Supporting Information

For Design of New, Chiral Phase Transfer Catalysts for Asymmetric Conjugate Additions of α-Substituted-α-cyanoacetates to Acetylenic Esters

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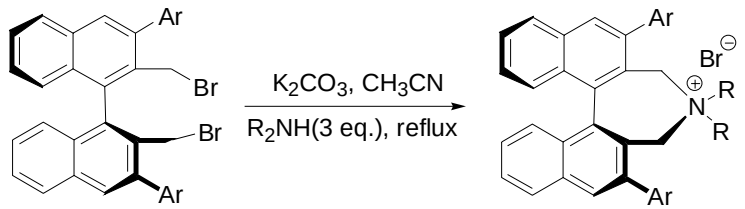
General Information:

Infrared (IR) spetra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-FX400 NMR instrument (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) at ambient temperature and calibrated using $SiMe_4$ (δ = 0 ppm) and the centeral line of $CDCl_3$ triplet (δ = 77 ppm) as internal references unless otherwise noted. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. Chemical shifts are reported in ppm from the residual solvent as an internal standard. High performed liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using a Daicel CHIRALPAK AD-H, OD-H or AS-H, 4.6 mm × 25 mm column. High-resolution mass spectra (HRMS) were performed on BRUKER micrOTOF focus–KR. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. All reactions were monitored by thin-layer chromatography carried out on

Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), visualization by using UV (254 nm), or dyes such as $KMnO_4$, PMA. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230~400 mesh). In experiments requiring dry solvents, ether and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Inc. as "dehydrated". Toluene was dried over sodium metal. Dichloromethane (CH_2Cl_2) was stored over 4 Å molecular sieves. Other simple chemicals were purchased and used as received.

Synthesis of Chiral Ammonium Salts:



(*S*)-**7** (*S*)-**1**

The key intermediate (*S*)-**7** was prepared according to literatures.[1]

Synthesis of (*S*)-1i: A mixture of (*S*)-**7i** (751 mg, 0.52 mmol), morpholine (136 μL, 1.56 mmol), and K_2CO_3 (360 mg, 2.6 mmol) in acetonitrile (10 mL) was heated to reflux and stirring was maintained for 10 h. After cooling to room temperature, the resulting mixture was filtrated through a celite pad to remove the inorganic salts and concentrated. The residue was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1:60-1:5 as eluant) to furnish (*S*)-**1i** (597 mg, 0.41 mmol, 79% yield). $[\alpha]_D^{28}$ -5.0° [*c* = 0.96, $CHCl_3$]; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 8.15 (s, 8H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.97 (s, 4H), 7.91 (s, 4H), 7.75-7.71 (m, 4H), 7.58-7.49 (m, 4H), 5.31 (d, *J* = 13.6 Hz, 2H), 4.06 (d, *J* = 13.6 Hz, 2H), 3.93 (br, 2H), 3.52 (br, 2H),

3.14 (br, 2H), 3.04 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 141.2, 141.0, 140.6, 138.6, 138.3, 134.0, 132.6 (q, $J_{C\text{-}F}$ = 34 Hz), 132.4 (q, $J_{C\text{-}F}$ = 34 Hz), 131.8, 131.0, 129.4, 128.8, 128.7, 128.2, 127.8, 127.6, 127.5, 126.5, 123.1 (q, $J_{C\text{-}F}$ = 275 Hz), 122.8, 122.1 (br), 60.5, 58.7, 57.6; IR (neat) 3057, 2876, 1620, 1589, 1366, 1277, 1171, 1126, 893, 845, 685 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{70}H_{40}F_{24}NNaO$ ($[M+Na]^+$): 1366.2721, Found: 1366.2712.

Chiral Ammonium Salt (*S*)-1b: 74% yield; $[\alpha]_D^{31}$ +19.8° [*c* = 1.03, $CHCl_3$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br, 2H), 8.15-7.92 (br, 2H), 8.10 (s, 2H), 8.09 (d, *J* = 5.2 Hz, 2H), 8.04 (s, 2H), 7.71 (t, *J* = 7.2 Hz, 2H), 7.48-7.38 (m, 4H), 4.81 (d, *J* = 13.6 Hz, 2H), 4.03 (d, *J* = 13.6 Hz, 2H), 3.33 (t, *J* = 12.8 Hz, 2H), 2.65 (t, *J* = 12.8 Hz, 2H), 1.09 (br, 4H), 0.87 (br, 2H), 0.63 (t, *J* = 7.2 Hz, 6H), 0.30 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.6, 136.6, 133.7, 132.4, 131.2, 130.4-129.8 (m), 128.8, 128.6, 128.3, 122.8 (q, $J_{C\text{-}F}$ = 275 Hz), 122.7, 122.2-122.0 (m), 57.6, 57.4, 24.4, 18.9, 13.2; IR (neat) 2965, 2359, 1470, 1368, 1281, 1173, 1134, 750 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{46}H_{38}F_{12}NNa$ ($[M+Na]^+$): 832.2807, Found: 832.2810.

Chiral Ammonium Salt (*S*)-1c: 62% yield; $[\alpha]_D^{32}$ -10.0° [*c* = 0.97, $CHCl_3$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.17 (m, 10H), 8.12 (d, *J* = 8.4 Hz, 2H), 8.03 (s, 2H), 7.98 (s, 2H), 7.92 (s, 4H), 7.77 (s, 2H), 7.73-7.69 (m, 2H), 7.47 (br, 4H), 5.16 (d, *J* = 14.0 Hz, 2H), 3.94 (d, *J* = 14.0 Hz, 2H), 3.47 (t, *J* = 13.2 Hz, 2H), 2.84 (t, *J* = 10.4 Hz, 2H), 1.15 (br, 2H), 0.99 (br, 2H), 0.82 (br, 2H), 0.60 (br, 2H), 0.53 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 141.6, 140.9, 138.7, 138.6, 134.0, 132.8 (q, $J_{C\text{-}F}$ = 34 Hz), 132.4 (q, $J_{C\text{-}F}$ = 34 Hz), 132.2, 131.2, 129.8, 128.9, 128.8, 128.7, 128.2, 128.1 (br), 127.8, 127.4 (br), 126.3, 123.4, 123.2 (q, $J_{C\text{-}F}$ = 273 Hz), 122.1 (br), 58.0, 57.9, 25.0, 19.6, 13.6; IR (neat) 2963, 2878, 1470, 1368, 1279, 1173, 1132, 901, 845, 771 cm^{-1};

HRMS (ESI-TOF) calcd for $C_{74}H_{50}F_{24}NNa$ ([M+Na]$^+$): 1408.3555, Found: 1408.3546.

Chiral Ammonium Salt (*S*)-1d: 91% yield; $[\alpha]_D^{34}$ +23.1° [*c* = 0.92, $CHCl_3$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 8.03 (s, 2H), 7.68 (t, *J* = 7.6 Hz, 2H), 7.46-7.38 (m, 4H), 7.17 (br, 4H), 5.21 (d, *J* = 13.6 Hz, 2H), 3.77 (br, 2H), 3.64 (d, *J* = 13.6 Hz, 2H), 3.11 (br, 2H), 1.63-1.58 (m, 2H), 1.53 (br, 2H), 1.01 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3 (d, $J_{C\text{-}F}$ = 253 Hz), 139.9 (dt, $J_{C\text{-}F}$ = 253, 14 Hz), 138.2, 137.0, 134.7 (br), 133.5, 131.3, 130.8, 128.6, 128.0, 127.3, 123.3, 114.7 (br), 58.7, 57.7, 20.1, 20.0; IR (neat) 3053, 2943, 2911, 1614, 1585, 1528, 1449, 1362, 1242, 1045, 895, 752 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{39}H_{28}F_6NNa$ ([M+Na]$^+$): 624.2120, Found: 624.2112.

Chiral Ammonium Salt (*S*)-1e: 66% yield; $[\alpha]_D^{34}$ +27.4° [*c* = 0.42, $CHCl_3$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.8 Hz, 2H), 8.03 (s, 2H), 7.67 (t, *J* = 6.8 Hz, 2H), 7.45-7.39 (m, 4H), 7.32-7.21 (m, 4H), 5.07 (d, *J* = 13.6 Hz, 2H), 3.93 (d, *J* = 13.6 Hz, 2H), 3.79 (br, 2H), 3.67 (br, 2H), 3.06 (br, 2H), 2.86 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1 (d, $J_{C\text{-}F}$ = 255 Hz), 139.8 (dt, $J_{C\text{-}F}$ = 255, 15 Hz), 138.3, 136.7, 134.7 (dd, $J_{C\text{-}F}$ = 12, 7 Hz), 133.6, 131.4, 130.9, 128.6, 128.5, 127.9, 127.4, 122.9, 114.8 (d, $J_{C\text{-}F}$ = 15 Hz), 60.5, 58.2, 57.6; IR (neat) 3053, 3007, 2878, 1614, 1526, 1447, 1362, 1242, 1047, 895, 752 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{38}H_{26}F_6NNaO$ ([M+Na]$^+$): 626.1913, Found: 626.1914.

Chiral Ammonium Salt (*S*)-1f: 84% yield; $[\alpha]_D^{33}$ +39.6° [*c* = 1.10, $CHCl_3$]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.68-7.64 (m, 2H), 7.50-7.18 (br, 4H), 7.45-7.40 (m, 4H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.99 (d, *J* = 13.6 Hz, 2H), 4.05 (d, *J* = 13.6 Hz, 2H), 3.87 (t, *J* = 8.8 Hz, 2H), 3.17-3.06 (m, 4H), 2.61 (t, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)

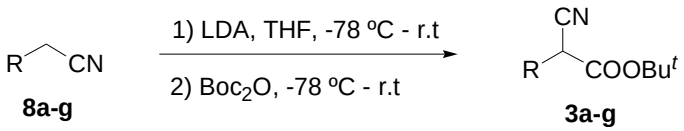
δ 151.3 (d, $J_{C\text{-}F}$ = 255 Hz), 148.4, 139.8 (dt, $J_{C\text{-}F}$ = 255, 15 Hz), 138.3, 136.7, 134.8 (q, $J_{C\text{-}F}$ = 7 Hz), 133.7, 131.6, 130.9, 129.2, 128.7, 128.5, 127.9, 127.4, 122.9, 121.7, 116.4, 114.9 (d, $J_{C\text{-}F}$ = 18 Hz), 58.3, 58.0, 43.5; IR (neat) 3057, 2920, 1618, 1614, 1526, 1447, 1362, 1242, 1045, 920, 864, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{44}H_{31}F_6N_2Na$ ($[M+Na]^+$): 701.2386, Found: 701.2390.

Chiral Ammonium Salt (*S*)-1g: 81% yield; $[\alpha]_D^{29}$ +32.3° [*c* = 0.89, $CHCl_3$]; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (br, 2H), 8.09 (s, 2H), 8.08 (d, *J* = 10.0 Hz, 2H), 8.04 (s, 2H), 7.91 (br, 2H), 7.73-7.69 (m, 2H), 7.48 (s, 2H), 7.47 (s, 2H), 4.87 (d, *J* = 13.6 Hz, 2H), 4.16 (d, *J* = 13.6 Hz, 2H), 3.86 (br, 2H), 3.50 (br, 2H), 2.86 (br, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.4, 136.5, 133.7, 133.1-132.2 (m), 132.0, 131.2, 130.3 (br), 128.8, 128.2, 127.5, 124.2 (q, $J_{C\text{-}F}$ = 275 Hz), 122.5, 122.3-122.2 (m), 60.5, 58.5, 57.6; IR (neat) 3057, 2876, 1468, 1373, 1323, 1279, 1177, 1130, 897, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{42}H_{28}F_{12}NNaO$ ($[M+Na]^+$): 790.1974, Found: 790.1978.

Chiral Ammonium Salt (*S*)-1h: 73% yield; $[\alpha]_D^{34}$ +21.8° [*c* = 0.43, CH_3OH]; ^1H NMR (400 MHz, CD_3OD) δ 8.34 (s, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 8.06 (s, 2H), 7.96 (s, 2H), 7.81 (s, 2H), 7.74-7.62 (m, 10H), 7.54-7.50 (m, 4H), 4.99 (d, *J* = 14.0 Hz, 2H), 3.93 (d, *J* = 14.0 Hz, 2H), 3.33 (br, 4H), 2.90 (br, 4H); ^{13}C NMR (100 MHz, $Cl_2CDCDCl_2$) δ 151.7 (d, $J_{C\text{-}F}$ = 255 Hz), 141.1, 140.9, 140.1, 140.0 (dt, $J_{C\text{-}F}$ = 255, 15 Hz), 138.7, 138.6, 135.8-135.4 (m), 134.3, 132.1, 131.2, 129.2, 128.6, 128.5, 127.9, 125.8, 122.8, 112.2-111.8 (m), 61.0, 59.0, 58.1; IR (neat) 2957, 1616, 1528, 1400, 1346, 1244, 1045, 852, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{62}H_{36}F_{12}NNaO$ ($[M+Na]^+$): 1038.2600, Found: 1038.2571.

Synthesis of Substrates 3a-g:

Substrates **3a-g** were prepared from nitriles **8a-g** and di-*t*-butyl dicarbonate according to literatures.[2, 3]



To a two-necked 200-mL round-bottomed flask equipped with magnetic stirrer were added diisopropylamine (6.60 mL, 47 mmol) and dry THF (40 mL). The solution was cooled to -78 °C (dry ice-methanol) and *n*-butyllithium (1.6 N in hexane, 29 mL, 46 mmol) was syringed in. The solution was stirred for 10 min at -78 °C and warmed to room temperature during 20 min. After cooling to -78 °C, a solution of nitrile **8** (20 mmol in 15 mL of dry THF) was syringed in during 10 min, and the mixture was allowed to stir for 0.5 h at -78 °C and 0.5 h while it warmed to room temperature. The anion solution was then cooled to -78 °C and a solution of di-*t*-butyl dicarbonate (4.82 mL in 10 mL dry THF, 21 mmol) was syringed in during 10 min and allowed to stir for 2 h at -78 °C. The reaction was quenched with 10 mL of saturated NH_4Cl. Ether (75 mL) and water (20 mL) were added, and the layers were separated. The organic layer was washed successively with HCl (10%, 30 mL × 3), water (30 mL × 3) and brine (30 mL), dried over Na_2SO_4. Evaporation and column chromatography on silica gel (ethyl acetate/hexane = 1:30-1:10 as eluant) afforded **3a-g**, all as colorless or pale yellow oils, with >95% yields.

2-Cyano-4-phenylbutyric Acid *tert*-Butyl Ester (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.20 (m, 5H), 3.35 (t, *J* = 7.6 Hz, 1H), 2.91-2.75 (m, 2H), 2.22 (dt, *J* = 7.6, 7.6 Hz,

2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 139.3, 128.7, 128.5, 126.7, 116.7, 84.1, 37.8, 32.7, 31.4, 27.8; IR (neat) 2980, 2936, 2249, 1740, 1371, 1278, 1260, 1152, 912, 839, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{19}NNaO_2$ ($[M+Na]^+$): 268.1308, Found: 268.1307.

2-Cyanohexanoic Acid *tert*-Butyl Ester (3b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (t, *J* = 7.2 Hz, 1H), 1.91 (q, *J* = 7.2 Hz, 2H), 1.50 (s, 9H), 1.47-1.33 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 116.9, 83.7, 38.5, 29.5, 28.7, 27.7, 21.9, 13.6; IR (neat) 2963, 2936, 2874, 2249, 1740, 1456, 1369, 1277, 1258, 1153, 912, 839, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{19}NNaO_2$ ($[M+Na]^+$): 220.1308, Found: 220.1310.

2-Cyanopentanoic Acid *tert*-Butyl Ester (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (t, *J* = 7.2 Hz, 1H), 1.89 (dt, *J* = 7.2, 7.2 Hz, 2H), 1.59-1.48 (m, 2H), 1.50 (s, 9H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 116.9, 83.8, 38.4, 31.8, 27.7, 20.0, 13.3; IR (neat) 2968, 2938, 2249, 1740, 1369, 1260, 1153, 842, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{17}NNaO_2$ ($[M+Na]^+$): 206.1151, Found: 206.1152.

2-Cyanobutyric Acid *tert*-Butyl Ester (3d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (dd, *J* = 7.2, 6.4 Hz, 1H), 2.01-1.93 (m, 2H), 1.50 (s, 9H), 1.12 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 116.8, 83.8, 39.9, 27.7, 23.6, 11.1; IR (neat) 2978, 2939, 2249, 1740, 1371, 1279, 1153, 840, 735 cm^{-1}; HRMS (ESI-TOF) calcd for $C_9H_{15}NNaO_2$ ($[M+Na]^+$): 192.0995, Found: 192.0987.

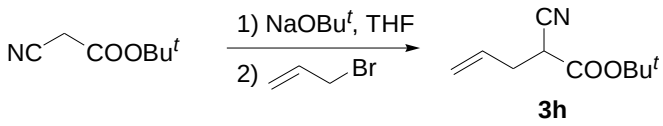
Cyanomethylacetic Acid *tert*-Butyl Ester (3e): reported compound.[3]

2-Cyano-3-methylbutyric Acid *tert*-Butyl Ester (3f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (d, *J* = 5.6 Hz, 1H), 2.44-2.32 (m, 1H), 1.51 (s, 9H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 115.7, 83.7, 46.3, 29.9, 27.8,

20.6, 18.7; IR (neat) 2972, 2936, 2249, 1738, 1468, 1371, 1283, 1260, 1155, 843, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{17}NNaO_2$ ($[M+Na]^+$): 206.1152, Found: 206.1152.

2-Cyanohex-5-enoic Acid *tert*-Butyl Ester (3g): ^1H NMR (400 MHz, $CDCl_3$) δ 5.81-5.71 (m, 1H), 5.16-5.11 (m, 1H), 5.10-5.07 (m, 1H), 3.42（dd, J = 8.0, 6.8 Hz, 1H), 2.33-2.20 (m, 2H), 2.04-1.98 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 135.5, 117.0, 116.7, 83.9, 37.7, 30.6, 28.9, 27.7; IR (neat) 2980, 2938, 2249, 1738, 1643, 1369, 1279, 1258, 1152, 918, 839, 739 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{17}NNaO_2$ ($[M+Na]^+$): 218.1152, Found: 218.1153.

Synthesis of Substrate 3h:

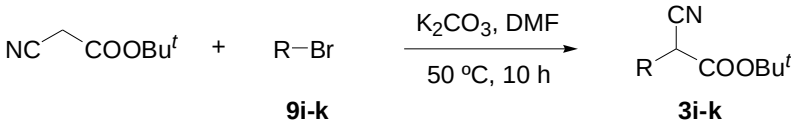


3h

A suspension of sodium *tert*-butoxide (461 mg, 4.8 mmol, 1.0 equiv) in dry THF (20 mL) was added cyanoacetic acid *tert*-butyl ester (1.02 g, 7.2 mmol, 1.5 equiv) dropwise at 0 °C under Ar. After stirring for 30 min at 0 °C, allyl bromide (406 μL, 4.8 mmol, 1 equiv) was added dropwise at that temperature. The reaction mixture was then stirred for 3 h at 0 °C before being quenched by water (20 mL). The layers were separated and the aqueous layer was extracted with ether (15 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (ethyl acetate/hexane = 1:50 as eluant) afforded **3h** (360 mg, 41% yield) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.87-5.77 (m, 1H),

5.29-5.22 (m, 2H), 3.47 (t, J = 6.8 Hz, 1H), 2.67-2.61 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 131.6, 119.7, 116.4, 84.1, 38.4, 33.9, 27.8; IR (neat) 2982, 2936, 2251, 1738, 1645, 1371, 1279, 1260, 1152, 926, 841, 741 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{21}NNaO_2$ ([M+Na]$^+$): 204.0995, Found: 234.1006.

Synthesis of Substrates 3i and 3j:



A stirred solution of **9i** (or **9j**, **9k)** (4.8 mmol), cyanoacetic acid *tert*-butyl ester (1.02 g, 7.2 mmol, 1.5 equiv), and K_2CO_3 (1.99 g, 14.4 mmol, 3.0 equiv) in DMF (8 mL) was heated to 50 °C for 10 h. The solution was cooled to room temperature and concentrated under reduced pressure. The resulting reaction mixture was suspended in diethyl ether (30 mL) and filtrated through a celite pad to remove inorganic salts. Evaporation and column chromatography on silica gel afforded **3i** (or **3j**, **3k)** (61% yield for **3i**, 76% yield for **3j**, 42% yield for **3k**) as colorless oils.

2-Cyano-5-methylhexanoic Acid *tert*-Butyl Ester (3i) (ethyl acetate/hexane = 1:60 as eluant) : ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (t, J = 6.8 Hz, 1H), 1.94-1.88 (m, 2H), 1.62-1.55 (m, 1H), 1.50 (s, 9H), 1.40-1.35 (m, 2H), 0.93 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 116.9, 83.8, 38.7, 35.6, 27.9, 27.7, 27.5, 22.3, 22.1; IR (neat) 2959, 2936, 2249, 1740, 1470, 1456, 1369, 1281, 1259, 1153, 841, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{21}NNaO_2$ ([M+Na]$^+$): 234.1465, Found: 234.1470.

2-Cyano-4-(trimethylsilyl)butyric Acid *tert*-Butyl Ester (3j) (ethyl acetate/hexane = 1:150-1:100 as eluant): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (t, *J* = 6.4 Hz, 1H), 1.91-1.84 (m, 2H), 1.50 (s, 9H), 0.72-0.59 (m, 2H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 117.0, 83.7, 41.6, 27.8, 25.3, 13.8, -2.0; IR (neat) 2980, 2955, 2899, 2247, 1740, 1371, 1250, 1153, 837, 750 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{23}NNaO_2Si$ ($[M+Na]^+$): 264.1390, Found: 264.1382.

2-Cyano-4-(4-Bromophenyl)-butyric Acid *tert*-Butyl Ester (3k) (ethyl acetate/hexane = 1:50 as eluant): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.34 (t, *J* = 7.2 Hz, 1H), 2.86-2.71 (m, 2H), 2.19 (q, *J* = 7.6 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 138.2, 131.8, 130.2, 120.5, 116.5, 84.2, 37.6, 32.0, 31.1, 27.7; IR (neat) 2980, 2933, 2868, 2249, 1738, 1489, 1456, 1369, 1275, 1258, 1148, 1072, 1011, 837, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{18}BrNNaO_2$ ($[M+Na]^+$): 346.0413, Found: 346.0401.

General Procedure of Catalytic Enantioselective Conjugate Addition of Cyanoacetates to Acetylenic Esters under Phase Transfer Condition.

To a reaction vessel containing cyanoacetate **3** (0.3 mmol) and chiral ammonium salt (*S*)-**1i** (0.003 mmol, 1 mol %) were added toluene (6.0 mL) and propiolic acid *tert*-butyl ester (82 μL, 0.6 mmol, 2 equiv) under Ar. After the reaction system was cooled to –40 °C, Cs_2CO_3 (118 mg, 0.36 mmol, 1.2 equiv) was added in a single portion. The reaction mixture was stirred vigorously at the same temperature for 6 h, quenched with saturated NH_4Cl solution (10 mL), extracted with diethyl ether (10 mL), dried over Na_2SO_4 and concentrated. The *E*/*Z* ratio was determined by ^{1}H NMR analysis of the crude sample. Purification of the residue by column chromatography on silica gel with hexane-ethyl

acetate as eluant afforded (*E*)-**4** and (*Z*)-**4**, respectively. The product was identified by NMR spectroscopy. The enantiomeric excess of the product was determined by chiral HPLC using a chiral column.

(*E*)-**4aa**: $[\alpha]_D^{30}$ +9.3° [*c* = 1.04, $CHCl_3$ (81% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.17 (m, 5H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.81-2.68 (m, 2H), 2.38 (dt, *J* = 13.6, 5.6 Hz, 1H), 2.14 (dt, *J* = 13.6, 5.6 Hz, 1H), 1.52 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 164.7, 140.3, 139.2, 128.6, 128.3, 126.6, 124.7, 116.4, 85.4, 61.0, 52.6, 39.0, 31.4, 27.7, 14.1; IR (neat) 2982, 2247, 1737, 1724, 1254, 1219, 1182, 1032, 837, 771, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{25}NNaO_4$ ($[M+Na]^+$): 366.1676, Found: 366.1670. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.1 min (major) and 11.0 min (minor).

(*Z*)-**4aa**: $[\alpha]_D^{33}$ -24.9° [*c* = 0.92, $CHCl_3$ (70% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 5H), 6.13 (d, *J* = 11.6 Hz, 1H), 6.07 (d, *J* = 11.6 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.93-2.78 (m, 2H), 2.43-2.31 (m, 2H), 1.53 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.4, 139.6, 139.5, 128.7, 128.4, 126.6, 125.5, 117.2, 84.4, 61.1, 48.7, 41.2, 31.4, 27.8, 14.1; IR (neat) 2982, 2245, 1736, 1722, 1256, 1219, 1194, 1028, 840, 771, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{25}NNaO_4$ ($[M+Na]^+$): 366.1676, Found: 366.1673. HPLC analysis: DAICEL Chiralpak OD-H, 2-propanol/hexane = 1:30, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 23.8 min (minor) and 26.6 min (major).

(*E*)-**4a**: $[\alpha]_D^{32}$ +8.7° [*c* = 1.05, $CHCl_3$ (94% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 2.84-2.67 (m, 2H), 2.37 (dt, *J* = 13.6, 5.2 Hz, 1H), 2.12 (dt, *J* = 13.6, 5.2 Hz, 1H), 1.52 (s, 9H), 1.50 (s, 9H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 165.0, 164.1, 139.3, 139.2, 128.6, 128.4, 126.6, 126.5, 116.7, 85.3, 81.5, 52.6, 39.2, 31.5, 28.0, 27.7; IR (neat) 2980, 2934, 2247, 1740, 1719, 1456, 1369, 1254, 1150, 837, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{29}NNaO_4$ ($[M+Na]^+$): 394.1989, Found: 394.2003. HPLC analysis: DAICEL Chiralpak AD-H + AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 39.6 min (major) and 41.4 min (minor).

(*Z*)-**4a**: $[\alpha]_D^{32}$ -29.7° [*c* = 1.01, $CHCl_3$ (84% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 5H), 6.05 (d, *J* = 12.0 Hz, 1H), 5.98 (d, *J* = 12.0 Hz, 1H), 2.93-2.78 (m, 2H), 2.42-2.30 (m, 2H), 1.53 (s, 9H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.7, 139.7, 138.4, 128.7, 128.4, 127.1, 126.5, 117.4, 84.2, 81.9, 48.4, 41.2, 31.4, 28.1, 27.8; IR (neat) 2980, 2934, 2245, 1724, 1705, 1456, 1371, 1261, 1153, 843, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{29}NNaO_4$ ($[M+Na]^+$): 394.1989, Found: 394.1988. HPLC analysis: DAICEL Chiralpak OD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 19.5 min (major) and 21.9 min (minor).

(*E*)-**4b**: $[\alpha]_D^{31}$ +15.5° [*c* = 1.11, $CHCl_3$ (95% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 2.07 (dt, *J* = 13.6, 4.4 Hz, 1H), 1.82 (dt, *J* = 13.6, 4.4 Hz, 1H), 1.51 (s, 9H), 1.50 (s, 9H), 1.43-1.33 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.2, 139.7, 126.0, 116.9, 85.0, 81.4, 52.7, 37.3, 28.0, 27.7, 27.1, 22.2, 13.6; IR (neat) 2980, 2938, 2247, 1740, 1719, 1369, 1256, 1150, 980, 839 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{29}NNaO_4$ ($[M+Na]^+$): 346.1989, Found: 346.1994. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.9 min (minor) and 12.9 min (major).

(*Z*)-**4b**: $[\alpha]_D^{33}$ -16.4° [*c* = 0.99, $CHCl_3$ (95% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 11.6 Hz, 1H), 5.94 (d, *J* = 11.6 Hz, 1H), 2.12-2.00 (m, 2H), 1.51 (s, 9H), 1.50 (s,

9H), 1.46-1.34 (m, 4H), 0.94 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.8, 138.9, 126.8, 117.7, 83.8, 81.8, 48.3, 39.3, 28.1 27.7, 26.9, 22.4, 13.7; IR (neat) 2978, 2934, 2245, 1742, 1719, 1369, 1252, 1152, 841, 773 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{29}NNaO_4$ ($[M+Na]^+$): 346.1989, Found: 346.1987. HPLC analysis: DAICEL Chiralpak AS-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 12.0 min (minor) and 13.7 min (major).

(*E*)-**4c**: $[\alpha]_D^{30}$ +28.3° [*c* = 1.05, $CHCl_3$ (94% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, J = 16.0 Hz, 1H), 6.23 (d, J = 16.0 Hz, 1H), 2.06 (dt, J = 12.8, 5.2 Hz, 1H), 1.81 (dt, J = 12.8, 5.2 Hz, 1H), 1.58-1.41 (m, 2H), 1.51 (s, 9H), 1.50 (s, 9H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.2, 139.7, 126.0, 116.9, 85.0, 81.4, 52.6, 39.5, 28.0, 27.7, 18.5, 13.5; IR (neat) 2978, 2936, 2247, 1740, 1719, 1369, 1254, 1150, 840 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{27}NNaO_4$ ($[M+Na]^+$): 332.1832, Found: 332.1829. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 12.9 min (minor) and 14.3 min (major).

(*Z*)-**4c**: $[\alpha]_D^{32}$ -20.6° [*c* = 0.80, $CHCl_3$ (93% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, J = 11.6 Hz, 1H), 5.94 (d, J = 11.6 Hz, 1H), 2.10-1.98 (m, 2H), 1.67-1.46 (m, 2H), 1.51 (s, 9H), 1.50 (s, 9H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.8, 138.9, 126.8, 117.6, 83.8, 81.8, 48.4, 41.6, 28.1, 27.7, 18.4, 13.8; IR (neat) 2978, 2936, 2247, 1740, 1717, 1369, 1248, 1152, 839 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{27}NNaO_4$ ($[M+Na]^+$): 332.1832, Found: 332.1823. HPLC analysis: DAICEL Chiralpak AS-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.6 min (minor) and 15.2 min (major).

(*E*)-**4d**: $[\alpha]_D^{34}$ +27.7° [*c* = 1.01, $CHCl_3$ (95% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, J = 16.0 Hz, 1H), 6.24 (d, J = 16.0 Hz, 1H), 2.14 (dt, J = 21.2, 7.6 Hz, 1H), 1.89 (dt, J =

21.2, 7.6 Hz, 1H), 1.51 (s, 9H), 1.50 (s, 9H), 1.09 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.2, 139.5, 126.3, 116.7, 85.0, 81.4, 53.4, 31.2, 28.0, 27.7, 9.4; IR (neat) 2980, 2938, 2247, 1742, 1719, 1369, 1254, 1152, 850, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{25}NNaO_4$ ($[M+Na]^+$): 318.1676, Found: 318.1672. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 12.7 min (minor) and 16.4 min (major).

(*Z*)-**4d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (d, *J* = 11.6 Hz, 1H), 5.93 (d, *J* = 11.6 Hz, 1H), 2.14 (q, *J* = 7.6 Hz, 2H), 1.51 (s, 9H), 1.50 (s, 9H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 163.8, 138.7, 127.0, 117.5, 83.9, 81.8, 49.0, 33.2, 28.1, 27.8, 9.4; IR (neat) 2978, 2936, 2245, 1742, 1717, 1369, 1248, 1150, 841, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{25}NNaO_4$ ($[M+Na]^+$): 318.1676, Found: 318.1670.

(*E*)-**4e**: $[\alpha]_D^{34}$ +31.8° [*c* = 1.05, $CHCl_3$ (93% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, *J* = 15.6 Hz, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 1.71 (s, 3H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.2, 140.1, 125.7, 117.6, 85.0, 81.4, 46.7, 27.9, 27.6, 23.9; IR (neat) 2980, 2938, 2247, 1742, 1717, 1369, 1255, 1151, 839 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{23}NNaO_4$ ($[M+Na]^+$): 304.1520, Found: 304.1516. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:200, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 14.6 min (minor) and 27.5 min (major).

(*Z*)-**4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 11.6 Hz, 1H), 5.98 (d, *J* = 11.6 Hz, 1H), 1.83 (s, 3H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 163.8, 139.7, 126.6, 118.6, 83.8, 81.8, 43.4, 28.1, 27.6, 26.1; IR (neat) 2980, 2936, 2247, 1742, 1717, 1369, 1254, 1153, 837 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{23}NNaO_4$ ($[M+Na]^+$): 304.1520, Found: 304.1516.

(*E*)-**4f**: $[\alpha]_D^{30}$ +36.6° [*c* = 1.02, $CHCl_3$ (96% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 2.43-2.33 (m, 1H), 1.51 (s, 9H), 1.50 (s, 9H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.1, 139.5, 126.7, 115.5, 84.9, 81.3, 59.1, 35.5, 28.0, 27.7, 18.3, 17.6; IR (neat) 2976, 2936, 2247, 1740, 1719, 1460, 1369, 1323, 1256, 1150, 982, 839, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{27}NNaO_4$ ($[M+Na]^+$): 332.1832, Found: 332.1825. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 9.9 min (minor) and 11.2 min (major).

(*Z*)-**4f**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (d, *J* = 11.6 Hz, 1H), 5.91 (d, *J* = 11.6 Hz, 1H), 2.39-2.29 (m, 1H), 1.51 (s, 9H), 1.50 (s, 9H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.8, 137.7, 127.2, 116.7, 83.8, 81.8, 53.5, 37.5, 28.1, 27.8, 18.0; IR (neat) 2974, 2932, 2247, 1722, 1711, 1393, 1369, 1288, 1221, 1153, 845, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{27}NNaO_4$ ($[M+Na]^+$): 332.1832, Found: 332.1826.

(*E*)-**4g**: $[\alpha]_D^{32}$ +27.0° [*c* = 1.08, $CHCl_3$ (92% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 5.82-5.72 (m, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 5.05 (d, *J* = 10.4 Hz, 1H), 2.27-2.14 (m, 3H), 1.95-1.89 (m, 1H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.1, 139.4, 135.5, 126.3, 116.6, 116.5, 85.2, 81.5, 52.3, 36.6, 29.2, 28.0, 27.7; IR (neat) 2980, 2936, 2247, 1742, 1719, 1645, 1369, 1323, 1256, 1150, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{27}NNaO_4$ ($[M+Na]^+$): 344.1832, Found: 344.1836. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.9 min (minor) and 15.5 min (major).

(*Z*)-**4g**: $[\alpha]_D^{33}$ -22.6° [*c* = 1.06, $CHCl_3$ (89% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (d,

J = 11.6 Hz, 1H), 5.95 (d, *J* = 11.6 Hz, 1H), 5.85-5.74 (m, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 5.05 (d, *J* = 10.4 Hz, 1H), 2.39-2.19 (m, 2H), 2.19-2.10 (m, 2H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.7, 138.5, 135.9, 127.0, 117.4, 116.3, 84.1, 81.9, 48.1, 38.6, 29.1, 28.1, 27.7; IR (neat) 2980, 2934, 2247, 1732, 1705, 1643, 1371, 1277, 1261, 1157, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{27}NNaO_4$ ($[M+Na]^+$): 344.1832, Found: 344.1828. HPLC analysis: DAICEL Chiralpak AS-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.2 min (minor) and 18.2 min (major).

(*E*)-**4h**: $[\alpha]_D^{33}$ +37.9° [*c* = 0.98, $CHCl_3$ (92% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 15.6 Hz, 1H), 6.24 (d, *J* = 15.6 Hz, 1H), 5.82-5.71 (m, 1H), 5.30-5.26 (m, 2H), 2.80 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.59 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.50 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.1, 139.0, 129.6, 126.5, 121.6, 116.5, 85.2, 81.5, 52.4, 41.8, 28.0, 27.7; IR (neat) 2980, 2936, 2247, 1742, 1719, 1651, 1371, 1256, 1150, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{25}NNaO_4$ ($[M+Na]^+$): 330.1676, Found: 330.1677. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 10.1 min (minor) and 15.6 min (major).

(*Z*)-**4h**: $[\alpha]_D^{33}$ -19.3° [*c* = 0.68, $CHCl_3$ (81% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (d, *J* = 11.6 Hz, 1H), 5.97 (d, *J* = 11.6 Hz, 1H), 5.92-5.82 (m, 1H), 5.30-5.25 (m, 2H), 2.88-2.77 (m, 2H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 163.8, 137.9, 130.4, 127.1, 121.2, 117.4, 84.1, 81.8, 47.7, 43.3, 28.1, 27.8; IR (neat) 2980, 2932, 2247, 1744, 1717, 1645, 1369, 1246, 1219, 1152, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{25}NNaO_4$ ($[M+Na]^+$): 330.1676, Found: 330.1672. HPLC analysis: DAICEL Chiralpak AS-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.1 min (minor) and 17.2 min (major).

(*E*)-**4i**: $[\alpha]_D^{32}$ +27.3° [*c* = 1.06, $CHCl_3$ (95% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 2.07 (dt, *J* = 12.8, 4.8 Hz, 1H), 1.82 (dt, *J* = 12.8, 4.8 Hz, 1H), 1.62-1.55 (m, 1H), 1.51 (s, 9H), 1.50 (s, 9H), 1.41-1.35 (m, 1H), 1.31-1.22 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.2, 139.7, 126.0, 116.9, 84.9, 81.4, 52.7, 35.7, 33.8, 28.0, 27.8, 27.7, 22.2, 22.1; IR (neat) 2978, 2961, 2936, 2247, 1740, 1719, 1653, 1369, 1256, 1150, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{31}NNaO_4$ ($[M+Na]^+$): 360.2145, Found: 360.2152. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 12.3 min (minor) and 13.7 min (major).

(*Z*)-**4i**: $[\alpha]_D^{32}$ -28.6° [*c* = 0.95, $CHCl_3$ (93% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 11.6 Hz, 1H), 5.93 (d, *J* = 11.6 Hz, 1H), 2.13-2.01 (m, 2H), 1.67-1.54 (m, 1H), 1.51 (s, 9H), 1.50 (s, 9H), 1.48-1.34 (m, 2H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.8, 138.8, 126.8, 117.7, 83.8, 81.8, 48.3, 37.6, 33.6, 28.1, 27.9, 27.8, 22.4, 22.3; IR (neat) 2959, 2936, 2245, 1732, 1717, 1369, 1250, 1153, 772 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{31}NNaO_4$ ($[M+Na]^+$): 360.2145, Found: 360.2146. HPLC analysis: DAICEL Chiralpak AS-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 10.4 min (minor) and 12.1 min (major).

(*E*)-**4j**: $[\alpha]_D^{32}$ +17.8° [*c* = 1.11, $CHCl_3$ (95% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 2.07 (dt, *J* = 14.0, 4.0 Hz, 1H), 1.80 (dt, *J* = 14.0, 4.0 Hz, 1H), 1.51 (s, 9H), 1.50 (s, 9H), 0.72 (dt, *J* = 14.0, 4.0 Hz, 1H), 0.55 (dt, *J* = 14.0, 4.0 Hz, 1H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.3, 139.6, 126.2, 116.9, 84.9, 81.4, 55.1, 33.5, 28.0, 27.7, 11.9, -2.1; IR (neat) 2980, 2955, 2247, 1740, 1719, 1647, 1369, 1323, 1252, 1150, 839, 771 cm^{-1}; HRMS (ESI-TOF) calcd for

$C_{19}H_{33}NNaO_4Si$ ([M+Na]$^+$): 390.2071, Found: 390.2071. HPLC analysis: DAICEL Chiralpak OD-H + OD-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 22.9 min (major) and 24.0 min (minor).

(*Z*)-**4j**: $[\alpha]_D^{32}$ -20.7° [*c* = 0.91, $CHCl_3$ (93% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (d, *J* = 11.6 Hz, 1H), 5.93 (d, *J* = 11.6 Hz, 1H), 2.14-2.01 (m, 2H), 1.50 (s, 18H), 0.80-0.65 (m, 2H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.8, 138.5, 126.9, 117.8, 83.7, 81.8, 50.2, 35.1, 28.1, 27.8, 11.7, -2.0; IR (neat) 2982, 2955, 2243, 1732, 1709, 1371, 1279, 1248, 1157, 842, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{33}NNaO_4Si$ ([M+Na]$^+$): 390.2071, Found: 390.2063. HPLC analysis: DAICEL Chiralpak AS-H, 2-propanol/hexane = 1:400, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.0 min (minor) and 13.0 min (major).

(*E*)-**4k**: $[\alpha]_D^{27}$ +3.9° [*c* = 1.21, $CHCl_3$ (95% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 15.6 Hz, 1H), 6.28 (d, *J* = 15.6 Hz, 1H), 2.80-2.63 (m, 2H), 2.34 (dt, *J* = 12.8, 5.2 Hz, 1H), 2.09 (dt, *J* = 12.8, 5.2 Hz, 1H), 1.52 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 164.0, 139.0, 138.2, 131.7, 130.1, 126.6, 120.4, 116.5, 85.4, 81.5, 52.4, 38.8, 30.9, 28.0, 27.7; IR (neat) 2980, 2934, 2247, 1740, 1717, 1489, 1456, 1369, 1255, 1152, 837, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{28}BrNNaO_4$ ([M+Na]$^+$): 472.1094 Found: 472.1092. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 16.8 min (major) and 18.0 min (minor).

(*Z*)-**4k**: $[\alpha]_D^{28}$ -13.6° [*c* = 1.06, $CHCl_3$ (91% *ee*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.05 (d, *J* = 11.6 Hz, 1H), 5.96 (d, *J* = 11.6 Hz, 1H), 2.89-2.72 (m, 2H), 2.39-2.27 (m, 2H), 1.53 (s, 9H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 163.7, 138.7, 138.2, 131.7, 130.1, 127.2, 120.3, 117.3, 84.3, 82.0,

48.4, 40.8, 30.8, 28.1, 27.8; IR (neat) 2980, 2932, 2245, 1740, 1717, 1489, 1456, 1369, 1254, 1150, 839, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{28}BrNNaO_4$ ($[M+Na]^+$): 472.1094 Found: 472.1101. HPLC analysis: DAICEL Chiralpak OD-H, 2-propanol/hexane = 1:100, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 9.1 min (major) and 11.1 min (minor).

(*E*)-**4l**: $[\alpha]_D^{27}$ +1.0° [*c* = 1.10, $CHCl_3$ (18% *ee*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.39 (m, 5H), 7.20 (d, *J* = 15.6 Hz, 1H), 6.28 (d, *J* = 15.6 Hz, 1H), 1.49 (s, 9H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 164.2, 139.5, 134.2, 129.3, 129.1, 126.1, 116.4, 85.6, 81.4, 56.2, 28.0, 27.5; IR (neat) 2980, 2936, 2249, 1742, 1717, 1651, 1450, 1369, 1251, 1146, 835, 756 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{25}NNaO_4$ ($[M+Na]^+$): 366.1676 Found: 366.1679. HPLC analysis: DAICEL Chiralpak AD-H, 2-propanol/hexane = 1:100, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 14.7 min (minor) and 16.4 min (major).

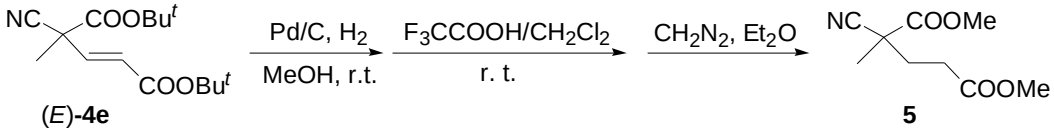
(*Z*)-**4l**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.44-7.37 (m, 3H), 6.33 (d, *J* = 11.6 Hz, 1H), 6.16 (d, *J* = 11.6 Hz, 1H), 1.46 (s, 9H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 163.8, 139.9, 136.6, 129.0, 128.7, 127.7, 126.4, 116.8, 84.3, 81.8, 53.3, 28.0, 27.4; IR (neat) 2980, 2934, 2249, 1746, 1717, 1450, 1369, 1258, 1150, 822, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{25}NNaO_4$ ($[M+Na]^+$): 366.1676 Found: 366.1675.

Catalytic Enantioselective Conjugate Addition of 2-Cyano-4-phenyl-butyric acid *tert*-butyl ester (3a) to 2-Cyclohexenone under Phase Transfer Condition.

To a reaction vessel containing 2-cyano-4-phenylbutyric acid *tert*-butyl ester **3a** (73.7

mg, 0.3 mmol) and chiral ammonium salt (*S*)-**1i** (4.4 mg, 0.003 mmol, 1 mol %) were added toluene (6.0 mL) and 2-cyclohexenone (58 μL, 0.6 mmol, 2 equiv) under Ar. After the reaction system was cooled to 0 °C, Cs_2CO_3 (49 mg, 0.15 mmol, 0.5 equiv) was added in a single portion. The reaction mixture was stirred vigorously at the same temperature for 2 h, quenched with saturated NH_4Cl solution (10 mL), extracted with diethyl ether (10 mL), dried over Na_2SO_4 and concentrated. Purification of the residue by column chromatography on silica gel with hexane-ethyl acetate (10:1-2:1) as eluant afforded **6** as a pale yellow oil. The products were identified by NMR spectroscopy. The *ee* and d. r. of the products were determined by chiral HPLC on chiral column. $[\alpha]_D^{33}$ +8.6° [*c* = 1.04, $CHCl_3$ (d. r. = 85/15, 91% *ee* (major)/4% *ee* (minor)]; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of isomers) δ 7.32-7.16 (m, 5H), 2.91-2.81 (m, 1H), 2.63-2.01 (m, 10H), 1.85-1.60 (m, 2H), 1.57 (s, 4H, minor), 1.56 (s, 5H, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 166.9 (minor), 166.7 (major), 139.7 (major), 139.6 (minor), 128.6, 128.2 (major), 128.1 (minor), 126.5, 117.8 (major), 117.7 (minor), 84.9 (major), 84.7 (minor), 55.3 (minor), 55.2 (major), 44.3 (major), 44.1 (minor), 43.9 (major), 42.7 (minor), 40.8 (minor), 40.7 (major), 37.4 (major), 36.8 (minor), 31.8 (major), 31.6 (minor), 27.8 (major), 27.5 (minor), 26.1, 24.2 (minor), 24.0 (major); IR (neat) 2976, 2936, 2241, 1732, 1717, 1454, 1369, 1252, 1152, 1030, 843, 770, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{27}NNaO_3$ ($[M+Na]^+$): 364.1883, Found: 364.1871. HPLC analysis: DAICEL Chiralpak AD-H + AD-H, 2-propanol/hexane = 1:30, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 57.3 min (major), 64.7 min (minor); 62.2 min (major), and 106.5 min (minor).

Determination of the Absolute Configuration of (*E*)-4e.



To a stirred solution of (*E*)-**4e** (93% *ee*) (80 mg, 0.28 mmol) in MeOH (3 mL) was added 10% Pd on carbon (17 mg) under Ar. The Ar was replaced by a stream of hydrogen, and then the mixture was stirred at 25 °C under 1 atm of hydrogen for 12 h. Insoluble materials were removed by filtration through a celite pad. The filtrate was concentrated under reduced pressure and then dissolved in CH_2Cl_2 (1 mL) and trifluoroacetic acid (2 mL). After stirring at 25 °C for 3 h, the reaction mixture was diluted with ether (10 mL) and water (10 mL) was added. The aqueous layer was extracted with ether (10 mL × 2) and the combined organic extracts were dried over Na_2SO_4. Ether and trifluoroacetic acid were evaporated under reduced pressure below 20 °C. To this crude mixture was added freshly prepared CH_2N_2 in ether until the color of the reaction mixture became yellow. Evaporation and column chromatography on silica gel afforded **5** (6.5 mg, 11% yield) as colorless oil. This product was found to be identical with the reported one by ^{1}H NMR and ^{13}C NMR analysis. The absolute configuration of (*E*)-**4e** was found to be *S*: $[\alpha]_D^{29}$ -1.63° (*c* = 0.30, $CHCl_3$) [Lit[3]: $[\alpha]_D^{20}$ +1.7° (*c* = 5.09, $CHCl_3$) (82% *ee*, *R* enantiomer)].

X-ray Structure Determination

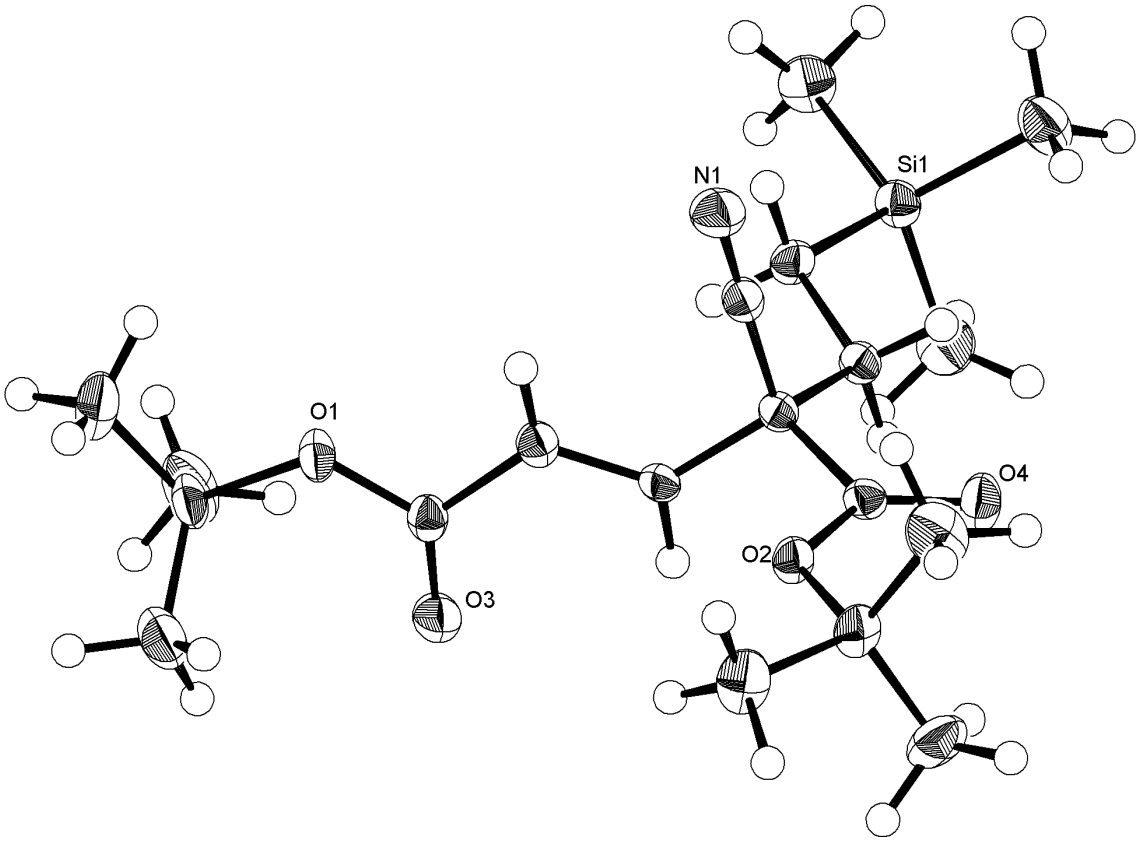
(*E*)-4j: The product was recrystallized by slow evaporation of ether. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected

by Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKα radiation (λ = 1.54187 Å) to a maximum 2θ value of 136.4 °. The structure was solved by direct methods[4] and expanded using Fourier techniques[5]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[6] on F^2 was based on 4007 observed reflections and 228 variable parameters. The absolute configuration was determined by reference to the Flack parameter[7] 0.02(3). The crystallographic data were summarized in the following table.

(*E*)-4j	
empirical formula	$C_{19}H_{33}NO_4Si$
formula weight	367.56
crystal system	Orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	6.32501(11)
b, Å	15.6014(3)
c, Å	22.1928(4)
V , Å^3	2189.96(7)
Z	4
D_{calc}, g/cm^3	1.115
T, °C	-140
μ (CuKα), cm^{-1}	11.135
no. of reflns meased	29093
no. of reflns obsd	4007

no. of reflns variable	228
R (All reflections)	0.0518
R_W (All reflections)	0.1438
goodness of fit	1.089
Flack Parameter (Friedel pairs = 1678)	0.02(3)

ORTEP Diagram of (*E*)-4j



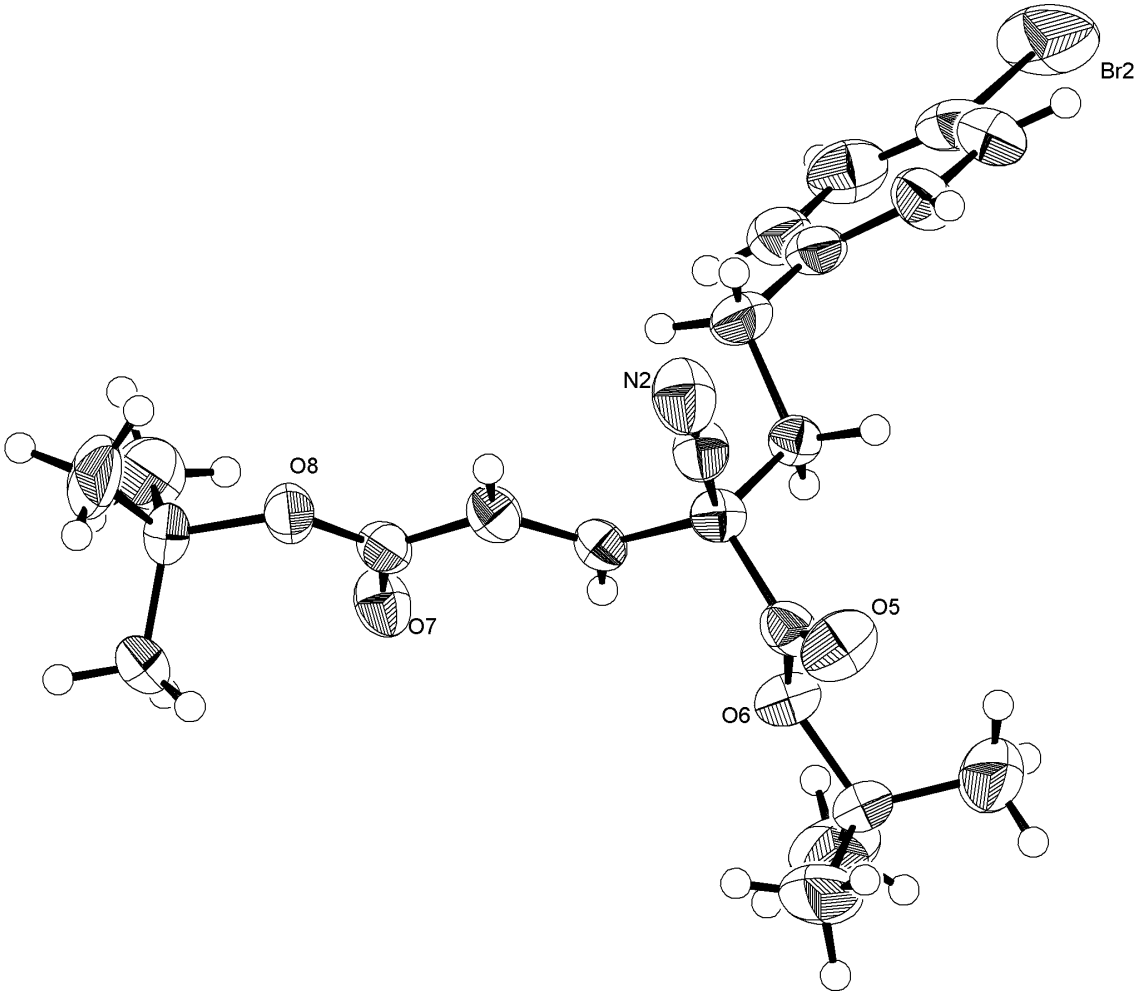
(*E*)-4k: The product was recrystallized from hot hexane. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKα radiation (λ = 1.54187 Å) to a maximum 2θ value of

136.4 °. The structure was solved by direct methods[8] and expanded using Fourier techniques[5]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[6] on F^2 was based on 8267 observed reflections and 506 variable parameters. The absolute configuration was determined by reference to the Flack parameter[7] -0.02(2). The crystallographic data were summarized in the following table.

(*E*)-4k	
empirical formula	$C_{22}H_{28}BrNO_4$
formula weight	450.37
crystal system	Orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	11.9583(3)
b, Å	18.0650(3)
c, Å	21.9228(5)
V , Å^3	4735.88(18)
Z	8
D_{calc}, g/cm^3	1.263
T, °C	-130
μ (CuKα), cm^{-1}	25.676
no. of reflns meased	34419
no. of reflns obsd	8267
no. of reflns variable	506
R (All reflections)	0.0882

R_W (All reflections)	0.1804
goodness of fit	1.039
Flack Parameter (Friedel pairs = 3554)	-0.02(2)

ORTEP Diagram of (*E*)-4k



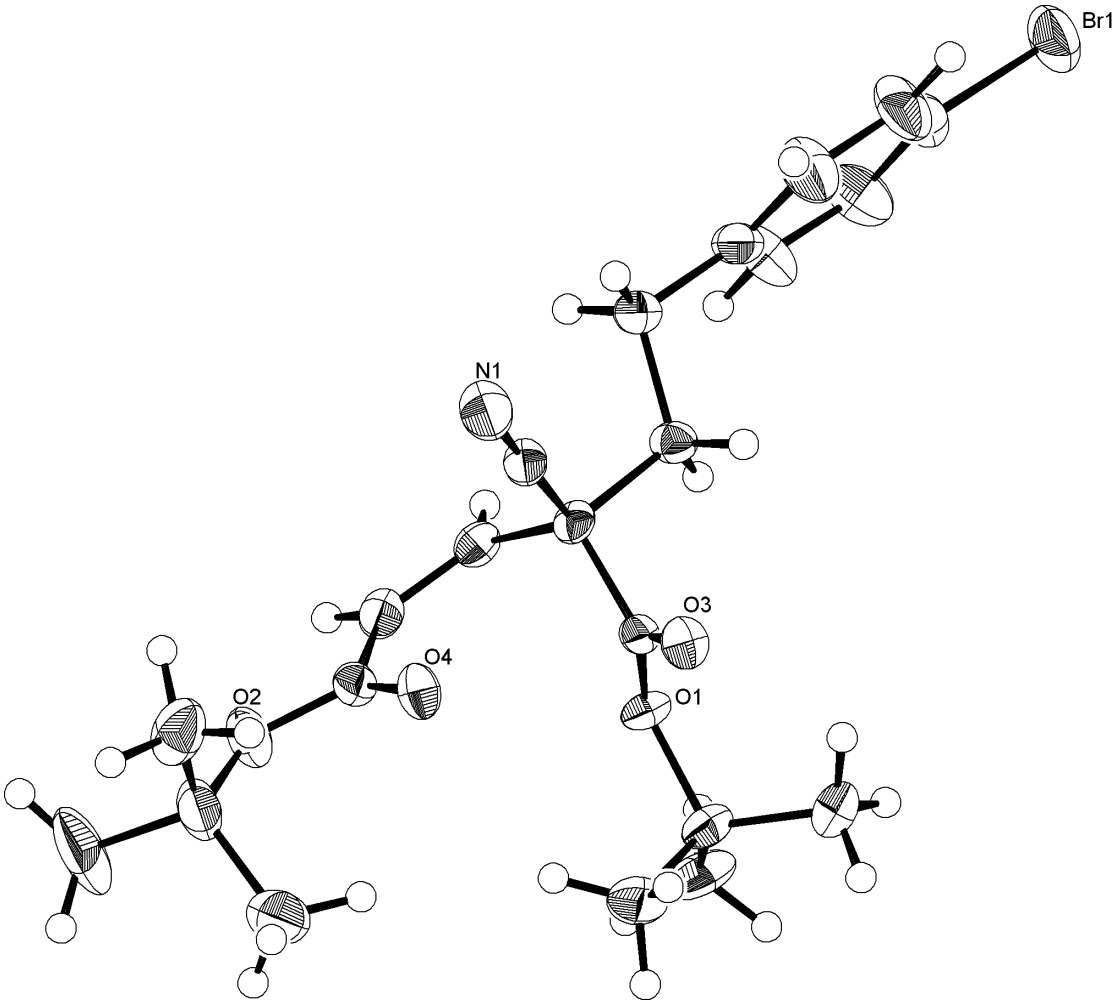
(Z)-4k: The product was recrystallized from CH_2Cl_2/hexane. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using

graphite-monochromated CuKα radiation (λ = 1.54187 Å) to a maximum 2θ value of 136.4 °. The structure was solved by direct methods[8] and expanded using Fourier techniques[5]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[6] on F^2 was based on 4010 observed reflections and 255 variable parameters. The absolute configuration was determined by reference to the Flack parameter[7] 0.01(2). The crystallographic data were summarized in the following table.

(*Z*)-4k	
empirical formula	$C_{22}H_{28}BrNO_4$
formula weight	450.37
crystal system	Orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	5.8517(3)
b, Å	18.9534(6)
c, Å	20.9196(6)
V , Å^3	2320.17(14)
Z	4
D_{calc}, g/cm^3	1.289
T, °C	-130
μ (CuKα), cm^{-1}	26.205
no. of reflns meased	15477
no. of reflns obsd	4010
no. of reflns variable	255

R (All reflections)	0.0672
R_W (All reflections)	0.1652
goodness of fit	1.072
Flack Parameter (Friedel pairs = 1635)	0.01(2)

ORTEP Diagram of (*Z*)-4k



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(6) Least Squares function minimized: (SHELXL97)

$\Sigma w(Fo^2-Fc^2)^2$ where w = Least Squares weights.

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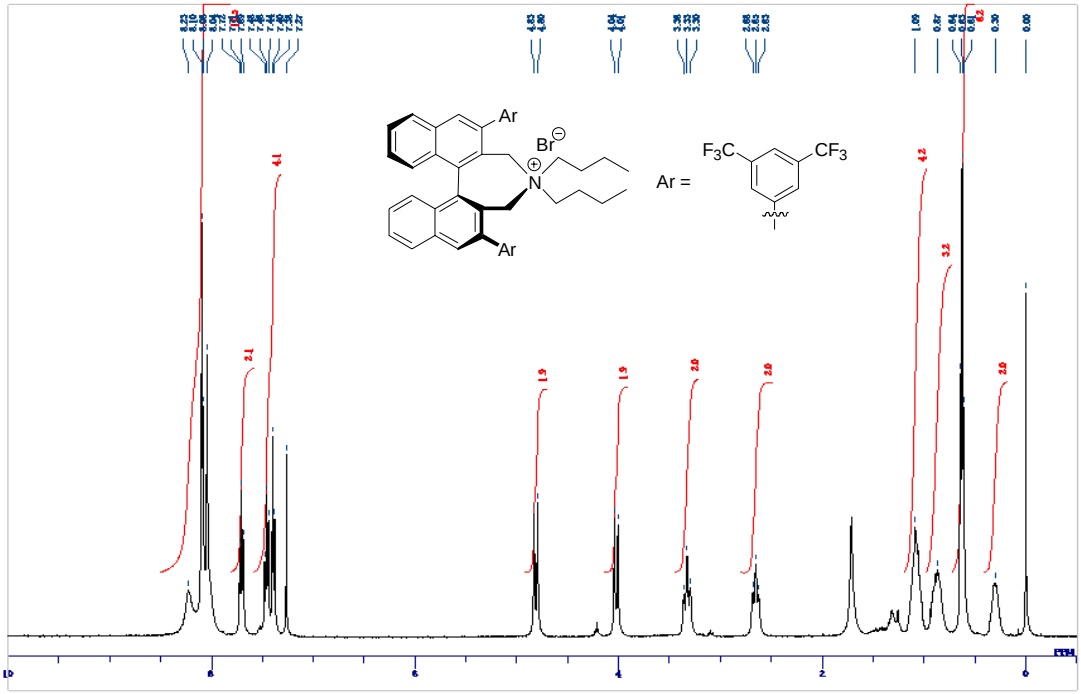
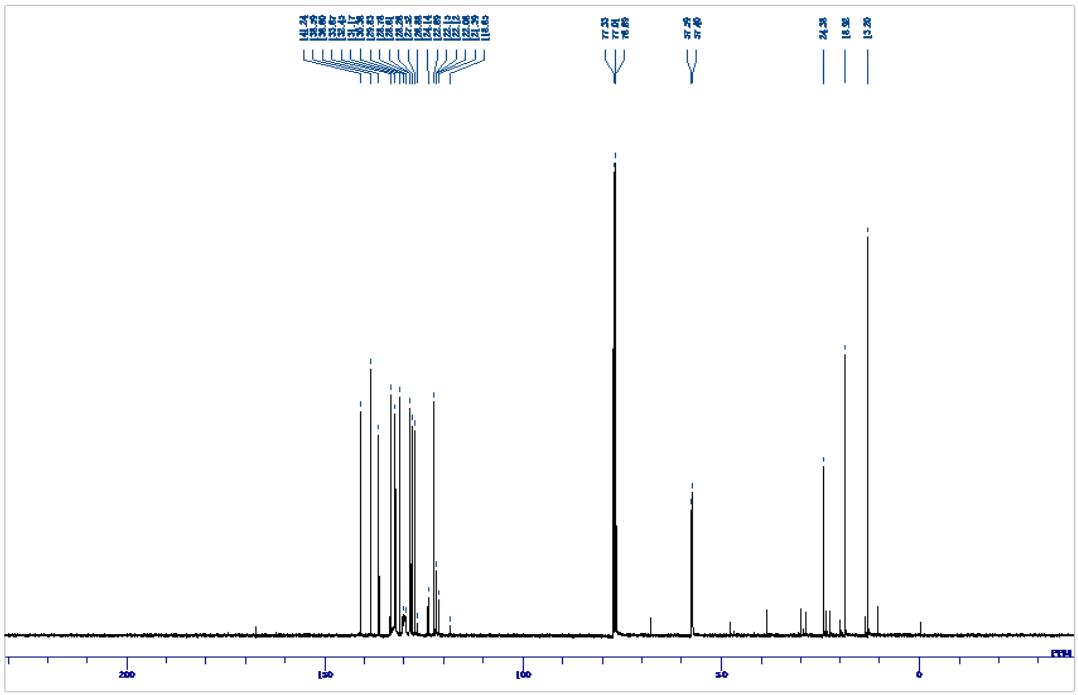
Copies of ^{1}H and ^{13}C NMR Spectra of Catalysts and Michael Addition Products:

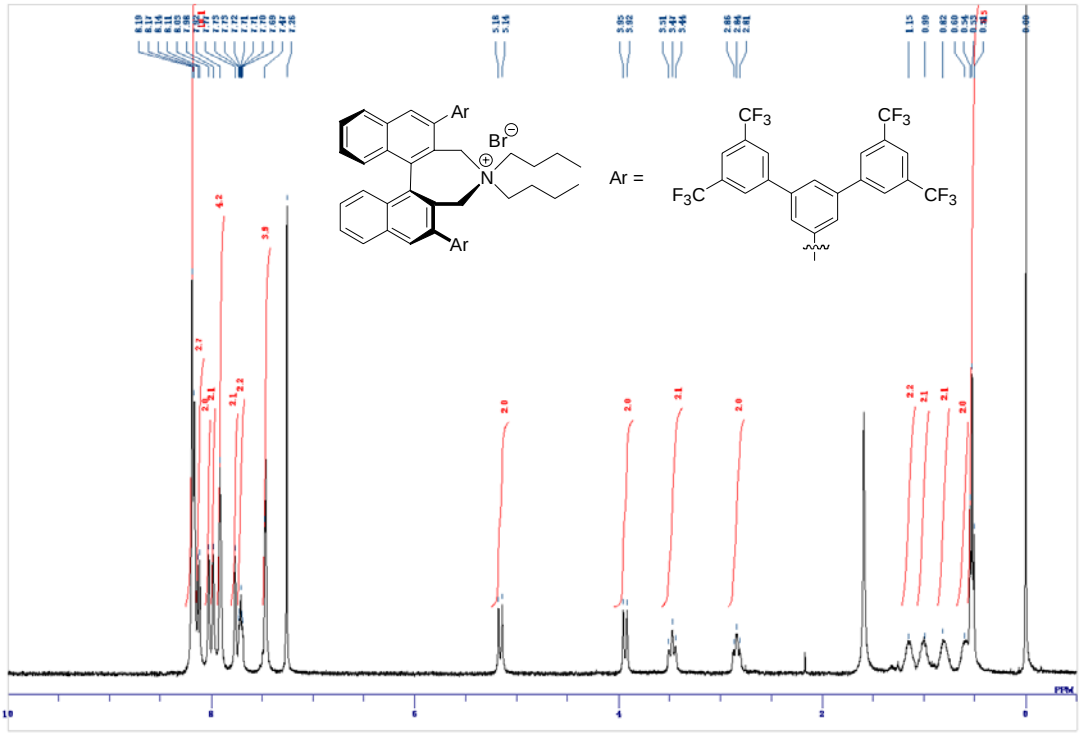
^{1}H NMR: Chiral ammonium salt (*S*)-**1b**



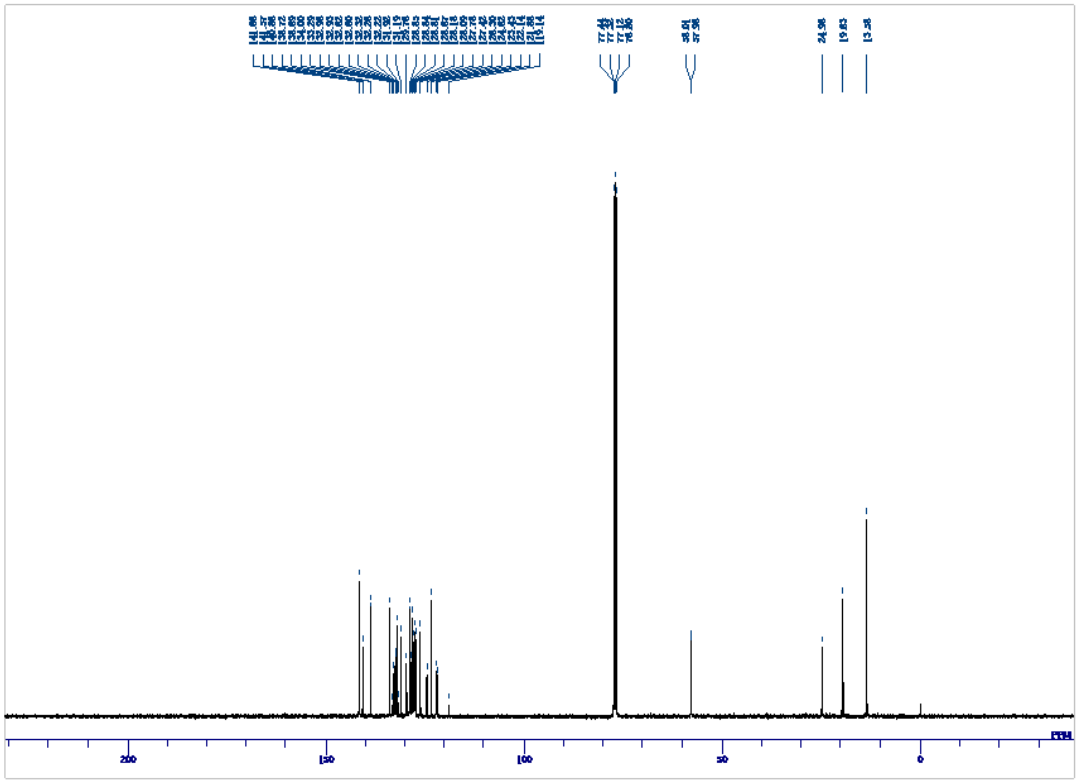
^{13}C NMR: Chiral ammonium salt (*S*)-**1b**



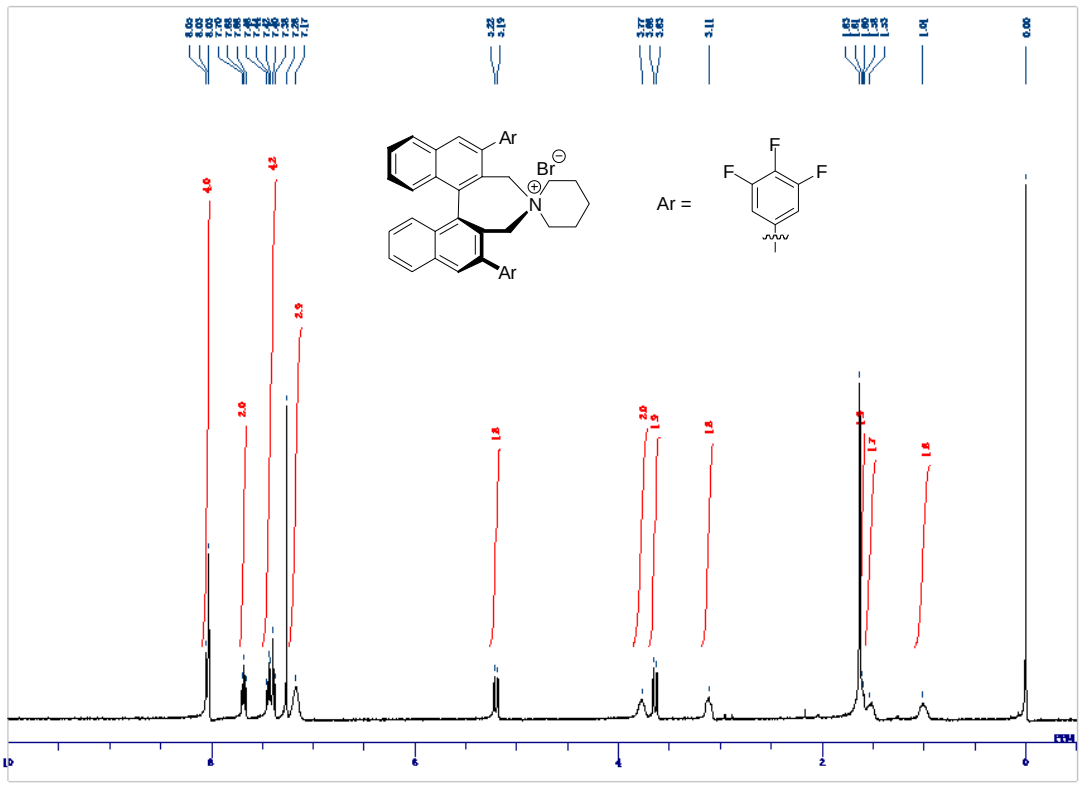
^{1}H NMR: Chiral ammonium salt (*S*)-**1c**



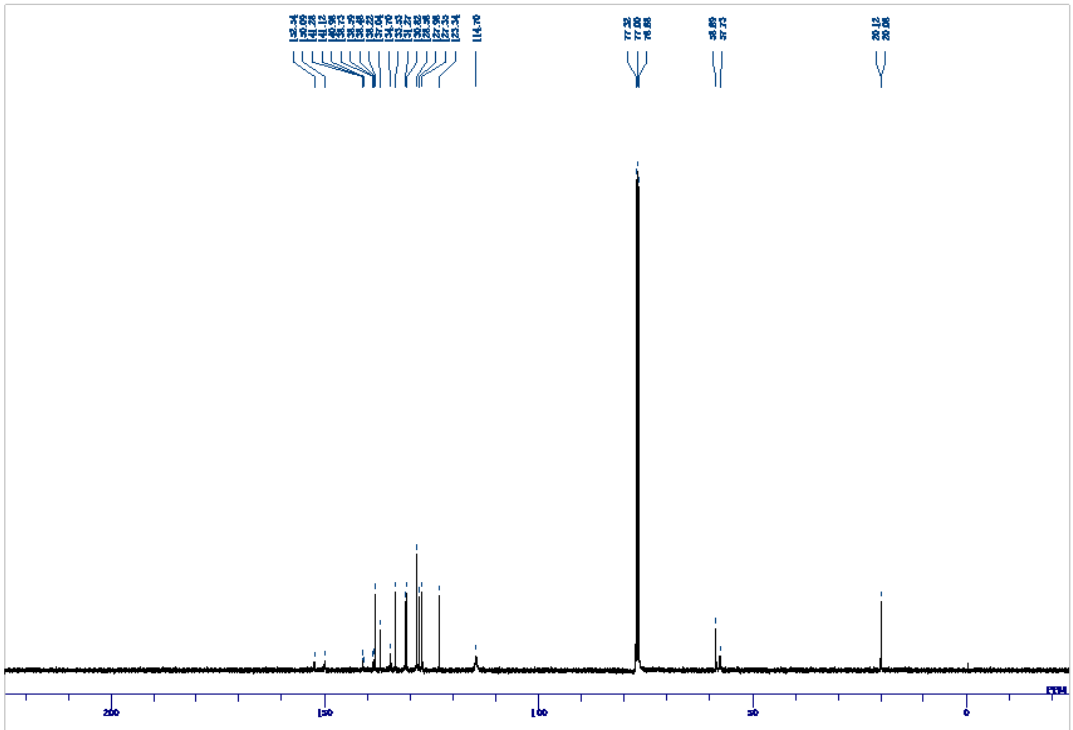
^{13}C NMR: Chiral ammonium salt (*S*)-**1c**



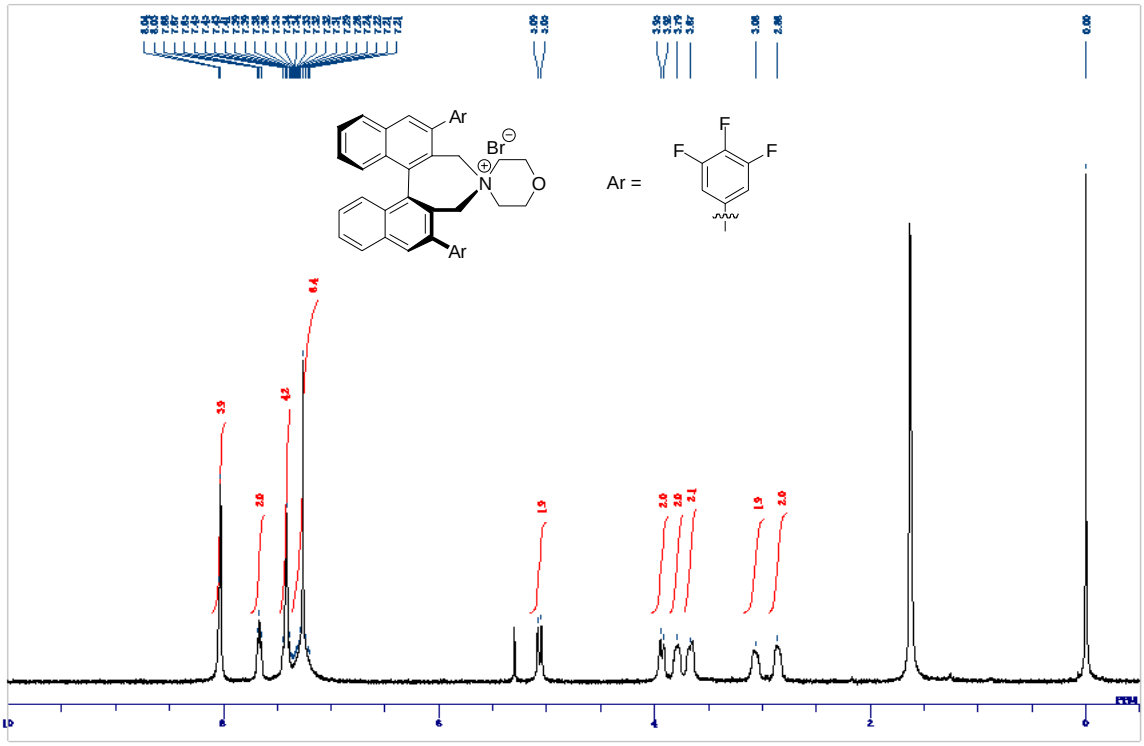
^{1}H NMR: Chiral ammonium salt (*S*)-**1d**



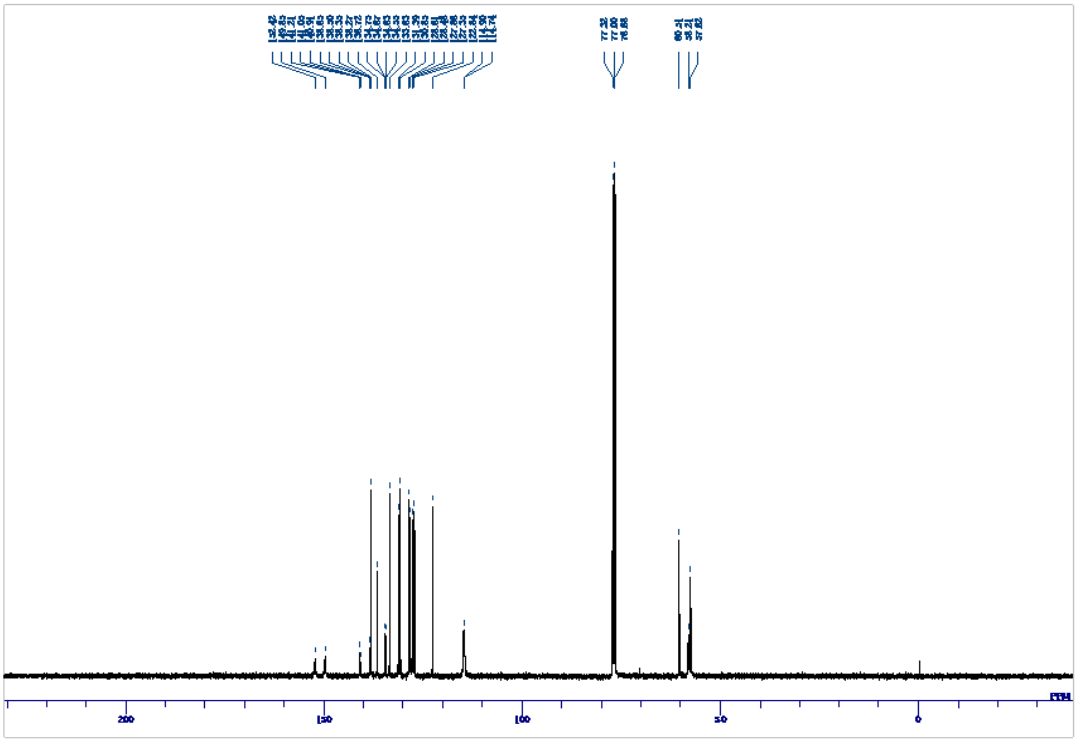
^{13}C NMR: Chiral ammonium salt (*S*)-**1d**



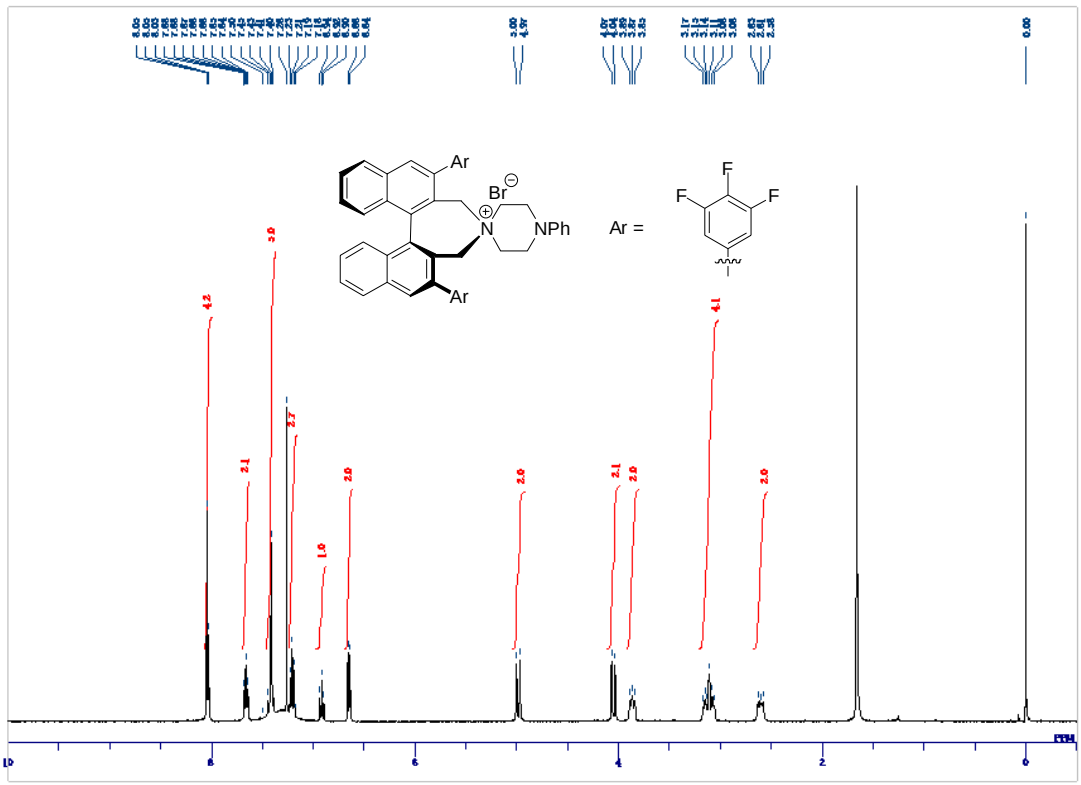
^{1}H NMR: Chiral ammonium salt (*S*)-**1e**



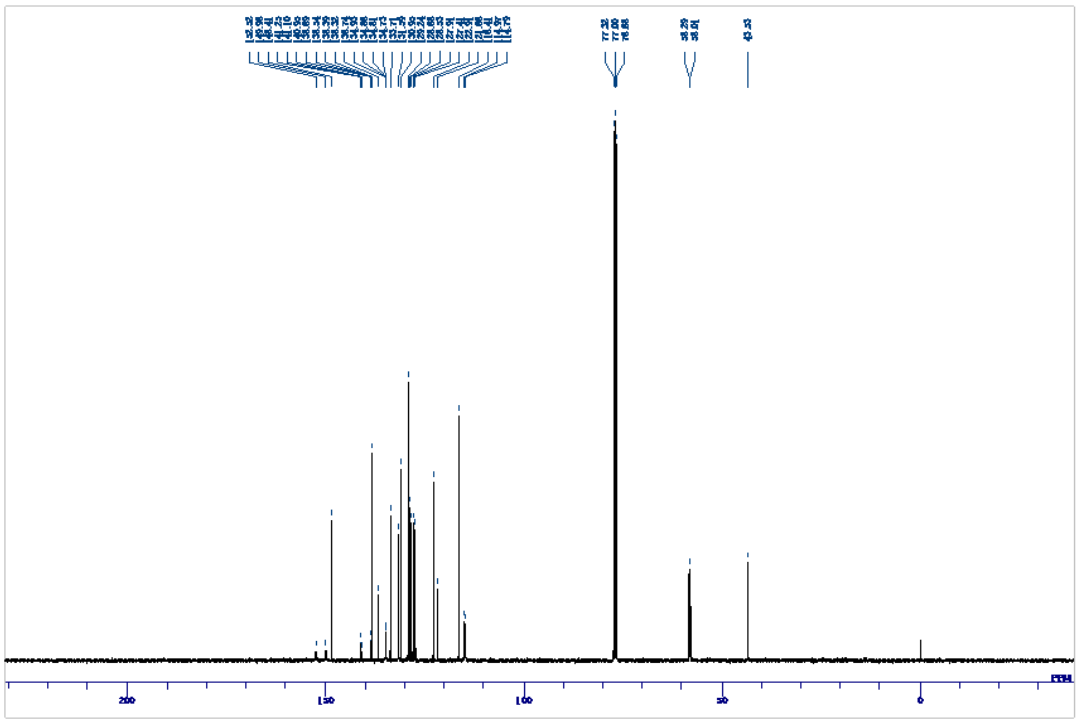
^{13}C NMR: Chiral ammonium salt (*S*)-**1e**



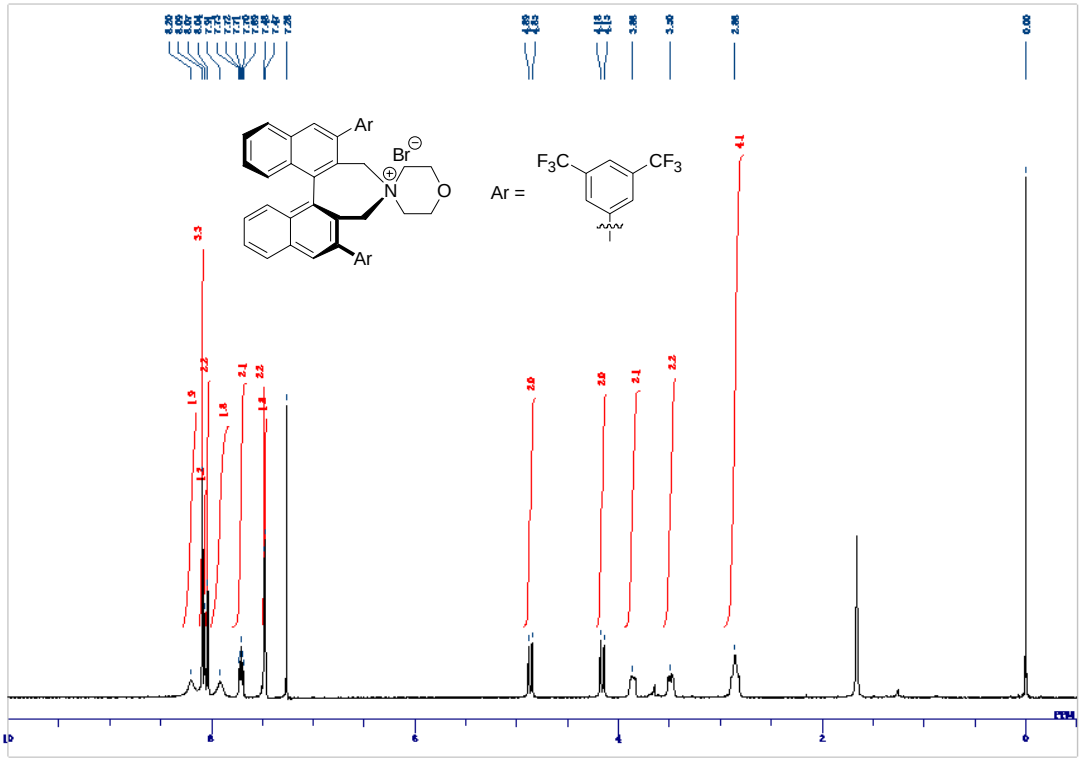
^{1}H NMR: Chiral ammonium salt (*S*)-**1f**



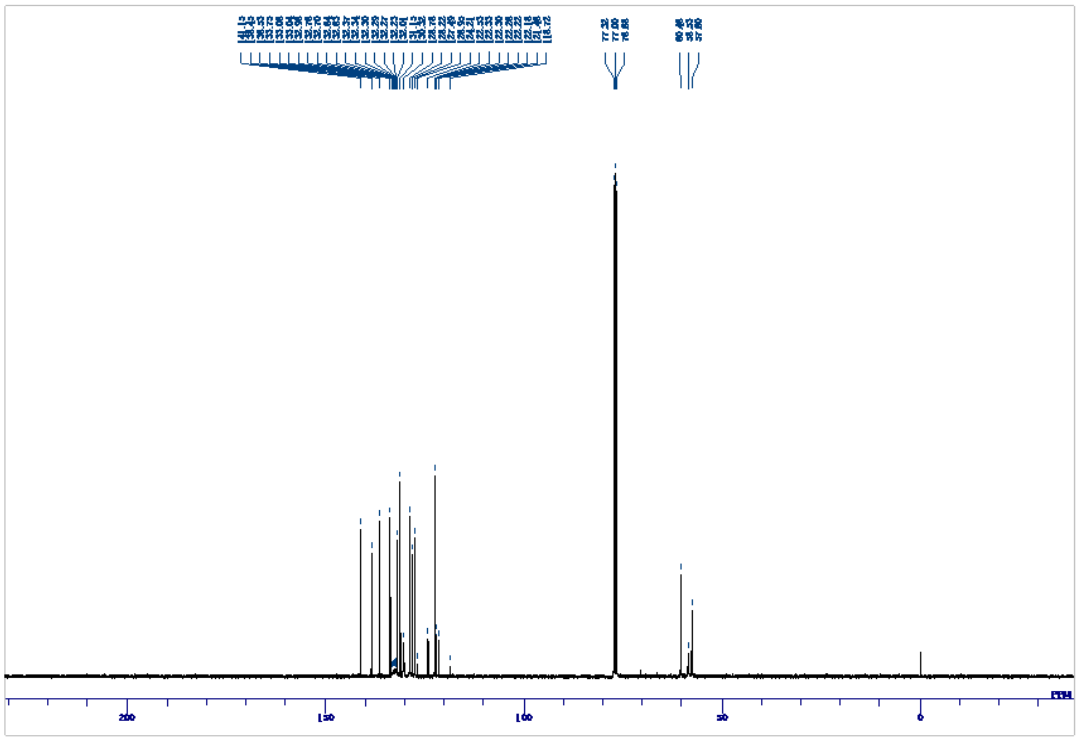
^{13}C NMR: Chiral ammonium salt (*S*)-**1f**



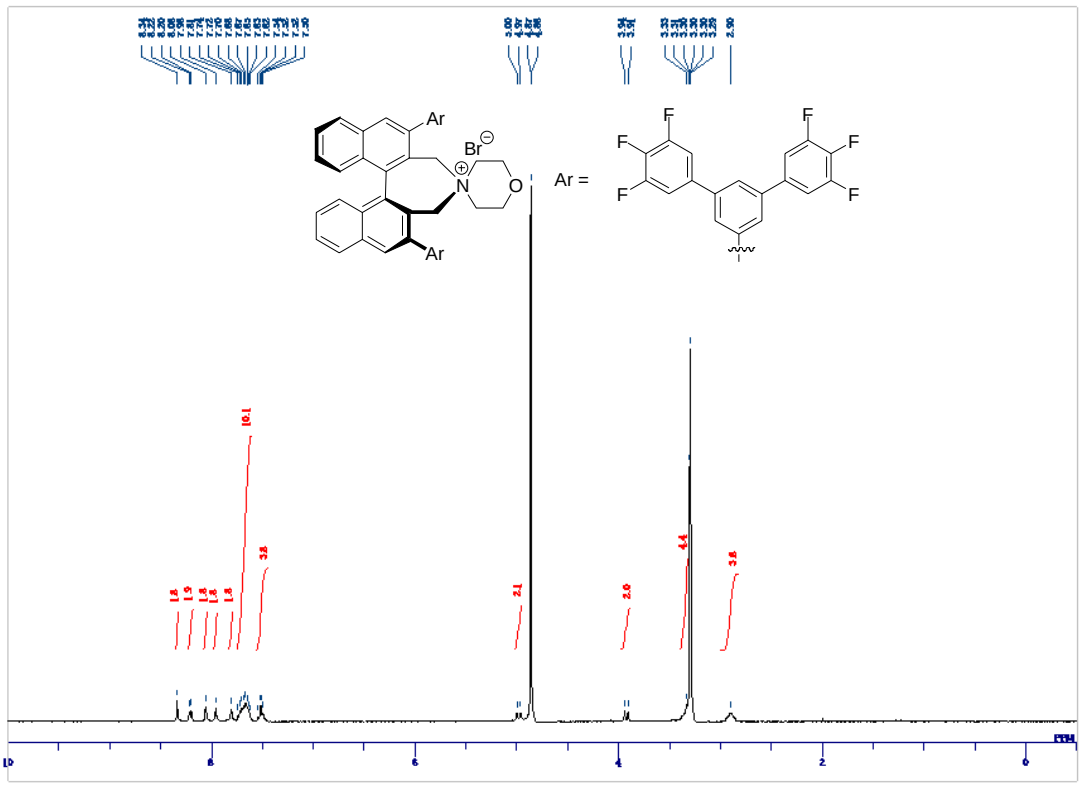
^{1}H NMR: Chiral ammonium salt (*S*)-**1g**



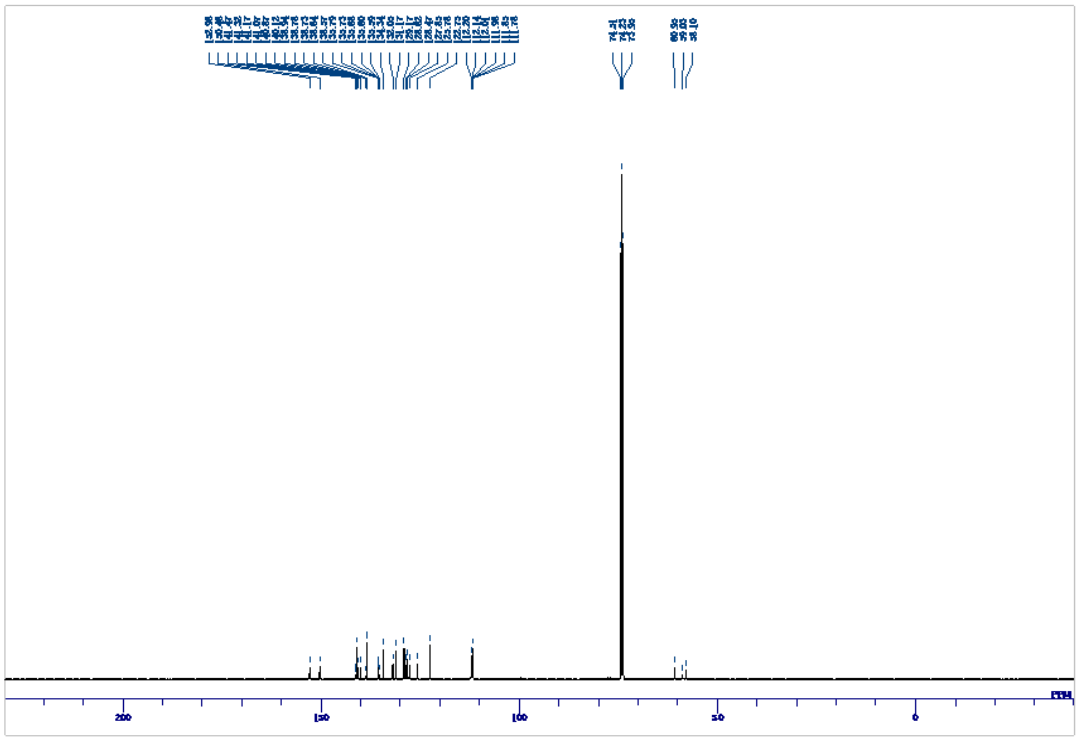
^{13}C NMR: Chiral ammonium salt (*S*)-**1g**



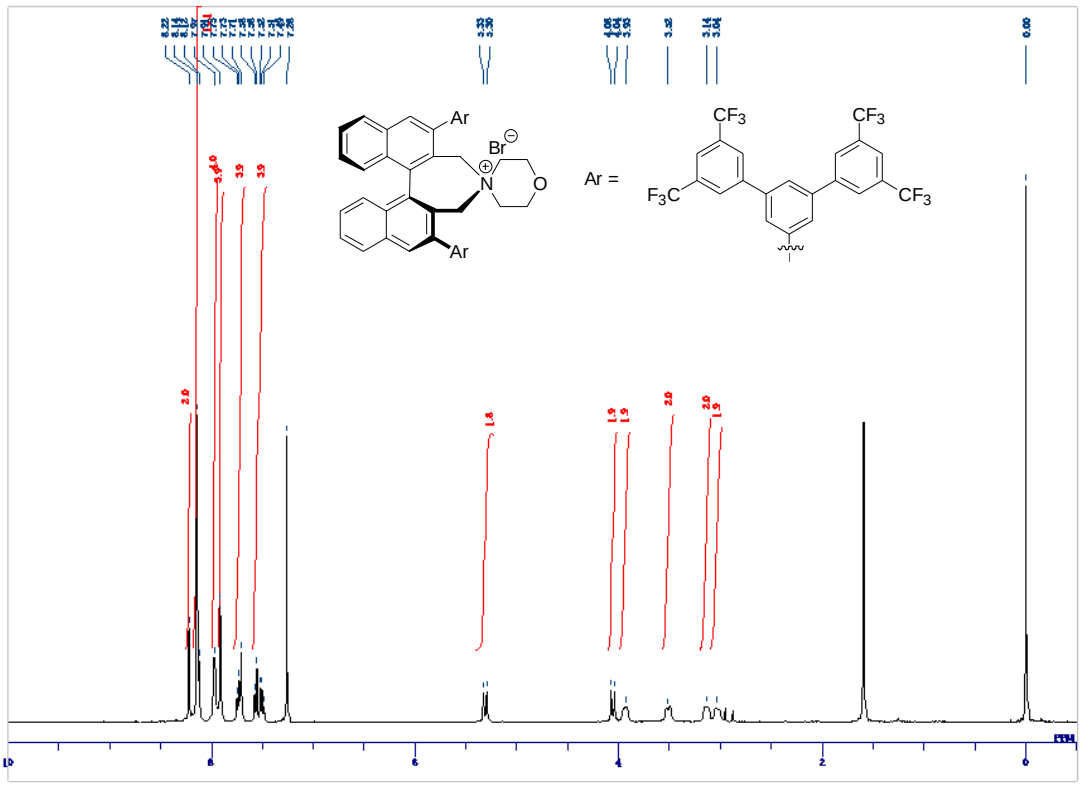
^{1}H NMR: Chiral ammonium salt (*S*)-**1h**



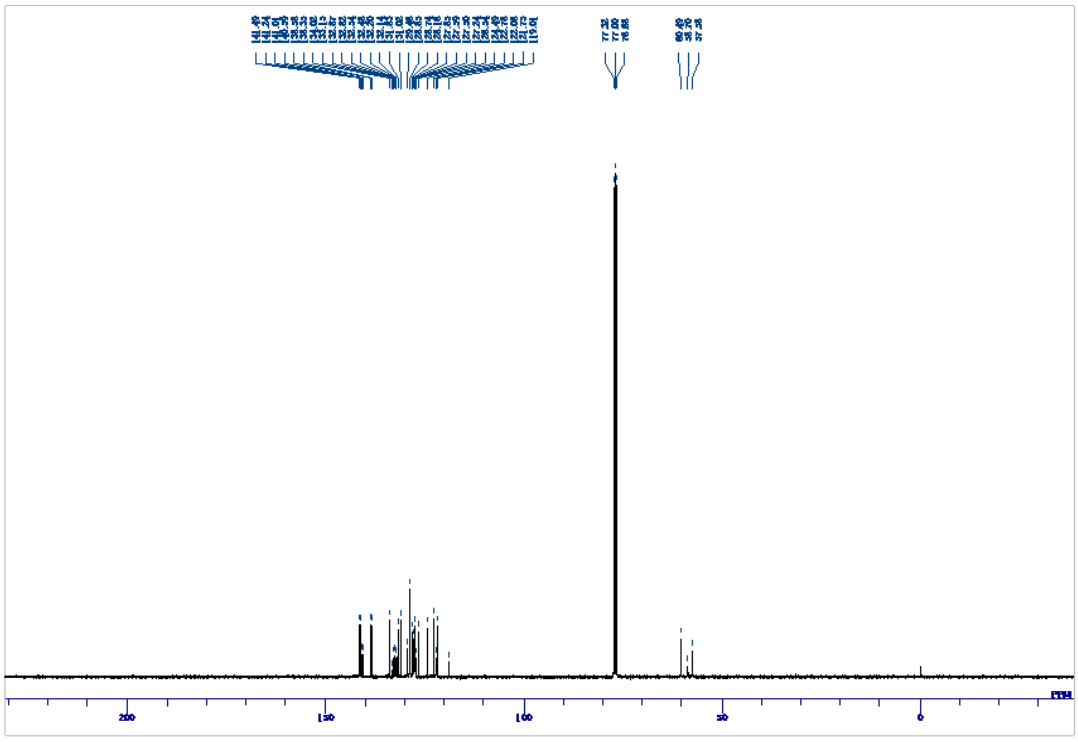
^{13}C NMR: Chiral ammonium salt (*S*)-**1h**



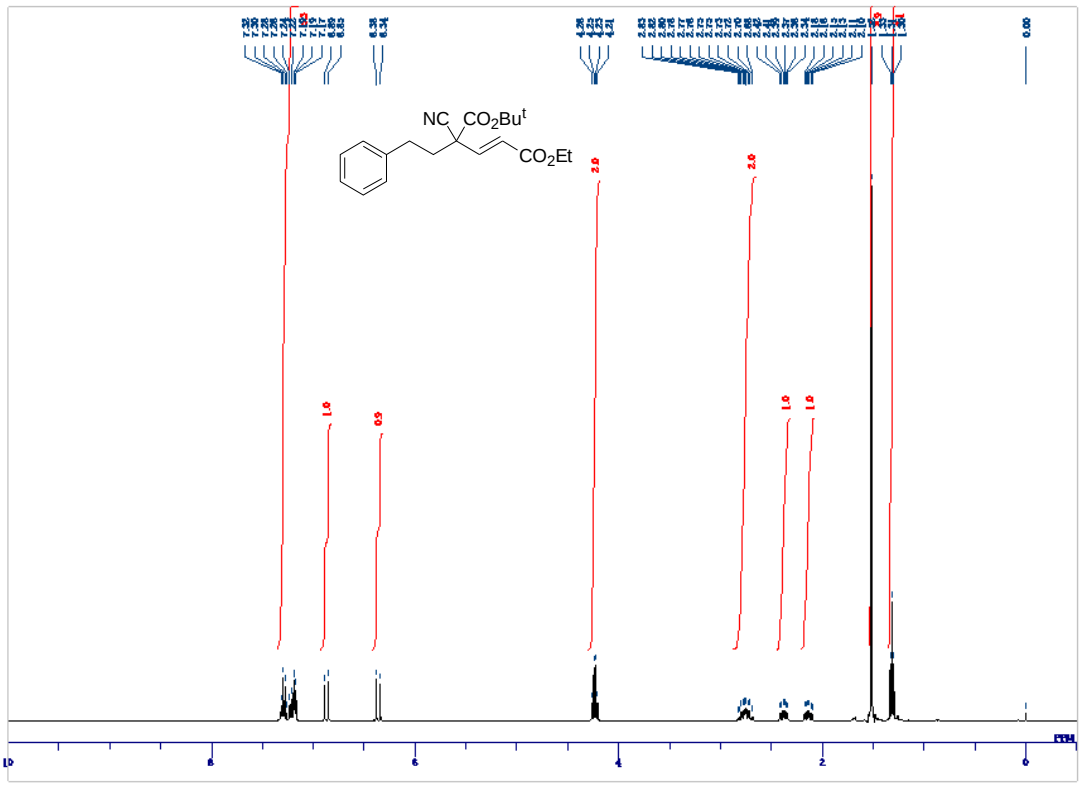
^{1}H NMR: Chiral ammonium salt (*S*)-**1i**



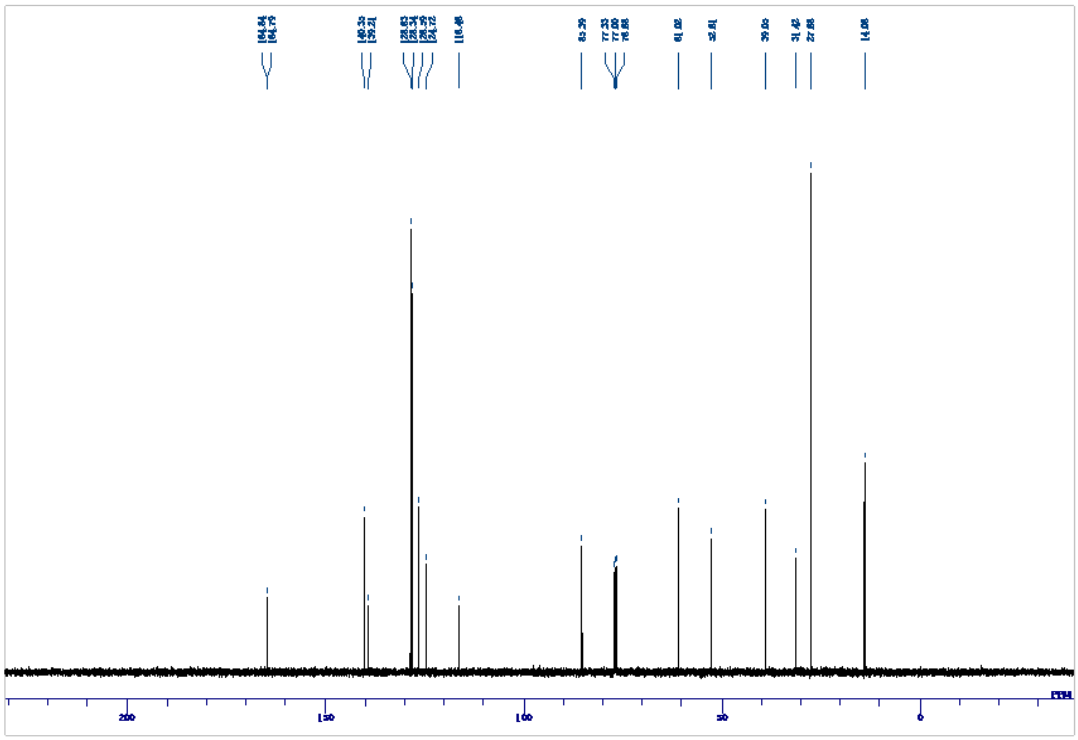
^{13}C NMR: Chiral ammonium salt (*S*)-**1i**



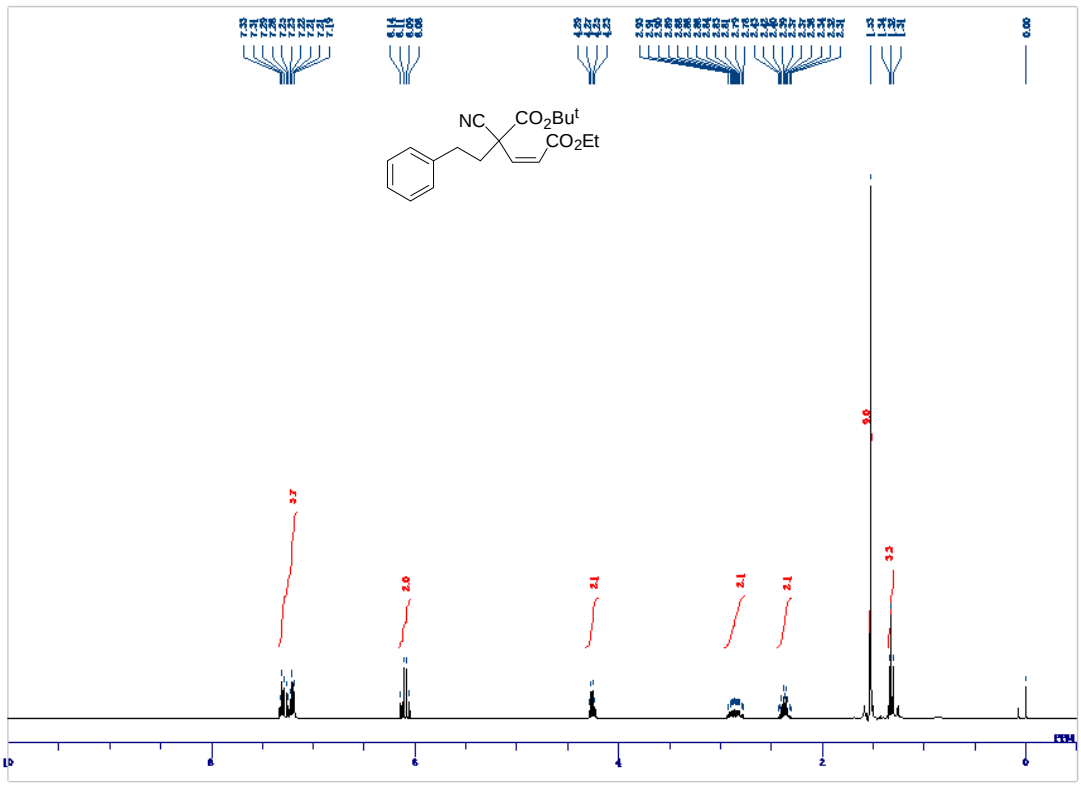
^{1}H NMR: (*E*)-**4aa**



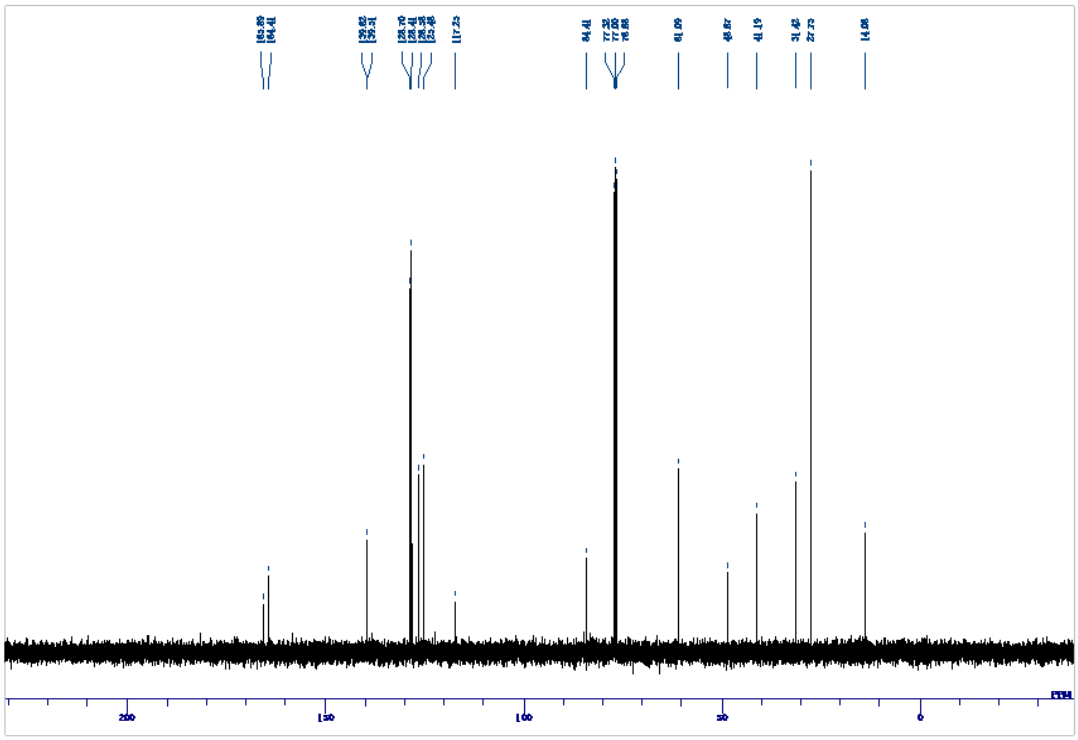
^{13}C NMR: (*E*)-**4aa**



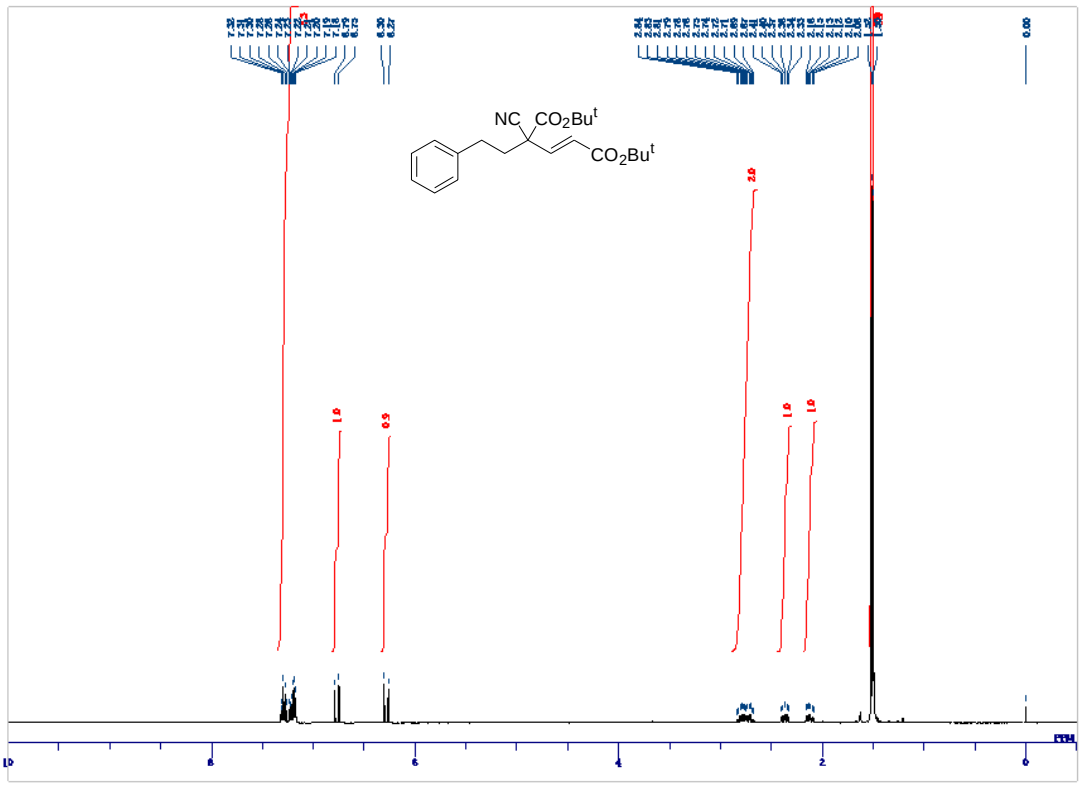
^{1}H NMR: (*Z*)-**4aa**



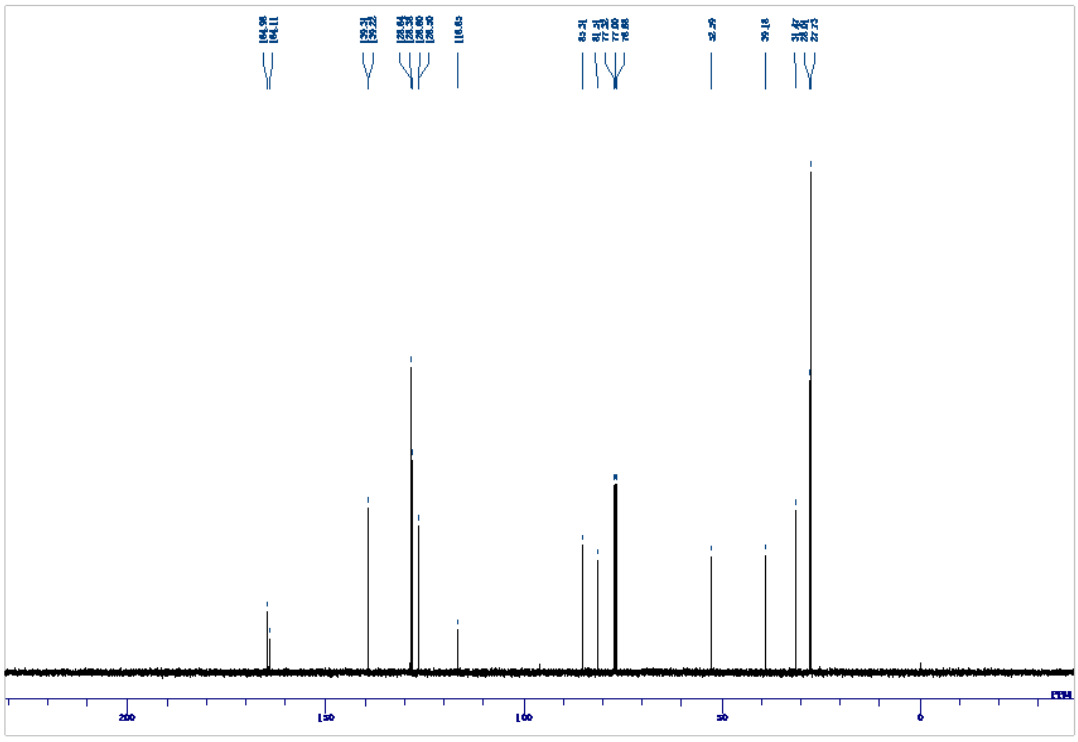
^{13}C NMR: (*Z*)-**4aa**



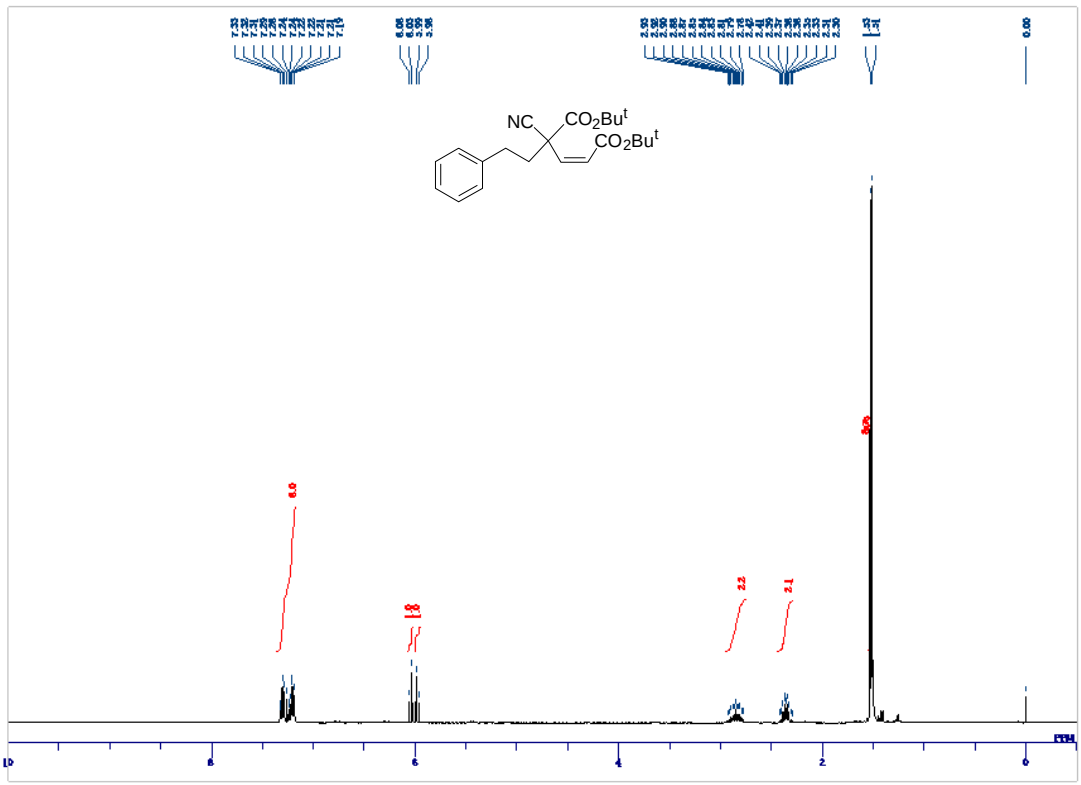
^{1}H NMR: (*E*)-**4a**



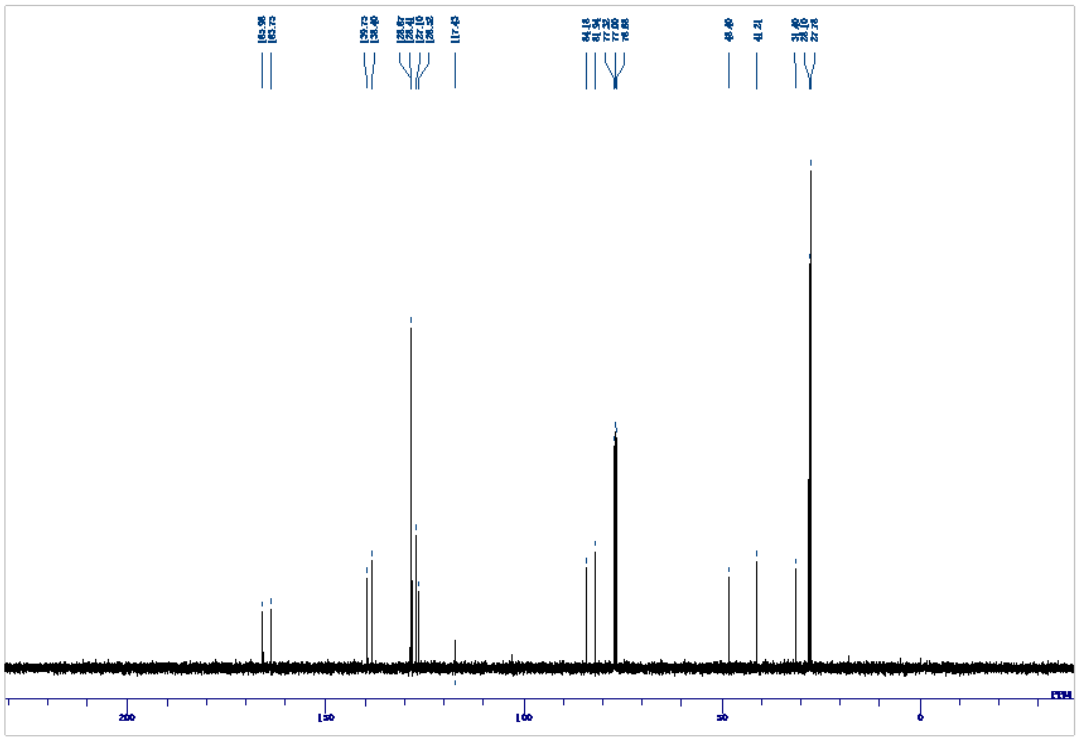
^{13}C NMR: (*E*)-**4a**



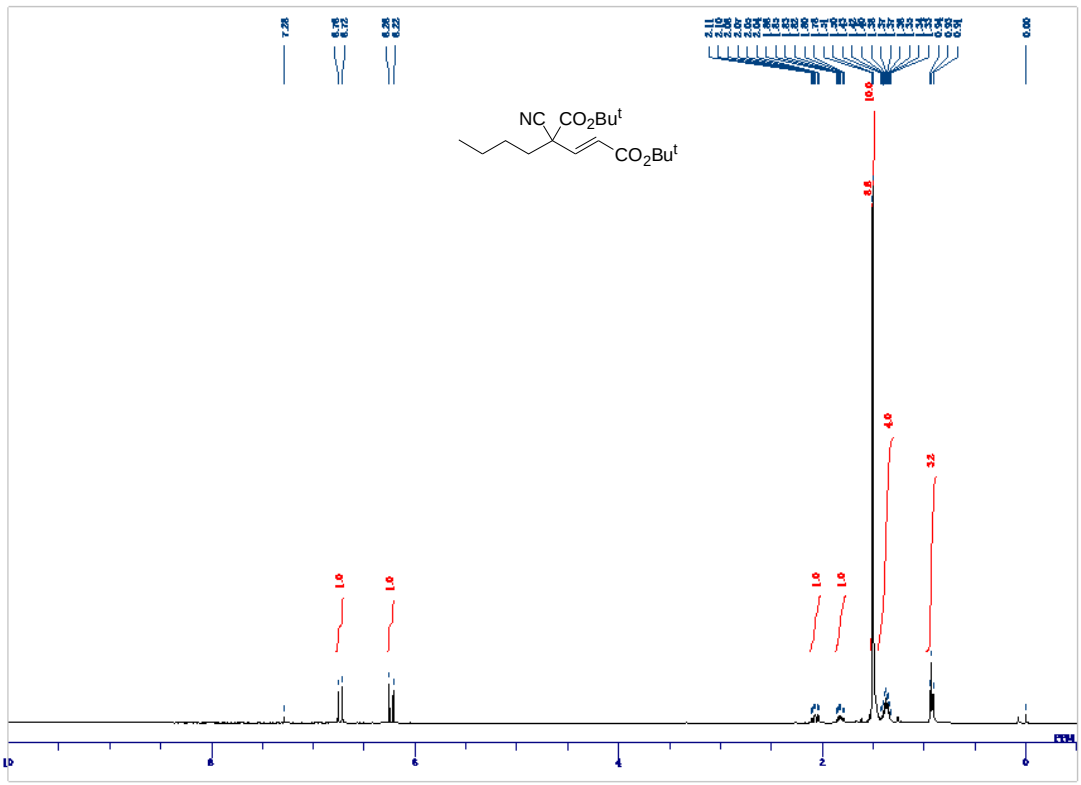
^{1}H NMR: (*Z*)-**4a**



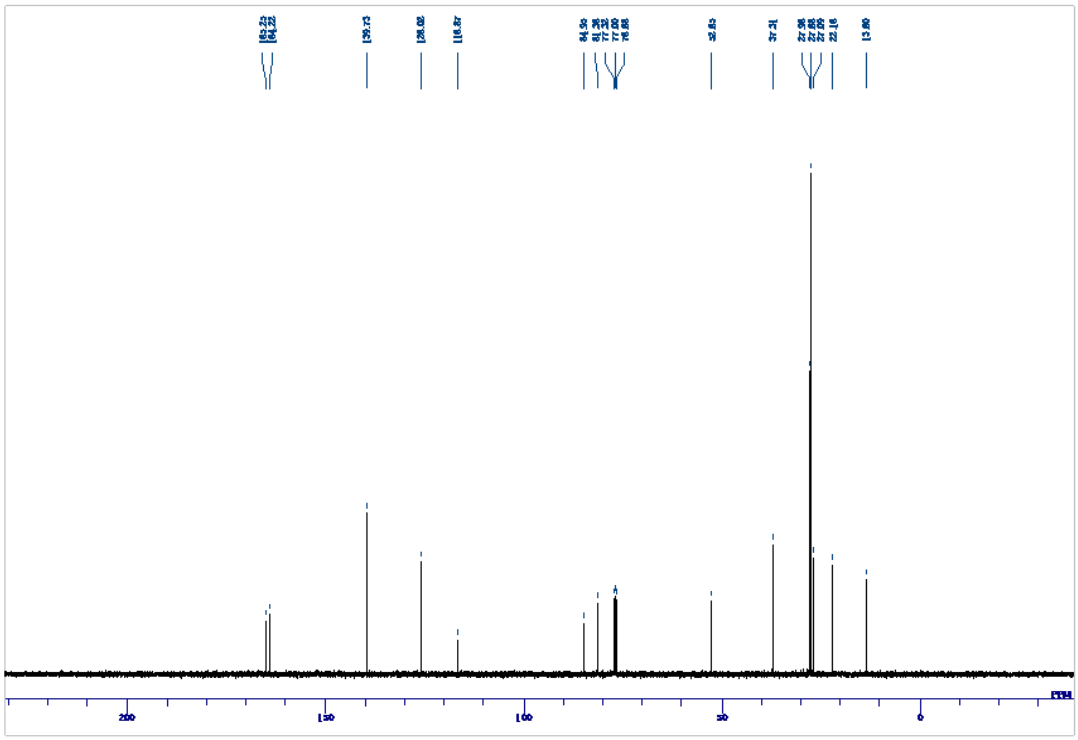
^{13}C NMR: (*Z*)-**4a**



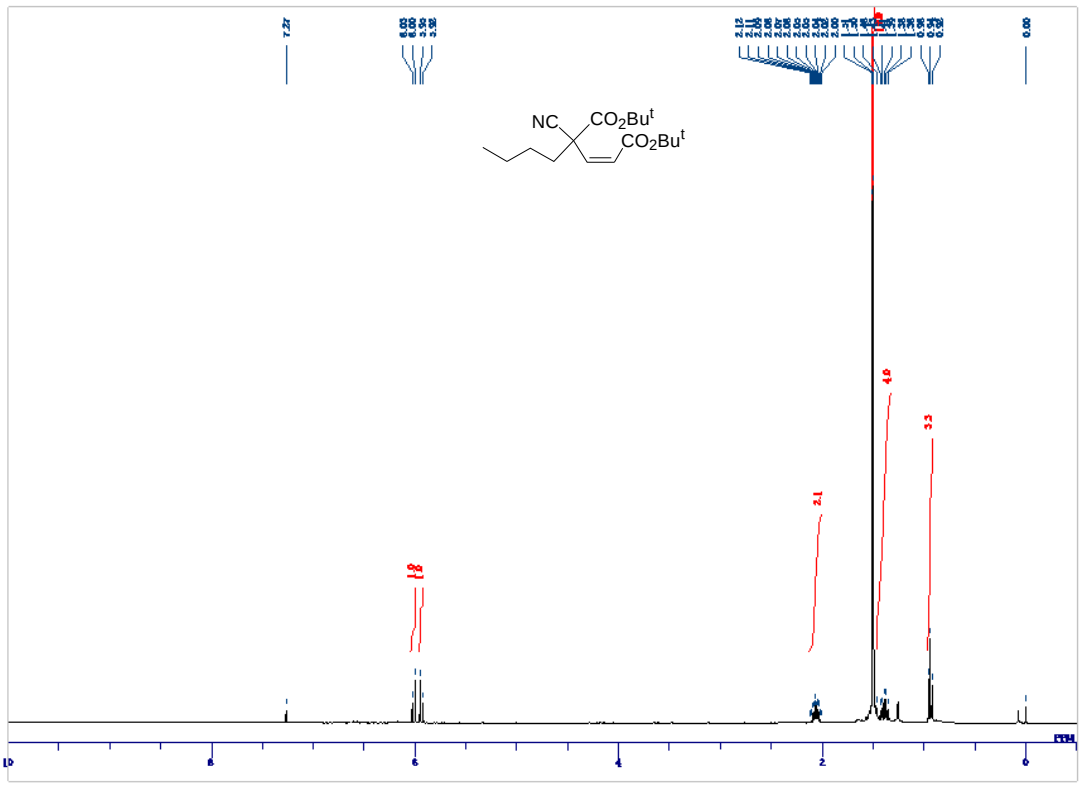
^{1}H NMR: (*E*)-**4b**



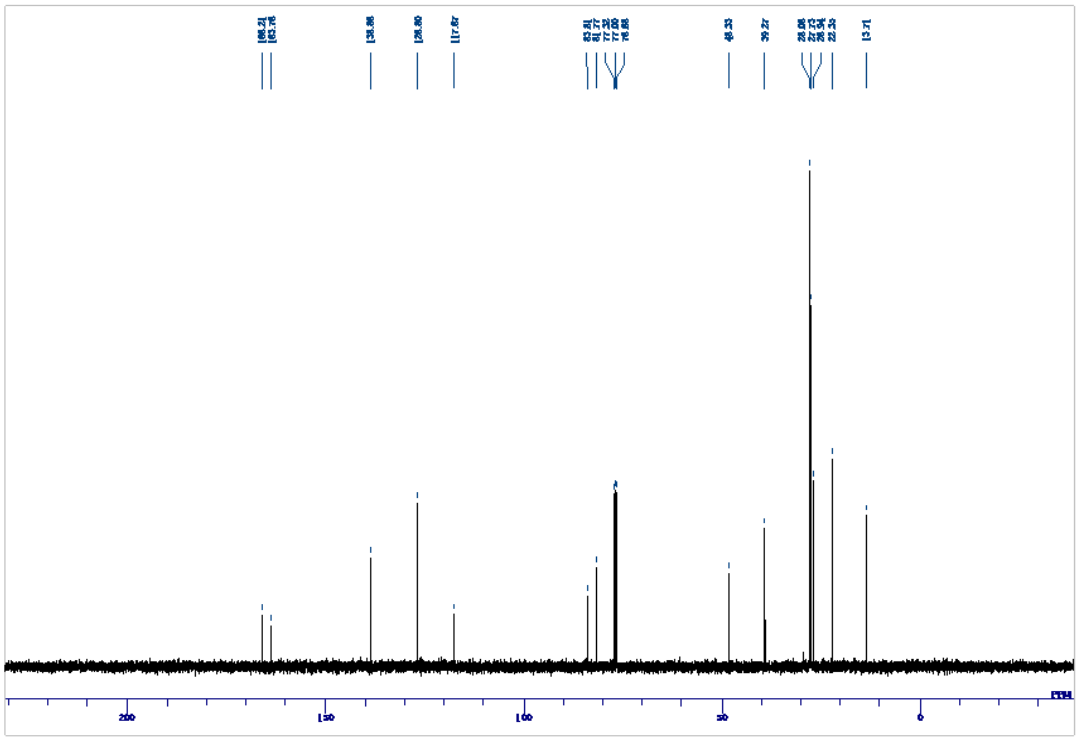
^{13}C NMR: (*E*)-**4b**



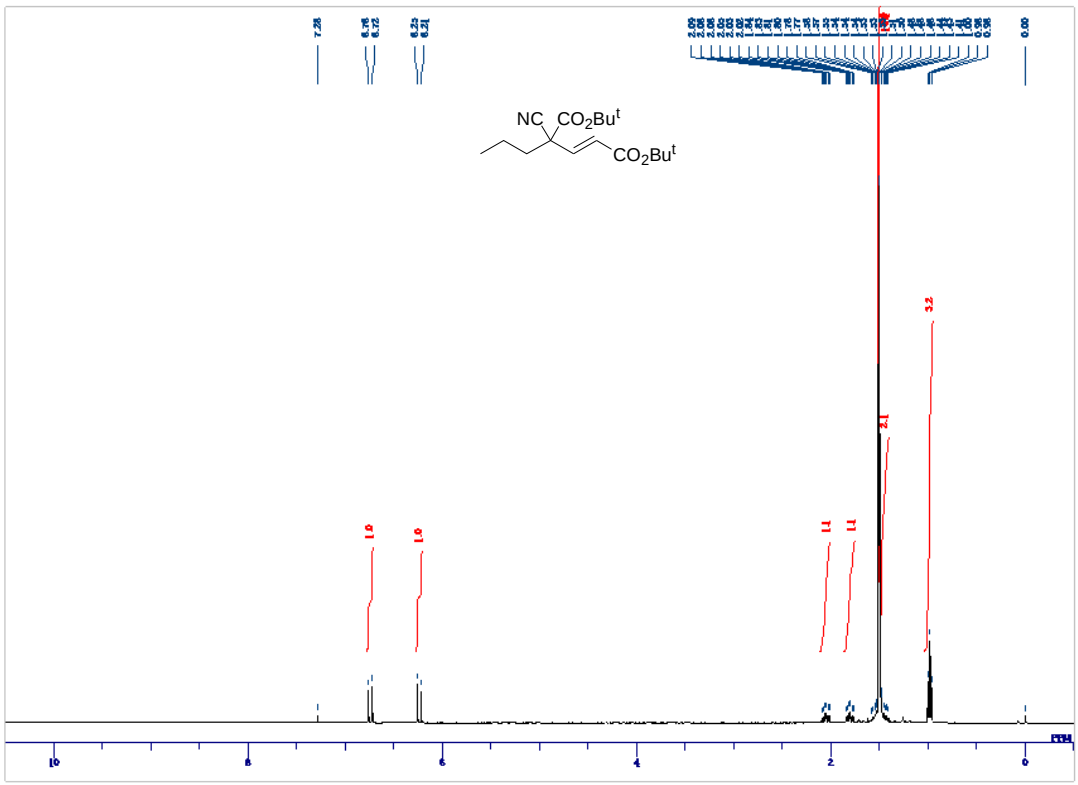
^{1}H NMR: (*Z*)-**4b**



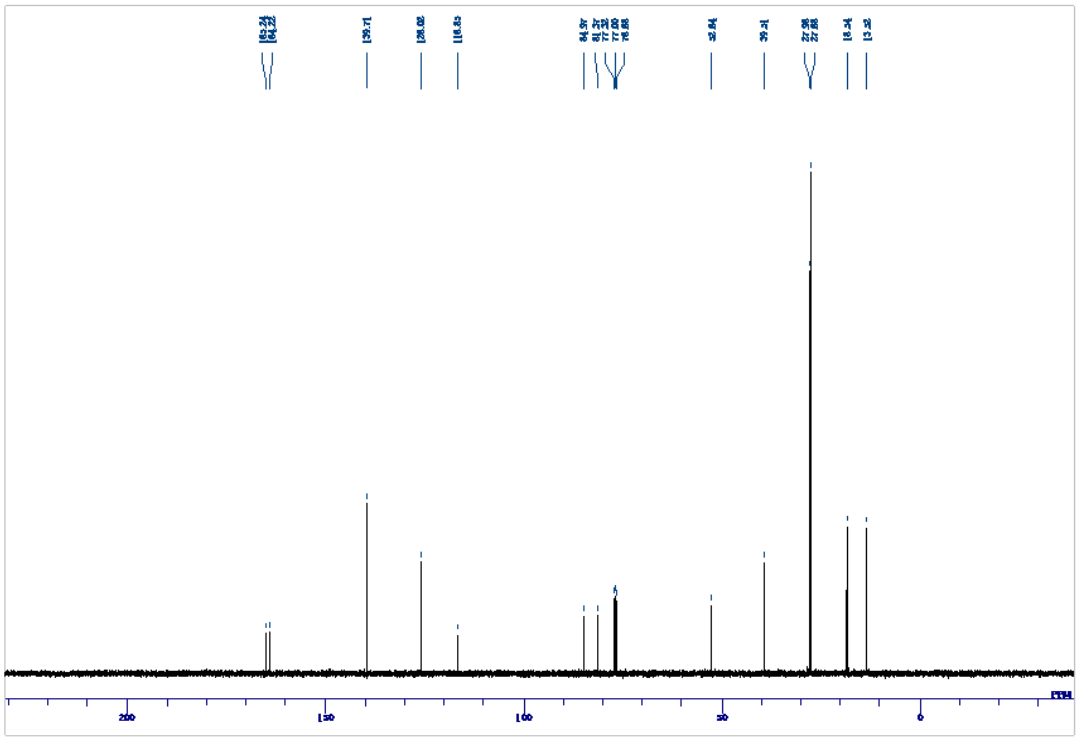
^{13}C NMR: (*Z*)-**4b**



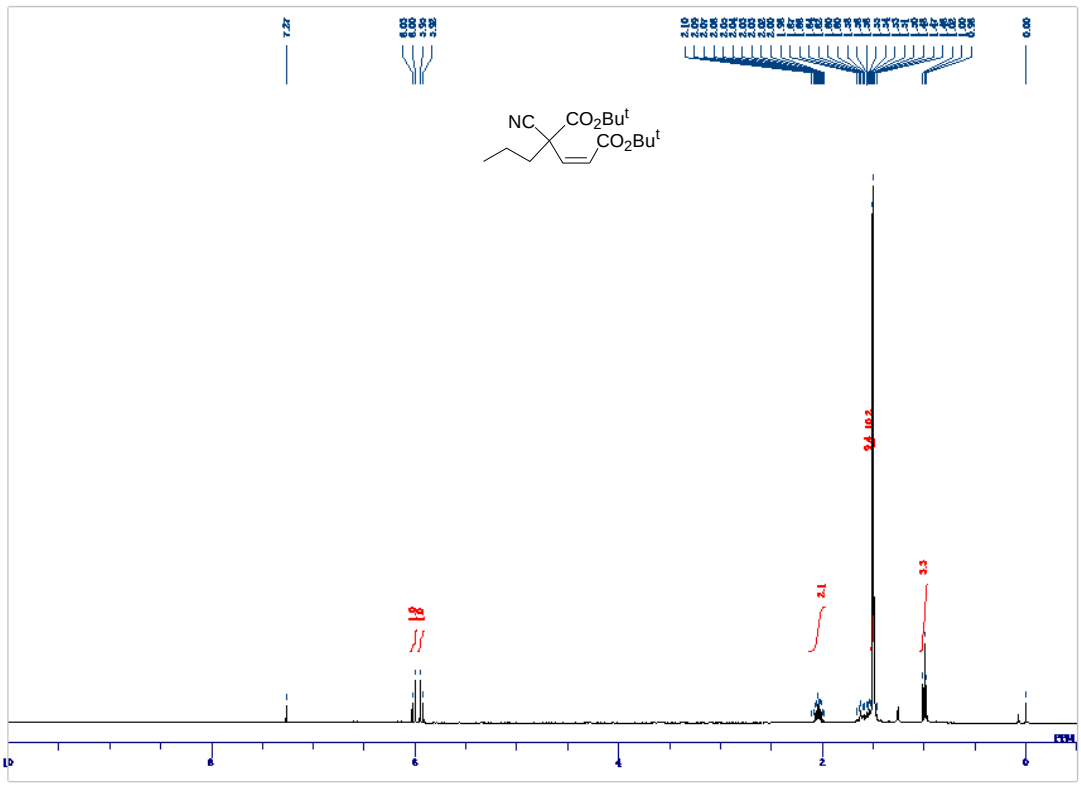
^{1}H NMR: (*E*)-**4c**



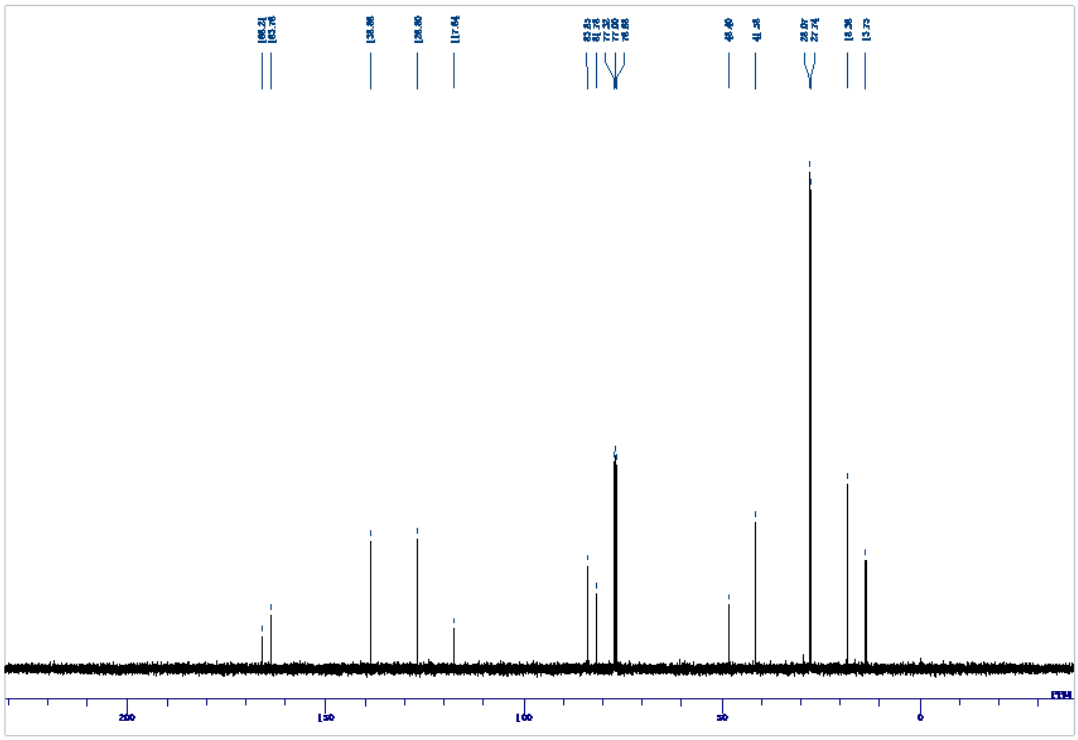
^{13}C NMR: (*E*)-**4c**



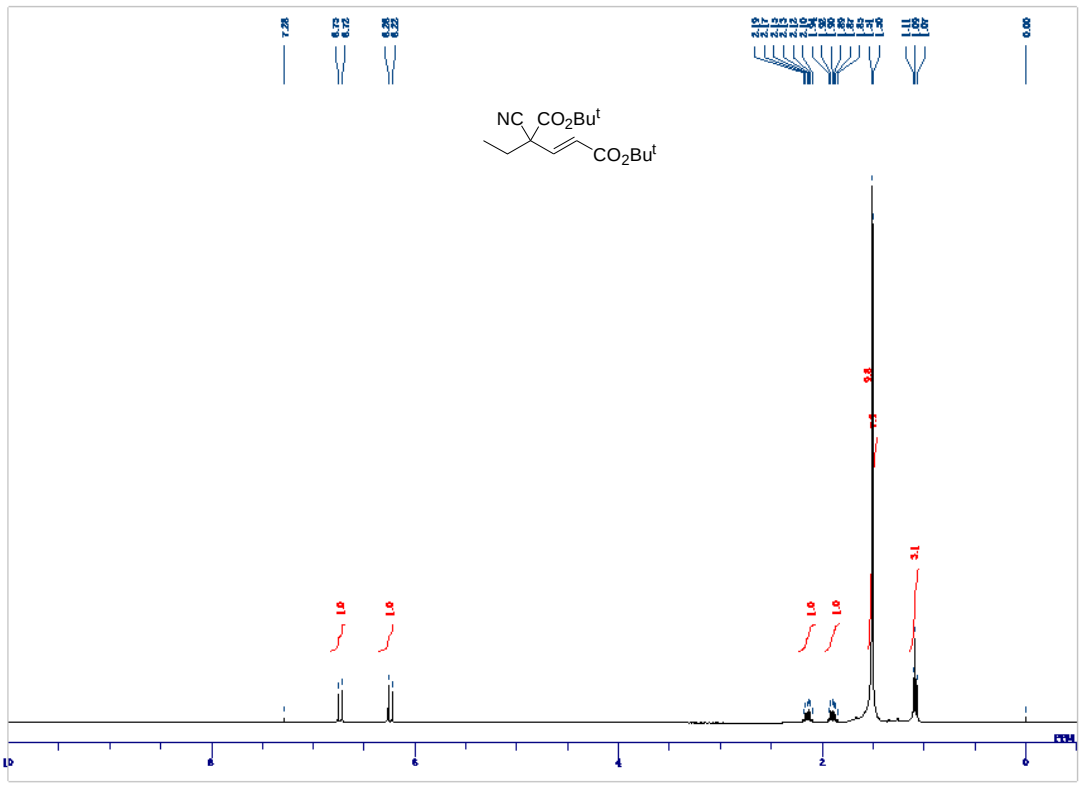
^{1}H NMR: (*Z*)-**4c**



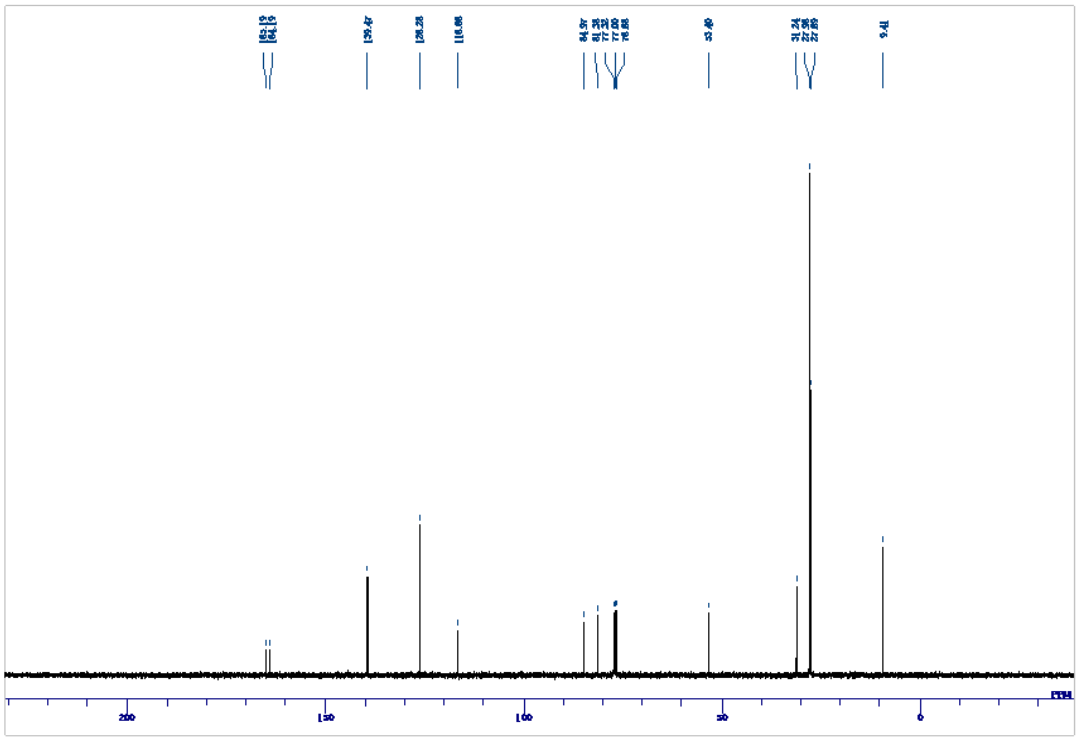
^{13}C NMR: (*Z*)-**4c**



^{1}H NMR: (*E*)-**4d**



^{13}C NMR: (*E*)-**4d**



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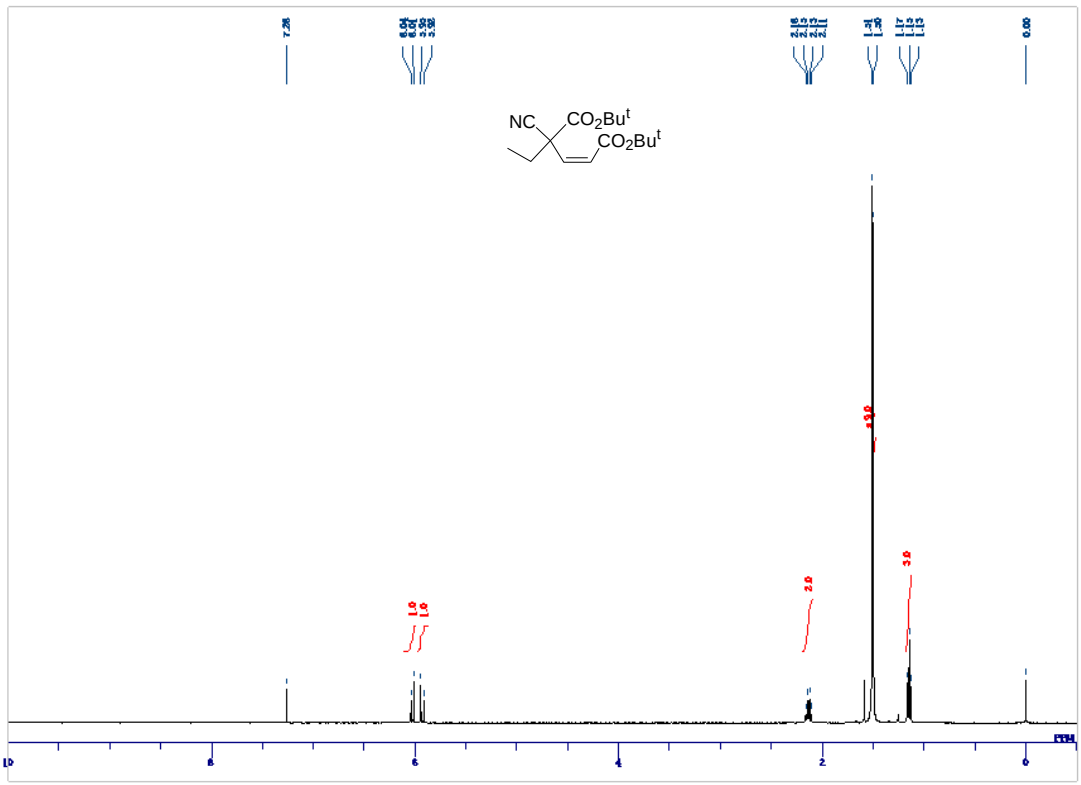

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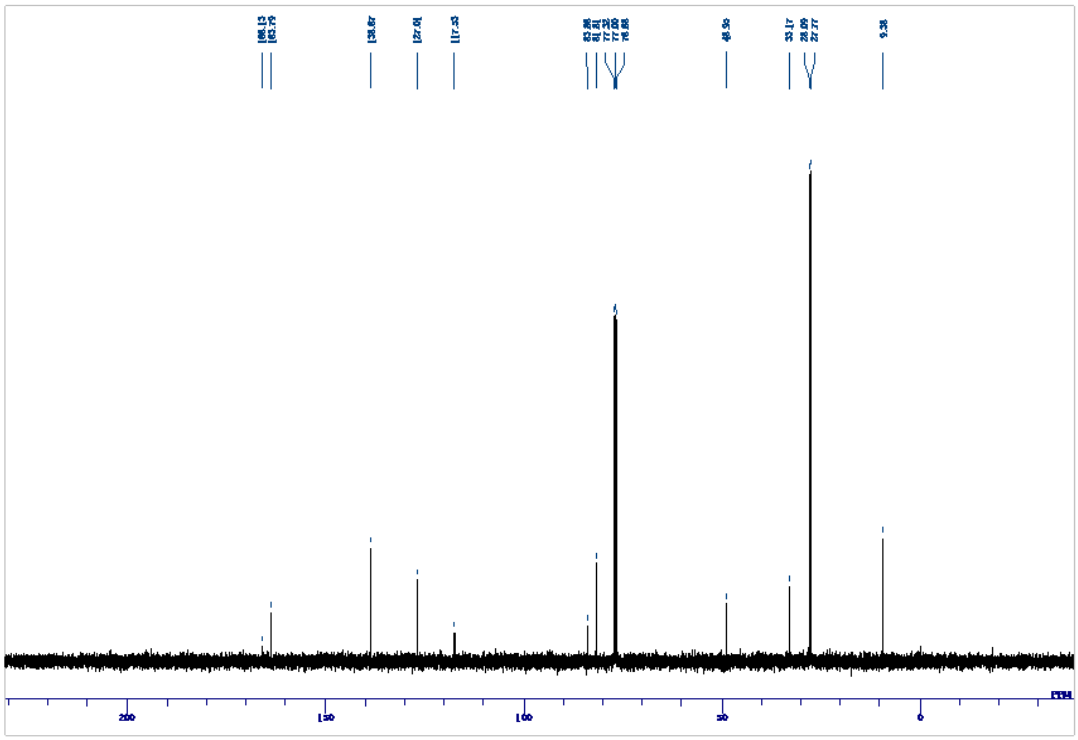
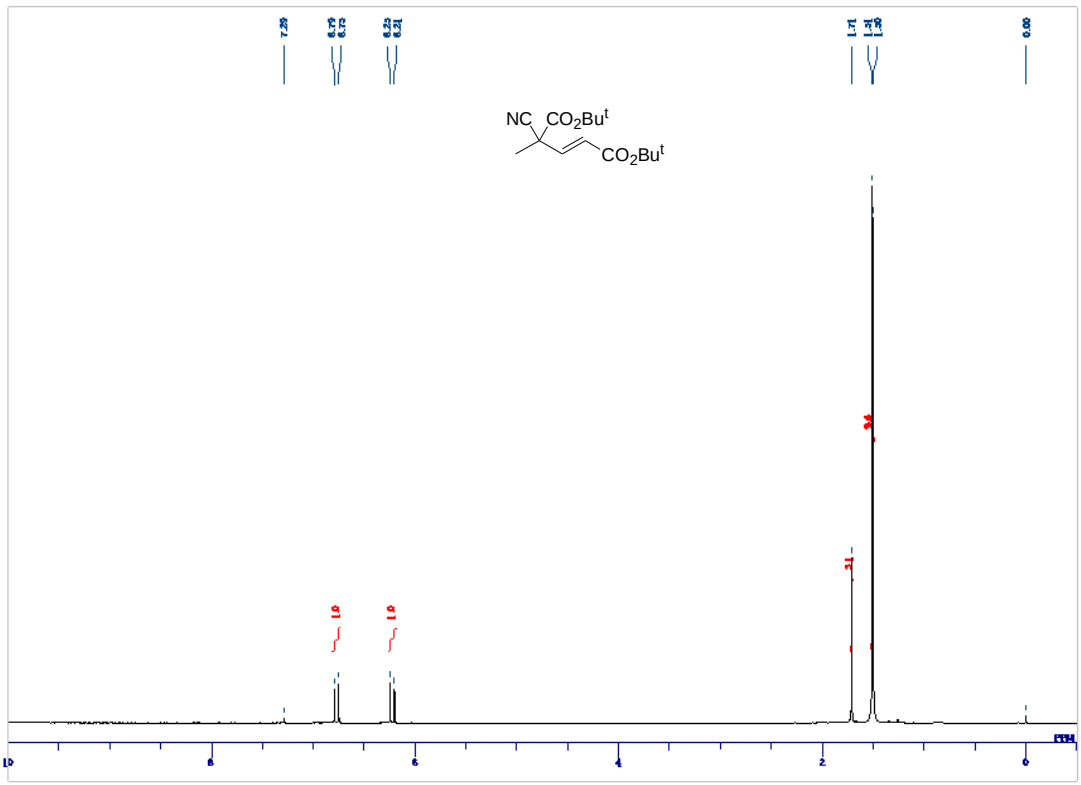


^{1}H NMR: (*E*)-**4e**



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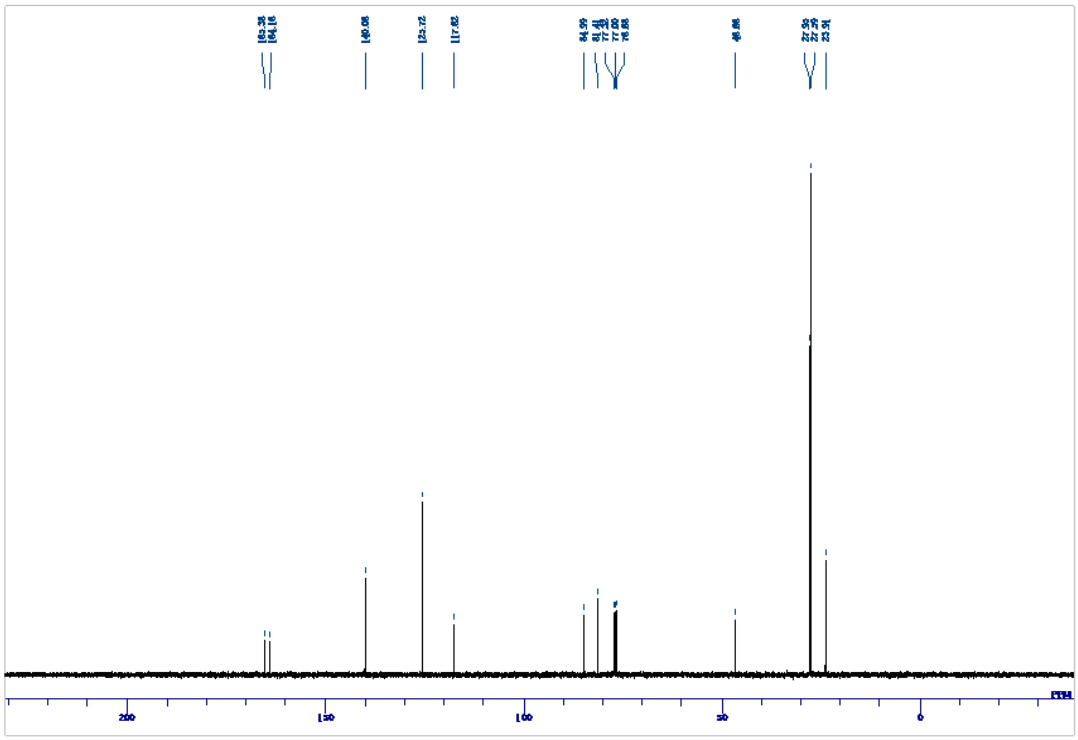
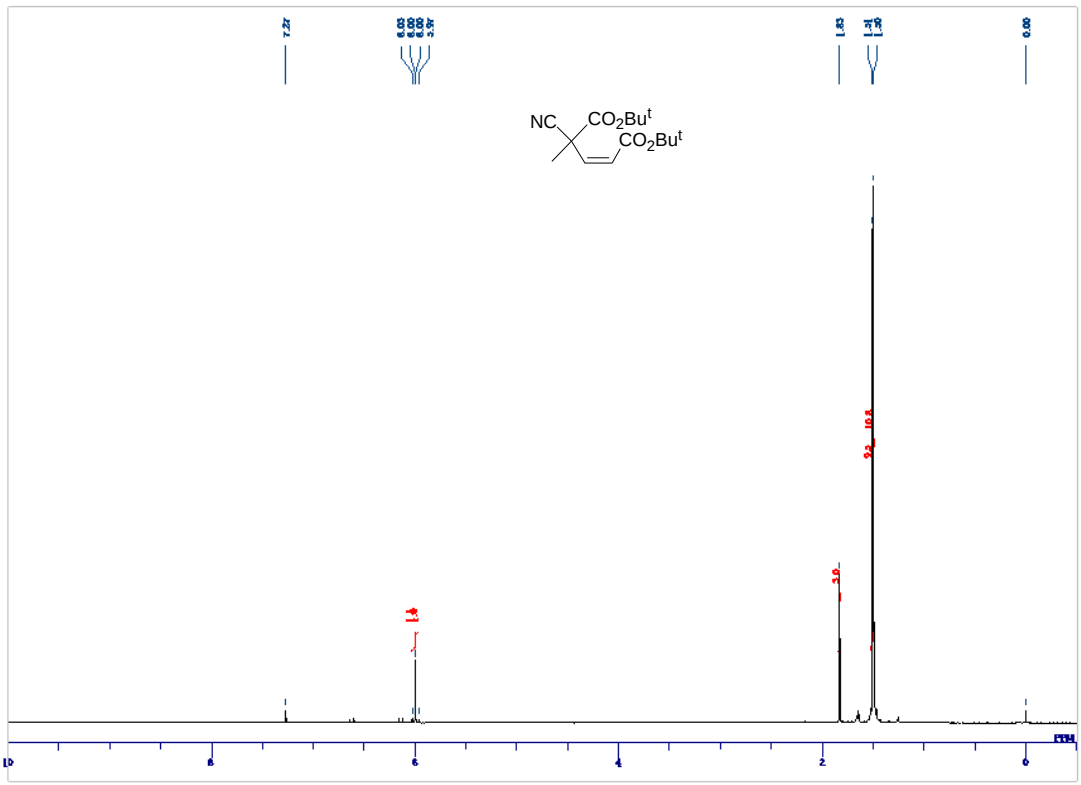
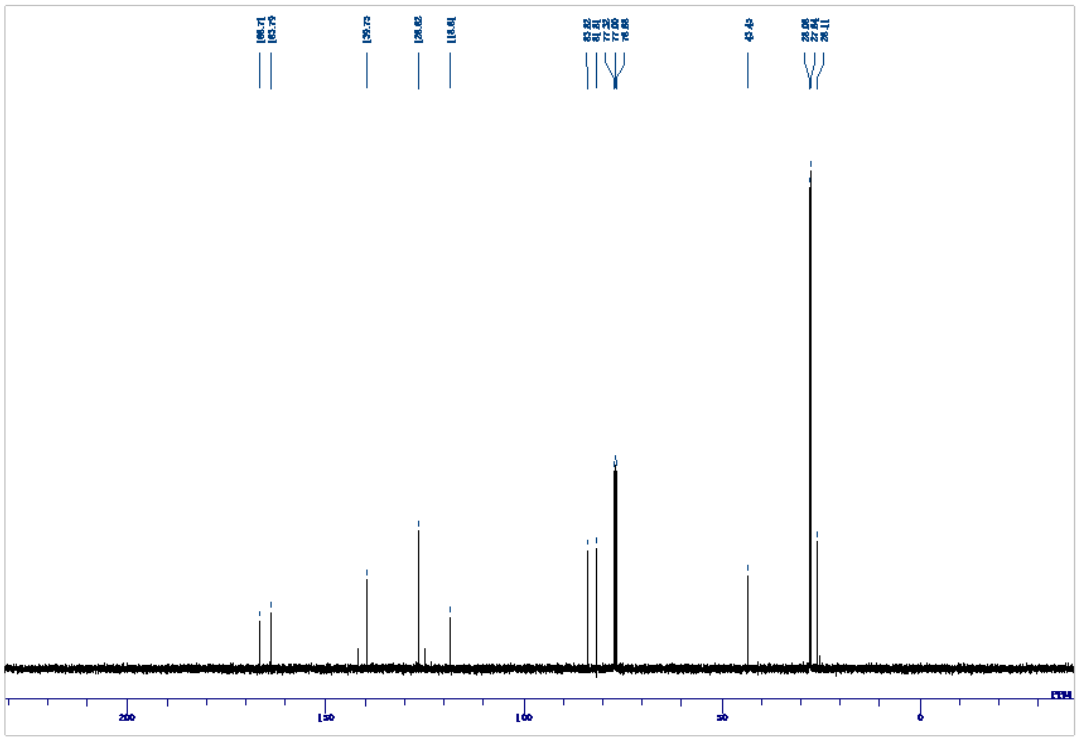


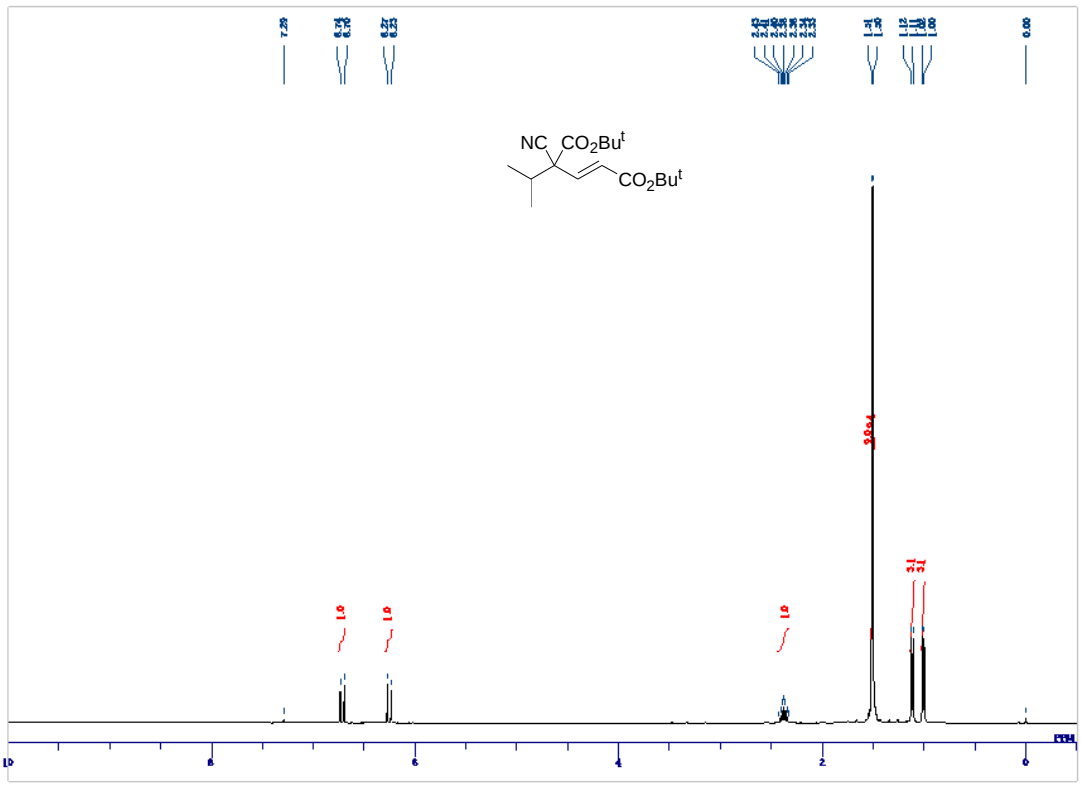
^{1}H NMR: (*Z*)-**4e**



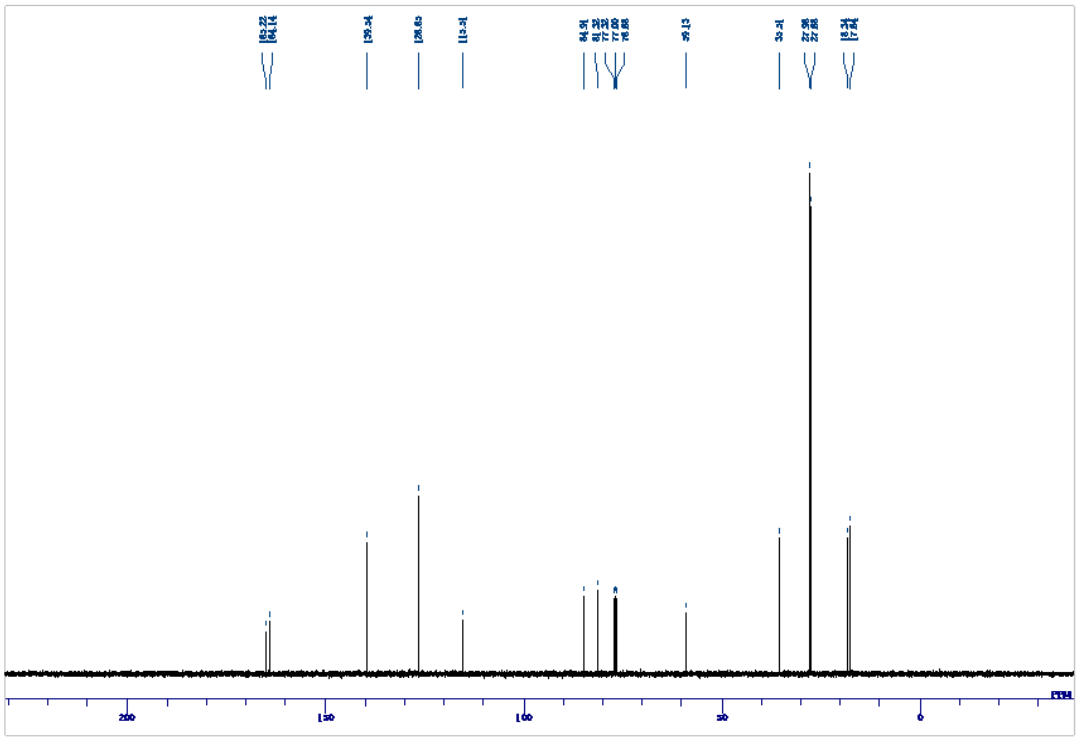
^{13}C NMR: (*Z*)-**4e**



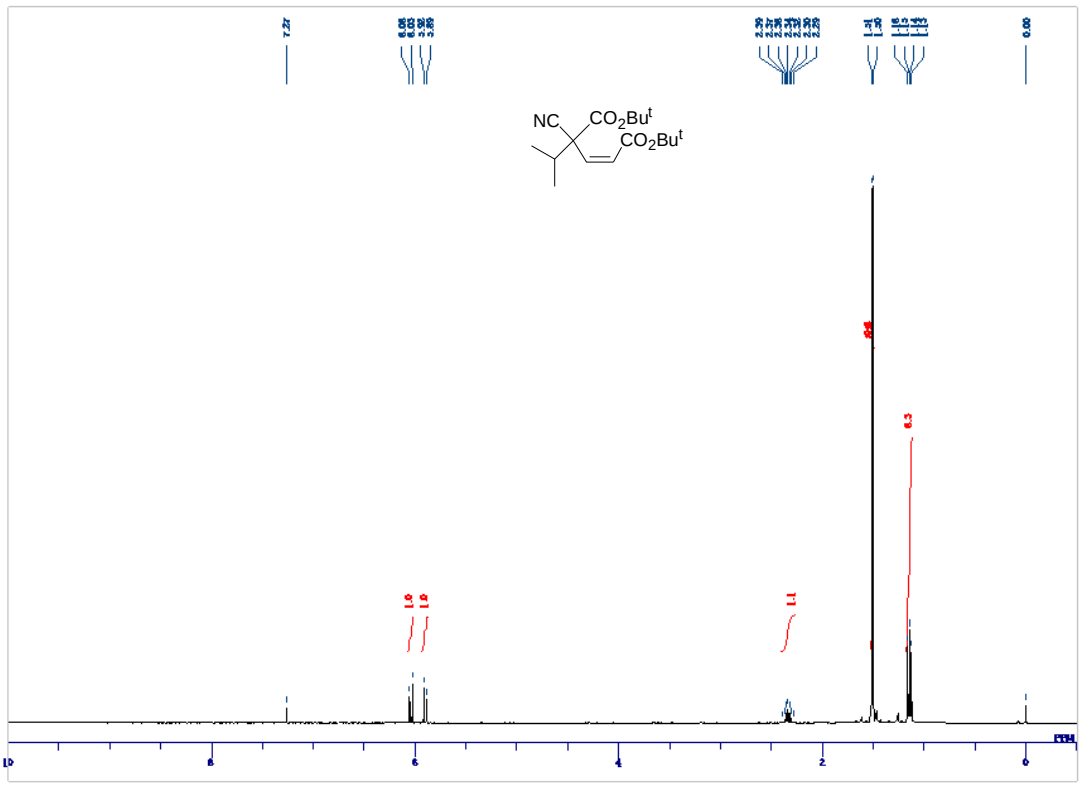
^{1}H NMR: (*E*)-**4f**



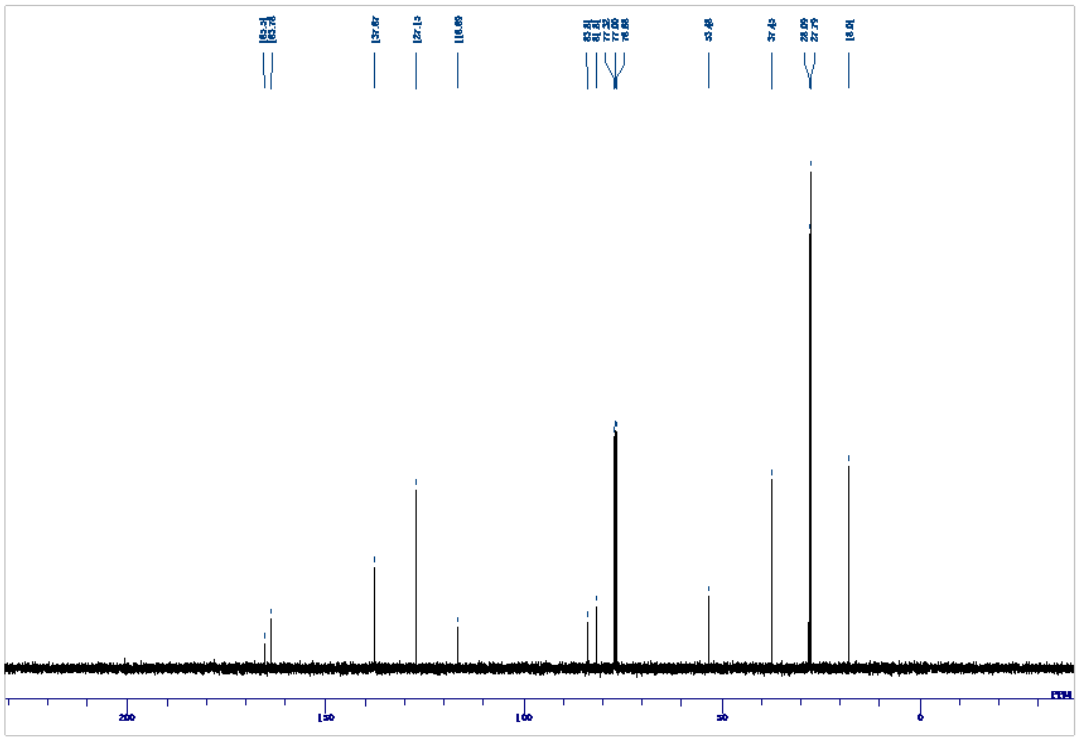
^{13}C NMR: (*E*)-**4f**



^{1}H NMR: (*Z*)-**4f**



^{13}C NMR: (*Z*)-**4f**



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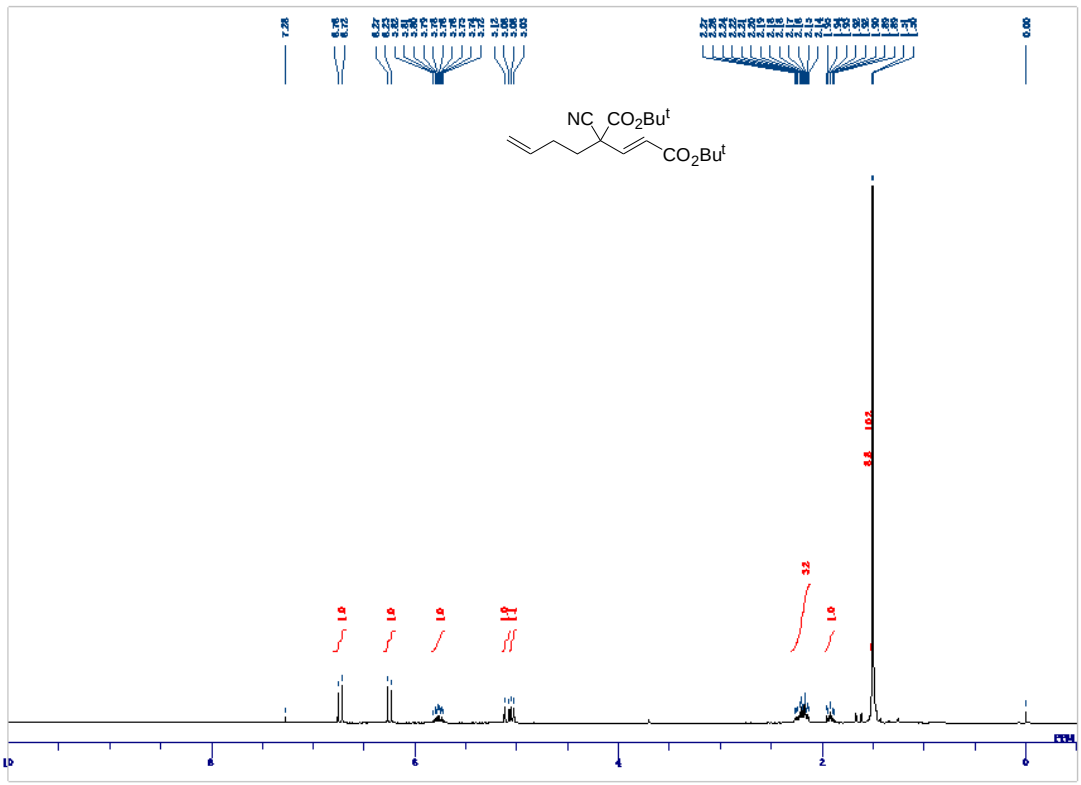
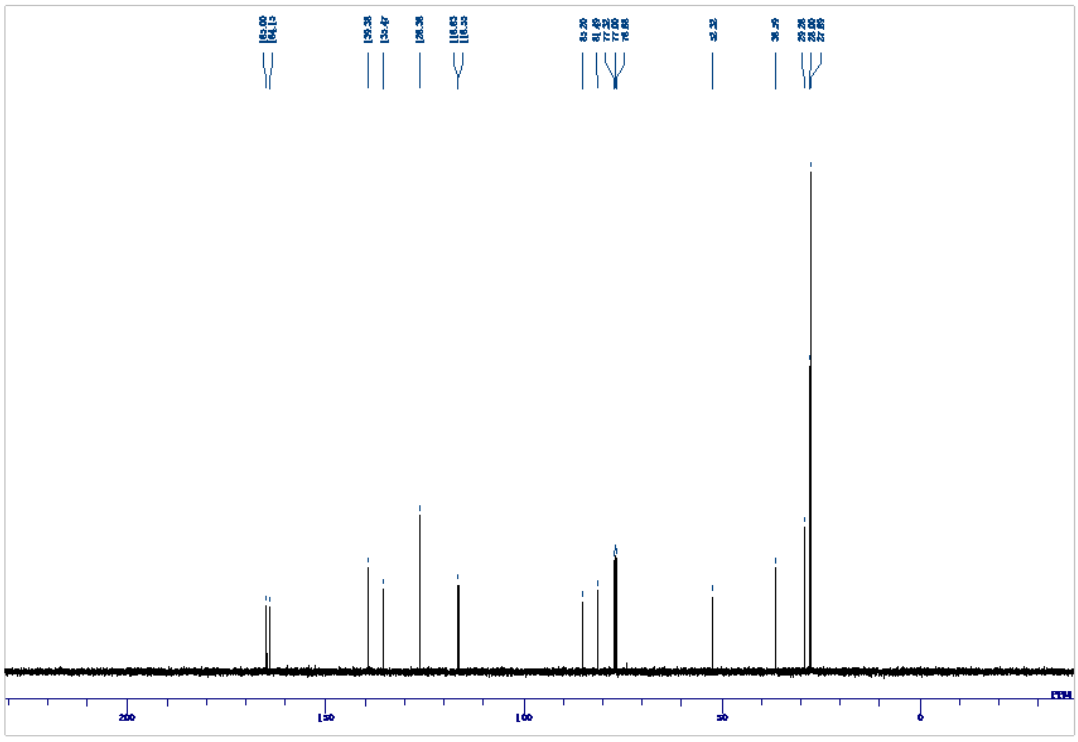
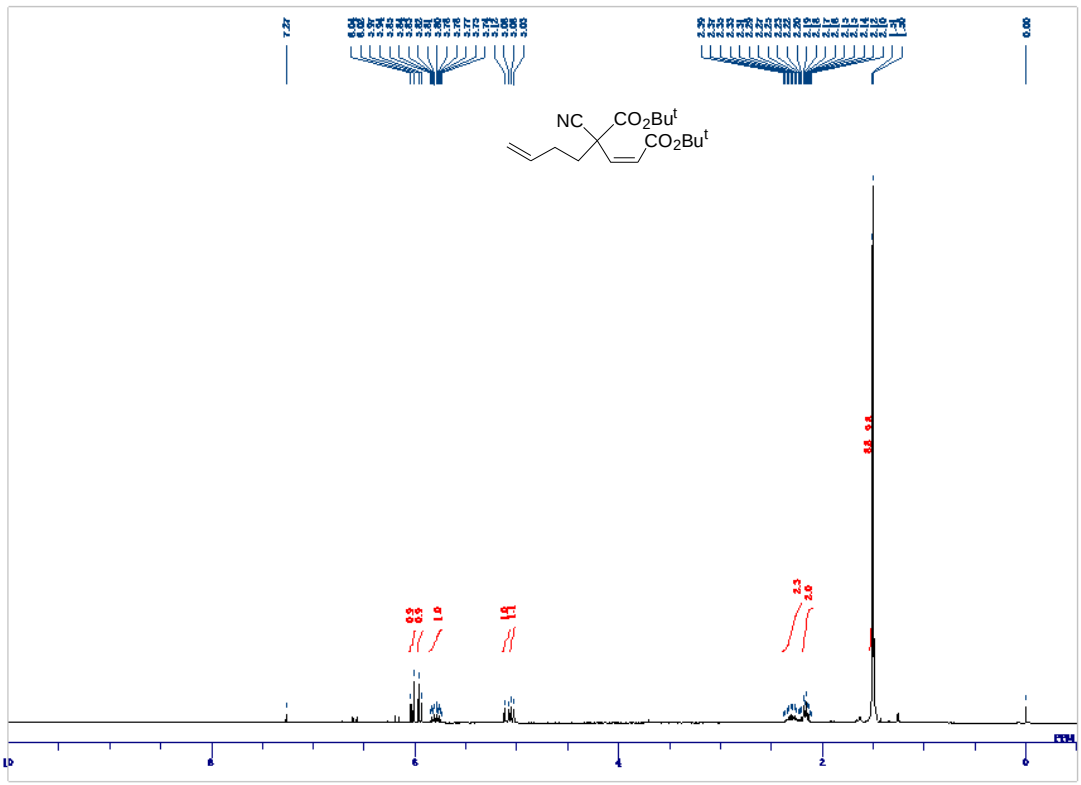


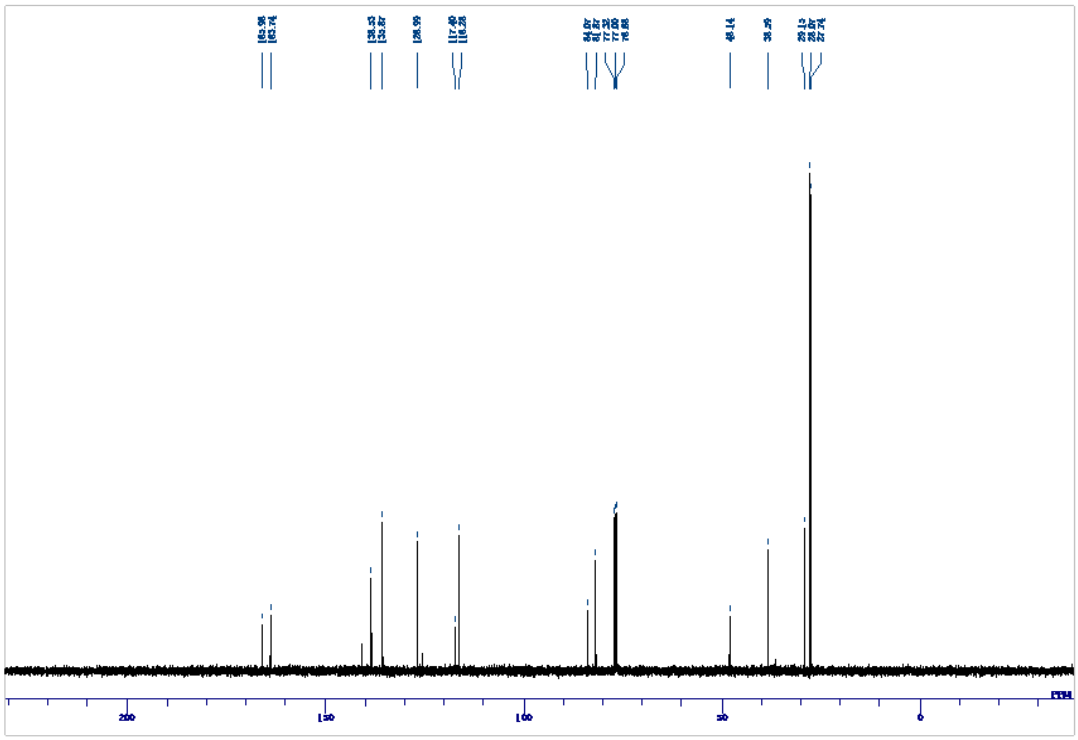
^{13}C NMR: (*E*)-**4g**



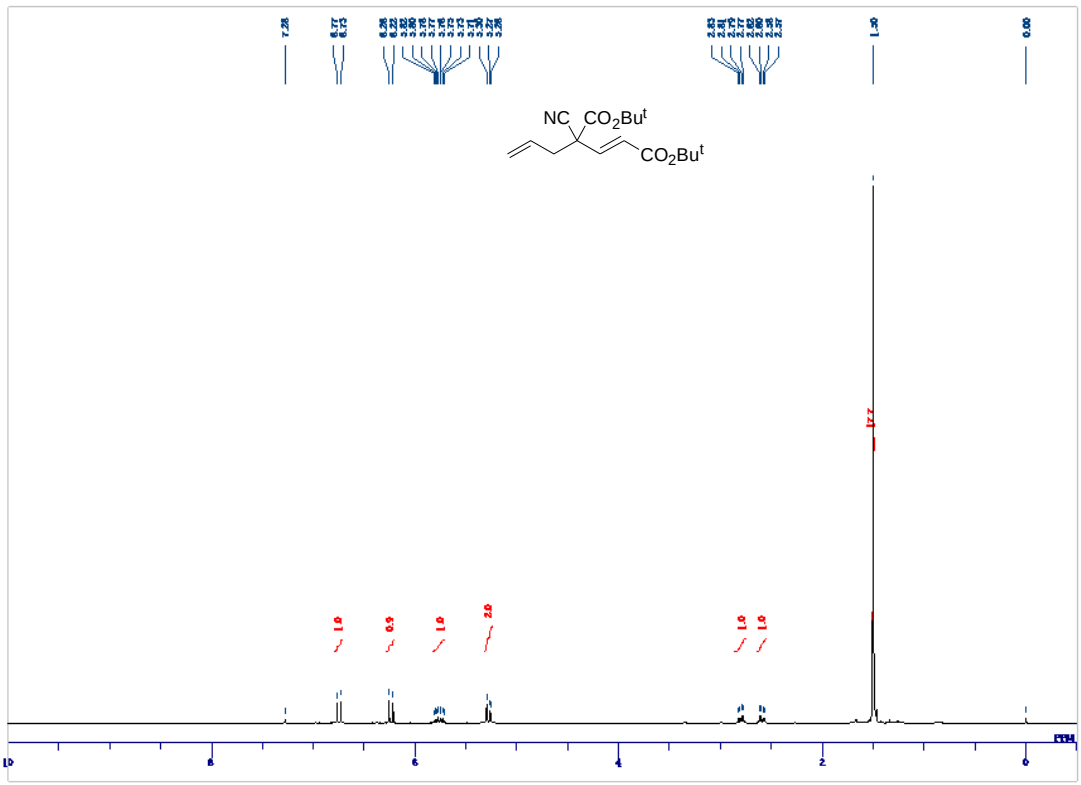
^{1}H NMR: (*Z*)-**4g**



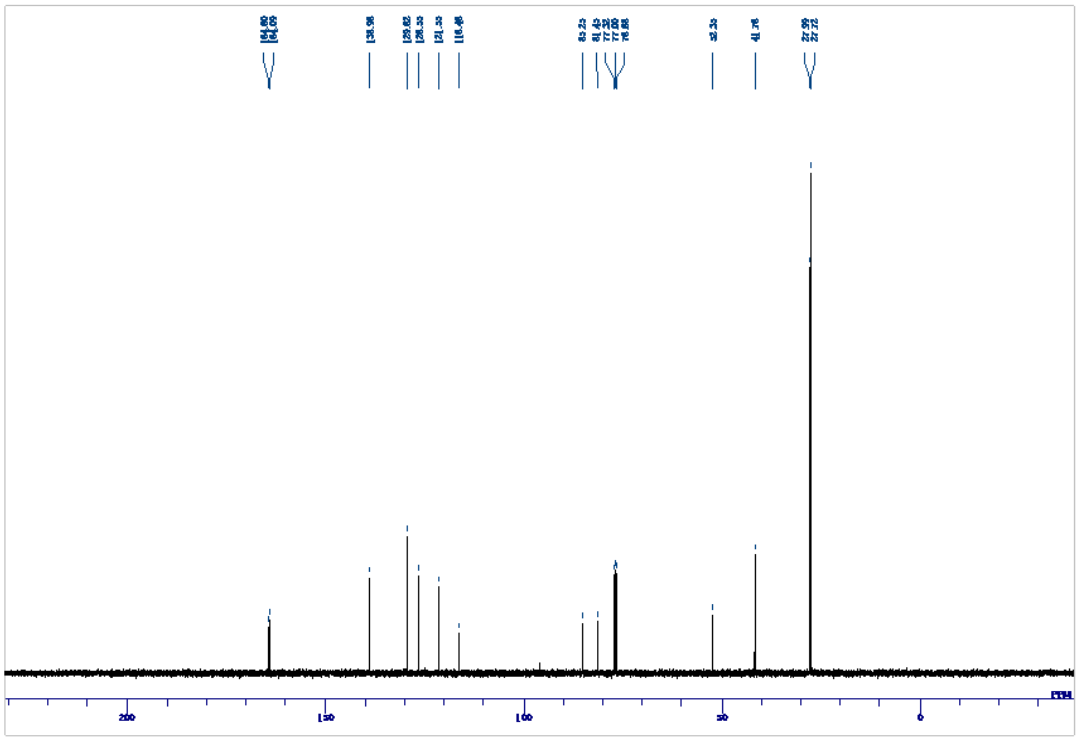
^{13}C NMR: (*Z*)-**4g**



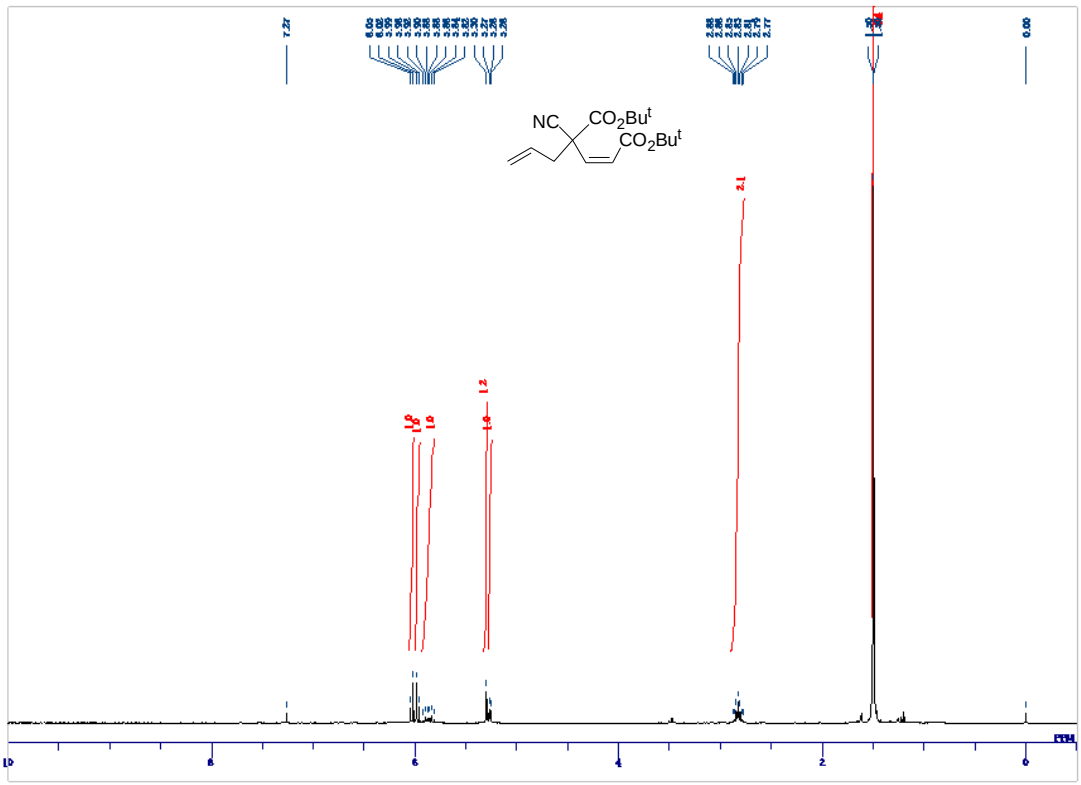
^{1}H NMR: (*E*)-**4h**



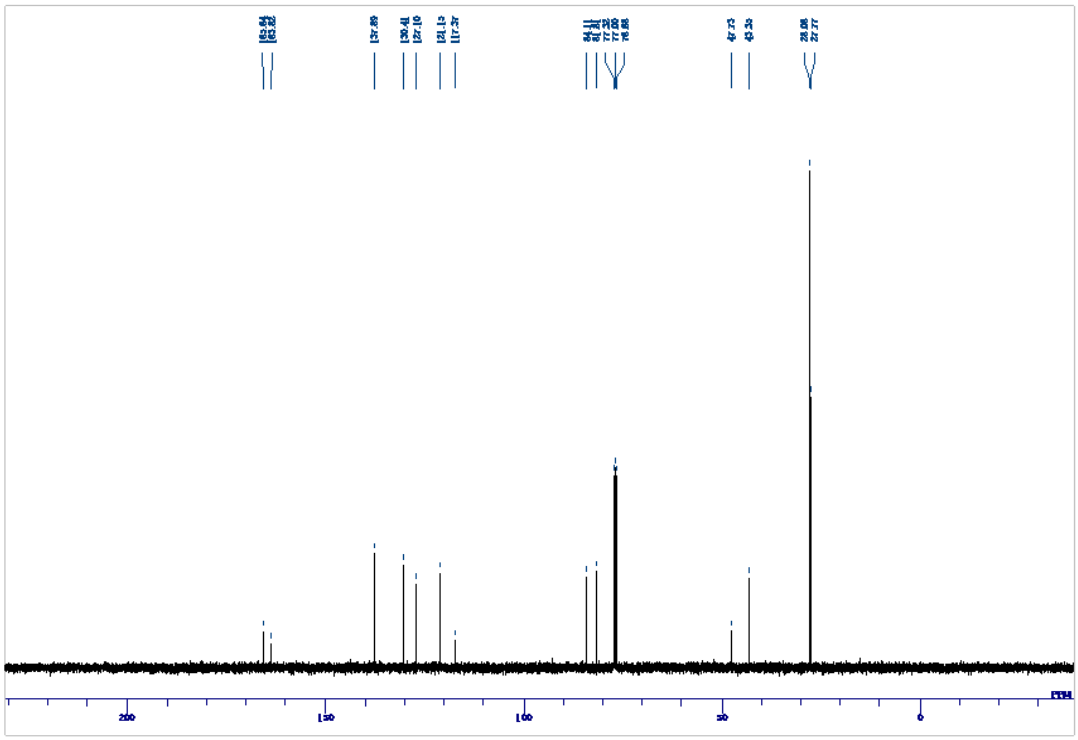
^{13}C NMR: (*E*)-**4h**



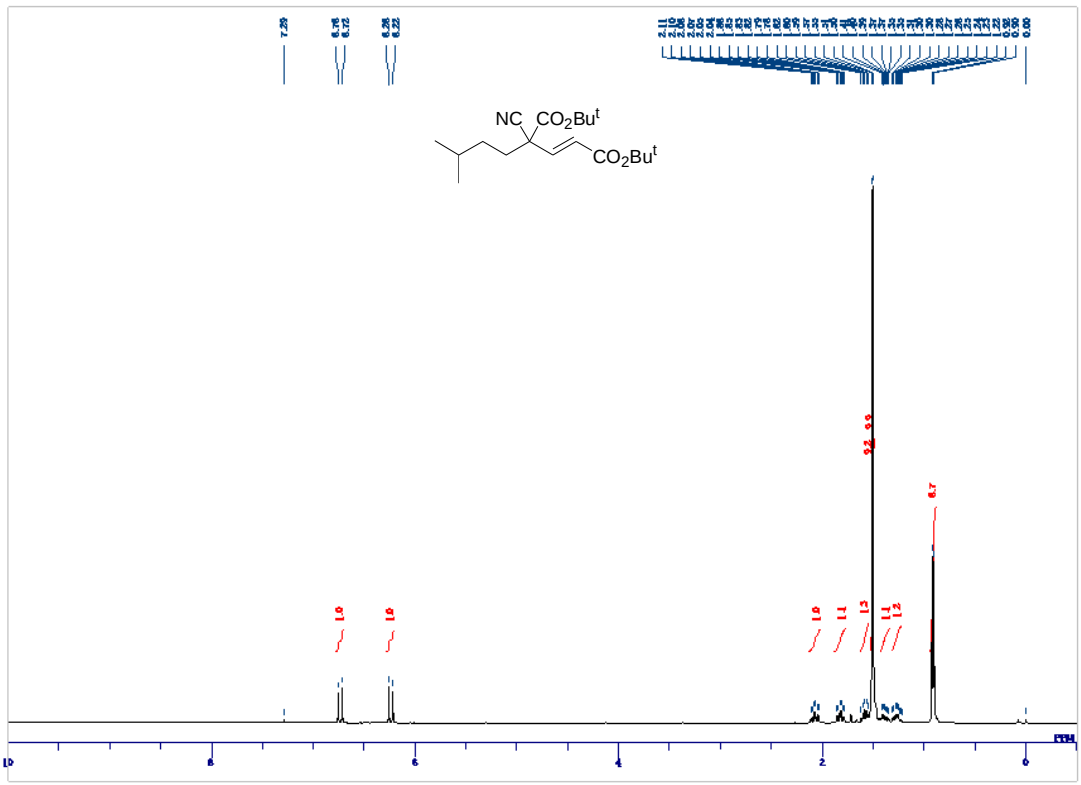
^{1}H NMR: (*Z*)-**4h**



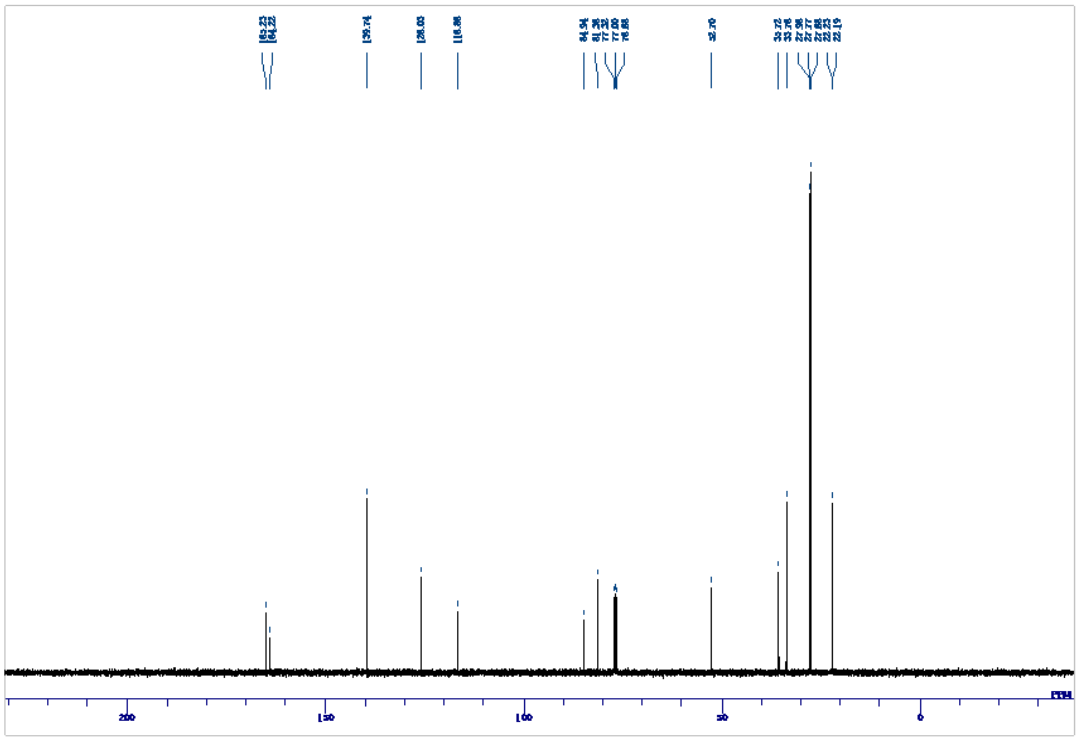
^{13}C NMR: (*Z*)-**4h**



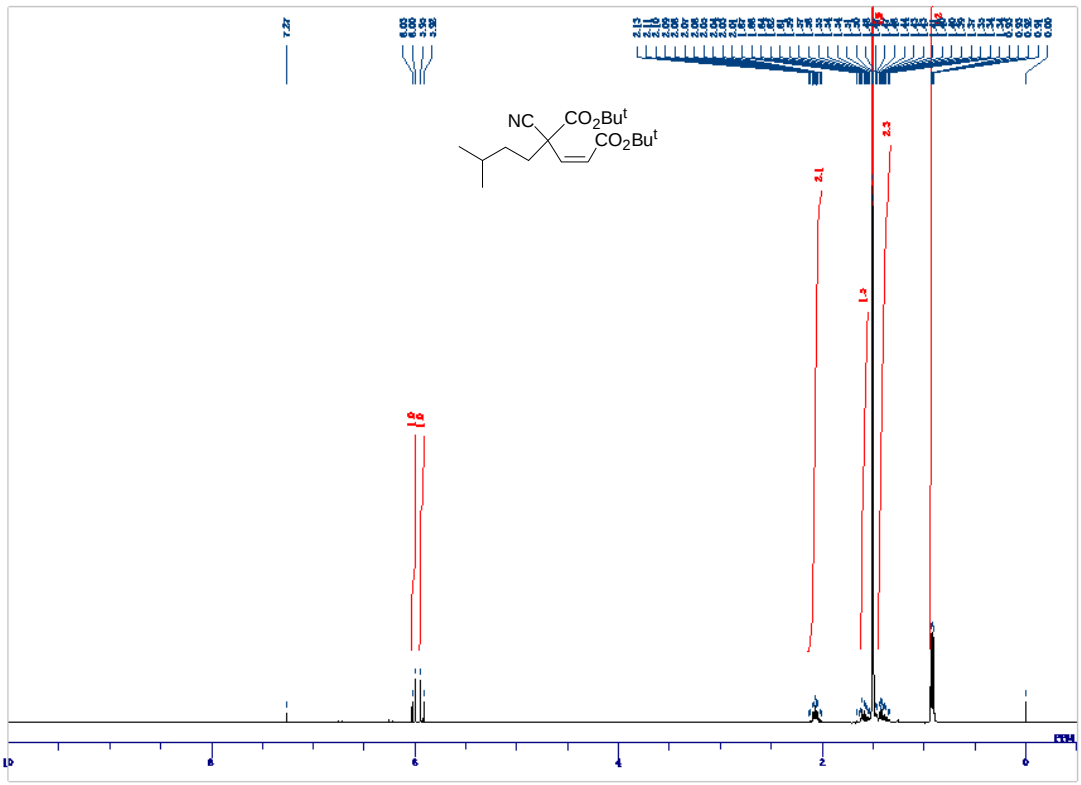
^{1}H NMR: (*E*)-**4i**



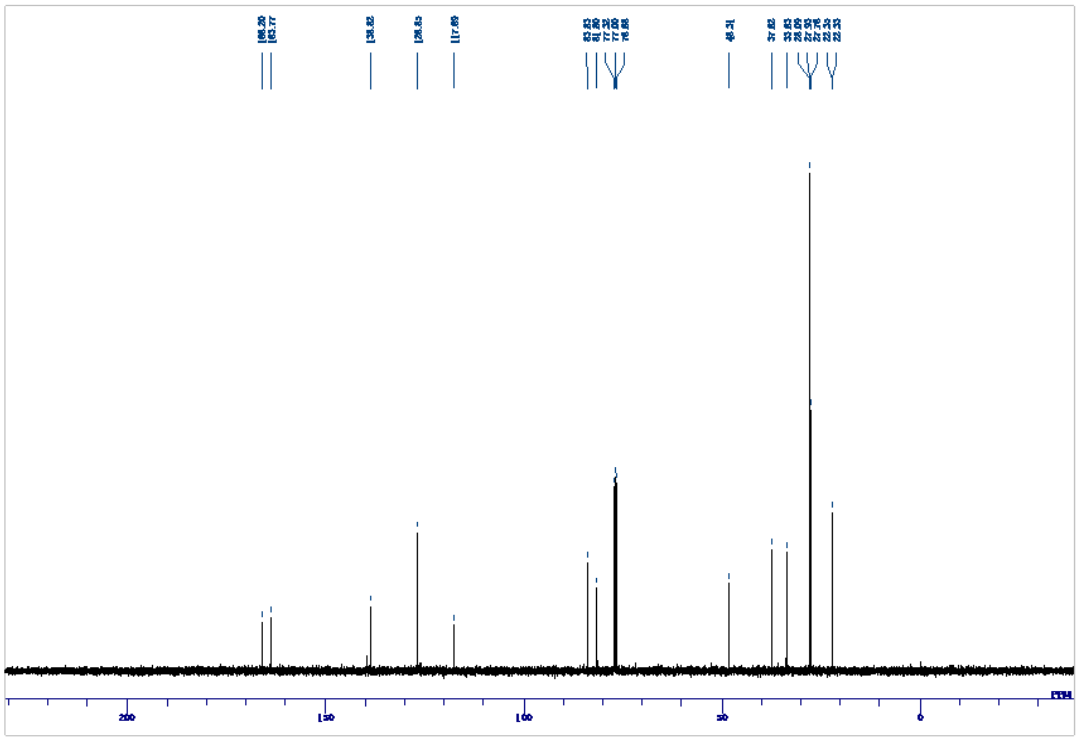
^{13}C NMR: (*E*)-**4i**



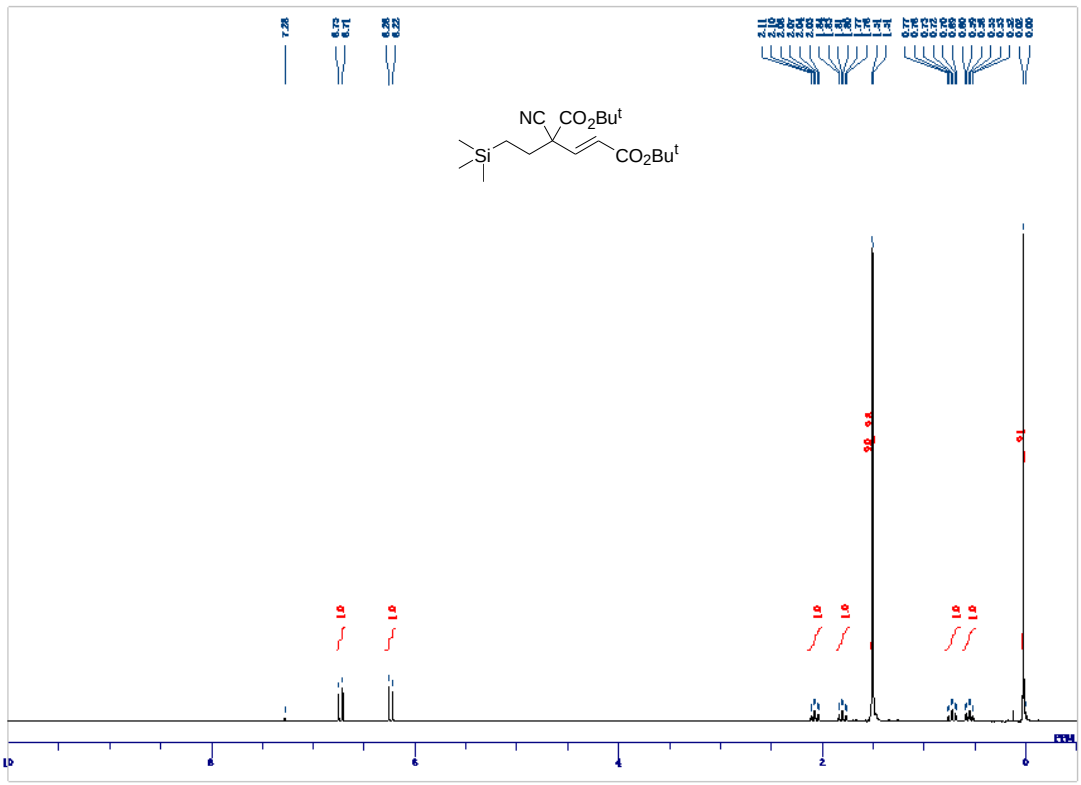
^{1}H NMR: (*Z*)-**4i**



^{13}C NMR: (*Z*)-**4i**



^{1}H NMR: (*E*)-**4j**



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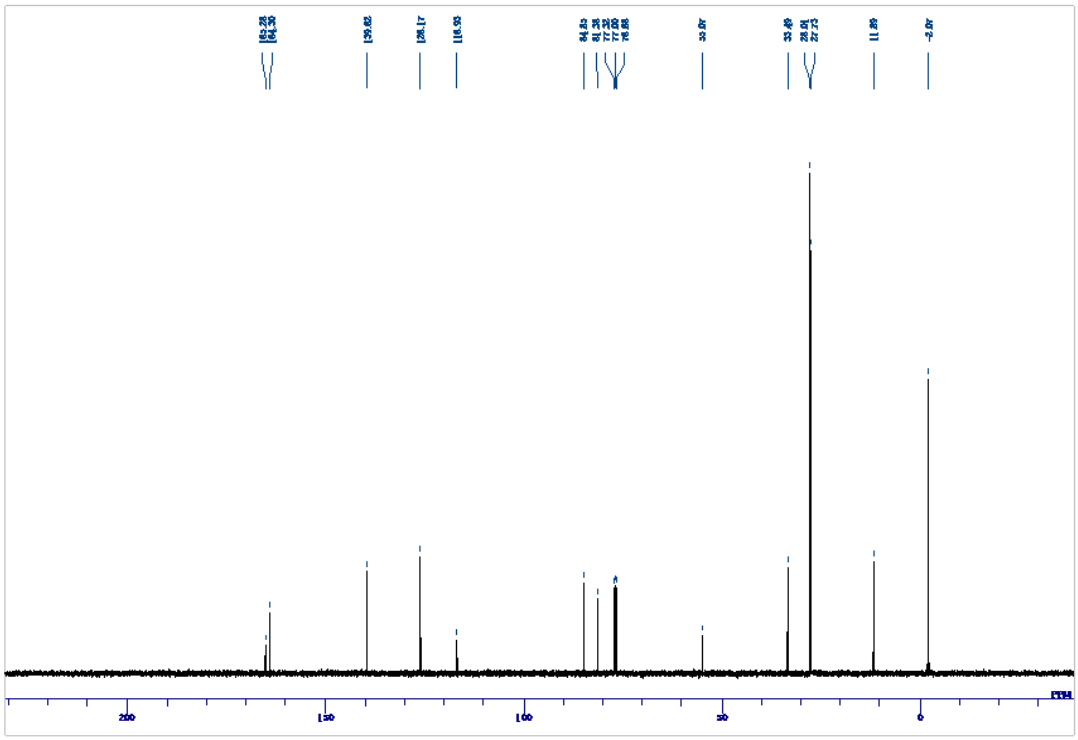
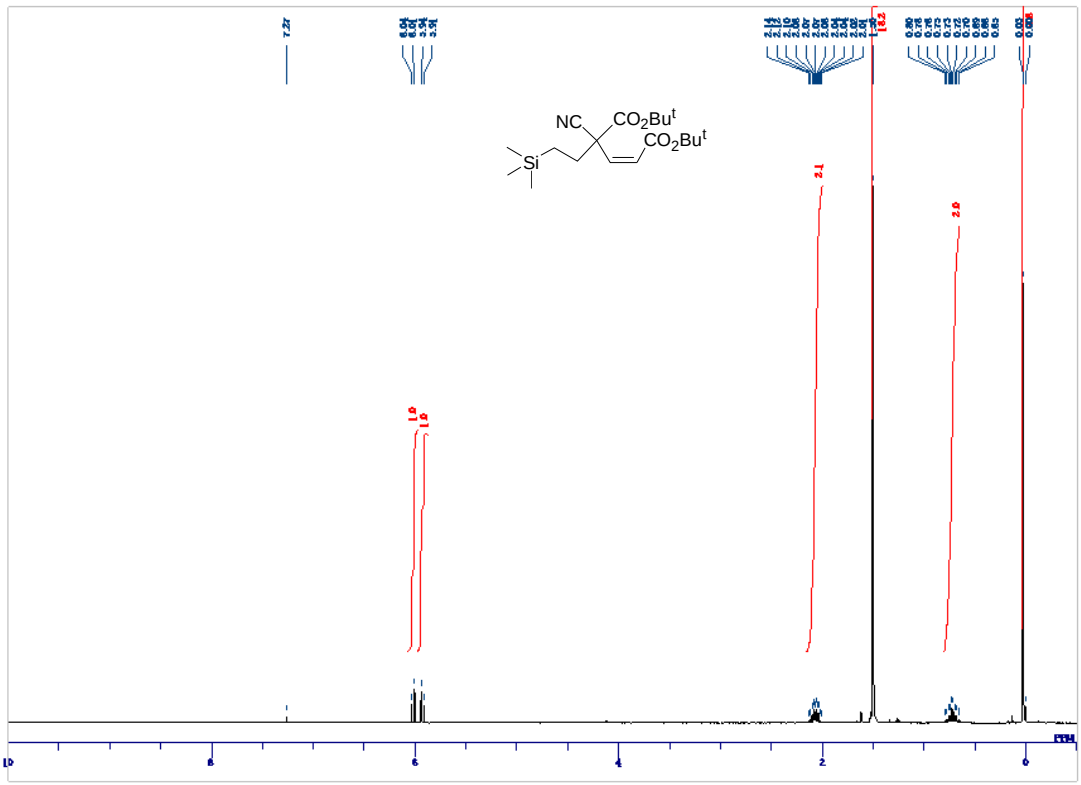
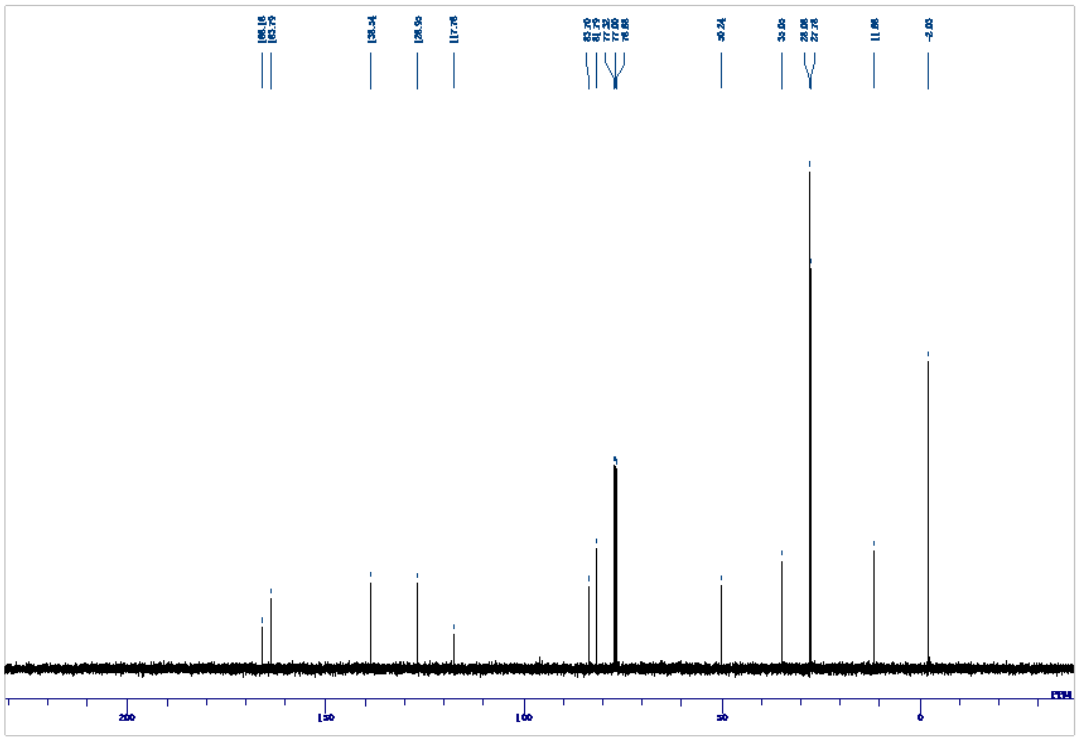


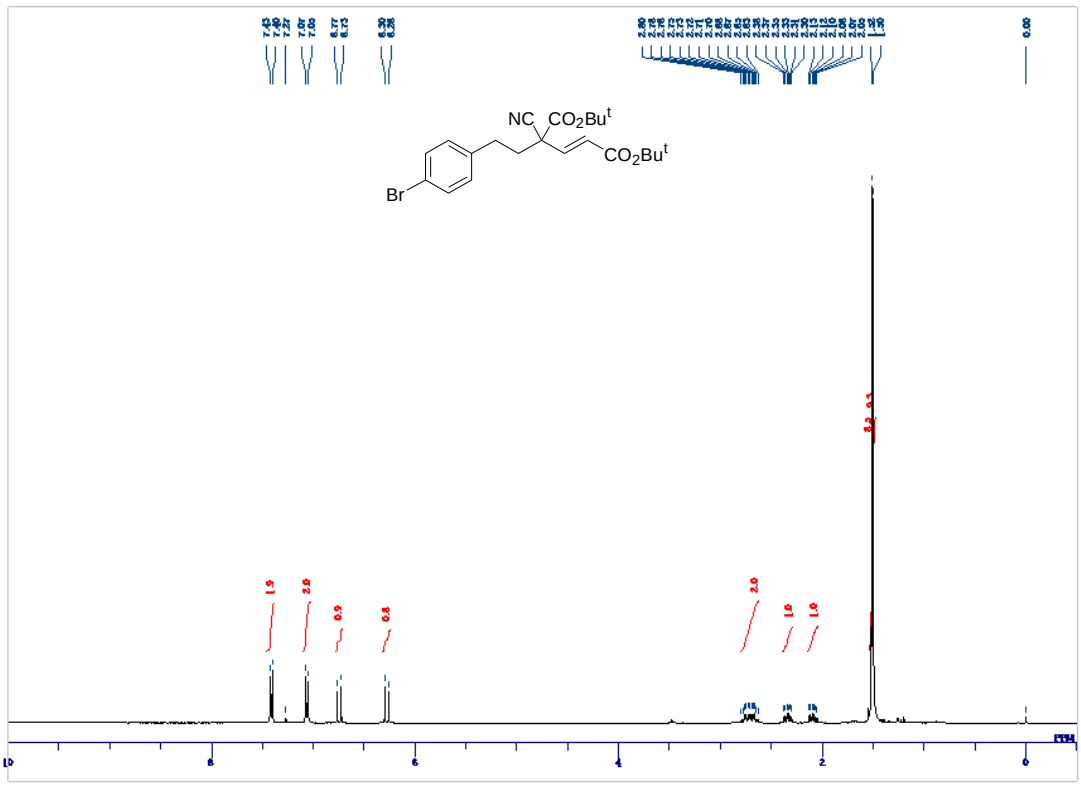
^{1}H NMR: (*Z*)-**4j**



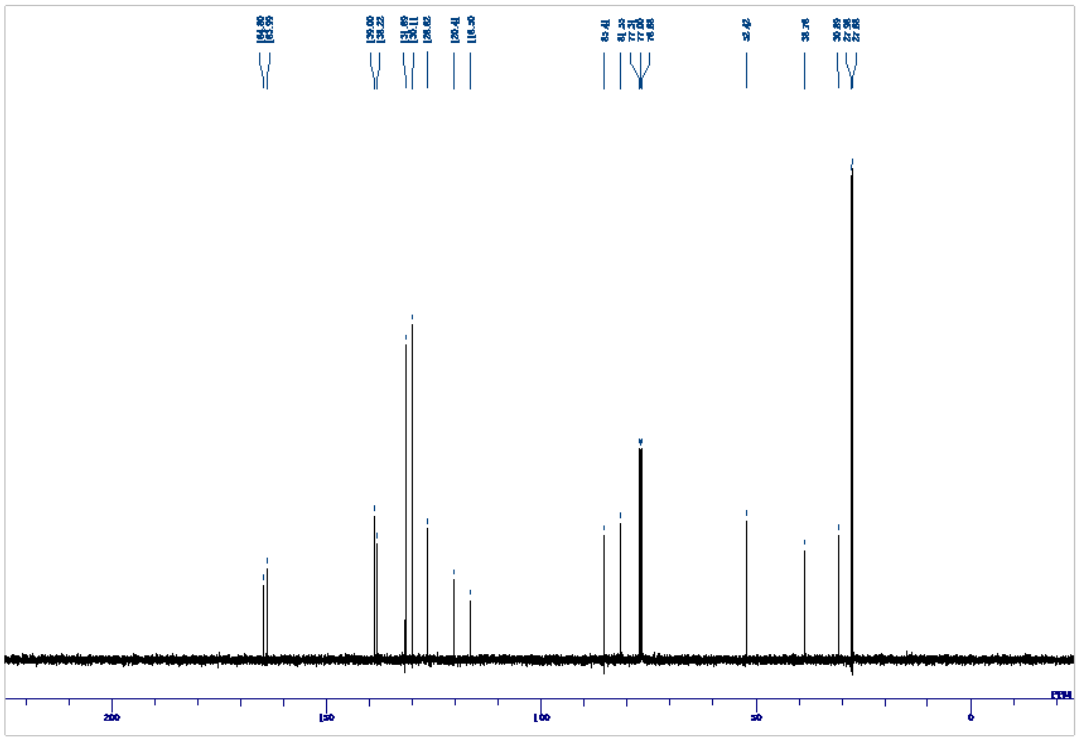
^{13}C NMR: (*Z*)-**4j**



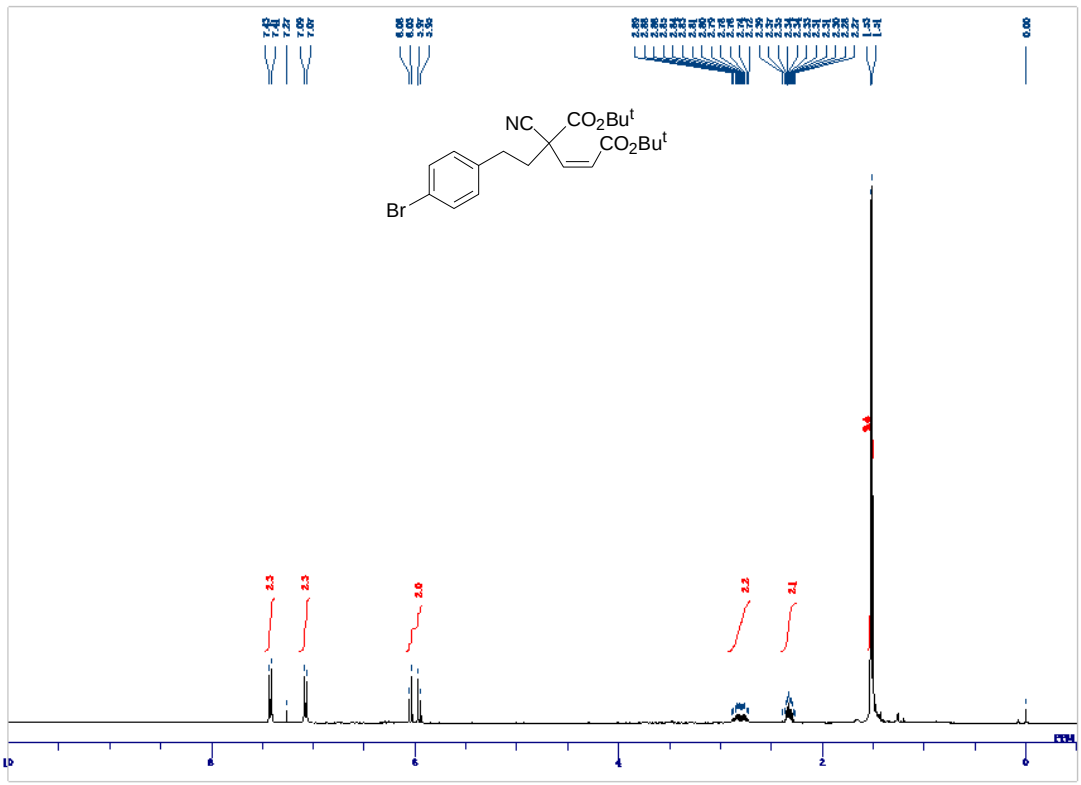
^{1}H NMR: (*E*)-**4k**



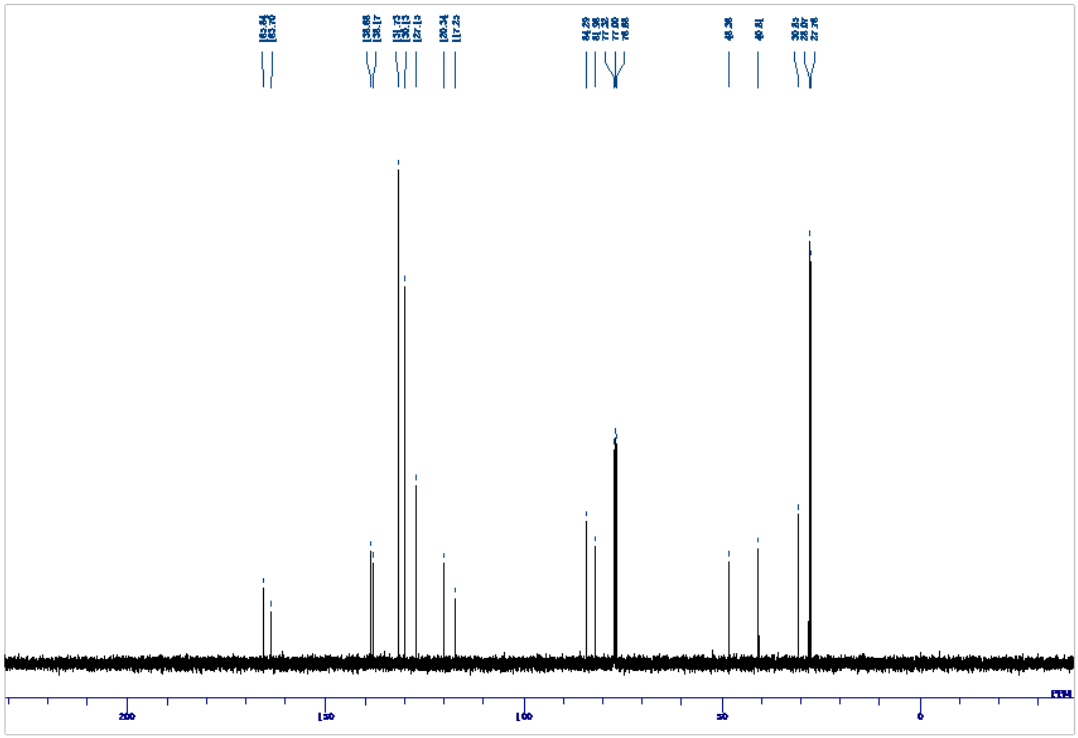
^{13}C NMR: (*E*)-**4k**



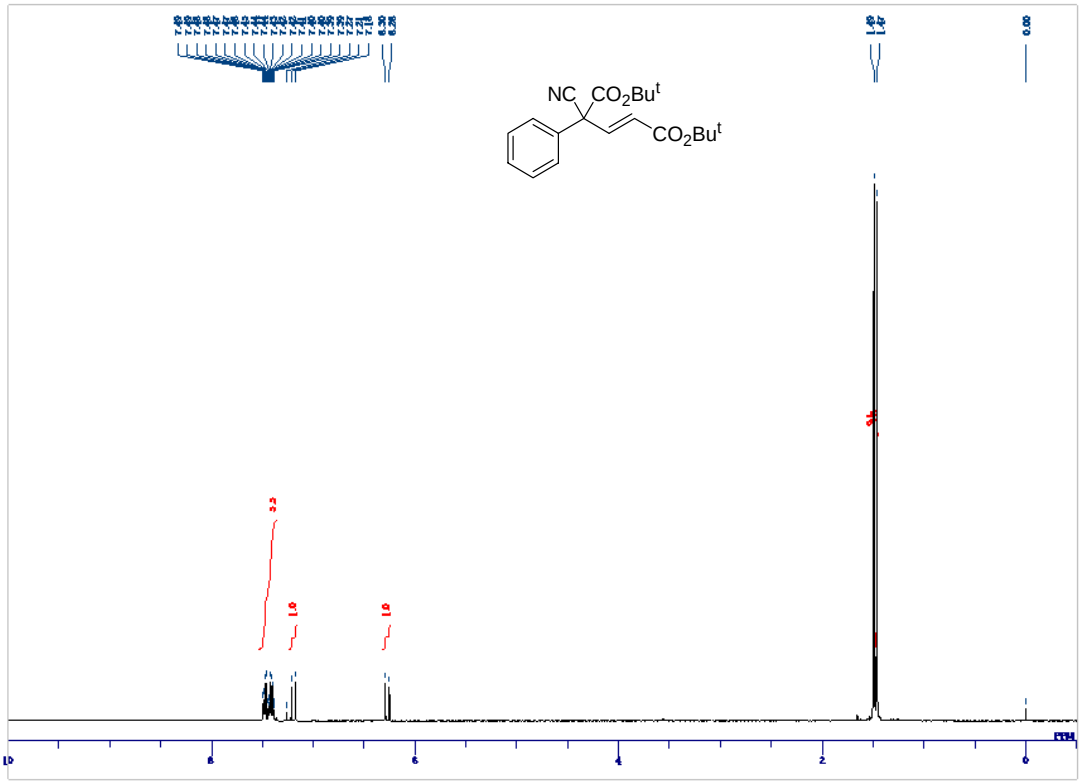
^{1}H NMR: (*Z*)-**4k**



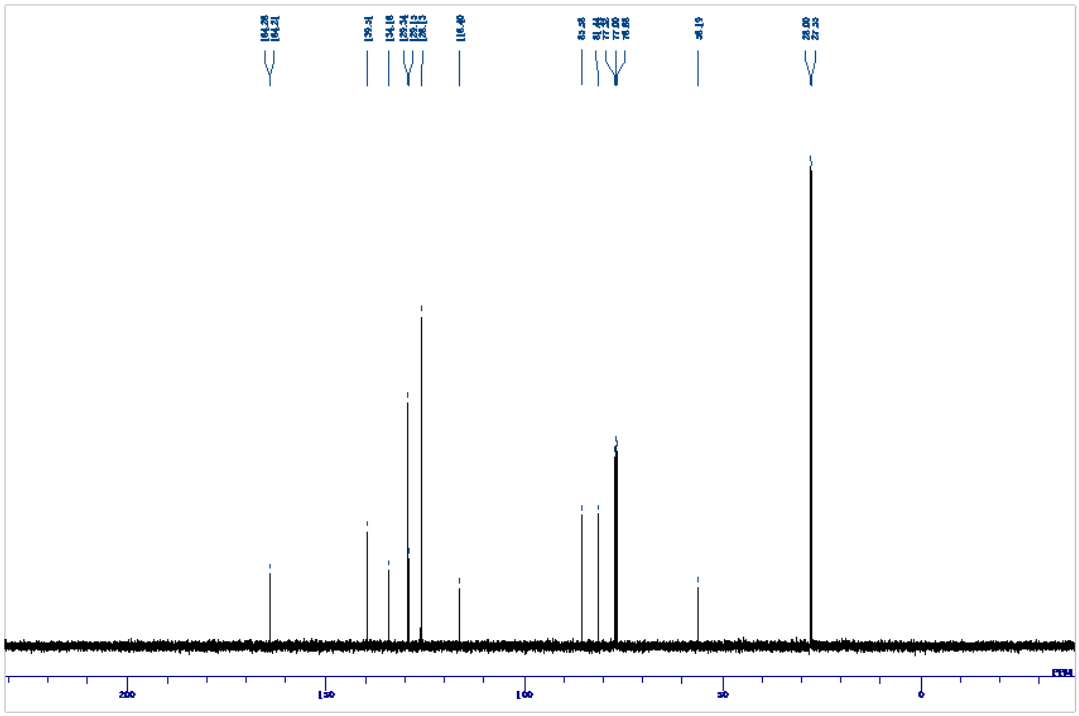
^{13}C NMR: (*Z*)-**4k**



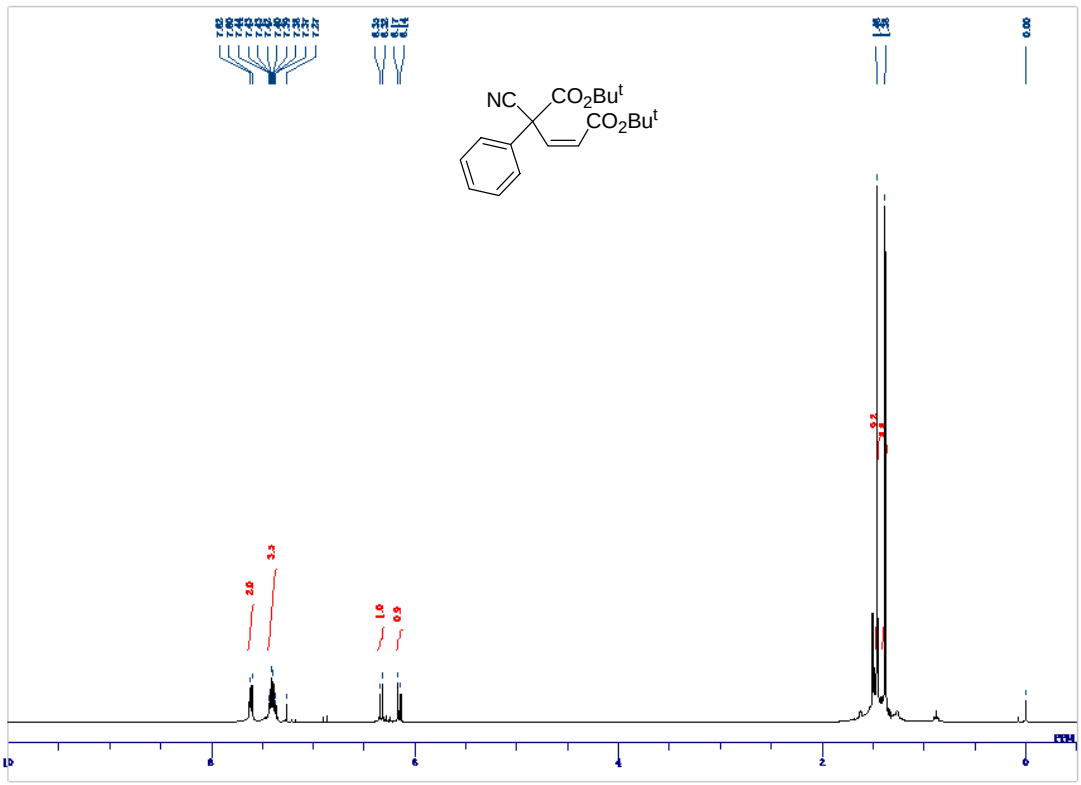
^{1}H NMR: (*E*)-**4l**



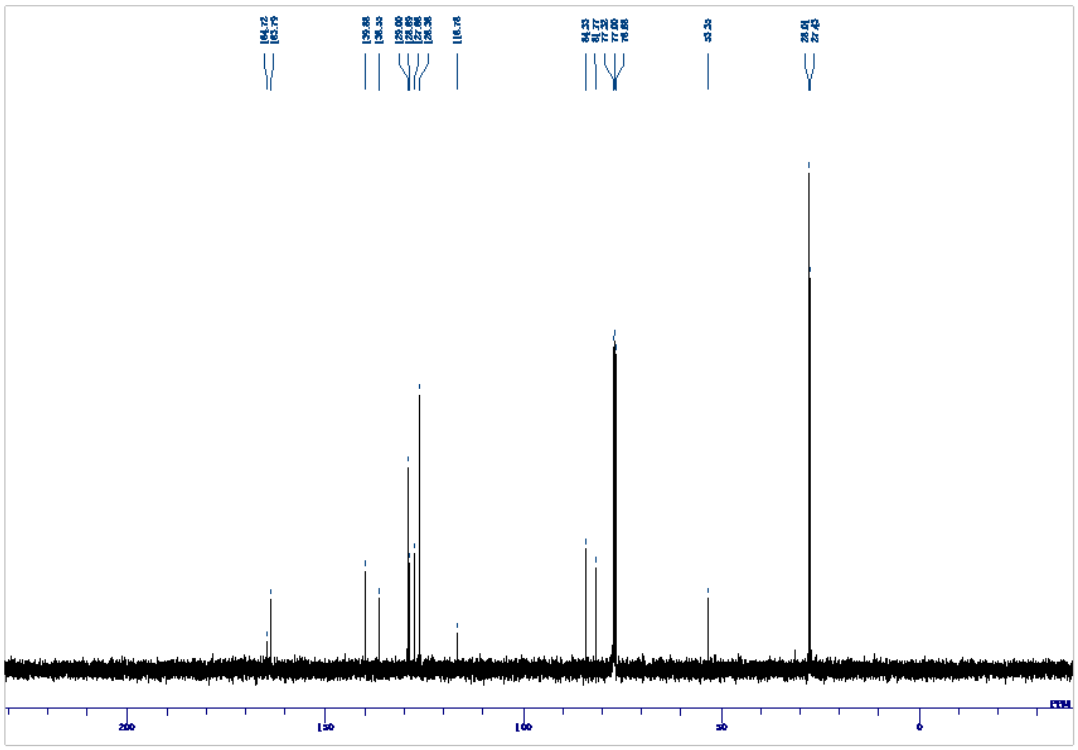
^{13}C NMR: (*E*)-**4l**



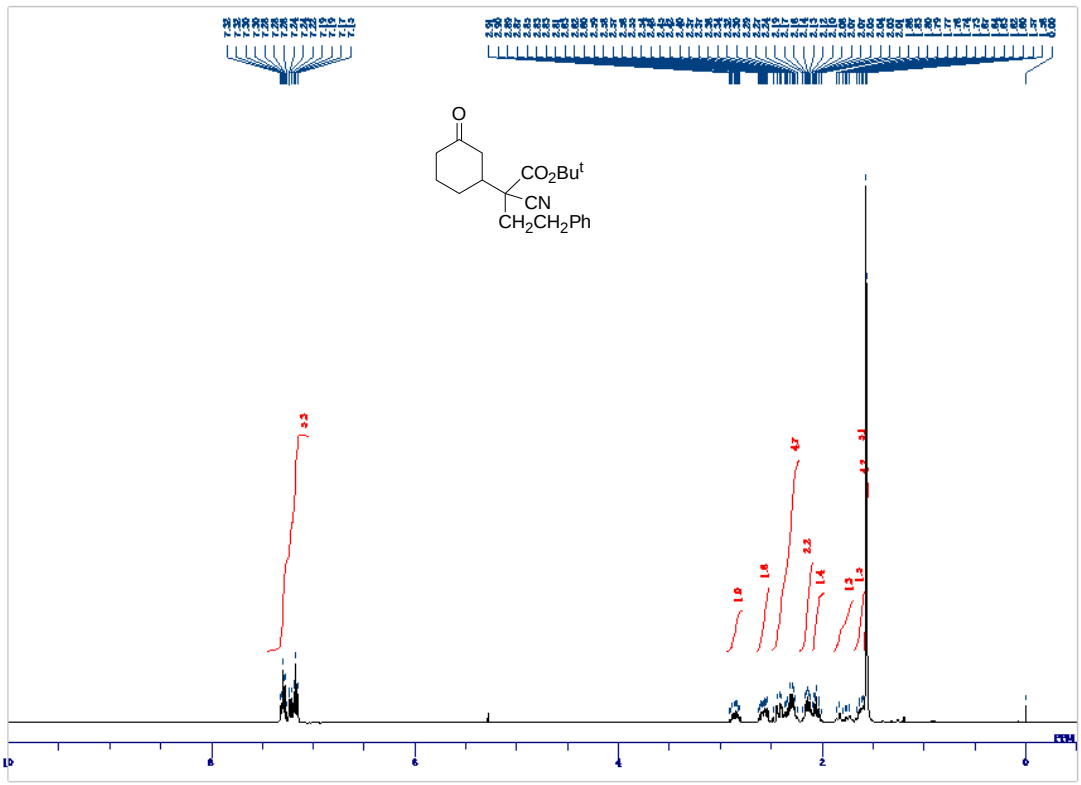
^{1}H NMR: (*Z*)-**4l**



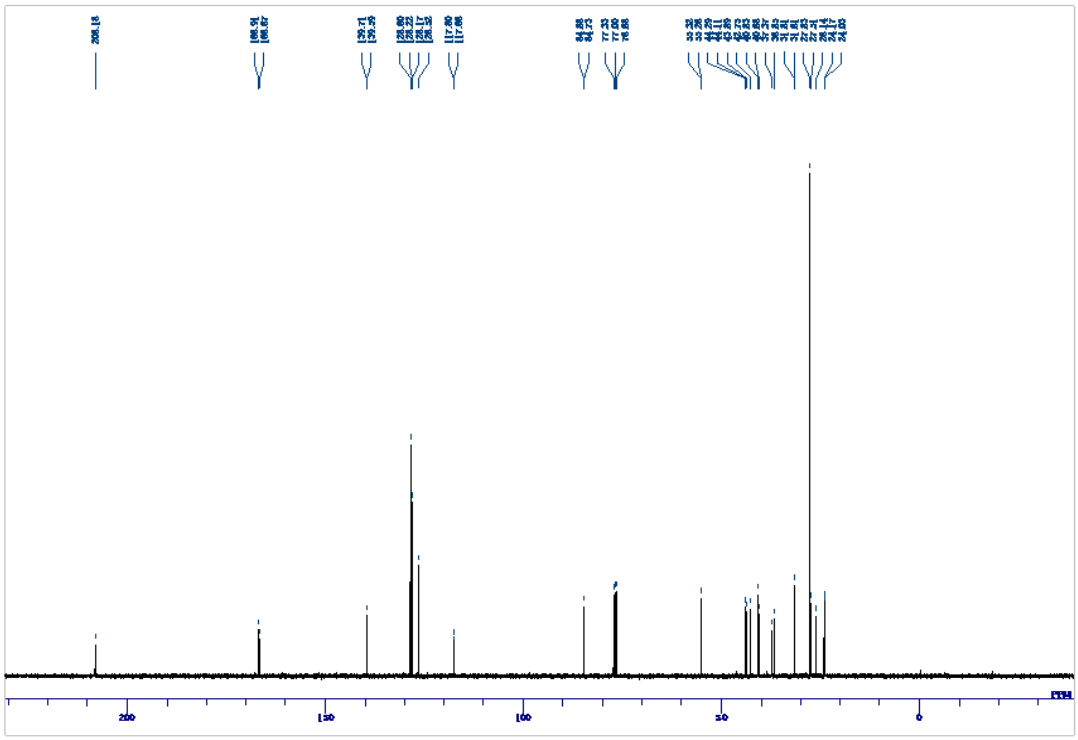
^{13}C NMR: (*Z*)-**4l**



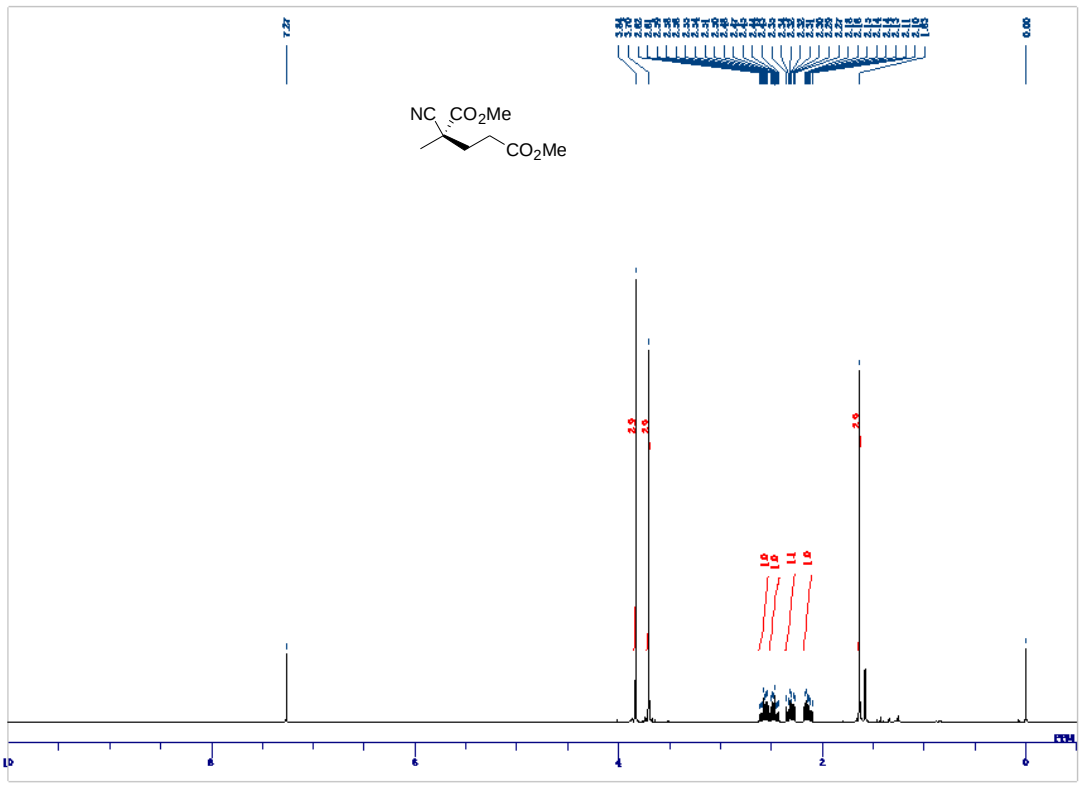
^{1}H NMR: Rac.-**6** (mixture of isomers)



^{13}C NMR: Rac.-**6** (mixture of isomers)



^{1}H NMR: (**5**)



^{13}C NMR: (**5**)