Supporting Information

Nickel-Catalyzed Synthesis of an Aryl Nitrile via Aryl Exchange between an Aromatic Amide and a Simple Nitrile

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I. General information

Unless otherwise noted, all nickel-catalyzed aryl exchange reactions were carried out under nitrogen atmosphere in glovebox.

Commercially available reagents, including bis(1,5-cyclooctadiene)nickel(0) $Ni(cod)_2$, 1,2-bis(dicyclohexylphosphino)ethane dcype and manganese Mn, were purchased and used without further purification. Solvents were dried and degassed before used.

NMR spectra, including ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), ^{19}F NMR (376 MHz) and ^{15}N NMR (41 MHz) spectra, were obtained on an Agilent 400-MR DD2 or Bruker AV II-400 spectrometer. The ^{1}H NMR chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm), and the ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet and br = broad), coupling constant (*J values* in Hz) and integration. The ^{13}C NMR chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm).

High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-IT-TOF (ESI), and the corresponding molecular ion, such as $[M]^+$, $[M+H]^+$, $[M+Na]^+$ or $[M-H]^-$, are given in m/z units. GC analysis was performed with Agilent 7890B (KB-1, 30 m × 0.32 mm × 0.25 μm), and GC-Mass analysis was performed with SHIMADZU GCMS-QP2020 (SH-Rtx-35MS, 30 m × 0.25 mm × 0.25μm). Melting points were determined in open glass capillaries and were uncorrected.

Analytical thin layer chromatography was performed on HG/T2354-92 GF254 plates (Qingdao Haiyang Chemical Co., Ltd.), and the visualization was assisted with irradiation of UV light at 254 nm or oxidative staining using $KMnO_4$ solution. Column chromatography was carried out using silica gel (200-300 mesh or 300-400 mesh) eluting with petroleum ether/ethyl acetate or petroleum ether/dichloromethane.

II. Synthesis of starting materials

All starting materials are shown in **Fig. S1**. Substrates **A2**-**A4**, **A10**-**A14** and **A20**-**A22** were prepared through Procedure I. Substrates **A1**, **A5**-**A9**, **A15**-**A19**, **A23**-**A35** and **A41**-**A44** were prepared through Procedure II, and substrates **A1b**, **A1d**-**A1f** were prepared through Procedure III. Substrates **A1c**, **A36**-**A40** and **A45** were prepared through other procedures. Detailed description of all procedures and the characterization data of starting materials were as follows:

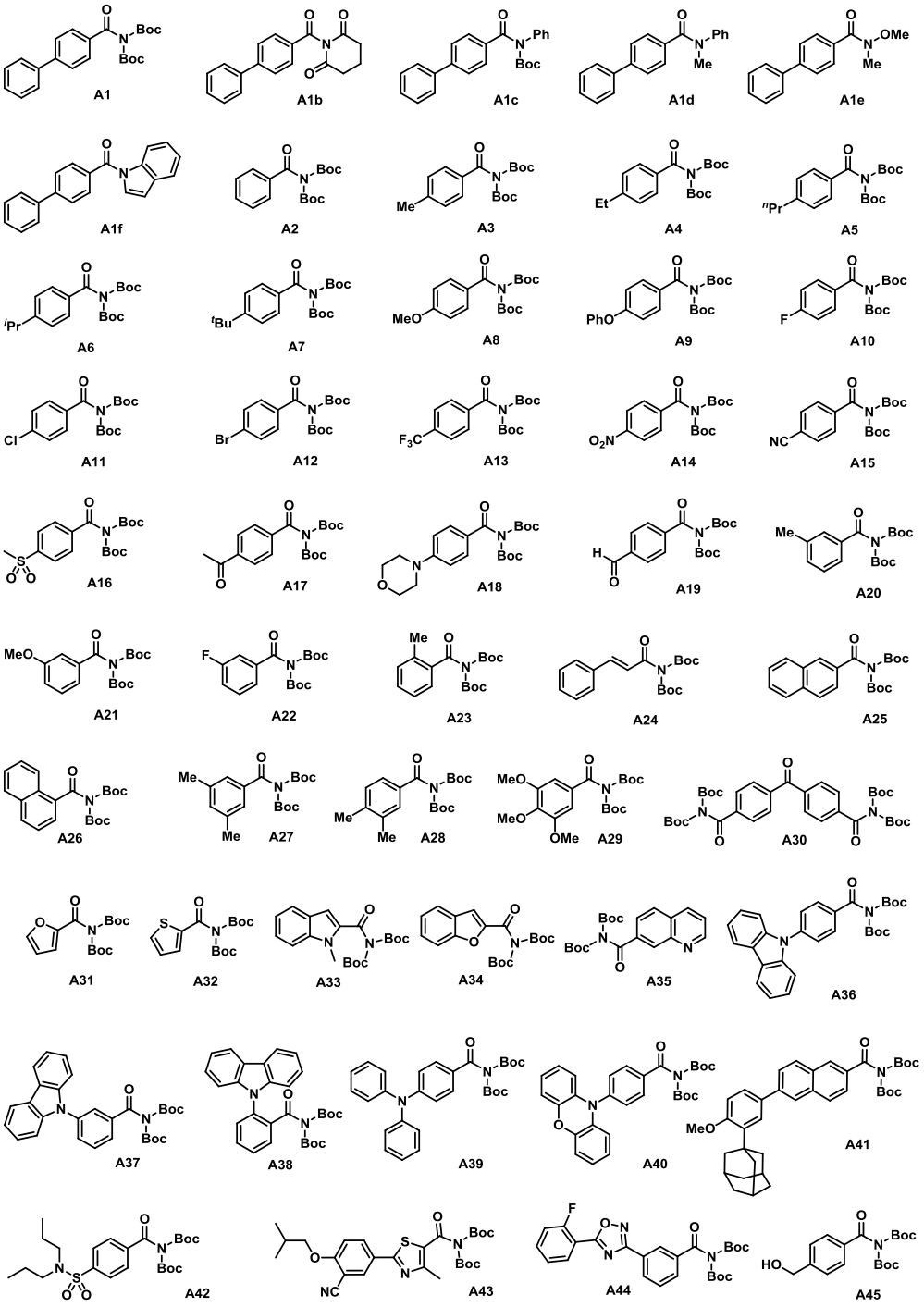
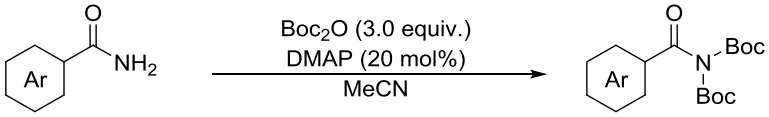


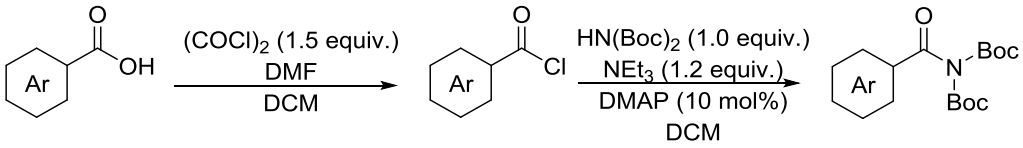
Fig. S1. List of starting materials.

Procedure I:



To a solution of primary benzamide derivatives (3.0 mmol) and 4-dimethylaminopyridine DMAP (0.6 mmol, 73.2 mg) in acetonitrile (15 mL) was added di-*tert*-butyl dicarbonate Boc_2O (9.0 mmol, 1.96 g) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford the corresponding products.

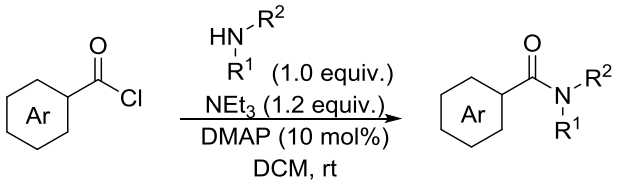
Procedure II:



To a solution of carboxylic acid derivatives (3.0 mmol) in dichloromethane (10 mL) was added oxalyl chloride (4.5 mmol, 0.38 mL) dropwise at 0 °C, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure, and the crude acyl chloride was used directly for the next step without further purification.

The obtained acyl chloride was dissolved in dichloromethane (5 mL), and the solution was added dropwise to a solution of di-*tert*-butyl iminodicarboxylate $HN(Boc)_2$ (3.0 mmol, 651.0 mg), NEt_3 (3.6 mmol, 0.5 mL) and DMAP (0.3 mmol, 36.6 mg) in dichloromethane (10 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (30 mL) and extracted with dichloromethane (30 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford the corresponding products.

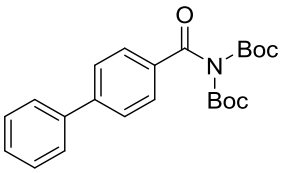
Procedure III:



To a solution of secondary amine (3.0 mmol), NEt_3 (3.6 mmol, 0.5 mL) and DMAP (0.3 mmol, 36.6 mg) in dichloromethane (10 mL) was added acyl chloride (3.0 mmol) dropwise at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with

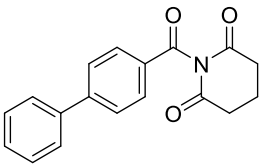
saturated $NaHCO_3$ solution (30 mL) and extracted with dichloromethane (30 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford the corresponding products.

Detailed procedures and characterization data of starting materials:



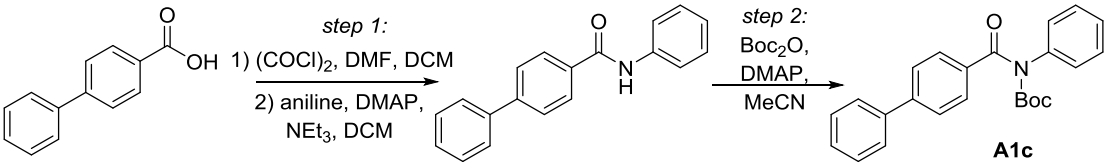
***N*,*N*-Boc$_2$-4-phenylbenzamide (A1)**

Procedure II was followed with 4-biphenylcarboxylic acid to afford **A1** (966.7 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.11, 150.07, 146.37, 139.56, 132.99, 129.91, 129.22, 128.66, 127.41, 115.76, 84.32, 27.76. HRMS (ESI)$^+$: calcd for $C_{23}H_{28}NO_5$ $[M+H]^+$ 398.1967, found: 398.1980.[1]



1-([1,1'-biphenyl]-4-carbonyl)piperidine-2,6-dione (A1b)

Procedure III was followed with 4-phenylbenzoyl chloride and glutarimide to afford **A1b** (780.2 mg, 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 2.80 (t, *J* = 6.5 Hz, 4H), 2.17 (p, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.96, 170.44, 147.81, 139.49, 130.77, 130.43, 129.04, 128.63, 127.83, 127.38, 32.45, 17.54. HRMS (ESI)$^+$: calcd for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1130, found: 294.1108.[2]



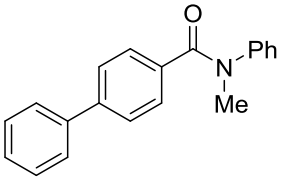
***N*-Boc-*N*-phenyl-[1,1'-biphenyl]-4-carboxamide (A1c)**

Step 1: To a solution of 4-biphenylcarboxylic acid (3.0 mmol, 594.0 mg) in dichloromethane (10 mL) was added oxalyl chloride (4.5 mmol, 0.38 mL) dropwise at 0 °C, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure. Then obtained acyl chloride was redissolved in dichloromethane (5 mL), and the

solution was added dropwise to a solution of aniline (3.0 mmol, 0.27 mL), NEt_3 (3.6 mmol, 0.5 mL) and and DMAP (0.3 mmol, 36.6 mg) in dichloromethane (10 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (30 mL) and extracted with dichloromethane (30 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford *N*-phenyl-[1,1'-biphenyl]-4-carboxamide (753.5 mg, 92%).[3]

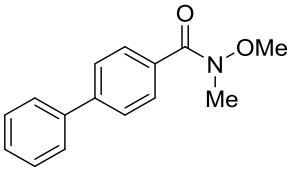
Step 2: To a solution of *N*-phenyl-[1,1'-biphenyl]-4-carboxamide (2.76 mmol, 753.5 mg) and 4-dimethylaminopyridine DMAP (0.55 mmol, 67.3 mg) in acetonitrile (15 mL) was added di-*tert*-butyl dicarbonate Boc_2O (4.2 mmol, 915.6 mg) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford **A1c** (875.0 mg, 85%).

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.61 (m, 4H), 7.50 – 7.32 (m, 6H), 7.31 – 7.27 (m, 2H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 153.36, 144.64, 140.00, 139.14, 135.52, 129.22, 128.96, 128.85, 128.12, 127.94, 127.79, 127.25, 126.93, 83.53, 27.55. HRMS (ESI)$^+$: calcd for $C_{24}H_{24}NO_3$ $[M+H]^+$ 374.1756, found: 374.1764.[4]



4-phenyl-*N*-methyl-*N*-phenylbenzamide (A1d)

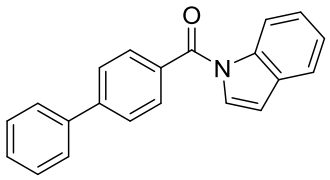
Procedure III was followed with 4-phenylbenzoyl chloride and *N*-methylaniline to afford **A1d** (695.0 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.45 – 7.39 (m, 6H), 7.37 – 7.32 (m, 1H), 7.30 – 7.24 (m, 2H), 7.20 – 7.15 (m, 1H), 7.13 – 7.09 (m, 2H), 3.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.35, 145.01, 142.26, 140.10, 134.65, 129.39, 129.25, 128.79, 127.72, 127.06, 126.92, 126.54, 126.36, 38.53. HRMS (ESI)$^+$: calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1388, found: 288.1402.[5]



***N*-methoxy-*N*-methyl-[1,1'-biphenyl]-4-carboxamide (A1e)**

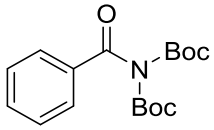
Procedure III was followed with 4-phenylbenzoyl chloride and *N,O*-dimethylhydroxylamine to afford **A1e** (672.9 mg, 93%) as a white solid. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.66 – 7.60 (m, 4H), 7.50 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 3.59 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.67, 143.40, 140.23, 132.80, 128.89, 128.85, 127.86, 127.19, 126.70, 61.12, 33.81. HRMS $(ESI)^+$: calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.1181, found: 242.1193.[6]



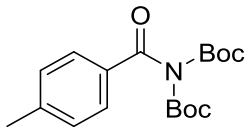
[1,1'-biphenyl]-4-yl(1*H*-indol-1-yl)methanone (A1f)

Procedure III was followed with 4-phenylbenzoyl chloride and 1*H*-indole to afford **A1f** (760.8 mg, 85%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.78 – 7.73 (m, 2H), 7.69 – 7.61 (m, 3H), 7.54 – 7.47 (m, 2H), 7.46 – 7.37 (m, 3H), 7.33 (td, *J* = 7.6, 1.1 Hz, 1H), 6.65 (dd, *J* = 3.7, 0.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.51, 144.84, 139.80, 136.07, 133.20, 130.79, 129.89, 129.04, 128.28, 127.62, 127.30, 127.25, 124.95, 123.95, 120.91, 116.41, 108.58. HRMS $(ESI)^+$: calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1232, found: 298.1326.[7]



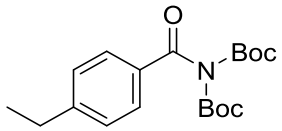
***N,N*-Boc$_2$-benzamide (A2)**

Procedure I was followed with benzamide to afford **A2** (817.4 mg, 85%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 – 7.42 (m, 2H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.27, 149.75, 134.21, 133.43, 129.02, 128.66, 84.22, 27.54. HRMS $(ESI)^+$: calcd for $C_{17}H_{24}NO_5$ $[M+H]^+$ 322.1654, found: 322.1634.[8]



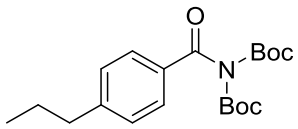
***N,N*-Boc$_2$-4-methylbenzamide (A3)**

Procedure I was followed with 4-methylbenzamide to afford **A3** (896.5 mg, 89%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H), 1.29 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.90, 149.76, 144.52, 131.27, 129.35, 129.24, 83.93, 27.52, 21.62. HRMS $(ESI)^+$: calcd for $C_{18}H_{26}NO_5$ $[M+H]^+$ 336.1811, found: 336.1809.[8]



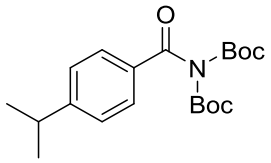
***N,N*-Boc$_2$-4-ethylbenzamide (A4)**

Procedure I was followed with 4-ethylbenzamide to afford **A4** (856.8 mg, 82%) as a white solid. Mp: 64-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.37 (s, 18H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.09, 150.69, 149.85, 131.61, 129.46, 128.19, 84.07, 29.00, 27.63, 15.16. HRMS (ESI)$^+$: calcd for $C_{19}H_{28}NO_5$ $[M+H]^+$ 350.1967, found: 350.1943.



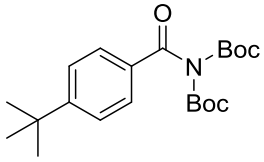
***N,N*-Boc$_2$-4-propylbenzamide (A5)**

Procedure II was followed with 4-propylbenzoic acid to afford **A5** (825.1 mg, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.66 – 1.53 (m, 2H), 1.31 (s, 18H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.01, 149.81, 149.12, 131.64, 129.25, 128.76, 83.96, 37.95, 27.52, 24.12, 13.58. HRMS (ESI)$^+$: calcd for $C_{20}H_{30}NO_5$ $[M+H]^+$ 364.2124, found: 364.2108.



***N,N*-Boc$_2$-4-isopropylbenzamide (A6)**

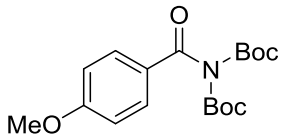
Procedure II was followed with 4-isopropylbenzoic acid to afford **A6** (913.6 mg, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.34 (s, 18H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.06, 155.24, 149.87, 131.75, 129.43, 126.75, 84.03, 34.27, 27.57, 23.64. HRMS (ESI)$^+$: calcd for $C_{20}H_{30}NO_5$ $[M+H]^+$ 364.2124, found: 364.2120.



***N,N*-Boc$_2$-4-(*tert*-butyl)benzamide (A7)**

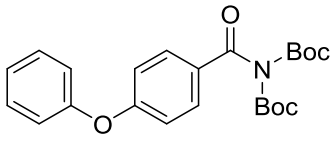
Procedure II was followed with 4-*tert*-butylbenzoic acid to afford **A7** (924.7 mg, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 1.36 (s, 18H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.09, 157.48,

149.91, 131.38, 129.16, 125.61, 84.06, 35.21, 31.08, 27.60. HRMS (ESI)$^+$: calcd for $C_{21}H_{32}NO_5$ $[M+H]^+$ 378.2280, found: 378.2264.[9]



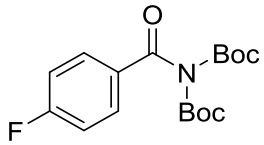
***N,N*-Boc$_2$-4-methoxybenzamide (A8)**

Procedure II was followed with 4-methoxybenzoic acid to afford **A8** (931.4 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 1.37 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.23, 164.03, 149.79, 131.74, 126.36, 114.00, 83.93, 55.57, 27.67. HRMS (ESI)$^+$: calcd for $C_{18}H_{26}NO_6$ $[M+H]^+$ 352.1760, found: 352.1754.[10]



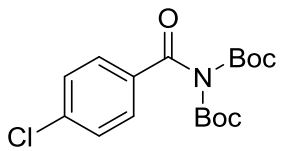
***N,N*-Boc$_2$-4-phenoxybenzamide (A9)**

Procedure II was followed with 4-phenoxybenzoic acid to afford **A9** (931.0 mg, 75%) as a white solid. Mp: 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.40 – 7.33 (m, 2H), 7.21 – 7.14 (m, 1H), 7.07 – 7.01 (m, 2H), 7.00 – 6.94 (m, 2H), 1.37 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.20, 162.52, 155.11, 149.79, 131.59, 130.13, 128.08, 124.90, 120.27, 117.28, 84.09, 27.65. HRMS (ESI)$^+$: calcd for $C_{23}H_{28}NO_6$ $[M+H]^+$ 414.1917, found: 414.1901.



***N,N*-Boc$_2$-4-fluorobenzamide (A10)**

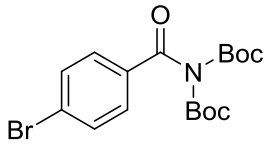
Procedure I was followed with 4-fluorobenzamide to afford **A10** (870.6 mg, 86%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 2H), 7.18 – 7.09 (m, 2H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.10, 165.89 (d, *J* = 256.0 Hz), 149.64, 131.77 (d, *J* = 9.5 Hz), 130.43 (d, *J* = 3.1 Hz), 115.97 (d, *J* = 22.2 Hz), 84.44, 27.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.99. HRMS (ESI)$^+$: calcd for $C_{17}H_{23}FNO_5$ $[M+H]^+$ 340.1560, found: 340.1552.[9]



***N,N*-Boc$_2$-4-chlorobenzamide (A11)**

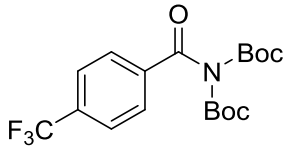
Procedure I was followed with 4-chlorobenzamide to afford **A11** (870.4 mg, 82%) as a

white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.35, 149.60, 139.92, 132.59, 130.45, 129.05, 84.57, 27.63. HRMS (ESI)$^{+}$: calcd for $C_{17}H_{23}ClNO_5$ $[M+H]^{+}$ 356.1265, found: 356.1231.[9]



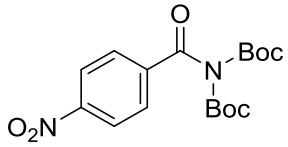
***N,N*-Boc$_2$-4-bromobenzamide (A12)**

Procedure I was followed with 4-bromobenzamide to afford **A12** (955.4 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.53, 149.58, 133.04, 132.04, 130.51, 128.53, 84.60, 27.63. HRMS (ESI)$^{+}$: calcd for $C_{17}H_{23}BrNO_5$ $[M+H]^{+}$ 400.0760, found: 400.0752.[11]



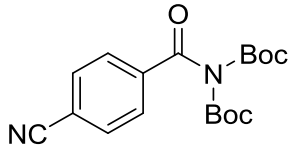
***N,N*-Boc$_2$-4-trifluoromethylbenzamide (A13)**

Procedure I was followed with 4-trifluoromethylbenzamide to afford **A13** (935.6 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.40, 149.54, 137.51, 134.55 (q, *J* = 32.9 Hz), 129.14, 125.65 (q, *J* = 3.7 Hz), 123.42 (d, *J* = 272.7 Hz), 84.91, 27.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.17. HRMS (ESI)$^{+}$: calcd for $C_{18}H_{23}F_3NO_5$ $[M+H]^{+}$ 390.1528, found: 390.1512.[8]



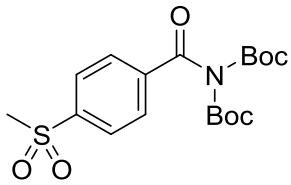
***N,N*-Boc$_2$-4-nitrobenzamide (A14)**

Procedure I was followed with 4-nitrobenzamide to afford **A14** (918.4 mg, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 1.41 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.90, 150.17, 149.40, 139.71, 129.59, 123.77, 85.30, 27.56. HRMS (ESI)$^{+}$: calcd for $C_{17}H_{23}N_2O_7$ $[M+H]^{+}$ 367.1505, found: 367.1493.[8]



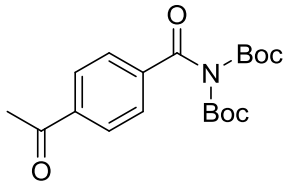
***N,N*-Boc$_2$-4-cyanobenzamide (A15)**

Procedure II was followed with 4-cyanobenzoic acid to afford **A15** (812.1 mg, 78%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 1.41 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.12, 149.43, 138.14, 132.39, 129.12, 117.68, 116.40, 85.19, 27.58. HRMS (ESI)$^{+}$: calcd for $C_{18}H_{23}N_2O_5$ $[M+H]^{+}$ 347.1607, found: 347.1593.[12]



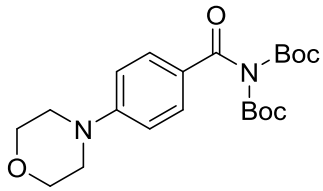
***N*,*N*-Boc$_2$-4-(methylsulfonyl)benzamide (A16)**

Procedure II was followed with 4-(methylsulfonyl)benzoic acid to afford **A16** (968.0 mg, 81%) as a white solid. Mp: 118-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 3.08 (s, 3H), 1.40 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.15, 149.46, 144.21, 139.02, 129.46, 127.71, 85.18, 44.30, 27.55. HRMS (ESI)$^{+}$: calcd for $C_{18}H_{26}NO_7S$ $[M+H]^{+}$ 400.1430, found: 400.1418.



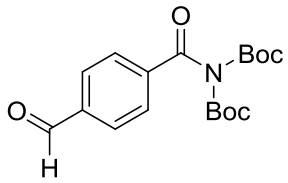
***N*,*N*-Boc$_2$-4-acetylbenzamide (A17)**

Procedure II was followed with 4-acetylbenzoic acid to afford **A17** (901.3 mg, 83%) as a white solid. Mp: 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 2.63 (s, 3H), 1.38 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.13, 168.69, 149.57, 140.24, 137.94, 129.04, 128.43, 84.77, 27.57, 26.87. HRMS (ESI)$^{+}$: calcd for $C_{19}H_{26}NO_6$ $[M+H]^{+}$ 364.1760, found: 364.1724.



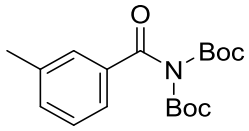
***N*,*N*-Boc$_2$-4-morpholinobenzamide (A18)**

Procedure II was followed with 4-morpholinobenzoic acid to afford **A18** (933.5 mg, 77%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.90 (t, *J* = 4.8 Hz, 4H), 3.37 (t, *J* = 4.8 Hz, 4H), 1.41 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.93, 154.31, 149.89, 131.71, 123.93, 113.53, 83.71, 66.39, 47.57, 27.74. HRMS (ESI)$^{+}$: calcd for $C_{21}H_{31}N_2O_6$ $[M+H]^{+}$ 407.2182, found: 407.2164.



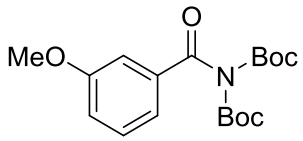
***N,N*-Boc$_2$-4-formylbenzamide (A19)**

Procedure II was followed with 4-formylbenzoic acid to afford **A19** (897.6 mg, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.24, 168.59, 149.49, 139.13, 139.07, 129.65, 129.21, 84.83, 27.48. HRMS (ESI)$^+$: calcd for $C_{18}H_{24}NO_6$ $[M+H]^+$ 350.1604, found: 350.1588.



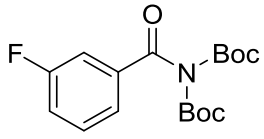
***N,N*-Boc$_2$-3-methylbenzamide (A20)**

Procedure I was followed with 3-methylbenzamide to afford **A20** (901.2 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.31 – 7.20 (m, 2H), 2.27 (s, 3H), 1.26 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.15, 149.78, 138.40, 134.15, 134.07, 129.34, 128.53, 126.12, 83.94, 27.39, 21.02. HRMS (ESI)$^+$: calcd for $C_{18}H_{26}NO_5$ $[M+H]^+$ 336.1811, found: 336.1807.[12]



***N,N*-Boc$_2$-3-methoxybenzamide (A21)**

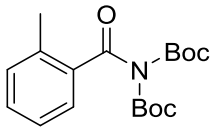
Procedure I was followed with 3-methoxybenzamide to afford **A21** (903.1 mg, 86%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 3H), 7.09 – 7.04 (m, 1H), 3.75 (s, 3H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.02, 159.76, 149.72, 135.43, 129.67, 121.26, 119.78, 113.48, 84.15, 55.36, 27.47. HRMS (ESI)$^+$: calcd for $C_{18}H_{26}NO_6$ $[M+H]^+$ 352.1760, found: 352.1748.[11]



***N,N*-Boc$_2$-3-fluorobenzamide (A22)**

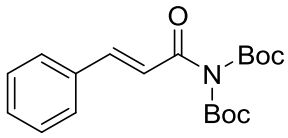
Procedure I was followed with 3-fluorobenzamide to afford **A22** (952.0 mg, 94%) as a white solid. Mp: 63-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 1H), 7.50 – 7.38 (m, 2H), 7.30 – 7.23 (m, 1H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.15 (d, *J* = 2.9 Hz), 162.58 (d, *J* = 248.6 Hz), 149.56, 136.34 (d, *J* = 7.1 Hz), 130.40 (d, *J* = 7.8 Hz), 124.60 (d, *J* = 3.1 Hz), 120.39 (d, *J* = 21.3 Hz), 115.82 (d, *J* = 23.2 Hz), 84.61,

27.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.59. HRMS (ESI)$^+$: calcd for $C_{17}H_{23}FNO_5$ $[M+H]^+$ 340.1560, found: 340.1534.



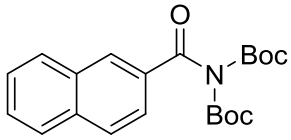
***N,N*-Boc$_2$-2-methylbenzamide (A23)**

Procedure II was followed with 2-methylbenzoic acid to afford **A23** (896.8 mg, 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.21 (m, 2H), 2.50 (s, 3H), 1.38 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.76, 149.91, 138.21, 134.84, 131.50, 131.18, 127.92, 125.70, 84.39, 27.45, 19.85. HRMS (ESI)$^+$: calcd for $C_{18}H_{26}NO_5$ $[M+H]^+$ 336.1811, found: 336.1803.[11]



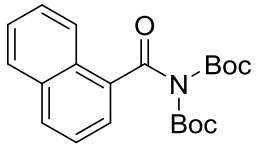
***N,N*-Boc$_2$-cinnamamide (A24)**

Procedure II was followed with cinnamic acid to afford **A24** (841.7 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.7 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.45 – 7.36 (m, 4H), 1.55 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 149.73, 145.98, 134.56, 130.58, 128.87, 128.51, 118.81, 84.72, 27.68. HRMS (ESI)$^+$: calcd for $C_{19}H_{26}NO_5$ $[M+H]^+$ 348.1811, found: 348.1803.[13]



***N,N*-Boc$_2$-2-naphthamide (A25)**

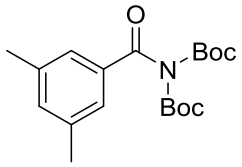
Procedure II was followed with 2-naphthoic acid to afford **A25** (946.7 mg, 85%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.97 – 7.85 (m, 4H), 7.66 – 7.53 (m, 2H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.29, 149.84, 135.68, 132.40, 131.39, 130.69, 129.41, 128.84, 128.70, 127.88, 127.13, 124.73, 84.31, 27.63. HRMS (ESI)$^+$: calcd for $C_{21}H_{26}NO_5$ $[M+H]^+$ 372.1811, found: 372.1803.[8]



***N,N*-Boc$_2$-1-naphthamide (A26)**

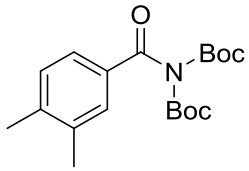
Procedure II was followed with 1-naphthoic acid to afford **A26** (892.1 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.00 – 7.92 (m, 1H), 7.89 – 7.82 (m, 1H), 7.80 – 7.73 (m, 1H), 7.61 – 7.40 (m, 3H), 1.25 (s, 18H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 169.39, 149.97, 133.50, 132.78, 132.52, 130.53, 128.44, 127.89, 126.91, 126.71, 124.85, 124.47, 84.50, 27.35. HRMS $(ESI)^+$: calcd for $C_{21}H_{26}NO_5$ $[M+H]^+$ 372.1811, found: 372.1807.[9]



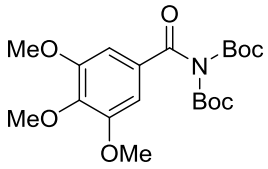
***N,N*-Boc$_2$-3,5-dimethylbenzamide (A27)**

Procedure II was followed with 3,5-dimethylbenzoic acid to afford **A27** (912.4 mg, 87%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 2H), 7.09 (s, 1H), 2.20 (s, 6H), 1.25 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.13, 149.85, 138.23, 134.96, 134.03, 126.62, 83.78, 27.34, 20.86. HRMS $(ESI)^+$: calcd for $C_{19}H_{28}NO_5$ $[M+H]^+$ 350.1967, found: 350.1961.[9]



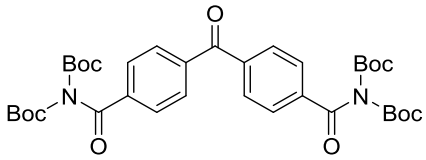
***N,N*-Boc$_2$-3,4-dimethylbenzamide (A28)**

Procedure II was followed with 3,4-dimethylbenzoic acid to afford **A28** (851.7 mg, 81%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.38 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.12, 149.93, 143.27, 137.15, 131.61, 130.36, 129.94, 126.98, 84.02, 27.64, 20.12, 19.64. HRMS $(ESI)^+$: calcd for $C_{19}H_{28}NO_5$ $[M+H]^+$ 350.1967, found: 350.1945.



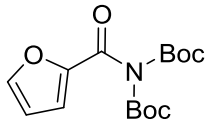
***N,N*-Boc$_2$-3,4,5-trimethoxybenzamide (A29)**

Procedure II was followed with 3,4,5-trimethylbenzoic acid to afford **A29** (980.4 mg, 80%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.77 (m, 2H), 3.71 – 3.57 (m, 9H), 1.15 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.16, 152.99, 149.66, 142.72, 128.80, 106.25, 83.80, 60.51, 55.95, 27.26. HRMS $(ESI)^+$: calcd for $C_{20}H_{30}NO_8$ $[M+H]^+$ 412.1971, found: 412.1969.[11]



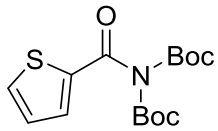
4,4'-carbonylbis(*N*,*N*-Boc$_2$-benzamide) (A30)

Procedure II was followed with 4,4'-carbonyldibenzoic acid and two equivalent of HN(Boc)$_2$ to afford **A30** (1.66 g, 83%) as a white solid. Mp: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 4H), 7.86 (d, *J* = 8.2 Hz, 4H), 1.42 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.58, 168.66, 149.63, 140.39, 137.89, 130.02, 128.88, 84.90, 27.62. HRMS (ESI)$^+$: calcd for $C_{17}H_{24}NO_5$ $[M+H]^+$ 669.3023, found: 669.3003.



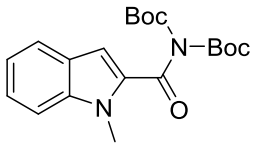
***N*,*N*-Boc$_2$-furan-2-carboxamide (A31)**

Procedure II was followed with furan-2-carboxylic acid to afford **A31** (842.8 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.6 Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.6 Hz, 1H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 149.22, 147.88, 146.74, 119.91, 112.93, 84.26, 27.69. HRMS (ESI)$^+$: calcd for $C_{15}H_{22}NO_6$ $[M+H]^+$ 312.1447, found: 312.1431.[13]



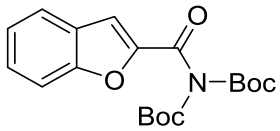
***N*,*N*-Boc$_2$-thiophene-2-carboxamide (A32)**

Procedure II was followed with thiophene-2-carboxylic acid to afford **A32** (808.4 mg, 82%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.57 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.0, 3.8 Hz, 1H), 1.27 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.13, 149.13, 138.46, 135.21, 134.03, 128.14, 84.10, 27.55. HRMS (ESI)$^+$: calcd for $C_{15}H_{22}NO_5S$ $[M+H]^+$ 328.1219, found: 328.1231.[13]



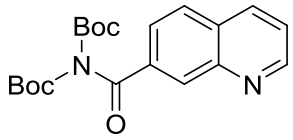
***N*,*N*-Boc$_2$-1-methyl-1*H*-indole-2-carboxamide (A33)**

Procedure II was followed with 1-methyl-1*H*-indole-2-carboxylic acid to afford **A33** (847.2 mg, 76%) as a white solid. Mp: 93-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 3.6 Hz, 2H), 7.22 – 7.13 (m, 2H), 4.03 (s, 3H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.04, 149.72, 140.67, 131.92, 126.33, 125.72, 123.21, 121.09, 111.99, 110.37, 84.05, 31.46, 27.74. HRMS (ESI)$^+$: calcd for $C_{20}H_{27}N_2O_5$ $[M+H]^+$ 375.1920, found: 375.1914.



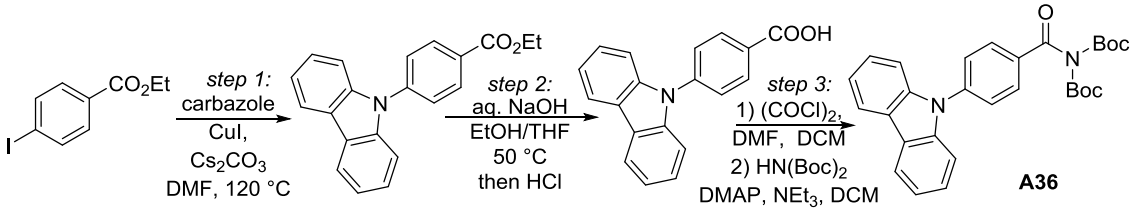
***N,N*-Boc$_2$-benzofuran-2-carboxamide (A34)**

Procedure II was followed with benzofuran-2-carboxylic acid to afford **A34** (900.6 mg, 83%) as a white solid. Mp: 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.61 (s, 1H), 7.56 – 7.45 (m, 2H), 7.36 – 7.30 (m, 1H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.51, 155.52, 149.20, 148.24, 128.67, 126.98, 124.22, 123.27, 115.44, 112.32, 84.57, 27.66. HRMS (ESI)$^+$: calcd for $C_{19}H_{23}NNaO_6$ $[M+Na]^+$ 384.1423, found: 384.1409.



***N,N*-Boc$_2$-quinoline-7-carboxamide (A35)**

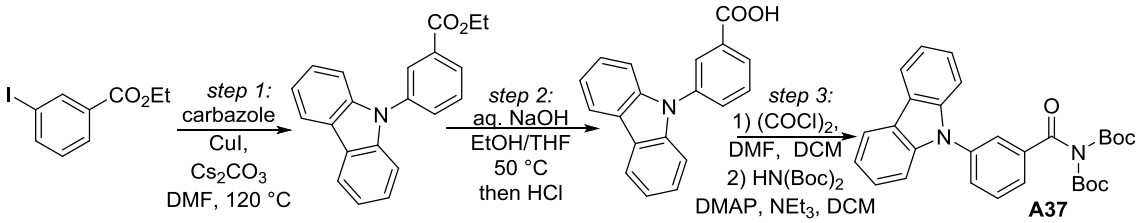
Procedure II was followed with quinoline-7-carboxylic acid to afford **A35** (827.3 mg, 74%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (br, 1H), 8.54 (s, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.83 (m, 2H), 7.51 – 7.42 (m, 1H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.15, 151.72, 149.69, 147.39, 135.87, 134.82, 131.32, 130.80, 128.63, 125.36, 123.18, 84.50, 27.59. HRMS (ESI)$^+$: calcd for $C_{20}H_{25}N_2O_5$ $[M+H]^+$ 373.1763, found: 373.1751.



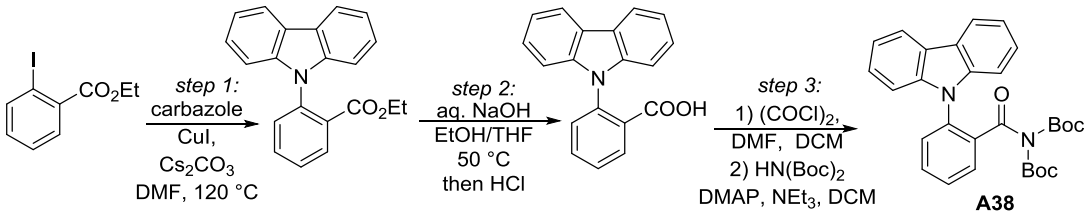
4-(9*H*-carbazol-9-yl)-*N,N*-Boc$_2$-benzamide (A36) was prepared according to the known literature with proper adjustment.[14]

Step 1: Ethyl 4-iodobenzoate (14.0 mmol, 3.86 g), carbazole (10.0 mmol. 1.67 g), CuI (2.0 mmol, 382.0 mg) and Cs_2CO_3 (20.0 mmol, 6.52 g) were added into a dried 100 mL two-neck flask equipped with a condenser pipe, and it was subjected to three cycles of vacuum and refilled with nitrogen. Then DMF (30 mL) was sequentially injected into it, and the mixture was stirred at 120 °C for 24 h. After the indicated time, the mixture was slowly cooled to room temperature and filtered with *Celite*. The filtrate was then poured into a large amount of water (200 mL) and extracted with ethyl acetate (150 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford the ethyl 4-(9*H*-carbazol-9-yl)benzoate (1.78 g, 57%).

Step 2: To a solution of ethyl 4-(9*H*-carbazol-9-yl)benzoate (5.65 mmol, 1.78 g) in EtOH/THF (v/v: 1:1, 30 mL) was added 1 M aqueous NaOH solution (11.3 mmol, 11.3 mL), and the mixture was stirred at 50 °C overnight. After the indicated time, the mixture was slowly cooled to room temperature and 1 M aqueous HCl solution was added to adjust the pH to 2. Then the precipitated solid was filtered, washed with water and dried under vacuum to give the 4-(9*H*-carbazol-9-yl)benzoic acid. (1.59 g, 98%).
Step 3: To a solution of 4-(9*H*-carbazol-9-yl)benzoic acid (5.54 mmol, 1.59 g) in dichloromethane (15 mL) was added oxalyl chloride (8.3 mmol, 0.7 mL) dropwise at 0 °C, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure. Then obtained acyl chloride was redissolved in dichloromethane (5 mL), and the solution was added dropwise to a solution of $HN(Boc)_2$ (5.6 mmol, 1.21 g), NEt_3 (6.5 mmol, 0.9 mL) and DMAP (0.5 mmol, 61.0 mg) in dichloromethane (20 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (50 mL) and extracted with dichloromethane (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford **A36** (2.45 g, 91%).
White solid. Mp: 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 15.4, 8.1 Hz, 4H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.37 – 7.30 (m, 2H), 1.53 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.60, 149.97, 142.46, 140.05, 132.57, 130.93, 126.47, 126.38, 123.98, 120.89, 120.58, 109.68, 84.56, 27.76. HRMS (ESI)$^+$: calcd for $C_{29}H_{31}N_2O_5$ $[M+H]^+$ 487.2233, found: 487.2209.

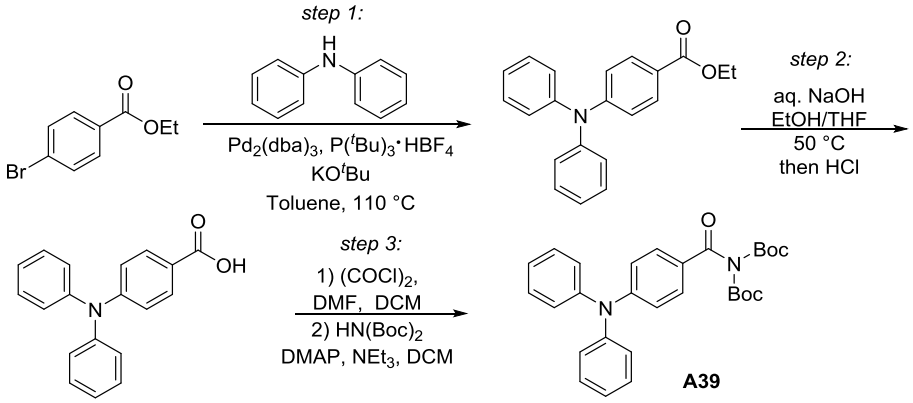


3-(9*H*-carbazol-9-yl)-*N*,*N*-Boc$_2$-benzamide (A37) was prepared through a similar procedure to **A36** by using ethyl 3-iodobenzoate as starting material (2.37 g, 49% overall yield for three steps).
White solid. Mp: 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.7 Hz, 2H), 8.07 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.38 – 7.31 (m, 2H), 1.49 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 149.78, 140.55, 138.35, 136.26, 131.67, 130.30, 127.68, 127.43, 126.19, 123.62, 120.48, 120.44, 109.47, 84.76, 27.70. HRMS (ESI)$^+$: calcd for $C_{29}H_{31}N_2O_5$ $[M+H]^+$ 487.2233, found: 487.2217.



2-(9*H*-carbazol-9-yl)-*N*,*N*-Boc$_2$-benzamide (A38) was prepared through a similar procedure to **A36** by using ethyl 2-iodobenzoate as starting material (2.12 g, 44% overall yield for three steps).

White solid. Mp: 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.82 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.70 (td, *J* = 7.7, 1.6 Hz, 1H), 7.62 (td, *J* = 7.6, 1.1 Hz, 1H), 7.48 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.42 – 7.25 (m, 6H), 1.22 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.99, 149.03, 141.60, 135.63, 134.27, 132.23, 129.96, 128.84, 128.07, 125.90, 123.73, 120.04, 119.98, 110.77, 84.44, 27.32. HRMS (ESI)$^+$: calcd for $C_{29}H_{31}N_2O_5$ $[M+H]^+$ 487.2233, found: 487.2207.

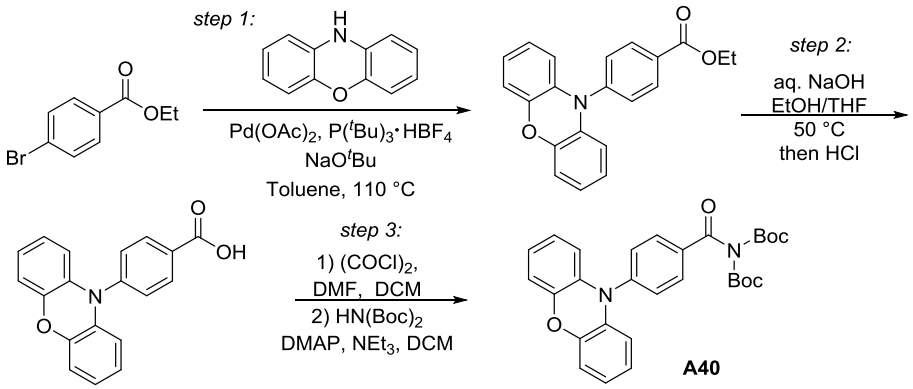


***N*,*N*-Boc$_2$-4-diphenylaminobenzamide (A39)** was prepared according to the known literature with proper adjustment.[15]

Step 1: Diphenylamine (10.0 mmol. 1.69 g), $Pd_2(dba)_3$ (0.3 mmol, 274.5 mg), $P(^tBu)_3{\cdot}HBF_4$ (0.6 mmol, 174.0 mg) and KO^{t}Bu (20.0 mmol, 2.24 g) were added into a dried 100 mL two-neck flask equipped with a condenser pipe, and it was subjected to three cycles of vacuum and refilled with nitrogen. Toluene (30 mL) was sequentially injected into it, and the mixture was stirred at room temperature for 15 min. Then ethyl 4-bromobenzoate (11.0 mmol, 2.52 g) was added dropwise to it and the mixture was transferred to 110 °C and stirred for 16 h. After the indicated time, the mixture was slowly cooled to room temperature, diluted with dichloromethane (50 mL) and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the ethyl 4-(diphenylamino)benzoate (2.84 g, 90%).

Step 2: To a solution of ethyl 4-(diphenylamino)benzoate (8.96 mmol, 2.84 g) in EtOH/THF (v/v: 1:1, 30 mL) was added 1 M aqueous NaOH solution (18.0 mmol, 18.0 mL), and the mixture was stirred at 50 °C overnight. After the indicated time, the mixture was slowly cooled to room temperature and 1 M aqueous HCl solution was added to adjust the pH to 2. Then the precipitated solid was filtered, washed with water

and dried under vacuum to give the 4-(diphenylamino)benzoic acid. (2.55 g, 98%).
Step 3: To a solution of 4-(diphenylamino)benzoic acid (8.82 mmol, 2.55 g) in dichloromethane (20 mL) was added oxalyl chloride (17.8 mmol, 1.5 mL) dropwise at 0 °C, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure. Then obtained acyl chloride was redissolved in dichloromethane (10 mL), and the solution was added dropwise to a solution of $HN(Boc)_2$ (8.82 mmol, 1.92 g), NEt_3 (10.8 mmol, 1.5 mL) and and DMAP (0.9 mmol, 109.8 mg) in dichloromethane (25 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (50 mL) and extracted with dichloromethane (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford **A39** (3.55 g, 82%).
White solid. Mp: 121-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.18 – 7.11 (m, 6H), 6.97 (d, *J* = 8.9 Hz, 2H), 1.48 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.47, 153.22, 149.79, 146.15, 132.10, 129.77, 126.28, 125.13, 120.17, 119.21, 81.97, 28.09. HRMS (ESI)$^+$: calcd for $C_{29}H_{33}N_2O_5$ $[M+H]^+$ 489.2389, found: 489.2397.

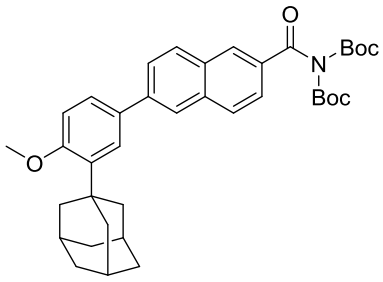


***N,N*-Boc$_2$-4-(10*H*-phenoxazin-10-yl)benzamide (A40)** was prepared according to the known literature with proper adjustment.[16]
Step 1: 10*H*-phenoxazine (10.0 mmol. 1.83 g), $Pd(OAc)_2$ (0.3 mmol, 67.3 mg), $P(^tBu)_3{\cdot}HBF_4$ (0.6 mmol, 174.0 mg) and NaO^tBu (15.0 mmol, 1.44 g) were added into a dried 100 mL two-neck flask equipped with a condenser pipe, and it was subjected to three cycles of vacuum and refilled with nitrogen. Toluene (30 mL) was sequentially injected into it, and the mixture was stirred at room temperature for 15 min. Then ethyl 4-bromobenzoate (11.0 mmol, 2.52 g) was added dropwise to it and the mixture was transferred to 110 °C and stirred for 24 h. After the indicated time, the mixture was slowly cooled to room temperature, diluted with dichloromethane (50 mL) and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the ethyl 4-(10*H*-phenoxazin-10-yl)benzoate (2.67 g, 81%).

Step 2: To a solution of ethyl 4-(10*H*-phenoxazin-10-yl)benzoate (8.07 mmol, 2.67 g) in EtOH/THF (v/v: 1:1, 30 mL) was added 1 M aqueous NaOH solution (17.0 mmol, 17.0 mL), and the mixture was stirred at 50 °C overnight. After the indicated time, the mixture was slowly cooled to room temperature and 1 M aqueous HCl solution was added to adjust the pH to 2. Then the precipitated solid was filtered, washed with water and dried under vacuum to give the 4-(10*H*-phenoxazin-10-yl)benzoic acid. (2.34 g, 96%).

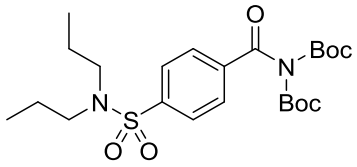
Step 3: To a solution of 4-(10*H*-phenoxazin-10-yl)benzoic acid (7.72 mmol, 2.34 g) in dichloromethane (20 mL) was added oxalyl chloride (16.5 mmol, 1.4 mL) dropwise at 0 °C, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure. Then obtained acyl chloride was redissolved in dichloromethane (10 mL), and the solution was added dropwise to a solution of $HN(Boc)_2$ (7.74 mmol, 1.68 g), NEt_3 (9.3 mmol, 1.3 mL) and DMAP (0.8 mmol, 97.6 mg) in dichloromethane (25 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (50 mL) and extracted with dichloromethane (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford **A40** (3.25 g, 84%).

Yellow solid. Mp: 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.75 – 6.65 (m, 4H), 6.64 – 6.56 (m, 2H), 5.95 (d, *J* = 7.7 Hz, 2H), 1.45 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.59, 149.80, 144.09, 143.94, 134.16, 133.51, 131.76, 131.09, 123.25, 122.05, 115.84, 113.35, 84.67, 27.67. HRMS (ESI)$^+$: calcd for $C_{29}H_{31}N_2O_6$ $[M+H]^+$ 503.2182, found: 503.2168.



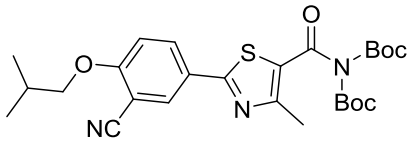
***N*,*N*-Boc$_2$-6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthamide (A41)**

Procedure II was followed with Adapalene to afford **A41** (1.56 g, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 (s, 1H), 8.00 – 7.93 (m, 2H), 7.90 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.83 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.18 (br, 6H), 2.11 (br, 3H), 1.81 (br, 6H), 1.37 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.22, 159.07, 149.85, 142.05, 139.09, 136.18, 132.29, 131.12, 130.83, 130.61, 129.79, 128.75, 126.93, 125.99, 125.75, 125.12, 124.78, 112.13, 84.24, 55.18, 40.62, 37.24, 37.13, 29.11, 27.66. HRMS (ESI)$^+$: calcd for $C_{38}H_{45}NNaO_6$ $[M+Na]^+$ 634.3145, found: 634.3141.[17]



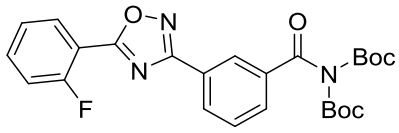
***N*,*N*-Boc$_2$-4-(*N*,*N*-dipropylsulfamoyl)benzamide (A42)**

Procedure II was followed with Probenecid to afford **A42** (1.17 g, 81%) as a white solid. Mp: 91-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (br, 4H), 3.08 (t, *J* = 7.6 Hz, 4H), 1.58 – 1.47 (m, 4H), 1.37 (s, 18H), 0.84 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.29, 149.48, 144.47, 137.56, 129.31, 127.20, 84.94, 49.87, 27.55, 21.88, 11.12. HRMS (ESI)$^+$: calcd for $C_{23}H_{36}N_2NaO_7S$ $[M+Na]^+$ 507.2141, found: 507.2137.



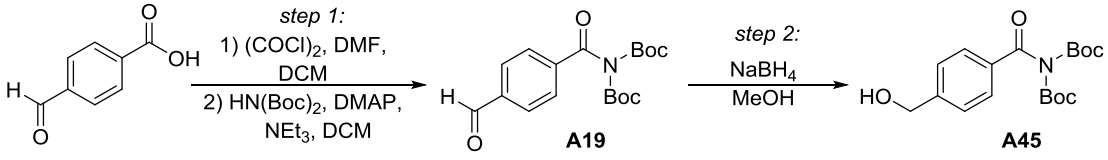
***N*,*N*-Boc$_2$-2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxamide (A43)**

Procedure II was followed with Febuxostat to afford **A43** (1.34 g, 87%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.3 Hz, 1H), 8.08 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.71 (s, 3H), 2.27 – 2.15 (m, 1H), 1.45 (s, 18H), 1.08 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.29, 162.85, 162.14, 161.78, 148.87, 132.76, 132.26, 127.15, 125.51, 115.23, 112.74, 103.17, 84.69, 75.78, 28.15, 27.78, 19.04, 17.54. HRMS (ESI)$^+$: calcd for $C_{26}H_{34}N_3O_6S$ $[M+H]^+$ 516.2168, found: 516.2148.[17]



***N*,*N*- Boc$_2$-3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)benzamide (A44)**

Procedure II was followed with Atuluren to afford **A44** (1.24 g, 86%) as a white solid. Mp: 112-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.46 – 8.39 (m, 1H), 8.25 (td, *J* = 7.8, 1.7 Hz, 1H), 8.04 – 7.97 (m, 1H), 7.70 – 7.59 (m, 2H), 7.41 – 7.27 (m, 2H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.19 (d, *J* = 4.4 Hz), 168.71, 167.71, 160.80 (d, *J* = 260.9 Hz), 149.73, 135.03, 134.85 (d, *J* = 8.7 Hz), 131.98, 131.56, 130.98, 129.38, 128.02, 127.53, 124.78 (d, *J* = 3.8 Hz), 117.20 (d, *J* = 20.9 Hz), 112.59 (d, *J* = 11.3 Hz), 84.65, 27.61. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.15. HRMS (ESI)$^+$: calcd for $C_{25}H_{27}FN_3O_6$ $[M+H]^+$ 484.1884, found: 484.1886.



***N*,*N*-Boc$_2$-4-(hydroxymethyl)benzamide (A45)**

Step 1: To a solution of 4-formylbenzoic acid (3.0 mmol, 450.0 mg) in dichloromethane (10 mL) was added oxalyl chloride (4.5 mmol, 0.38 mL) dropwise at 0 °C, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure. The obtained mixture was redissolved in dichloromethane (5 mL), and the solution was added dropwise to a solution of $HN(Boc)_2$ (3.0 mmol, 651.0 mg), NEt_3 (3.6 mmol, 0.5 mL) and DMAP (0.3 mmol, 36.6 mg) in dichloromethane (10 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (30 mL) and extracted with dichloromethane (30 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford **A19** (897.6 mg, 86%).

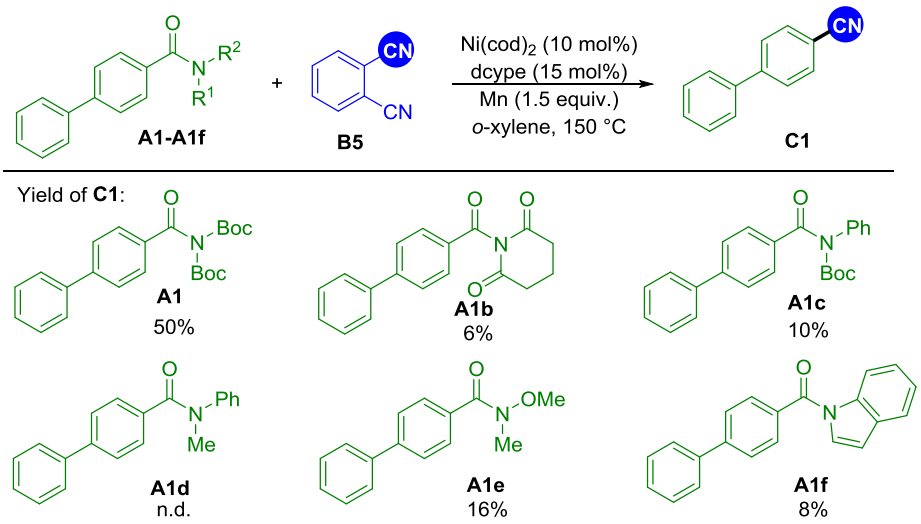
Step 2: To a solution of **A19** (897.6 mg, 2.57 mmol) in methanol (20 mL) was slowly added $NaBH_4$ (136.8 mg, 3.6 mmol) at 0 °C, and the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the resulting mixture was cooled to 0 °C, diluted with water (20 mL) and concentrated under reduced pressure, and the residue was sequentially extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford **A45** (821.4 mg, 91%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 4.77 (s, 2H), 2.25 (s, 1H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.00, 149.79, 147.06, 133.03, 129.41, 126.58, 84.34, 64.36, 27.62. HRMS (ESI)$^+$: calcd for $C_{18}H_{25}NNaO_6$ $[M+Na]^+$ 374.1580, found: 374.1570.

III. Optimization of reaction conditions

3.1 Screening of amide N substituents.

Six amides with different N substituents (**A1**-**A1f**) were tested as shown in **Scheme S1**. The results showed that benzamide with *N*,*N*-Boc_2 substituents gave the best yield, so **A1** was chosen as model substrate for further evaluation.

Scheme S1. Screening of Amide N Substituents[a,b]

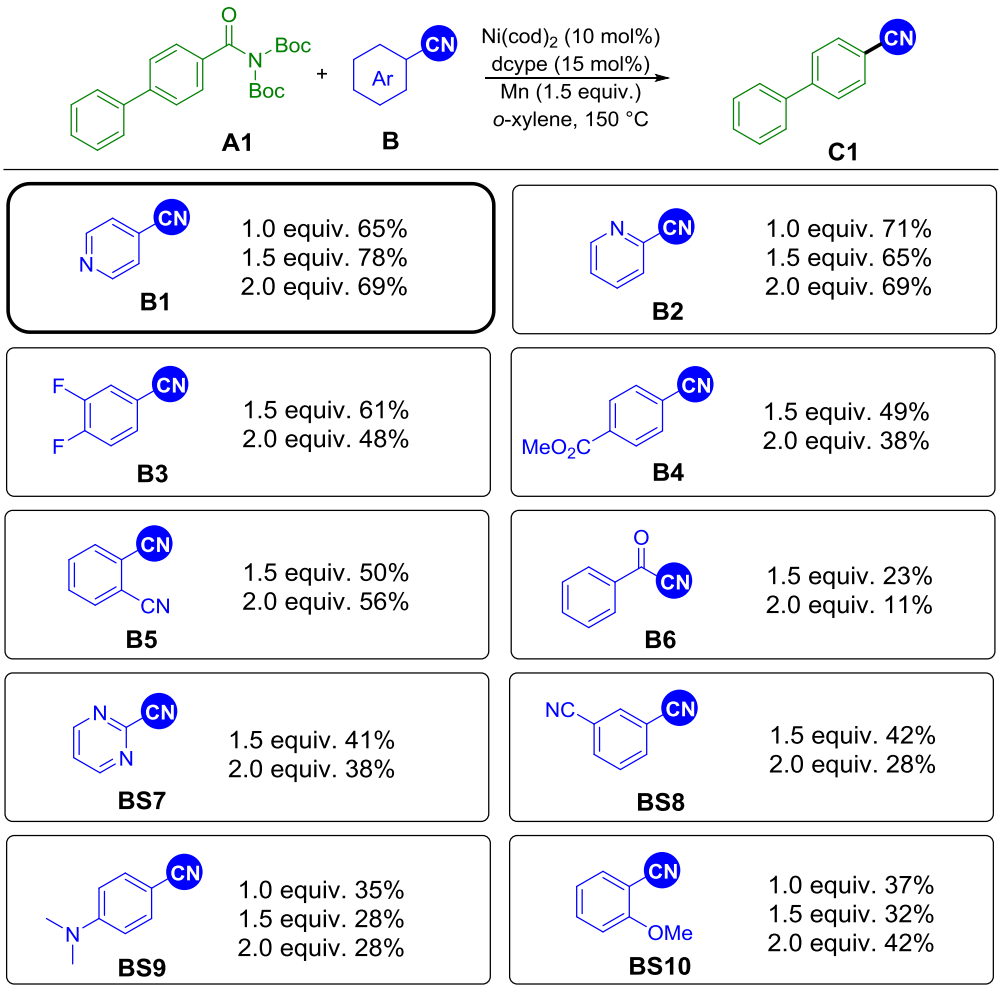


[a]All reactions were carried out with **A** (0.1 mmol), **B5** (0.15 mmol), $Ni(cod)_2$ (10 mol%), dcype (15 mol%) and Mn (0.15 mmol) in *o*-xylene (1 mL) at 150 °C for 24 h. [b]GC yields by using 4-methoxybiphenyl as internal standard.

3.2 Screening of aryl nitrile donors.

Ten different aryl nitrile donors (**B1**-**BS10**) were tested as shown in **Scheme S2**. The results showed that 4-cyanopyridine **B1** gave the best yield, so **B1** was chosen as optimal cyano donor for further evaluation.

Scheme S2. Screening of Aryl Nitrile Donors.[a,b]

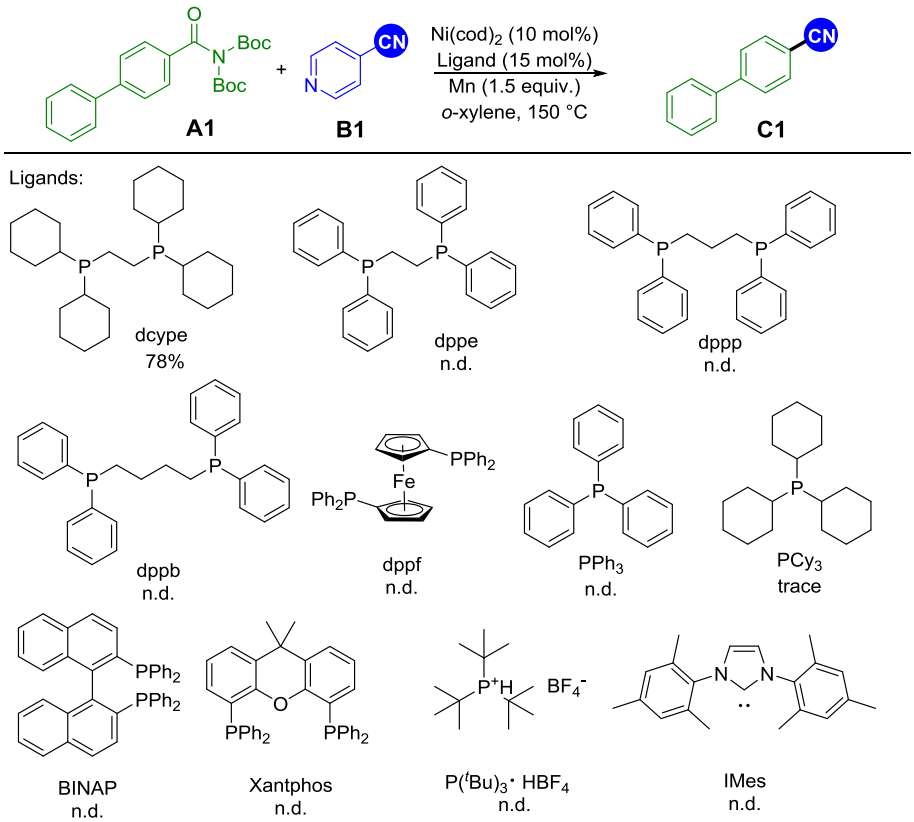


[a]All reactions were carried out with **A1** (0.1 mmol), **B**, $Ni(cod)_2$ (10 mol%), dcype (15 mol%) and Mn (0.15 mmol) in *o*-xylene (1 mL) at 150 °C for 24 h. [b]GC yields by using 4-methoxybiphenyl as internal standard.

3.3 Screening of ligands

Eleven different ligands were surveyed as shown in Scheme S3. The results showed that 1,2-bis-(dicyclohexylphosphino)ethane dcype gave the best yield, so dcype was chosen as optimal ligand for further evaluation.

Scheme S3. Screening of Ligands.[a,b]

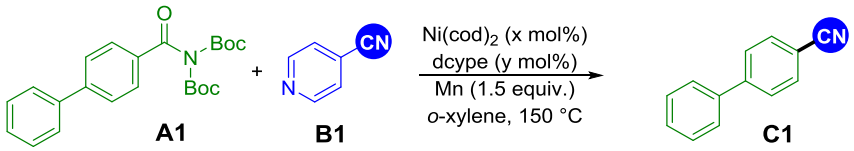


[a]All reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(cod)_2$ (10 mol%), dcype (15 mol%) and Mn (0.15 mmol) in *o*-xylene (1 mL) at 150 °C for 24 h. [b]GC yields by using 4-methoxybiphenyl as internal standard.

3.4 Screening of catalyst loading

Different catalyst loadings were surveyed as shown in Table S1. The results showed that the conditions in Entry 1 gave a comparable yield to the conditions in Entry 5, so the conditions in entry 1 was chosen for further evaluation.

Table S1. Screening of Catalyst Loading.[a,b]



Entry	$Ni(cod)_2$	dcype	Yield
1	10 mol%	15 mol%	78%
2	15 mol%	15 mol%	69%
3	15 mol%	20 mol%	71%
4	20 mol%	20 mol%	70%
5	20 mol%	25 mol%	80%
6	10 mol%	w/o	trace
7	w/o	15 mol%	n.d.

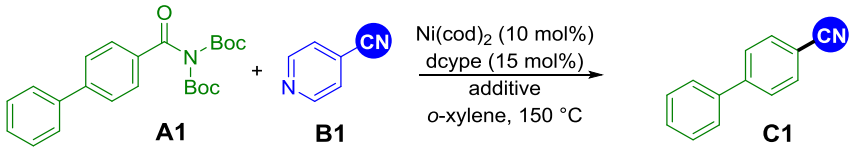
[a]All reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(cod)_2$ (x mol%), dcype (y

mol%) and Mn (0.15 mmol) in *o*-xylene (1 mL) at 150 °C for 24 h. [b]GC yields by using 4-methoxybiphenyl as internal standard.

3.5 Screening of additives

Various additives were surveyed as shown in Table S2. The results showed that 1.5 equivalent of Mn gave the best yield, so Mn was chosen as for further evaluation.

Table S2. Screening of Additives.[a,b]



Entry	Additives	Yield
1	Mn (1.0 equiv.)	71%
2	Mn (1.5 equiv)	78%
3	Mn (2.0 equiv)	77%
4	Mn (2.5 equiv)	70%
5	Zn (1.0 equiv.)	61%
6	Zn (1.5 equiv.)	71%
7	Zn (2.0 equiv.)	73%
8	NaO^{t}Bu (1.0 equiv.)	19%
9	Cs_2CO_3 (1.0 equiv)	9%
10	K_2CO_3 (1.0 equiv)	11%
11	NaOMe (1.0 equiv)	16%
12	NaSEt (1.0 equiv)	2%
13	NaH (1.0 equiv)	10%
14	DBU (1.0 equiv)	trace
15	$Na_2C_2O_4$ (1.0 equiv)	n.d.
16	K_3PO_4 (1.0 equiv)	14%
17	w/o additive	57%

[a]All reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(cod)_2$ (10 mol%), dcype (15 mol%) and additive in *o*-xylene (1 mL) at 150 °C for 24 h. [b]GC yields by using 4-methoxybiphenyl as internal standard.

3.6 Screening of solvents and temperature

Different solvents and temperature were surveyed as shown in Table S3. The results showed that *o*-xylene as solvent (entry 1) gave the best yield, and 150 °C as temperature (entry 2) gave the best yield.

Table S3. Screening of Solvents and Temperature.[a,b]

A1 B1 C1

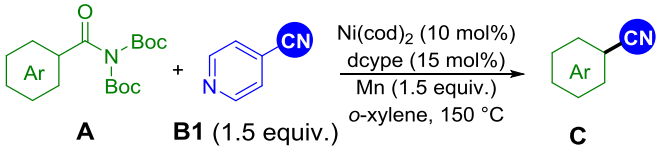
Entry	Solvent	Temperature	Yield
1	*o*-xylene	150 °C	78%
2	toluene	150 °C	64%
3	mesitylene	150 °C	70%
4	1,4-dioxane	150 °C	56%
6	*o*-xylene	140 °C	68%
7	*o*-xylene	160 °C	75%

[a]All reactions were carried out with **A1** (0.1 mmol), **B1** (0.15 mmol), $Ni(cod)_2$ (10 mol%), dcype (15 mol%) and Mn (0.15 mmol) in solvent (1 mL) at indicated temperature for 24 h. [b]GC yields by using 4-methoxybiphenyl as internal standard.

IV. General procedure for Ni-catalyzed synthesis of aryl nitrile from aromatic amide and characterization data of the products

Aryl nitrile products **C1-C14**, **C16-C29** and **C31-C44** were synthesized through Procedure IV. Aryl nitrile product **C15** was synthesized through both Procedure IV and Procedure V, and aryl nitrile product **C30** was synthesized through Procedure VI. Detailed description of all procedures and the characterization data of products were as follows:

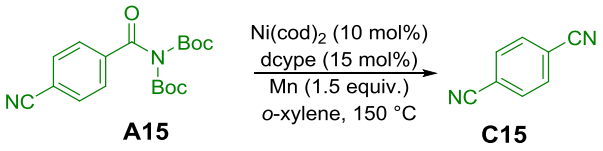
Procedure IV:



A B1 (1.5 equiv.) C

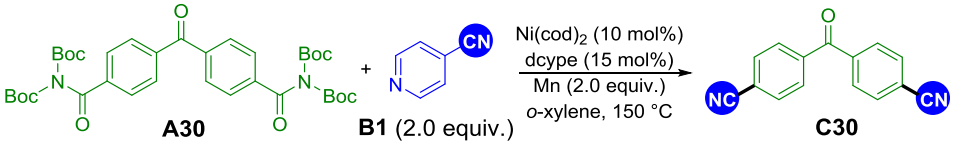
N,*N*-Boc_2 substituted aromatic amide **A** (0.1 mmol), 4-cyanopyridine **B1** (0.15 mmol, 15.6 mg), $Ni(cod)_2$ (0.01 mmol, 2.8 mg), dcype (0.015 mmol, 6.4 mg), Mn (0.15 mmol, 8.3 mg) and *o*-xylene (1.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the corresponding products.

Procedure V:



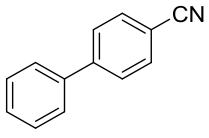
N,*N*-Boc$_2$ 4-cyanobenzamide **A15** (0.2 mmol, 69.2 mg), Ni(cod)$_2$ (0.01 mmol, 2.8 mg), dcype (0.015 mmol, 6.4 mg), Mn (0.15 mmol, 8.3 mg) and *o*-xylene (1.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the corresponding products, and the yield was calculated based on the theoretical yield obtained from the decyanation and cyanation of **A15** in a 1:1 ratio. (Note: 0.1 mmol of **A15** was treated as cyanating agent in this reaction.)

Procedure VI:



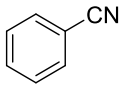
4,4'-Carbonylbis(*N*,*N*-Boc$_2$-benzamide) **A30** (0.1 mmol, 66.8 mg), 4-cyanopyridine **B1** (0.2 mmol, 20.8 mg), Ni(cod)$_2$ (0.01 mmol, 2.8 mg), dcype (0.015 mmol, 6.4 mg), Mn (0.2 mmol, 11.0 mg) and *o*-xylene (1.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the corresponding products.

Characterization of the products:



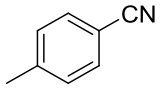
[1,1'-Biphenyl]-4-carbonitrile (C1)

Procedure IV was followed to afford **C1** (13.8 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 4H), 7.62 – 7.57 (m, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.68, 139.18, 132.61, 129.13, 128.68, 127.74, 127.24, 118.96, 110.93.[18]



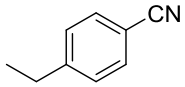
Benzonitrile (C2)

Procedure IV was followed to afford **C2** (7.8 mg, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.63 – 7.58 (m, 1H), 7.50 – 7.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.78, 132.16, 129.13, 118.85, 112.46.[19]



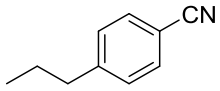
4-Methylbenzonitrile (C3)

Procedure IV was followed to afford **C3** (9.6 mg, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70, 132.05, 129.84, 119.17, 109.32, 21.85.[18]



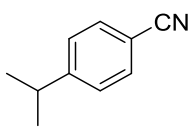
4-Ethylbenzonitrile (C4)

Procedure IV was followed to afford **C4** (10.2 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.81, 132.18, 128.68, 119.20, 109.49, 29.08, 15.04.[20]



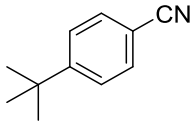
4-Propylbenzonitrile (C5)

Procedure IV was followed to afford **C5** (10.3 mg, 71%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.63 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.33, 132.11, 129.25, 119.25, 109.50, 38.13, 24.13, 13.70.[21]



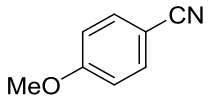
4-Isopropylbenzonitrile (C6)

Procedure IV was followed to afford **C6** (10.3 mg, 71%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.36, 132.24, 127.30, 119.18, 109.61, 34.40, 23.54.[22]



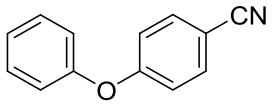
4-(*tert*-Butyl)benzonitrile (C7)

Procedure IV was followed to afford **C7** (12.3 mg, 77%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.64, 131.97, 126.17, 119.17, 109.32, 35.28, 30.96.[21]



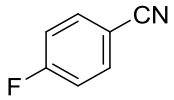
4-Methoxybenzonitrile (C8)

Procedure IV was followed to afford **C8** (10.3 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.85, 133.98, 119.24, 114.76, 103.96, 55.55.[21]



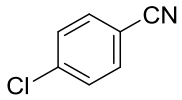
4-Phenoxybenzonitrile (C9)

Procedure IV was followed to afford **C9** (14.3 mg, 73%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.47 – 7.41 (m, 2H), 7.29 – 7.23 (m, 1H), 7.11 – 7.06 (m, 2H), 7.05 – 7.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.67, 154.81, 134.13, 130.24, 125.15, 120.42, 118.86, 117.92, 105.82.[23]



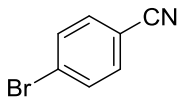
4-Fluorobenzonitrile (C10)

Procedure IV was followed to afford **C10** (7.9 mg, 65%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.23 – 7.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.04 (d, *J* = 256.6 Hz), 134.69 (d, *J* = 9.3 Hz), 118.03, 116.87 (d, *J* = 22.7 Hz), 108.59 (d, *J* = 3.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.43.[24]



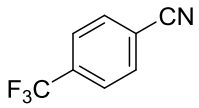
4-Chlorobenzonitrile (C11)

Procedure IV was followed to afford **C11** (9.8 mg, 71%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.56, 133.39, 129.70, 117.97, 110.79.[24]



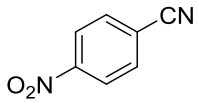
4-Bromobenzonitrile (C12)

Procedure IV was followed to afford **C12** (7.7 mg, 42%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.41, 132.65, 128.02, 118.05, 111.26. (Note: Through Procedure IV, except for 4-bromobenzonitrile, 28% yield of the debrominating product benzonitrile was also detected.) [24]



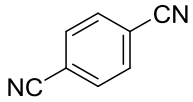
4-(Trifluoromethyl)benzonitrile (C13)

Procedure IV was followed to afford **C13** (12.8 mg, 75%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6 (q, *J* = 34.4 Hz), 132.69, 126.19 (q, *J* = 3.7 Hz), 123.05 (q, *J* = 273.9 Hz), 117.44, 116.06. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.56.[25]



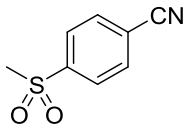
4-Nitrobenzonitrile (C14)

Procedure IV was followed to afford **C14** (10.0 mg, 68%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.05, 133.49, 124.30, 118.34, 116.80.[26]



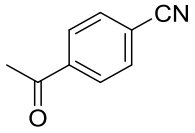
Terephthalonitrile (C15)

Procedure IV was followed to afford **C15** (9.0 mg, 70%), and Procedure V was followed to afford **C15** (10.5 mg, 82%). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.80, 117.02, 116.72.[27]



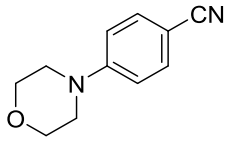
4-(Methylsulfonyl)benzonitrile (C16)

Procedure IV was followed to afford **C16** (15.3 mg, 85%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.49, 133.22, 128.22, 117.65, 117.04, 44.25.[28]



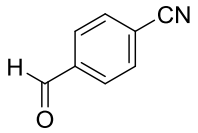
4-Acetylbenzonitrile (C17)

Procedure IV was followed to afford **C17** (11.2 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.53, 139.92, 132.53, 128.70, 117.93, 116.43, 26.78.[29]



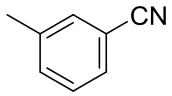
4-Morpholinobenzonitrile (C18)

Procedure IV was followed to afford **C18** (15.2 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 9.1 Hz, 2H), 6.87 (d, *J* = 9.1 Hz, 2H), 3.85 (t, *J* = 4.8 H, 4H), 3.28 (t, *J* = 4.8 H, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.46, 133.53, 119.85, 114.13, 101.06, 66.45, 47.36.[30]



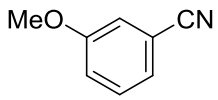
4-Formylbenzonitrile (C19)

Procedure IV was followed to afford **C19** (7.3 mg, 56%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.59, 138.74, 132.91, 129.89, 117.71, 117.62.[31]



3-Methylbenzonitrile (C20)

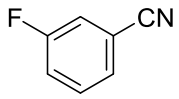
Procedure IV was followed to afford **C20** (9.4 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.43 – 7.39 (m, 1H), 7.38 – 7.32 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.22, 133.66, 132.51, 129.30, 128.99, 119.08, 112.24, 21.19.[26]



3-Methoxybenzonitrile (C21)

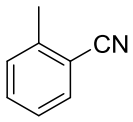
Procedure IV was followed to afford **C21** (9.0 mg, 68%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 1H), 7.25 – 7.20 (m, 1H), 7.15 – 7.09 (m, 2H),

3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.64, 130.34, 124.47, 119.30, 118.75, 116.85, 113.18, 55.54.[26]



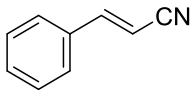
3-Fluorobenzonitrile (C22)

Procedure IV was followed to afford **C22** (8.8 mg, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.39 – 7.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.21 (d, *J* = 250.3 Hz), 131.16 (d, *J* = 8.3 Hz), 128.20 (d, *J* = 3.6 Hz), 120.53 (d, *J* = 21.0 Hz), 119.18 (d, *J* = 24.5 Hz), 117.54 (d, *J* = 3.1 Hz), 113.94 (d, *J* = 9.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.64.[27]



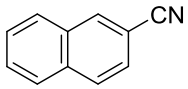
2-Methylbenzonitrile (C23)

Procedure IV was followed to afford **C23** (7.4 mg, 63%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.49 (td, *J* = 7.7, 1.3 Hz, 1H), 7.36 – 7.25 (m, 2H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.91, 132.64, 132.49, 130.23, 126.22, 118.14, 112.75, 20.46.[24]



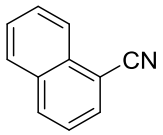
Cinnamonitrile (C24)

Procedure IV was followed to afford **C24** (6.5 mg, 50%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 6H), 5.89 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.60, 133.54, 131.23, 129.13, 127.37, 118.15, 96.37.[24]



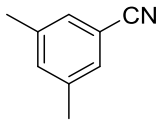
2-Naphthonitrile (C25)

Procedure IV was followed to afford **C25** (12.4 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.94 – 7.87 (m, 3H), 7.68 – 7.57 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.66, 134.17, 132.26, 129.21, 129.05, 128.42, 128.06, 127.67, 126.36, 119.27, 109.39.[26]



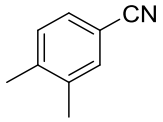
1-Naphthonitrile (C26)

Procedure IV was followed to afford **C26** (9.7 mg, 63%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.70 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.63 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.53 (dd, *J* = 8.2, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.29, 132.94, 132.65, 132.38, 128.67, 128.62, 127.57, 125.18, 124.94, 117.83, 110.22.[26]



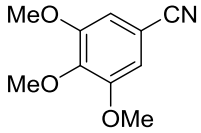
3,5-Dimethylbenzonitrile (C27)

Procedure IV was followed to afford **C27** (9.8 mg, 75%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 7.24 (s, 1H), 2.36 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.03, 134.60, 129.66, 119.22, 112.04, 21.03.[32]



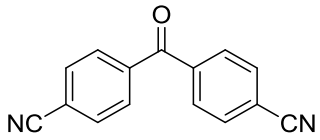
3,4-Dimethylbenzonitrile (C28)

Procedure IV was followed to afford **C28** (10.6 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.46, 137.88, 132.85, 130.29, 129.65, 119.31, 109.53, 20.14, 19.56.[28]



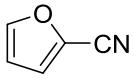
3,4,5-Trimethoxybenzonitrile (C29)

Procedure IV was followed to afford **C29** (15.2 mg, 79%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 2H), 3.89 (s, 3H), 3.87 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.57, 142.36, 118.98, 109.46, 106.72, 61.06, 56.40.[28]



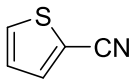
4,4'-Carbonyldibenzonitrile (C30)

Procedure V was followed to afford **C30** (18.3 mg, 79%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 4H), 7.82 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.46, 139.76, 132.49, 130.27, 117.70, 116.57.[33]



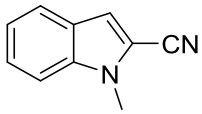
Furan-2-carbonitrile (C31)

Procedure IV was followed to afford **C31** (6.2 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 6.54 (dd, *J* = 3.6, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.34, 126.34, 121.99, 111.58, 111.45.[34]



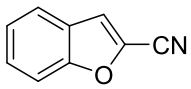
Thiophene-2-carbonitrile (C32)

Procedure IV was followed to afford **C32** (7.3 mg, 67%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H), 7.13 (dd, *J* = 4.8, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.42, 132.57, 127.65, 114.24, 109.95.[35]



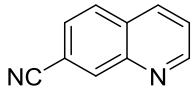
1-Methyl-1H-indole-2-carbonitrile (C33)

Procedure IV was followed to afford **C33** (12.0 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.99, 126.12, 125.83, 122.34, 121.37, 113.68, 112.67, 110.23, 110.13, 31.52.[36]



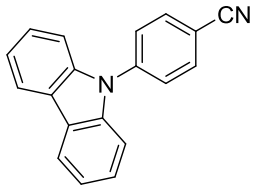
Benzofuran-2-carbonitrile (C34)

Procedure IV was followed to afford **C34** (7.4 mg, 52%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.46 (s, 1H), 7.40 – 7.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.69, 128.46, 127.32, 125.50, 124.57, 122.59, 118.48, 112.11, 111.85.[37]



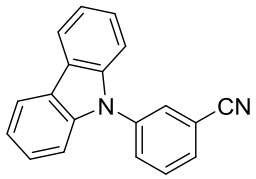
Quinoline-7-carbonitrile (C35)

Procedure IV was followed to afford **C35** (7.4 mg, 48%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 4.1 Hz, 1H), 8.51 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 8.4, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.40, 147.17, 136.62, 135.60, 130.61, 129.68, 127.76, 123.92, 118.72, 113.51.[38]



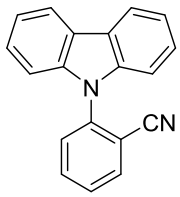
4-(9*H*-carbazol-9-yl)benzonitrile (C36)

Procedure IV was followed to afford **C36** (20.4 mg, 76%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.7 Hz, 2H), 7.93 – 7.87 (m, 2H), 7.76 – 7.71 (m, 2H), 7.50 – 7.41 (m, 4H), 7.35 (ddd, *J* = 6.1, 2.2, 1.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.08, 139.91, 133.94, 127.11, 126.40, 124.02, 121.03, 120.61, 118.41, 110.48, 109.55. HRMS (ESI)$^{+}$: calcd for $C_{19}H_{13}N_2$ $[M+H]^{+}$ 269.1079, found: 269.1061.[39]



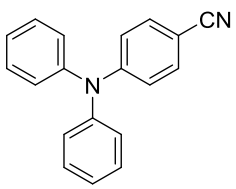
3-(9*H*-carbazol-9-yl)benzonitrile (C37)

Procedure IV was followed to afford **C37** (21.5 mg, 80%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.93 – 7.83 (m, 2H), 7.79 – 7.71 (m, 2H), 7.48 – 7.41 (m, 2H), 7.40 – 7.30 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.26, 138.94, 131.53, 131.00, 130.76, 130.35, 126.35, 123.77, 120.80, 120.59, 117.93, 114.25, 109.29. HRMS (ESI)$^{+}$: calcd for $C_{19}H_{13}N_2$ $[M+H]^{+}$ 269.1079, found: 269.1059.[39]



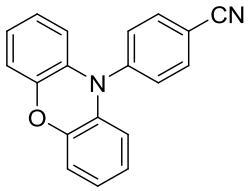
2-(9*H*-carbazol-9-yl)benzonitrile (C38)

Procedure IV was followed to afford **C38** (16.6 mg, 62%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.95 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.82 (td, *J* = 7.8, 1.4 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.48 – 7.41 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.73, 140.61, 134.56, 134.36, 129.71, 128.51, 126.24, 123.91, 120.83, 120.59, 116.10, 112.84, 109.73. HRMS (ESI)$^{+}$: calcd for $C_{19}H_{13}N_2$ $[M+H]^{+}$ 269.1079, found: 269.1071.[39]



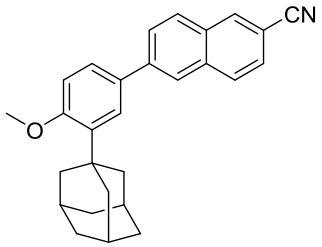
4-(Diphenylamino)benzonitrile (C39)

Procedure IV was followed to afford **C39** (22.9 mg, 85%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.30 (m, 4H), 7.19 – 7.12 (m, 6H), 6.99 – 6.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.61, 145.98, 133.19, 129.80, 126.18, 125.15, 119.71, 102.51. HRMS (ESI)$^{+}$: calcd for $C_{19}H_{15}N_2$ $[M+H]^{+}$ 271.1235, found: 271.1217.[40]



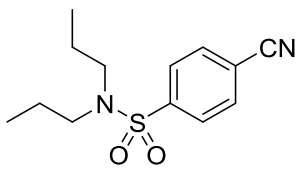
4-(10*H*-phenoxazin-10-yl)benzonitrile (C40)

Procedure IV was followed to afford **C40** (21.9 mg, 77%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.77 – 6.68 (m, 4H), 6.67 – 6.60 (m, 2H), 5.94 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.08, 143.77, 135.00, 133.26, 131.81, 123.38, 122.32, 118.13, 115.97, 113.42, 112.21. HRMS (ESI)$^{+}$: calcd for $C_{19}H_{13}N_2O$ $[M+H]^{+}$ 285.1028, found: 285.1016.[41]



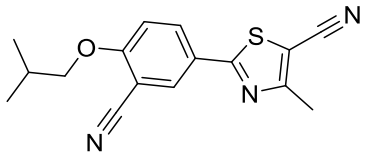
6-(3-((1r,3R,5S)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthonitrile (C41)

Procedure IV was followed to afford **C41** (31.0 mg, 79%) as a white solid. Mp: 169-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.01 (s, 1H), 7.97 – 7.90 (m, 2H), 7.85 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.19 (br, 6H), 2.11 (br, 3H), 1.81 (br, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.17, 142.23, 139.16, 135.13, 133.90, 132.01, 130.99, 129.22, 128.76, 127.46, 126.69, 125.98, 125.80, 124.87, 119.46, 112.16, 108.67, 55.19, 40.61, 37.24, 37.12, 29.11. HRMS (ESI)$^{+}$: calcd for $C_{28}H_{28}NO$ $[M+H]^{+}$ 394.2171, found: 394.2167.



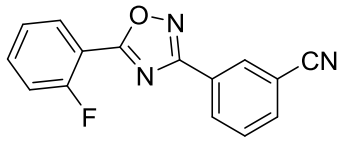
4-Cyano-N,N-dipropylbenzenesulfonamide (C42)

Procedure IV was followed to afford **C42** (22.3 mg, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 3.10 (t, *J* = 7.8 Hz, 4H), 1.60 – 1.48 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.65, 132.85, 127.60, 117.41, 115.96, 49.93, 21.94, 11.13. HRMS (ESI)$^{+}$: calcd for $C_{13}H_{19}N_2O_2S$ $[M+H]^{+}$ 267.1167, found: 267.1161.[42]



2-(3-Cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonitrile (C43)

Procedure IV was followed to afford **C43** (13.7 mg, 46%) as a white solid. Mp: 87-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 2.65 (s, 3H), 2.27 – 2.15 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.00, 164.91, 162.98, 132.76, 132.37, 125.02, 115.12, 112.80, 112.60, 103.29, 100.57, 75.83, 28.15, 19.04, 17.07. HRMS (ESI)$^{+}$: calcd for $C_{16}H_{16}N_3OS$ $[M+H]^{+}$ 298.1014, found: 298.1002.



3-(5-(2-Fluorophenyl)-1,2,4-oxadiazol-3-yl)benzonitrile (C44)

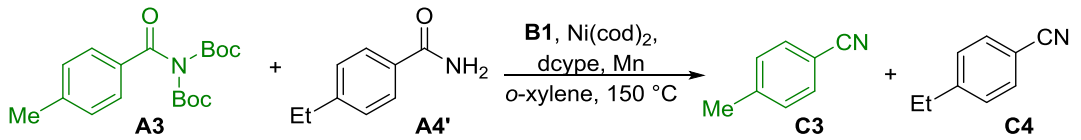
Procedure IV was followed to afford **C44** (18.8 mg, 71%) as a white solid. Mp: 118-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.44 – 8.39 (m, 1H), 8.21 (td, *J* = 7.9, 1.6 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.68 – 7.60 (m, 2H), 7.40 – 7.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.38 (d, *J* = 4.3 Hz), 167.12, 160.82 (d, *J* = 261.0 Hz), 135.01 (d, *J* = 8.7 Hz), 134.45, 131.52, 131.18, 130.92, 129.84, 128.24, 124.83 (d, *J* = 3.8 Hz), 118.02, 117.28 (d, *J* = 20.8 Hz), 113.41, 112.45 (d, *J* = 11.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.00. HRMS (ESI)$^{+}$: calcd for $C_{15}H_9FN_3O$ $[M+H]^{+}$ 266.0730, found: 266.0722.

V. Synthetic applications

5.1 Comparison of various cyanation methods

A mixture of **A3** (0.1 mmol) and **A4'** (0.1 mmol) was placed under nine different conditions respectively to determine the selectivity and activity. Detailed procedure and results (Table S4 & Scheme S4) for each method were as follows:

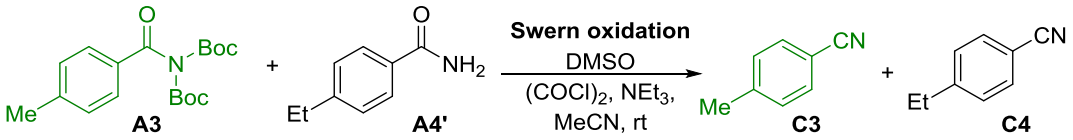
Method A:



N,*N*-Boc_2-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg), 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg), 4-cyanopyridine **B1** (0.2 mmol, 20.8 mg), $Ni(cod)_2$ (0.02 mmol, 5.6 mg), dcype (0.03 mmol, 12.8 mg), Mn (0.3 mmol, 16.5 mg) and *o*-xylene (2.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the

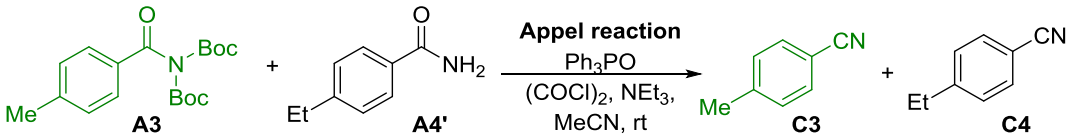
glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

Method B:



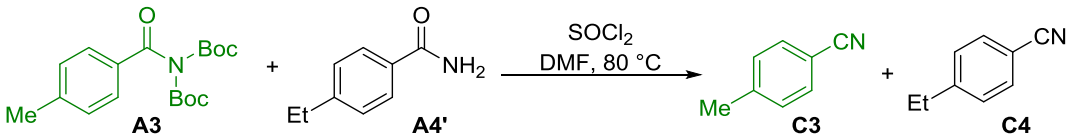
Method B was performed according to the known literature.[19] To a solution of *N,N*-Boc_2-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg) and 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) in anhydrous MeCN (1.0 mL) was added DMSO (in MeCN, 0.01 M, 0.2 mL) and NEt_3 (0.25 mmol, 70 μL). Subsequently, oxalyl chloride (0.24 mmol, 21 μL) in anhydrous MeCN (0.5 mL) was added dropwise at 20 °C and further stirred at room temperature for 40 min. After the indicated time, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

Method C:



Method C was performed according to the known literature.[43] To a solution of *N,N*-Boc_2-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg), 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) and Ph_3PO (0.002 mmol, 0.6 mg) in MeCN (1.0 mL) was added NEt_3 (0.6 mmol, 84 μL). Subsequently, oxalyl chloride (0.4 mmol, 34 μL) was added dropwise and the mixture was further stirred at room temperature for 10 min. After the indicated time, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

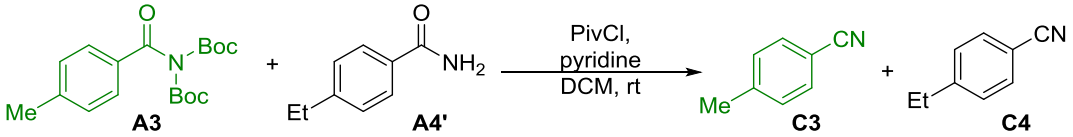
Method D:



Method D was performed according to the known literature.[44] A solution of thionyl chloride (1.0 mmol, 73 μL) in DMF (0.5 mL) was added dropwise to another solution

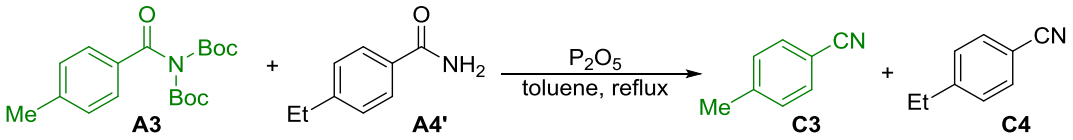
of *N*,*N*-Boc$_2$-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg) and 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) in DMF (1.0 mL). The mixture was then stirred at 80 °C for 30 min. After the indicated time, the mixture was slowly cooled to room temperature and the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added. Subsequently, the mixture was diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

Method E:



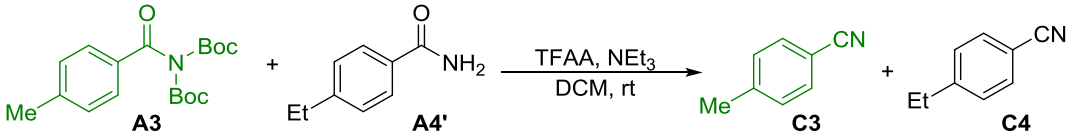
Method E was performed according to the known literature.[45] To a solution of *N*,*N*-Boc$_2$-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg), 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) and pivaloyl choride (0.22 mmol, 27 μL) in dichloromethane (1.0 mL) was added pyridine (0.24 mmol, 20 μL), and the mixture was stirred at room temperature for 6 h. After the indicated time, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

Method F:



Method F was performed according to the known literature.[46] A solution of *N*,*N*-Boc$_2$-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg), 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) in toluene (1.0 mL) was added P_2O_5 (1.0 mmol, 142.0 mg). Then the mixture was refluxed for 18 h. After the indicated time, the mixture was slowly cooled to room temperature and the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added. Subsequently, the mixture was diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

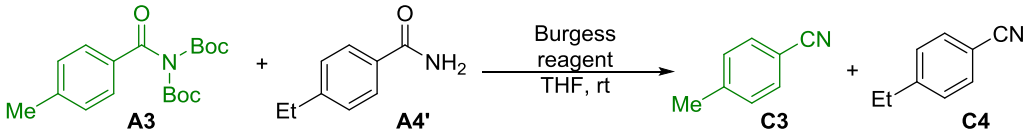
Method G:



Method G was performed according to the known literature.[47] To a solution of *N*,*N*-Boc$_2$-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg), 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) and NEt_3 (0.9 mmol, 125 μL) in anhydrous dichloromethane (1.0 mL) was added trifluoroacetic anhydride (in dichloromethane, 1 M, 0.4 mL) at 0 °C. Then the

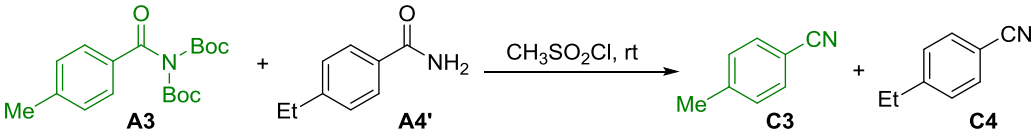
mixture was transferred to room temperature and stirred at the same temperature for 12 h. After the indicated time, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

Method H:



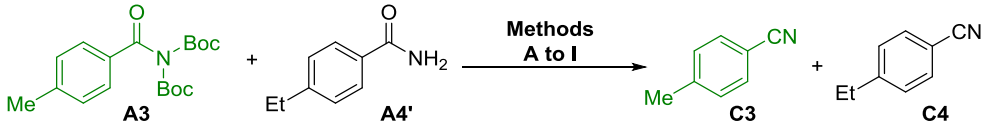
Method H was performed according to the known literature.[48] To a solution of *N,N*-Boc_2-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg) and 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) in anhydrous THF (1.0 mL) was added Burgess reagent (0.3 mmol, 71.4 mg) and the mixture was stirred at room temperature for 2 h. After the indicated time, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

Method I:



Method I was performed according to the known literature.[49] To a mixture of *N,N*-Boc_2-4-methylbenzamide **A3** (0.1 mmol, 33.5 mg) and 4-ethylbenzamide **A4'** (0.1 mmol, 14.9 mg) was added methanesulfonyl chloride (2.0 mL) dropwise over 5 min at 0 °C. Then the mixture was slowly warmed to room temperature and stirred at the same temperature overnight. After the indicated time, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 5 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC to analyze the composition of the reaction.

Table S4. Summary of Different Cyanation Methods.[a,b]

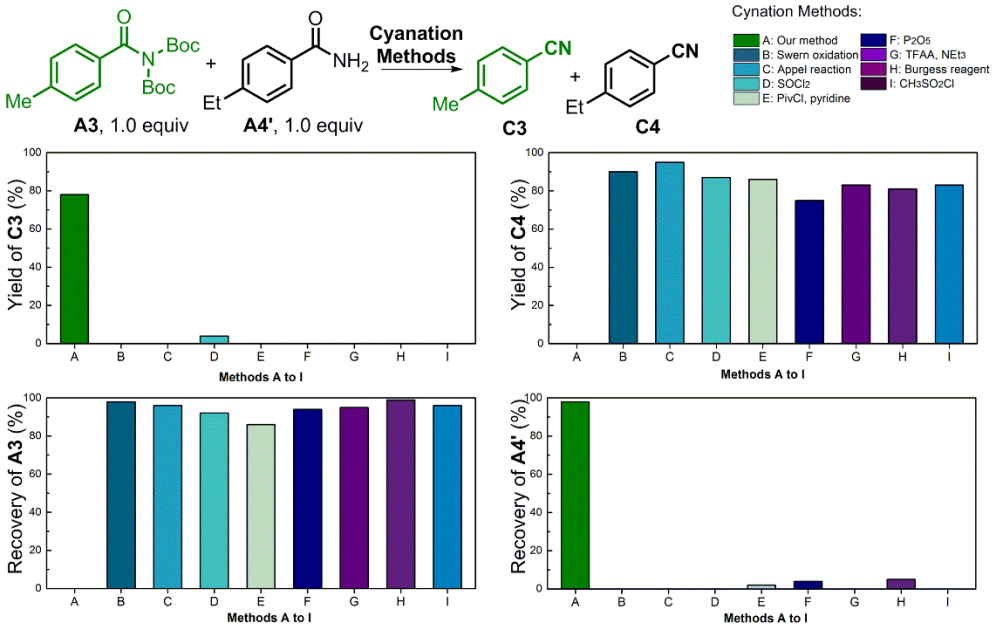


Methods	Yield of **C3**	Yield of **C4**	Recovery of **A3**	Recovery of **A4'**
A	77%	0%	0%	98%
B	0%	90%	98%	0%
C	0%	95%	96%	0%
D	4%	87%	92%	0%
E	0%	86%	86%	2%

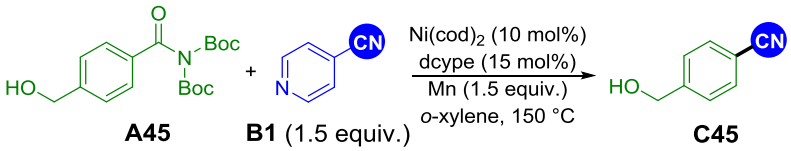
F	0%	75%	94%	4%
G	0%	83%	95%	0%
H	0%	81%	99%	5%
I	0%	83%	96%	0%

[a]All reactions were carried out with **A3** (0.1 mmol) and **A4'** (0.1 mmol) under the corresponding conditions. [b]GC yields by using 4-methoxybiphenyl as internal standard.

Scheme S4. Comparison of Various Cyanation Methods.

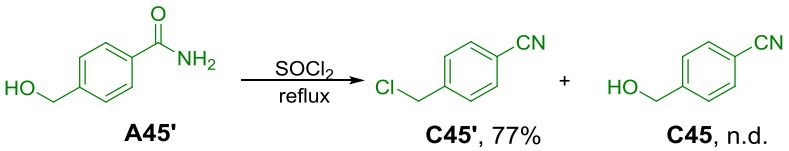


5.2 Cyanation of amide A44 and A44'



N,*N*-Boc$_2$-4-(hydroxymethyl)benzamide **A45** (0.1 mmol), 4-cyanopyridine **B1** (0.15 mmol, 15.6 mg), Ni(cod)$_2$ (0.01 mmol, 2.8 mg), dcype (0.015 mmol, 6.4 mg), Mn (0.15 mmol, 8.3 mg) and *o*-xylene (1.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the 4-(hydroxymethyl)benzonitrile **C45** (6.8 mg, 51%).

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 4.77 (s, 2H), 2.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.25, 132.32, 127.02, 118.86, 111.12, 64.20.[50]

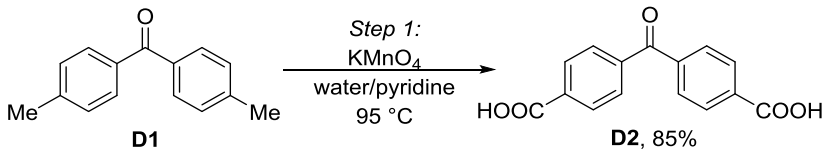


A45' **C45'**, 77% **C45**, n.d.

4-(Hydroxymethyl)benzamide **A45'** was prepared according to the known literature.[51] **A45'** (1.0 mmol, 151.0 mg) was added into a dried 25 mL two-neck flask equipped with a condenser pipe, and it was subjected to three cycles of vacuum and refilled with nitrogen. Then thionyl chloride (15 mL) was sequentially injected into it, and the mixture was refluxed for 12 h. After the indicated time, the reaction was concentrated under reduced pressure to remove the excess thionyl chloride. The residue was further dissolved in 10 mL of dichloromethane, and 1.0 μL of the solution was subjected to GC-Mass for composition analysis. The undesired chlorinated product 4-(chloromethyl)benzonitrile **C45'** was detected, while the targeted product 4-(hydroxymethyl)benzonitrile **C45** was not detected. Further purification of the residue by flash column chromatography on silica gel afforded 4-(chloromethyl)benzonitrile **C45'** (116.9 mg, 77%).

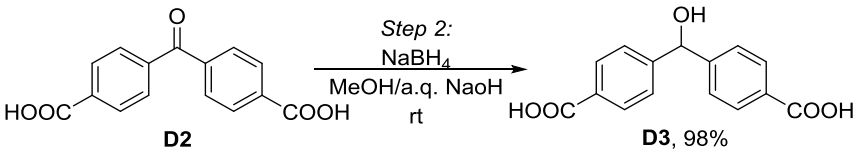
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 4.60 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.42, 132.54, 129.16, 118.40, 112.27, 44.93.[52]

5.3 Synthesis of Letrozole



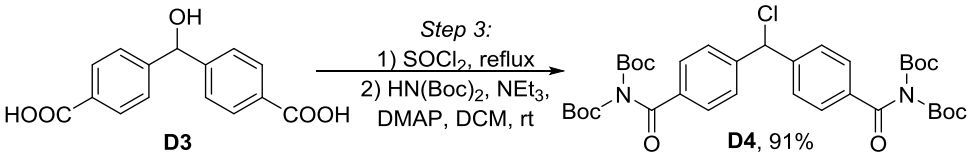
D1 **D2**, 85%

Step 1: this step was performed according to the known literature.[53] To a solution of di-*p*-tolylmethanone (1.0 mmol, 210.0 mg) in pyridine (10.0 mL) and water (10.0 mL) was added $KMnO_4$ (8.0 mmol, 1.27 g), and the mixture was stirred at 95 °C for 6 h. After the indicated time, the mixture was quenched with methanol, filtrated and washed with hot water to remove the MnO_2. Concentrated HCl was further added to the filtrate to adjust the pH to 1. Then the precipitated solid was filtered and redissolved in aqueous NaOH (5 %) to remove the insoluble impurity. The solution was once again acidified with concentrated HCl, and the precipitated solid was filtered, washed with water and dried under vacuum to give the 4,4'-carbonyldibenzoic acid **D2** (230.1 mg, 85% yield). White solid. Mp: 360-361 °C. ^{1}H NMR (400 MHz, DMSO) δ 13.37 (s, 2H), 8.11 (d, *J* = 8.4 Hz, 4H), 7.85 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ 195.46, 167.06, 140.43, 134.78, 130.27, 129.95. HRMS $(ESI)^-$: calcd for $C_{15}H_9O_5$ $[M-H]^-$ 269.0450, found: 269.0438.



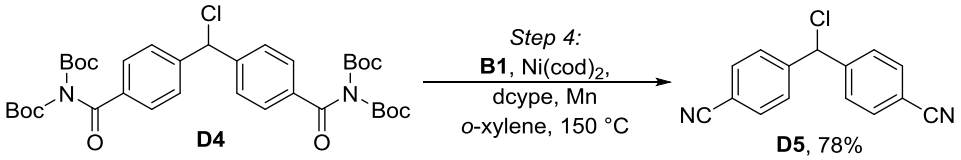
Step 2: this step was performed according to the known literature.[54] To a mixed solution of MeOH (10 mL) and 0.2 M aqueous NaOH (10 mL) was added 4,4'-carbonyldibenzoic acid **D2** (0.85 mmol, 230.1 mg). After the solid was dissolved, $NaBH_4$ (1.0 mmol, 38.0 mg) was added to the solution for three portions and the mixture was stirred at room temperature for 6 h. After the indicated time, concentrated HCl was added to the mixture to adjust the pH to 1, and the precipitated solid was filtered, washed with water and dried under vacuum to give the 4,4'-(hydroxymethylene)dibenzoic acid **D3** (225.8 mg, 98%), which was directly used for next step without further purification.

White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.86 (s, 2H), 7.89 (d, J = 8.1 Hz, 4H), 7.52 (d, J = 8.1 Hz, 4H), 6.21 (d, J = 3.6 Hz, 1H), 5.86 (d, J = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.59, 150.37, 129.89, 129.81, 126.81, 73.95. HRMS (ESI)$^-$: calcd for $C_{15}H_{11}O_5$ $[M-H]^-$ 271.0623, found: 271.0615.[55]



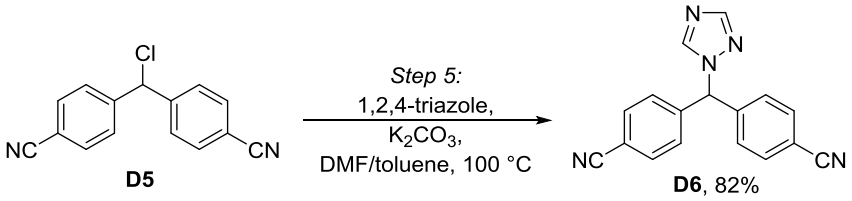
Step 3: 4,4'-(hydroxymethylene)dibenzoic acid **D3** (0.83 mmol, 225.8 mg) was added into a dried 25 mL two-neck flask equipped with a condenser pipe, and it was subjected to three cycles of vacuum and refilled with nitrogen. Then thionyl chloride (15 mL) was sequentially injected into it, and the mixture was refluxed for 12 h. After the indicated time, the reaction was concentrated under reduced pressure to remove the excess thionyl chloride. Then the residue was dissolved in DCM (10 mL), and the solution was added dropwise to a mixture of $HN(Boc)_2$ (1.0 mmol, 217.0 mg), DMAP (0.1 mmol, 12.2 mg) and NEt_3 (1.5 mmol, 0.2 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford the 4,4'-(chloromethylene)bis(*N*,*N*-Boc_2-benzamide) **D4** (518.2 mg, 91%).

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 4H), 7.46 (d, J = 8.4 Hz, 4H), 6.17 (s, 1H), 1.30 (s, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.60, 149.65, 145.53, 134.14, 129.30, 127.94, 84.39, 62.13, 27.47. HRMS (ESI)$^+$: calcd for $C_{35}H_{45}ClN_2NaO_{10}$ $[M+Na]^+$ 711.2660, found: 711.2605.



Step 4: 4,4'-(chloromethylene)bis(*N*,*N*-Boc$_2$-benzamide) **D4** (0.75 mmol, 518.2 mg), 4-cyanopyridine **B1** (1.5 mmol, 156.0 mg), Ni(cod)$_2$ (0.075 mmol, 20.6 mg), dcype (0.113 mmol, 47.5 mg), Mn (1.5 mmol, 82.5 mg) and *o*-xylene (7.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The mixture was then diluted with 20 mL of dichloromethane and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the 4,4'-(chloromethylene)dibenzonitrile **D5** (147.3 mg, 78%).

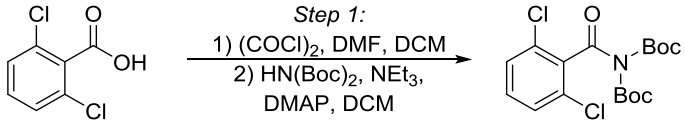
White solid. Mp: 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 4H), 7.59 (d, *J* = 8.4 Hz, 4H), 6.29 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.77, 132.71, 128.54, 118.36, 112.28, 61.91. HRMS (ESI)$^+$: calcd for $C_{15}H_{10}ClN_2$ $[M+H]^+$ 253.0533, found: 253.0519.



Step 5: this step was performed according to the known literature.[56] 1,2,4-Triazole (0.87 mmol, 60.0 mg), K_2CO_3 (1.2 mmol, 165.6 mg) were added into a dried 50 mL two-neck flask equipped with a condenser pipe, and it was subjected to three cycles of vacuum and refilled with nitrogen. Then DMF (10 mL) and toluene (10 mL) was sequentially injected into it, and the mixture was stirred at room temperature for 1 h. After the indicated time, a solution of 4,4'-(chloromethylene)dibenzonitrile **D5** (0.58 mmol, 147.3 mg) in DMF (10 mL) was added dropwise to the flask, and the mixture was stirred at 100 °C for 24 h. After the indicated time, the mixture was slowly cooled to room temperature and filtered with *Celite*. The filtrate was then poured into a large amount of water (200 mL) and extracted with ethyl acetate (150 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford the 4,4'-((1*H*-1,2,4-triazol-1-yl)methylene)dibenzonitrile Letrozole **D6** (136.0 mg, 82%).

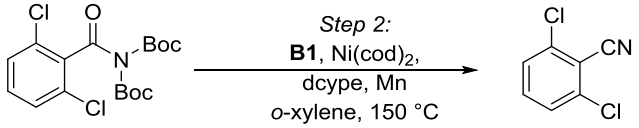
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.06 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 4H), 7.28 (d, *J* = 8.3 Hz, 4H), 6.80 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.08, 143.73, 141.80, 132.95, 128.94, 117.87, 113.30, 66.38.[28]

5.4 Synthesis of Dichlobenil



E1 **E2**, 89%

Step 1: To a solution of 2,6-dichlorobenzoic acid **E1** (0.5 mmol, 95.5 mg) in dichloromethane (10 mL) was added oxalyl chloride (0.75 mmol, 64 μL) dropwise at 0 °C, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure. The obtained mixture was redissolved in dichloromethane (5 mL), and the solution was added dropwise to a solution of $HN(Boc)_2$ (0.5 mmol, 108.5 mg), NEt_3 (0.6 mmol, 84 μL) and DMAP (0.05 mmol, 6.1 mg) in dichloromethane (10 mL) at 0 °C. Then the mixture was transferred to room temperature and stirred at the same temperature for 16 h. After the indicated time, the mixture was quenched with saturated $NaHCO_3$ solution (10 mL) and extracted with dichloromethane (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel to afford the *N*,*N*-Boc_2-2,6-dichlorobenzamide **E2** (173.9 mg, 89%).
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (br, 3H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.89, 148.38, 135.11, 131.28, 130.90, 127.74, 85.34, 27.31. HRMS (ESI)$^+$: calcd for $C_{17}H_{21}Cl_2NNaO_5$ $[M+Na]^+$ 412.0694, found: 412.0686.

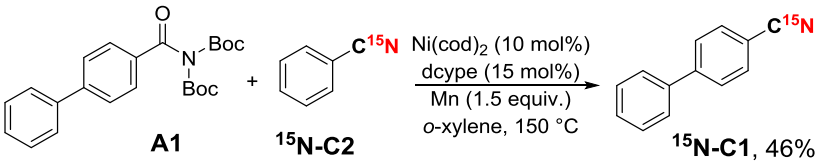


E2 **E3**, 62%

Step 2: *N*,*N*-Boc_2-2,6-dichlorobenzamide **E2** (0.45 mmol, 173.9 mg), 4-cyanopyridine **B1** (0.675 mmol, 70.2 mg), $Ni(cod)_2$ (0.045 mmol, 12.4 mg), dcype (0.068 mmol, 28.5 mg), Mn (0.675 mmol, 37.1 mg) and *o*-xylene (4.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The mixture was then diluted with 10 mL of dichloromethane and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the 2,6-dichlorobenzonitrile **E3** (48.1 mg, 62%).
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 7.41 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.50, 133.88, 128.18, 114.43, 113.35.[57]

VI. Control experiments

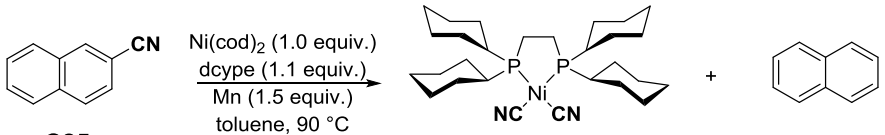
6.1 ^{15}N-labeling experiment



A1 ^{15}N-C2 ^{15}N-C1, 46%

^{15}N-benzonitrile **^{15}N-C2** was prepared according to the known literature.[58] *N*,*N*-Boc$_2$-4-phenylbenzamide **A1** (0.1 mmol, 39.7 mg), ^{15}N-benzonitrile **^{15}N-C2** (0.15 mmol, 10.4 mg), Ni(cod)$_2$ (0.01 mmol, 2.8 mg), dcype (0.015 mmol, 6.4 mg), Mn (0.15 mmol, 8.3 mg) and *o*-xylene (1.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. The mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was concentrated under reduced pressure, and the residue was further purified by flash column chromatography on silica gel to afford the ^{15}N-[1,1'-biphenyl]-4-carbonitrile **^{15}N-C1** (8.3 mg, 46%).
White solid. Mp: 86-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (q, *J* = 8.5 Hz, 4H), 7.63 – 7.57 (m, 2H), 7.52 – 7.40 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.69, 139.19, 132.61, 129.12, 128.67, 127.74, 127.24, 118.93 (d, *J* = 17.8 Hz), 110.93 (d, *J* = 2.9 Hz). ^{15}N NMR (41 MHz, $CDCl_3$) δ 255.57. HRMS (ESI)$^+$: calcd for $C_{13}H_{10}{}^{15}N$ $[M+H]^+$ 181.0784, found: 181.0766.

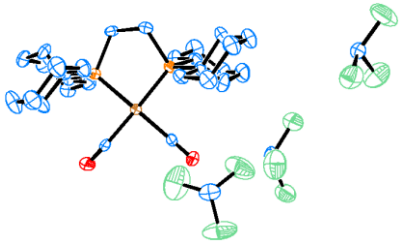
6.2 Oxidative addition of nickel to amide and nitrile



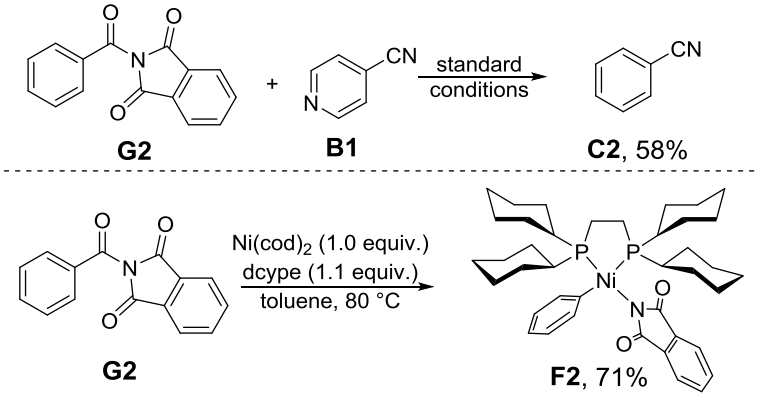
C25 F1, 85% G1, 63%

2-Naphthonitrile **C25** (0.2 mmol, 30.6 mg), Ni(cod)$_2$ (0.2 mmol, 55.0 mg), dcype (0.22 mmol, 92.8 mg), Mn (0.3 mmol, 16.5 mg) and toluene (2.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 90 °C for 16 h. After the indicated time, the tube was slowly cooled to room temperature, transferred into the glovebox and opened the cap. Subsequently, the mixture was filtrated by cannula filtration and washed with toluene (3.0 mL). Hexane (1.0 mL) was sequentially added to the filtrate, and the tube was taken out of the glovebox and was cooled to −45 °C to crystalize the complex. Then, the tube was transferred into the glovebox and the precipitated solid was collected by cannula filtration, washed with hexane (1.0 mL ×3) and dried under reduced pressure to give complex **F1** (45.5 mg, 85% yield based on nitrile) as an orange solid. The filtrate was further taken out of the glovebox and concentrated under reduced pressure. The

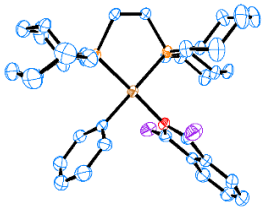
residue was diluted with dichloromethane (5.0 mL), filtrated with *Celite* and added the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg), and 1.0 μL of the solution was subjected to GC-Mass for composition analysis, which showed 63% yield of naphthalene **G1**. (Note: this procedure was performed three times to provide enough **F1** for characterization and further experiments).



Complex **F1** is a known compound, and its characterization data are in consistent with the reported literature.[59] The structure of complex **F1** was unambiguously determined by X-ray crystallography, and the single crystals were grown from a solution in $CHCl_3$ by slow evaporation. Detailed information for complex **F1** see Table S6.

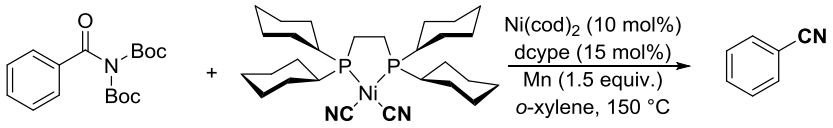


2-Benzoylisoindoline-1,3-dione **G2** was prepared according to the known literature.[60] Initially, **G2** amide was employed as amide substrate with **B1** under standard conditions to afford **C2** in 58% yield, which allowed amide **G2** for further organometallic reactions. Synthesis of **F2**: **G2** (0.2 mmol, 50.2 mg), $Ni(cod)_2$ (0.2 mmol, 55.0 mg), dcype (0.22 mmol, 92.8 mg) and toluene (2.0 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 80 °C for 16 h. After the indicated time, the tube was slowly cooled to room temperature, transferred into the glovebox and opened the cap. Subsequently, hexane (1.0 mL) was added to the solution, and the tube was taken out of the glovebox and was cooled to −45 °C to crystalize the complex. Then, the tube was transferred into the glovebox and the precipitated solid was collected by cannula filtration, washed with hexane (1.0 mL ×3) and dried under reduced pressure. The solid was further dissolved in THF (0.5 mL) to remove the impurity, and the filtrate was evaporated under reduced pressure to give complex **F2** (100.6 mg, 71%) as a yellow solid.



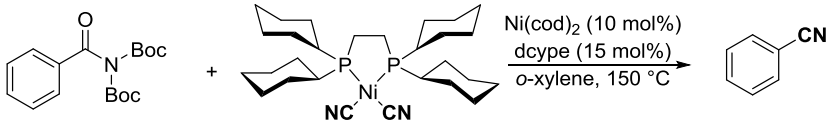
(dcype)Ni(Ph)(Phthalimide) **F2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.44 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.30 (dd, *J* = 5.3, 3.0 Hz, 2H), 6.87 – 6.81 (m, 2H), 6.70 – 6.62 (m, 1H), 2.54 – 2.34 (m, 4H), 1.94 – 1.07 (m, 42H), 0.84 – 0.67 (m, 2H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.66 (d, *J* = 14.8 Hz), 60.63 (d, *J* = 14.8 Hz). IR (KBr, cm^{-1}): 3042 w, 2931 s, 2849 s, 1651 s, 1645 s, 1621 m, 1562 w, 1446 m, 1372 s, 1347 m, 1303 s, 1171 m, 1122 s, 1056 m, 1018 w, 1003 w, 889 m, 852 m, 793 m, 721 s, 701 s, 663 m, 644 m, 532 s. HRMS (ESI)$^{+}$: calcd for $C_{40}H_{58}NNiO_2P_2$ $[M+H]^{+}$ 704.3296, found: 704.3306. The structure of complex **F2** was unambiguously determined by X-ray crystallography, and the single crystals were grown from a solution in THF by slow evaporation. Detailed information for complex **F2** see Table S7.

6.3 Reaction with complex F1



A2 **F1** (1.0 equiv.) **C2**, 81%

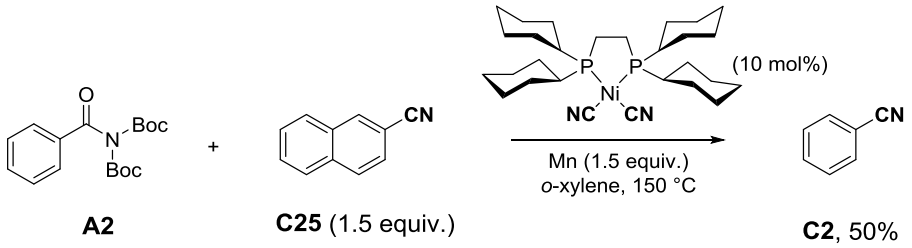
N,*N*-Boc_2-benzamide **A2** (0.05 mmol, 19.9 mg), **F1** (0.05 mmol, 26.6 mg), $Ni(cod)_2$ (0.005 mmol, 1.4 mg), dcype (0.008 mmol, 3.2 mg), Mn (0.075 mmol, 4.1 mg) and *o*-xylene (0.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. Subsequently, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC for composition analysis, which showed 81% yield of benzonitrile **C2**.



A2 **F1** (1.0 equiv.) **C2**, 78%

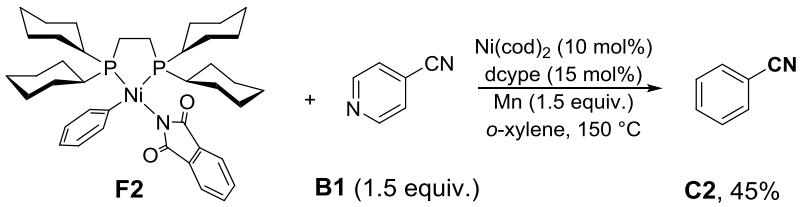
N,*N*-Boc_2-benzamide **A2** (0.05 mmol, 19.9 mg), **F1** (0.05 mmol, 26.6 mg), $Ni(cod)_2$ (0.005 mmol, 1.4 mg), dcype (0.008 mmol, 3.2 mg) and *o*-xylene (0.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the

mixture was cooled to room temperature and the tube was slowly opened in the fume hood. Subsequently, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC for composition analysis, which showed 78% yield of benzonitrile **C2**.

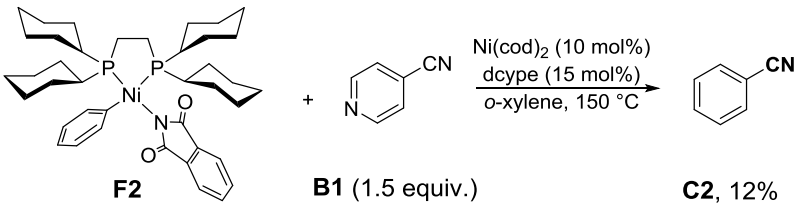


N,*N*-Boc_2-benzamide **A2** (0.05 mmol, 19.9 mg), 2-naphthonitrile **C25** (0.075 mmol, 11.5 mg), **F1** (0.005 mmol, 2.7 mg), Mn (0.075 mmol, 4.1 mg) and *o*-xylene (0.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. Subsequently, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC for composition analysis, which showed 50% yield of benzonitrile **C2**.

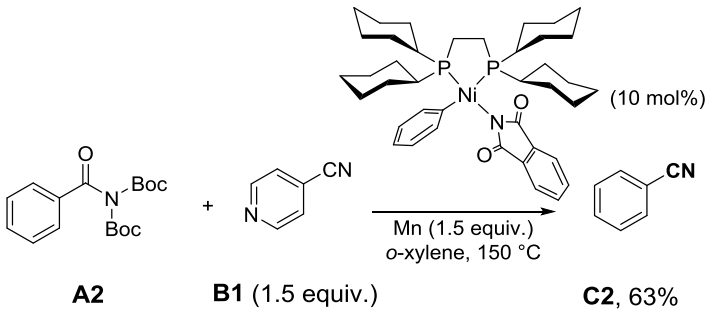
6.4 Reaction with complex F2



F2 (0.05 mmol, 35.2 mg), 4-cyanopyridine **B1** (0.075 mmol, 7.8 mg), $Ni(cod)_2$ (0.005 mmol, 1.4 mg), dcype (0.008 mmol, 3.2 mg), Mn (0.075 mmol, 4.1 mg) and *o*-xylene (0.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. Subsequently, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC for composition analysis, which showed 45% yield of benzonitrile **C2**.

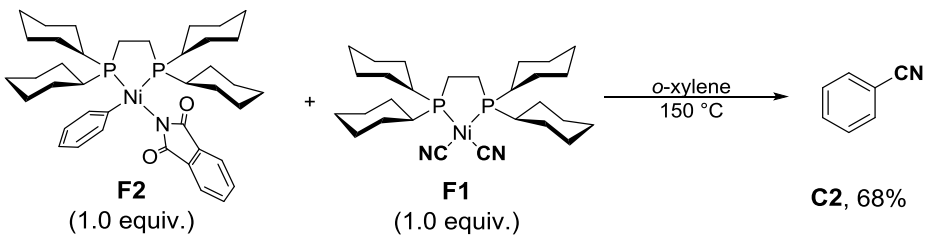


Complex **F2** (0.05 mmol, 35.2 mg), 4-cyanopyridine **B1** (0.075 mmol, 7.8 mg), $Ni(cod)_2$ (0.005 mmol, 1.4 mg), dcype (0.008 mmol, 3.2 mg) and *o*-xylene (0.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. Subsequently, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC for composition analysis, which showed 12% yield of benzonitrile **C2**.



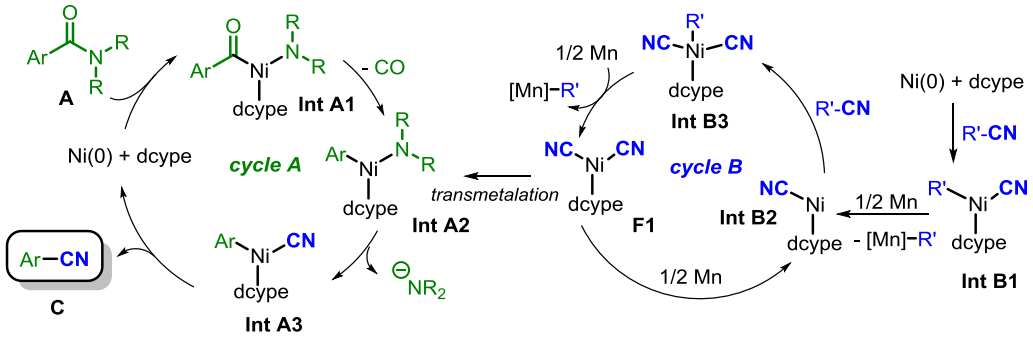
N,*N*-Boc_2-benzamide **A2** (0.05 mmol, 19.9 mg), 4-cyanopyridine **B1** (0.075 mmol, 7.8 mg), **F2** (0.005 mmol, 3.5 mg), Mn (0.075 mmol, 4.1 mg) and *o*-xylene (0.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. Subsequently, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC for composition analysis, which showed 63% yield of benzonitrile **C2**.

6.5 Reaction between complexes F1 and F2



Complex **F2** (0.05 mmol, 35.2 mg), **F1** (0.05 mmol, 26.6 mg) and *o*-xylene (0.5 mL) were added to a dried Schlenk tube equipped with a Teflon-sealed screwcap in the glovebox filled with nitrogen. After the addition, the cap was closed and the tube was taken out of the glovebox. The mixture was then stirred at 150 °C for 24 h. After the indicated time, the mixture was cooled to room temperature and the tube was slowly opened in the fume hood. Subsequently, the internal standard 4-methoxybiphenyl (0.1 mmol, 18.4 mg) was added and the mixture was then diluted with 3 mL of dichloromethane and filtered with *Celite*. The filtrate was sequentially submitted to GC for composition analysis, which showed 68% yield of benzonitrile **C2**.

6.6 Working hypothesis



Based on our work and the literatures[61], a plausible reaction pathway was proposed as shown above. Initially, a successive C–N/C–C bond activation of amide by Ni^0 resulted in the formation of **Int A2**. Meanwhile, the oxidative addition of nickel to C–CN bond delivered **Int B1**. Next, the reduction of **Int B1** by Mn afforded **Int B2**,[61a-c, 61h] partially due to the resonance stabilization of negative charge on pyridine ring and the stability of pyridyl metal salts,[61d-g] which was also supported by the formation of complex **F1** and the results obtained from screening aryl nitrile donors. Moreover, the sequential oxidative addition and reductive elimination processes gave complex **F1**, which further underwent transmetalation with **Int A2** to provide cyano group. Finally, the reductive elimination of **Int A3** afforded the cyanation product **C**. Besides, the catalytic competency of complex **F1** and **F2** for this reaction might be derived from its reduced Ni^0 species.[62] In addition, although our proposed mechanism provided a plausible pathway for the cyanation of **Int A2**, the possibility of other potential cyanation source cannot be excluded.

VII. X-ray crystallographic data

Detailed X-ray crystallographic data of compound **C43**, complex **F1** and complex **F2**, is shown in Table S5, Table S6 and Table S7 respectively.

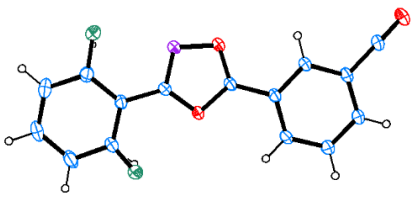


Table S5. Crystal Data and Structure Refinement for Compound C43 (CCDC 2143514)

Empirical formula	$C_{15}H_8FN_3O$
Formula weight	265.24
Temperature/K	150.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.202(3)
b/Å	13.933(4)
c/Å	12.252(4)
α/°	90
β/°	92.89(2)
γ/°	90
Volume/Å^3	1227.9(7)
Z	4
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	0.871
F(000)	544.0
Crystal size/mm^3	0.45 × 0.13 × 0.07
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.62 to 140.04
Index ranges	$-8 \le h \le 5$, $-13 \le k \le 16$, $-14 \le l \le 14$
Reflections collected	8546
Independent reflections	2257 [R_{int} = 0.0630, R_{sigma} = 0.0556]
Data/restraints/parameters	2257/0/191
Goodness-of-fit on F^2	1.132
Final R indexes [I>=2σ (I)]	R_1 = 0.0841, wR_2 = 0.2499
Final R indexes [all data]	R_1 = 0.0884, wR_2 = 0.2564
Largest diff. peak/hole / e Å^{-3}	0.39/-0.38

Note: the fluorine atom might appear in two positions with a same percent probability of 50%, which caused the split during the measurement of the single crystal structure.[63]

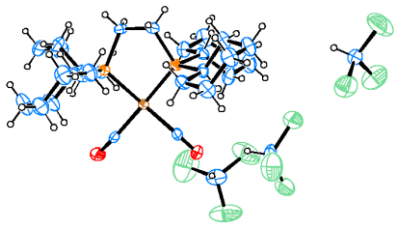


Table S6. Crystal Data and Structure Refinement for Complex F1 (CCDC 2116202)

Empirical formula	$C_{31}H_{51}Cl_9N_2NiP_2$
Formula weight	891.43
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	26.5408(11)
b/Å	10.7490(5)
c/Å	15.0781(7)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	4301.6(3)
Z	4
$\rho_{calc}g/cm^3$	1.376
μ/mm^{-1}	1.108
F(000)	1848.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.14 to 52.736
Index ranges	$-33 \leq h \leq 32$, $-11 \leq k \leq 13$, $-17 \leq l \leq 18$
Reflections collected	14292
Independent reflections	7659 [R_{int} = 0.0306, R_{sigma} = 0.0534]
Data/restraints/parameters	7659/1/406
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0598, wR_2 = 0.1341
Final R indexes [all data]	R_1 = 0.0798, wR_2 = 0.1481
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.44
Flack parameter	-0.013(12)

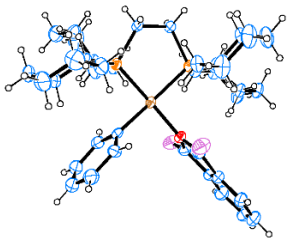


Table S7. Crystal Data and Structure Refinement for Complex F2 (CCDC 2125411)

Empirical formula	$C_{40}H_{57}NNiO_2P_2$
Formula weight	704.51
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.8456(6)
b/Å	22.0902(10)
c/Å	16.2886(8)
α/°	90
β/°	92.103(4)
γ/°	90
Volume/Å^3	4259.4(4)
Z	4
ρ_{calc}g/cm^3	1.099
μ/mm^{-1}	0.561
F(000)	1512.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.218 to 52.736
Index ranges	$-13 \le h \le 14$, $-26 \le k \le 27$, $-20 \le l \le 20$
Reflections collected	20135
Independent reflections	8701 [R_{int} = 0.0376, R_{sigma} = 0.0747]
Data/restraints/parameters	8701/0/409
Goodness-of-fit on F^2	1.000
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1258
Final R indexes [all data]	R_1 = 0.0867, wR_2 = 0.1381
Largest diff. peak/hole / e Å^{-3}	0.45/-0.31

There is an Alert A of Solvent Accessible VOID(S) in structure. The formation of voids is caused by the disorder of solvent, and X-ray single crystal diffraction cannot locate them. Then, the disorder of solvents has to be screened out in structural refinement by Solvent Mask. In addition, there is an Alert B of Hirshfeld Test Diff for C11-C12 (9.0 s.u.), and this little difference is caused by the thermal vibration between C11 and C12.

VIII. References

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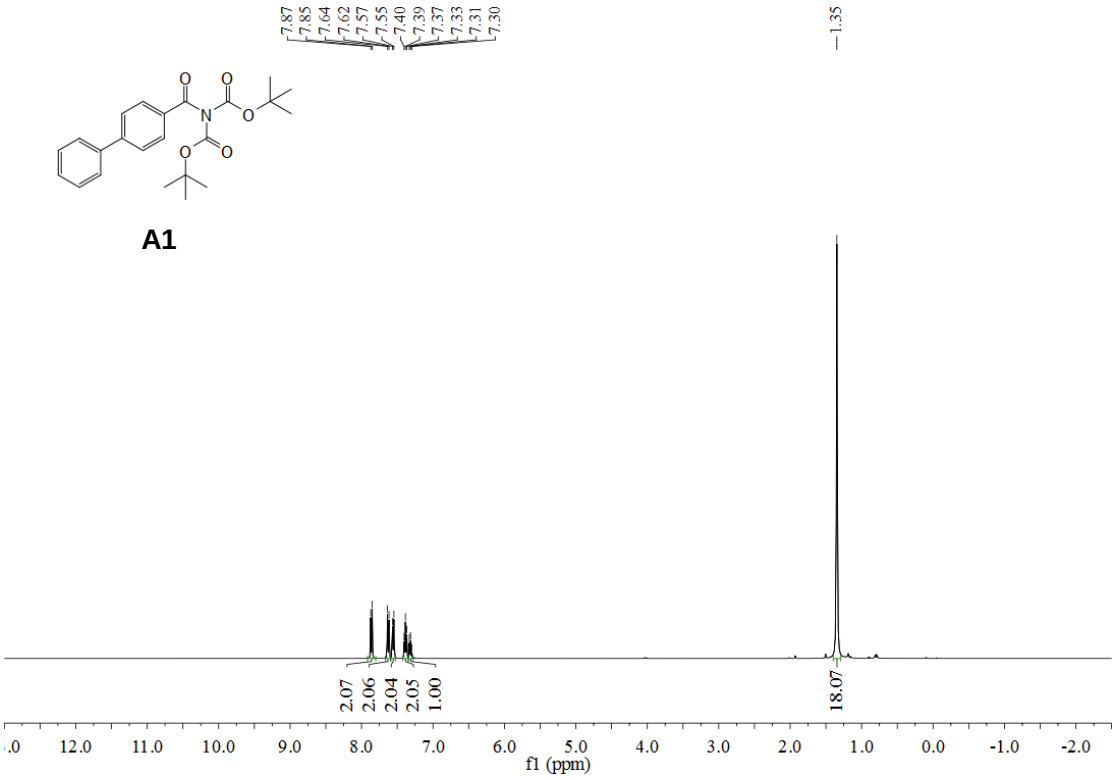
IX. Copies of NMR spectra



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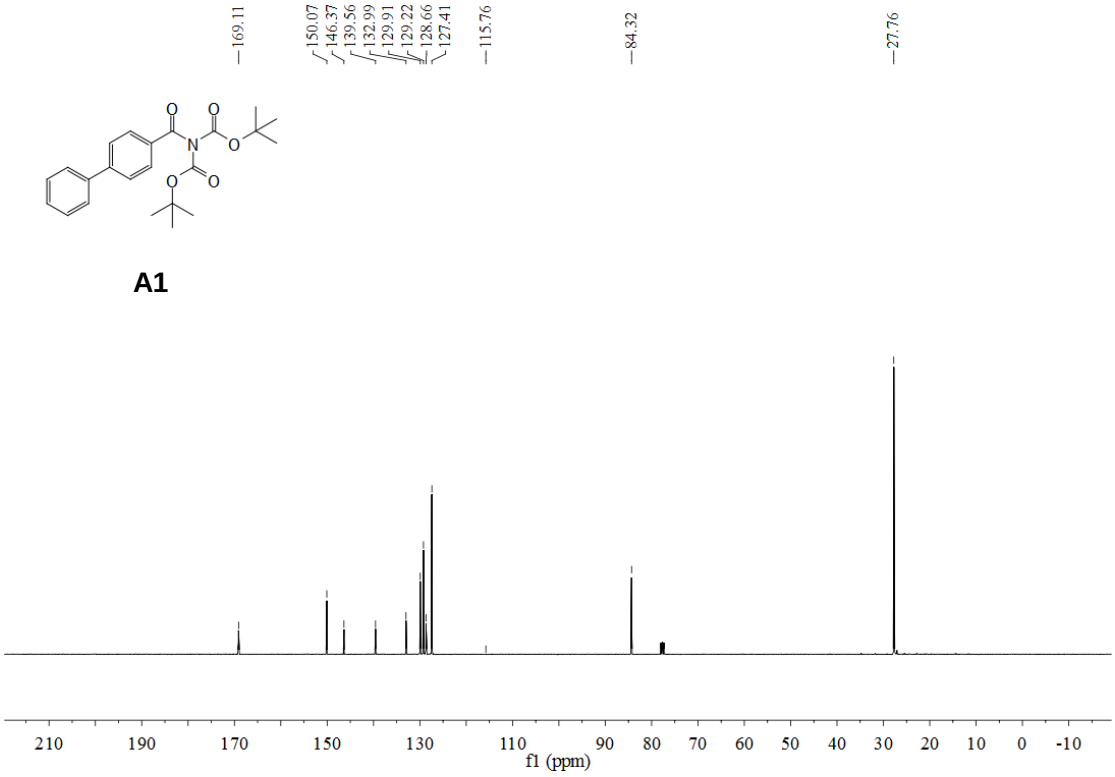

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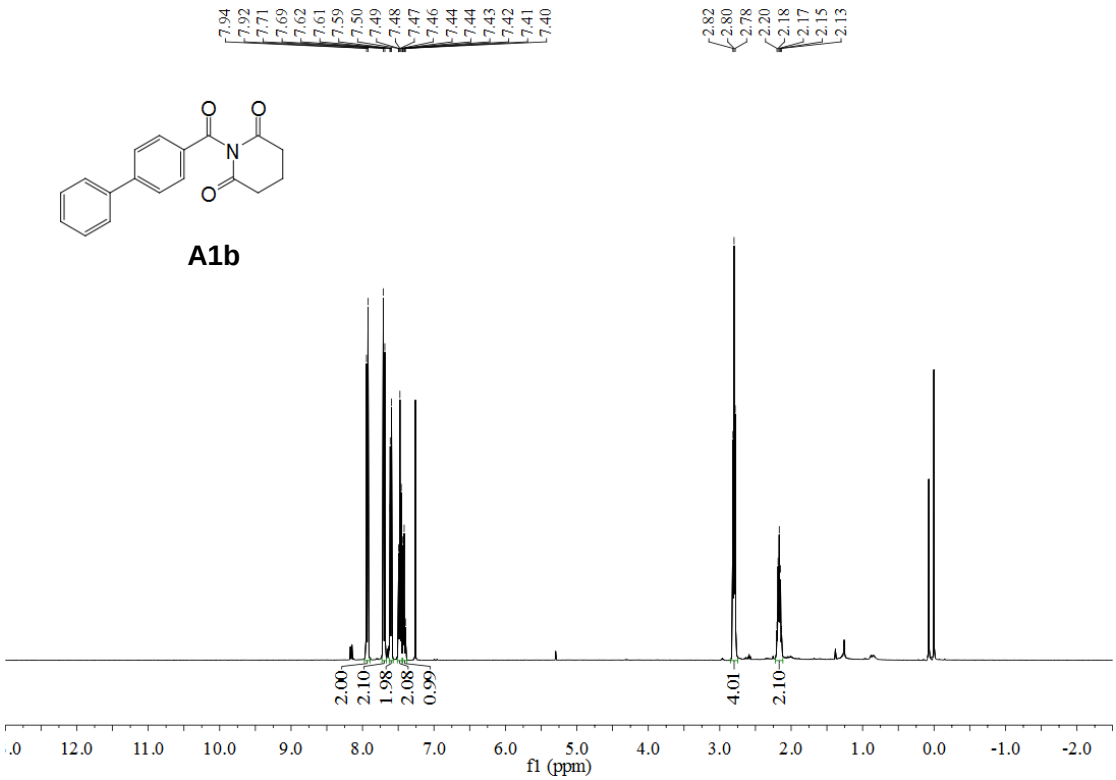
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7.44
7.43
7.42
7.41
7.40
2.82
2.80
2.78
2.20
2.18
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2.13
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2.08
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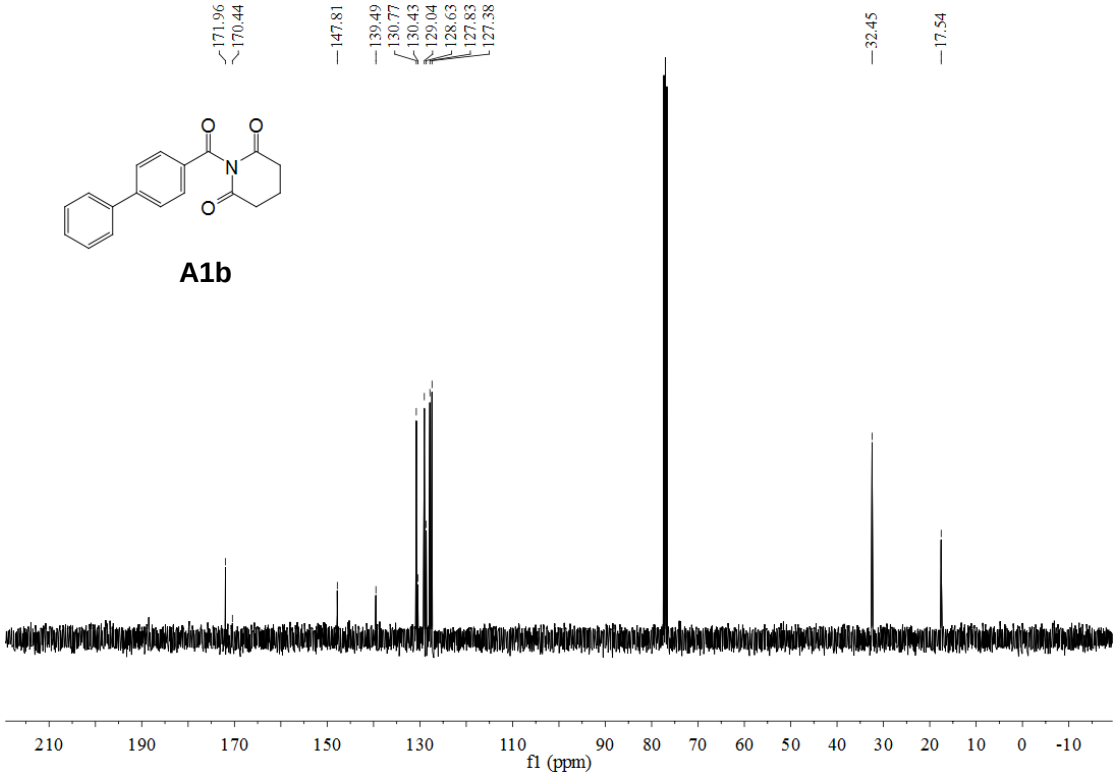
f1 (ppm)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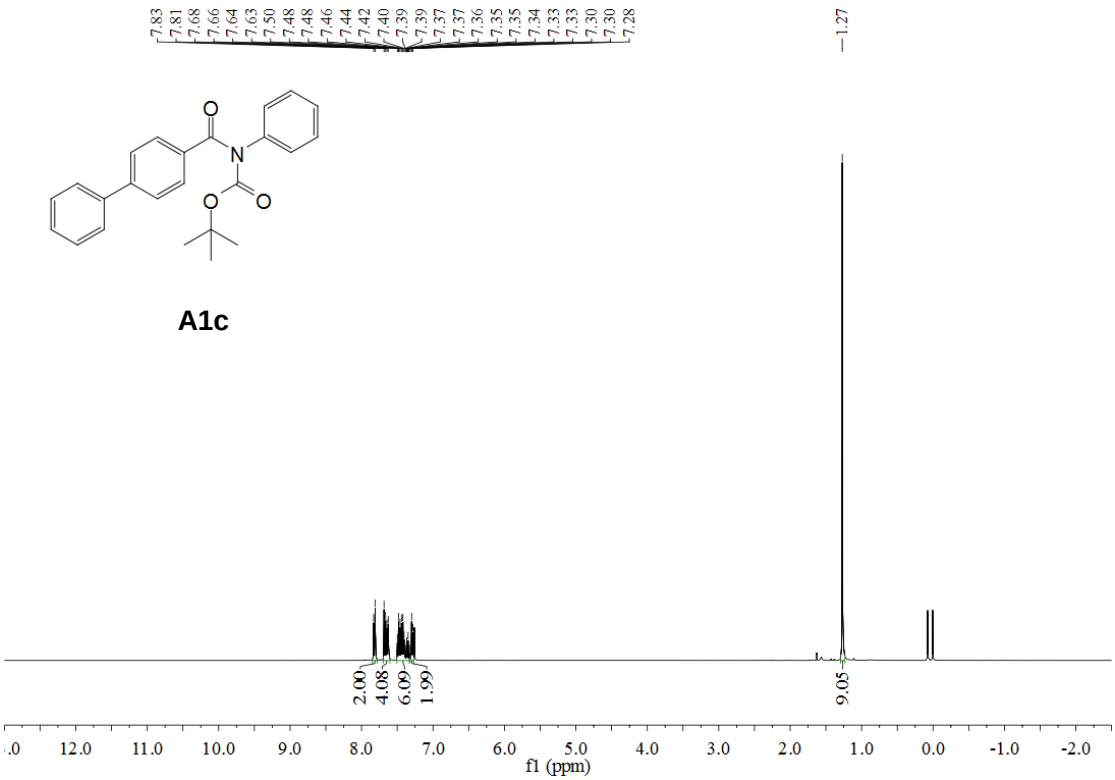
f1 (ppm)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7.39
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7.35
7.34
7.33
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f1 (ppm)

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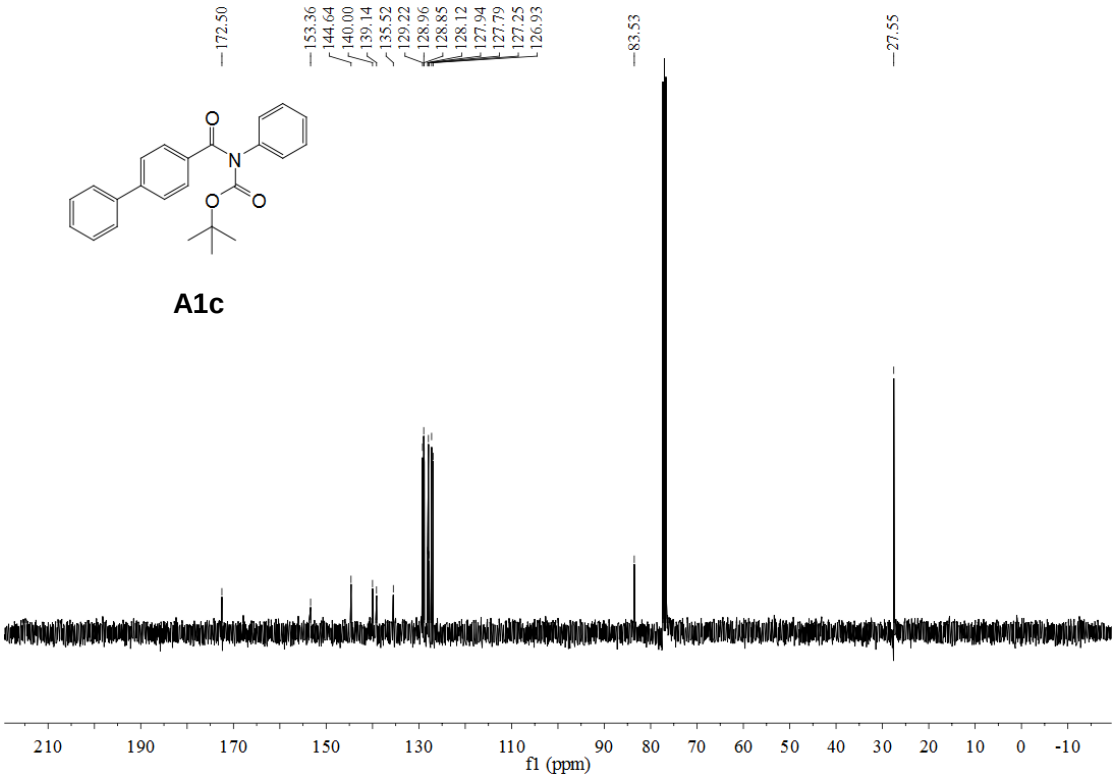
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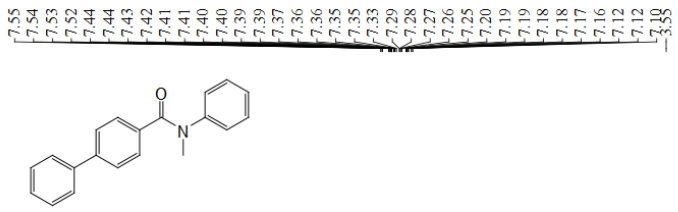
A1c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7.35
7.35
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7.25
7.20
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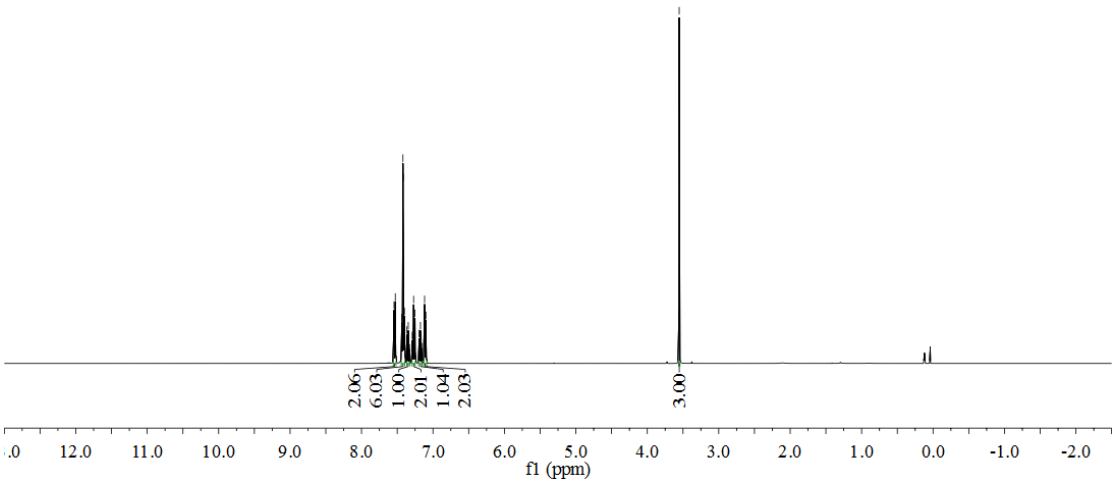
7.12
7.10
3.55
O
N

A1d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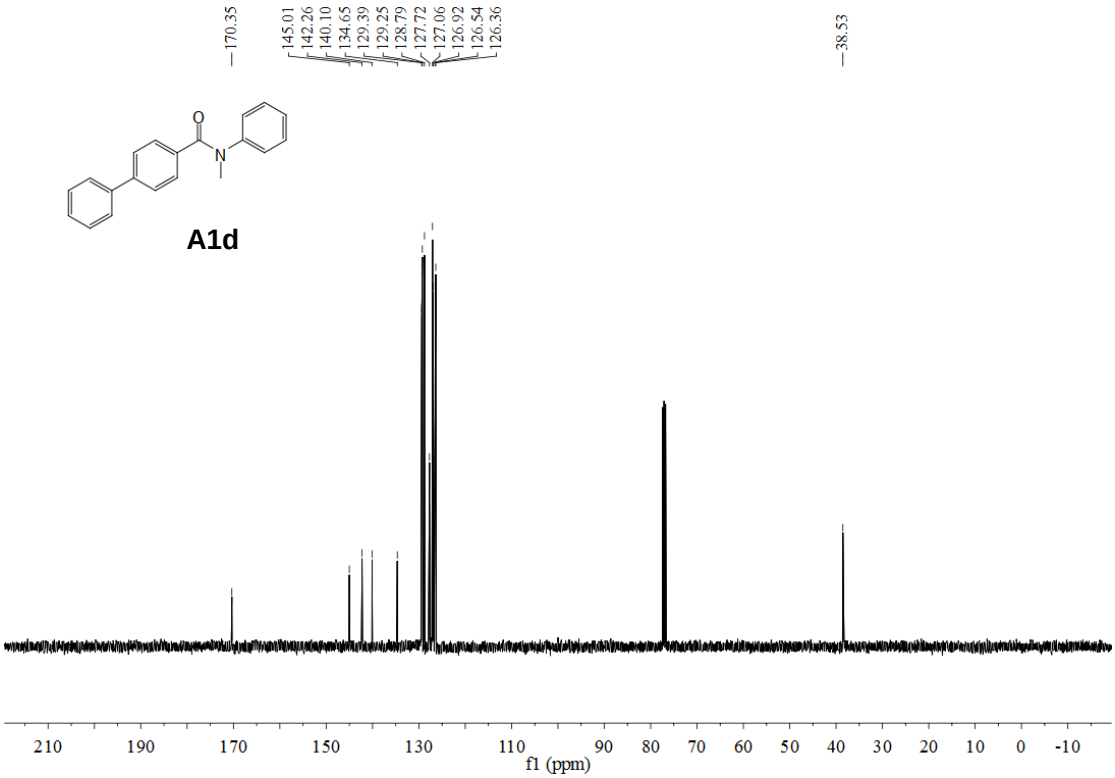
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O
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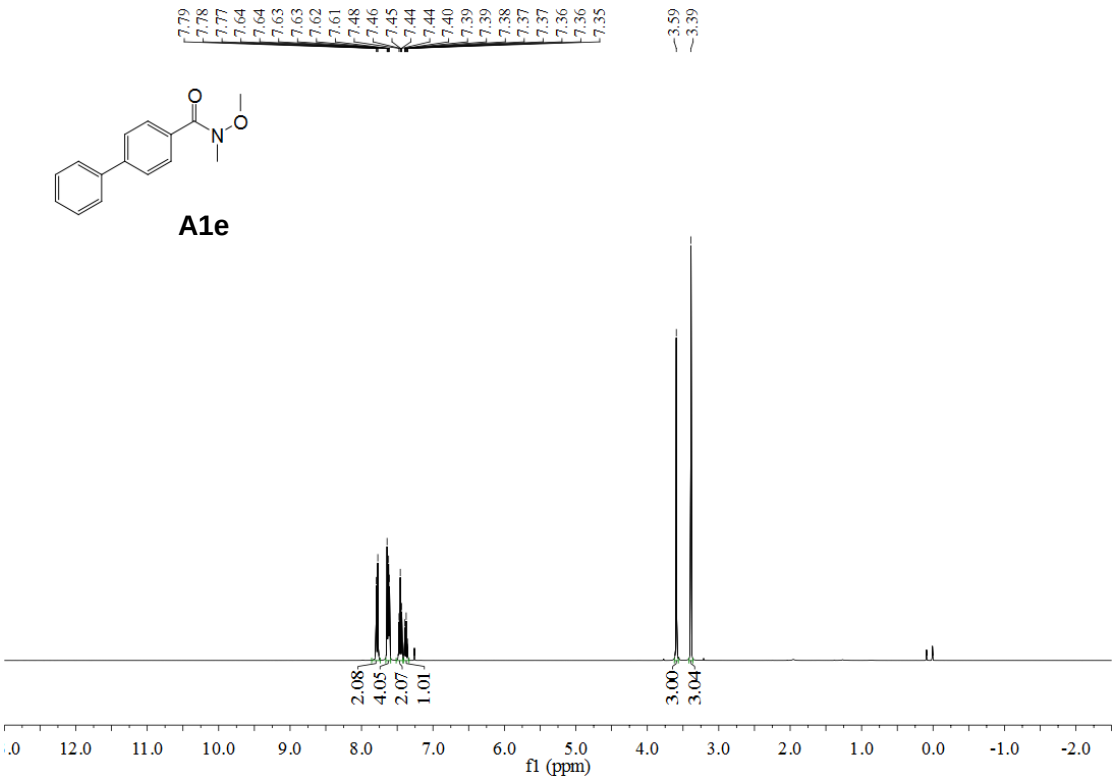
f1 (ppm)

A1d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7.39
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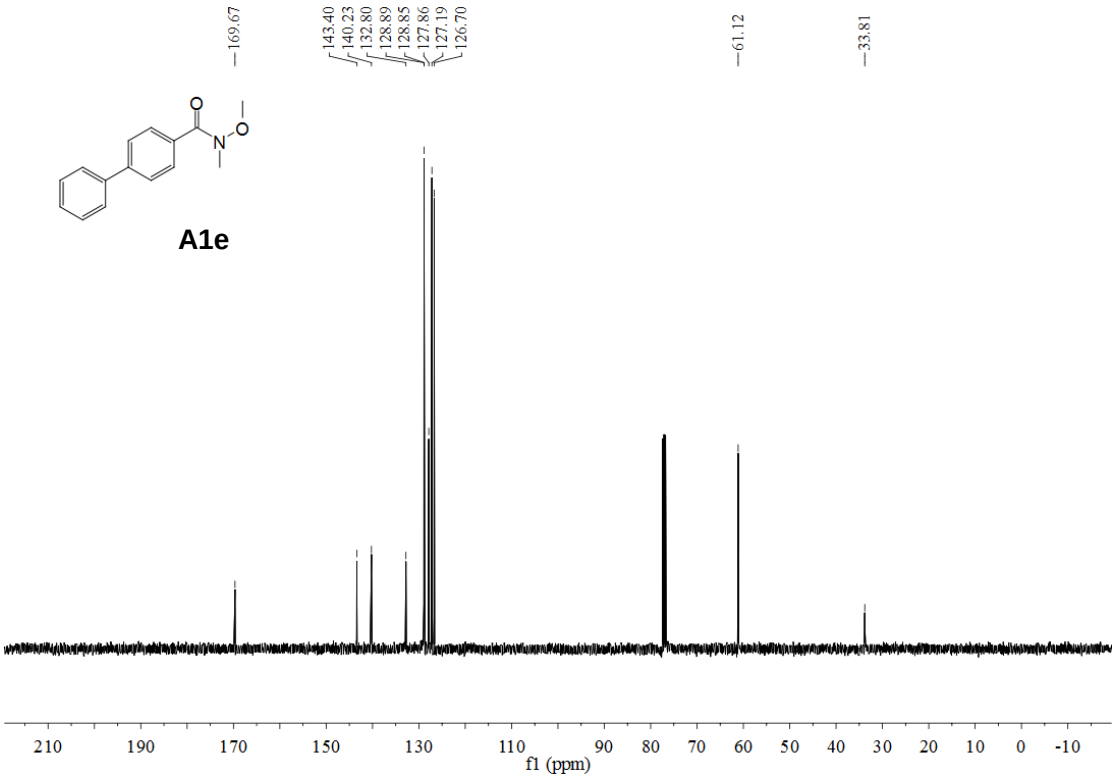
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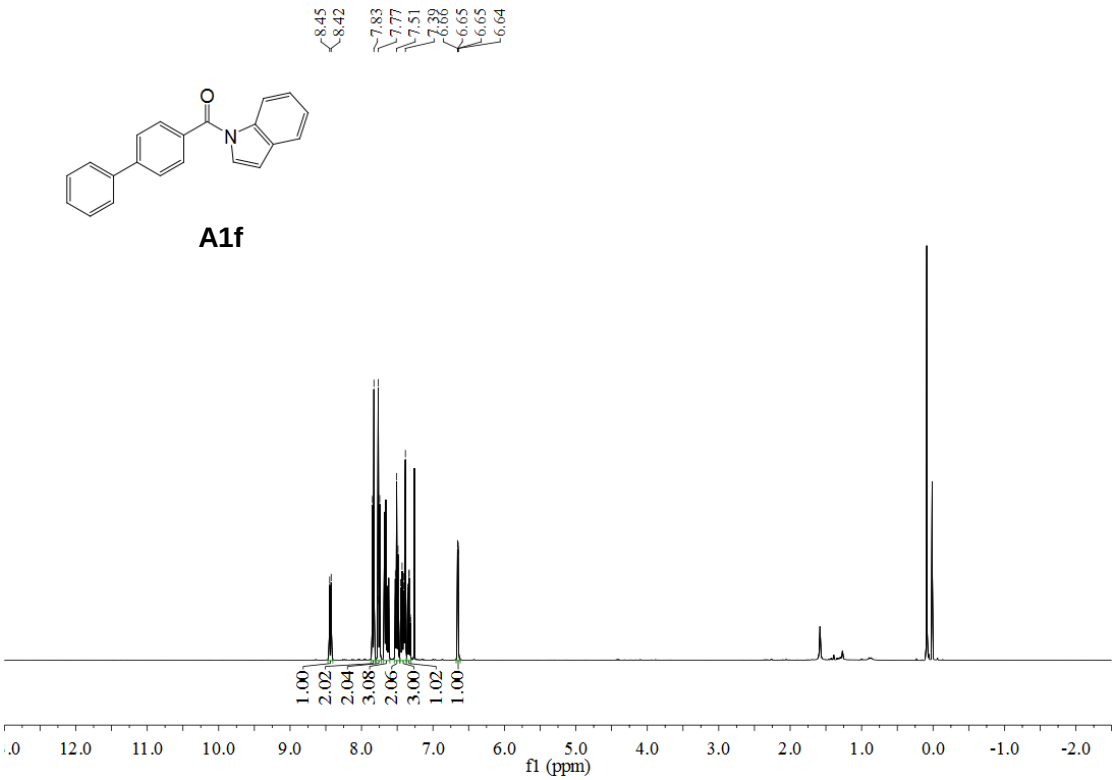
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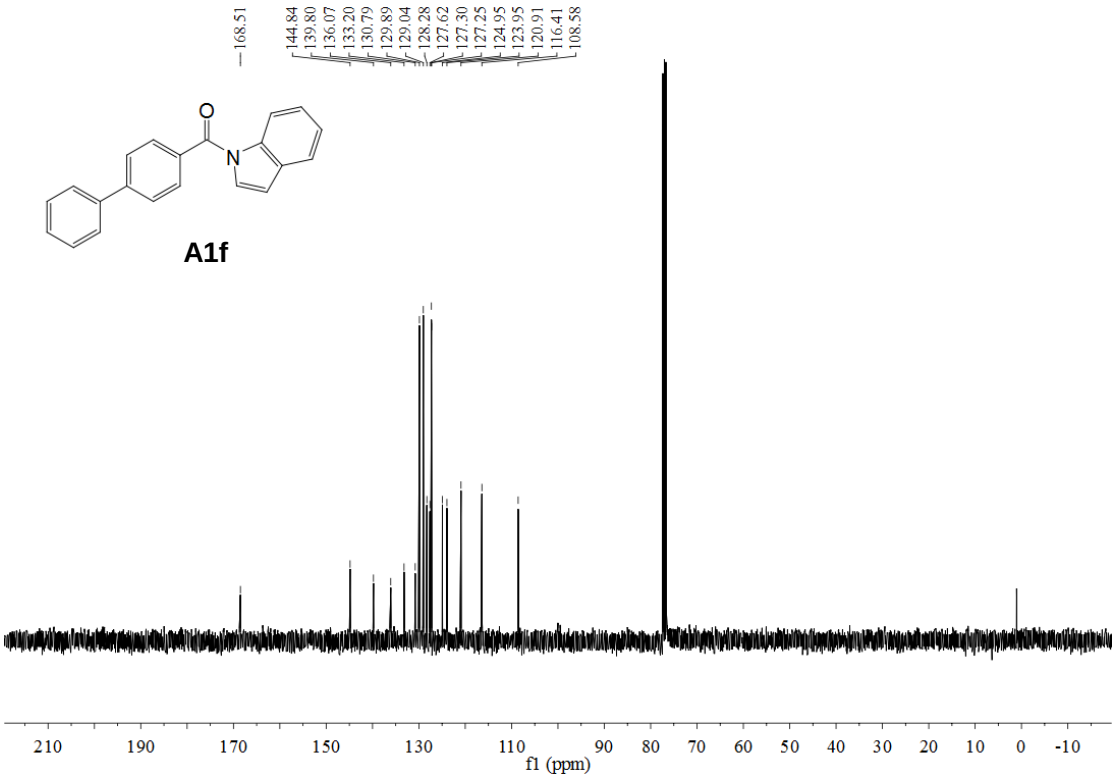
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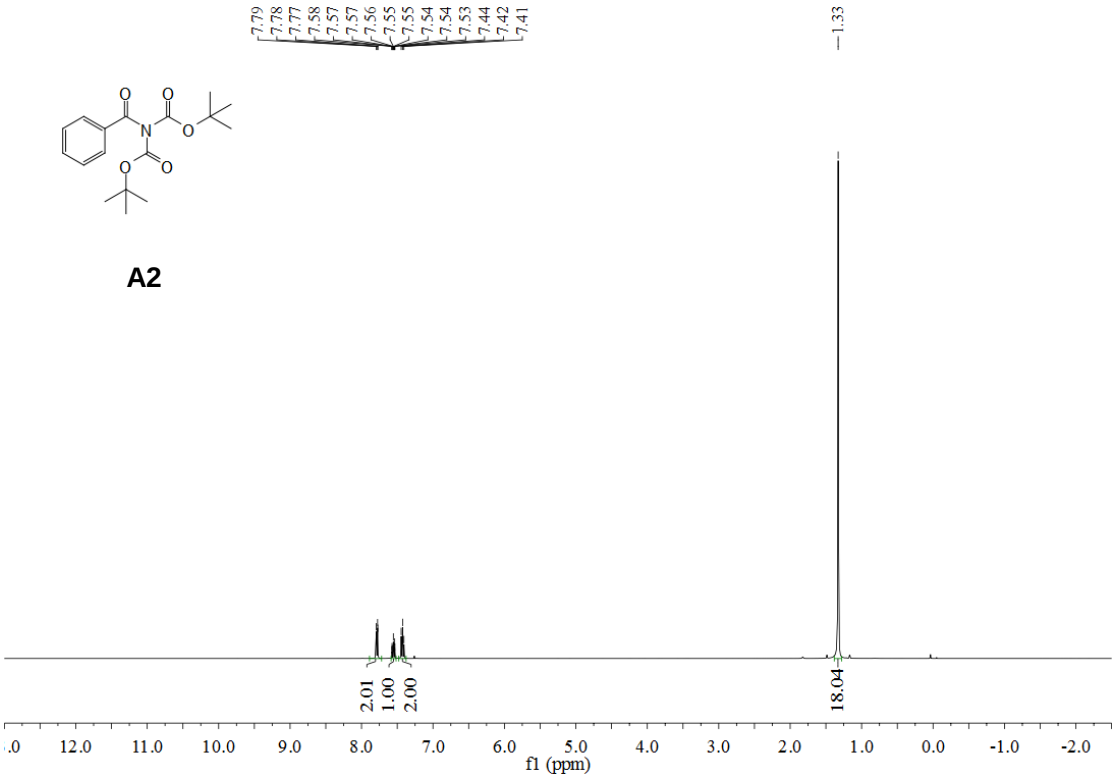
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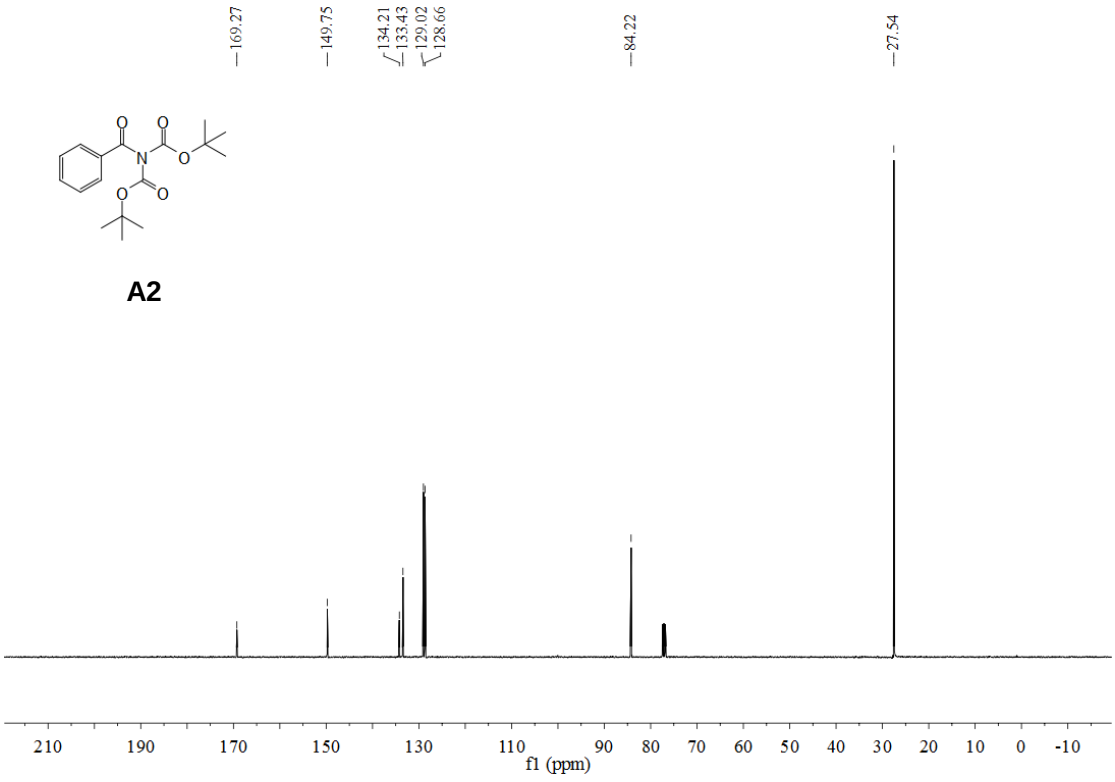
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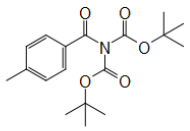

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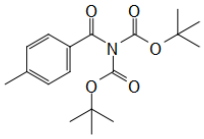

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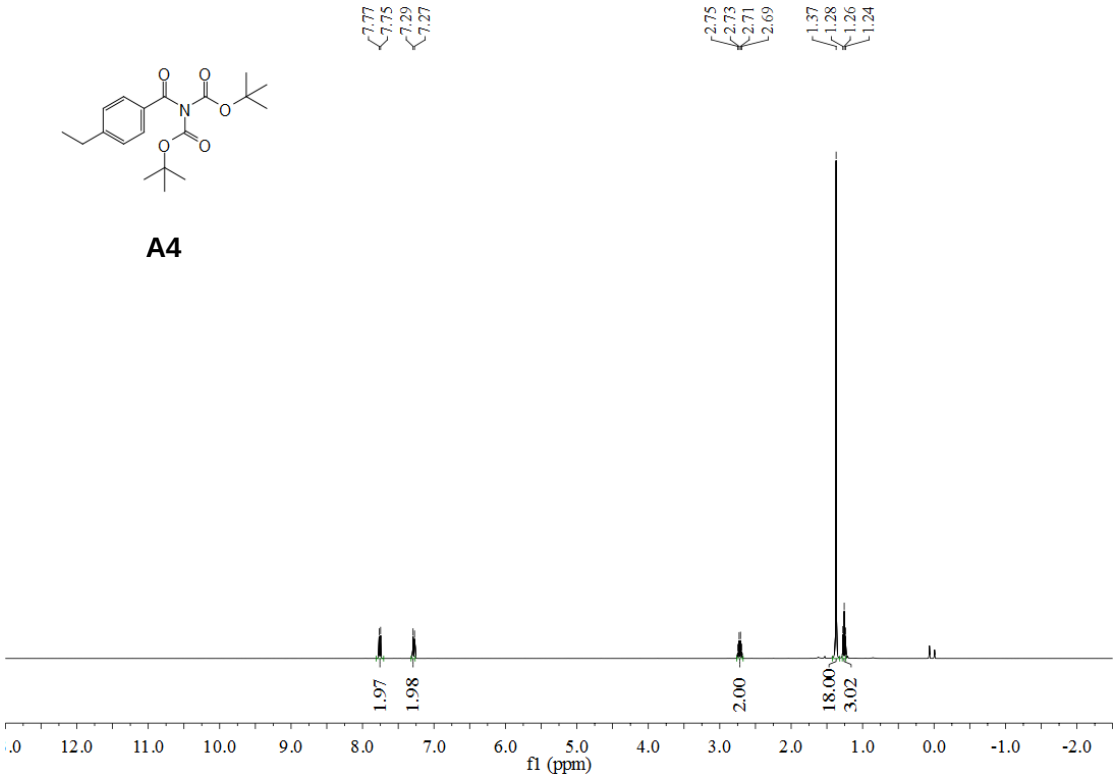
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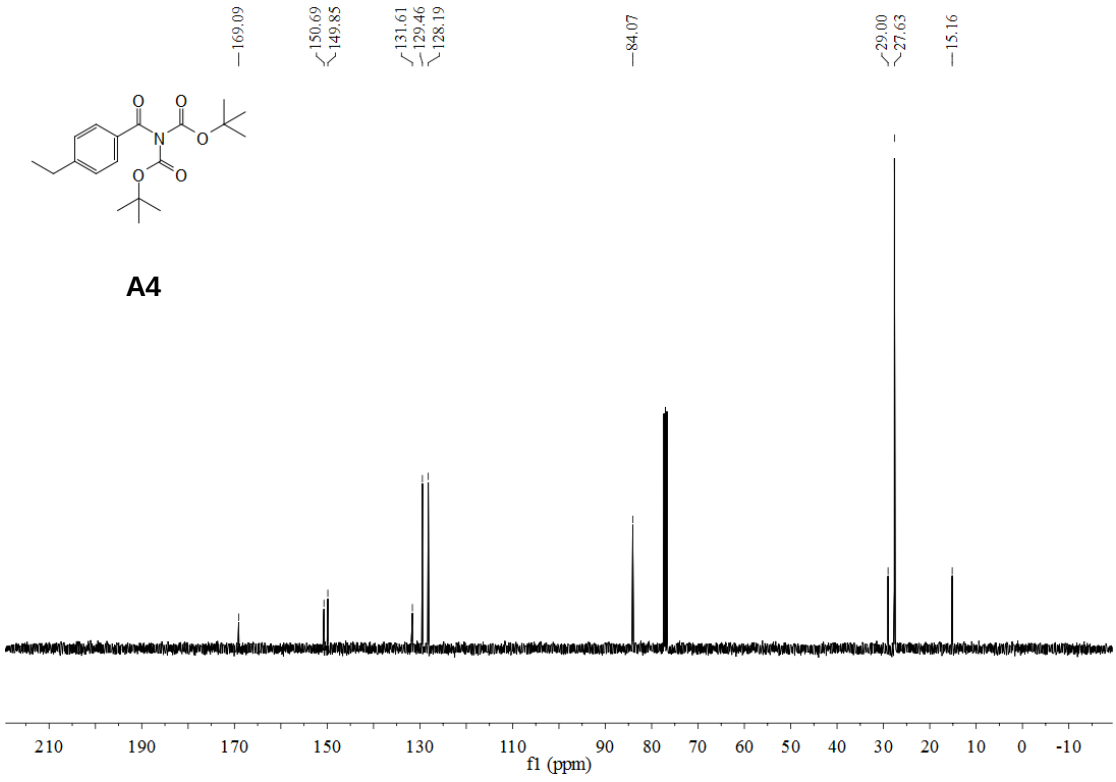
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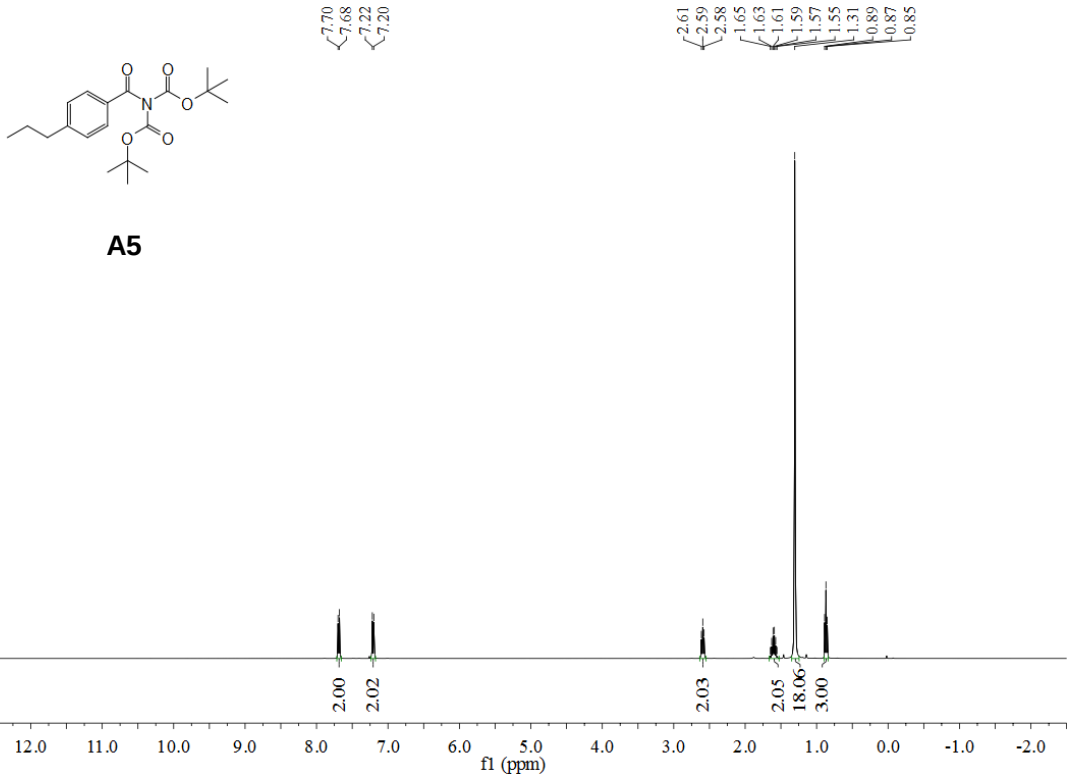
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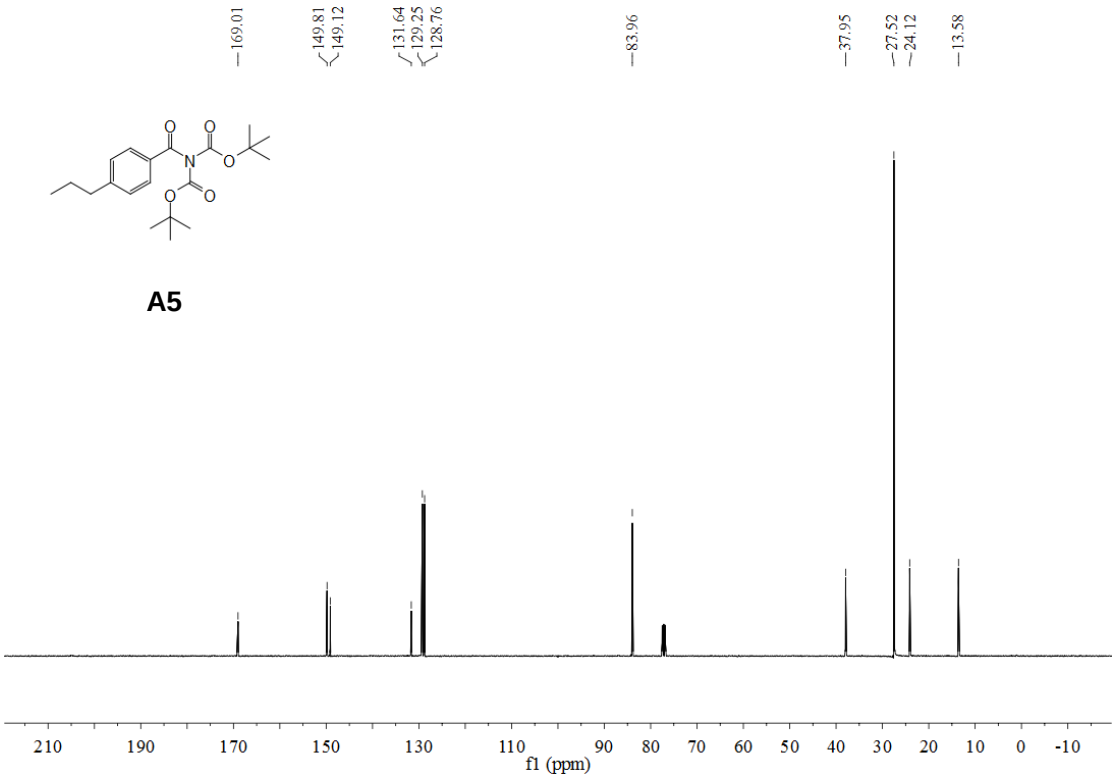
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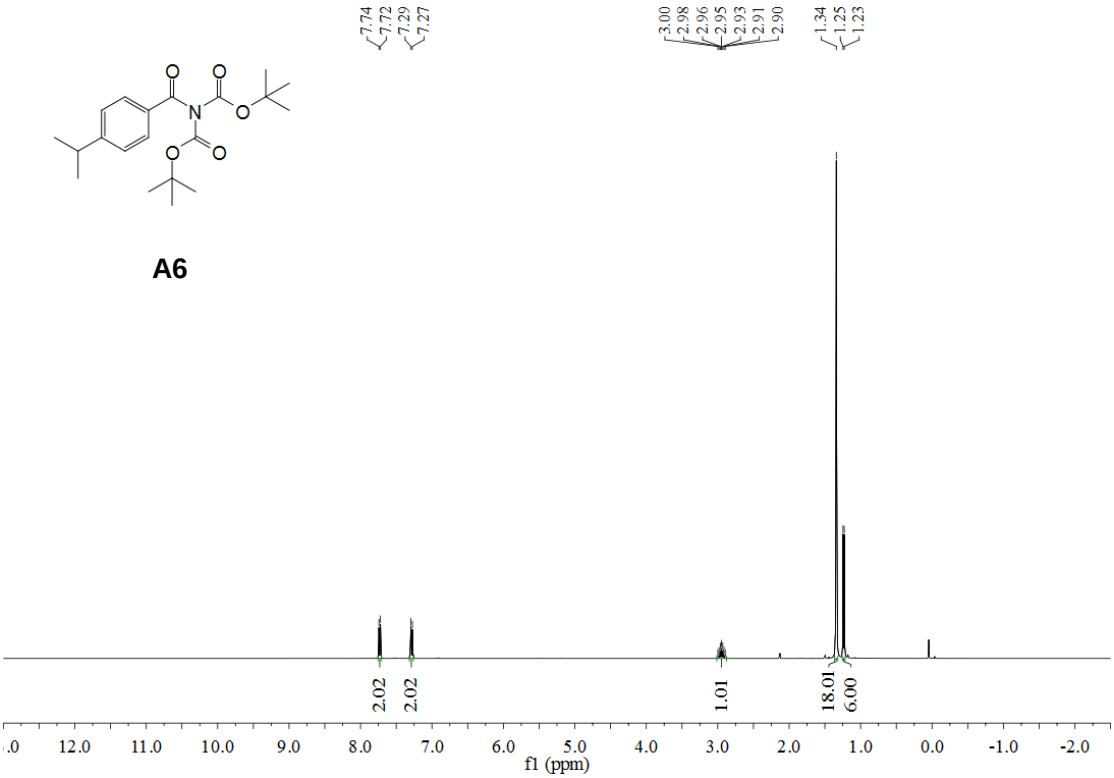
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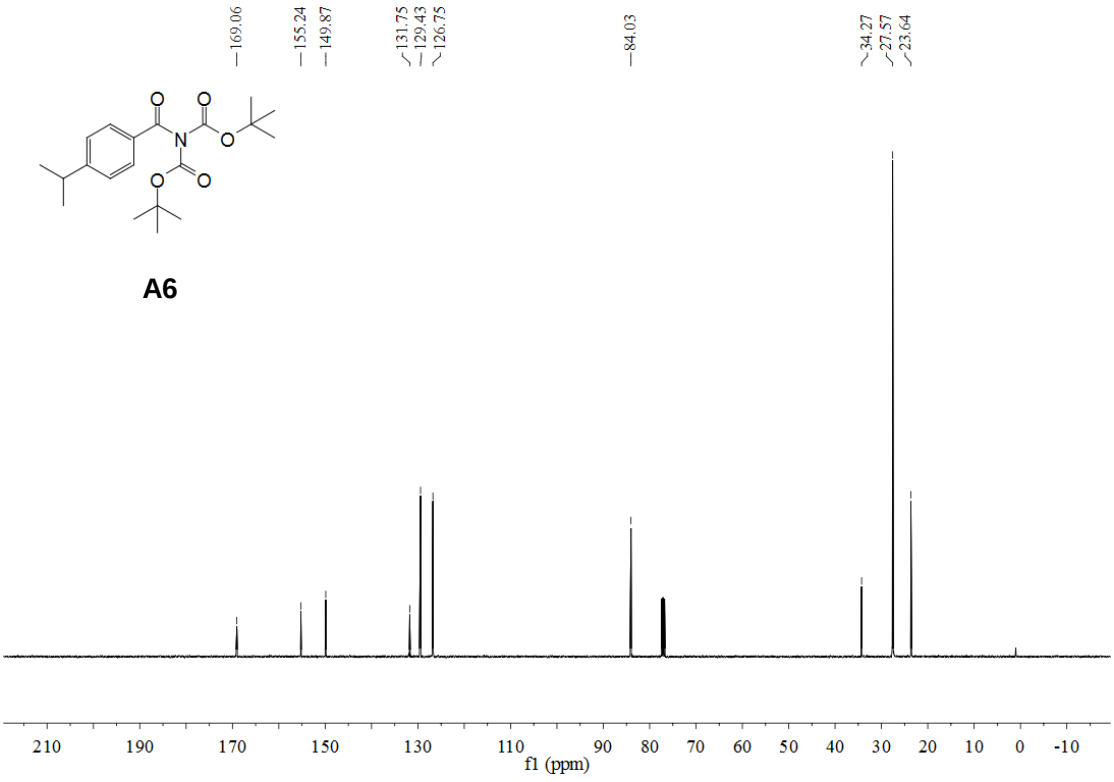
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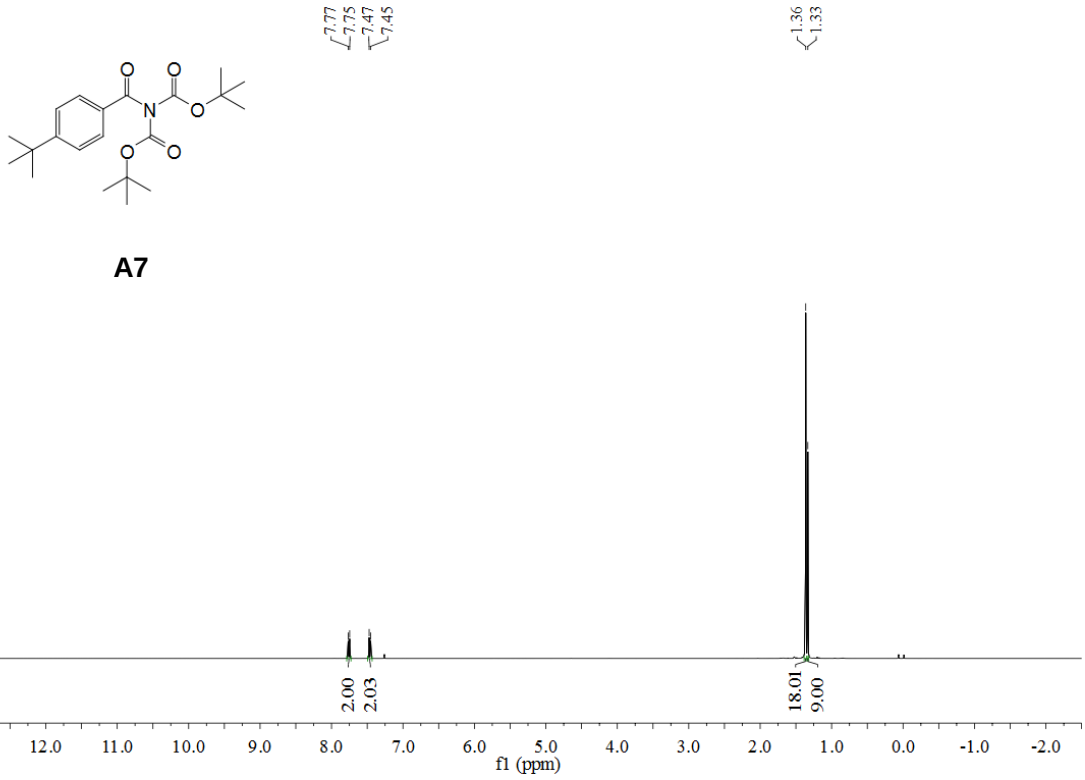
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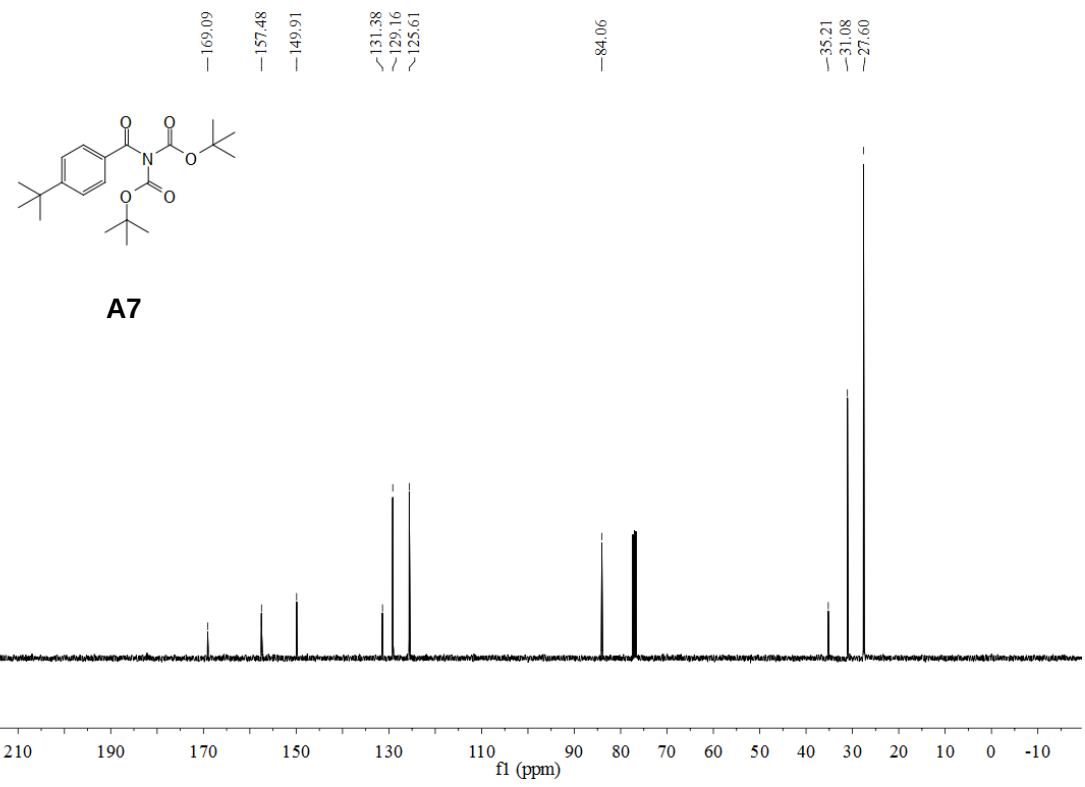
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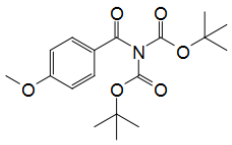

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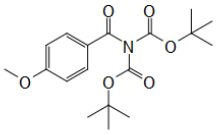

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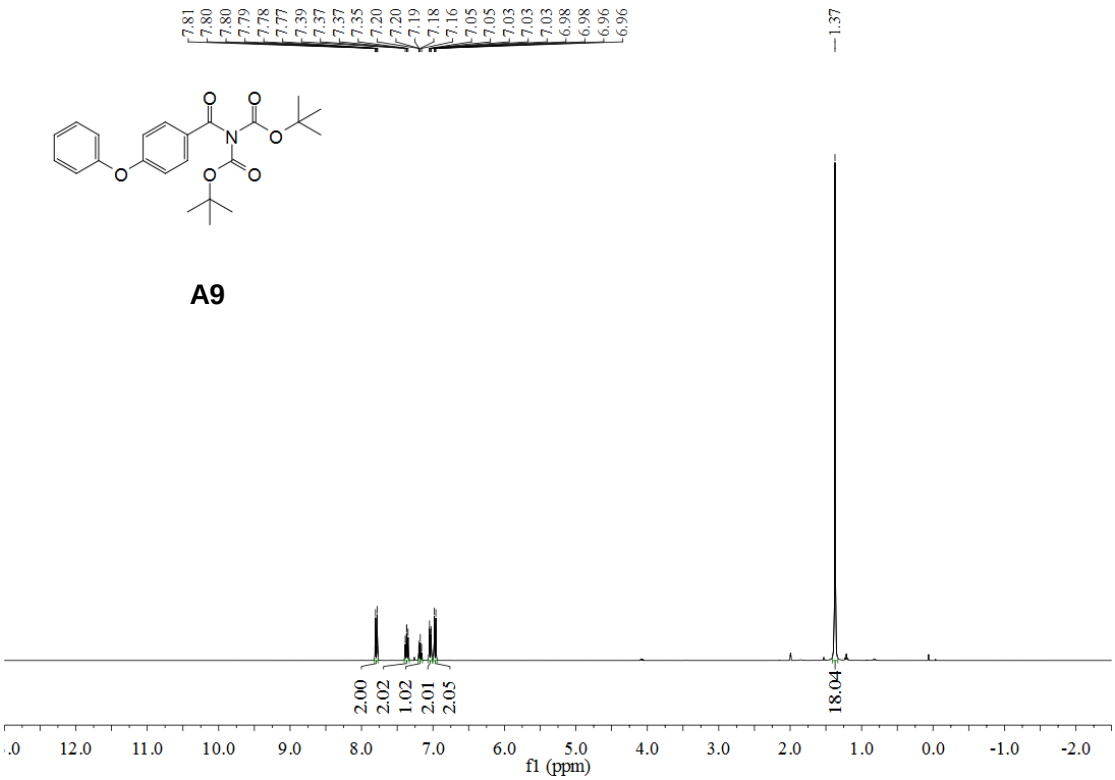
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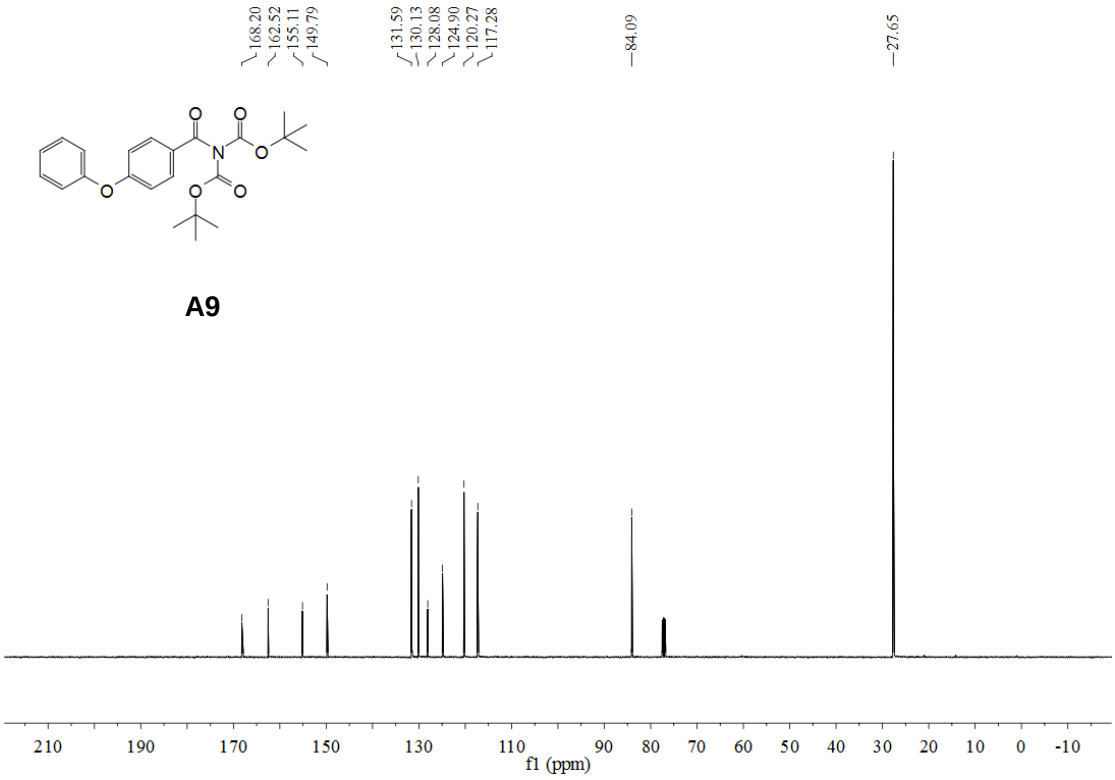
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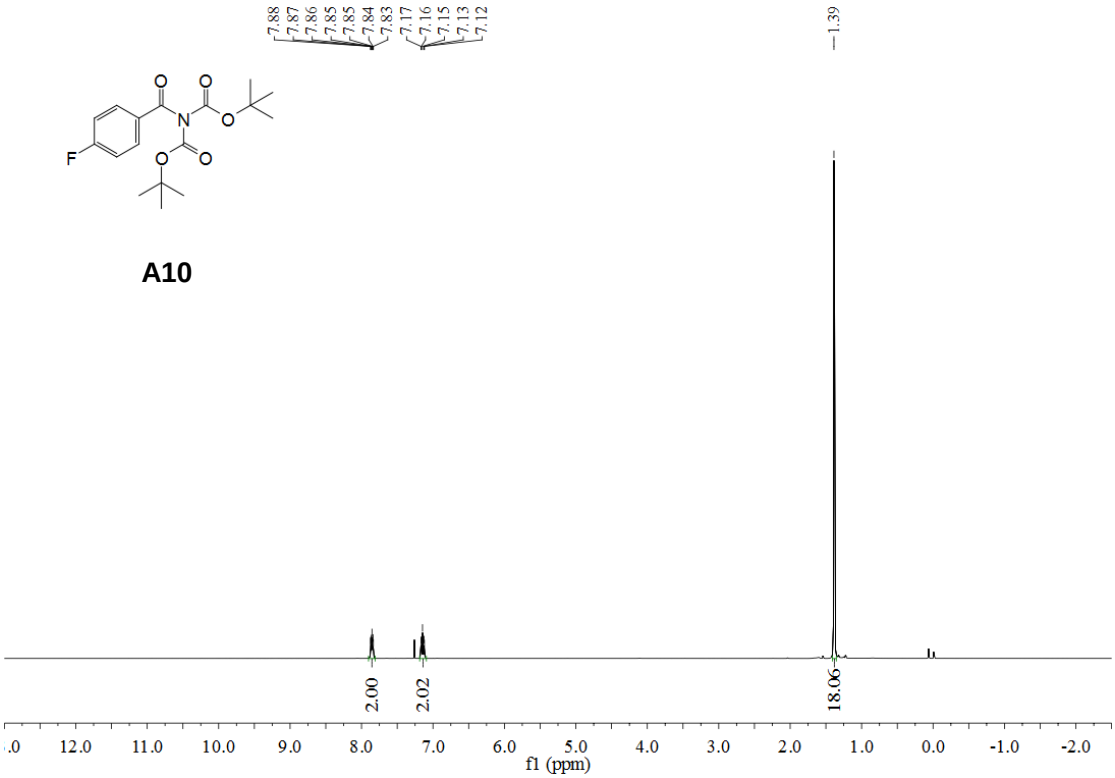
A9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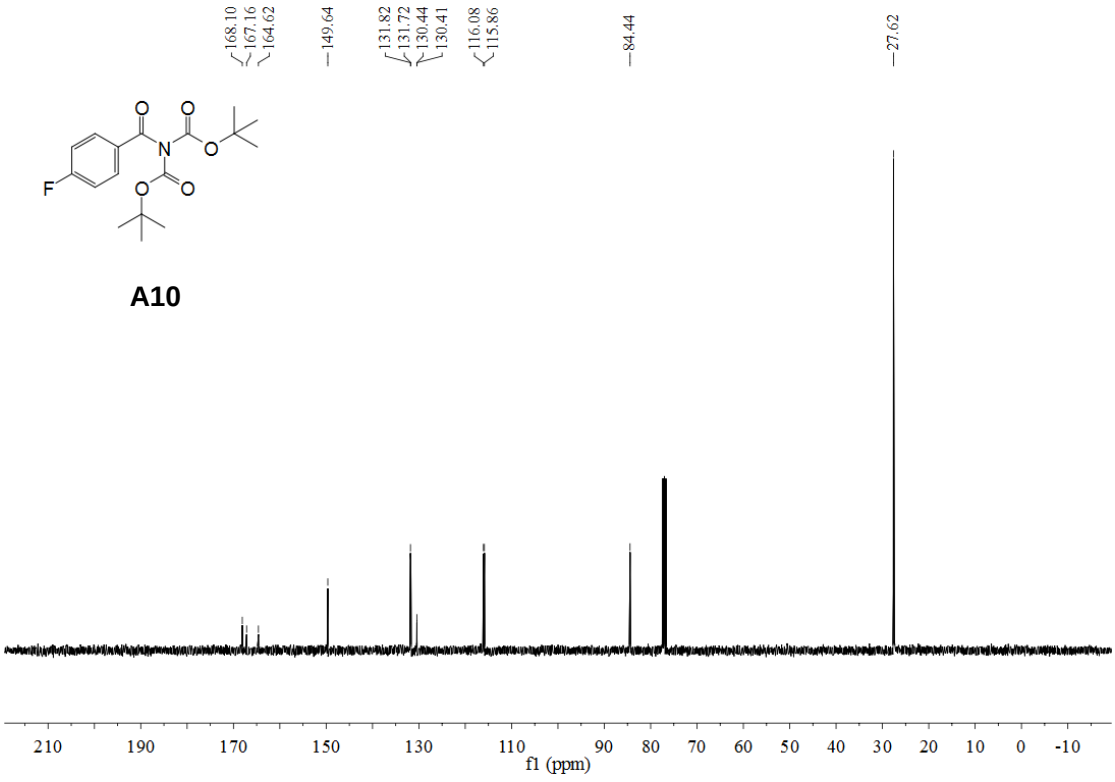
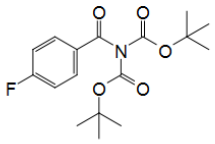
F
2.00
2.02
18.06
f1 (ppm)

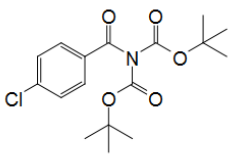
A10


168.10
167.16
164.62
149.64
131.82
131.72
130.44
130.41
116.08
115.86
84.44
27.62
F
f1 (ppm)

A10

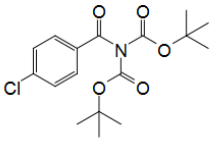


A10



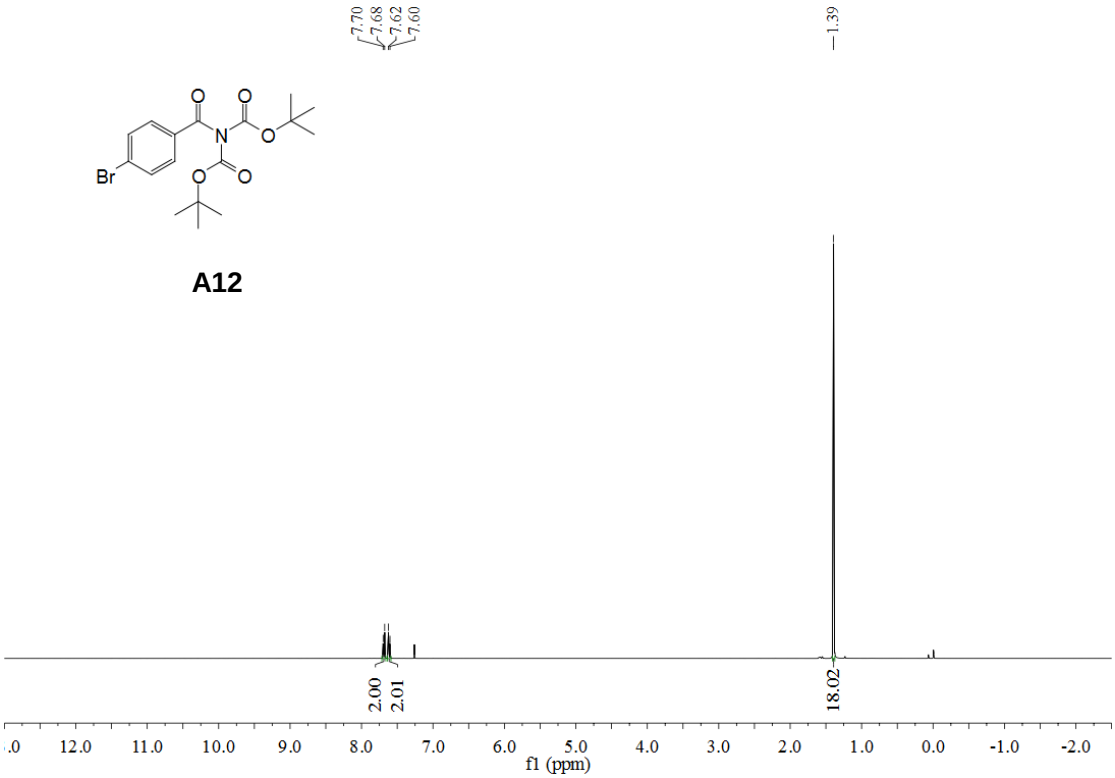
A11

7.78
7.76
7.46
7.44
1.39
2.00
2.03
18.09
f1 (ppm)

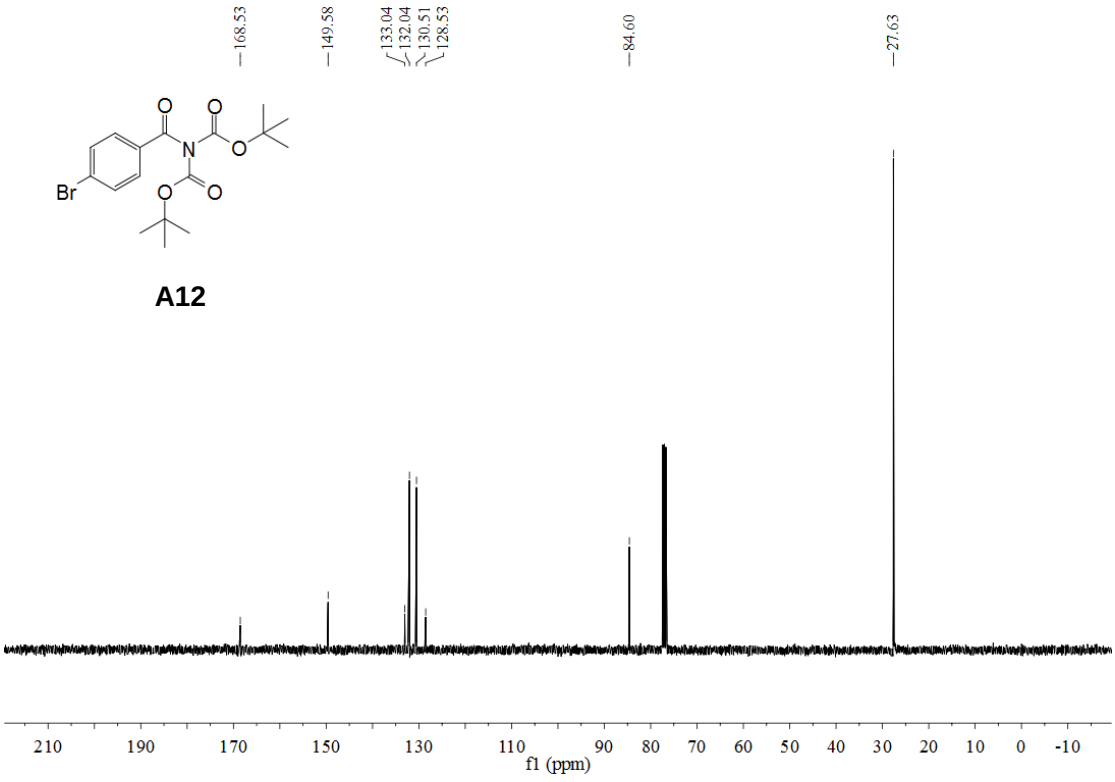


A11

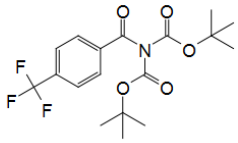
168.35
149.60
139.92
132.59
130.45
129.05
84.57
27.63
f1 (ppm)


7.70
7.68
7.62
7.60
1.39
Br
2.00
2.01
18.02
f1 (ppm)

A12

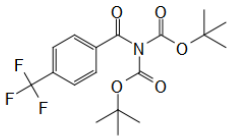

168.53
149.58
133.04
132.04
130.51
128.53
84.60
27.63
Br
f1 (ppm)

A12



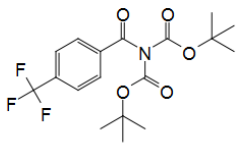
A13

7.91
7.89
7.73
7.71
1.39
2.04
2.03
18.00
f1 (ppm)

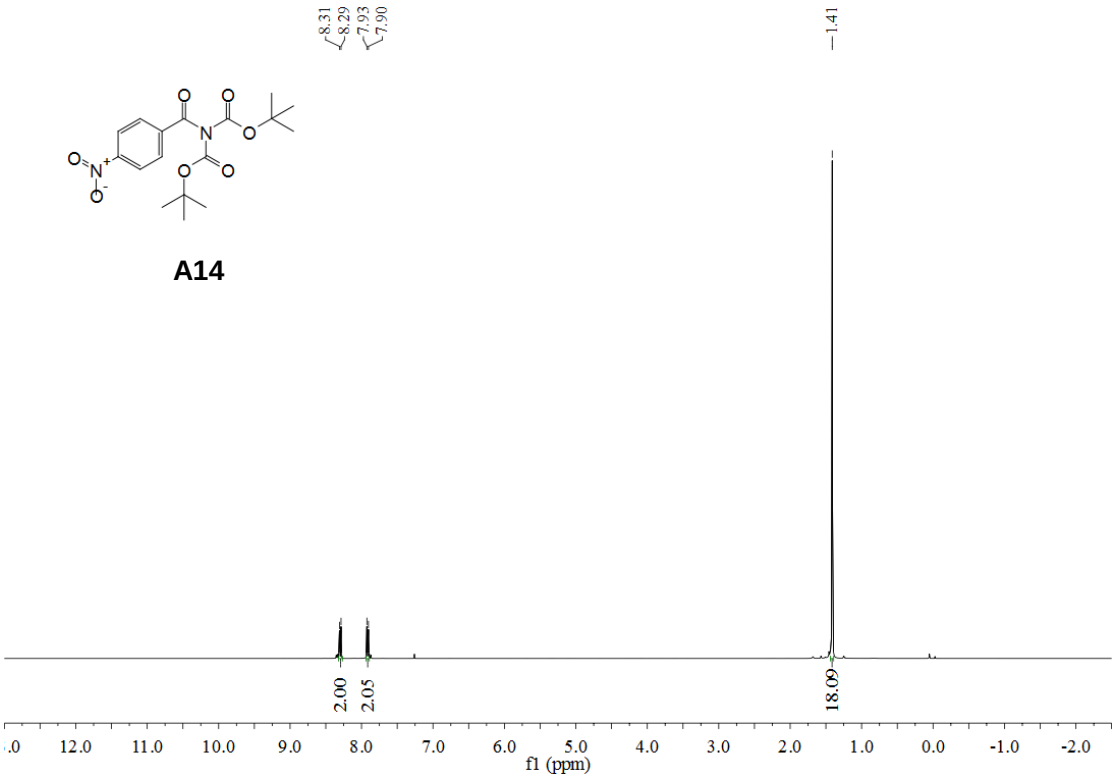


A13

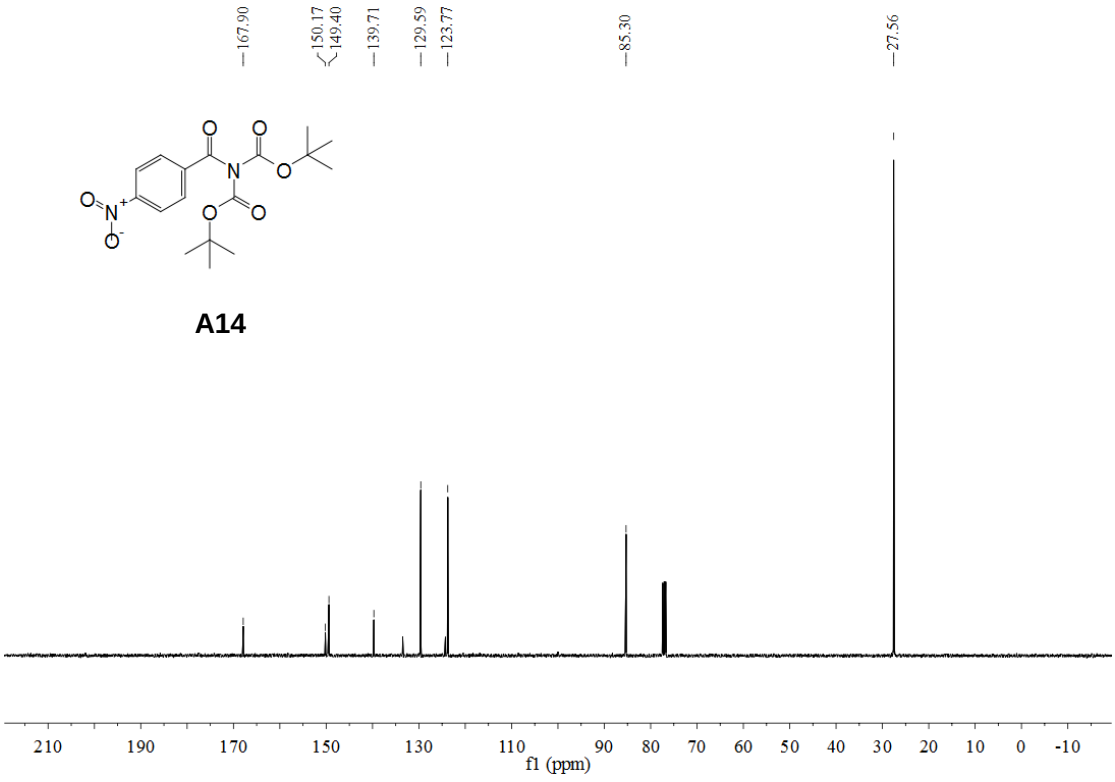
168.40
149.54
137.51
135.04
134.72
134.39
134.06
129.14
125.71
125.67
125.63
125.60
124.78
122.07
84.91
27.54
f1 (ppm)



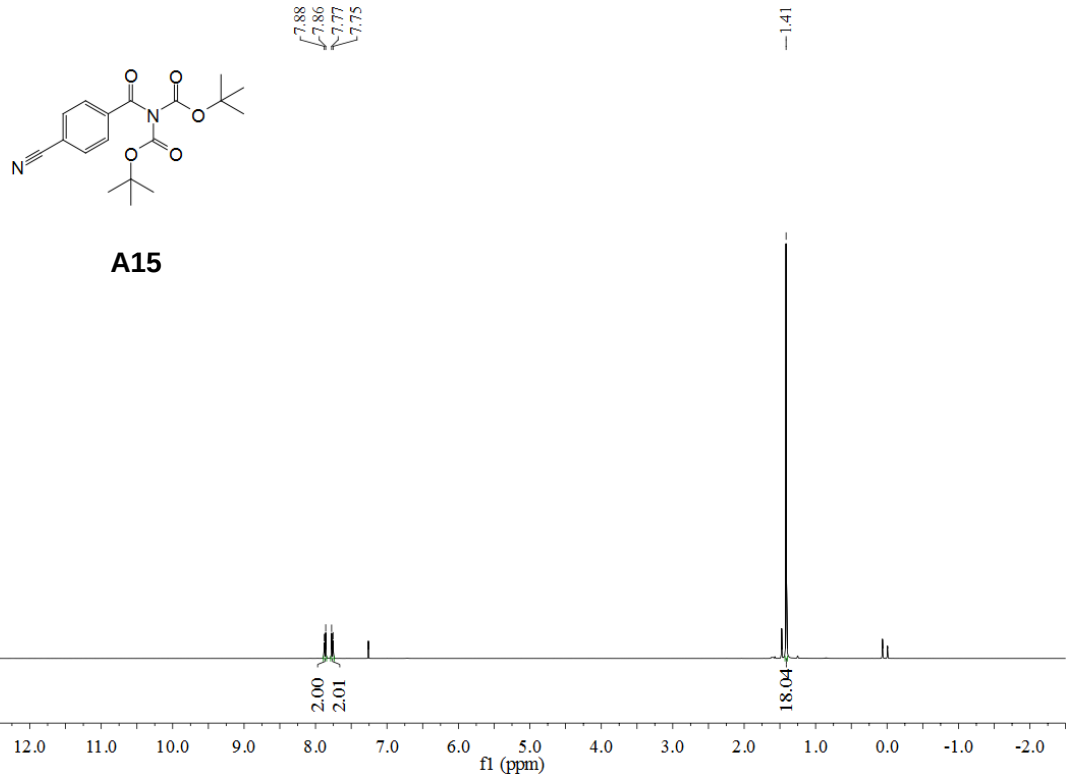
A13


8.31
8.29
7.93
7.90
1.41
2.00
2.05
18.09
f1 (ppm)

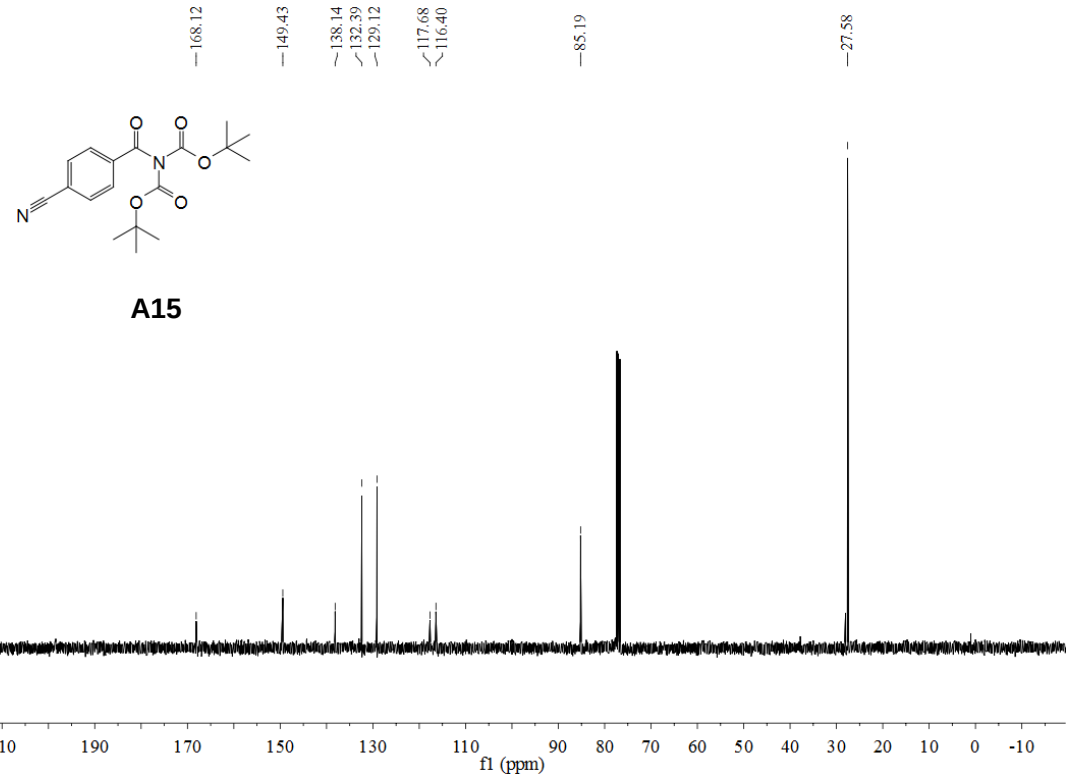
A14


167.90
150.17
149.40
139.71
129.59
123.77
85.30
27.56
f1 (ppm)

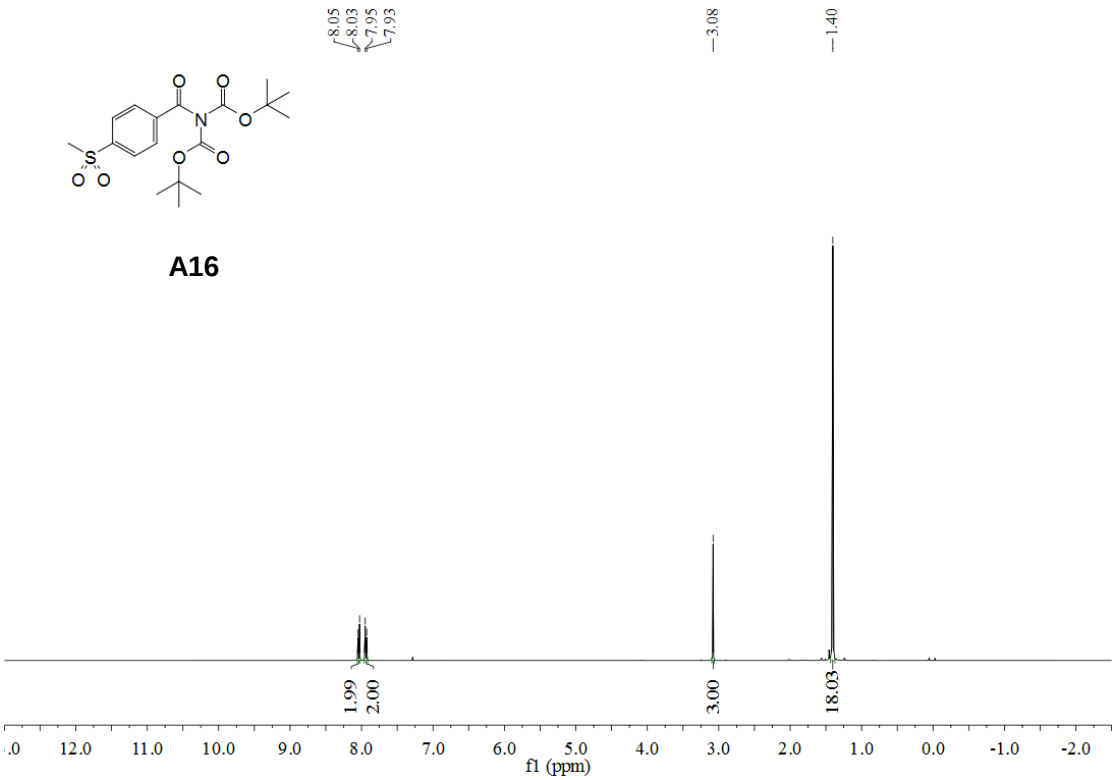
A14


7.88
7.86
7.77
7.75
1.41
2.00
2.01
18.04
f1 (ppm)

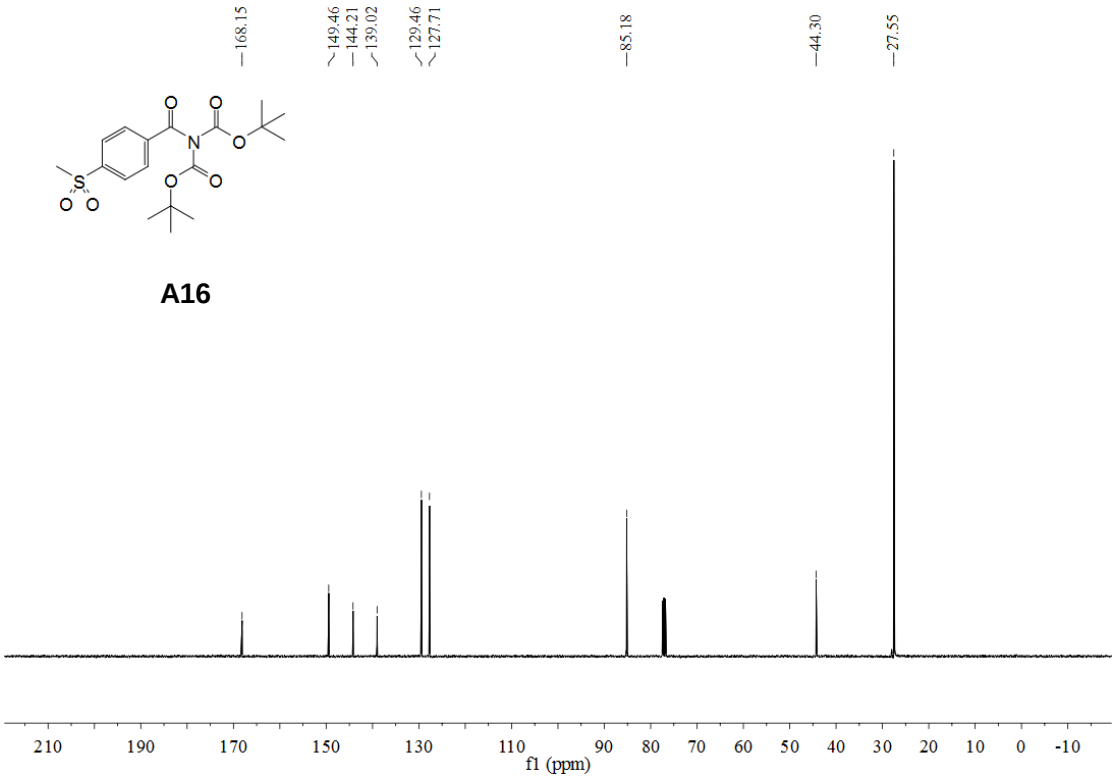
A15


168.12
149.43
138.14
132.39
129.12
117.68
116.40
85.19
27.58
f1 (ppm)

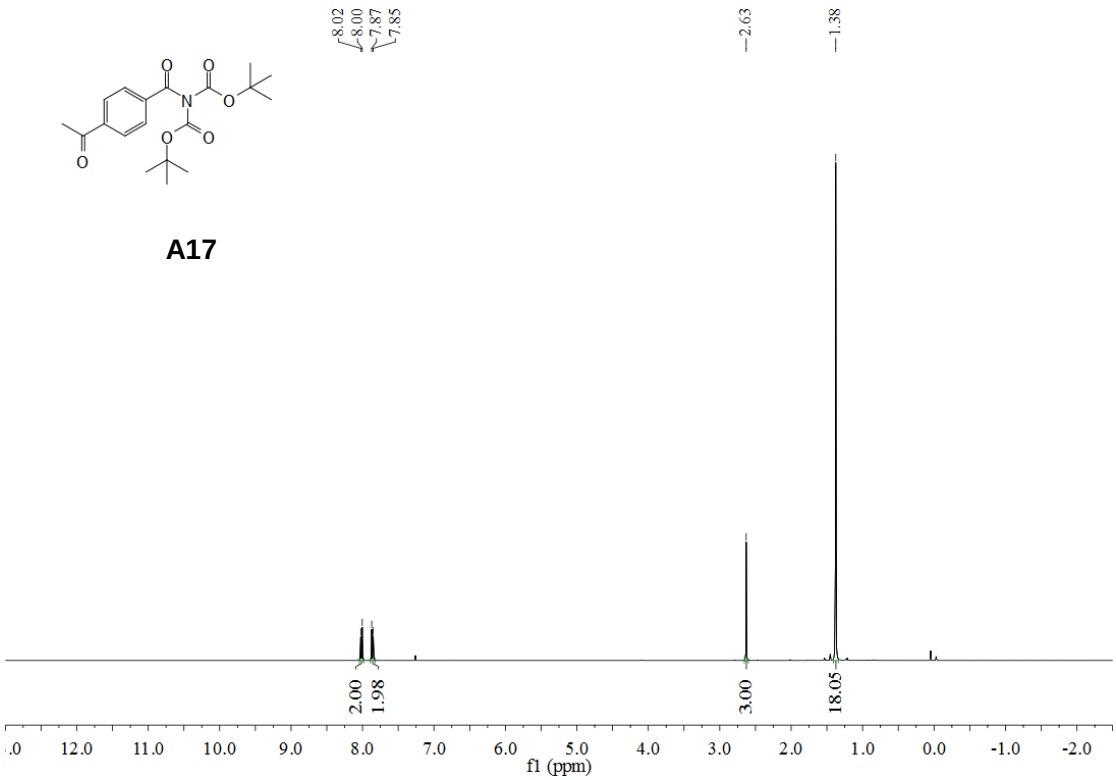
A15


8.05
8.03
7.95
7.93
3.08
1.40
1.99
2.00
3.00
18.03
f1 (ppm)

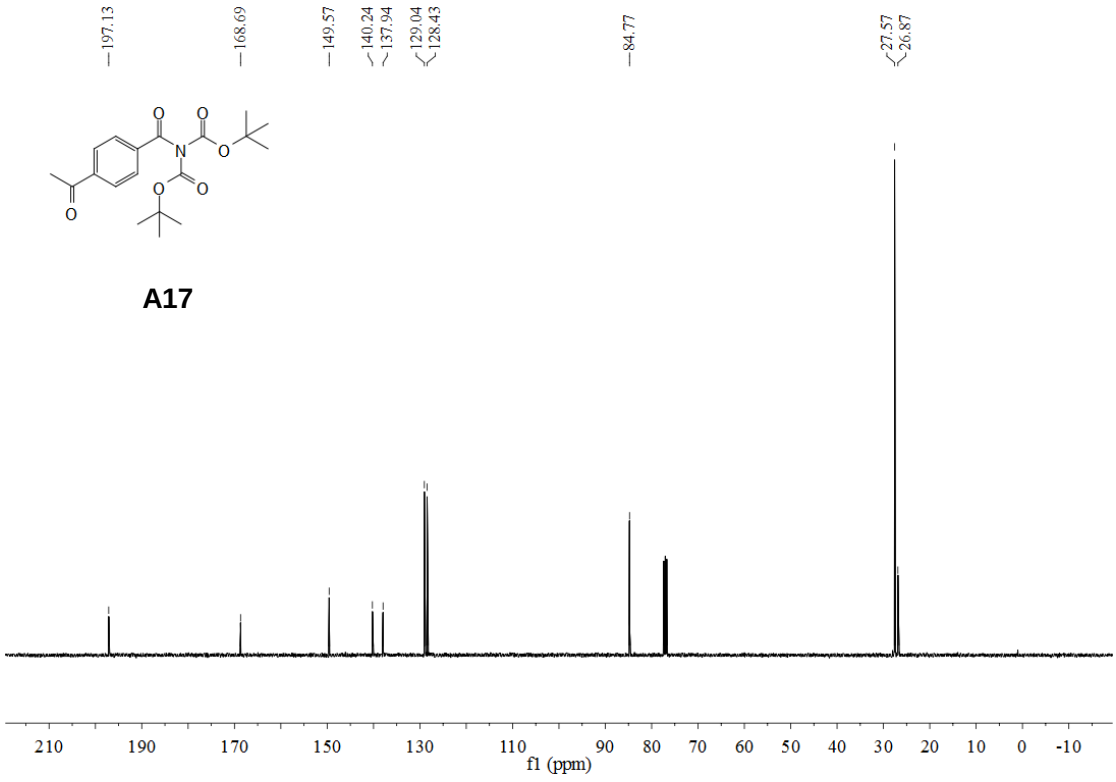
A16


168.15
149.46
144.21
139.02
129.46
127.71
85.18
44.30
27.55
f1 (ppm)

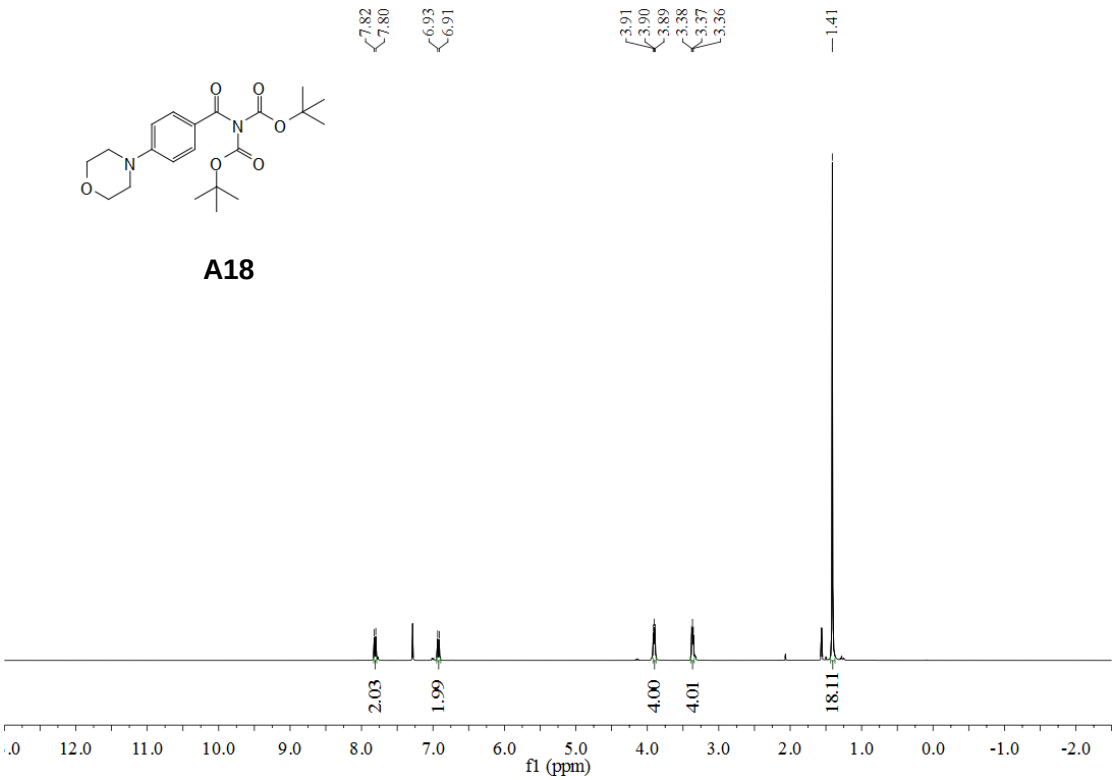
A16


8.02
8.00
7.87
7.85
2.63
1.38
2.00
1.98
3.00
18.05
f1 (ppm)

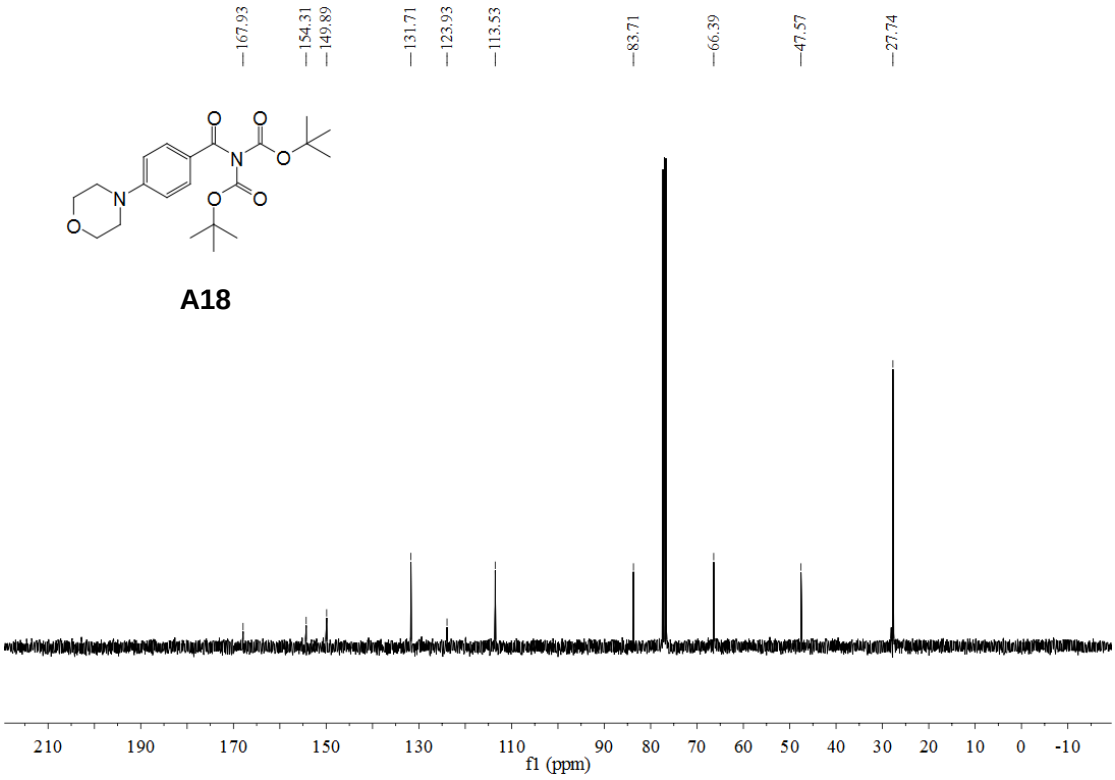
A17


197.13
168.69
149.57
140.24
137.94
129.04
128.43
84.77
27.57
26.87
f1 (ppm)

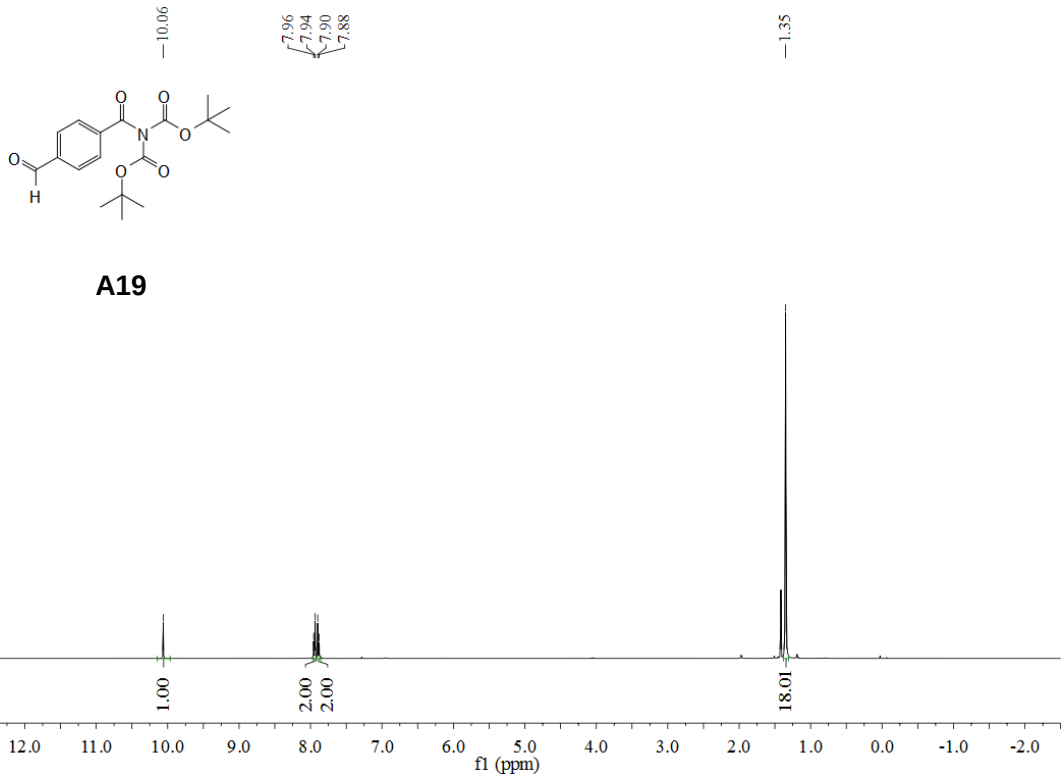
A17


7.82
7.80
6.93
6.91
3.91
3.90
3.89
3.38
3.37
3.36
1.41
2.03
1.99
4.00
4.01
18.11
f1 (ppm)

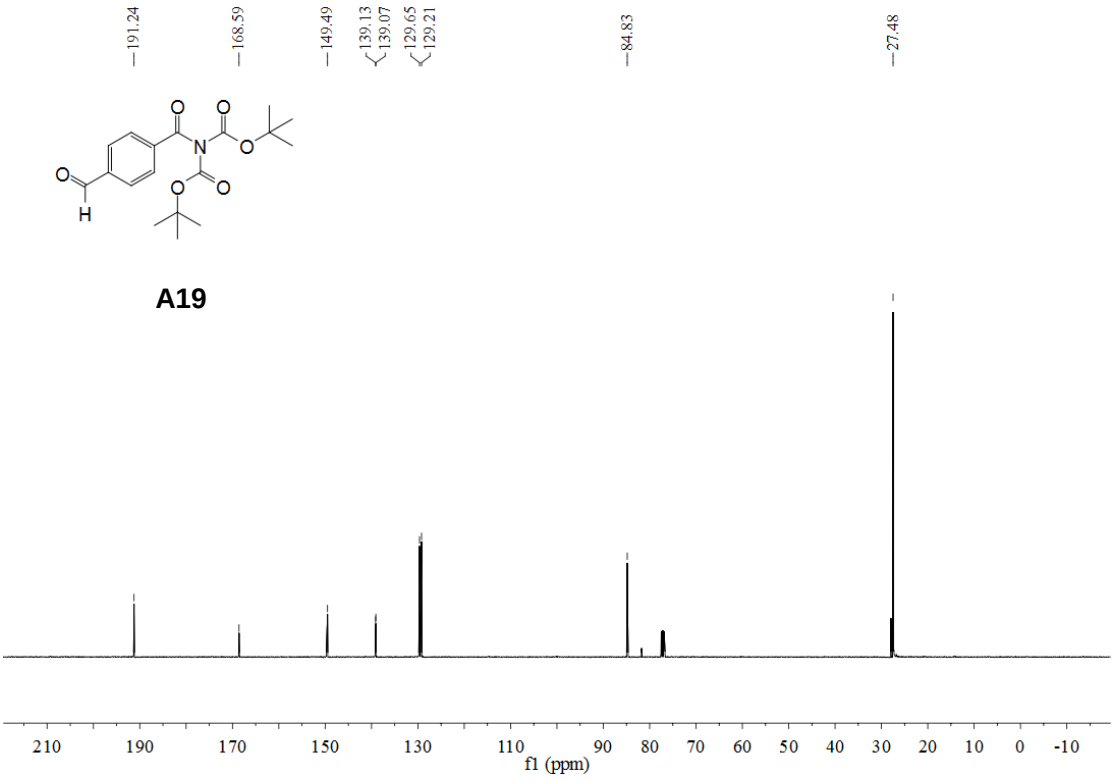
A18


167.93
154.31
149.89
131.71
123.93
113.53
83.71
66.39
47.57
27.74
f1 (ppm)

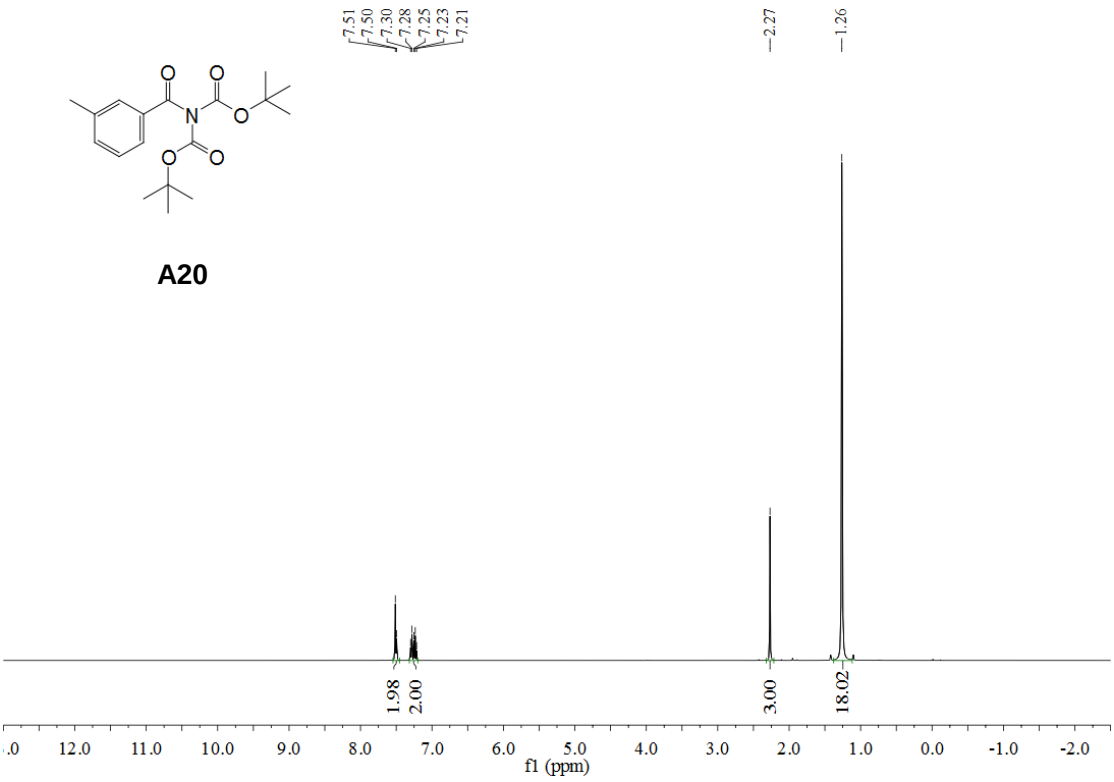
A18


10.06
7.96
7.94
7.90
7.88
1.35
1.00
2.00
2.00
18.01
f1 (ppm)

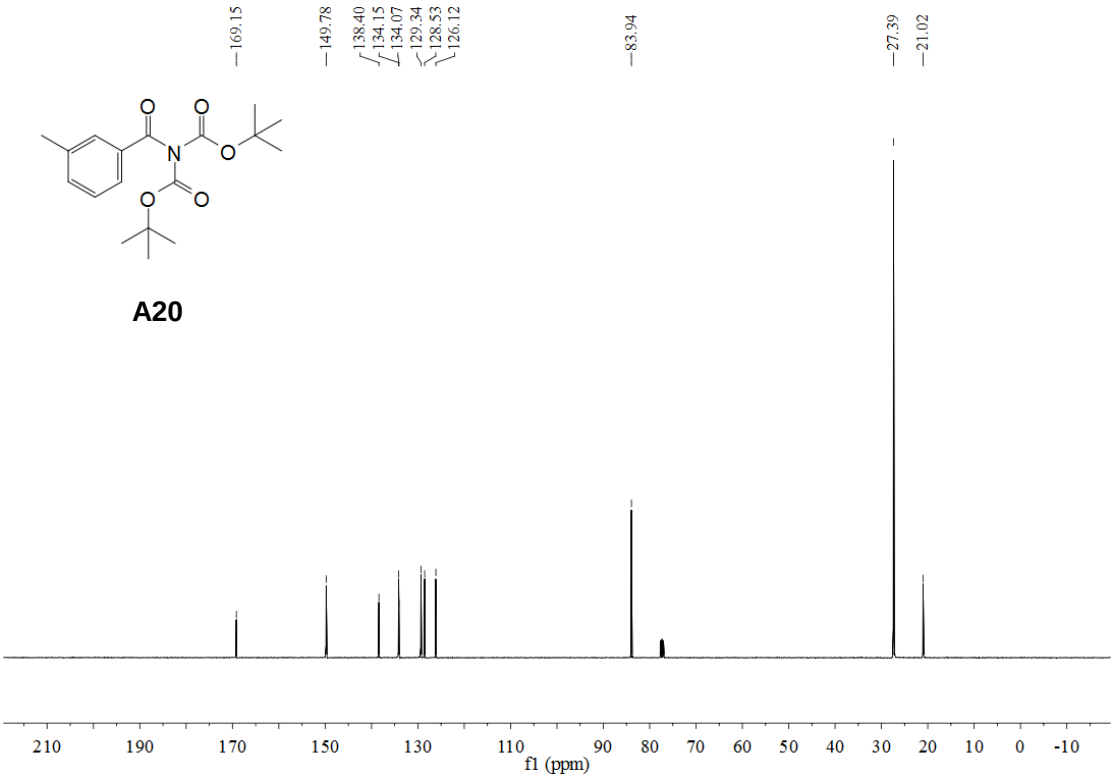
A19


191.24
168.59
149.49
139.13
139.07
129.65
129.21
84.83
27.48
f1 (ppm)

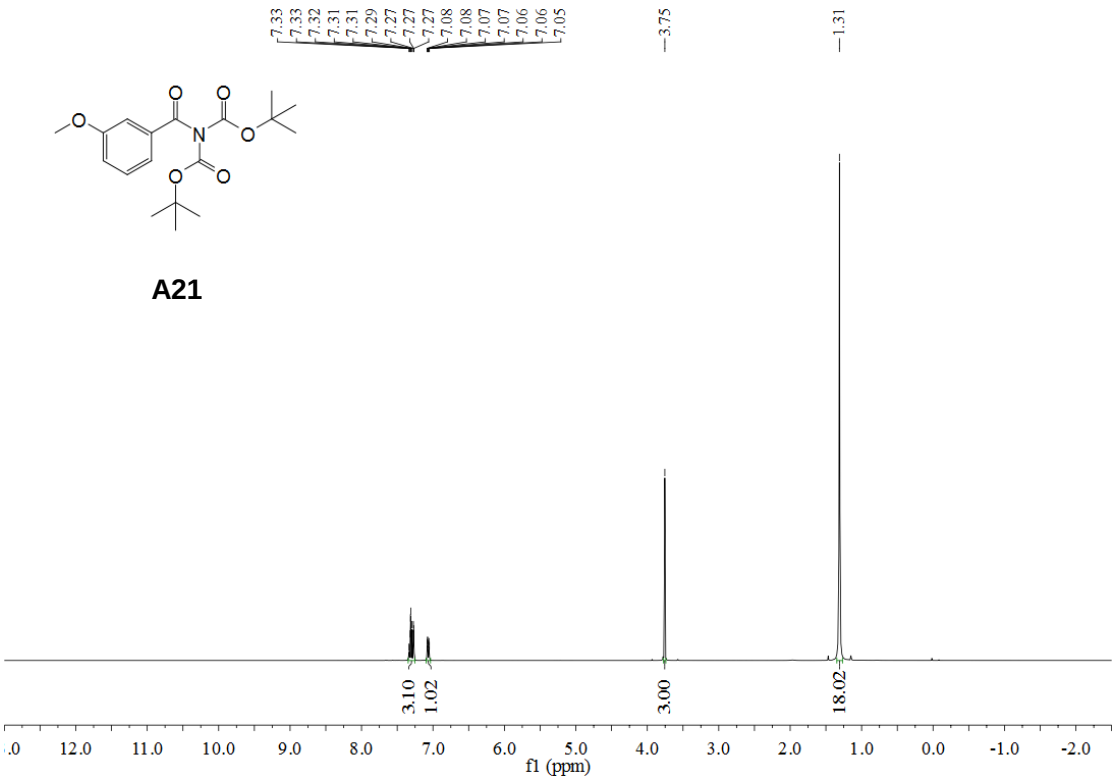
A19


7.51
7.50
7.30
7.28
7.25
7.23
7.21
2.27
1.26
1.98
2.00
3.00
18.02
f1 (ppm)

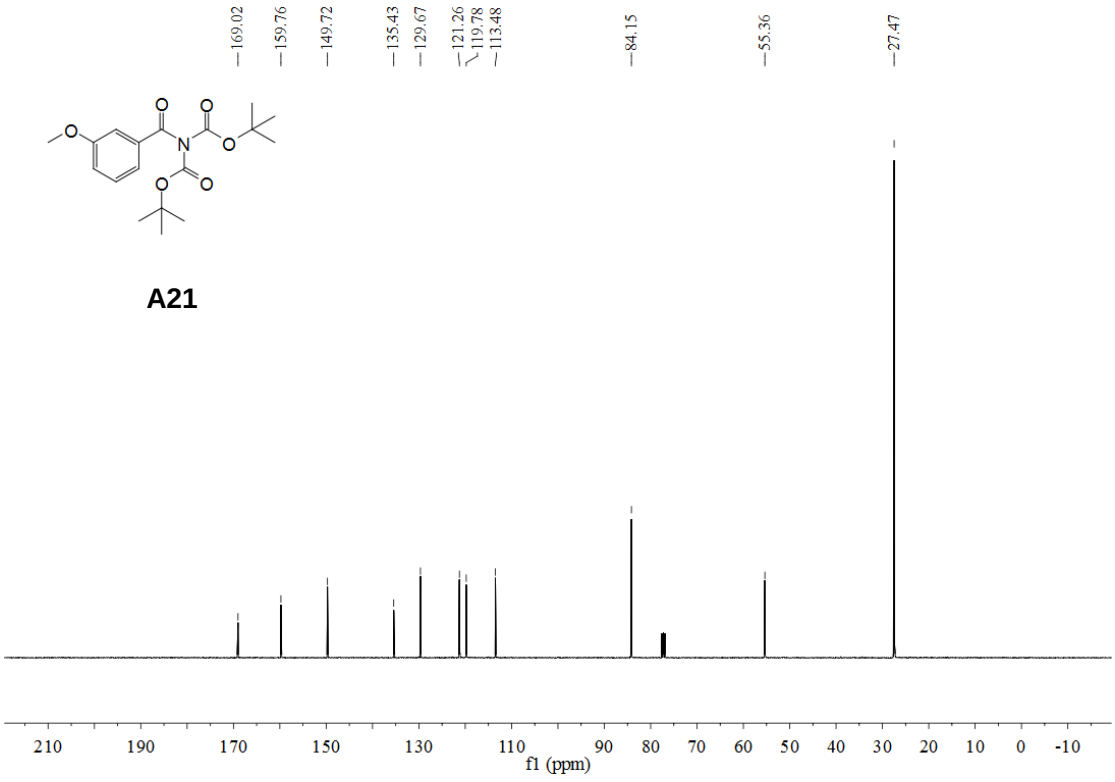
A20


169.15
149.78
138.40
134.15
134.07
129.34
128.53
126.12
83.94
27.39
21.02
f1 (ppm)

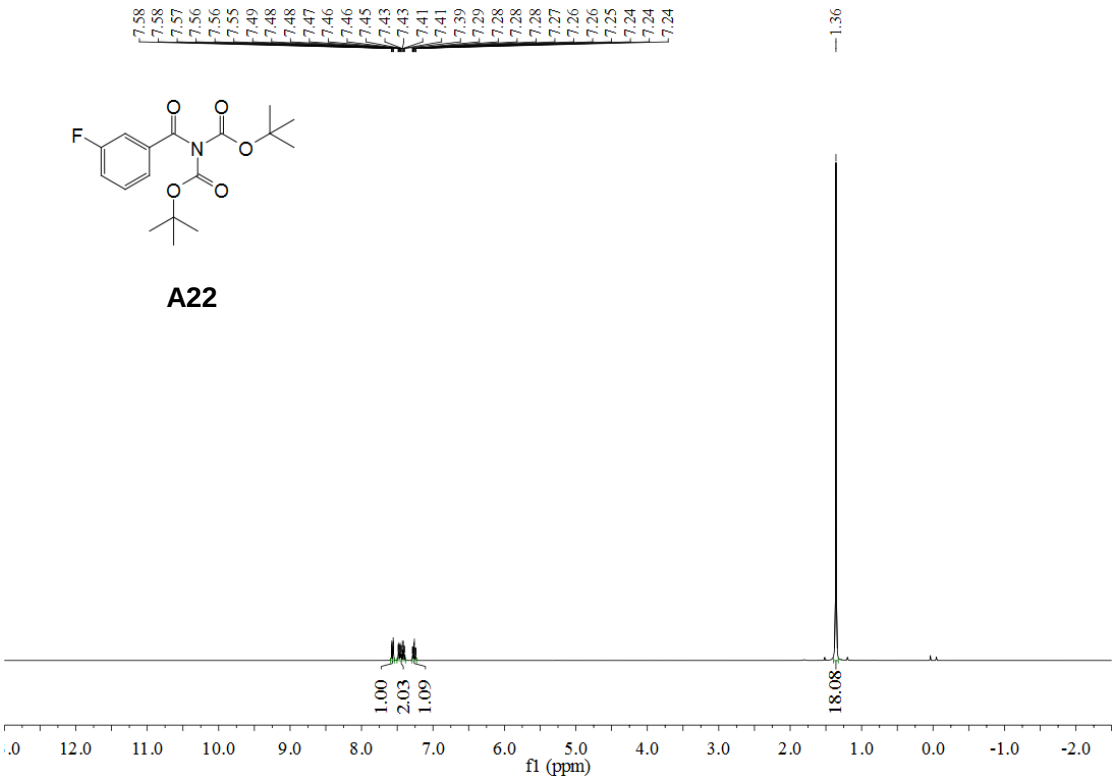
A20


7.33
7.33
7.32
7.31
7.31
7.29
7.27
7.27
7.27
7.08
7.08
7.07
7.07
7.06
7.06
7.05
3.75
1.31
3.10
1.02
3.00
18.02
f1 (ppm)

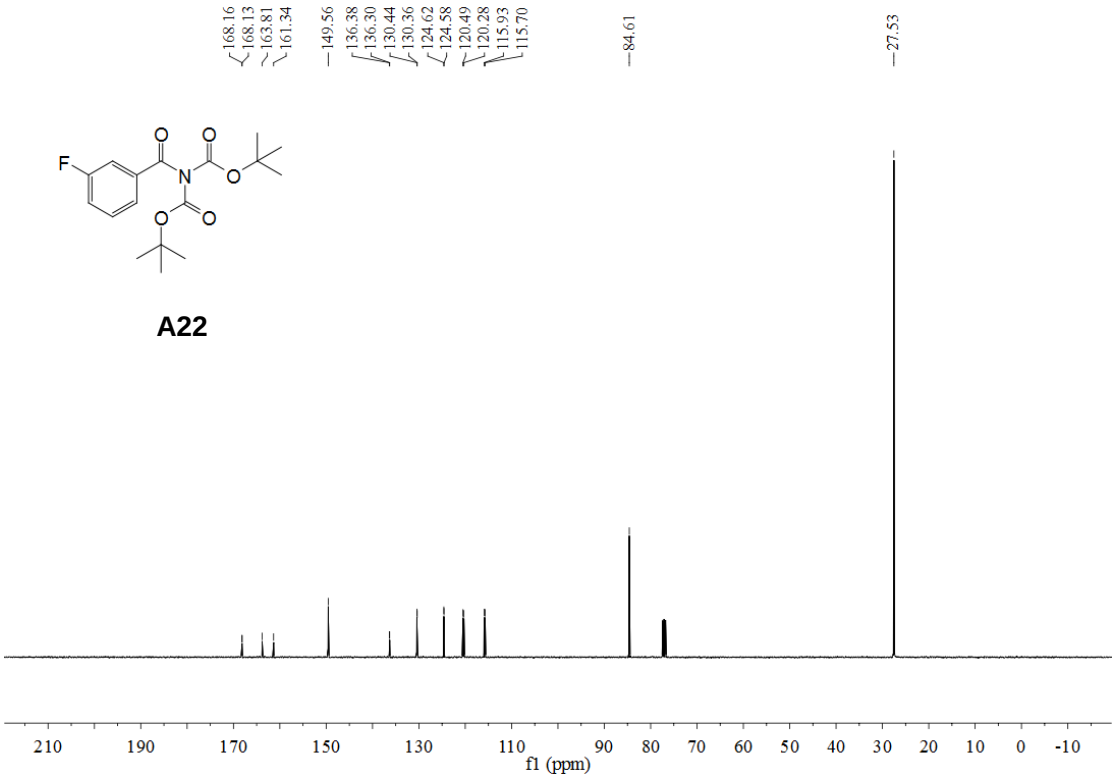
A21


169.02
159.76
149.72
135.43
129.67
121.26
119.78
113.48
84.15
55.36
27.47
f1 (ppm)

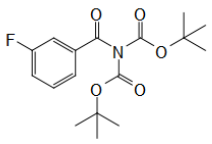
A21


7.58
7.58
7.57
7.56
7.56
7.55
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.43
7.43
7.41
7.41
7.39
7.29
7.28
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.24
1.36
F
O
N
O
O
O
O
O
1.00
2.03
1.09
18.08
f1 (ppm)

A22

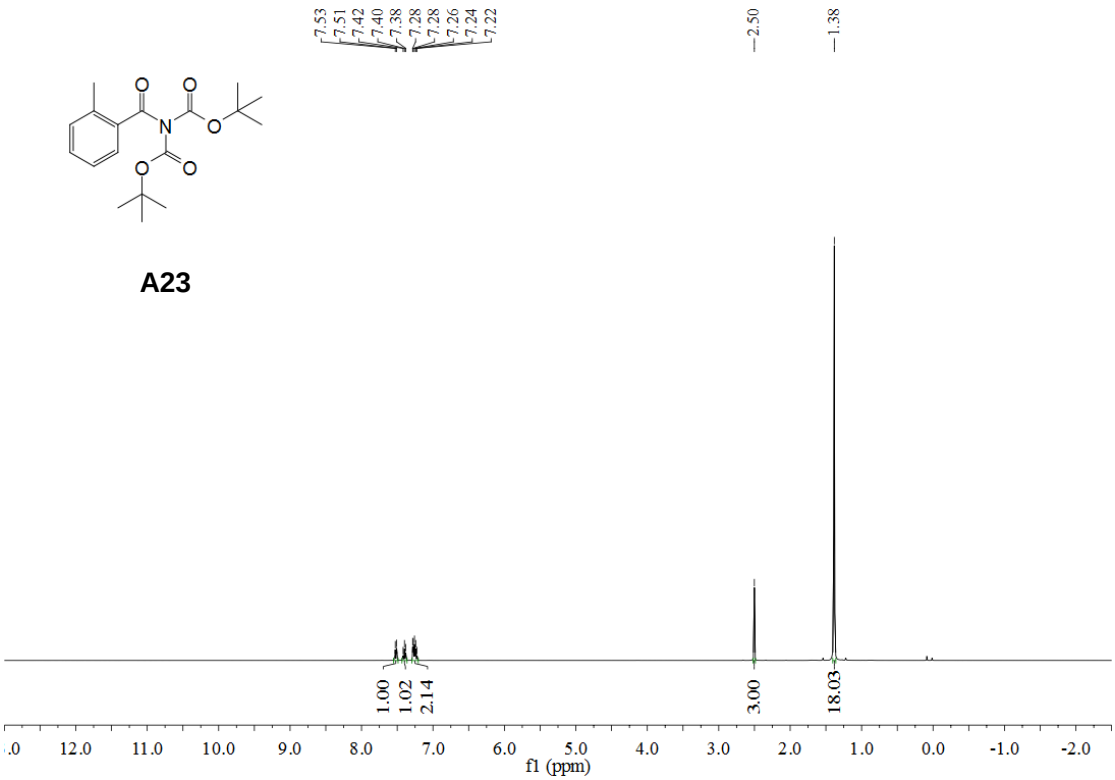

168.16
168.13
163.81
161.34
149.56
136.38
136.30
130.44
130.36
124.62
124.58
120.49
120.28
115.93
115.70
84.61
27.53
F
O
N
O
O
O
O
O
f1 (ppm)

A22

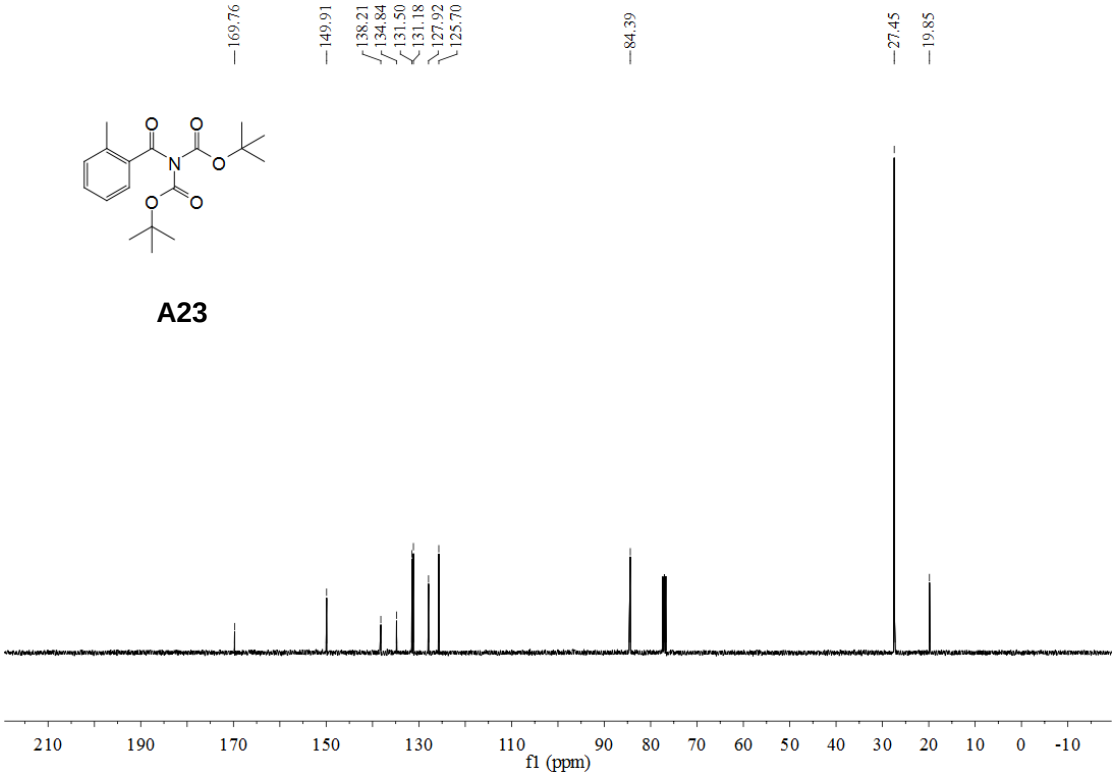

F
O
N
O
O
O
O
O

A22

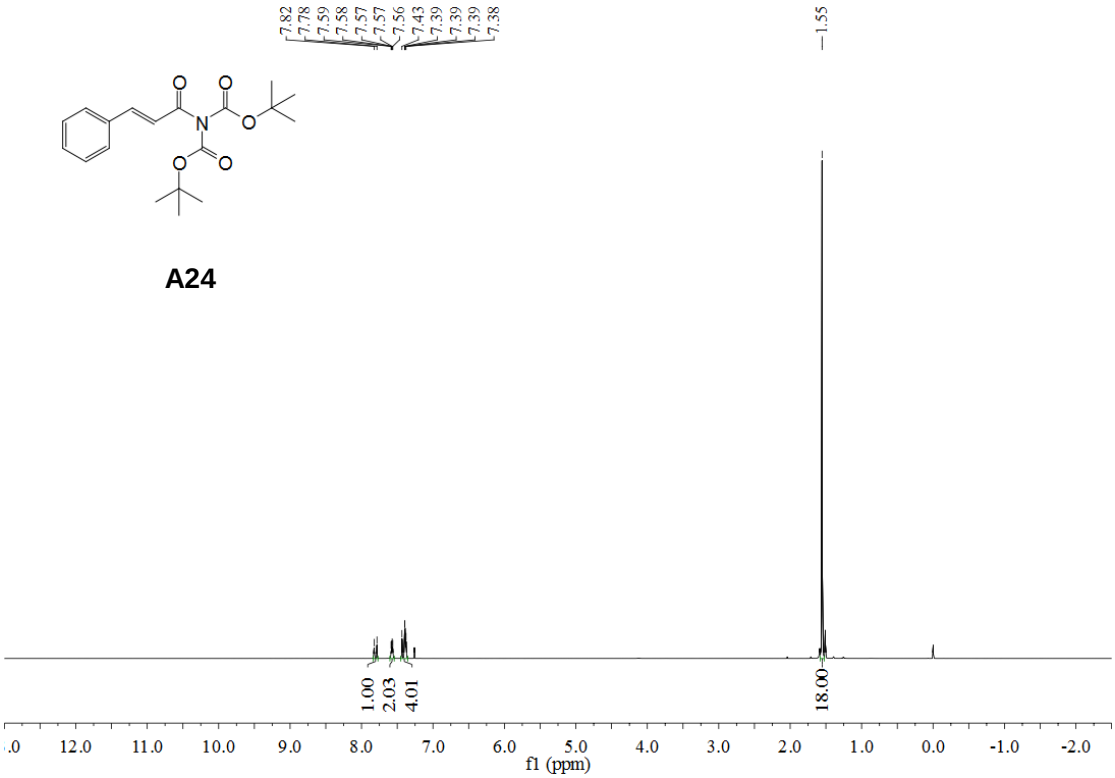
-111.59
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.53
7.51
7.42
7.40
7.38
7.28
7.28
7.26
7.24
7.22
2.50
1.38
1.00
1.02
2.14
3.00
18.03
f1 (ppm)

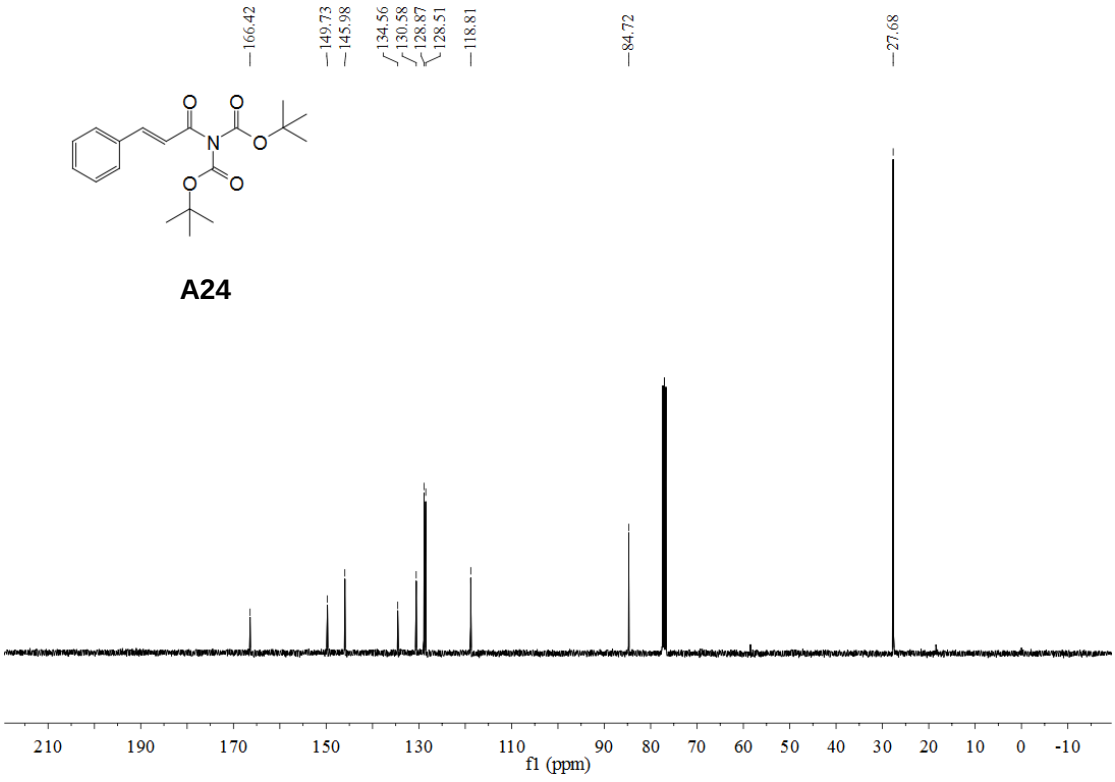
A23


169.76
149.91
138.21
134.84
131.50
131.18
127.92
125.70
84.39
27.45
19.85
f1 (ppm)

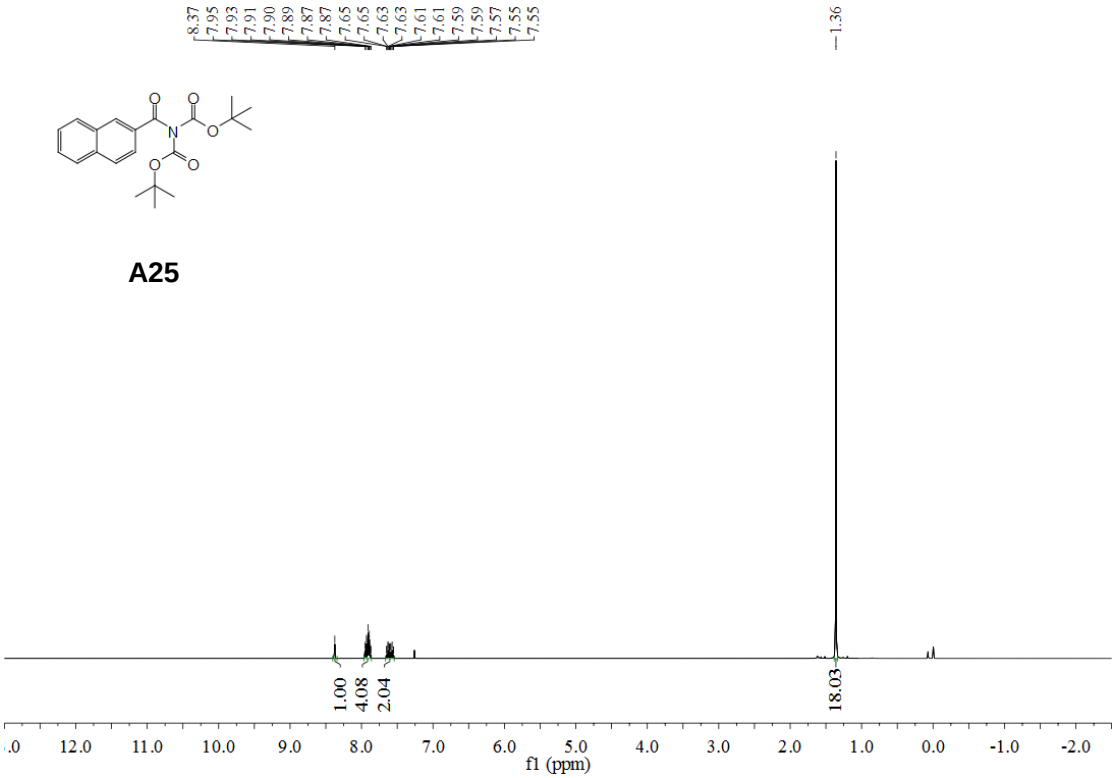
A23


7.82
7.78
7.59
7.58
7.57
7.57
7.56
7.43
7.39
7.39
7.39
7.38
1.55
1.00
2.03
4.01
18.00
f1 (ppm)

A24


166.42
149.73
145.98
134.56
130.58
128.87
128.51
118.81
84.72
27.68
f1 (ppm)

A24


8.37
7.95
7.93
7.91
7.90
7.89
7.87
7.87
7.65
7.65
7.63
7.63
7.61
7.61
7.59
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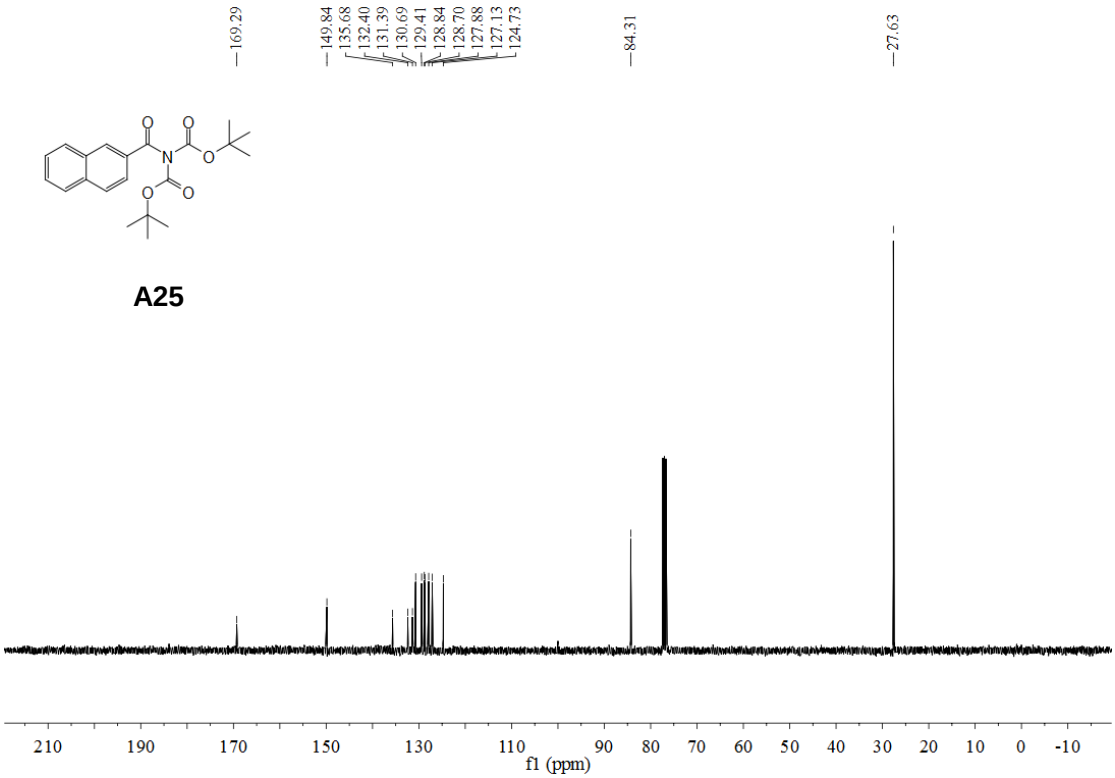
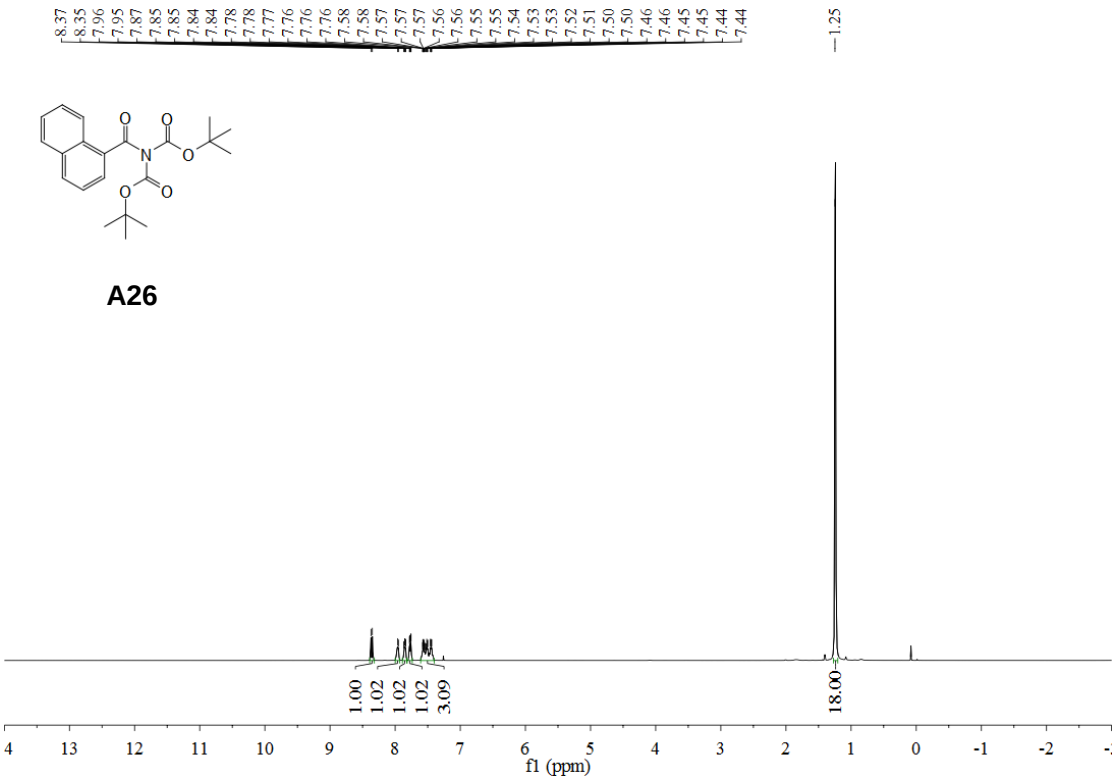
7.55
7.55
1.36
1.00
4.08
2.04
18.03
f1 (ppm)

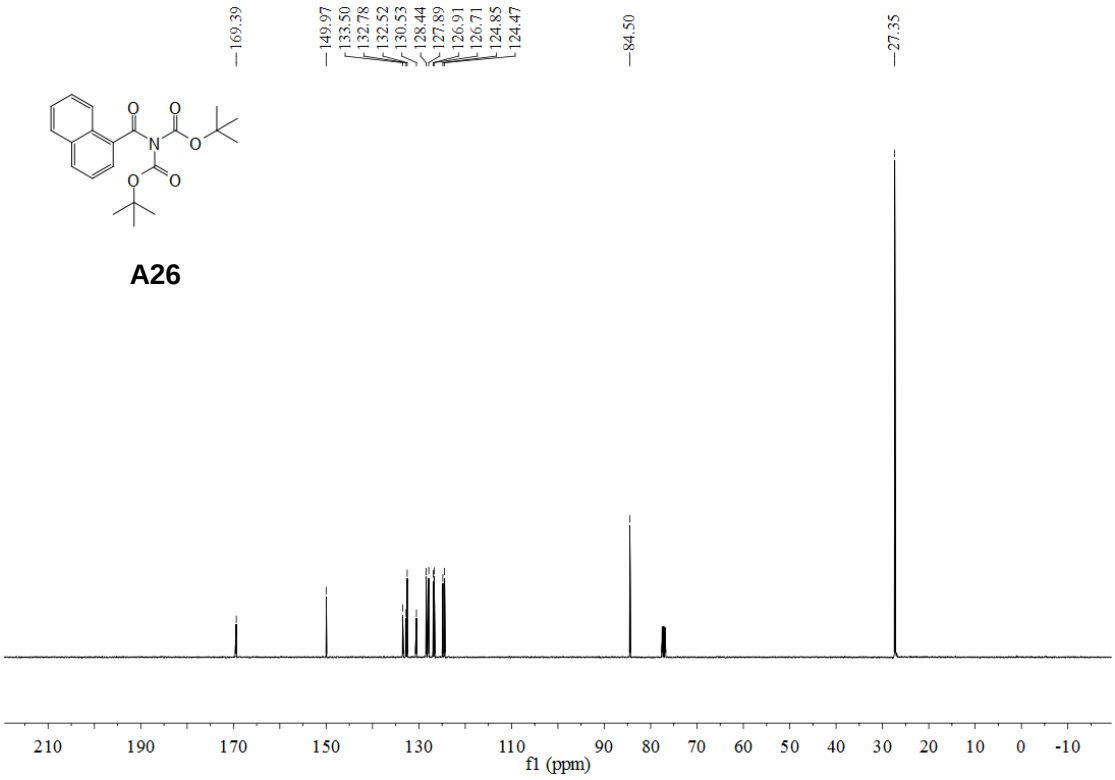
A25


169.29
149.84
135.68
132.40
131.39
130.69
129.41
128.84
128.70
127.88
127.13
124.73
84.31
27.63
f1 (ppm)

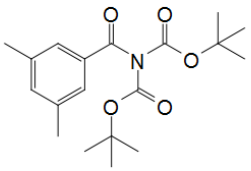
A25


8.37
8.35
7.96
7.95
7.87
7.85
7.85
7.84
7.84
7.78
7.78
7.77
7.76
7.76
7.76
7.58
7.58
7.57
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.50
7.46
7.46
7.45
7.45
7.44
7.44
1.25
1.00
1.02
1.02
1.02
3.09
18.00
f1 (ppm)

A26

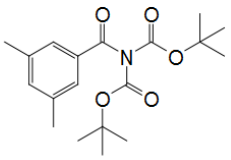

169.39
149.97
133.50
132.78
132.52
130.53
128.44
127.89
126.91
126.71
124.85
124.47
84.50
27.35
f1 (ppm)

A26



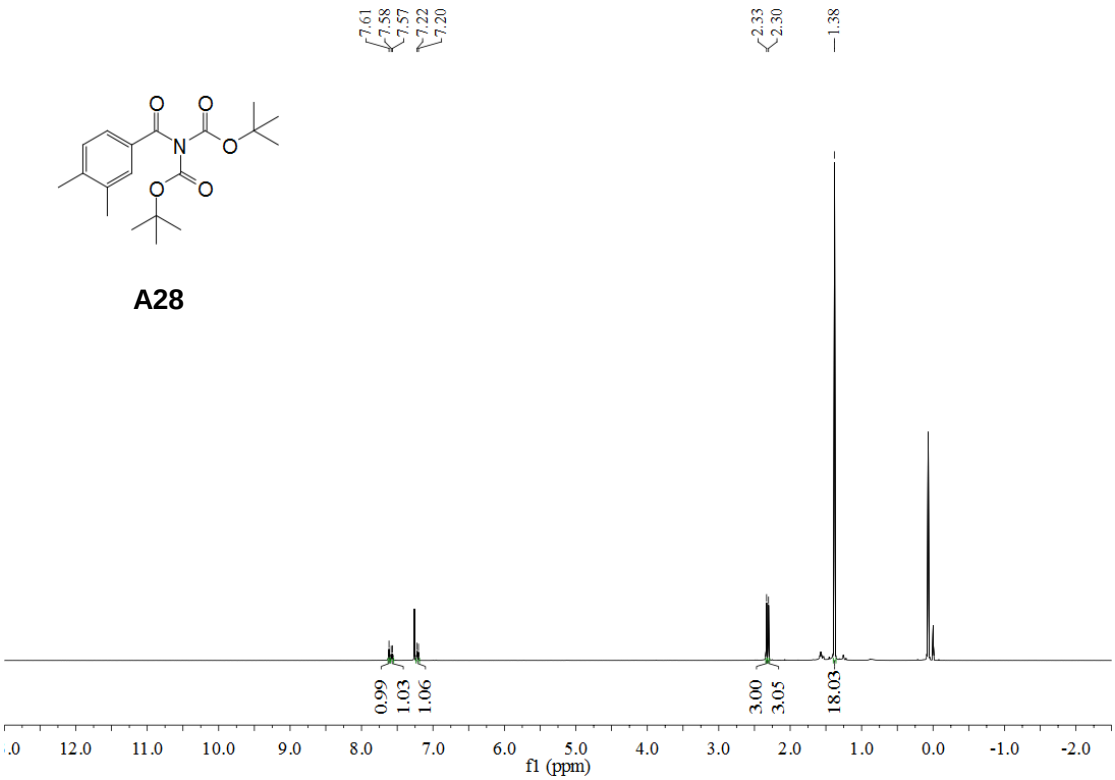
A27

7.29
7.09
2.20
1.25
2.02
1.00
6.00
18.06
f1 (ppm)

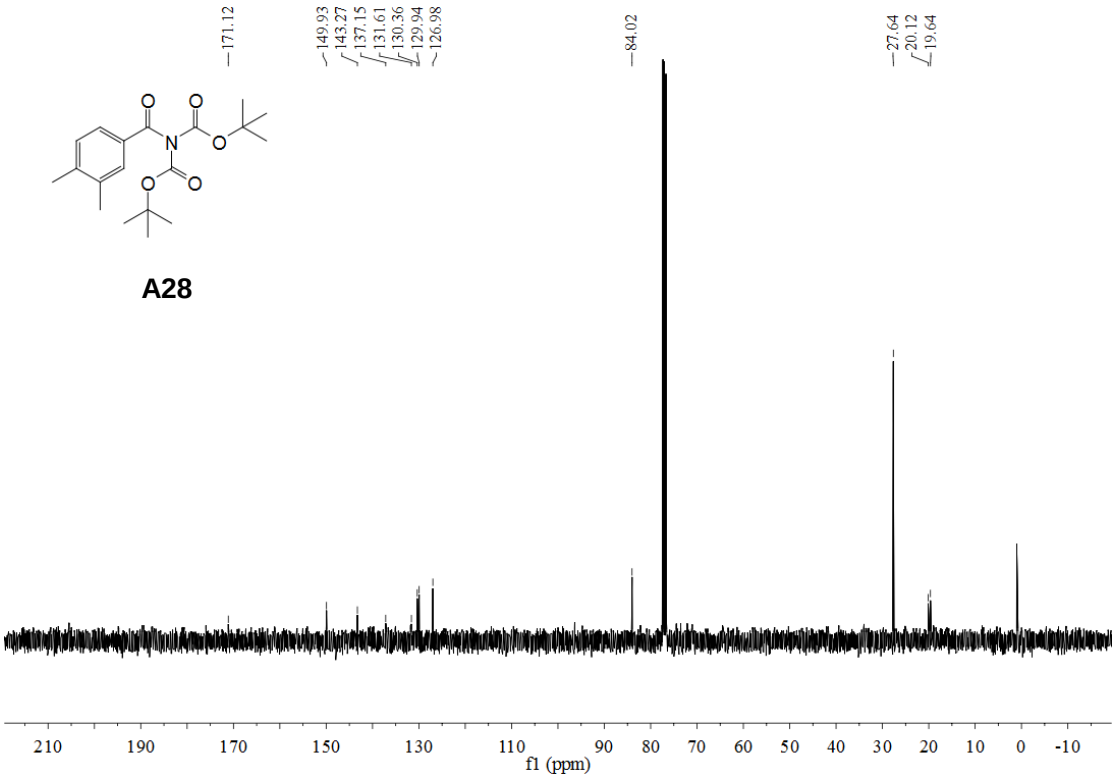


A27

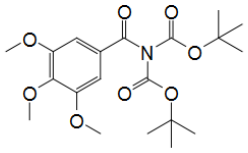
169.13
149.85
138.23
134.96
134.03
126.62
83.78
27.34
20.86
f1 (ppm)


7.61
7.58
7.57
7.22
7.20
2.33
2.30
1.38
0.99
1.03
1.06
3.00
3.05
18.03
f1 (ppm)

A28

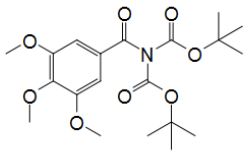

171.12
149.93
143.27
137.15
131.61
130.36
129.94
126.98
84.02
27.64
20.12
19.64
f1 (ppm)

A28



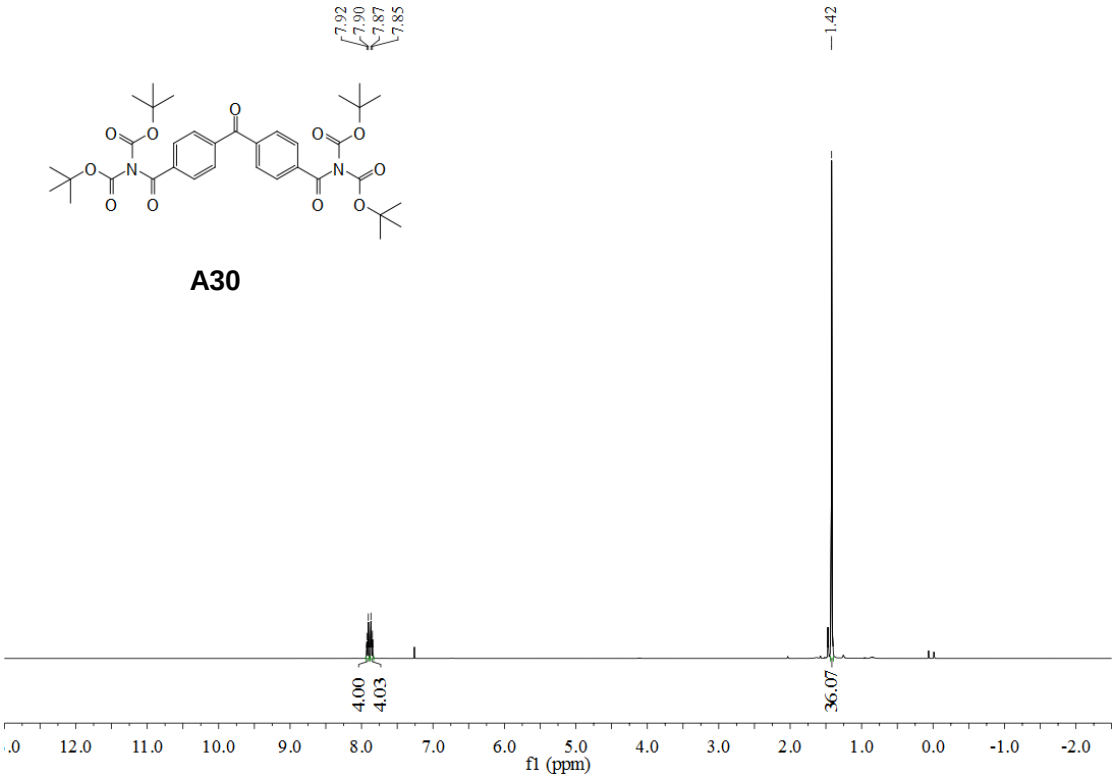
A29

6.83
6.82
3.63
3.62
1.15
2.00
9.04
18.07
f1 (ppm)

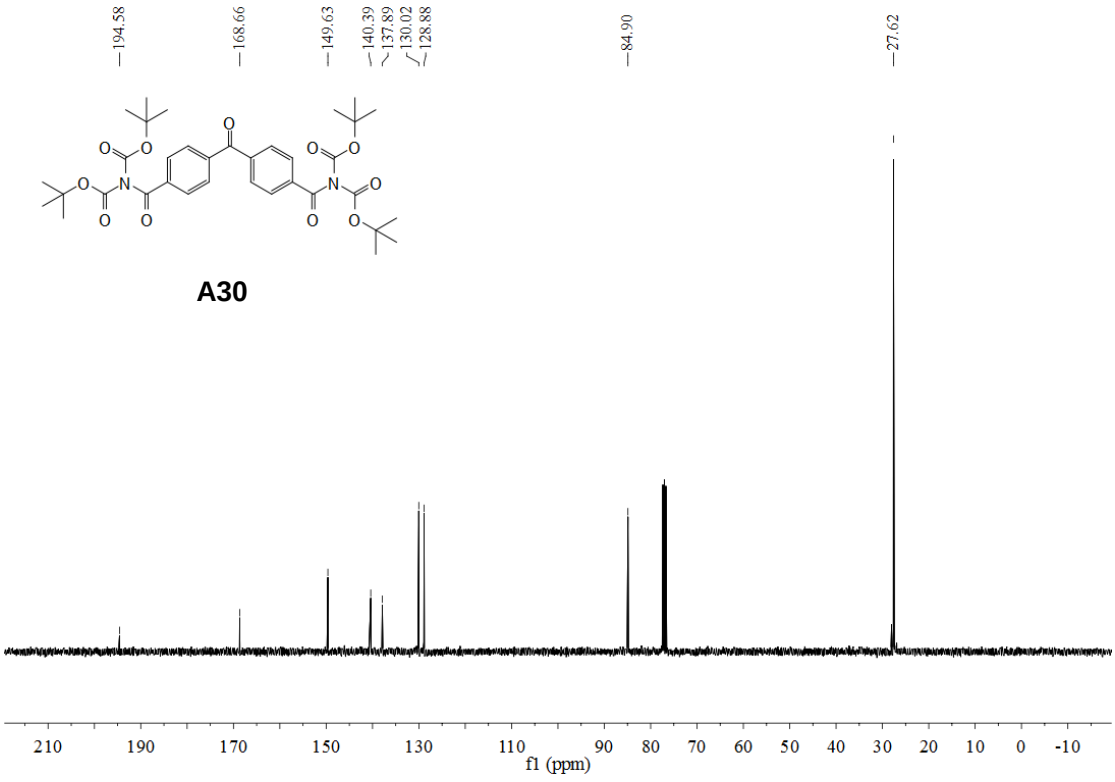


A29

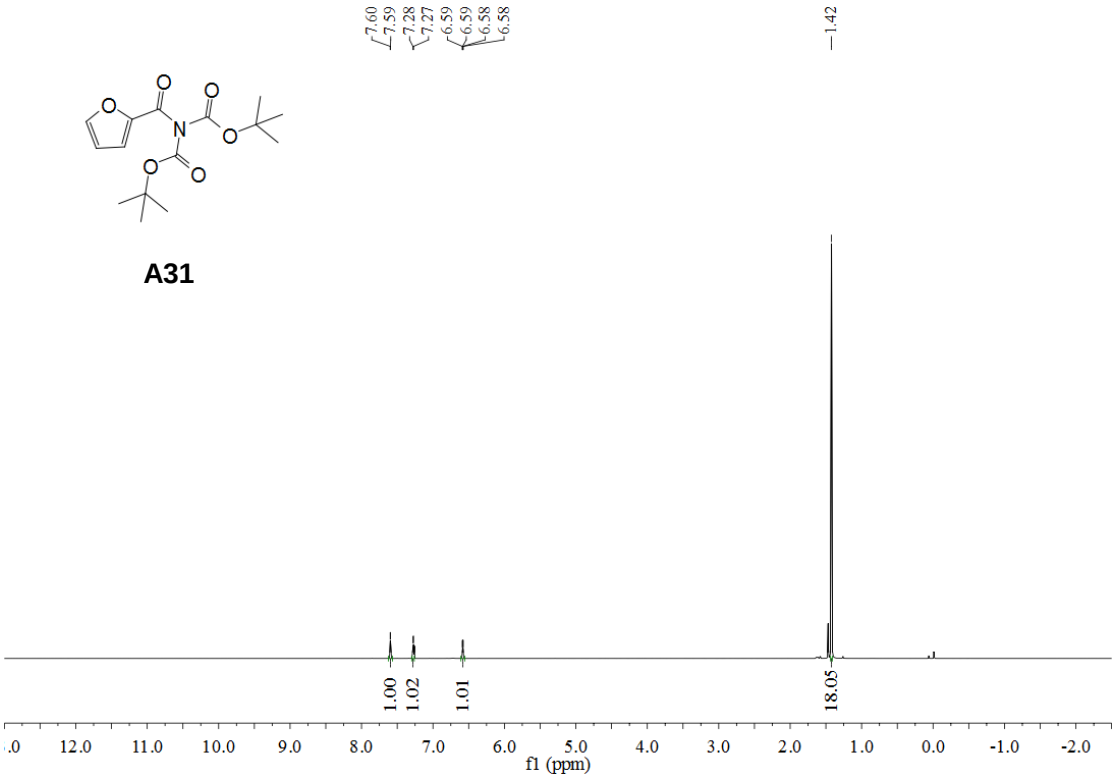
168.16
152.99
149.66
142.72
128.80
106.25
83.80
60.51
55.95
27.26
f1 (ppm)


7.92
7.90
7.87
7.85
1.42
4.00
4.03
36.07
f1 (ppm)

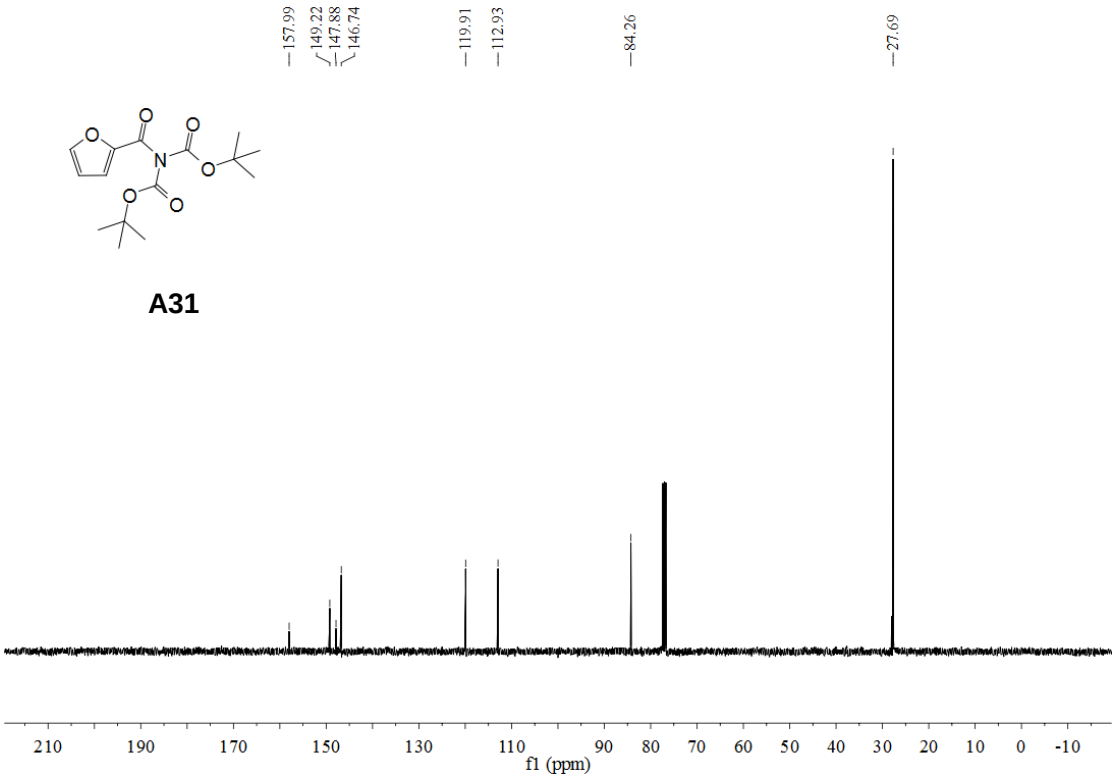
A30


194.58
168.66
149.63
140.39
137.89
130.02
128.88
84.90
27.62
f1 (ppm)

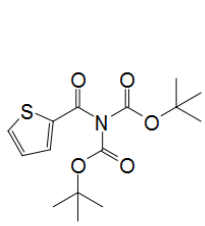
A30


7.60
7.59
7.28
7.27
6.59
6.59
6.58
6.58
1.42
1.00
1.02
1.01
18.05
f1 (ppm)

A31

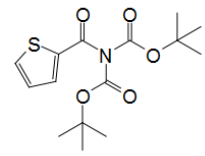

157.99
149.22
147.88
146.74
119.91
112.93
84.26
27.69
f1 (ppm)

A31



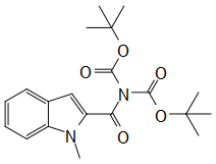
A32

7.64
7.64
7.63
7.62
7.57
7.57
7.56
7.56
7.04
7.03
7.02
7.01
1.27
1.00
1.00
1.02
18.06
f1 (ppm)



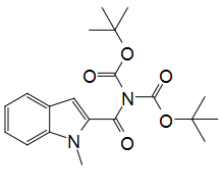
A32

162.13
149.13
138.46
135.21
134.03
128.14
84.10
27.55
f1 (ppm)



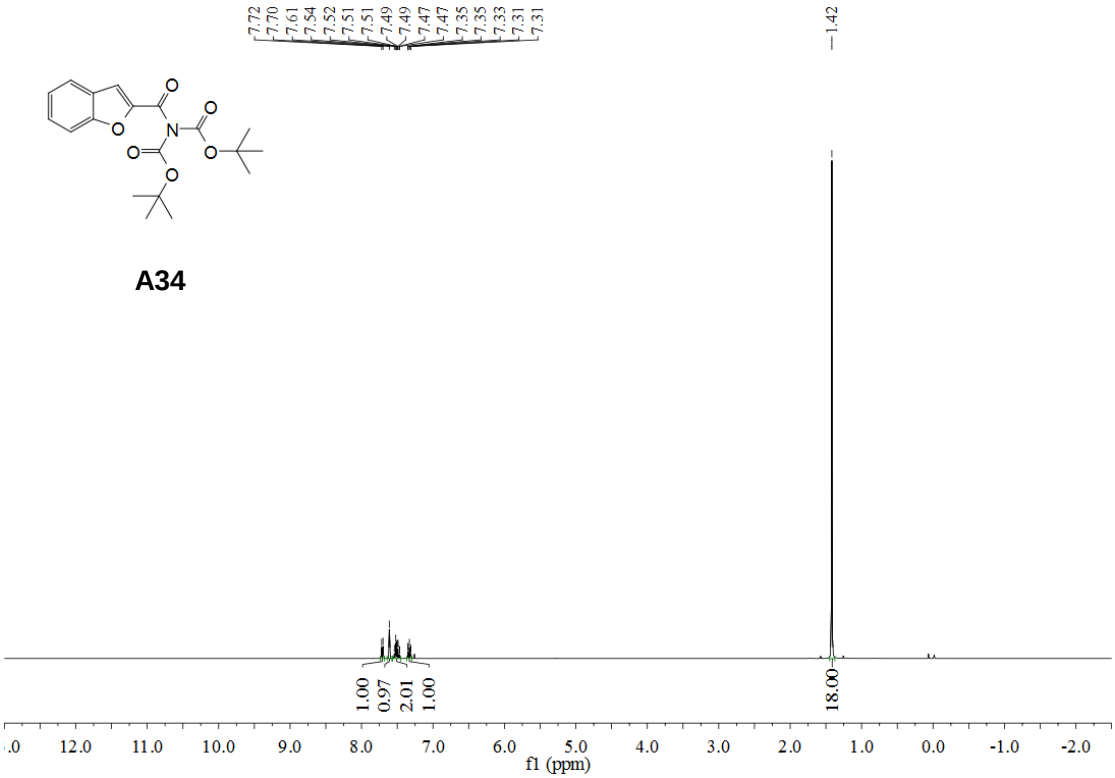
A33

7.69
7.67
7.41
7.40
7.20
7.19
7.18
7.17
7.16
7.15
4.03
1.39
1.00
2.00
2.00
3.00
18.04
f1 (ppm)

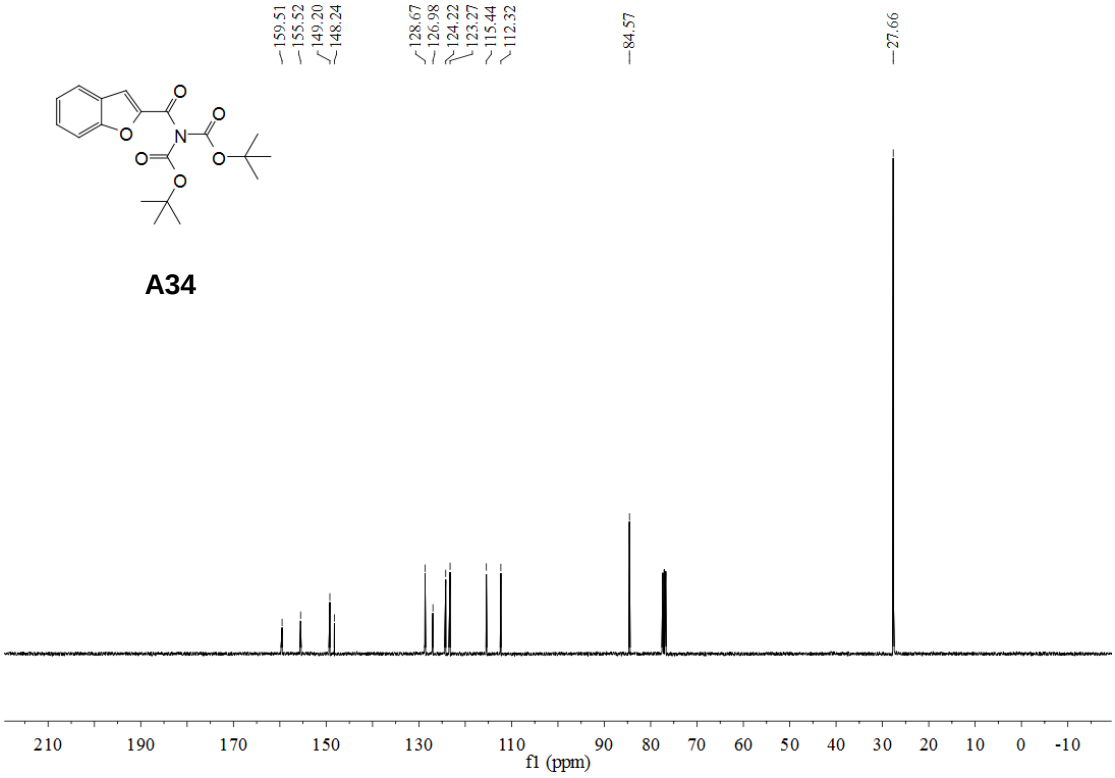


A33

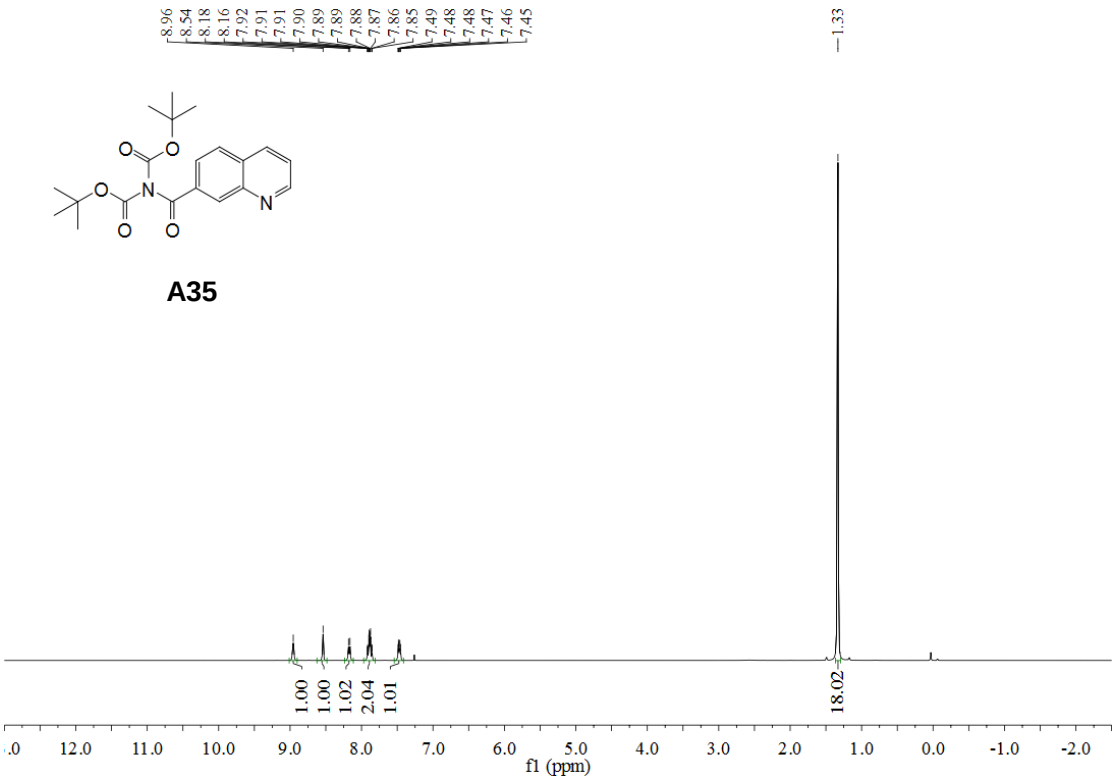
162.04
149.72
140.67
131.92
126.33
125.72
123.21
121.09
111.99
110.37
84.05
31.46
27.74
f1 (ppm)


7.72
7.70
7.61
7.54
7.52
7.51
7.51
7.49
7.49
7.47
7.47
7.35
7.35
7.33
7.31
7.31
1.42
1.00
0.97
2.01
1.00
18.00
f1 (ppm)

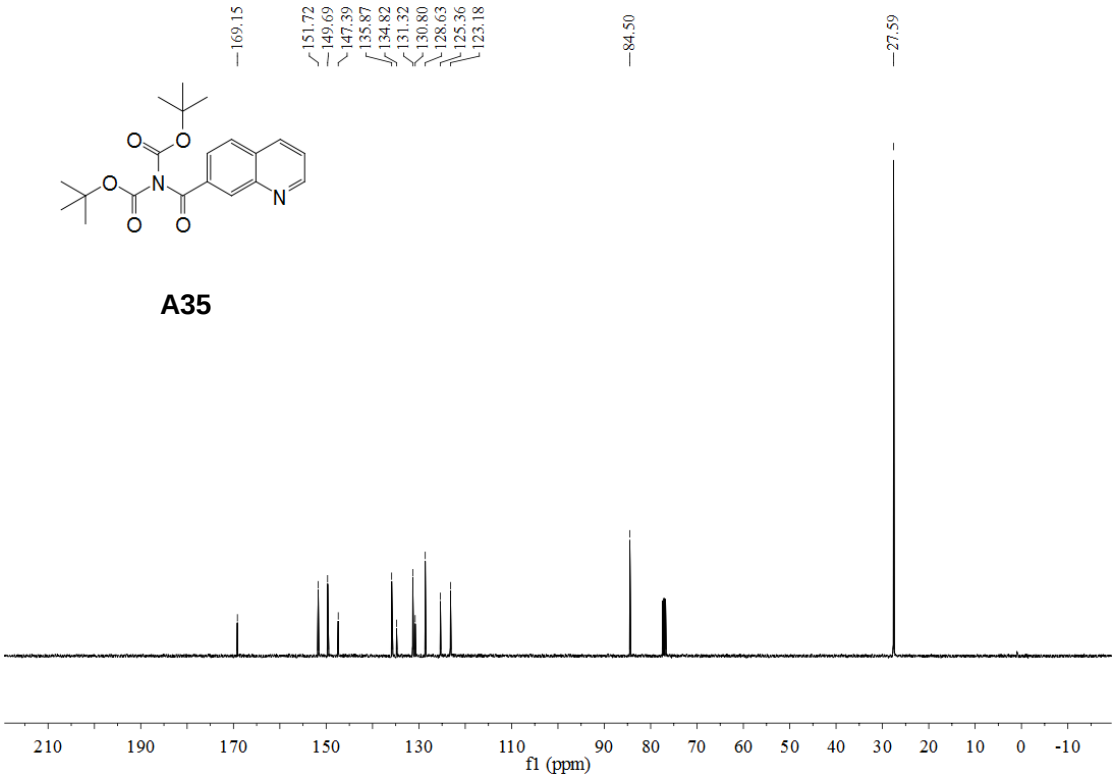
A34


159.51
155.52
149.20
148.24
128.67
126.98
124.22
123.27
115.44
112.32
84.57
27.66
f1 (ppm)

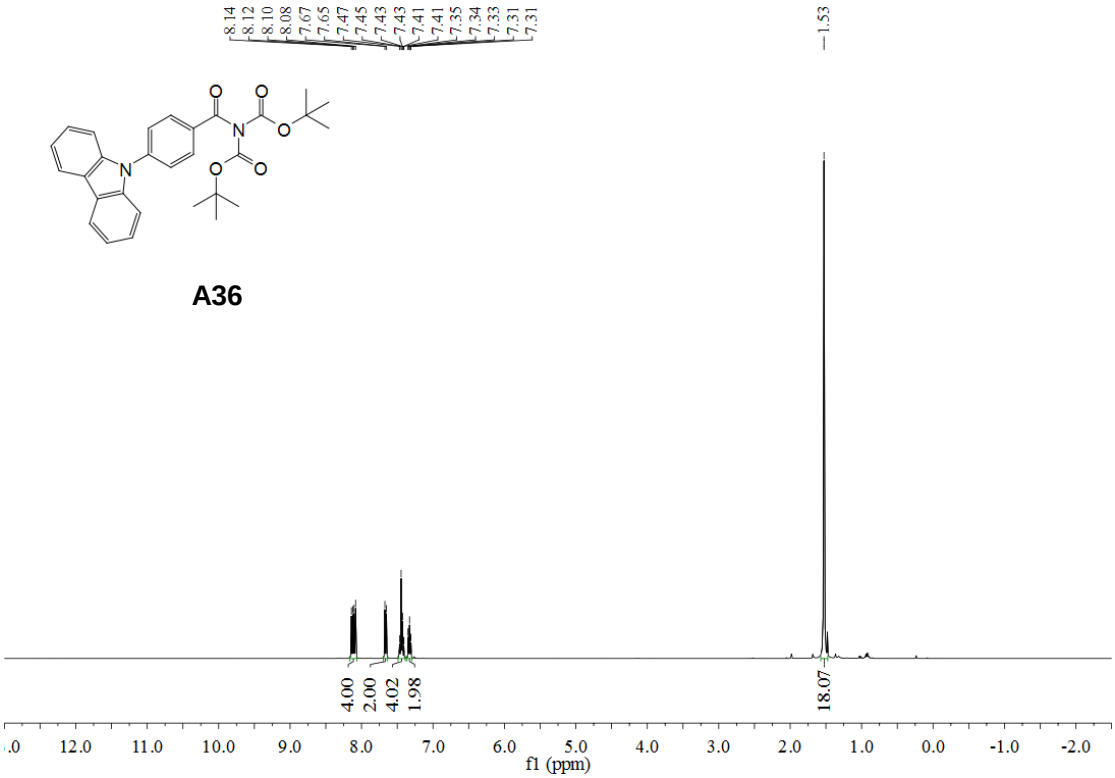
A34


8.96
8.54
8.18
8.16
7.92
7.91
7.91
7.90
7.89
7.89
7.88
7.87
7.86
7.85
7.49
7.48
7.48
7.47
7.46
7.45
1.33
1.00
1.00
1.02
2.04
1.01
18.02
f1 (ppm)

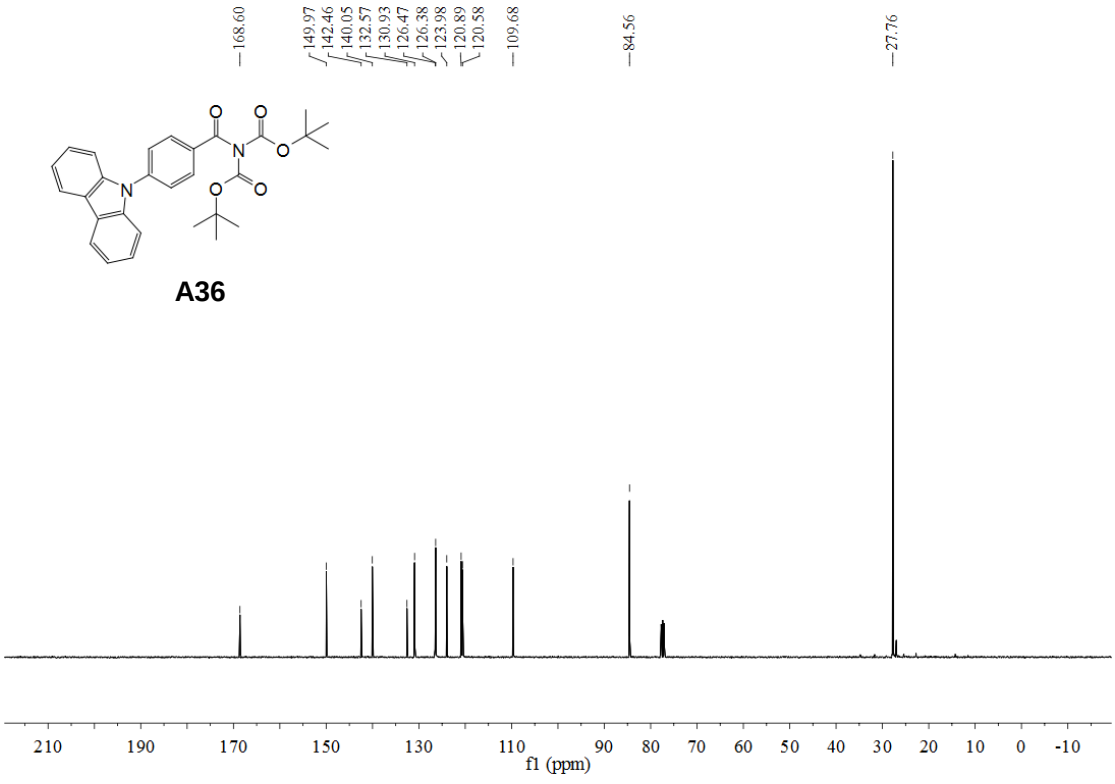
A35


169.15
151.72
149.69
147.39
135.87
134.82
131.32
130.80
128.63
125.36
123.18
84.50
27.59
f1 (ppm)

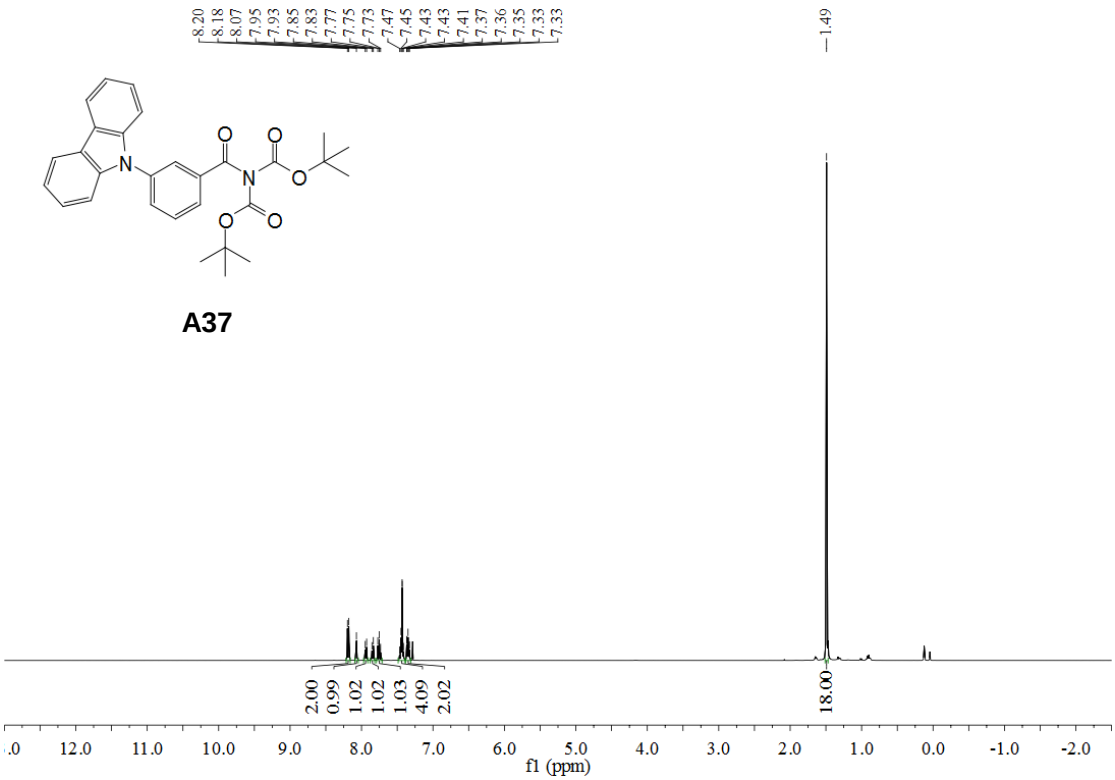
A35


8.14
8.12
8.10
8.08
7.67
7.65
7.47
7.45
7.43
7.43
7.41
7.41
7.35
7.34
7.33
7.31
7.31
1.53
4.00
2.00
4.02
1.98
18.07
f1 (ppm)

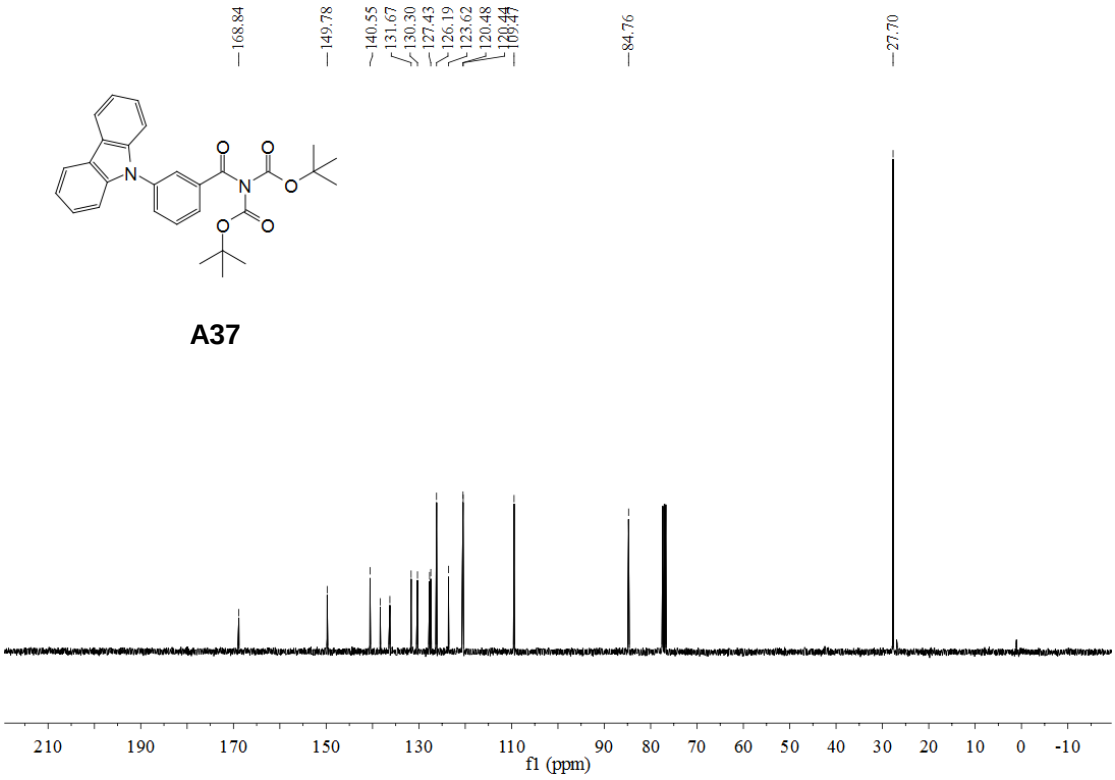
A36


168.60
149.97
142.46
140.05
132.57
130.93
126.47
126.38
123.98
120.89
120.58
109.68
84.56
27.76
f1 (ppm)

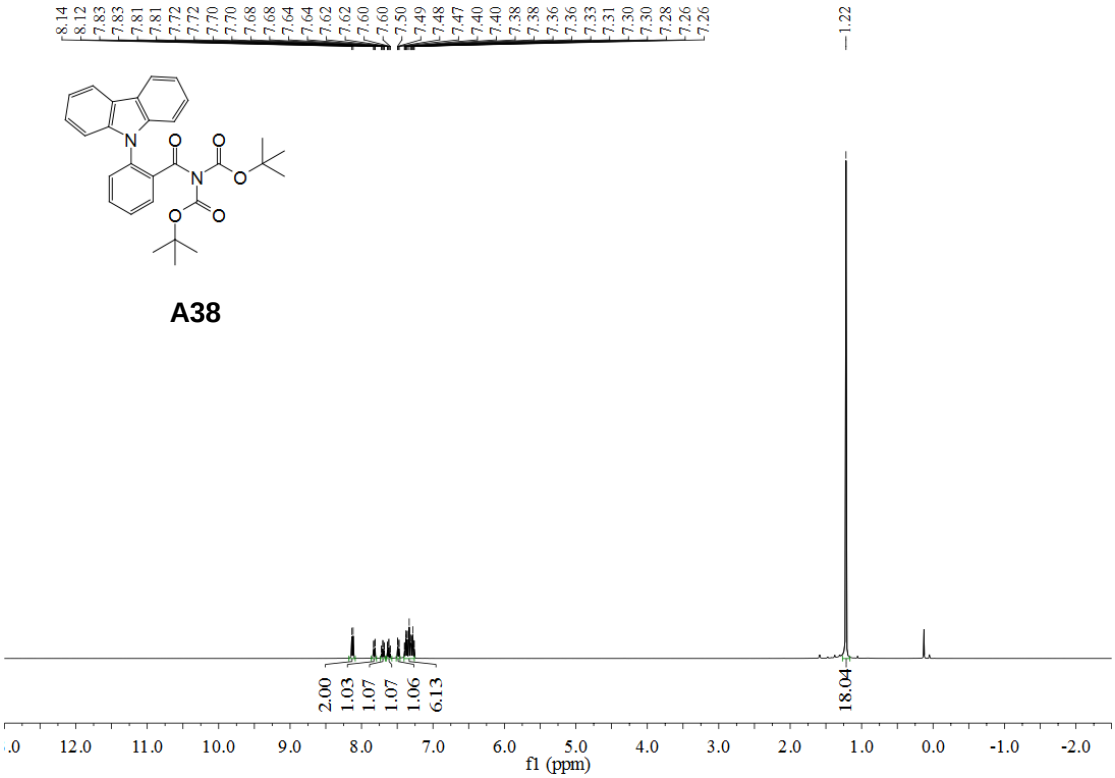
A36


8.20
8.18
8.07
7.95
7.93
7.85
7.83
7.77
7.75
7.73
7.47
7.45
7.43
7.43
7.41
7.37
7.36
7.35
7.33
7.33
1.49
2.00
0.99
1.02
1.02
1.03
4.09
2.02
18.00
f1 (ppm)

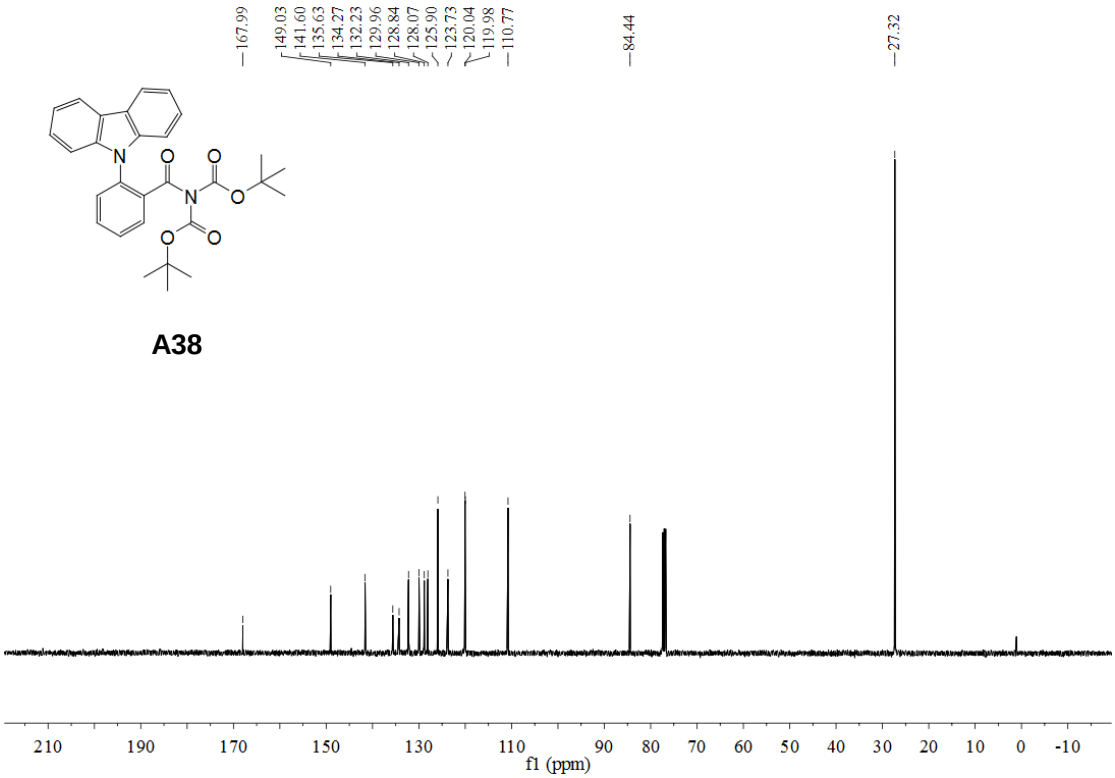
A37


168.84
149.78
140.55
131.67
130.30
127.43
126.19
123.62
120.48
120.44
109.47
84.76
27.70
f1 (ppm)

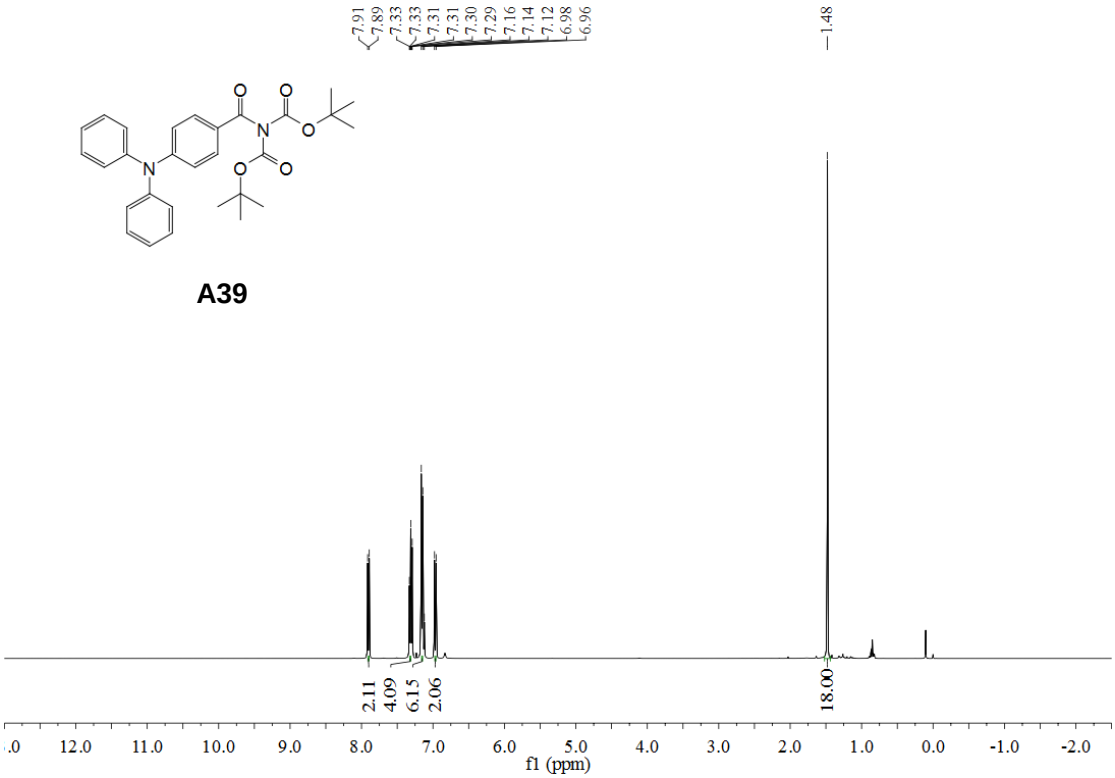
A37


8.14
8.12
7.83
7.83
7.81
7.81
7.72
7.72
7.70
7.70
7.68
7.68
7.64
7.64
7.62
7.62
7.60
7.60
7.50
7.49
7.48
7.47
7.40
7.40
7.38
7.38
7.36
7.36
7.33
7.31
7.30
7.30
7.28
7.26
7.26
1.22
2.00
1.03
1.07
1.07
1.06
6.13
18.04
f1 (ppm)

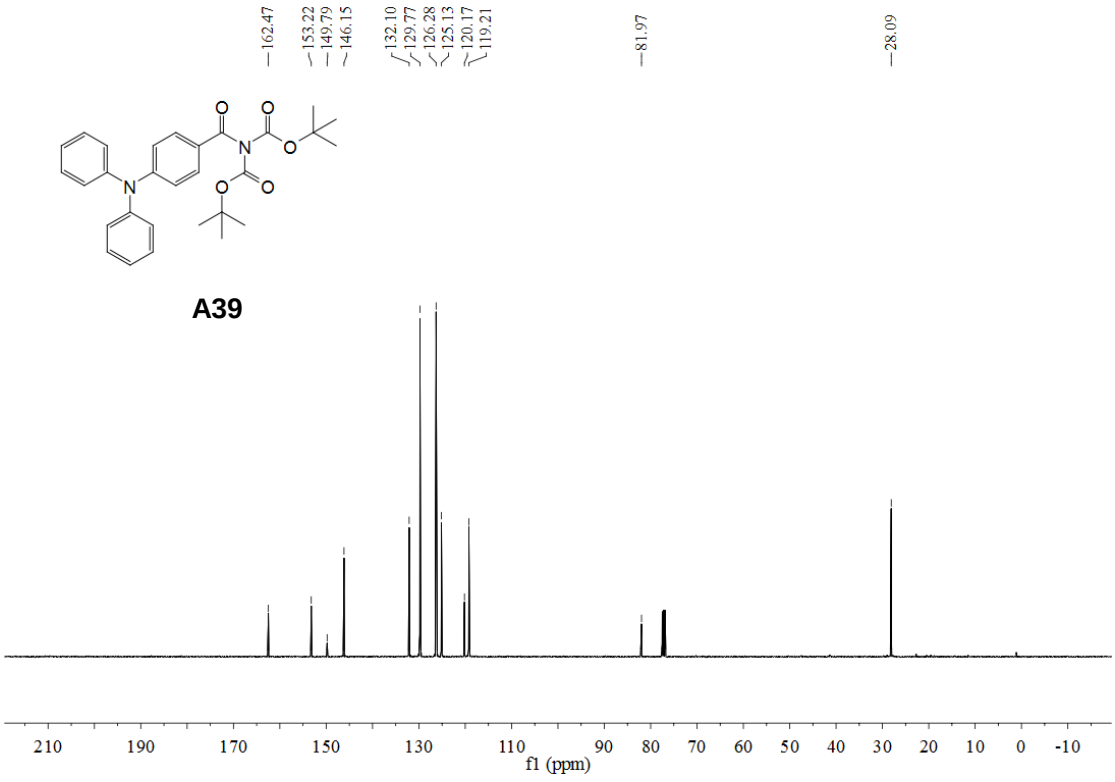
A38


167.99
149.03
141.60
135.63
134.27
132.23
129.96
128.84
128.07
125.90
123.73
120.04
119.98
110.77
84.44
27.32
f1 (ppm)

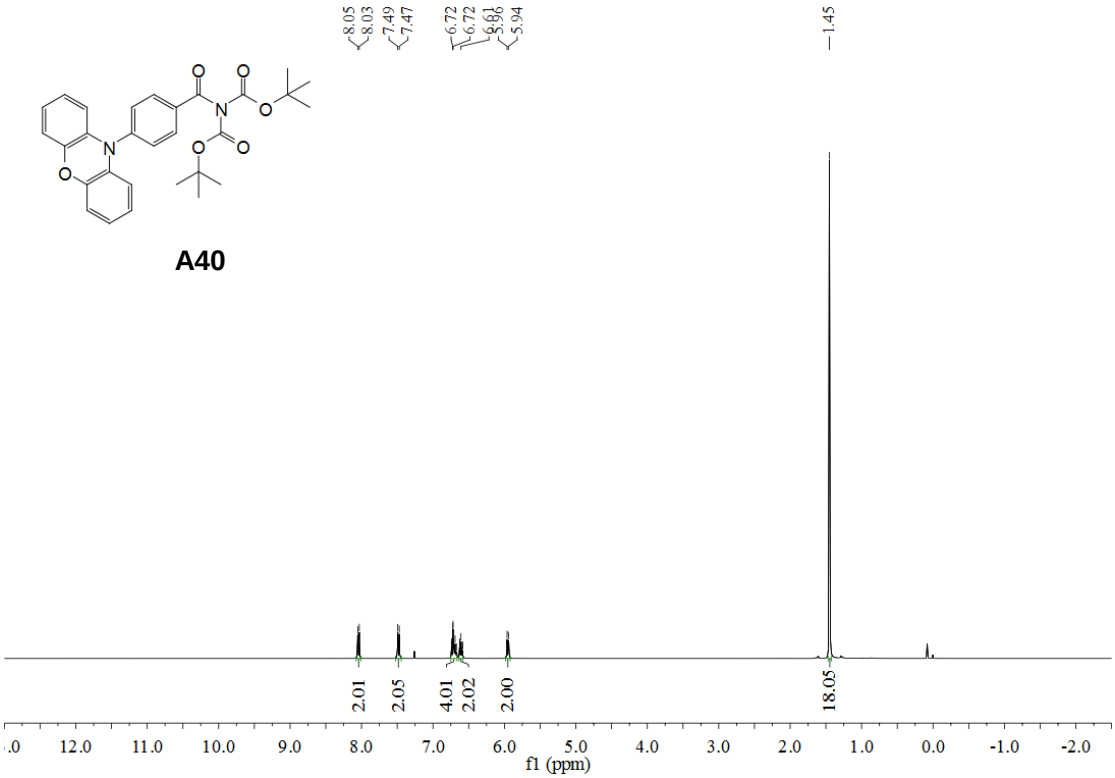
A38


7.91
7.89
7.33
7.33
7.31
7.31
7.30
7.29
7.16
7.14
7.12
6.98
6.96
1.48
2.11
4.09
6.15
2.06
18.00
f1 (ppm)

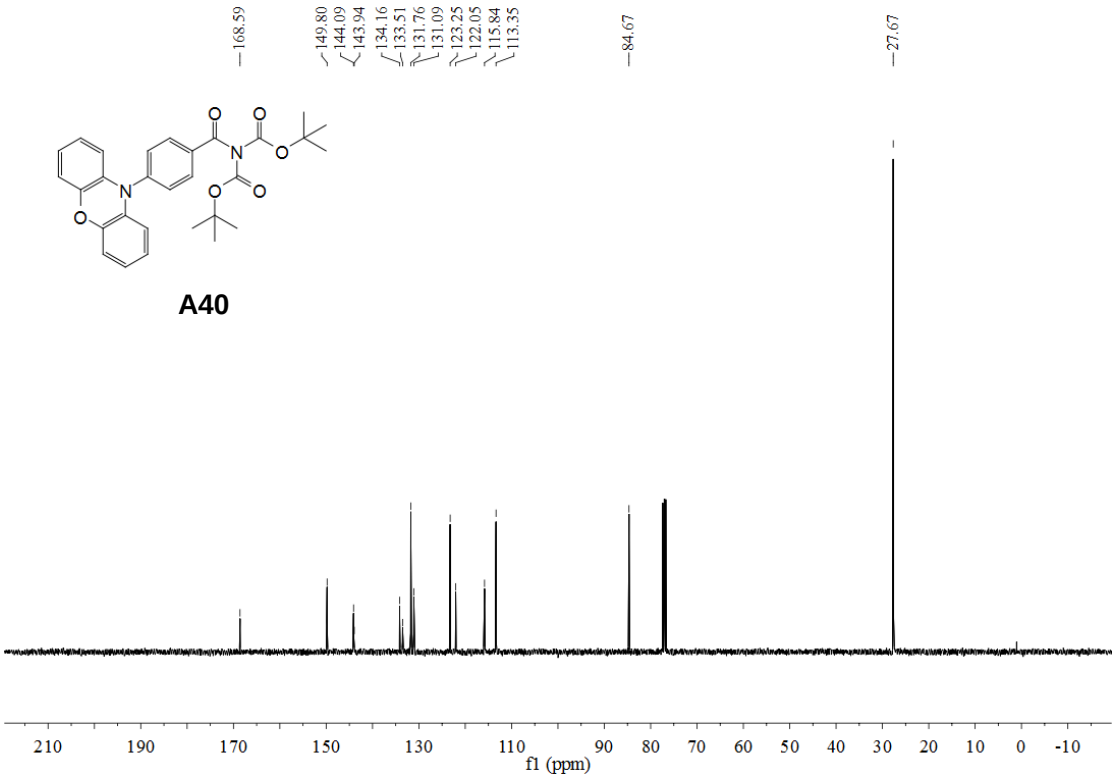
A39


162.47
153.22
149.79
146.15
132.10
129.77
126.28
125.13
120.17
119.21
81.97
28.09
f1 (ppm)

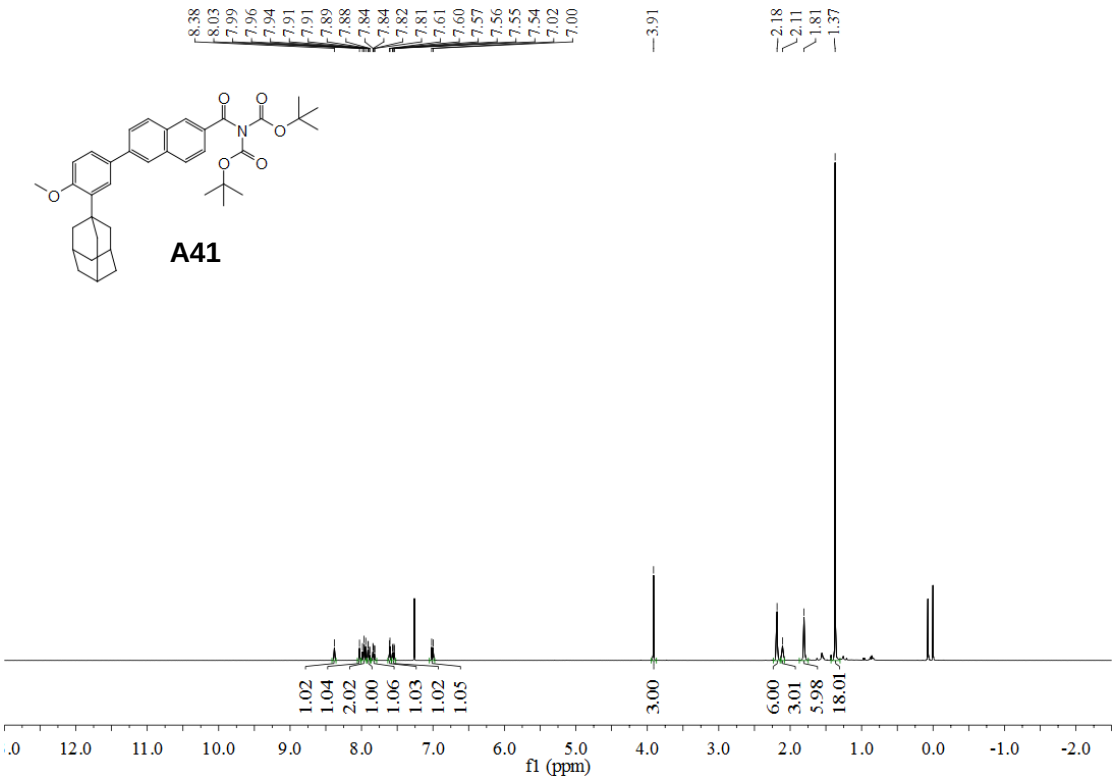
A39

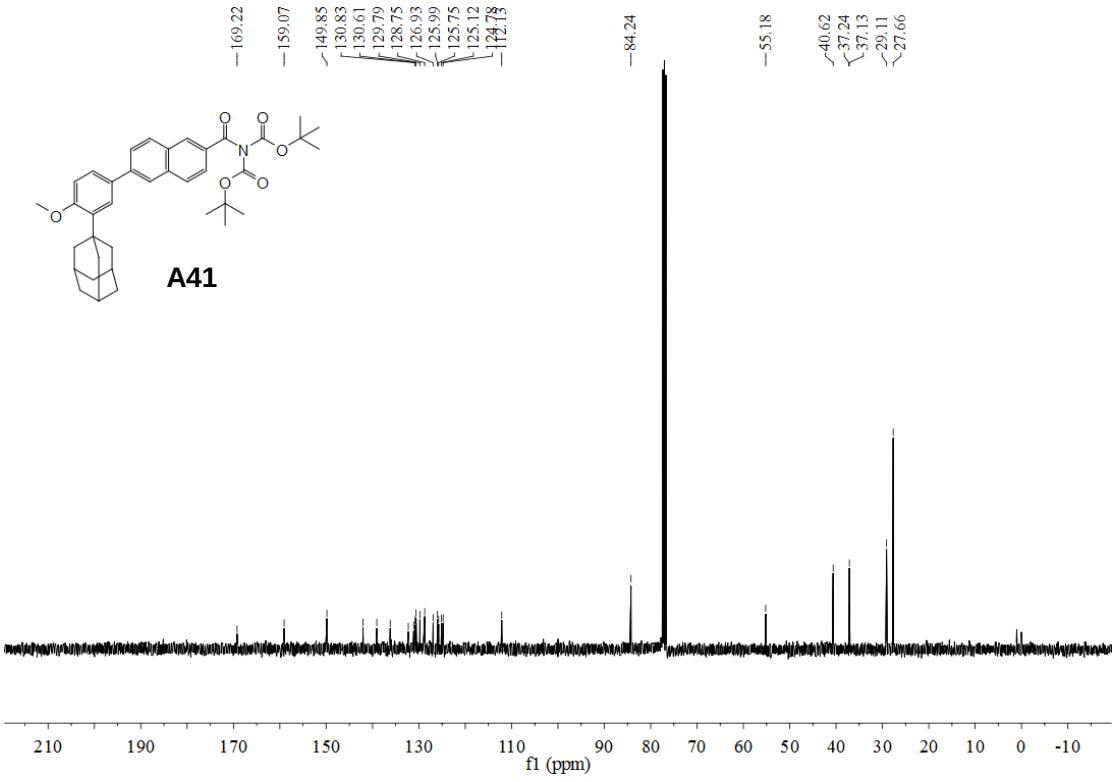

8.05
8.03
7.49
7.47
6.72
6.72
6.61
5.96
5.94
1.45
2.01
2.05
4.01
2.02
2.00
18.05
f1 (ppm)

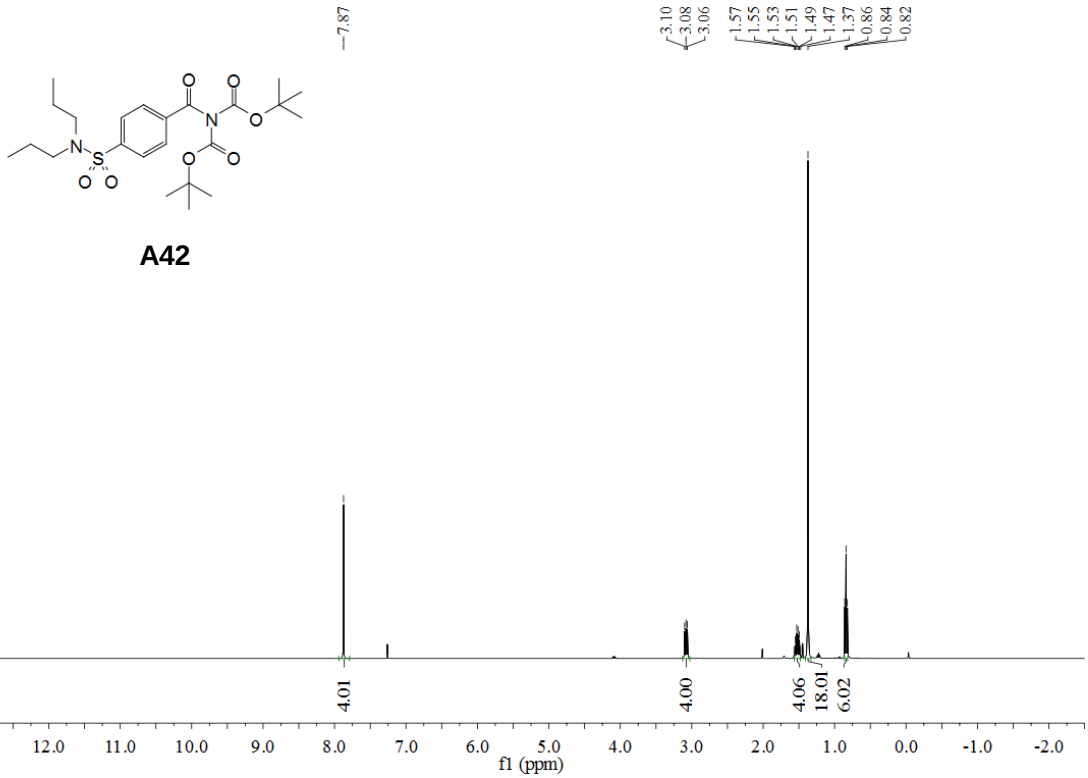
A40


168.59
149.80
144.09
143.94
134.16
133.51
131.76
131.09
123.25
122.05
115.84
113.35
84.67
27.67
f1 (ppm)

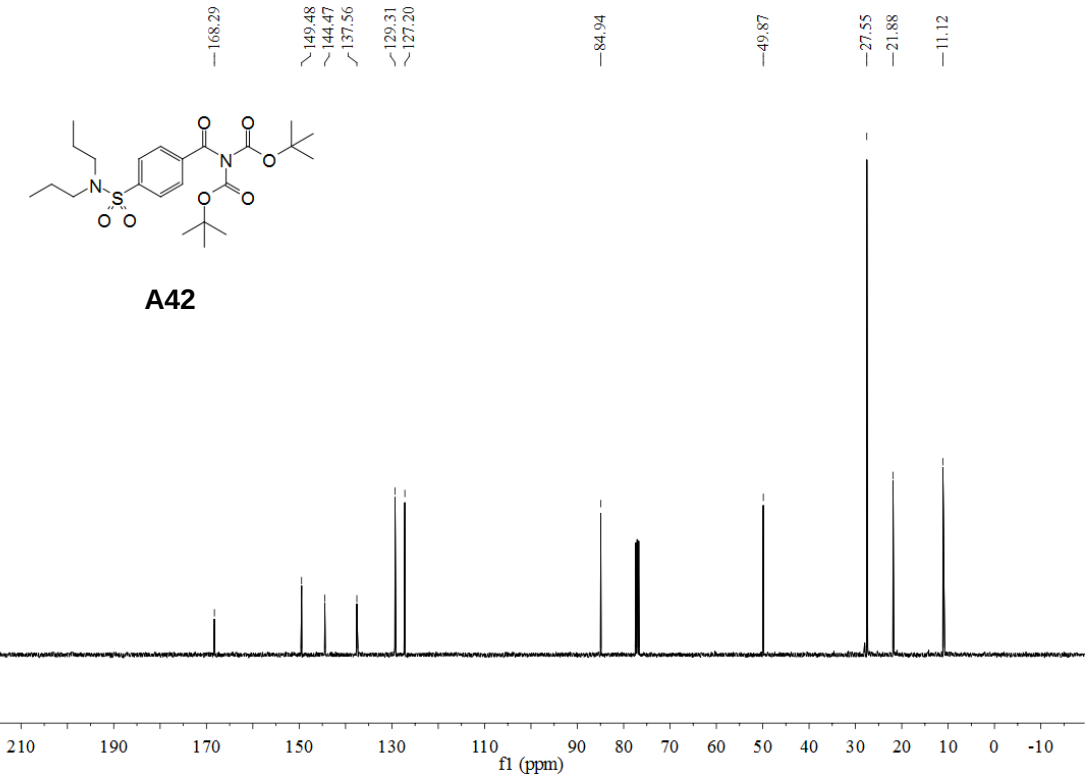
A40


8.38
8.03
7.99
7.96
7.94
7.91
7.91
7.89
7.88
7.84
7.84
7.82
7.81
7.61
7.60
7.57
7.56
7.55
7.54
7.02
7.00
3.91
2.18
2.11
1.81
1.37
A41
1.02
1.04
2.02
1.00
1.06
1.03
1.02
1.05
3.00
6.00
3.01
5.98
18.01
f1 (ppm)

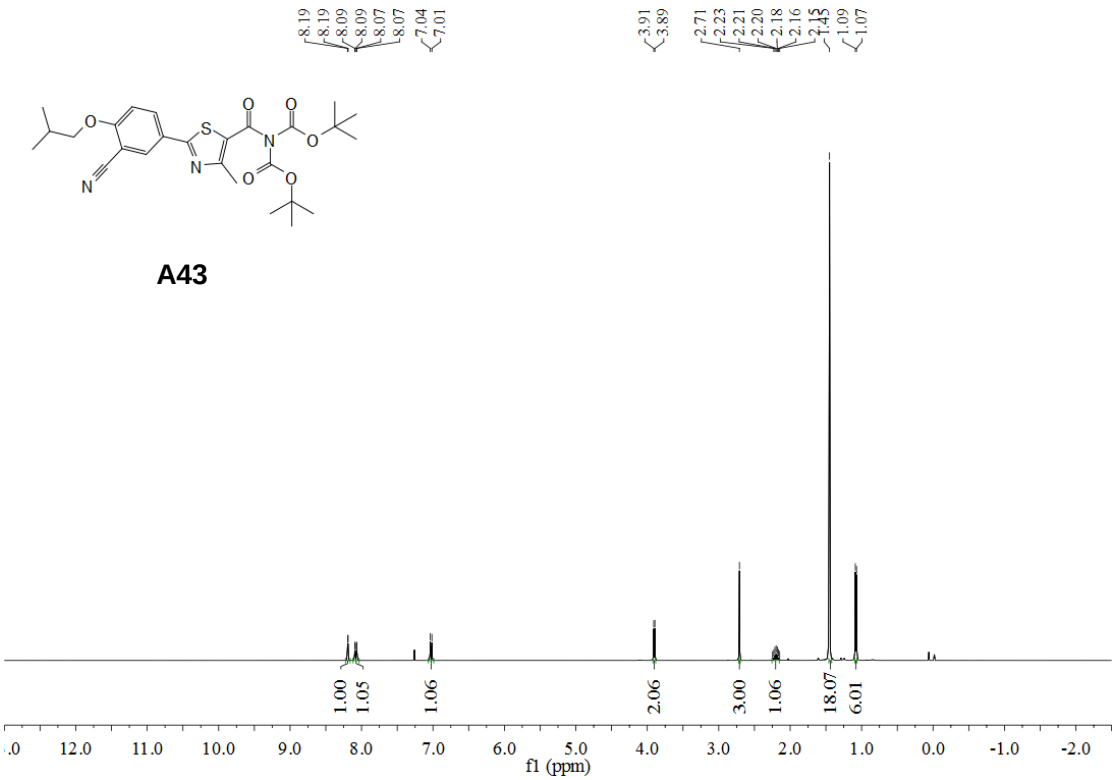

169.22
159.07
149.85
130.83
130.61
129.79
128.75
126.93
125.99
125.75
125.12
84.24
55.18
40.62
37.24
37.13
29.11
27.66
A41
f1 (ppm)


7.87
3.10
3.08
3.06
1.57
1.55
1.53
1.51
1.49
1.47
1.37
0.86
0.84
0.82
4.01
4.00
4.06
18.01
6.02
f1 (ppm)

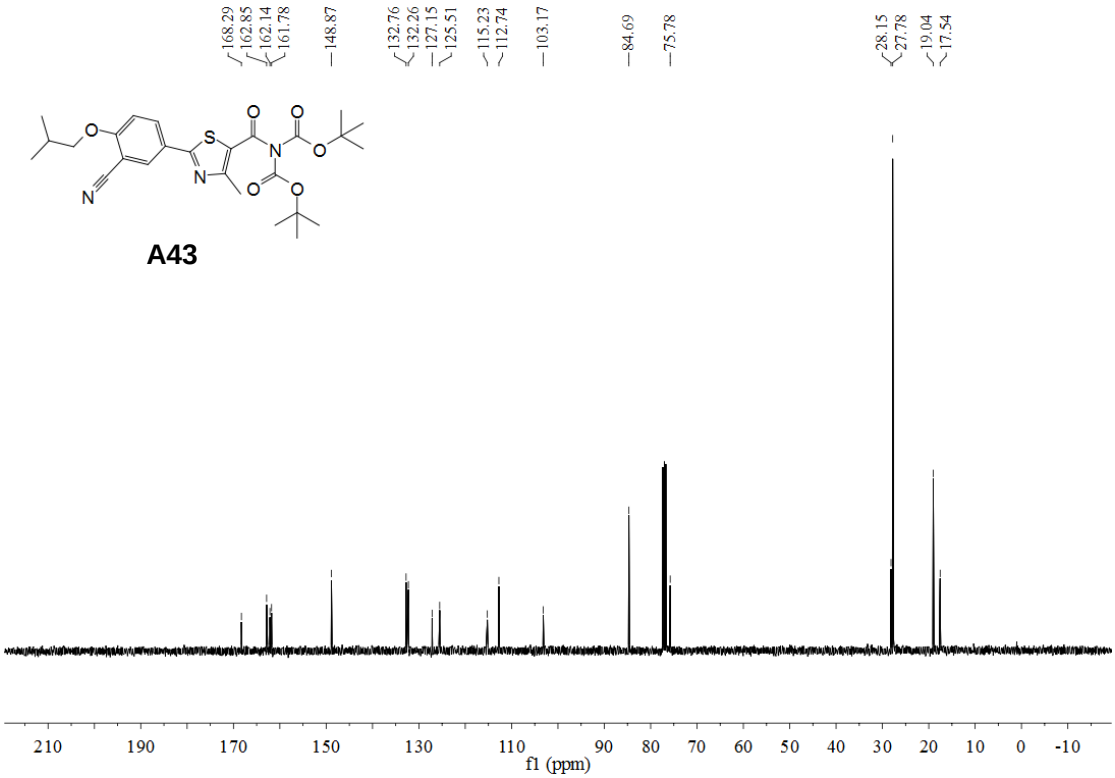
A42


168.29
149.48
144.47
137.56
129.31
127.20
84.94
49.87
27.55
21.88
11.12
f1 (ppm)

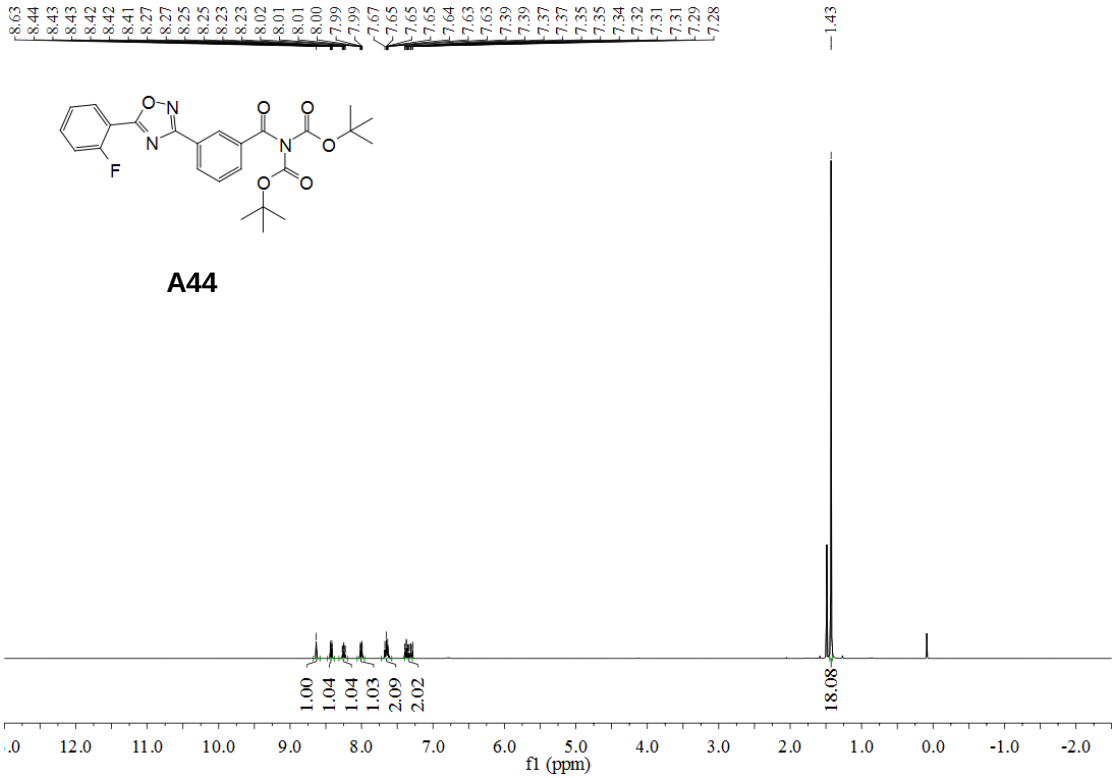
A42


8.19
8.19
8.09
8.09
8.07
8.07
7.04
7.01
3.91
3.89
2.71
2.23
2.21
2.20
2.18
2.16
1.45
1.09
1.07
1.00
1.05
1.06
2.06
3.00
1.06
18.07
6.01
f1 (ppm)

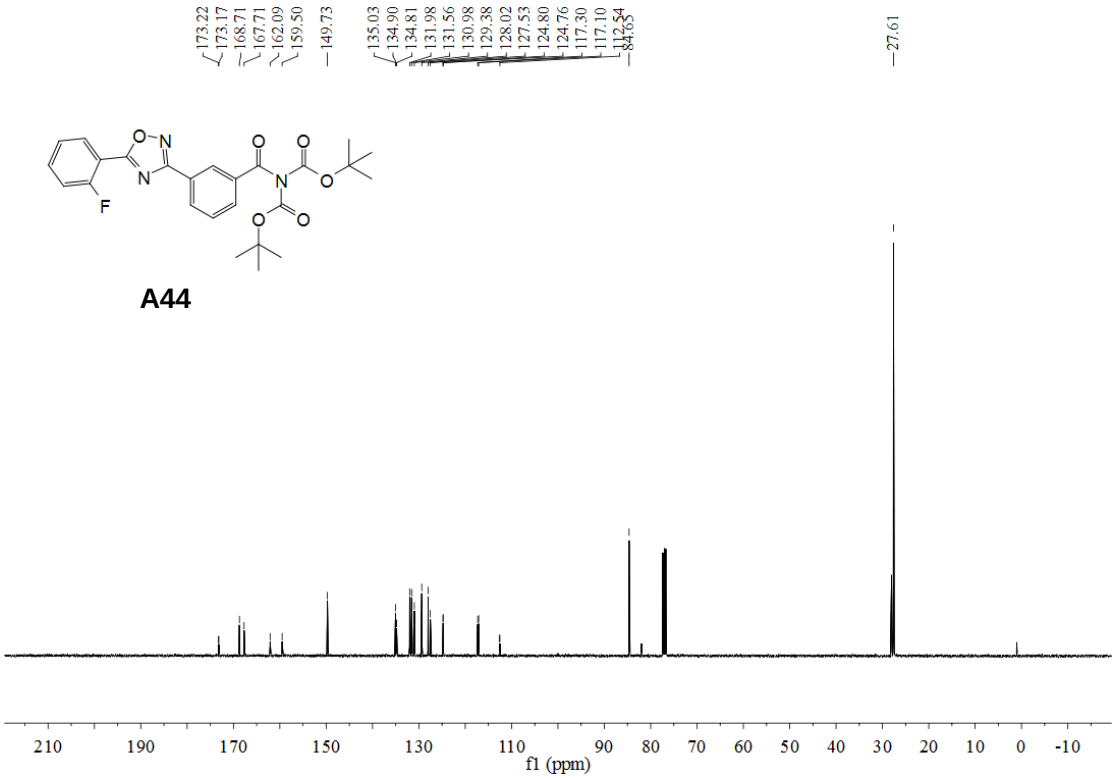
A43


168.29
162.85
162.14
161.78
148.87
132.76
132.26
127.15
125.51
115.23
112.74
103.17
84.69
75.78
28.15
27.78
19.04
17.54
f1 (ppm)

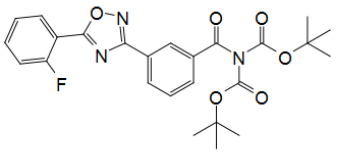
A43


8.63
8.44
8.43
8.43
8.42
8.42
8.41
8.27
8.27
8.25
8.25
8.23
8.23
8.02
8.01
8.01
8.00
7.99
7.99
7.67
7.65
7.65
7.65
7.64
7.63
7.63
7.39
7.39
7.37
7.37
7.35
7.35
7.34
7.32
7.31
7.31
7.29
7.28
1.43
1.00
1.04
1.04
1.03
2.09
2.02
18.08
f1 (ppm)

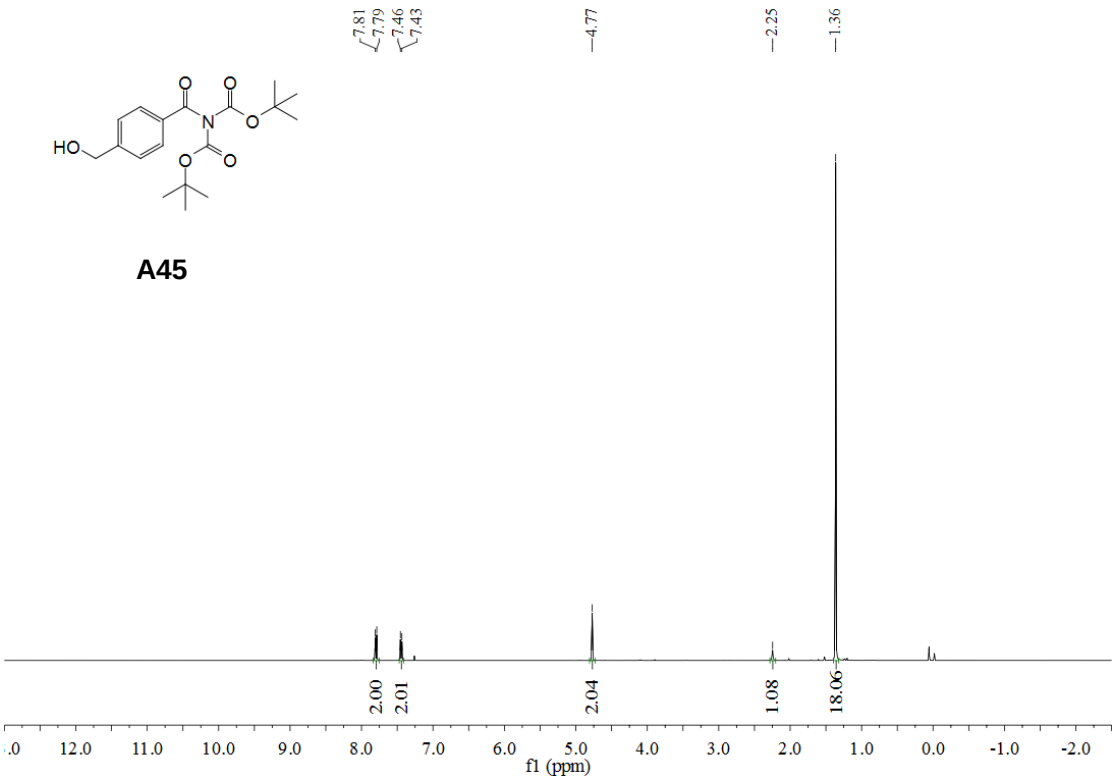
A44


173.22
173.17
168.71
167.71
162.09
159.50
149.73
135.03
134.90
134.81
131.98
131.56
130.98
129.38
128.02
127.53
124.80
124.76
117.30
117.10
112.54
84.65
27.61
f1 (ppm)

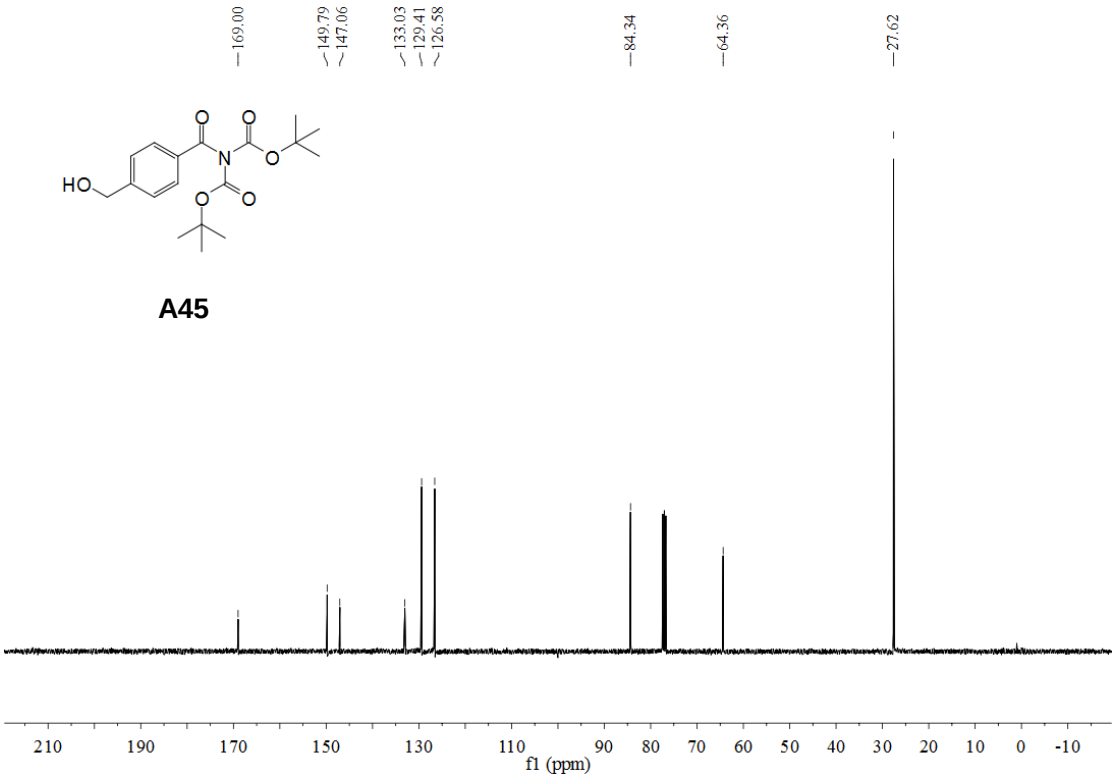
A44



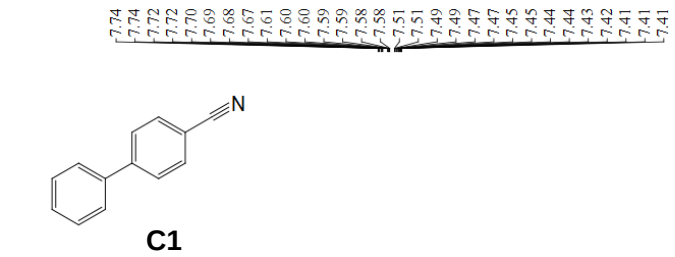
A44


7.81
7.79
7.46
7.43
4.77
2.25
1.36
HO
O
N
O
O
O
O
2.00
2.01
2.04
1.08
18.06
f1 (ppm)

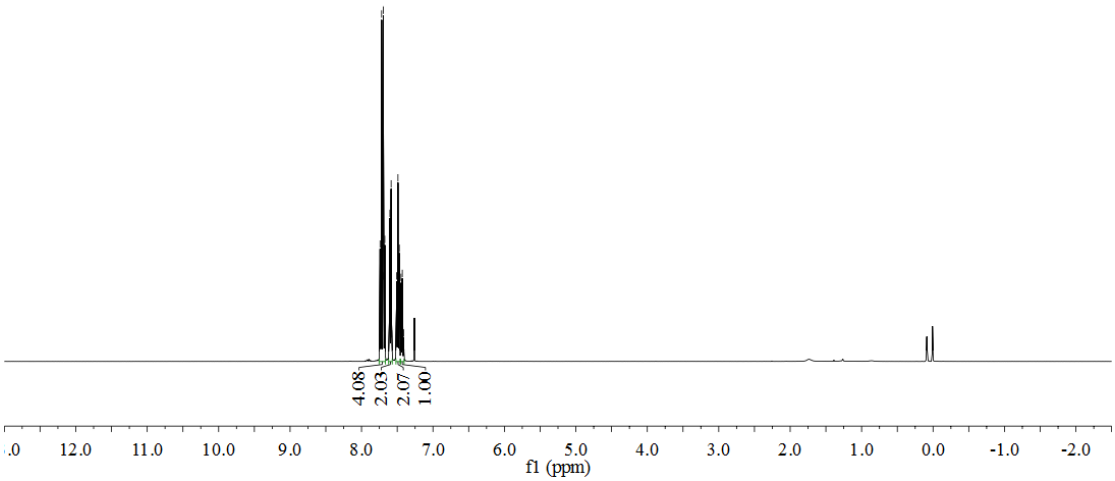
A45

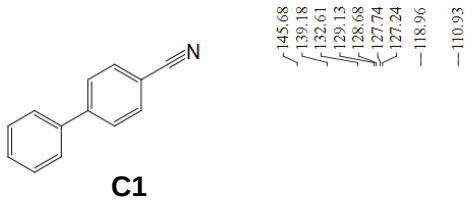

169.00
149.79
147.06
133.03
129.41
126.58
84.34
64.36
27.62
HO
O
N
O
O
O
O
f1 (ppm)

A45

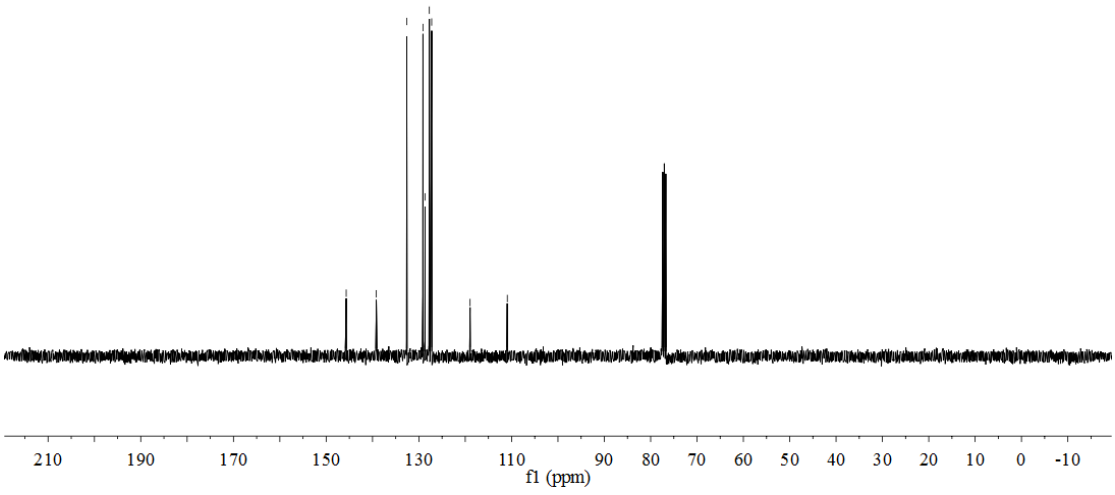

7.74
7.74
7.72
7.72
7.70
7.69
7.68
7.67
7.61
7.60
7.60
7.59
7.59
7.58
7.58
7.51
7.51
7.49
7.49
7.47
7.47
7.45
7.45
7.44
7.44
7.43
7.42
7.41
7.41
7.41
N

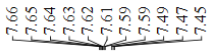
C1

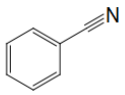

4.08
2.03
2.07
1.00
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)


145.68
139.18
132.61
129.13
128.68
127.74
127.24
118.96
110.93
N

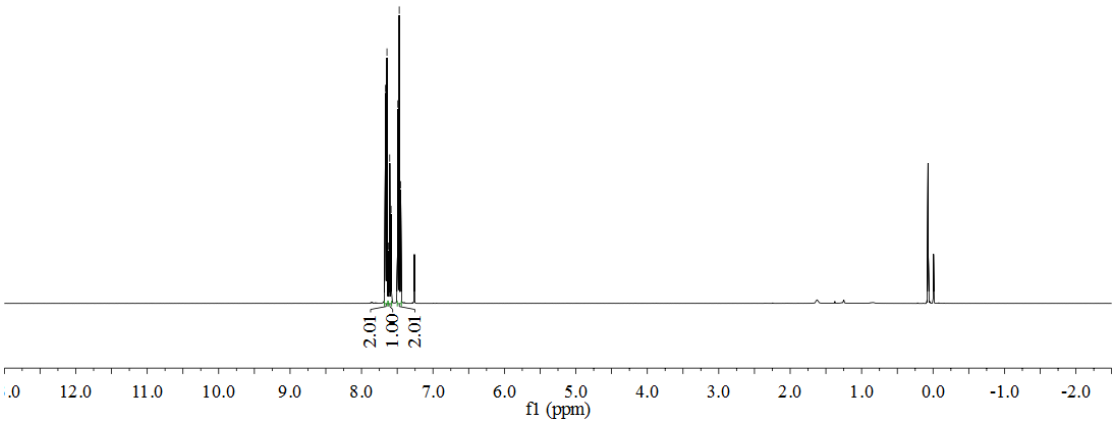
C1

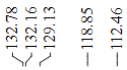

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

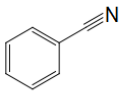

7.66
7.65
7.64
7.63
7.62
7.61
7.59
7.59
7.49
7.47
7.45


N

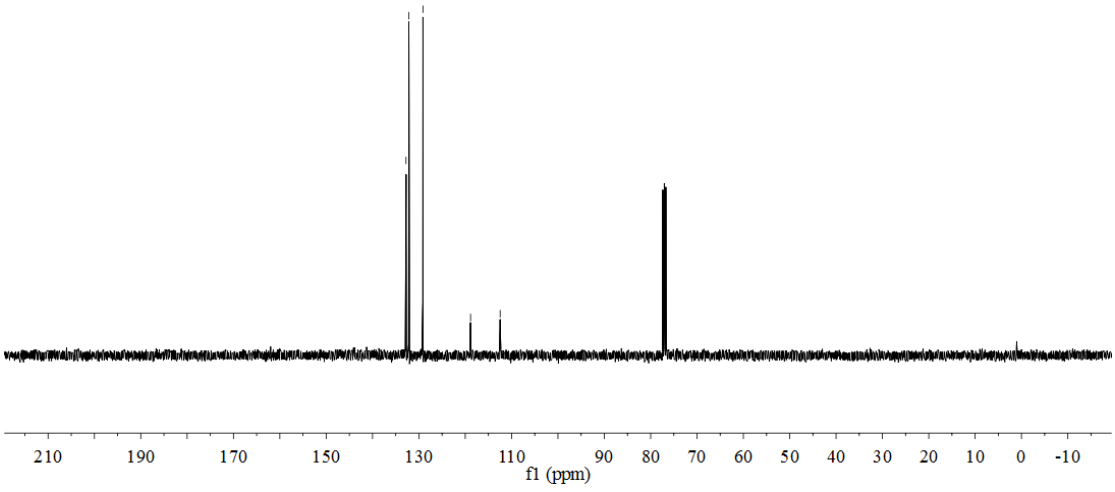
C2

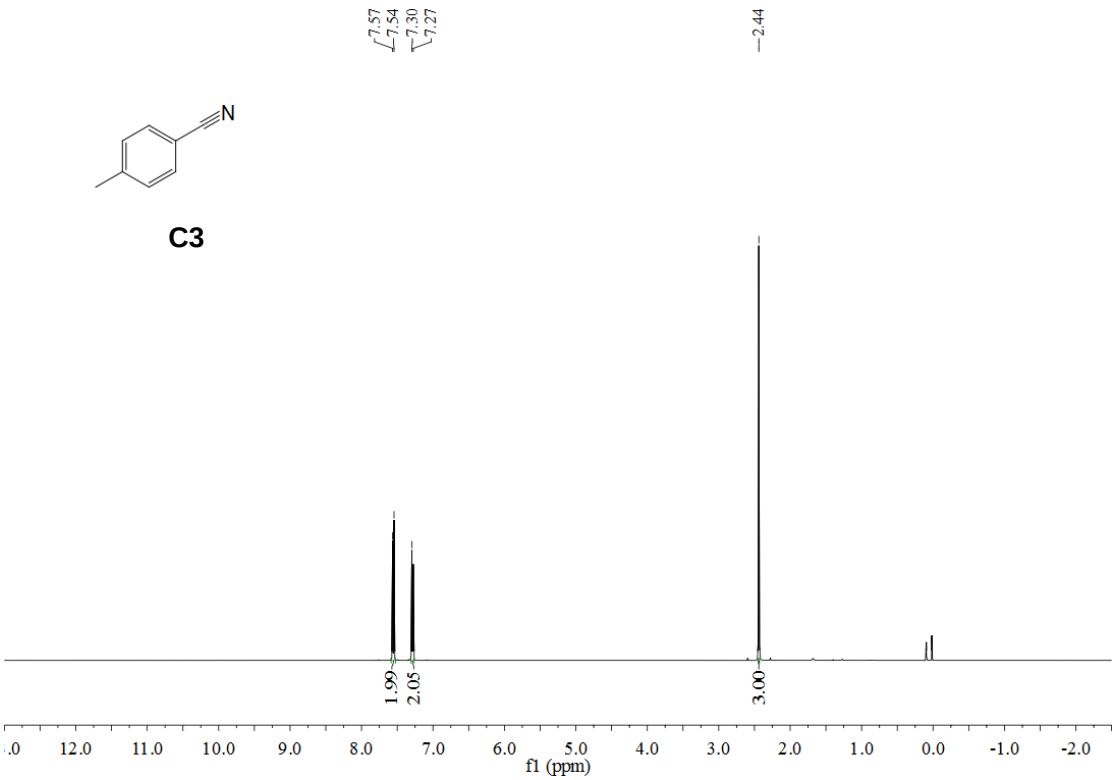

2.01
1.00
2.01
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

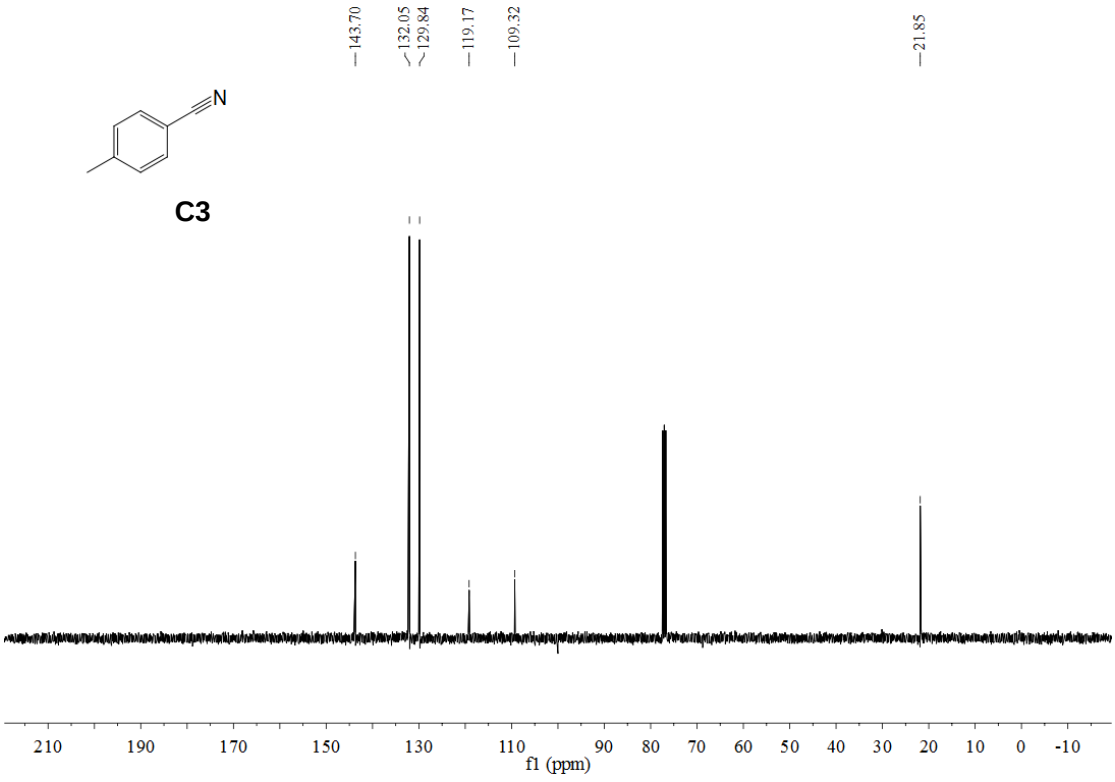

132.78
132.16
129.13
118.85
112.46

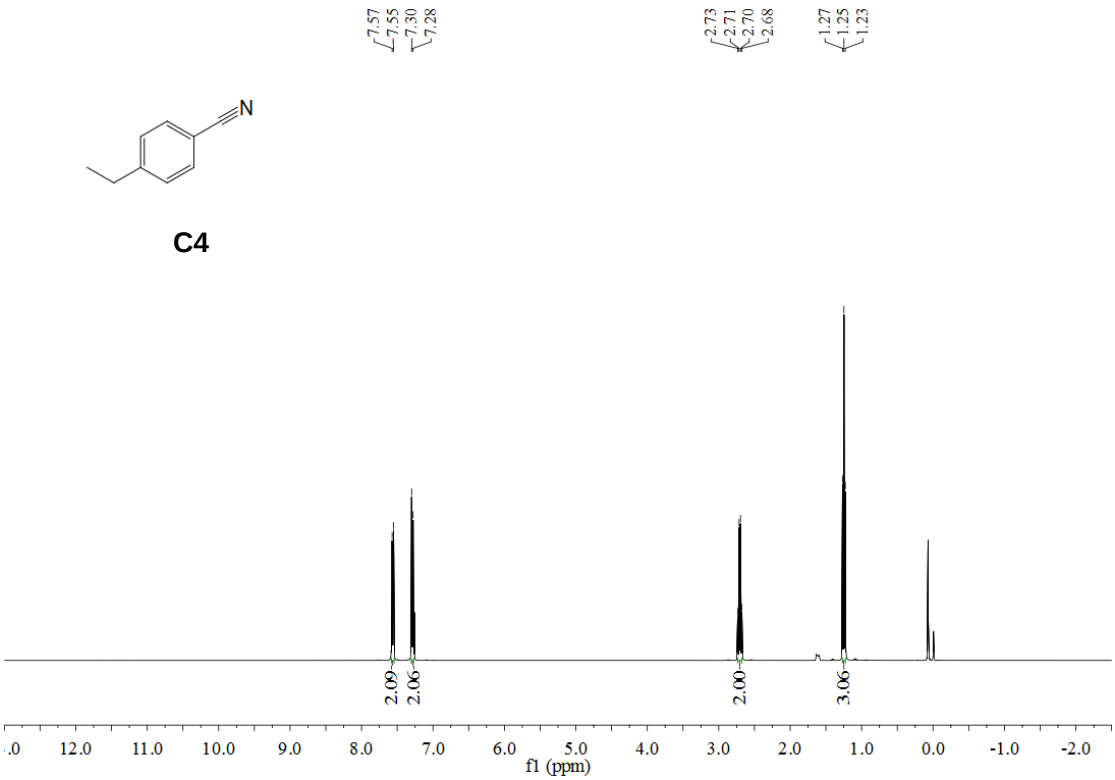

N

C2

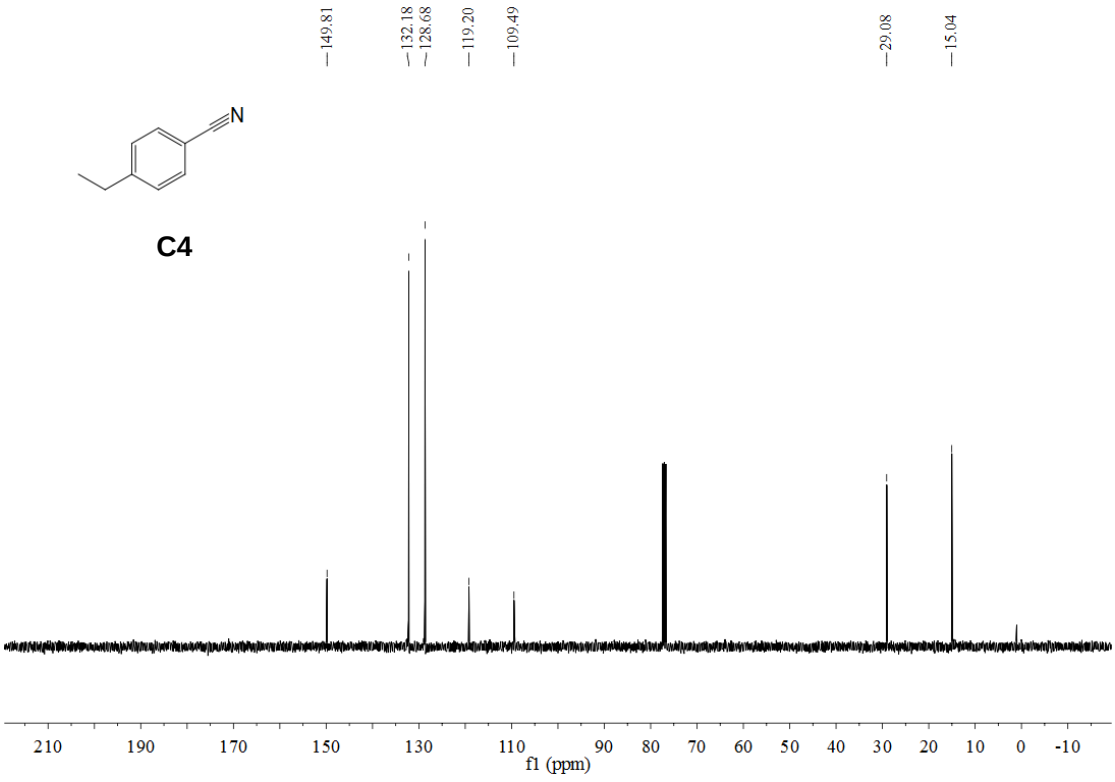

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.57
7.54
7.30
7.27
2.44
N
C3
1.99
2.05
3.00
f1 (ppm)

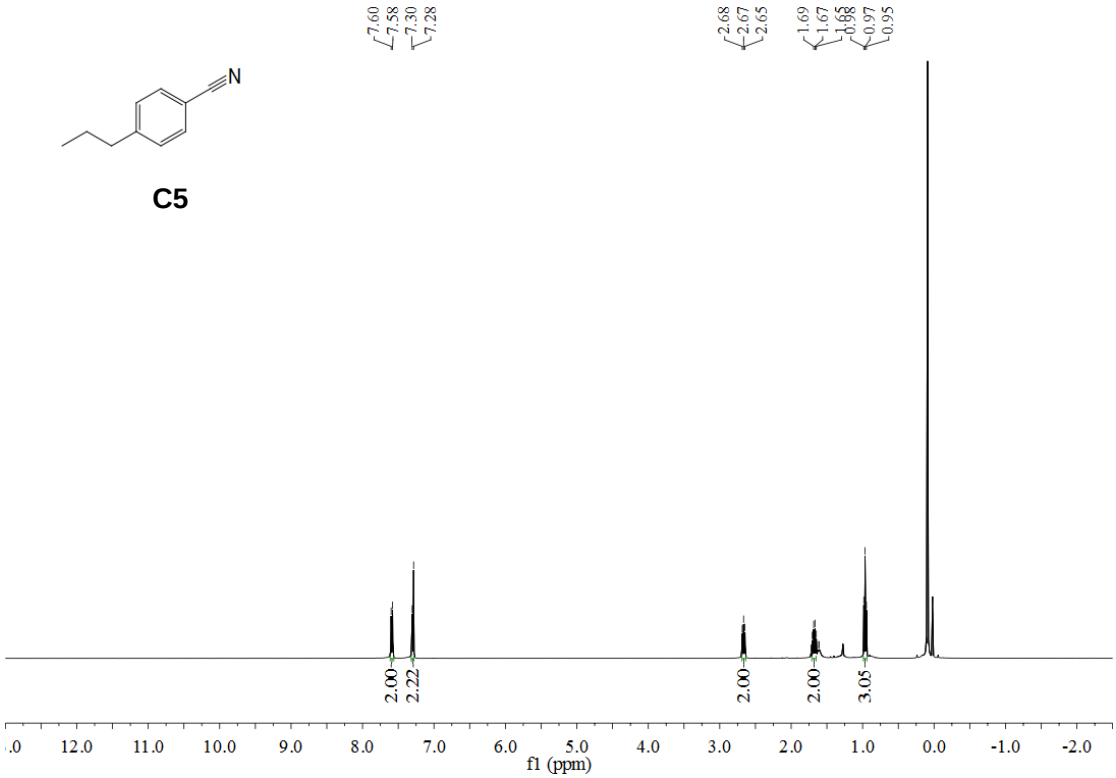

143.70
132.05
129.84
119.17
109.32
21.85
N
C3
f1 (ppm)


7.57
7.55
7.30
7.28
2.73
2.71
2.70
2.68
1.27
1.25
1.23
N
2.09
2.06
2.00
3.06
f1 (ppm)

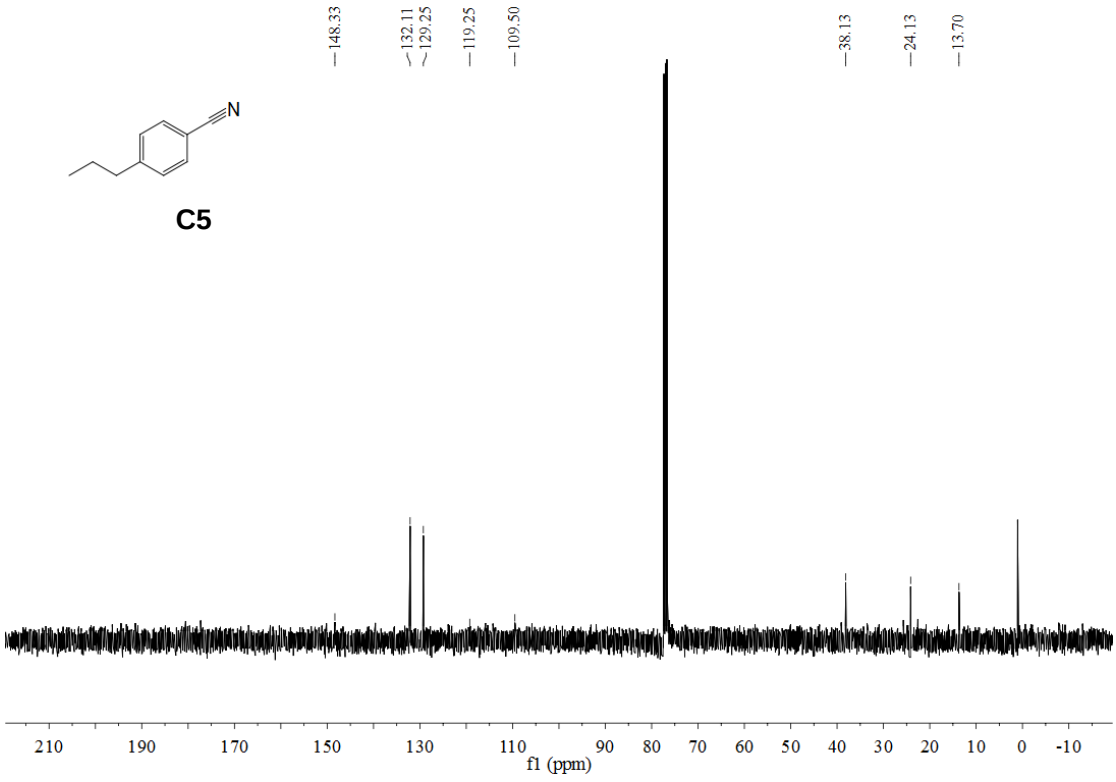
C4


149.81
132.18
128.68
119.20
109.49
29.08
15.04
N
f1 (ppm)

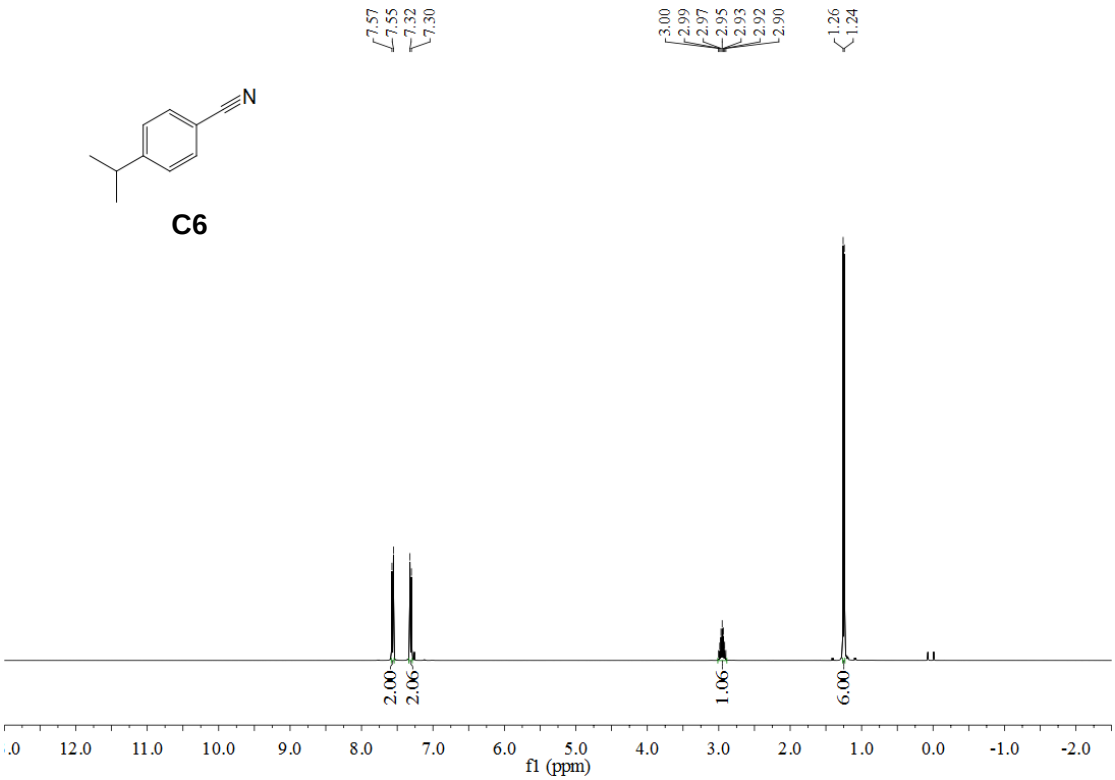
C4

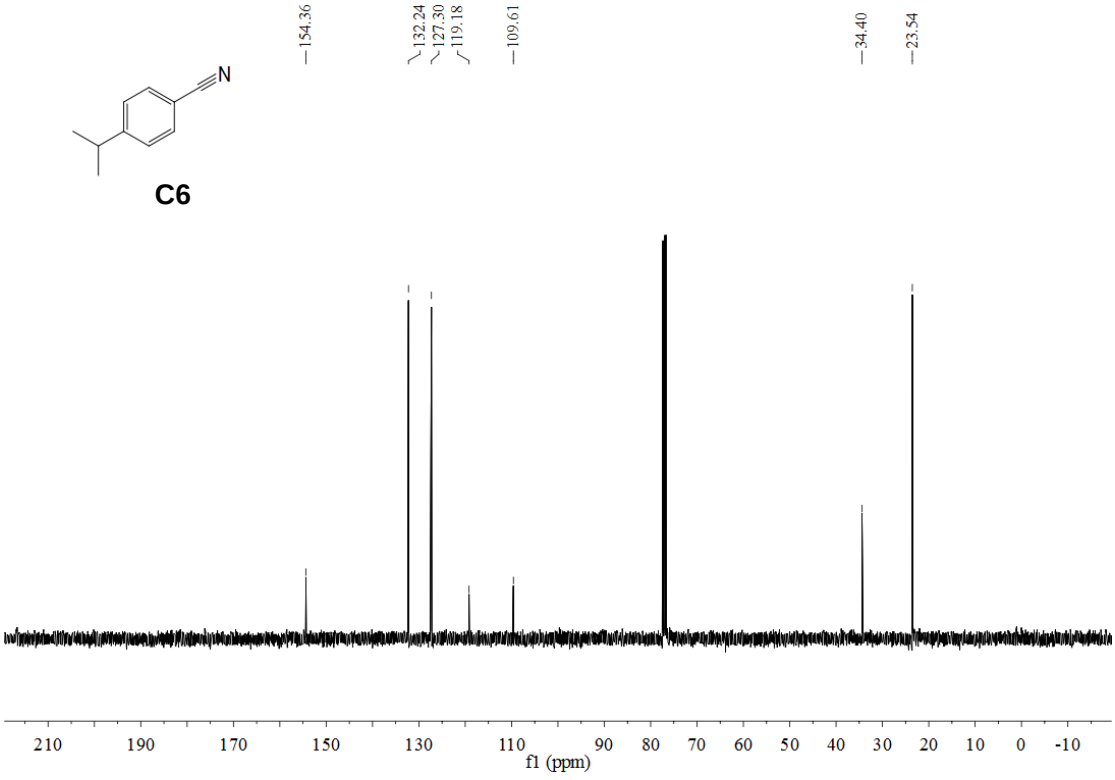

7.60
7.58
7.30
7.28
2.68
2.67
2.65
1.69
1.67
1.65
0.98
0.97
0.95
N
2.00
2.22
2.00
2.00
3.05
f1 (ppm)

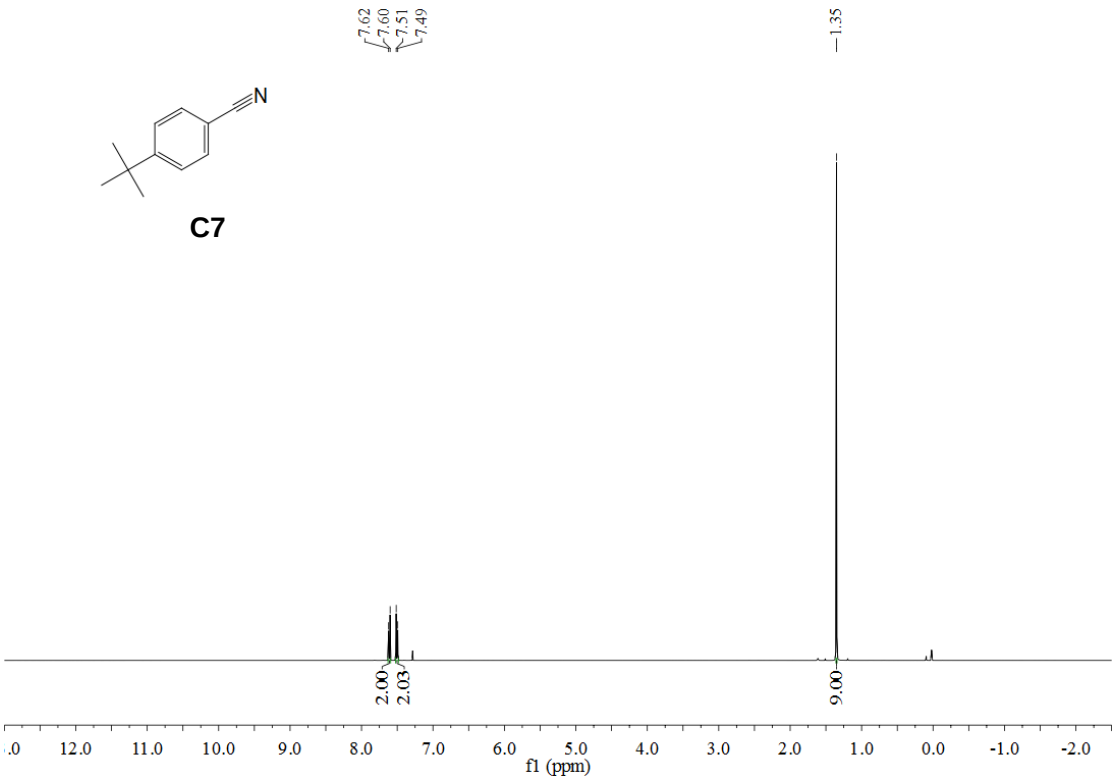
C5

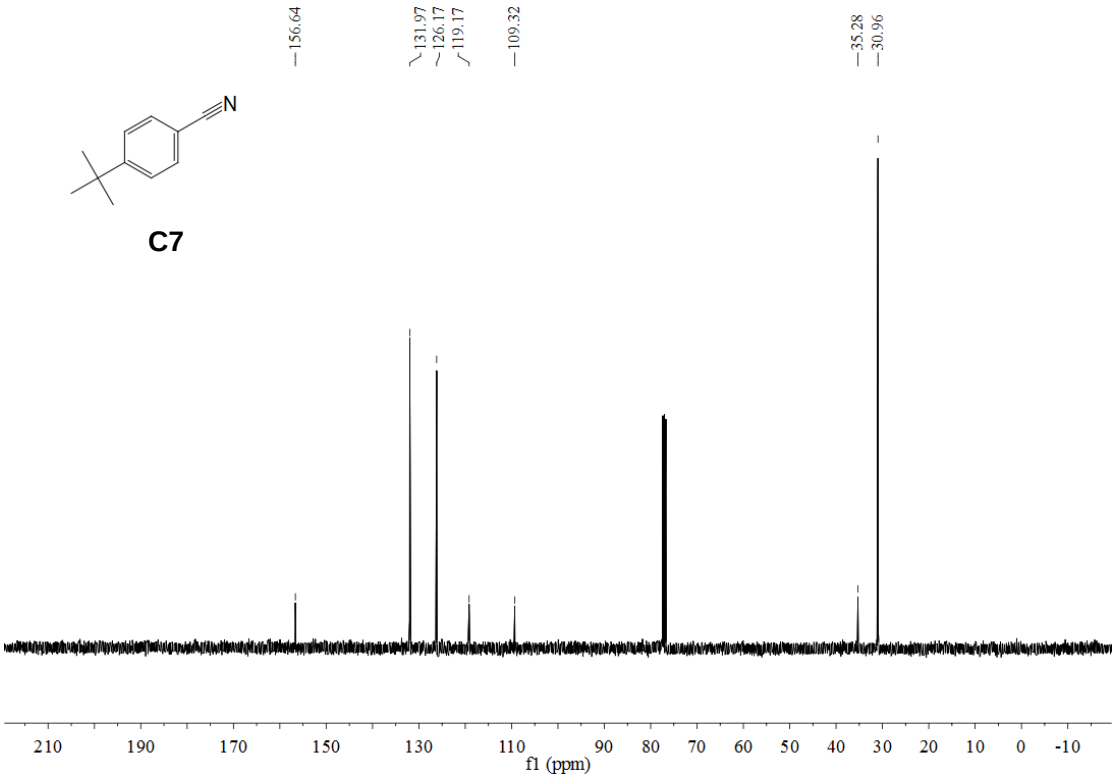

148.33
132.11
129.25
119.25
109.50
38.13
24.13
13.70
N
f1 (ppm)

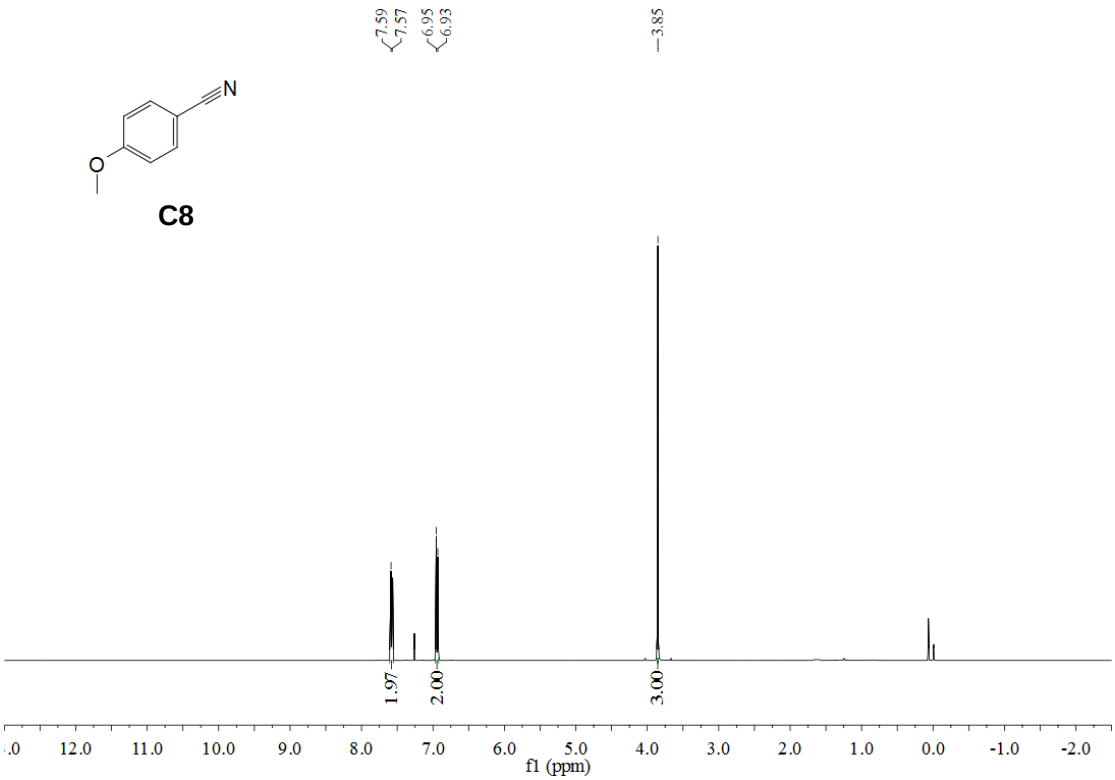
C5

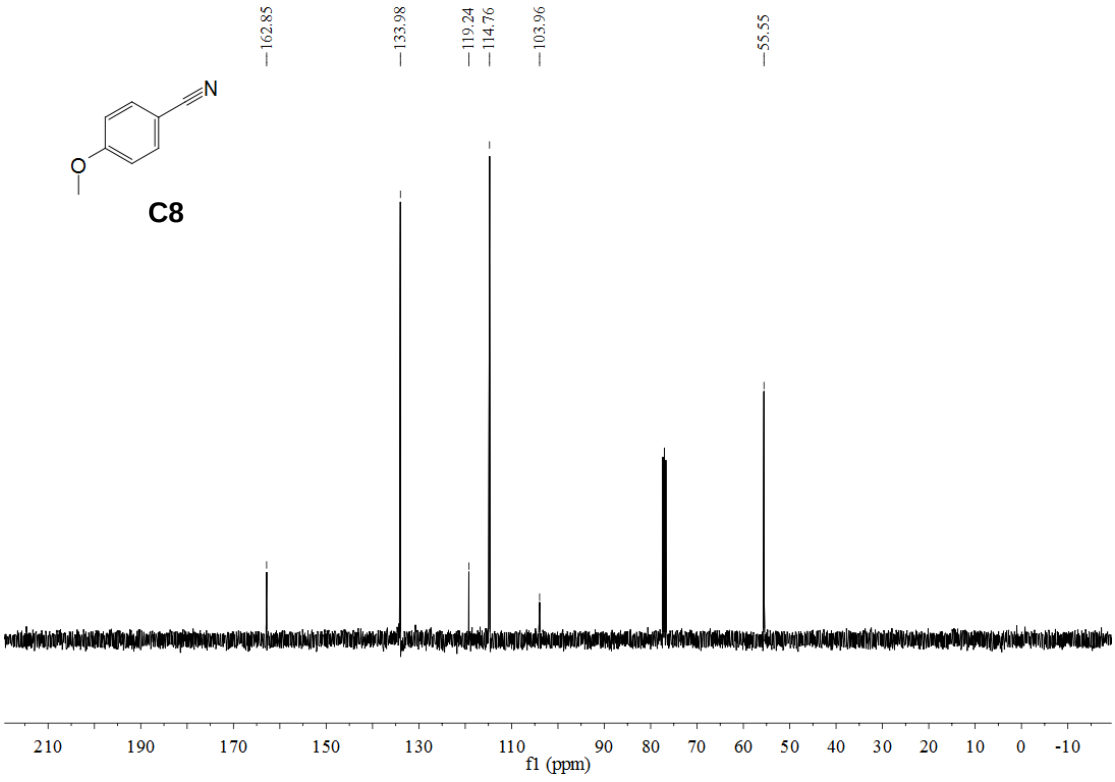

7.57
7.55
7.32
7.30
3.00
2.99
2.97
2.95
2.93
2.92
2.90
1.26
1.24
N
C6
2.00
2.06
1.06
6.00
f1 (ppm)

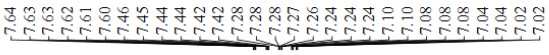

154.36
132.24
127.30
119.18
109.61
34.40
23.54
N
C6
f1 (ppm)


7.62
7.60
7.51
7.49
1.35
N
C7
2.00
2.03
9.00
f1 (ppm)


156.64
131.97
126.17
119.17
109.32
35.28
30.96
N
C7
f1 (ppm)


7.59
7.57
6.95
6.93
3.85
N
O
C8
1.97
2.00
3.00
f1 (ppm)


162.85
133.98
119.24
114.76
103.96
55.55
N
O
C8
f1 (ppm)


7.64
7.63
7.63
7.62
7.61
7.60
7.46
7.45
7.44
7.44
7.42
7.42
7.28
7.28
7.28
7.27
7.26
7.24
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7.10
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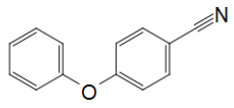
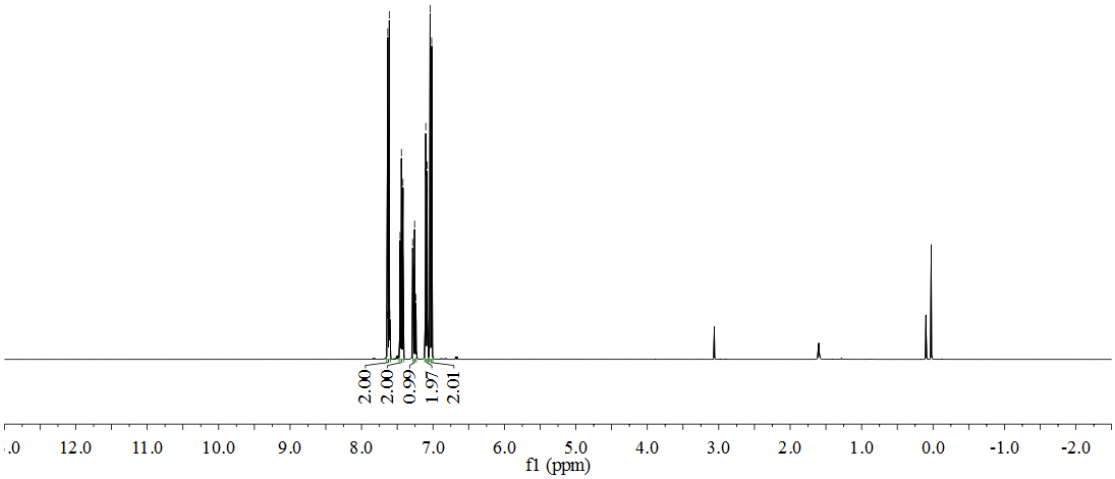
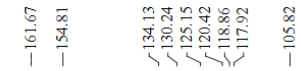
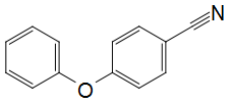
7.08
7.08
7.08
7.04
7.04
7.02
7.02


N
O

C9

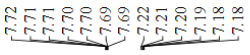

2.00
2.00
0.99
1.97
2.01
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

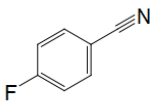

161.67
154.81
134.13
130.24
125.15
120.42
118.86
117.92
105.82


N
O

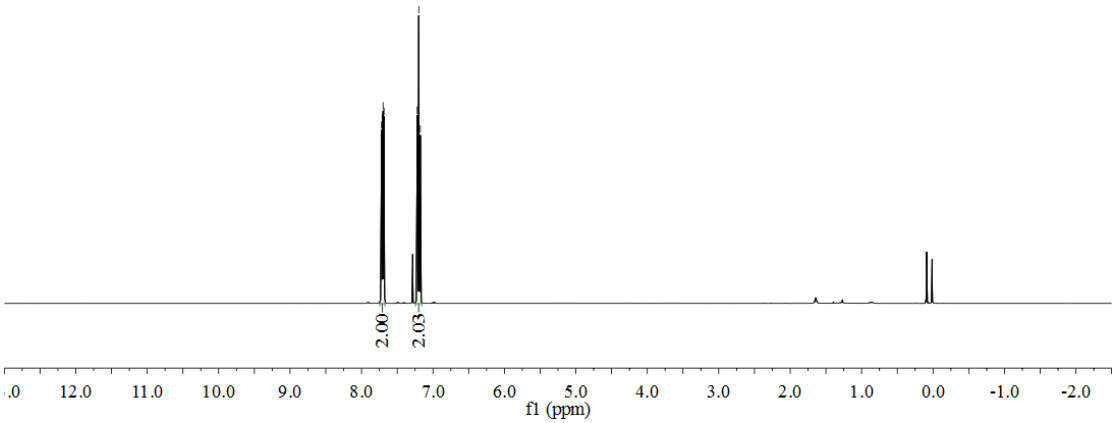
C9

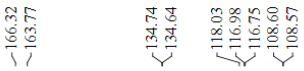
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

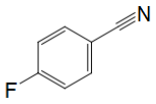

7.72
7.71
7.71
7.70
7.70
7.69
7.69
7.22
7.21
7.20
7.19
7.18
7.18


N
F

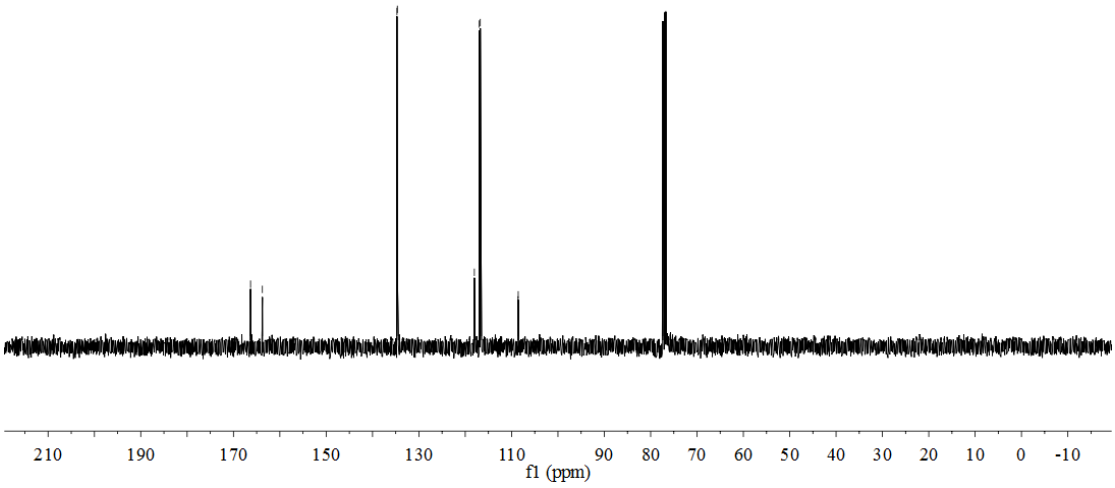
C10

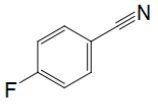

2.00
2.03
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)


166.32
163.77
134.74
134.64
118.03
116.98
116.75
108.60
108.57


N
F

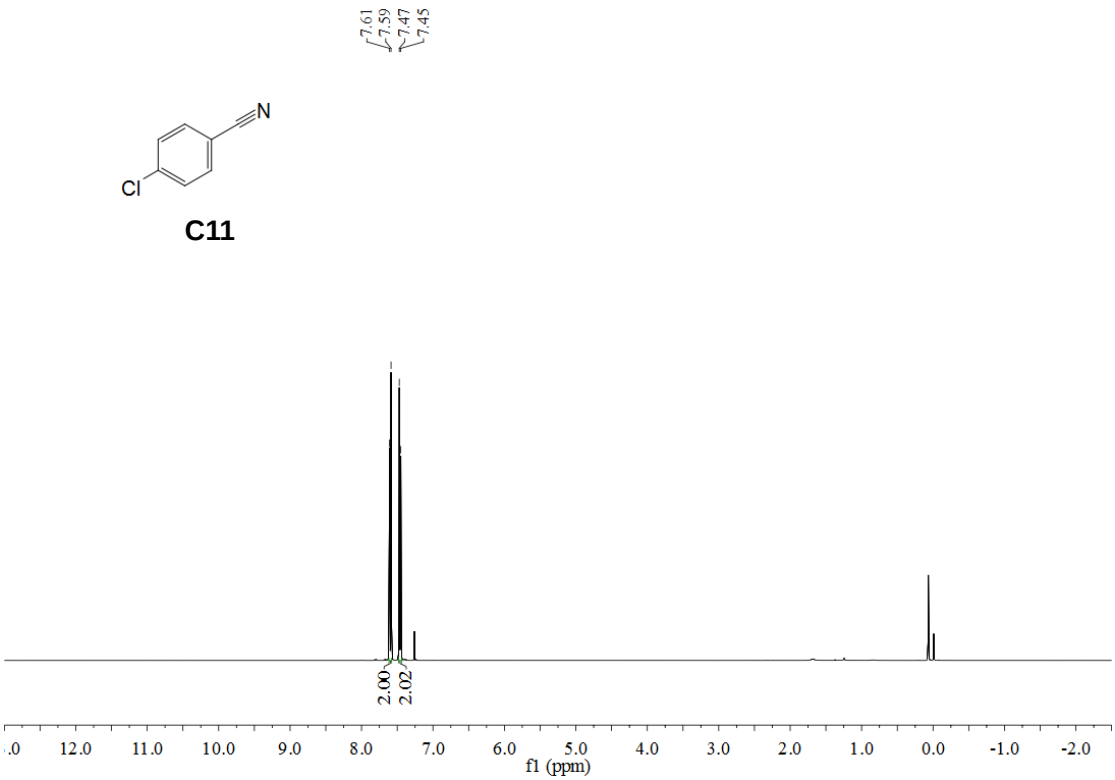
C10


210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

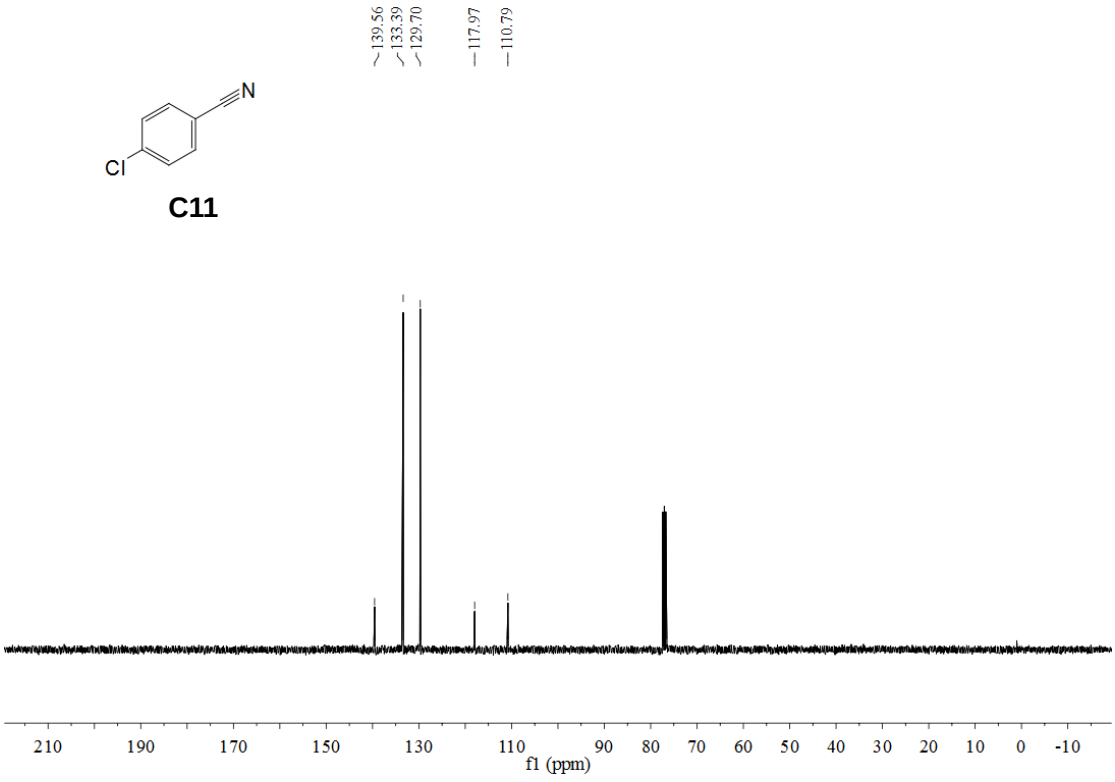

N
F

C10

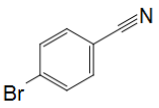
-102.43
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.61
7.59
7.47
7.45
N
Cl
2.00
2.02
f1 (ppm)

C11

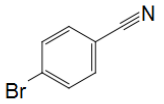

139.56
133.39
129.70
117.97
110.79
N
Cl
f1 (ppm)

C11


N
Br

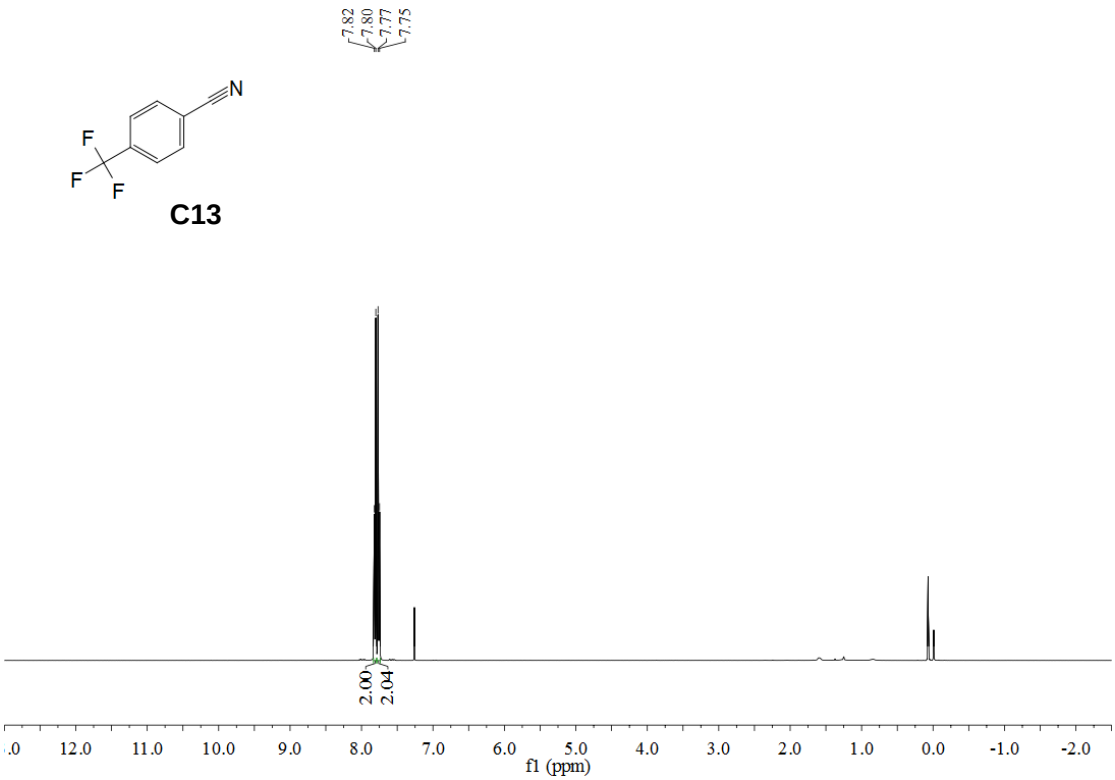
C12

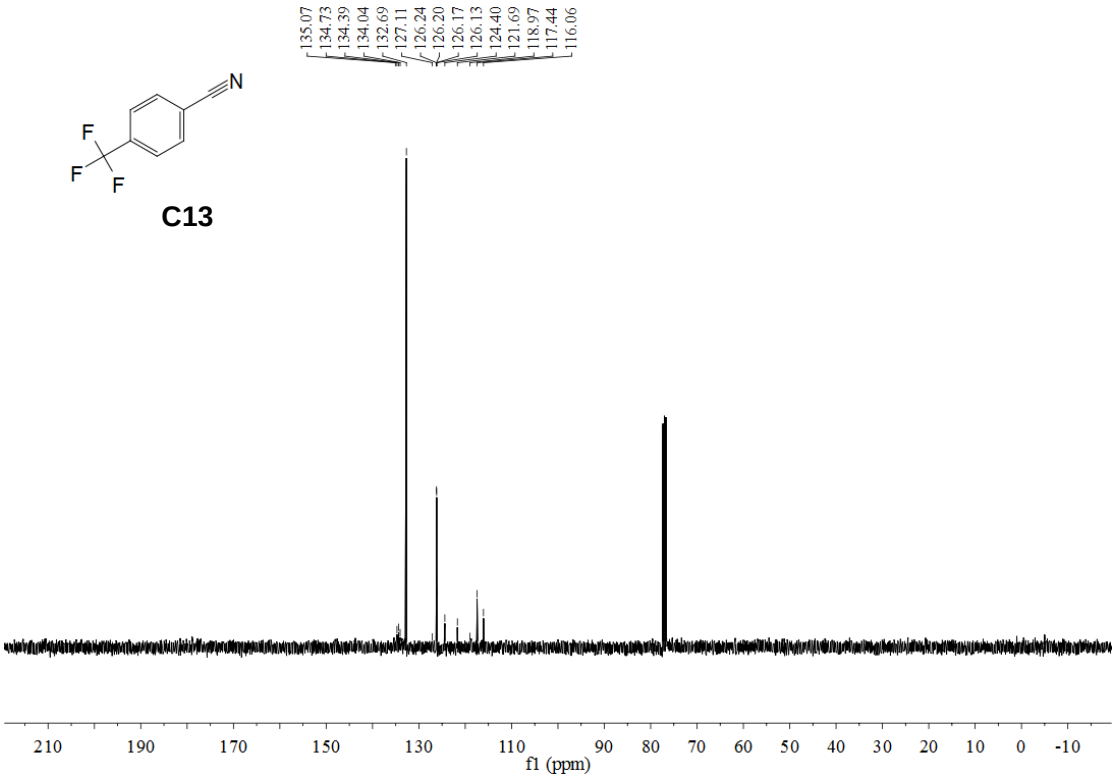
7.64
7.62
7.53
7.51
2.01
2.00
.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

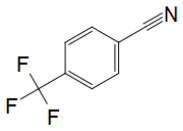

N
Br

C12

133.41
132.65
128.02
118.05
111.26
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

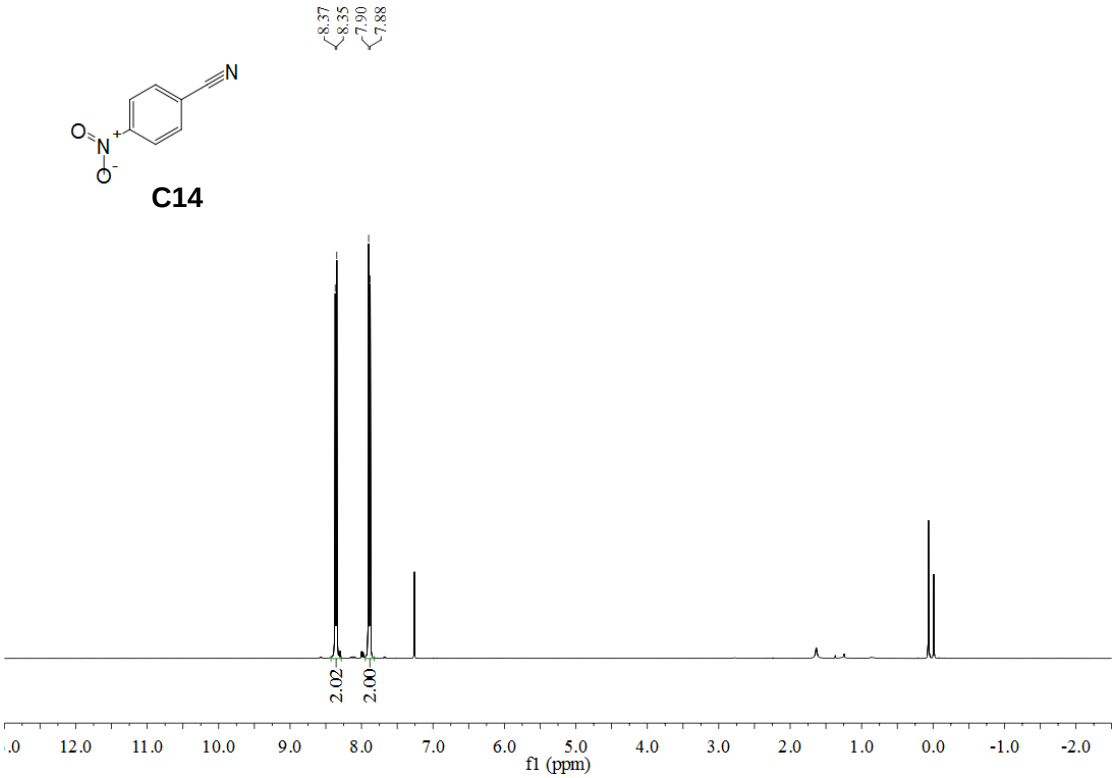

7.82
7.80
7.77
7.75
N
F
F
F
C13
2.00
2.04
f1 (ppm)

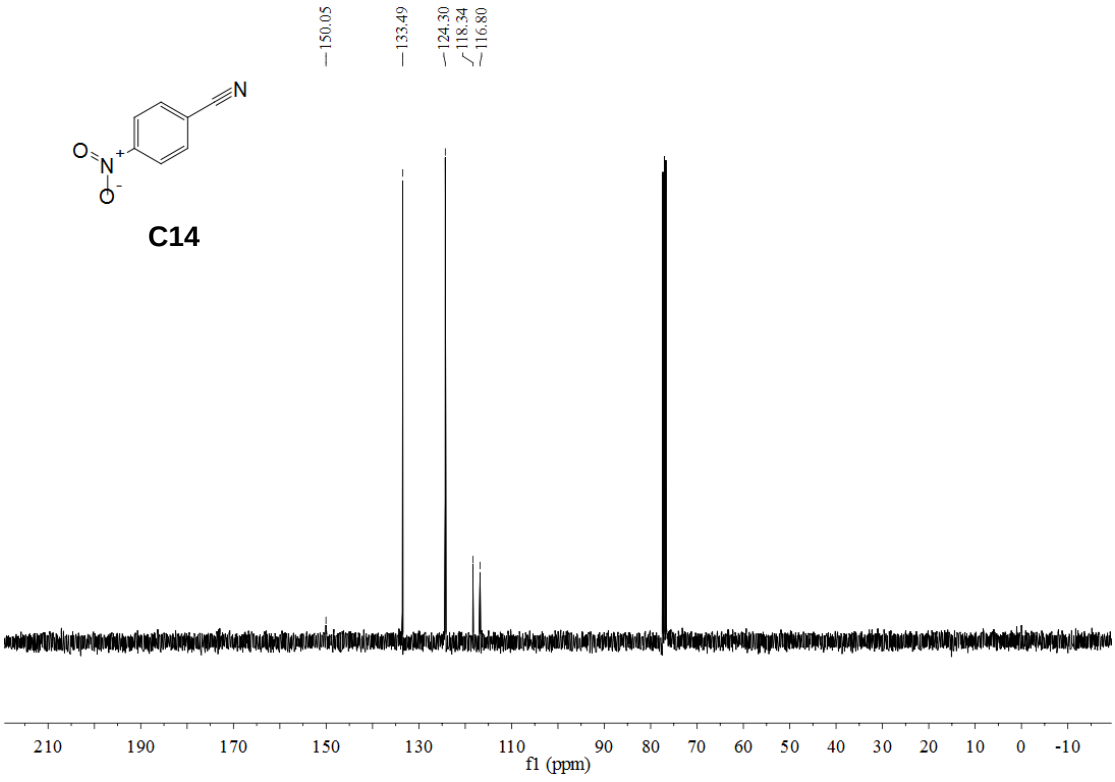

135.07
134.73
134.39
134.04
132.69
127.11
126.24
126.20
126.17
126.13
124.40
121.69
118.97
117.44
116.06
N
F
F
F
C13
f1 (ppm)

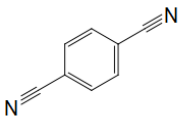

N
F
F
F

C13

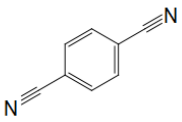
-63.56
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


8.37
8.35
7.90
7.88
C14
2.02
2.00
f1 (ppm)

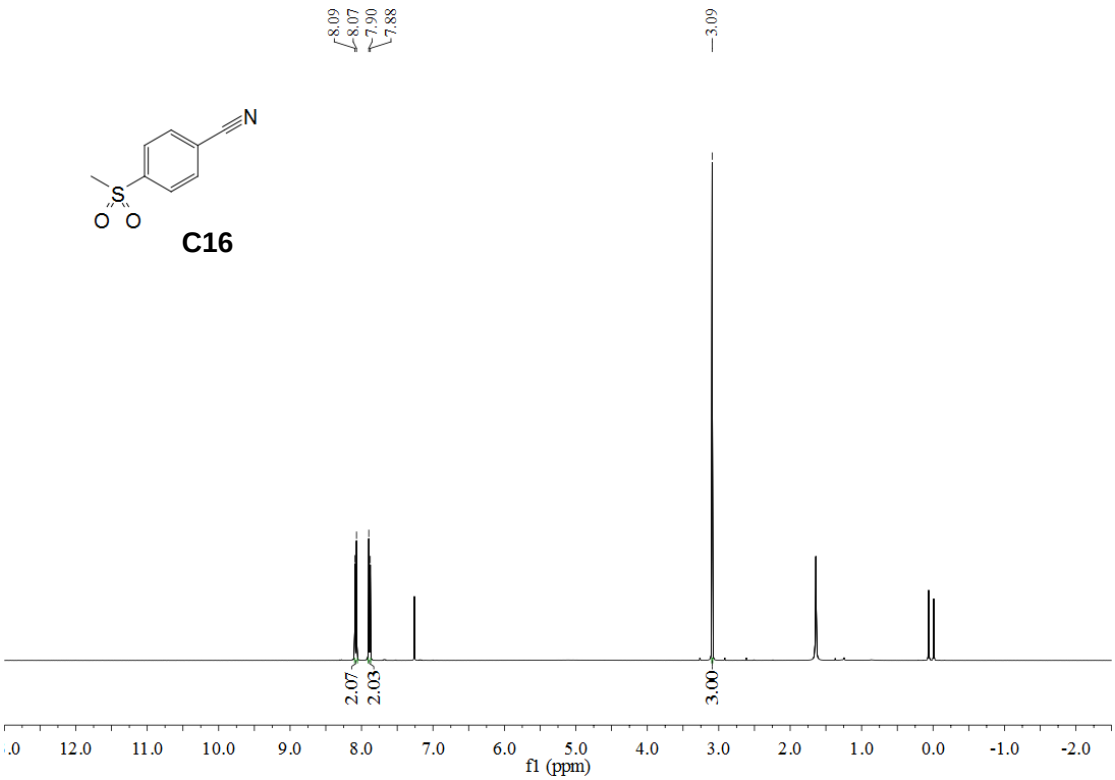

150.05
133.49
124.30
118.34
116.80
C14
f1 (ppm)

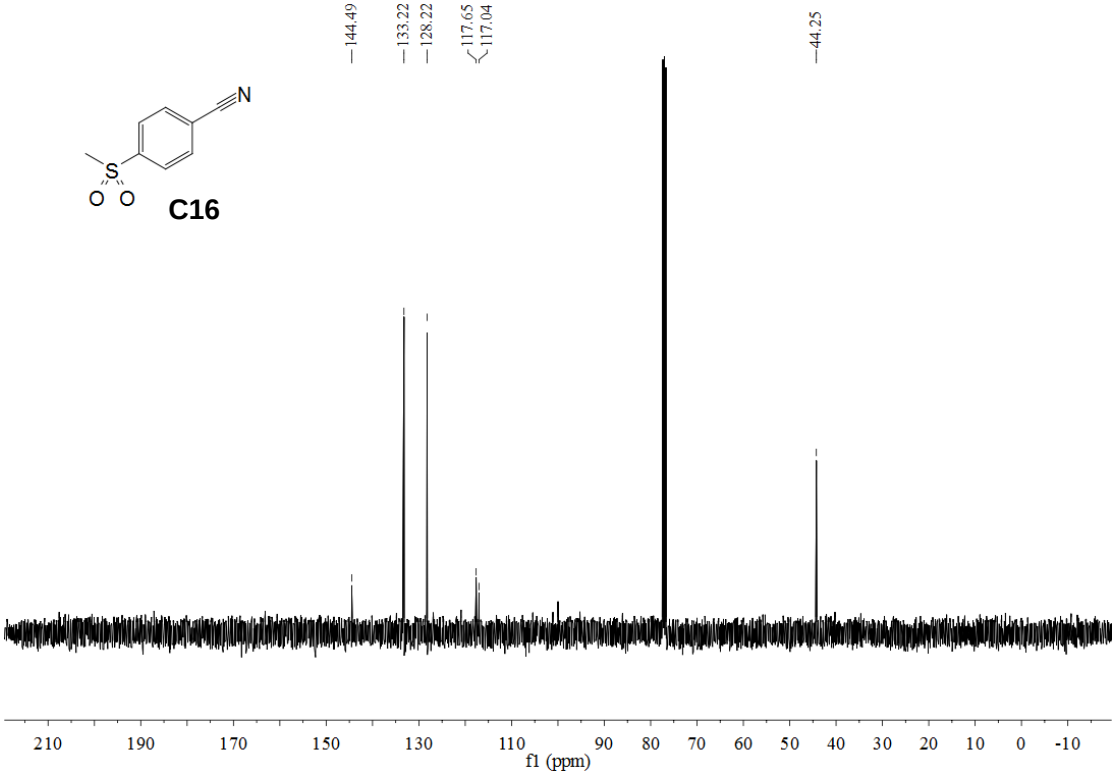


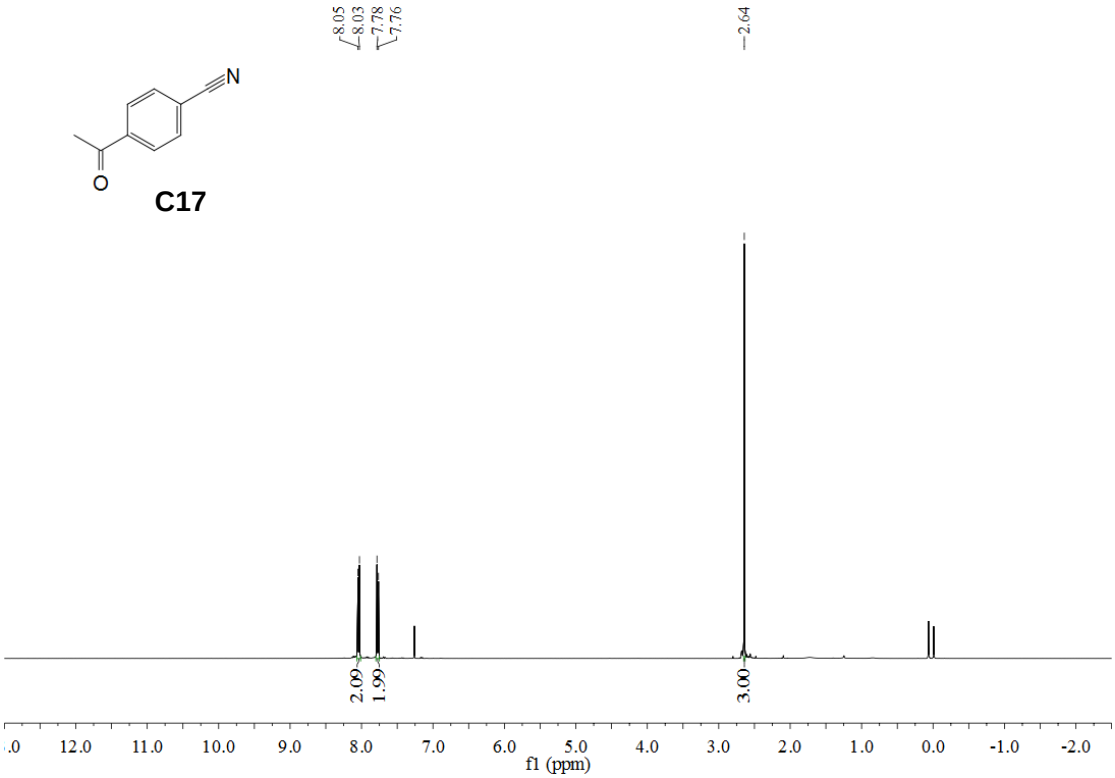
C15

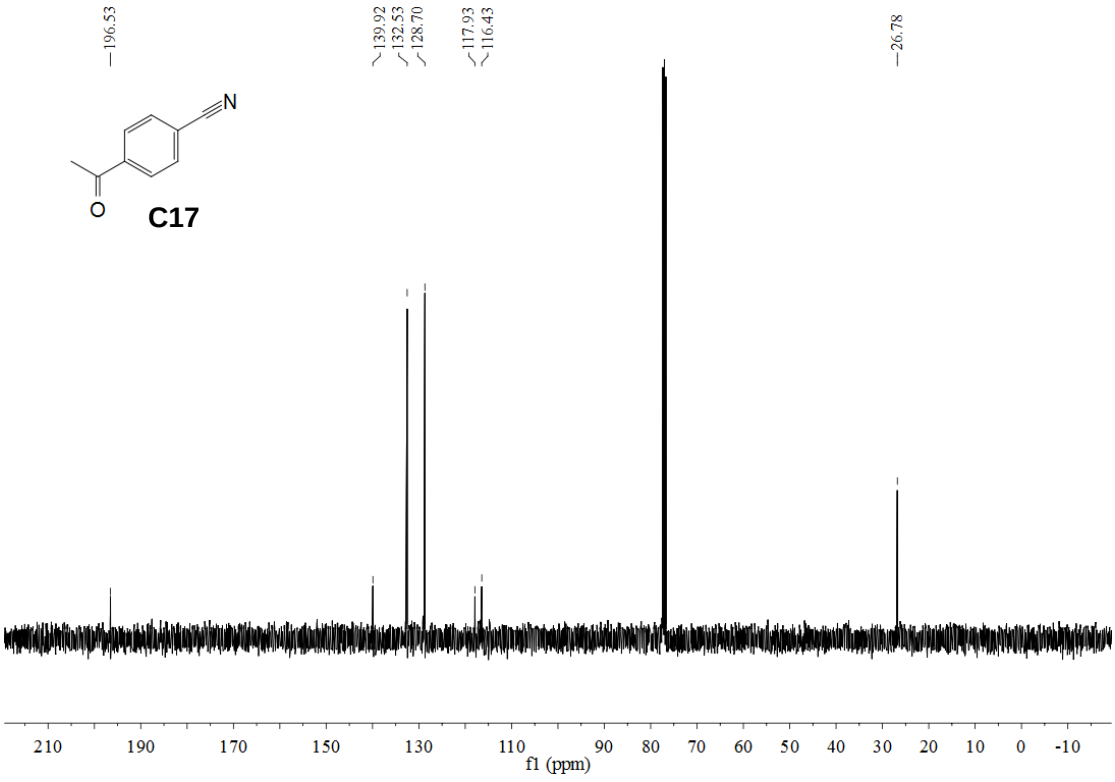


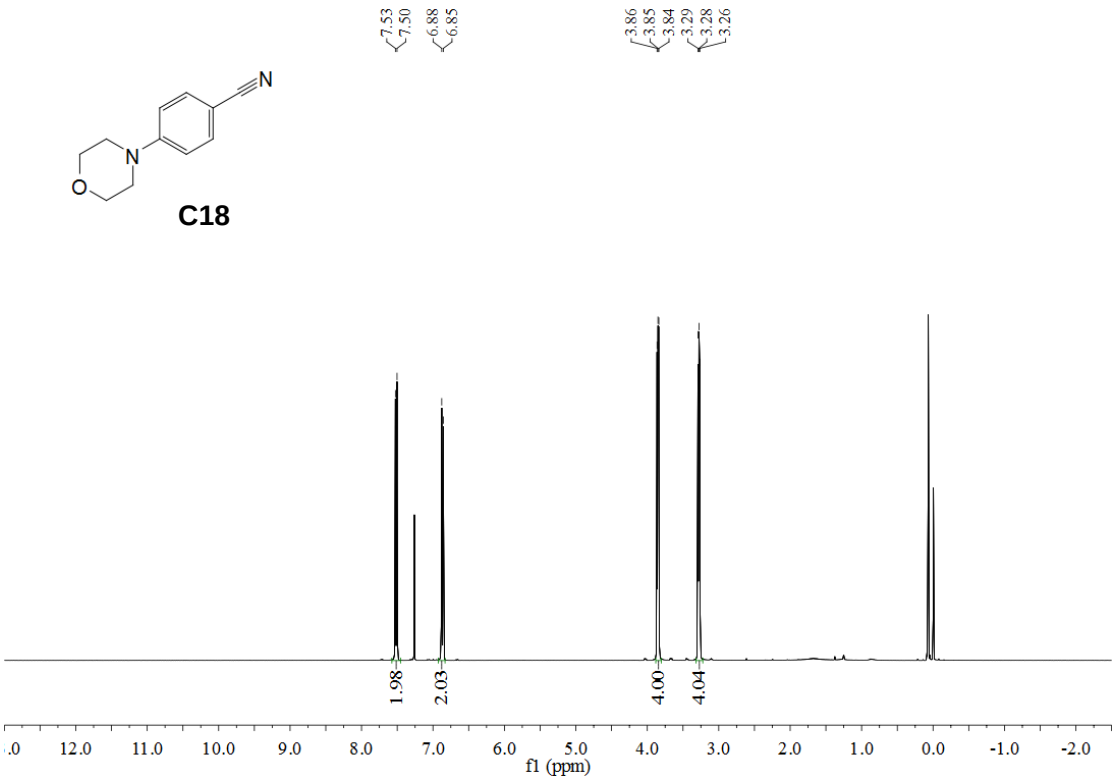
C15

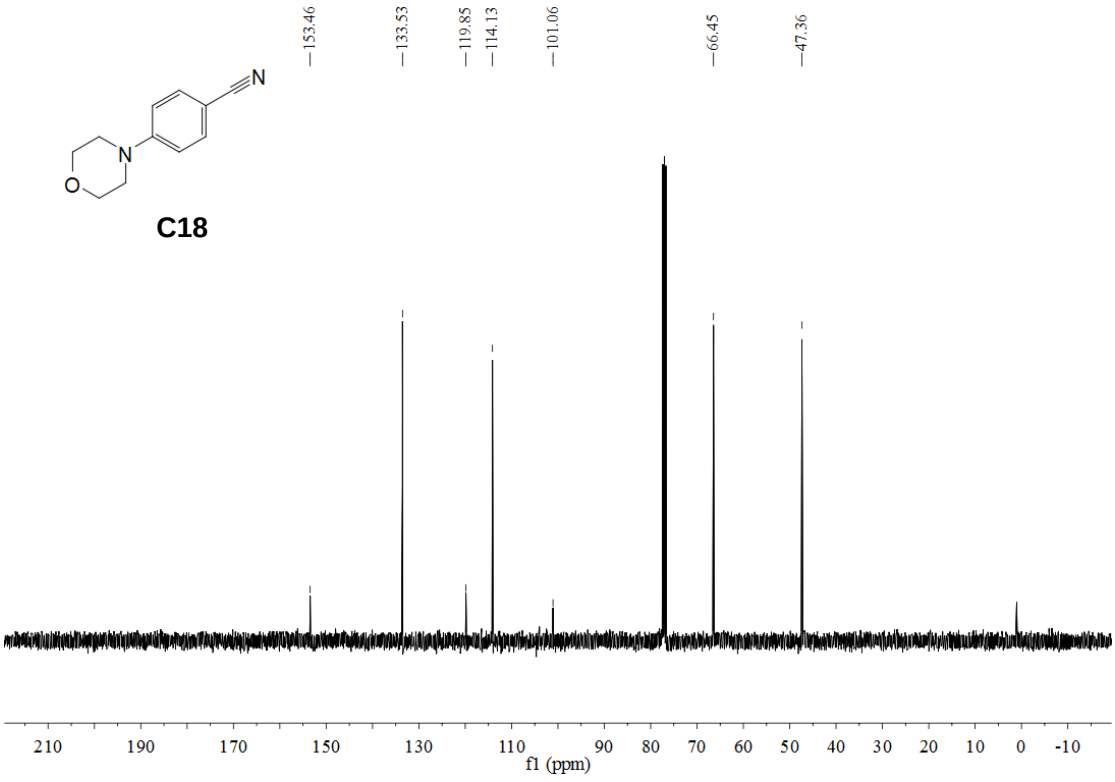

8.09
8.07
7.90
7.88
3.09
N
S
O
O
C16
2.07
2.03
3.00
f1 (ppm)

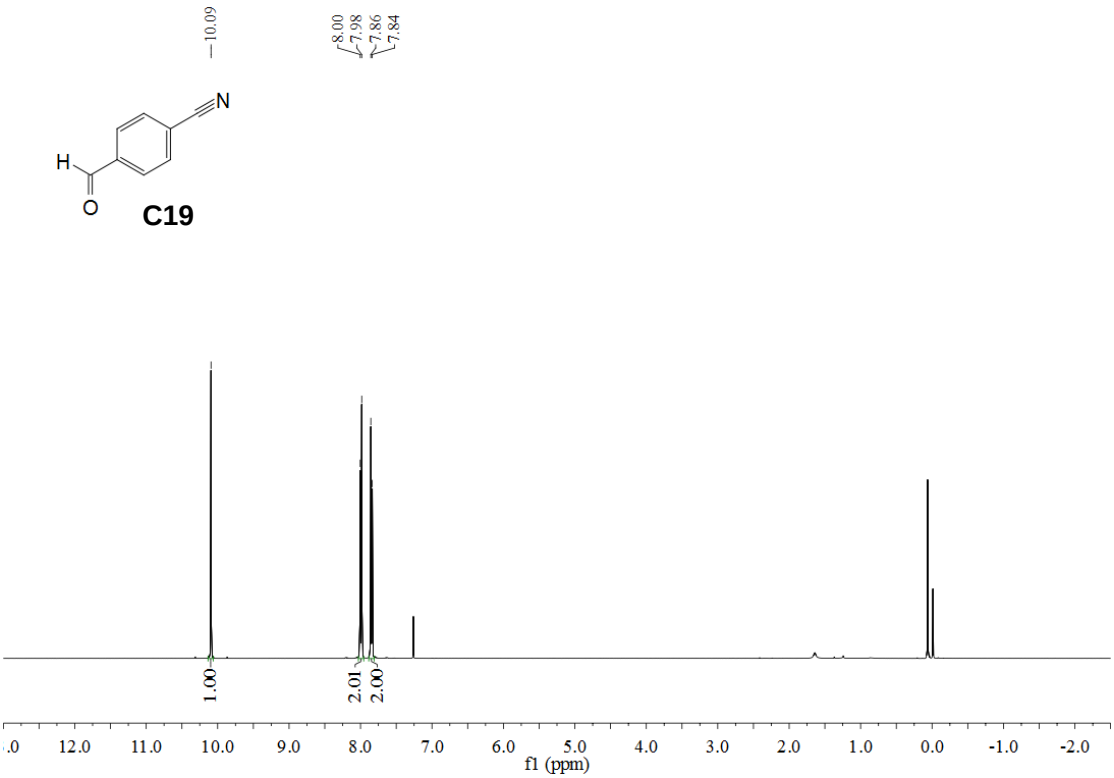

144.49
133.22
128.22
117.65
117.04
44.25
N
S
O
O
C16
f1 (ppm)

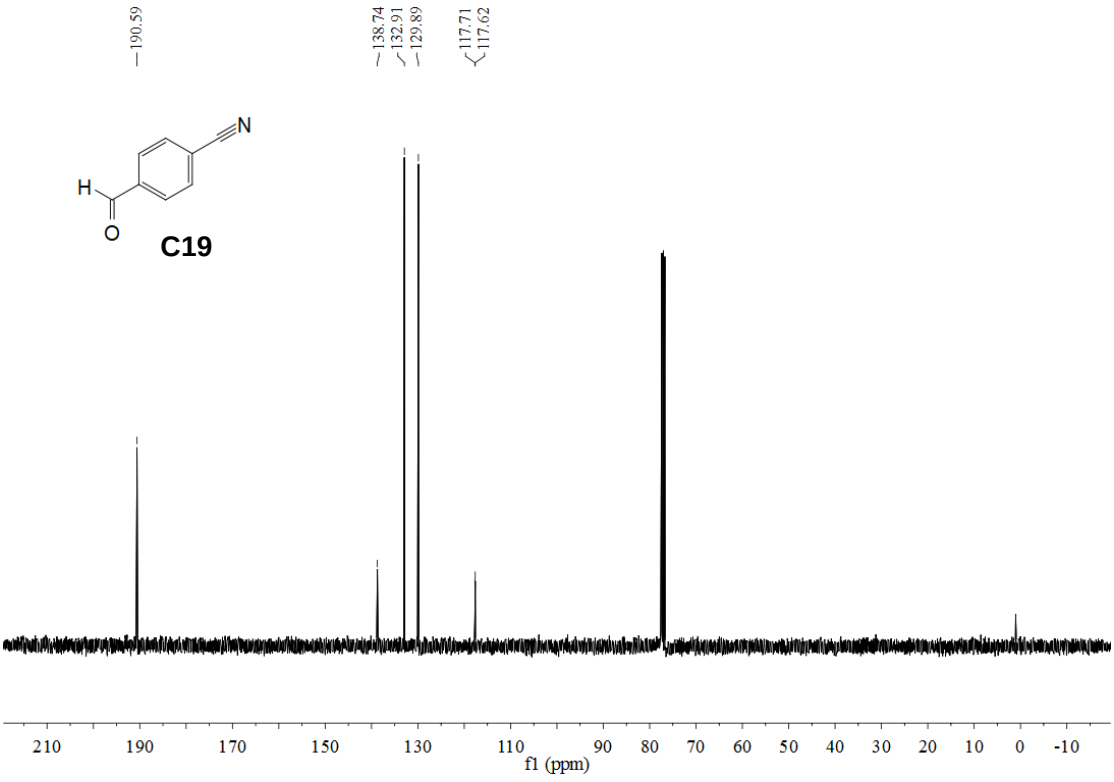

8.05
8.03
7.78
7.76
2.64
N
O
C17
2.09
1.99
3.00
f1 (ppm)

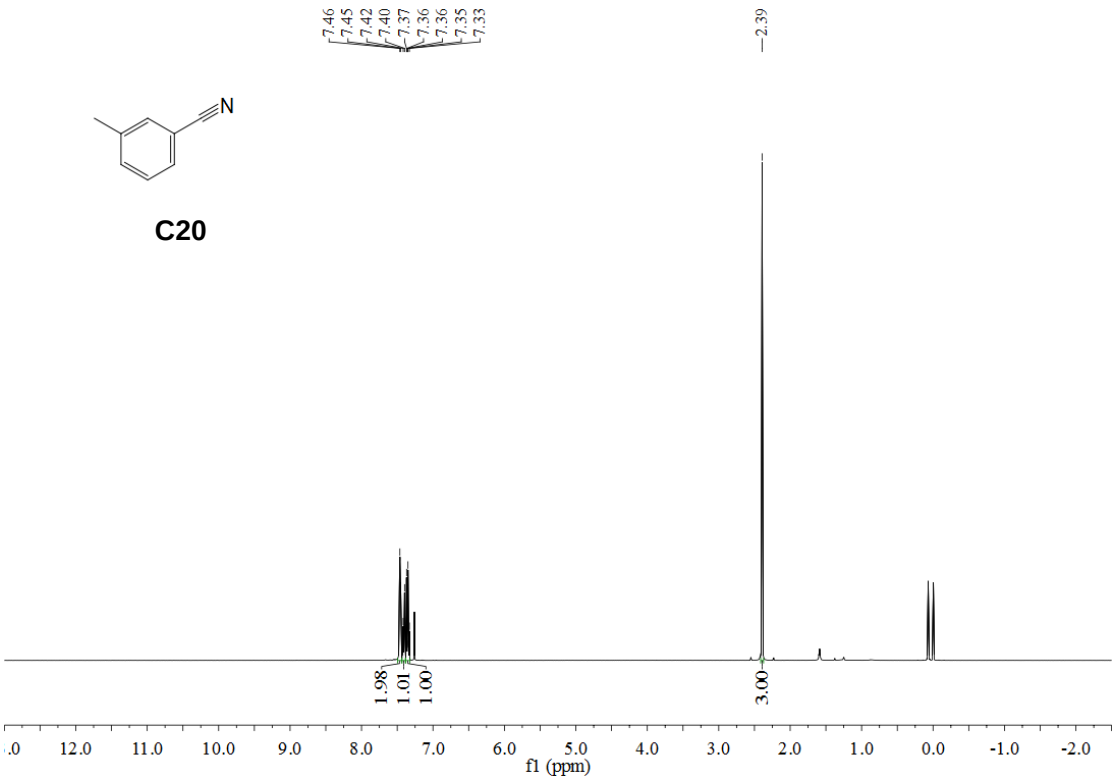

196.53
139.92
132.53
128.70
117.93
116.43
26.78
N
O
C17
f1 (ppm)

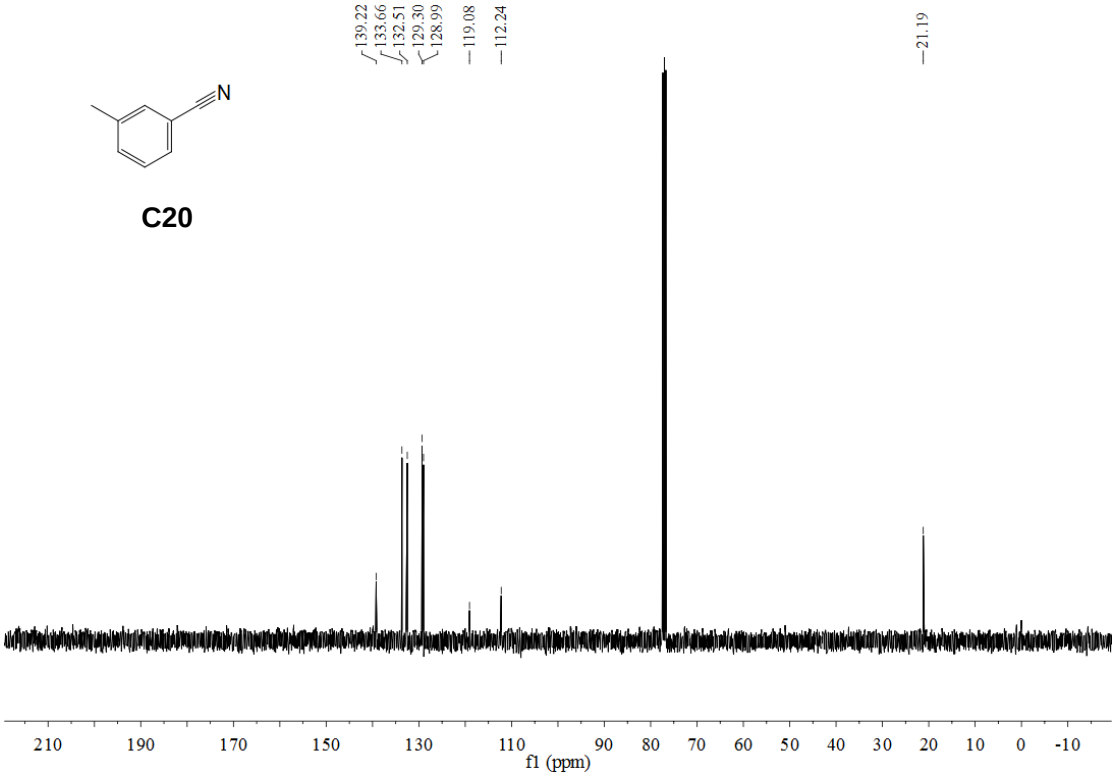

7.53
7.50
6.88
6.85
3.86
3.85
3.84
3.29
3.28
3.26
N
N
O
C18
1.98
2.03
4.00
4.04
f1 (ppm)

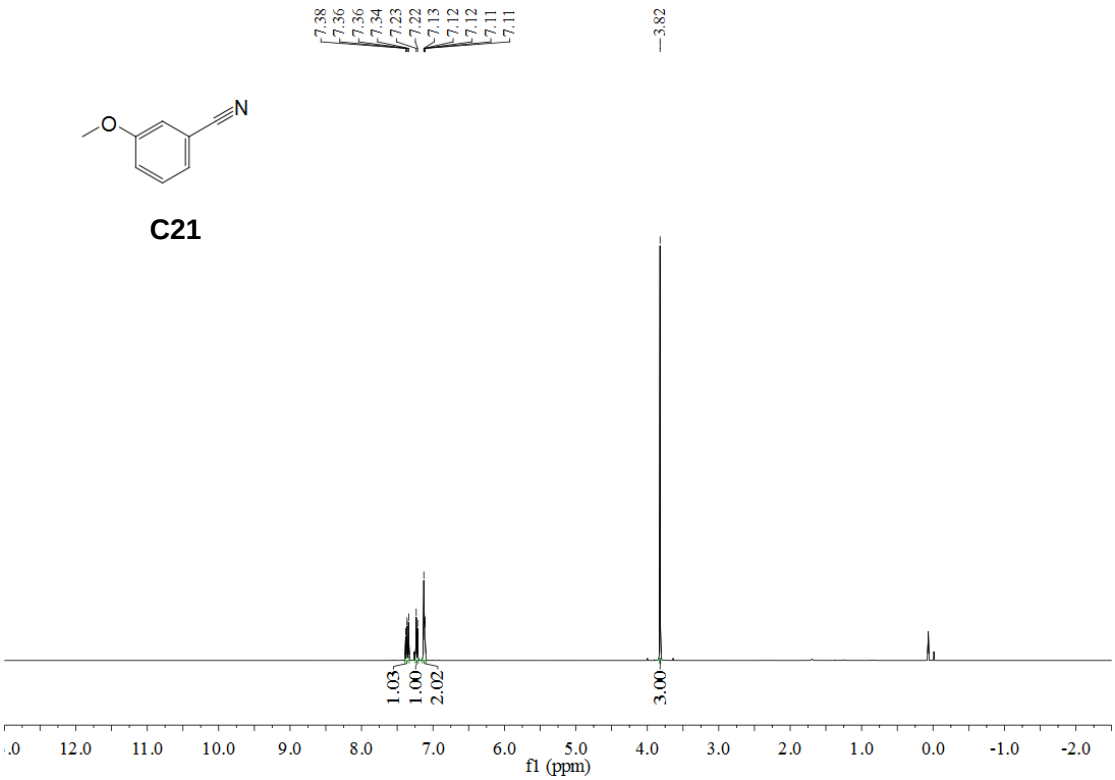

153.46
133.53
119.85
114.13
101.06
66.45
47.36
N
N
O
C18
f1 (ppm)


10.09
8.00
7.98
7.86
7.84
N
H
O
C19
1.00
2.01
2.00
f1 (ppm)

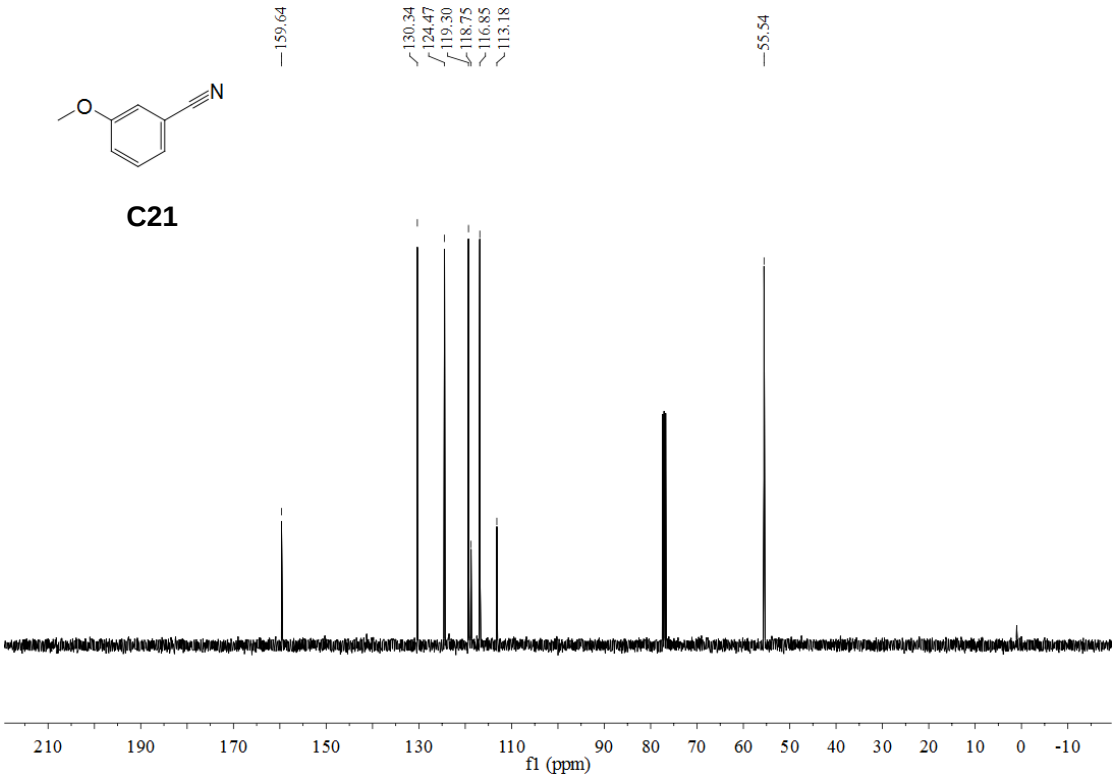

190.59
138.74
132.91
129.89
117.71
117.62
N
H
O
C19
f1 (ppm)


7.46
7.45
7.42
7.40
7.37
7.36
7.36
7.35
7.33
2.39
N
C20
1.98
1.01
1.00
3.00
f1 (ppm)

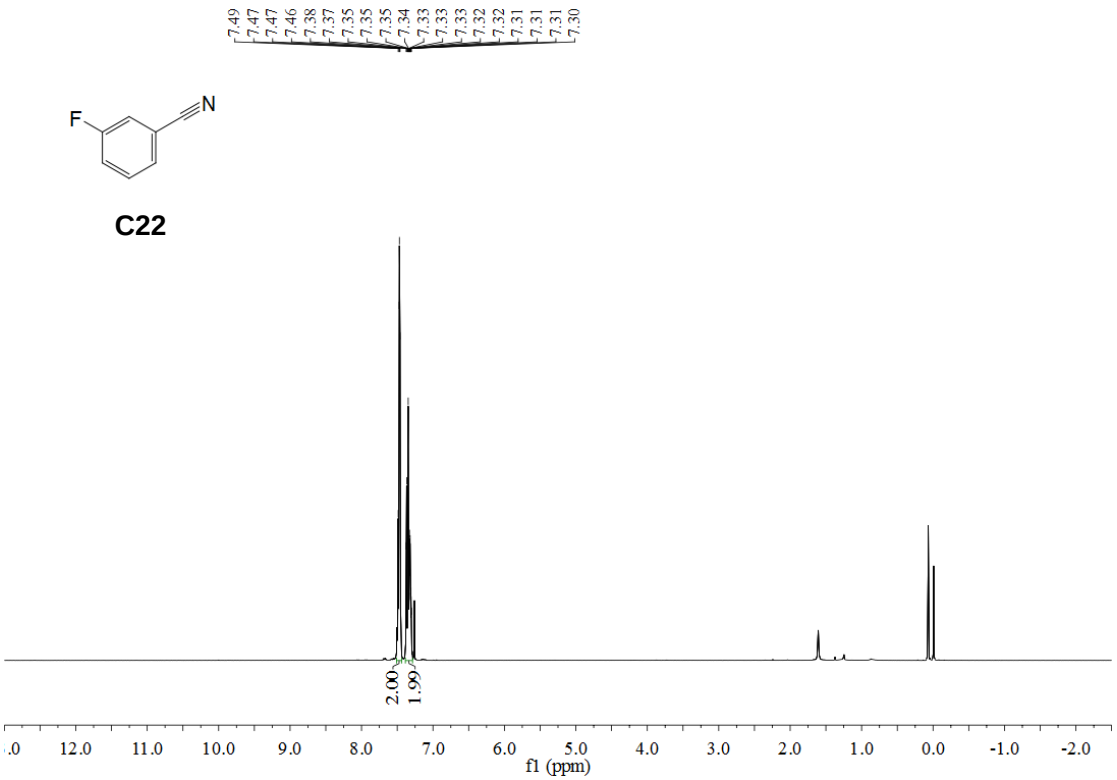

139.22
133.66
132.51
129.30
128.99
119.08
112.24
21.19
N
C20
f1 (ppm)


7.38
7.36
7.36
7.34
7.23
7.22
7.13
7.12
7.12
7.11
7.11
3.82
O
N
1.03
1.00
2.02
3.00
f1 (ppm)

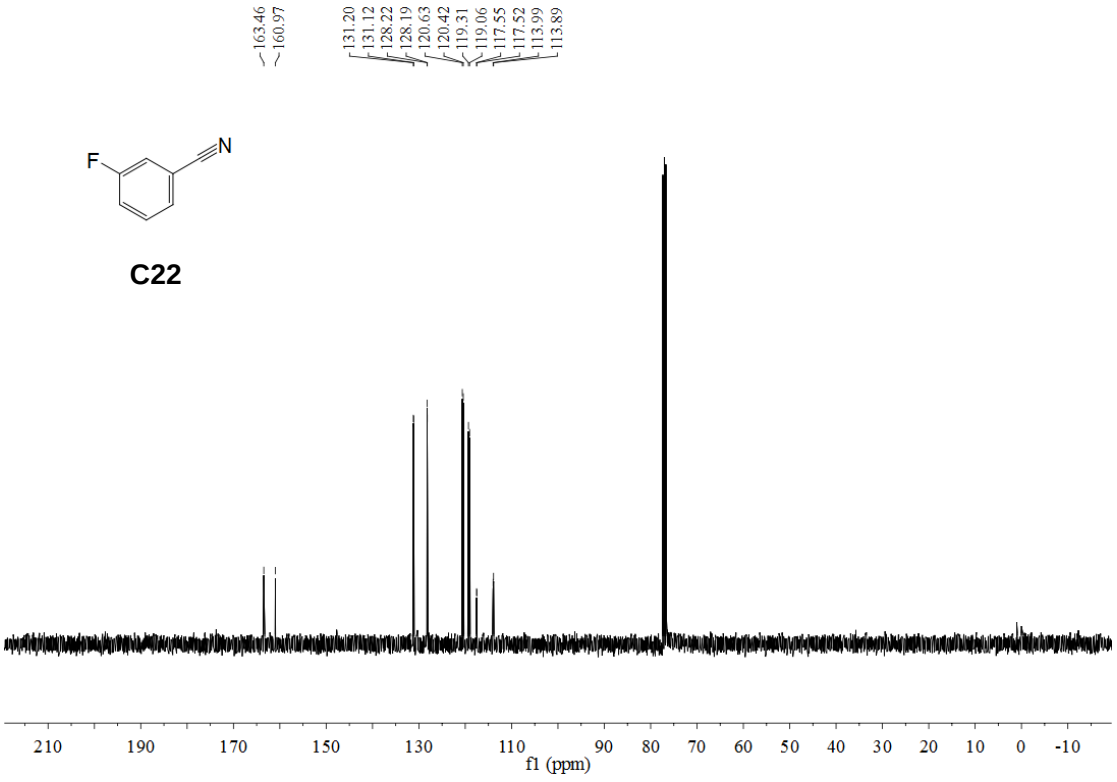
C21


159.64
130.34
124.47
119.30
118.75
116.85
113.18
55.54
O
N
f1 (ppm)

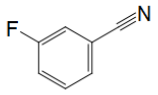
C21


7.49
7.47
7.47
7.46
7.38
7.37
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.30
F
N
2.00
1.99
f1 (ppm)

C22

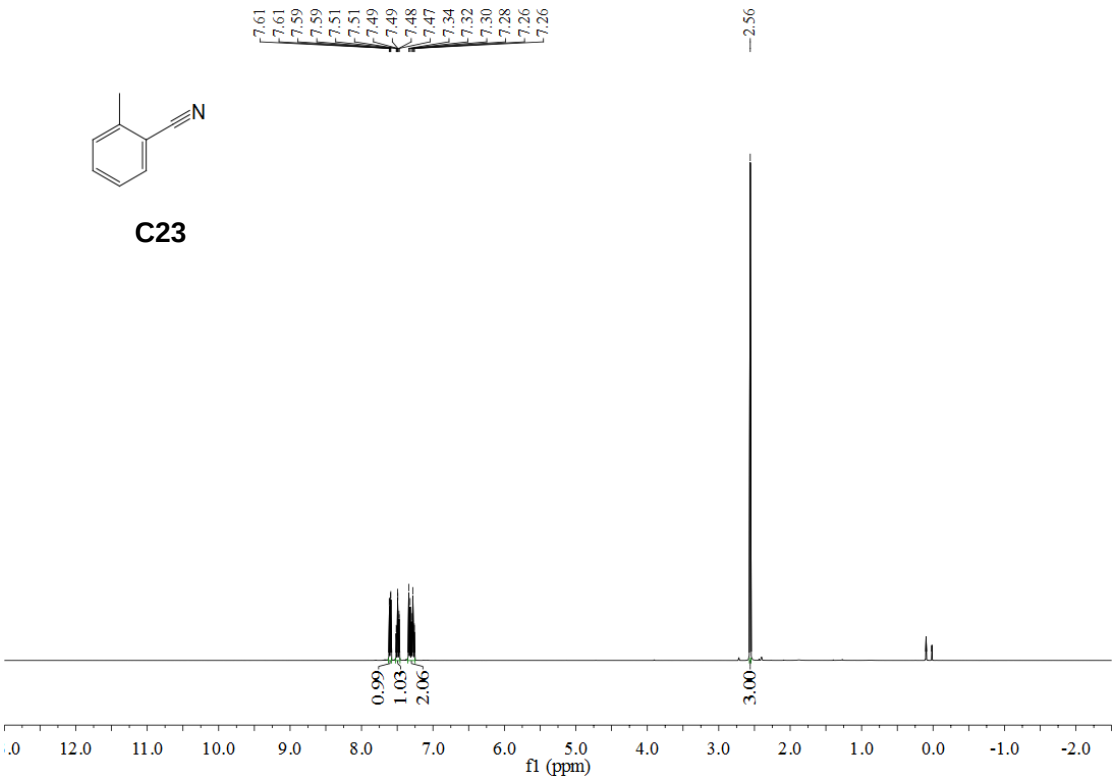

163.46
160.97
131.20
131.12
128.22
128.19
120.63
120.42
119.31
119.06
117.55
117.52
113.99
113.89
F
N
f1 (ppm)

C22

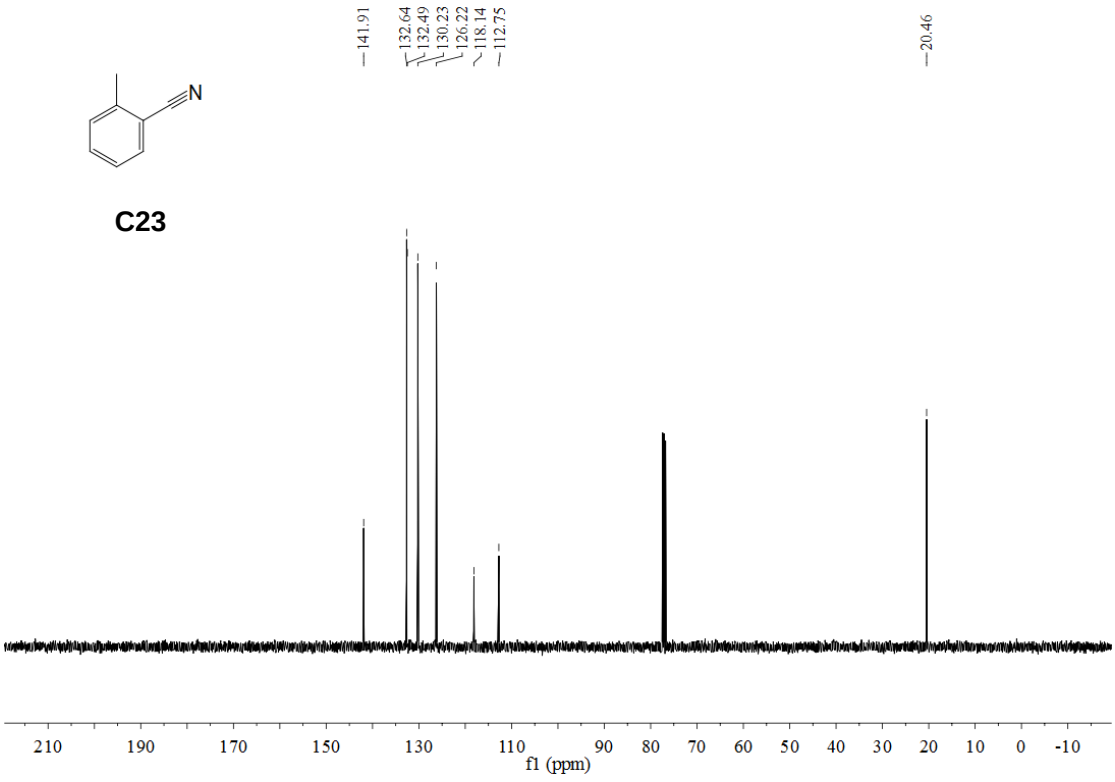

F
N

C22

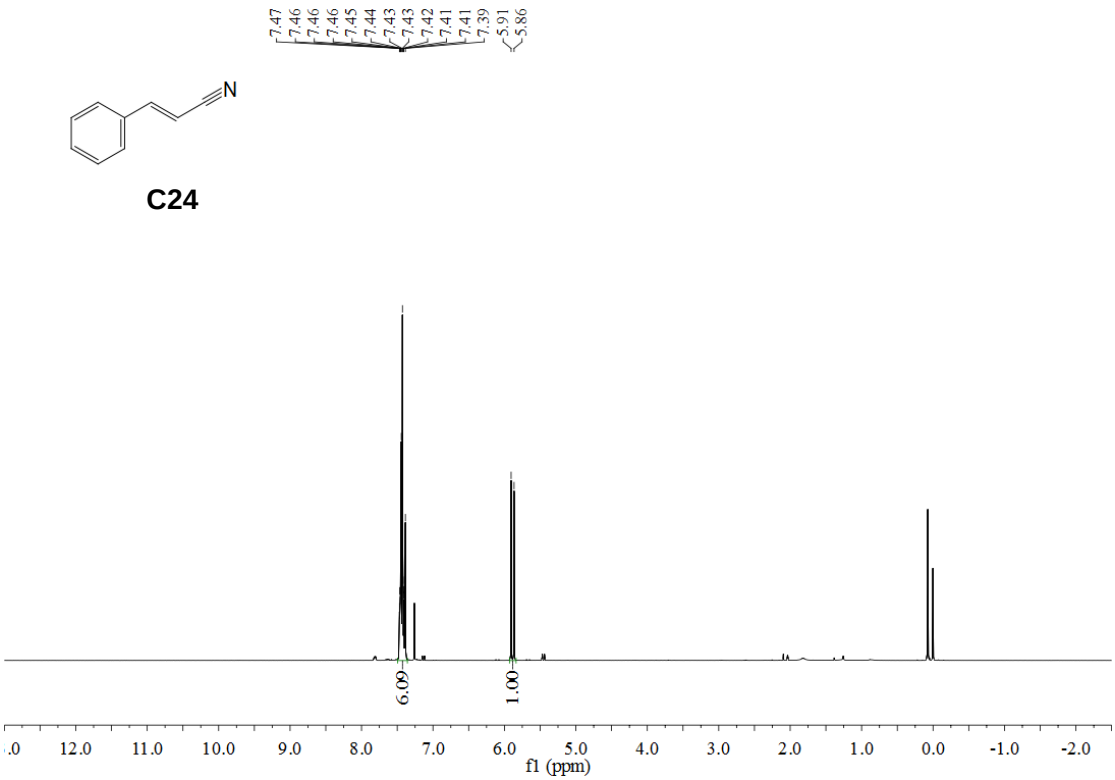
-109.64
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

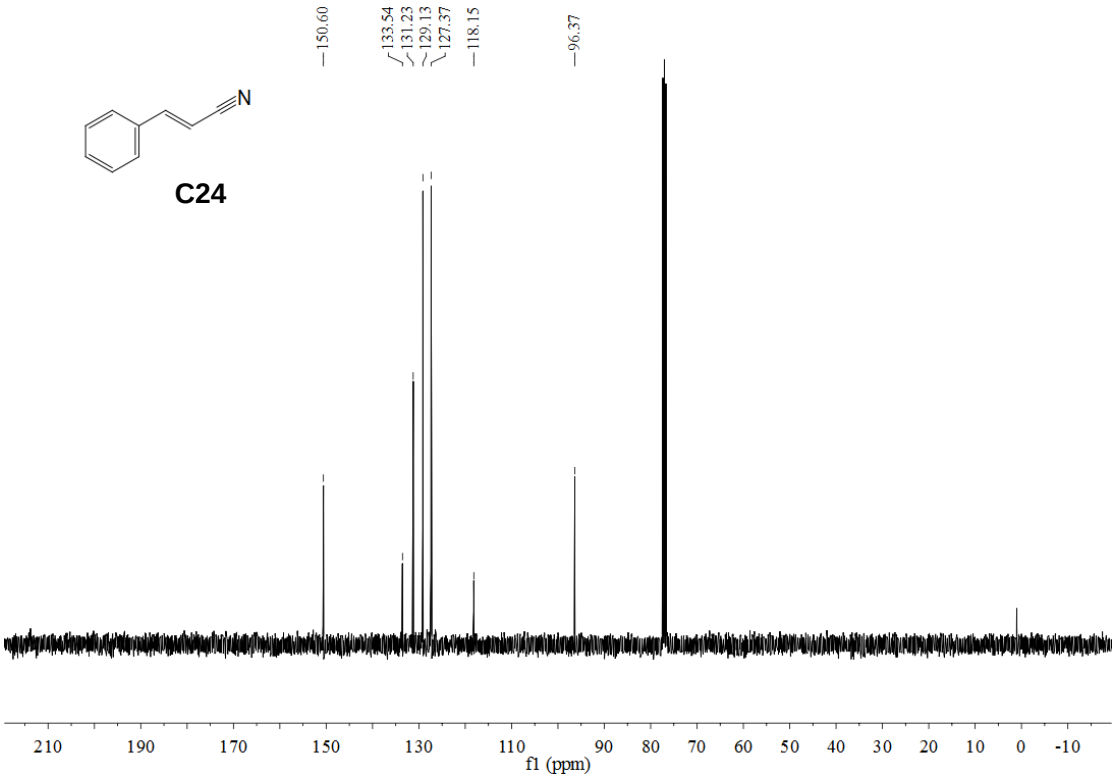

7.61
7.61
7.59
7.59
7.51
7.51
7.49
7.49
7.48
7.47
7.34
7.32
7.30
7.28
7.26
7.26
2.56
N
0.99
1.03
2.06
3.00
f1 (ppm)

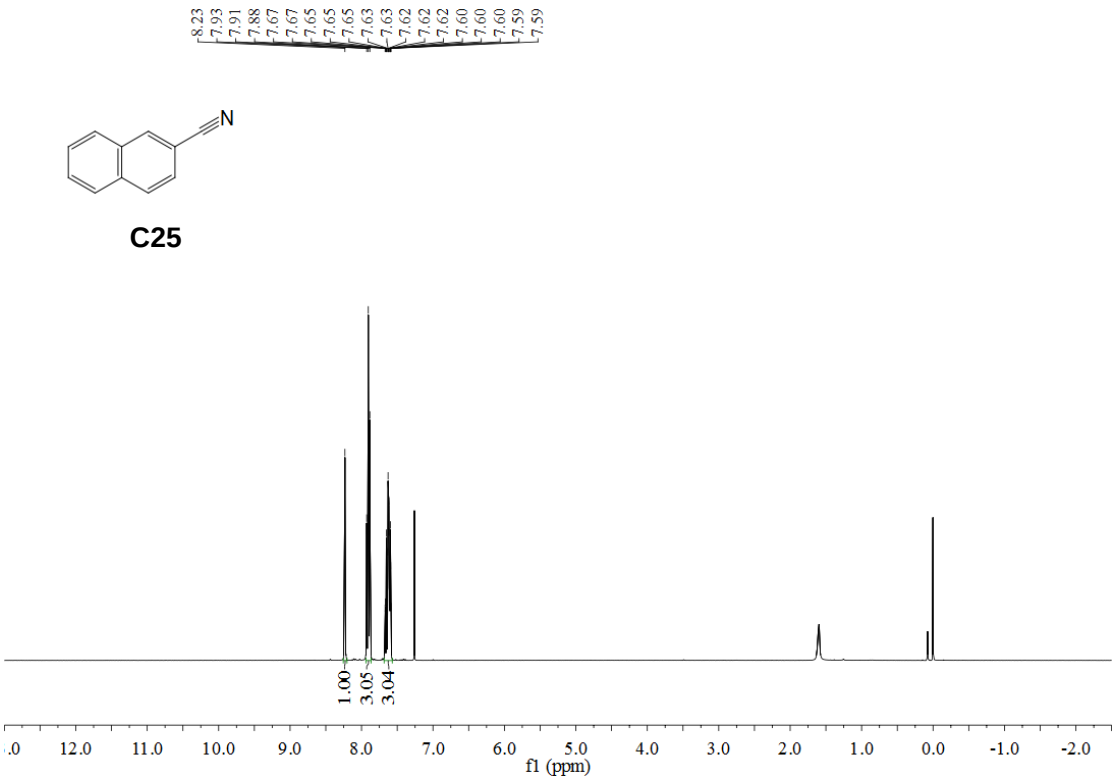
C23

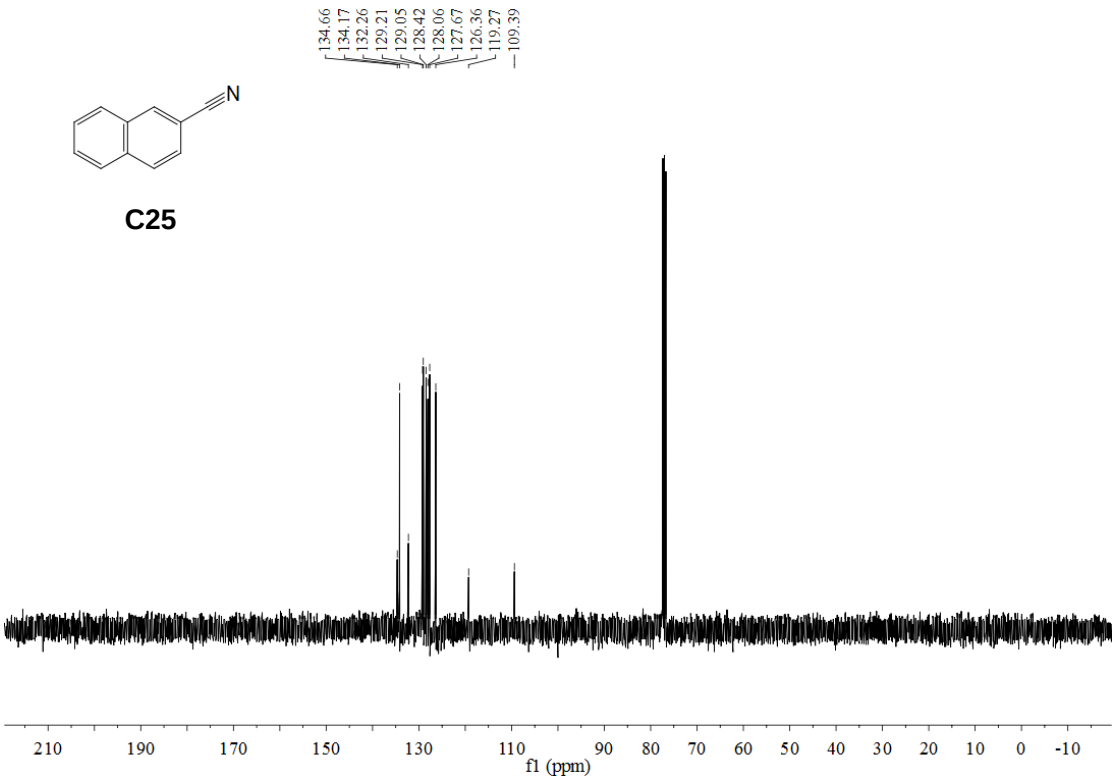

141.91
132.64
132.49
130.23
126.22
118.14
112.75
20.46
N
f1 (ppm)

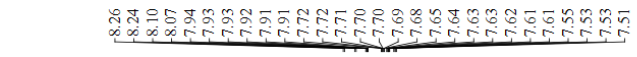
C23

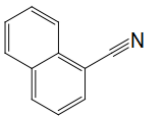

7.47
7.46
7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.39
5.91
5.86
N
C24
6.09
1.00
f1 (ppm)


150.60
133.54
131.23
129.13
127.37
118.15
96.37
N
C24
f1 (ppm)

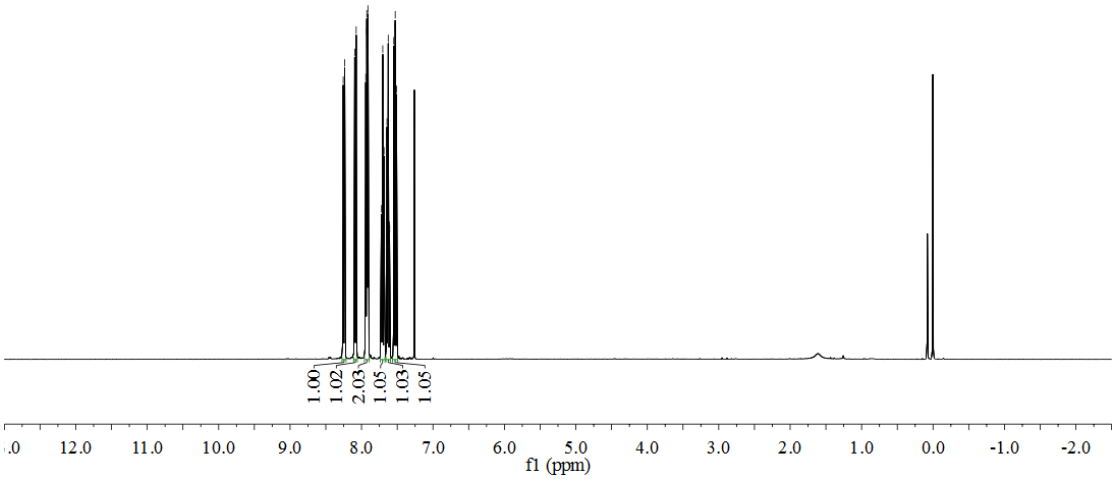

8.23
7.93
7.91
7.88
7.67
7.67
7.65
7.65
7.65
7.63
7.63
7.62
7.62
7.62
7.60
7.60
7.60
7.59
7.59
N
C25
1.00
3.05
3.04
f1 (ppm)

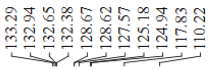

134.66
134.17
132.26
129.21
129.05
128.42
128.06
127.67
126.36
119.27
109.39
N
C25
f1 (ppm)

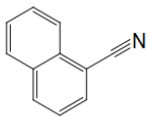

8.26
8.24
8.10
8.07
7.94
7.93
7.93
7.92
7.91
7.91
7.72
7.72
7.71
7.70
7.70
7.69
7.68
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.55
7.53
7.53
7.51


N

C26

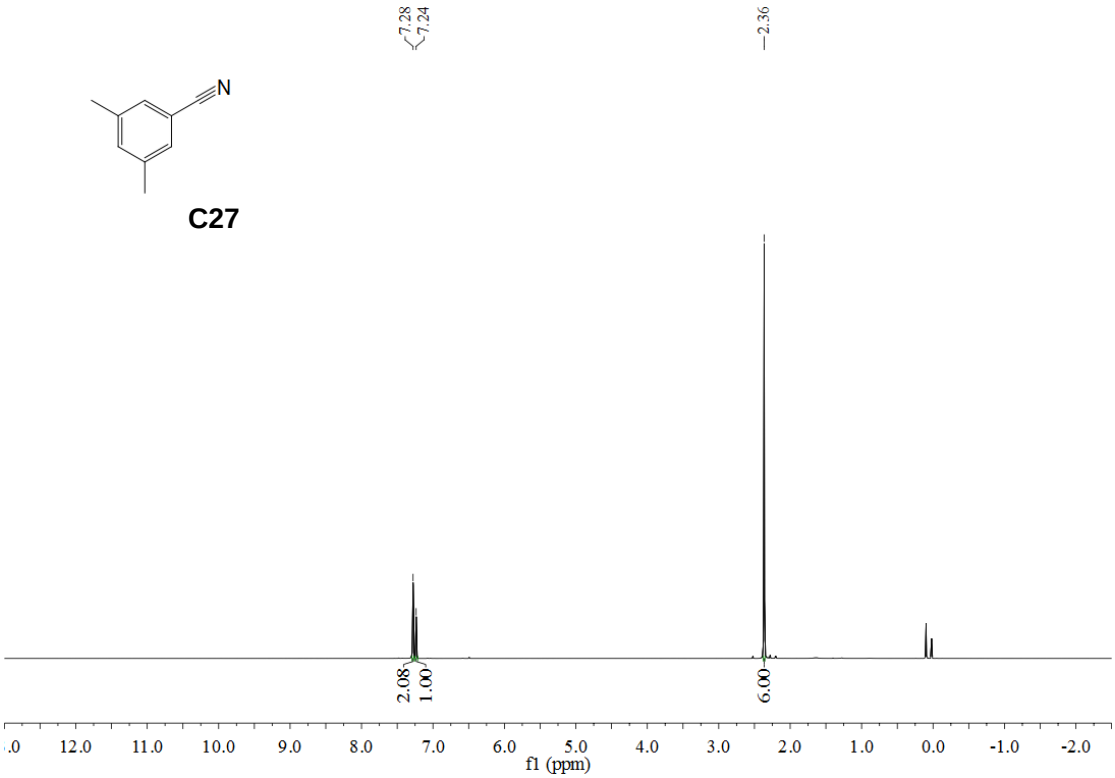

1.00
1.02
2.03
1.05
1.03
1.05
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

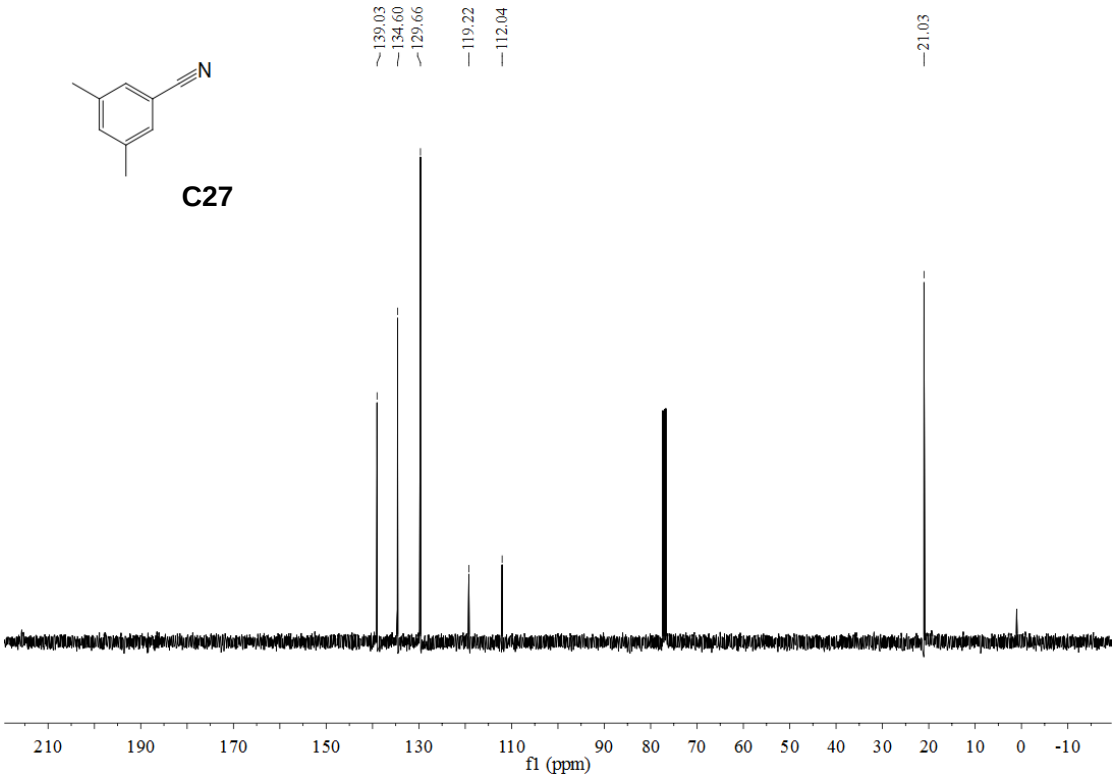

133.29
132.94
132.65
132.38
128.67
128.62
127.57
125.18
124.94
117.83
110.22

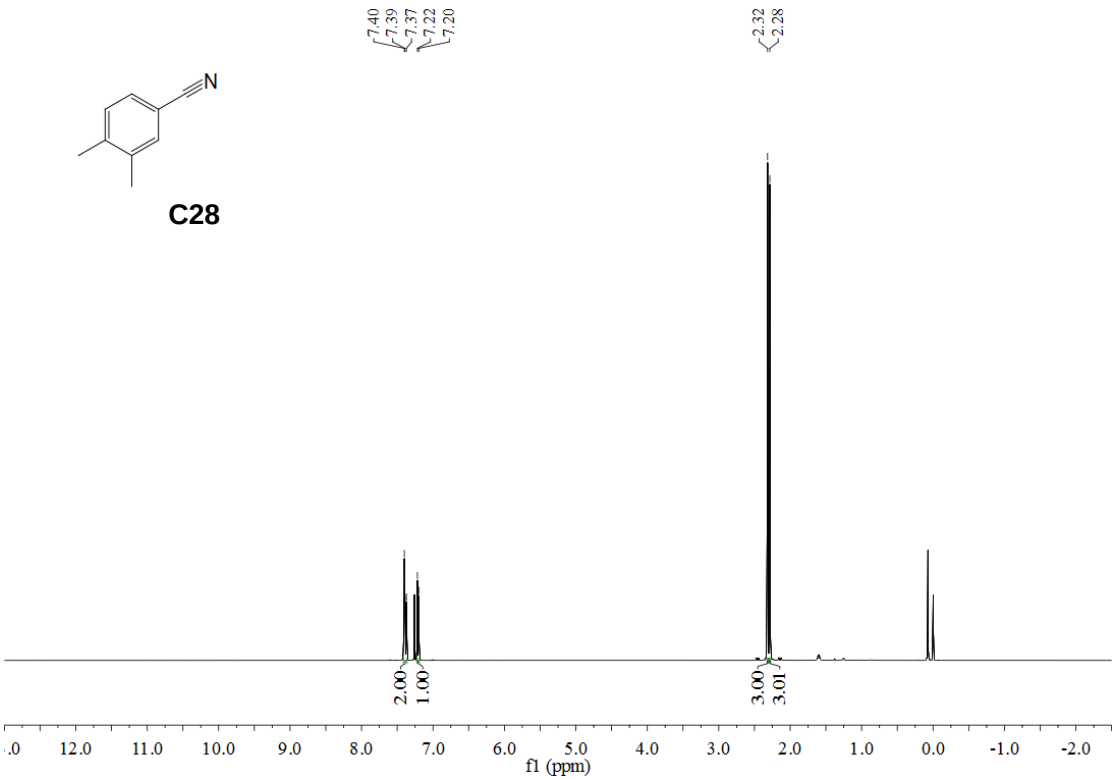

N

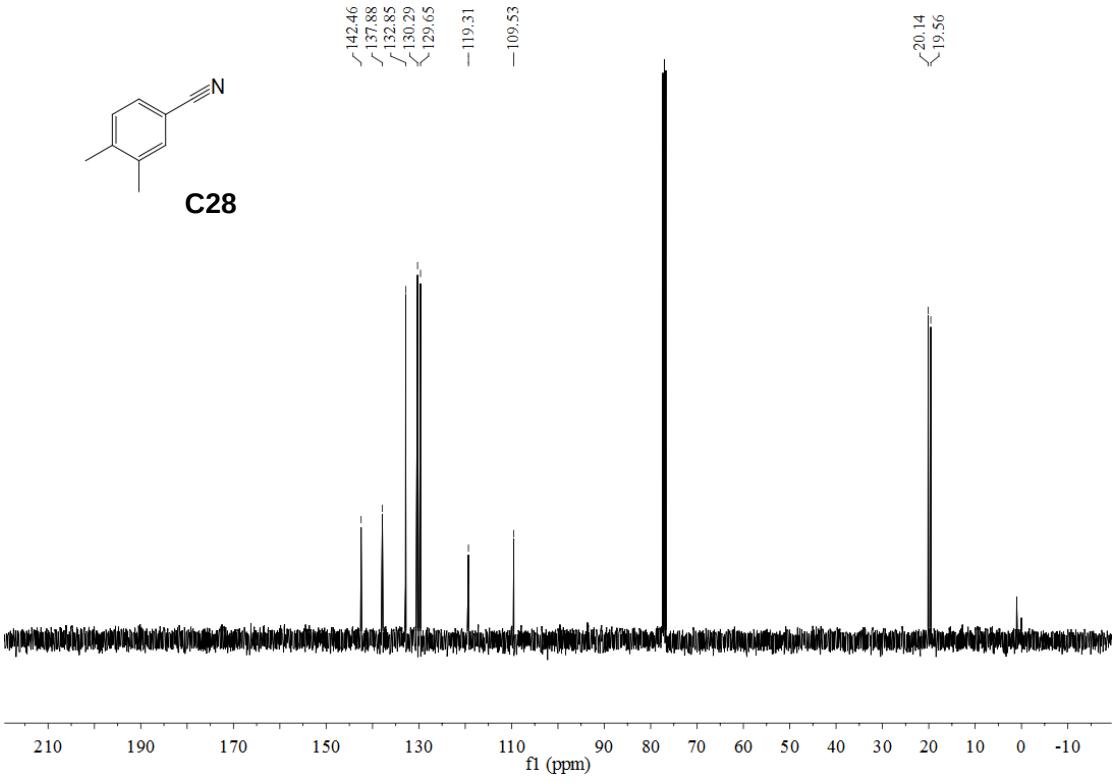
C26

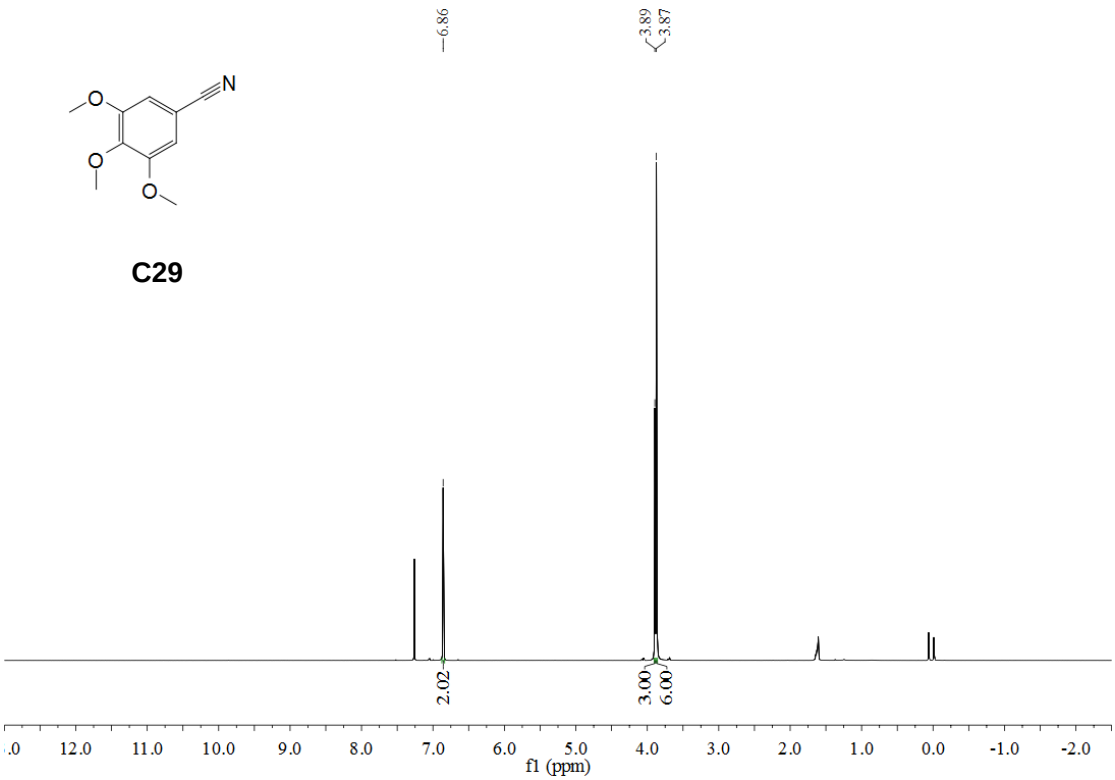
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

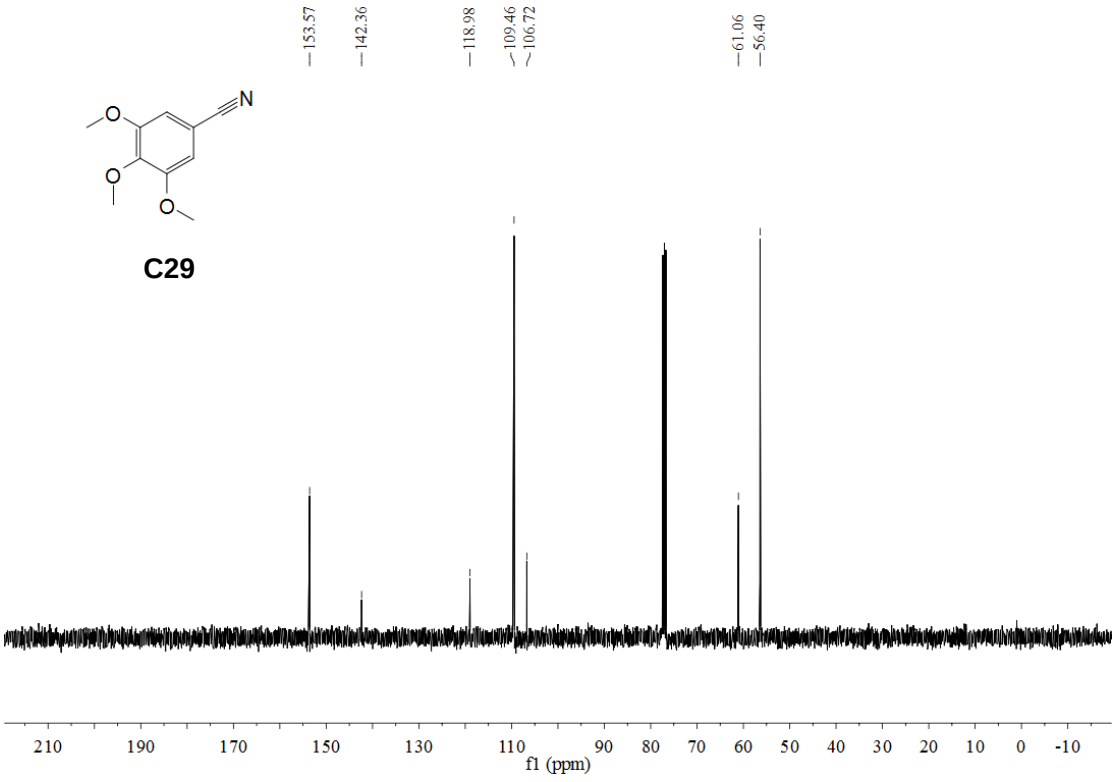

7.28
7.24
2.36
N
C27
2.08
1.00
6.00
f1 (ppm)

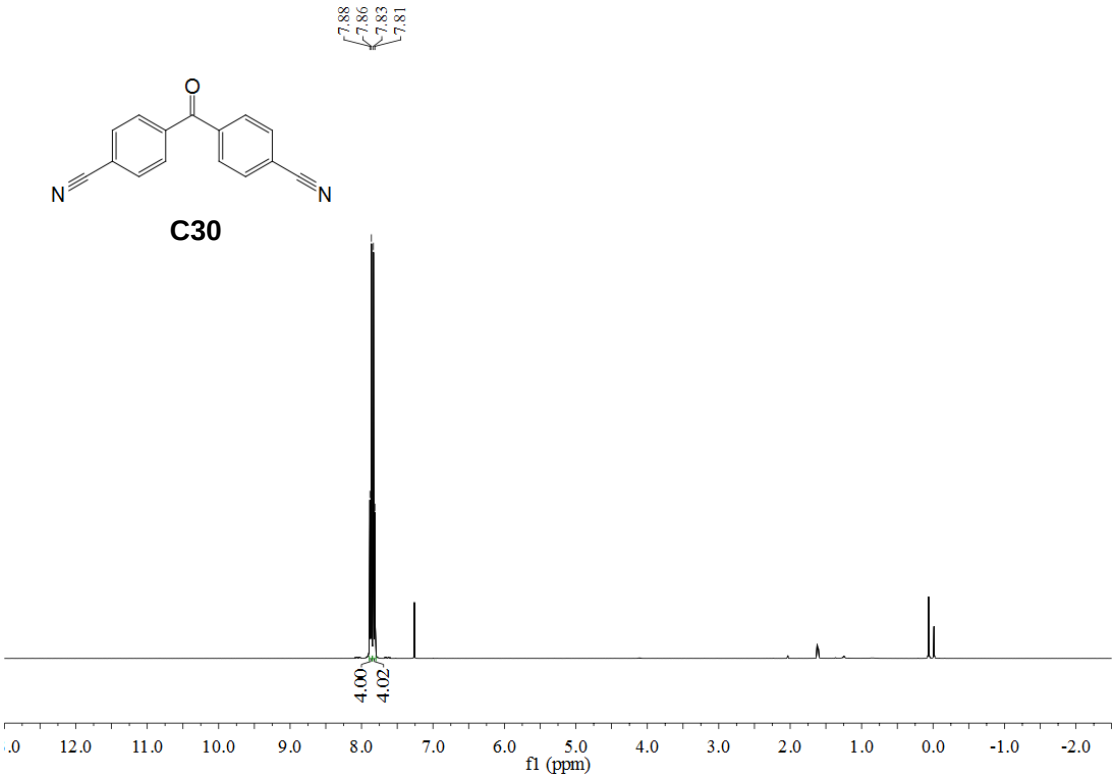

139.03
134.60
129.66
119.22
112.04
21.03
N
C27
f1 (ppm)

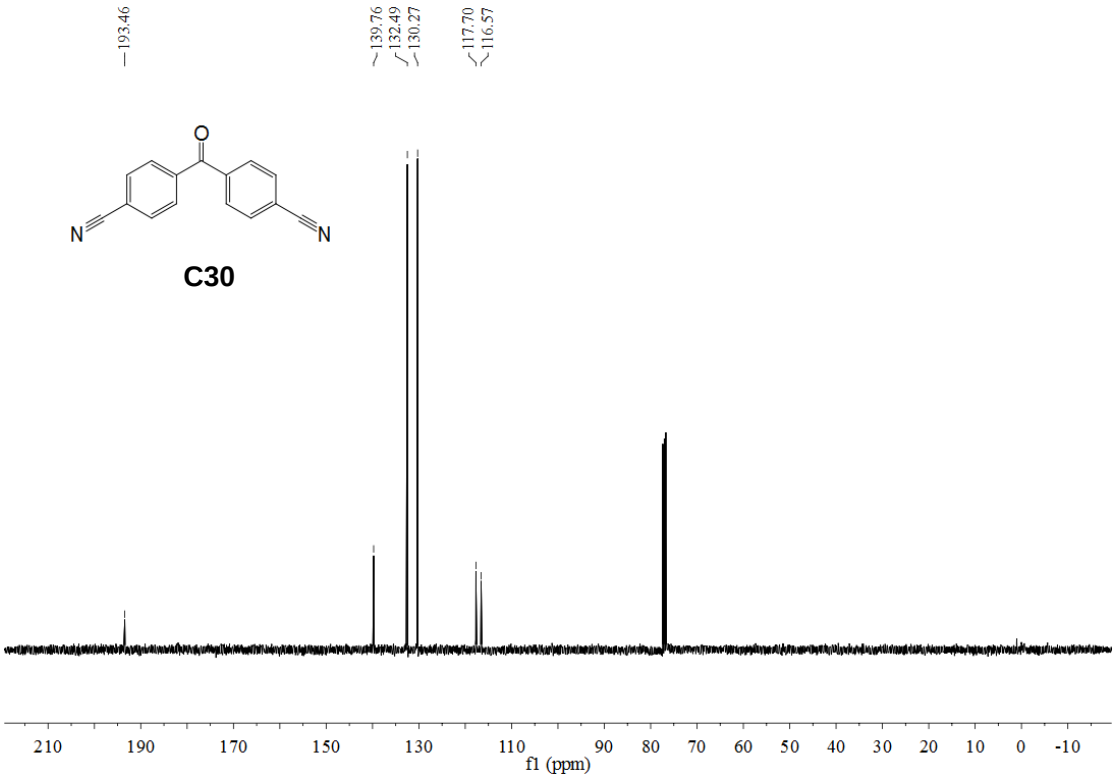

7.40
7.39
7.37
7.22
7.20
2.32
2.28
N
C28
2.00
1.00
3.00
3.01
f1 (ppm)

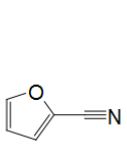

142.46
137.88
132.85
130.29
129.65
119.31
109.53
20.14
19.56
N
C28
f1 (ppm)


6.86
3.89
3.87
N
O
O
O
C29
2.02
3.00
6.00
f1 (ppm)


153.57
142.36
118.98
109.46
106.72
61.06
56.40
N
O
O
O
C29
f1 (ppm)

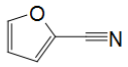

7.88
7.86
7.83
7.81
O
N
N
C30
4.00
4.02
.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)


193.46
139.76
132.49
130.27
117.70
116.57
O
N
N
C30
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



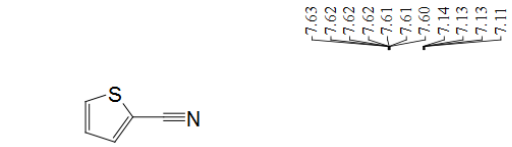
C31

7.59
7.59
7.11
7.10
6.54
6.54
6.53
6.53
1.00
1.00
1.01
f1 (ppm)

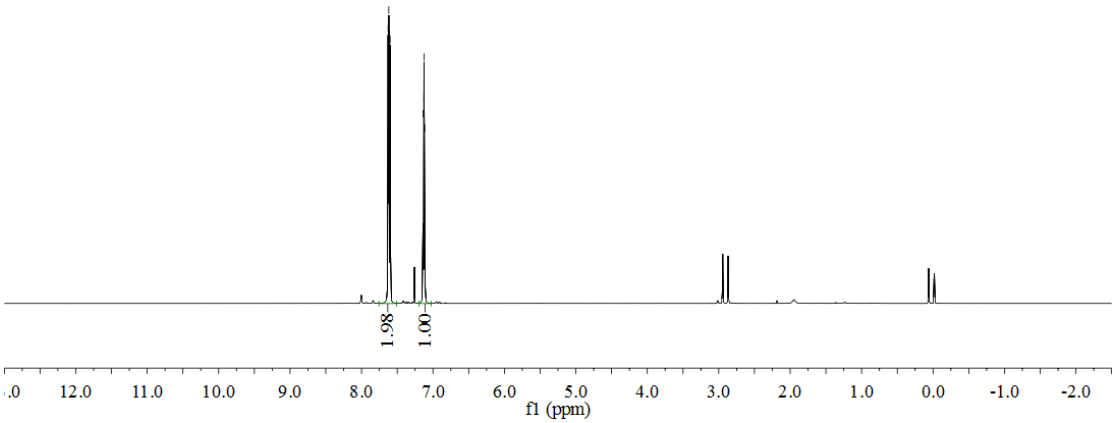


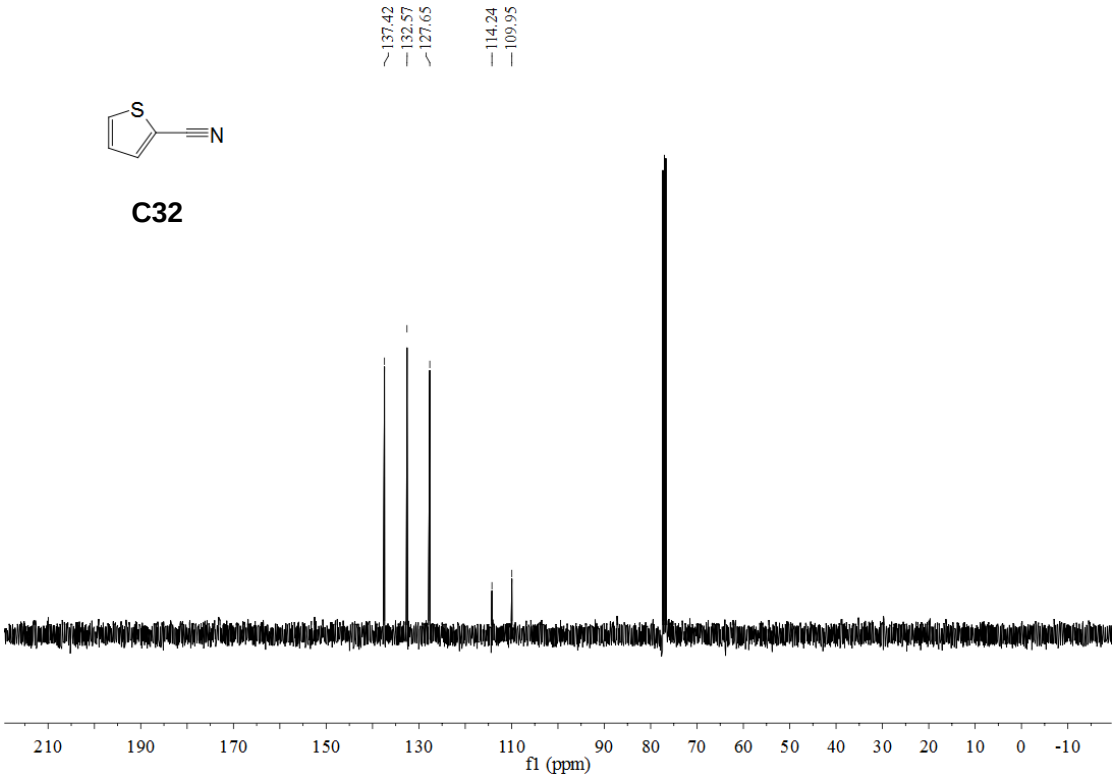
C31

147.34
126.34
121.99
111.58
111.45
f1 (ppm)

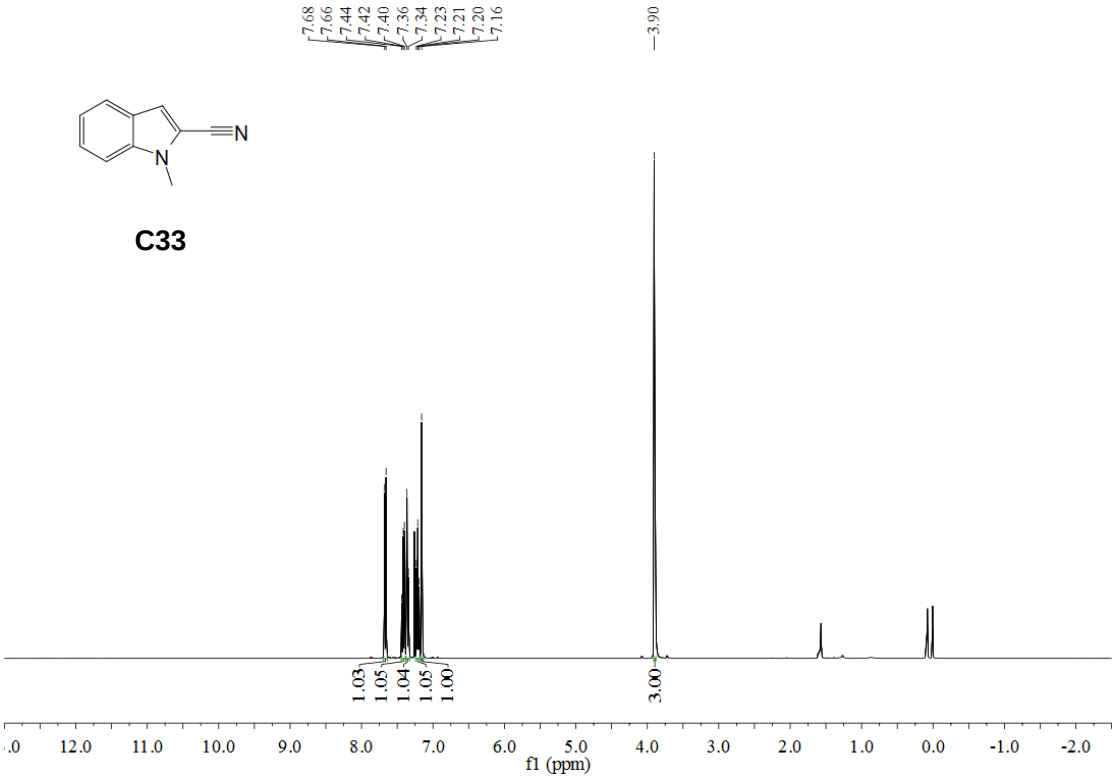

7.63
7.62
7.62
7.62
7.61
7.61
7.60
7.14
7.13
7.13
7.11
S
N

C32

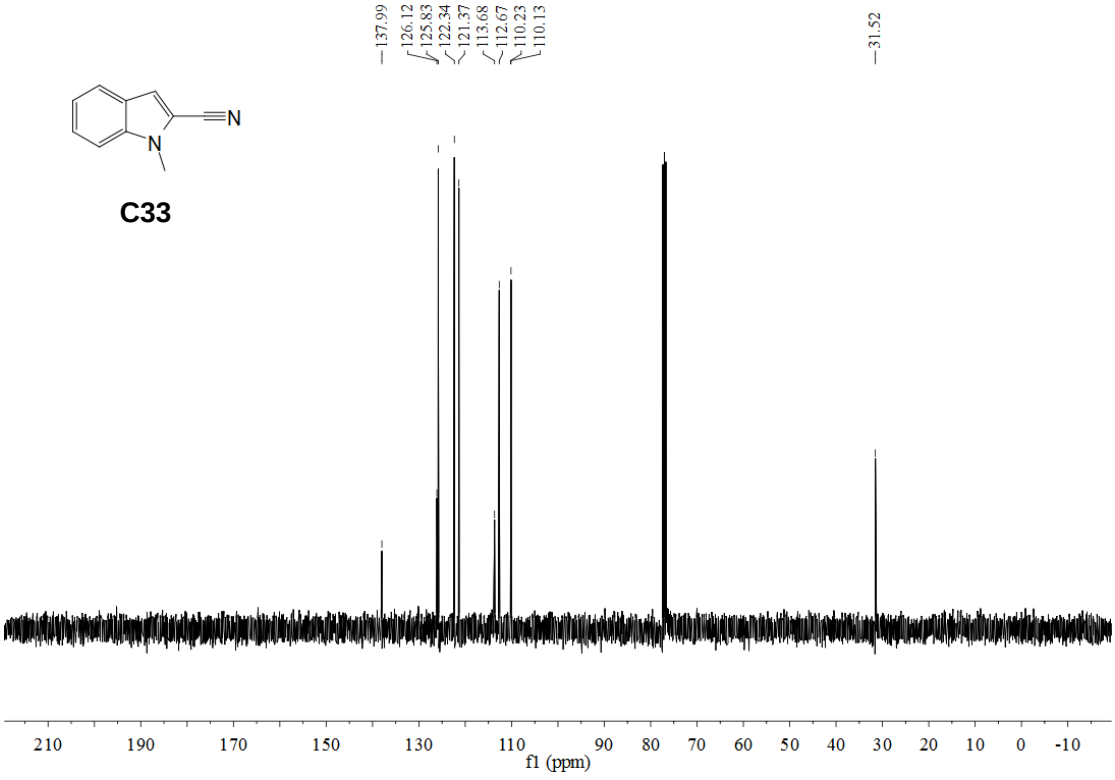

1.98
1.00
.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)


137.42
132.57
127.65
114.24
109.95
S
N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

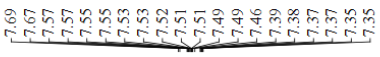
C32

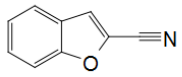

7.68
7.66
7.44
7.42
7.40
7.36
7.34
7.23
7.21
7.20
7.16
3.90
N
N
1.03
1.05
1.04
1.05
1.00
3.00
f1 (ppm)

C33

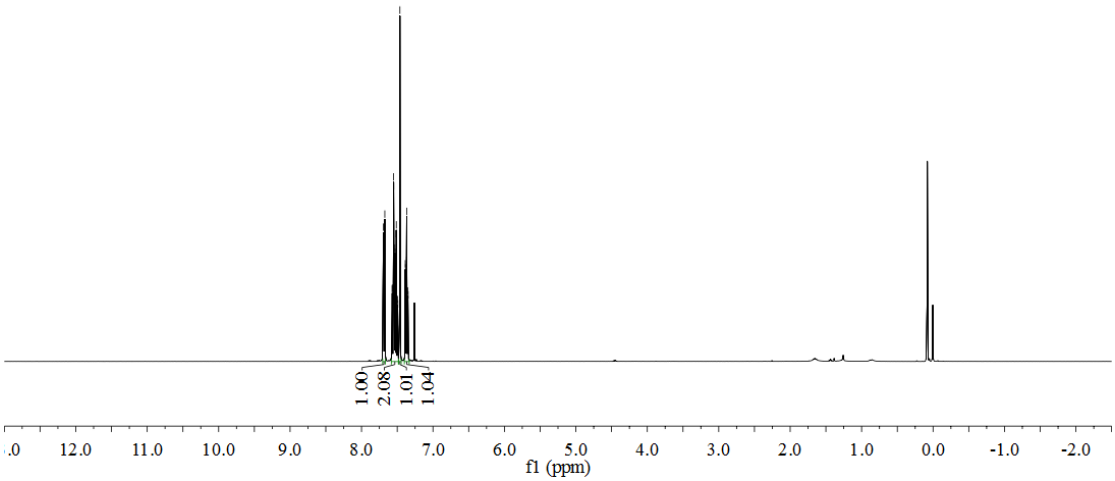

137.99
126.12
125.83
122.34
121.37
113.68
112.67
110.23
110.13
31.52
N
N
f1 (ppm)

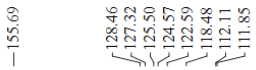
C33

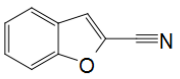

7.69
7.67
7.57
7.57
7.55
7.55
7.53
7.53
7.52
7.51
7.51
7.49
7.49
7.46
7.39
7.38
7.37
7.37
7.35
7.35


N
O

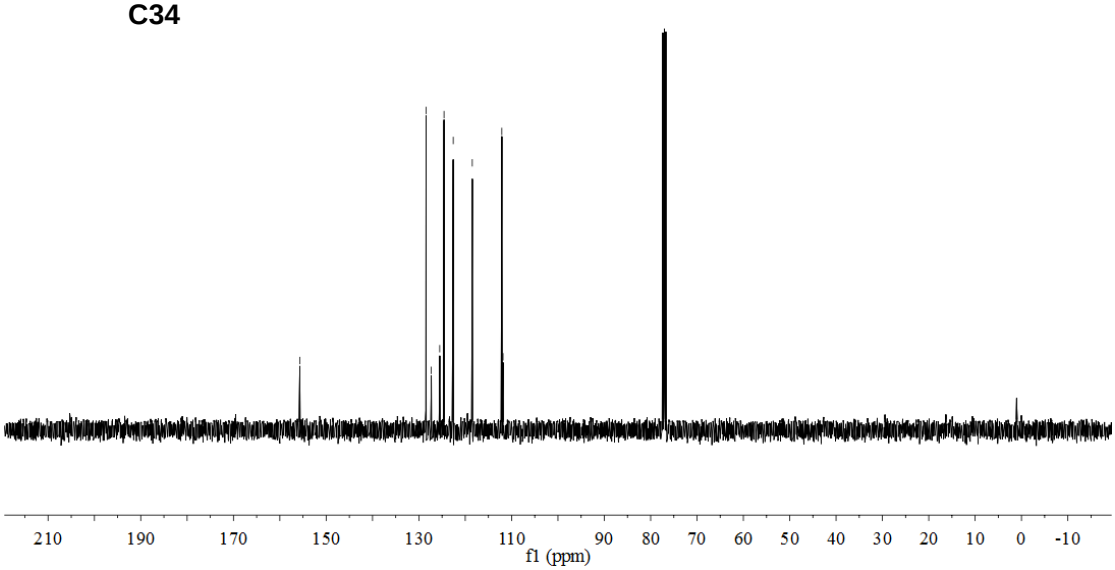
C34

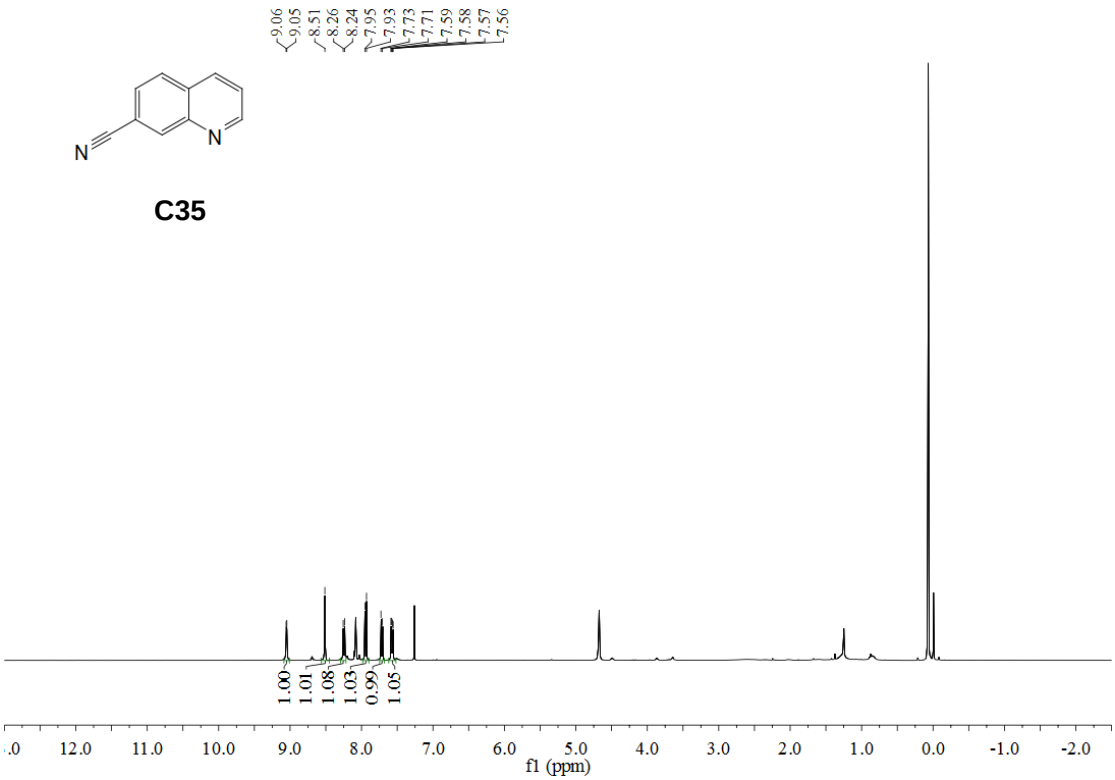

1.00
2.08
1.01
1.04
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)


155.69
128.46
127.32
125.50
124.57
122.59
118.48
112.11
111.85

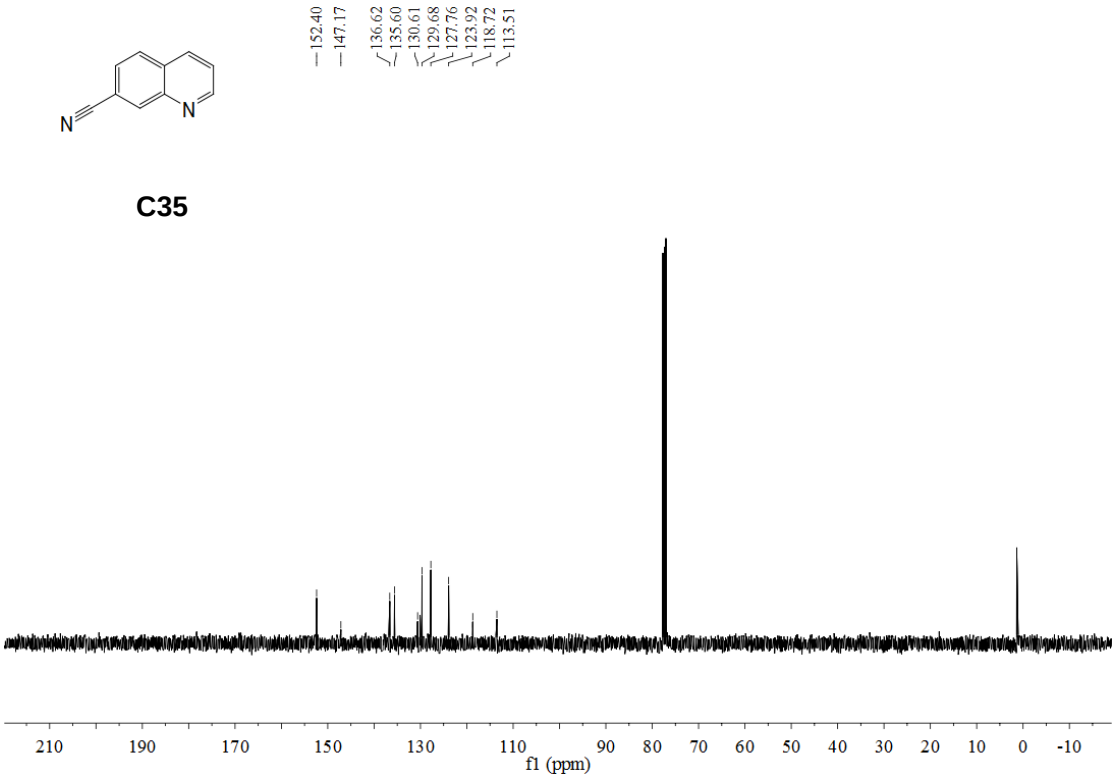

N
O

C34

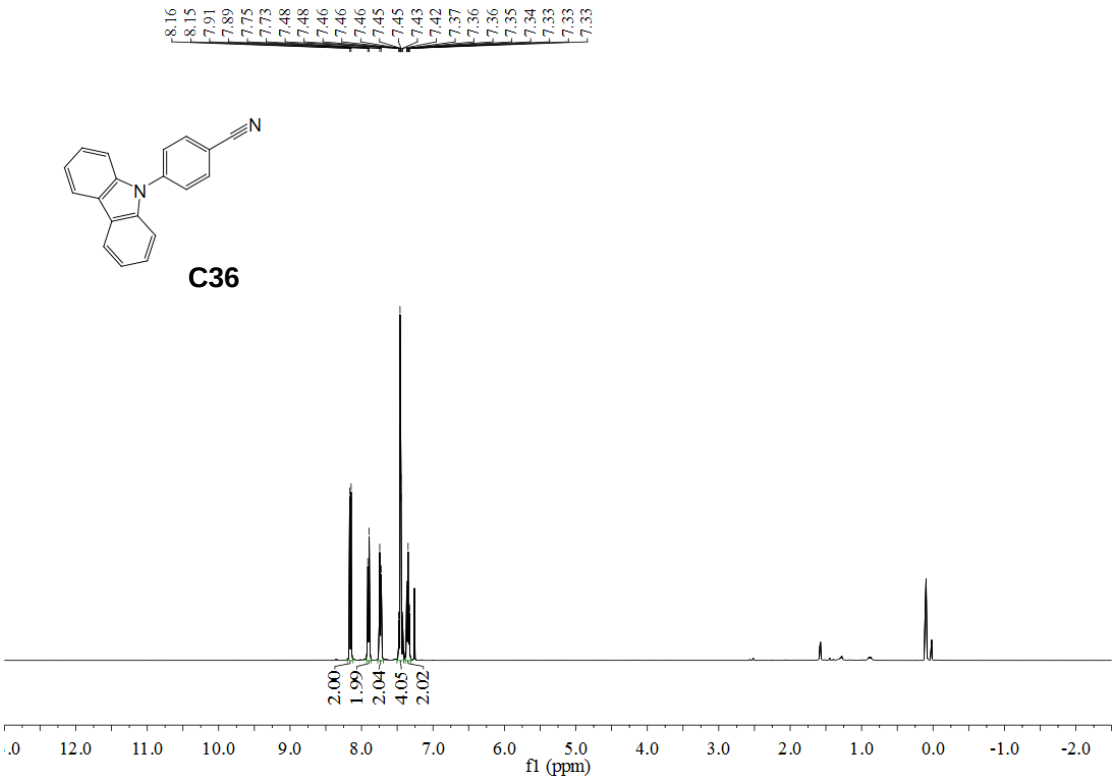

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

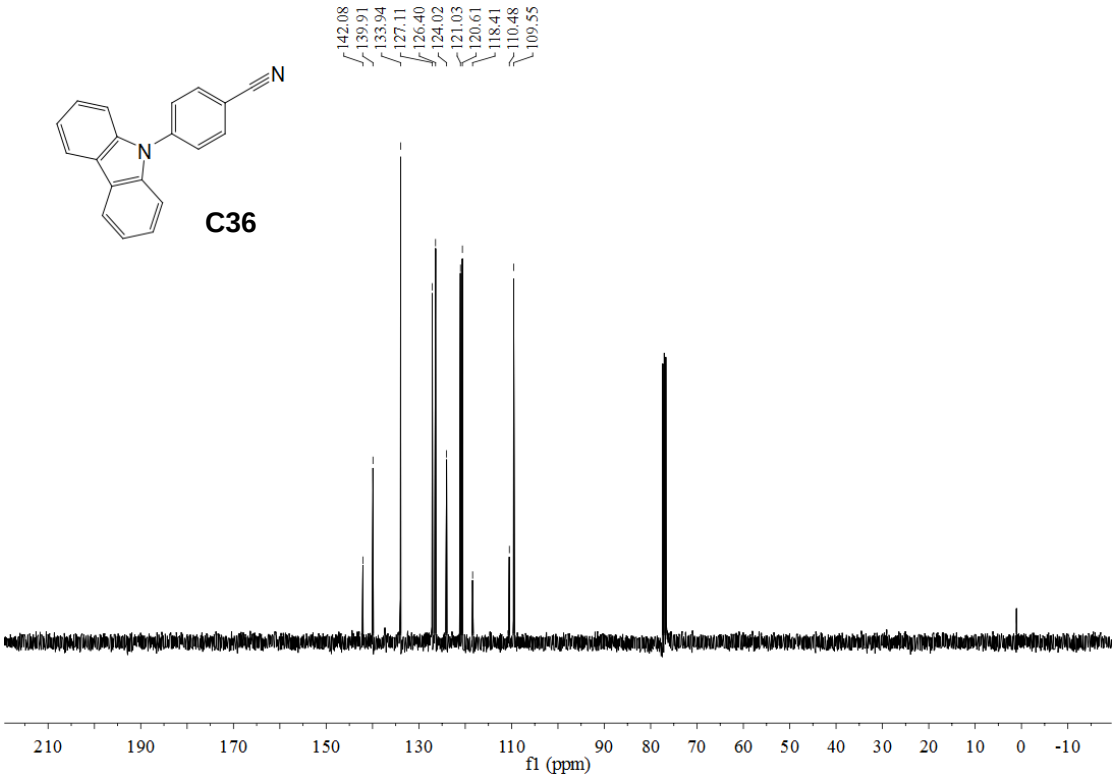

9.06
9.05
8.51
8.26
8.24
7.95
7.93
7.73
7.71
7.59
7.58
7.57
7.56
N
N
1.00
1.01
1.08
1.03
0.99
1.05
f1 (ppm)

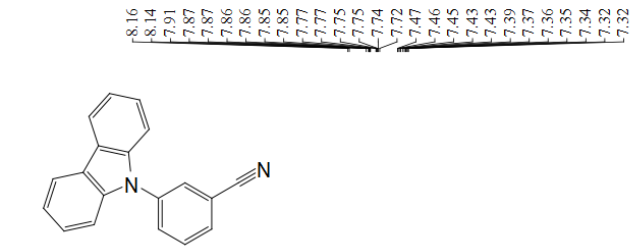
C35


152.40
147.17
136.62
135.60
130.61
129.68
127.76
123.92
118.72
113.51
N
N
f1 (ppm)

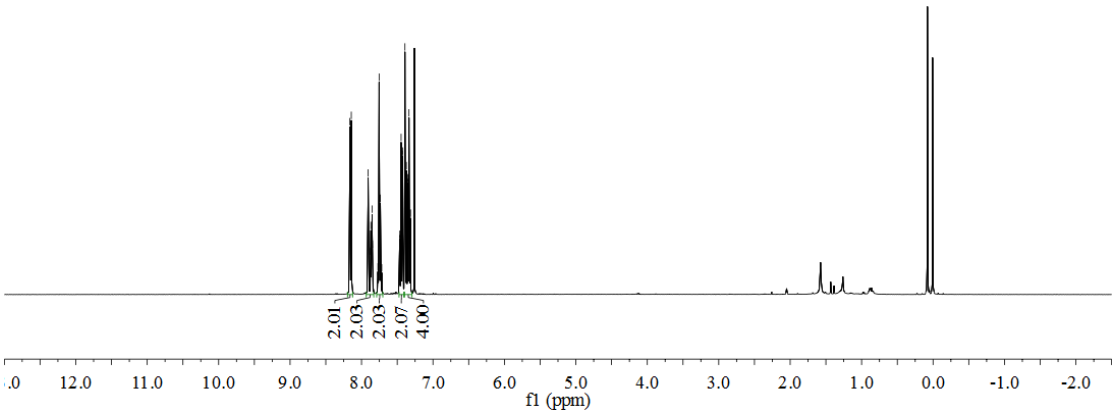
C35

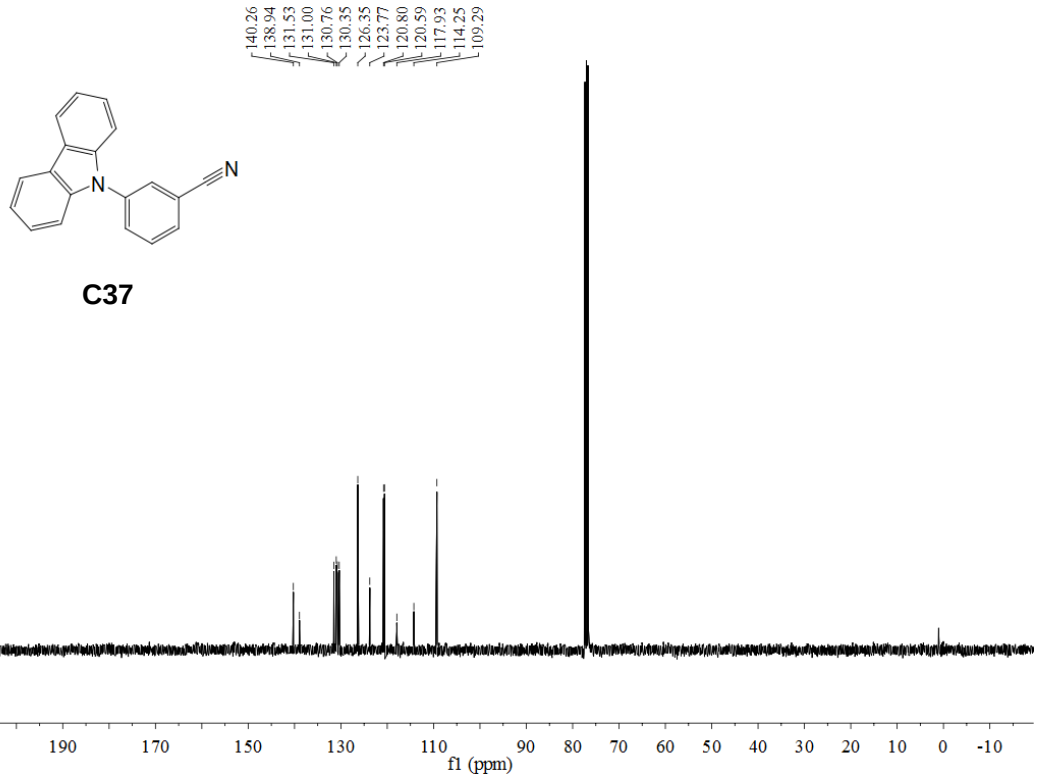

8.16
8.15
7.91
7.89
7.75
7.73
7.48
7.48
7.46
7.46
7.46
7.45
7.45
7.43
7.42
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.33
N
C36
2.00
1.99
2.04
4.05
2.02
f1 (ppm)


142.08
139.91
133.94
127.11
126.40
124.02
121.03
120.61
118.41
110.48
109.55
N
C36
f1 (ppm)

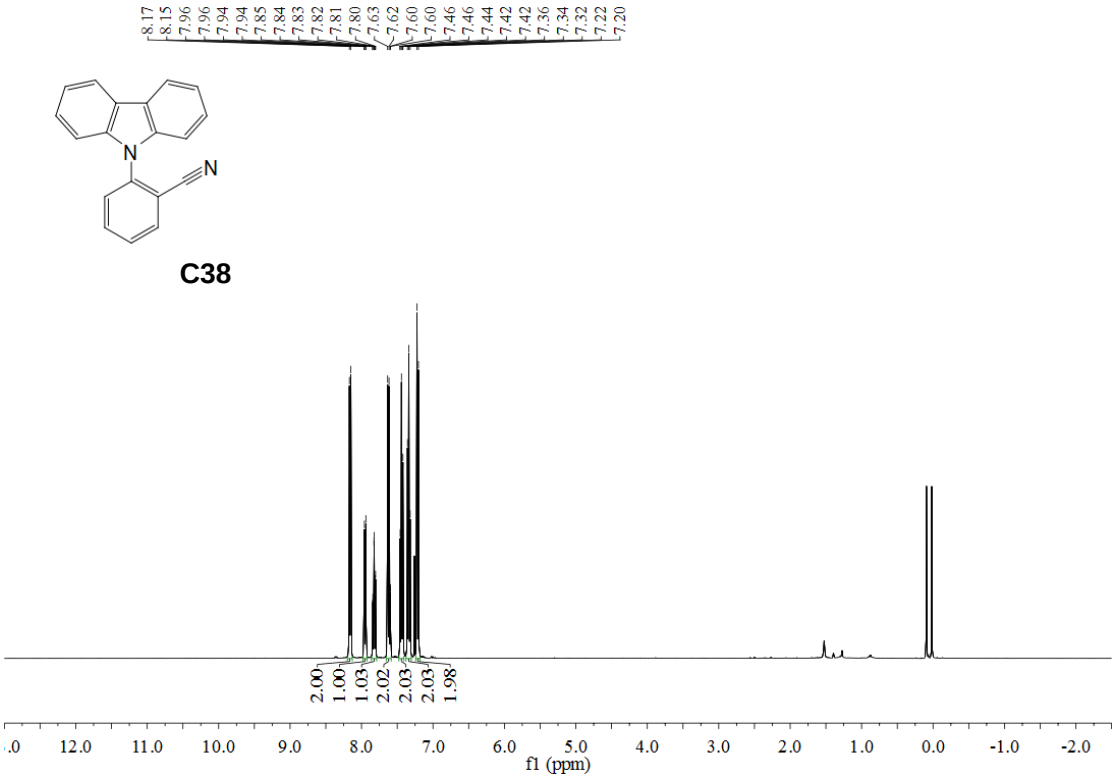

8.16
8.14
7.91
7.87
7.87
7.86
7.86
7.85
7.85
7.77
7.77
7.75
7.75
7.74
7.72
7.47
7.46
7.45
7.43
7.43
7.39
7.37
7.36
7.35
7.34
7.32
7.32
N

C37

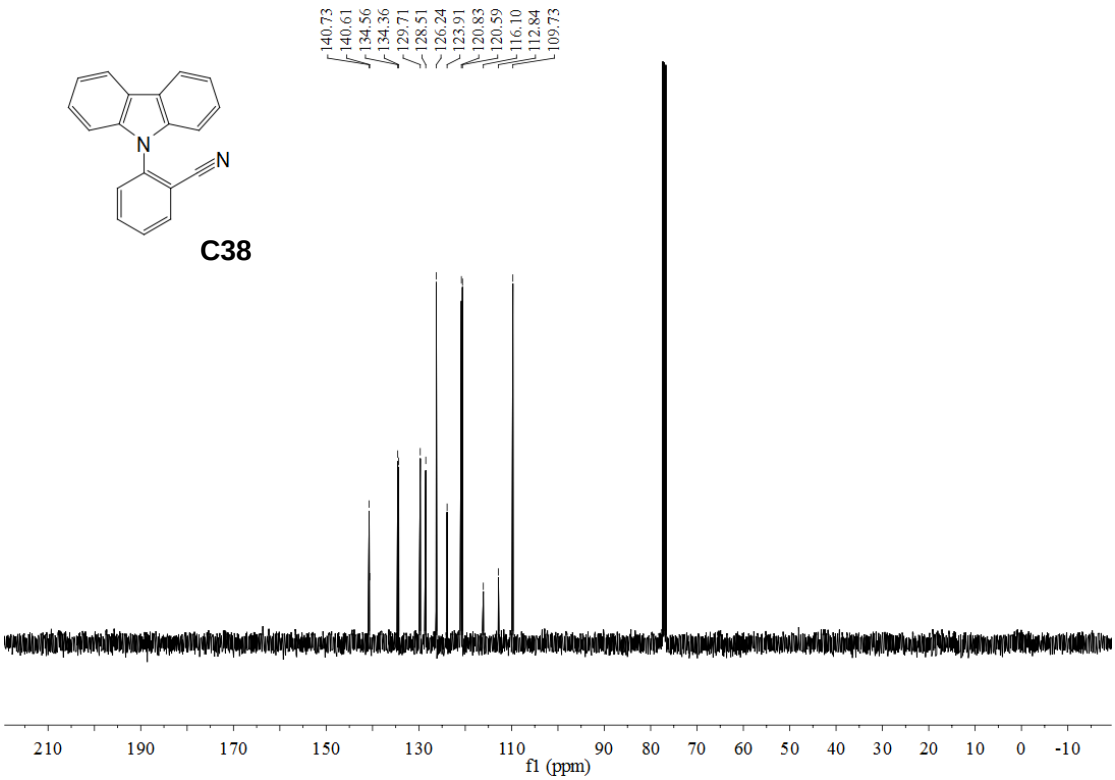

2.01
2.03
2.03
2.07
4.00
f1 (ppm)


140.26
138.94
131.53
131.00
130.76
130.35
126.35
123.77
120.80
120.59
117.93
114.25
109.29
N
f1 (ppm)

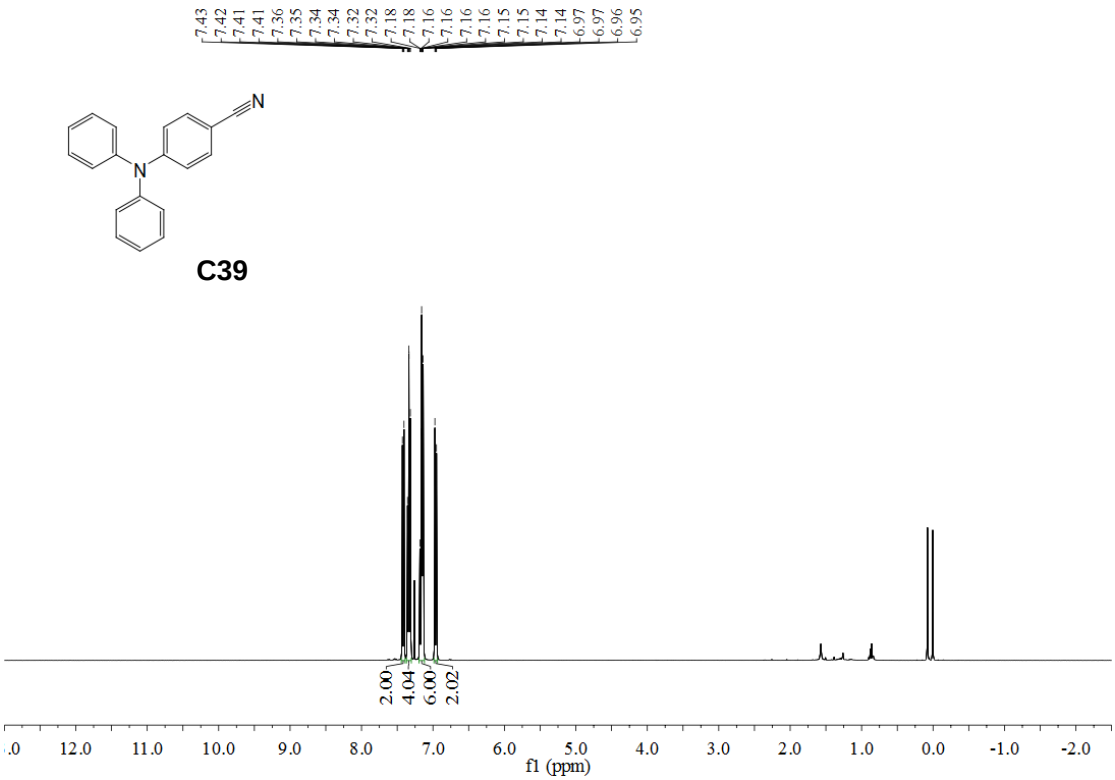
C37

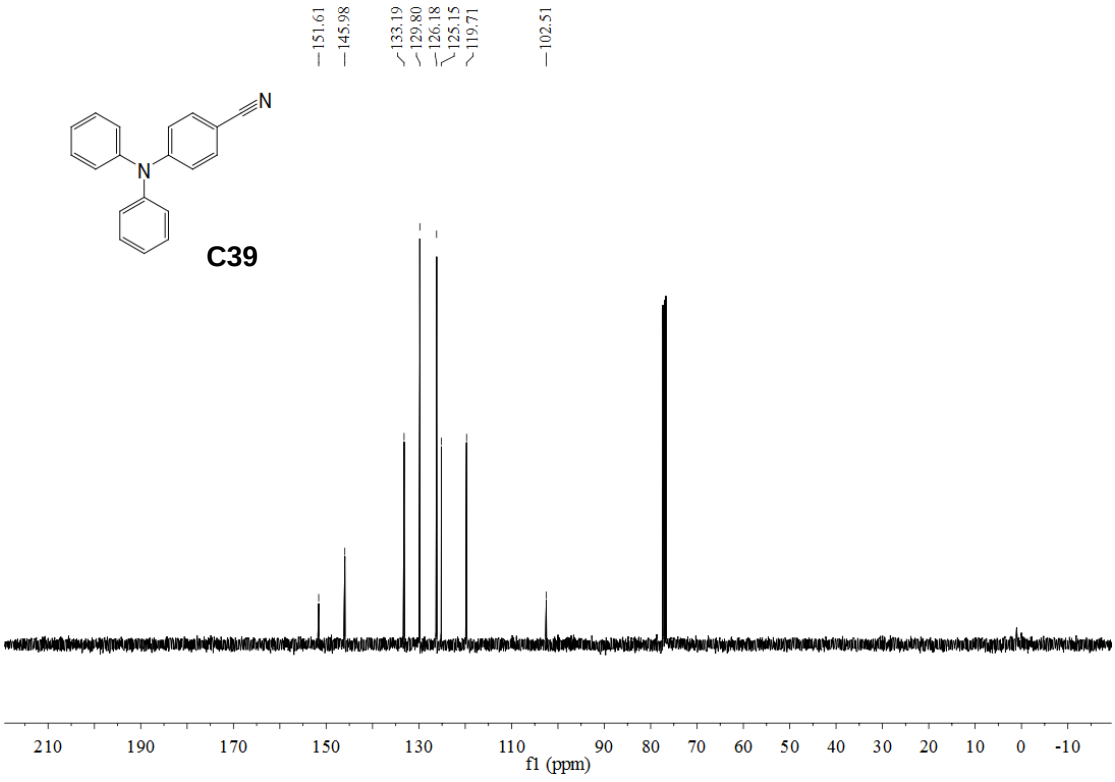

8.17
8.15
7.96
7.96
7.94
7.94
7.85
7.84
7.83
7.82
7.81
7.80
7.63
7.62
7.60
7.60
7.46
7.46
7.44
7.42
7.42
7.36
7.34
7.32
7.22
7.20
N
N
2.00
1.00
1.03
2.02
2.03
2.03
1.98
f1 (ppm)

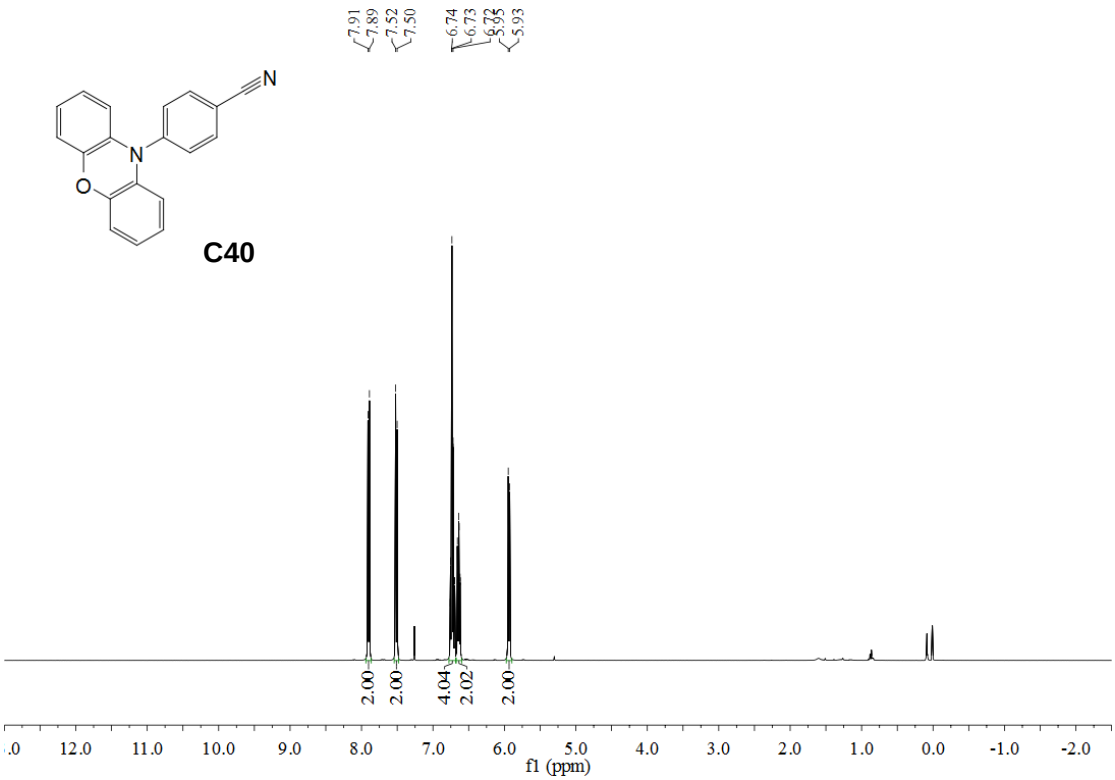
C38

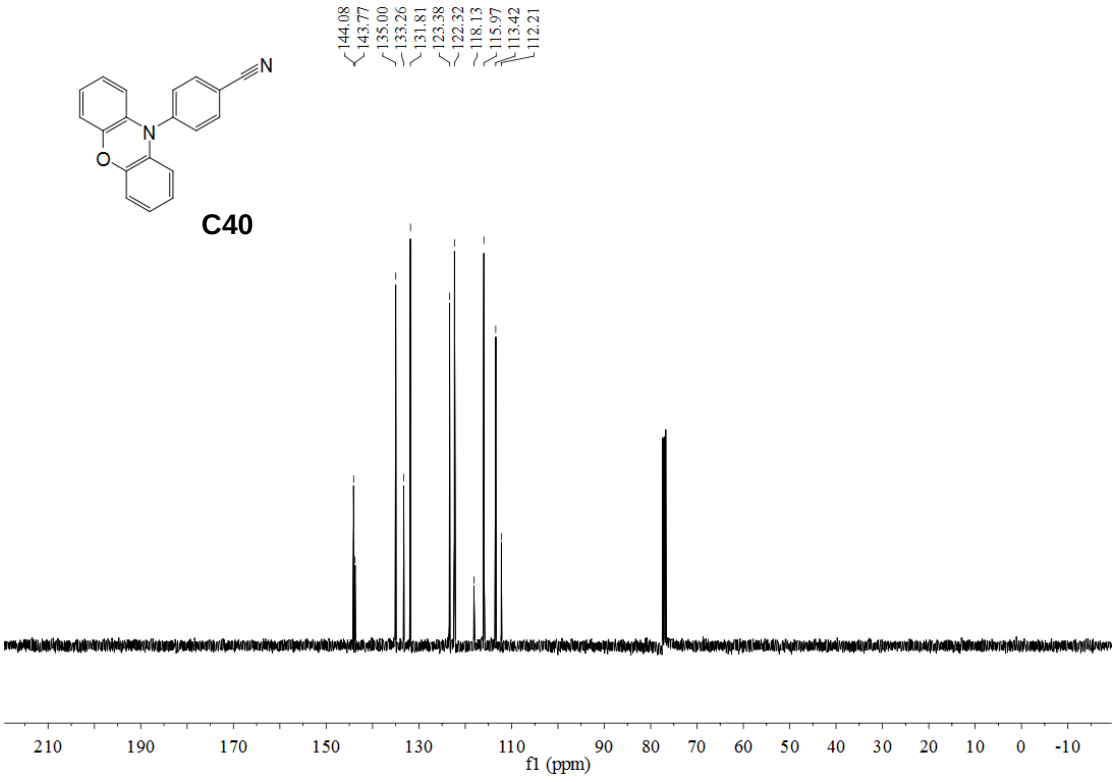

140.73
140.61
134.56
134.36
129.71
128.51
126.24
123.91
120.83
120.59
116.10
112.84
109.73
N
N
f1 (ppm)

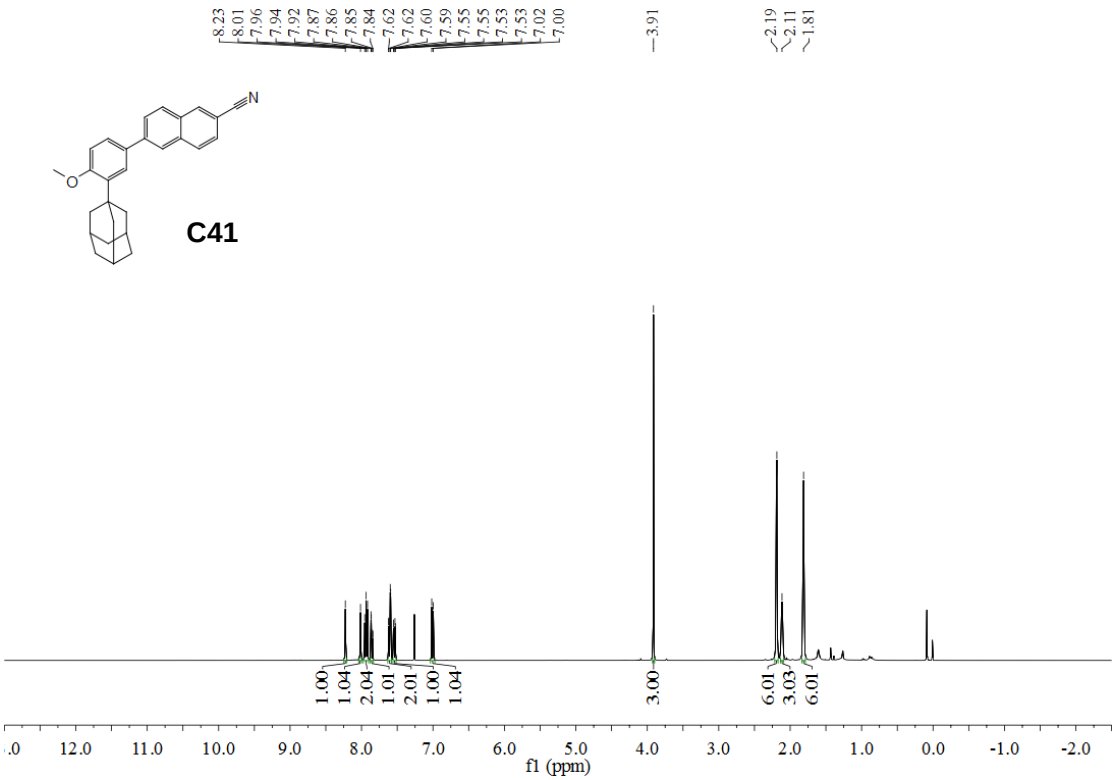
C38

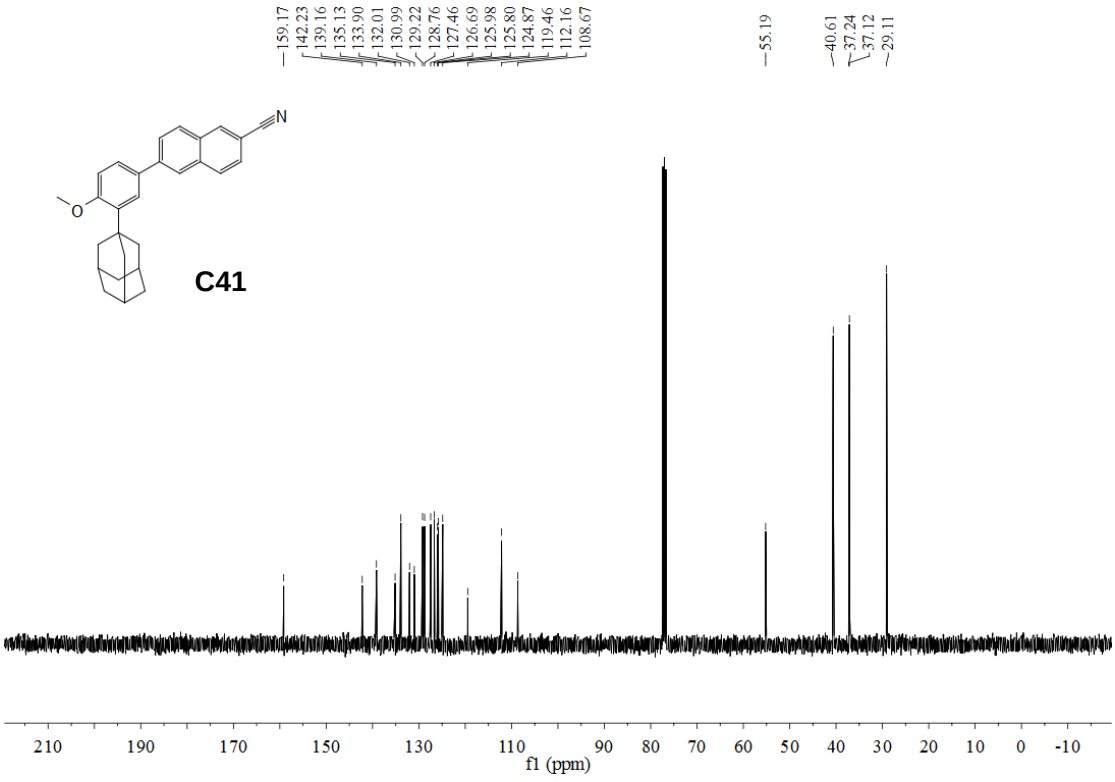

7.43
7.42
7.41
7.41
7.36
7.35
7.34
7.34
7.32
7.32
7.18
7.18
7.16
7.16
7.16
7.16
7.15
7.15
7.14
7.14
6.97
6.97
6.96
6.95
N
N
C39
2.00
4.04
6.00
2.02
f1 (ppm)

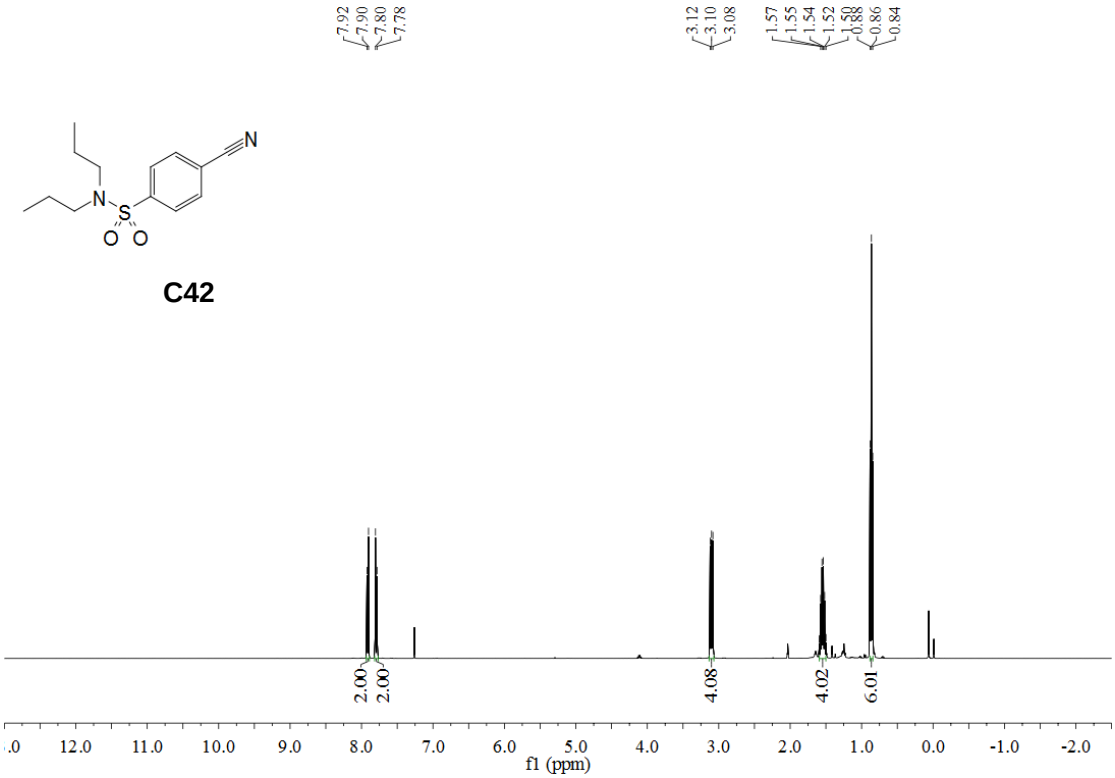

151.61
145.98
133.19
129.80
126.18
125.15
119.71
102.51
N
N
C39
f1 (ppm)


7.91
7.89
7.52
7.50
6.74
6.73
5.95
5.93
N
O
C40
2.00
2.00
4.04
2.02
2.00
f1 (ppm)

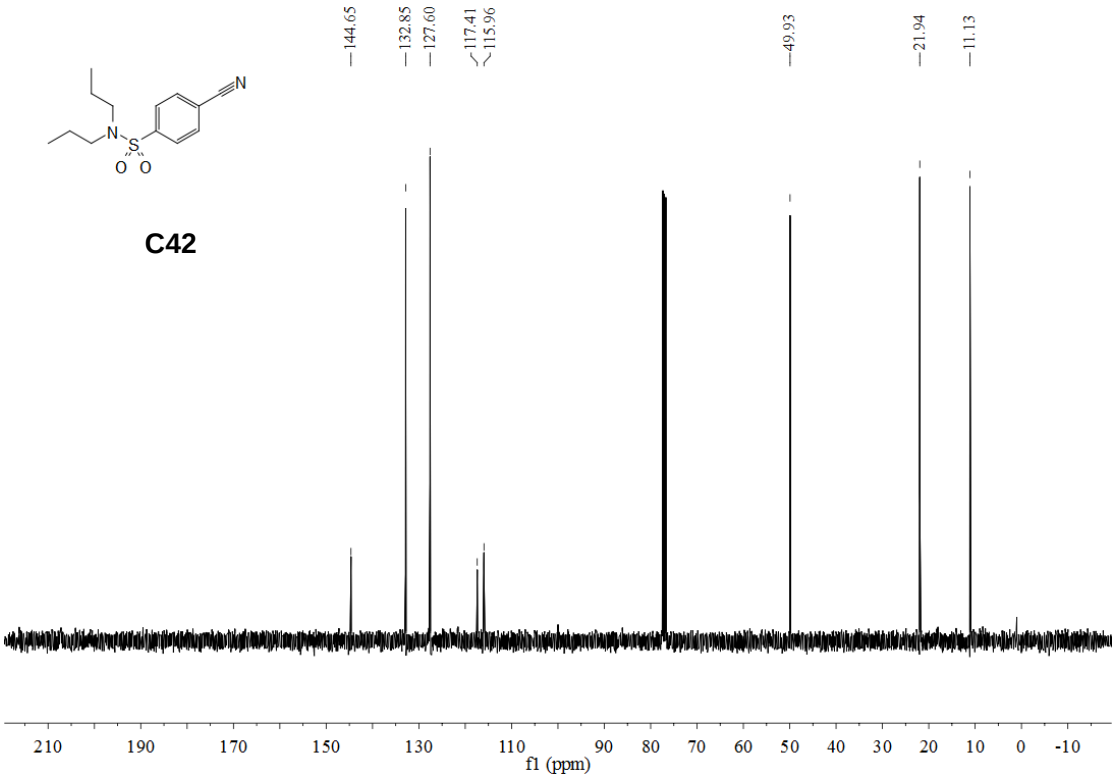

144.08
143.77
135.00
133.26
131.81
123.38
122.32
118.13
115.97
113.42
112.21
N
O
C40
f1 (ppm)


8.23
8.01
7.96
7.94
7.92
7.87
7.86
7.85
7.84
7.62
7.62
7.60
7.59
7.55
7.55
7.53
7.53
7.02
7.00
3.91
2.19
2.11
1.81
N
O
C41
1.00
1.04
2.04
1.01
2.01
1.00
1.04
3.00
6.01
3.03
6.01
f1 (ppm)

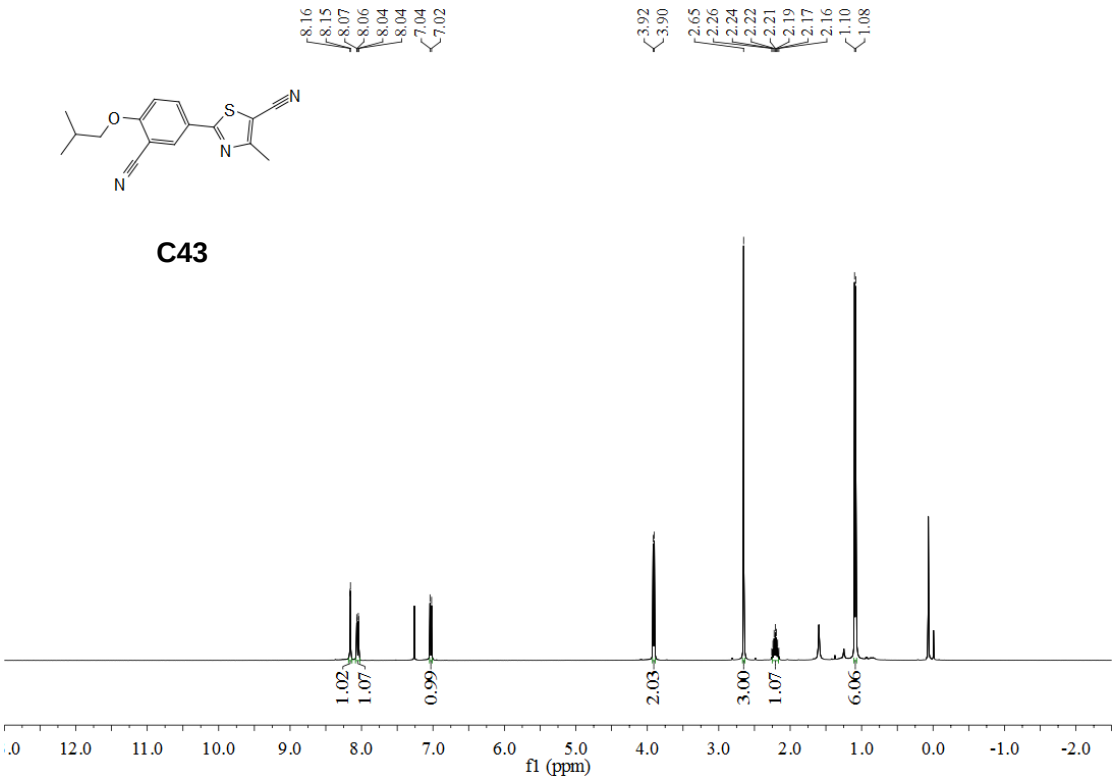

159.17
142.23
139.16
135.13
133.90
132.01
130.99
129.22
128.76
127.46
126.69
125.98
125.80
124.87
119.46
112.16
108.67
55.19
40.61
37.24
37.12
29.11
N
O
C41
f1 (ppm)

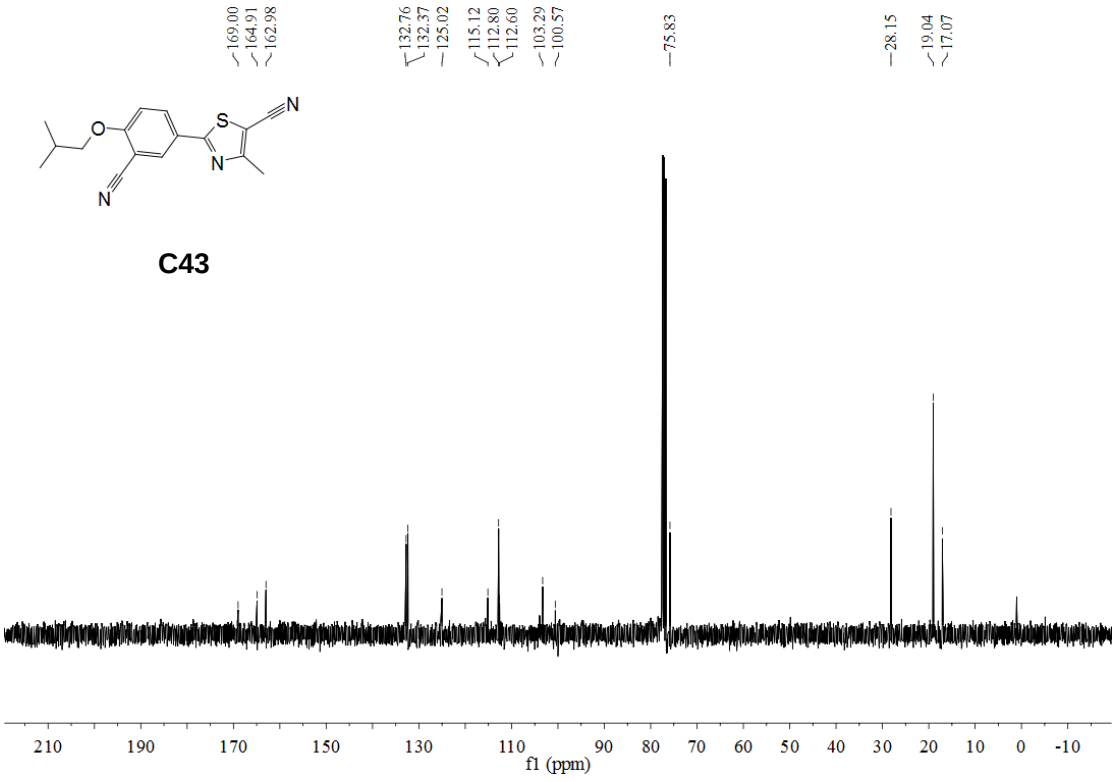

7.92
7.90
7.80
7.78
3.12
3.10
3.08
1.57
1.55
1.54
1.52
0.88
0.86
0.84
N
S
O O
2.00
2.00
4.08
4.02
6.01
f1 (ppm)

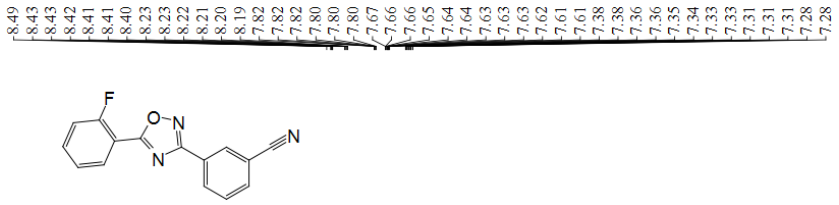
C42


144.65
132.85
127.60
117.41
115.96
49.93
21.94
11.13
N
S
O O
f1 (ppm)

C42

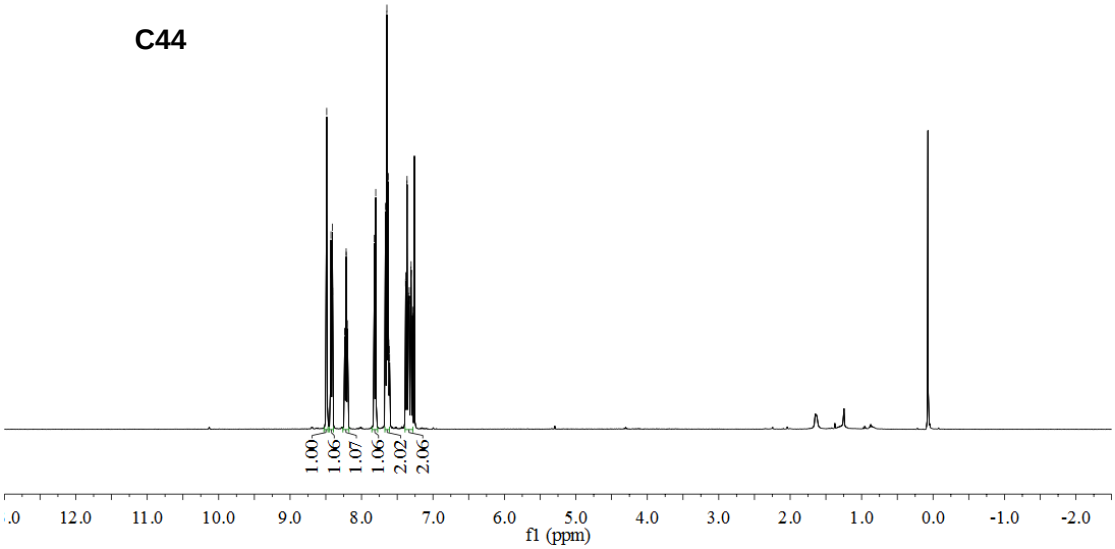

8.16
8.15
8.07
8.06
8.04
8.04
7.04
7.02
3.92
3.90
2.65
2.26
2.24
2.22
2.21
2.19
2.17
2.16
1.10
1.08
O
S
N
N
N
C43
1.02
1.07
0.99
2.03
3.00
1.07
6.06
f1 (ppm)

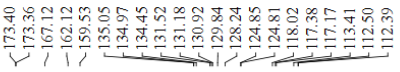

169.00
164.91
162.98
132.76
132.37
125.02
115.12
112.80
112.60
103.29
100.57
75.83
28.15
19.04
17.07
O
S
N
N
N
C43
f1 (ppm)

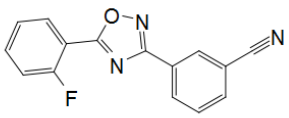

8.49
8.43
8.43
8.42
8.41
8.41
8.40
8.23
8.23
8.22
8.21
8.20
8.19
7.82
7.82
7.82
7.80
7.80
7.80
7.67
7.66
7.66
7.65
7.64
7.64
7.63
7.63
7.63
7.62
7.61
7.61
7.38
7.38
7.36
7.36
7.35
7.34
7.33
7.33
7.31
7.31
7.31
7.28
7.28

F
O
N
N
N

C44

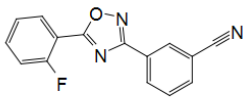

1.00
1.06
1.07
1.06
2.02
2.06
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)


173.40
173.36
167.12
162.12
159.53
135.05
134.97
134.45
131.52
131.18
130.92
129.84
128.24
124.85
124.81
118.02
117.38
117.17
113.41
112.50
112.39


O
N
N
N
F

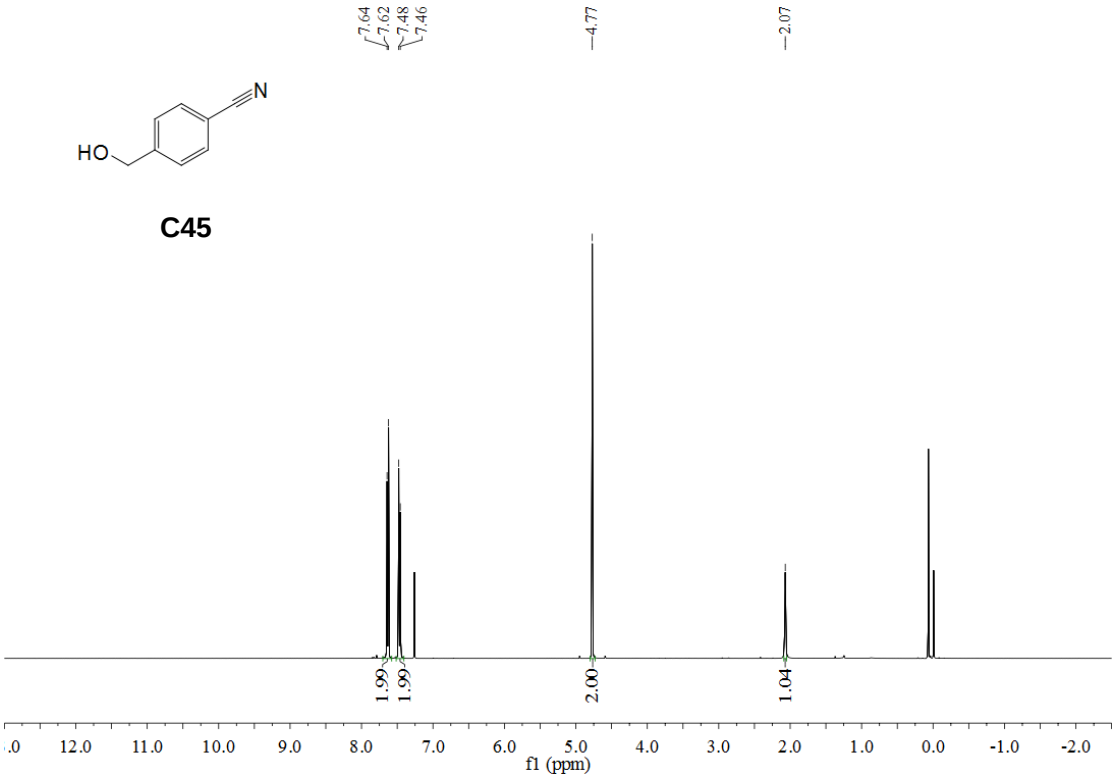
C44

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

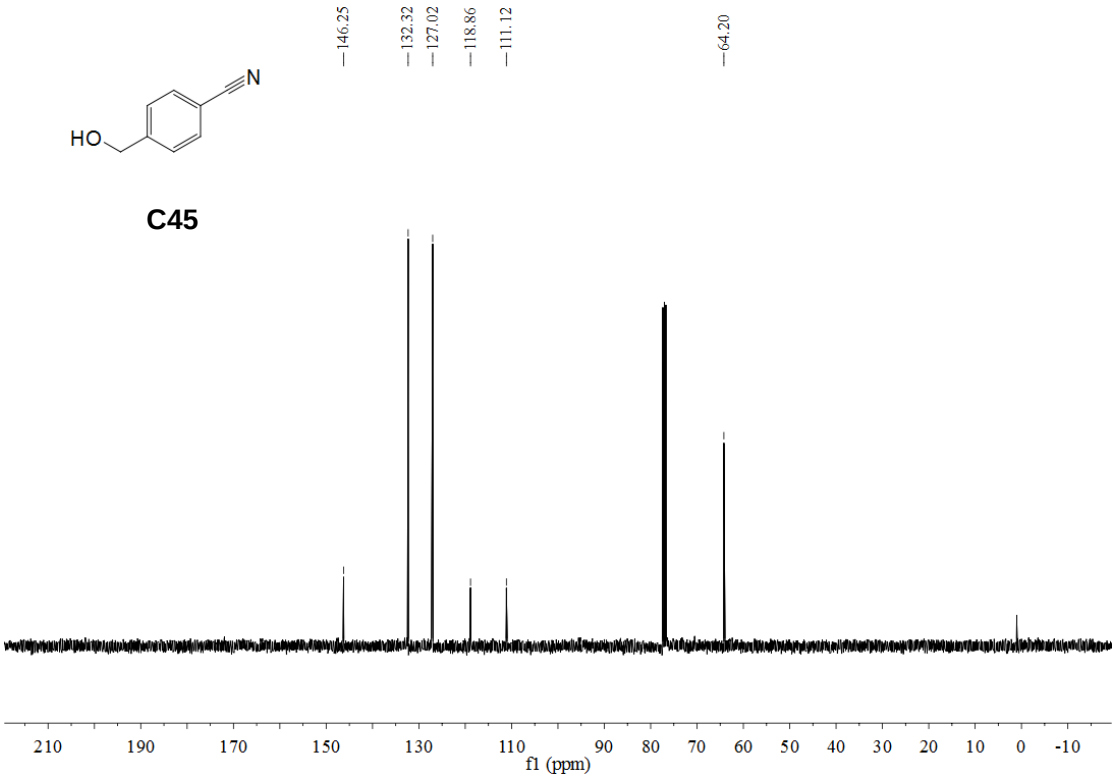

O
N
N
F
N

C44

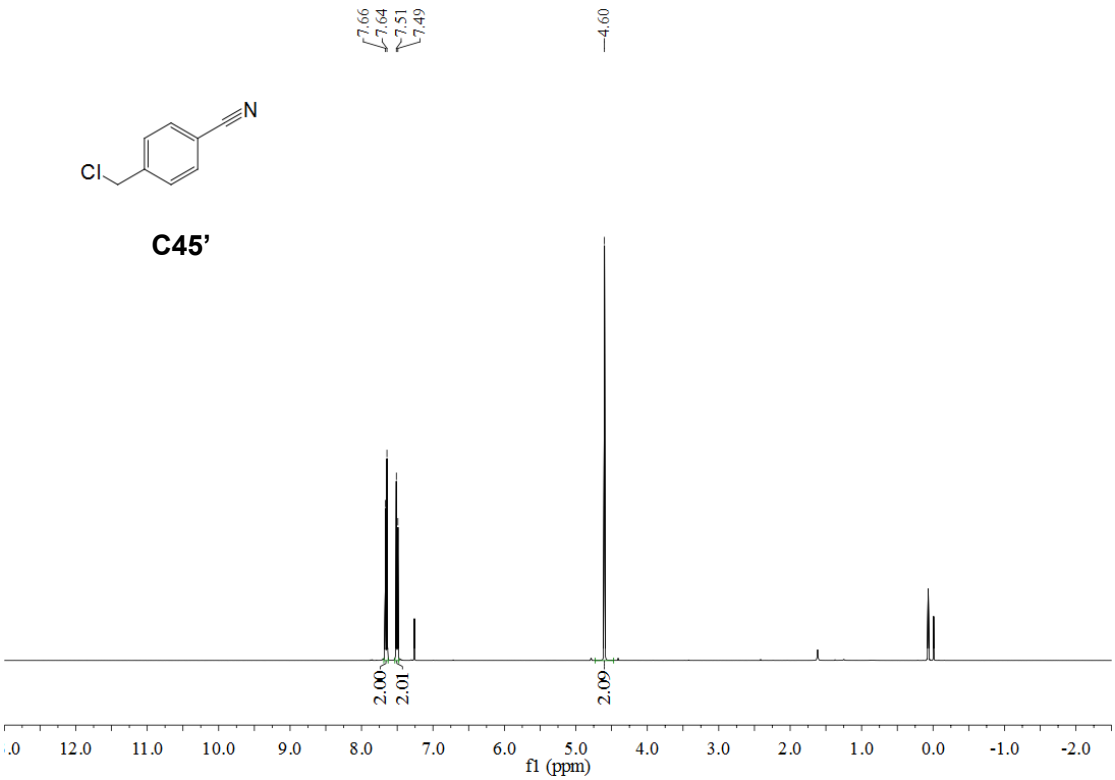
-108.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.64
7.62
7.48
7.46
4.77
2.07
HO
N
1.99
1.99
2.00
1.04
f1 (ppm)

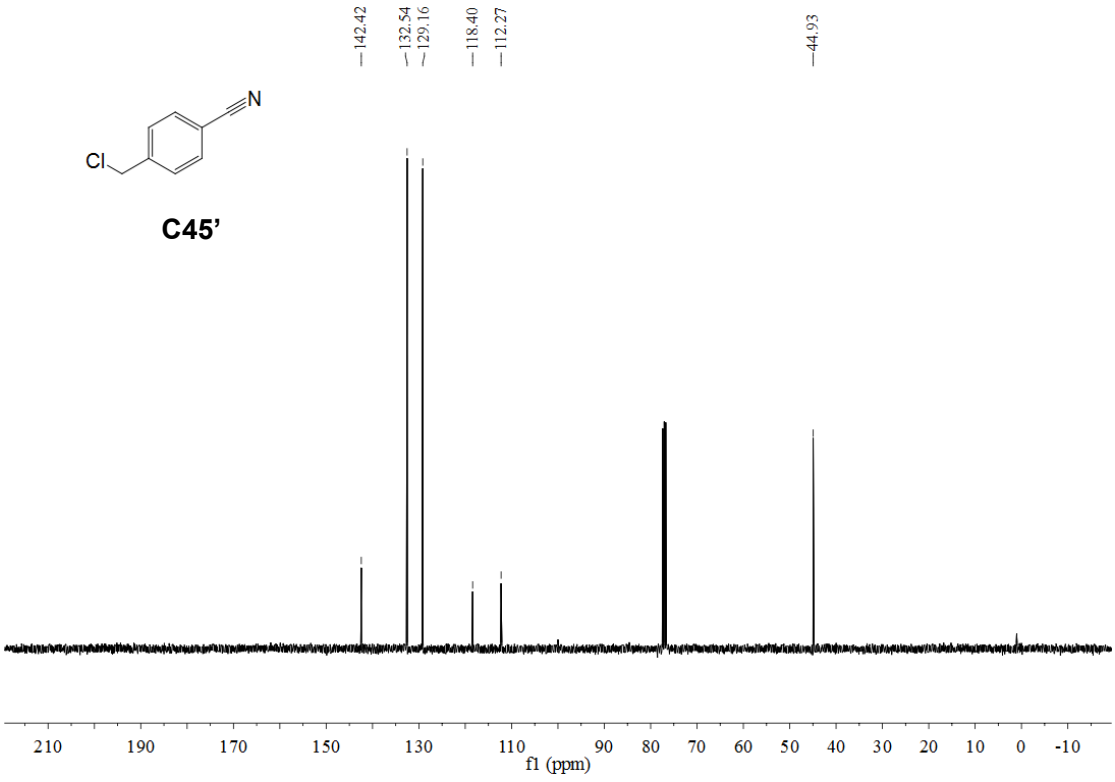
C45


146.25
132.32
127.02
118.86
111.12
64.20
HO
N
f1 (ppm)

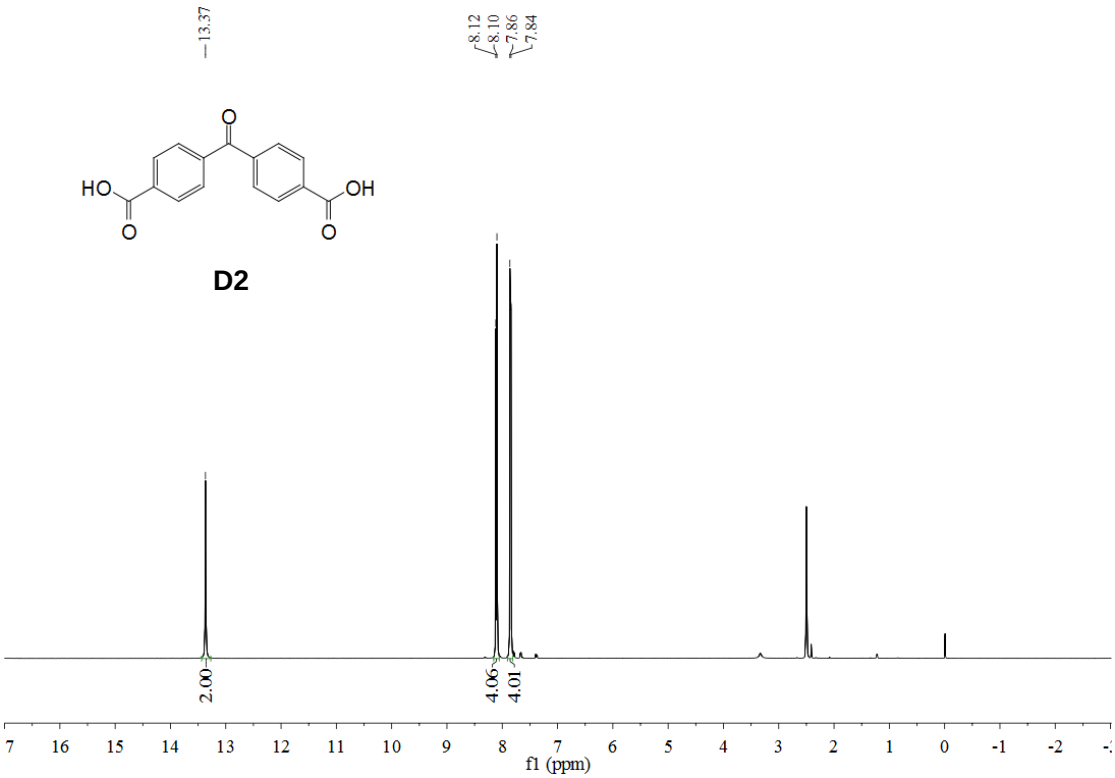
C45

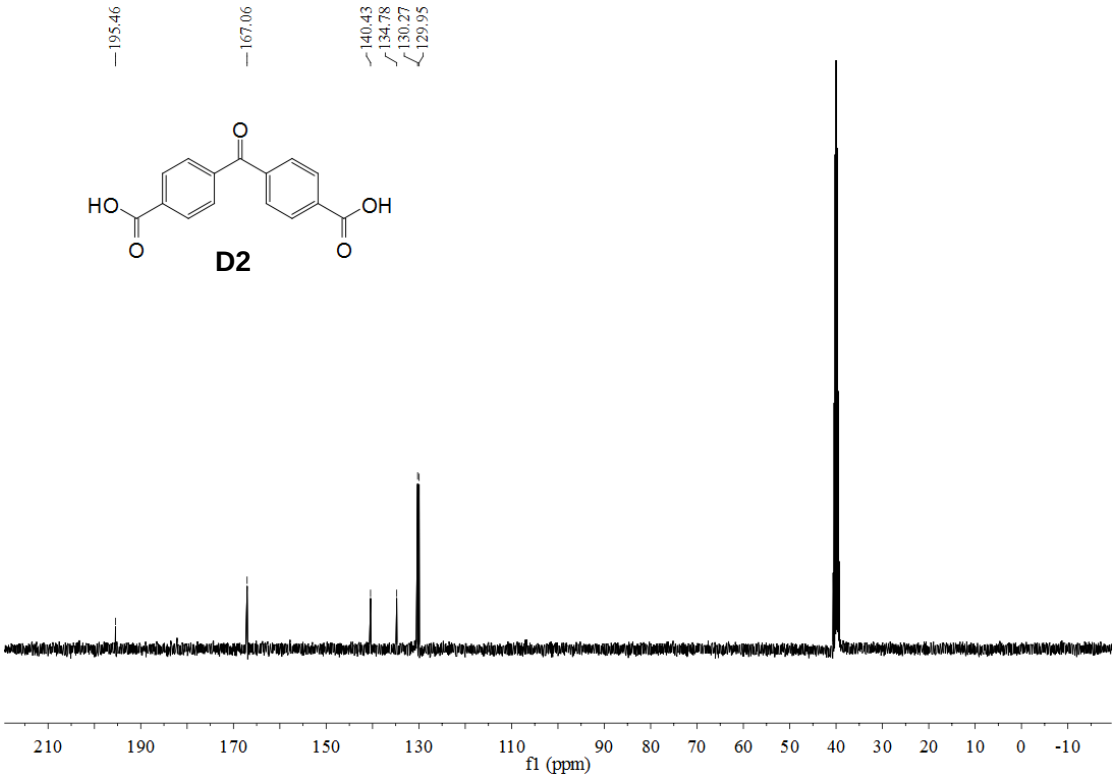

7.66
7.64
7.51
7.49
4.60
N
Cl
2.00
2.01
2.09
f1 (ppm)

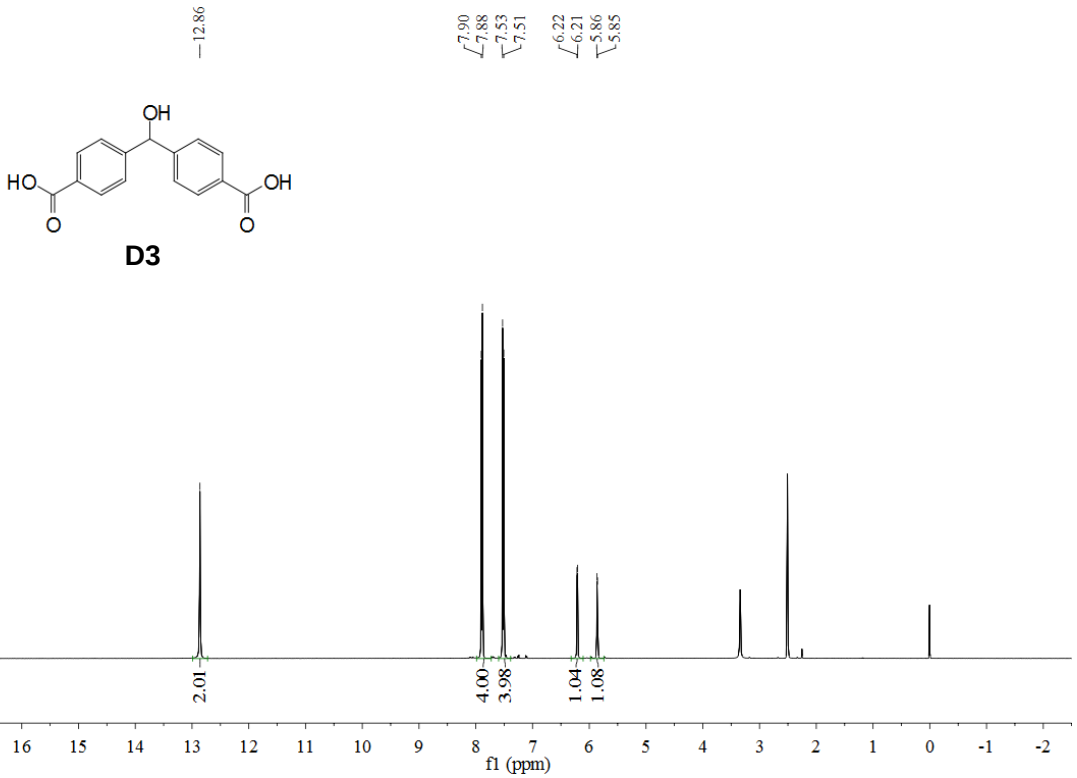
C45’

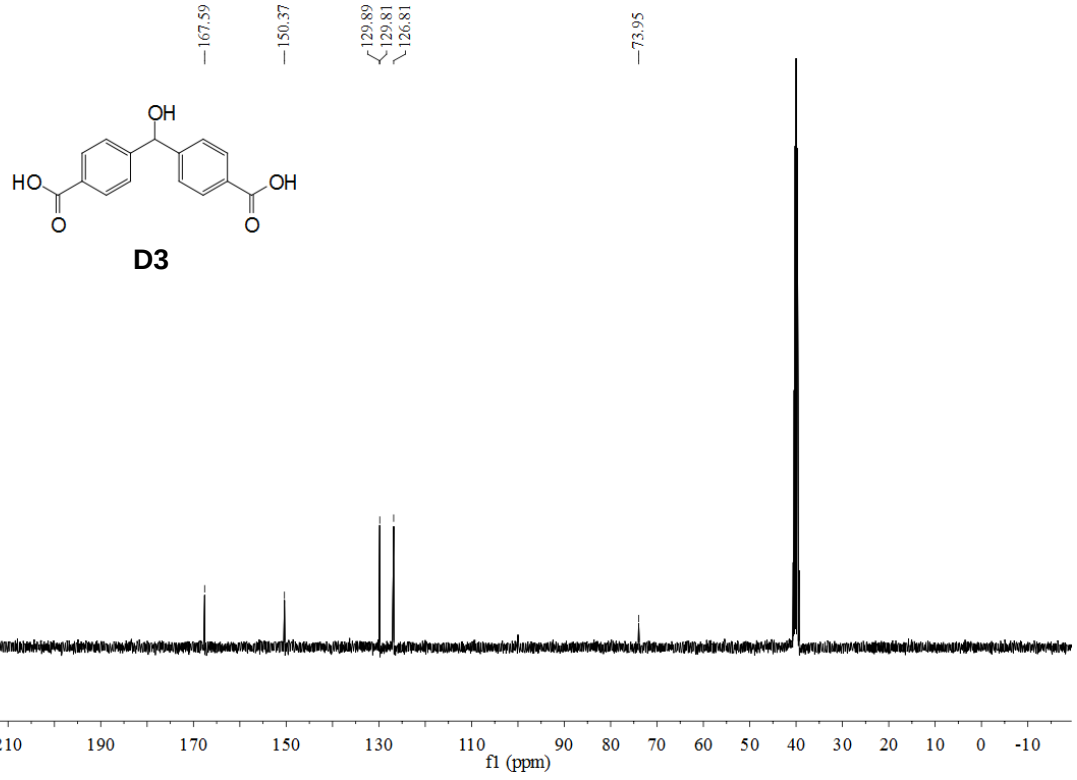

142.42
132.54
129.16
118.40
112.27
44.93
N
Cl
f1 (ppm)

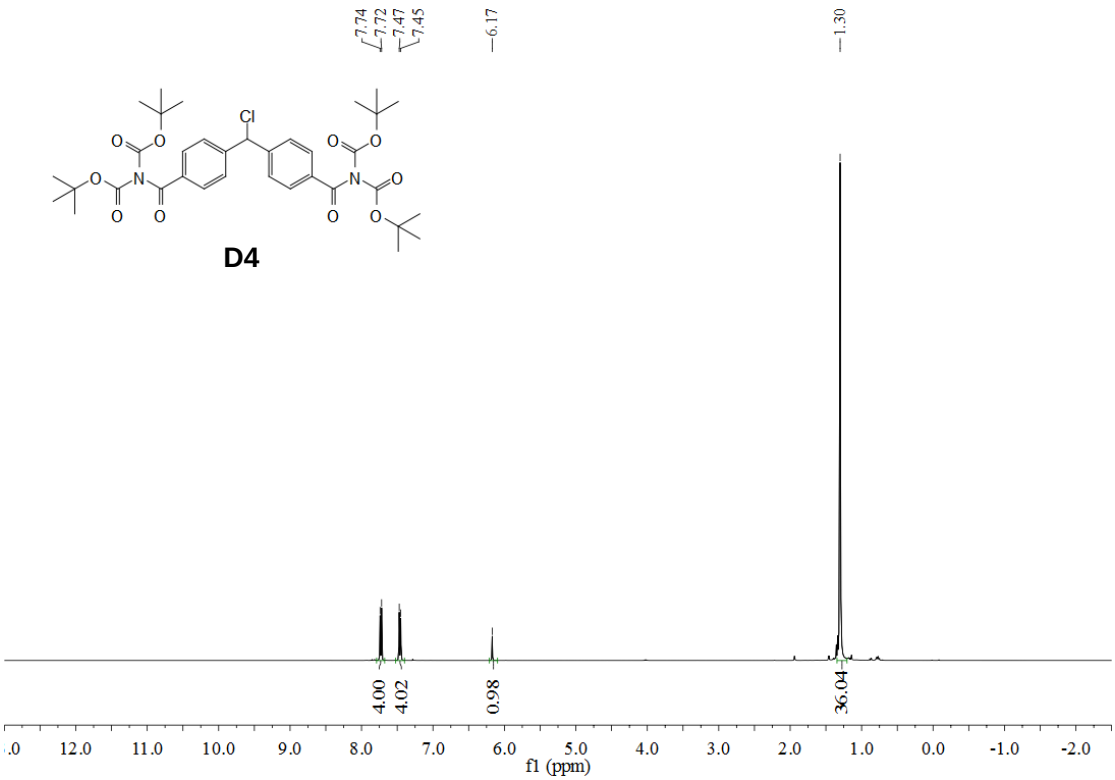
C45’

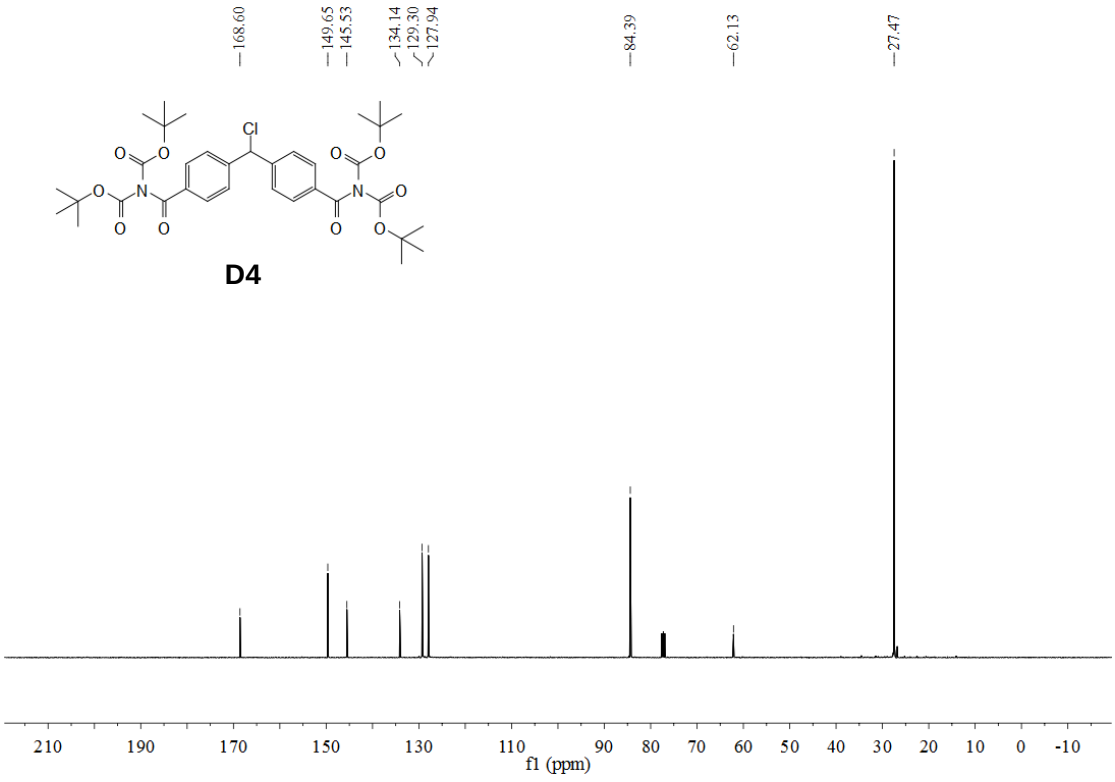

13.37
8.12
8.10
7.86
7.84
HO
OH
O
O
O
O
D2
2.00
4.06
4.01
7 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

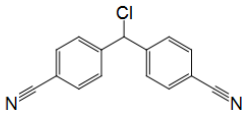

195.46
167.06
140.43
134.78
130.27
129.95
HO
OH
O
O
O
O
D2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


12.86
7.90
7.88
7.53
7.51
6.22
6.21
5.86
5.85
OH
HO
OH
O
O
D3
2.01
4.00
3.98
1.04
1.08
f1 (ppm)


167.59
150.37
129.89
129.81
126.81
73.95
OH
HO
OH
O
O
D3
f1 (ppm)

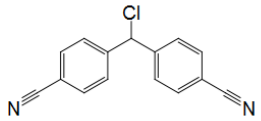

7.74
7.72
7.47
7.45
6.17
1.30
Cl
O
N
D4
4.00
4.02
0.98
36.04
f1 (ppm)


168.60
149.65
145.53
134.14
129.30
127.94
84.39
62.13
27.47
Cl
O
N
D4
f1 (ppm)


Cl
N
N

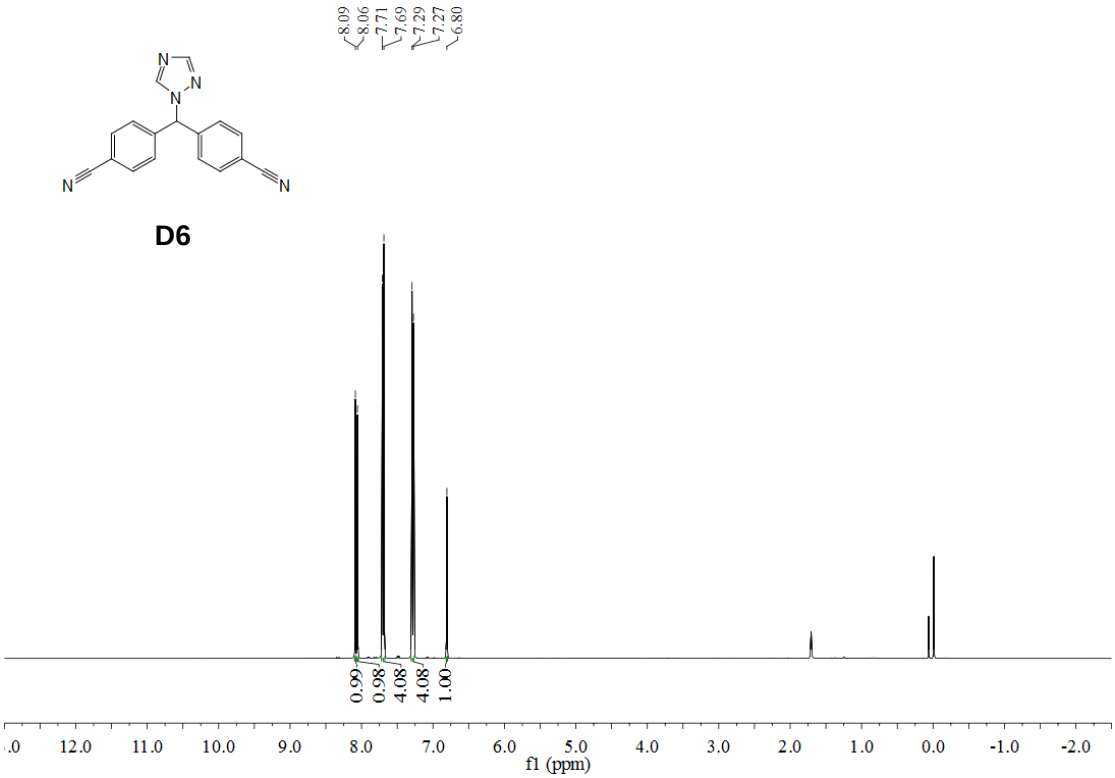
D5

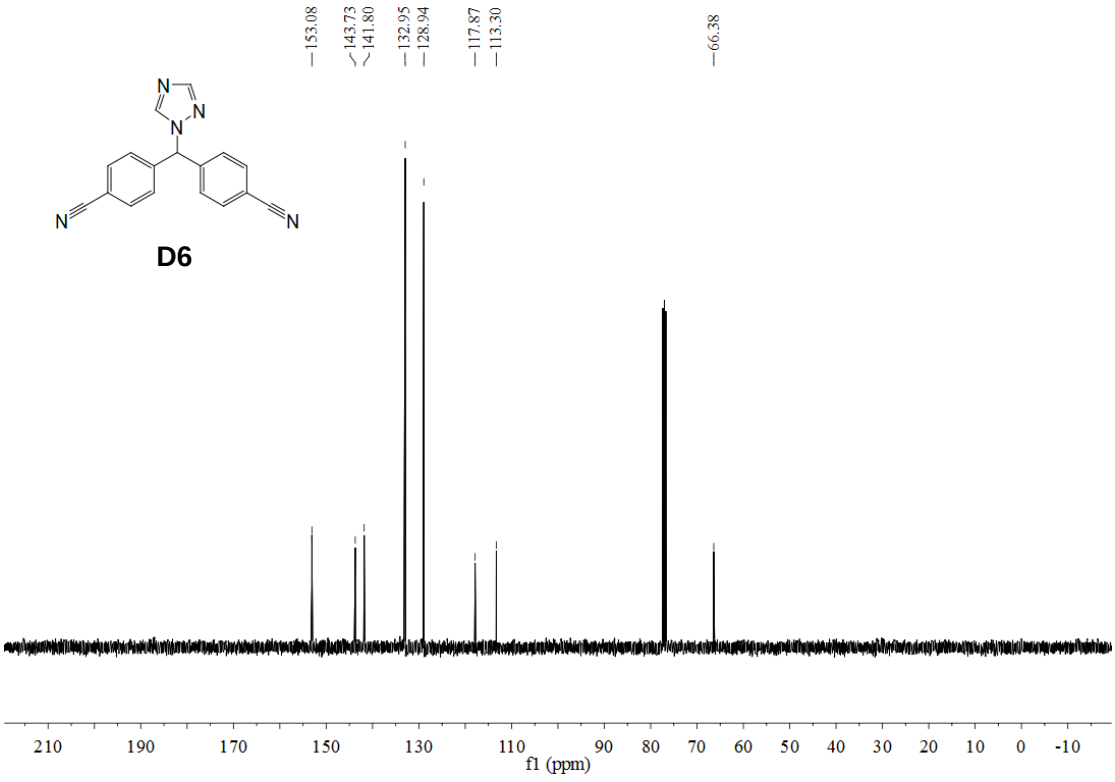
7.69
7.67
7.60
7.58
6.29
4.00
4.08
0.99
f1 (ppm)

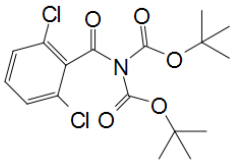

Cl
N
N

D5

144.77
132.71
128.54
118.36
112.28
61.91
f1 (ppm)

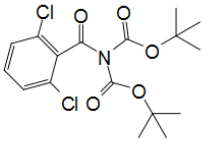

8.09
8.06
7.71
7.69
7.29
7.27
6.80
D6
0.99
0.98
4.08
4.08
1.00
f1 (ppm)


153.08
143.73
141.80
132.95
128.94
117.87
113.30
66.38
D6
f1 (ppm)



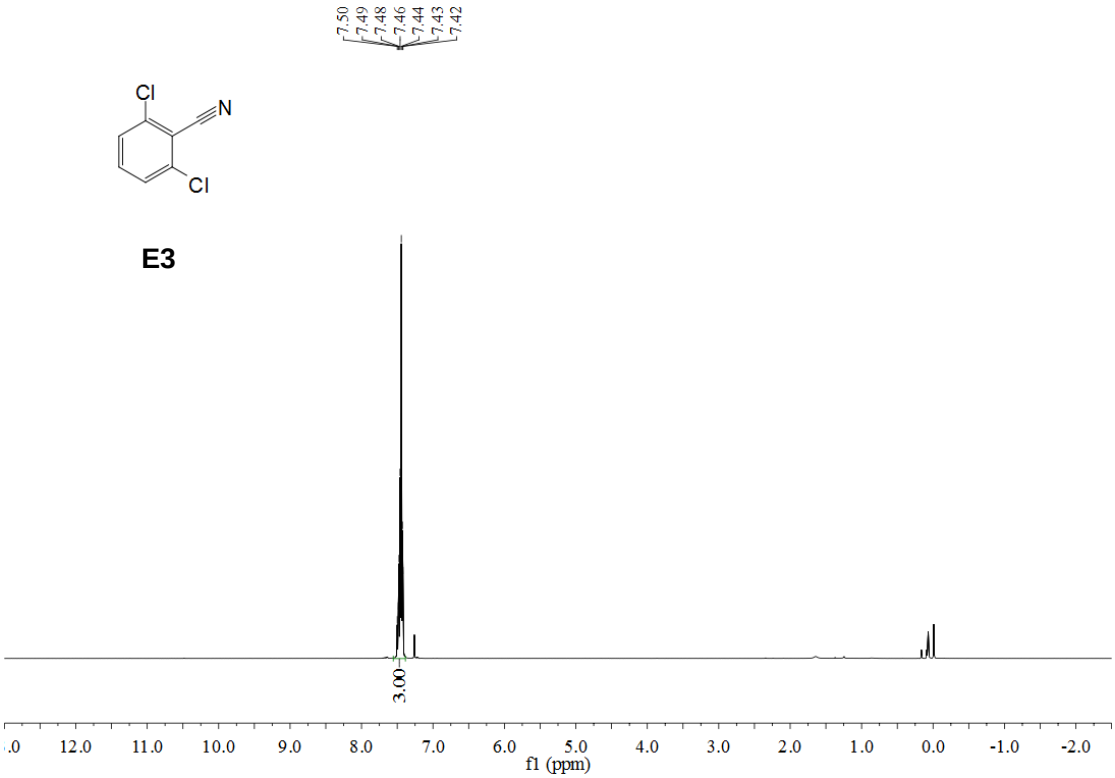
E2

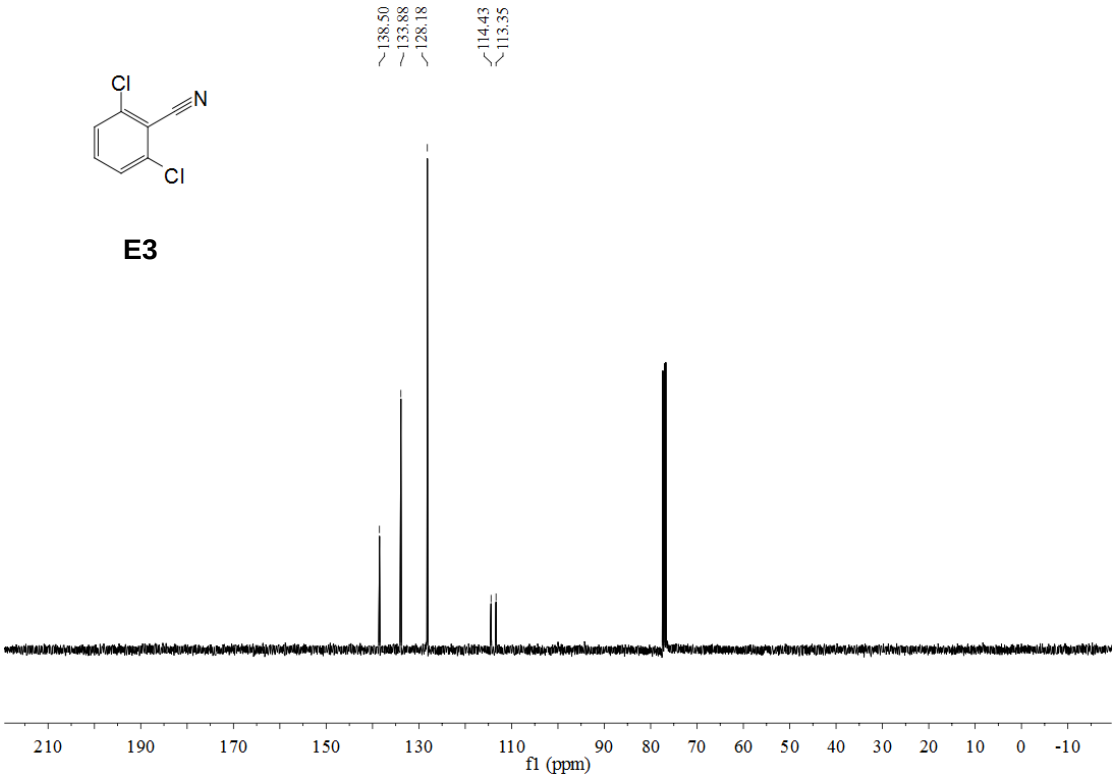
7.23
1.39
3.03
18.00
f1 (ppm)

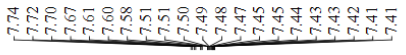


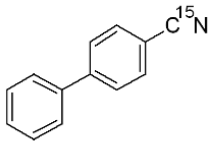
E2

163.89
148.38
135.11
131.28
130.90
127.74
85.34
27.31
f1 (ppm)

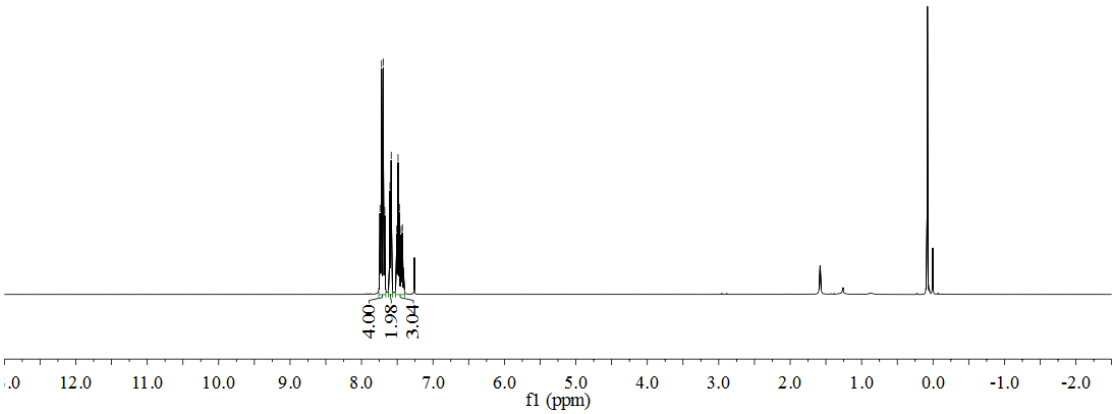

7.50
7.49
7.48
7.46
7.44
7.43
7.42
Cl
N
Cl
E3
3.00
.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

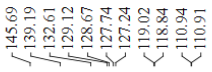

138.50
133.88
128.18
114.43
113.35
Cl
N
Cl
E3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

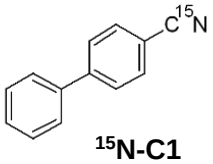

7.74
7.72
7.70
7.67
7.61
7.60
7.58
7.51
7.51
7.50
7.49
7.48
7.47
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.41


C
15
N

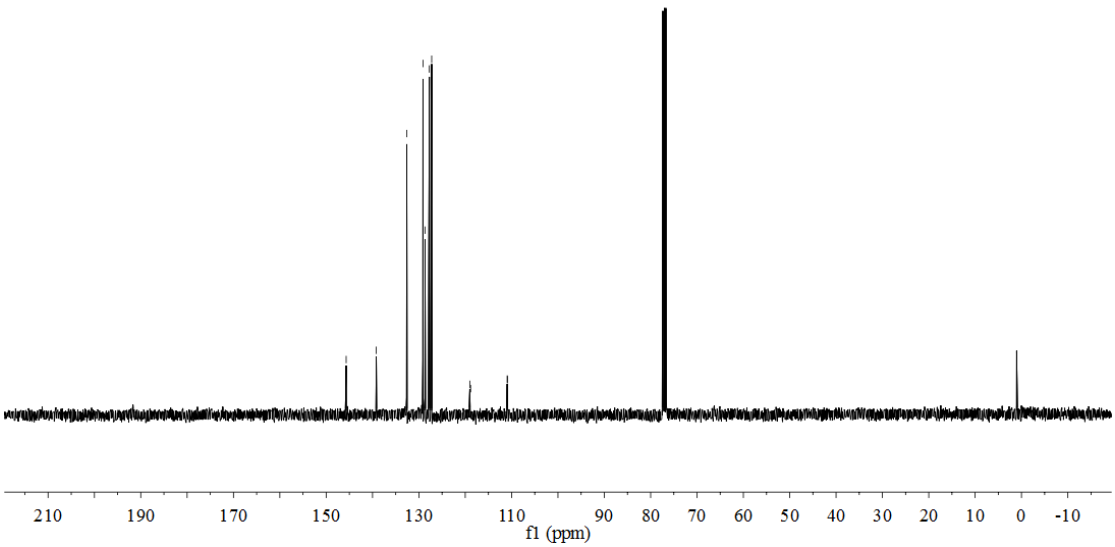
^{15}N-C1

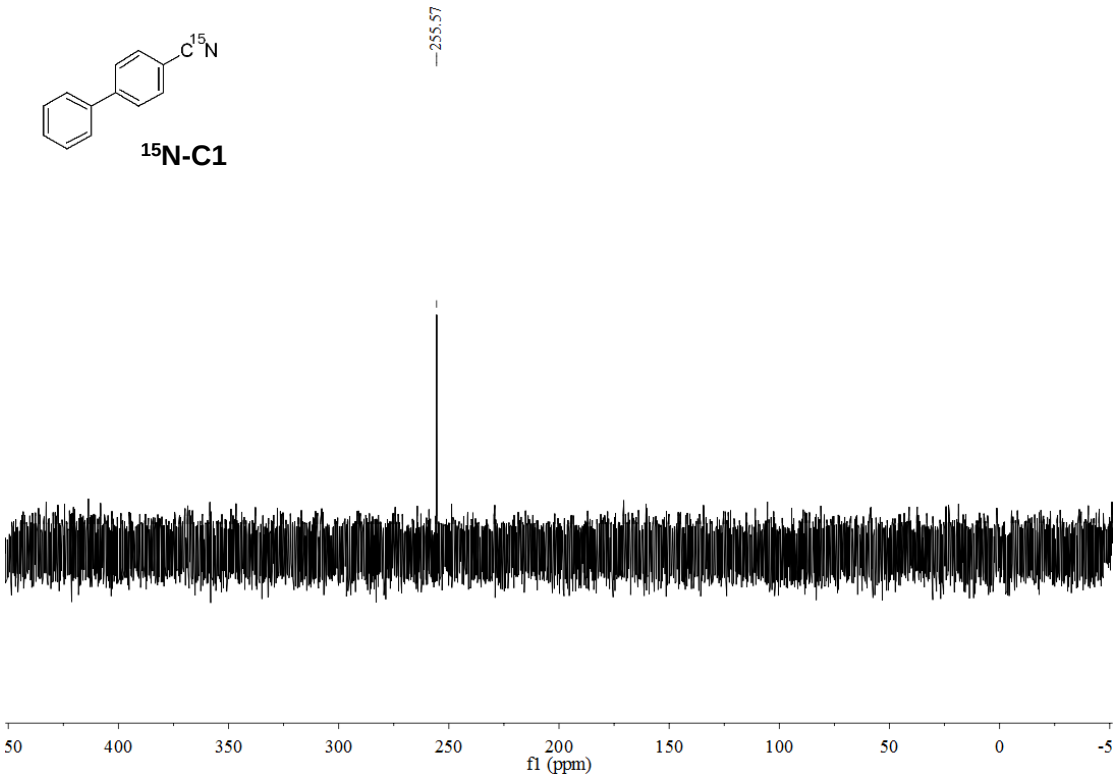

4.00
1.98
3.04
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)


145.69
139.19
132.61
129.12
128.67
127.74
127.24
119.02
118.84
110.94
110.91

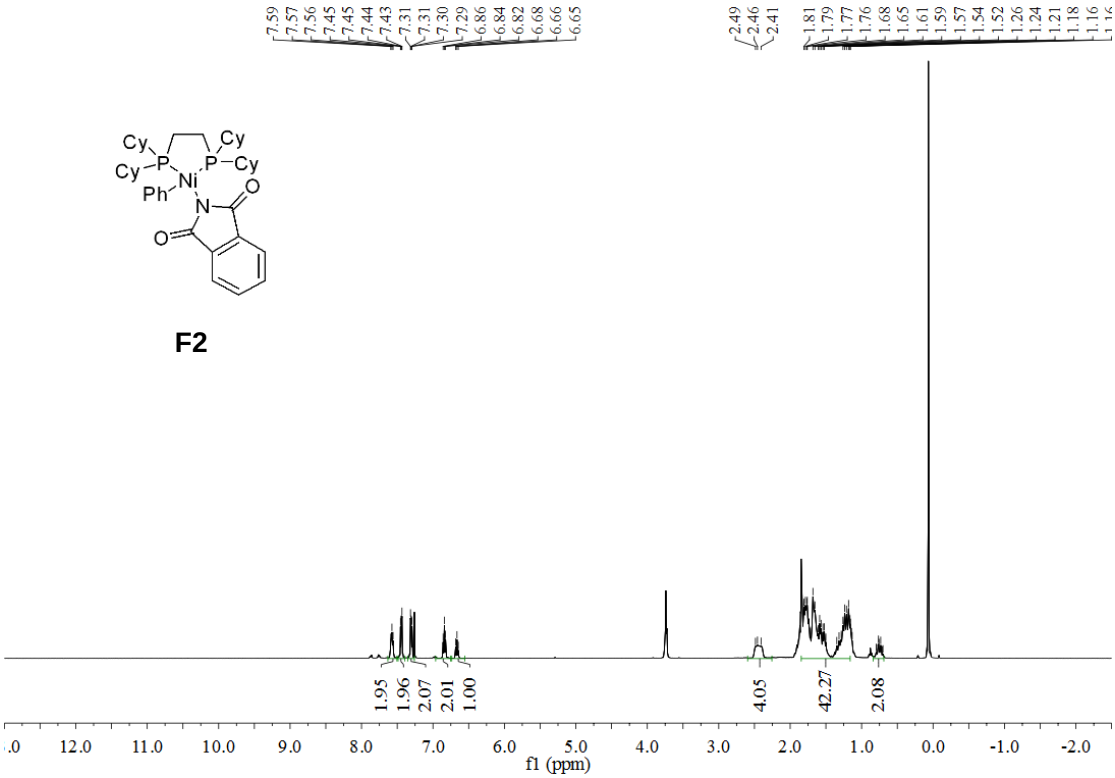

C
15
N

^{15}N-C1

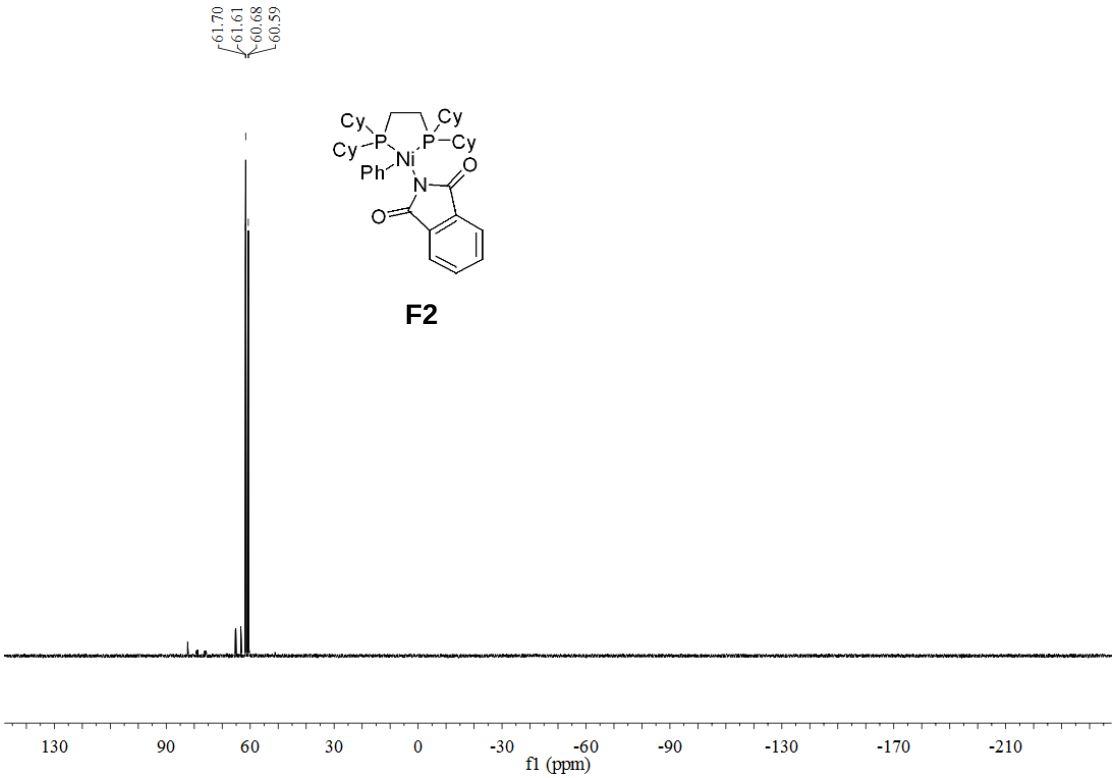

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



^{15}N-C1


7.59
7.57
7.56
7.45
7.45
7.44
7.43
7.31
7.31
7.30
7.29
6.86
6.84
6.82
6.68
6.66
6.65
2.49
2.46
2.41
1.81
1.79
1.77
1.76
1.68
1.65
1.61
1.59
1.57
1.54
1.52
1.26
1.24
1.21
1.18
1.16
Cy
Cy
P
Ni
Ph
N
O
O
P
Cy
Cy
1.95
1.96
2.07
2.01
1.00
4.05
42.27
2.08
.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

F2


61.70
61.61
60.68
60.59
Cy
Cy
P
Ni
Ph
N
O
O
P
Cy
Cy
130
90
60
30
0
-30
-60
-90
-130
-170
-210
f1 (ppm)

F2