

SUPPORTING INFORMATION

Nickel-Catalyzed Reductive Dicarbonylation of Alkenes

Andrés García-Domínguez, Zhaodong Li and Cristina Nevado

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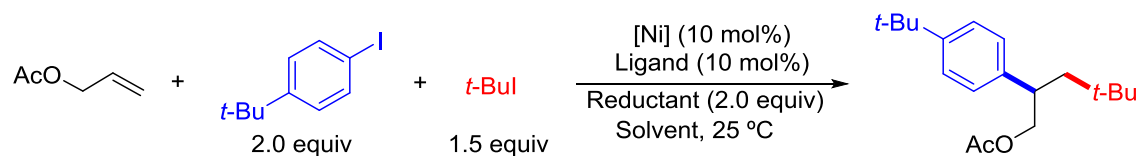
1. General Information

NMR spectra were recorded on AV2 400 Bruker spectrometers. Chemical shifts are given in ppm and the spectra are calibrated using the residual chloroform signals: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), multiplet (m) and broad (br). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution mass spectrometry was performed on a Finnigan MAT 900 (ThermoFinnigan, San Jose, CA; USA) double focusing magnetic sector mass spectrometer. A mass accuracy ≤ 2 ppm was obtained in the peak matching acquisition mode by using a solution containing 2<1 PEG200, 2<1 PPG450, and 1.5 mg NaOAc (all obtained from Sigma-Aldrich, CH-Buchs) dissolved in 100 mL MeOH (HPLC Supra grade, Scharlau, E-Barcelona) as internal standard.

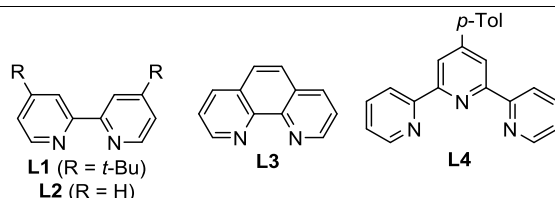
Materials and Methods: Unless otherwise stated, all the reactions were performed using Schlenk techniques under N_2 atmosphere outside the glovebox. The following compounds were prepared according to the procedures described previously in the literature: $\text{NiCl}_2(\text{Py})_4$,¹ 2-iodo-2-methylbutane,² 6-iodo-6-methyl-1-heptene,³ 1-chloro-4-iodo-4-methylpenten,⁴ 1-iodo-1-methylcyclohexene,⁵ 2-iodo-2-methyl-1-phenylbutane,⁶ 4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl acetate⁷ and $(\text{dtbbpy})\text{NiI}_2$.⁸

The remaining chemicals presented in this work were purchased from Aldrich, Fluka, TCI Europe, Fluorochem and/or ABCR and used as received except TDAE, which was transferred into a Schlenck under N_2 and stored at 4 °C. THF was dried using a solvent purification system (Pure Solv PS-MD-4EN, Innovative Technology Inc.) equipped with alumina drying columns under Ar. Thin Layer Chromatography was performed using Merck TLC silica gel 60 F₂₅₄ plates and visualized using UV light at 254 nm and/or stained with an ethanolic solution of phosphomolybdic acid. Flash column chromatography was performed over silica gel (230-400 mesh).

2. Optimization of Reaction Conditions^a



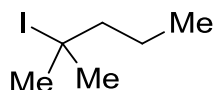
Entry	[Ni]	Ligand	Reductant	Solvent	Yield of 1 (%) ^b
1	NiCl ₂ ·DME	L1	Zn	THF (0.4M)	0
2	NiCl ₂ ·DME	L1	Mn	THF (0.4M)	0
3	NiCl ₂ ·DME	L1	B ₂ pin ₂ /KO ^t Bu	THF (0.4M)	0
4	NiCl ₂ ·DME	L1	TDAE ^c	THF (0.4M)	17
5	NiCl ₂ ·DME	L1	TDAE ^c	DCM (0.4M)	8
6	NiCl ₂ ·DME	L1	TDAE ^c	CH ₃ CN (0.4M)	0
7	NiCl ₂ ·DME	L1	TDAE ^c	DMF (0.4M)	12
8	NiCl ₂ ·DME	L1	TDAE ^c	THF (0.05M)	17
9	NiCl ₂ ·DME	L1	TDAE ^c	THF (0.1M)	2
10	NiCl ₂ ·DME	L1	TDAE ^c	THF (0.7M)	4
11	NiCl ₂ ·DME	L2	TDAE ^c	THF (0.4M)	1
12	NiCl ₂ ·DME	L3	TDAE ^c	THF (0.4M)	2
13	NiCl ₂ ·DME	L4	TDAE ^c	THF (0.4M)	0
14	NiBr ₂ ·DME	L1	TDAE ^c	THF (0.4M)	54
15	Ni(acac) ₂	L1	TDAE ^c	THF (0.4M)	27
16	NiCl ₂ (Py) ₄	L1	TDAE ^c	THF (0.4M)	82 (83)
17	NiCl ₂ (Py) ₄	L1	TDAE ^d	THF (0.4M)	33
18	-	L1	TDAE ^c	THF (0.4M)	0
19	NiCl ₂ (Py) ₄	-	TDAE ^c	THF (0.4M)	0



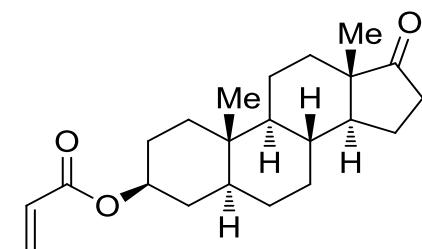
^a Conditions: Allyl acetate (20.0 mg, 0.2 mmol, 1.0 equiv), 4-*tert*-butyliodobenzene (104.4 mg, 0.4 mmol, 2.0 equiv), *tert*-butyl iodide (55.2 mg, 0.3 mmol, 1.5 equiv), nickel catalyst (0.02 mmol, 10 mol%), ligand (0.02 mmol, 10 mol%), reductant (0.4 mmol, 2.0 equiv), solvent, 25 °C, 15 h. ^b Yield determined by ¹H NMR with *p*-nitroacetophenone as internal standard. In brackets: Isolated yield after column chromatography. ^c TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was used.

^d TDAE (47 μL, 0.2 mmol, 1.0 equiv) was used.

3. Synthesis and Characterization of New Substrates



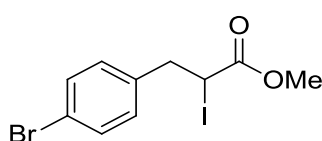
2-iodo-2-methylpentane (S1). The title compound was prepared following a reported procedure.^{3,5} Diphosphorous tetraiodide (769 mg, 1.35 mmol) was placed in a two necked 50 mL round bottomed flask. The flask was evacuated and back filled with N₂ three times and CS₂ (15 mL) added. The orange suspension was cooled at 0 °C (ice bath), 2-methylpentan-2-ol (0.61 mL, 511 mg, 5.00 mmol) was added and the brown red mixture stirred until complete consumption of the starting alcohol (TLC monitoring). The ice bath was removed and solid potassium carbonate, followed by a saturated aqueous solution of potassium carbonate (25 mL) were added. The orange water layer was extracted with Et₂O (6 x 25 mL) and the combined organic layers dried over MgSO₄. After filtration, the solvent was removed carefully under reduced pressure to obtain 2-iodo-2-methylpentane (738 mg, 3.48 mmol, 70% yield) as a yellow oil which was used without further purification. ¹H NMR (300 MHz, CDCl₃) δ 1.92 (s, 6H), 1.65 – 1.46 (m, 4H), 0.97 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 52.96, 38.22 (2 x C), 21.98, 13.98; IR (film): ν (cm⁻¹) 2958, 2932, 2872, 2826, 1463, 1455, 1384, 1367, 1306, 1291, 1249, 1221, 1179, 1133, 1111, 1090, 1075, 1059, 1039, 1007, 998, 961, 900, 860, 811; HR-MS (EI) *m/z* calcd for C₆H₁₃ [M – I]: 85.10118, found 85.10190.



(3S,5S,8R,9S,10S,13S,14S)-10,13-Dimethyl-17-oxohexadecahydro-1H-

cyclopenta[a]phenanthren-3-yl acrylate (S2). To a solution of epiandrosterone (1.45 g, 5.0 mmol) and Et₃N (1.5 mL, 10.0 mmol) in CH₂Cl₂ (50.0 mL) at 0 °C was added acryloyl chloride (0.54 g, 6.0 mmol). The reaction mixture was warmed to 25 °C and stirred for 12 h. The mixture was quenched with H₂O (10.0 mL), extracted with CH₂Cl₂ (3 x 20.0 mL) and the combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel using Hexane/EtOAc 20/1 (v/v) as eluent to afford the product as a colourless solid (1.63 g, 4.75 mmol, 95% yield). ¹H NMR (400 MHz,

CDCl₃) δ 6.36 (dd, J = 17.3, 1.5 Hz, 1H), 6.07 (dd, J = 17.3, 10.4 Hz, 1H), 5.77 (dd, J = 10.4, 1.6 Hz, 1H), 4.87 – 4.67 (m, 1H), 2.42 (dd, J = 19.1, 8.8 Hz, 1H), 2.05 (dt, J = 19.1, 9.0 Hz, 1H), 1.96 – 1.70 (m, 5H), 1.70 – 1.60 (m, 2H), 1.60 – 1.16 (m, 10H), 1.11 – 0.90 (m, 2H), 0.85 (s, 3H), 0.84 (s, 3H), 0.77 – 0.66 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 221.21, 165.86, 130.29, 129.19, 73.76, 54.45, 51.50, 47.88, 44.79, 36.83, 35.94, 35.78, 35.17, 34.05, 31.66, 30.93, 28.39, 27.52, 21.89, 20.59, 13.93, 12.34; IR (film): ν (cm⁻¹) 2951, 2917, 1735, 1713, 1616, 1471, 1453, 1440, 1407, 1269, 1197, 1150, 1130, 1110, 1079, 1049, 1014, 997, 982, 971, 937, 920, 902, 893, 884, 863, 844, 831, 812; HR-MS (ESI) m/z calcd for C₂₂H₃₂O₃Na [M + Na⁺]: 367.22437, found 367.22429.

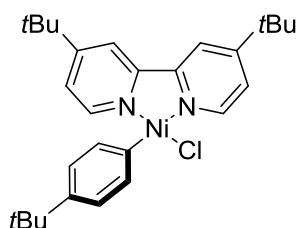


Methyl 3-(4-bromophenyl)-2-iodopropanoate (S3).

Step 1: Red phosphorus (150 mg, 4.84 mmol) was added at 25 °C to 3-phenylpropanoyl chloride (3.36 g, 20 mmol) while stirring. Then, Br₂ (2.05 mL, 40 mmol) was added dropwise maintaining the temperature below 100 °C. When the addition was finished, the reaction mixture was heated at 100 °C for 12 h and cooled to 25 °C. Then, the mixture was cooled to 0 °C (ice bath) and dry methanol (40.0 mL) was added dropwise. The reaction mixture was warmed to 25 °C and then heated at reflux for 6 h. After cooling the reaction mixture to 25 °C, cold water was added and the aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL). The combined organic layer was dried over MgSO₄, filtered and the solvent removed under reduced pressure. The crude product was purified by chromatography on silica gel using Hexane/EtOAc 20/1 (v/v) as eluent to afford methyl 2-bromo-3-(4-bromophenyl)propanoate as a brown oil (3.83 g, 60% yield).

Step 2: To a solution of methyl 2-bromo-3-(4-bromophenyl)propanoate (3.19 g, 10.0 mmol) in acetone (30.0 mL) was added NaI (2.98 g, 20.0 mmol) at 25 °C. The reaction mixture was heated at reflux for 12 h and after cooling to 25 °C, quenched with H₂O (10.0 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting residue was purified by chromatography on silica gel using Hexane/EtOAc 20/1 (v/v) as eluent to afford methyl 3-(4-bromophenyl)-2-iodopropanoate as a brown oil (3.50 g, 95% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 4.46 (dd, J = 9.0, 6.8 Hz, 1H), 3.70 (s, 3H), 3.41 (dd, J = 14.3, 9.1 Hz, 1H), 3.20 (dd, J = 14.3, 6.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 171.40, 137.52, 131.97,

130.74, 121.40, 53.08, 41.86, 19.20; IR (film): ν (cm⁻¹) 3027, 2950, 1732, 1487, 1434, 1404, 1355, 1308, 1291, 1275, 1223, 1158, 1116, 1071, 1057, 1045, 1011, 979, 910, 839;



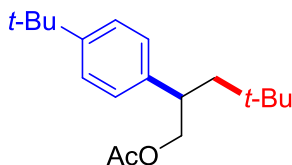
[(dtbbpy)Ni(4-*t*-Bu-C₆H₄)Cl] (43): In a nitrogen filled glove box, a 50 mL round bottom flask containing a PTFE-coated stir bar was charged with [Ni(cod)₂] (550 mg, 2.0 mmol, 1.0 equiv), 4,4'-di-*tert*-butyl-2,2'-pyridine (537 mg, 2.0 mmol, 1.0 equiv) and dry THF (8.0 mL) giving a deep purple mixture which was stirred for 2 hours at 25 °C. 4-*tert*-butylchlorobenzene (5.0 g, 29.6 mmol, 14.8 equiv) was added and stirred for additional 30 minutes. Dry pentane (30 mL) was added to the deep red coloured mixture and filtered. The resulting precipitate was washed with pentane (3 x 10 mL) and dried under vacuum to give the desired complex **43** as an orange powder (803 mg, 1.62 mmol, 81% yield). The product was used as such without further purification. The complex was stored in a nitrogen filled glove box at -35 °C and showed to be stable in solid form. In solution (CH₂Cl₂) significant decomposition was observed after 8h. ¹H NMR (300 MHz, CD₂Cl₂) δ 9.02 (s, 1H), 7.84 (d, *J* = 13.4 Hz, 2H), 7.53 (s, 1H), 7.45 – 7.26 (m, 3H), 7.15 (s, 1H), 7.03 (d, *J* = 7.1 Hz, 2H), 1.42 (s, 9H), 1.35 (s, 9H), 1.31 (s, 9H); ¹³C NMR (101 MHz, CD₂Cl₂) 163.34, 162.35, 155.62, 152.45, 151.71, 148.86, 144.72, 144.60, 135.41, 123.15, 123.01, 122.83, 117.27, 116.58, 35.09, 33.43, 31.20, 30.78, 29.90, 29.67; IR (film): ν (cm⁻¹) 3056, 3035, 2962, 2905, 2867, 1614, 1550, 1480, 1464, 1408, 1365, 1267, 1251, 1200, 1178, 1110, 1078, 1053, 1020, 1008, 936, 921, 897, 849, 822, 809, 792, 763, 749, 735, 721, 699, 687, 677, 654, 645, 632, 606.

4. Synthesis and Characterization of New Products

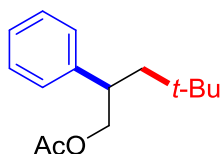
4.1 General Procedure for the Reductive Alkene Dicarbonylation

$\text{NiCl}_2(\text{Py})_4$ (8.9 mg, 0.02 mmol, 10 mol%), **L1** (5.4 mg, 0.02 mmol, 10 mol%) and aryl iodide if solid (0.4 mmol, 2.0 equiv) were placed in an oven dried Schlenk flask. The reaction vessel was evacuated and filled back with nitrogen three times. THF (0.5 mL), unsaturated substrate (0.2 mmol, 1.0 equiv), aryl iodide if liquid (0.4 mmol, 2.0 equiv) and alkyl iodide (0.3 mmol, 1.5 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N_2 . The mixture was diluted with Et_2O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et_2O twice. The combined organic layers were dried over anhydrous MgSO_4 and after filtration and removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel to obtain the corresponding products in pure form.

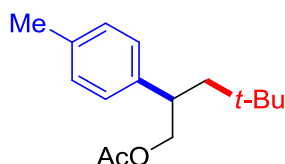
4.2 Characterization of New Products



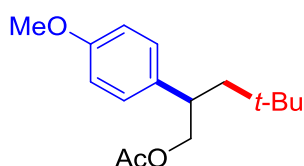
2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylpentyl acetate (1). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 4.09 (dd, J = 9.3, 5.8 Hz, 1H), 4.05 (dd, J = 9.3, 5.8 Hz, 1H), 3.01 – 2.94 (m, 1H), 1.98 (s, 3H), 1.69 (dd, J = 14.0, 8.0 Hz, 1H), 1.58 (dd, J = 14.0, 3.7 Hz, 1H), 1.30 (s, 9H), 0.82 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.22, 149.34, 140.85, 127.76, 125.35, 69.91, 46.06, 41.20, 34.51, 31.55, 31.27, 30.11, 21.12. IR (film): ν (cm^{-1}) 3092, 3051, 3026, 2954, 2904, 2867, 1741, 1511, 1466, 1413, 1393, 1382, 1364, 1229, 1121, 1079, 1032, 976, 919, 887, 829; HR-MS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 313.21380, found 313.21364.



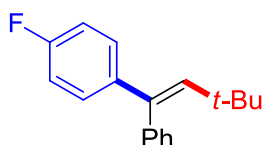
4,4-Dimethyl-2-phenylpentyl acetate (2). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.25 (m, 2H), 7.25 – 7.17 (m, 3H), 4.12 (dd, J = 9.4, 5.7 Hz, 1H), 4.08 (dd, J = 9.4, 6.1 Hz, 1H), 3.08 – 2.98 (m, 1H), 1.97 (s, 3H), 1.71 (dd, J = 14.0, 8.4 Hz, 1H), 1.59 (dd, J = 14.1, 3.5 Hz, 1H), 0.82 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.12, 144.00, 128.53, 128.23, 126.59, 69.83, 46.00, 41.81, 31.28, 30.11, 21.04; IR (film): ν (cm^{-1}) 3086, 3063, 3028, 2953, 2867, 1739, 1610, 1495, 1467, 1454, 1383, 1365, 1228, 1031, 912; HR-MS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 257.15120, found 257.15107.



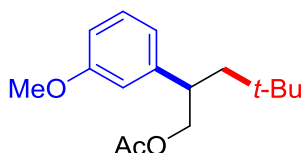
4,4-Dimethyl-2-(4-tolyl)pentyl acetate (3). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.10 (br s, 4H), 4.09 (dd, J = 10.7, 7.0 Hz, 1H), 4.04 (dd, J = 10.7, 7.4 Hz, 1H), 3.04 – 2.92 (m, 1H), 2.32 (s, 3H), 1.97 (s, 3H), 1.68 (dd, J = 14.0, 8.3 Hz, 1H), 1.57 (dd, J = 14.0, 3.5 Hz, 1H), 0.82 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.17, 140.94, 136.04, 129.23, 128.06, 69.96, 46.02, 41.35, 31.28, 30.12, 21.17, 21.08; IR (film): ν (cm^{-1}) 3020, 2953, 2865, 1741, 1653, 1514, 1467, 1382, 1364, 1230, 1165, 1114, 1095, 1076, 1032, 1006, 983, 920, 886, 860, 844, 834; HR-MS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 271.16685, found 271.16680.



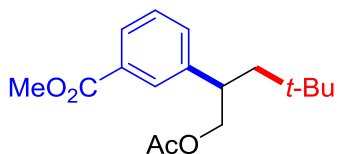
4,4-Dimethyl-2-(4-methoxyphenyl)pentyl acetate (4). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.07 (dd, J = 8.9, 5.4 Hz, 1H), 4.03 (dd, J = 8.9, 5.6 Hz, 1H), 3.78 (s, 3H), 3.06 – 2.88 (m, 1H), 1.97 (s, 3H), 1.66 (dd, J = 14.0, 8.5 Hz, 1H), 1.56 (dd, J = 14.0, 3.5 Hz, 1H), 0.81 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.11, 158.30, 135.93, 129.06, 113.91, 69.96, 55.29, 46.03, 40.92, 31.21, 30.12, 21.04; IR (film): ν (cm^{-1}) 3032, 2999, 2951, 2865, 2836, 1737, 1612, 1584, 1511, 1465, 1444, 1382, 1364, 1301, 1239, 1228, 1178, 1111, 1031, 975, 887 828; HR-MS (ESI) m/z calcd $\text{C}_{16}\text{H}_{24}\text{O}_3\text{Na}$ [$\text{M} + \text{Na}^+$]: 287.16177, found 287.16159.



(E)-1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-fluorobenzene (5). Colorless oil. NMR (400 MHz, CDCl_3) δ 7.38 – 7.28 (m, 3H), 7.21 – 7.12 (m, 4H), 6.92 (t, J = 8.8 Hz, 2H), 6.03 (s, 1H), 0.97 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.98 (d, J = 245.7 Hz), 140.76, 140.38 (d, J = 3.2 Hz), 140.08 (d, J = 1.4 Hz), 138.28, 130.38, 128.52 (d, J = 7.9 Hz), 127.99, 127.02, 114.85 (d, J = 21.3 Hz), 34.11, 31.44; ^{19}F NMR (376 MHz, CDCl_3) δ -116.71 (tt, J = 8.5, 5.5 Hz, 1F); IR (film): ν (cm^{-1}) 3077, 3055, 3020, 2957, 2901, 2865, 1600, 1576, 1505, 1474, 1460, 1441, 1409, 1393, 1361, 1299, 1281, 1265, 1230, 1189, 1158, 1099, 1072, 1028, 1013, 958, 922, 889, 831, 811; HR-MS (EI) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{F}$ [M^+]: 254.14653, found 254.14683.

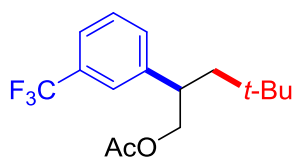


2-(3-Methoxyphenyl)-4,4-dimethylpentyl acetate (6). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.20 (td, J = 7.7, 0.7 Hz, 1H), 6.81 (dd, J = 7.6, 1.1 Hz, 1H), 6.78 – 6.73 (m, 2H), 4.12 (m, 2 H), 3.80 (s, 3H), 3.03 – 2.94 (m, 1H), 1.98 (s, 3H), 1.69 (dd, J = 14.1, 8.3 Hz, 1H), 1.57 (dd, J = 14.1, 3.5 Hz, 1H), 0.82 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.15, 159.77, 145.74, 129.48, 120.70, 114.27, 111.58, 69.78, 55.31, 45.99, 41.84, 31.29, 30.09, 21.08; IR (film): ν (cm^{-1}) 3047, 2952, 2865, 2835, 1738, 1600, 1585, 1487, 1466, 1455, 1437, 1382, 1364, 1315, 1262, 1229, 1152, 1093, 1035, 995, 976, 946, 923, 865, 855, 835; HR-MS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{Na}$ [$\text{M} + \text{Na}^+$]: 287.16177, found 287.16181.

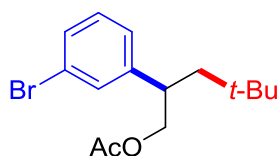


3-(1-acetoxy-4,4-dimethylpentan-2-yl)phenyl acetate (7). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.81 (t, J = 1.6 Hz, 1H), 7.78 (dt, J = 7.5, 1.5 Hz, 1H), 7.31 (dt, J = 7.7, 1.5 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 4.03 (dd, J = 10.8, 6.7 Hz, 1H), 3.96 (dd, J = 10.8, 7.8 Hz, 1H), 3.81 (s, 3H), 3.03 – 2.93 (m, 1H), 1.84 (s, 3H), 1.62 (dd, J = 14.1, 8.4 Hz, 1H), 1.50 (dd, J = 14.1, 3.5 Hz, 1H), 0.70 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.98, 167.21, 144.48, 132.88, 130.45, 129.32, 128.59, 127.94, 69.53, 52.19, 45.92, 41.65, 31.29, 30.08, 20.94; IR (film): ν (cm^{-1}) 3056, 2952, 2907, 2867, 1721, 1606, 1588,

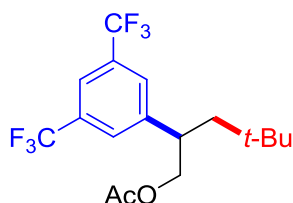
1467, 1445, 1433, 1382, 1365, 1281, 1226, 1204, 1109, 1089, 1034, 980, 908, 847, 818; HR-MS (ESI) m/z calcd for $C_{17}H_{24}O_4Na$ $[M + Na^+]$: 315.15668, found 315.15665.



4,4-Dimethyl-2-(3-(trifluoromethyl)phenyl)pentyl acetate (8). Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.44 – 7.39 (m, 2H), 4.13 (dd, J = 10.8, 6.5 Hz, 1H), 4.07 (dd, J = 10.8, 7.8 Hz, 1H), 3.16 – 3.04 (m, 1H), 1.95 (s, 3H), 1.72 (dd, J = 14.2, 8.2 Hz, 1H), 1.62 (dd, J = 14.2, 3.7 Hz, 1H), 0.82 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.97, 145.09, 131.58, 130.89 (q, J = 32.0 Hz), 129.01, 125.04 (q, J = 3.7 Hz), 124.34 (q, J = 272.2 Hz), 123.56 (q, J = 3.8 Hz), 69.42, 45.87, 41.72, 31.32, 30.07, 20.90; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.59 (s, 3F); IR (film): ν (cm^{-1}) 3067, 3026, 2956, 2869, 1740, 1469, 1450, 1366, 1324, 1226, 1161, 1122, 1073, 1034, 897, 829, 802; HR-MS (ESI) m/z calcd for $C_{16}H_{21}O_2F_3Na$ $[M + Na^+]$: 325.13859, found 325.13871.

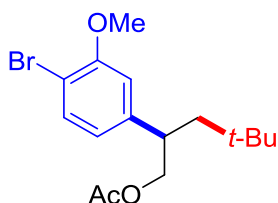


2-(3-Bromophenyl)-4,4-dimethylpentyl acetate (9). Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.19 – 7.12 (m, 2H), 4.10 (dd, J = 10.8, 6.7 Hz, 1H), 4.04 (dd, J = 10.8, 7.7 Hz, 1H), 3.04 – 2.94 (m, 1H), 1.97 (s, 3H), 1.67 (dd, J = 14.1, 8.2 Hz, 1H), 1.57 (dd, J = 14.1, 3.6 Hz, 1H), 0.82 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 146.54, 131.29, 130.14, 129.79, 126.91, 122.62, 69.49, 45.93, 41.60, 31.32, 30.09, 21.00; IR (film): ν (cm^{-1}) 3060, 2953, 2866, 1738, 1592, 1566, 1474, 1429, 1382, 1364, 1226, 1168, 1072, 1034, 997, 979, 913, 880, 838; HR-MS (ESI) m/z calcd for $C_{15}H_{21}BrO_2Na$ $[M + Na^+]$: 335.06171, found 335.06185.

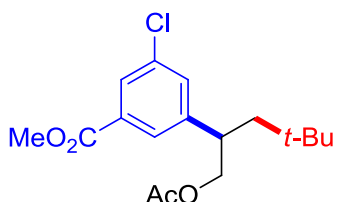


2-(3,5-bis(trifluoromethyl)phenyl)-4,4-dimethylpentyl acetate (10). Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.75 (br s, 1H), 7.67 (br s, 2H), 4.18 (dd, J = 10.9, 5.9 Hz, 1H), 4.06 (dd, J = 10.9, 8.0 Hz, 1H), 3.26 – 3.13 (m, 1H), 1.95 (s, 3H), 1.73 (dd, J = 14.3, 7.8 Hz, 1H), 1.66 (dd, J = 14.3, 4.0 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (101 MHz,

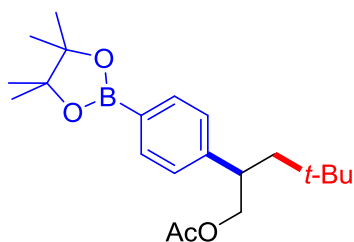
CDCl₃) δ 170.80, 146.83, 131.85 (q, J = 33.2 Hz), 128.44 (q, J = 2.7 Hz), 123.51 (q, J = 272.6 Hz), 121.01 – 119.93 (m), 69.02, 45.80, 41.68, 31.38, 30.04, 20.79; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.87 (s, 6F); IR (film): ν (cm⁻¹) 3056, 2959, 2910, 2870, 1741, 1622, 1469, 1377, 1368, 1353, 1276, 1266, 1228, 1170, 1131, 1081, 1062, 1037, 982, 950, 935, 924, 895, 843; HR-MS (ESI) m/z calcd for C₁₇H₂₀F₆O₂Na [M + Na⁺]: 393.12597, found 393.12595.



2-(4-Bromo-3-methoxyphenyl)-4,4-dimethylpentan-2-yl acetate (11). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 1.9 Hz, 1H), 6.71 (dd, J = 8.1, 2.0 Hz, 1H), 4.09 (dd, J = 9.7, 5.9 Hz, 1H), 4.05 (dd, J = 9.7, 6.6 Hz, 1H), 3.89 (s, 3H), 3.08 – 2.92 (m, 1H), 1.97 (s, 3H), 1.66 (dd, J = 14.1, 8.2 Hz, 1H), 1.57 (dd, J = 14.1, 3.6 Hz, 1H), 0.82 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 171.03, 155.95, 145.11, 133.25, 121.65, 112.03, 109.63, 69.48, 56.36, 46.03, 41.77, 31.31, 30.08, 21.03; IR (film): ν (cm⁻¹) 3062, 3010, 2952, 2866, 1736, 1589, 1578, 1483, 1464, 1412, 1394, 1381, 1364, 1280, 1226, 1165, 1137, 1037, 1025, 978, 945, 913, 852, 811; HR-MS (ESI) m/z calcd for C₁₆H₂₃BrO₃Na [M + Na⁺]: 365.07228, found 365.07231.

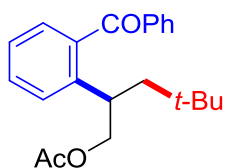


Methyl 3-(1-acetoxy-4,4-dimethylpentan-2-yl)-5-chlorobenzoate (12). White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (t, J = 1.6 Hz, 1H), 7.80 (t, J = 1.6 Hz, 1H), 7.40 (t, J = 2.0 Hz, 1H), 4.14 (dd, J = 10.8, 6.4 Hz, 1H), 4.04 (dd, J = 9.7, 8.0 Hz, 1H), 3.93 (s, 3H), 3.10 – 3.04 (m, 1H), 1.97 (s, 3H), 1.70 (dd, J = 14.4, 8.0 Hz, 1H), 1.57 (dd, J = 14.4, 4.0 Hz, 1H), 0.83 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 170.80, 165.90, 146.52, 134.46, 132.62, 131.89, 127.88, 127.46, 69.08, 52.39, 45.73, 41.39, 31.20, 29.93, 20.79; IR (film): ν (cm⁻¹) 3059, 3020, 2953, 1728, 1448, 1365, 1287, 1227, 1036, 770; HR-MS (ESI) m/z calcd for C₁₇H₂₃ClO₄Na [M + Na⁺]: 349.11771, found 349.11778.

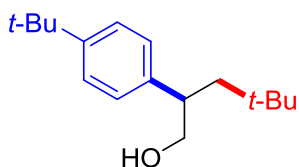


4,4-Dimethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pentyl

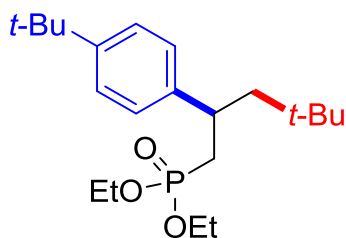
acetate (13). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 4.12 (dd, J = 10.7, 6.8 Hz, 2H), 4.05 (dd, J = 10.7, 7.7 Hz, 1H), 3.03 (ddd, J = 15.2, 7.8, 3.4 Hz, 1H), 1.95 (s, 3H), 1.72 (dd, J = 14.1, 8.4 Hz, 1H), 1.57 (dd, J = 14.1, 3.4 Hz, 1H), 1.34 (s, 12H), 0.80 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.11, 147.39, 135.06, 127.70, 83.84, 69.71, 45.90, 42.00, 31.30, 30.11, 25.06, 25.00, 21.03; IR (film): ν (cm^{-1}) 3047, 2976, 2954, 2867, 1739, 1611, 1560, 1516, 1467, 1448, 1398, 1358, 1321, 1266, 1228, 1187, 1165, 1143, 1106, 1092, 1034, 1020, 962, 920, 888, 859, 828; HR-MS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{33}\text{O}_4\text{BNa}$ [$\text{M} + \text{Na}^+$]: 383.23641, found 383.23679.



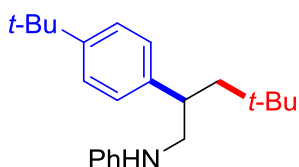
2-(2-Benzoylphenyl)-4,4-dimethylpentyl acetate (14). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.81 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.42 (m, 4H), 7.29 – 7.25 (m, 2H), 4.20 (dd, J = 10.7, 6.2 Hz, 1H), 4.01 (dd, J = 10.7, 7.4 Hz, 1H), 3.49 – 3.39 (m, 1H), 1.86 (s, 3H), 1.78 (dd, J = 14.2, 7.8 Hz, 1H), 1.61 (dd, J = 14.2, 4.2 Hz, 1H), 0.79 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.35, 171.10, 143.41, 138.99, 138.12, 133.34, 130.61, 130.41, 128.86, 128.49, 128.23, 125.51, 70.10, 46.35, 36.50, 31.37, 30.06, 21.00; IR (film): ν (cm^{-1}) 3060, 3022, 2953, 2907, 2866, 1737, 1664, 1596, 1579, 1468, 1448, 1382, 1365, 1315, 1285, 1264, 1241, 1179, 1152, 1073, 1034, 1001, 975, 927, 891, 847; HR-MS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{26}\text{O}_3\text{Na}$ [$\text{M} + \text{Na}^+$]: 361.17742, found 361.17732.



2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylpentan-1-ol (15). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 8.3 Hz, 1H), 3.67 (dd, J = 10.6, 5.7 Hz, 1H), 3.58 (dd, J = 10.6, 8.7 Hz, 1H), 2.90 – 2.80 (m, 1H), 1.64 (dd, J = 14.0, 7.9 Hz, 1H), 1.50 (dd, J = 14.0, 3.8 Hz, 1H), 1.31 (s, 9H), 0.83 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.49, 141.07, 127.99, 125.63, 69.15, 45.98, 44.91, 34.53, 31.55, 31.30, 30.16; IR (film): ν (cm^{-1}) 3352, 3088, 3052, 3026, 2953, 2906, 2866, 1511, 1474, 1466, 1412, 1393, 1364, 1269, 1245, 1202, 1120, 1062, 1031, 1002, 945, 908, 871, 829; HR-MS (EI) m/z calcd for $\text{C}_{17}\text{H}_{28}\text{O}$ [M^+]: 248.21347, found 248.21363.

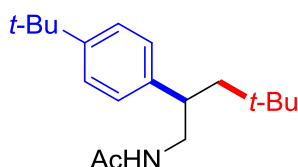


Diethyl (2-(4-(*tert*-butyl)phenyl)-4,4-dimethylpentyl)phosphonate (16). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 3.97 – 3.76 (m, 3H), 3.75 – 3.63 (m, 1H), 3.21 – 3.01 (m, 1H), 2.10 – 1.96 (m, 2H), 1.78 – 1.65 (m, 2H), 1.28 (s, 9H), 1.16 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H), 0.77 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.17, 143.40 (d, J = 7.3 Hz), 127.46, 125.23, 61.27 (d, J = 6.5 Hz), 61.08 (d, J = 6.3 Hz), 51.46 (d, J = 12.9 Hz), 36.71 (d, J = 3.4 Hz), 35.94 (d, J = 137.2 Hz), 34.47, 31.54, 31.50, 30.15, 16.38 (d, J = 6.4 Hz); IR (film): ν (cm^{-1}) 3051, 3022, 2953, 2904, 2866, 1511, 1475, 1444, 1408, 1393, 1364, 1294, 1244, 1162, 1097, 1054, 1027, 958, 892, 850, 827; HR-MS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{38}\text{O}_3\text{P}$ [$\text{M} + \text{H}^+$]: 369.25531, found 369.25480.

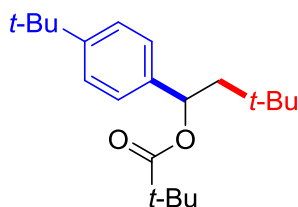


***N*-(2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylpentyl)aniline (17).** Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 8.3 Hz, 2H), 7.19 – 7.11 (m, 4H), 6.69 (t, J = 7.3 Hz, 1H), 6.60 – 6.49 (m, 2H), 3.51 (brs, 1H), 3.36 (dd, J = 12.0, 5.5 Hz, 1H), 3.10 (dd, J = 12.0, 9.4 Hz, 1H), 3.01 – 2.88 (m, 1H), 1.77 (dd, J = 14.0, 7.9 Hz, 1H), 1.60 (dd, J = 14.0, 3.6

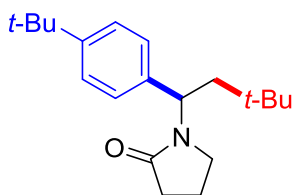
Hz, 1H), 1.33 (s, 9H), 0.84 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.35, 148.30, 141.95, 129.31, 127.71, 125.58, 117.40, 113.25, 51.78, 48.21, 41.50, 34.54, 31.56, 31.47, 30.19; IR (film): ν (cm^{-1}) 3417, 3086, 3051, 3022, 2954, 2904, 2865, 1601, 1505, 1473, 1430, 1412, 1394, 1363, 1319, 1265, 1201, 1179, 1154, 1109, 1072, 1017, 991, 968, 912, 865, 831; HR-MS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{34}\text{N}$ [$\text{M} + \text{H}^+$]: 324.26858, found 324.26850.



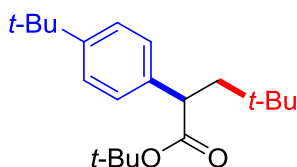
***N*-(2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylpentyl)acetamide (18).** White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 5.19 (br s, 1H), 3.79 – 3.62 (m, 1H), 3.08 – 2.93 (m, 1H), 2.86 – 2.74 (m, 1H), 1.85 (s, 3H), 1.66 (dd, J = 14.0, 7.8 Hz, 1H), 1.50 (dd, J = 14.0, 3.9 Hz, 1H), 1.31 (s, 9H), 0.81 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.97, 149.50, 141.61, 127.64, 125.65, 47.72, 47.02, 41.89, 34.54, 31.53, 31.34, 30.13, 23.46; IR (film): ν (cm^{-1}) 3286, 3087, 2958, 2901, 2869, 1650, 1556, 1510, 1466, 1435, 1407, 1394, 1364, 1288, 1268, 1249, 1241, 1164, 1101, 1075, 1066, 1054, 1018, 908, 880, 870, 829; HR-MS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{32}\text{NO}$ [$\text{M} + \text{H}^+$]: 290.24784, found 290.24783.



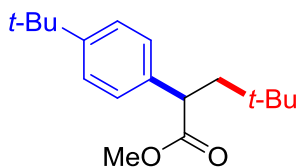
1-(4-(*tert*-Butyl)phenyl)-3,3-dimethylbutyl pivalate (19). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 5.81 (dd, J = 9.3, 2.6 Hz, 1H), 1.96 (dd, J = 14.9, 9.3 Hz, 1H), 1.57 (dd, J = 14.9, 2.7 Hz, 1H), 1.30 (s, 9H), 1.18 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.60, 150.16, 140.02, 125.45, 125.28, 73.70, 50.49, 38.56, 34.46, 31.34, 30.45, 29.93, 27.09; IR (film): ν (cm^{-1}) 3058, 3029, 2956, 2905, 2869, 1727, 1511, 1478, 1464, 1412, 1395, 1365, 1317, 1280, 1245, 1216, 1202, 1150, 1119, 1109, 1079, 1045, 1029, 1021, 963, 940, 924, 896, 860, 830; HR-MS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 341.24510, found 341.24526.



1-(1-(4-(*tert*-Butyl)phenyl)-3,3-dimethylbutyl)pyrrolidin-2-one (20). White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 5.47 (dd, J = 9.6, 4.0 Hz, 1H), 3.44 – 3.35 (m, 1H), 3.09 – 2.96 (m, 1H), 2.42 – 2.22 (m, 2H), 1.98 – 1.82 (m, 3H), 1.78 (dd, J = 14.4, 4.1 Hz, 1H), 1.30 (s, 9H), 0.96 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.31, 150.29, 138.17, 127.42, 125.41, 50.98, 43.05, 42.51, 34.57, 31.79, 31.46, 30.81, 29.89, 17.98; IR (film): ν (cm^{-1}) 3051, 3027, 2952, 2905, 2867, 1681, 1512, 1476, 1461, 1419, 1363, 1281, 1268, 1243, 1223, 1201, 1165, 1150, 1122, 1109, 1076, 1040, 1018, 998, 934, 915, 895, 860, 840, 824; HR-MS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{31}\text{NONa}$ [$\text{M} + \text{Na}^+$]: 324.22979, found 324.22933.

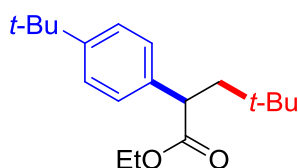


***tert*-Butyl 2-(4-(*tert*-butyl)phenyl)-4,4-dimethylpentanoate (21).** White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 3.50 (dd, J = 9.8, 3.0 Hz, 1H), 2.27 (dd, J = 14.0, 9.8 Hz, 1H), 1.47 (dd, J = 14.0, 3.0 Hz, 1H), 1.38 (s, 9H), 1.30 (s, 9H), 0.91 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.27, 149.55, 138.75, 127.31, 125.48, 80.38, 48.87, 47.58, 34.53, 31.52, 31.19, 29.64, 28.05. IR (film): ν (cm^{-1}) 3093, 3057, 3022, 2956, 2906, 2868, 1730, 1508, 1477, 1392, 1366, 1251, 1216, 1163, 1142, 1020, 962, 941, 843, 831; HR-MS (EI) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_2$ [M^+]: 318.25533, found 318.25578.

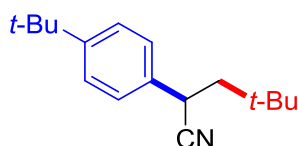


Methyl 2-(4-(*tert*-butyl)phenyl)-4,4-dimethylpentanoate (22). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 3.69 – 3.60 (m, 4H), 2.32 (dd, J = 14.0, 9.7 Hz, 1H), 1.56 (dd, J = 14.0, 3.4 Hz, 1H), 1.30 (s, 9H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 175.57, 149.98, 138.01, 127.46, 125.65, 52.08, 47.69, 47.66, 34.56, 31.49, 31.12, 29.50; IR (film): ν (cm^{-1}) 3091, 3058, 3020, 2953,

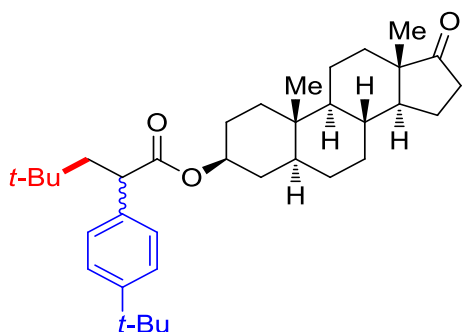
1737, 1476, 1465, 1435, 1365, 1281, 1270, 1241, 1211, 1196, 1165, 1150, 910, 833; HR-MS (ESI) m/z calcd for $C_{18}H_{28}O_2Na$ [$M + Na^+$]: 299.19815, found 299.19765.



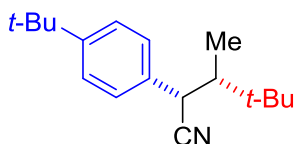
Ethyl 2-(4-(*tert*-butyl)phenyl)-4,4-dimethylpentanoate (23). Yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 4.15 (dq, $J = 10.9$, 7.1 Hz, 1H), 4.04 (dq, $J = 10.8$, 7.1 Hz, 1H), 3.62 (dd, $J = 9.8$, 3.2 Hz, 1H), 2.33 (dd, $J = 14.0$, 9.8 Hz, 1H), 1.55 (dd, $J = 14.0$, 3.2 Hz, 1H), 1.31 (s, 9H), 1.22 (t, $J = 7.1$ Hz, 3H), 0.91 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.10, 149.86, 138.20, 127.44, 125.59, 60.76, 47.88, 47.70, 34.54, 31.49, 31.16, 29.54, 14.19; IR (film): ν (cm^{-1}) 3092, 3059, 3023, 2954, 2905, 2867, 1733, 1476, 1465, 1366, 1280, 1270, 1241, 1210, 1194, 1170, 1148, 1027, 829; HR-MS (ESI) m/z calcd for $C_{19}H_{30}O_2Na$ [$M + Na^+$]: 313.21380, found 313.21373.



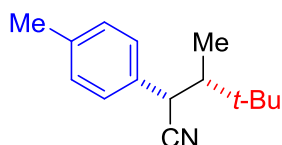
2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylpentanenitrile (24). Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 3.72 (dd, $J = 10.4$, 3.4 Hz, 1H), 2.04 (dd, $J = 14.2$, 10.4 Hz, 1H), 1.65 (dd, $J = 14.2$, 3.4 Hz, 1H), 1.31 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.01, 134.92, 126.92, 126.16, 122.42, 50.40, 34.66, 32.89, 31.41, 31.27, 29.51; IR (film): ν (cm^{-1}) 3057, 3033, 2959, 2905, 2868, 2238, 1513, 1476, 1411, 1397, 1367, 1268, 1108, 1019, 831; HR-MS (EI) m/z calcd for $C_{17}H_{25}N$ [M^+]: 243.19815, found 243.19824.



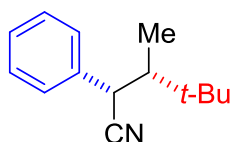
(3S,5S,8R,9S,10S,13S,14S)-10,13-Dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(4-(tert-butyl)phenyl)-4,4-dimethylpentanoate (dr = 1:1) (25).⁹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.71 – 4.59 (m, 1H), 3.57 (dd, *J* = 10.0, 2.8 Hz, 1H), 2.42 (dd, *J* = 19.2, 8.9 Hz, 1H), 2.31 (dd, *J* = 13.9, 10.0 Hz, 1H), 2.12 – 1.99 (m, 1H), 1.85 – 1.12 (m, 17H), 1.29 (s, 9H), 1.08 – 0.87 (m, 3H), 0.91 (s, 9H), 0.85 (s, 3H), 0.84 (s, 3H), 0.76 – 0.65 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 221.12, 174.47, 149.58, 138.21, 127.18, 125.37, 73.58, 54.27, 51.34, 47.94, 47.91, 47.73, 47.52, 47.48, 44.66, 44.65, 36.66, 36.63, 35.80, 35.62, 35.00, 34.35, 33.68, 33.63, 31.49, 31.31, 31.01, 30.78, 29.42, 28.25, 28.20, 27.23, 27.17, 21.73, 20.42, 13.77, 12.21 ; IR (film): ν (cm⁻¹) 2950, 1732, 1365, 1148, 1013, 910, 731; HR-MS (EI) *m/z* calcd for C₃₆H₅₄O₃ [M⁺]: 557.39652, found 557.39624.



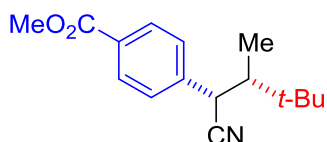
2-(4-(tert-Butyl)phenyl)-3,4,4-trimethylpentanenitrile (26) (dr > 20:1). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.13 (d, *J* = 1.5 Hz, 1H), 1.59 (qd, *J* = 7.0, 1.9 Hz, 1H), 1.32 (s, 9H), 1.08 (s, 9H), 1.01 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.70, 134.12, 127.27, 125.85, 120.17, 49.74, 38.13, 34.64, 33.91, 31.44, 27.87, 10.51; IR (film): ν (cm⁻¹) 3055, 3027, 2962, 2904, 2870, 2238, 1508, 1470, 1414, 1400, 1380, 1366, 1268, 1221, 1202, 1108, 1053, 1019, 995, 932, 902, 844; HR-MS (EI) *m/z* calcd for C₁₉H₃₀O₂Na [M⁺]: 257.21380, found 257.21337.



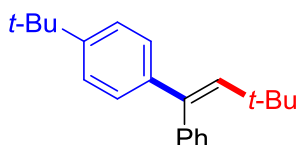
3,4,4-Trimethyl-2-(p-tolyl)pentanenitrile (27) (dr > 20:1). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 4.13 (d, J = 1.5 Hz, 1H), 1.57 (qd, J = 7.0, 2.0 Hz, 1H), 0.99 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.44, 134.19, 129.60, 127.46, 120.16, 49.89, 38.23, 33.91, 27.88, 21.12, 10.41; IR (film): ν (cm^{-1}) 3056, 3024, 2965, 2238, 1541, 1469, 1415, 1400, 1380, 1369, 1320, 1261, 1222, 1188, 1122, 1101, 1077, 1053, 1022, 994, 964, 913, 892, 880, 834; HR-MS (EI) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{N}$ [M^+]: 215.16685, found 215.16665.



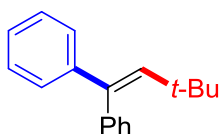
3,4,4-Trimethyl-2-phenylpentanenitrile (28) (dr > 20:1). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.26 (m, 5H), 4.16 (d, J = 1.7 Hz, 1H), 1.60 (qd, J = 7.0, 2.0 Hz, 1H), 1.09 (s, 9H), 1.00 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.18, 128.94, 127.68, 127.59, 119.97, 49.85, 38.61, 33.93, 27.87, 10.39; IR (film): ν (cm^{-1}) 3082, 3062, 2964, 2891, 2239, 1598, 1495, 1470, 1453, 1380, 1369, 1219, 1102, 757, 717; HR-MS (EI) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}$ [M^+]: 201.15120, found 201.15100.



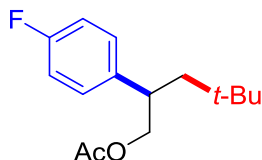
Methyl 4-(1-cyano-2,3,3-trimethylbutyl)benzoate (29) (dr > 20:1). White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 4.20 (d, J = 1.8 Hz, 1H), 3.92 (s, 3H), 1.60 (qd, J = 7.0, 2.0 Hz, 1H), 1.09 (s, 9H), 0.98 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.62, 142.15, 130.25, 129.78, 127.70, 119.39, 52.36, 49.84, 38.75, 34.04, 27.86, 10.44; IR (film): ν (cm^{-1}) 3080, 3063, 2964, 2241, 1724, 1611, 1471, 1434, 1415, 1381, 1369, 1280, 1218, 1185, 1110, 1020, 969, 943, 914, 861, 823; HR-MS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 282.14645, found 282.14643.



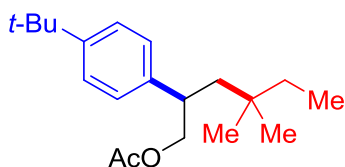
(E)-1-(tert-Butyl)-4-(3,3-dimethyl-1-phenylbut-1-en-1-yl)benzene (30). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.28 (m, 3H), 7.25 (d, J = 8.7 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.09 (s, 1H), 1.28 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.65, 141.22, 141.03, 139.53, 138.80, 130.51, 127.85, 126.79, 126.49, 125.06, 34.51, 34.06, 31.49, 31.47. The experimental data match with those reported in the literature.¹⁰



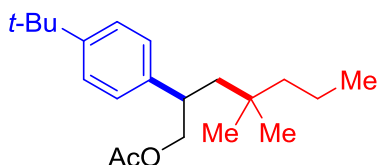
(3,3-Dimethylbut-1-ene-1,1-diyl)dibenzene (31). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.18 (m, 3H), 7.18 – 6.98 (m, 7H), 6.01 (s, 1H), 0.88 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.23, 140.91, 140.23, 139.19, 130.49, 128.12, 127.88, 126.99, 126.87, 126.69, 34.12, 31.47. The experimental data match with those reported in the literature.¹¹



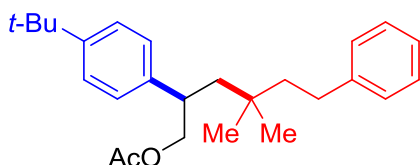
4,4-Dimethyl-2-(4-fluorophenyl)pentyl acetate (32). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (dd, J = 8.7, 5.4 Hz, 2H), 6.97 (t, J = 8.7 Hz, 2H), 4.08 (dd, J = 9.1, 5.3 Hz, 1H), 4.04 (dd, J = 9.1, 5.9 Hz, 1H), 3.06 – 2.96 (m, 1H), 1.96 (s, 3H), 1.64 (d, J = 8.4 Hz, 1H), 1.57 (dd, J = 14.1, 3.6 Hz, 1H), 0.81 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.04, 161.70 (d, J = 244.3 Hz), , 139.62 (d, J = 3.1 Hz), 129.53 (d, J = 7.8 Hz), 115.34 (d, J = 21.1 Hz), 69.72, 46.09, 41.09, 31.26, 30.10, 20.98; ^{19}F NMR (376 MHz, CDCl_3) δ -116.74 (tt, J = 8.8, 5.4 Hz, 1F); IR (film): ν (cm^{-1}) 3041, 2954, 2866, 2716, 1737, 1604, 1509, 1468, 1383, 1365, 1223, 1158, 1110, 1034, 910, 832; HR-MS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{FO}_2\text{Na}[\text{M} + \text{Na}^+]$: 275.14178, found 275.14215.



2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylhexyl acetate (33). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 4.09 (dd, J = 9.2, 5.7 Hz, 1H), 4.05 (dd, J = 9.2, 5.6 Hz, 1H), 3.05 – 2.89 (m, 1H), 1.98 (s, 3H), 1.67 (dd, J = 14.1, 8.0 Hz, 1H), 1.58 (dd, J = 14.1, 3.6 Hz, 1H), 1.27 – 1.12 (m, 2H), 0.77 – 0.71 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.18, 149.31, 140.92, 127.76, 125.32, 69.96, 43.56, 40.73, 34.73, 34.50, 33.73, 31.54, 27.29, 27.24, 21.10, 8.44; IR (film): ν (cm^{-1}) 3086, 3054, 3025, 2960, 2904, 2869, 1741, 1511, 1463, 1412, 1381, 1363, 1228, 1121, 1111, 1079, 1032, 976, 946, 934, 912, 891, 879, 829; HR-MS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 327.22945, found 327.22969.

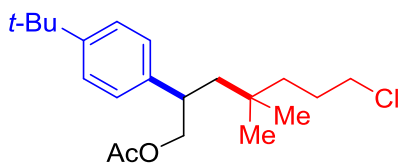


2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylheptyl acetate (34). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 4.09 (dd, J = 8.2, 4.8 Hz, 1H), 4.05 (dd, J = 8.2, 4.6 Hz, 1H), 3.08 – 2.89 (m, 1H), 1.98 (s, 3H), 1.69 (dd, J = 14.1, 8.3 Hz, 1H), 1.56 (dd, J = 14.1, 3.3 Hz, 1H), 1.30 (s, 9H), 1.24 – 1.02 (m, 4H), 0.82 – 0.72 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.17, 149.32, 140.81, 127.78, 125.31, 69.93, 44.86, 43.75, 40.80, 34.50, 33.75, 31.54, 28.04, 27.94, 21.09, 17.25, 14.92; IR (film): ν (cm^{-1}) 3093, 3051, 3020, 2957, 2932, 2870, 1735, 1511, 1466, 1411, 1384, 1364, 1231, 1155, 1121, 1111, 1080, 1032, 979, 908, 856, 830; HR-MS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 341.24510, found 341.24500.

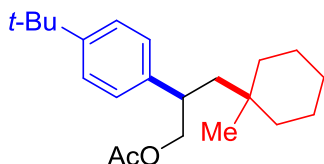


2-(4-(*tert*-Butyl)phenyl)-4,4-dimethyl-6-phenylhexyl acetate (35). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.31 (m, 2H), 7.25 – 7.11 (m, 5H), 7.00 – 6.93 (m, 2H), 4.10 (d, J = 7.3 Hz, 2H), 3.04 (qd, J = 7.4, 2.9 Hz, 1H), 2.55 – 2.43 (m, 1H), 2.41 – 2.29 (m, 1H), 2.00 (s, 3H), 1.85 (dd, J = 14.2, 8.6 Hz, 1H), 1.66 (dd, J = 14.2, 2.9 Hz, 1H), 1.48 – 1.36 (m, 2H), 1.33 (s, 9H), 0.90 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.14, 149.52, 143.37, 140.53, 128.38, 128.33, 127.87, 125.59, 125.49,

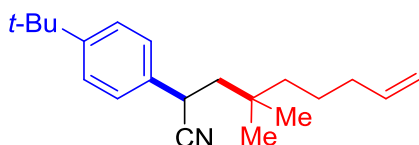
69.96, 44.36, 43.33, 40.87, 34.53, 33.91, 31.55, 30.75, 28.23, 28.07, 21.09; IR (film): ν (cm^{-1}) 3085, 3061, 3025, 2956, 2905, 2866, 1739, 1603, 1584, 1557, 1510, 1496, 1465, 1455, 1411, 1382, 1363, 1227, 1156, 1111, 1067, 1031, 976, 938, 921, 886, 830; HR-MS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{36}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 403.26075, found 403.26101.



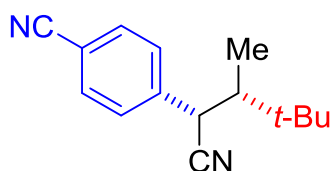
(2-(4-(*tert*-Butyl)phenyl)-7-chloro-4,4-dimethylheptyl acetate (36). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 4.06 (d, $J = 7.2$ Hz, 2H), 3.30 – 3.17 (m, 2H), 3.04 – 2.92 (m, 1H), 1.99 (s, 3H), 1.73 (dd, $J = 14.2$, 8.8 Hz, 1H), 1.68 – 1.44 (m, 3H), 1.31 (s, 9H), 1.28 – 1.08 (m, 2H), 0.82 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.11, 149.59, 140.33, 127.78, 125.42, 69.78, 45.67, 43.38, 40.82, 39.17, 34.51, 33.52, 31.51, 28.03, 28.00, 27.80, 21.07; IR (film): ν (cm^{-1}) 3088, 3056, 3023, 2957, 2906, 2868, 1740, 1511, 1466, 1412, 1383, 1364, 1312, 1288, 1229, 1111, 1304, 975, 945, 921, 893, 831; HR-MS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{33}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 375.20613, found 375.20625.



2-(4-(*tert*-Butyl)phenyl)-3-(1-methylcyclohexyl)propyl acetate (37). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.09 (dd, $J = 9.0$, 5.6 Hz, 1H), 4.05 (dd, $J = 9.0$, 5.5 Hz, 1H), 3.06 – 2.95 (m, 1H), 1.98 (s, 3H), 1.70 (dd, $J = 14.1$, 7.8 Hz, 1H), 1.60 (dd, $J = 14.2$, 3.6 Hz, 1H), 1.47 – 1.35 (m, 3H), 1.30 (s, 9H), 1.31 – 1.22 (m, 5H), 1.15 – 1.07 (m, 2H), 0.77 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.23, 149.27, 141.13, 127.75, 125.32, 70.01, 40.17, 38.45, 38.37, 34.52, 33.67, 31.55, 26.54, 22.19, 22.08, 21.13; IR (film): ν (cm^{-1}) 3088, 3056, 3030, 2952, 2925, 2861, 2849, 1741, 1510, 1461, 1416, 1379, 1362, 1229, 1149, 1111, 1031, 977, 946, 932, 888, 874, 830; HR-MS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{34}\text{O}_2\text{Na}$ [$\text{M} + \text{Na}^+$]: 353.24510, found 353.24499.



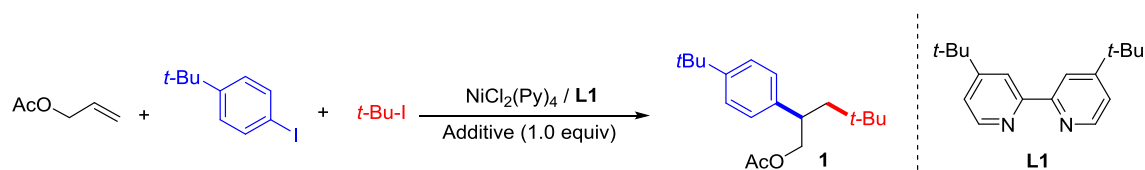
2-(4-(*tert*-Butyl)phenyl)-4,4-dimethylnon-8-enenitrile (40). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.01 (ddd, J = 17.1, 3.6, 1.6 Hz, 1H), 4.96 (ddt, J = 10.2, 2.1, 1.1 Hz, 1H), 3.71 (dd, J = 10.2, 3.5 Hz, 1H), 2.10 – 1.98 (m, 3H), 1.65 (dd, J = 14.3, 3.6 Hz, 1H), 1.44 – 1.24 (m, 4H), 1.32 (s, 9H), 1.03 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.06, 138.86, 135.00, 126.97, 126.20, 122.41, 114.76, 48.29, 41.60, 34.68, 34.46, 33.68, 32.49, 31.42, 27.30, 27.22, 23.50; IR (film): ν (cm^{-1}) 3075, 3030, 2959, 2936, 2905, 2868, 2238, 1641, 1512, 1472, 1440, 1412, 1391, 1366, 1318, 1268, 1234, 1202, 1138, 1120, 878, 829; HR-MS (EI) m/z calcd for $\text{C}_{21}\text{H}_{31}\text{N}$ [M^+]: 297.24510, found 297.24515.



4-(1-cyano-2,3,3-trimethylbutyl)benzonitrile (44) (dr > 20:1). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 4.20 (d, J = 1.5 Hz, 1H), 1.58 (qd, J = 7.0, 1.9 Hz, 1H), 1.09 (s, 9H), 0.97 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 142.43, 132.78, 128.49, 118.81, 118.33, 112.02, 49.89, 38.90, 34.08, 27.81, 10.43; IR (film): ν (cm^{-1}) 3065, 3037, 2966, 2884, 2360, 2230, 1609, 1609, 1505, 1472, 1414, 1402, 1382, 1370, 1262, 1218, 1187, 1175, 1120, 1100, 1079, 1053, 1021, 995, 957, 945, 931, 920, 898, 876, 850.

5. Control Experiments

5.1 Radical Inhibition Experiments

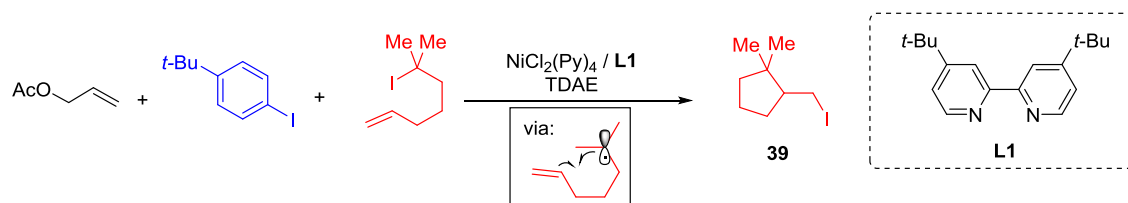


Additive	^1H NMR yield of 1
none	82%
BHT	23%
1,1-Diphenylethylene	0%
1,4-cyclohexadiene	23%

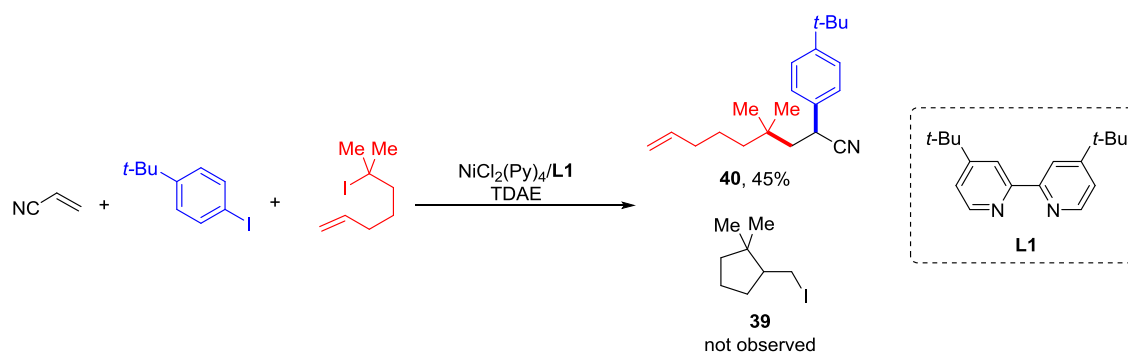
Experimental procedure: $\text{NiCl}_2(\text{Py})_4$ (8.9 mg, 0.02 mmol, 10 mol%), **L1** (5.4 mg, 0.02 mmol, 10 mol%) and additive if solid (BTH, 0.2 mmol, 1.0 equiv) were placed in an oven dried Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. THF (0.5 mL), allyl acetate (20.0 mg, 0.2 mmol, 1.0 equiv), 4-*tert*-butyliodobenzene (104.0 mg, 0.4 mmol, 2.0 equiv), 2-iodo-2-methylpropane (55.2 mg, 0.3 mmol, 1.5 equiv) and additive if liquid (1,1-diphenylethylene or 1,4-cyclohexadiene, 0.2 mmol, 1.0 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N_2 . The resulting mixture was diluted with Et_2O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et_2O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO_4 and filtered. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added as internal standard, redissolved in CDCl_3 (1.0 mL) and the crude mixture analyzed by ^1H NMR.

Conclusions: The partial or complete suppression of the reaction suggests the participation of radical species in this transformation.

5.2 Radical Clock Experiments (Scheme 3, equations 1 and 2)



Experimental procedure: $\text{NiCl}_2(\text{Py})_4$ (8.9 mg, 0.02 mmol, 10 mol%) and **L1** (5.4 mg, 0.02 mmol, 10 mol%) were placed in an oven dried Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. THF (0.5 mL), allyl acetate (20.0 mg, 0.2 mmol, 1.0 equiv), 4-*tert*-butyl iodobenzene (104.0 mg, 0.4 mmol, 2.0 equiv) and 6-iodo-6-methylhept-1-ene (71.4 mg, 0.3 mmol, 1.5 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N_2 . The resulting mixture was diluted with Et_2O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et_2O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO_4 and filtered. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added as internal standard, redissolved in CDCl_3 (1.0 mL) and the crude mixture analyzed by ^1H NMR confirming the formation of compound **39** in 17% yield.



Experimental procedure: $\text{NiCl}_2(\text{Py})_4$ (8.9 mg, 0.02 mmol, 10 mol%) and **L1** (5.4 mg, 0.02 mmol, 10 mol%) were placed in an oven dried Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. THF (0.5 mL), acrylonitrile (15.9 mg, 0.2 mmol, 1.0 equiv), 4-*tert*-butyl iodobenzene (104.0 mg, 0.4 mmol, 2.0 equiv) and 6-iodo-6-methylhept-1-ene (71.4 mg, 0.3 mmol, 1.5 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N_2 . The resulting mixture was diluted with Et_2O (5 mL) and transferred into a separatory funnel

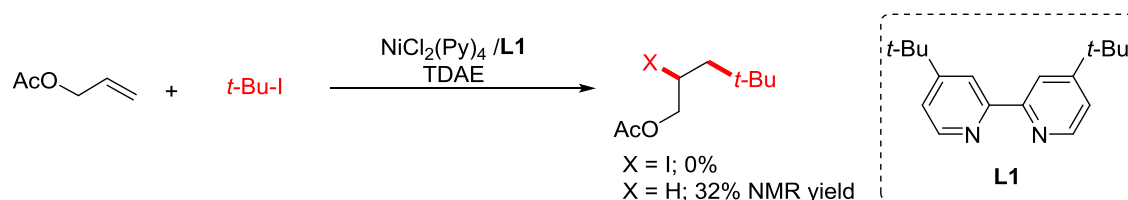
containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et₂O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO₄ and filtered and after removal of the solvent under reduced the crude product was purified by column chromatography on silica gel to obtain 2-(4-(*tert*-butyl)phenyl)-4,4-dimethylnon-8-enenitrile **40** (26.9 mg, 0.09 mmol, 45% yield) as a yellow oil. Cyclized product **39** was not observed in the reaction mixture.

Conclusions: According to previously reported kinetic data,¹² the cyclization of the 1-hexen-5-yl radical takes place approximately 10 times slower than the addition of a tertiary radical to acrylonitrile. In these experiments, the starting iodide produced the cyclized product when an unactivated olefin was used (no addition product detected), whereas the use of acrylonitrile gave exclusively the addition product (no cyclization observed). The different outcome observed in these reactions depending on the degree of activation of the olefin is in agreement with the kinetics of the radical clocks suggesting that the C-Halide bond is homolytically cleaved generating a C-centered radical.

5.3 Evaluation of potential intermediates

5.3.1 Evaluation of secondary alkyl iodides

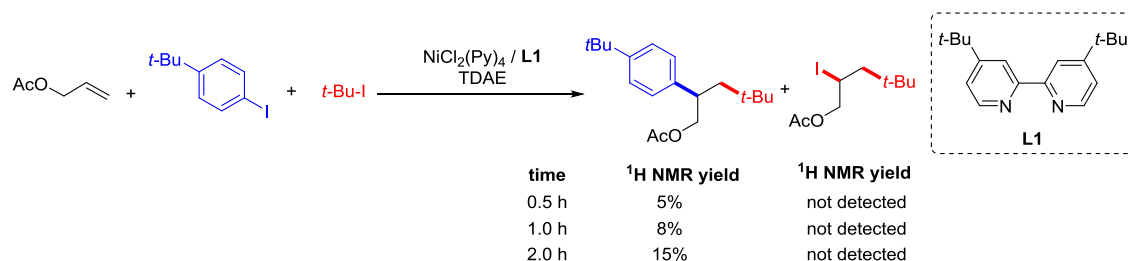
a) Reaction in absence of aryl iodide (Scheme 3, equation 5)



Experimental procedure: $\text{NiCl}_2(\text{Py})_4$ (8.9 mg, 0.02 mmol, 10 mol%) and **L1** (5.4 mg, 0.02 mmol, 10 mol%) were placed in an oven dried Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. THF (0.5 mL), allyl acetate (20.0 mg, 0.2 mmol, 1.0equiv) and 2-iodo-2-methylpropane (55.2 mg, 0.3 mmol, 1.5 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N₂. The resulting mixture was diluted with Et₂O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et₂O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO₄ and filtered. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added

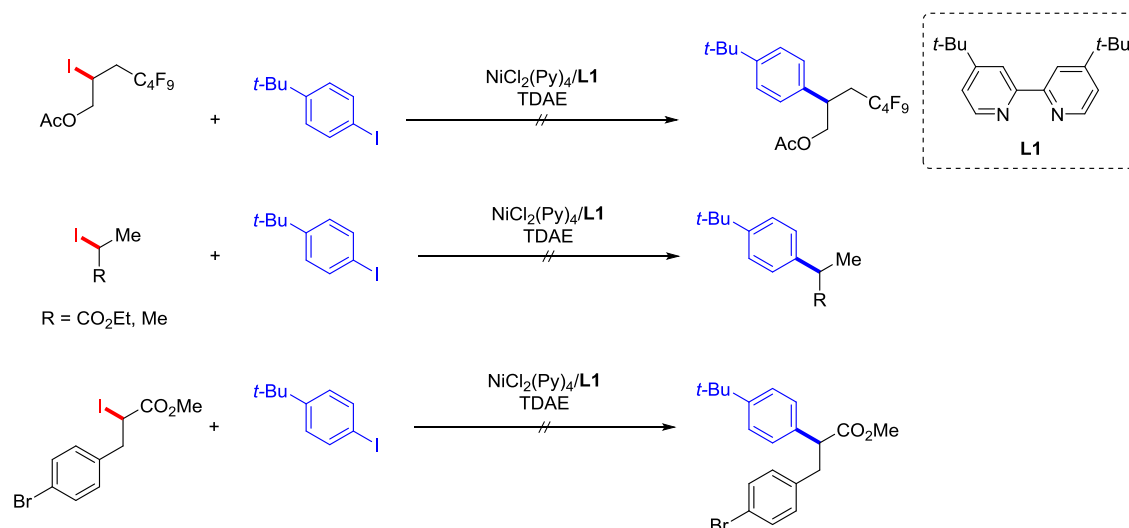
as internal standard, redissolved in CDCl_3 (1.0 mL) and the crude mixture analyzed by ^1H NMR revealing the formation of hydroalkylation product in 32% yield. Additionally, the same reaction in the absence of Ni showed no conversion for any of the starting materials.

b) Monitoring the reaction mixture at low conversion



Following the general experimental procedure, three reactions were set up in parallel. After the indicated periods of time the standard work-up was carried out for each of them and the reaction mixtures were analyzed by ^1H NMR with *p*-nitroacetophenone as internal standard. No alkyl iodide was detected in any of the cases.

c) Reductive coupling of aryl iodides with secondary alkyl iodides (Scheme 3, equation 3)

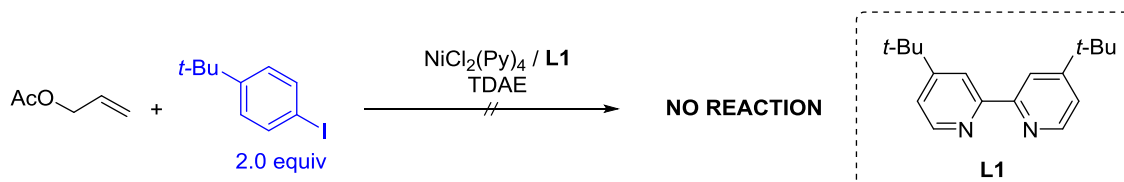


Experimental procedure: $\text{NiCl}_2(\text{Py})_4$ (8.9 mg, 0.02 mmol, 10 mol%) and **L1** (5.4 mg, 0.02 mmol, 10 mol%) were placed in an oven dried Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. THF (0.5 mL), 4-*tert*-butyliodobenzene (104.0 mg, 0.4 mmol, 2.0 equiv) and secondary iodide (0.2 mmol, 1.0 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for

additional 15 h at 25 °C under N₂. The resulting mixture was diluted with Et₂O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et₂O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO₄ and filtered. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added as internal standard, redissolved in CDCl₃ (1.0 mL) and the crude mixture analyzed by ¹H NMR. The corresponding cross-coupling products were not detected in the reaction mixture.

Conclusions: The experiments in absence of aryl iodide showed that the nickel catalyst is, to a small extent, able to reduce the alkyl iodide. Although the activation of the alkyl electrophile was possible in absence of the aromatic partner, only hydroalkylation products and no secondary alkyl iodides were detected. In the experiments performed at low conversion, secondary alkyl iodides were not observed either, whereas the reactions using secondary iodides failed to give the coupled product under the reaction conditions. Therefore, these experiments seem to rule out the participation of secondary alkyl iodides in the reaction.

5.3.2 Evaluation of Heck type products (Scheme 3, equation 4)

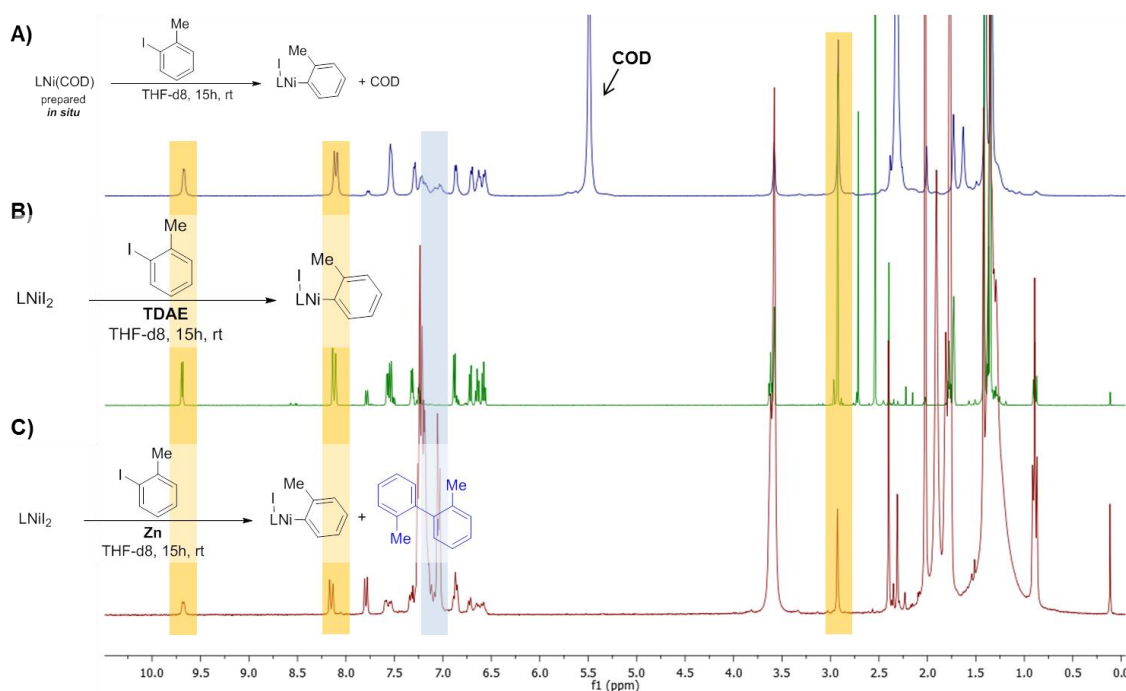


Experimental procedure: NiCl₂(Py)₄ (8.9 mg, 0.02 mmol, 10 mol%) and L1 (5.4 mg, 0.02 mmol, 10 mol%) were placed in an oven dried Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. THF (0.5 mL), allyl acetate (20.0 and 4-*tert*-butyliodobenzene (104.0 mg, 0.4 mmol, 2.0 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N₂. The resulting mixture was diluted with Et₂O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et₂O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO₄ and filtered. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added as internal standard, redissolved in CDCl₃ (1.0 mL) and the crude mixture analyzed by ¹H NMR. No reaction was observed.

Conclusions: In absence of alkyl iodide no reaction is observed suggesting that Heck type adducts are not intermediates in the reaction.

5.3.3 Evaluation of potential nickel intermediates (Scheme 3, equations 7 and 8)

a) Reduction of LNiI_2 with TDAE or Zn in the presence of 2-iodotoluene ($\text{L} = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine)



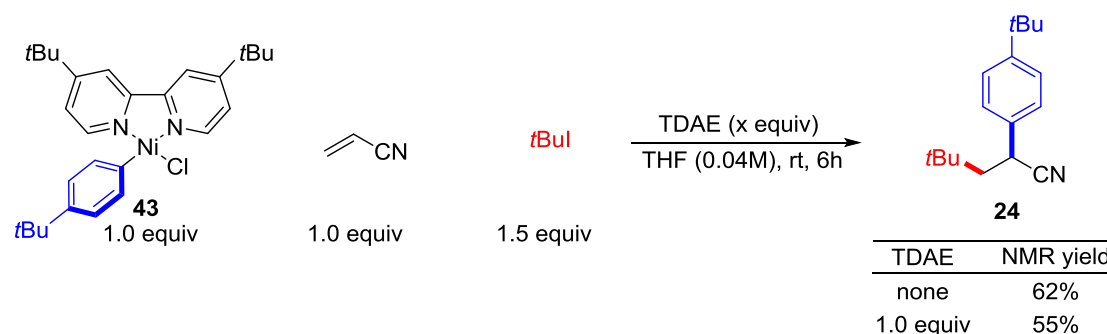
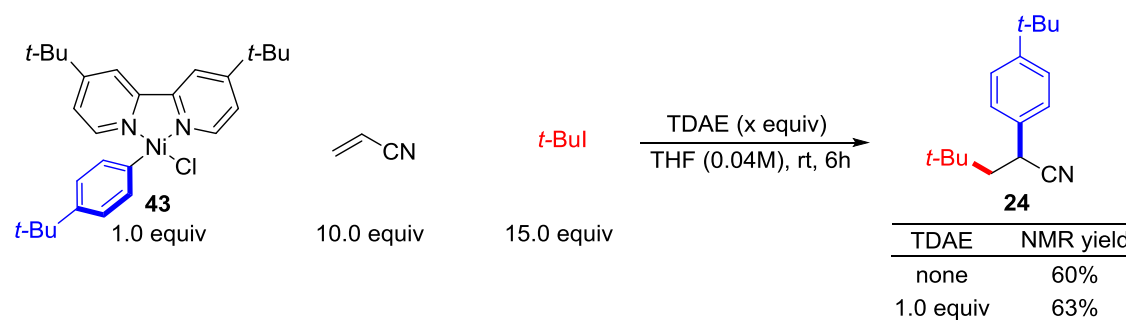
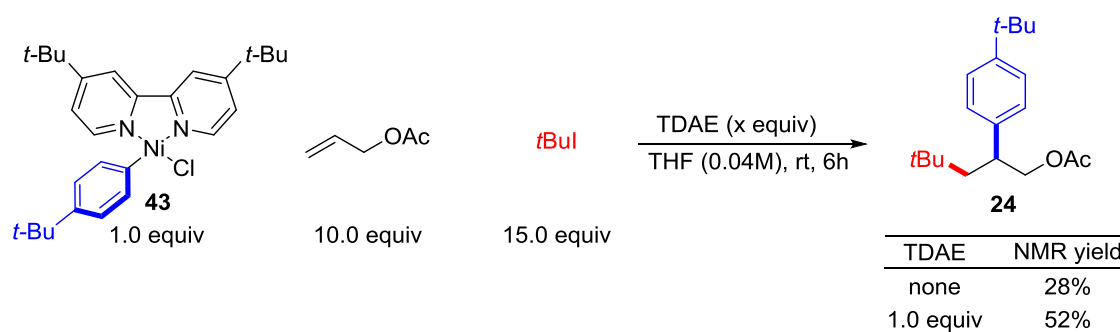
Experimental procedure for the reaction of $(\text{dtbbpy})\text{NiI}_2$ with either TDAE or Zn in presence of *o*-iodo toluene (NMR traces B and C): In a nitrogen filled glove box, a 5 mL vial containing a PTFE-coated stir bar was charged with $(\text{dtbbpy})\text{NiI}_2$ (58 mg, 0.1 mmol, 1.0 equiv), 2-iodotoluene (15 μL , 0.12 mmol, 1.2 equiv) and THF- d_8 (1 mL). After stirring two minutes at 25 $^\circ\text{C}$, the reductant (0.1 mmol, 1.0 equiv) was added and the mixture stirred overnight at 25 $^\circ\text{C}$ for additional 15h. The mixture was filtered over celite and the filtrate transferred to a J-Young NMR tube and analyzed by ^1H NMR which showed characteristic signals for the arylNi(II) complex **42**¹³ (highlighted in orange) together with small amounts of homocoupling product (highlighted in blue).

As a control experiment, complex **42** was also generated in situ by oxidative addition of 2-iodotoluene with LNi(COD) (**NMR trace A**): In a nitrogen filled glove box, a 5 mL vial containing a PTFE-coated stir bar was charged with the Ni(COD)_2 (27.5 mg, 0.1 mmol, 1.0 equiv) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (26.8 mg, 0.1 mmol, 1.0 equiv) and THF- d_8 (1 mL) resulting in a deep purple mixture which was stirred overnight at 25 $^\circ\text{C}$. 2-iodotoluene (15 μL , 0.12 mmol, 1.2 equiv) was added and the deep red mixture stirred

at 25 °C for additional 15h. The mixture was filtered over celite and the filtrate transferred to a J-Young NMR tube and analyzed by ^1H NMR which showed characteristic signals for the arylNi(II) complex **42** (highlighted in orange) together with small amounts of homocoupling product (highlighted in blue).

Conclusions: The formation of the Aryl-Ni(II) complex **42** from a mixture containing LNiI_2 and aryl iodide upon addition of Zn or TDAE demonstrates the ability of these species to act as reductants for Ni(II) in THF at 25 °C.

b) Stoichiometric reactions with aryl-nickel(II)



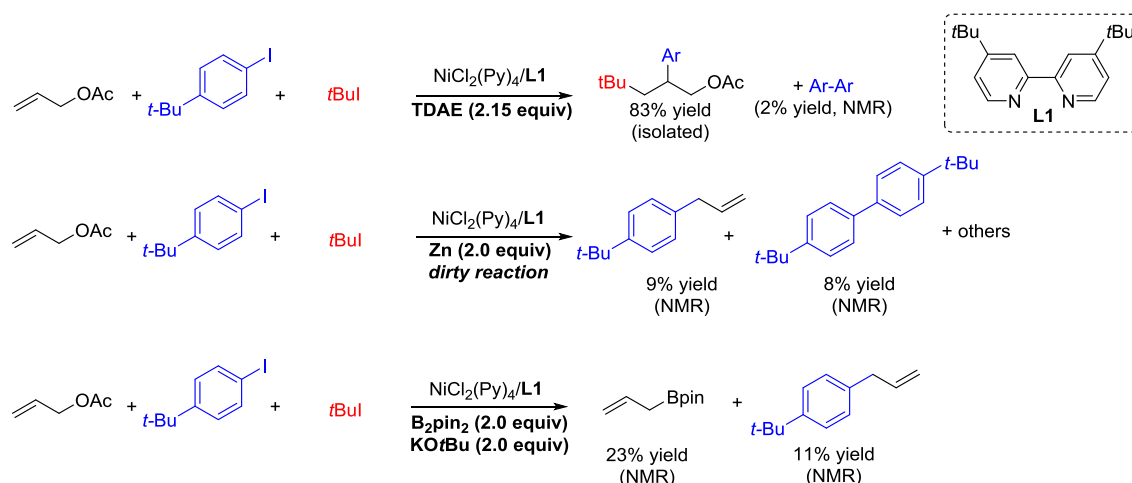
Experimental procedure: In a nitrogen filled glove box, a 5 mL vial containing a PTFE-coated stir bar was charged with the arylnickel complex **43** (24.8 mg, 0.05 mmol, 1.0 equiv) and a solution with the corresponding amount of olefin and *tert*-butyl iodide in THF (1.25 mL). TDAE (if needed, 12 μL , 0.05 mmol, 1.0 equiv) was added and the reaction mixture stirred 6h at 25 °C. The vial was taken out of the glovebox and the mixture was diluted with Et_2O (3 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous

phase extracted with Et₂O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO₄ and filtered. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added as internal standard, redissolved in CDCl₃ (1.0 mL) and the crude mixture analyzed by ¹H NMR.

Conclusions: Aryl-Ni(II) complex **43** prepared independently was able to produce efficiently the desired dicarbofunctionalization products either in presence or absence of the organic reductant. These results suggest that aryl-Ni(II) complexes might be potential intermediates along the reaction pathway.

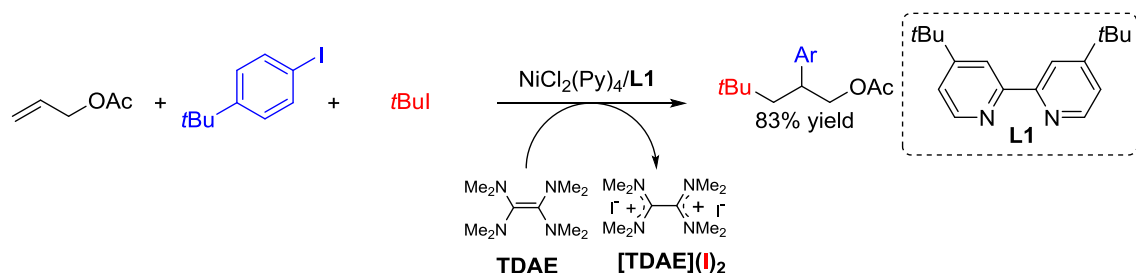
5.4 TDAE as reductant

5.4.1 Comparison between common reductants



Experimental procedure for the reactions using Zn and B₂pin₂/KOtBu as reductant: NiCl₂(Py)₄ (8.9 mg, 0.02 mmol, 10 mol%), **L1** (5.4 mg, 0.02 mmol, 10 mol%) and reductant (0.4 mmol, 2.0 equiv) were placed in an oven dried Schlenk flask. The reaction vessel was evacuated and filled back with nitrogen three times. THF (0.5 mL), allyl acetate (20.0 mg, 0.2 mmol, 1.0 equiv), 4-*tert*-butyliodobenzene (104.4 mg, 0.4 mmol, 2.0 equiv) and *tert*-butyl iodide (55.2 mg, 0.3 mmol, 1.5 equiv) were sequentially added and stirred (1400 rpm) 15 h at 25 °C under N₂. The mixture was diluted with Et₂O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et₂O twice. The combined organic layers were dried over anhydrous MgSO₄ and filter. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added as internal standard, redissolved in CDCl₃ (1.0 mL) and the crude mixture analyzed by ¹H NMR.

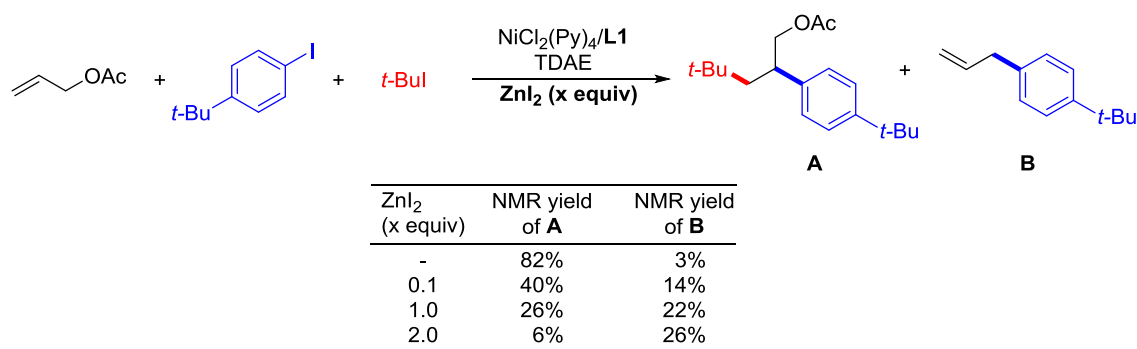
5.4.2 Transformation of TDAE into [TDAE](I)₂



Experimental procedure for the isolation of [TDAE](I)₂: NiCl₂(Py)₄ (8.9 mg, 0.02 mmol, 10 mol%), **L1** (5.4 mg, 0.02 mmol, 10 mol%) were placed in an oven dried Schlenk flask. The reaction vessel was evacuated and filled back with nitrogen three times. THF (0.5 mL), allyl acetate (20.0 mg, 0.2 mmol, 1.0 equiv), 4-*tert*-butyliodobenzene (104.4 mg, 0.4 mmol, 2.0 equiv) and *tert*-butyl iodide (55.2 mg, 0.3 mmol, 1.5 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C under N₂. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N₂. The mixture was filter with a frit and the solid washed with Et₂O (10 mL) and dry under vacuum to give [TDAE](I)₂ as a light yellow powder. ¹H NMR (400 MHz, D₂O) δ 3.64 (s, 12H), 3.36 (s, 12H); ¹³C NMR (101 MHz, D₂O) δ 155.87, 43.29, 42.36; IR (film): ν (C=N) 1666, 1652 cm⁻¹; HR-MS (ESI, positive mode) m/z calcd for C₁₀H₂₄N₄ [TDAE⁺]: 200.19955, found 200.19959; HR-MS (ESI, negative mode) m/z calcd for [I]⁻: 126.90502, found 126.90507.

Conclusions: [TDAE](I)₂ is formed in the reaction according to both, spectroscopy and HR-MS data analysis.¹⁴

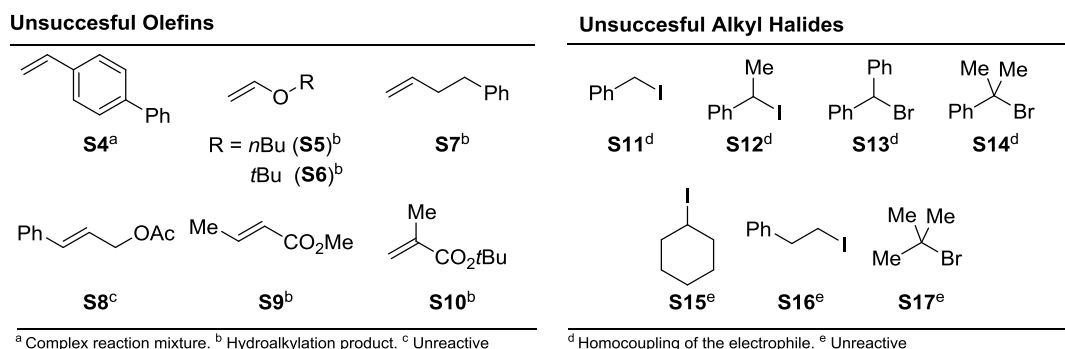
5.4.3 Effect of Zn²⁺ in the reaction outcome



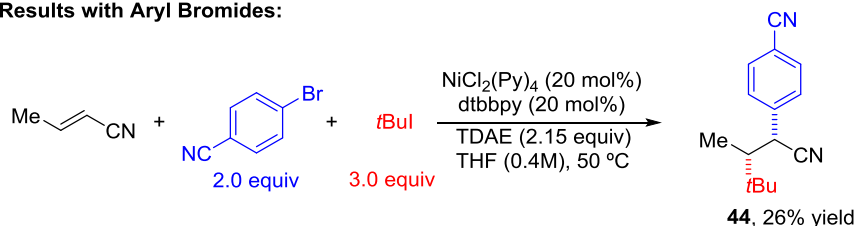
Experimental procedure: NiCl₂(Py)₄ (8.9 mg, 0.02 mmol, 10 mol%), **L1** (5.4 mg, 0.02 mmol, 10 mol%) and ZnI₂ were placed in an oven dried Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. THF (0.5 mL), 4-*tert*-butyliodobenzene (104.0 mg, 0.4 mmol, 2.0 equiv) and *tert*-butyl iodide (55.2 mg, 0.3 mmol, 1.5 equiv) were sequentially added and stirred (1400 rpm) one minute at 25 °C. TDAE (0.1 mL, 0.43 mmol, 2.15 equiv) was added dropwise and the reaction stirred for additional 15 h at 25 °C under N₂. The resulting mixture was diluted with Et₂O (5 mL) and transferred into a separatory funnel containing aqueous HCl 1M (5 mL). The phases were separated and the aqueous phase extracted with Et₂O (2 x 5 mL). The combined organic layers were dried over anhydrous MgSO₄ and filtered. After removal of the solvent under reduced pressure *p*-nitroacetophenone (33.0 mg, 0.2 mmol) was added as internal standard, redissolved in CDCl₃ (1.0 mL) and the crude mixture analyzed by ¹H NMR.

Conclusions: The decreased yield of the desired product in presence of Zn²⁺, suggest that *this Lewis acid might compete with nickel for the coordinating/directing group of the olefinic partner, which is needed for a succesful transformation.*

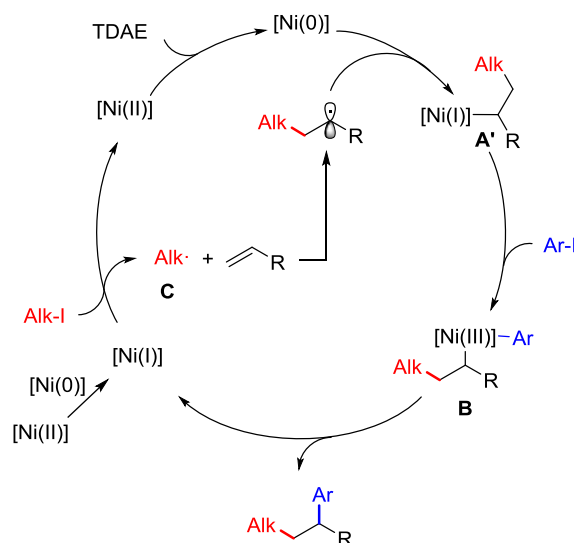
6. Additional Results



Results with Aryl Bromides:

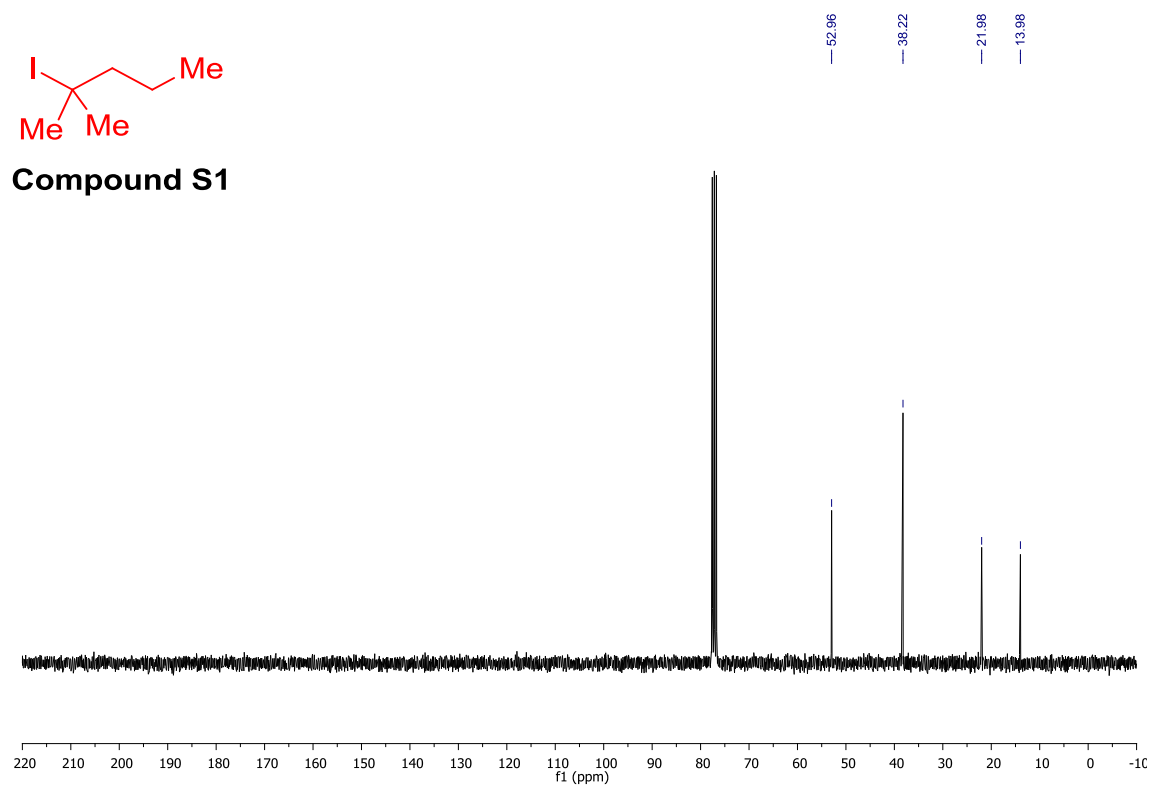
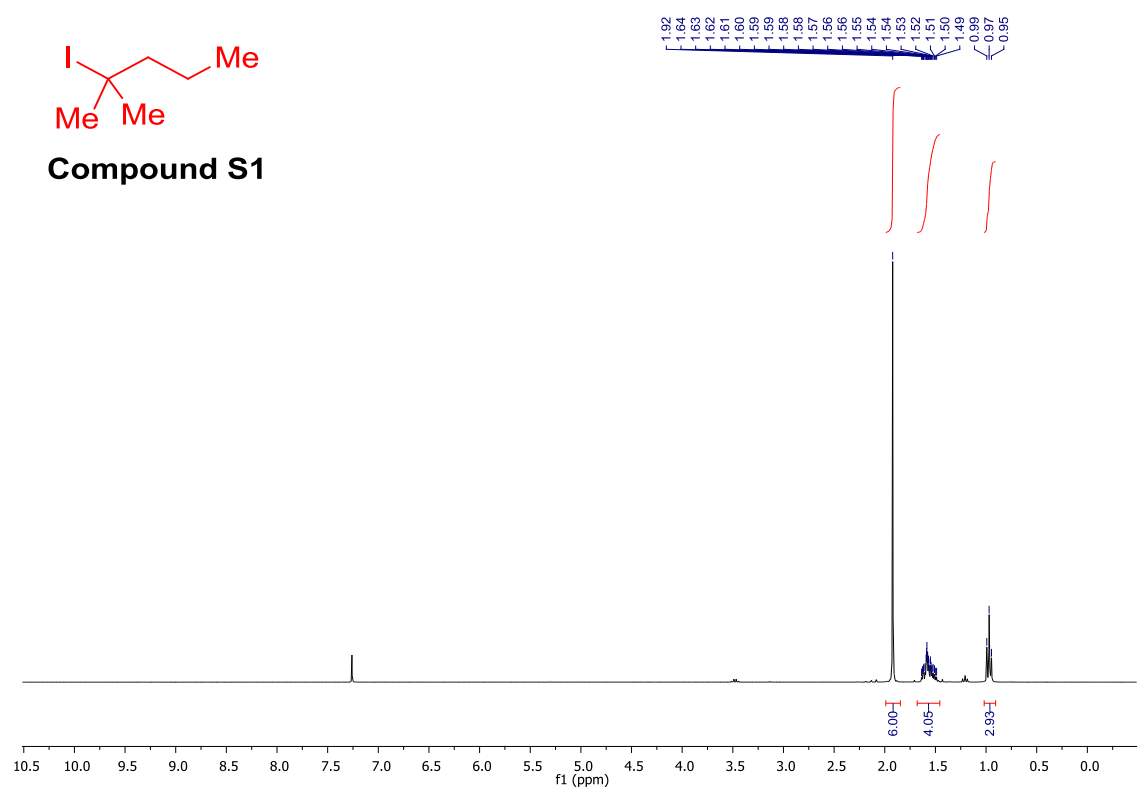


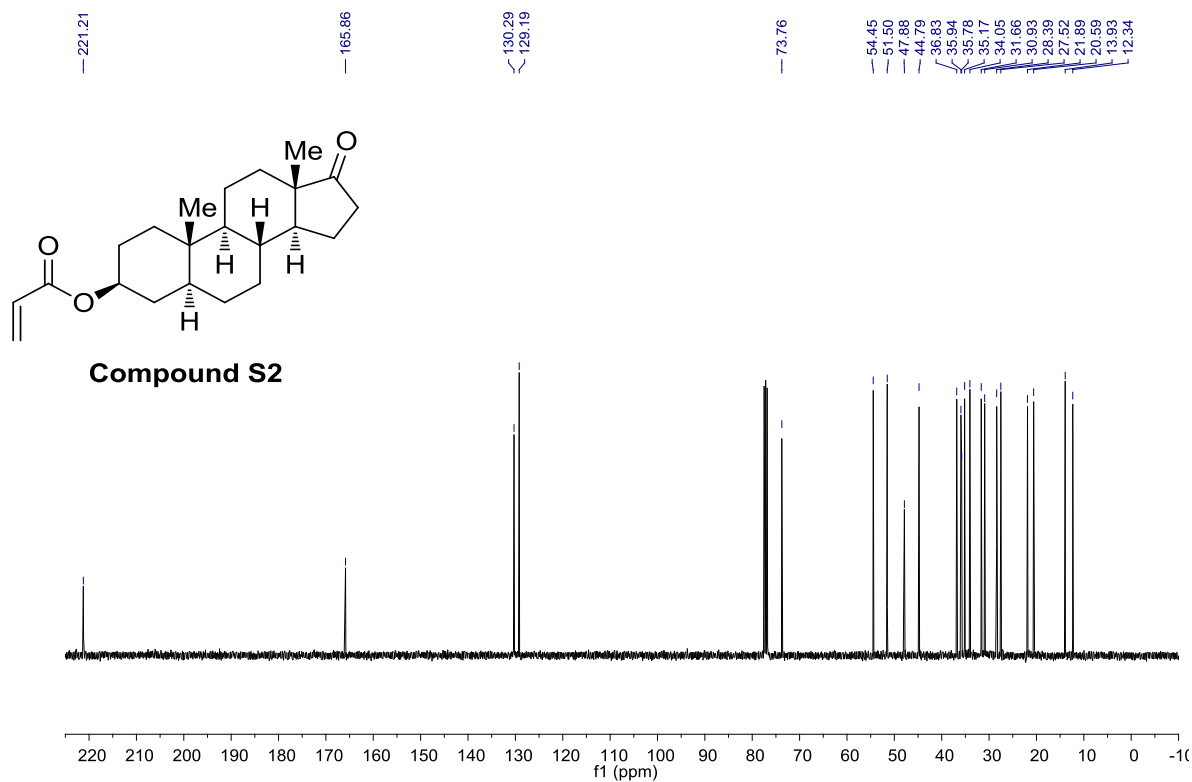
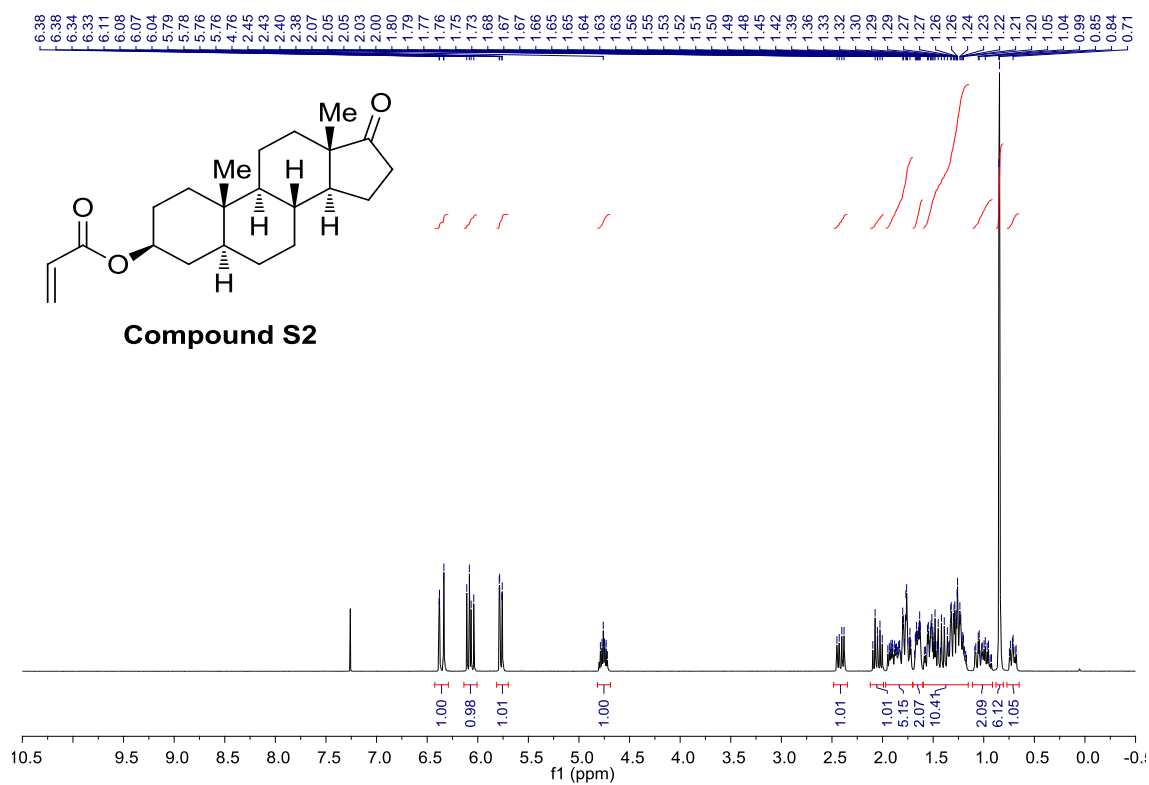
7. Alternative Mechanistic Proposal

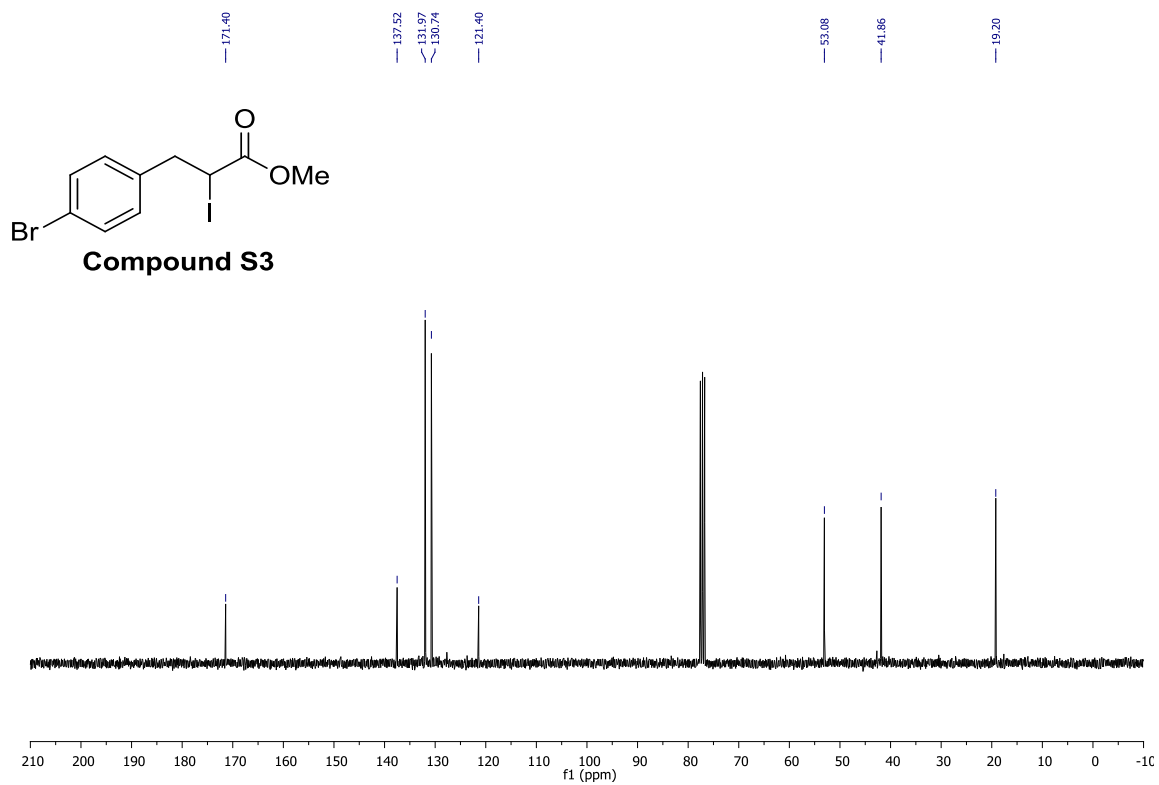
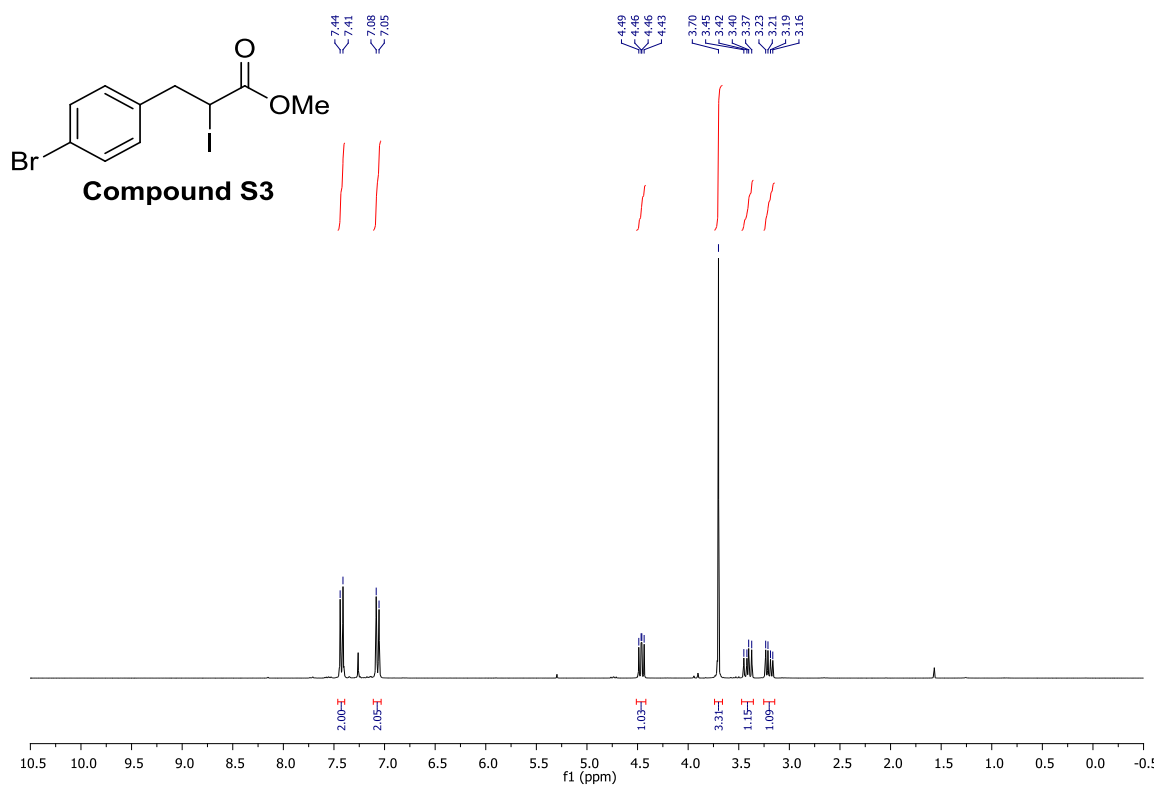


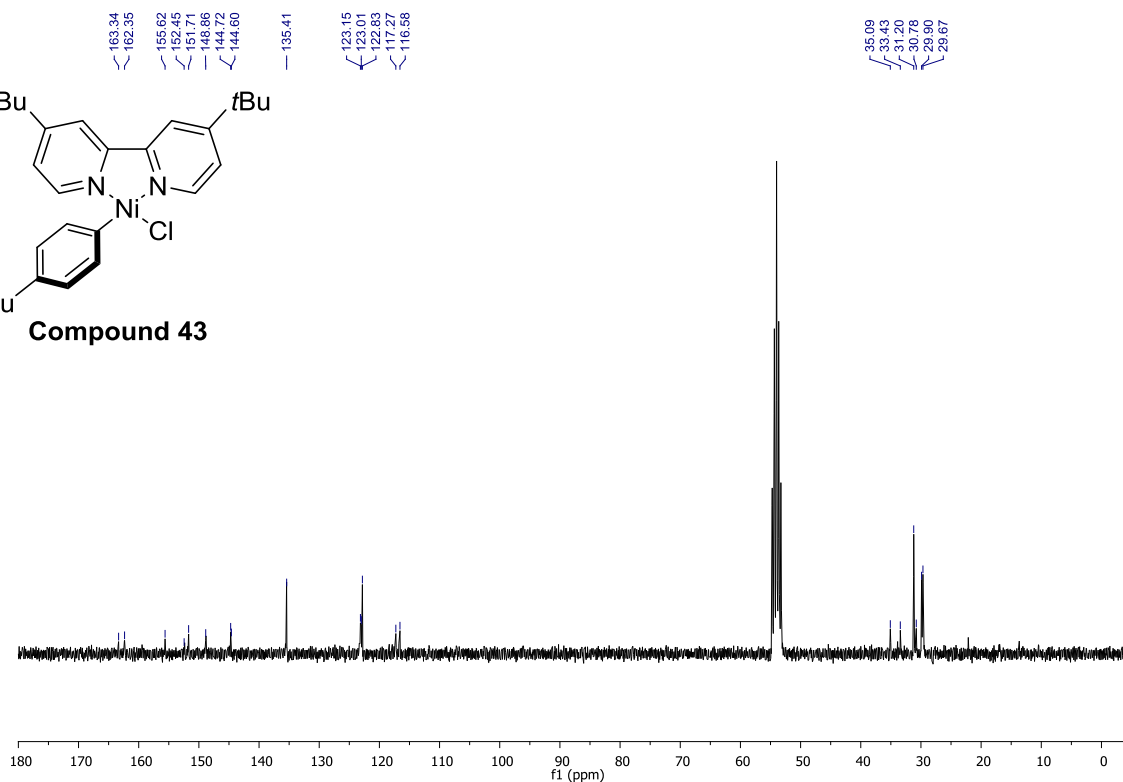
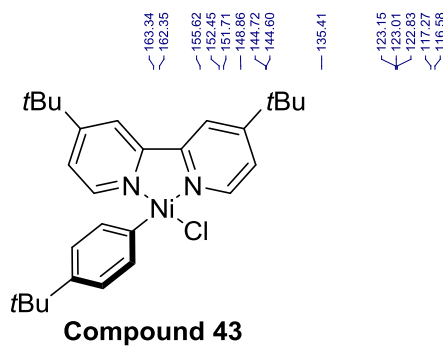
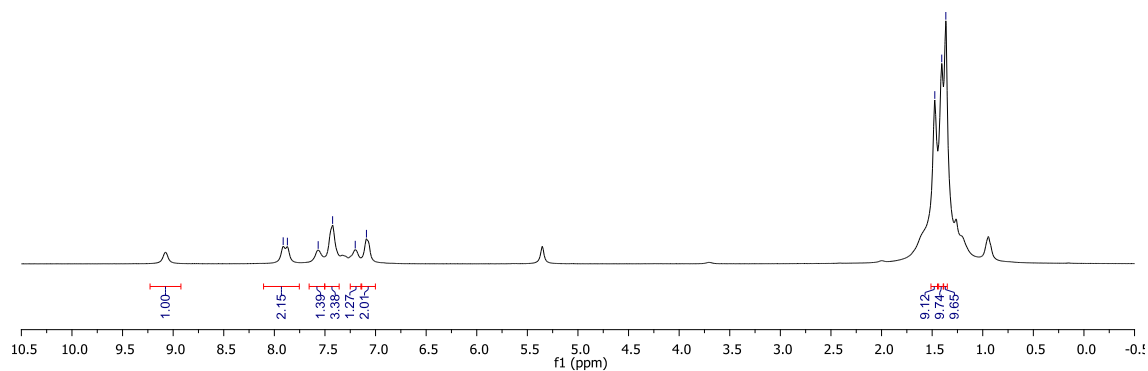
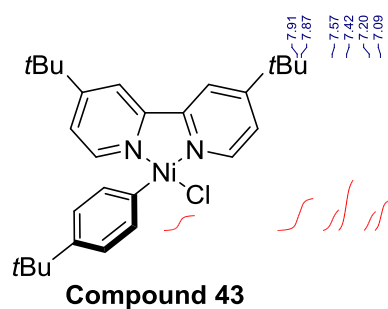
Under the reductive reaction conditions, Ni(I) species generated *in situ* induce the formation of alkyl radicals **C** delivering Ni(II) species which are further reduced to Ni(0) by the organic reductant. The alkyl radicals generated add onto the terminal carbon of the olefin leading to secondary C-centered radicals which recombine with the Ni(0) species generated previously giving an alkyl-Ni(I) intermediate (**A'**). Oxidative addition of the aryl iodide give rise to the formation of Ni(III) complexes **B** that close the catalytic cycle delivering the desired product upon reductive elimination.

8. NMR Spectra of New Substrates

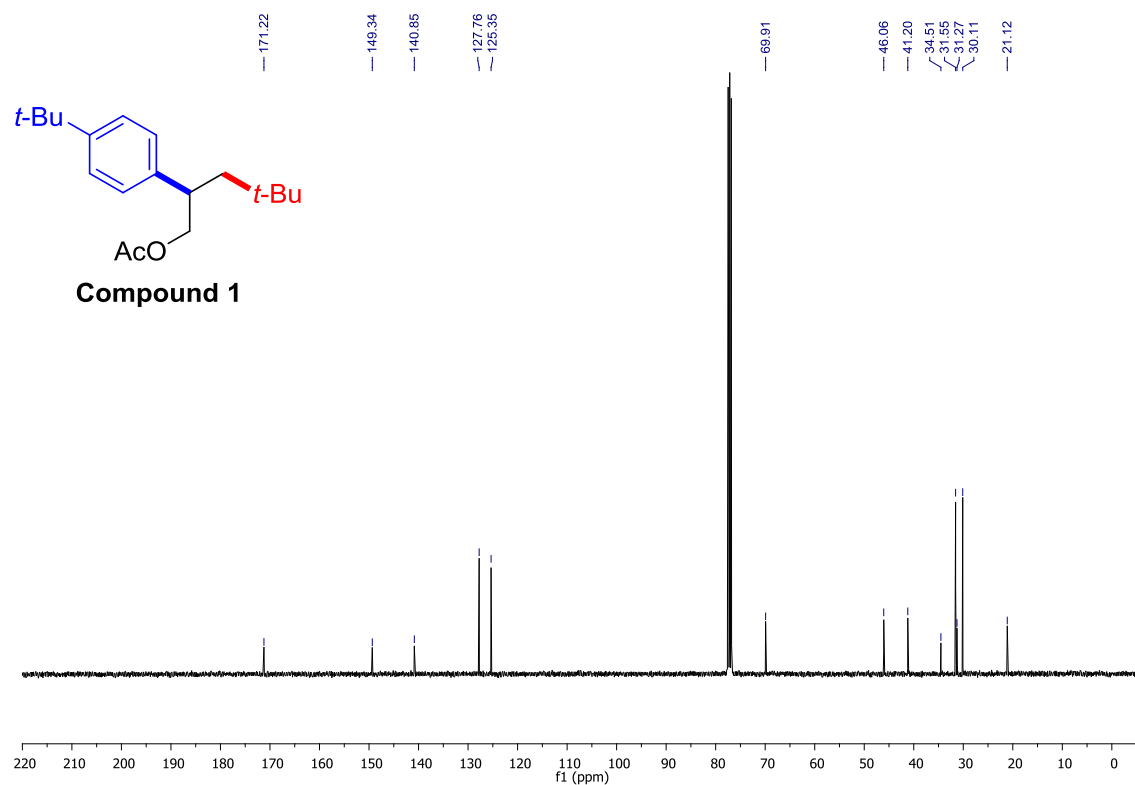
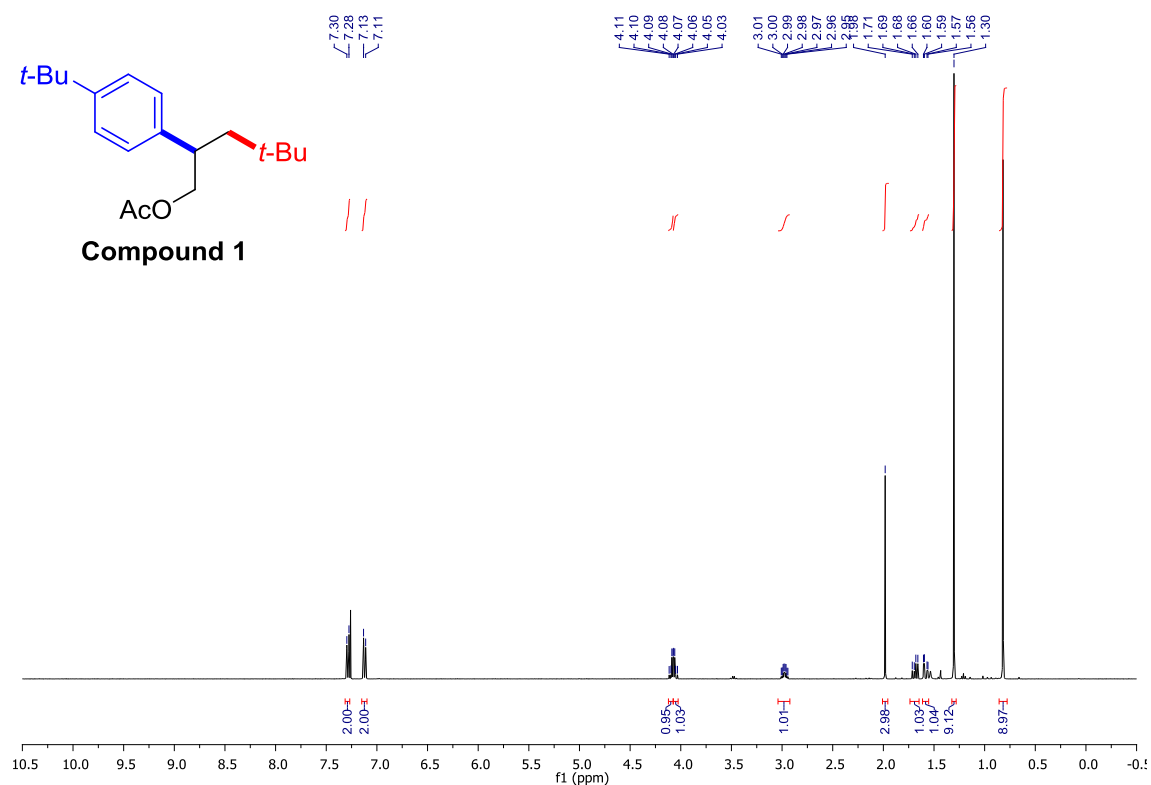


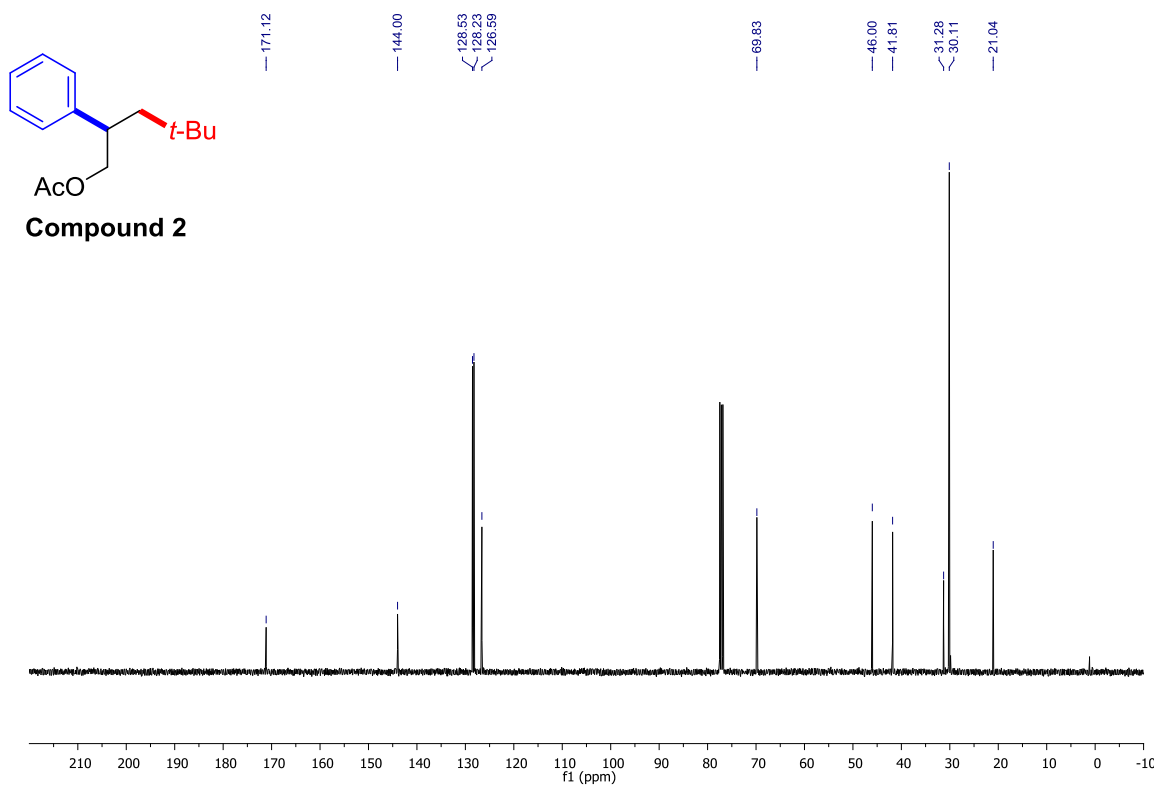
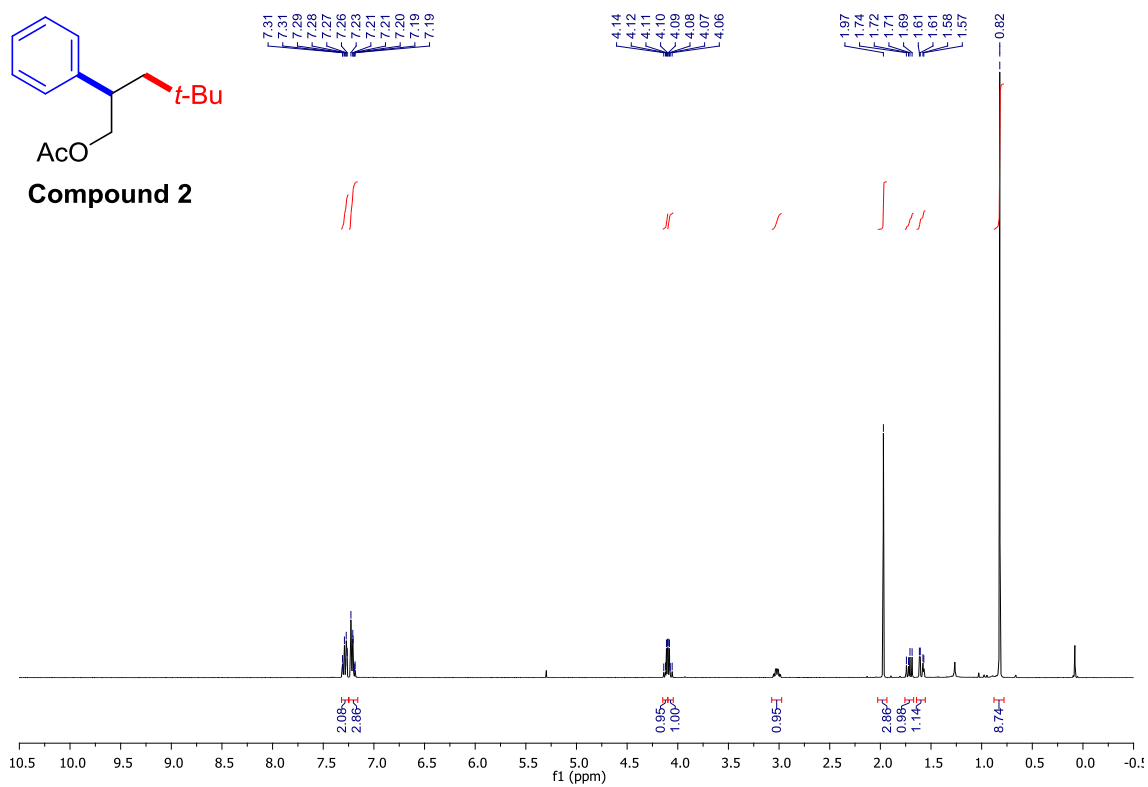


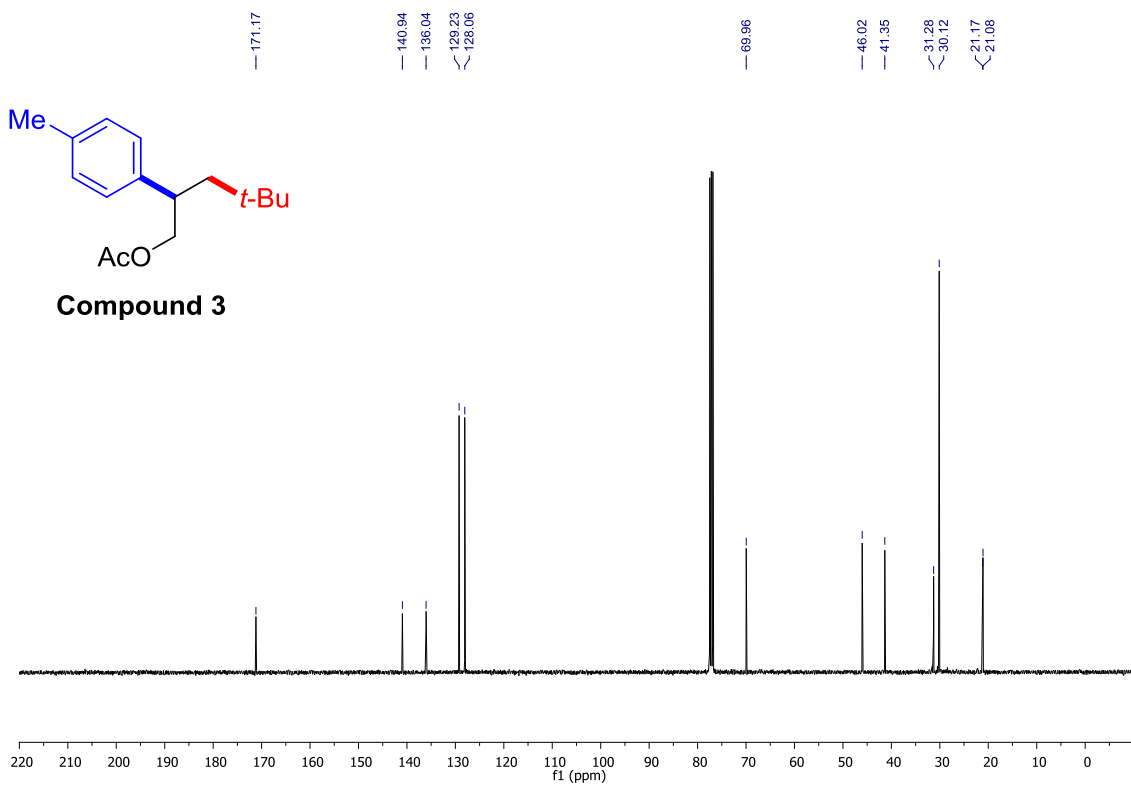
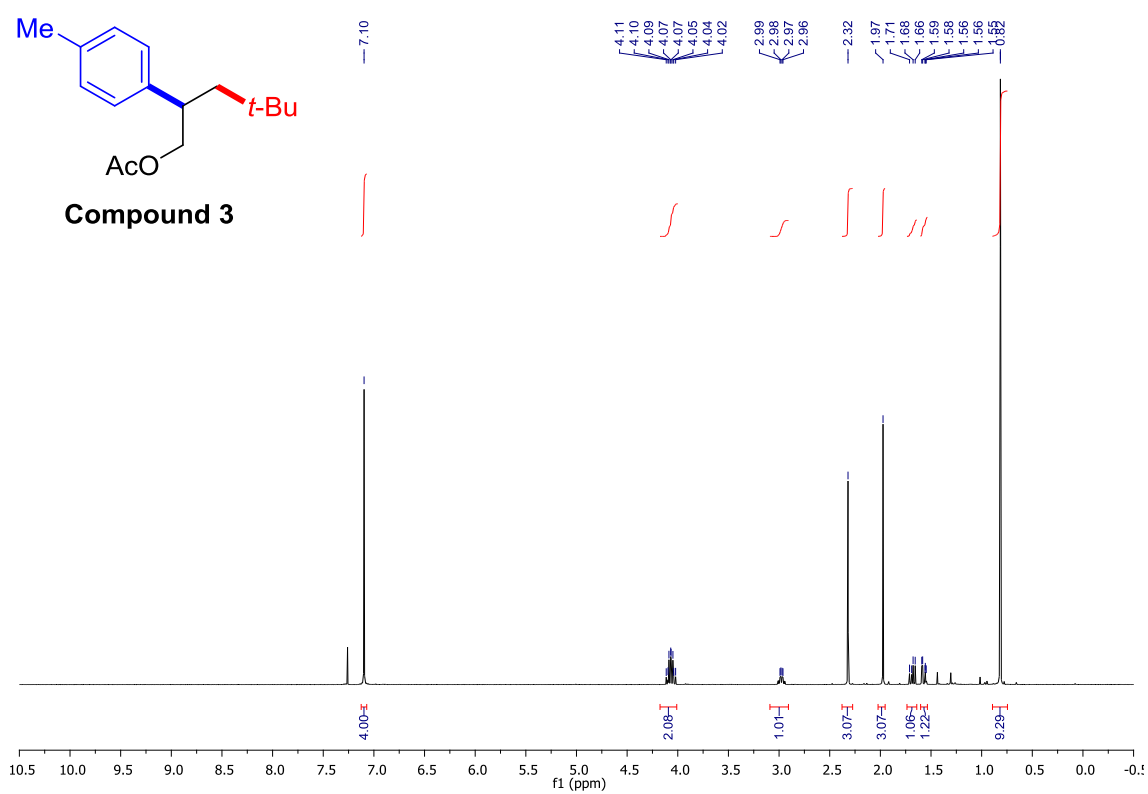


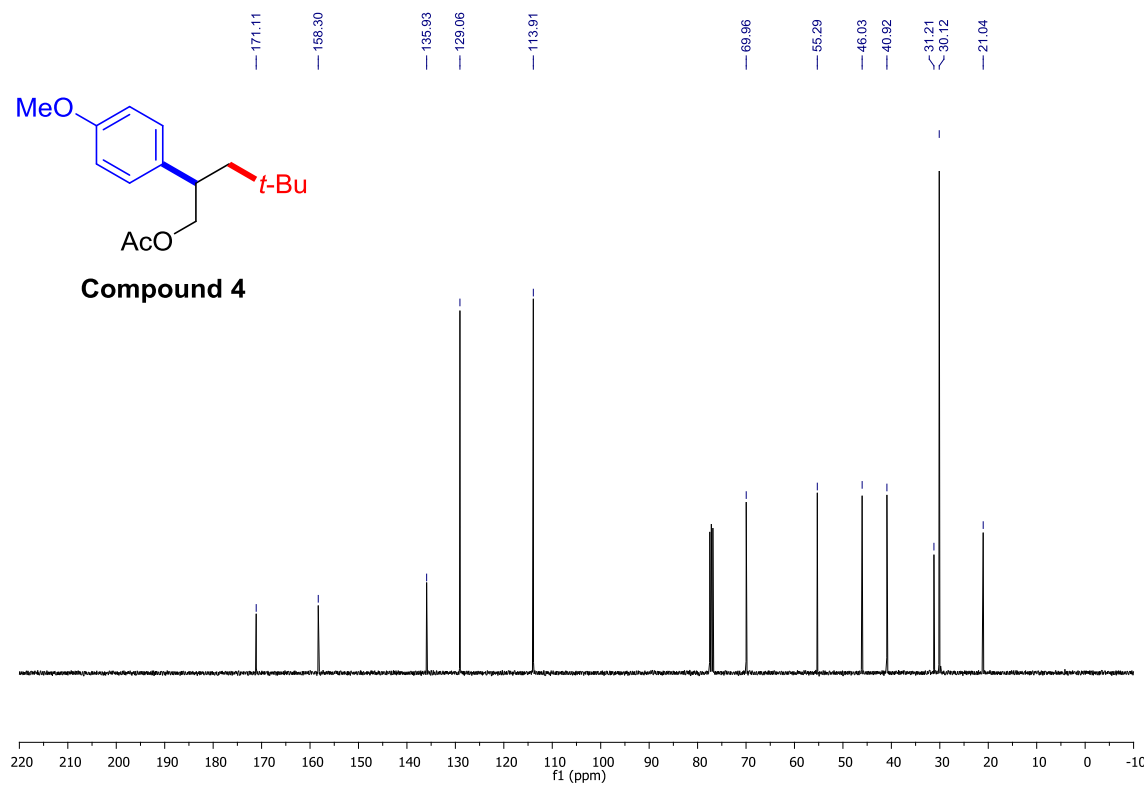
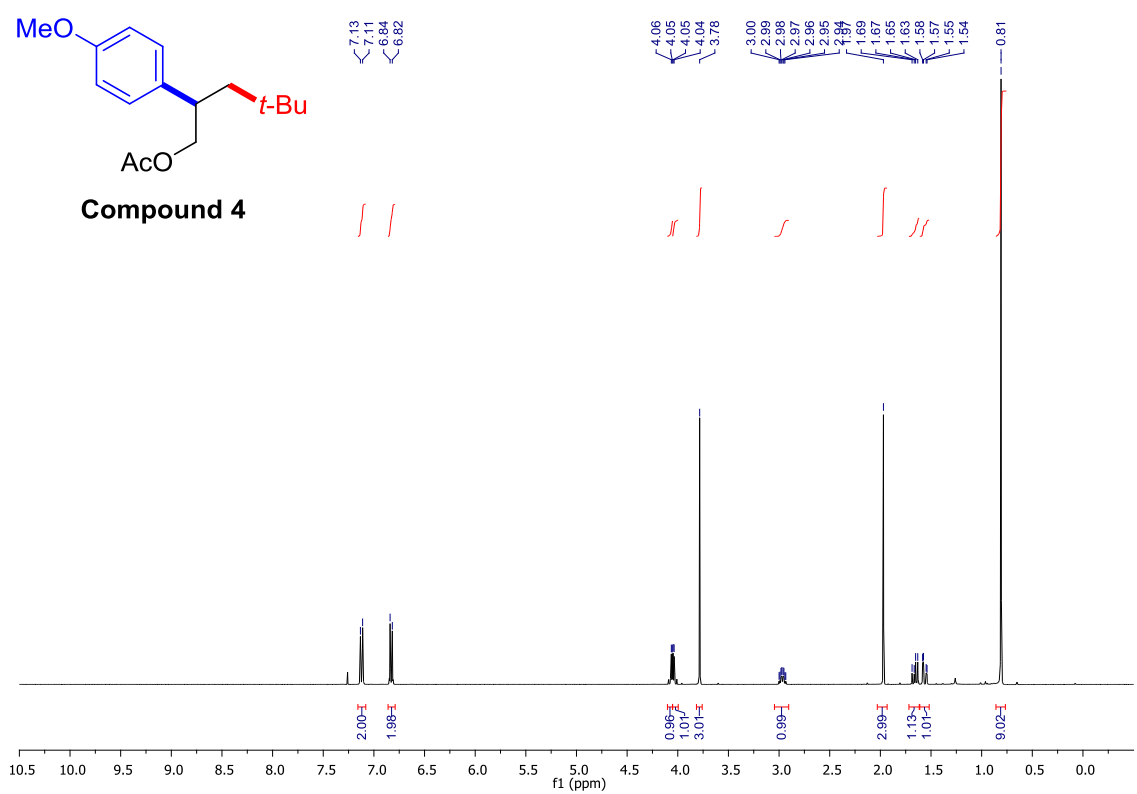


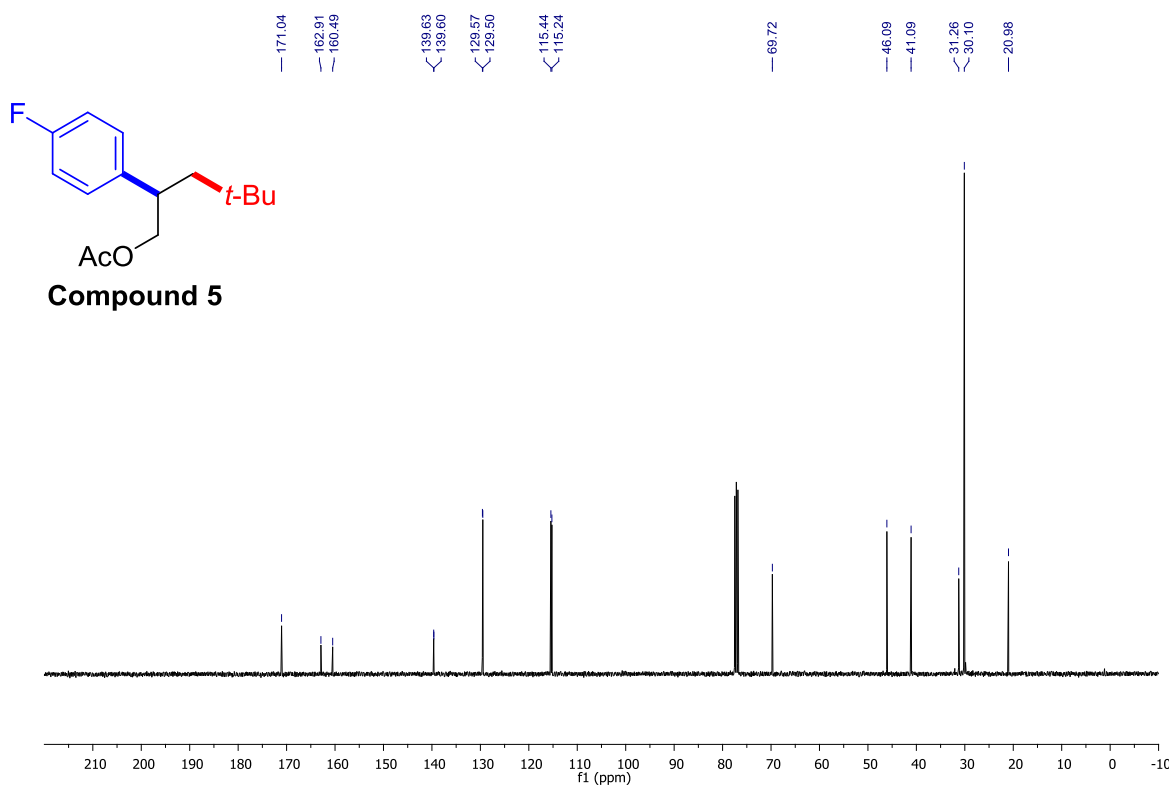
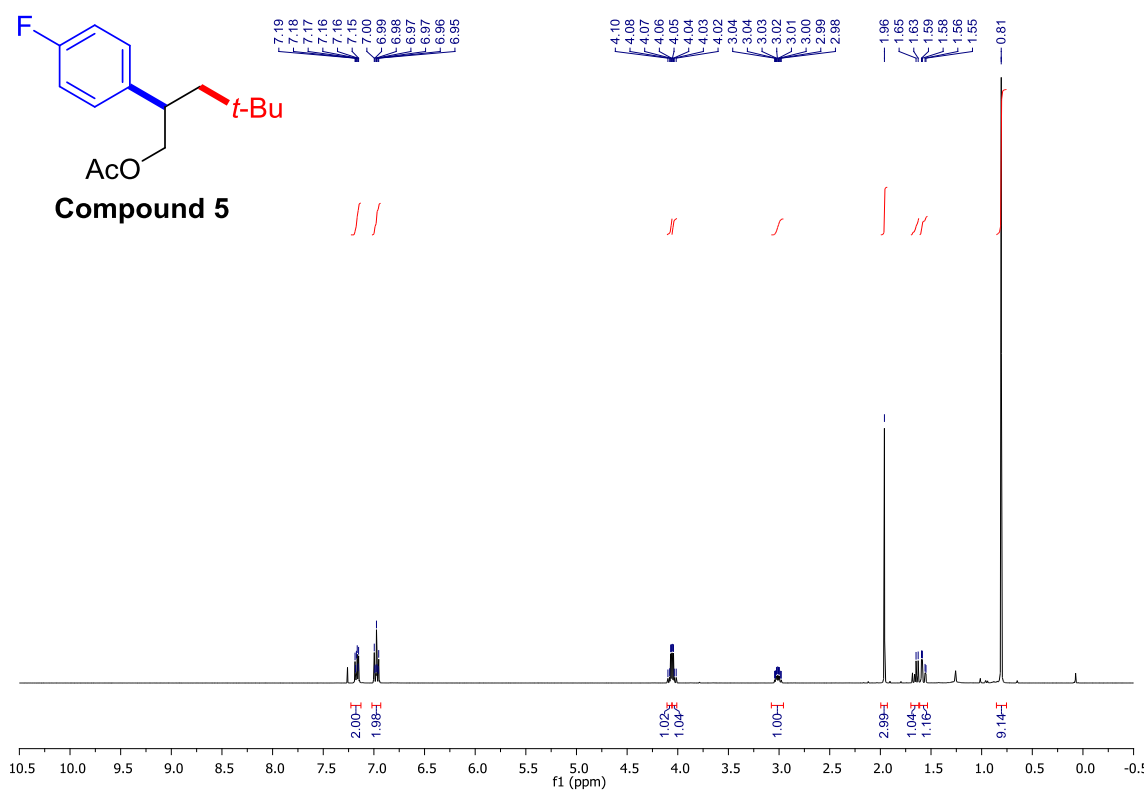
9. NMR Spectra of New Products

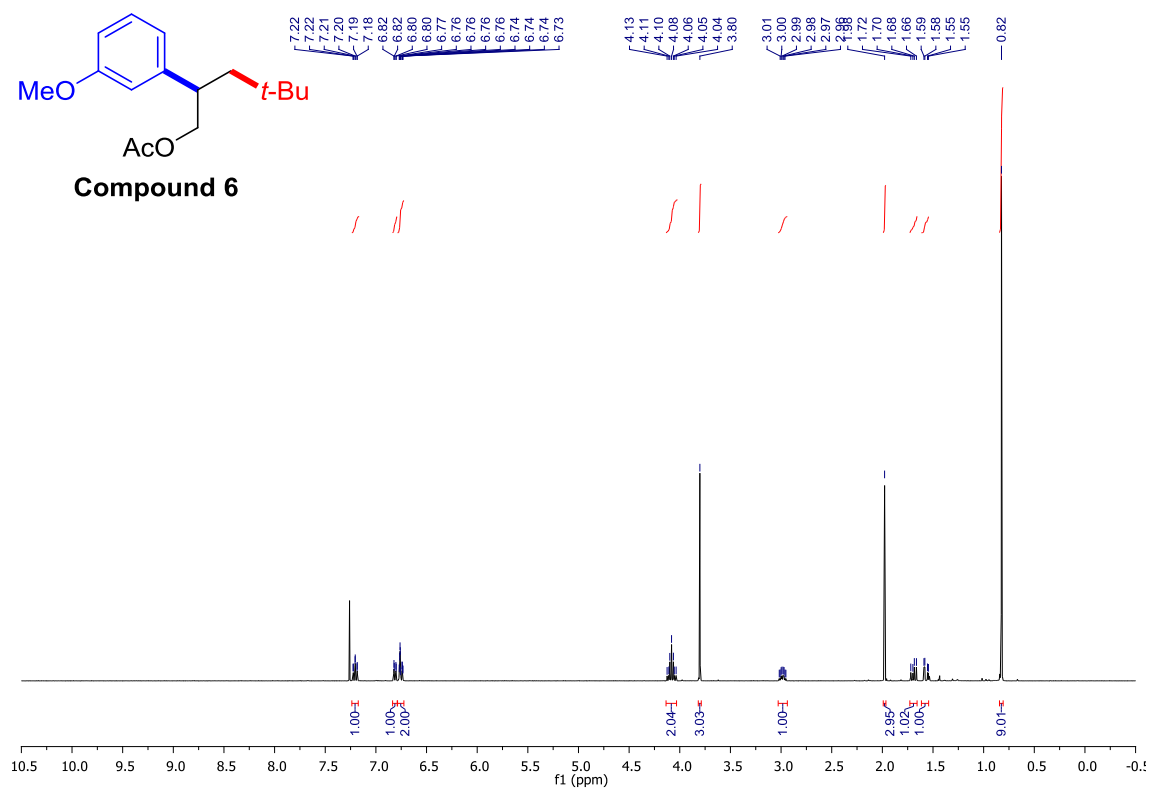
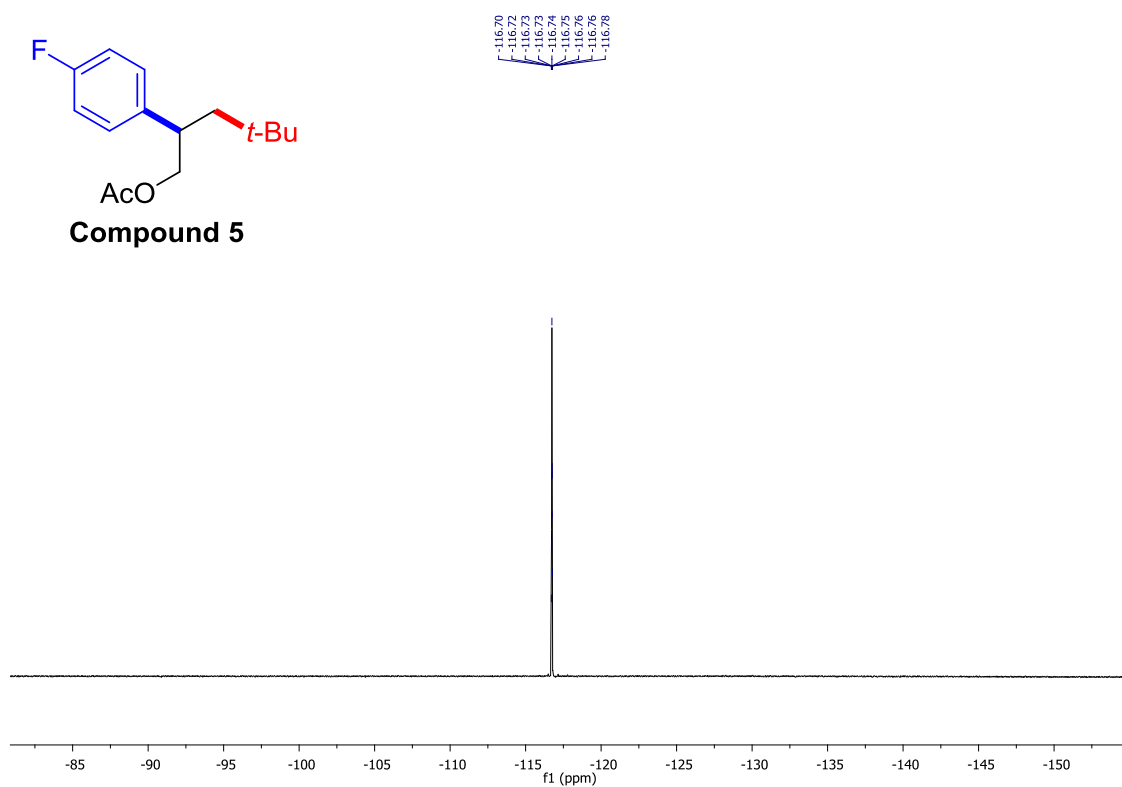


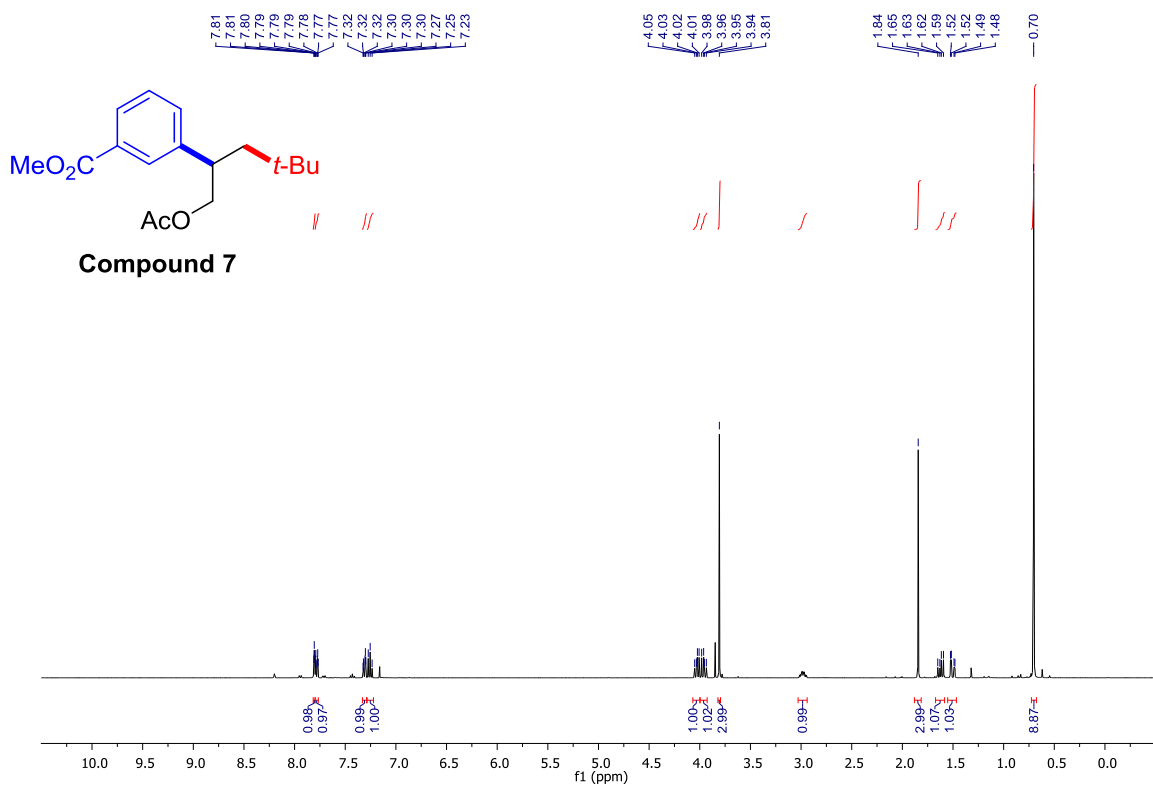
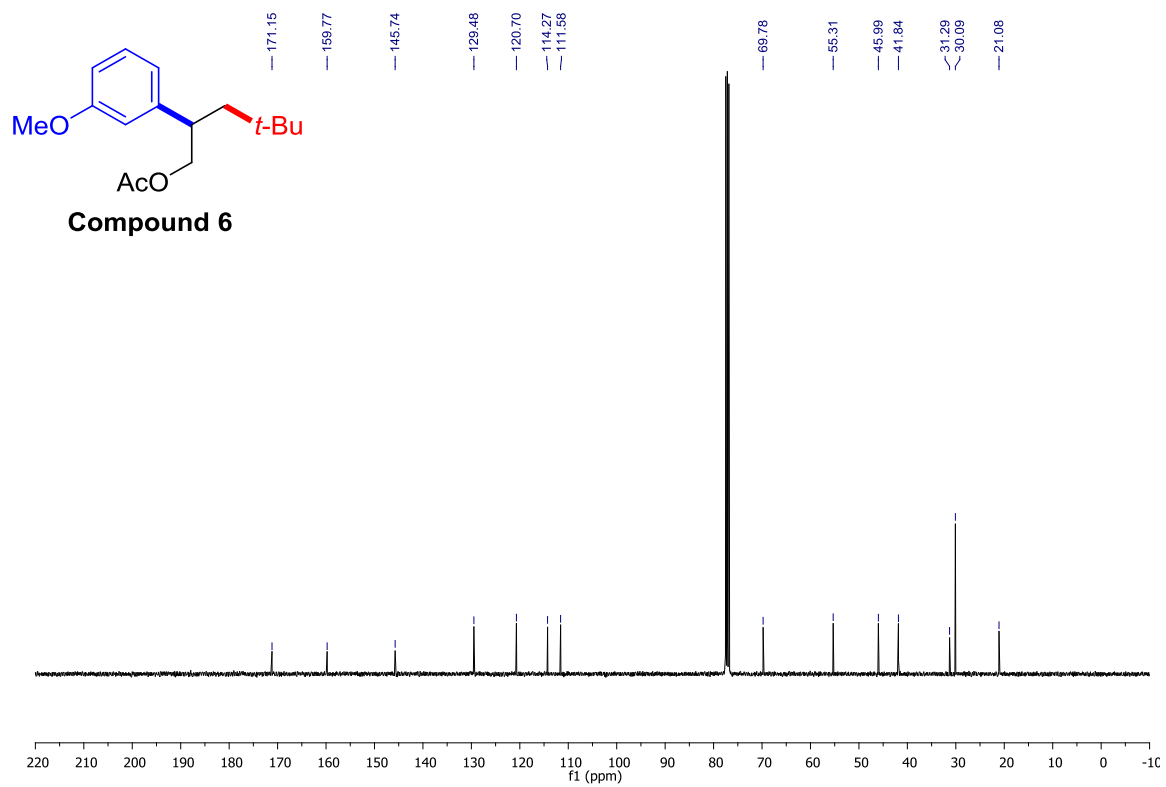


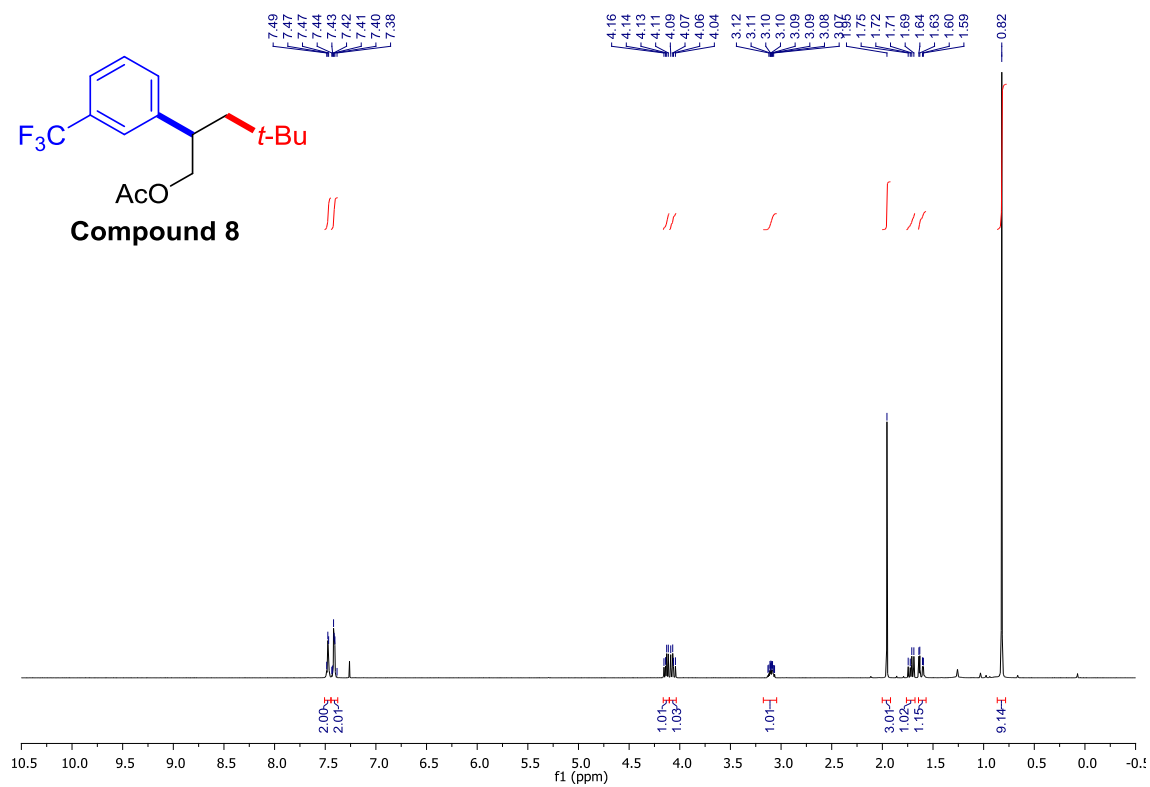
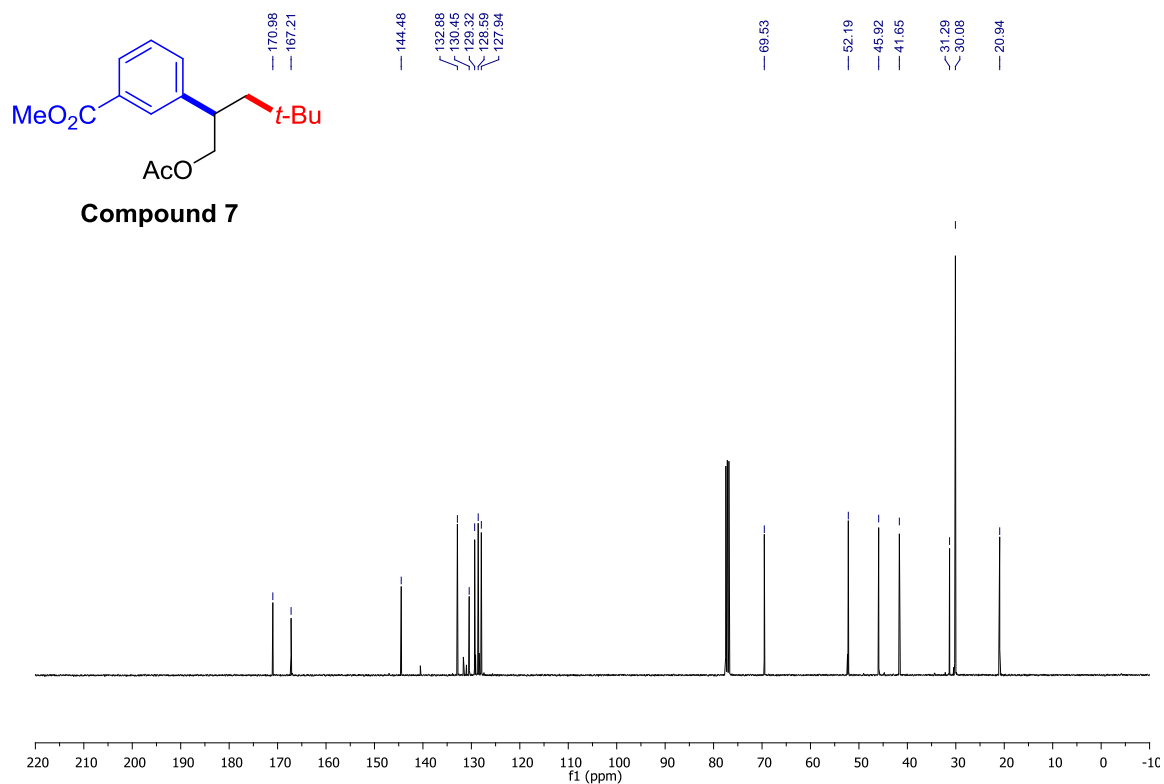


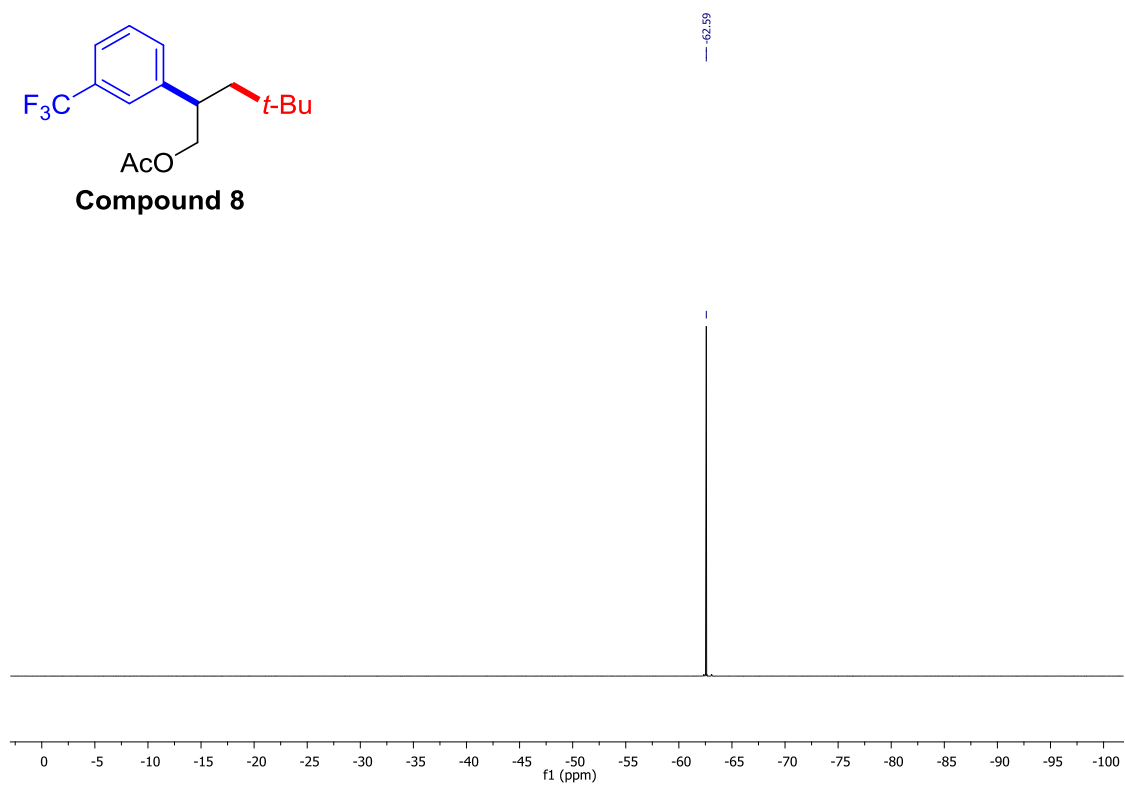
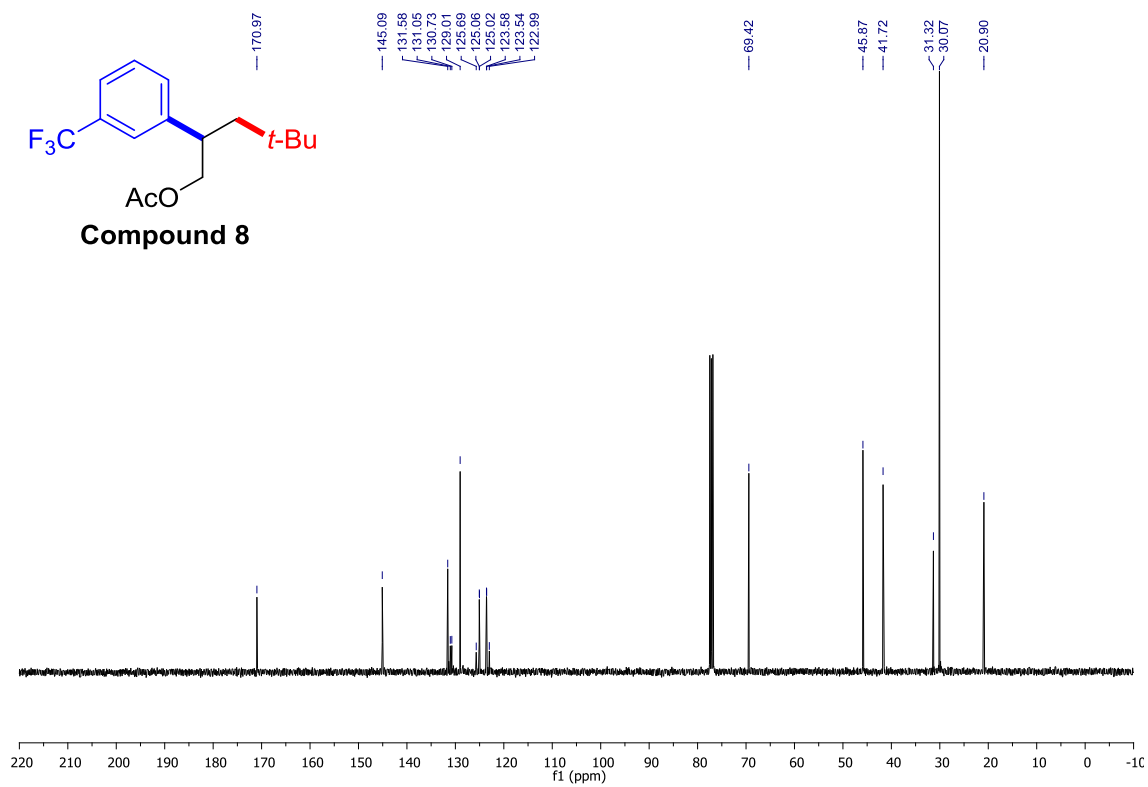


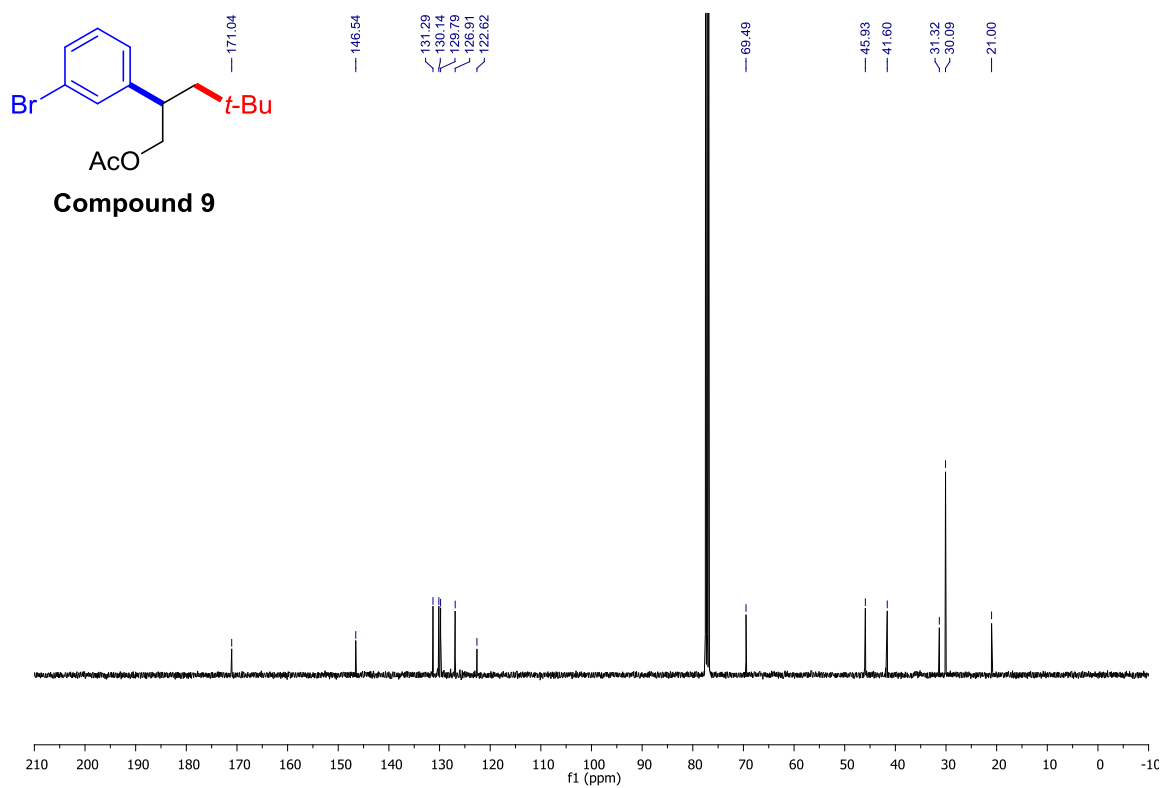
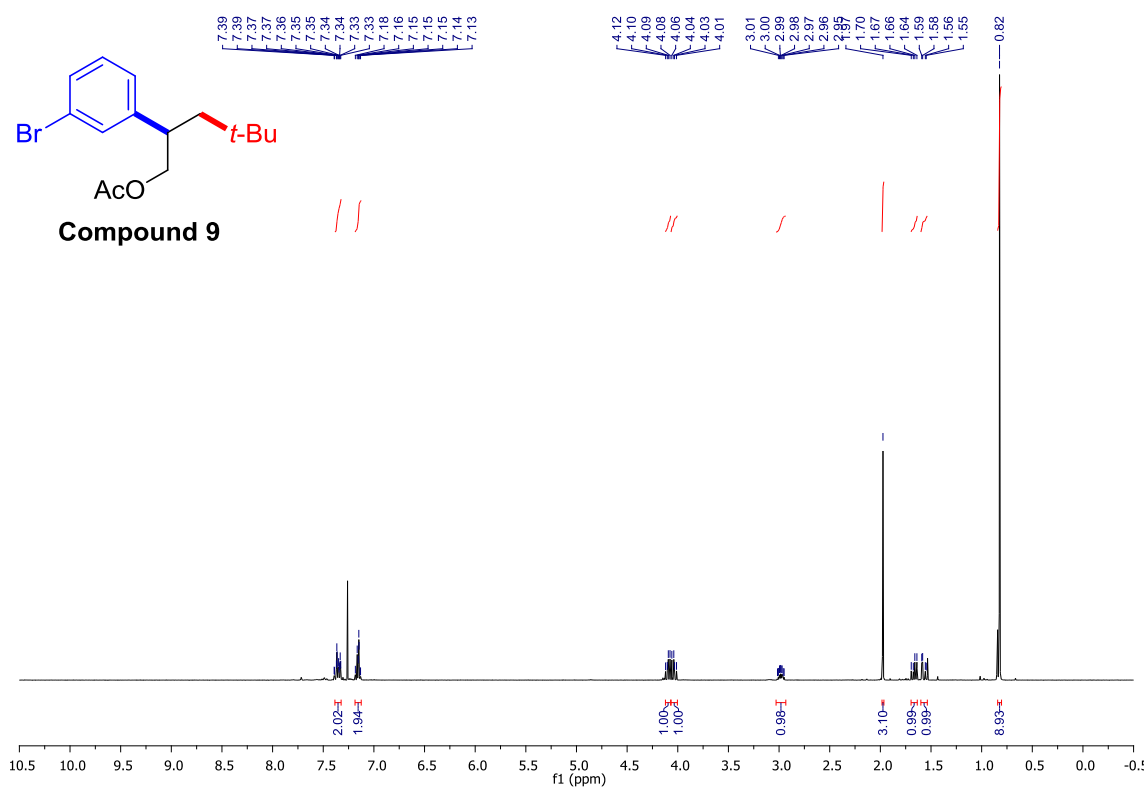


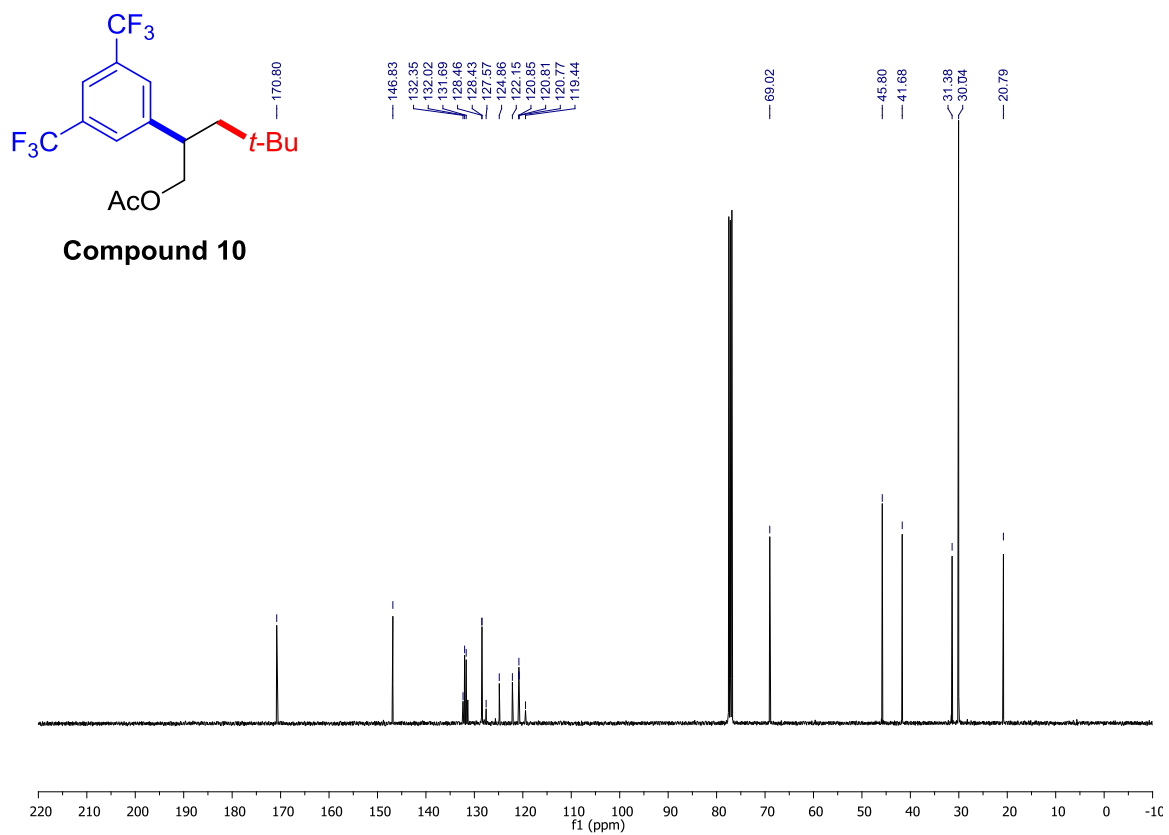
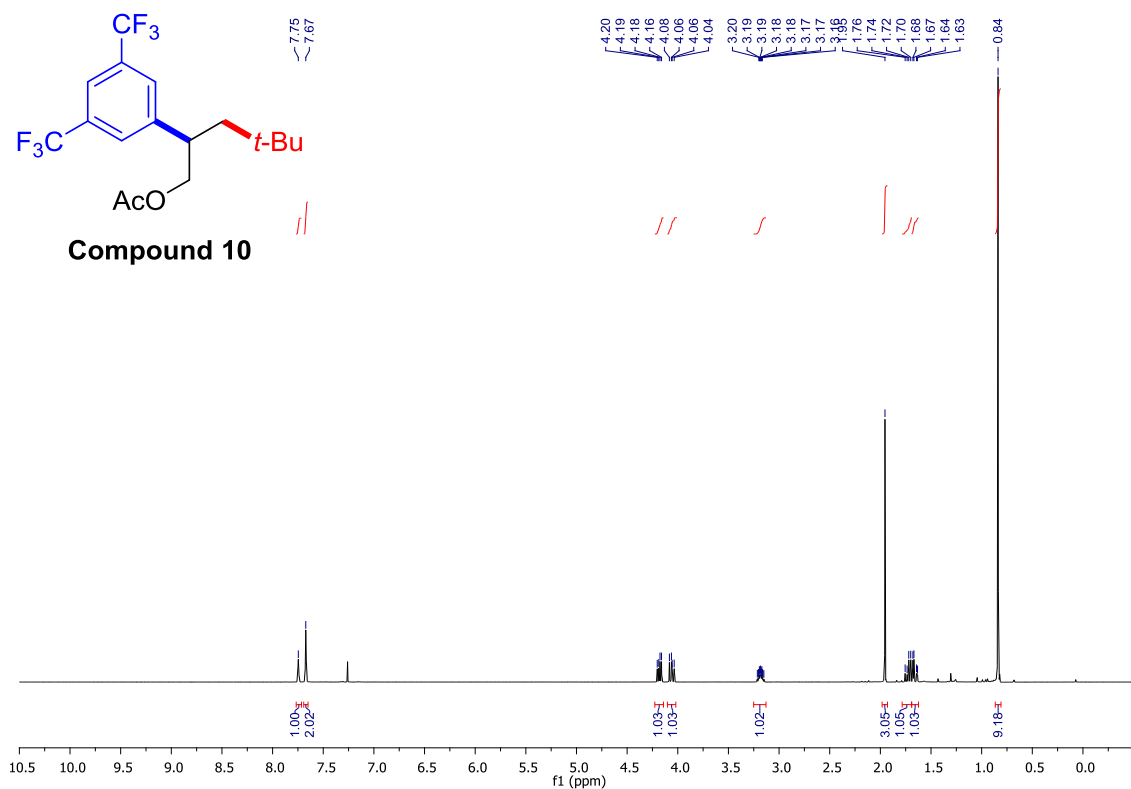


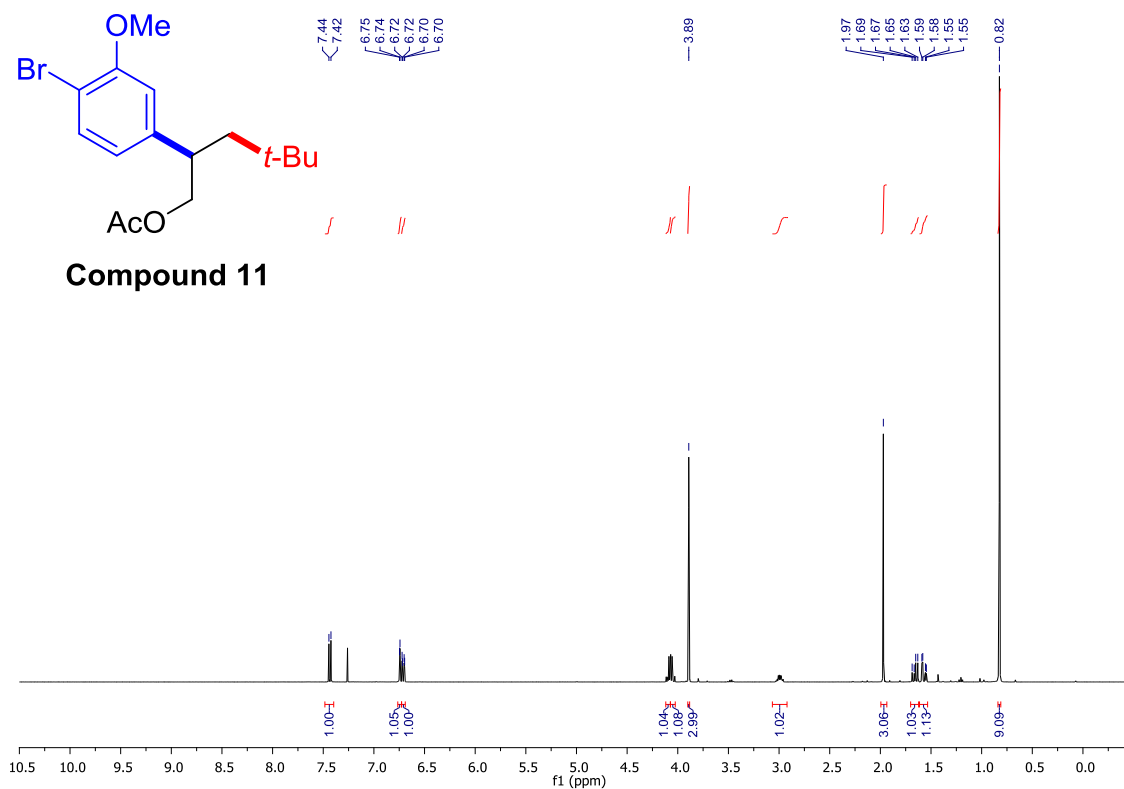
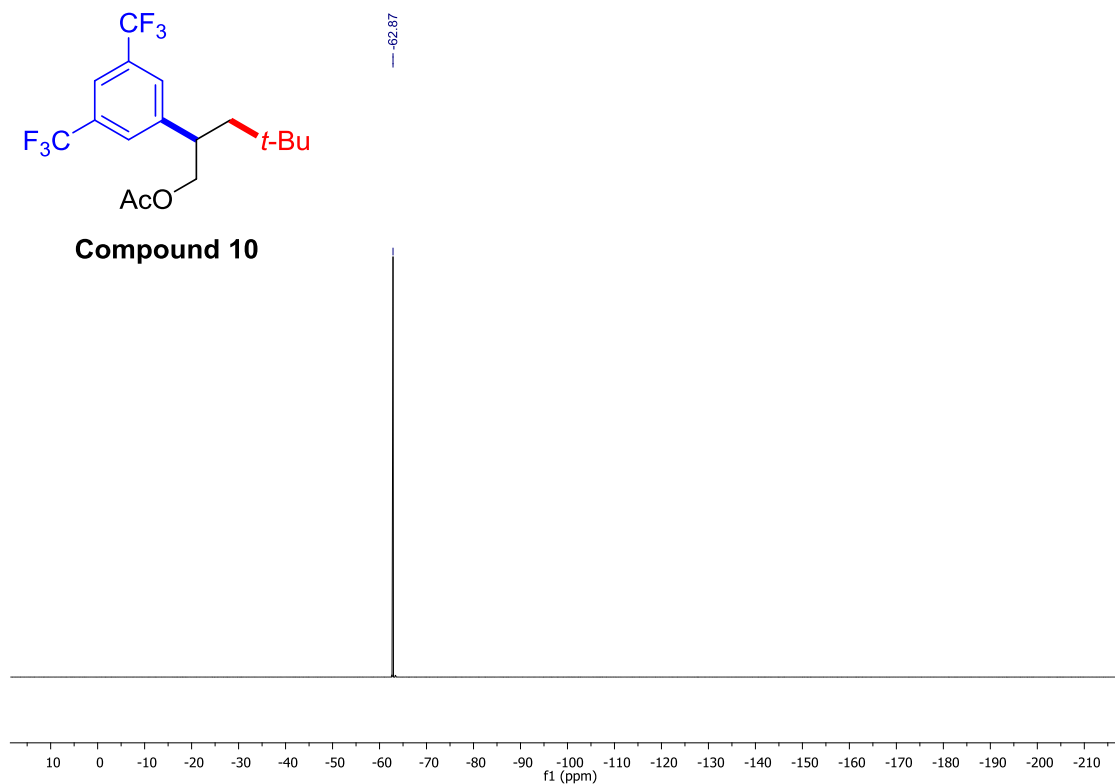


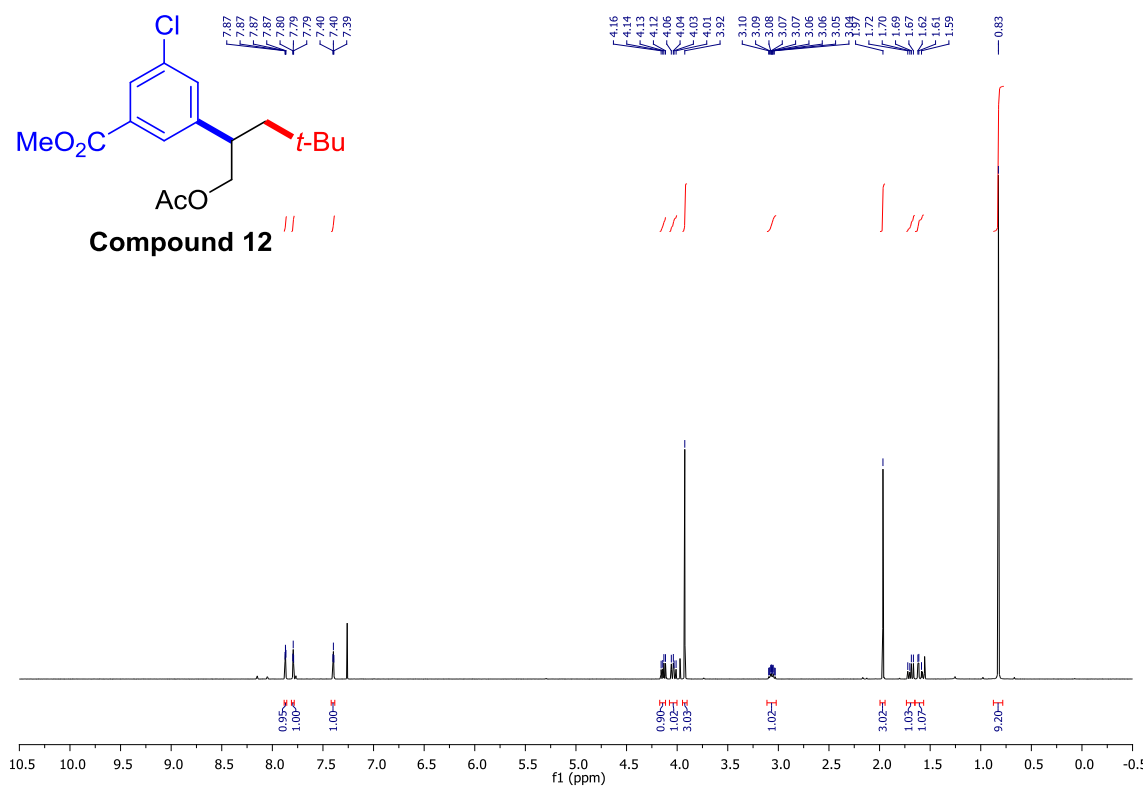
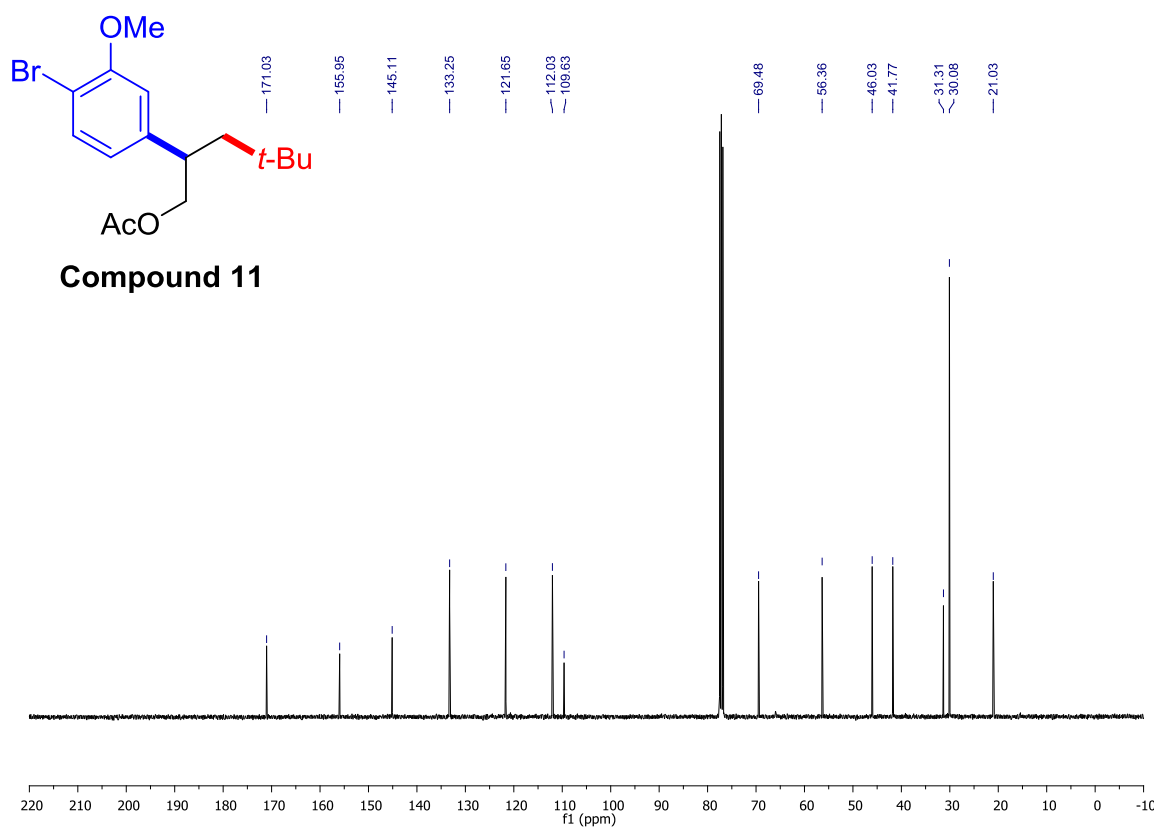


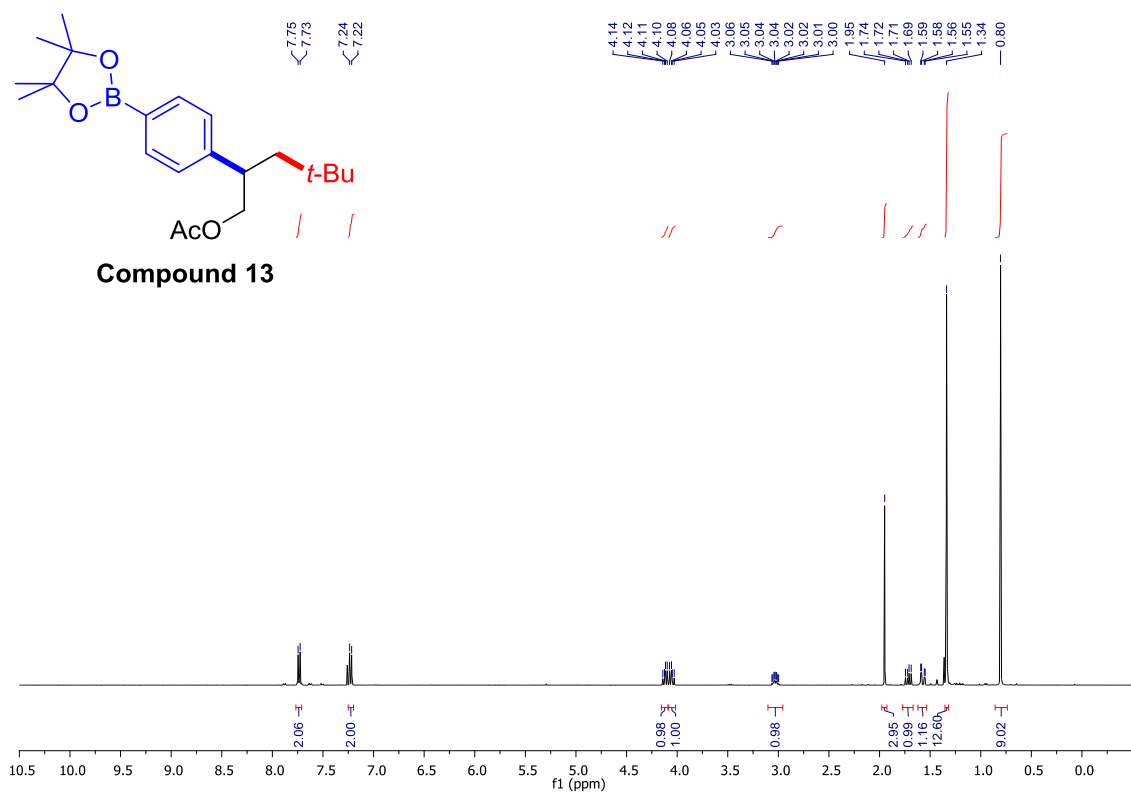
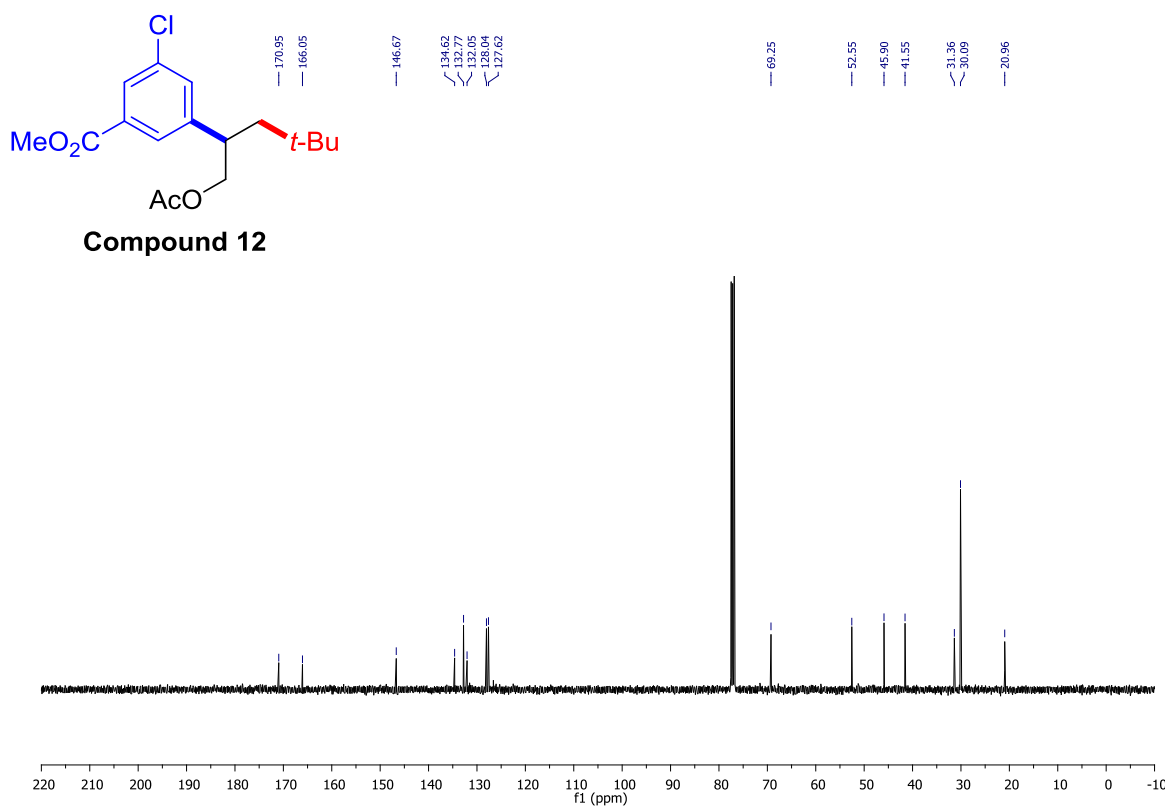


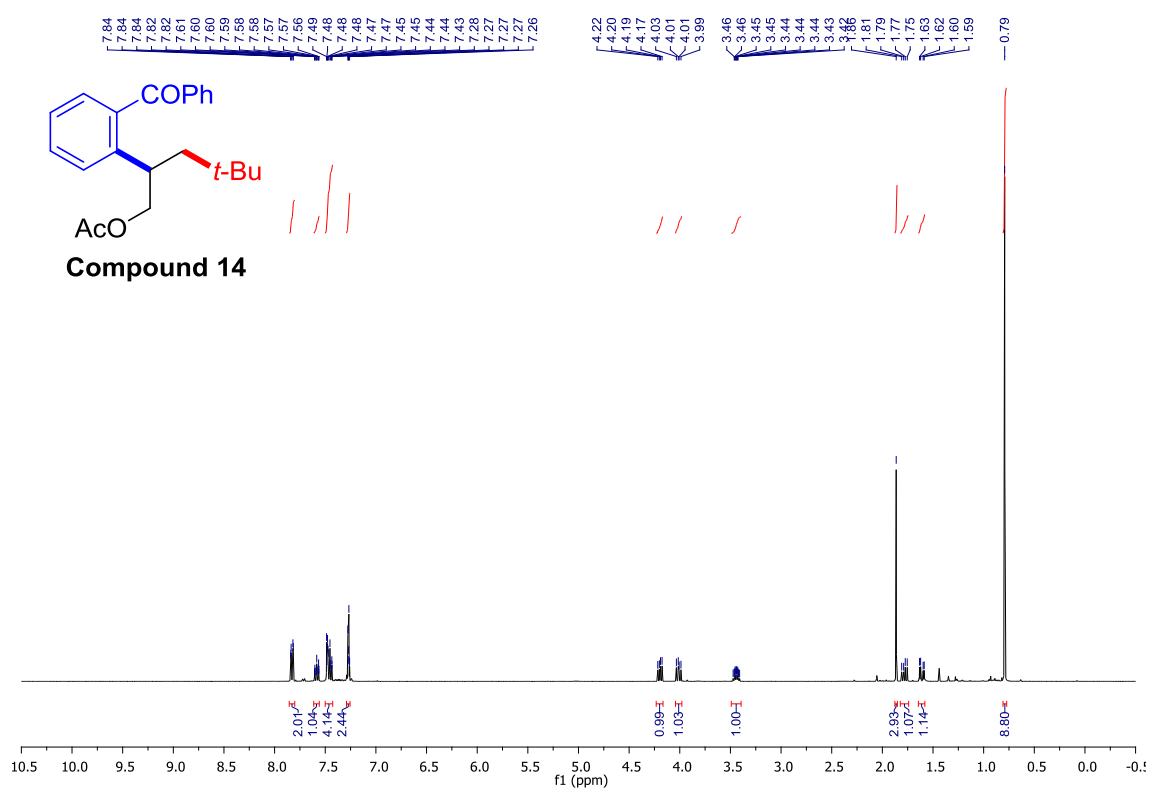
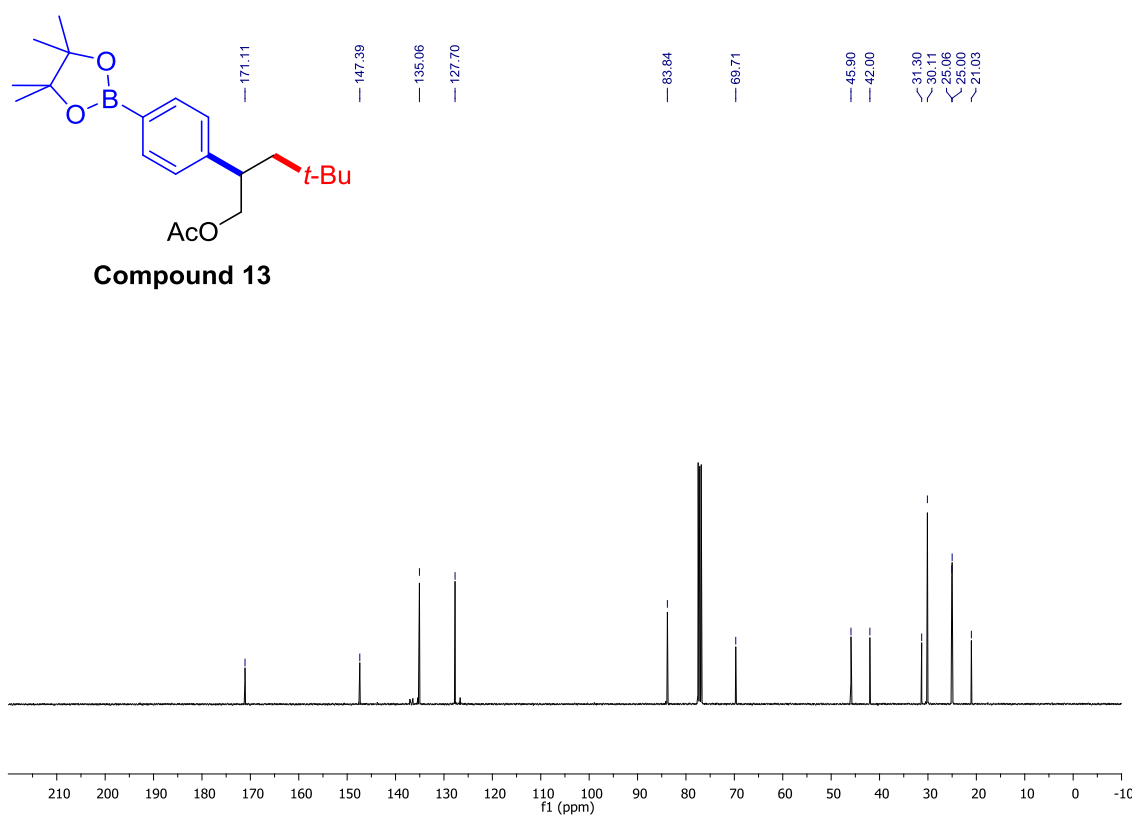


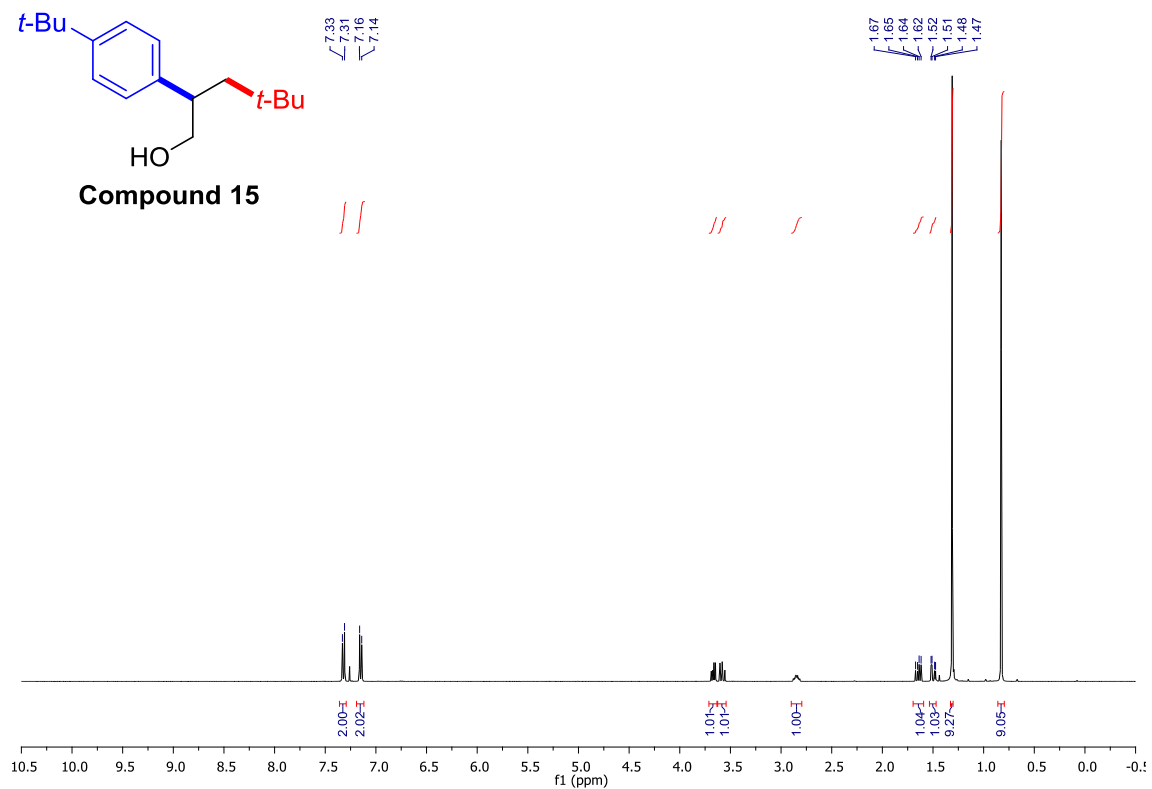
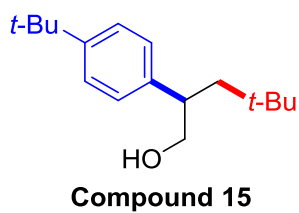
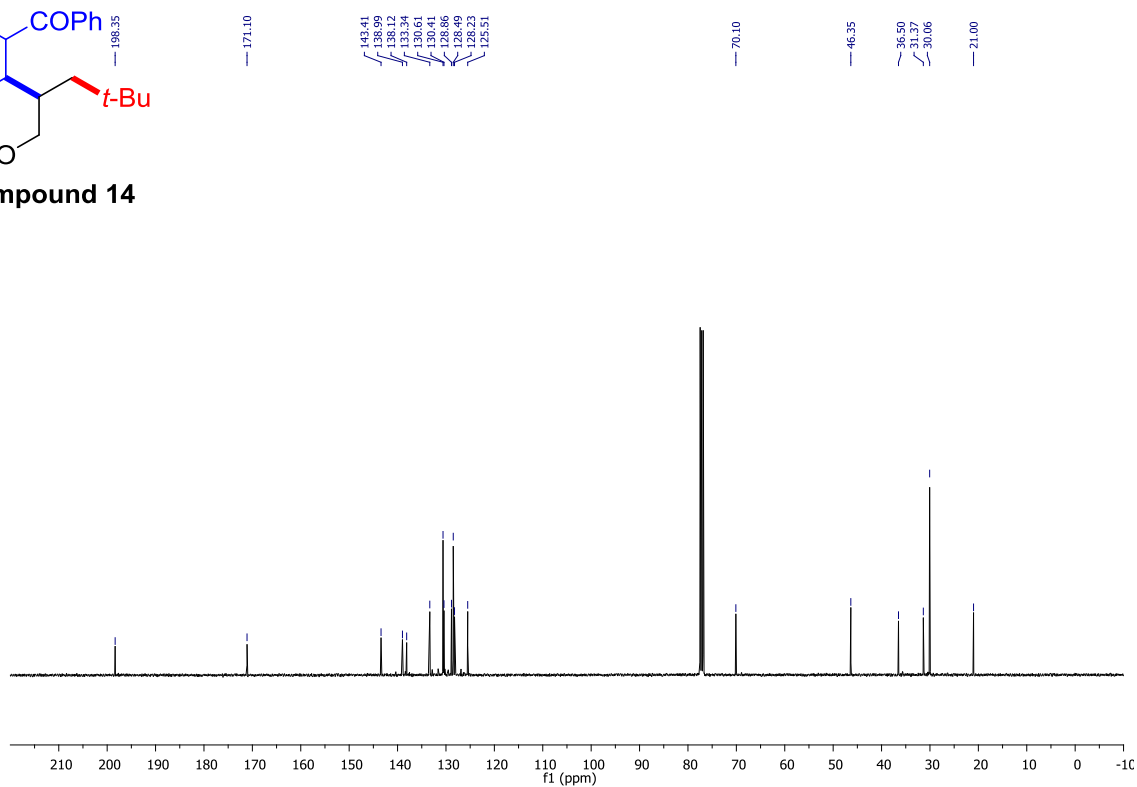
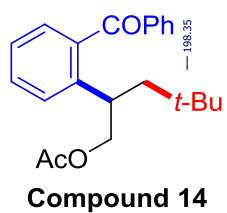


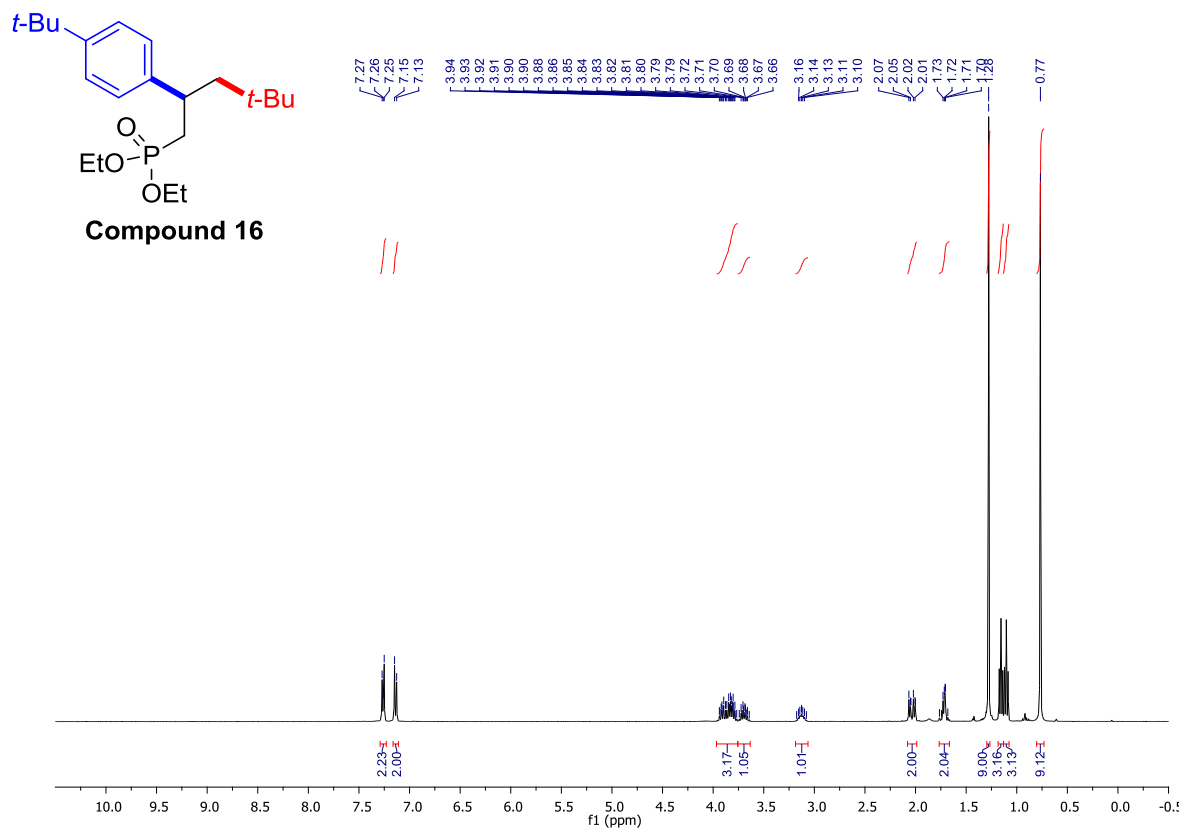
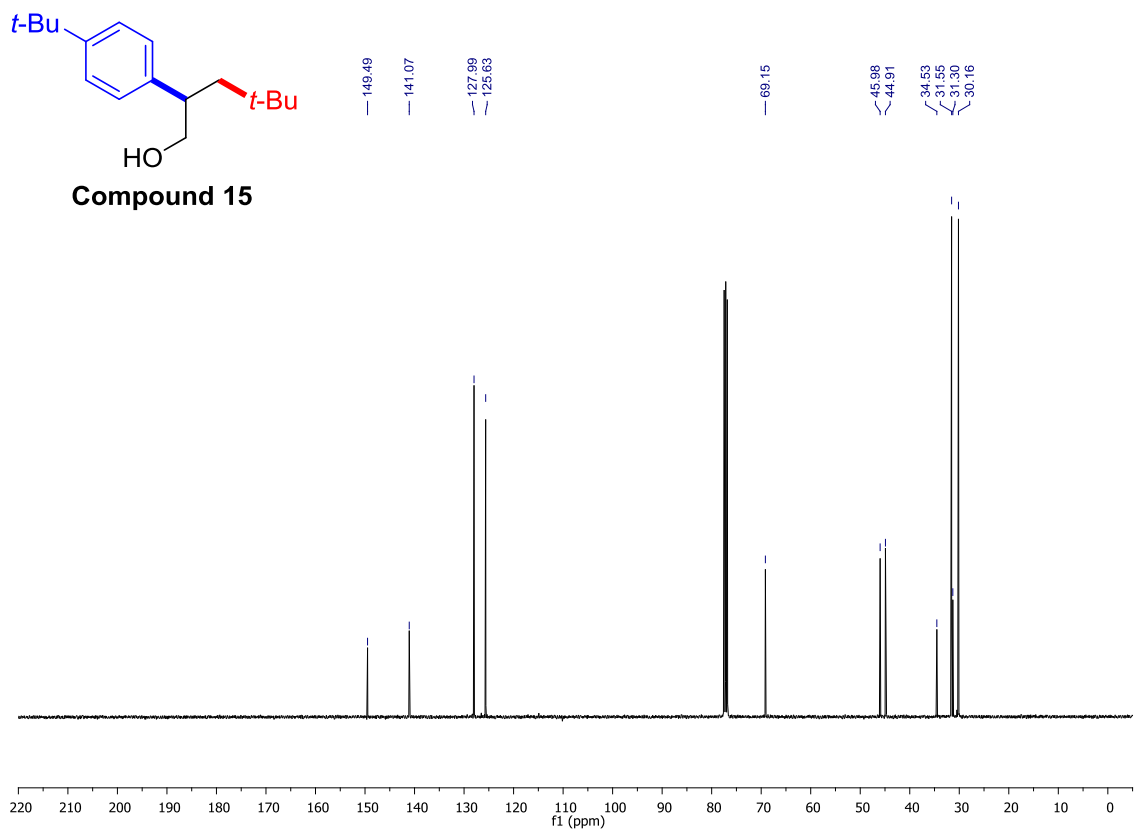


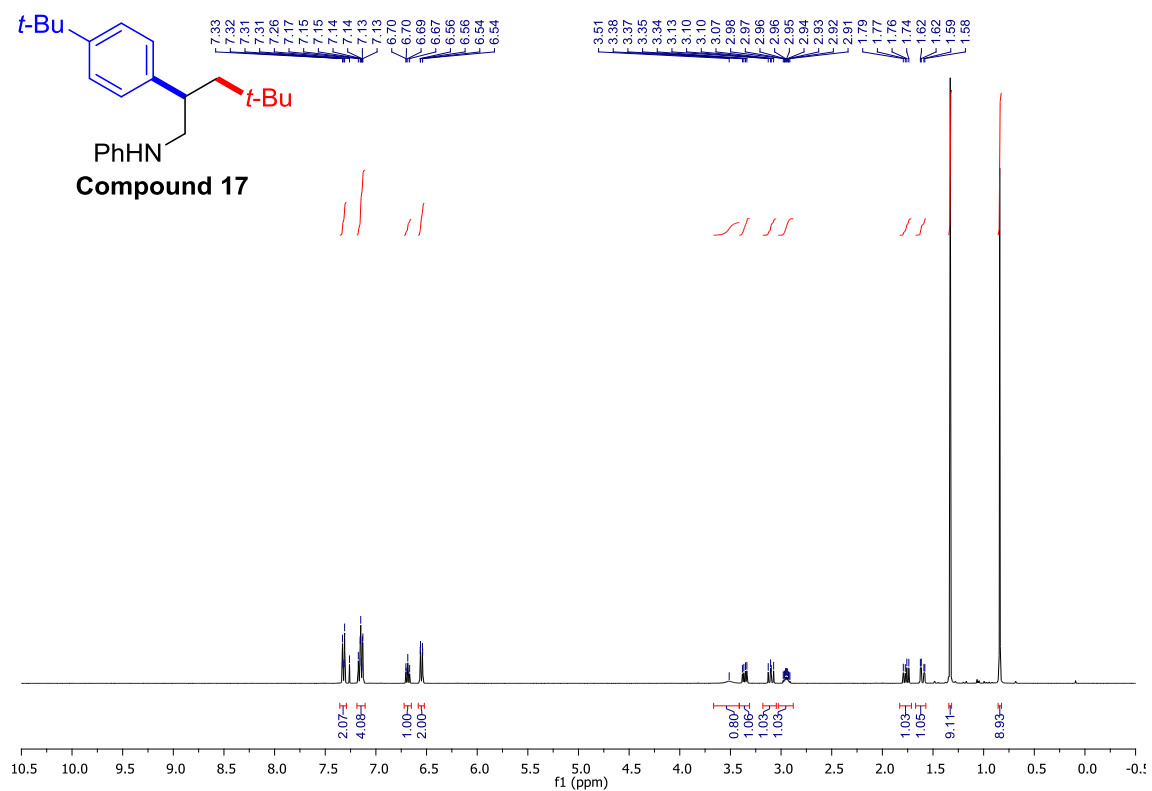
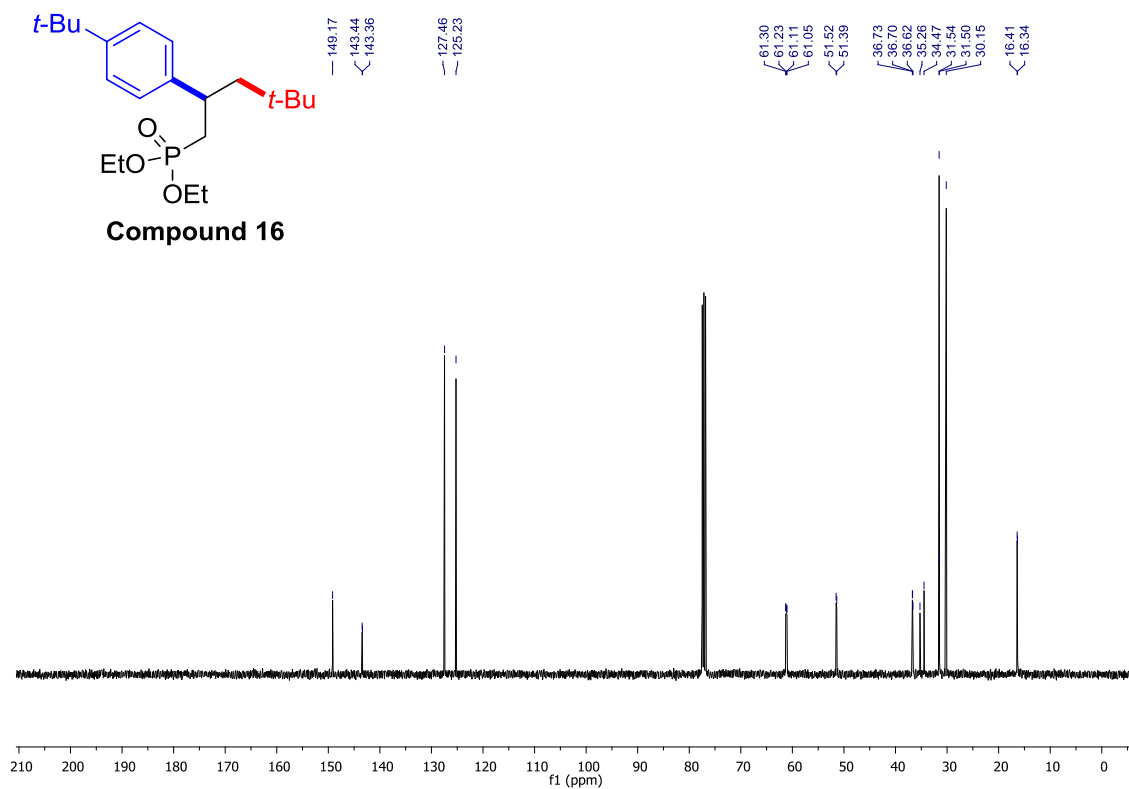


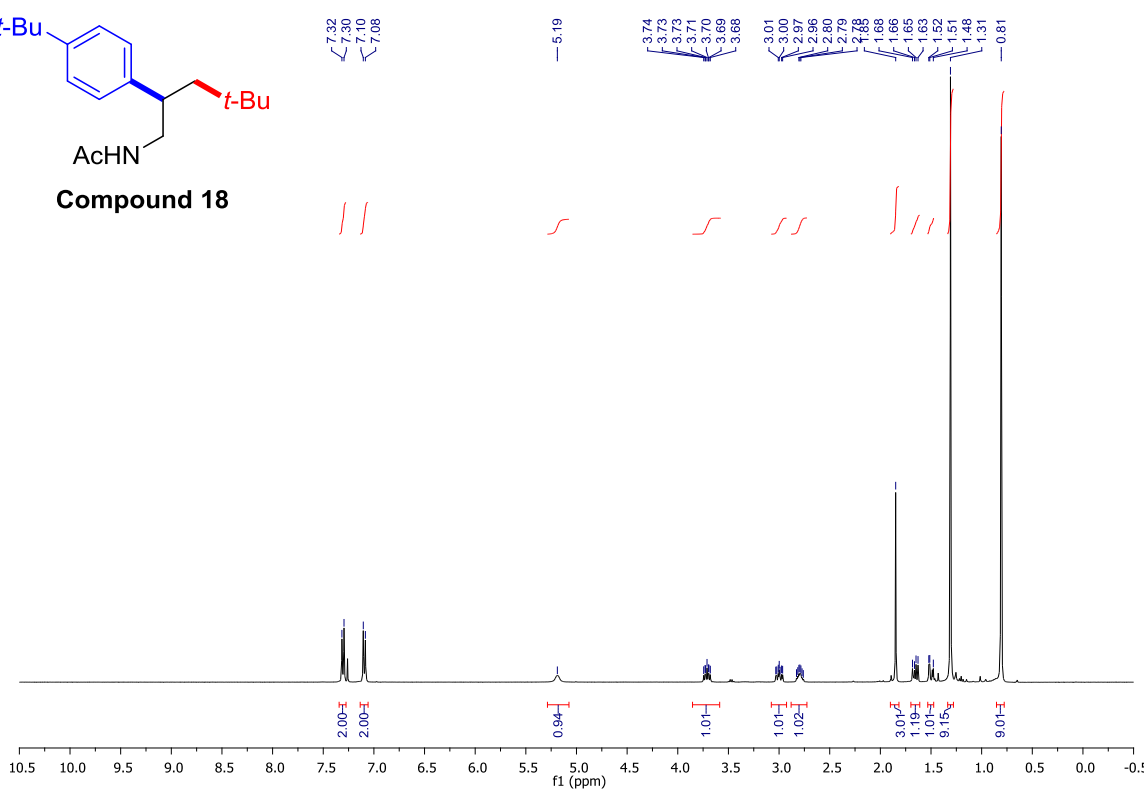
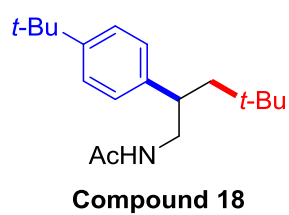
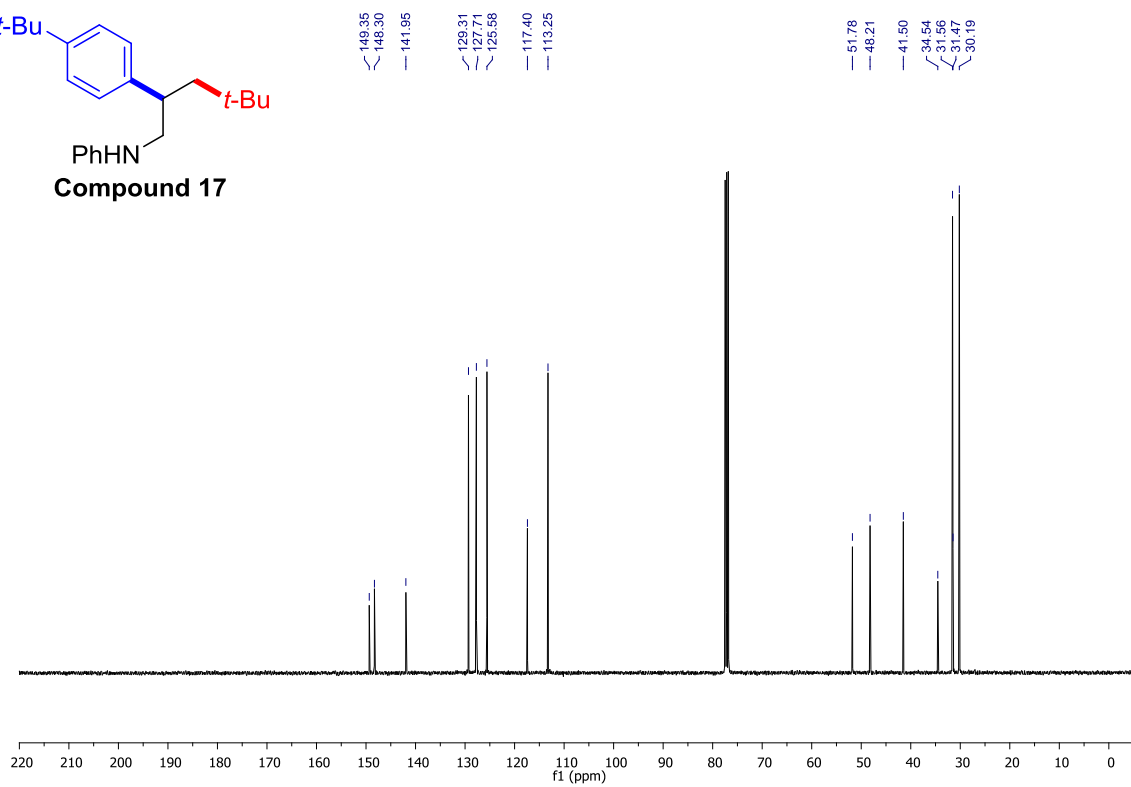
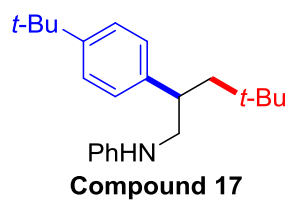


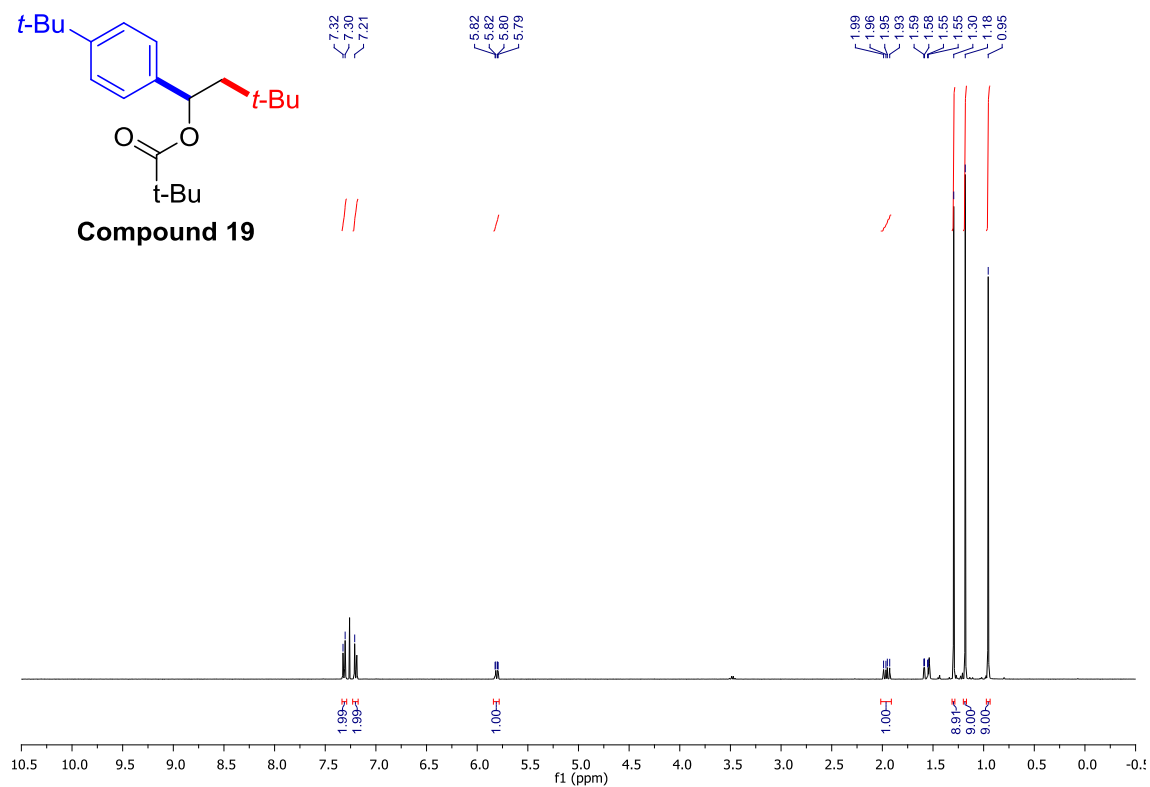
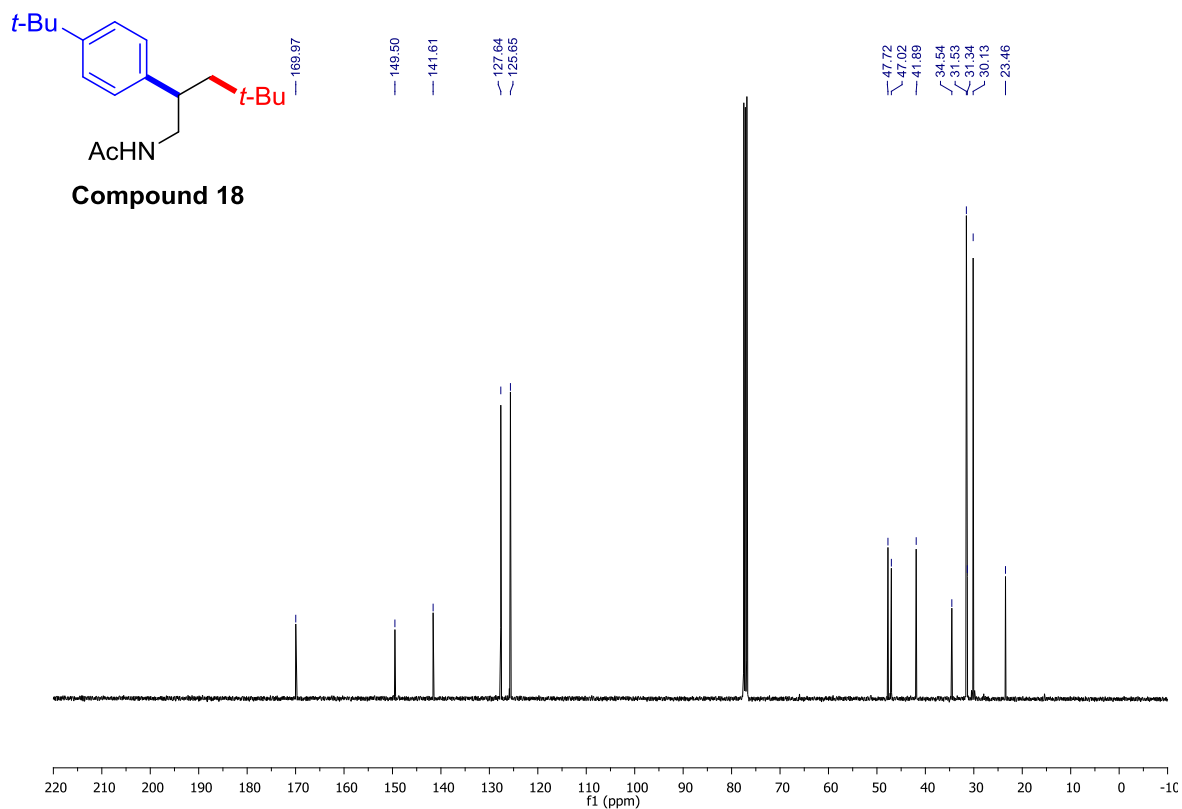


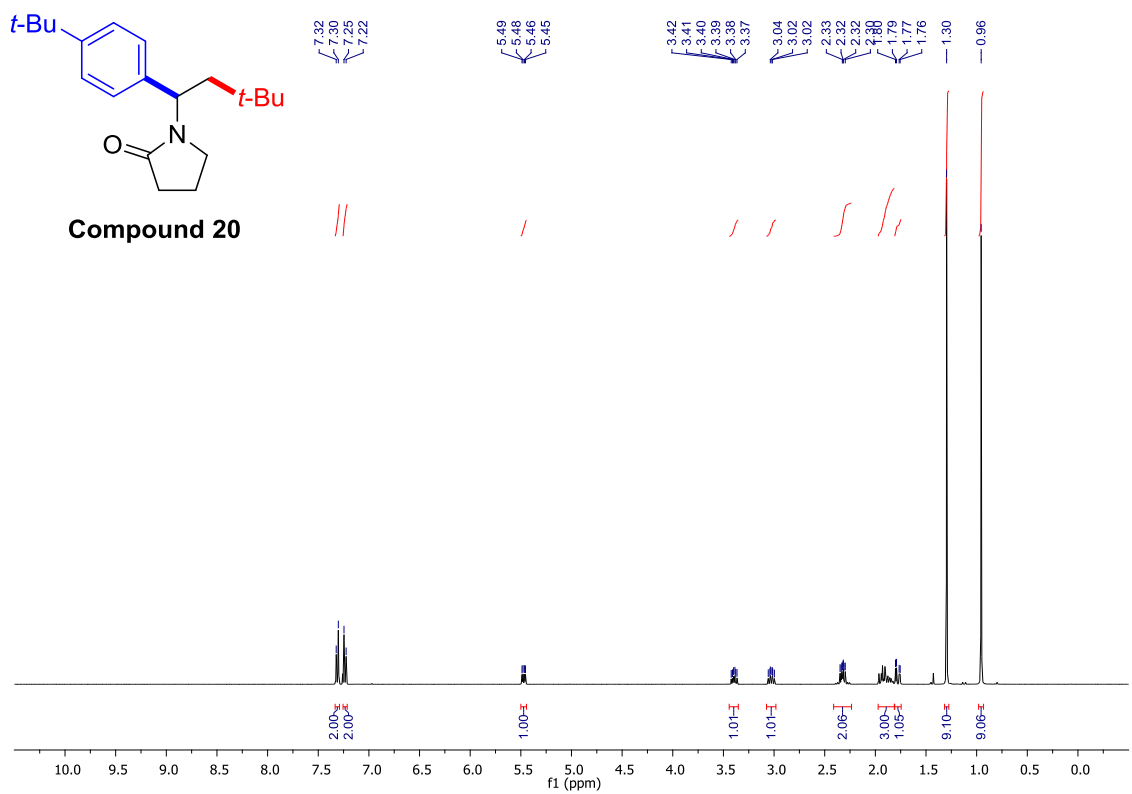
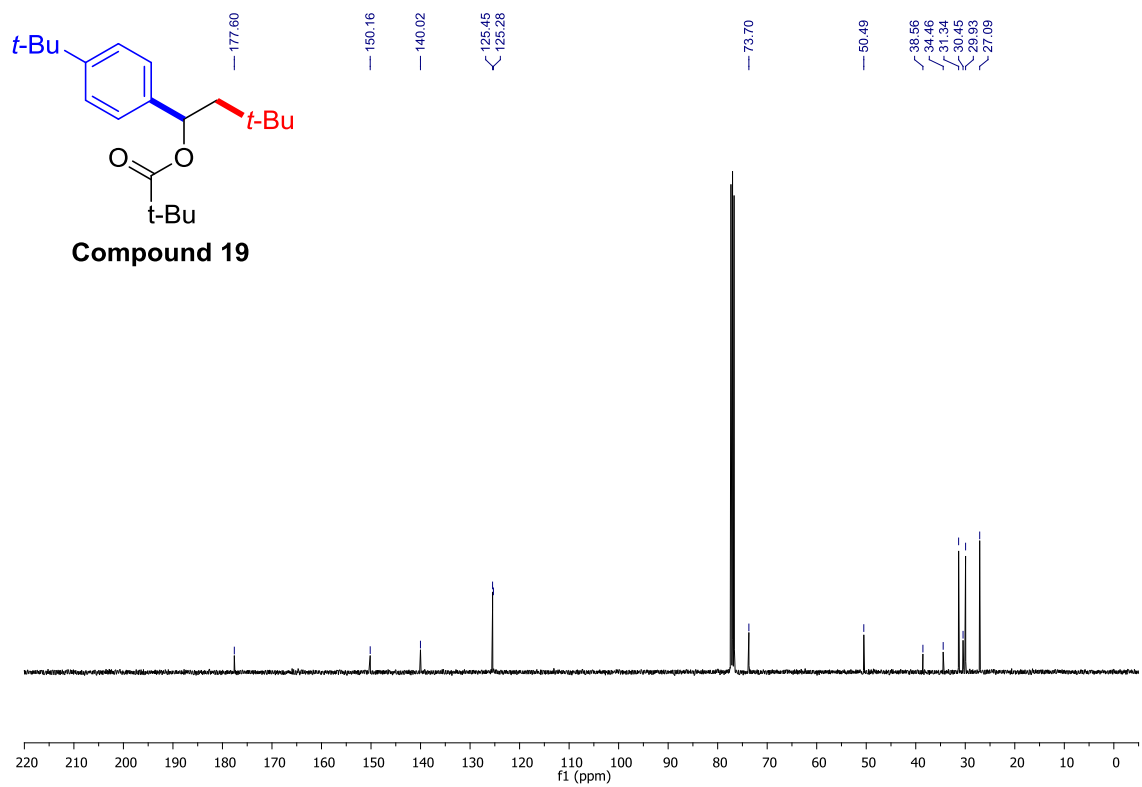


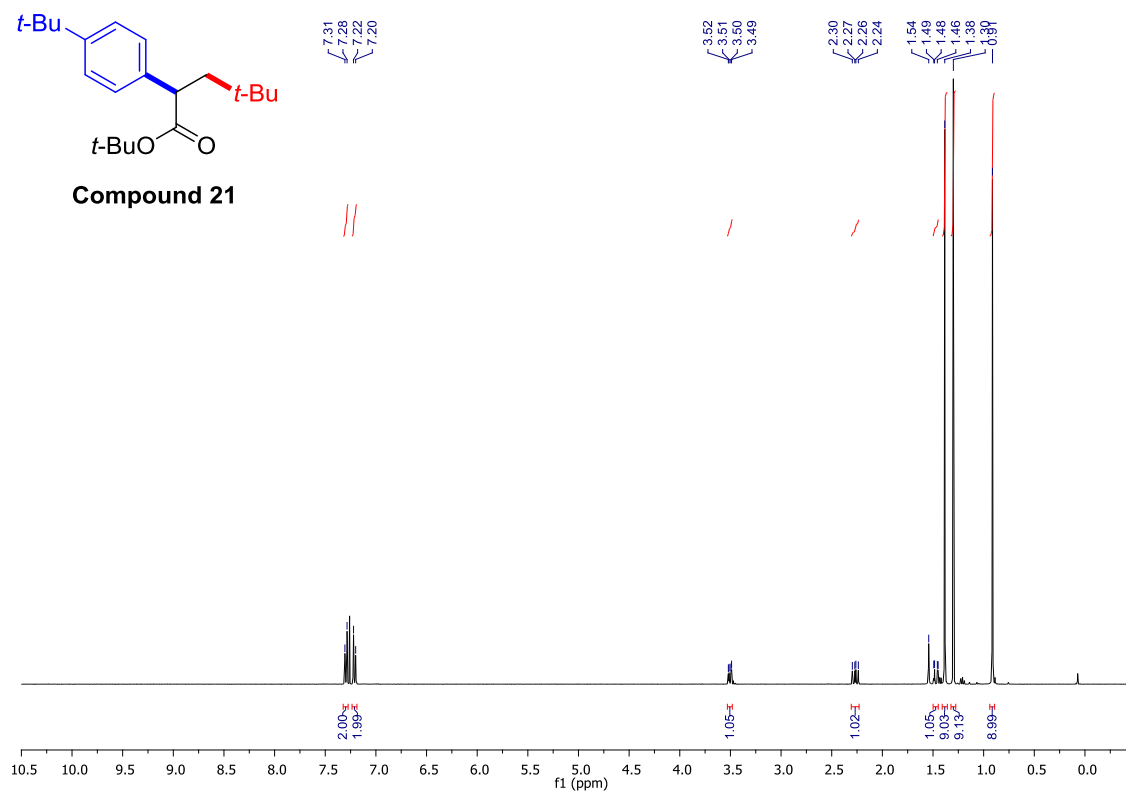
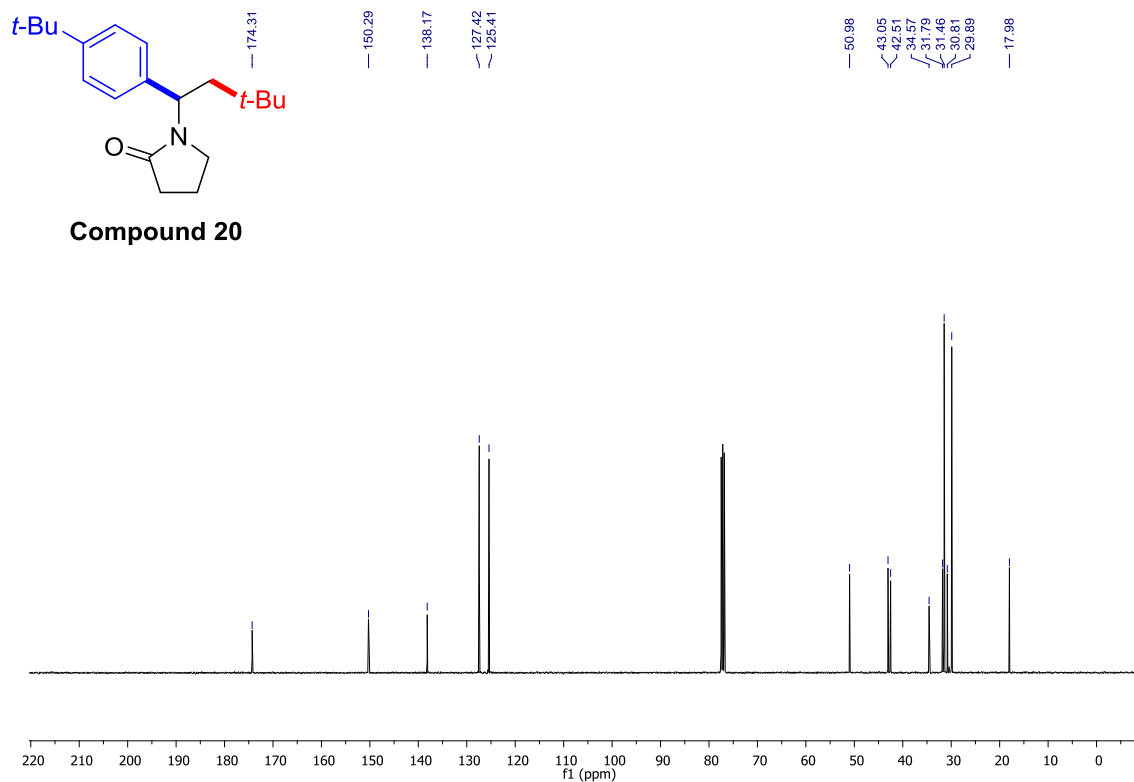


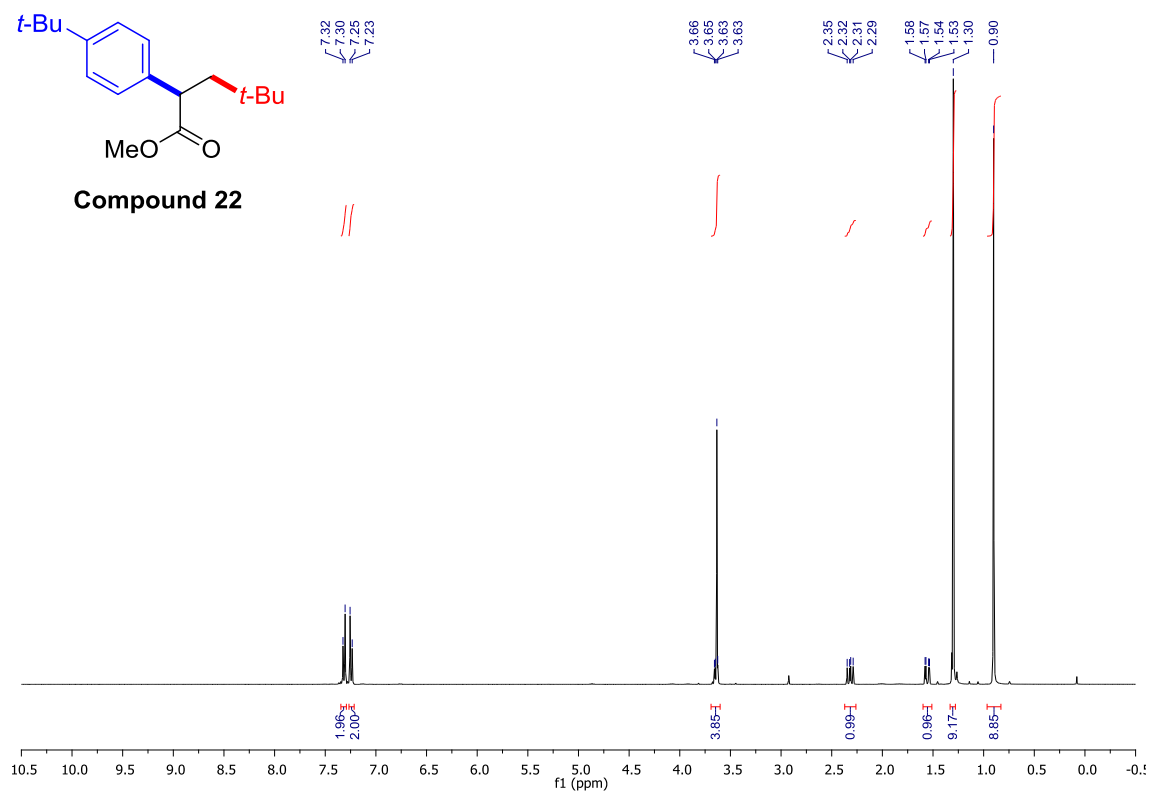
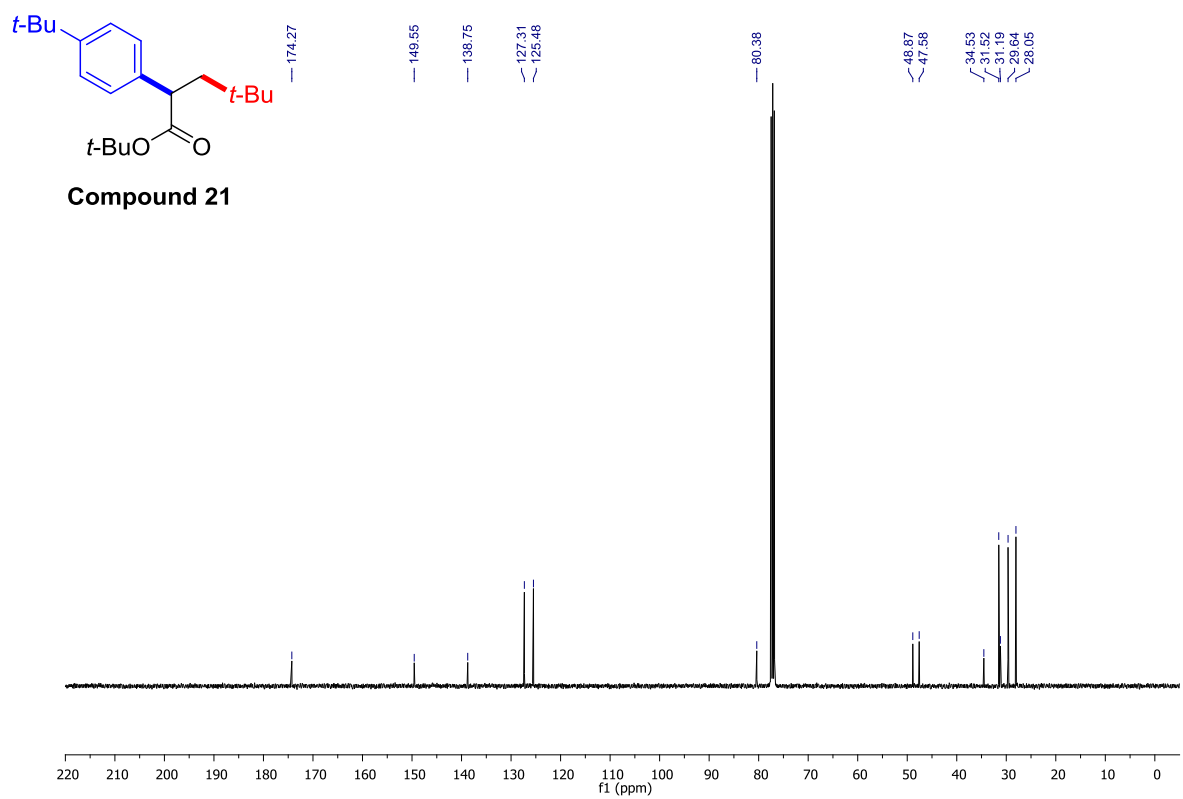


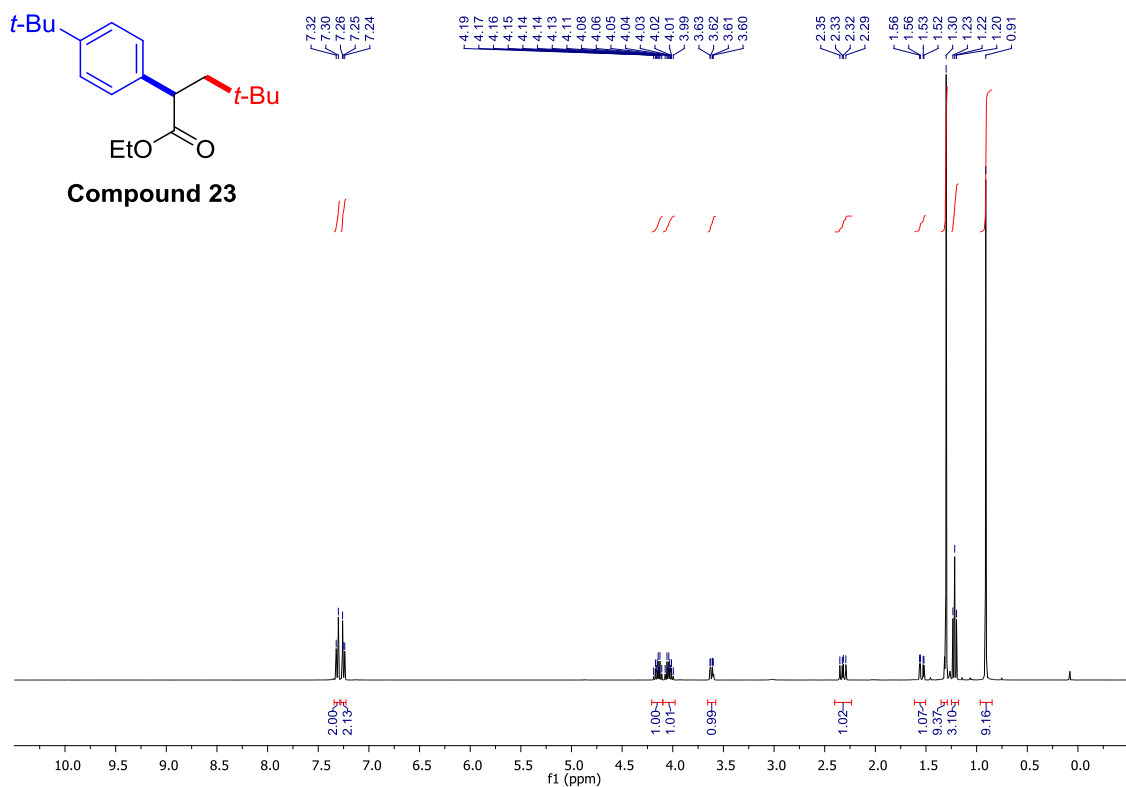
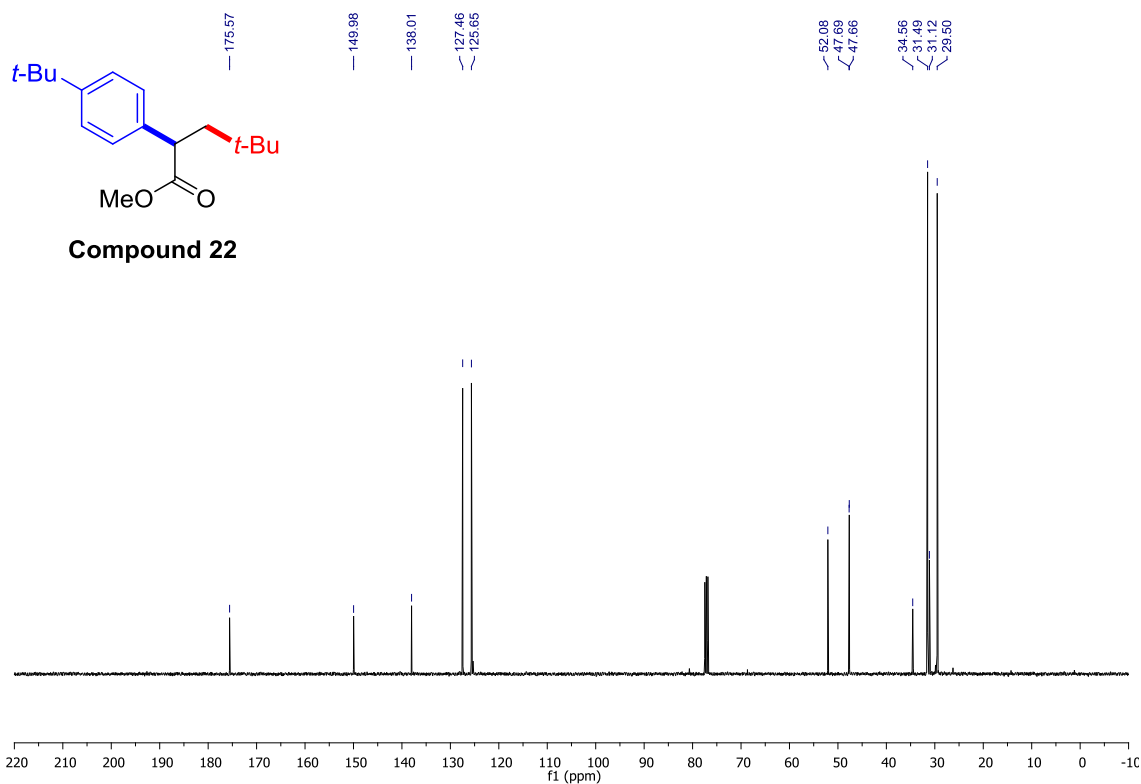


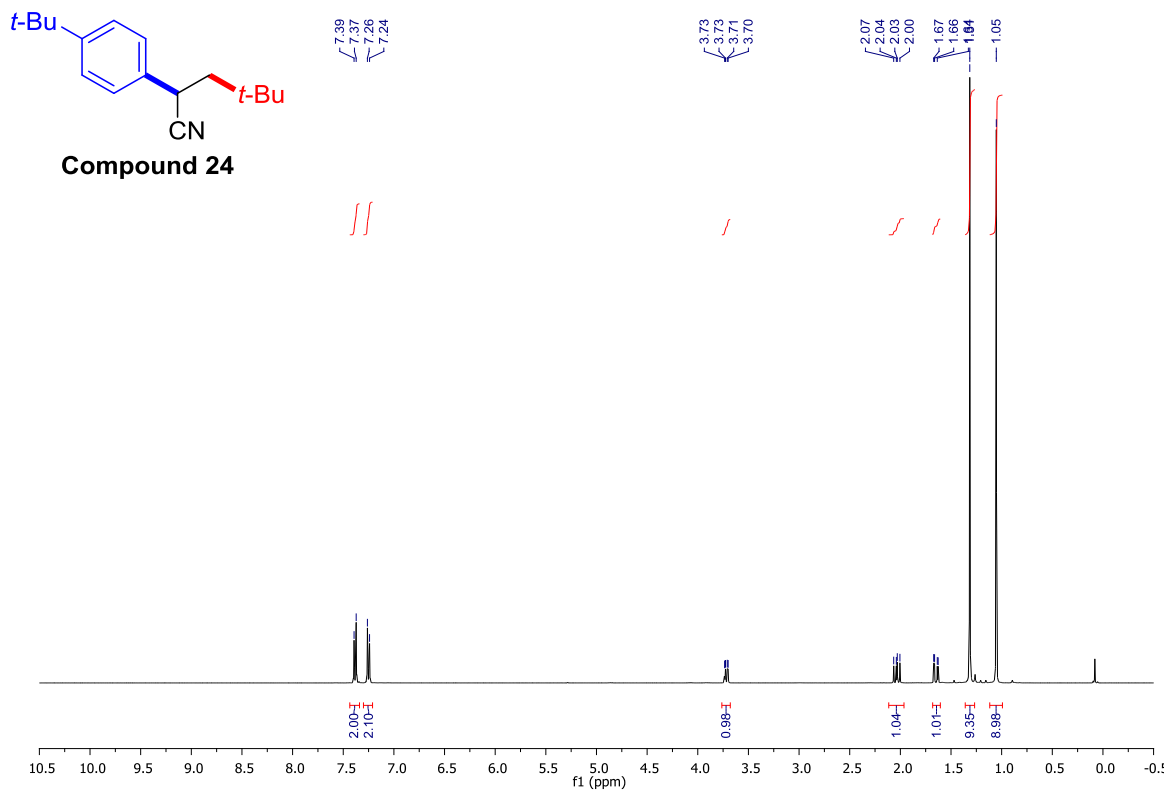
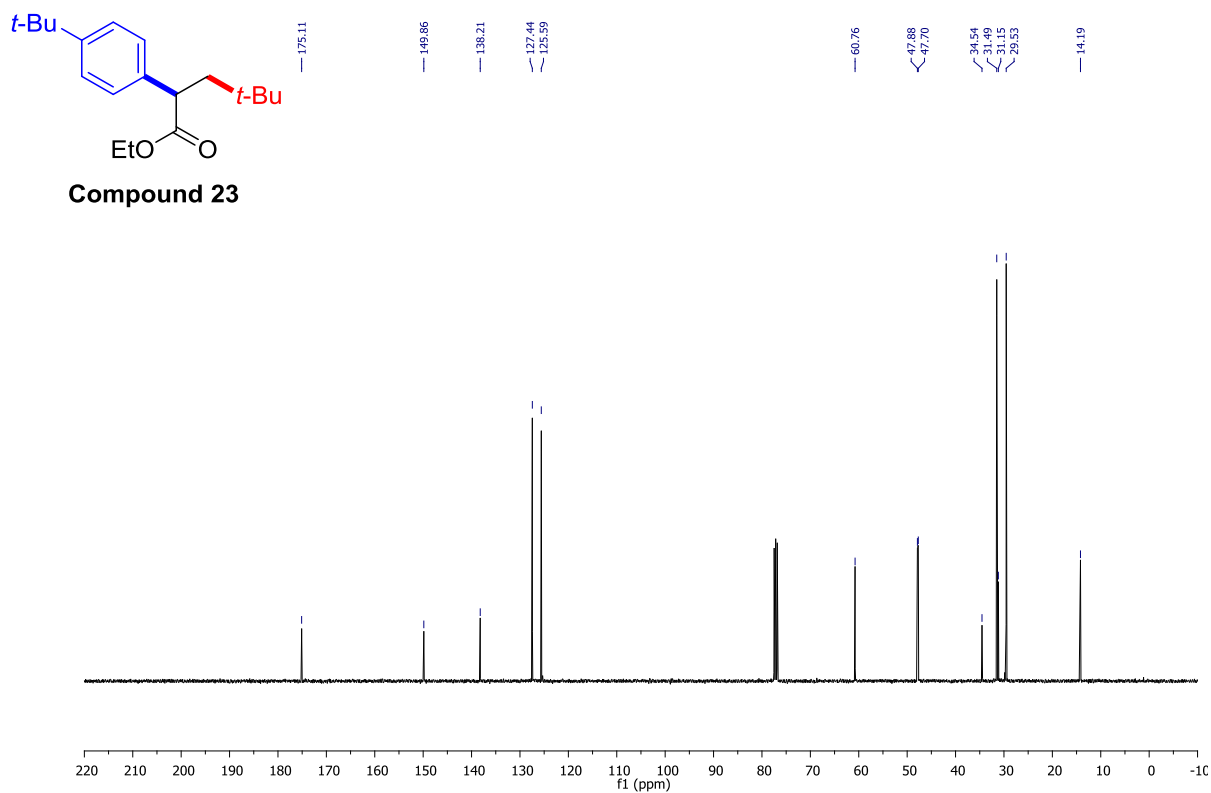


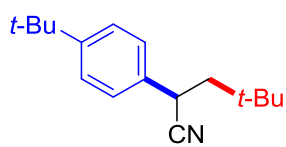




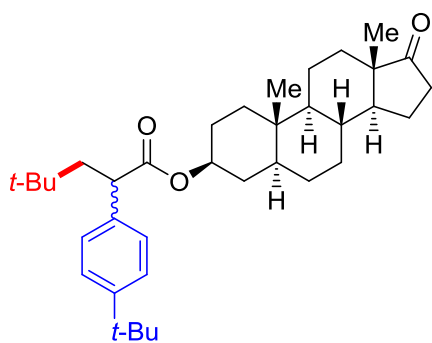
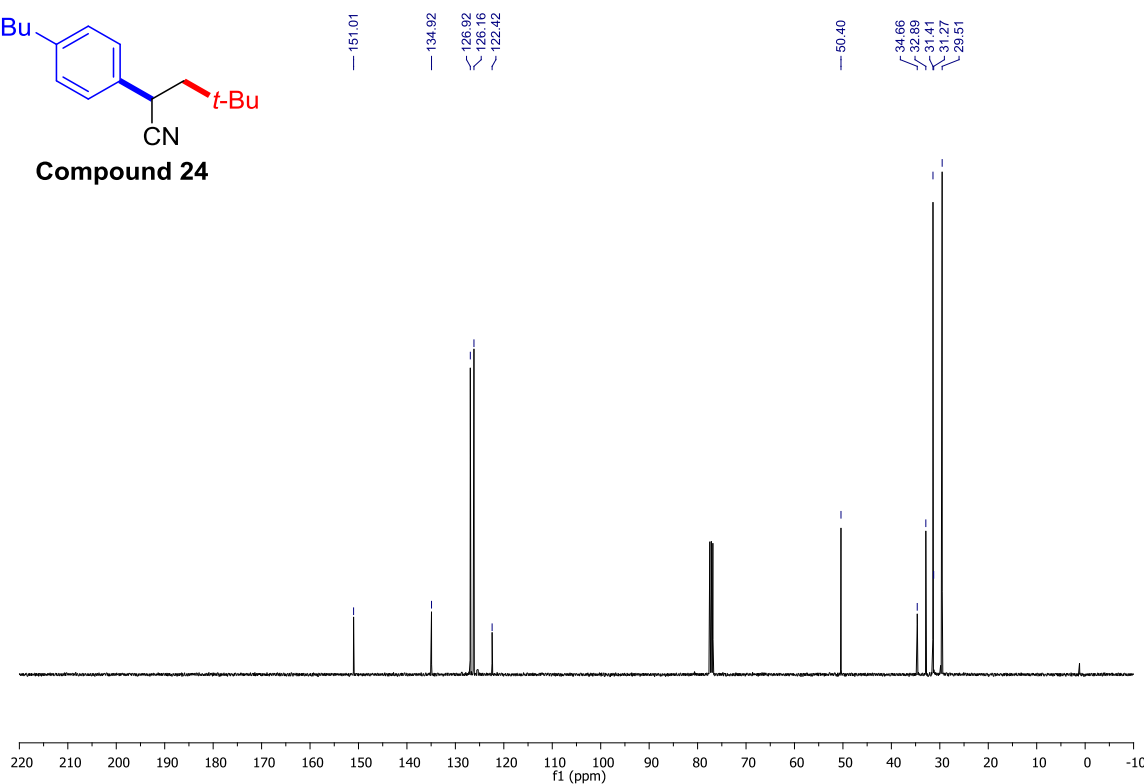




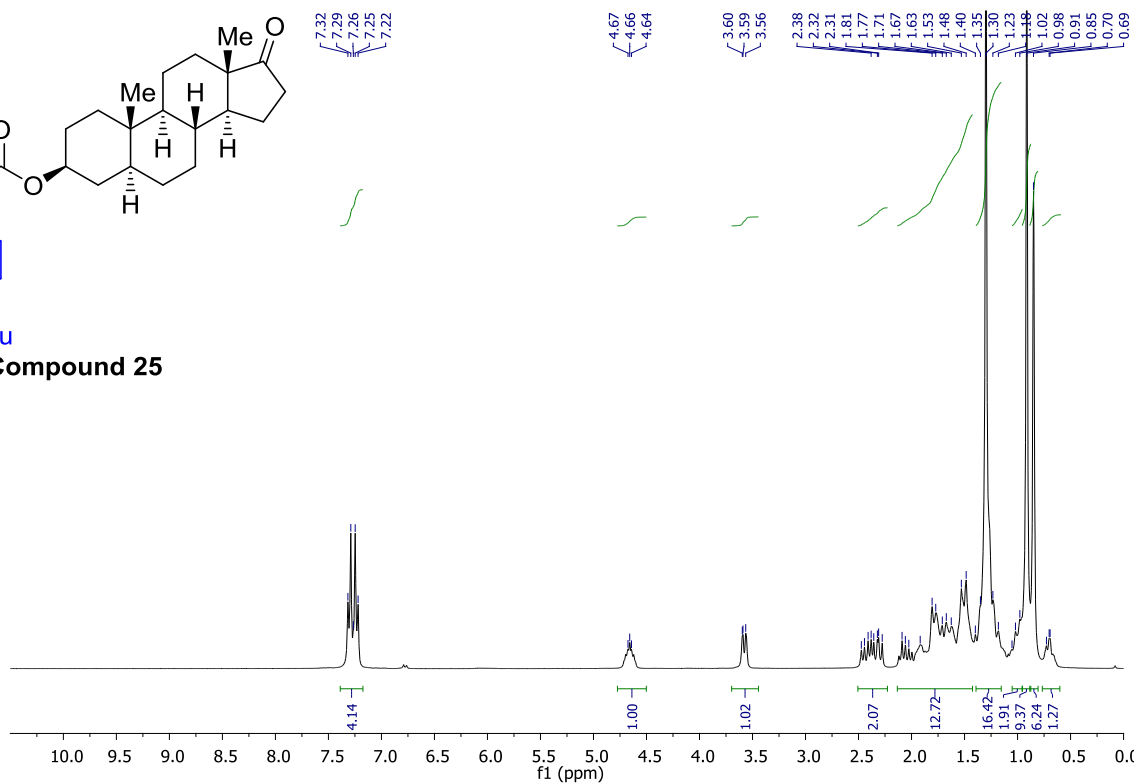


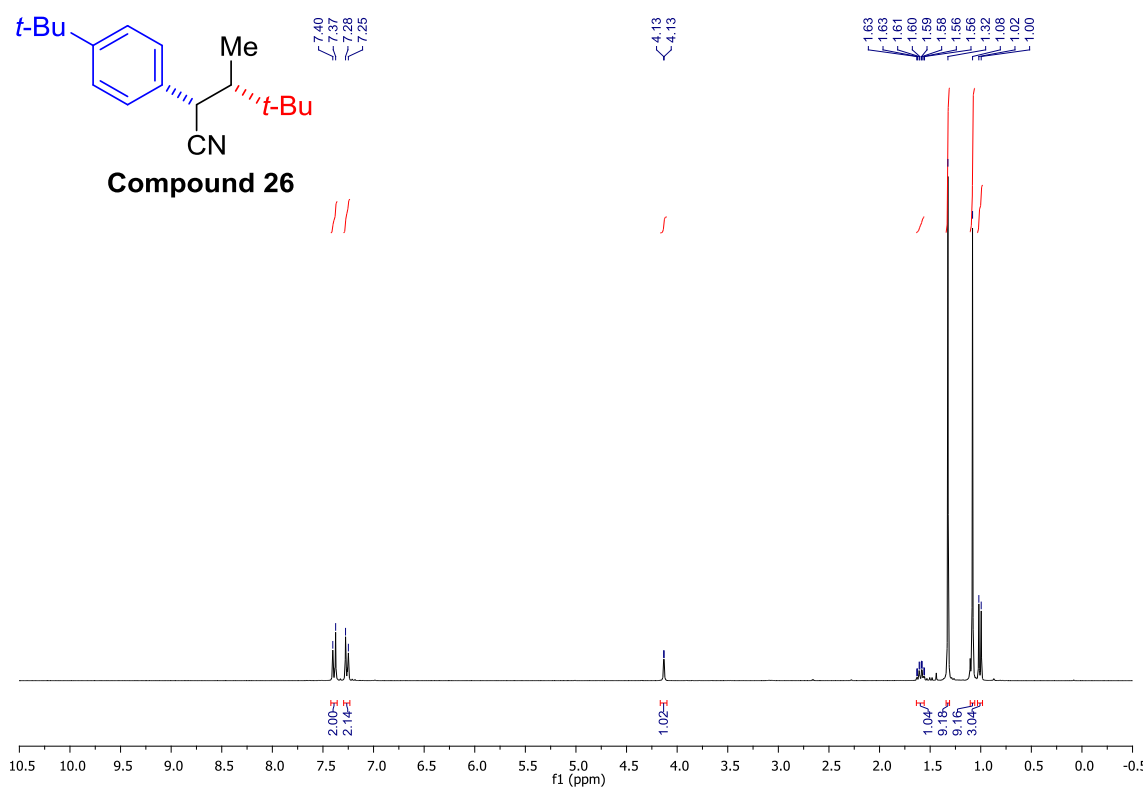
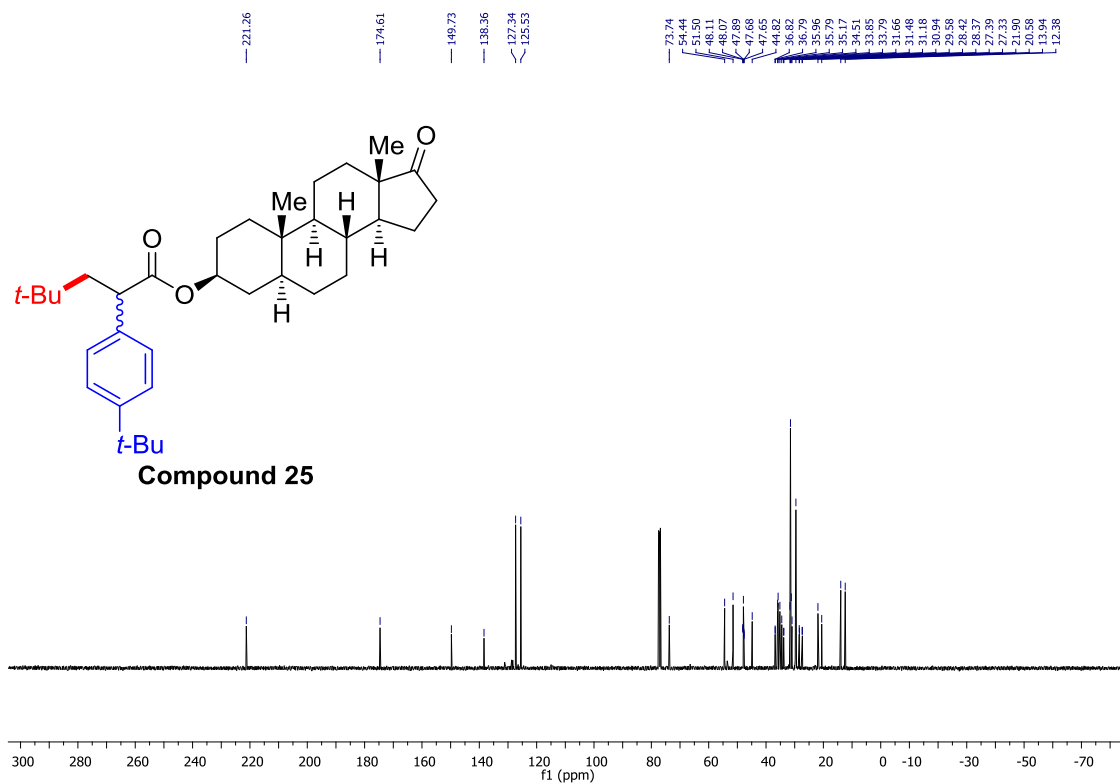


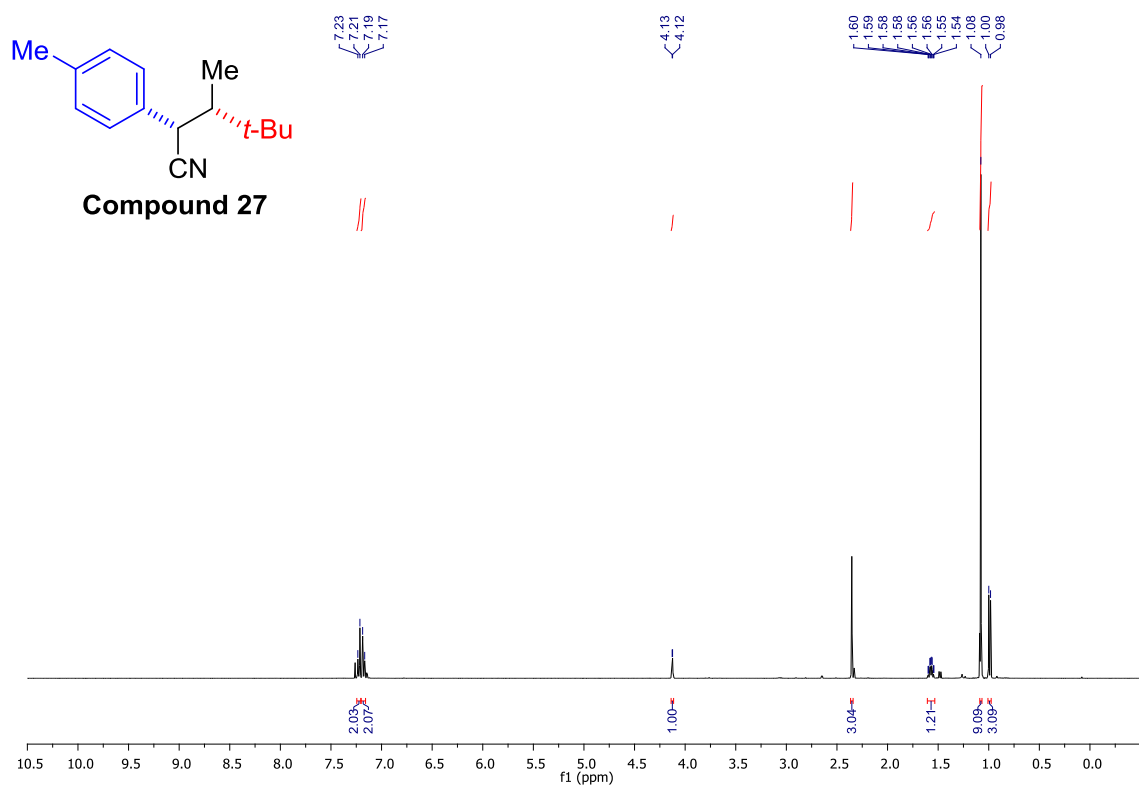
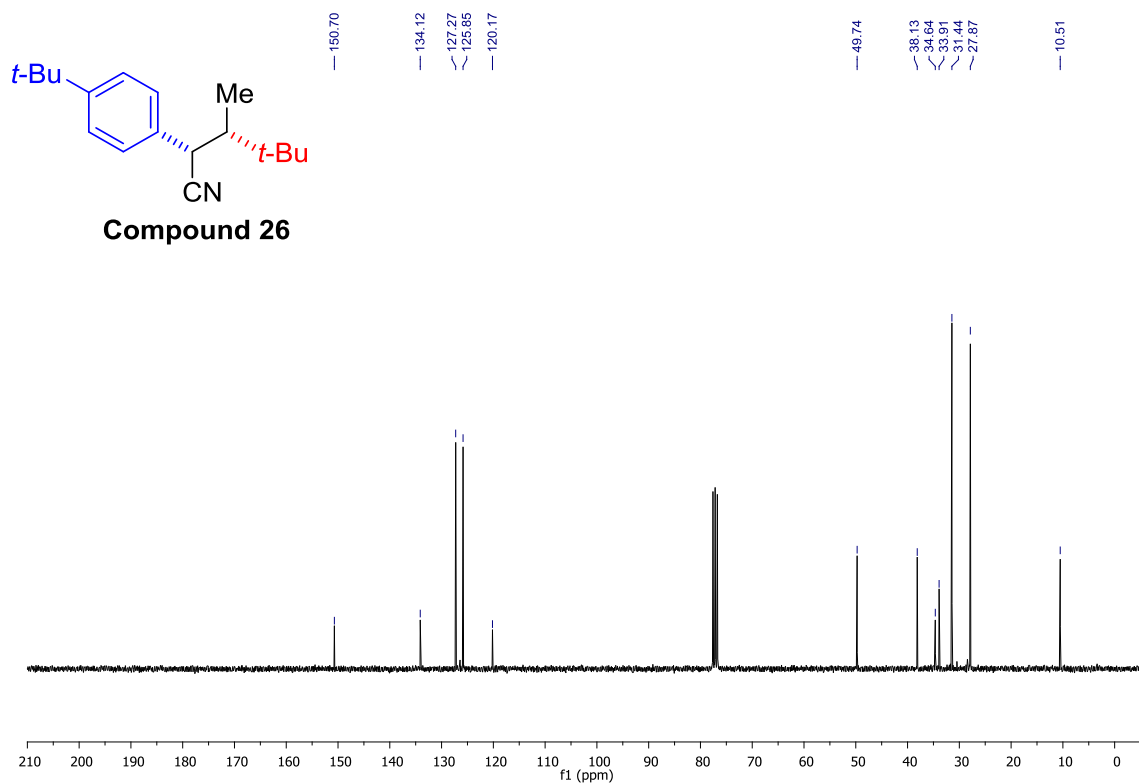
Compound 24

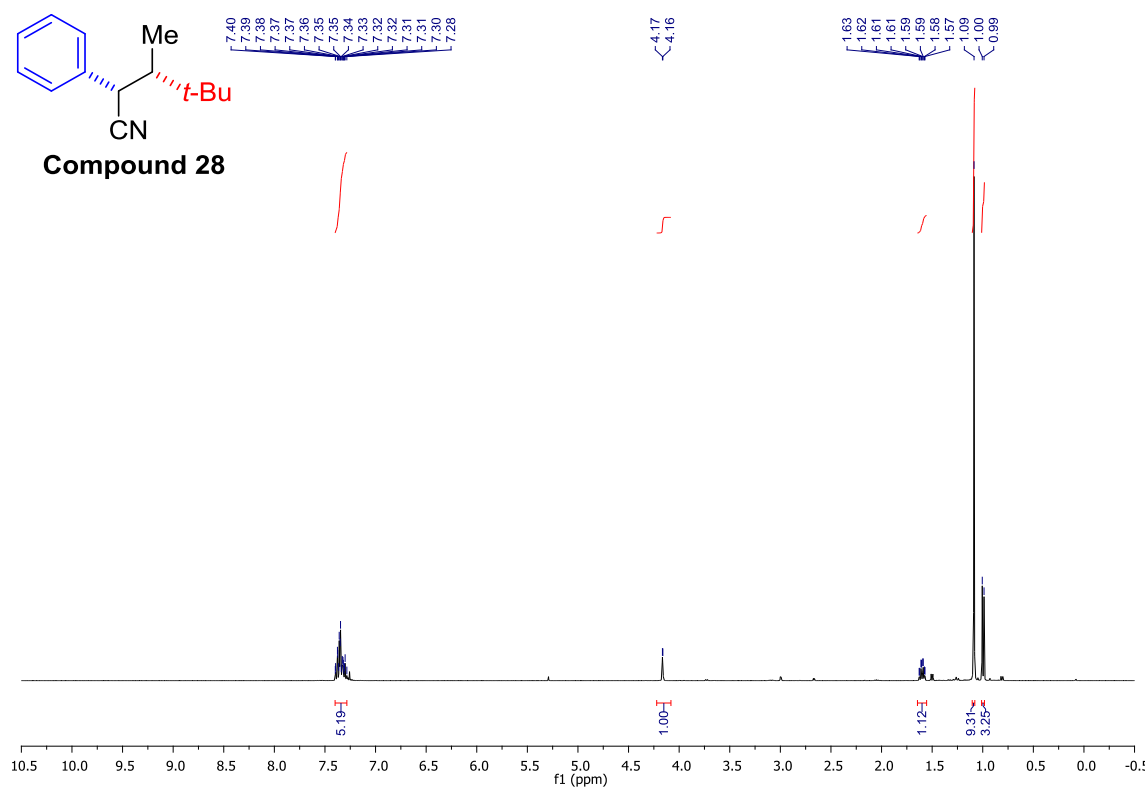
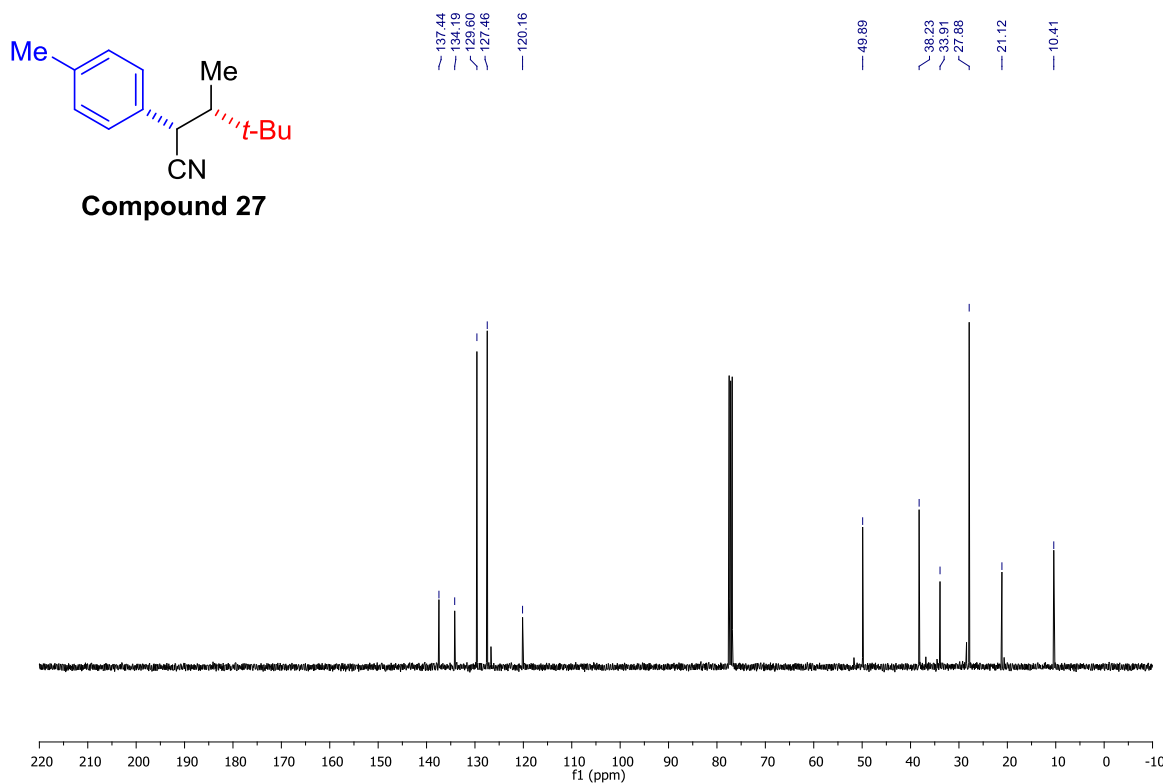


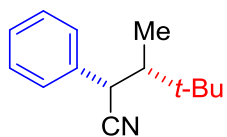
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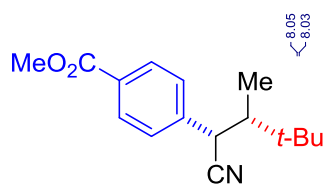
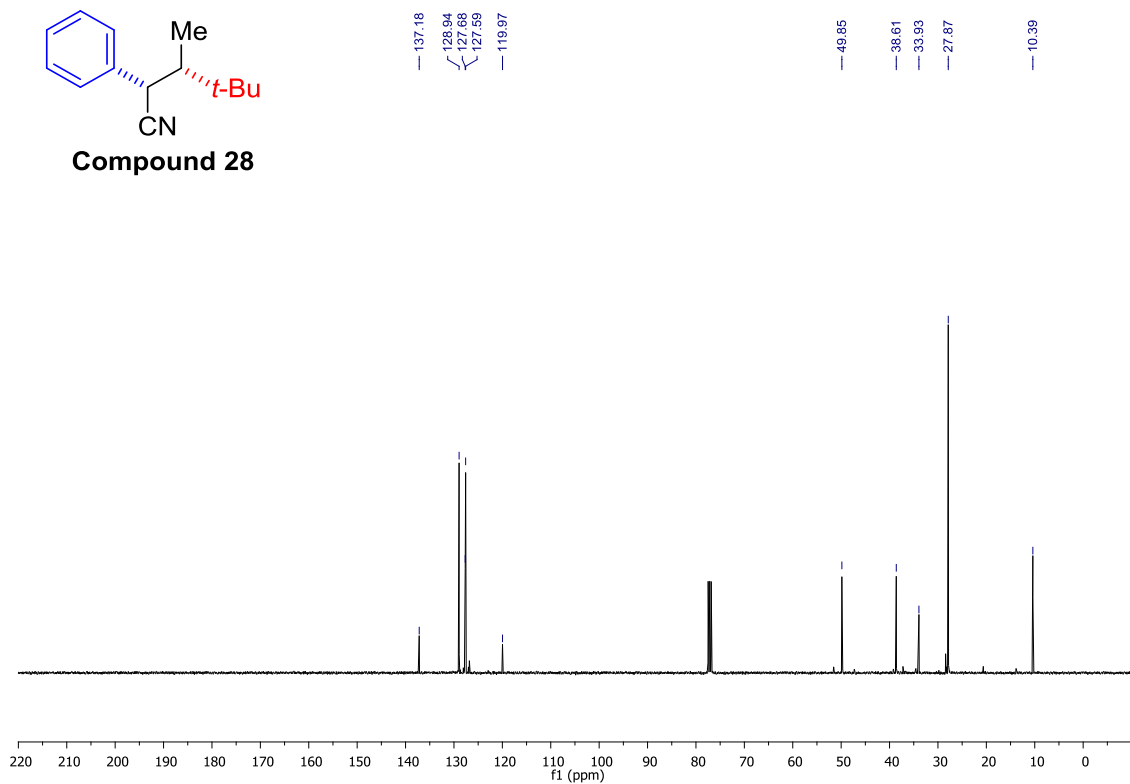




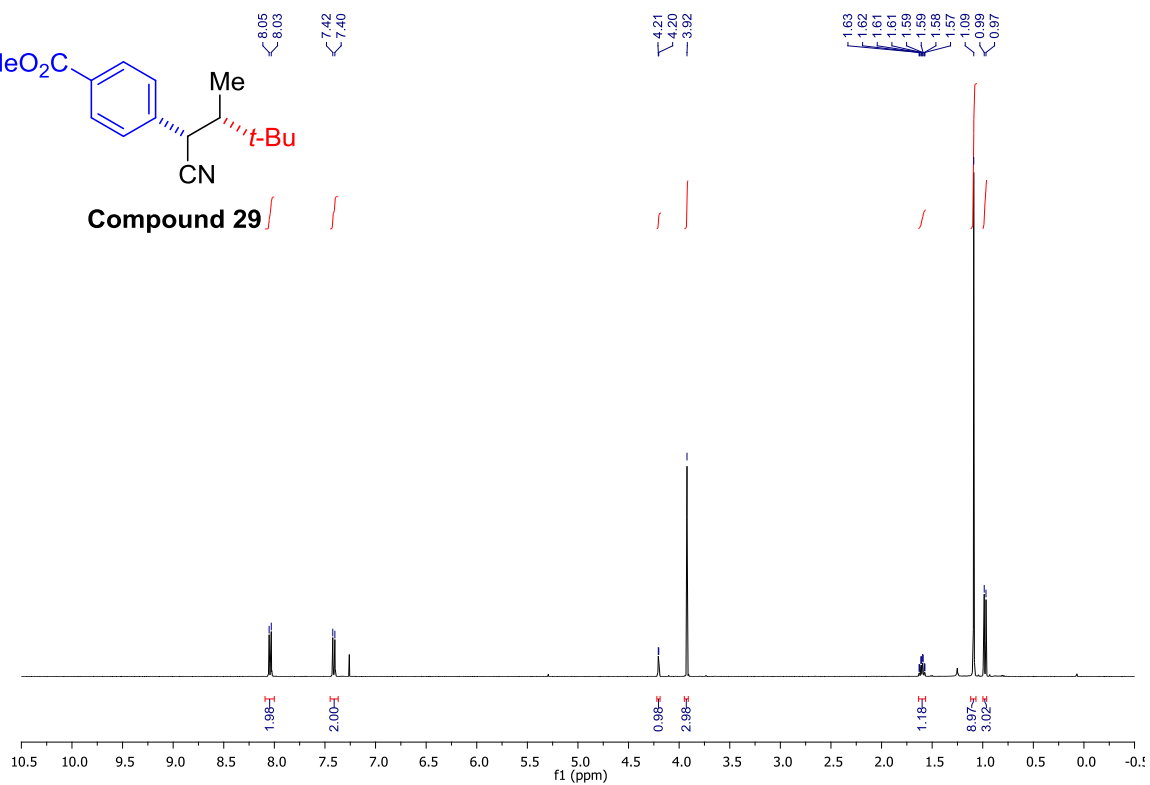


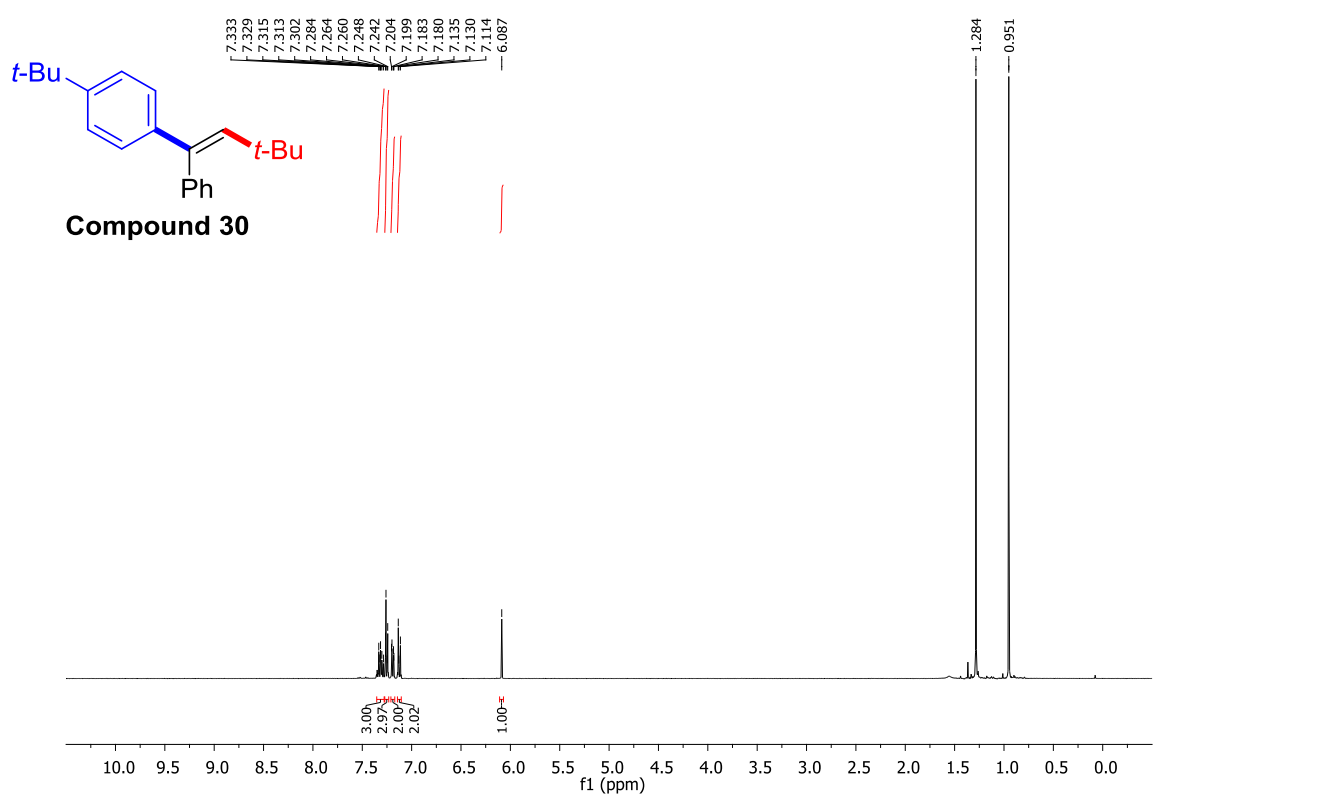
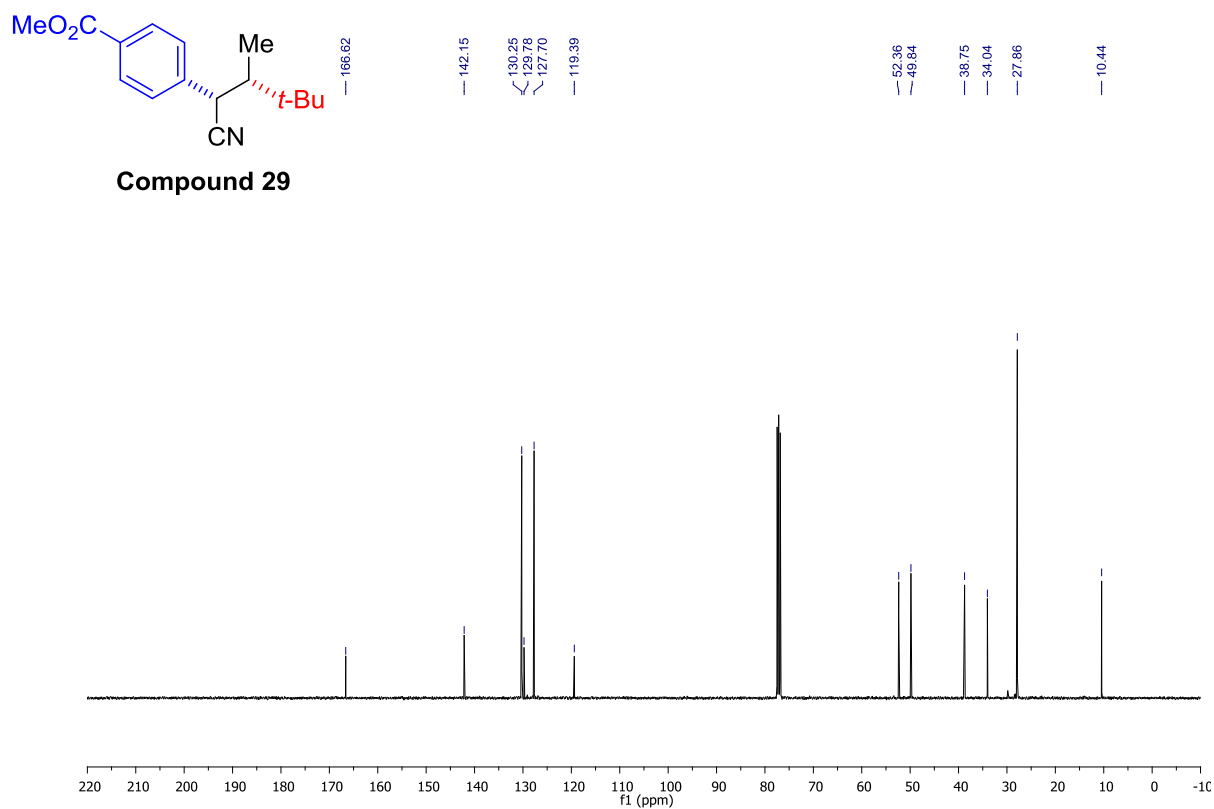


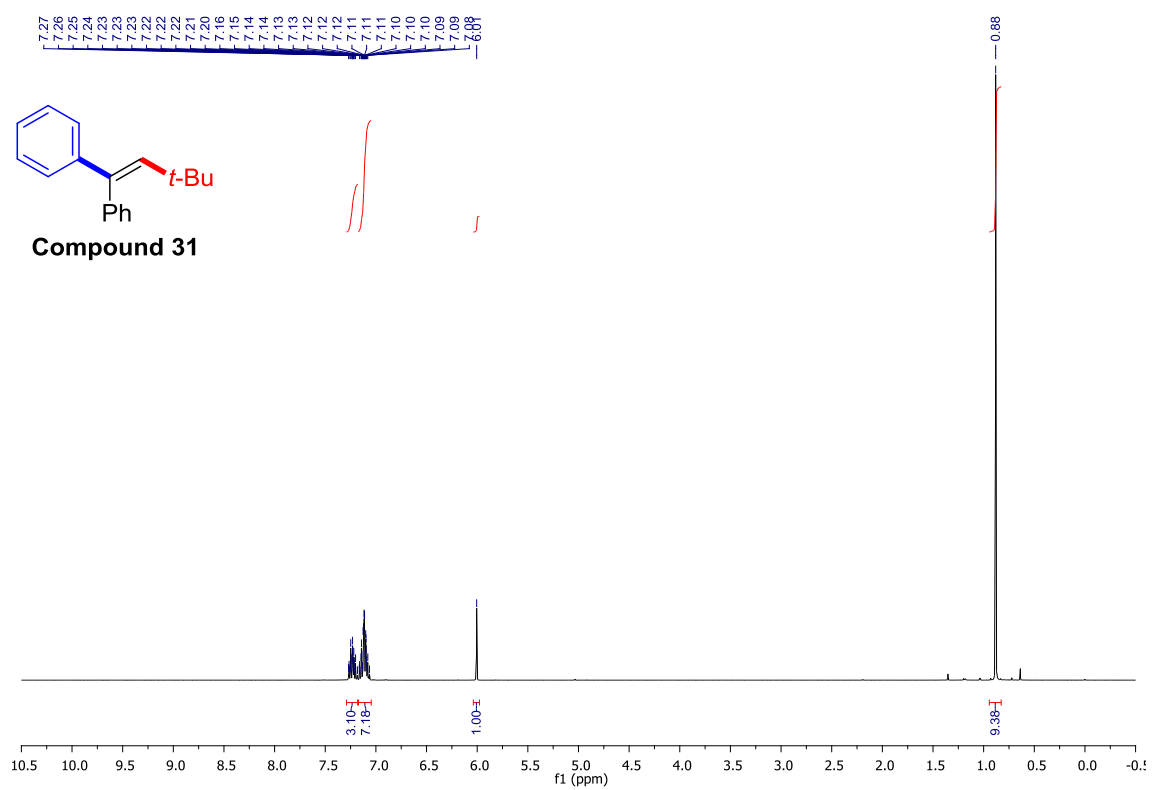
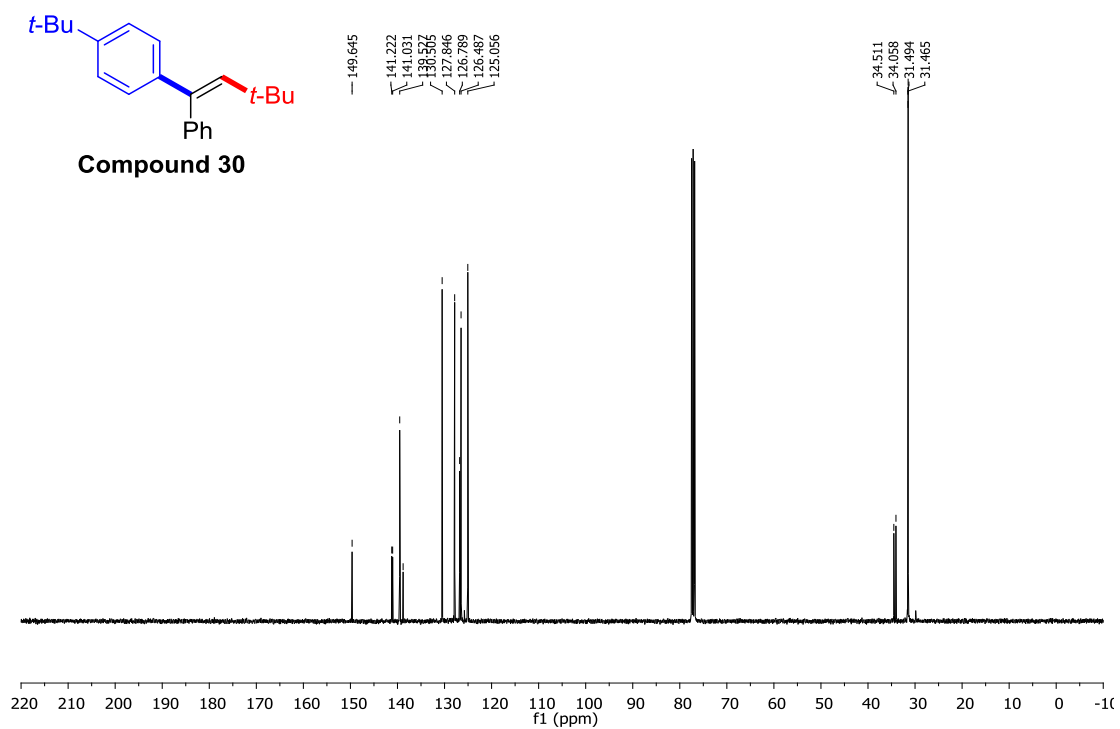
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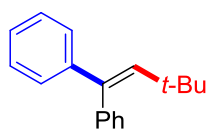


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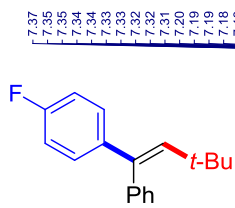
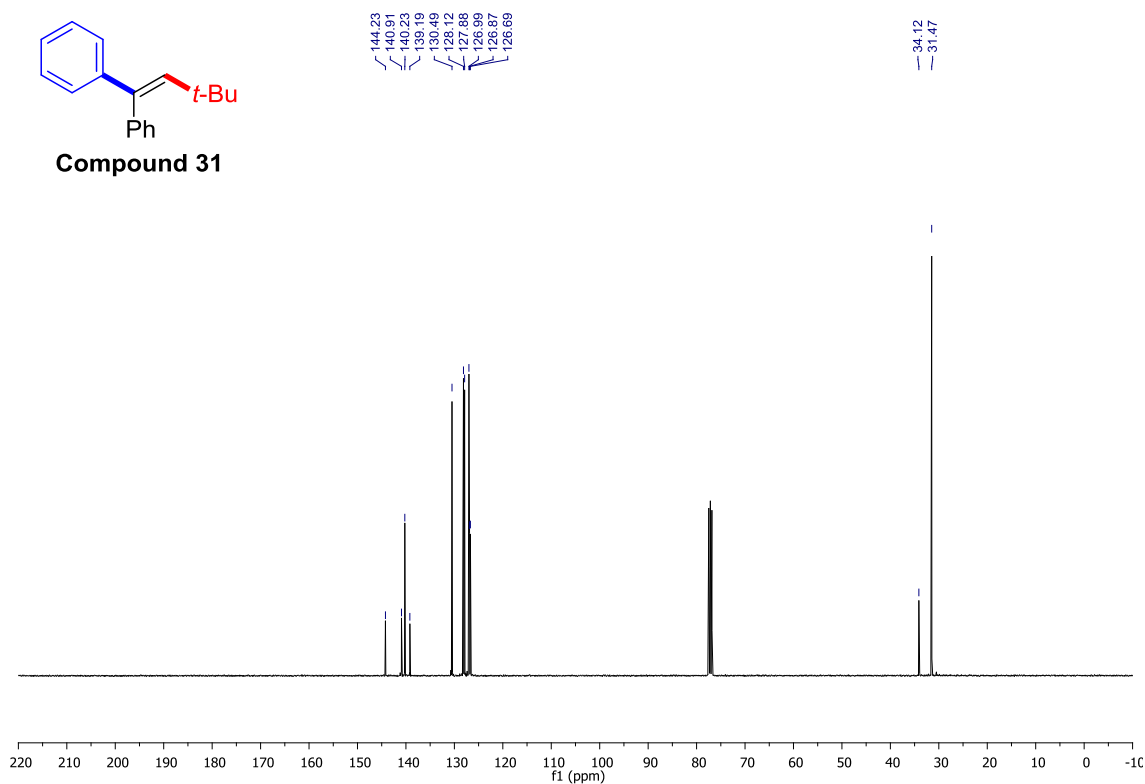




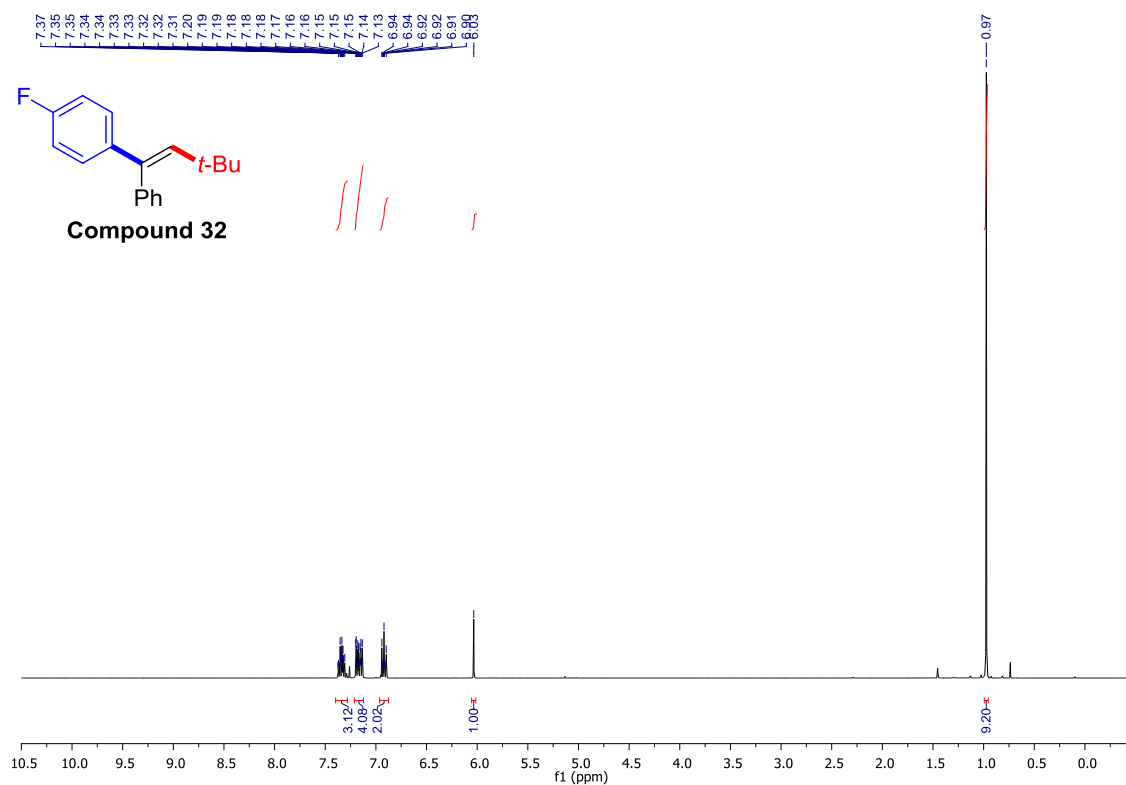


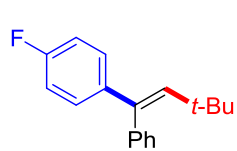


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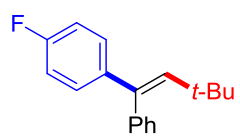
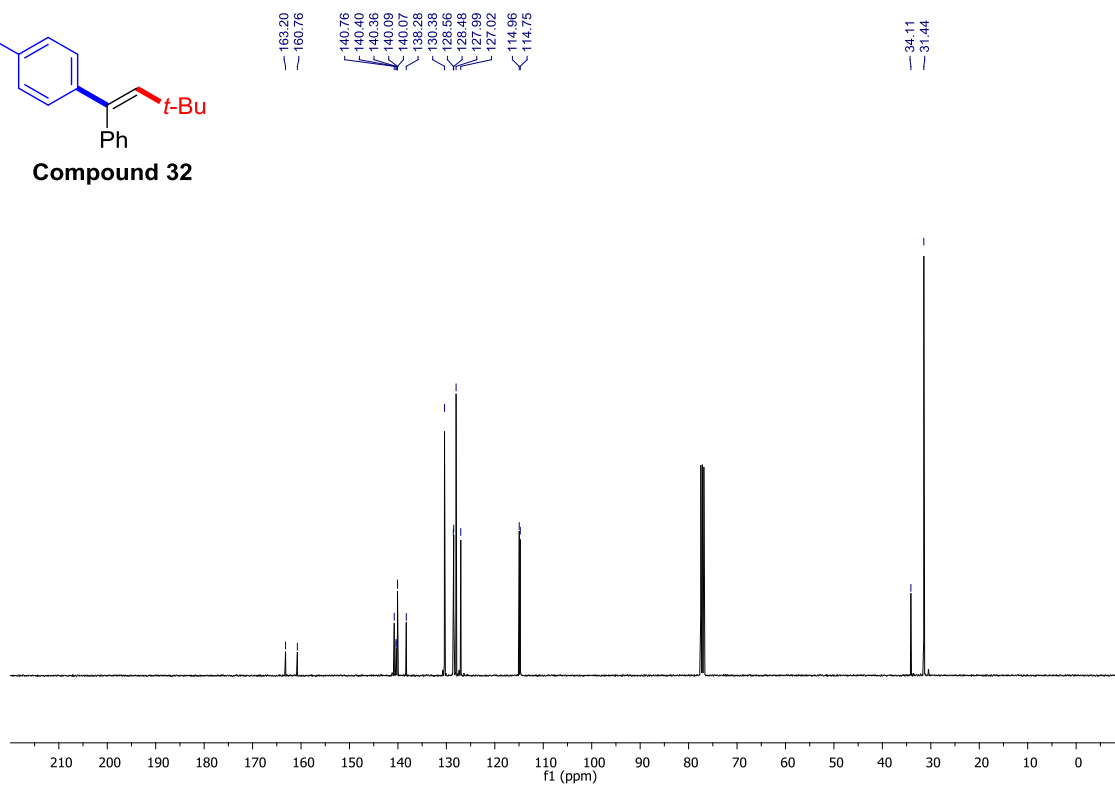


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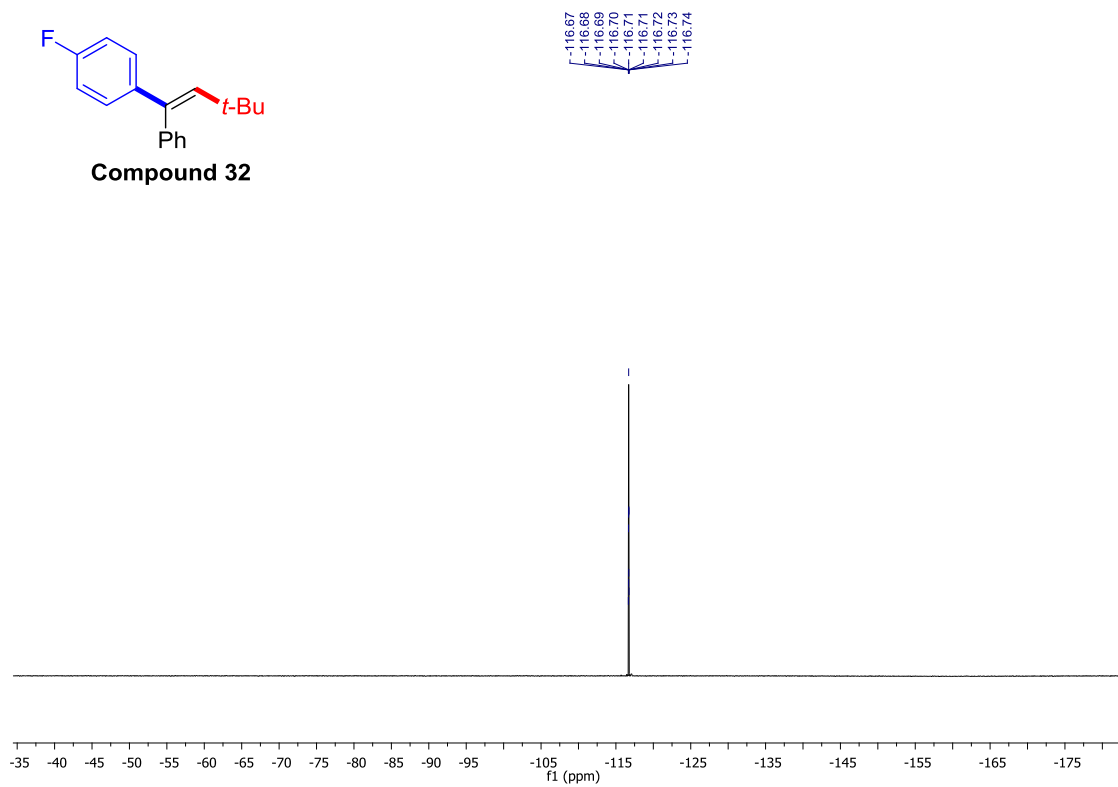


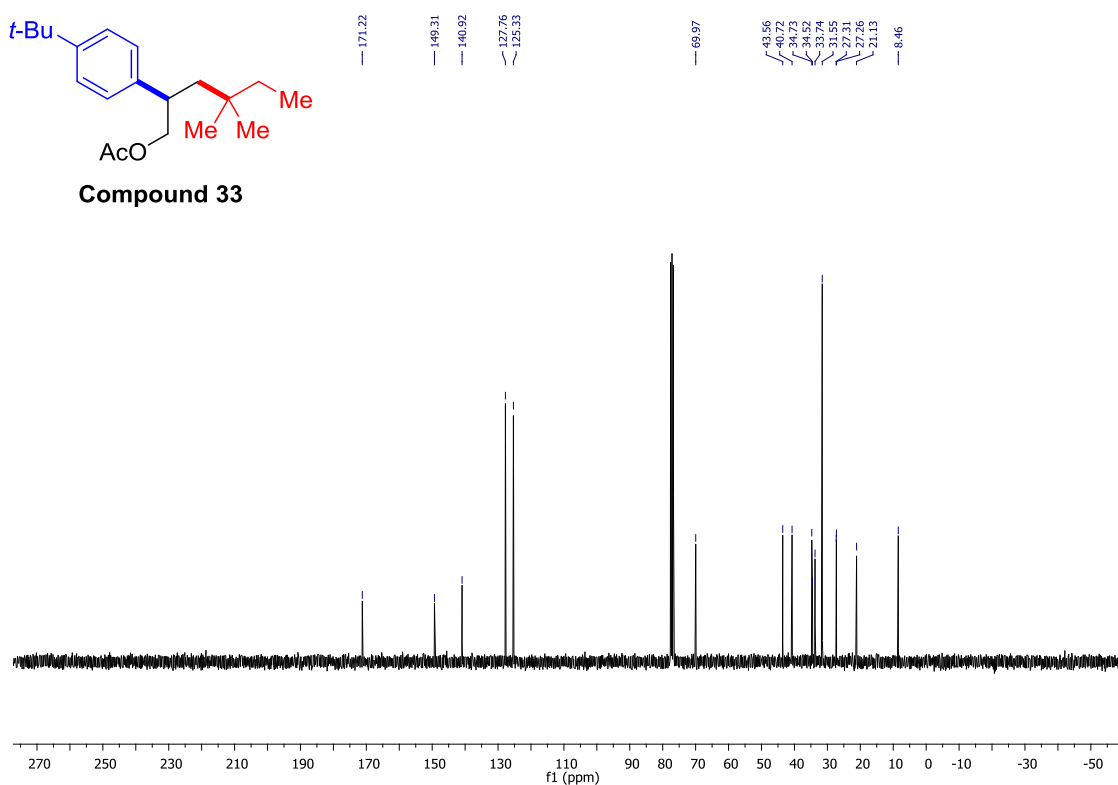
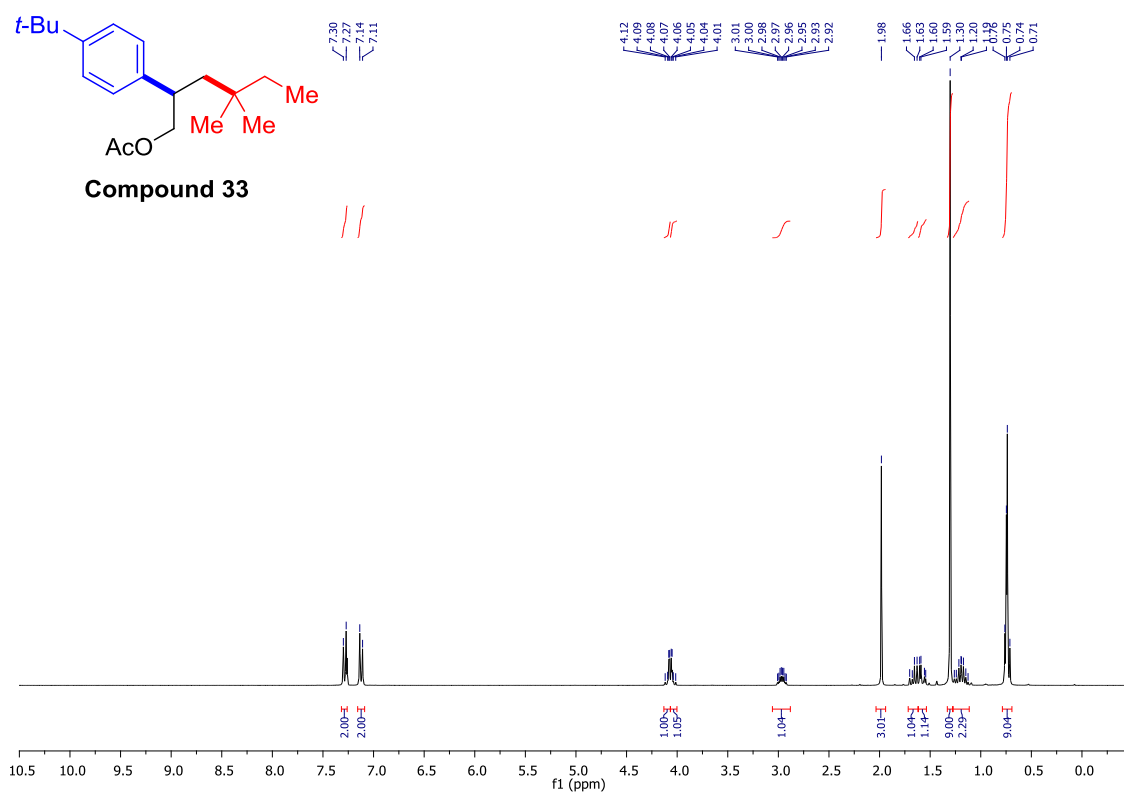


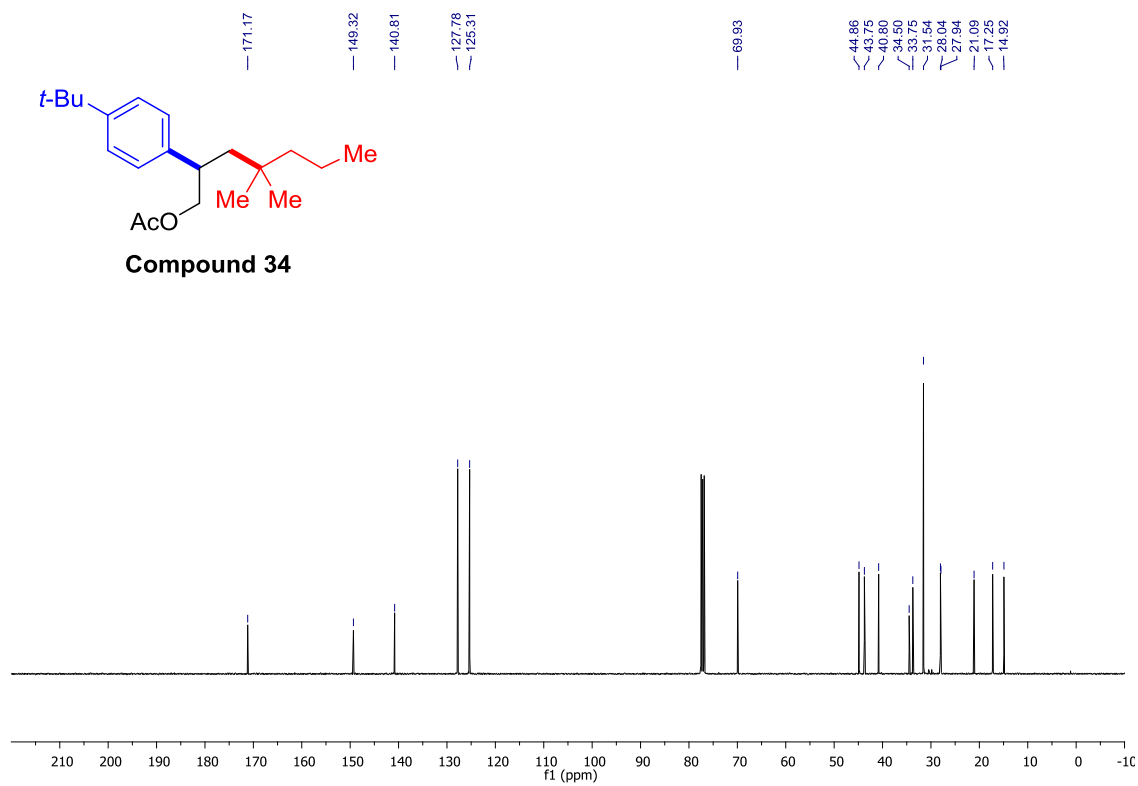
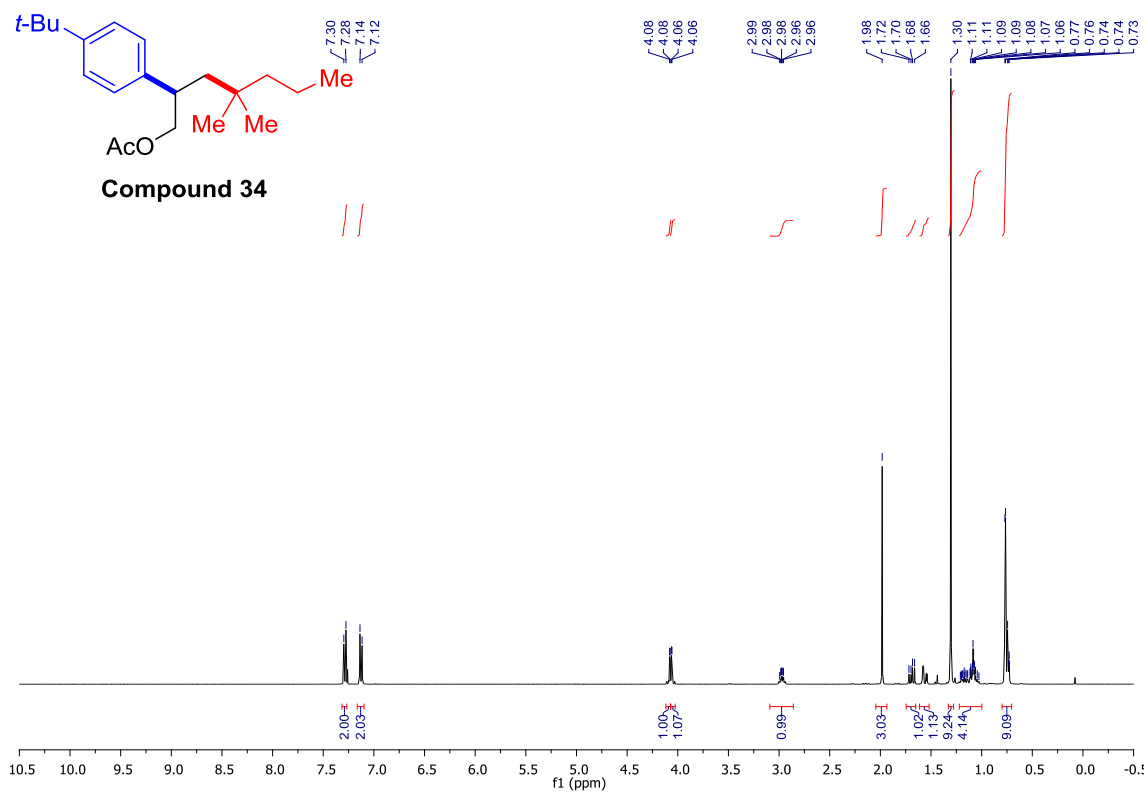
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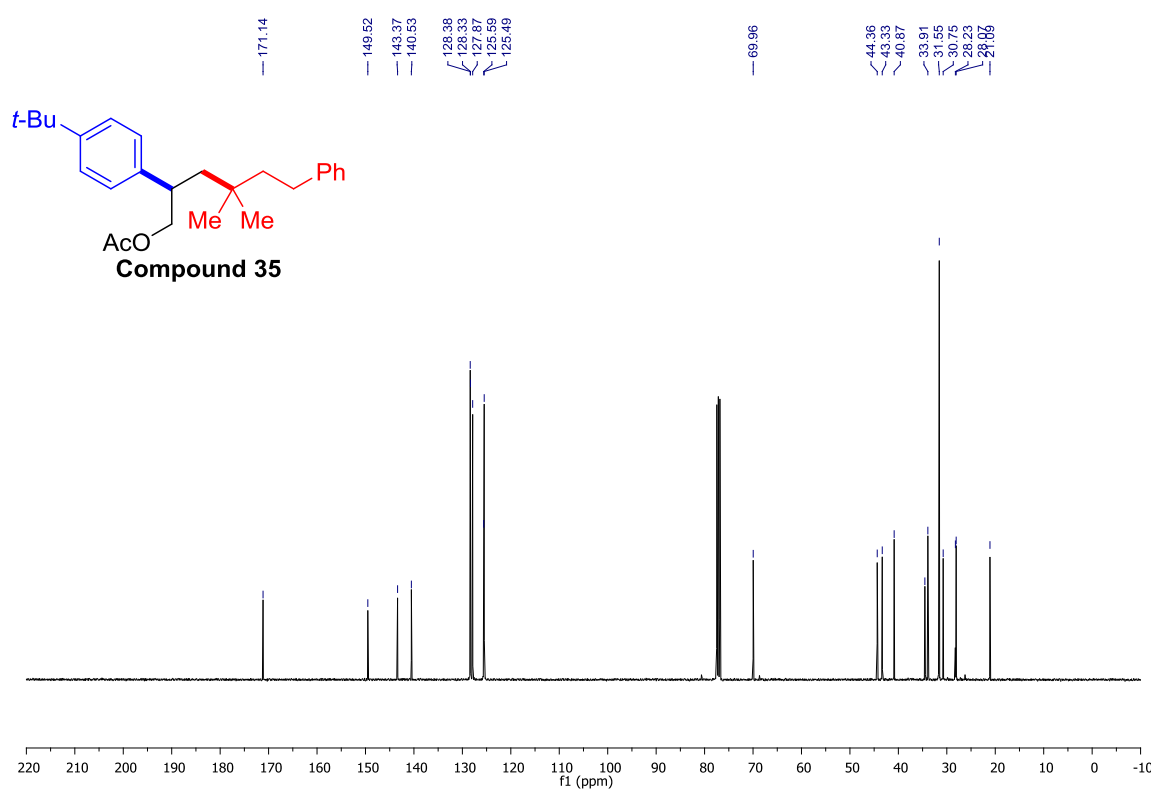
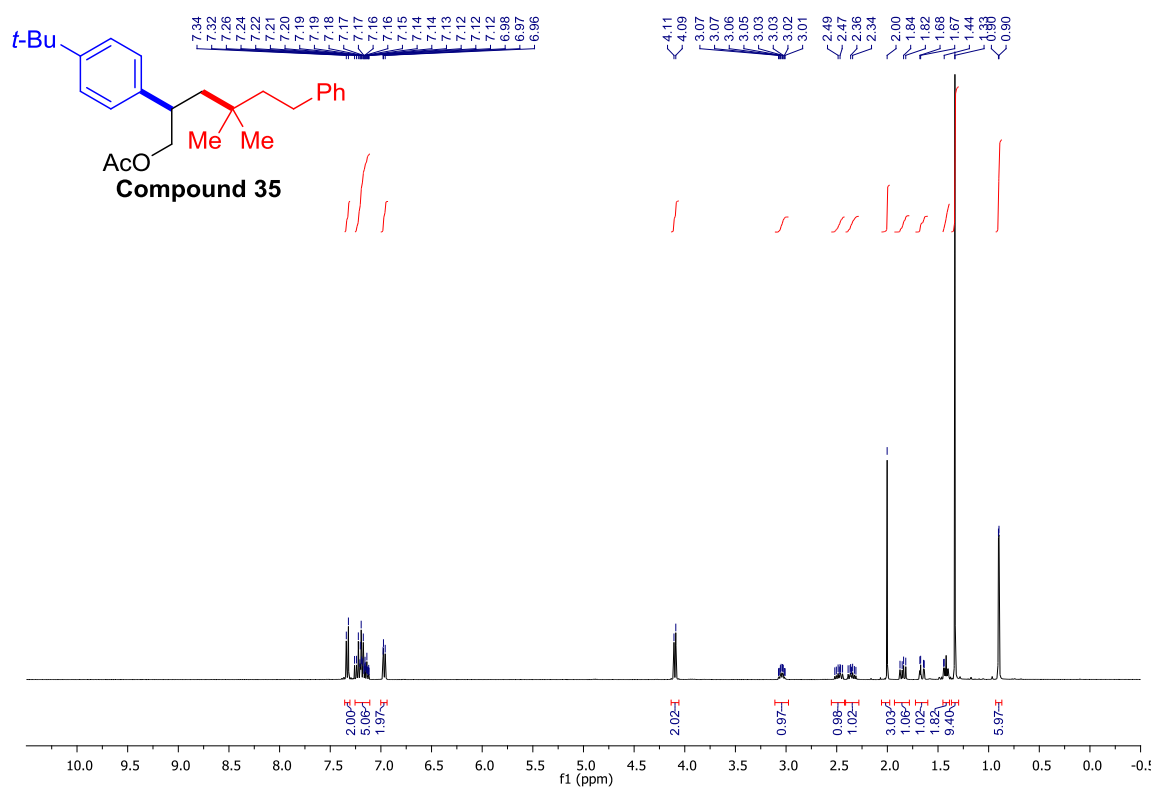


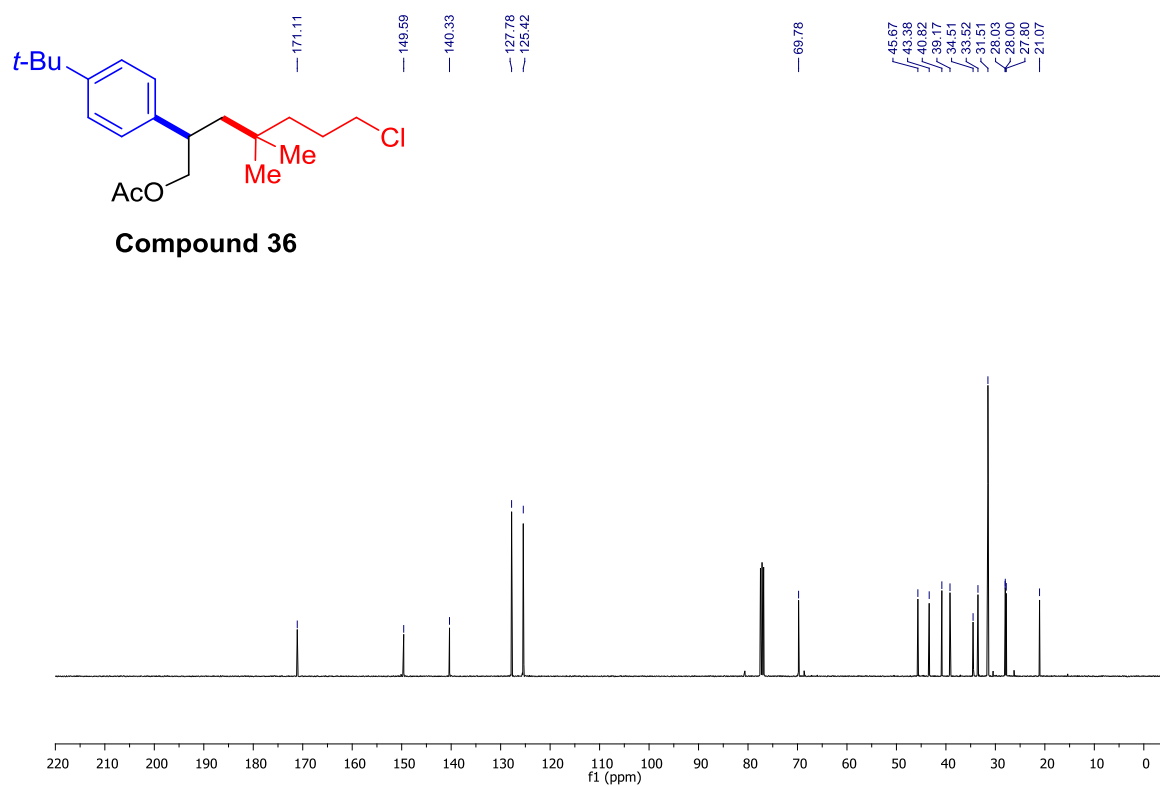
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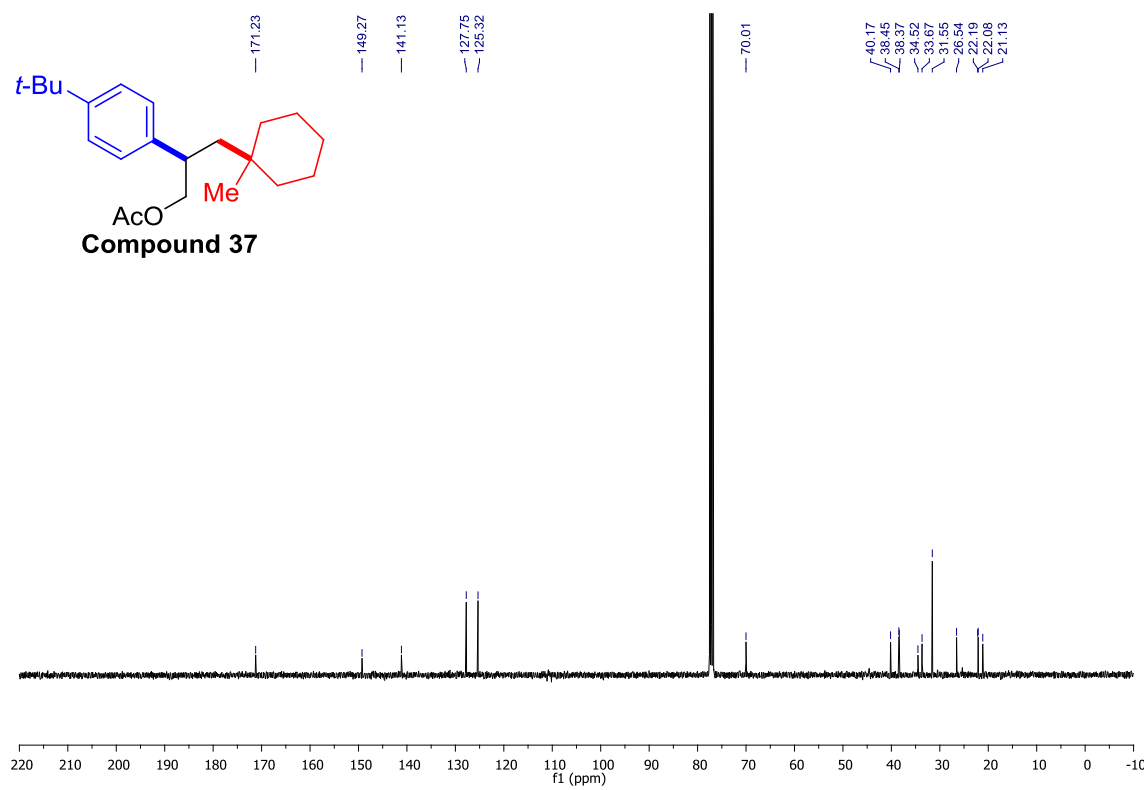
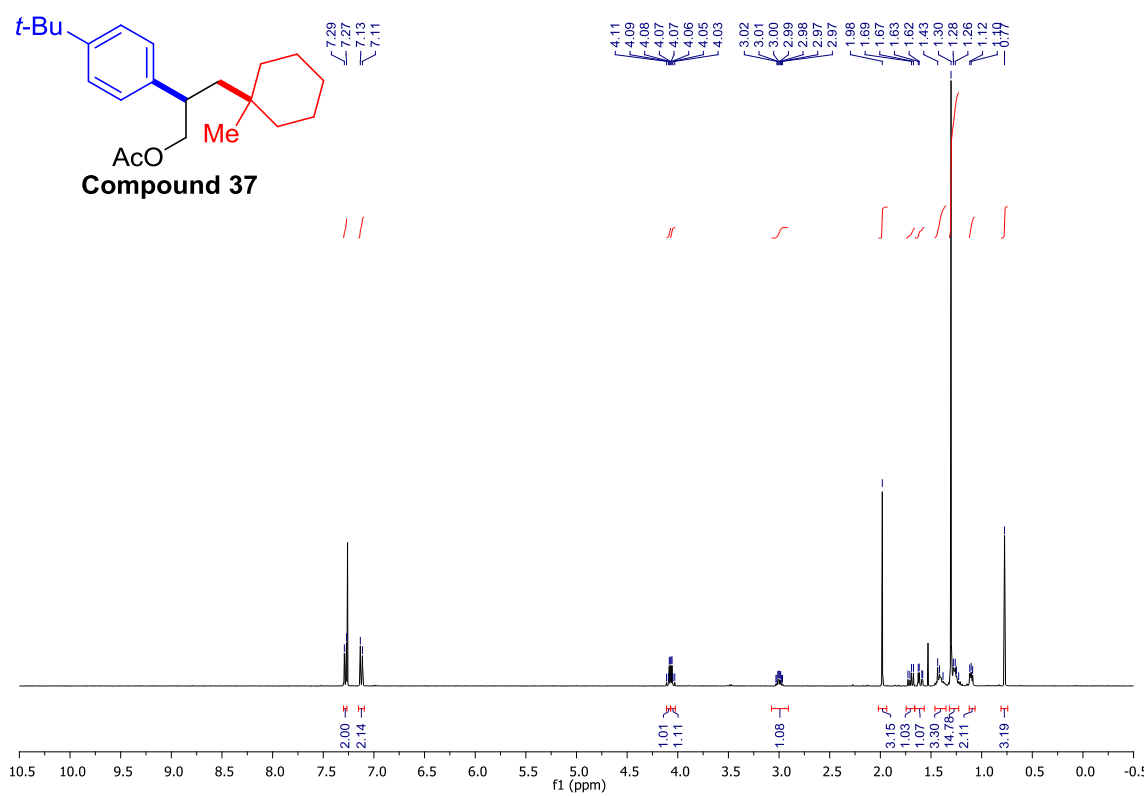


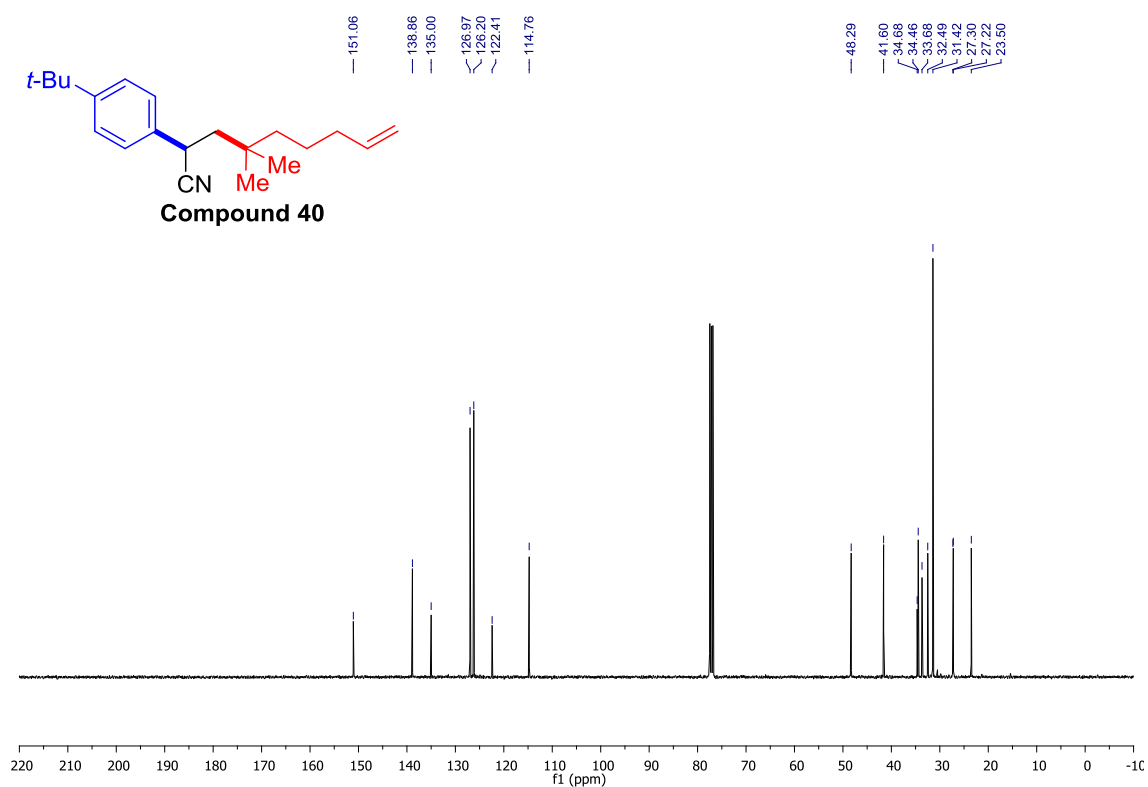
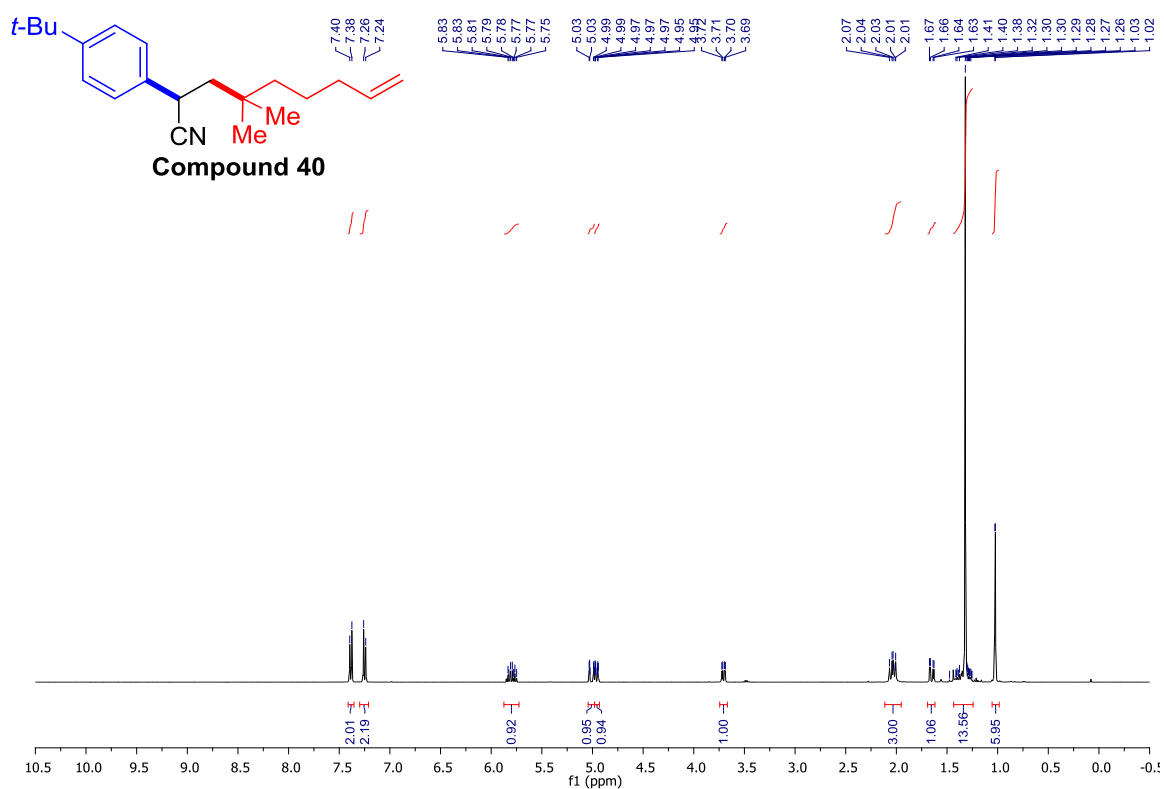


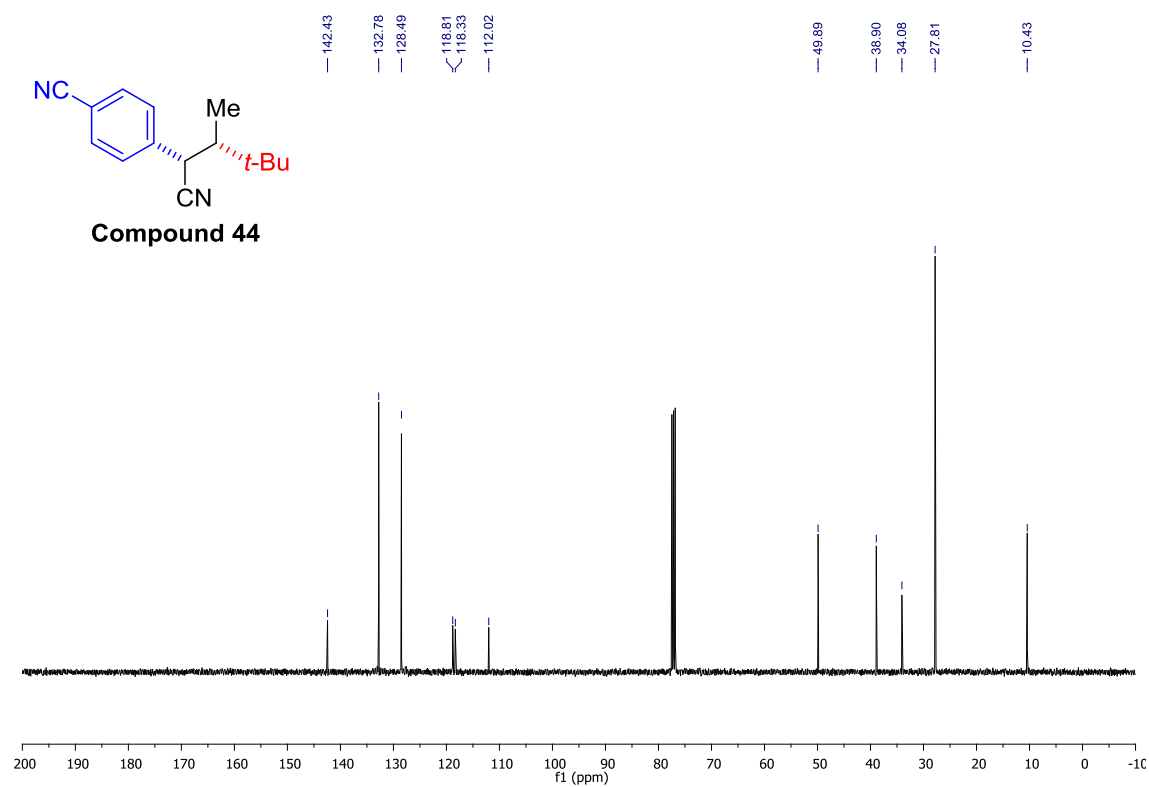
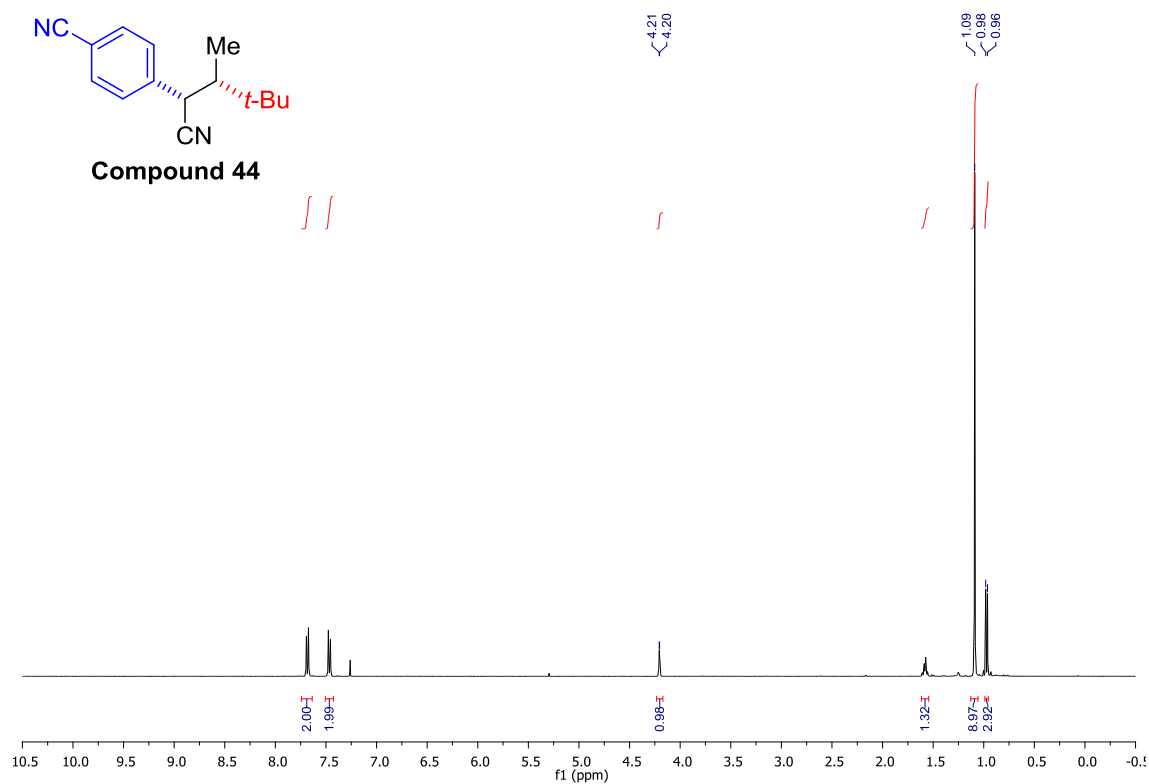


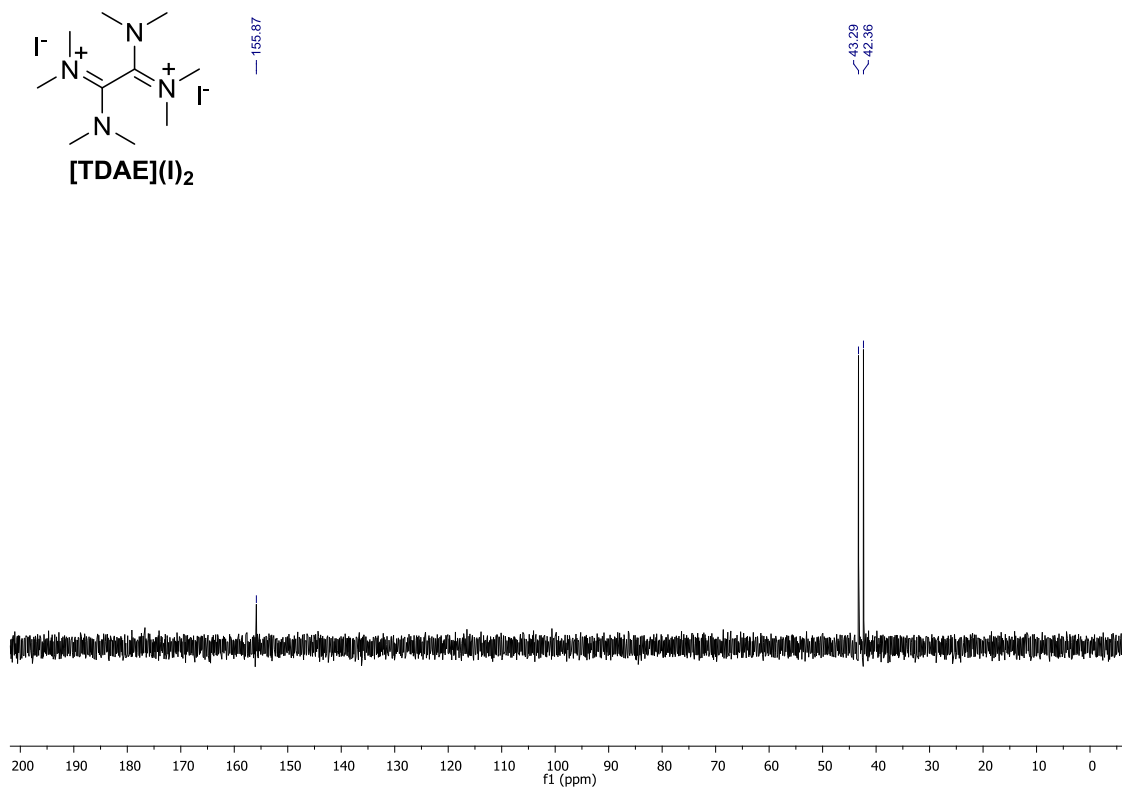
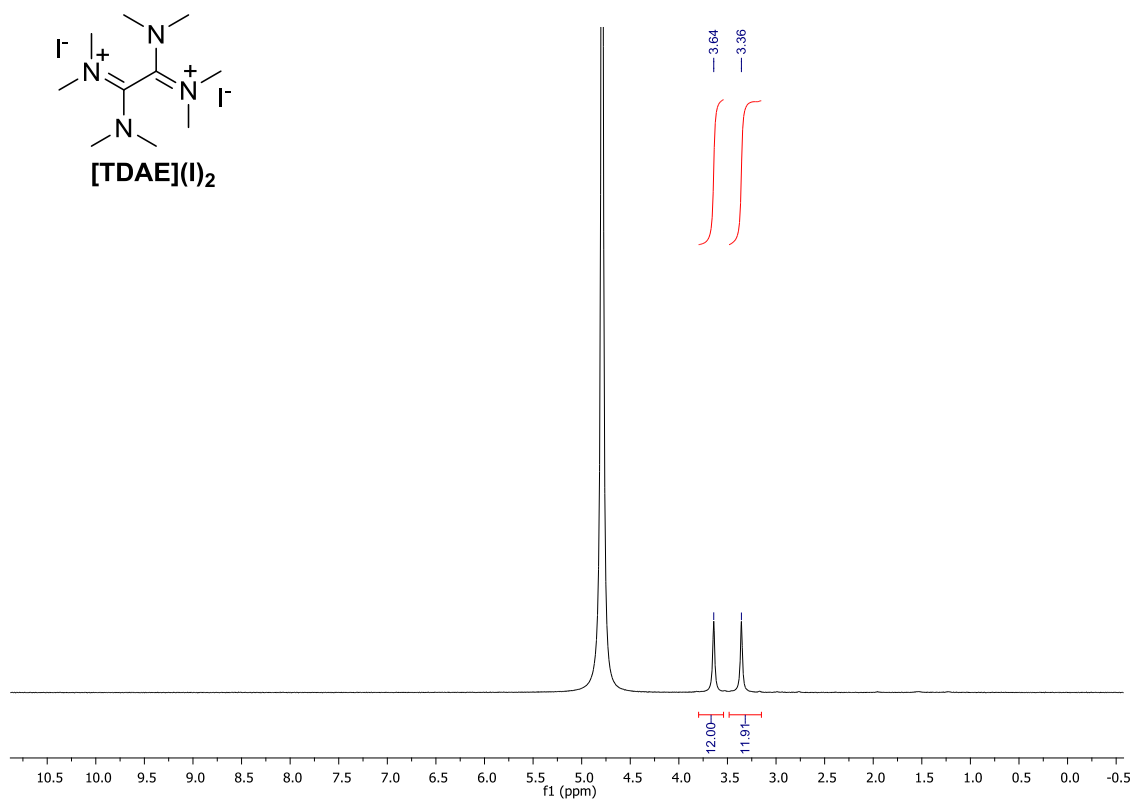












10. X-Ray Diffraction Data

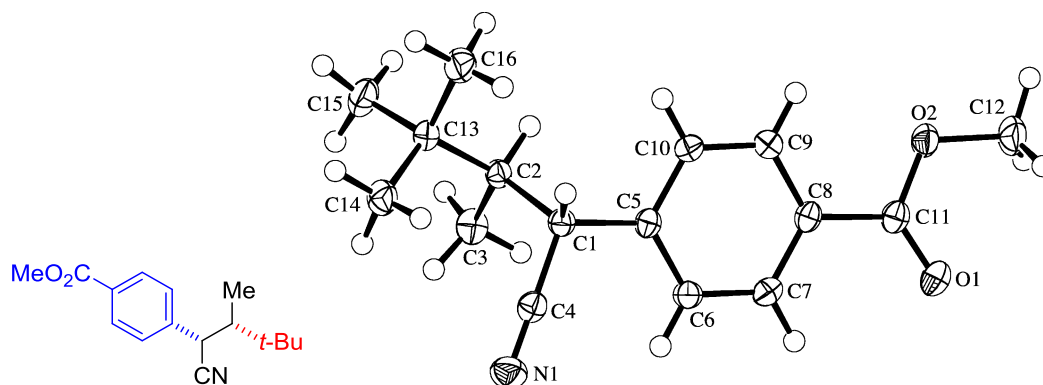


Figure S1. ORTEP representation of the molecule **29** (50% probability ellipsoids; H-atoms given arbitrary displacement parameters for clarity).

Table S1. Crystallographic Data

Crystallised from	CH ₂ Cl ₂ / hexane
Empirical formula	C ₁₆ H ₂₁ NO ₂
Formula weight [g mol ⁻¹]	259.34
Crystal colour, habit	colourless, prism
Crystal dimensions [mm]	0.12 × 0.20 × 0.27
Temperature [K]	160(1)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)
<i>Z</i>	4
Reflections for cell determination	9907
2 θ range for cell determination [°]	7–149
Unit cell parameters	
<i>a</i> [Å]	6.29308(6)
<i>b</i> [Å]	12.62973(10)
<i>c</i> [Å]	18.01319(14)
α [°]	90
β [°]	93.0741(8)
γ [°]	90
<i>V</i> [Å ³]	1429.63(2)
<i>F</i> (000)	560
<i>D</i> _x [g cm ⁻³]	1.205

$\mu(\text{Cu } K\alpha)$ [mm ⁻¹]	0.625
Scan type	ω
$2\theta_{(\text{max})}$ [°]	148.4
Transmission factors (min; max)	0.814; 1.000
Total reflections measured	13859
Symmetry independent reflections	2867
R_{int}	0.012
Reflections with $I > 2\sigma(I)$	2763
Reflections used in refinement	2867
Parameters refined	178
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0339
$wR(F^2)$ (all data)	0.0884
Weights:	$w = [\sigma^2(F_o^2) + (0.0433P)^2 + 0.3995P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness of fit	1.055
Secondary extinction coefficient	0.0035(6)
Final $\Delta_{\text{max}}/\sigma$	0.001
$\Delta\rho$ (max; min) [e Å ⁻³]	0.31; -0.14
$\sigma(d_{\text{C-C}})$ [Å]	0.0012 – 0.0014

Table S2. Bond lengths (Å) with standard uncertainties in parentheses.

O (1)	–C (11)	1.2058 (12)	C (5)	–C (10)	1.3953 (13)
O (2)	–C (11)	1.3414 (12)	C (6)	–C (7)	1.3891 (14)
O (2)	–C (12)	1.4428 (12)	C (7)	–C (8)	1.3877 (14)
N (1)	–C (4)	1.1434 (14)	C (8)	–C (9)	1.3961 (14)
C (1)	–C (4)	1.4733 (13)	C (8)	–C (11)	1.4900 (13)
C (1)	–C (5)	1.5269 (12)	C (9)	–C (10)	1.3832 (14)
C (1)	–C (2)	1.5640 (12)	C (13)	–C (14)	1.5294 (13)
C (2)	–C (3)	1.5291 (13)	C (13)	–C (16)	1.5322 (14)
C (2)	–C (13)	1.5561 (13)	C (13)	–C (15)	1.5340 (14)
C (5)	–C (6)	1.3893 (13)			

Table S3. Bond angles (°) with standard uncertainties in parentheses.

C (11) -O (2) -C (12)	115.17 (8)	C (7) -C (8) -C (11)
118.44 (8)		
C (4) -C (1) -C (5)	110.89 (8)	C (9) -C (8) -C (11)
121.94 (9)		
C (4) -C (1) -C (2)	110.48 (7)	C (10) -C (9) -C (8)
119.87 (9)		
C (5) -C (1) -C (2)	112.25 (7)	C (9) -C (10) -C (5)
120.96 (9)		
C (3) -C (2) -C (13)	114.99 (8)	O (1) -C (11) -O (2)
123.53 (9)		
C (3) -C (2) -C (1)	109.94 (8)	O (1) -C (11) -C (8)
124.12 (9)		
C (13) -C (2) -C (1)	113.45 (7)	O (2) -C (11) -C (8)
112.35 (8)		
N (1) -C (4) -C (1)	178.39 (10)	C (14) -C (13) -C (16)
108.96 (9)		
C (6) -C (5) -C (10)	118.75 (9)	C (14) -C (13) -C (15)
108.78 (8)		
C (6) -C (5) -C (1)	123.44 (8)	C (16) -C (13) -C (15)
107.33 (9)		
C (10) -C (5) -C (1)	117.79 (8)	C (14) -C (13) -C (2)
113.34 (8)		
C (7) -C (6) -C (5)	120.65 (9)	C (16) -C (13) -C (2)
108.97 (8)		
C (8) -C (7) -C (6)	120.25 (9)	C (15) -C (13) -C (2)
109.28 (8)		
C (7) -C (8) -C (9)	119.52 (9)	

Table S4. Torsion angles (°) with standard uncertainties in parentheses.

C (4) -C (1) -C (2) -C (3)	-47.0 (1)	C (8) -C (9) -C (10) -C (5)
-0.3 (2)		
C (5) -C (1) -C (2) -C (3)	77.36 (9)	C (6) -C (5) -C (10) -C (9)
-0.2 (1)		
C (4) -C (1) -C (2) -C (13)	83.4 (1)	C (1) -C (5) -C (10) -C (9)
178.27 (9)		
C (5) -C (1) -C (2) -C (13)	-152.31 (8)	C (12) -O (2) -C (11) -O (1)
-7.2 (1)		
C (4) -C (1) -C (5) -C (6)	6.9 (1)	C (12) -O (2) -C (11) -C (8)
171.85 (9)		

C (2) -C (1) -C (5) -C (6) -117.18 (9)	C (7) -C (8) -C (11) -O (1)
-6.4 (2)	
C (4) -C (1) -C (5) -C (10) -171.49 (8)	C (9) -C (8) -C (11) -O (1)
169.9 (1)	
C (2) -C (1) -C (5) -C (10) 64.4 (1)	C (7) -C (8) -C (11) -O (2)
174.59 (8)	
C (10) -C (5) -C (6) -C (7) 0.5 (1)	C (9) -C (8) -C (11) -O (2)
-9.1 (1)	
C (1) -C (5) -C (6) -C (7) -177.88 (8)	C (3) -C (2) -C (13) -C (14)
75.3 (1)	
C (5) -C (6) -C (7) -C (8) -0.3 (1)	C (1) -C (2) -C (13) -C (14)
-52.5 (1)	
C (6) -C (7) -C (8) -C (9) -0.2 (1)	C (3) -C (2) -C (13) -C (16)
-163.21 (9)	
C (6) -C (7) -C (8) -C (11) 176.18 (8)	C (1) -C (2) -C (13) -C (16)
69.0 (1)	
C (7) -C (8) -C (9) -C (10) 0.5 (1)	C (3) -C (2) -C (13) -C (15)
-46.2 (1)	
C (11) -C (8) -C (9) -C (10) -175.75 (9)	C (1) -C (2) -C (13) -C (15)
-173.96 (8)	

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