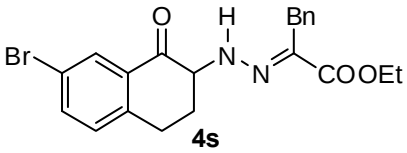
yellow solid; 88% yield, 94% ee. $[\alpha]_D^{16}$ = –51.3 (c = 0.60 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AS-H, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.36 min (major), 21.06 min (minor). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.4 Hz, 1H), 8.32 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.21 (m, 5H), 7.08 (d, *J* = 2.4 Hz, 1H), 4.47 – 4.23 (m, 3H), 4.06 (d, *J* = 15.7 Hz, 1H), 3.85 (d, *J* = 15.7 Hz, 1H), 3.30 – 3.12 (m, 2H), 2.90 – 2.80 (m, 1H), 2.05 (qd, *J* = 13.1, 4.9 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.88, 164.03, 149.22, 146.10, 135.64, 134.05, 131.22, 129.39, 127.96, 127.35, 126.69, 125.91, 121.86, 63.07, 60.35, 30.44, 28.90, 27.22, 13.36. HRMS (ESI-TOF) calcd for $C_{21}H_{21}N_3O_5Na$ ([M+Na^+]) = 418.1379, Found 418.1373.



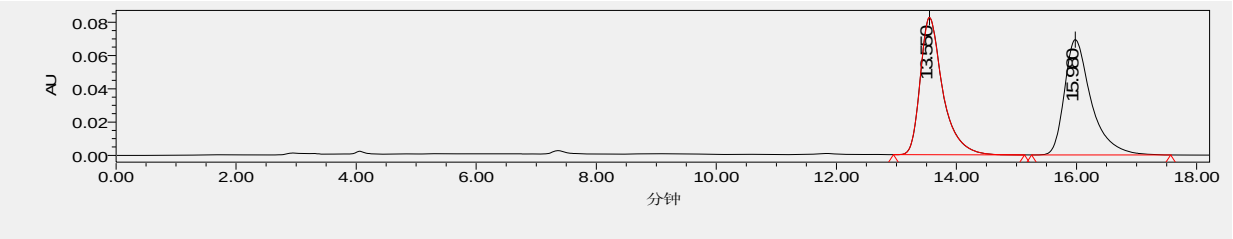


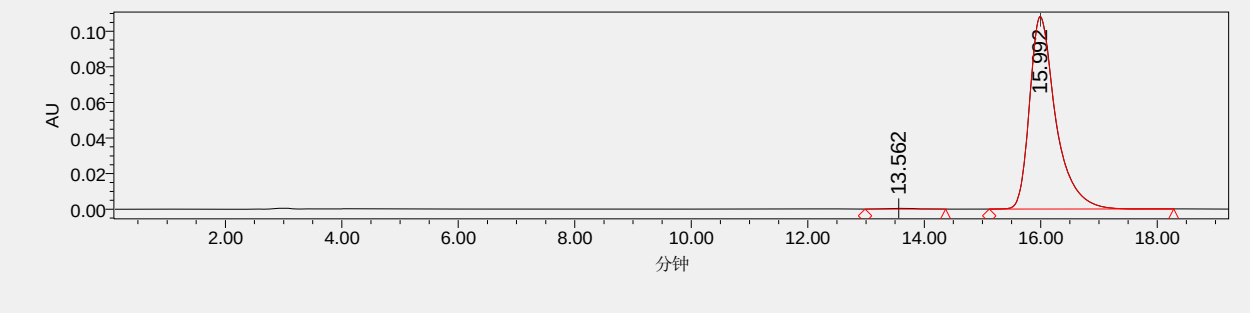
ethyl 2-(2-(7-bromo-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4s)



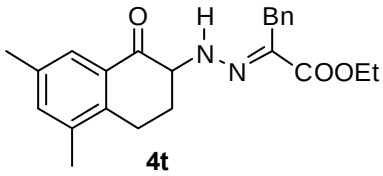
4s

yellow solid; 96% yield, 99% ee. $[\alpha]_D^{16}$ = –69.3 (c = 0.82 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.56 min (minor), 15.99 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.9 Hz, 1H), 7.59 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.23 (t, *J* = 6.9 Hz, 1H), 7.15 – 7.09 (m, 2H), 4.38 – 4.29 (m, 3H), 4.04 (d, *J* = 15.6 Hz, 1H), 3.86 (d, *J* = 15.6 Hz, 1H), 3.08 (ddd, *J* = 17.1, 13.0, 4.3 Hz, 1H), 3.03 – 2.94 (m, 1H), 2.82 – 2.73 (m, 1H), 1.97 (qd, *J* = 13.1, 4.5 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.61, 165.17, 142.52, 136.74, 136.06, 135.22, 132.79, 130.70, 130.27, 128.93, 128.40, 126.84, 120.83, 64.03, 61.31, 31.39, 30.42, 27.60, 14.41. HRMS (ESI-TOF) calcd for $C_{21}H_{22}BrN_2O_3$ ([M+H^+]) = 429.0814, Found 429.0824.



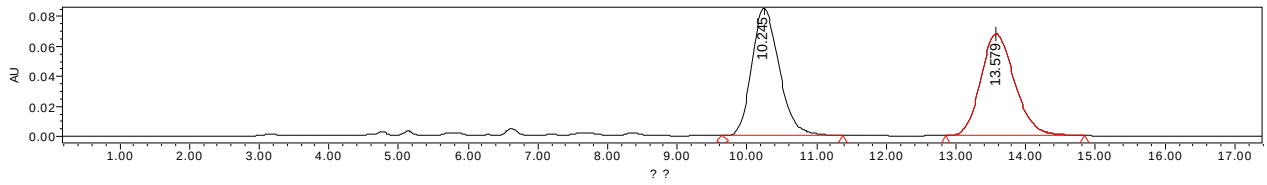


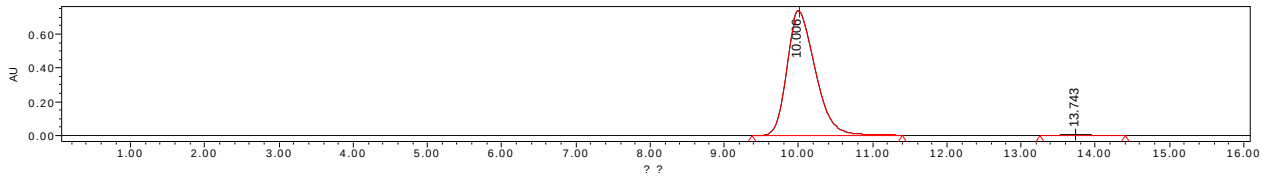
ethyl 2-(2-(5,7-dimethyl-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4t)



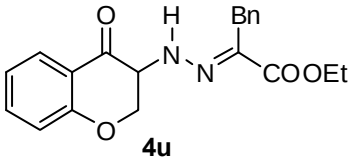
4t

yellow solid; m.p. 100-102 °C; 80% yield, 99% ee. $[\alpha]_D^{12}$ = –80.4 (c = 0.23 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OD-H, n-hexane/2-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.01 min (major), 13.74 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.25 – 7.18 (m, 3H), 4.42 – 4.26 (m, 3H), 4.03 (d, *J* = 15.6 Hz, 1H), 3.88 (d, *J* = 15.6 Hz, 1H), 3.01 – 2.91 (m, 1H), 2.90 – 2.74 (m, 2H), 2.31 (s, 3H), 2.26 (s, 3H), 2.00 – 1.77 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.36, 165.32, 139.19, 136.51, 136.16, 135.42, 135.32, 131.32, 128.88, 128.45, 126.76, 125.36, 63.43, 61.24, 31.32, 30.12, 24.92, 20.80, 19.27, 14.43. HRMS (ESI-TOF) calcd for $C_{23}H_{27}N_2O_3$ ([M+H$^+$]) = 379.2022, Found 379.2016.



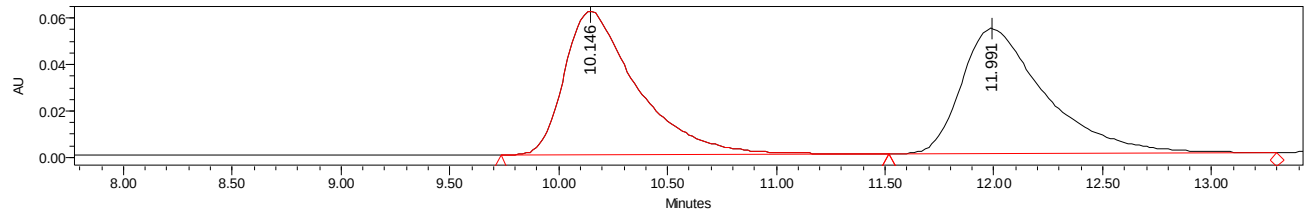


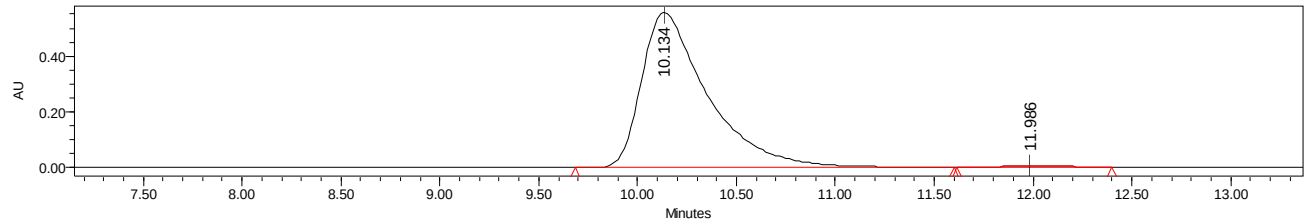
ethyl 2-(2-(4-oxochroman-3-yl)hydrazono)-3-phenylpropanoate (4u)



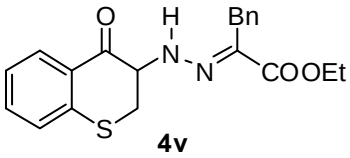
4u

yellow oil; 75% yield, 98% ee. $[\alpha]_D^{16}$ = –108.1 (c = 0.37 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.13 min (major), 11.99 min (minor). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.35-7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 4.8 Hz, 1H), 6.98 (d, *J* = 5.6 Hz, 1H), 6.84 (d, *J* = 1.5 Hz, 1H), 4.89 (dd, *J* = 10.9, 6.0 Hz, 1H), 4.59 (ddd, *J* = 13.2, 6.0, 2.3 Hz, 1H), 4.36-4.30 (m, 2H), 4.20 – 4.13 (m, 1H), 4.03 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.6 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.42, 164.93, 161.86, 137.93, 136.55, 134.84, 129.01, 128.35, 127.27, 126.98, 121.74, 119.54, 117.97, 70.15, 61.47, 60.24, 31.39, 14.35. HRMS (ESI-TOF) calcd for $C_{20}H_{21}N_2O_4$ ([M+H$^+$]) = 353.1501, Found 353.1491.



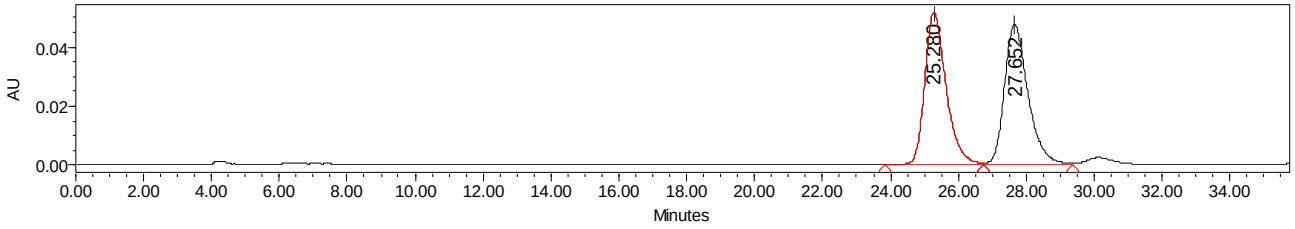


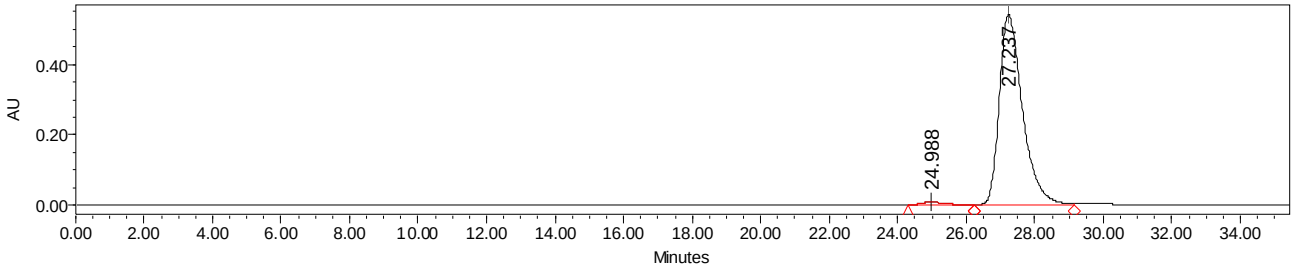
ethyl 2-(2-(4-oxothiochroman-3-yl)hydrazono)-3-phenylpropanoate (4v)



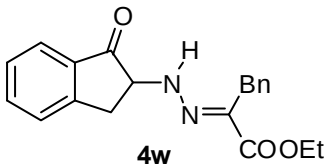
4v

yellow solid; m.p. 58-61 °C; 90% yield, 98% ee. $[\alpha]_D^{16}$ = –199.3 (c = 0.58 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 24.99 min (minor), 27.24 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.34 – 7.29 (m, 5H), 7.26 – 7.22 (m, 2H), 7.19 – 7.15 (m, 1H), 4.65 (ddd, *J* = 13.7, 4.7, 2.4 Hz, 1H), 4.39 – 4.25 (m, 2H), 4.03 (d, *J* = 15.6 Hz, 1H), 3.86 (d, *J* = 15.6 Hz, 1H), 3.54 (dd, *J* = 12.9, 4.7 Hz, 1H), 3.26 (t, *J* = 13.3 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.94, 165.09, 141.88, 136.87, 135.09, 133.90, 129.66, 129.50, 128.95, 128.41, 127.41, 126.89, 125.00, 62.76, 61.39, 31.65, 31.46, 14.40. HRMS (ESI-TOF) calcd for $C_{20}H_{21}N_2O_3S$ ([M+H$^+$]) = 369.1273, Found 369.1281.





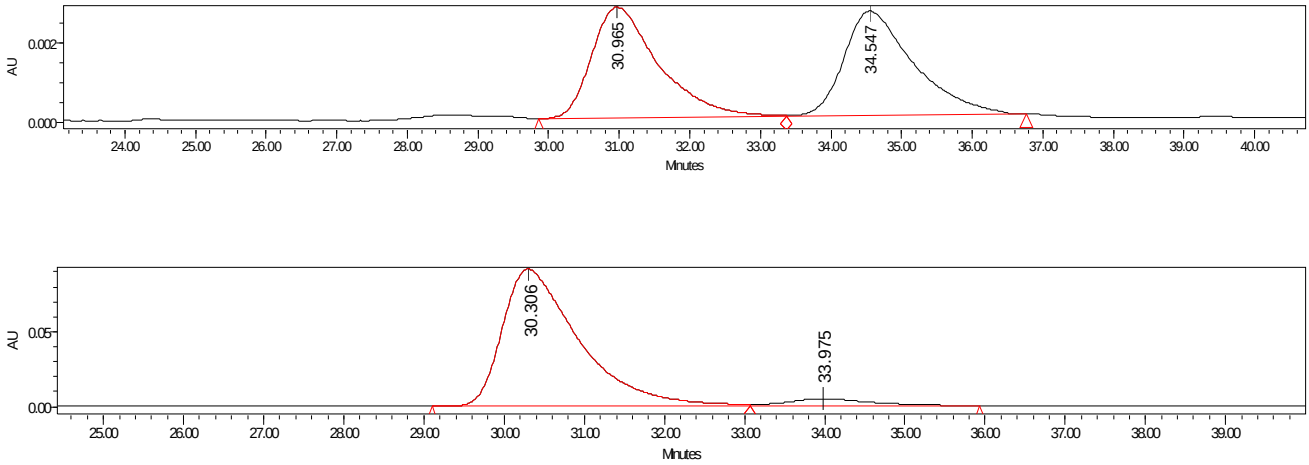
ethyl 2-(2-(1-oxo-2,3-dihydro-1H-inden-2-yl)hydrazono)-3-phenylpropanoate (4w)



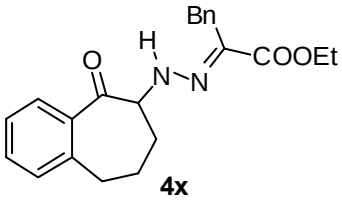
4w

yellow solid; m.p. 80-84 °C; 53% yield, 89% ee. $[\alpha]_D^{15}$ = –43.7 (c = 0.35 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 30.31 min (major), 33.98 min (minor). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.64-7.61 (m, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 3H), 6.55 (d, *J* = 3.2 Hz,

1H), 4.45 – 4.37 (m, 1H), 4.33 – 4.26 (m, 2H), 3.97 (d, *J* = 15.9 Hz, 1H), 3.89 (d, *J* = 15.9 Hz, 1H), 3.63 (dd, *J* = 16.8, 8.1 Hz, 1H), 3.18 (dd, *J* = 16.8, 5.2 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.45, 165.01, 151.71, 136.61, 135.67, 134.95, 134.82, 128.99, 128.21, 127.89, 126.89, 126.75, 124.29, 64.58, 61.26, 33.69, 31.22, 14.30. HRMS (ESI-TOF) calcd for $C_{20}H_{21}N_2O_3$ ([M+H$^+$]) = 337.1552, Found 337.1561.

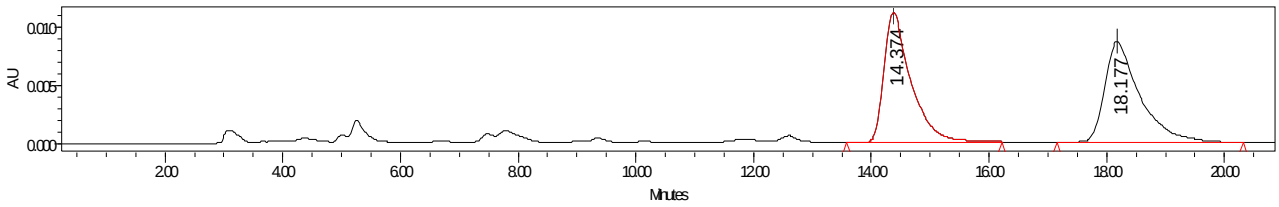


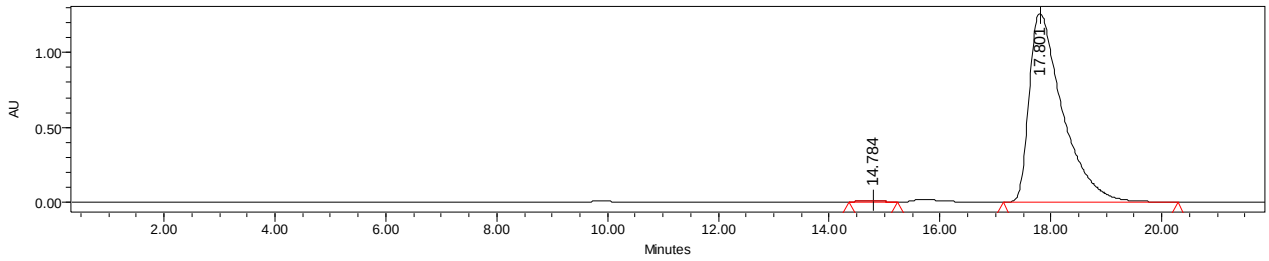
ethyl 2-(2-(5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulen-6-yl)hydrazono)-3-phenylpropanoate(4x)



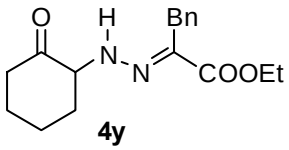
4x

yellow oil; 98% yield, 99% ee. $[\alpha]_D^{16}$ = +97.5 (c = 0.68 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.78 min (minor), 17.80 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.26-7.22 (m, 2H), 6.91 (d, *J* = 6.5 Hz, 1H), 4.74-4.70 (m, 1H), 4.33 – 4.23 (m, 2H), 4.01 (d, *J* = 15.8 Hz, 1H), 3.90 (d, *J* = 15.8 Hz, 1H), 3.07 (dd, *J* = 18.6, 8.7 Hz, 1H), 2.94 (ddd, *J* = 24.1, 13.4, 6.6 Hz, 1H), 2.47 – 2.29 (m, 1H), 2.21 – 2.07 (m, 1H), 1.65 – 1.54 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.89, 165.22, 143.21, 136.61, 135.37, 135.11, 132.37, 130.40, 129.18, 128.86, 128.37, 126.73, 126.57, 66.90, 61.22, 33.84, 31.22, 30.99, 24.07, 14.40. HRMS (ESI-TOF) calcd for $C_{22}H_{25}N_2O_3$ ([M+H$^+$]) = 365.1865, Found 365.1860.



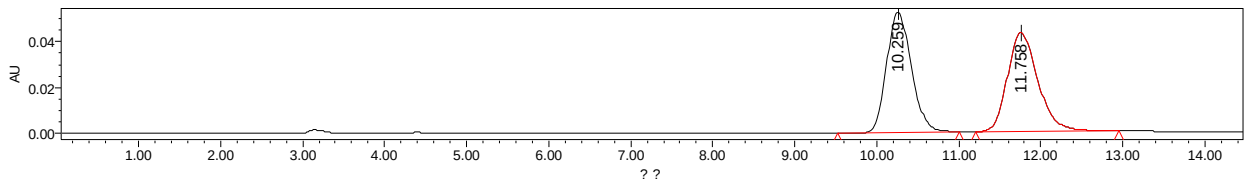


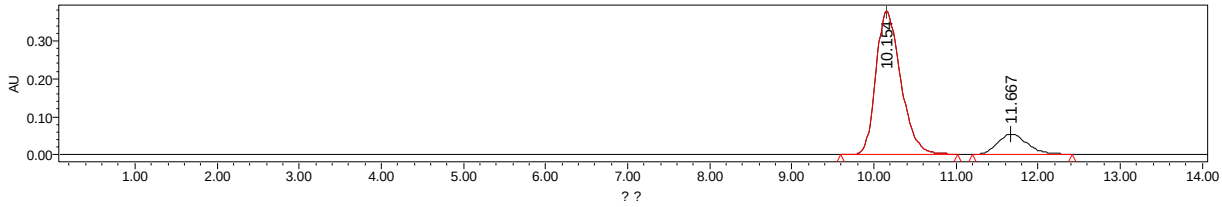
ethyl 2-(2-(2-oxocyclohexyl)hydrazono)-3-phenylpropanoate (4y)



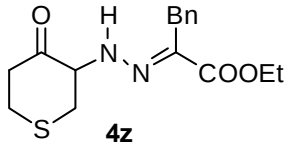
4y

colorless oil; 83% yield, 71% ee. $[\alpha]_D^{16}$ = –14.7 (c = 0.40 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.15 min (major), 11.67 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 5H), 6.84 (d, *J* = 4.5 Hz, 1H), 4.35-4.27 (m, 2H), 4.25 – 4.12 (m, 1H), 3.89 (dd, *J* = 36.5, 15.7 Hz, 2H), 2.61-2.55 (m, 1H), 2.47-2.42 (m, 1H), 2.37-2.28 (m, 1H), 2.16 – 2.01 (m, 1H), 1.88 (d, *J* = 14.9 Hz, 1H), 1.74 – 1.55 (m, 2H), 1.40 (dd, *J* = 12.8, 3.7 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.13, 165.24, 135.36, 134.79, 128.80, 128.34, 126.69, 66.62, 61.12, 41.06, 35.81, 31.19, 27.55, 23.88, 14.38. HRMS (ESI-TOF) calcd for $C_{17}H_{22}N_2O_3Na$ ([M+Na$^+$]) = 325.1528, Found 325.1554.



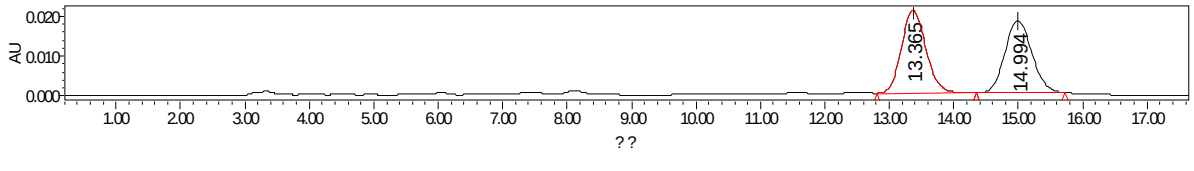


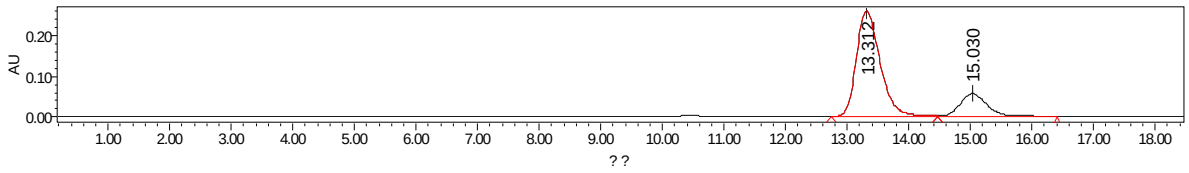
ethyl 2-(2-(4-oxotetrahydro-2H-thiopyran-3-yl)hydrazono)-3-phenylpropanoate (4z)



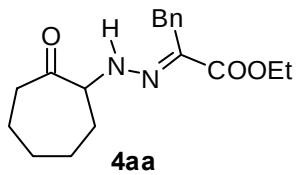
4z

yellow oil; 70% yield, 61% ee. $[\alpha]_D^{17}$ = –22.2 (c = 0.35 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.31 min (major), 15.03 min (minor). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.22 (m, 3H), 7.04 (d, *J* = 4.2 Hz, 1H), 4.53 – 4.44 (m, 1H), 4.35-4.29 (m, 2H), 3.95 (d, *J* = 15.6 Hz, 1H), 3.83 (d, *J* = 15.7 Hz, 1H), 3.36 (dd, *J* = 13.3, 5.4 Hz, 1H), 2.87 (dd, *J* = 9.2, 3.0 Hz, 2H), 2.79 – 2.71 (m, 2H), 2.63 (dd, *J* = 13.3, 11.4 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.53, 165.11, 136.04, 135.08, 128.92, 128.35, 126.87, 67.49, 61.36, 44.17, 37.39, 31.36, 30.70, 14.39. HRMS (ESI-TOF) calcd for $C_{16}H_{21}N_2O_3S$ ([M+H$^+$]) = 321.1273, Found 321.1270.





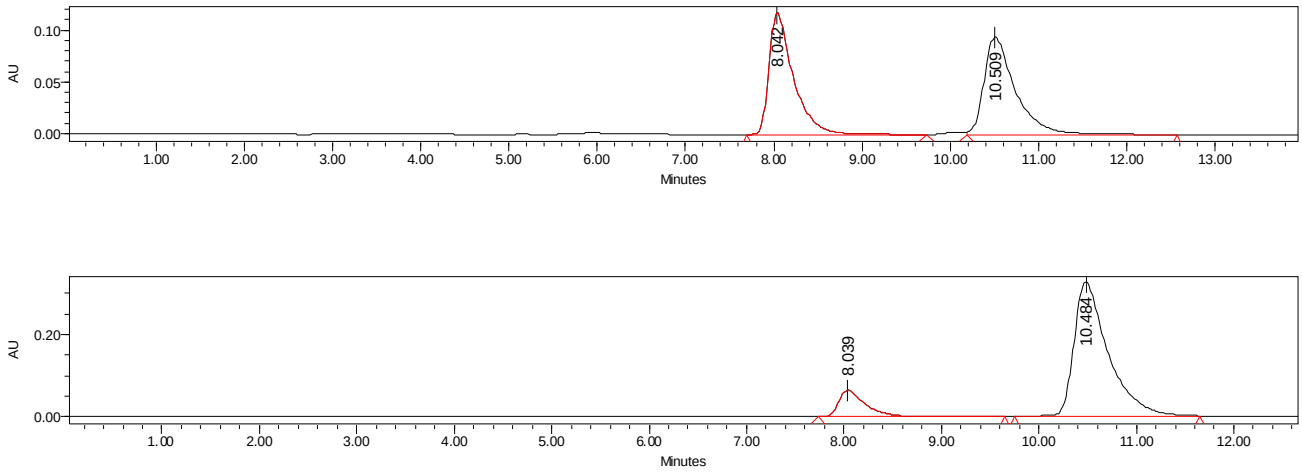
ethyl 2-(2-(2-oxocycloheptyl)hydrazono)-3-phenylpropanoate (4aa)



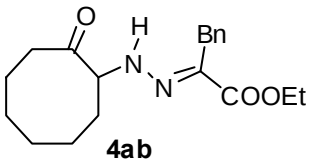
4aa

colorless oil; 81% yield, 74% ee. $[\alpha]_D^{15}$ = +2.4 (c = 0.46 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0

mL/min, λ = 254 nm, retention time: 8.40 min (minor), 10.48 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 6.89 (d, *J* = 4.4 Hz, 1H), 4.46 – 4.40 (m, 1H), 4.35 – 4.27 (m, 2H), 3.89 (q, *J* = 15.7 Hz, 2H), 2.63 – 2.57 (m, 1H), 2.43 – 2.26 (m, 2H), 2.11 (m, 1H), 1.89 – 1.82 (m, 1H), 1.73 – 1.62 (m, 4H), 1.50 (m,1H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.08, 165.29, 135.37, 134.71, 128.79, 128.36, 126.70, 67.63, 61.20, 41.72, 32.50, 31.24, 28.93, 27.07, 23.30, 14.39. HRMS (ESI-TOF) calcd for $C_{18}H_{25}N_2O_3$ ([M+H$^+$]) = 317.1865, Found 317.1863.



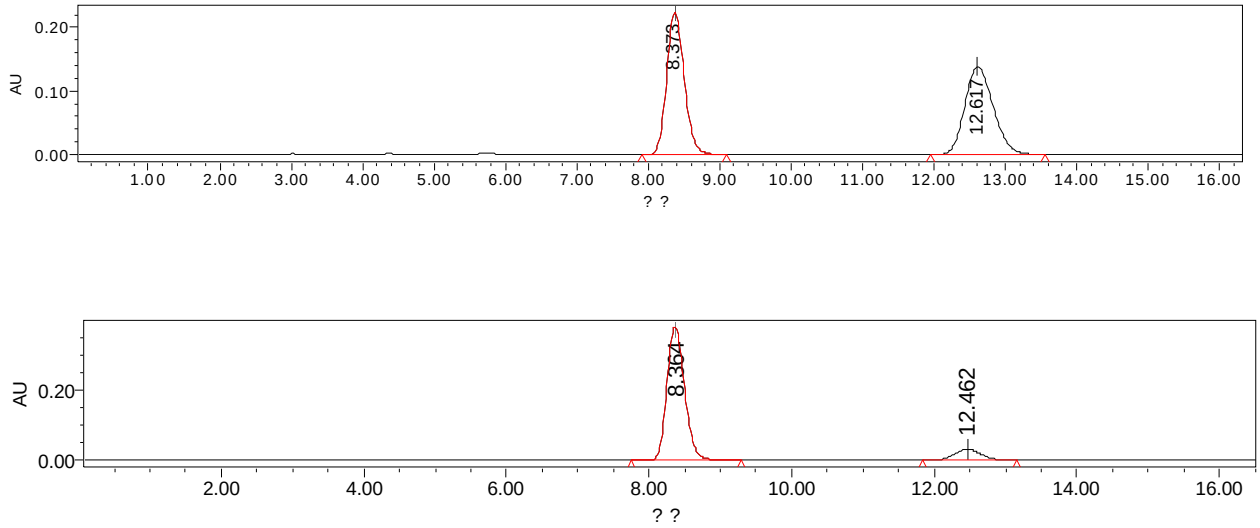
ethyl 2-(2-(2-oxocyclooctyl)hydrazono)-3-phenylpropanoate (4ab)



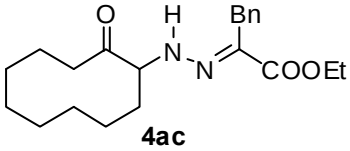
4ab

colorless oil; 45% yield, 77% ee. $[\alpha]_D^{21}$ = –1.8 (c = 0.22 in CH_2Cl_2). HPLC DAICEL CHIRALCEL OD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.36 min (major), 12.46 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 3H), 7.26-7.24 (m, 1H), 7.23 – 7.20 (m, 1H), 6.79 (d, *J* = 4.8 Hz, 1H), 4.39 – 4.34 (m, 1H), 4.34 – 4.28 (m, 2H), 3.96 (d, *J* = 15.7 Hz, 1H), 3.83 (d, *J* = 15.7 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.29 – 2.20 (m, 2H), 2.03 – 1.94 (m, 1H), 1.90 – 1.83 (m, 1H), 1.77 – 1.71 (m, 1H), 1.63 – 1.56 (m, 2H), 1.45-1.40 (m, 2H), 1.37 – 1.30 (m, 4H), 0.84-0.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.60, 165.31, 135.44, 134.63, 128.81, 128.38, 126.71, 66.27, 61.18, 40.27, 31.25, 30.67,

26.56, 26.36, 24.42, 22.42, 14.40. HRMS (ESI-TOF) calcd for $C_{19}H_{27}N_2O_3$ ([M+H$^+$]) = 331.2022, Found 331.2015.

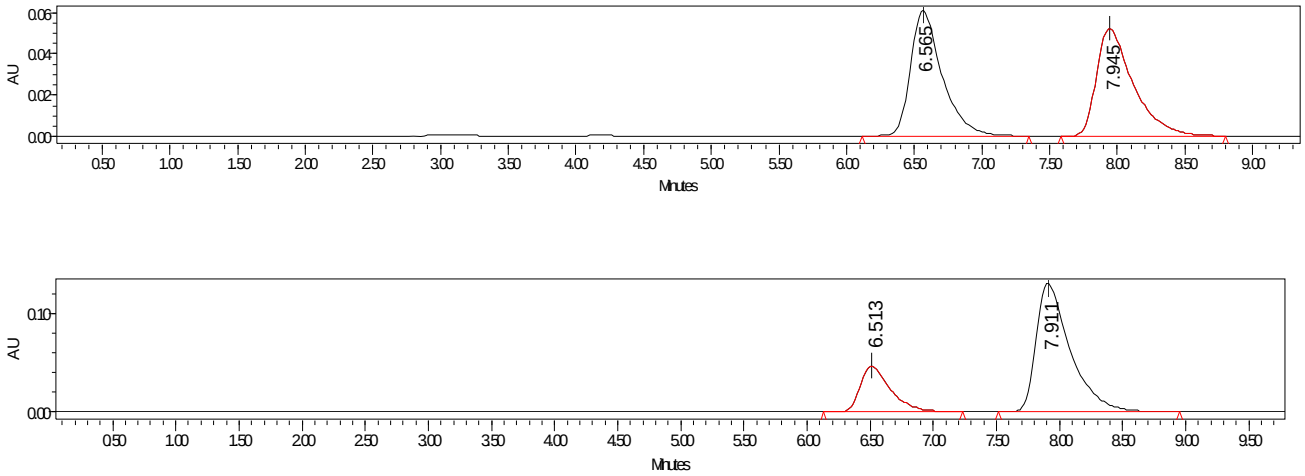


ethyl 2-(2-(2-oxocyclodecyl)hydrazono)-3-phenylpropanoate (4ac)

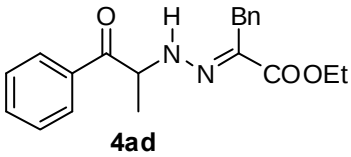


4ac

colorless oil; 75% yield, 52% ee. $[\alpha]_D^{17}$ = –1.7 (c = 0.52 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.51 min (minor), 7.91 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 6.79 (d, *J* = 5.5 Hz, 1H), 4.35-4.25 (m, 3H), 3.95 (d, *J* = 15.6 Hz, 1H), 3.84 (d, *J* = 15.7 Hz, 1H), 2.94 (ddd, *J* = 17.5, 10.9, 3.3 Hz, 1H), 2.26 – 2.18 (m, 1H), 2.15 – 2.07 (m, 1H), 2.07 – 1.97 (m, 2H), 1.64 – 1.56 (m, 1H), 1.55-1.50 (m, 1H), 1.40 – 1.25 (m, 8H), 1.22 – 1.11 (m, 3H), 1.00-0.94 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.12, 165.33, 135.51, 134.35, 128.85, 128.37, 126.73, 67.40, 61.13, 37.69, 31.28, 28.98, 25.16, 24.96, 23.77, 23.40, 22.44, 20.76, 14.38. HRMS (ESI-TOF) calcd for $C_{21}H_{31}N_2O_3$ ([M+H$^+$]) = 359.2335, Found 359.2328.

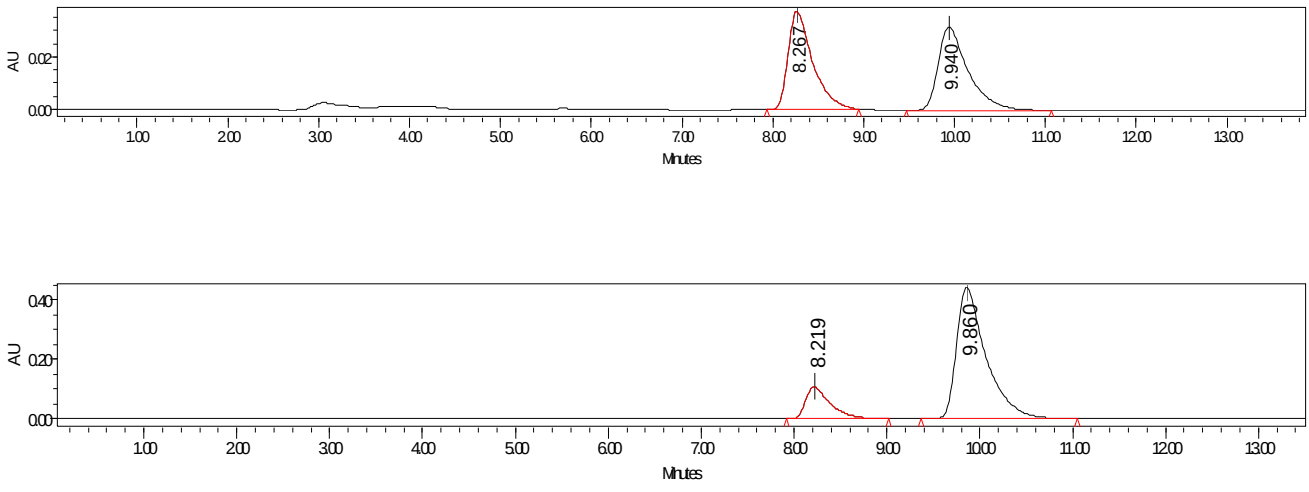


ethyl 2-(2-(1-oxo-1-phenylpropan-2-yl)hydrazono)-3-phenylpropanoate (4ad)

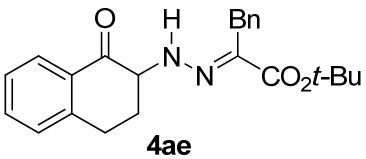


4ad

colorless oil; 45% yield, 66% ee. $[\alpha]_D^{21}$ = +20.0 (c = 0.50 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.22 min (minor), 9.86 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.42 (m, 2H), 7.34 – 7.19 (m, 5H), 6.79 (d, *J* = 7.2 Hz, 1H), 5.33-5.25 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.01 (d, *J* = 15.8 Hz, 1H), 3.88 (d, *J* = 15.8 Hz, 1H), 1.37-1.31 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.73, 165.20, 135.31, 135.23, 134.21, 133.80, 128.88, 128.86, 128.61, 128.31, 126.77, 61.24, 59.81, 31.19, 19.82, 14.40. HRMS (ESI-TOF) calcd for $C_{20}H_{23}N_2O_3$ ([M+H$^+$]) = 339.1709, Found 339.1705.

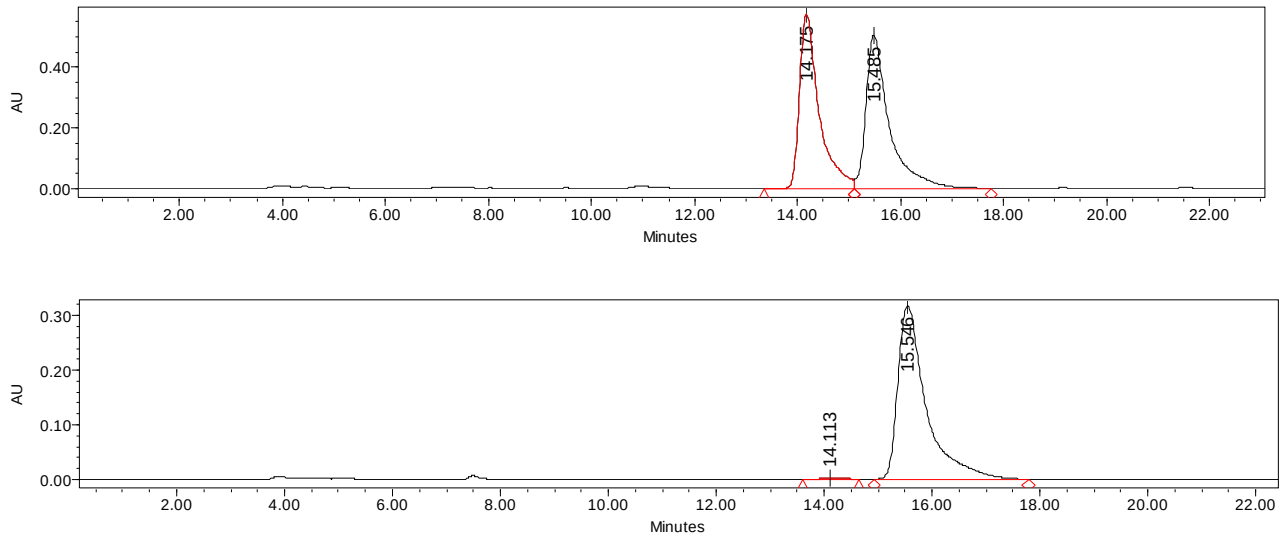


(E)-tert-butyl 2-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)hydrazono)-3-phenylpropanoate (4ae)

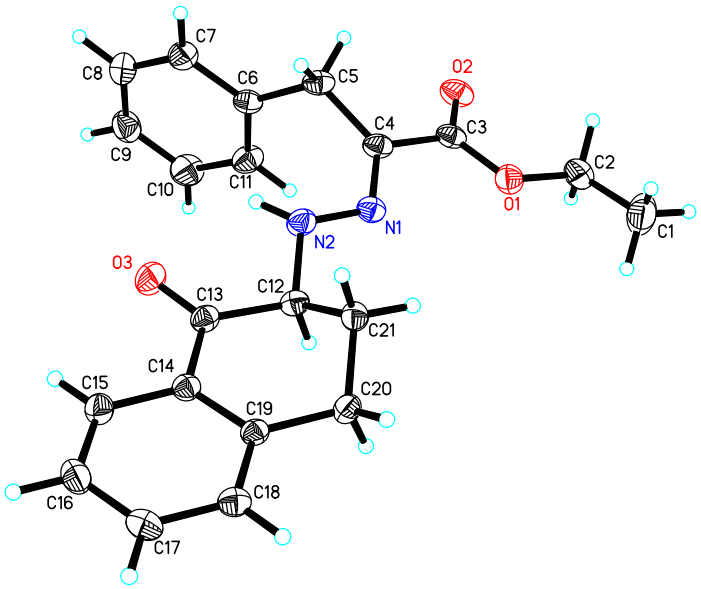


4ae

yellow oil; 9% yield, 99% ee. $[\alpha]_D^{17}$ = –74.5 (c = 0.22 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 95/5, flow rate = 0.8 mL/min, λ = 254 nm, retention time: 14.11 min (minor), 15.55 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 11.1, 3.8 Hz, 1H), 7.33-7.30 (m, 5H), 7.26-7.21 (m, 2H), 7.13 (s, 1H), 4.32 (ddd, *J* = 13.5, 4.9, 2.2 Hz, 1H), 3.97 (d, *J* = 15.6 Hz, 1H), 3.80 (d, *J* = 15.6 Hz, 1H), 3.18-3.12 (m, 1H), 3.05 – 2.98 (m, 1H), 2.86 – 2.73 (m, 1H), 2.00 (qd, *J* = 13.1, 4.4 Hz, 1H), 1.53 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.99, 164.08, 143.99, 137.02, 135.75, 133.97, 131.30, 128.90, 128.81, 128.41, 127.48, 126.77, 126.66, 81.14, 64.16, 31.40, 30.62, 29.70, 28.16, 28.08. HRMS (ESI-TOF) calcd for $C_{23}H_{26}N_2NaO_3$ ([M+H$^+$]) = 401.1841, Found 401.1830.



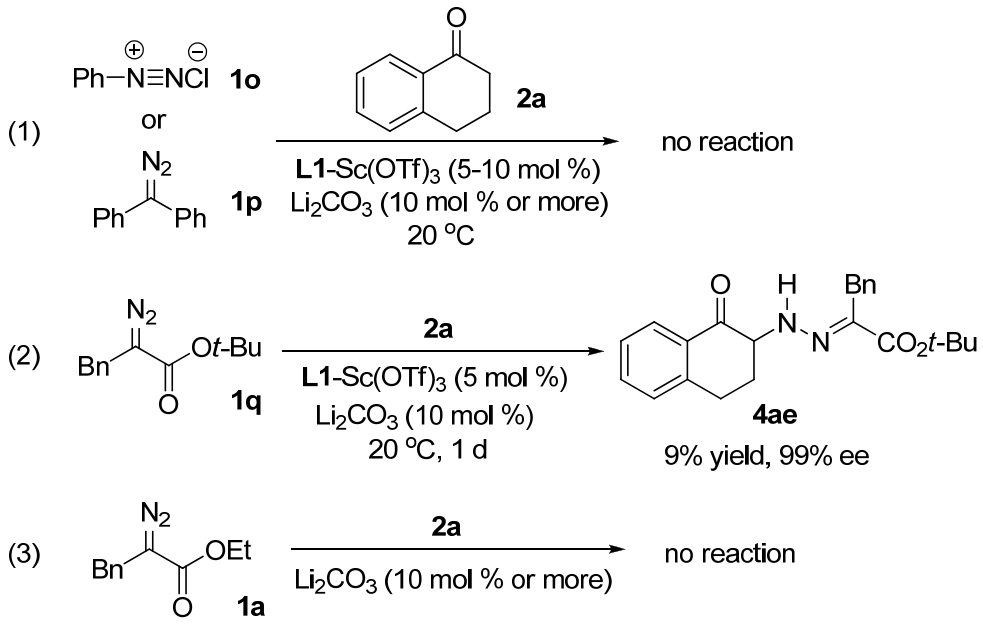
(I) X-ray structure of 4a



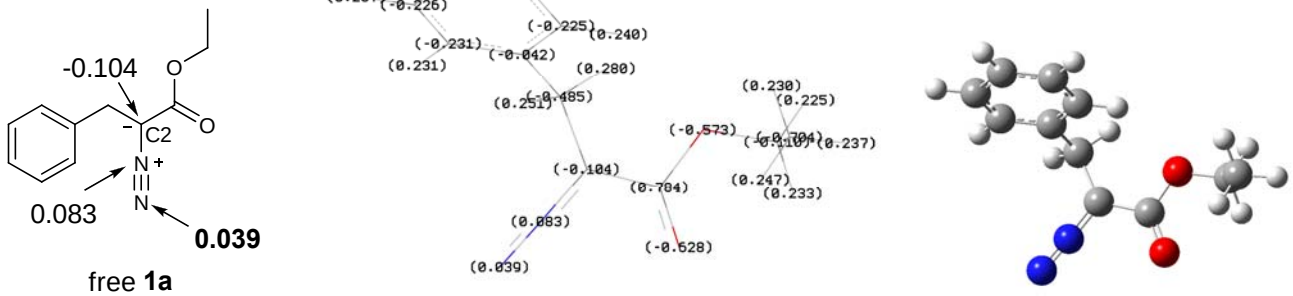
CCDC 825021 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

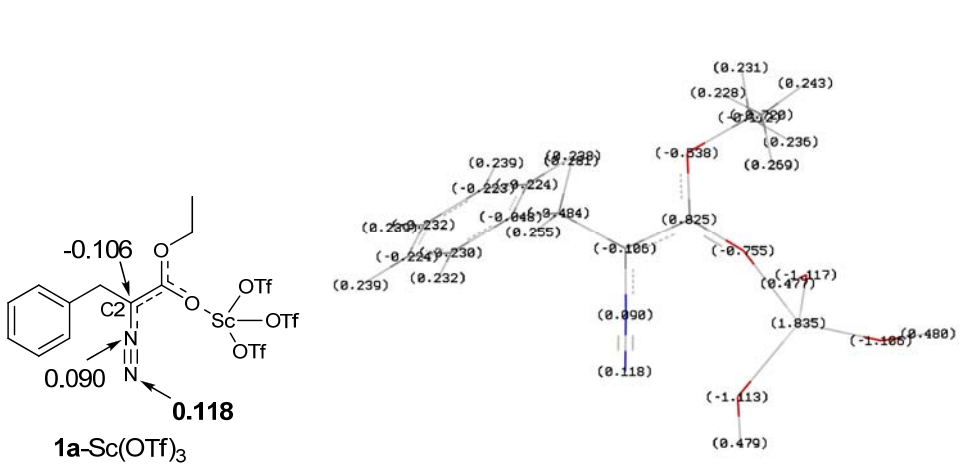
(J) Study of mechanism

a. Control experiments

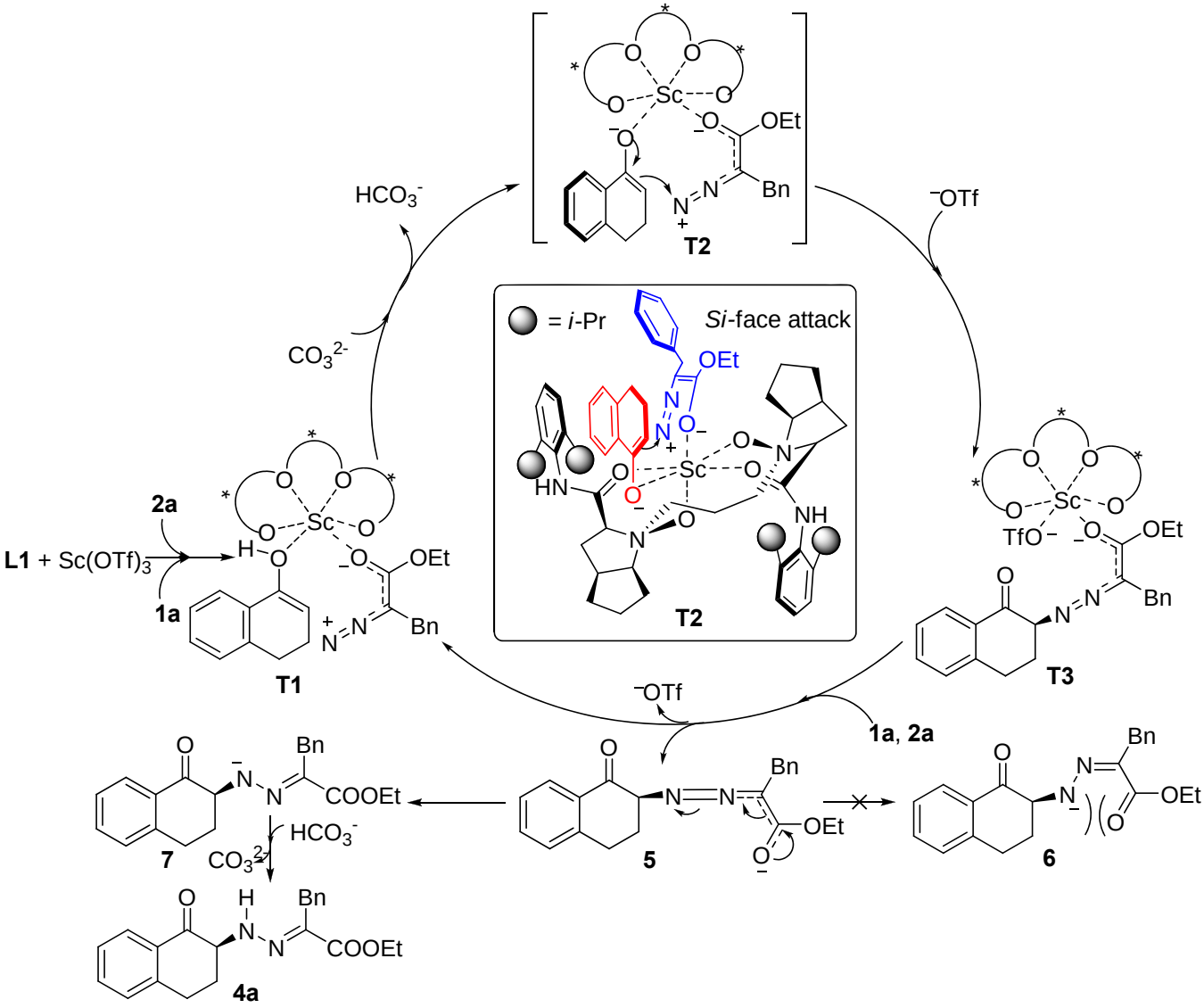


b. Computed natural bond orbital (NBO) charges





c. Proposed catalytic process for the catalytic asymmetric C–N bond formation.

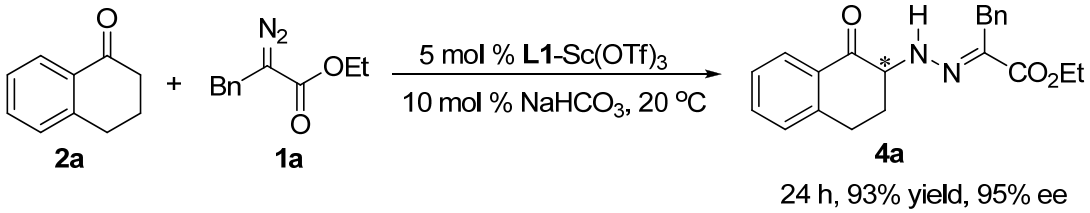


In the light of the X-ray structure of the *N*,*N*'-dioxide-Sc(III) complex[3] and the product **4a**, a proposed catalytic model was outlined.

d. Study of the role of Li_2CO_3

What is the essential role of lithium carbonate in this catalytic system, whether there is any association of Li_2CO_3 with Sc-catalyst?

Some observations are helpful for this question. First, the bases do not influence the ee values (Table 1), which imply that the bases may not effect the spatial environment of the catalyst. Second, lithium carbonate was not dissolved in the system, while the catalyst could dissolve well in the system. The most useful information is that similar good result (93% yield, 95% ee) was obtained when using the $NaHCO_3$ instead of Li_2CO_3 under the same conditions. These results indicate that Li_2CO_3 may not have association with the Sc-catalyst.



Maybe Li_2CO_3 give the best PH environment for this reaction system.

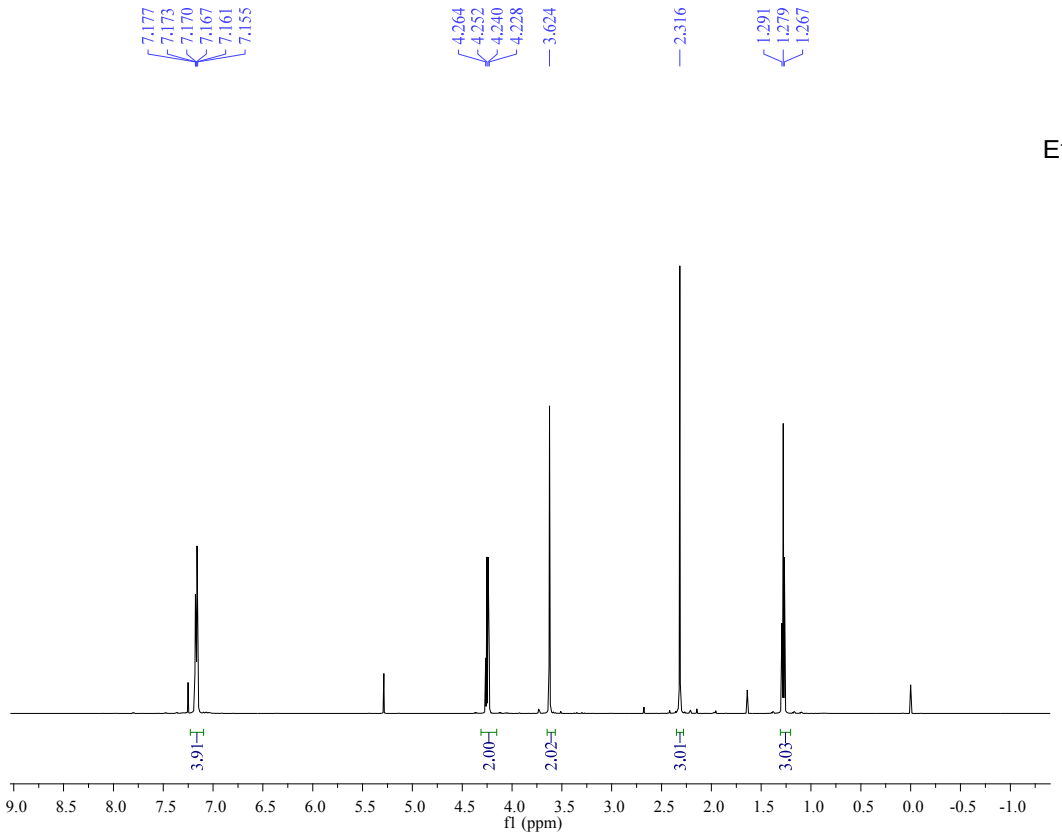
(K) References

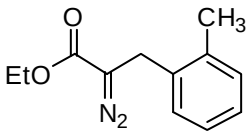
1. (a) Li, W.; Wang, J.; Hu, X. L.; Shen, K.; Wang, W. T.; Chu, Y. Y.; Lin, L. L.; Liu, X. H.; Feng, X. M. *J. Am. Chem. Soc.* **2010**, *132*, 8532. (b) Maier, T. C.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 4594.

2. (a) Wen, Y. H.; Huang, X.; Huang, J. L.; Xiong, Y.; Qin, B.; Feng, X. M. *Synlett* **2005**, 2445. (b) Yu, Z. P.; Liu, X. H.; Dong, Z. H.; Xie, M. S.; Feng, X. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 1308. (c) Zheng, K.; Qin, B.; Liu, X. H.; Feng, X. M. *J. Org. Chem.* **2007**, *72*, 8478. (d) Zhang, X.; Chen, D. H.; Liu, X. H.; Feng, X. M. *J. Org. Chem.* **2007**, *72*, 5227. (e) Zhou, X.; Shang, D. J.; Zhang, Q.; Lin, L. L.; Liu, X. H.; Feng, X. M. *Org. Lett*. **2009**, *11*, 1401.

3. Liu, Y. L.; Shang, D. J.; Zhou, X.; Liu, X. H.; Feng, X. M. *Chem. Eur. J.* **2009**, *15*, 2055.

(L) Copies of NMR spectra





1d

Current Data Parameters

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AQ: undefined
TE: 292.9 C

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P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
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LB: 0.30 Hz
First Point: 0.50
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Phase: Manual
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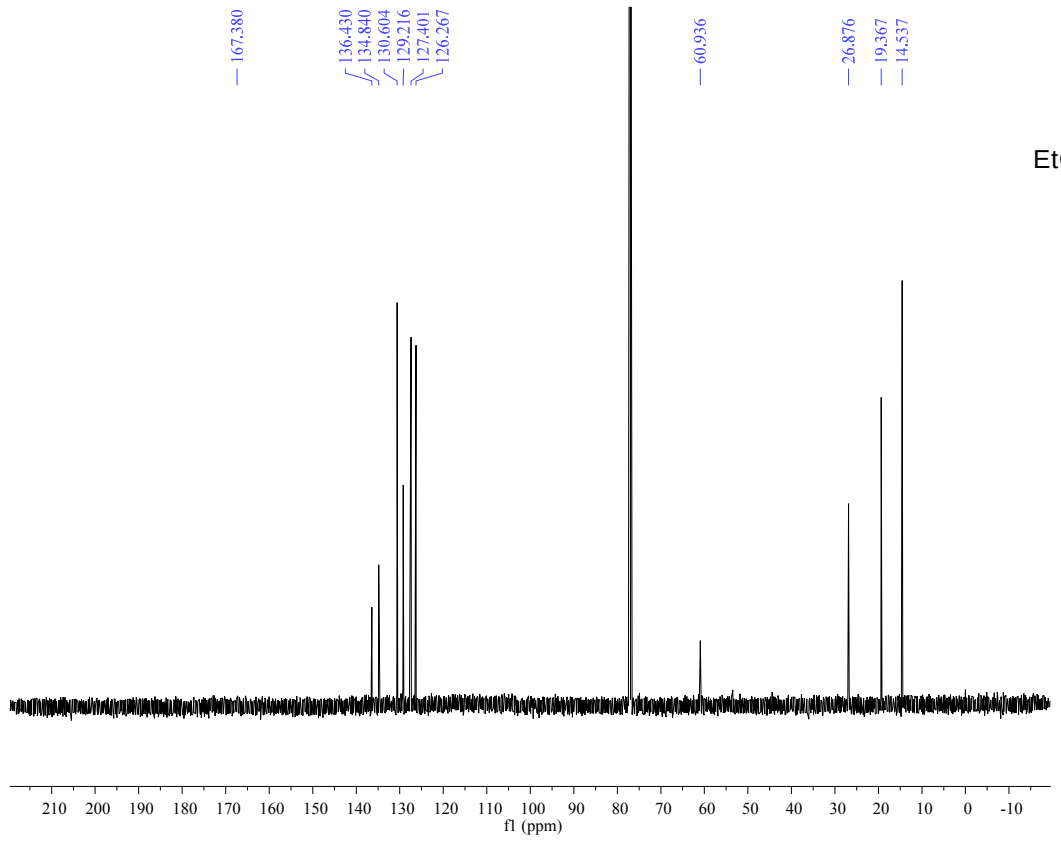
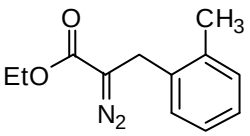
Ph1: 31.64





1d

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AQ: undefined
TE: 293.1 C

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NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
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LB: 1.00 Hz
First Point: 0.50
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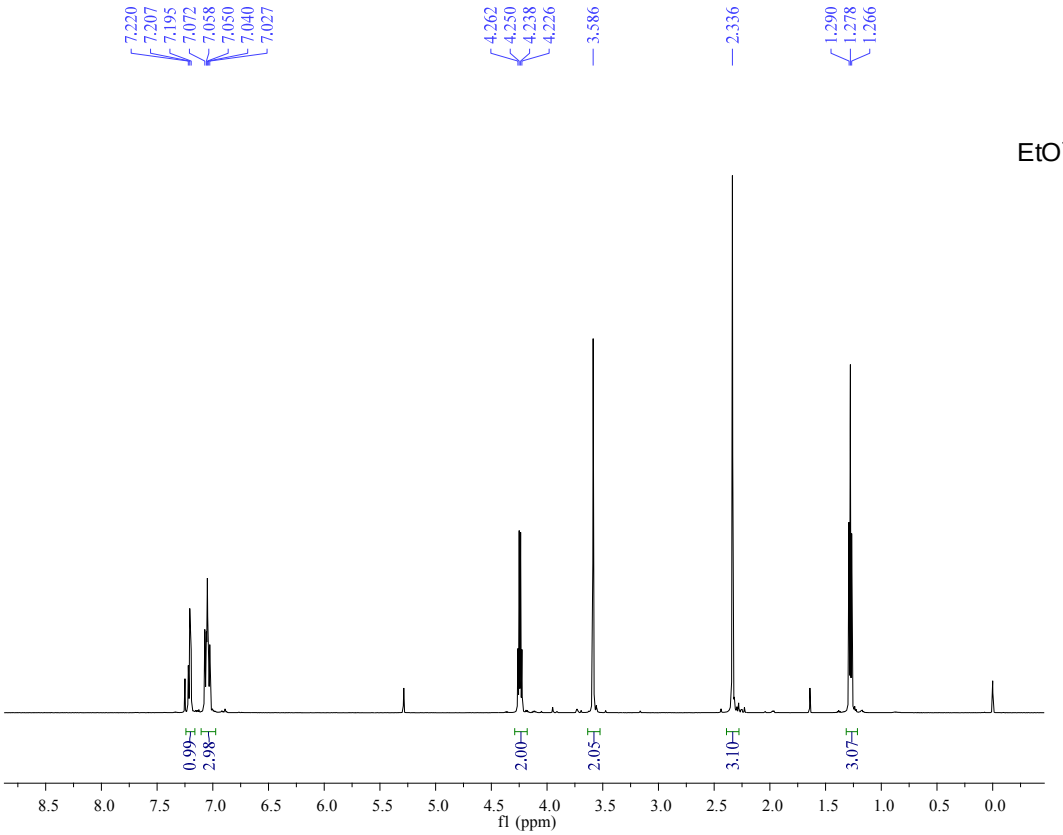

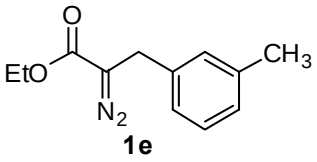

1e

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AQ: undefined
TE: 292.8 C

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NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
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LB: 0.60 Hz
First Point: 0.50
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Phase: Manual
Ph0: 119.50
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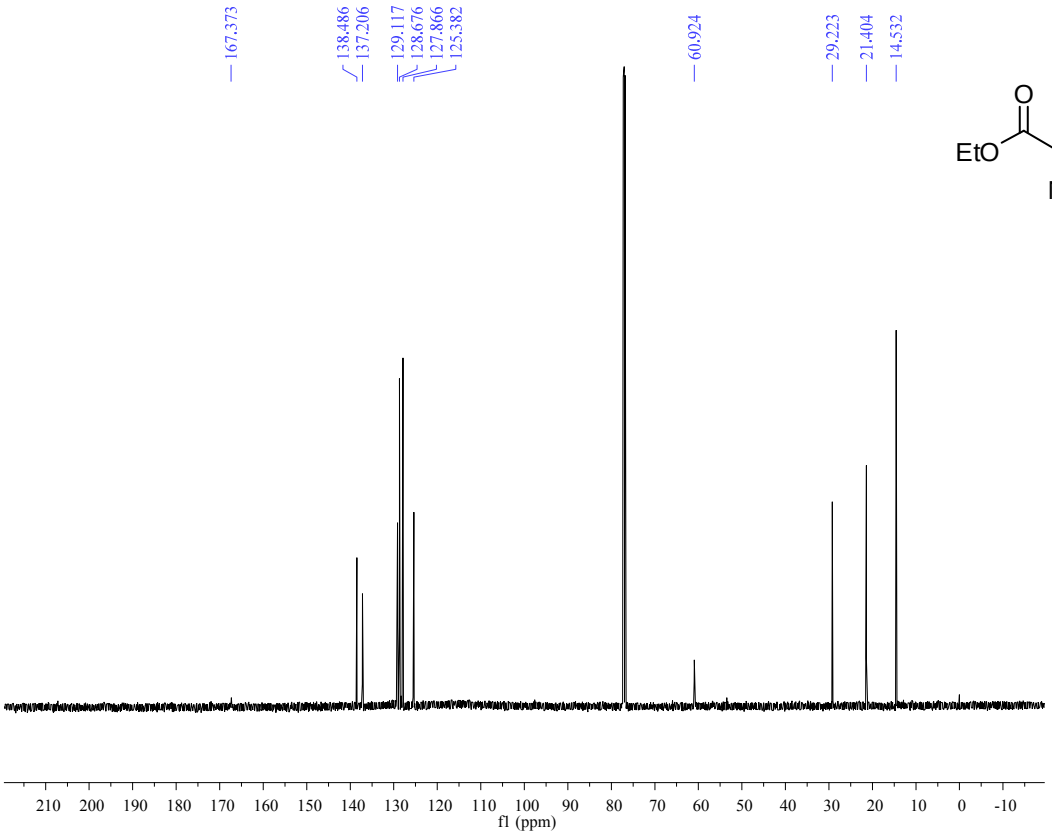

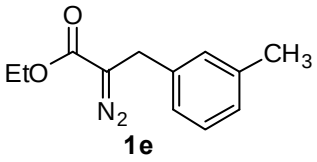

1e

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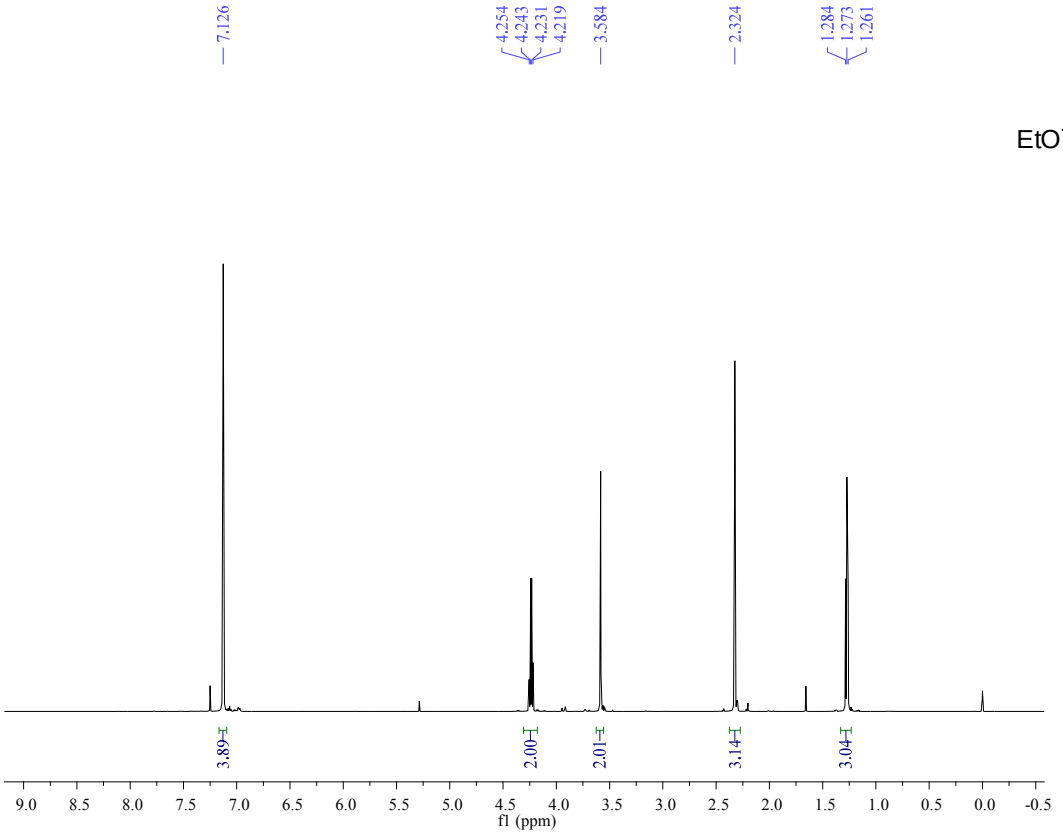
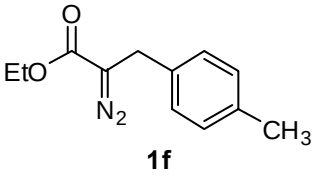
SWH: 36057.7 Hz
AQ: undefined
TE: 293.1 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 76.42
Ph1: 56.86





1f

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AQ: undefined
TE: 293.1 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
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DC: 0.05
LB: 0.30 Hz
First Point: 0.50
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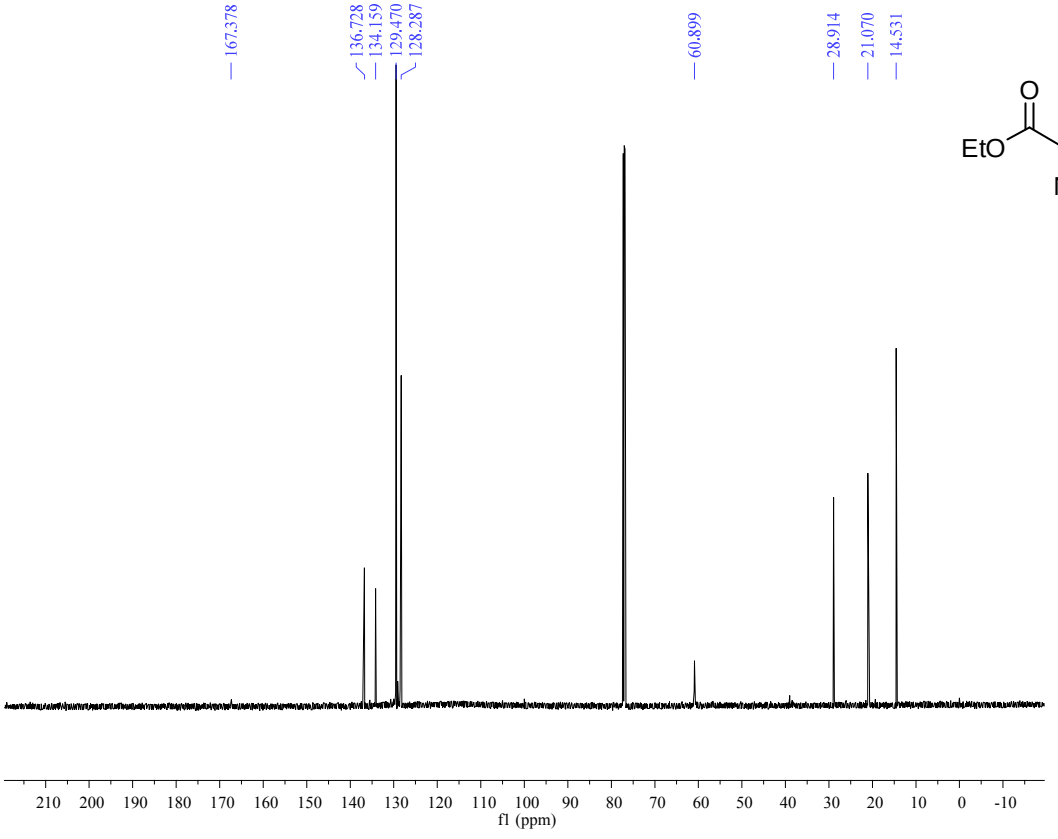
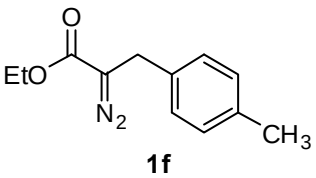
Ph1: 31.44





1f

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AQ: undefined
TE: 293.3 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
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LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
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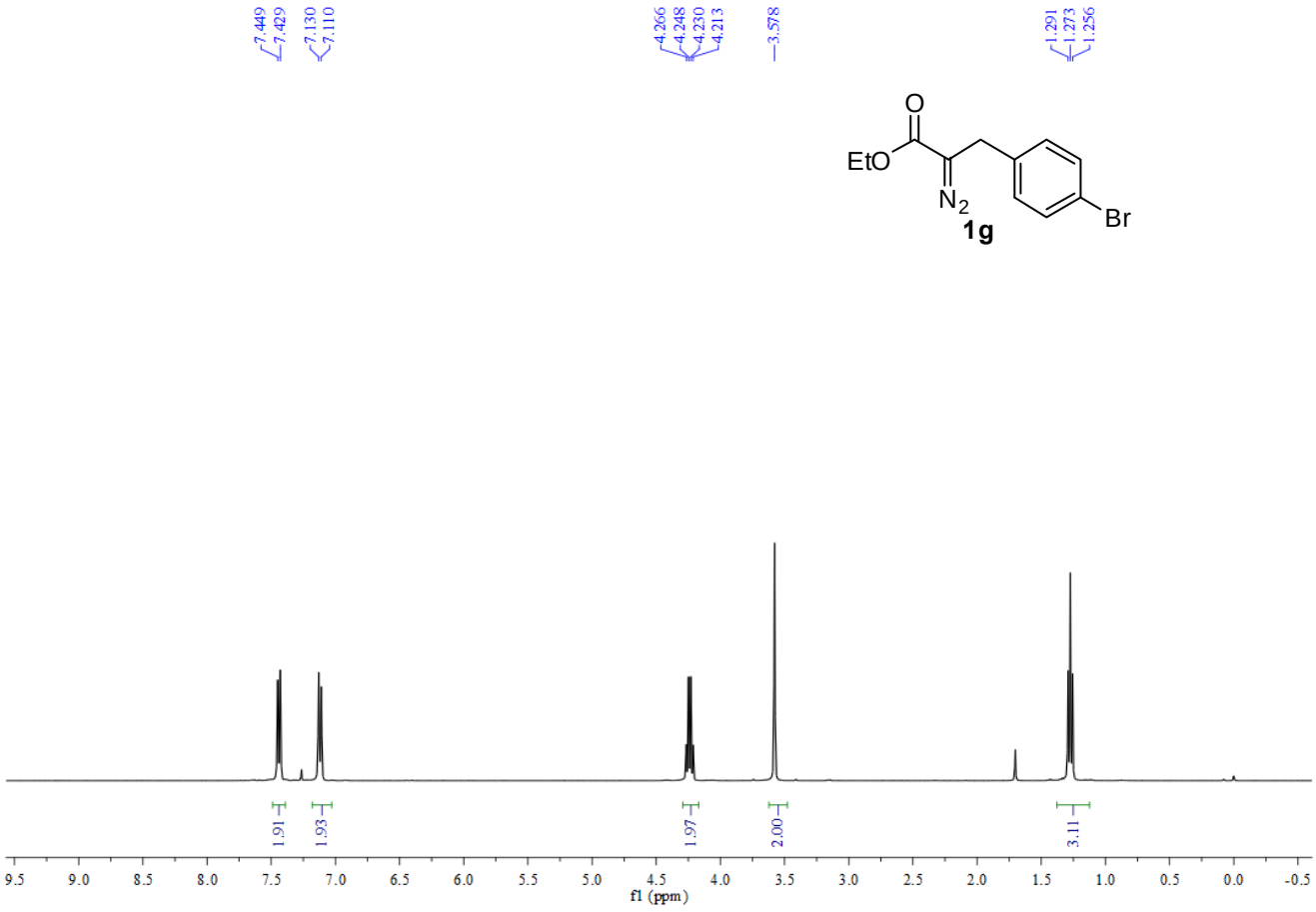
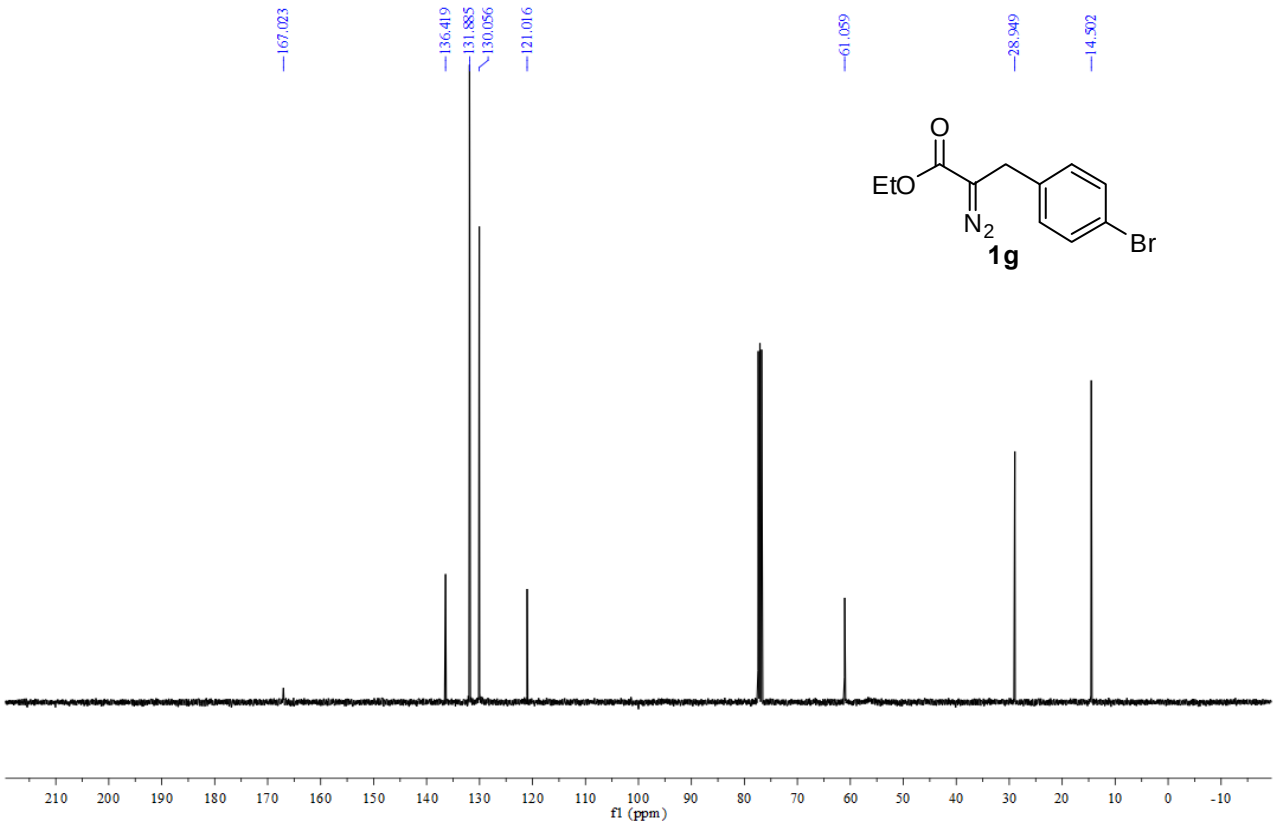
Ph1: 67.50


7.449
7.429
7.130
7.110
4.266
4.248
4.230
4.213
3.578
1.291
1.273
1.256
EtO
O
N2
Br
1g
1.91
1.93
1.97
2.00
3.11
f1 (ppm)


167.023
136.419
131.885
130.056
121.016
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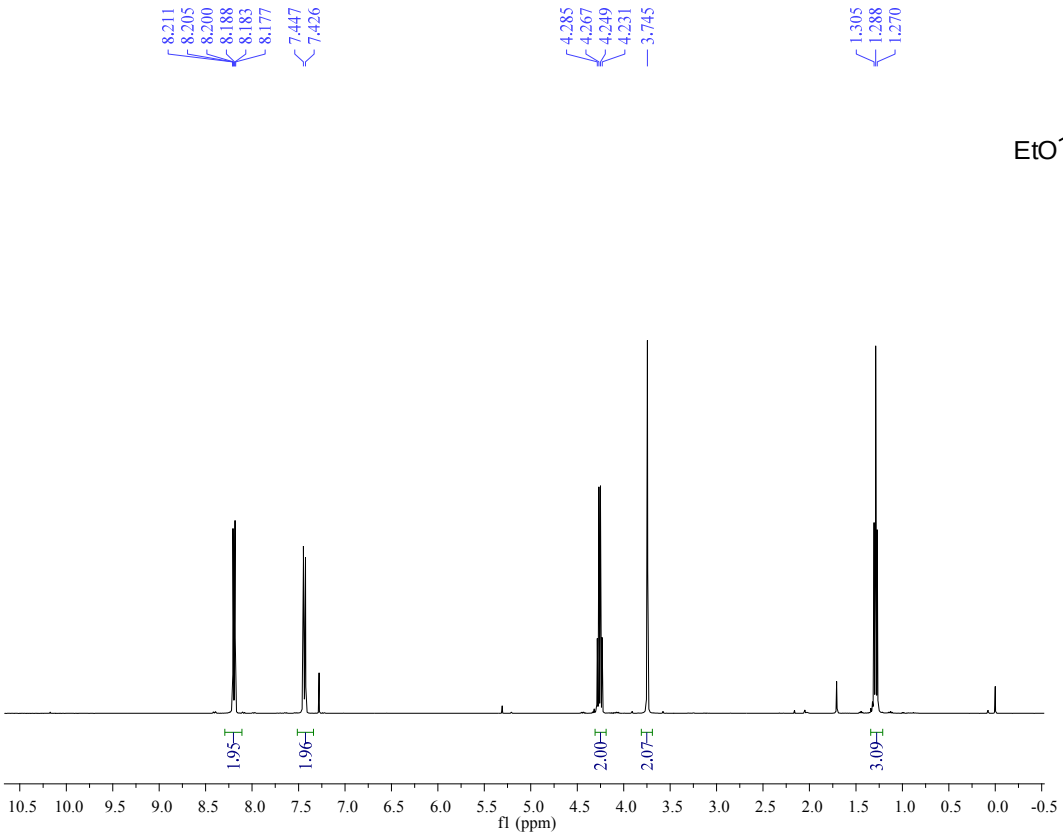
28.949
14.502
EtO
O
N2
Br
1g
f1 (ppm)



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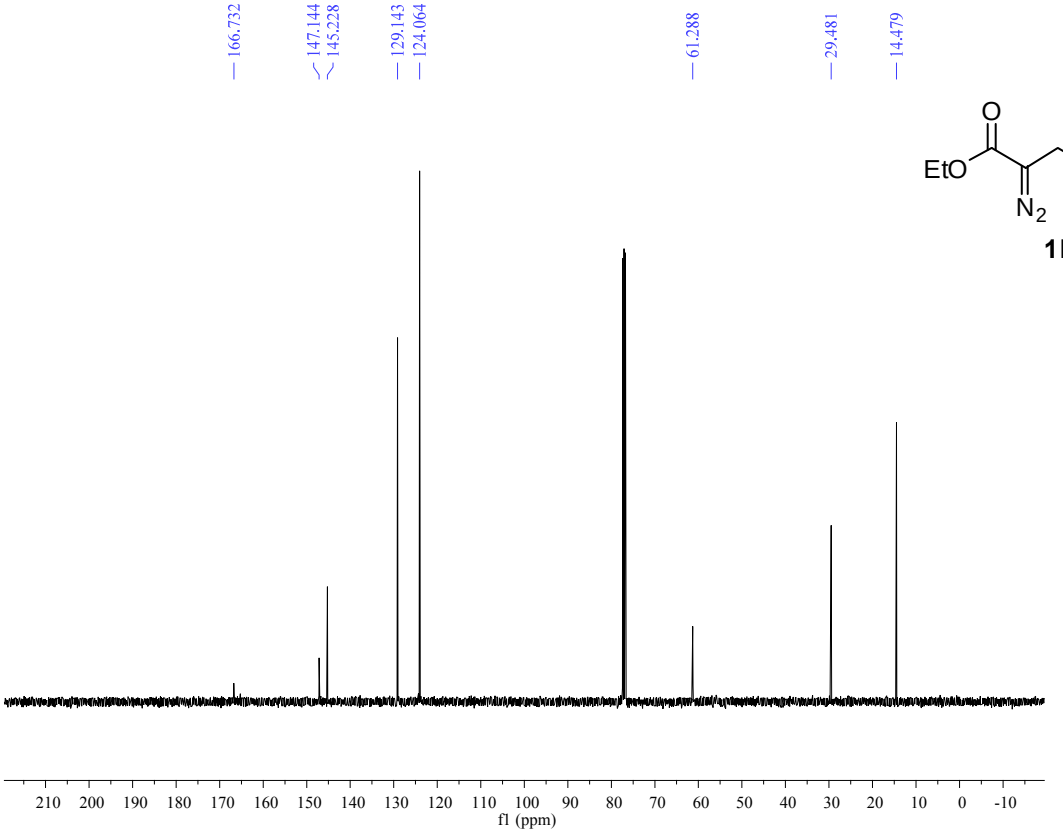
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 292.5 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -0.03
Ph1: 20.05



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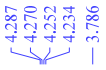
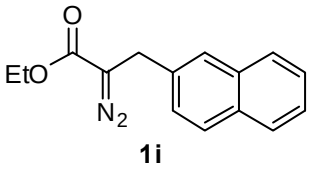
Solvent: CDCl3
NS: 162
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293 C

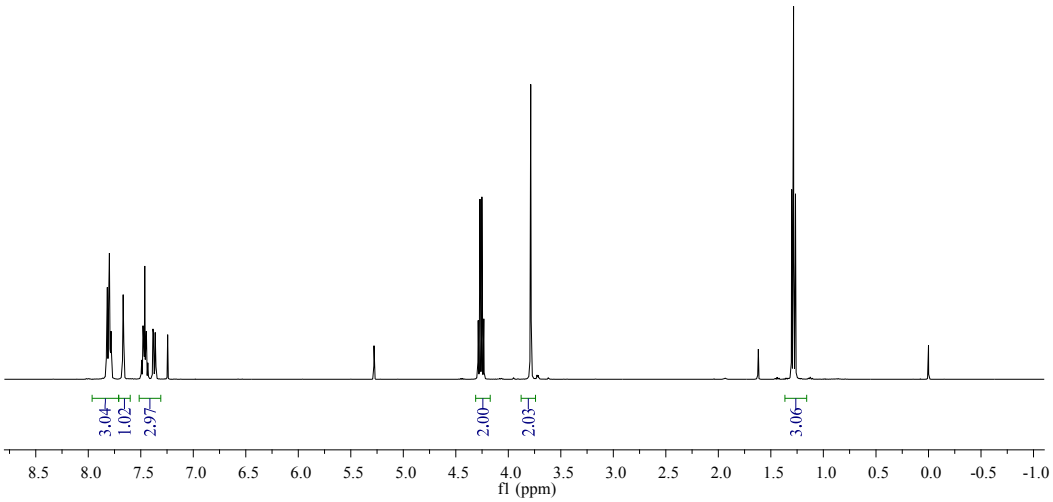
======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -122.84
Ph1: 87.77





1i



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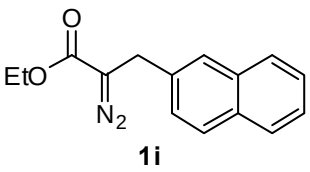
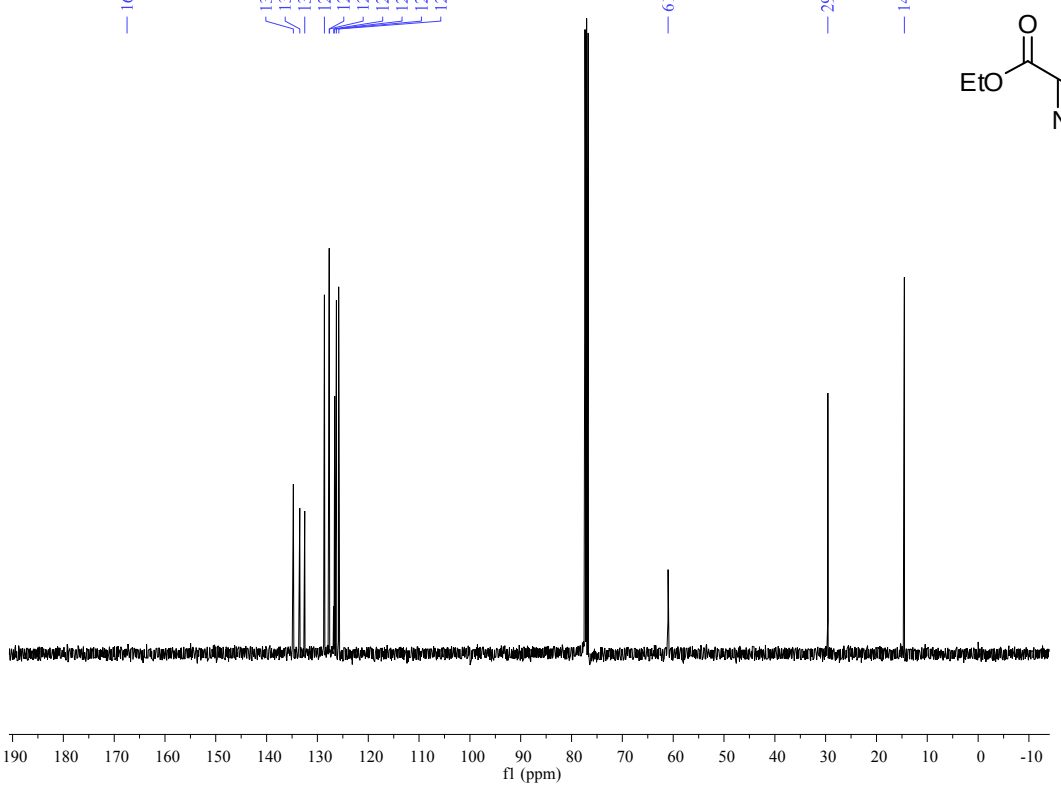
AQ: undefined
TE: 293.7 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -27.52
Ph1: 20.43



1i



Current Data Parameters

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SWH: 24038.5 Hz
AQ: undefined
TE: 294.6 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
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LB: 1.00 Hz
First Point: 0.50
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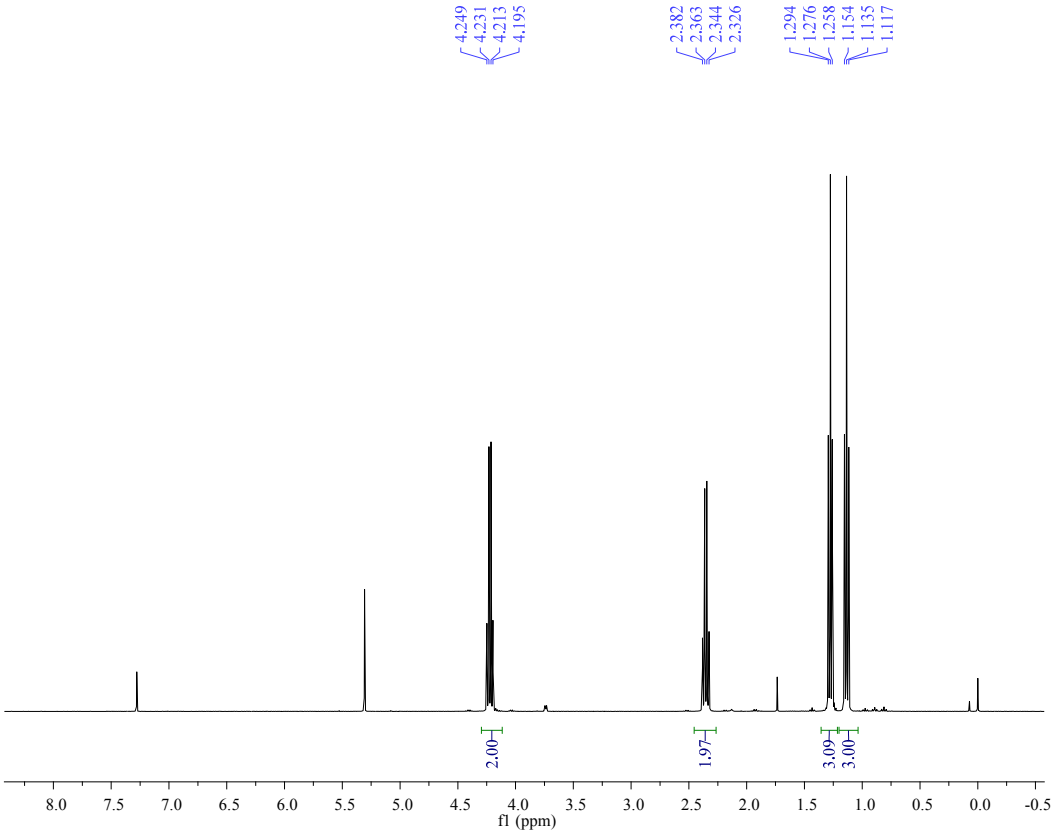
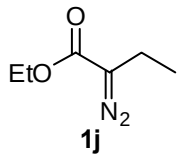
Ph1: 80.51





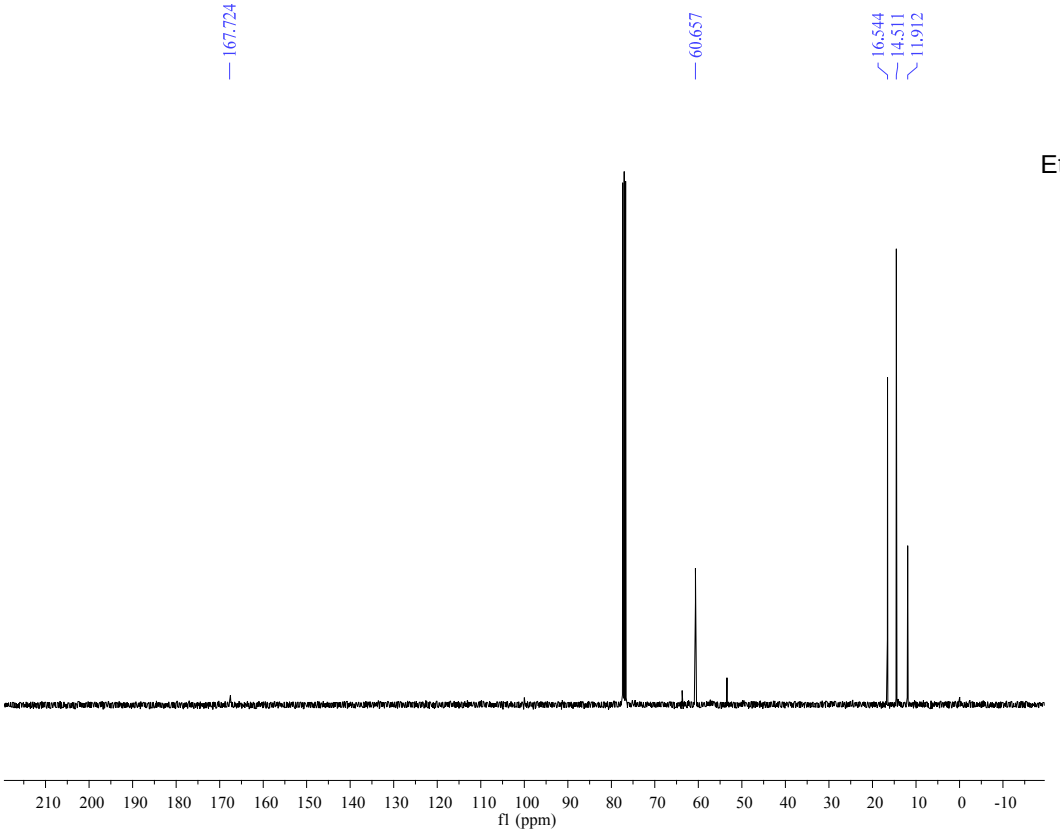
1j

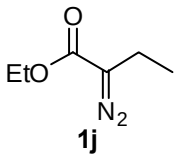
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-11T11:14:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.5 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -28.33
Ph1: 20.90





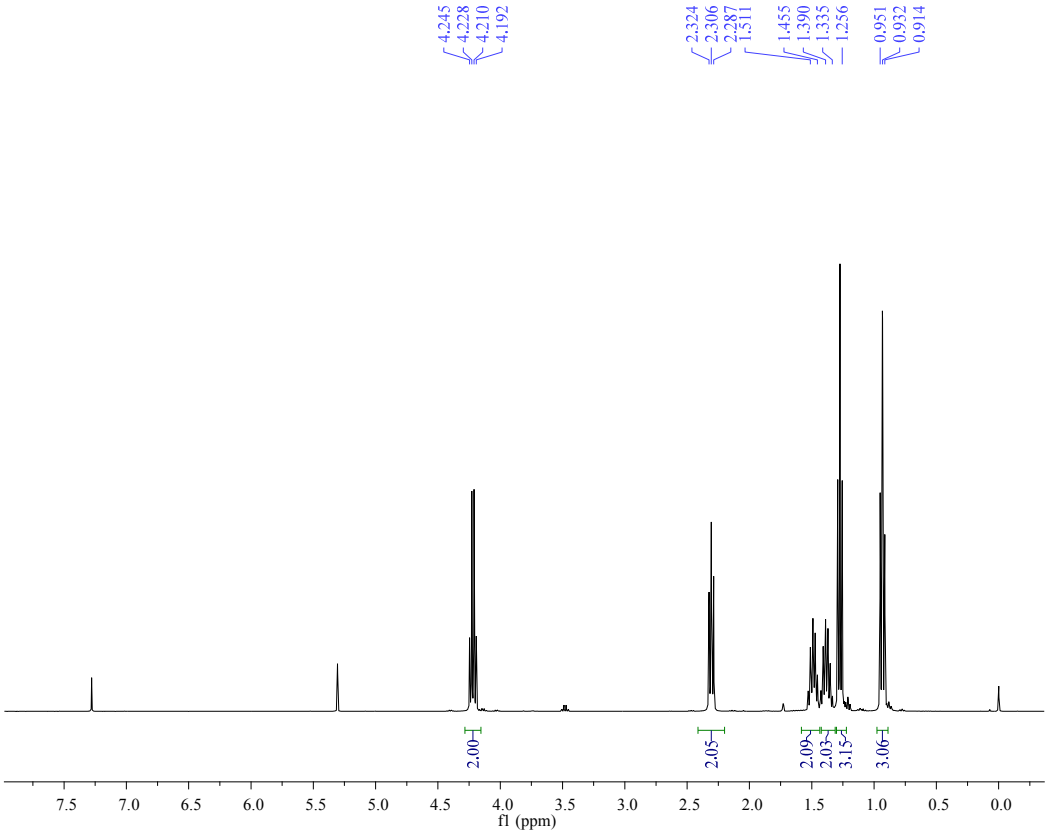
1j

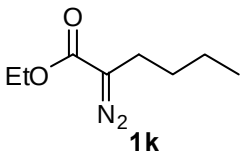
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-11T11:43:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.4 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -107.90
Ph1: 80.51





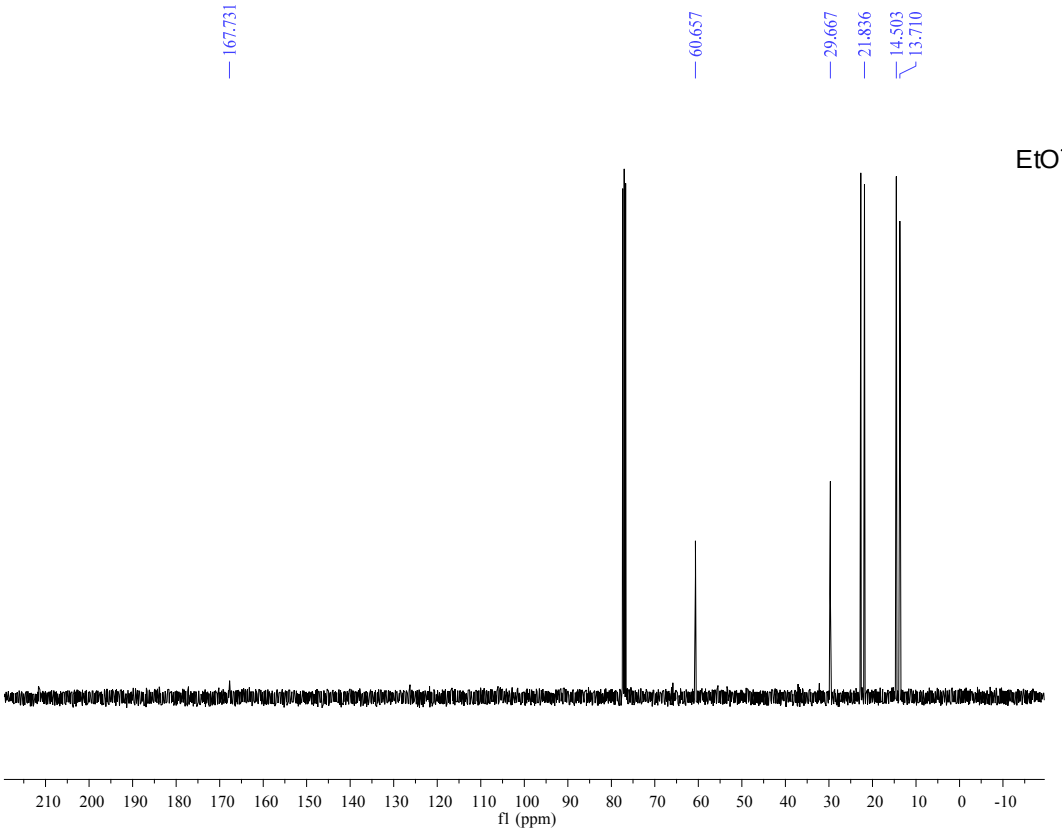
1k

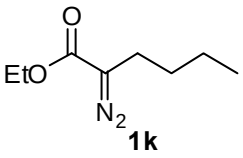
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-11T11:02:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.8 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -28.96
Ph1: 20.33





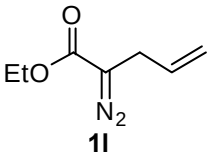
1k

Current Data Parameters

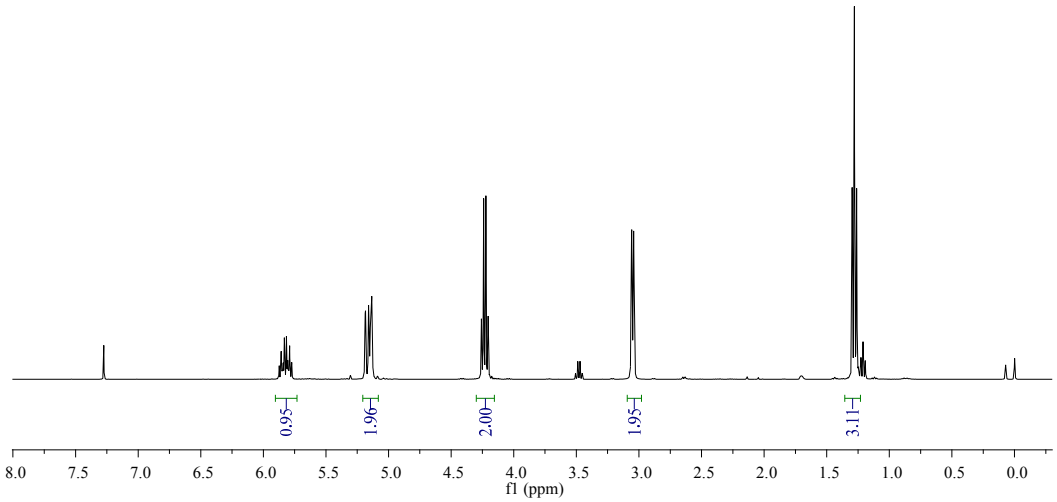
F2 - Acquisition Parameters
DATE: 2011-01-11T11:09:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 128
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.6 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -109.68
Ph1: 89.15



1l

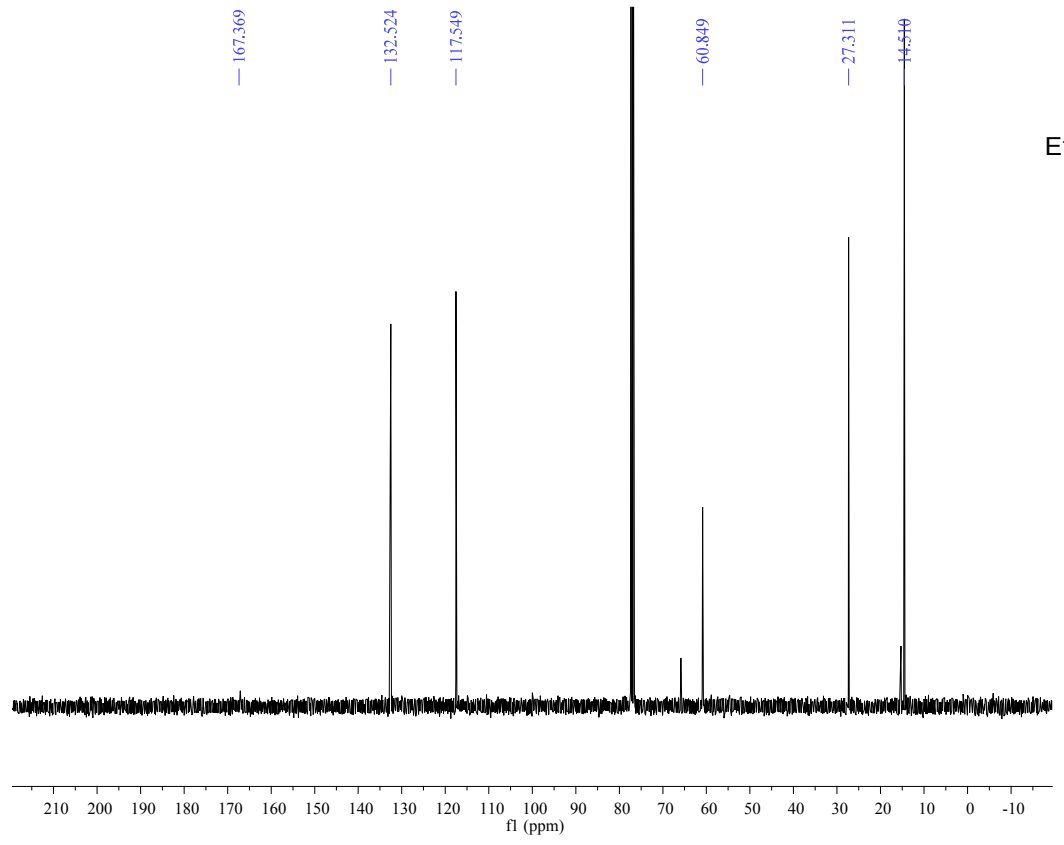


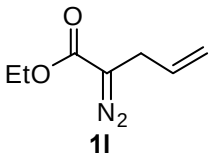
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T20:45:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.7 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -1.33
Ph1: 17.97





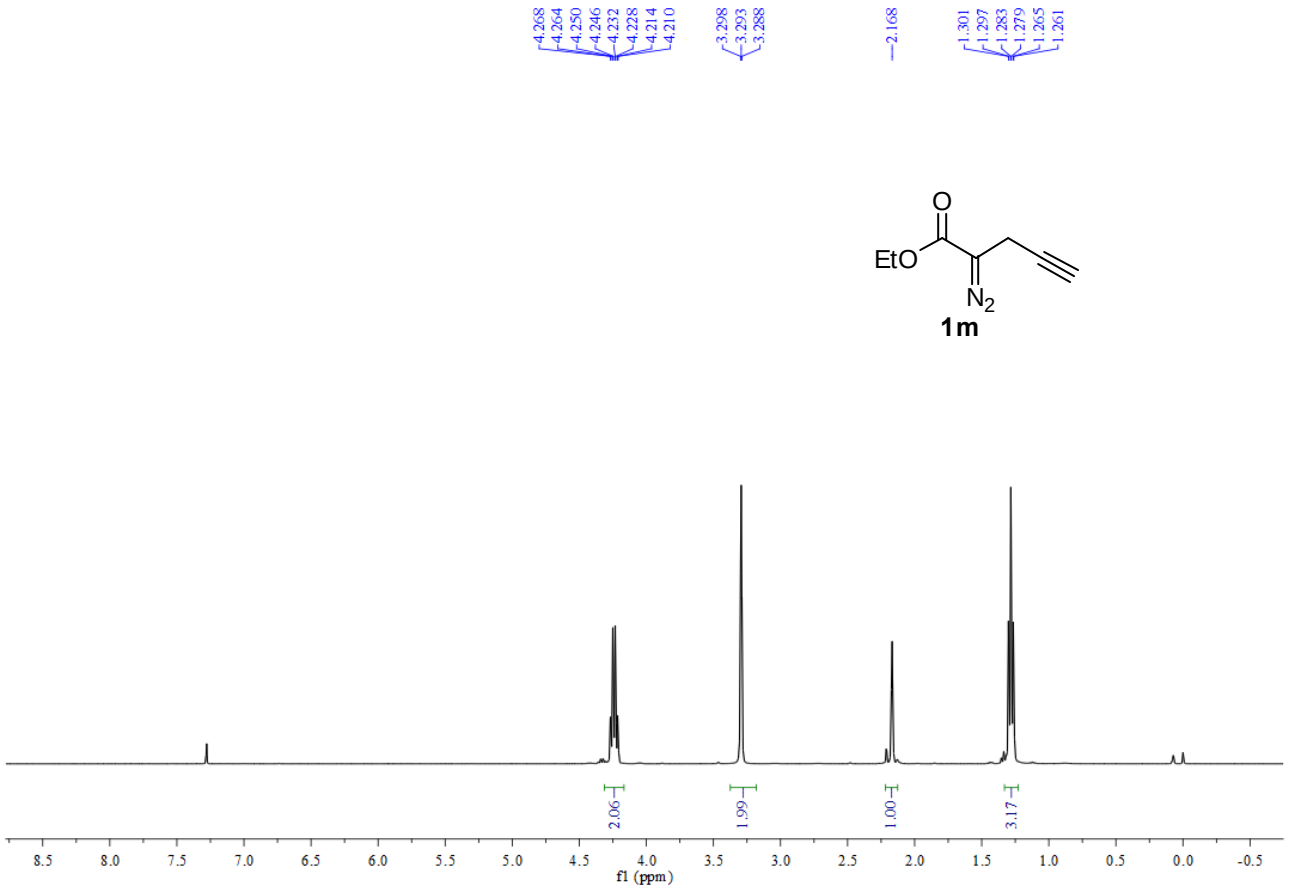
1l

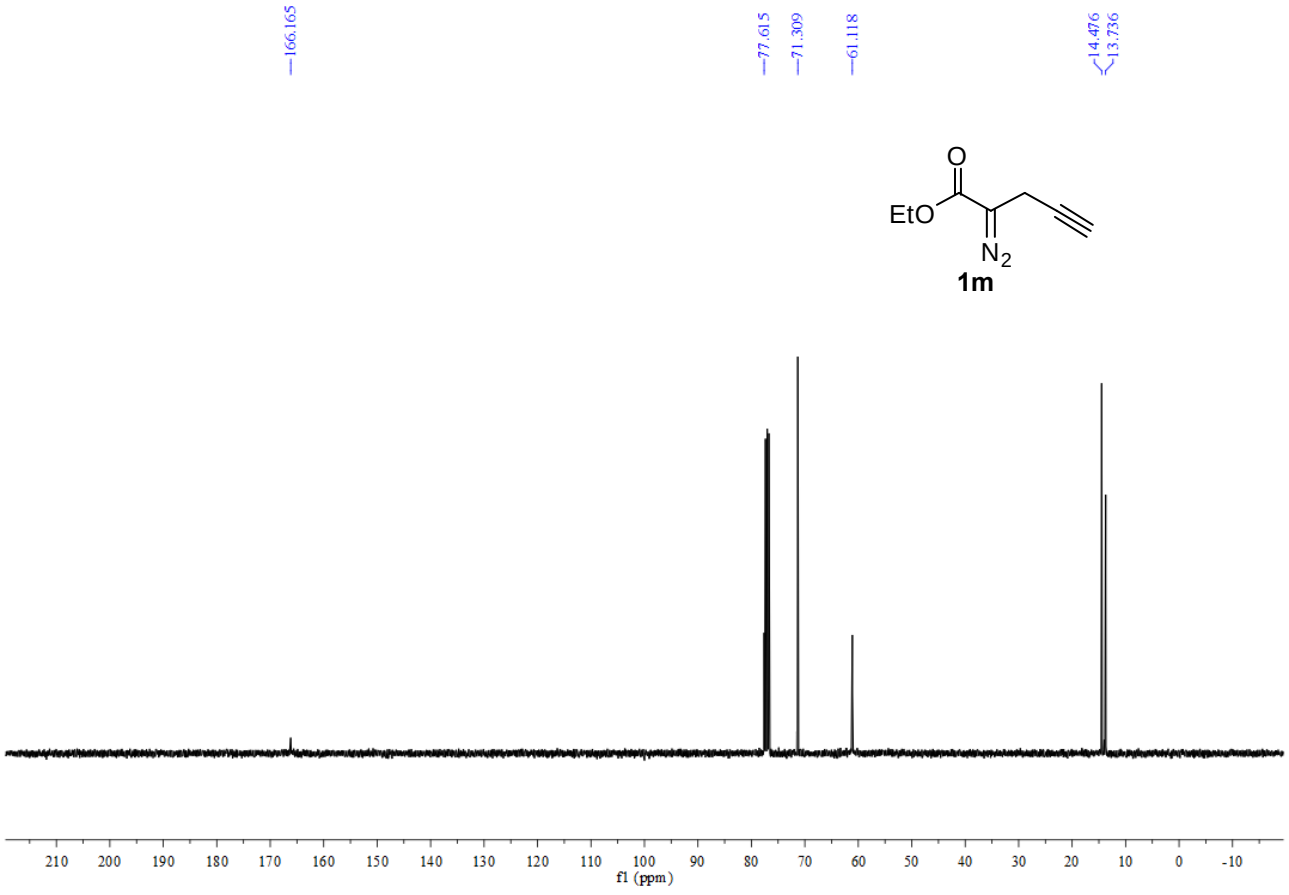
Current Data Parameters

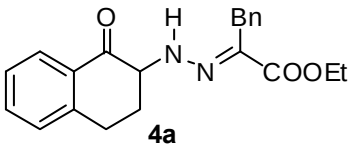
F2 - Acquisition Parameters
DATE: 2011-01-16T21:00:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.9 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

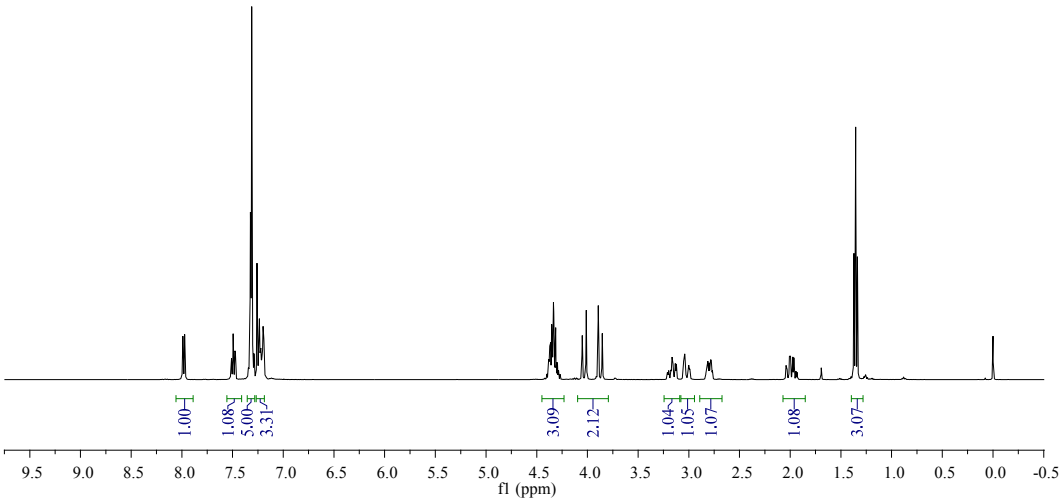
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -118.80
Ph1: 86.28


4.268
4.264
4.250
4.246
4.232
4.228
4.214
4.210
3.298
3.293
3.288
2.168
1.301
1.297
1.283
1.279
1.265
1.261
O
EtO
N2
1m
2.06
1.99
1.00
3.17
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 0.5 0.0 -0.5
f1 (ppm)


166.165
77.615
71.309
61.118
14.476
13.736
O
EtO
N2
1m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4a

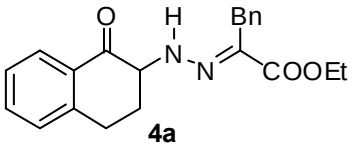


Current Data Parameters

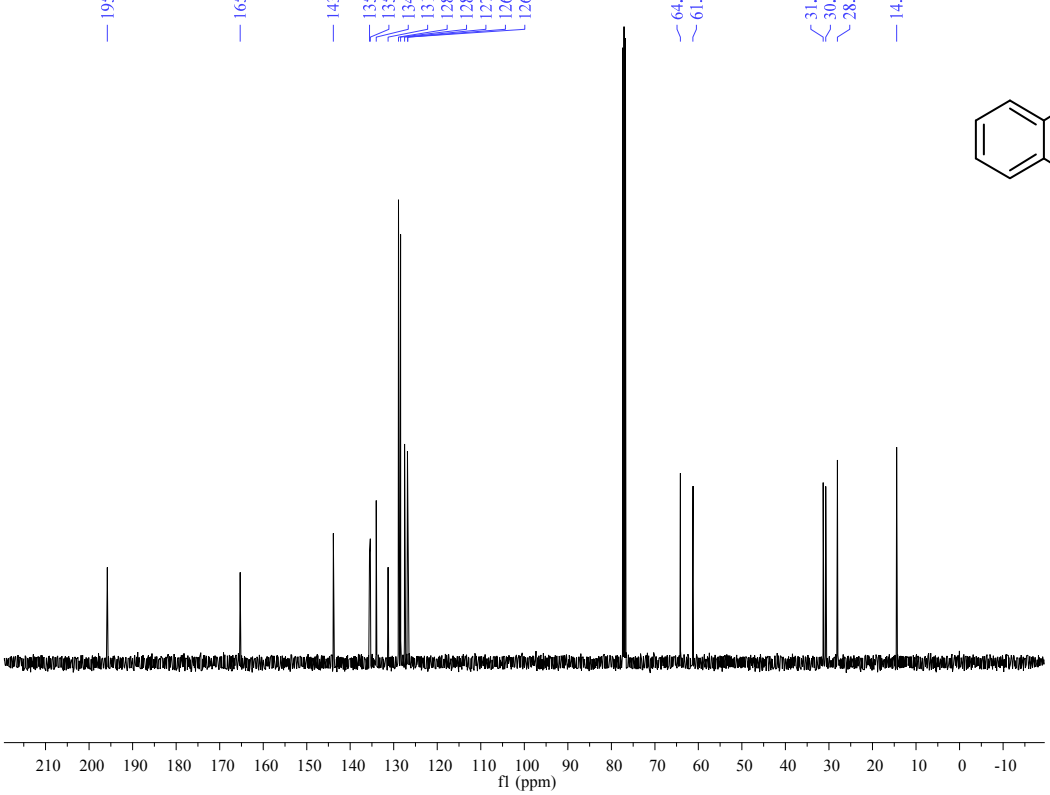
F2 - Acquisition Parameters
DATE: 2010-12-27T15:44:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.8 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -32.27
Ph1: 20.51



4a

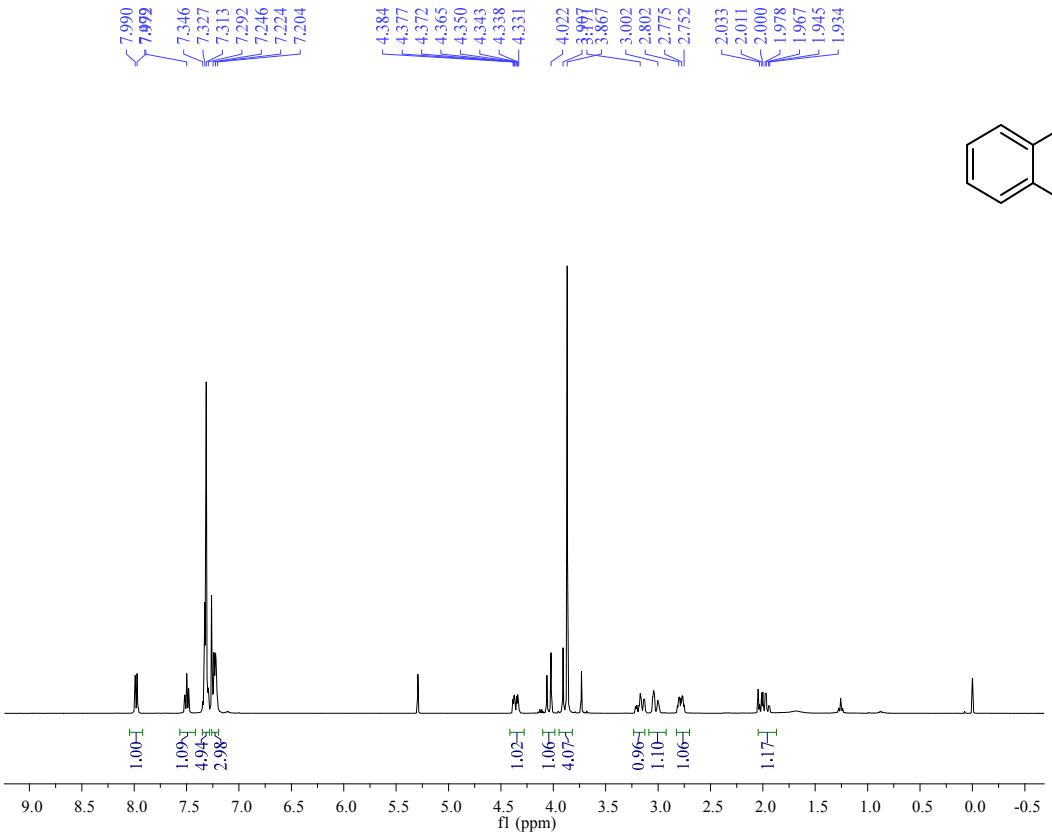


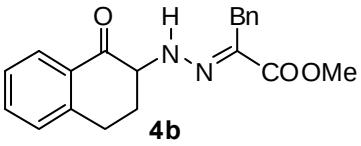
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-12-27T15:56:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 129
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.6 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -113.76
Ph1: 79.52





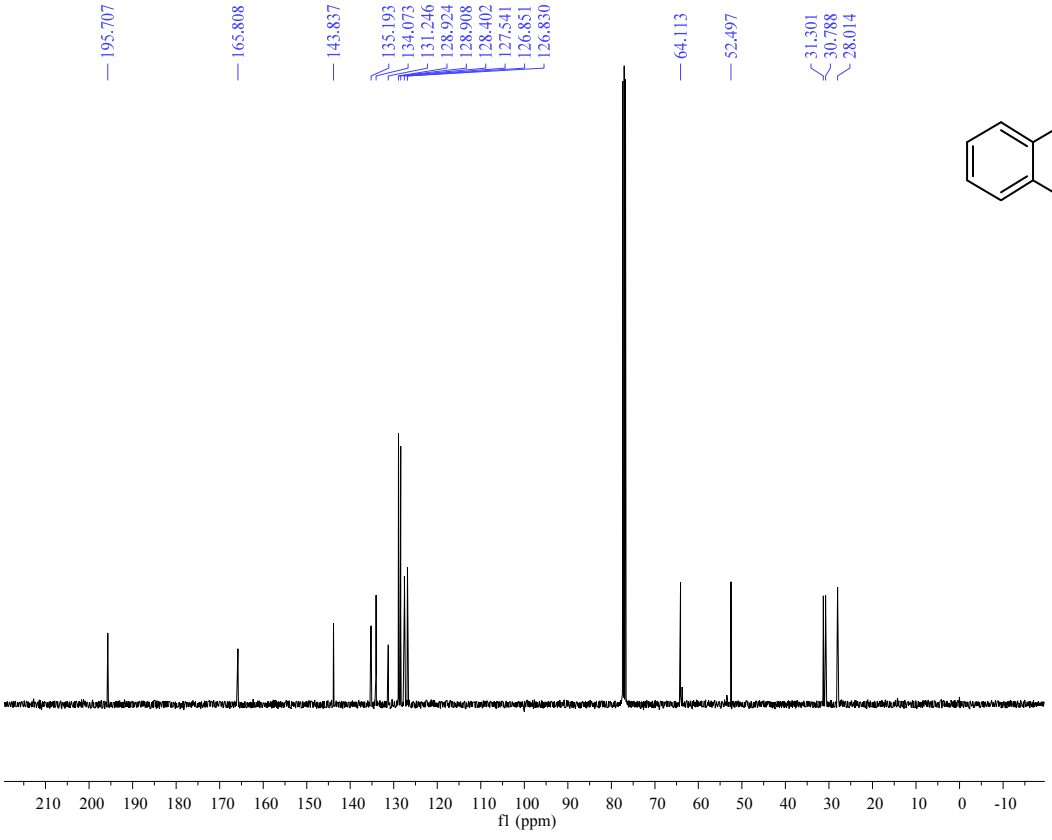
4b

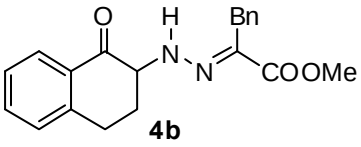
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-12-28T16:37:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 294 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 1.56
Ph1: 18.24





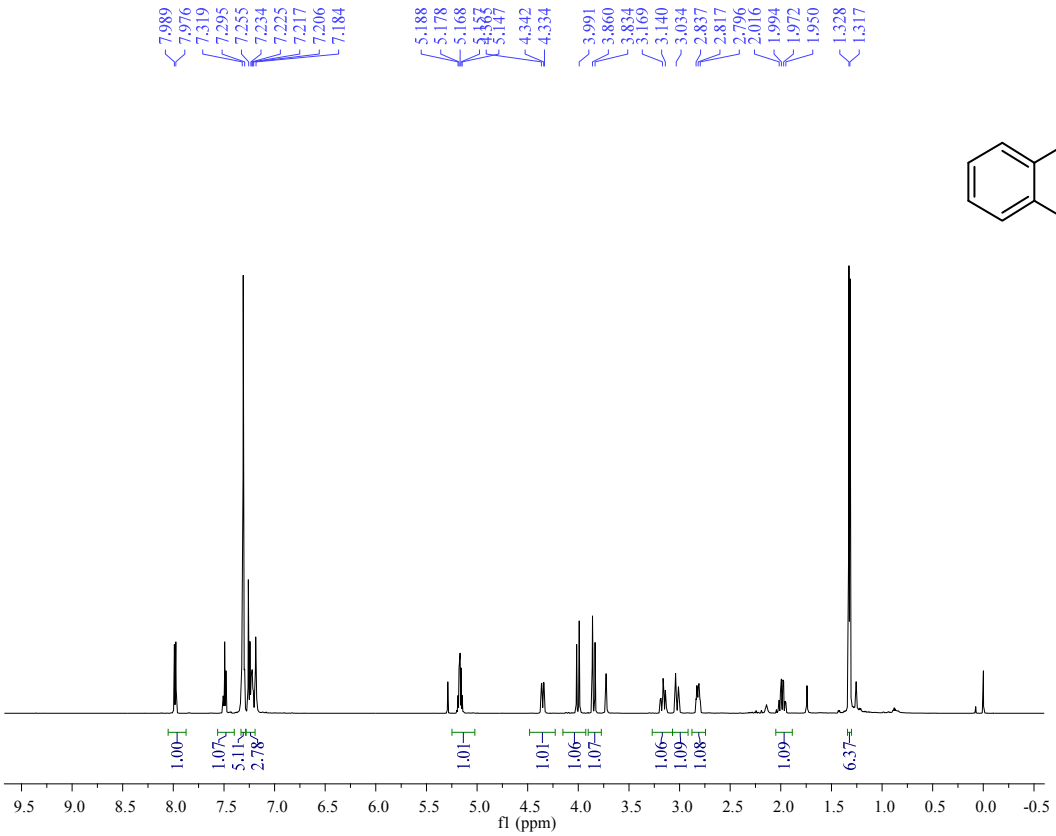
4b

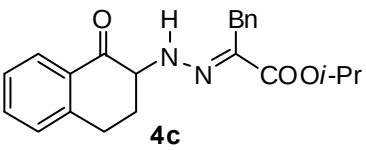
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-12-28T17:06:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.5 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -147.71
Ph1: 78.62





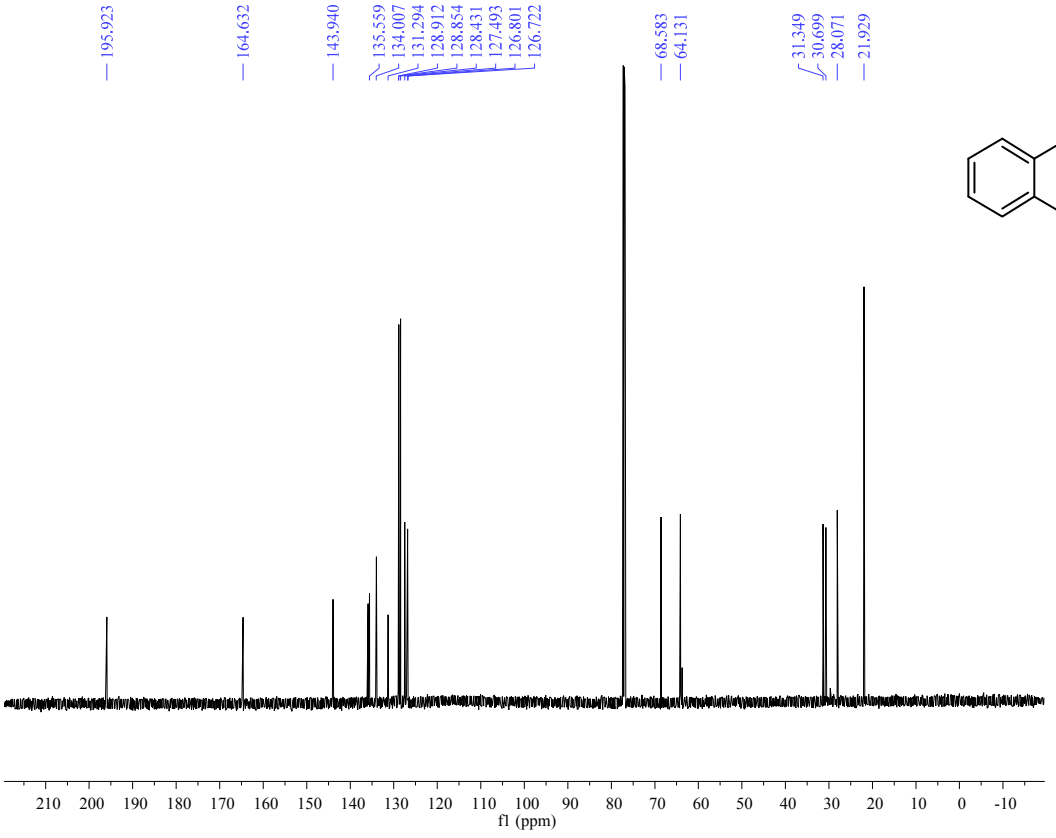
4c

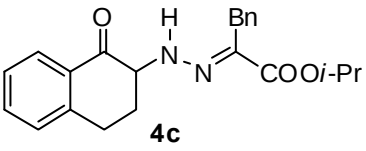
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-12-27T16:05:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 294.2 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 26.65
Ph1: 29.85





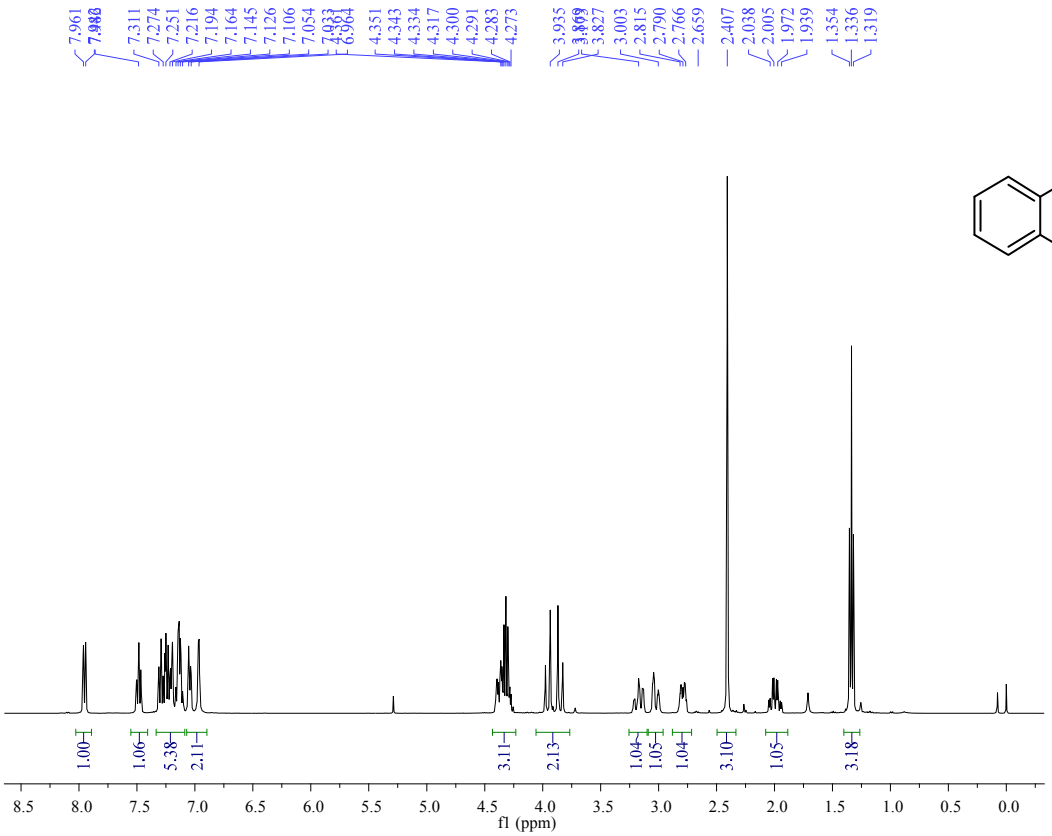
4c

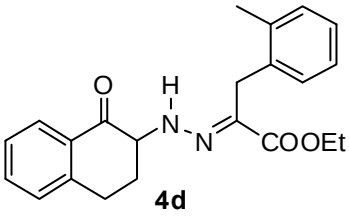
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-12-27T16:17:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 223
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 294.3 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 65.27
Ph1: 71.41





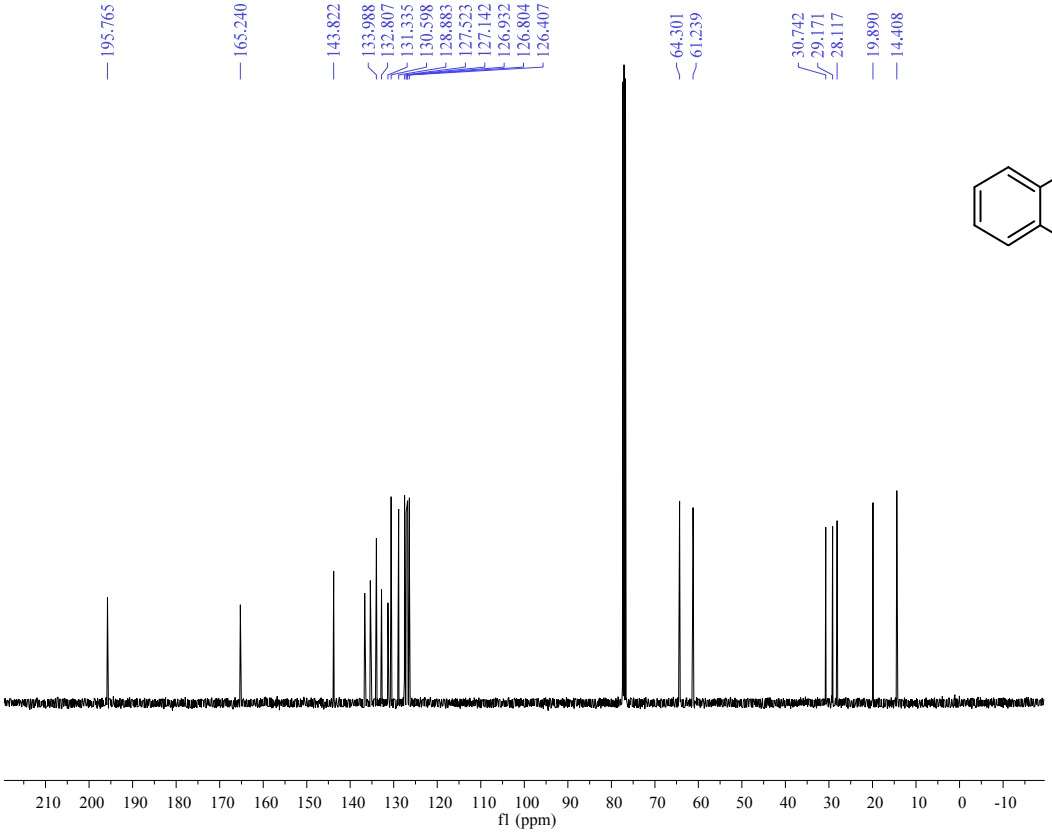
4d

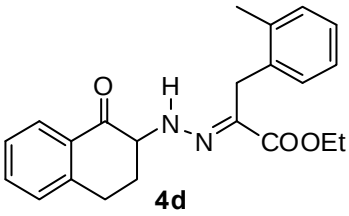
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T21:06:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.5 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -4.24
Ph1: 23.25





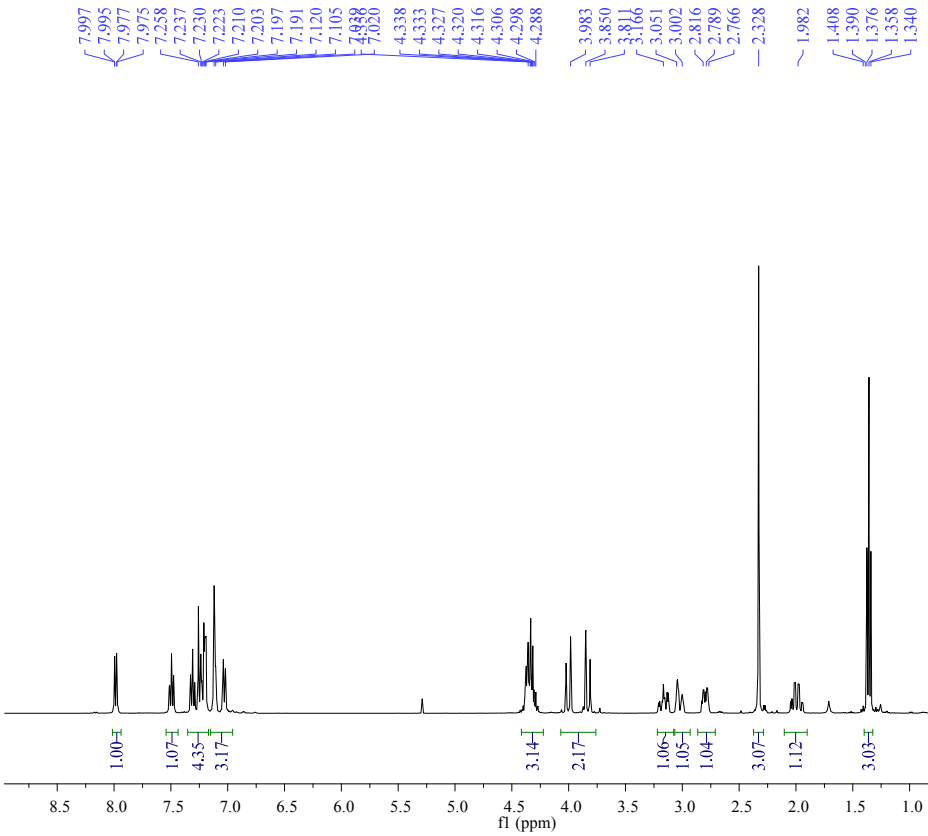
4d

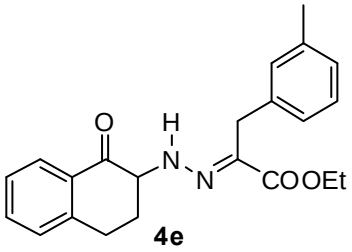
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T21:21:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.5 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -116.27
Ph1: 86.72





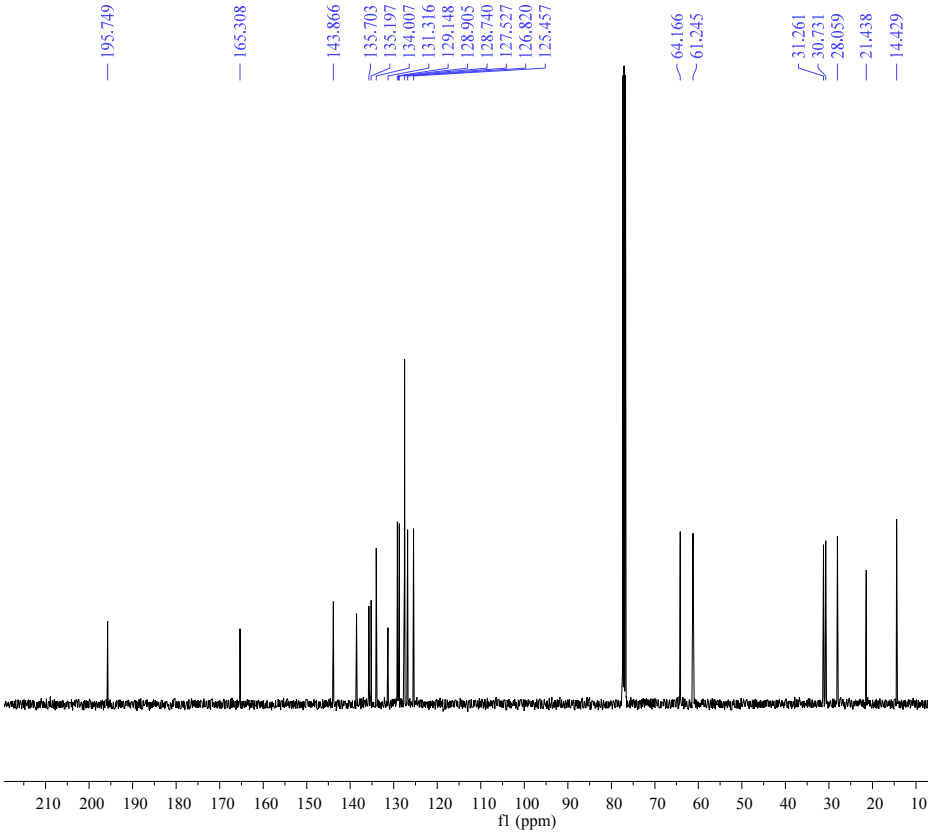
4e

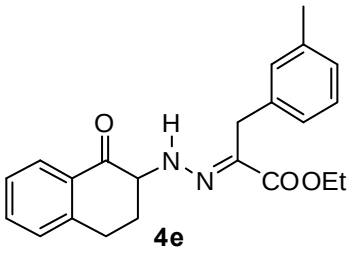
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T21:26:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.6 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -4.05
Ph1: 22.08





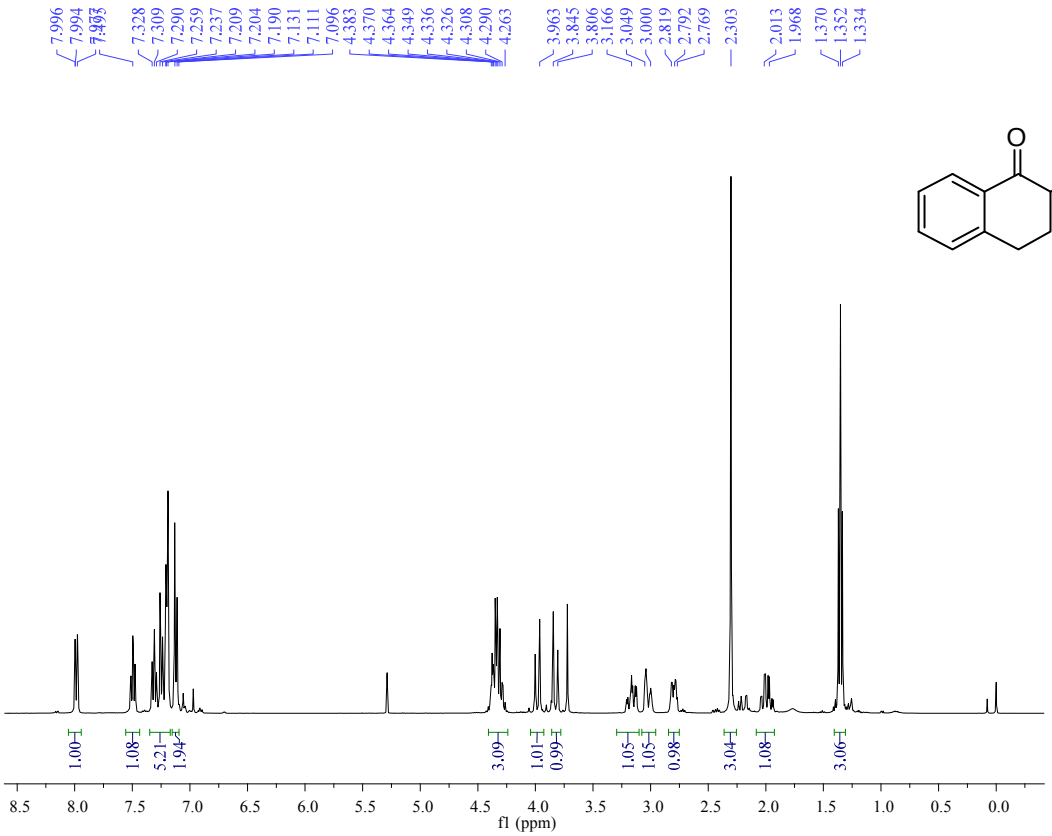
4e

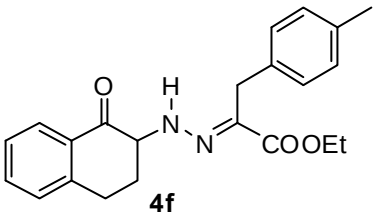
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T21:41:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.5 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 2.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -101.80
Ph1: 58.34





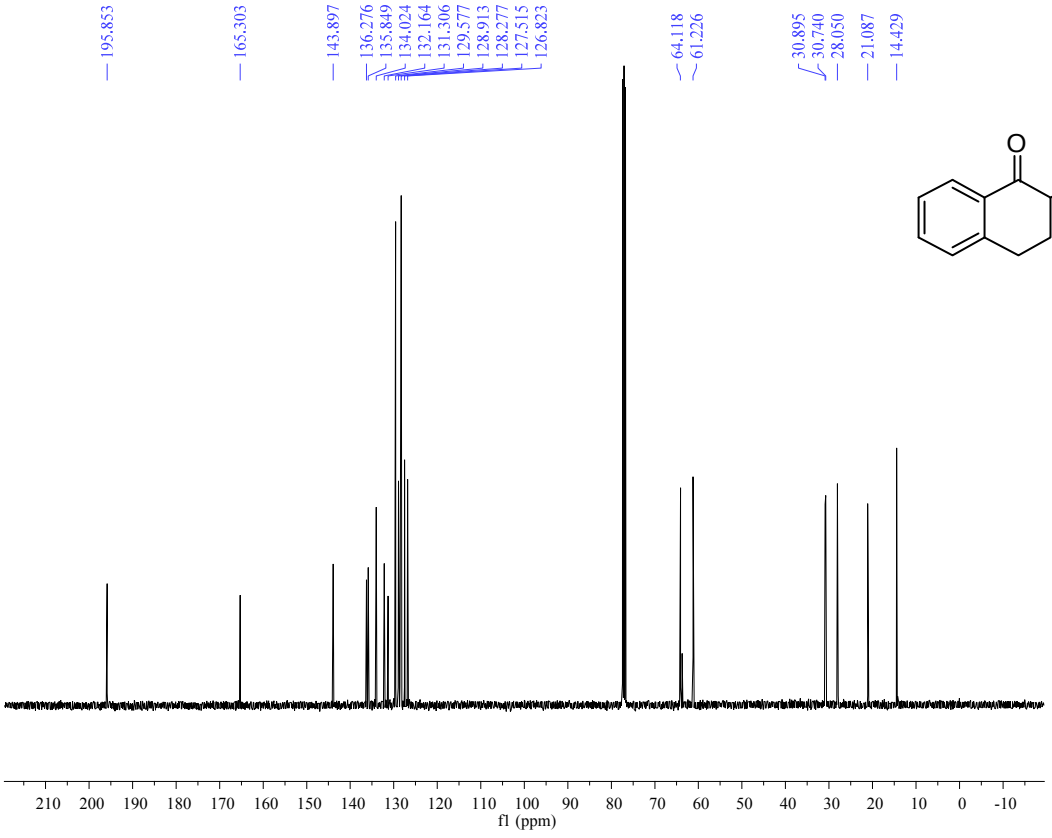
4f

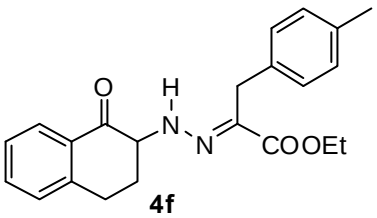
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T21:45:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 300 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -4.22
Ph1: 20.23





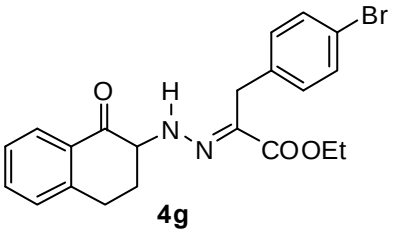
4f

Current Data Parameters

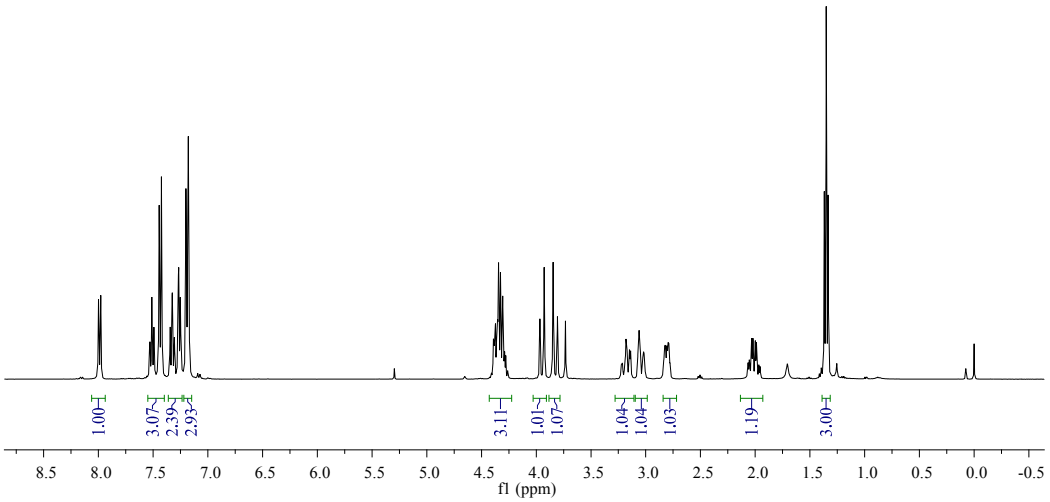
F2 - Acquisition Parameters
DATE: 2011-01-16T21:46:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 525
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.8 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -102.68
Ph1: 72.62



4g

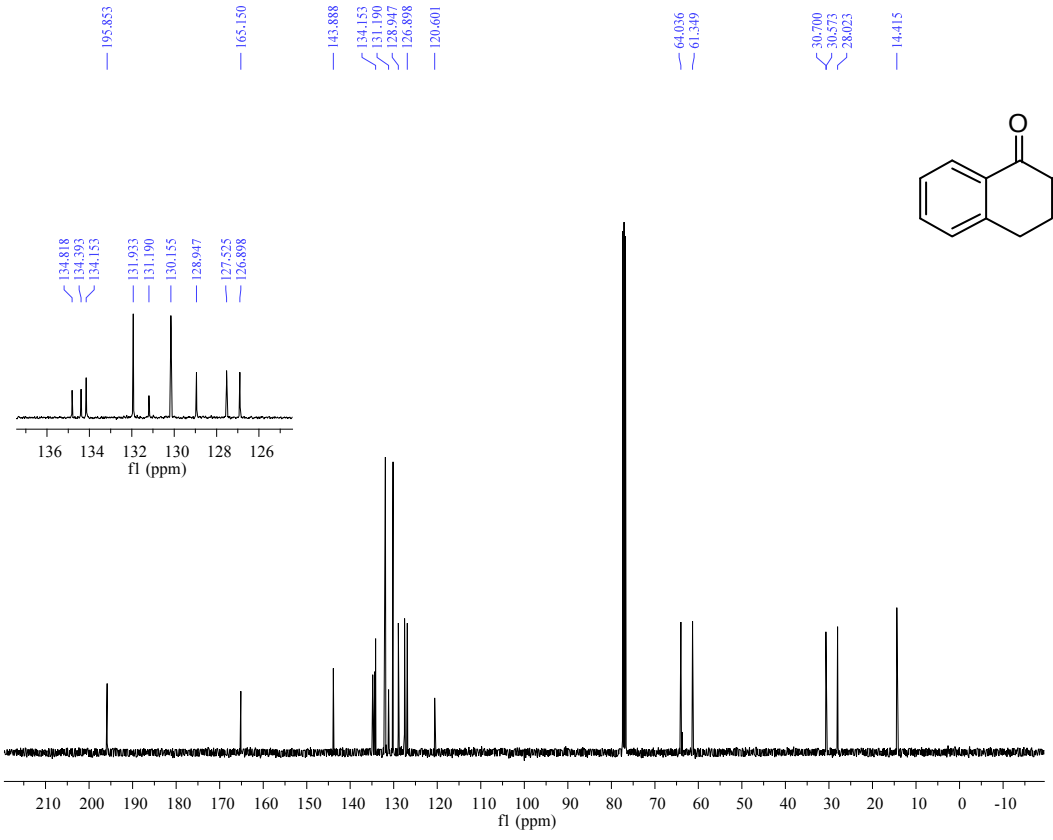


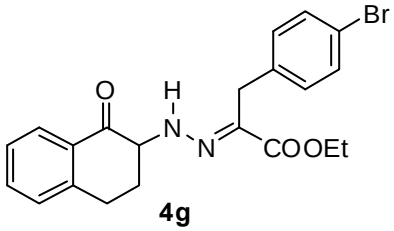
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T22:56:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.3 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -2.64
Ph1: 18.87





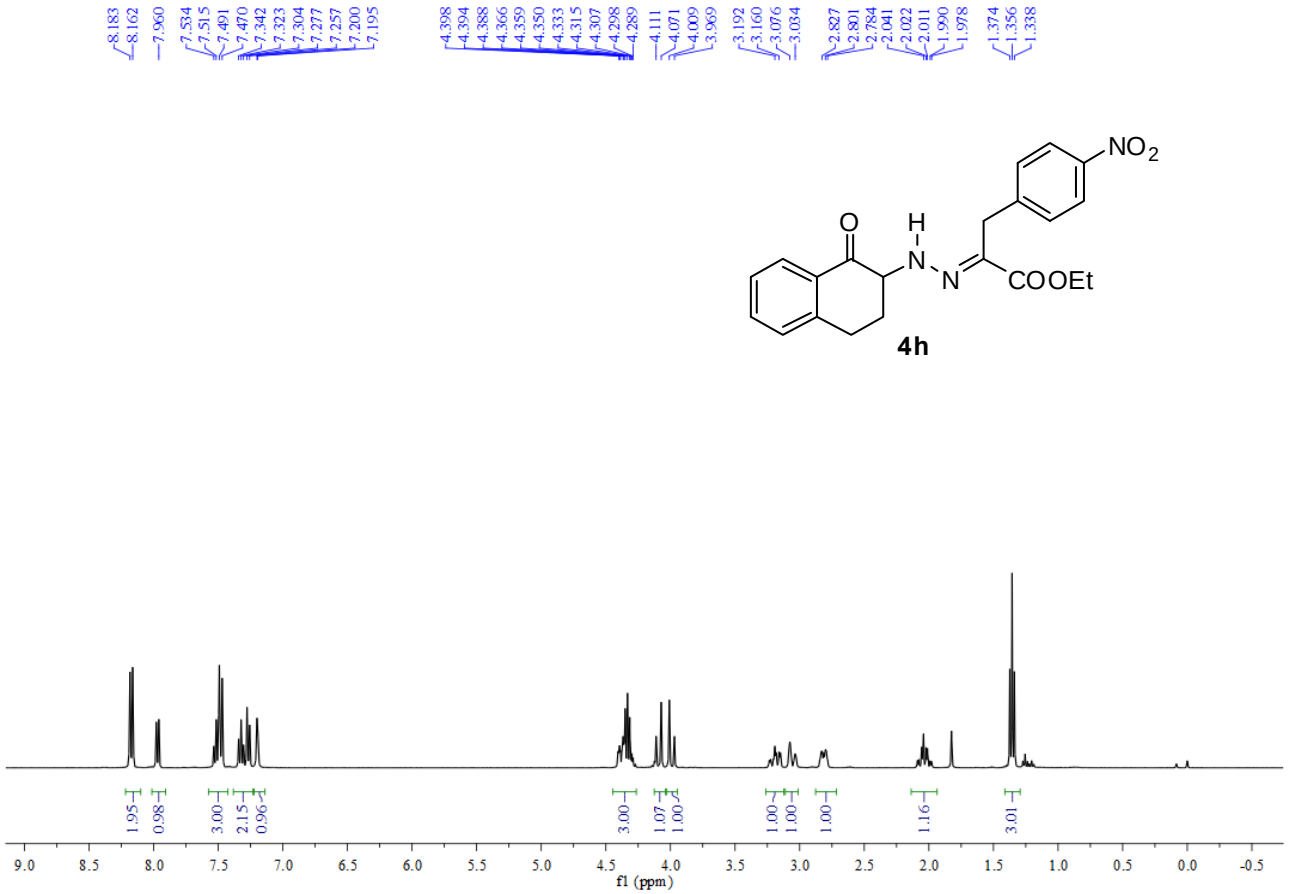
4g

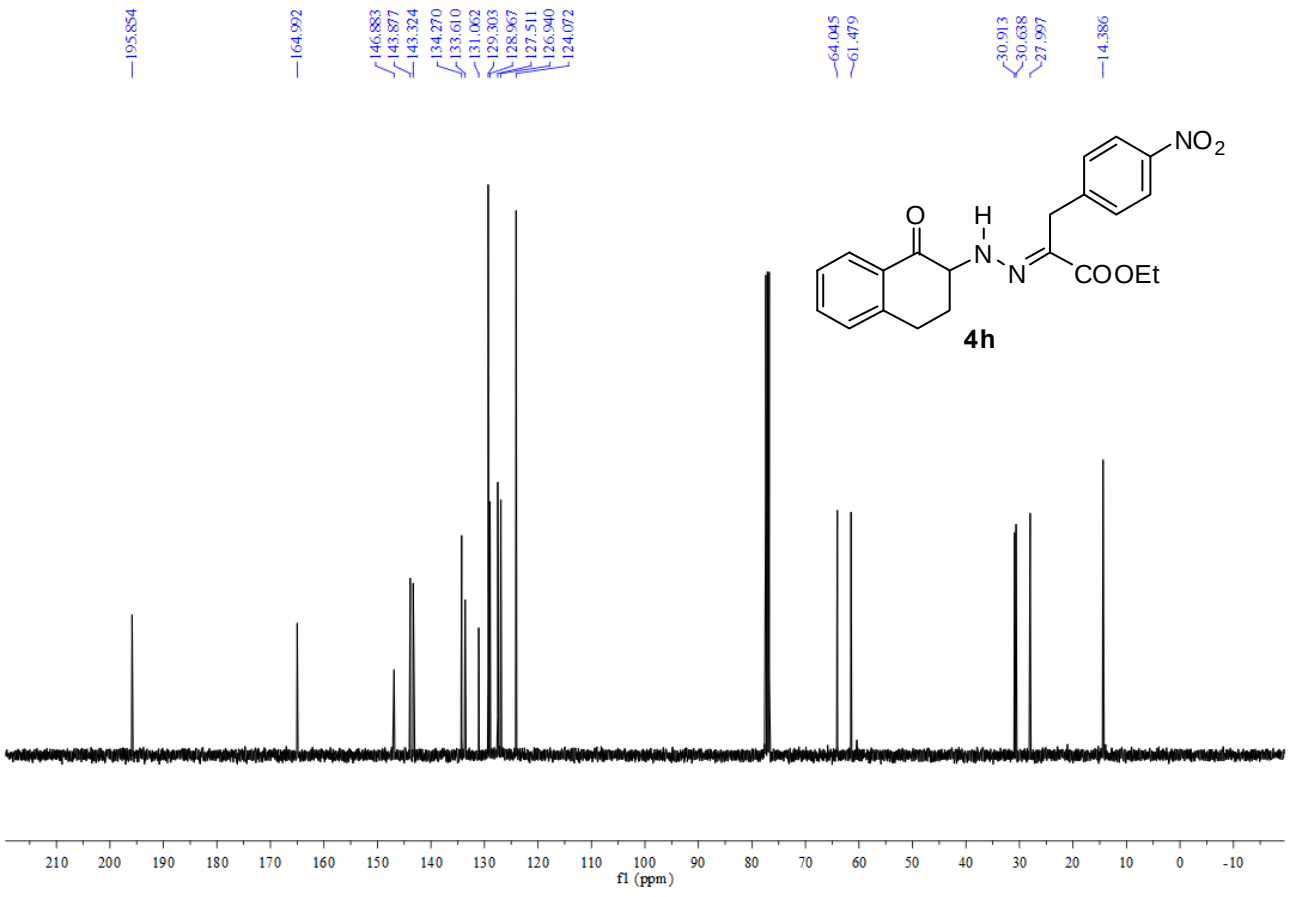
Current Data Parameters

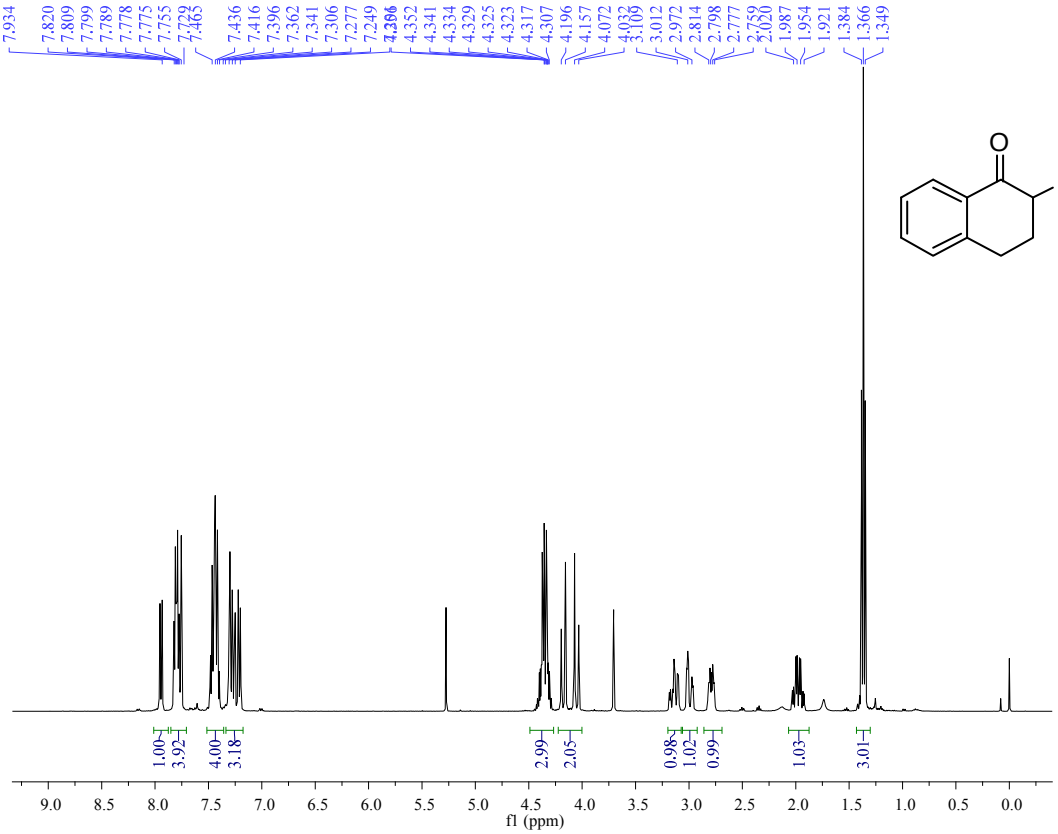
F2 - Acquisition Parameters
DATE: 2011-01-16T23:02:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 255
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.8 C

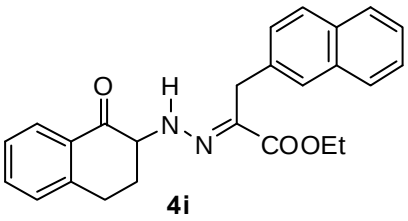
======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -108.32
Ph1: 70.89


8.183
8.162
7.960
7.534
7.515
7.491
7.470
7.342
7.323
7.304
7.277
7.257
7.200
7.195
4.398
4.394
4.388
4.366
4.359
4.350
4.333
4.315
4.307
4.298
4.289
4.111
4.071
4.009
3.969
3.192
3.160
3.076
3.034
2.827
2.801
2.784
2.041
2.022
2.011
1.990
1.978
1.374
1.356
1.338
NO2
O
H
N
N
COOEt
4h
1.95
0.98
3.00
2.15
0.96
3.00
1.07
1.00
1.00
1.00
1.00
1.16
3.01
f1 (ppm)


195.854
164.992
146.883
143.877
143.324
134.270
133.610
131.062
129.303
128.967
127.511
126.940
124.072
64.045
61.479
30.913
30.638
27.997
14.386
NO2
O
H
N
N
COOEt
4h
f1 (ppm)





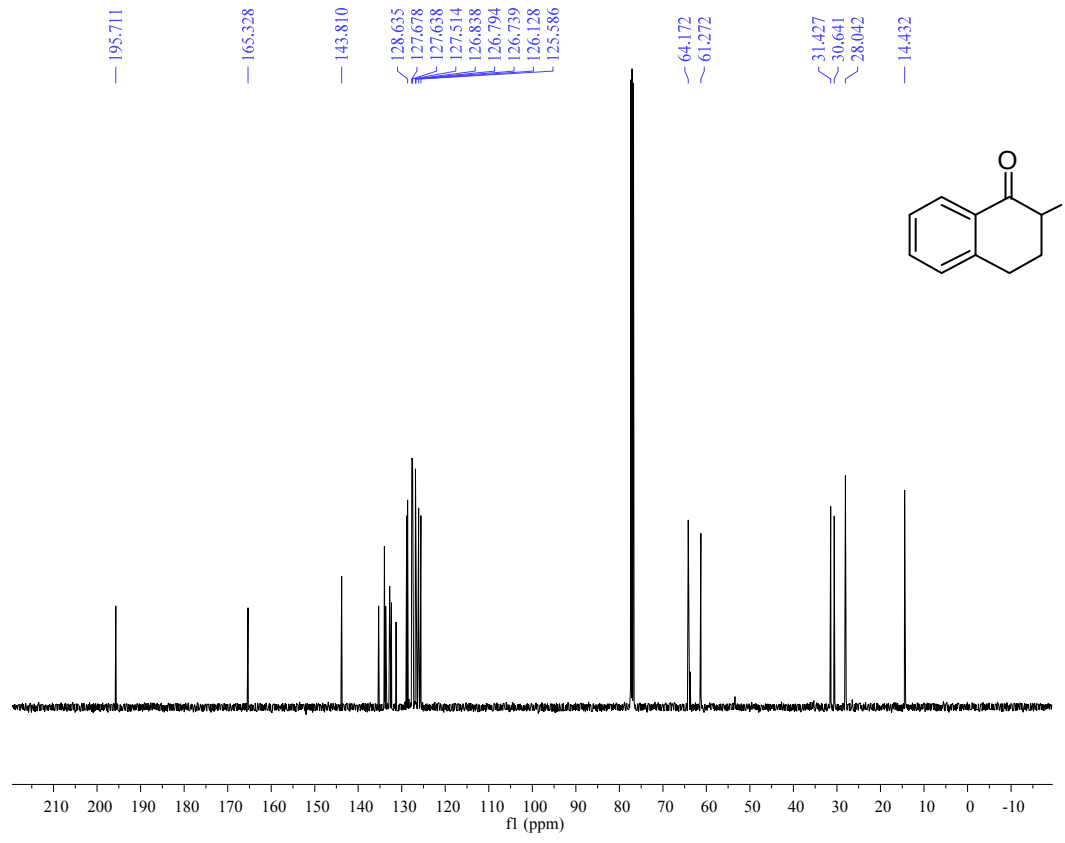
4i

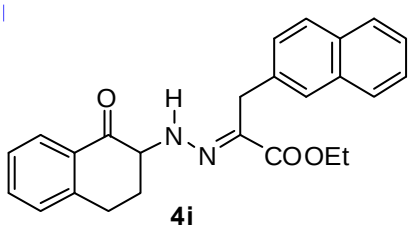
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T23:16:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.1 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -6.03
Ph1: 20.62





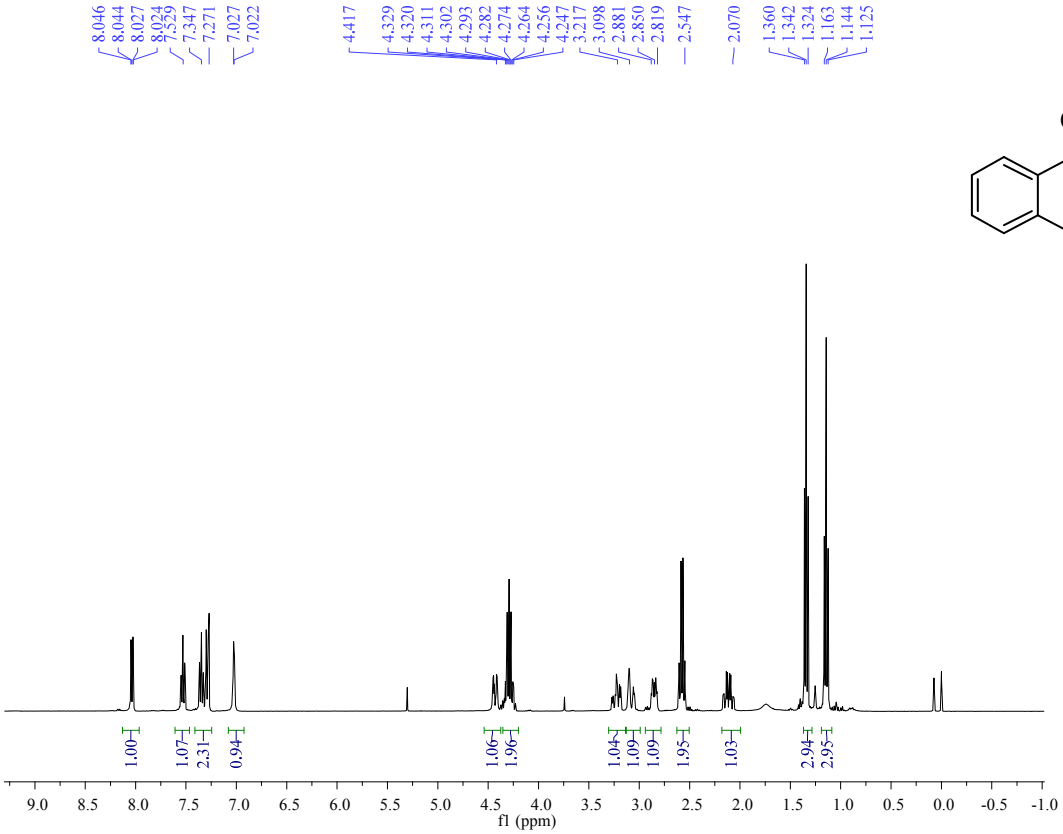
4i

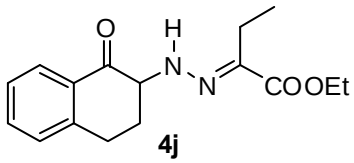
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-16T23:46:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.9 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -105.91
Ph1: 72.03





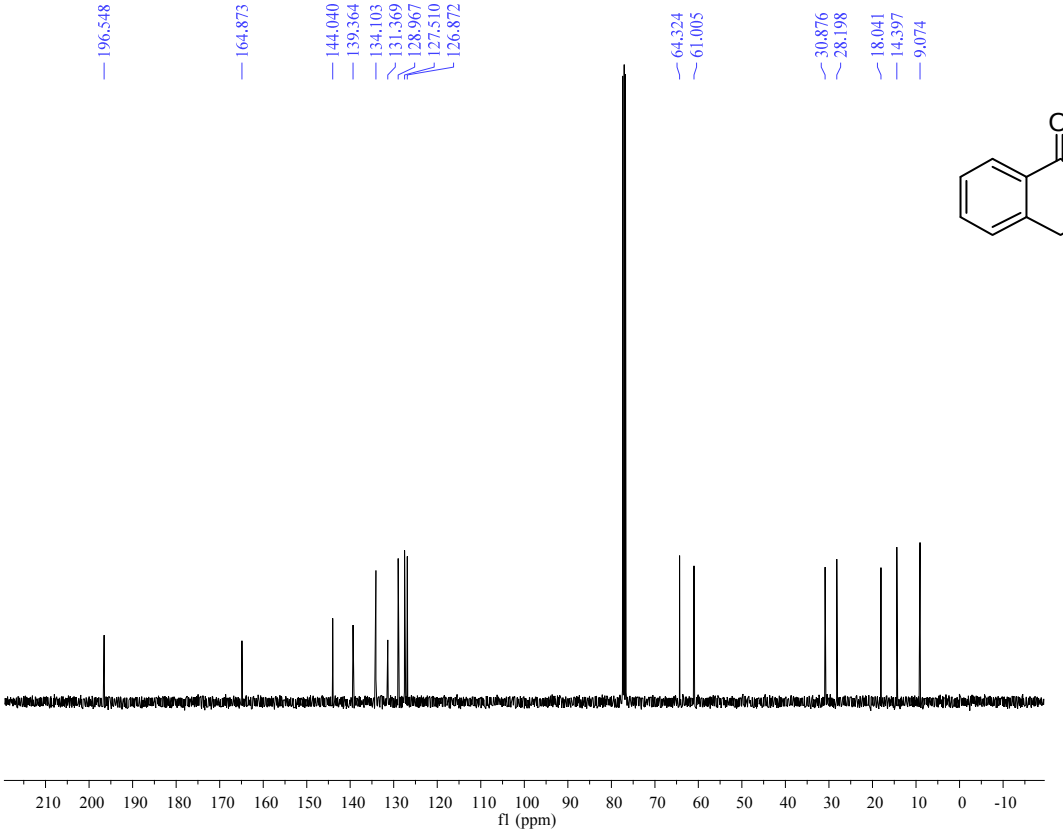
4j

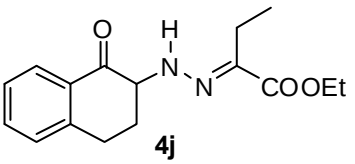
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T15:32:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 292.2 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 0.62
Ph1: 19.00





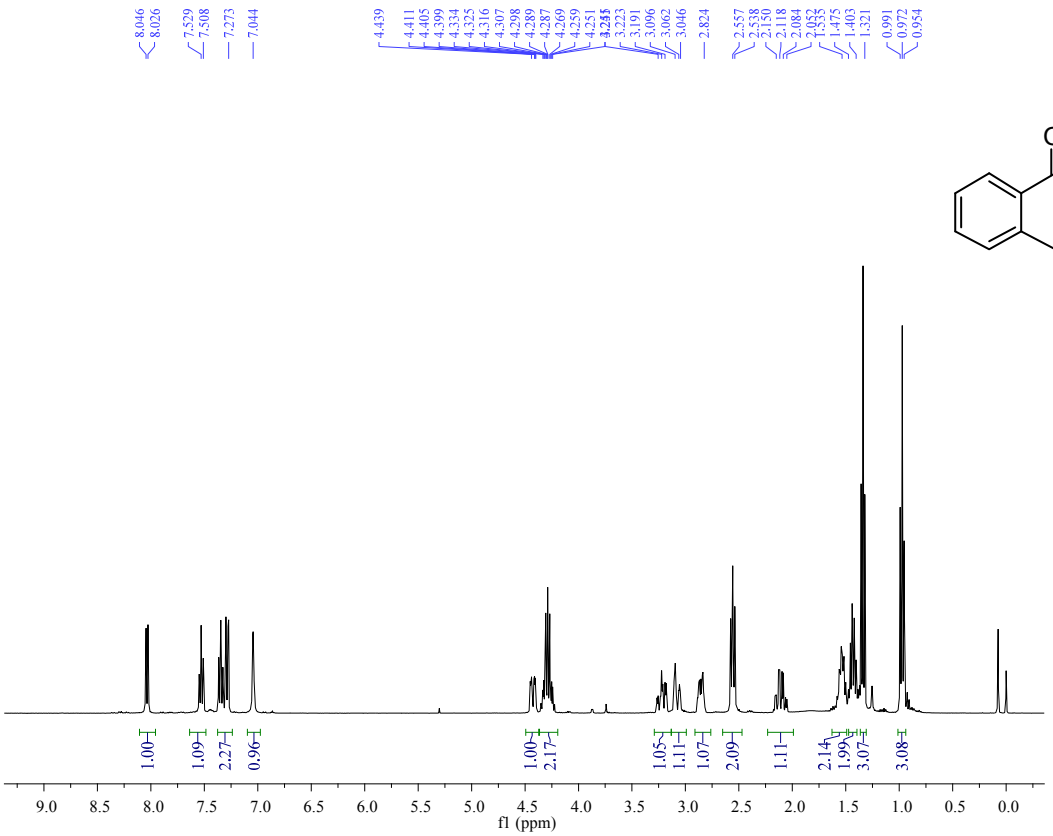
4j

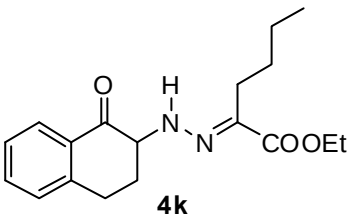
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T15:44:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 198
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 292.9 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -114.87
Ph1: 68.94





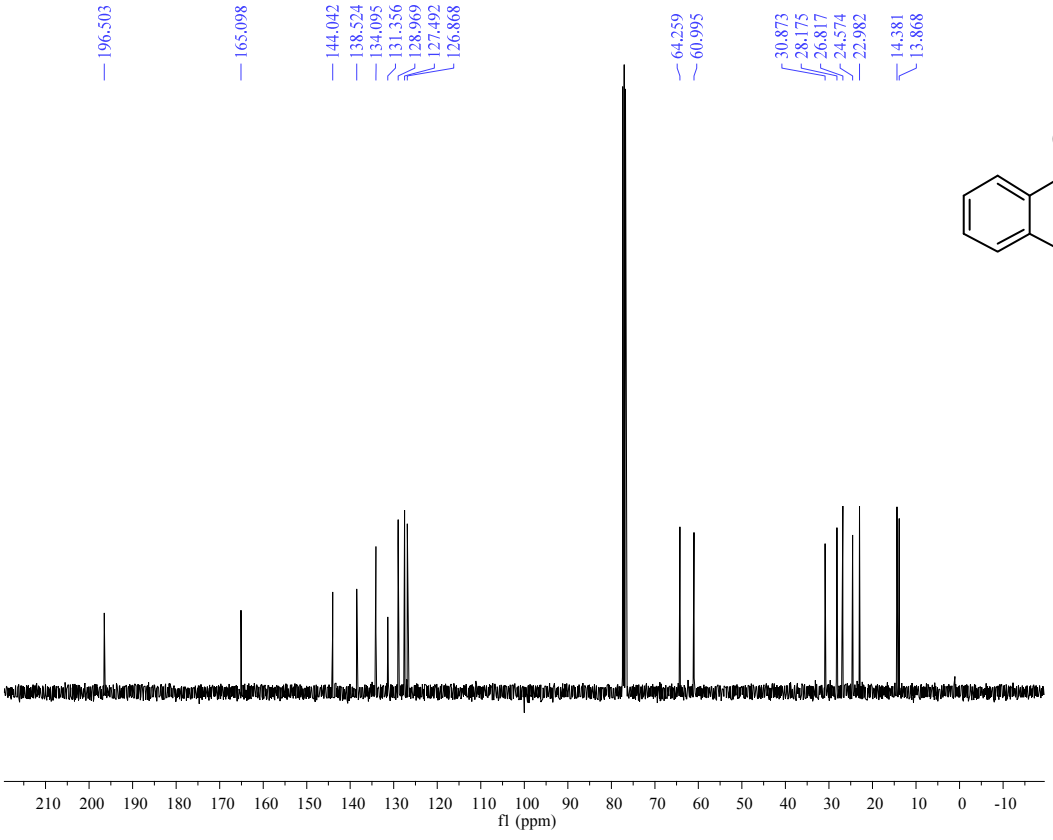
4k

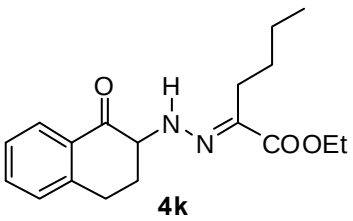
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T15:49:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 292.3 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -2.50
Ph1: 20.53





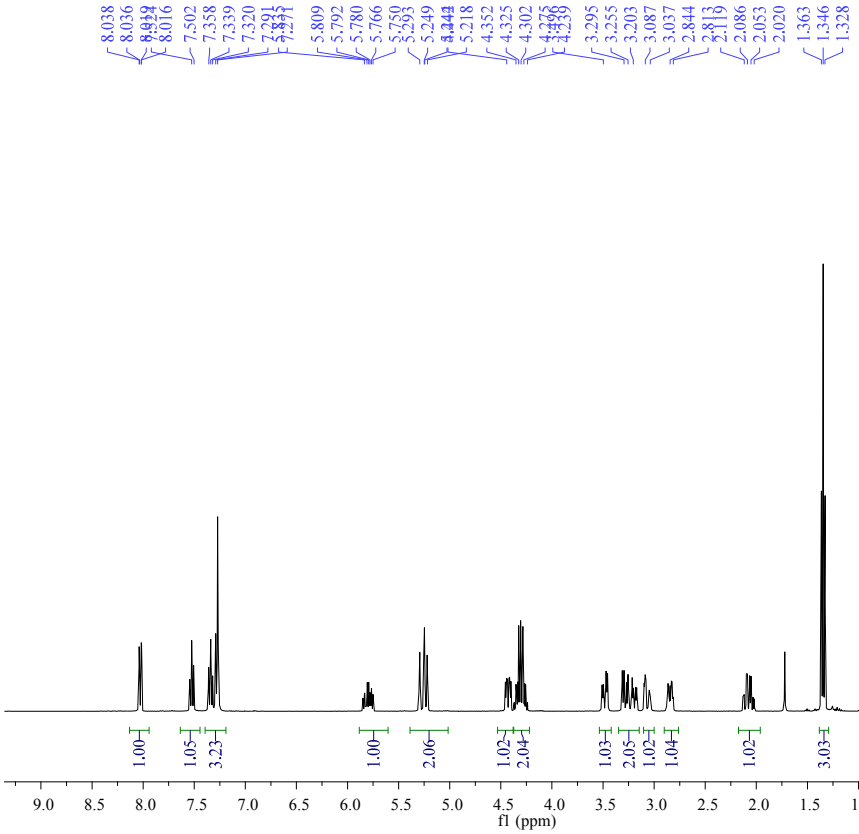
4k

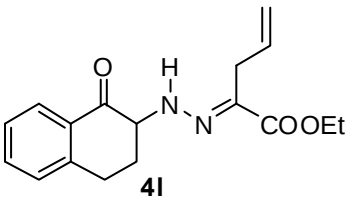
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T15:54:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 101
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.8 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -120.62
Ph1: 85.74





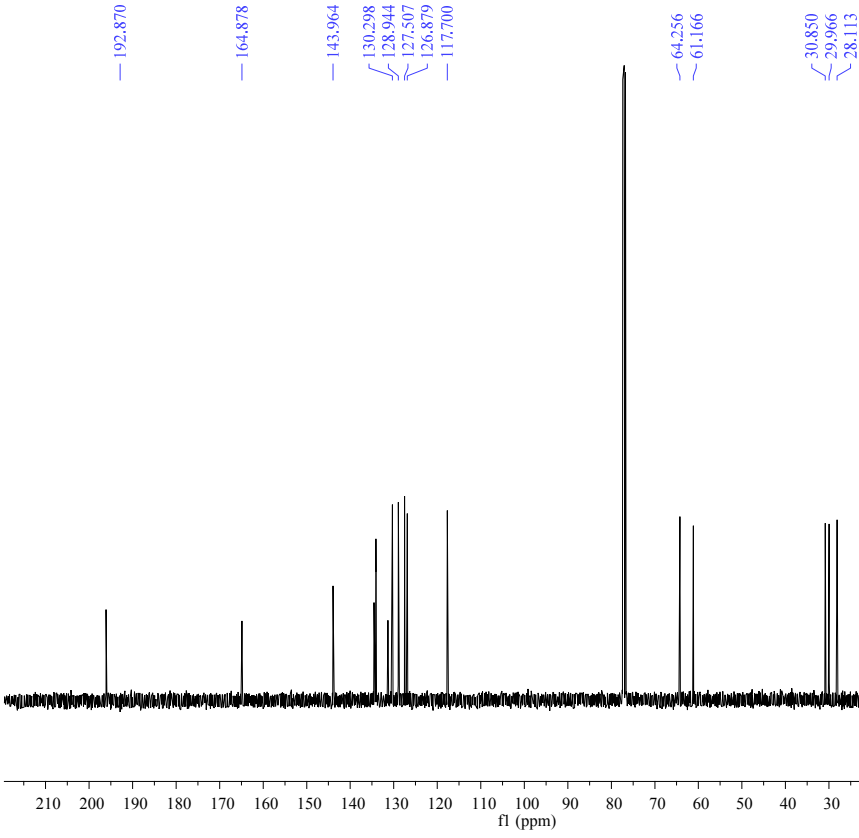
4l

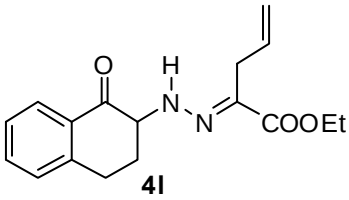
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-02-18T17:34:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.9 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 5.01
Ph1: 19.08





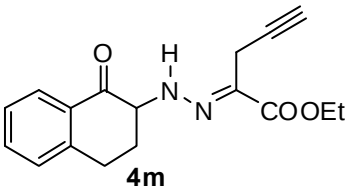
4l

Current Data Parameters

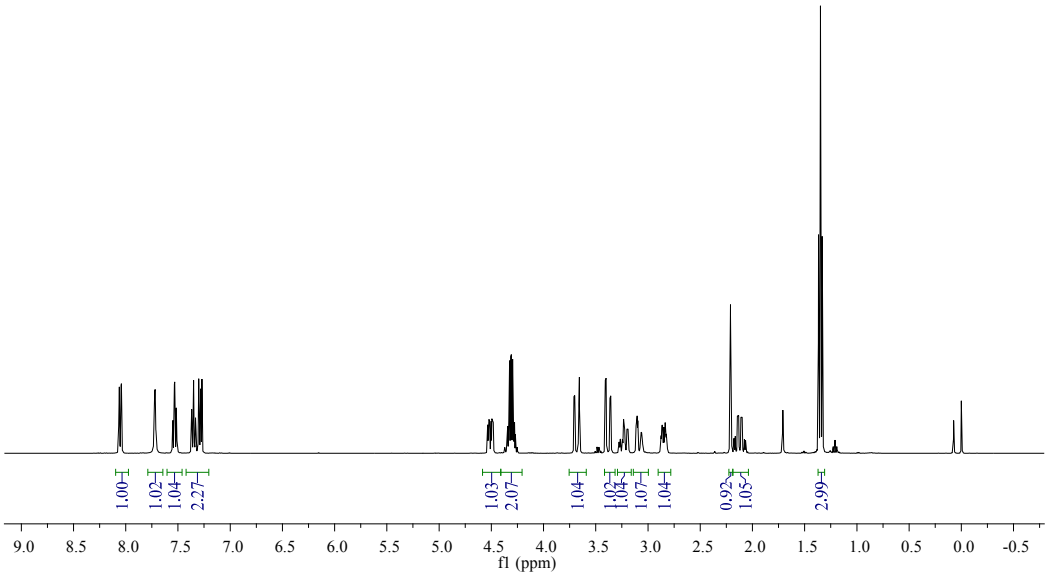
F2 - Acquisition Parameters
DATE: 2011-02-18T17:40:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 114
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.5 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -110.63
Ph1: 79.66



4m

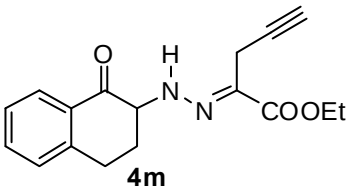


Current Data Parameters

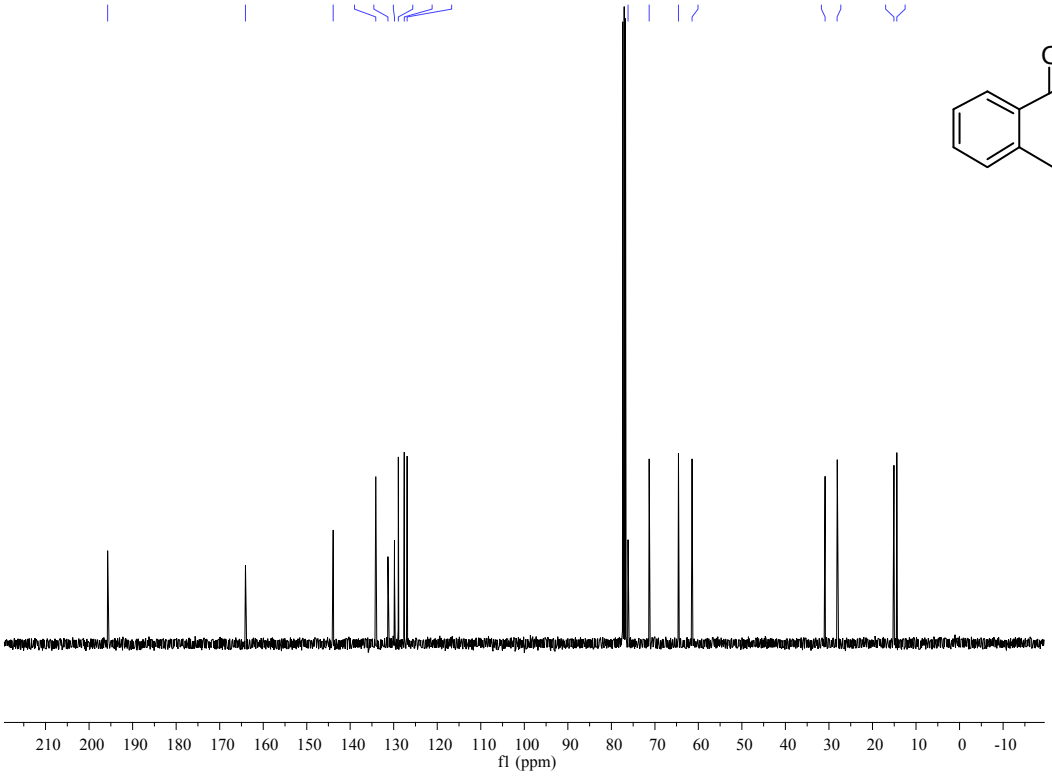
F2 - Acquisition Parameters
DATE: 2011-02-18T17:18:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 294.3 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 6.54
Ph1: 20.56



4m

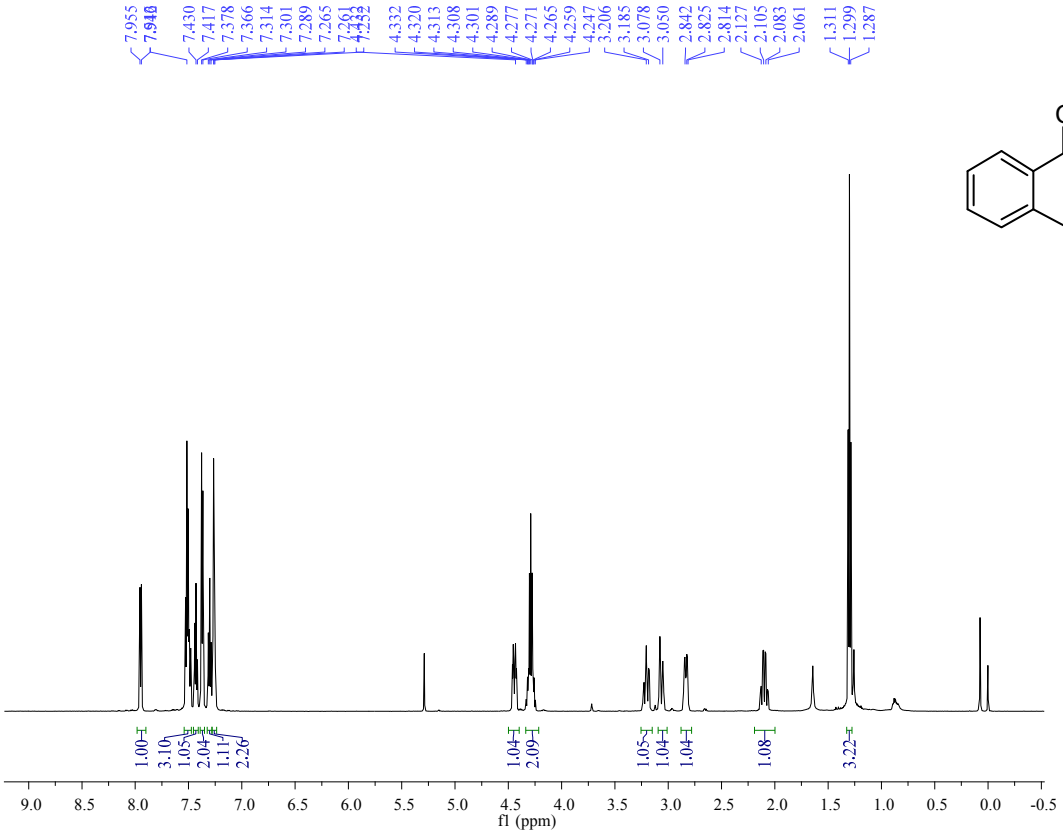


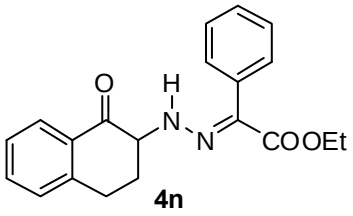
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-02-18T17:29:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 183
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.7 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -105.72
Ph1: 75.06





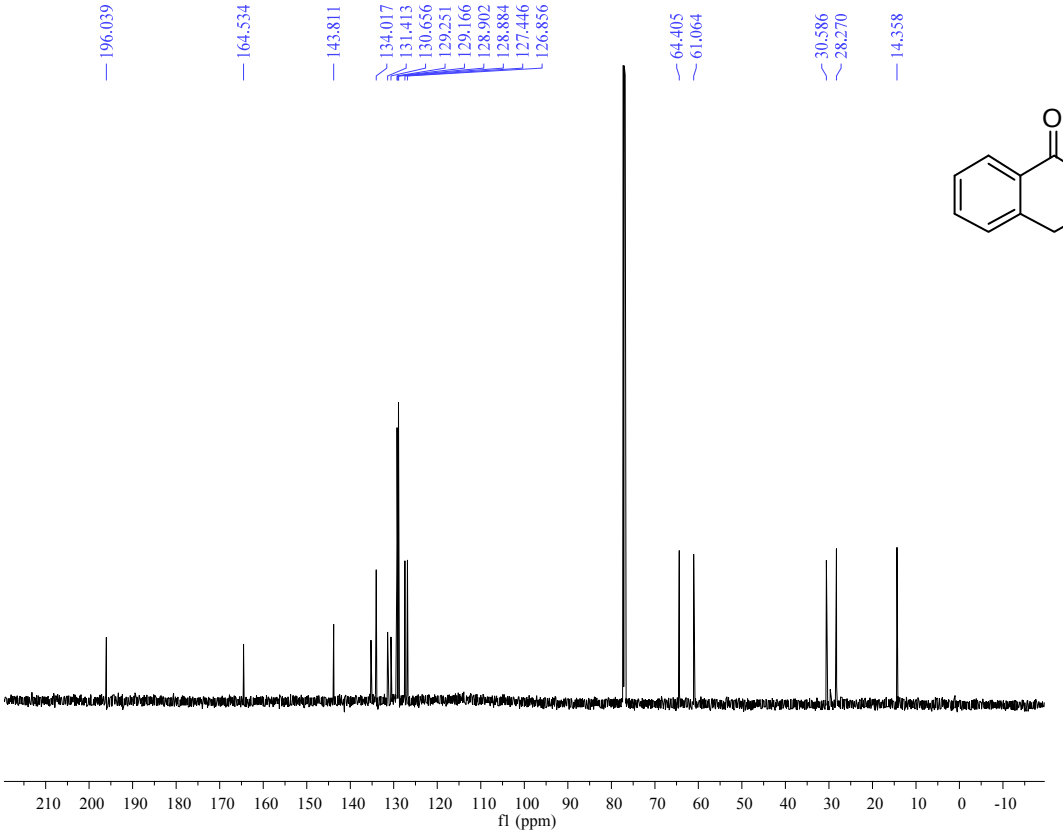
4n

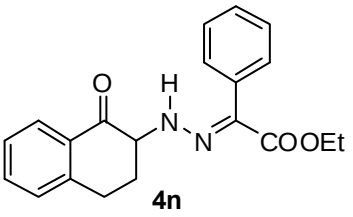
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-22T09:50:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 300.1 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.6 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -115.36
Ph1: 30.50





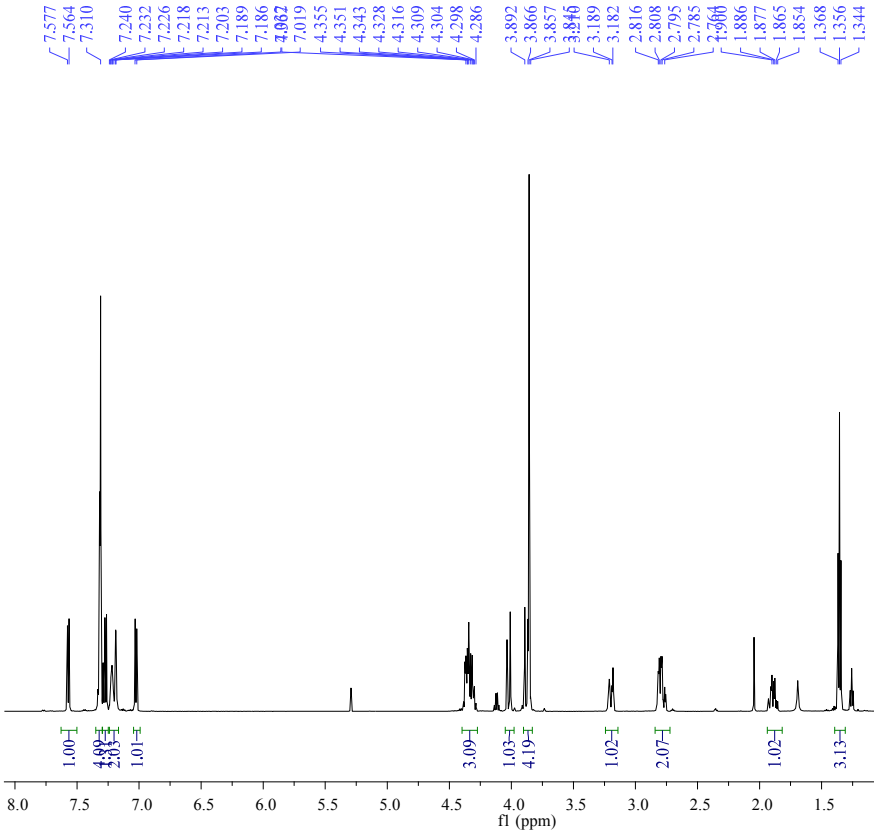
4n

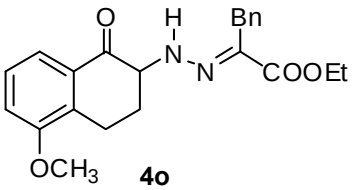
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-22T10:03:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 255
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 299.9 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 2.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 85.00
Ph1: 52.88





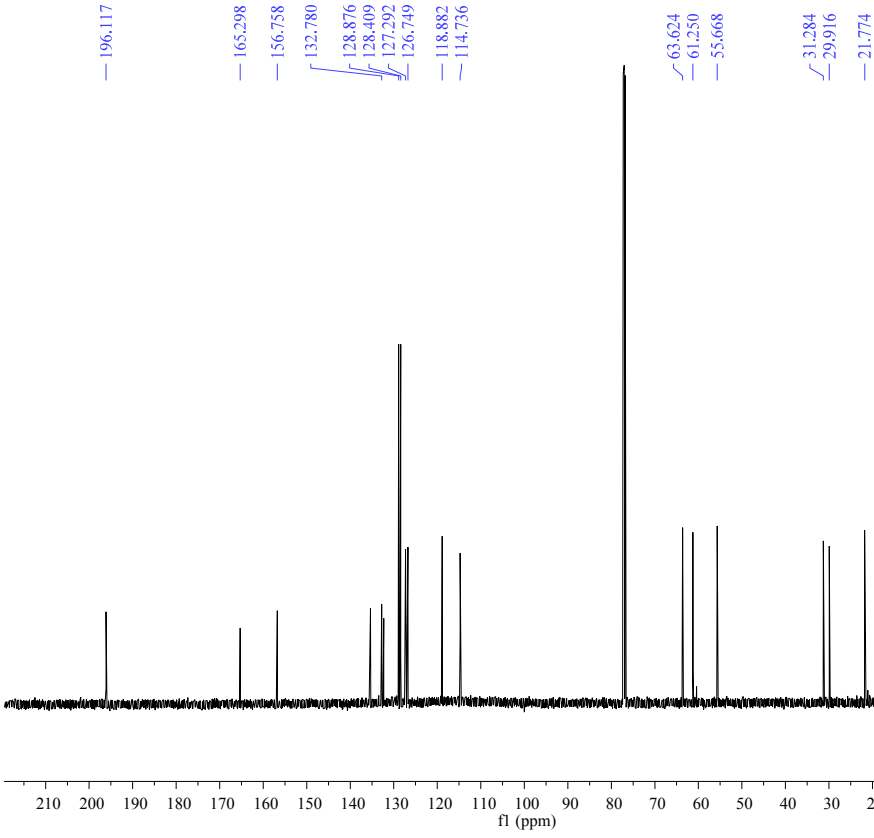
4o

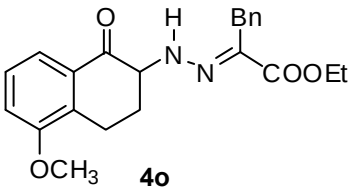
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T14:25:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 293.1 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 85.78
Ph1: 33.25





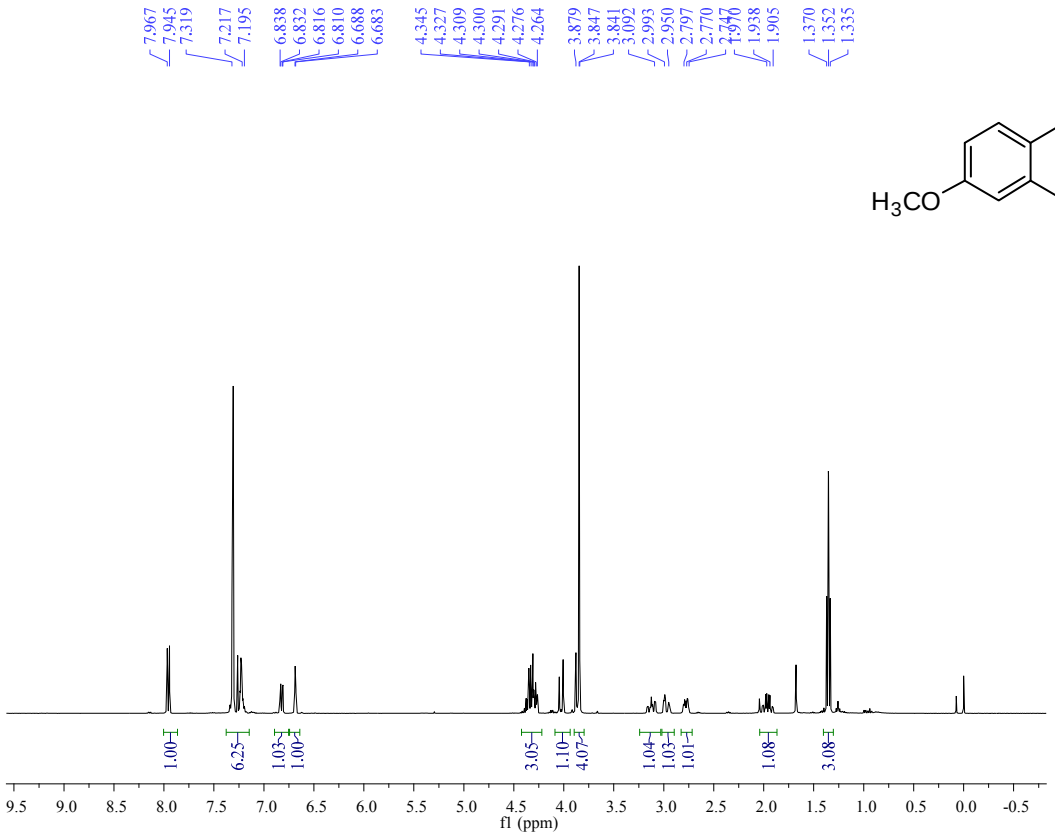
4o

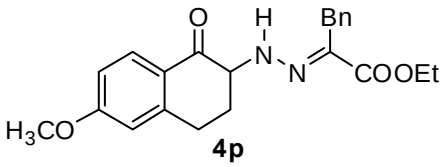
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T14:40:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 296
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 293.1 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 74.21
Ph1: 57.54





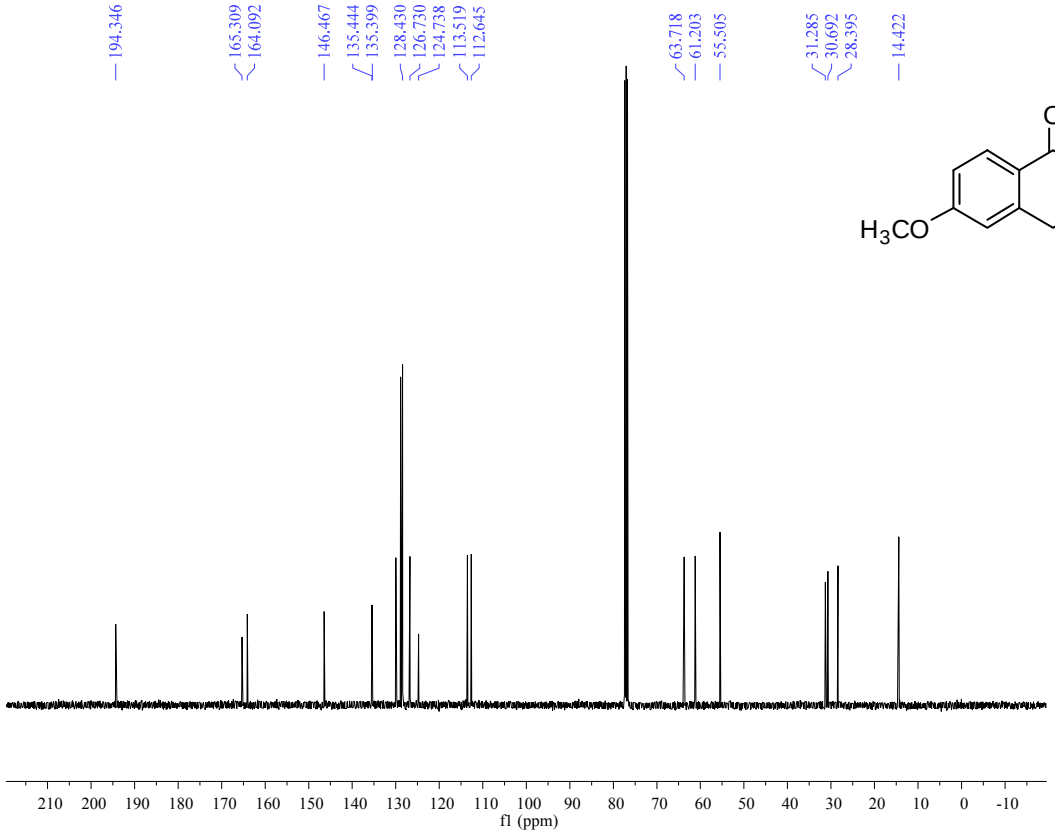
4p

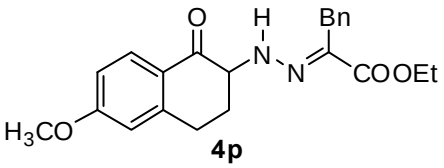
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-01T15:38:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 300 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -2.37
Ph1: 18.27





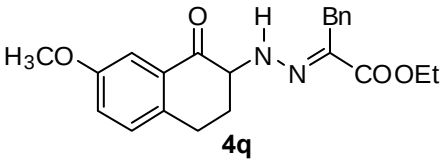
4p

Current Data Parameters

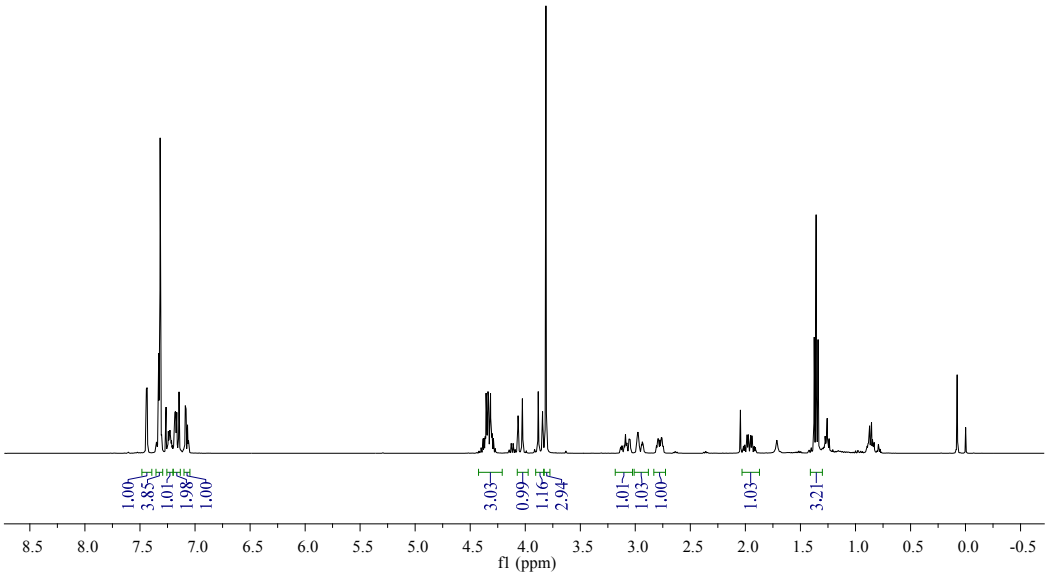
F2 - Acquisition Parameters
DATE: 2011-03-01T16:08:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -112.02
Ph1: 86.03



4q

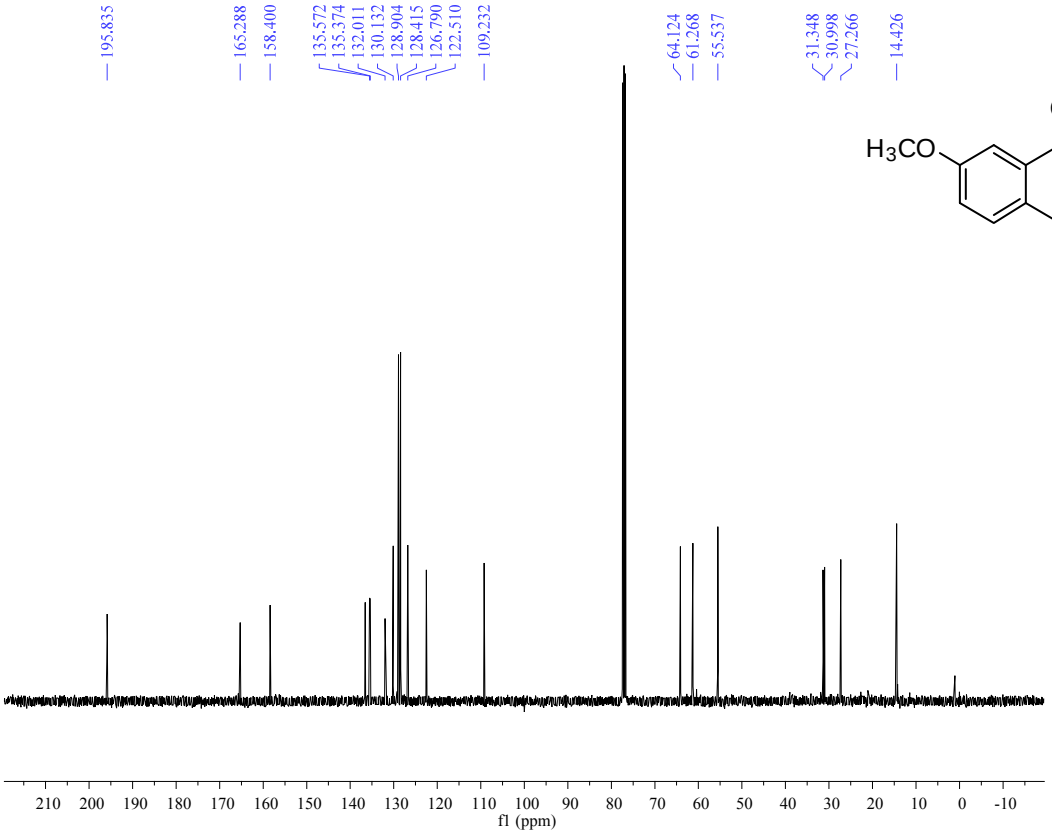


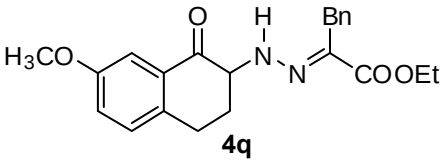
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T14:42:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 292.9 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 3.10
Ph1: 19.91





4q

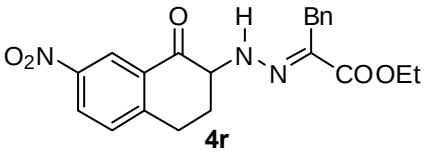
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T14:56:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 247
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.2 C

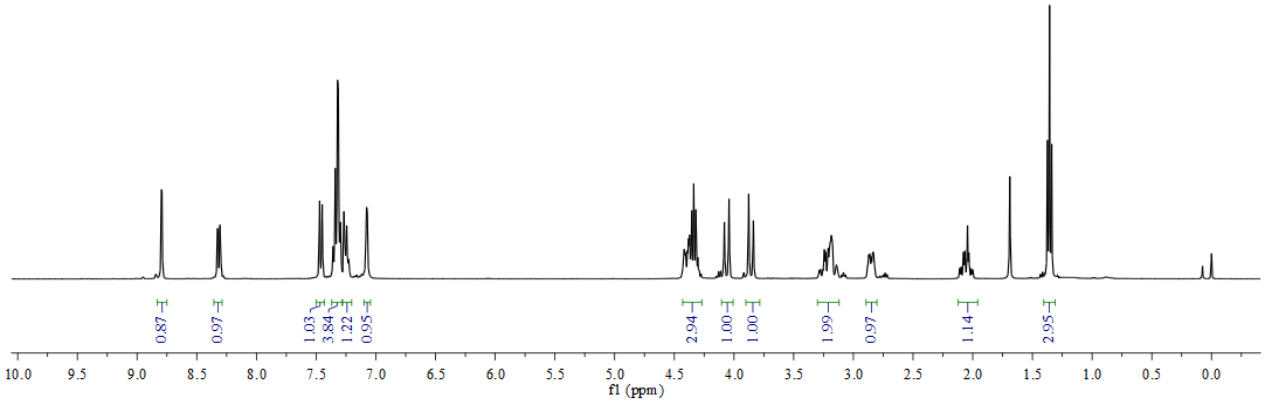
======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -116.41
Ph1: 73.52

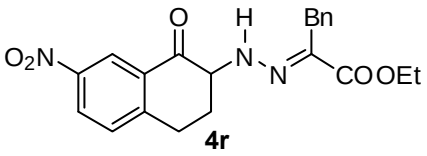

8.797
8.791
8.327
8.322
8.306
8.301
7.471
7.450
7.339
7.321
7.314
7.297
7.267
7.244
7.227
7.078
7.074
4.417
4.390
4.381
4.371
4.362
4.354
4.337
4.320
4.303
4.293
4.041
3.876
3.837
3.256
3.211
3.142
2.870
2.850
2.831
2.065
2.044
2.033
2.012
2.000
1.374
1.357
1.339


O
H
Bn
O2N
N
N
COOEt

4r

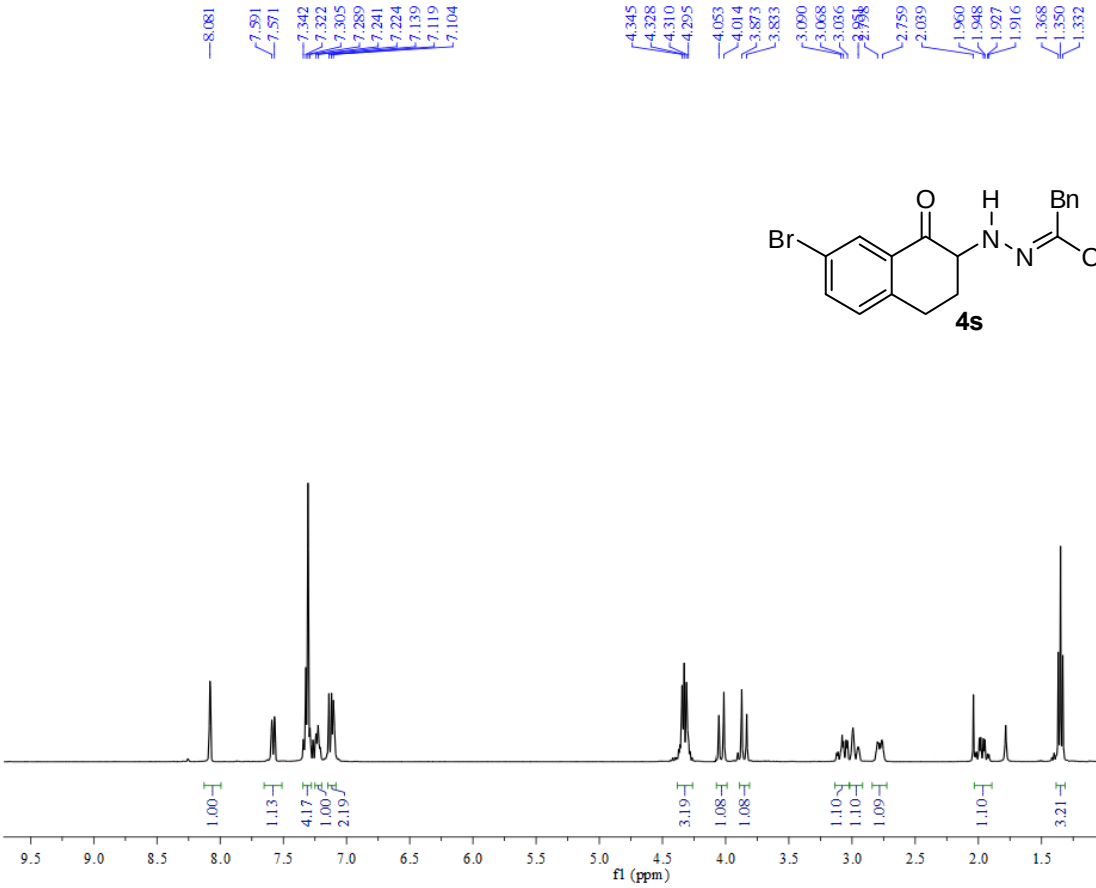

0.87
0.97
1.03
3.84
1.22
0.95
2.94
1.00
1.00
1.99
0.97
1.14
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

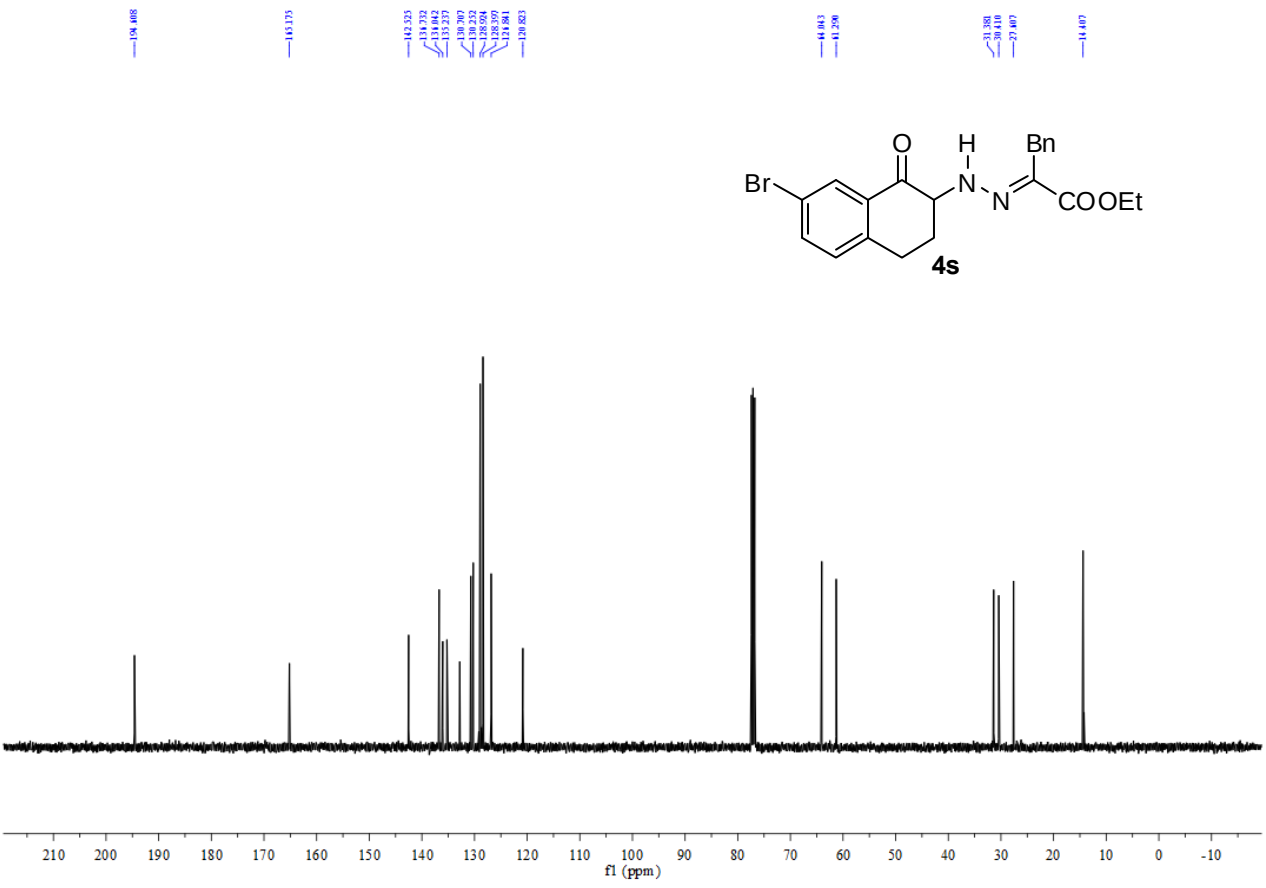

193.910
165.062
150.237
147.134
130.421
128.984
128.376
127.714
126.932
122.885
64.100
61.370
31.472
29.923
28.249
14.385

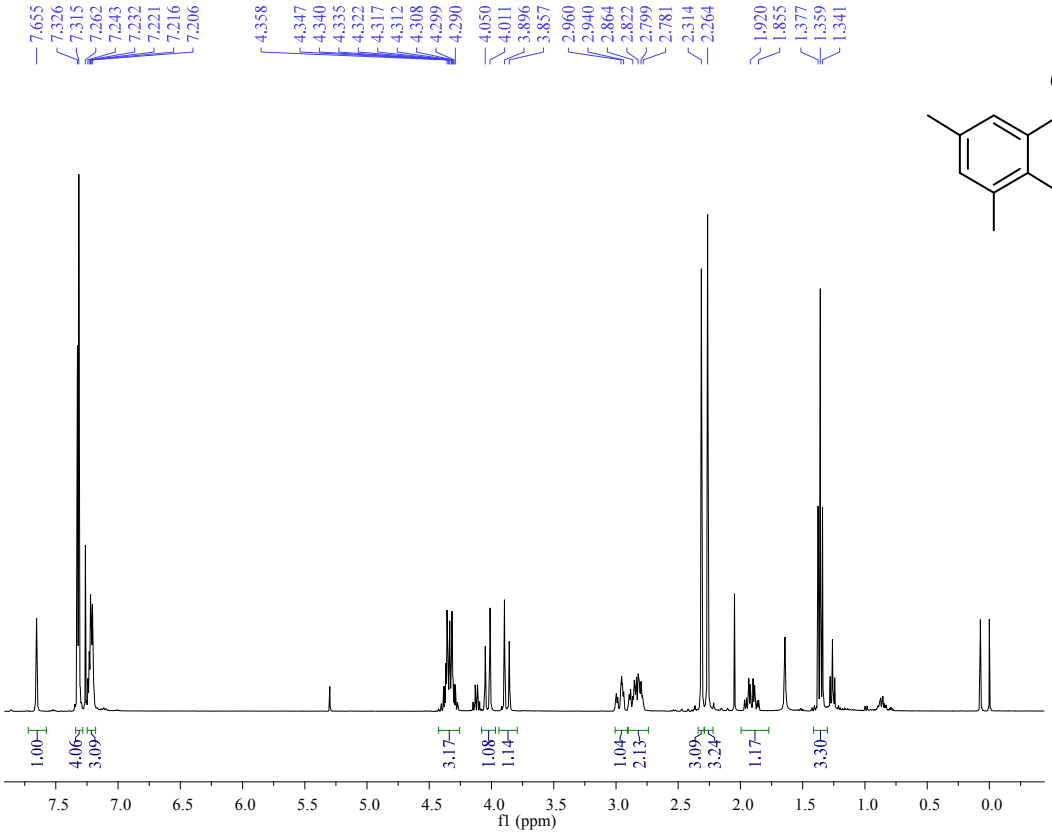

O
H
Bn
O2N
N
N
COOEt

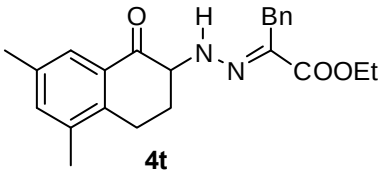
4r

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.081
7.591
7.571
7.342
7.322
7.305
7.289
7.241
7.224
7.139
7.119
7.104
4.345
4.328
4.310
4.295
4.053
4.014
3.873
3.833
3.090
3.068
3.036
2.759
2.039
1.960
1.948
1.927
1.916
1.368
1.350
1.332
Br
O
H
N
N
Bn
COOEt
4s
1.00
1.13
4.17
1.00
2.19
3.19
1.08
1.08
1.10
1.10
1.09
1.10
3.21
f1 (ppm)


194.468
143.175
142.535
134.732
134.364
133.237
130.707
130.252
128.594
128.397
124.041
120.823
44.043
41.290
31.388
29.410
22.407
14.107
Br
O
H
N
N
Bn
COOEt
4s
f1 (ppm)





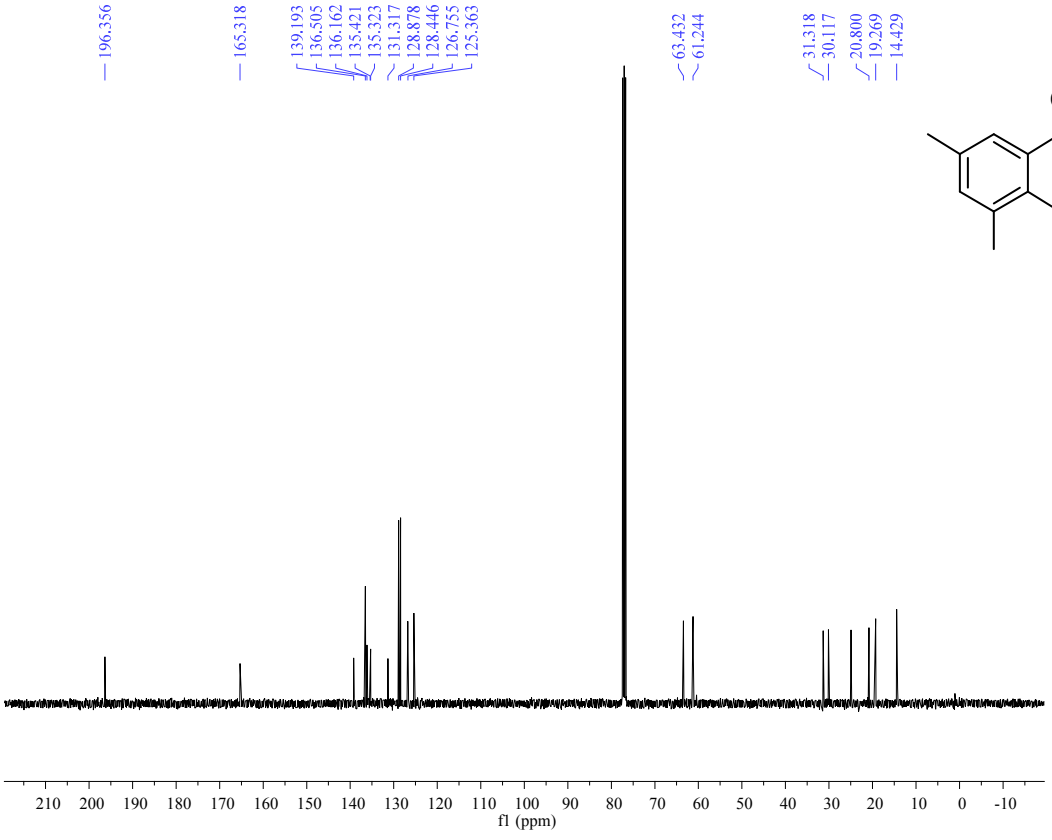
4t

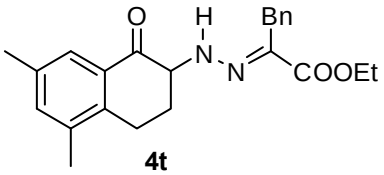
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-01-17T14:18:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 292.7 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 13.3 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -6.03
Ph1: 20.62





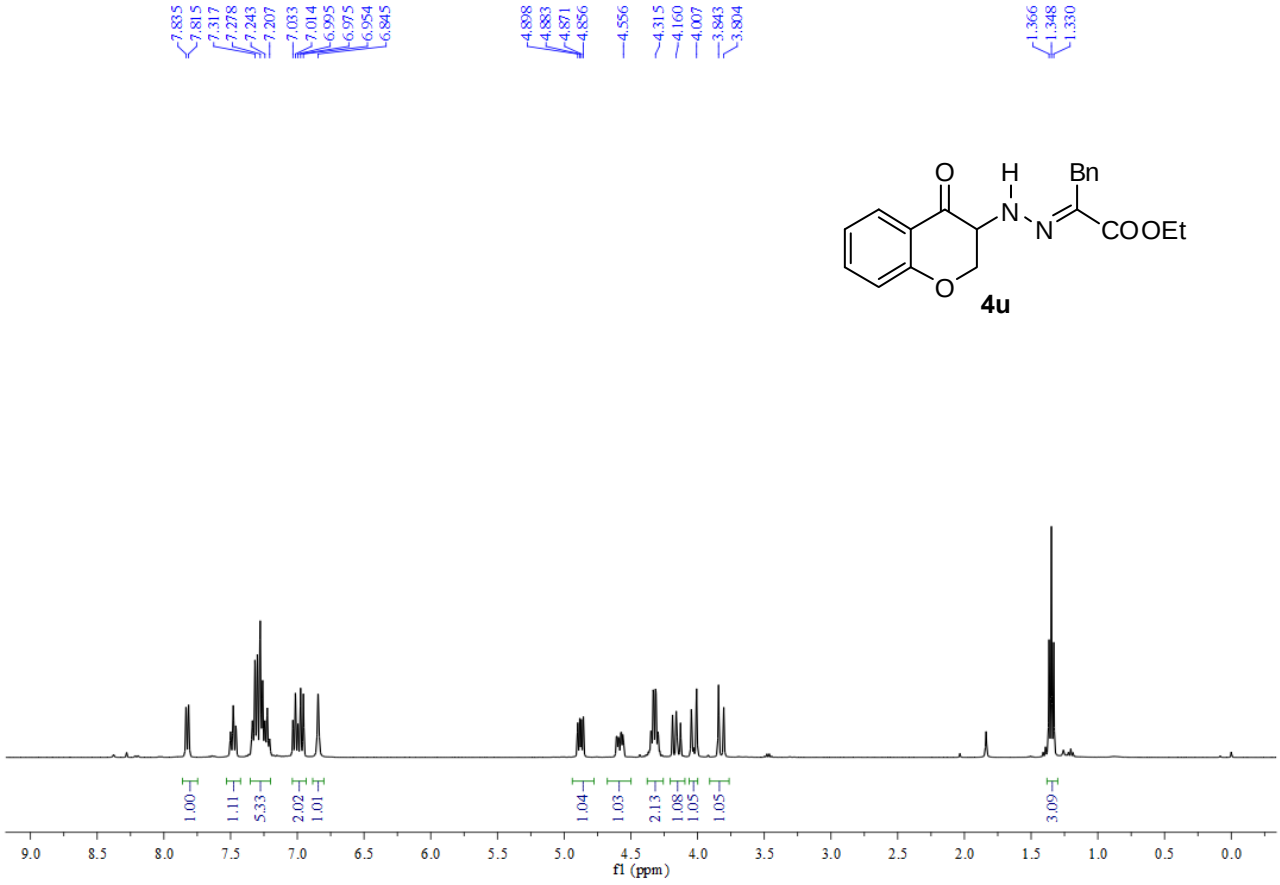
4t

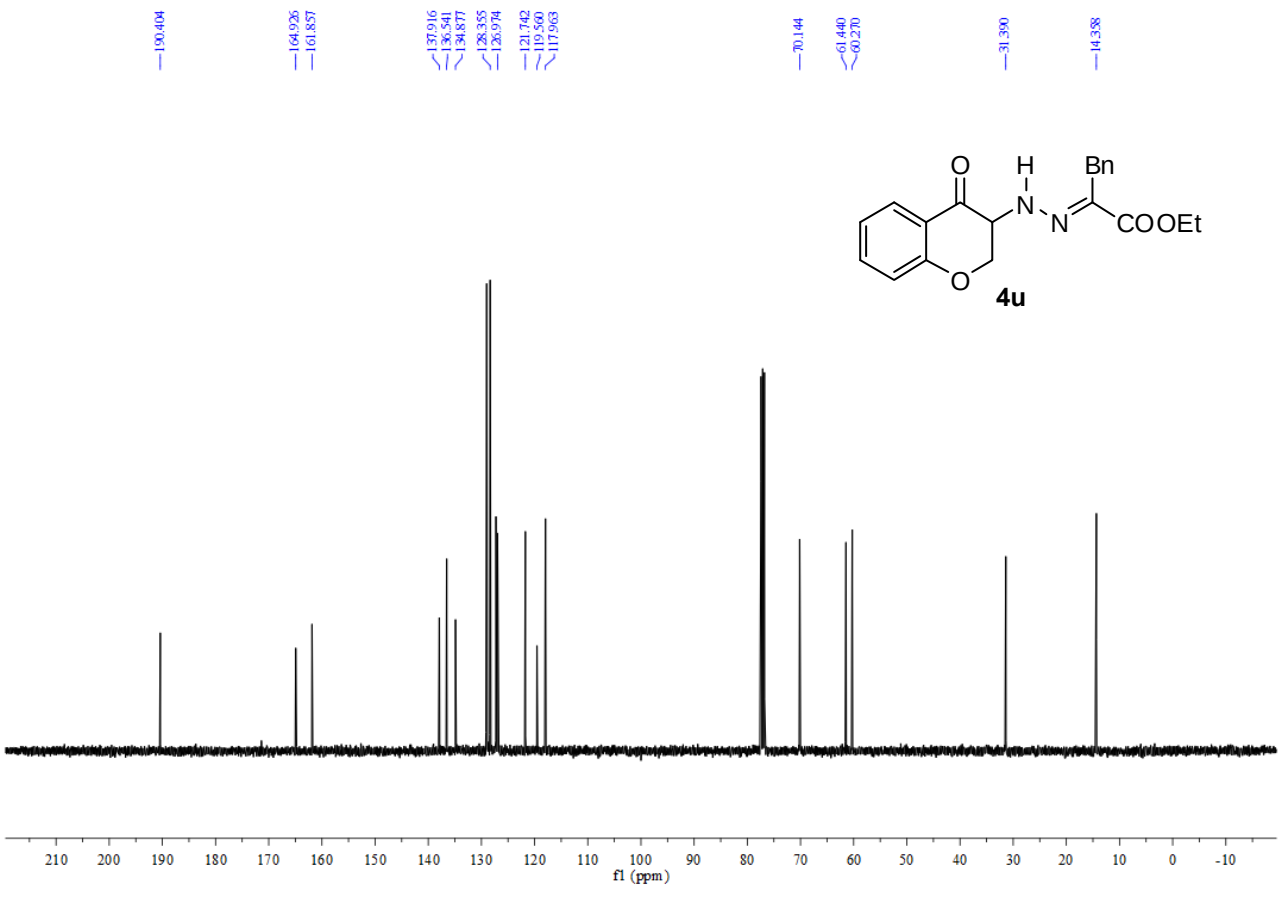
Current Data Parameters

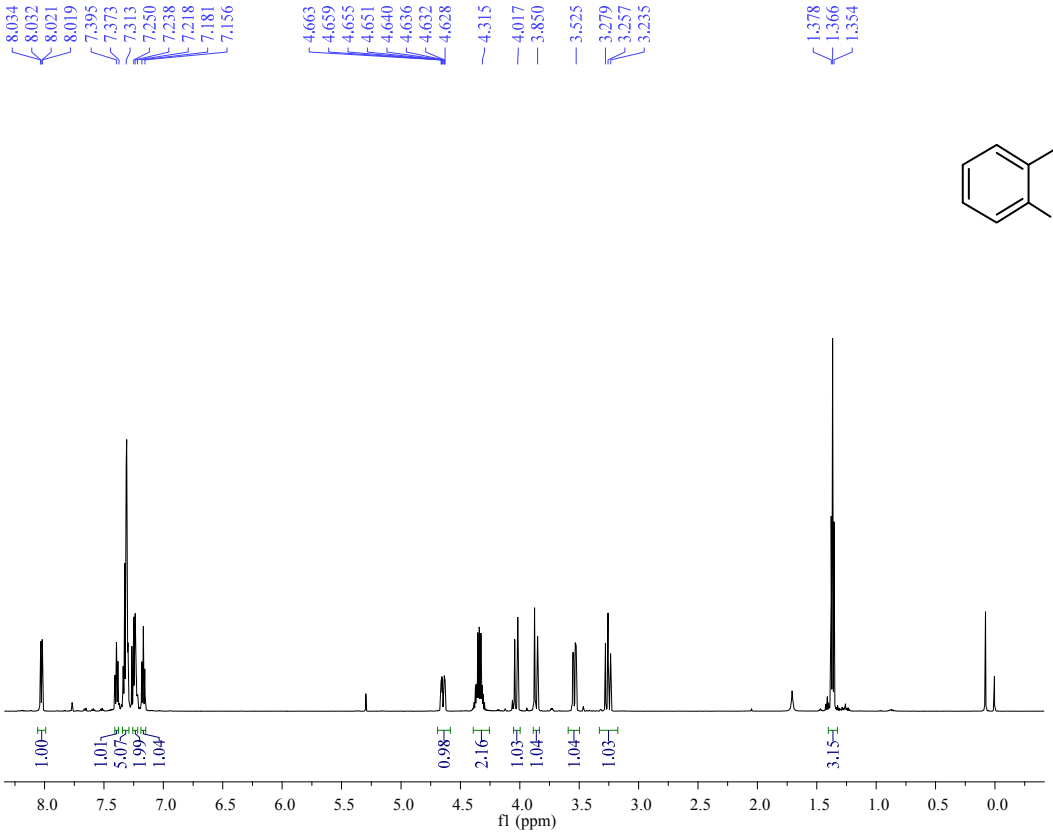
F2 - Acquisition Parameters
DATE: 2011-01-17T14:37:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 321
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.5 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -112.47
Ph1: 76.87


7.835
7.815
7.317
7.278
7.243
7.207
7.033
7.014
6.995
6.975
6.954
6.845
4.898
4.883
4.871
4.856
4.556
4.315
4.160
4.007
3.843
3.804
1.366
1.348
1.330
O
H
N
N
Bn
COOEt
O
4u
1.00
1.11
5.33
2.02
1.01
1.04
1.03
2.13
1.08
1.05
1.05
3.09
f1 (ppm)


190.404
164.926
161.857
137.916
136.541
134.877
128.355
126.974
121.742
119.560
117.963
70.144
61.440
60.270
31.390
14.358
O
H
N
N
Bn
COOEt
O
4u
f1 (ppm)

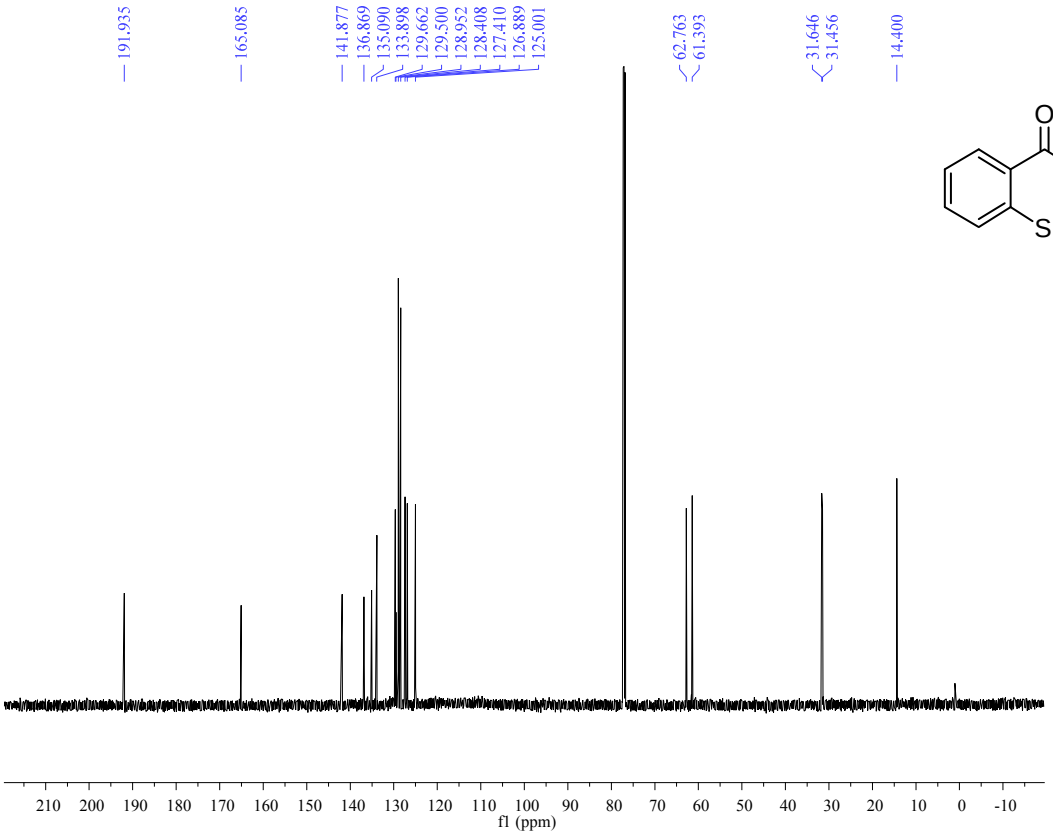


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-22T17:29:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 293.6 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.6 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -142.45
Ph1: 32.64

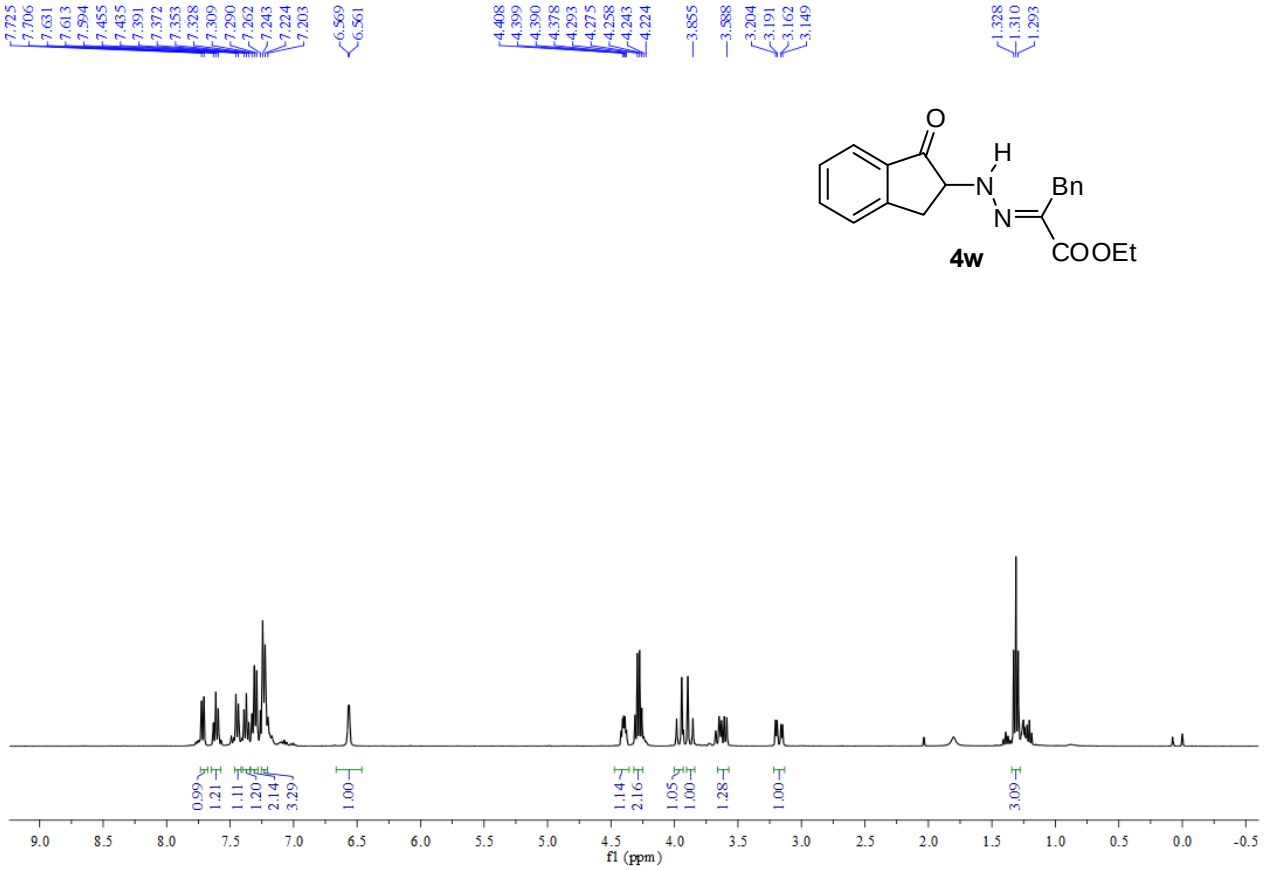


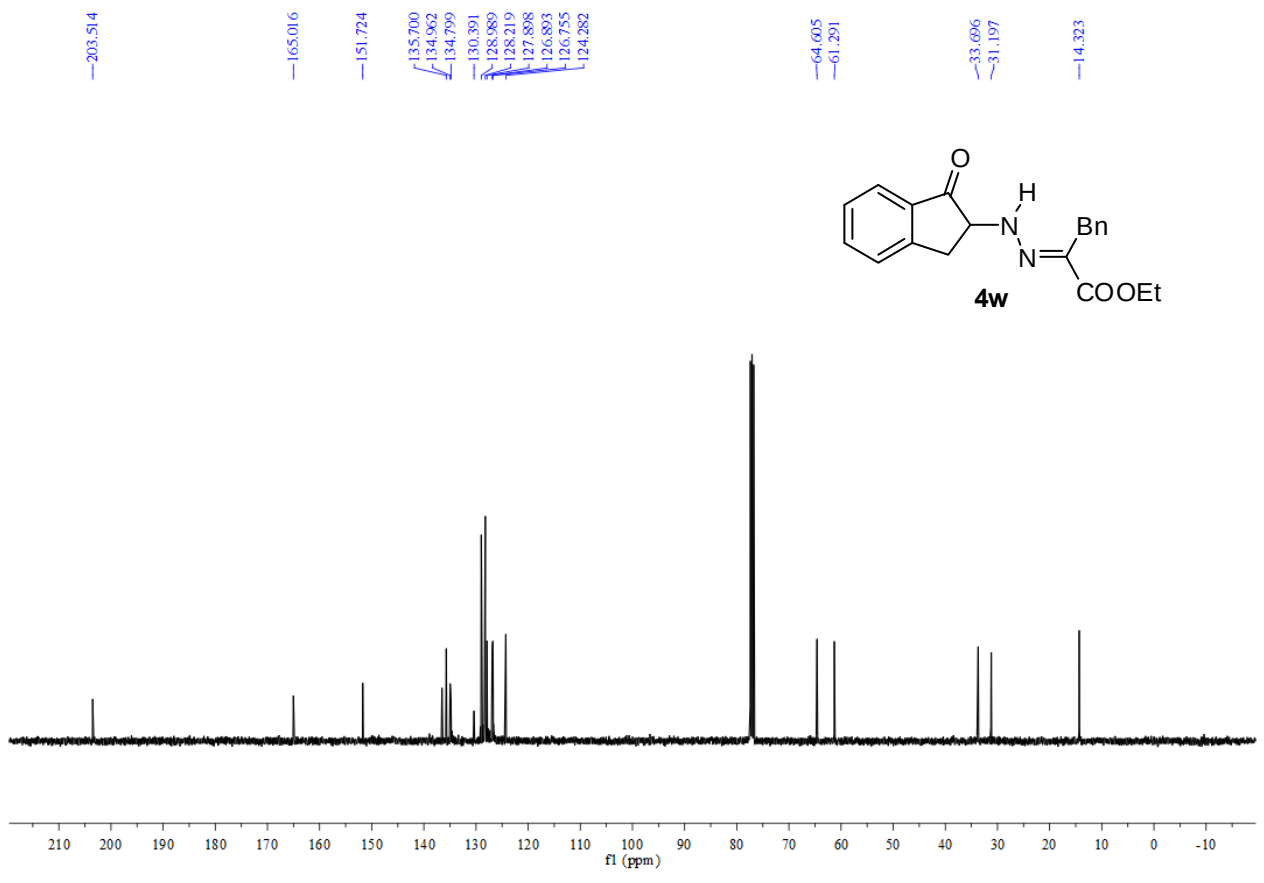
Current Data Parameters

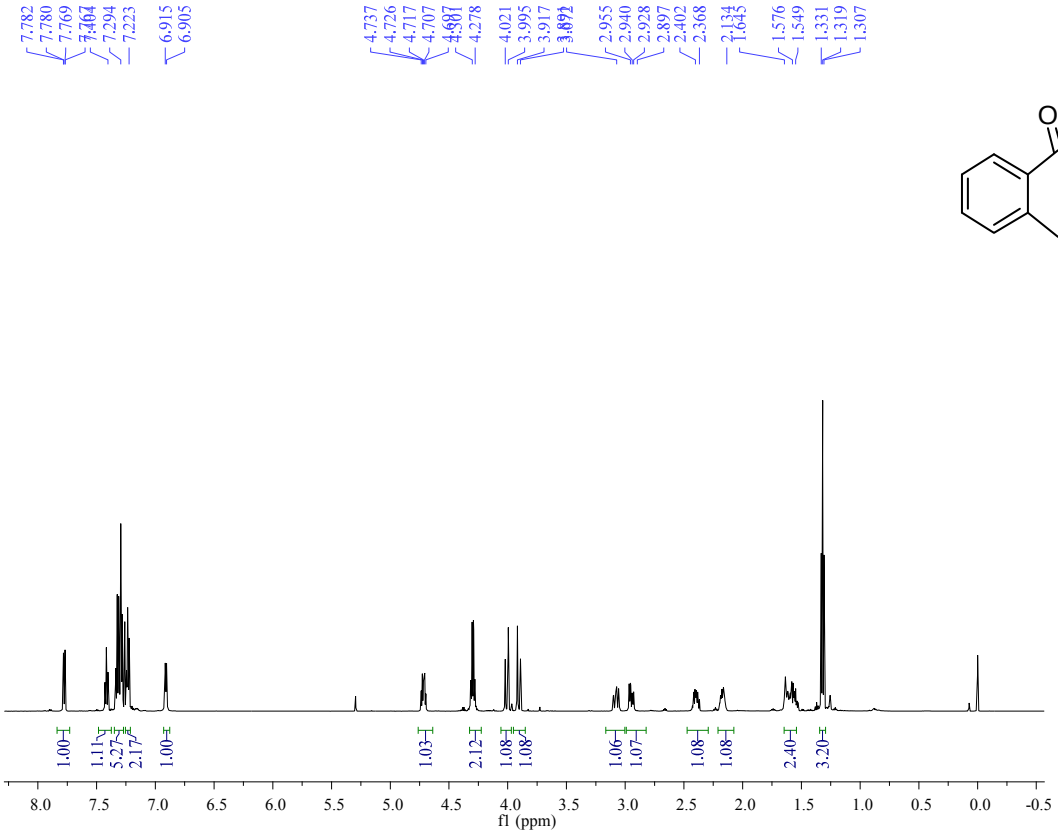
F2 - Acquisition Parameters
DATE: 2011-03-22T17:42:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 293.8 C

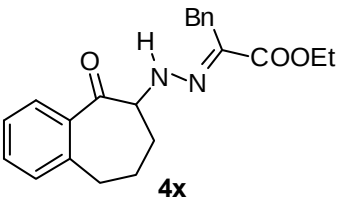
======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 70.25
Ph1: 66.45


7.725
7.706
7.631
7.613
7.594
7.455
7.435
7.391
7.372
7.353
7.328
7.309
7.290
7.262
7.243
7.224
7.203
6.569
6.561
4.408
4.399
4.390
4.378
4.293
4.275
4.258
4.243
4.224
3.855
3.588
3.204
3.191
3.162
3.149
1.328
1.310
1.293
O
H
N
N
Bn
COOEt
4w
0.99
1.21
1.11
1.20
2.14
3.29
1.00
1.14
2.16
1.05
1.00
1.28
1.00
3.09
9.0
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
0.5
0.0
-0.5
f1 (ppm)


203.514
165.016
151.724
135.700
134.962
134.799
130.391
128.989
128.219
127.898
126.893
126.755
124.282
64.605
61.291
33.696
31.197
14.323
O
H
N
N
Bn
COOEt
4w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)





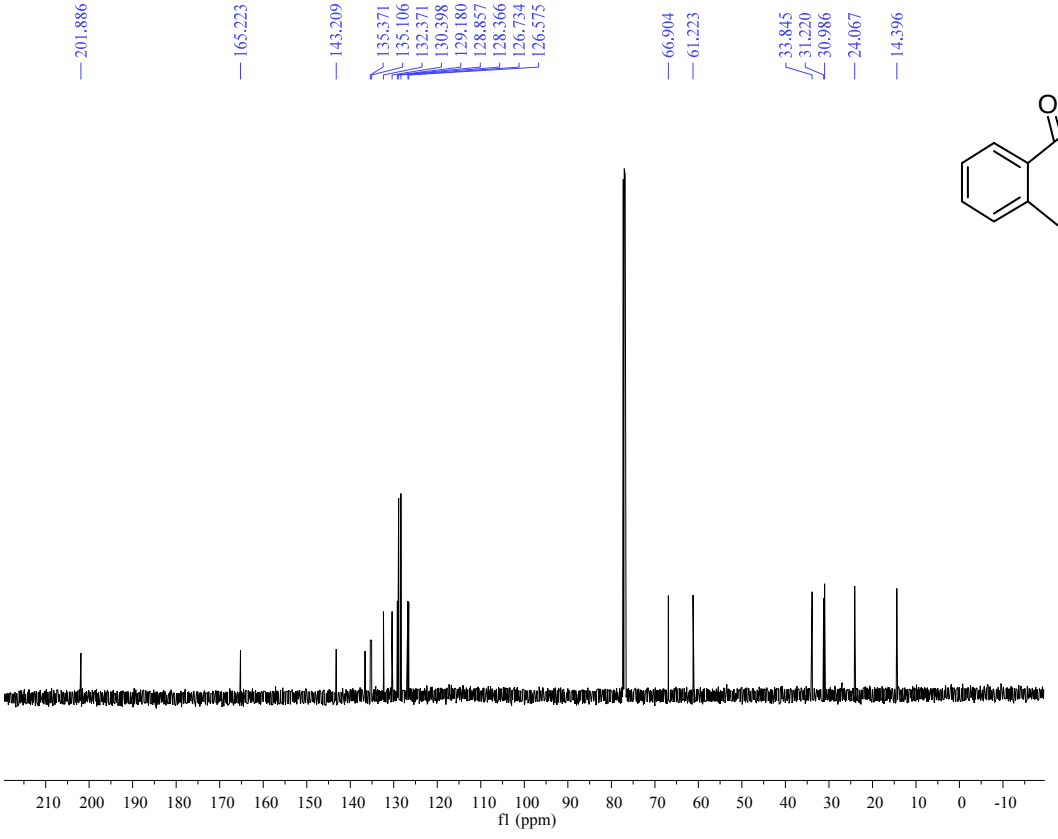
4x

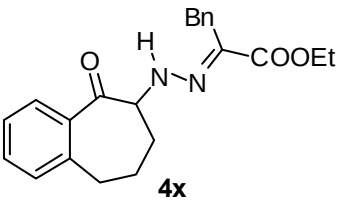
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-14T15:53:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 293.9 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.6 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 32.46
Ph1: 31.61





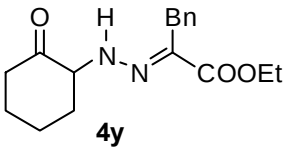
4x

Current Data Parameters

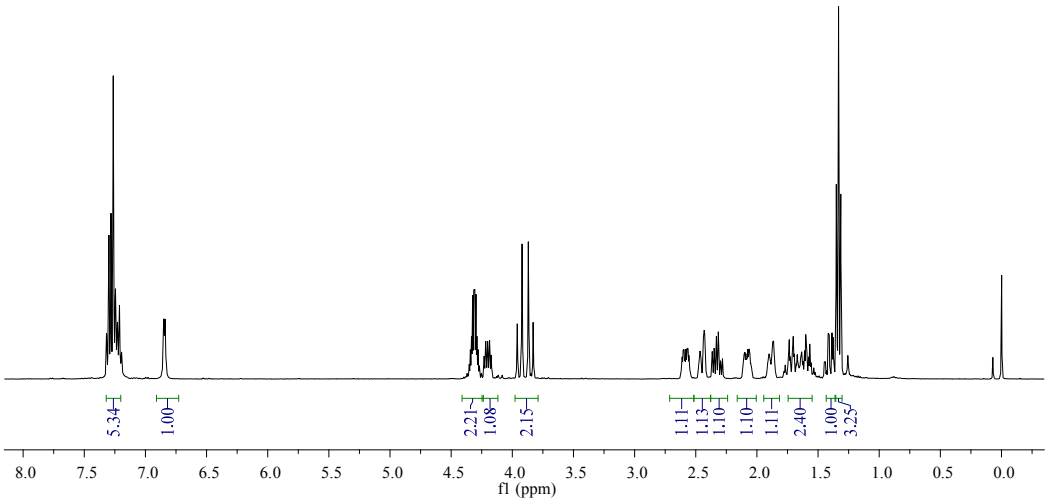
F2 - Acquisition Parameters
DATE: 2011-03-14T15:59:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 129
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 294.2 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 59.08
Ph1: 77.09



4y

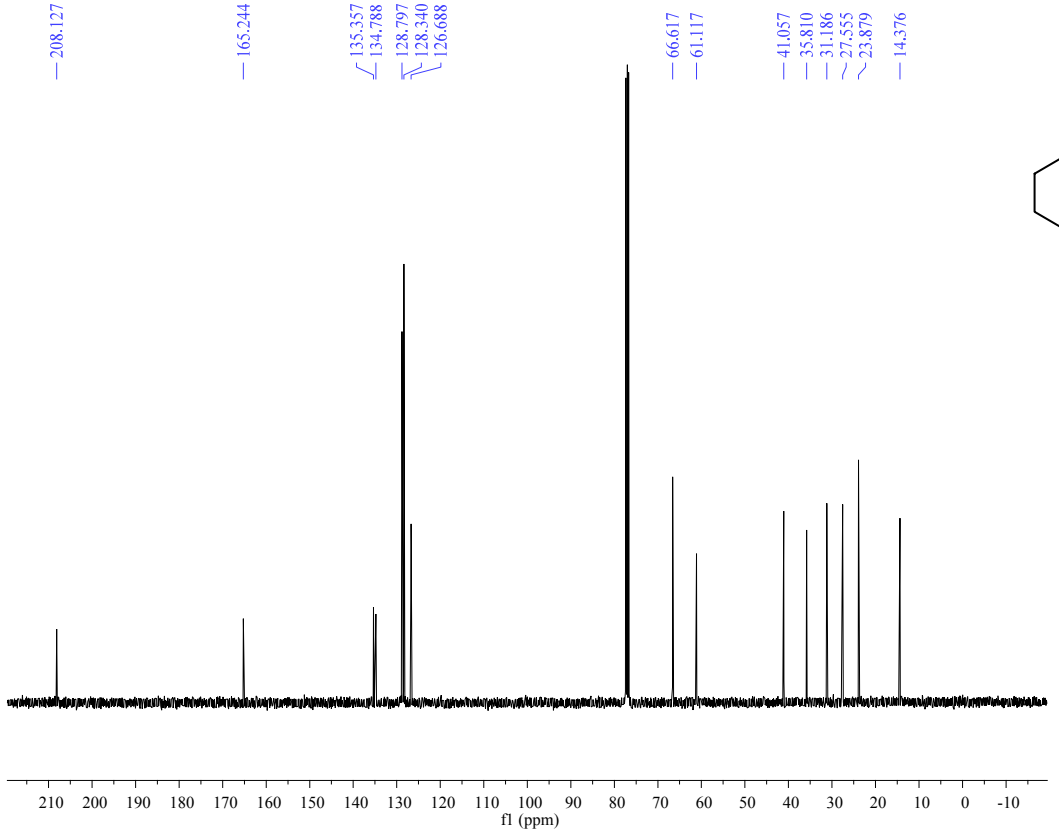


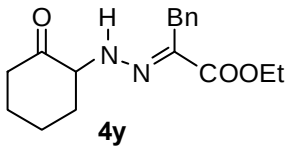
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-04-26T10:52:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 297.4 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 12 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 5.82
Ph1: 17.06





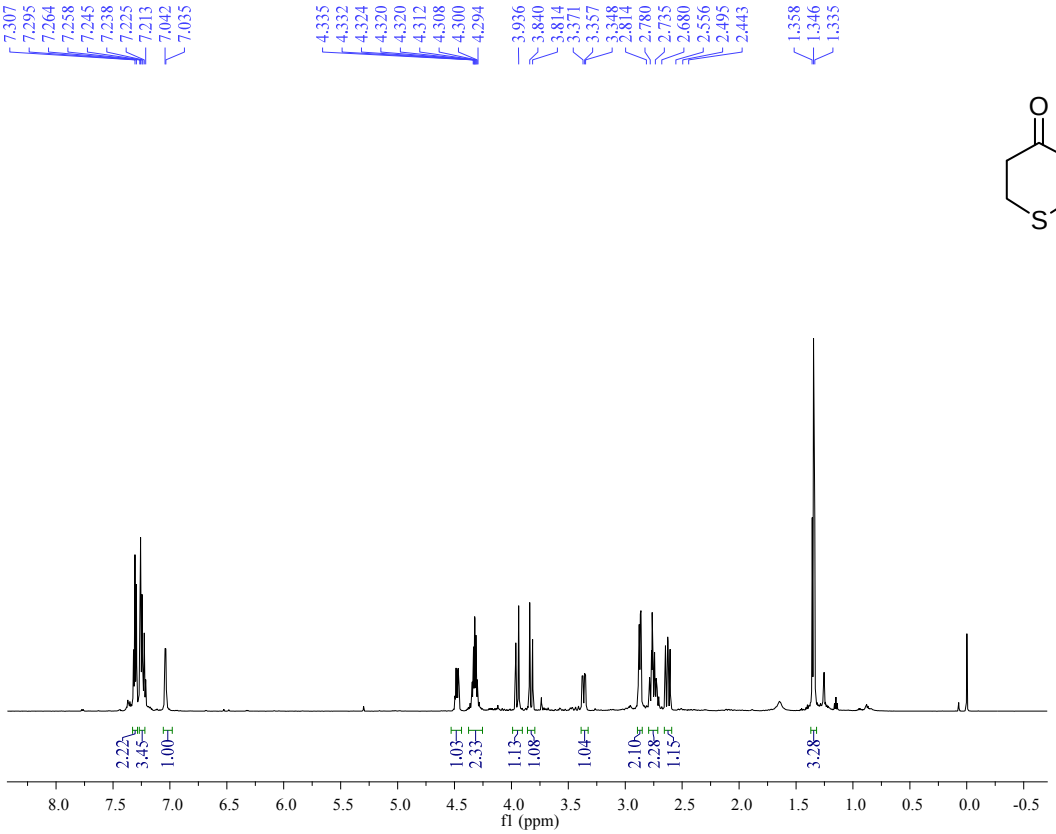
4y

Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-04-27T00:27:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 300.7 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -107.20
Ph1: 68.38

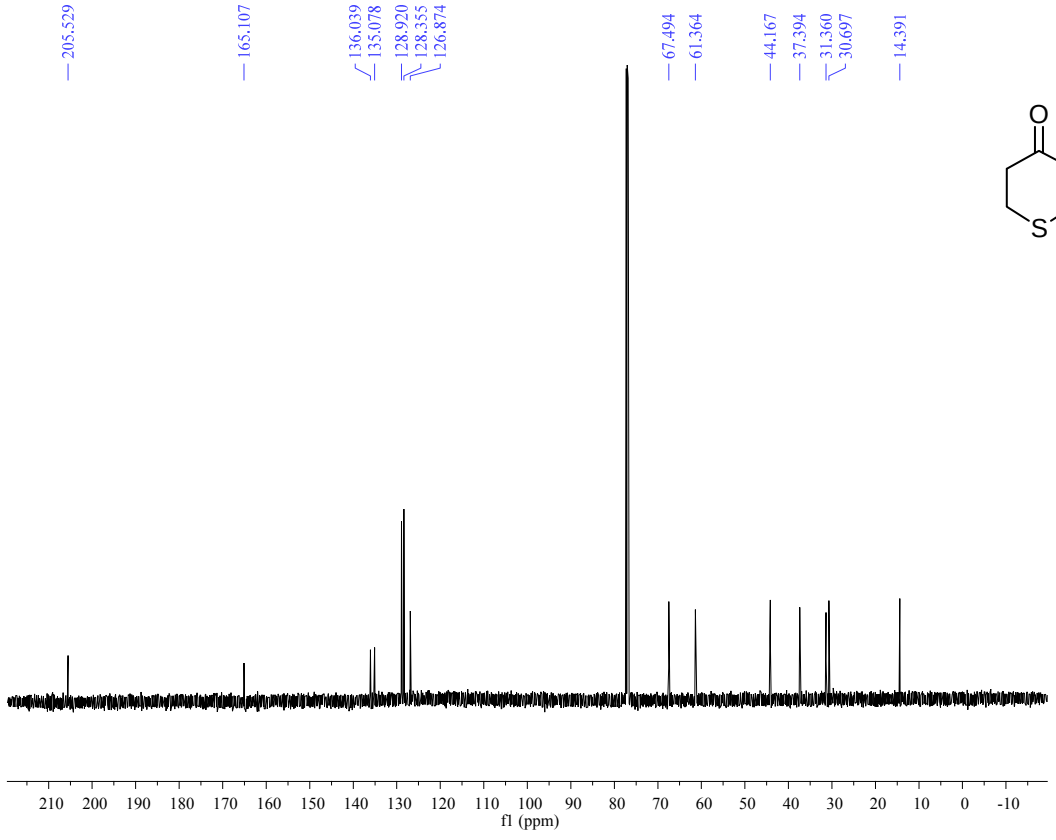


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-14T16:27:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 294.2 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.6 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 11.60
Ph1: 29.54



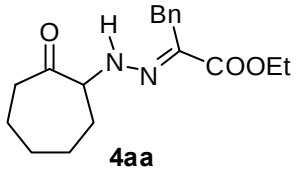
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-14T16:34:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 137
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 294.2 C

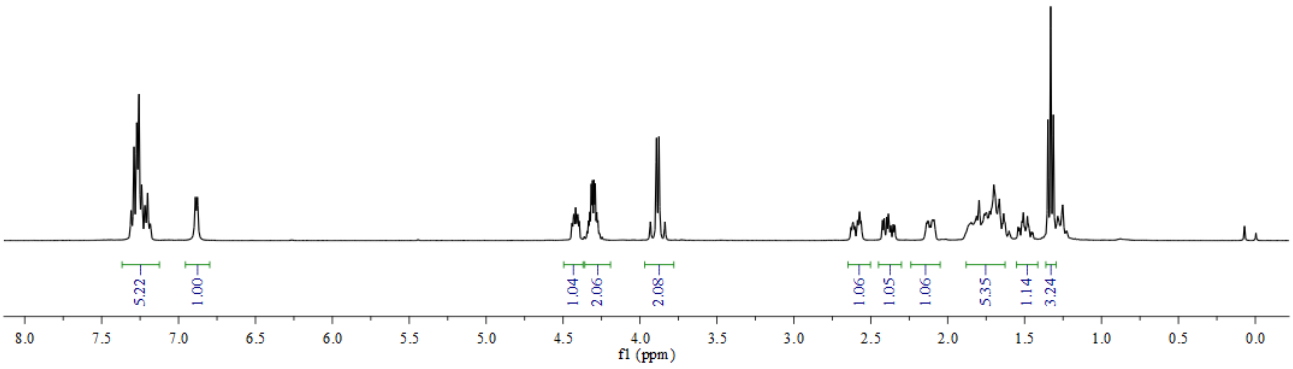
======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

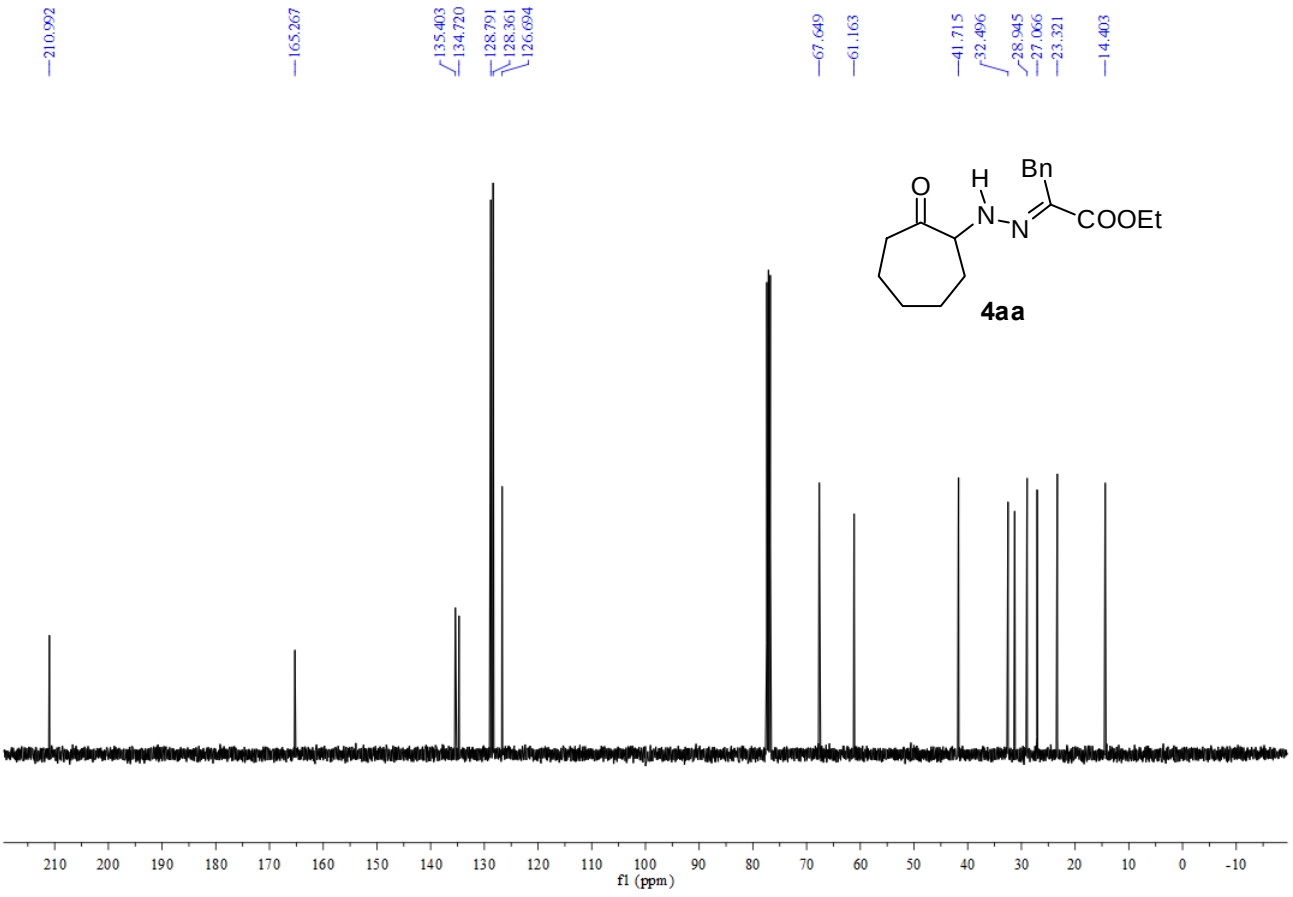
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 62.53
Ph1: 73.78

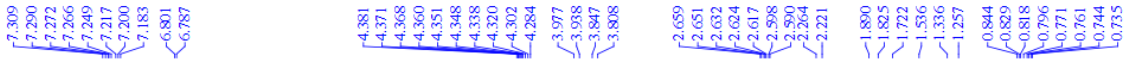

7.308
7.289
7.271
7.257
7.240
7.218
7.201
7.184
6.890
6.878
4.418
4.395
4.344
4.334
4.326
4.317
4.309
4.299
4.291
4.281
4.273
4.264
3.932
3.893
3.877
3.838
2.628
2.615
2.604
2.586
2.573
2.562
2.344
2.089
1.795
1.726
1.700
1.671
1.644
1.629
1.601
1.542
1.516
1.500
1.482
1.455
1.366
1.330
1.284
1.269
1.253

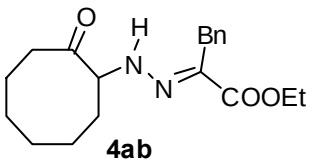

O
H
N
N
Bn
COOEt

4aa

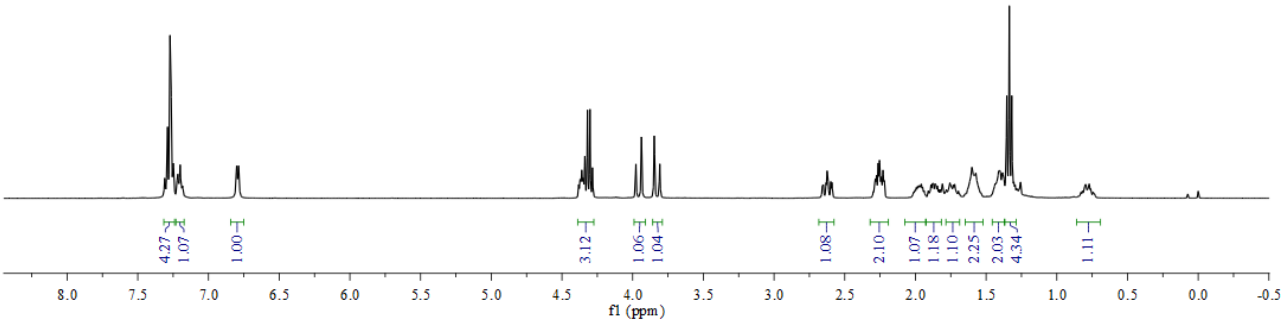

5.22
1.00
1.04
2.06
2.08
1.06
1.05
1.06
5.35
1.14
3.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210.992
165.267
135.403
134.720
128.791
128.361
126.694
67.649
61.163
41.715
32.496
28.945
27.066
23.321
14.403
O
H
N
N
Bn
COOEt
4aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

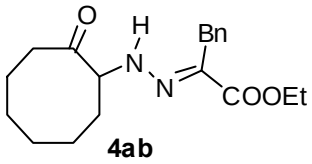

7.309
7.290
7.272
7.266
7.249
7.217
7.200
7.183
6.801
6.787
4.381
4.371
4.368
4.360
4.351
4.348
4.338
4.320
4.302
4.284
3.977
3.938
3.847
3.808
2.659
2.651
2.632
2.624
2.617
2.598
2.590
2.264
2.221
1.890
1.825
1.722
1.536
1.336
1.257
0.844
0.829
0.818
0.796
0.771
0.761
0.744
0.735


O
H
N
N
Bn
COOEt

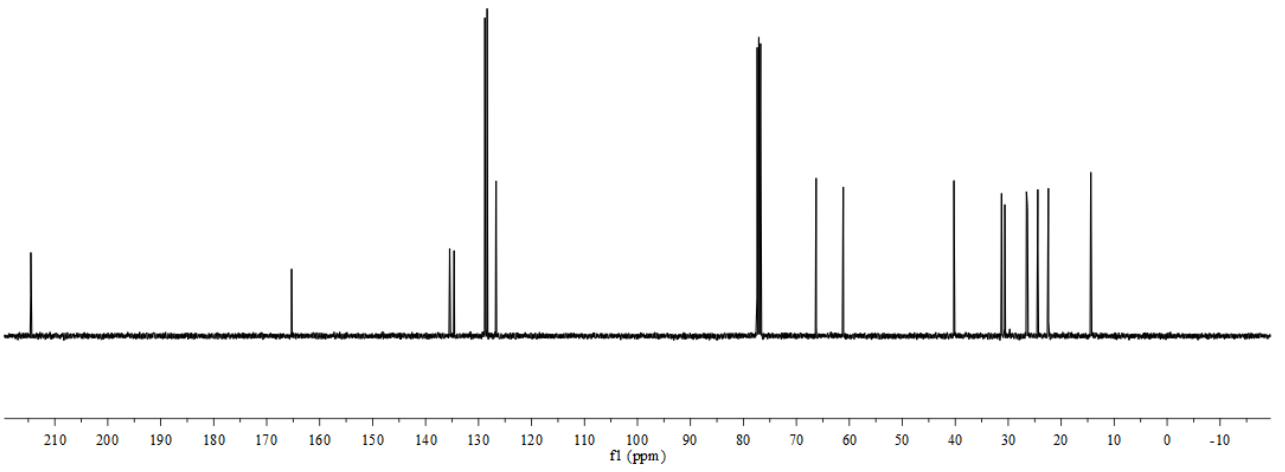
4ab

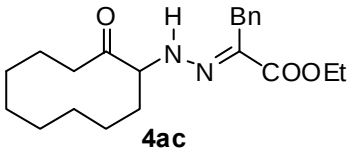

4.27
1.07
1.00
3.12
1.06
1.04
1.08
2.10
1.07
1.18
1.10
2.25
2.03
4.34
1.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


214.527
165.296
135.449
134.618
128.806
128.376
126.702
66.270
61.152
40.249
31.250
30.646
26.553
24.419
22.422
14.408

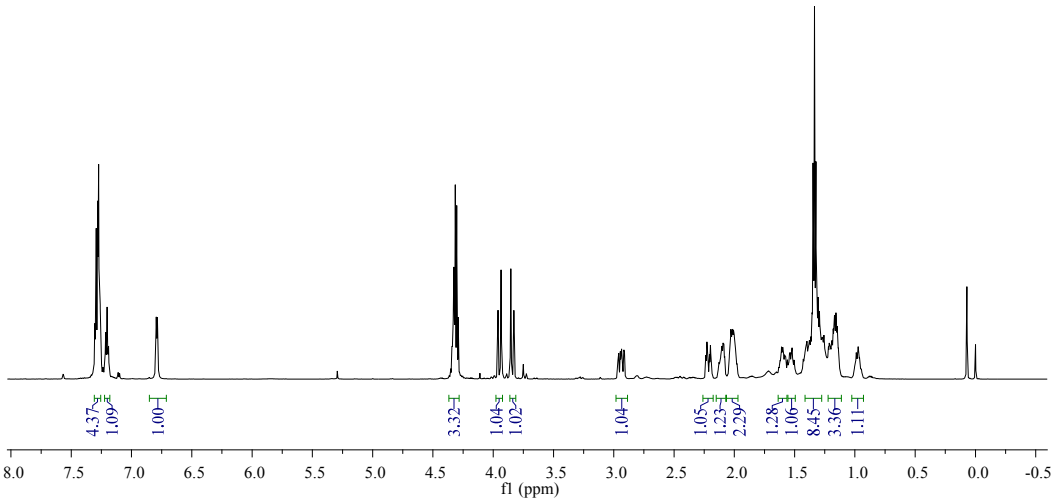

O
H
N
N
Bn
COOEt

4ab


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4ac

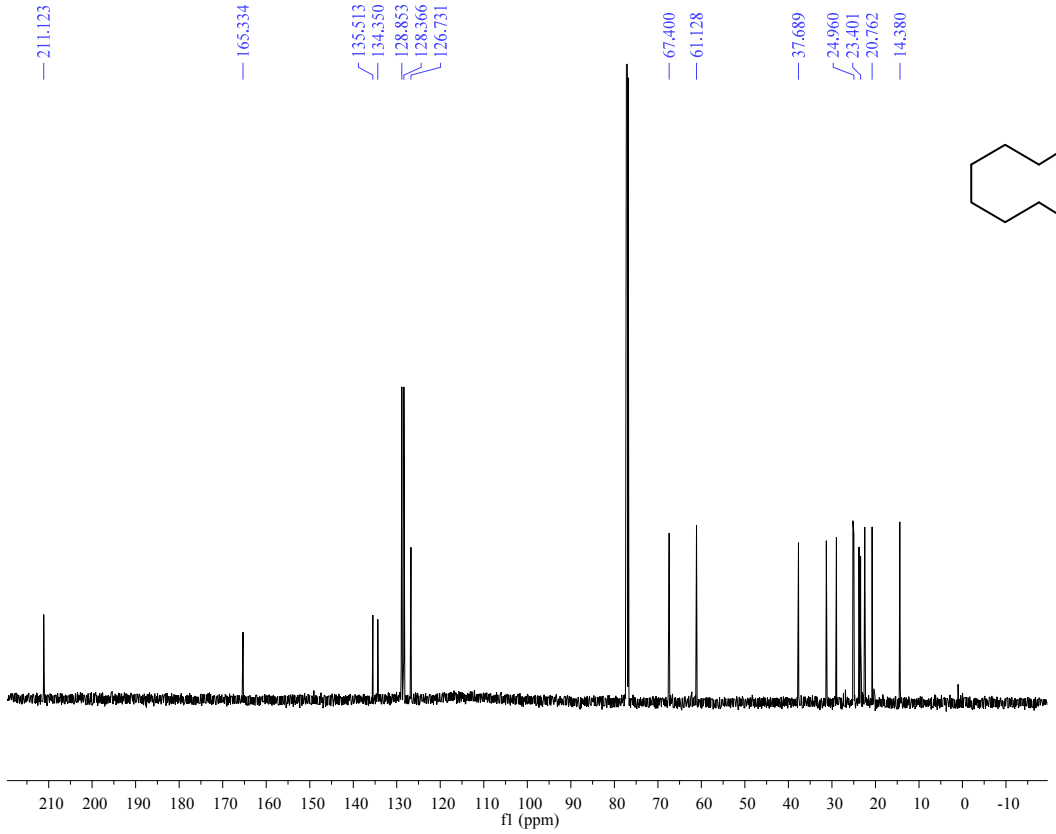


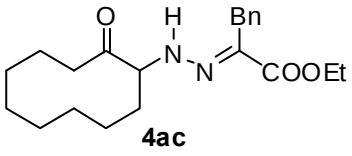
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-22T10:10:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 300.1 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.6 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -139.40
Ph1: 30.91





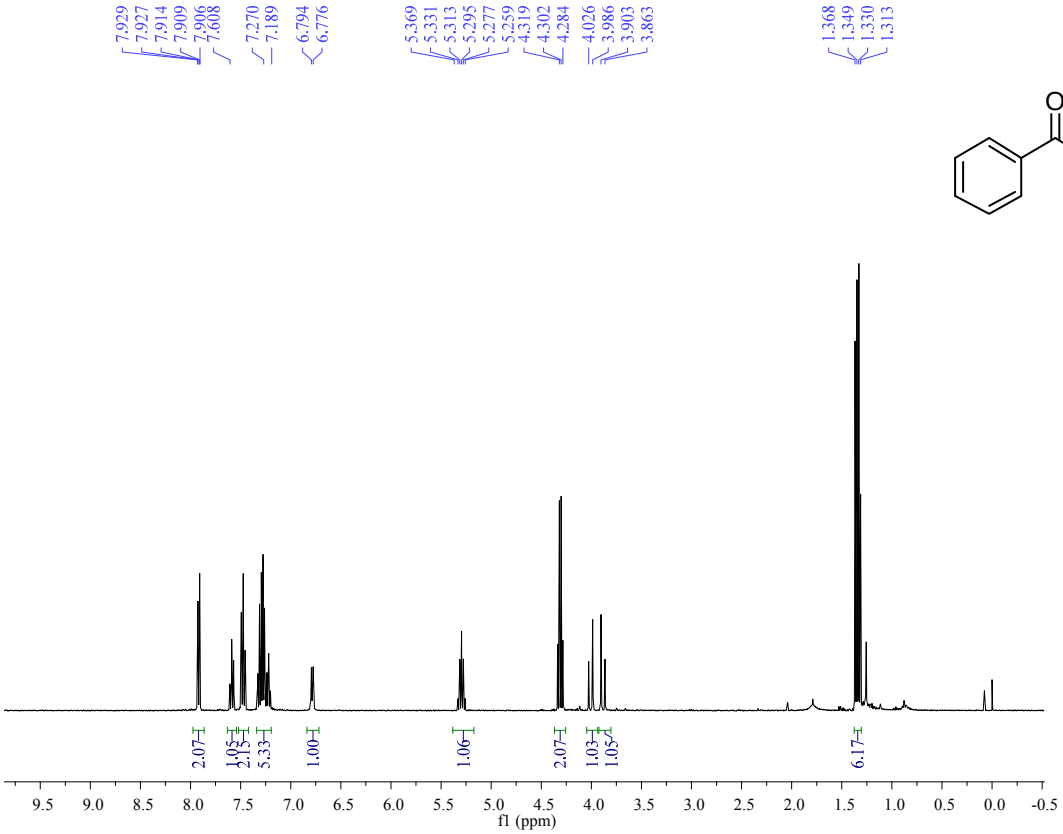
4ac

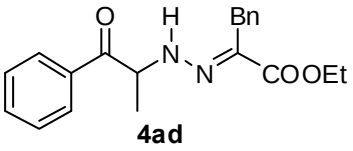
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-03-22T10:23:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 258
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 299.6 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 2.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 77.59
Ph1: 66.45





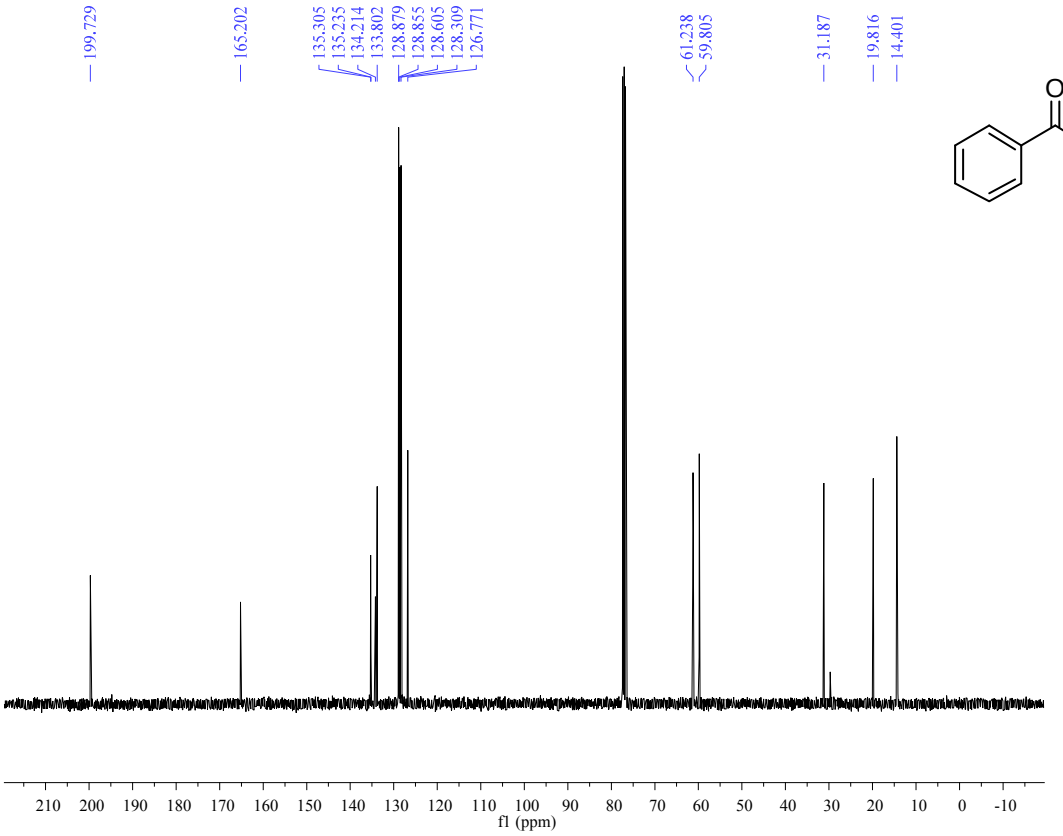
4ad

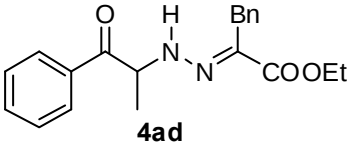
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2011-04-02T17:14:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.4 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 12 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: -0.20 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 4.65
Ph1: 12.00





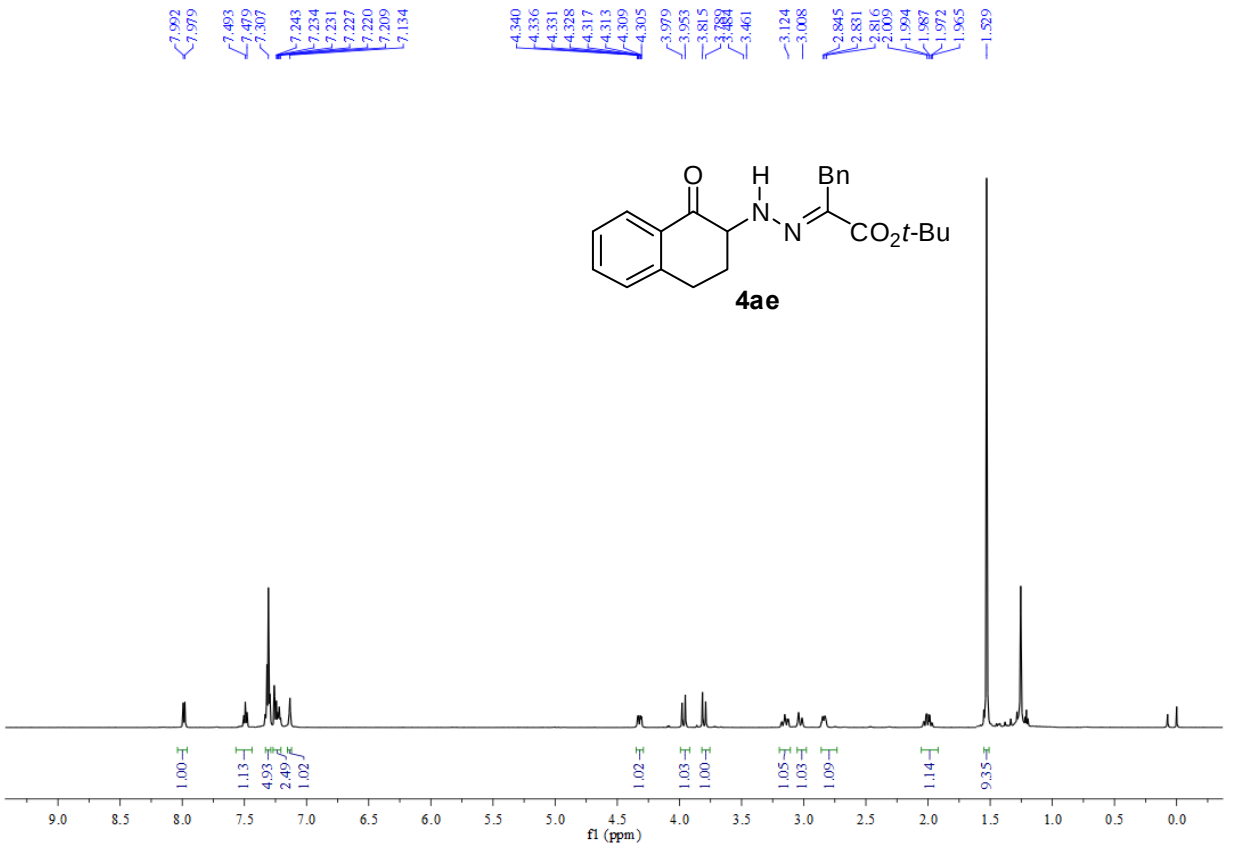
4ad

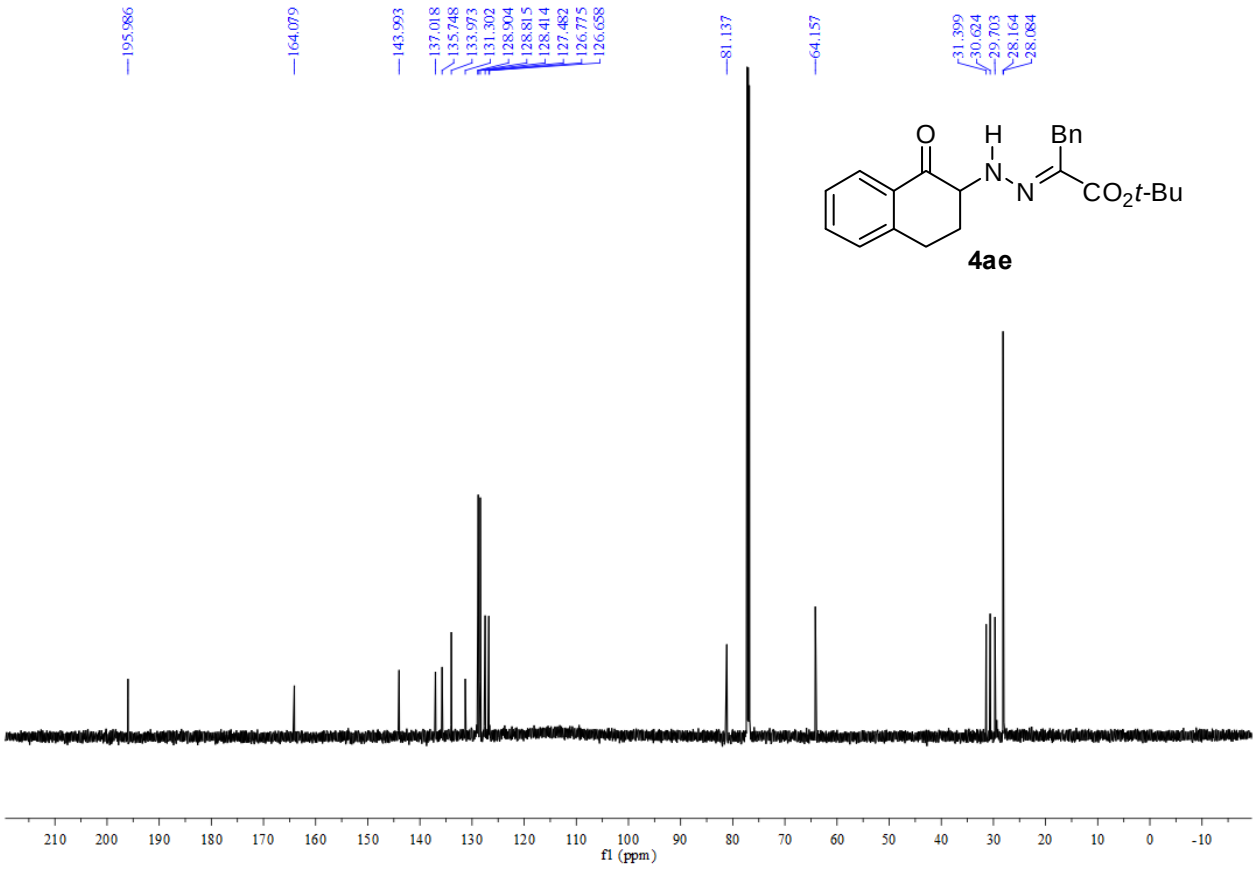
Current Data Parameters

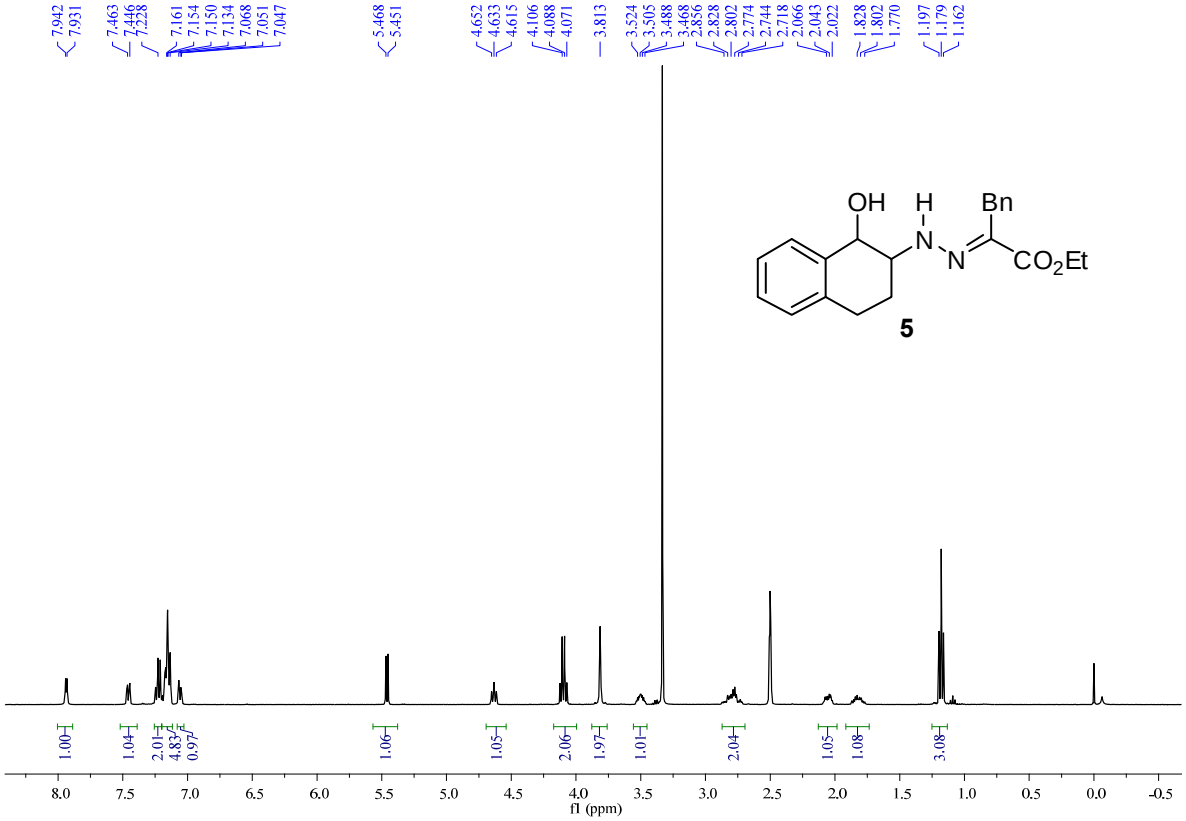
F2 - Acquisition Parameters
DATE: 2011-04-02T17:29:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.3 C

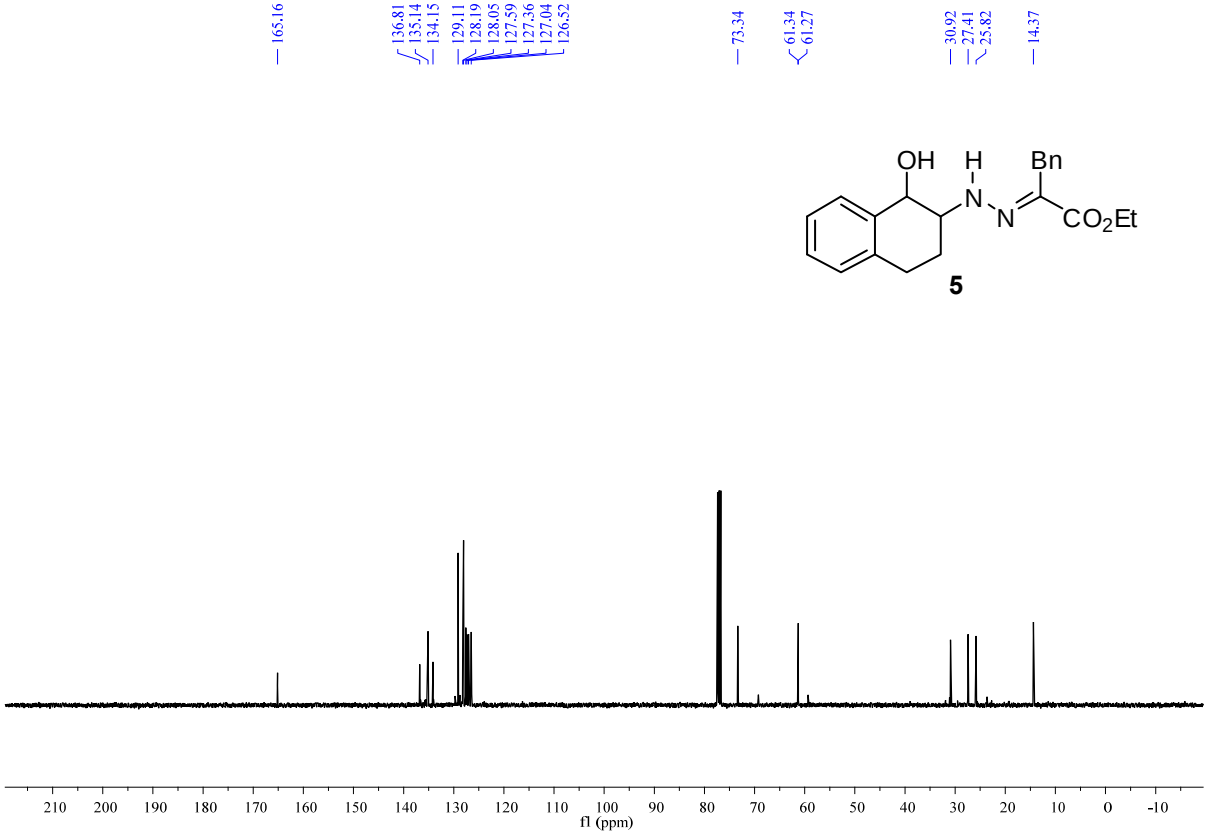
======== CHANNEL f1 ========
NUC1: 13C
P1: 19.4 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -110.57
Ph1: 82.06


7.992
7.979
7.493
7.479
7.307
7.243
7.234
7.231
7.227
7.220
7.209
7.134
4.340
4.336
4.331
4.328
4.317
4.313
4.309
4.305
3.979
3.953
3.815
3.461
3.124
3.008
2.845
2.831
2.816
2.009
1.994
1.987
1.972
1.965
1.529
O
H
N
N
Bn
CO2t-Bu
4ae
1.00
1.13
4.93
2.49
1.02
1.02
1.03
1.00
1.05
1.03
1.09
1.14
9.35
f1 (ppm)


195.986
164.079
143.993
137.018
135.748
133.973
131.302
128.904
128.815
128.414
127.482
126.775
126.658
81.137
64.157
31.399
30.624
29.703
28.164
28.084
O
H
N
N
Bn
CO2t-Bu
4ae
f1 (ppm)


7.942
7.931
7.463
7.446
7.228
7.161
7.154
7.150
7.134
7.068
7.051
7.047
5.468
5.451
4.652
4.633
4.615
4.106
4.088
4.071
3.813
3.524
3.505
3.488
3.468
2.856
2.828
2.802
2.774
2.744
2.718
2.066
2.043
2.022
1.828
1.802
1.770
1.197
1.179
1.162
OH
H
N
N
Bn
CO2Et
5
1.00
1.04
2.01
4.83
0.97
1.06
1.05
2.06
1.97
1.01
2.04
1.05
1.08
3.08
f1 (ppm)


165.16
136.81
135.14
134.15
129.11
128.19
128.05
127.59
127.36
127.04
126.52
73.34
61.34
61.27
30.92
27.41
25.82
14.37
OH
H
N
N
Bn
CO2Et
5
f1 (ppm)