Electronic Supplementary Material (ESI) for Chemical Science
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Aryl Nitrenium Ions from N-*Alkyl*-N-*arylamino-diazonium Precursors: Synthesis and Reactivity*

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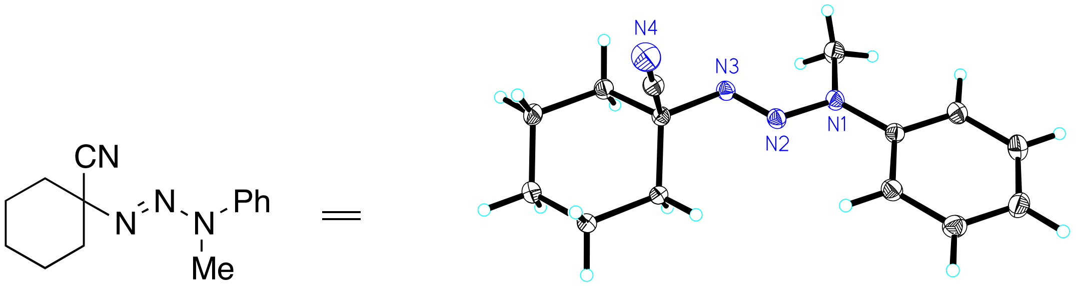
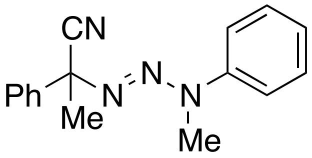
A. Synthesis of triazenes 2

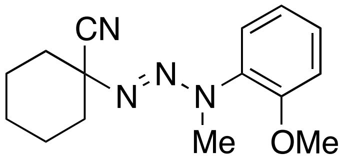
Typical reaction conditions for the synthesis of triazenes 2. To a stirred solution of diisopropylamine (1.1 mmol) in THF (5 mL, 0.2M) was added *n*-BuLi solution in hexanes (2.50–2.57 M, 1.05 mmol) at -78 °C. The resulting mixture was stirred for 20 min at -78 °C. The appropriate carbonitrile (1.0 mmol) was added dropwise at -78 °C, and subsequently stirred for 20 minutes. Aryl azide (1.20 mmol) dissolved in HPMA (1.2 mL) was added dropwise, and then the resulting mixture was warmed to rt. After an hour, alkylating or acylating reagent (1.5 mmol) was added dropwise, while the reaction flask was submerged in a water bath to avoid excessive heat generation. The resulting mixture was stirred for an hour, then concentrated under reduced pressure. The resulting crude mixture was partitioned between Et_2O (50 mL) and water (50 ml). The organic layer was separated, and the aqueous later was further extracted with Et_2O (2 × 30 mL). The combined organic layer was washed with water (20 mL) and brine (20 mL). The resulting crude material was dried (Na_2SO_4), filtered, concentrated, and purified by automated column chromatography (silica gel, 10% EtOAc in hexanes) to afford triazene (**2a–2aa**).



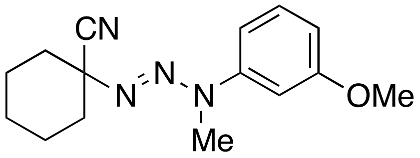
1-(3-Methyl-3-phenyltriaz-1-en-1-yl)cyclohexanecarbonitrile (**2a**): white solid, mp 64–66 °C (hexanes); IR (neat) 1600, 1474, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.32 (m, 4H), 7.10 (tt, *J* = 7.2, 1.3 Hz, 1H), 3.44 (s, 3H), 2.15–2.00 (m, 2H), 1.90-1.82 (m, 4H), 1.81–1.67 (m, 3H), 1.42–1.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 129.4, 123.8, 121.3, 116.8, 66.4, 36.4, 32.1, 25.0, 22.8; HRMS calcd for $C_{14}H_{19}N_4$ $[M+H]^+$: 243.1610, found 243.1620.



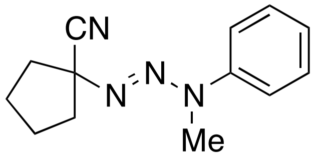
2-(3-Methyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2b**): brown oil; IR (neat) 1599, 1471, 1446 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.64 (m, 2H), 7.51–7.35 (m, 7H), 7.15 (tt, *J* = 7.3, 1.2 Hz, 1H), 3.52 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 140.0, 129.4, 129.0, 128.6, 126.2, 124.0, 120.9, 117.0, 67.7, 32.4, 29.1; HRMS calcd for $C_{16}H_{17}N_4$ $[M+H]^+$: 265.1453, found 265.1445.



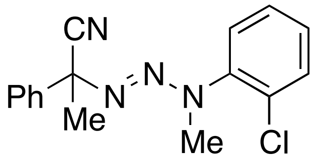
1-(3-(2-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)cyclohexanecarbonitrile (**2c**): white solid, mp 67–70 °C (hexanes); IR (neat) 1596, 1505, 1467, 1452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.16 (m, 2H), 7.07–6.86 (m, 2H), 3.87 (s, 3H), 3.33 (s, 3H), 2.24–2.00 (m, 2H), 1.91–1.78 (m, 4H), 1.78–1.63 (m, 3H), 1.40–1.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 134.9, 127.6, 126.0, 121.5, 121.2, 112.3, 65.6, 55.9, 36.4, 25.0, 22.9; HRMS calcd for $C_{15}H_{21}N_4O$ $[M+H]^+$: 273.1715, found 273.1710.



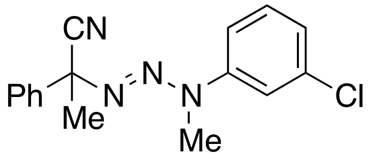
1-(3-(3-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)cyclohexanecarbonitrile (**2d**): yellow oil; IR (neat) 1602, 1477 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.2 Hz, 1H), 7.05 (t, *J* = 2.3 Hz, 1H), 6.97 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 6.66 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 3.84 (s, 3H), 3.43 (s, 3H), 2.13–2.01 (m, 2H), 1.87 (tdd, *J* = 10.7, 9.5, 5.4, 2.1 Hz, 4H), 1.81–1.68 (m, 2H), 1.44–1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 146.3, 130.1, 121.1, 109.3, 109.0, 102.8, 66.6, 55.5, 36.4, 32.0, 24.9, 22.8; HRMS calcd for $C_{15}H_{21}N_4O$ [M+H]$^+$: 273.1715, found 273.1717.



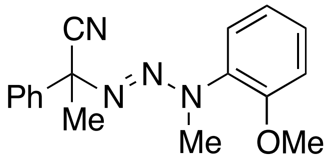
1-(3-Methyl-3-phenyltriaz-1-en-1-yl)cyclopentanecarbonitrile (**2e**): pale yellow solid, mp 55–57 °C (hexanes); IR (neat) 1599, 1474, 1450 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.31 (m, 4H), 7.09 (tt, *J* = 7.2, 1.3 Hz, 1H), 3.42 (s, 3H), 2.40–2.08 (m, 3H), 1.99–1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 129.3, 123.7, 122.1, 116.7, 70.0, 39.5, 32.0, 24.4; HRMS calcd for $C_{13}H_{17}N_4$ [M+H]$^+$: 229.1453, found 229.1449.



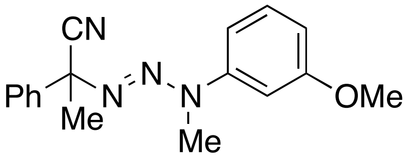
2-(3-(2-Chlorophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2f**): pale yellow oil; IR (neat) 1594, 1472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.60 (m, 2H), 7.46–7.36 (m, 3H), 7.36–7.30 (m, 1H), 7.30–7.24 (m, 2H), 7.23–7.17 (m, 1H), 3.42 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 140.1, 130.7, 129.2, 128.9, 128.5, 128.2, 127.7, 127.4, 126.1, 120.7, 67.2, 37.8, 29.2; HRMS calcd for $C_{16}H_{16}ClN_4$ [M+H]$^+$: 299.1063, found 299.1057.



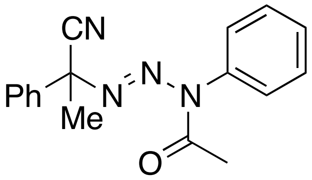
2-(3-(3-Chlorophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2g**): orange-yellow oil; IR (neat) 1467, 1446 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.57 (m, 2H), 7.48–7.39 (m, 2H), 7.39–7.32 (m, 3H), 7.30–7.22 (m, 1H), 7.07 (s, 1H), 3.46 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 139.6, 135.1, 130.4, 129.0, 128.7, 126.1, 123.8, 120.6, 116.7, 114.9, 68.0, 32.2, 29.0; HRMS calcd for $C_{16}H_{16}ClN_4$ [M+H]$^+$: 299.1063, found 299.1061.



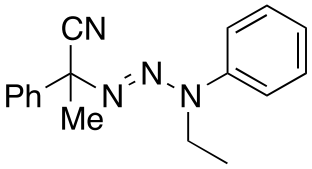
2-(3-(2-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2h**): orange-yellow oil; IR (neat) 1596, 1504, 1466, 1445 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.58 (m, 2H), 7.44–7.35 (m, 2H), 7.35–7.27 (m, 1H), 7.27–7.16 (m, 1H), 7.00–6.89 (m, 2H), 3.81 (s, 3H), 3.38 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 140.5, 134.5, 128.8, 128.4, 127.7, 126.2, 126.0, 121.1, 112.2, 66.9, 55.8, 37.4, 29.3; HRMS calcd for $C_{17}H_{19}N_4O$ [M+H]$^+$: 295.1559, found 295.1551.



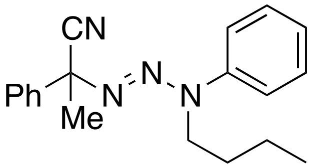
2-(3-(3-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2i**): orange-yellow oil; IR (neat) 1602, 1474, 1463, 1446, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.56 (m, 2H), 7.46–7.37 (m, 2H), 7.37–7.31 (m, 1H), 7.25 (t, *J* = 8.2 Hz, 1H), 7.11–7.04 (m, 1H), 6.97 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.66 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.82 (s, 3H), 3.48 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 146.2, 139.9, 130.1, 129.0, 128.6, 126.2, 120.8, 109.7, 109.0, 102.9, 68.0, 55.5, 32.4, 29.1; HRMS calcd for $C_{17}H_{19}N_4O$ [M+H]$^+$: 295.1559, found 295.1554.



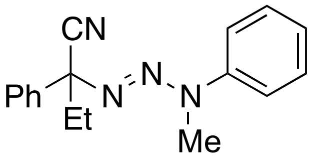
2-(3-Acetyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2j**): brown oil; IR (neat) 1716, 1513, 1374 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.40 (m, 3H), 7.39–7.29 (m, 5H), 7.06–6.99 (m, 2H), 2.68 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 138.0, 134.9, 129.5, 129.4, 129.1, 129.1, 128.8, 125.8, 119.0, 70.0, 28.6, 22.9; HRMS calcd for $C_{17}H_{17}N_4O$ [M+H]$^+$: 293.1402, found 293.1391.



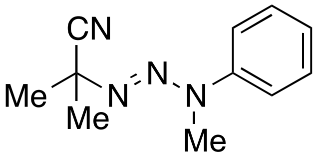
2-(3-Ethyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2k**): pale yellow oil; IR (neat) 1599, 1475, 1439 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 6.9, 1.4 Hz, 2H), 7.45–7.35 (m, 4H), 7.35–7.26 (m, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.98 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 140.0, 129.4, 128.9, 128.5, 126.0, 123.7, 120.7, 116.4, 67.8, 39.7, 28.0, 10.9; HRMS calcd for $C_{17}H_{19}N_4$ [M+H]$^+$: 279.1610, found 279.1605.



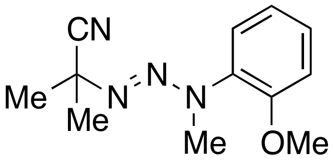
2-(3-Butyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2l**): red-orange oil; IR (neat) 1598, 1475, 1447 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.57 (m, 2H), 7.48–7.39 (m, 4H), 7.39–7.31 (m, 3H), 7.10 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.19–4.01 (m, 2H), 2.01 (s, 3H), 1.71–1.55 (m, 2H), 1.36 (tq, *J* = 14.8, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 140.1, 129.5, 129.0, 128.6, 126.2, 123.8, 120.9, 116.6, 68.0, 44.6, 29.2, 27.9, 20.6, 14.0; HRMS calcd for $C_{19}H_{23}N_4$ [M+H]$^+$: 307.1923, found 307.1937.



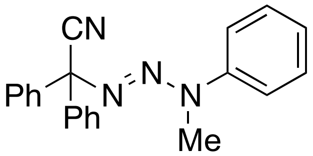
2-(3-Methyl-3-phenyltriaz-1-en-1-yl)-2-phenylbutanenitrile (**2m**): orange-yellow oil; IR (neat) 1599, 1474, 1447 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 2H), 7.44–7.36 (m, 4H), 7.36–7.29 (m, 3H), 7.08 (tt, *J* = 7.4, 1.2 Hz, 1H), 3.47 (s, 3H), 2.32 (A of ABX_3, J_{AB} = 13.6, J_{AX} = 7.2 Hz, 1H), 2.26 (B of ABX_3, J_{AB} = 13.6, J_{BX} = 7.2 Hz, 1H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.1, 129.3, 128.8, 128.5, 126.4, 123.8, 119.6, 116.8, 73.5, 35.7, 32.3, 9.2; HRMS calcd for $C_{17}H_{19}N_4$ $[M+H]^+$: 279.1610, found 279.1595.



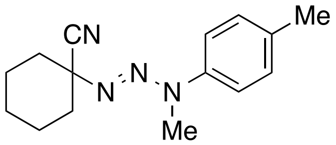
2-Methyl-2-(3-methyl-3-phenyltriaz-1-en-1-yl)propanenitrile (**2n**): yellow oil; IR (neat) 1600, 1475, 1451 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.31 (m, 4H), 7.11 (tt, *J* = 6.8, 1.4 Hz, 1H), 3.44 (s, 3H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 129.4, 123.9, 122.3, 116.9, 60.7, 32.2, 27.6; HRMS calcd for $C_{11}H_{15}N_4$ $[M+H]^+$: 203.1297, found 203.1287.



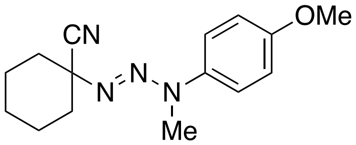
2-(3-(2-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)-2-methylpropanenitrile (**2o**): off-whte solid, mp 78–79 °C; IR (neat) 1596, 1505, 1468 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 2H), 7.02–6.94 (m, 2H), 3.87 (s, 3H), 3.33 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 127.7, 126.0, 122.6, 121.2, 112.2, 100.2, 60.0, 55.9, 37.2, 27.6; HRMS calcd for $C_{12}H_{17}N_4O$ $[M+H]^+$: 233.1402, found 233.1411.



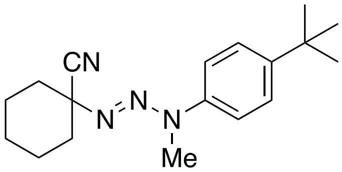
2-(3-Methyl-3-phenyltriaz-1-en-1-yl)-2,2-diphenylacetonitrile (**2p**): off-white solid, mp 98–102 °C; IR (neat) 1598, 1470, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.50 (m, 4H), 7.47–7.41 (m, 3H), 7.40–7.27 (m, 7H), 7.09 (tt, *J* = 7,4, 1.2 Hz, 1H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 140.3, 129.4, 128.9, 128.7, 127.5, 124.1, 119.7, 117.0, 74.8, 32.7; HRMS calcd for $C_{21}H_{19}N_4$ $[M+H]^+$: 327.1610, found 327.1599.



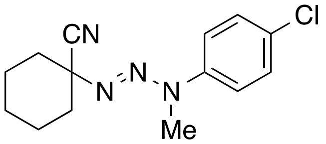
1-(3-methyl-3-(*p*-tolyl)triaz-1-en-1-yl)cyclohexane-1-carbonitrile (**2q**): off-white solid, mp 103–105 °C (hexanes); IR (neat) 1612, 1516, 1470 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2H), 7.19–7.12 (m, 2H), 3.41 (s, 3H), 2.33 (s, 3H), 2.14–2.02 (m, 2H), 1.94–1.79 (m, 4H), 1.79–1.65 (m, 3H), 1.40–1.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 133.4, 129.9, 121.3, 117.0, 66.2, 36.5, 32.4, 25.0, 22.8, 20.9; HRMS calcd for $C_{15}H_{21}N_4$ $[M+H]^+$: 257.1766, found 257.1783.



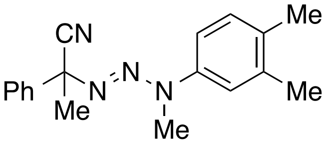
1-(3-(4-methoxyphenyl)-3-methyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile (**2r**): white solid, mp 45–46 °C (hexanes); IR (neat) 1612, 1516, 1470 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 6.94–6.86 (m, 2H), 3.80 (s, 3H), 3.40 (s, 3H), 2.12–2.02 (m, 2H), 1.93–1.79 (m, 4H), 1.79–1.66 (m, 3H), 1.39–1.25 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.4, 138.9, 121.4, 118.6, 114.6, 66.1, 55.7, 36.4, 32.9, 24.9, 22.8. HRMS calcd for $C_{15}H_{21}N_4O$ [M+H]$^+$: 273.1715, found 273.1704.



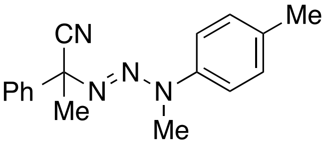
1-(3-(4-(*tert*-butyl)phenyl)-3-methyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile (**2s**): white solid, mp 81–82 °C (hexanes); IR (neat) 1610, 1516, 1467 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41–7.36 (m, 2H), 7.36–7.31 (m, 2H), 3.42 (s, 3H), 2.14–2.02 (m, 2H), 1.86 (dtt, *J* = 14.0, 8.6, 2.9 Hz, 4H), 1.79–1.66 (m, 4H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.8, 142.7, 126.2, 121.3, 116.7, 66.3, 36.4, 34.5, 32.3, 31.6, 25.0, 22.8; HRMS calcd for $C_{18}H_{27}N_4$ [M+H]$^+$: 299.2236, found 299.2223.



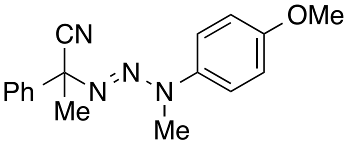
1-(3-(4-chlorophenyl)-3-methyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile (**2t**): white solid, mp 108–109 °C (hexanes); IR (neat) 1596, 1496, 1474 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39–7.28 (m, 4H), 3.41 (s, 3H), 2.13–2.01 (m, 2H), 1.91– 1.83 (m, 4H), 1.82–1.69 (m, 3H), 1.42–1.26 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.6, 129.4, 128.9, 121.0, 117.8, 66.6, 36.3, 32.0, 24.9, 22.8; HRMS calcd for $C_{14}H_{18}ClN_4$ [M+H]$^+$: 277.1220, found 277.1230.



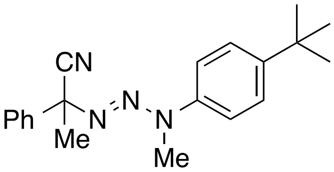
2-(3-(3,4-dimethylphenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2u**): brown oil; IR (neat) 1613, 1466, 1446 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67–7.59 (m, 2H), 7.45–7.37 (m, 2H), 7.37–7.30 (m, 1H), 7.22–7.17 (m, 1H), 7.17–7.07 (m, 2H), 3.46 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.0, 140.3, 137.7, 132.5, 130.4, 128.9, 128.5, 126.2, 121.1, 118.6, 114.8, 67.5, 32.9, 29.2, 20.4, 19.2; HRMS calcd for $C_{18}H_{21}N_4$ [M+H]$^+$: 293.1766, found 293.1747.



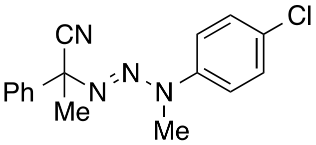
2-(3-methyl-3-(*p*-tolyl)triaz-1-en-1-yl)-2-phenylpropanenitrile (**2v**): orange oil; IR (neat) 1612, 1516, 1470 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32–7.26 (m, 2H), 7.19–7.12 (m, 2H), 3.41 (s, 3H), 2.33 (s, 3H), 2.14–2.02 (m, 2H), 1.94–1.79 (m, 4H), 1.79–1.65 (m, 3H), 1.40–1.28 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.8, 133.4, 129.9, 121.3, 117.0, 66.2, 36.5, 32.4, 25.0, 22.8, 20.9; HRMS calcd for $C_{17}H_{19}N_4$ [M+H]$^+$: 279.1610, found 279.1591.



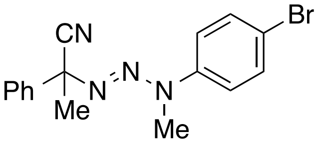
2-(3-(4-methoxyphenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2w**): brown oil; IR (neat) 1512, 1462, 1245 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.61 (m, 1H), 7.44–7.38 (m, 1H), 7.36–7.31 (m, 2H), 6.93–6.89 (m, 1H), 3.80 (s, 3H), 3.47 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 140.3, 138.8, 128.9, 128.5, 126.2, 121.1, 118.8, 114.6, 67.5, 55.8, 33.3, 29.3; HRMS calcd for $C_{17}H_{19}N_4O$ $[M+H]^+$: 295.1559, found 295.1542.



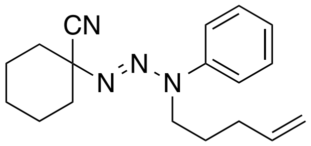
2-(3-(4-(*tert*-butyl)phenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2x**): colorless oil; IR (neat) 1610, 1516, 1465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.60 (m, 2H), 7.43–7.32 (m, 7H), 3.48 (s, 3H), 2.00 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 142.6, 140.2, 129.0, 128.6, 126.3, 126.2, 121.0, 116.9, 67.6, 34.5, 32.7, 31.6, 29.2; HRMS calcd for $C_{20}H_{25}N_4$ $[M+H]^+$: 321.2079, found 321.2058.



2-(3-(4-chlorophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2y**): brown oil; IR (neat) 1596, 1496, 1474 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.59 (m, 2H), 7.45–7.29 (m, 7H), 3.47 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 139.8, 129.4, 129.3, 129.0, 128.7, 126.2, 120.7, 118.0, 68.0, 32.4, 29.2; HRMS calcd for $C_{16}H_{16}ClN_4$ $[M+H]^+$: 299.1063, found 299.1043.



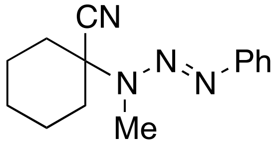
2-(3-(4-bromophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**2z**): yellow oil; IR (neat) 1591, 1492, 1472 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.58 (m, 2H), 7.50–7.27 (m, 7H), 3.47 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 139.7, 132.4, 129.1, 128.8, 126.2, 120.7, 118.3, 116.8, 68.0, 32.3, 29.1; HRMS calcd for $C_{16}H_{16}BrN_4$ $[M+H]^+$: 343.0558, found 343.0537.



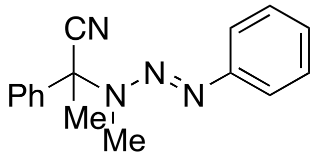
1-(3-(pent-4-en-1-yl)-3-phenyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile (**2aa**): yellow oil; IR (neat) 1641, 1599, 1479, 1452 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.30 (m, 4H), 7.09 (tt, *J* = 7.1, 1.3 Hz, 1H), 5.83 (ddt, *J* = 17.2, 10.4, 6.6 Hz, 1H), 5.21–4.91 (m, 2H), 4.15–3.94 (m, 2H), 2.14–2.02 (m, 4H), 1.92–1.81 (m, 4H), 1.81–1.66 (m, 5H), 1.42–1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.7, 129.5, 123.5, 121.3, 116.5, 115.5, 66.4, 44.0, 36.3, 31.4, 25.0, 24.6, 22.8. HRMS calcd for $C_{18}H_{25}N_4$ $[M+H]^+$: 297.2079, found 297.2063.

B. Characterization of Triazenes 3 Obtained as minor isomer

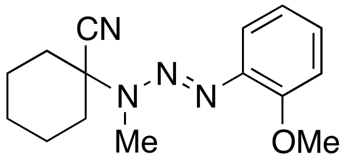
All compounds listed in section B were obtained as minor isomer, and only the characteristic ^{1}H NMR peaks were given. For the full characterization of **3a** and **3b**, see section C.



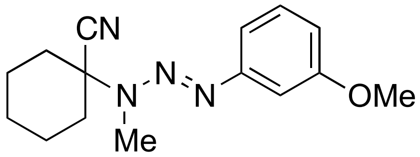
1-(1-Methyl-3-phenyltriaz-2-en-1-yl)cyclohexanecarbonitrile (**3a**): see section C



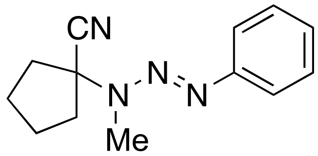
2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3b**): see section C



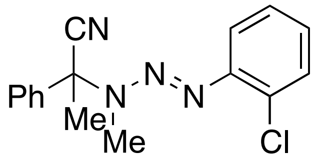
1-(3-(2-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)cyclohexanecarbonitrile (**3c**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.30 (s, 3H).



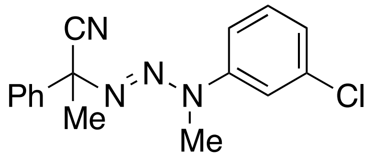
1-(3-(3-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)cyclohexanecarbonitrile (**3d**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (s, 3H).



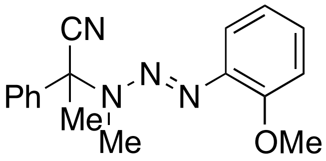
1-(1-Methyl-3-phenyltriaz-2-en-1-yl)cyclopentanecarbonitrile (**3e**):
^{1}H NMR (400 MHz, CDCl3) δ 3.21 (s, 3H).



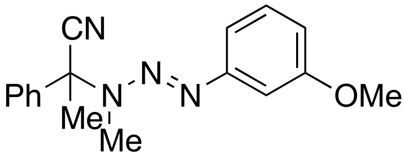
2-(3-(2-Chlorophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3f**) :
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09 (s, 3H), 2.25 (s, 3H).



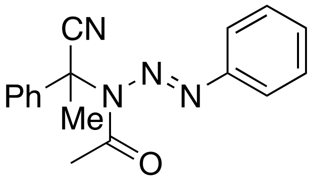
2-(3-(3-Chlorophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3g**) :
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (s, 3H), 2.25 (s, 3H).



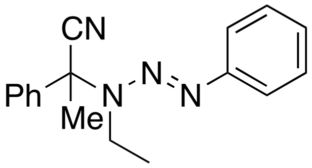
2-(3-(2-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3h**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 3.07 (s, 3H), 2.25 (s, 3H).



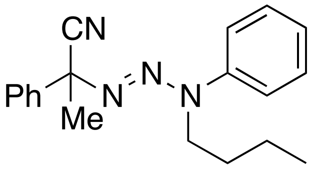
2-(3-(3-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3i**) :
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.03 (s, 3H), 2.25 (s, 3H).



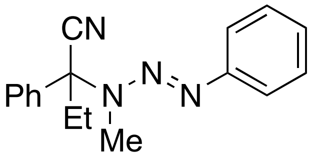
2-(1-Acetyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3j**): not observed.



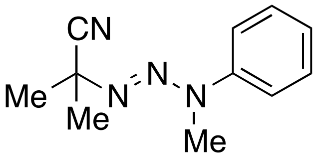
2-(1-Ethyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3k**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (A of ABX_3, J_{AB} = 14.0, J_{AX} = 7.0 Hz, 1H), 3.52 (A of ABX_3, J_{AB} = 13.9, J_{AX} = 7.0 Hz, 1H), 2.20 (s, 3H).



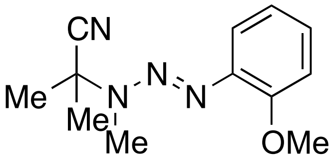
2-(3-Butyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (**3l**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (t, J = 6.5 Hz, 2H), 1.78–1.71 (m, 2H), 1.51–1.41 (m, 1H), 0.96 (t, J = 7.4 Hz, 3H).



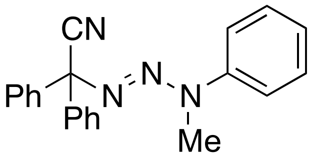
2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2-phenylbutanenitrile (**3m**): not observed.



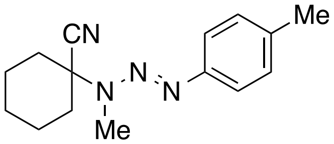
2-Methyl-2-(1-methyl-3-phenyltriaz-2-en-1-yl)propanenitrile (**3n**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H), 1.88 (s, 6H).



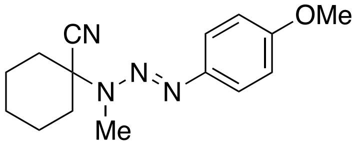
2-(3-(2-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)-2-methylpropanenitrile (**3o):**
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.28 (s, 3H), 1.87 (s, 6H).



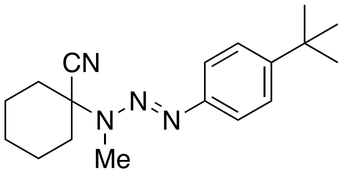
2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2,2-diphenylacetonitrile (**3p**): not observed.



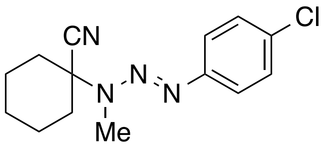
1-(1-methyl-3-(*p*-tolyl)triaz-2-en-1-yl)cyclohexane-1-carbonitrile (**3q**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (s, 3H).



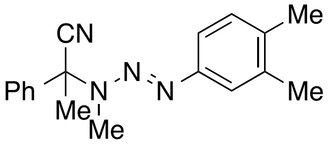
1-(3-(4-methoxyphenyl)-1-methyltriaz-2-en-1-yl)cyclohexane-1-carbonitrile (**3r**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.20 (s, 3H).



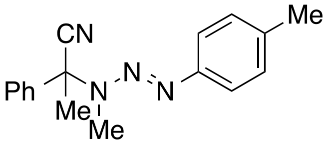
1-(3-(4-(*tert*-butyl)phenyl)-1-methyltriaz-2-en-1-yl)cyclohexane-1-carbonitrile (**3s**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H).



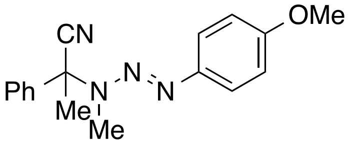
1-(3-(4-chlorophenyl)-1-methyltriaz-2-en-1-yl)cyclohexane-1-carbonitrile (**3t**):
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.25 (s, 3H).



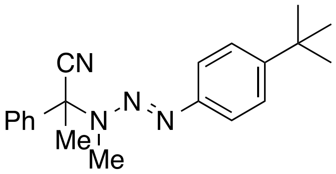
(*E*)-2-(3-(3,4-dimethylphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3u**):
^{1}H NMR (400 MHz, CDCl$_3$) δ 2.99 (s, 3H).



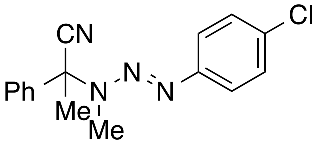
2-(1-methyl-3-(*p*-tolyl)triaz-2-en-1-yl)-2-phenylpropanenitrile (**3v**):
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.00 (s, 3H), 2.04 (s, 3H).



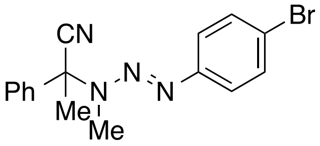
2-(3-(4-methoxyphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3w**):
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.60 (s, 3H), 2.86 (s, 3H).



2-(3-(4-(*tert*-butyl)phenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3x**):
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.00 (s, 3H), 2.25 (s, 3H).



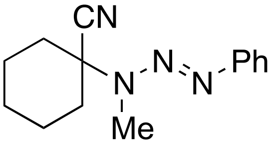
2-(3-(4-chlorophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3y**):
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.02 (s, 3H), 2.24 (s, 3H).



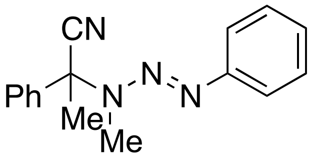
2-(3-(4-bromophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3z**):
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.02 (s, 3H), 2.25 (s, 3H).

C. Synthesis of Triazene 3

Typical reaction conditions for the synthesis of triazenes 3. To a stirred solution of diisopropylamine (1.1 mmol) in THF (5 mL, 0.2M) was added *n*-BuLi solution in hexanes (2.50–2.57 M, 1.05 mmol) at -78 °C. The resulting mixture was stirred for 20 min at -78 °C. The appropriate carbonitrile (1.0 mmol) was added dropwise at -78 °C, and subsequently stirred for 20 minutes. Aryl azide (1.20 mmol) dissolved in HPMA (1.2 mL) was added dropwise, and then the resulting mixture was warmed to rt. After an hour, alkylating or acylating reagent (1.5 mmol) was added dropwise, while the reaction flask was submerged in a water bath to avoid excessive heat generation. The resulting mixture was stirred for an hour, then concentrated under reduced pressure. The resulting crude mixture was partitioned between Et_2O (50 mL) and water (50 ml). The organic layer was separated, and the aqueous layer was further extracted with Et_2O (2 × 30 mL). The combined organic layer was washed with water (20 mL) and brine (20 mL). The resulting crude material was dried (Na_2SO_4), filtered, concentrated, and purified by automated column chromatography (silica gel, 10% EtOAc in hexanes) to afford triazenes (**3a, 3b**).

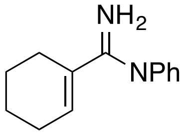


1-(1-Methyl-3-phenyltriaz-2-en-1-yl)cyclohexanecarbonitrile (**3a**): colorless oil; IR (neat) 1596, 1465, 1442 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.40–7.30 (m, 2H), 7.25–7.17 (m, 1H), 3.25 (s, 3H), 2.50–2.39 (m, 2H), 2.05 (ddd, *J* = 13.6, 11.5, 3.7 Hz, 2H), 1.95–1.83 (m, 2H), 1.81–1.66 (m, 3H), 1.41–1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 128.6, 126.4, 120.9, 119.1, 62.9, 34.5, 30.8, 24.3, 22.3; HRMS calcd for $C_{21}H_{19}N_4$ $[M+H]^+$: 243.1610, found 243.1606.



2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (**3b**): colorless oil; IR (neat) 1597, 1465, 1444 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 4H), 7.48–7.34 (m, 5H), 7.29–7.22 (m, 1H), 3.03 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 138.9, 129.5, 129.4, 129.2, 127.2, 125.5, 121.5, 119.4, 66.6, 33.5, 28.8; HRMS calcd for $C_{16}H_{17}N_4$ $[M+H]^+$: 265.1453, found 265.1461.

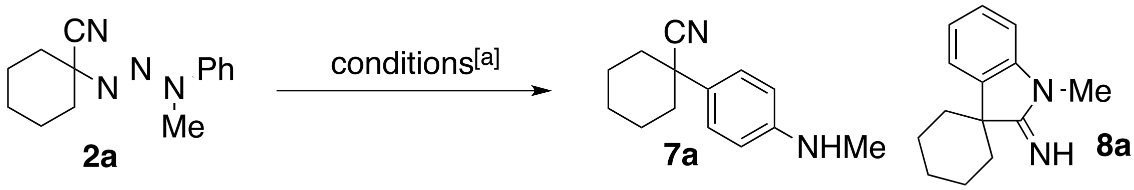
D. Synthesis of cyclohexenecarboxyimidamide 4a



N'-phenylcyclohex-1-ene-1-carboximidamide (**4a**) To a stirred solution of diisopropylamine (0.31 mL, 2.2 mmol) in THF (10 mL) was added 2.45M *n*-BuLi solution in hexanes (0.86, 2.1 mmol) at -78 °C. The resulting mixture was stirred for 20 min at -78 °C. Cyclohexanecarbonitrile (0.24 mL, 2.0 mmol) was added dropwise at -78 °C, and subsequently stirred for 20 minutes. Phenyl azide (290 mg, 2.4 mmol) dissolved in THF (2.4 mL) was added dropwise, and then the resulting mixture was stirred at -78 °C for 30 min. Then the reaction mixture was warmed to rt. After an hour, sat. aq. NH_4Cl solution (5 mL) was added. The resulting crude mixture extracted with Et_2O (3 × 20 mL). The combined organic layer was washed with brine (20 mL). The resulting crude material was dried (Na_2SO_4), filtered, concentrated, and purified by automated column chromatography (silica gel, 90:9:1 CH_2Cl_2/MeOH/NH_4OH) to afford **4a** (327 mg); brown oil; Rf = 0.29 (90:9:1 CH_2Cl_2/MeOH/NH_4OH); IR (neat) 1621, 1581 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.43–6.40 (m, 1H), 4.32 (s, 2H), 2.40–2.35 (m, 2H), 2.21–2.15 (m, 2H), 1.75–1.61 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 149.5, 134.4, 130.4, 129.6, 129.5, 123.0, 121.9, 121.9, 25.7, 25.4, 22.5, 21.9; HRMS calcd for $C_{13}H_{17}N_2$ $[M+H]^+$: 201.1392, found 201.1408.

E. Optimization of α-arylation conditions

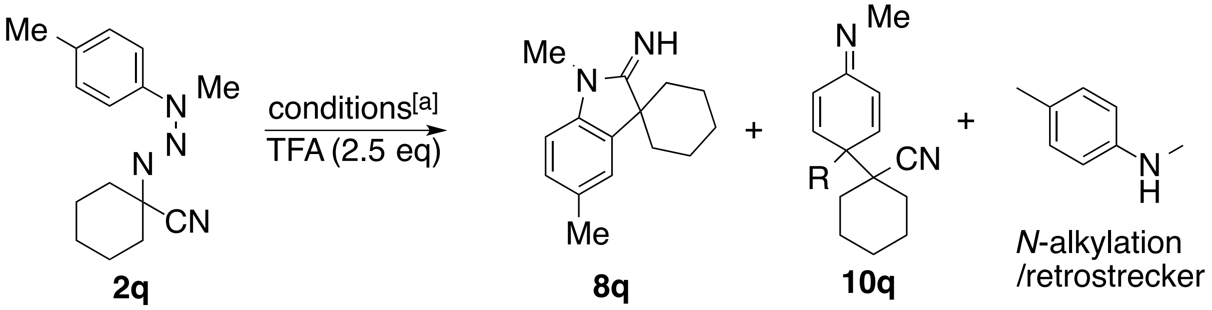
a. Optimization of *para*-selective arylation conditions



entry	acid	solvent	conditions	yield(**7a**)	crude nmr ratio	
					7a	**8a**
1	BF_3•OEt_2	CH_2Cl_2	0 °C, 1h	41%	89	11
2	BF_3•OEt_2	MeCN	0 °C, 1h	43%	89	11
3	BF_3•OEt_2	CH_2Cl_2	-20 °C, 1h	39%	87	13
4	BF_3•OEt_2	CH_2Cl_2	-45 °C, 1h	22%	78	22
5	BF_3•OEt_2	CH_2Cl_2	-78 °C, 1h	0%		
6	BF_3•OEt_2	EtOAc	0 °C, 1h	34%	89	11
7	BF_3•OEt_2	$CHCl_3$	0 °C, 1h	21%	87	13
8	BF_3•OEt_2	ether	0 °C, 1h	7%	90	10
9	BF_3•OEt_2	acetone	0 °C, 1h	7%	63	37
10	BF_3•OEt_2	toluene	0 °C, 1h	28%	91	9
11	$TiCl_4$	CH_2Cl_2	0 °C, 1h	—%[b]	59	41
12	$SnCl_4$	CH_2Cl_2	0 °C, 1h	20%	84	16
13	BBr_3	CH_2Cl_2	0 °C, 1h	32%	overlap with impurity	
14	$AlCl_3$	CH_2Cl_2	0 °C, 1h	30%	55	45
15	$MgCl_2$	CH_2Cl_2	rt, 1h	17%	56	44
16	$HfCl_4$	CH_2Cl_2	0 °C, 1h	24%	58	42
17	$ZrCl_4$	CH_2Cl_2	0 °C, 1h	22%	72	28
18	$Sc(OTf)_3$	CH_2Cl_2	0 °C, 1h	19%	95[c]	5
19	MeOTf	CH_2Cl_2	0 °C, 1h	0%		
20	TMSOTf	CH_2Cl_2	0 °C, 1h	0%		
21	TFA	CH_2Cl_2	0 °C, 1h	37%[d]	62	38
22	CSA	CH_2Cl_2	0 °C, 1h	10%	58	42
23	TfOH	CH_2Cl_2	0 °C, 1h	26%	62	38
24	TfOH	MeOH	0 °C, 1h	22%		
25		toluene	reflux	—%[b]		
26		acetone	$h\nu$ |	15%[d]	100	0
27	CuCl	MeCN/water	rt, 18 h	15%	66	34

[a] reaction conditions: **2** (0.25 mmol), solvent (0.2M), acid (0.3 mmol) [b] the existence of the productin the complex mixture was confirmed by crude ^{1}H NMR. However, not isolated. [c]large amount of unidentified side product produced. [d] The yields were inconsistent under given conditions. Average yield from 23–52%

b. Optimization of ortho-selective arylation conditions

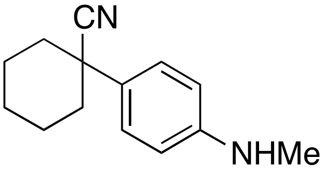


entry	solvent	conditions	yield	crude nmr ratio		
				8q	**10q**	*N*-alkylation
1	CH_2Cl_2	0 °C - rt, 1h	39%	45	35	30
2	CH_2Cl_2	rt, 1h	38%	42	31	27
3	CH_2Cl_2	-20 °C, 1h	36%	40	35	25
4	CH_2Cl_2	-45 °C, 1h	41%	38	35	27
5	CH_2Cl_2	0 °C, 18h	48%	45	32	22
6	toluene	0 °C - rt, 1h	–%[b]	42	24	35
7	THF	0 °C - rt, 1h	–%[b]	45	23	32
8	ether	0 °C - rt, 1h	–%[b]	42	19	39
9	DMSO	0 °C - rt, 1h	37%	67	26	7
10	MeOH	0 °C - rt, 1h	45%	54	24	22
11	MeOH	0 °C, 18h	48%	57	28	15
12	CF_3CH_2OH	0 °C - rt, 1h	32%	41	39	20
13	CF_3CH_2OH	50 °C[c]	40%	62	15	23
14	$(CF_3)_2CH_2OH$[d]	0 °C - rt, 1h	38%	50	41	9

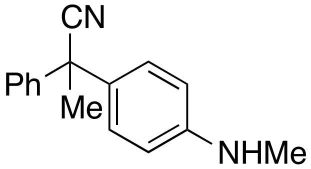
[a] reaction conditions: 2 (0.25 mmol), solvent (0.2M), acid (0.3 mmol) [b] not isolated. [c] 10 mol% of TFA was used. [d] Acidic solvent promoted the reaction without acid. [d] reaction proceed without acid.

F. The *para*-selective arylation of α-carbonitriles

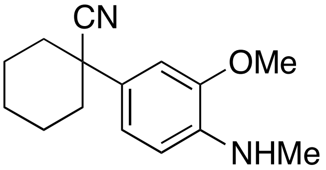
Typical reaction conditions for the synthesis of α-(4-aminoaryl)carbonitrile products 7. To a solution of triazene (0.25 mmol) in CH_2Cl_2 (0.2M, 1.25 mL) at 0 °C was added BF_3•OEt_2 (0.3 mmol) dropwise. Gentle bubbling continued for approximately 3 to 5 minutes. The resulting mixture was continued stirring for an hour at 0 °C. The reaction solution gradually turned brown or black. The reaction mixture was quenched with 1M NaOH (3 mL), and the aq. layer was extracted 3 times with CH_2Cl_2 (5 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The resulting crude material was purified by automated column chloromatography (SiO_2, 20% EtOAc/hexanes) to afford the corresponding α-(4-aminoaryl)carbonitrile products (**7a–7p, 7aa**).



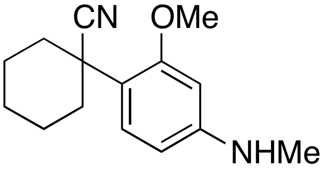
1-(4-(Methylamino)phenyl)cyclohexanecarbonitrile (**7a**): white solid, mp 91–95 °C; IR (neat) 3413, 2229, 1615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2H), 6.64–6.57 (m, 2H), 3.77 (bs, 1H), 2.84 (s, 3H), 2.24–2.06 (m, 2H), 1.92–1.75 (m, 5H), 1.74–1.63 (m, 2H), 1.33–1.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 130.1, 126.6, 123.5, 112.6, 43.5, 37.7, 30.8, 25.3, 23.9; HRMS calcd for $C_{14}H_{19}N_2$ [M+H]$^+$: 215.1548, found 215.1558.



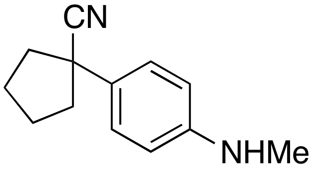
2-(4-(Methylamino)phenyl)-2-phenylpropanenitrile (**7b**): brown oil; IR (neat) 3413, 2233, 1613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.22 (m, 5H), 7.20–7.12 (m, 2H), 6.61–6.48 (m, 2H), 3.79 (bs, 1H), 2.81 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 142.4, 129.5, 128.9, 127.8, 127.8, 126.7, 124.1, 112.5, 45.6, 30.7, 28.5; HRMS calcd for $C_{16}H_{17}N_2$ [M+H]$^+$: 237.1392, found 237.1392.



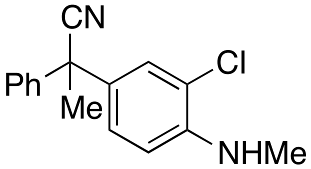
1-(3-Methoxy-4-(methylamino)phenyl)cyclohexanecarbonitrile (**7c**): off-white solid, mp 76–79 °C; IR (neat) 3431, 2231, 1613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 4.26 (bs, 1H), 3.87 (s, 3H), 2.86 (s, 3H), 2.24–2.09 (m, 2H), 1.89–1.79 (m, 5H), 1.78–1.65 (m, 2H), 1.36–1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 139.1, 129.5, 123.5, 118.1, 109.0, 107.3, 55.7, 43.8, 37.8, 30.5, 25.3, 23.9; HRMS calcd for $C_{15}H_{21}N_2O$ [M+H]$^+$: 245.1654, found 245.1656.



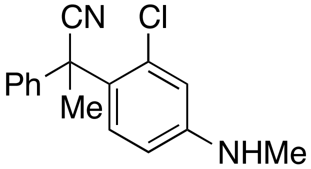
1-(2-Methoxy-4-(methylamino)phenyl)cyclohexanecarbonitrile (**7d**): yellow solid, mp 100–102 °C; IR (neat) 3402, 2230, 1614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.2 Hz, 1H), 6.19 (q, *J* = 2.3 Hz, 3H), 6.17 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 2.84 (s, 3H), 2.34 (ddt, *J* = 13.5, 3.1, 1.7 Hz, 2H), 1.91–1.75 (m, 5H), 1.69 (td, *J* = 12.7, 3.9 Hz, 2H), 1.31–1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 150.5, 126.8, 123.3, 118.2, 104.1, 97.3, 55.6, 40.3, 35.1, 30.84, 25.58, 23.61; HRMS calcd for $C_{15}H_{21}N_2O$ [M+H]$^+$: 245.1654, found 245.1656.



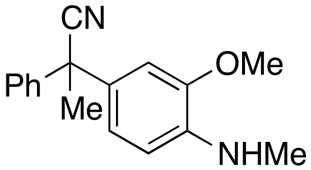
1-(4-(Methylamino)phenyl)cyclopentanecarbonitrile (**7e**): off-white solid, mp 76–78 °C; IR (neat) 3399, 2222, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.20 (m, 2H), 6.64–6.52 (m, 2H), 3.78 (bs, 1H), 2.83 (s, 3H), 2.49–2.36 (m, 2H), 2.11–1.95 (m, 4H), 1.93–1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 128.1, 127.1, 125.2, 112.6, 47.1, 40.4, 30.8, 24.2; HRMS calcd for $C_{13}H_{17}N_2$ [M+H]$^+$: 201.1392, found 201.1398.



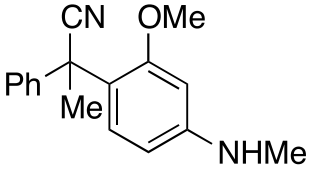
2-(3-Chloro-4-(methylamino)phenyl)-2-phenylpropanenitrile (**7f**): brown oil; IR (neat) 3421, 2235, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 4H), 7.33–7.27 (m, 1H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.17 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.41 (q, *J* = 5.1 Hz, 1H), 2.90 (d, *J* = 5.2 Hz, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.8, 129.8, 129.1, 128.0, 127.5, 126.6, 126.5, 123.7, 119.2, 110.6, 45.4, 30.5, 28.4; HRMS calcd for $C_{16}H_{16}ClN_2$ [M+H]$^+$: 271.1002, found 271.0996.



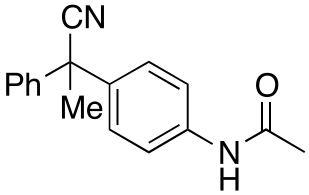
2-(2-Chloro-4-(methylamino)phenyl)-2-phenylpropanenitrile (**7g**): brown oil; IR (neat) 3412, 2235, 1608 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 1H), 7.34–7.23 (m, 5H), 6.61 (d, *J* = 2.6 Hz, 1H), 6.54 (dd, *J* = 8.6, 2.6 Hz, 1H), 2.82 (s, 4H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 142.4, 135.4, 128.8, 128.8, 127.5, 125.9, 124.3, 122.6, 114.9, 110.6, 45.0, 30.6, 30.0; HRMS calcd for $C_{16}H_{16}ClN_2$ [M+H]$^+$: 271.1002, found 271.1000.



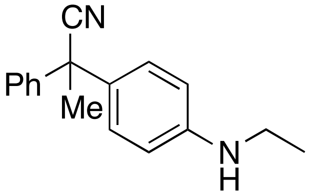
2-(3-Methoxy-4-(methylamino)phenyl)-2-phenylpropanenitrile (**7h**): brown oil; IR (neat) 3430, 2233, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.20 (m, 5H), 6.88 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.69 (d, *J* = 2.1 Hz, 1H), 6.52 (d, *J* = 8.2 Hz, 1H), 4.28 (bs, 1H), 3.76 (s, 3H), 2.84 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 142.3, 139.2, 128.9, 128.6, 127.8, 126.7, 124.2, 119.4, 108.6, 108.4, 55.6, 45.9, 30.4, 28.6; HRMS calcd for $C_{17}H_{19}N_2O$ [M+H]$^+$: 267.1497, found 267.1501.



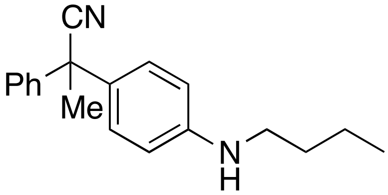
2-(2-Methoxy-4-(methylamino)phenyl)-2-phenylpropanenitrile (**7i**): brown oil; IR (neat) 3410, 2235, 1613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.18 (m, 5H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.21 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.11 (d, *J* = 2.3 Hz, 1H), 3.85 (s, 1H), 3.56 (s, 3H), 2.83 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 151.1, 143.3, 128.4, 127.7, 127.0, 125.8, 123.8, 117.3, 103.7, 97.5, 55.6, 42.9, 30.8, 28.5; HRMS calcd for $C_{17}H_{19}N_2O$ [M+H]$^+$: 267.1497, found 267.1499.



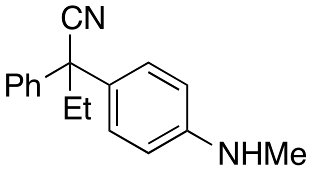
N-(4-(1-Cyano-1-phenylethyl)phenyl)acetamide (**7j**): yellow oil; IR (neat) 3300, 1672, 1601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.48 (m, 2H), 7.47 (s, 1H), 7.38–7.34 (m, 4H), 7.33–7.28 (m, 3H), 2.16 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 141.4, 137.8, 137.0, 129.1, 128.2, 127.6, 126.7, 123.6, 120.3, 45.9, 28.3, 24.8; HRMS calcd for $C_{17}H_{20}N_3O$ [M+NH$_4$$^+$: 282.1606, found 282.1598.



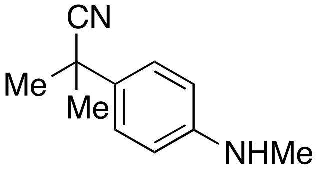
2-(4-(Ethylamino)phenyl)-2-phenylpropanenitrile (**7k**): pale brown oil; IR (neat) 3396, 2233, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.21 (m, 5H), 7.17–7.05 (m, 2H), 6.61–6.47 (m, 2H), 3.66 (bs, 1H), 3.13 (q, *J* = 7.1 Hz, 2H), 2.02 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 142.4, 129.4, 128.9, 127.8, 127.8, 126.7, 124.1, 112.7, 45.6, 38.5, 28.5, 15.0; HRMS calcd for $C_{17}H_{19}N_2$ [M+H]$^+$: 251.1548, found 251.1560.



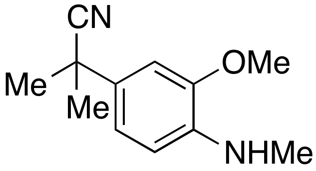
2-(4-(Butylamino)phenyl)-2-phenylpropanenitrile (**7l**): brown oil; IR (neat) 3400, 2234, 1613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.23 (m, 5H), 7.18–7.10 (m, 2H), 6.58–6.49 (m, 2H), 3.69 (bs, 1H), 3.08 (t, *J* = 7.1 Hz, 2H), 2.02 (s, 3H), 1.67–1.49 (m, 2H), 1.48–1.33 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 142.4, 129.3, 128.9, 127.8, 127.8, 126.7, 124.1, 112.7, 45.6, 43.7, 31.7, 28.5, 20.4, 14.1; HRMS calcd for $C_{19}H_{23}N_2$ [M+H]$^+$: 279.1861, found 279.1877.



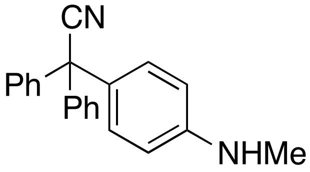
2-(4-(Methylamino)phenyl)-2-phenylbutanenitrile (**7m**): pale yellow oil; IR (neat) 3413, 2233, 1613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.29 (m, 4H), 7.28–7.22 (m, 1H), 7.21–7.12 (m, 2H), 6.60–6.51 (m, 2H), 2.81 (s, 3H), 2.36 (p, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.1, 128.9, 128.5, 128.10, 127.7, 127.1, 122.9, 112.5, 52.0, 33.1, 30.8, 10.4; HRMS calcd for $C_{17}H_{19}N_2$ [M+H]$^+$: 251.1548, found 251.1553.



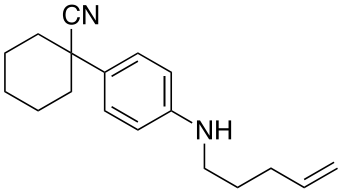
2-Methyl-2-(4-(methylamino)phenyl)propanenitrile (**7n**): pale yellow oil; IR (neat) 3410, 2234, 1615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.13 (m, 1H), 6.76–6.30 (m, 1H), 2.83 (s, 2H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 129.9, 126.2, 125.3, 112.6, 36.4, 30.8, 29.4; HRMS calcd for $C_{11}H_{15}N_2$ [M+H]$^+$: 175.1235, found 175.1228.



2-(3-Methoxy-4-(methylamino)phenyl)-2-methylpropanenitrile (**7o**): colorless oil; IR (neat) 3428, 2233, 1614 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 2.86 (s, 3H), 1.70 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 139.1, 129.3, 125.4, 117.6, 109.0, 106.8, 55.7, 36.8, 30.5, 29.5; HRMS calcd for $C_{12}H_{17}N_2O$ [M+H]$^+$: 205.1341, found 205.1356.



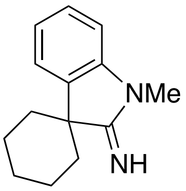
2-(4-(Methylamino)phenyl)-2,2-diphenylacetonitrile (**7p**): yellow solid, mp 109–112 °C; IR (neat) 3416, 2235, 1613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 6H), 7.27–7.19 (m, 3H), 7.03–6.92 (m, 2H), 6.59–6.50 (m, 2H), 3.85 (bs, 1H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 141.1, 129.9, 129.0, 128.7, 128.5, 128.1, 124.1, 112.3, 57.0, 30.7; HRMS calcd for $C_{21}H_{19}N_2$ [M+H]$^+$: 299.1548, found 299.1555.



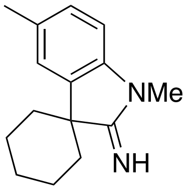
1-(4-(pent-4-en-1-ylamino)phenyl)cyclohexane-1-carbonitrile (**5aa**): yellow oil; IR (neat) 3394, 1599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.21 (m, 2H), 6.61–6.56 (m, 2H), 5.84 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.06 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.00 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 3.70 (s, 1H), 3.13 (t, *J* = 7.1 Hz, 2H), 2.22–2.06 (m, 4H), 1.90–1.77 (m, 5H), 1.76–1.64 (m, 4H), 1.34–1.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 138.1, 130.0, 126.6, 123.5, 115.4, 112.9, 43.51, 43.48, 37.7, 31.4, 28.8, 25.3, 23.9; HRMS calcd for $C_{18}H_{25}N_2$ [M+H]$^+$: 269.2018, found 269.2003.

G. The *ortho*-selective arylation of α-carbonitriles

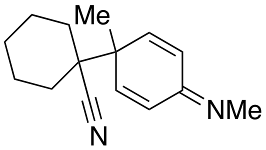
Typical reaction conditions for the synthesis of benzoamidine products 8. To a solution of triazene **2** (0.20 mmol) in Methanol (0.2M, 1.0 mL) at 0 °C was added trifluoroacetic acid (0.5 mmol) dropwise. Gentle bubbling continued for approximately 3 to 5 minutes. The resulting mixture was kept in a refrigerator at 0 °C for 12 h. The reaction mixture was quenched with 1M NaOH (3 mL), and the aq. layer was extracted 3 times with dichloromethane (3 × 5 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The resulting crude material was purified by automated column chloromatography (SiO_2, eluted with 90:9:1 CH_2Cl_2:MeOH:NH_4OH) to afford the corresponding benzoamidine (**8q–8z**).



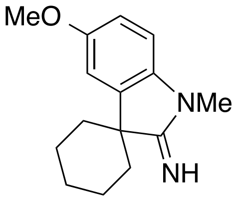
1'-methylspiro[cyclohexane-1,3'-indolin]-2'-imine (**8a**): colorless oil; IR (neat) 1644, 1604 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.24 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 6.92 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.23 (s, 3H), 1.92–1.76 (m, 6H), 1.69–1.59 (m, 4H), 1.58–1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 145.0, 135.3, 127.8, 124.6, 120.1, 107.0, 48.3, 35.6, 27.3, 25.3, 21.6; HRMS calcd for $C_{14}H_{19}N_2$ $[M+H]^+$: 215.1548, found 215.1538.



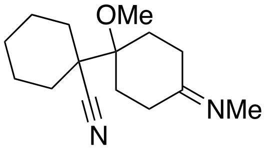
1',5'-dimethylspiro[cyclohexane-1,3'-indolin]-2'-imine (**8q**): yellow solid, mp 109-112 °C; IR (neat) 1641, 1610, 1596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 3.21 (s, 3H), 2.34 (s, 3H), 1.94–1.75 (m, 5H), 1.71–1.57 (m, 4H), 1.57–1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 142.7, 135.5, 129.4, 127.9, 125.7, 106.6, 48.4, 35.6, 27.4, 25.3, 21.6, 21.4. HRMS calcd for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1705, found 229.1697.



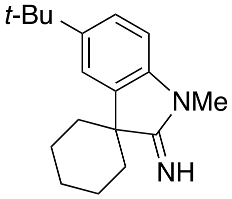
1'-methyl-4'-(methylimino)-[1,1'-bi(cyclohexane)]-2',5'-diene-1-carbonitrile (**10q**): pale yellow oil; IR (neat) 1656, 1607, 1591 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 10.5, 2.0 Hz, 1H), 6.46 (dd, *J* = 10.5, 2.8 Hz, 1H), 6.39 (dd, *J* = 10.2, 2.0 Hz, 1H), 6.26 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.35 (s, 3H), 1.99 (dd, *J* = 13.2, 1.6 Hz, 1H), 1.91 (dd, *J* = 13.2, 1.6 Hz, 1H), 1.81–1.71 (m, 2H), 1.64 (m, 2H), 1.36 (s, 3H), 1.36–1.23 (m, 3H), 1.07 (dtt, *J* = 12.8, 12.8, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 143.2, 138.6, 132.1, 121.9, 119.1, 47.1, 44.9, 38.2, 30.9, 30.5, 25.3, 23.5, 23.5, 23.0; HRMS calcd for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1705, found 229.1692.



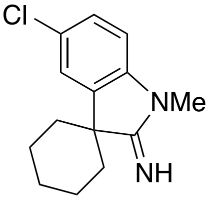
5'-methoxy-1'-methylspiro[cyclohexane-1,3'-indolin]-2'-imine (**8r**): colorless oil; IR (neat) 1592 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 2.5 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.20 (s, 3H), 1.91–1.75 (m, 5H), 1.71–1.57 (m, 4H), 1.57–1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 154.1, 138.9, 136.6, 113.5, 110.9, 106.5, 56.1, 48.5, 35.4, 27.3, 25.2, 21.5; HRMS calcd for $C_{15}H_{21}N_2O$ [M+H]$^+$: 245.1654, found 245.1643.



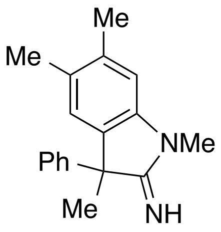
1'-methoxy-4'-(methylimino)-[1,1'-bi(cyclohexane)]-2',5'-diene-1-carbonitrile (**10r**): colorless oil; IR (neat) 1642, 1596 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 10.7, 2.1 Hz, 1H), 6.60 (dd, *J* = 10.4, 2.1 Hz, 1H), 6.41 (dd, *J* = 10.7, 2.8 Hz, 1H), 6.23 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.45 (s, 3H), 3.18 (s, 3H), 2.08 (d, *J* = 13.5 Hz, 1H), 1.97 (d, *J* = 13.4 Hz, 1H), 1.83–1.70 (m, 3H), 1.70–1.55 (m, 2H), 1.29 (tdd, *J* = 13.2, 3.7, 2.0 Hz, 2H), 1.14–1.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 138.4, 136.4, 133.8, 122.3, 121.7, 52.6, 48.9, 39.0, 30.3, 30.0, 25.5, 23.1, 23.1; HRMS calcd for $C_{15}H_{21}N_2O$ [M+H]$^+$: 245.1654, found 245.1647.



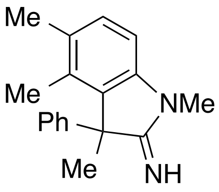
5'-(*tert*-butyl)-1'-methylspiro[cyclohexane-1,3'-indolin]-2'-imine (**8s**): white solid, mp 107–111 °C; IR (neat) 1640, 1611, 1594 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.0 Hz, 1H), 7.27 (dd, *J* = 8.0, 1.8 Hz, 2H), 6.68 (d, *J* = 8.1 Hz, 1H), 3.21 (s, 3H), 1.94–1.77 (m, 5H), 1.73–1.59 (m, 4H), 1.59–1.48 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 143.1, 142.7, 135.2, 124.2, 122.0, 106.1, 48.4, 35.6, 34.6, 31.9, 27.3, 25.4, 21.8; HRMS calcd for $C_{18}H_{27}N_2$ [M+H]$^+$: 271.2174, found 271.2157.



5'-chloro-1'-methylspiro[cyclohexane-1,3'-indolin]-2'-imine (**8t**): white solid, mp 53–58 °C; IR (neat) 1643, 1599, 1594 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.1 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 3.22 (s, 3H), 1.92–1.77 (m, 5H), 1.73–1.57 (m, 4H), 1.56–1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 143.6, 136.9, 127.6, 125.4, 125.1, 107.7, 48.6, 35.4, 27.6, 25.1, 21.5; HRMS calcd for $C_{14}H_{18}ClN_2$ [M+H]$^+$: 249.1159, found 249.1159.

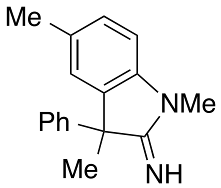


8u

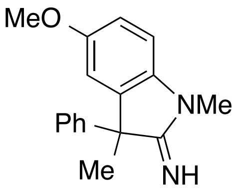


8u'

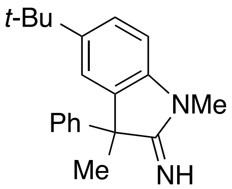
1,3,5,6-tetramethyl-3-phenylindolin-2-imine (**8u**): yellow oil; IR (neat) 1645, 1618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.19 (m, 5H), 6.74 (s, 1H), 6.61 (s, 1H), 3.29 (s, 3H), 2.28 (s, 3H), 2.15 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 143.4, 143.2, 136.4, 133.7, 128.9, 128.8, 127.2, 126.8, 124.8, 108.7, 53.2, 27.5, 25.4, 20.4, 19.5; HRMS calcd for $C_{18}H_{21}N_2$ $[M+H]^+$: 265.1705, found 265.1694. 1,3,4,5-tetramethyl-3-phenylindolin-2-imine (**8u'**) not seperable from **8u**.^1H NMR (400 MHz, $CDCl_{3,}$ diagnostic peaks ony) δ 7.07 (d, *J* = 7.9 Hz, 1H), 3.25 (s, 3H), 2.17 (s, 3H), 1.78 (s, 3H), 1.77 (s, 3H).



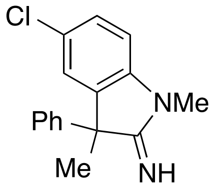
1,3,5-trimethyl-3-phenylindolin-2-imine (**8v**): white solid, mp 87-89 °C; IR (neat) 1644, 1594 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.26–7.19 (m, 3H), 7.02 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 3.29 (s, 3H), 2.24 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 143.0, 142.9, 136.4, 130.6, 128.8, 128.5, 127.3, 126.8, 124.4, 106.9, 53.3, 27.6, 25.3, 21.1; HRMS calcd for $C_{17}H_{19}N_2$ $[M+H]^+$: 251.1548, found 251.1537.



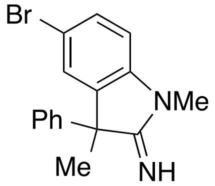
5-methoxy-1,3-dimethyl-3-phenylindolin-2-imine (**8w**): brown oil; IR (neat) 1644, 1596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.27–7.19 (m, 3H), 6.78 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 2.5 Hz, 1H), 3.72 (s, 3H), 3.29 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 155.2, 142.7, 139.2, 137.6, 128.9, 127.4, 126.8, 112.5, 111.3, 107.2, 56.0, 53.6, 27.7, 25.3; HRMS calcd for $C_{17}H_{19}N_2O$ $[M+H]^+$: 267.1497, found 267.1480.



5-(*tert*-butyl)-1,3-dimethyl-3-phenylindolin-2-imine (**8x**): pale yellow oil; IR (neat) 1645, 1615, 1595 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.26–7.19 (m, 4H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 3.29 (s, 3H), 1.75 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 144.4, 143.1, 143.0, 135.9, 128.8, 127.3, 126.8, 124.8, 120.8, 106.5, 53.5, 34.6, 31.8, 27.5, 25.5; HRMS calcd for $C_{20}H_{25}N_2$ $[M+H]^+$: 293.2018, found 293.2001.



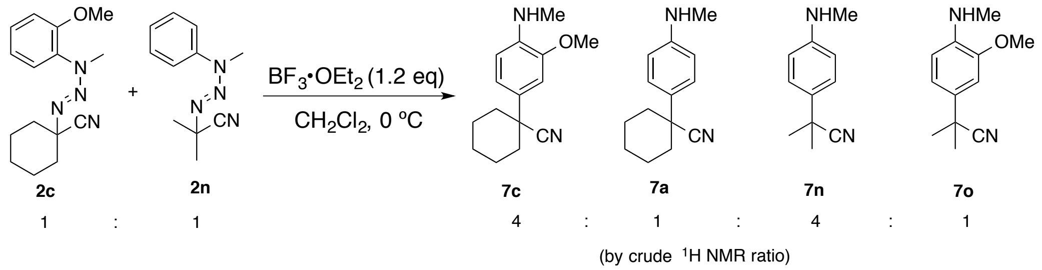
5-chloro-1,3-dimethyl-3-phenylindolin-2-imine (**8y**): yellow solid, mp 107–111 °C; IR (neat) 1646, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.23 (m, 3H), 7.22–7.17 (m, 3H), 6.93 (d, *J* = 2.1 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 3.30 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 143.9, 142.0, 137.9, 129.0, 128.2, 127.7, 126.7, 126.3, 124.0, 108.0, 53.3, 27.7, 25.3; HRMS calcd for $C_{16}H_{16}ClN_2$ [M+H]$^+$: 271.1002, found 271.0986.

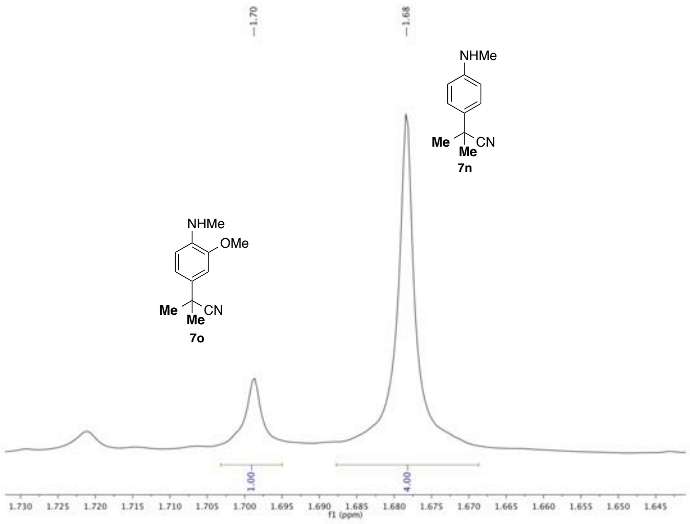


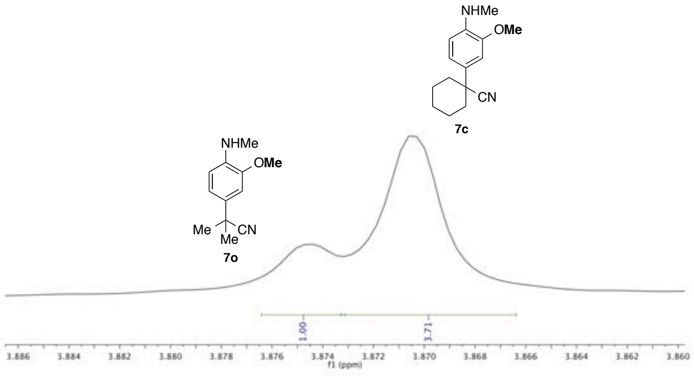
5-bromo-1,3-dimethyl-3-phenylindolin-2-imine (**8z**): dark brown oil; IR (neat) 1649, 1600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.24 (m, 4H), 7.23–7.17 (m, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 3.29 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 144.4, 142.0, 138.3, 131.1, 129.0, 127.7, 126.8, 126.7, 113.5, 108.6, 53.3, 27.6, 25.3; HRMS calcd for $C_{16}H_{16}BrN_2$ [M+H]$^+$: 315.0497, found 315.0478.

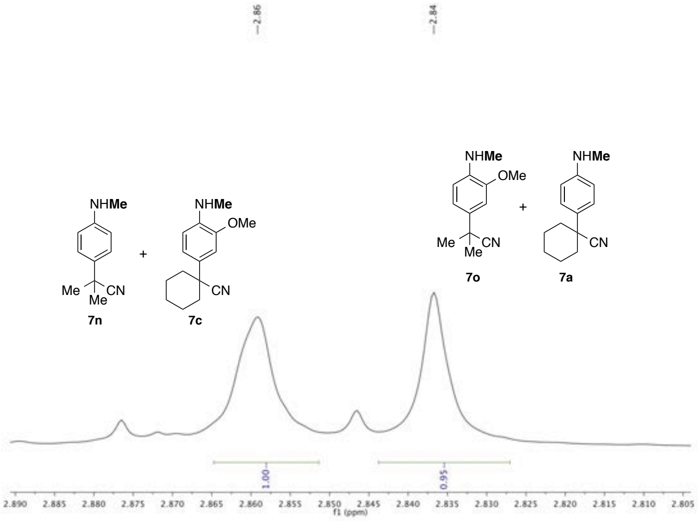
H. Crossover Experiment with a mixture of 2c and 2n

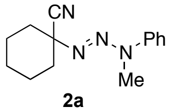
Two substrates, **2c** and **2n**, which have similar reactivity toward the α–arylation reaction, were subjected to a crossover experiment. A mixture of **2c** and **2n** (1:1) was submitted to typical reaction conditions (see S14). The ^{1}H NMR spectrum of the resulting crude mixture was carefully compared with the known spectra of **7c**, **7a**, **7n**, and **7o**. The observed ratio of **7c**:**7a**:**7n**:**7o** was ca. 4:1:4:1 (see below).



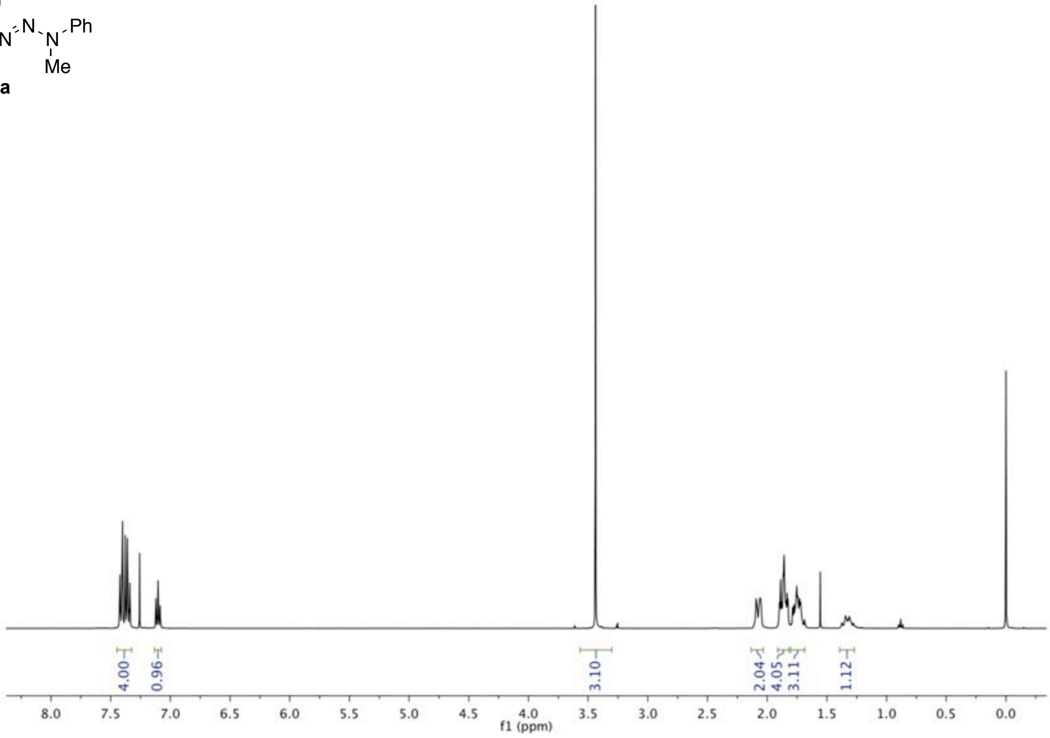





2.86
2.84
NHMe
Me
CN
7n
+
NHMe
OMe
CN
7c
NHMe
OMe
Me
CN
Me
7o
+
NHMe
CN
7a
1.00
0.95
2.890 2.885 2.880 2.875 2.870 2.865 2.860 2.855 2.850 2.845 2.840 2.835 2.830 2.825 2.820 2.815 2.810 2.805
f1 (ppm)


CN
N
N
N
Ph
Me

2a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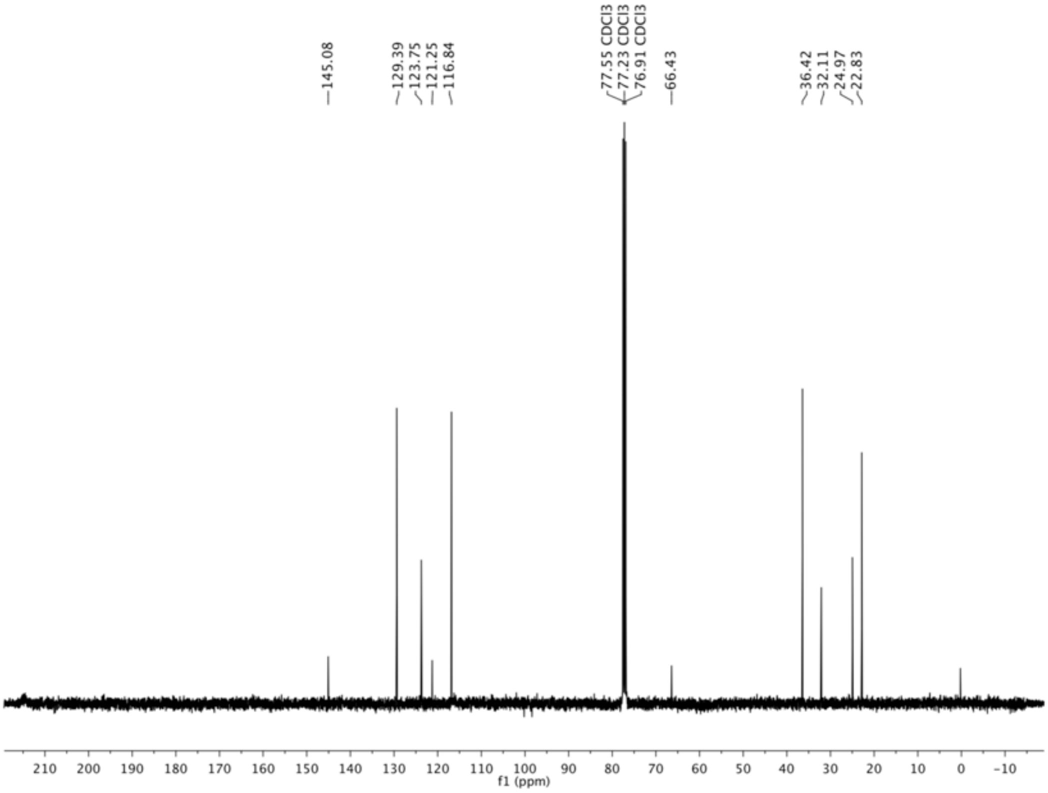
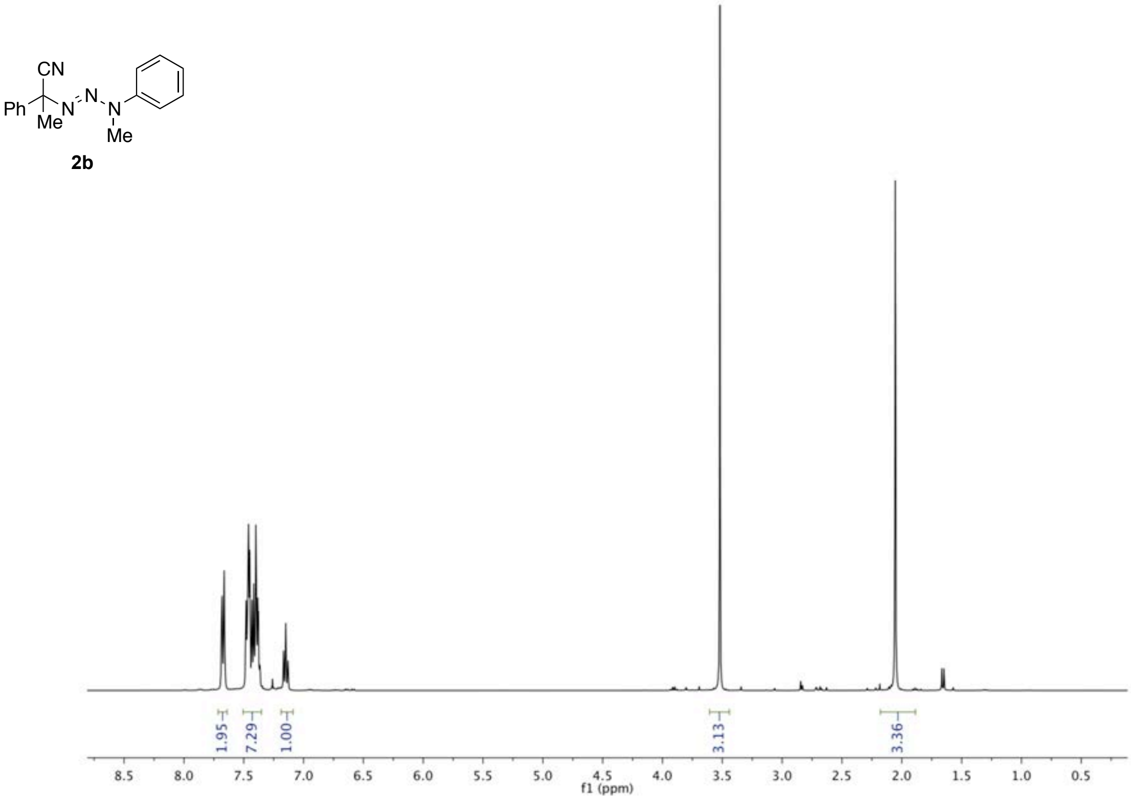
0.96
3.10
2.04
4.05
3.11
1.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.08
129.39
123.75
121.25
116.84
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
66.43
36.42
32.11
24.97
22.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

CN
Ph
N
N
N
Me
Me

2b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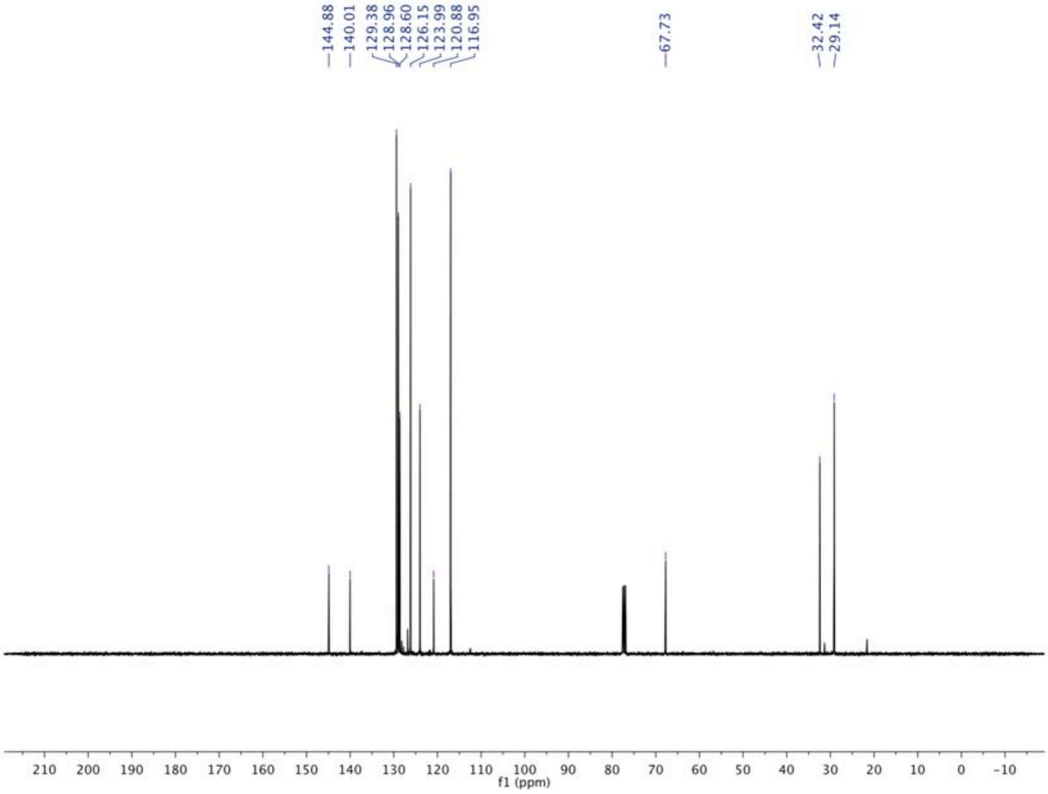
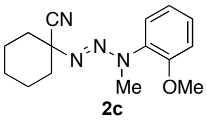
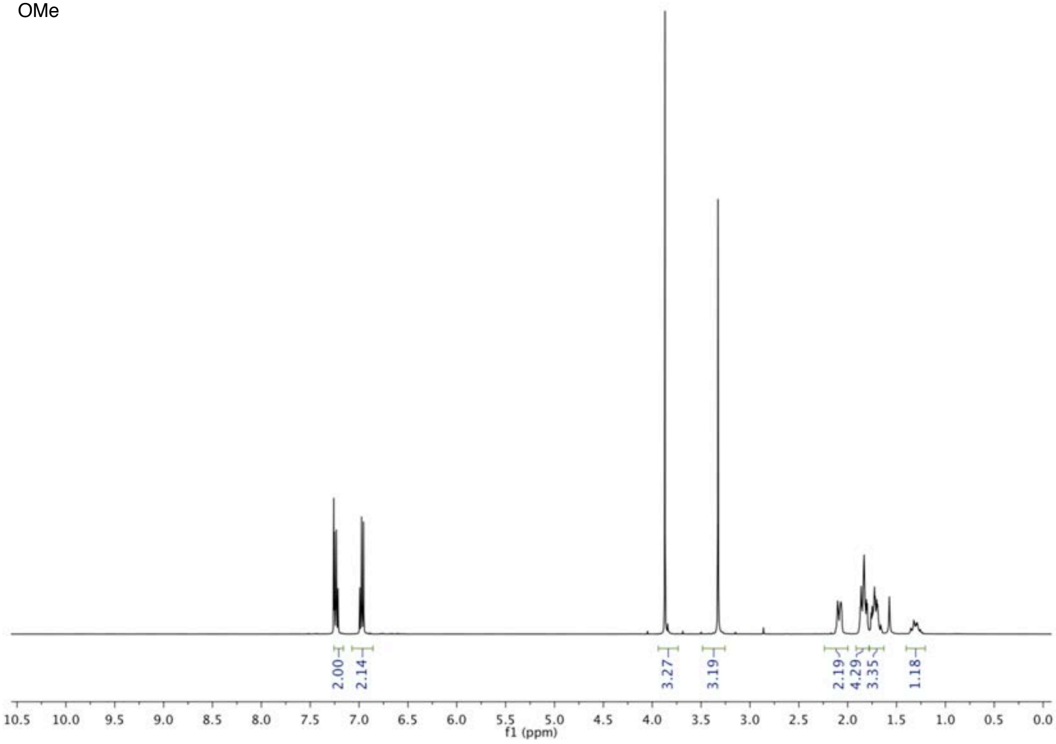
7.29
1.00
3.13
3.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


144.88
140.01
129.38
128.96
128.60
126.15
123.99
120.88
116.95
67.73
32.42
29.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
N
N
N
Me
OMe

2c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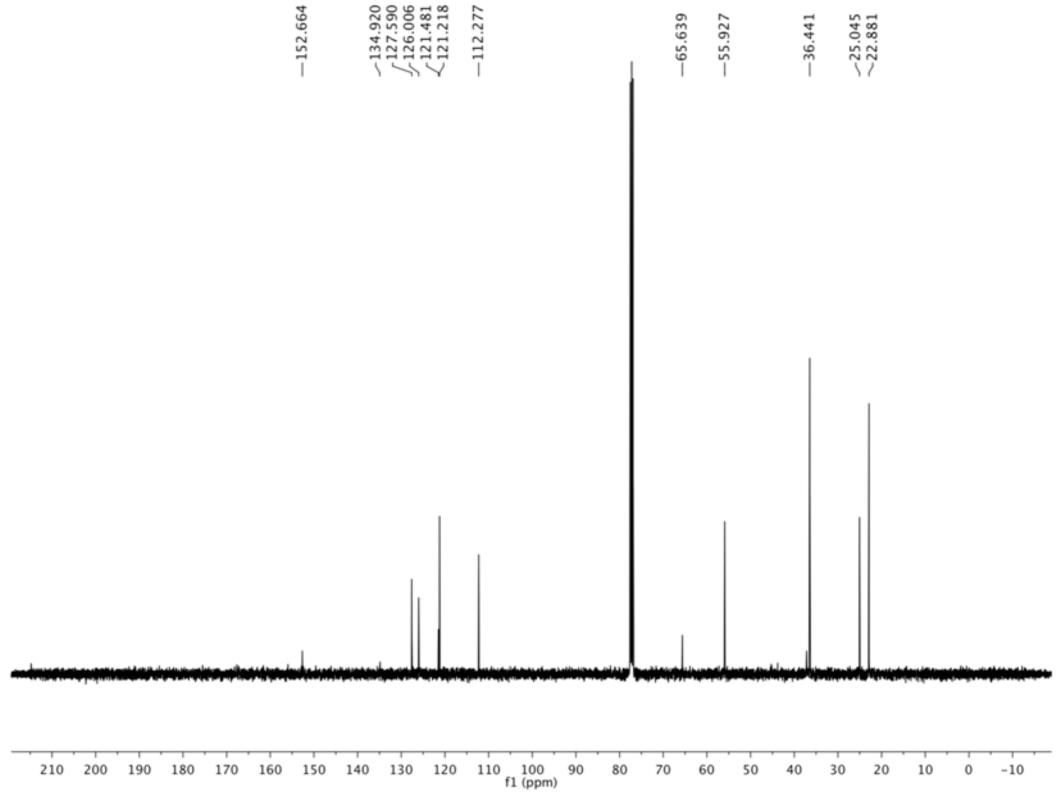
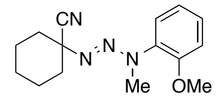
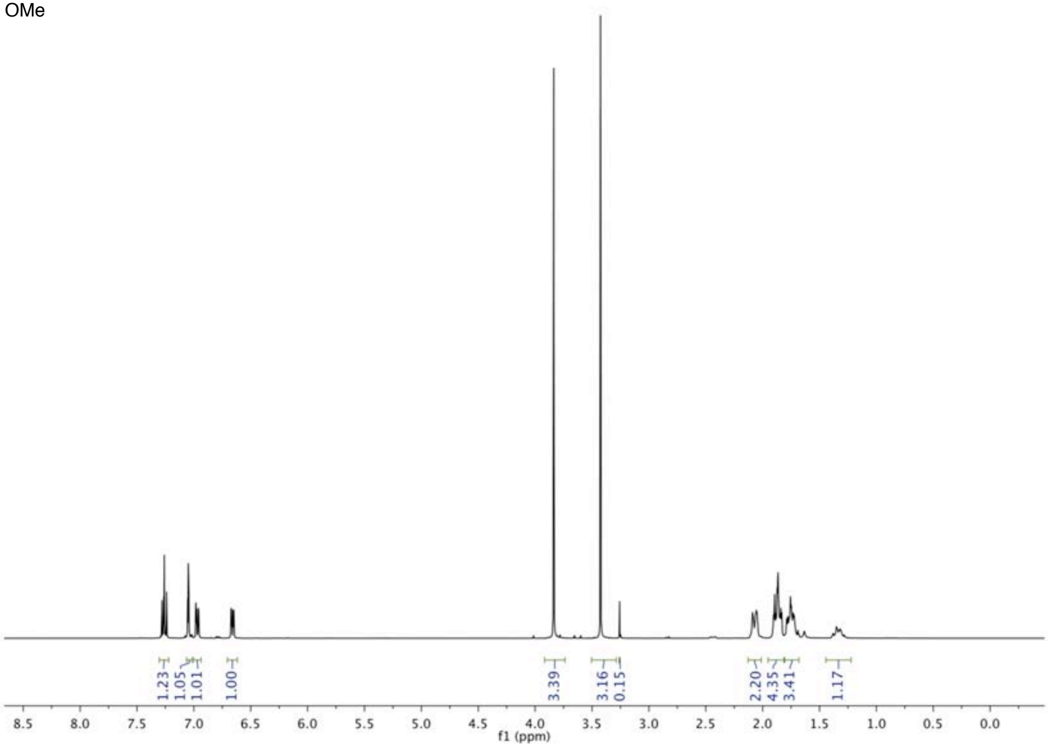
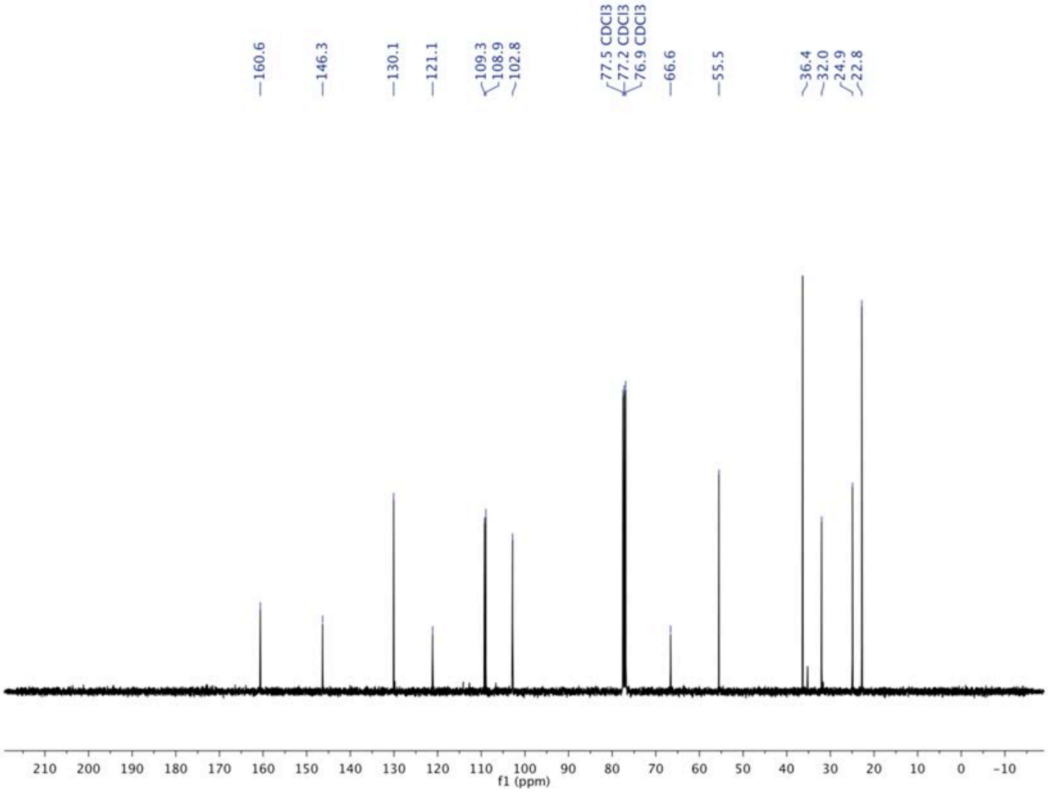
2.14
3.27
3.19
2.19
4.29
3.35
1.18
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

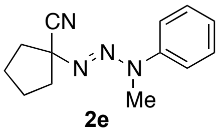

152.664
134.920
127.590
126.006
121.481
121.218
112.277
65.639
55.927
36.441
25.045
22.881
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
N
N
N
Me
OMe

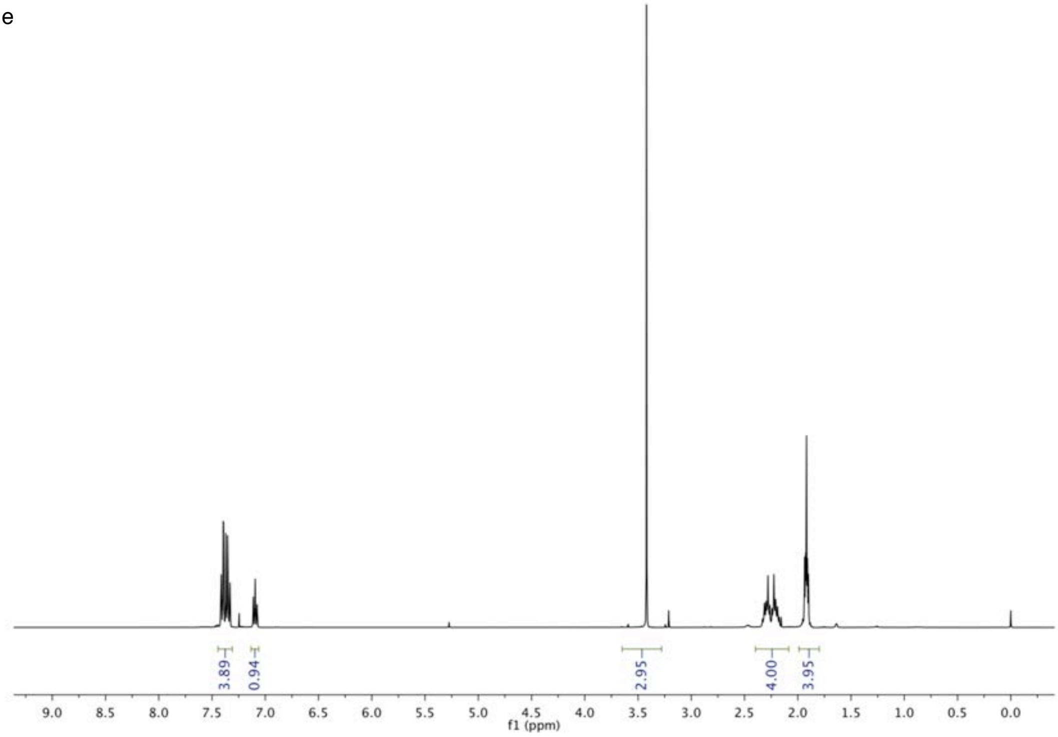
2d


1.23
1.05
1.01
1.00
3.39
3.16
0.15
2.20
4.35
3.41
1.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.6
146.3
130.1
121.1
109.3
108.9
102.8
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
66.6
55.5
36.4
32.0
24.9
22.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
N
N
N
Me

2e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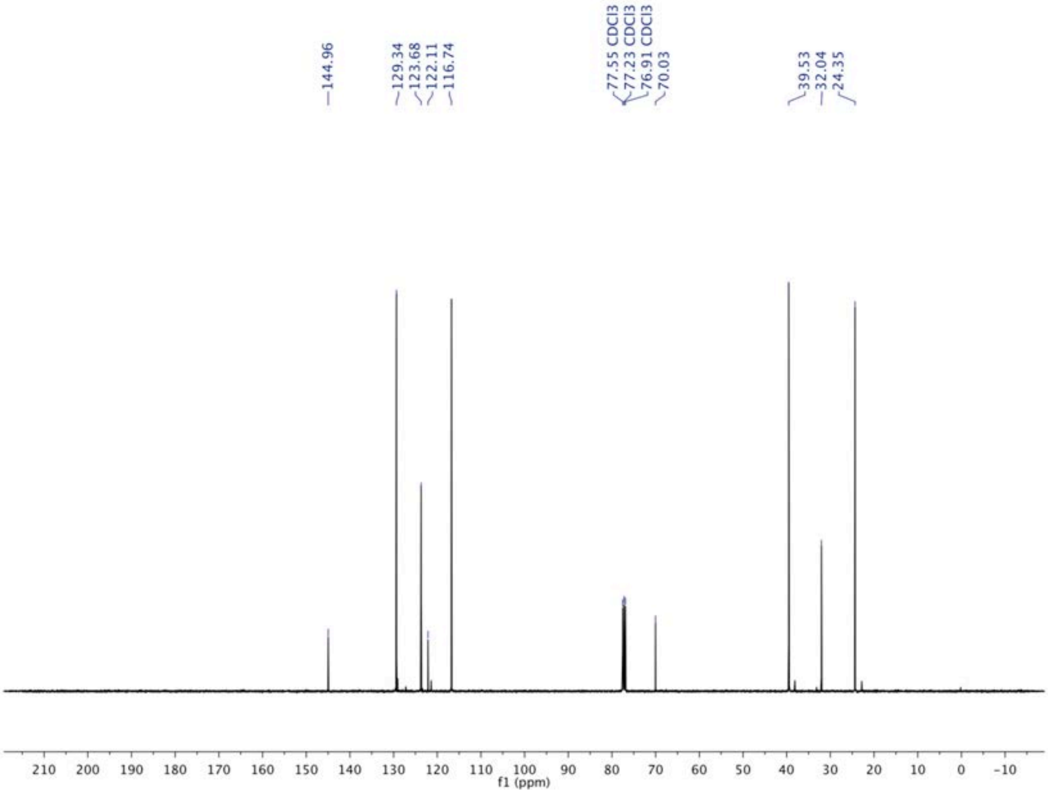
4.00
3.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.34
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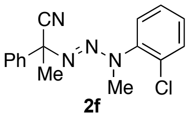
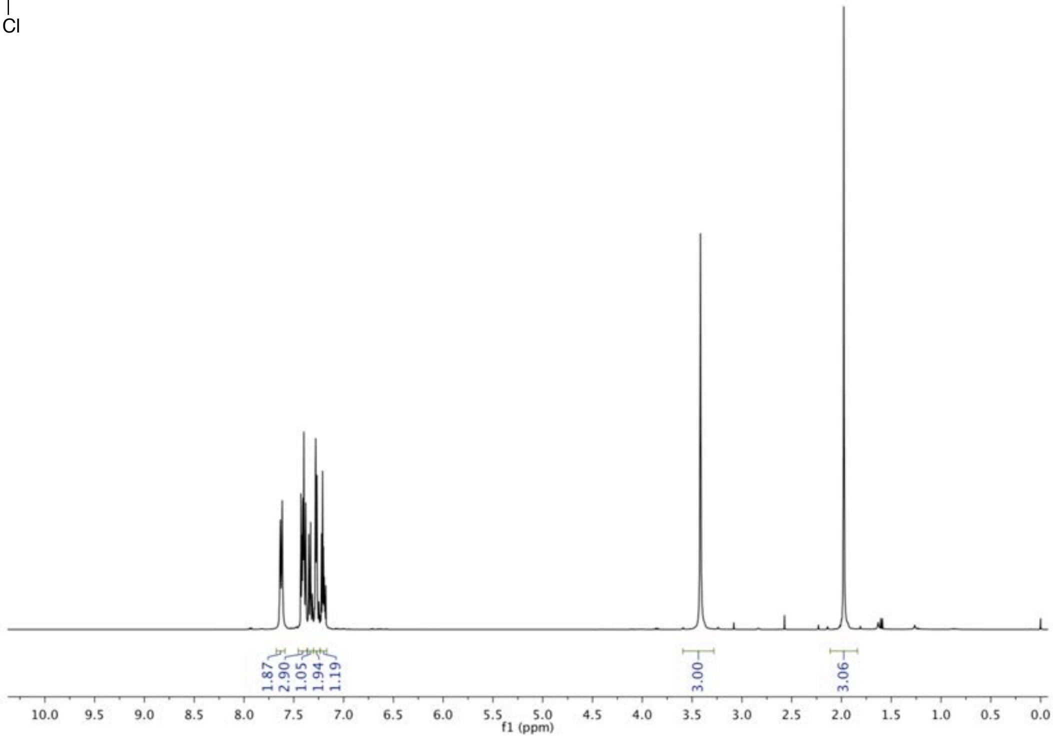
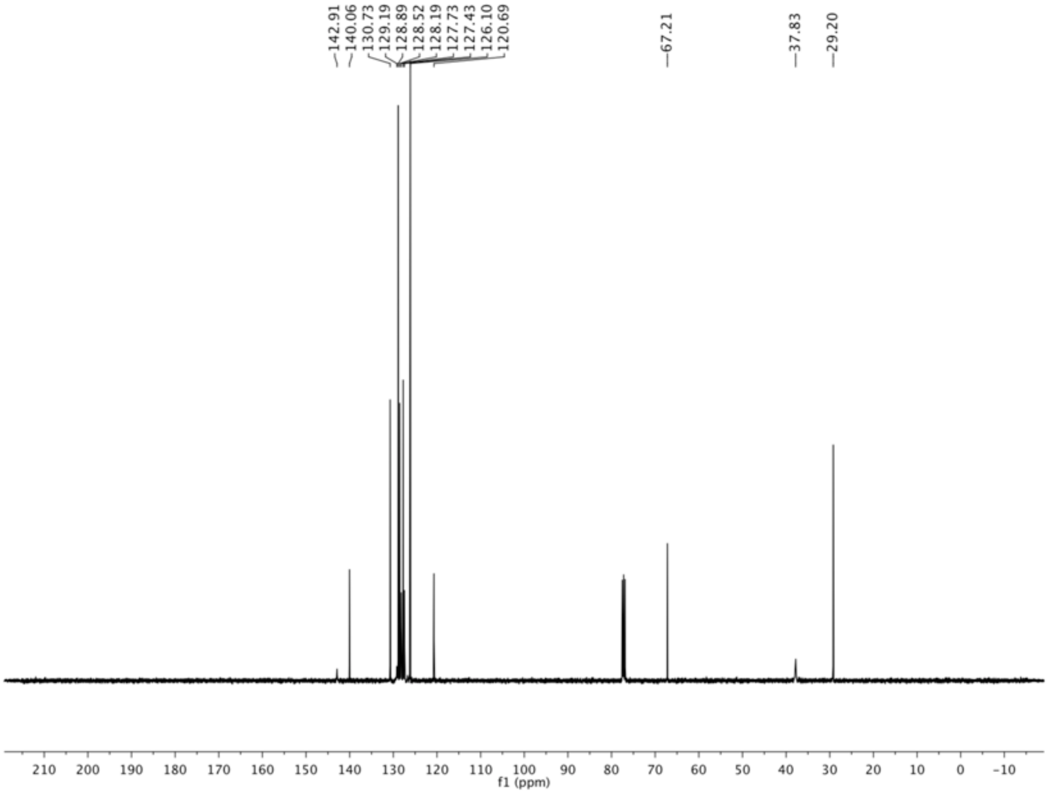
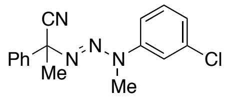
122.11
116.74
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
70.03
39.53
32.04
24.35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
N
N
Me
Cl

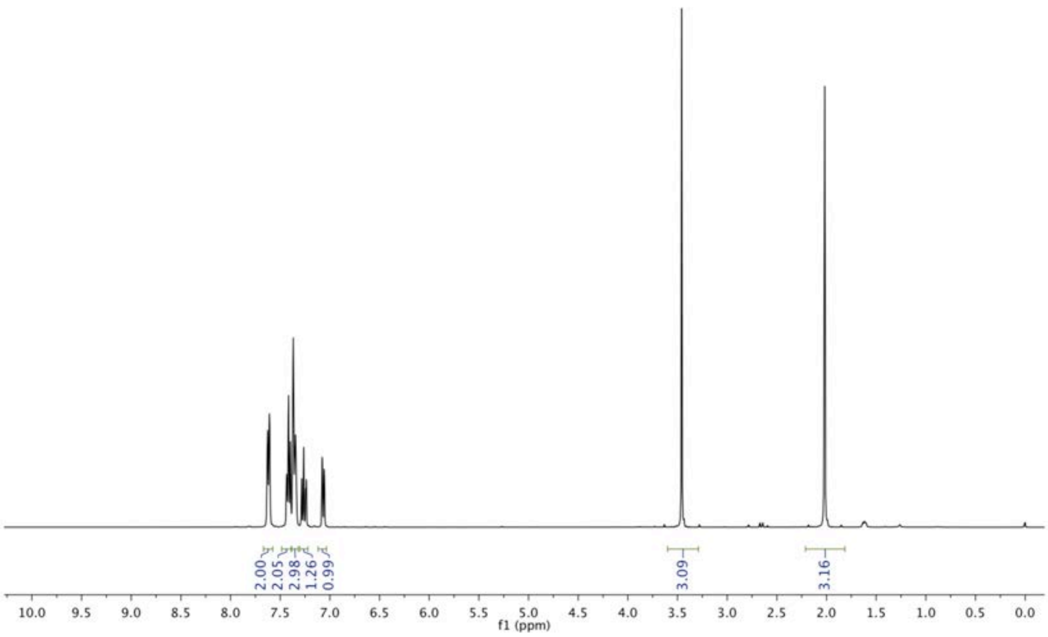
2f


1.87
2.90
1.05
1.94
1.19
3.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.91
140.06
130.73
129.19
128.89
128.52
128.19
127.73
127.43
126.10
120.69
67.21
37.83
29.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
N
N
Me
Cl

2g


2.00
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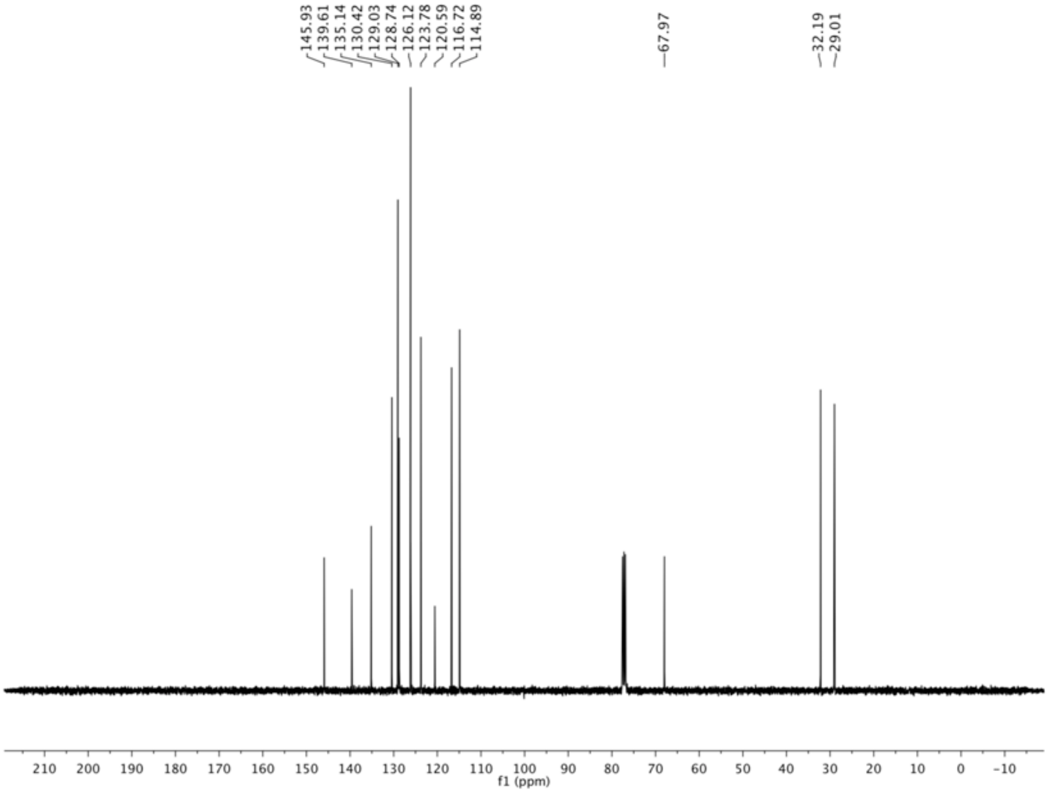
1.26
0.99
3.09
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.03
128.74
126.12
123.78
120.59
116.72
114.89
67.97
32.19
29.01
210
200
190
180
170
160
150
140
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120
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100
90
80
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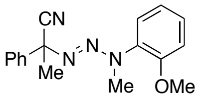
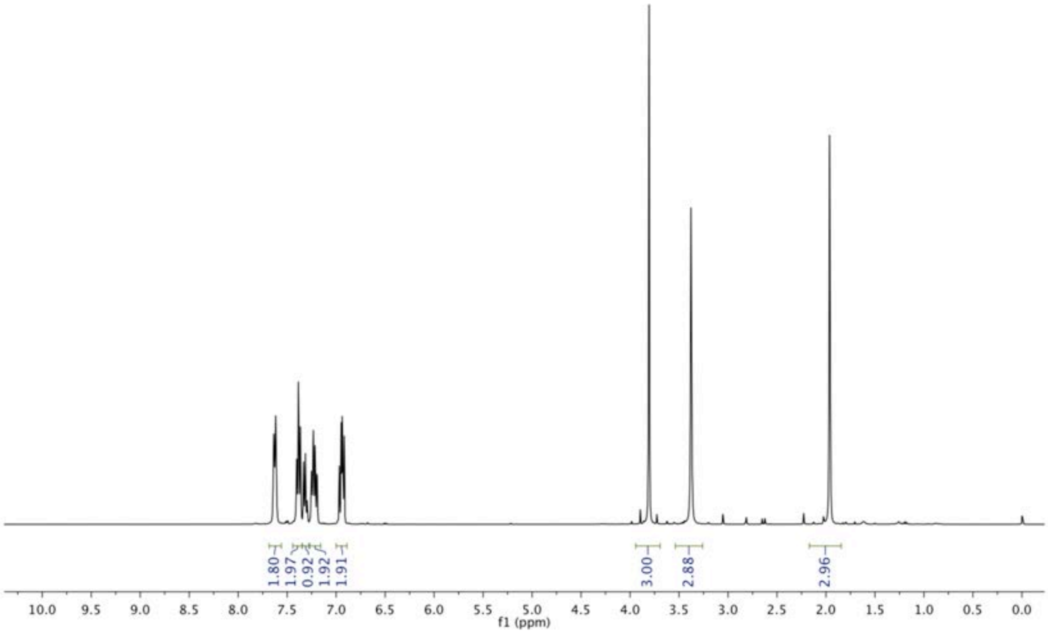
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
N
N
Me
OMe

2h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1.91
3.00
2.88
2.96
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9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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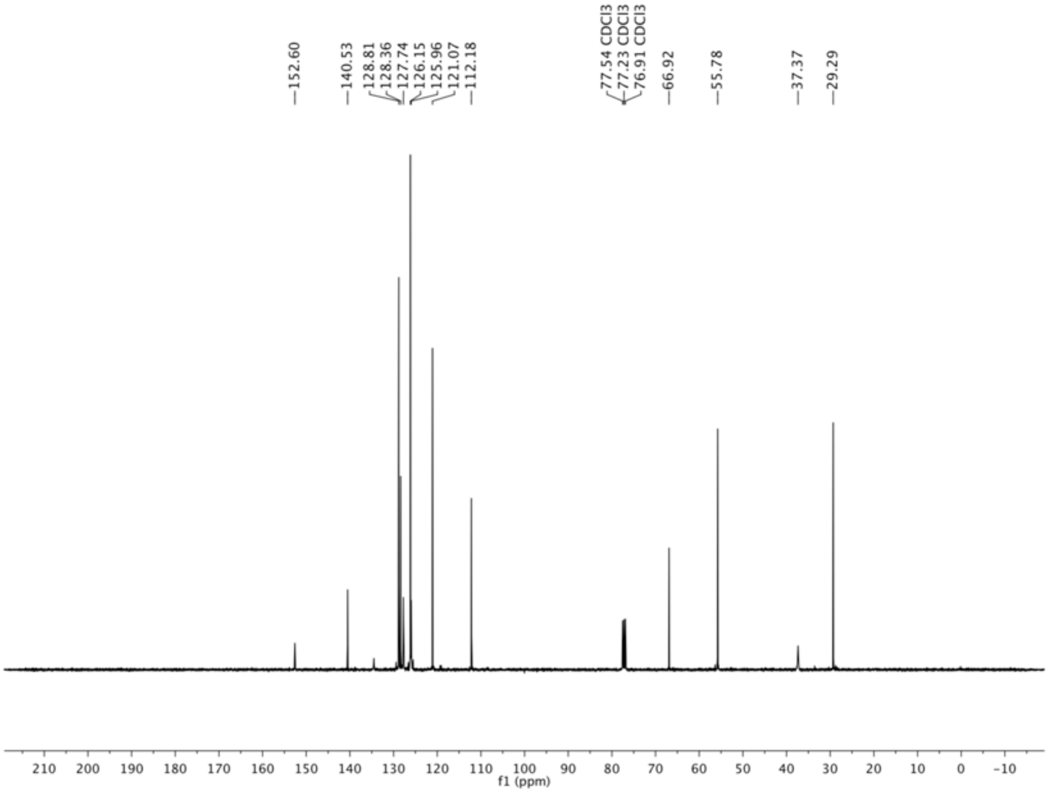
0.0
f1 (ppm)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128.36
127.74
126.15
125.96
121.07
112.18
77.54 CDCl3
77.23 CDCl3
76.91 CDCl3
66.92
55.78
37.37
29.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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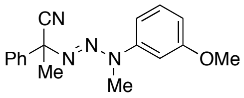
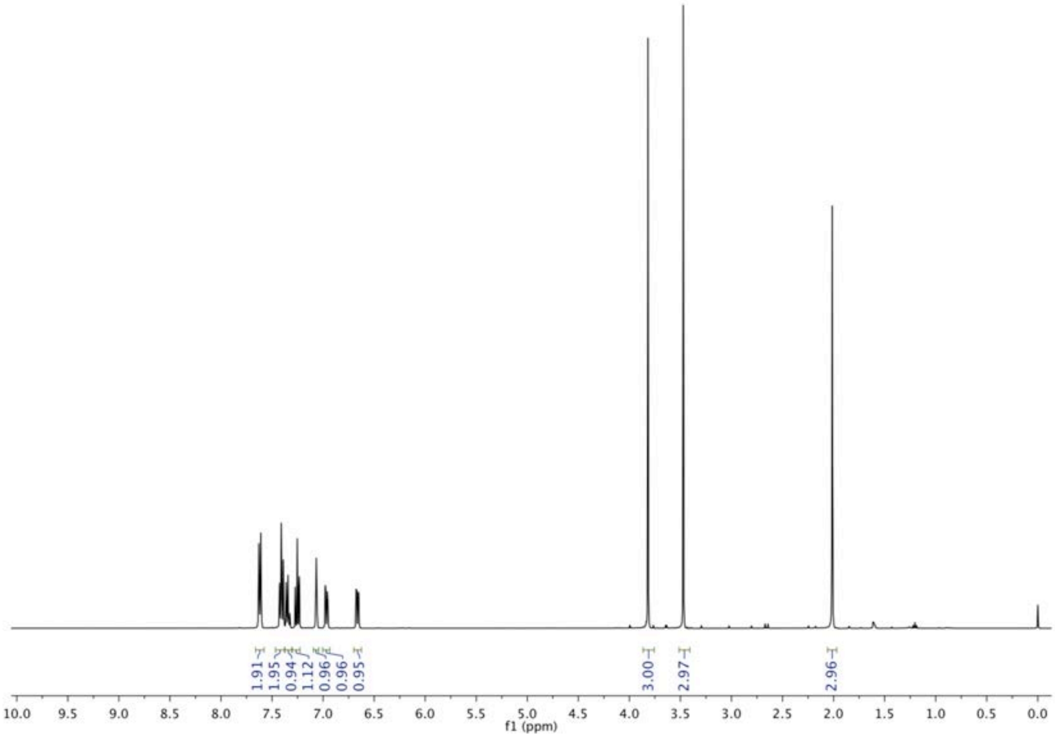
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
N
N
Me
OMe

2i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0.96
0.95
3.00
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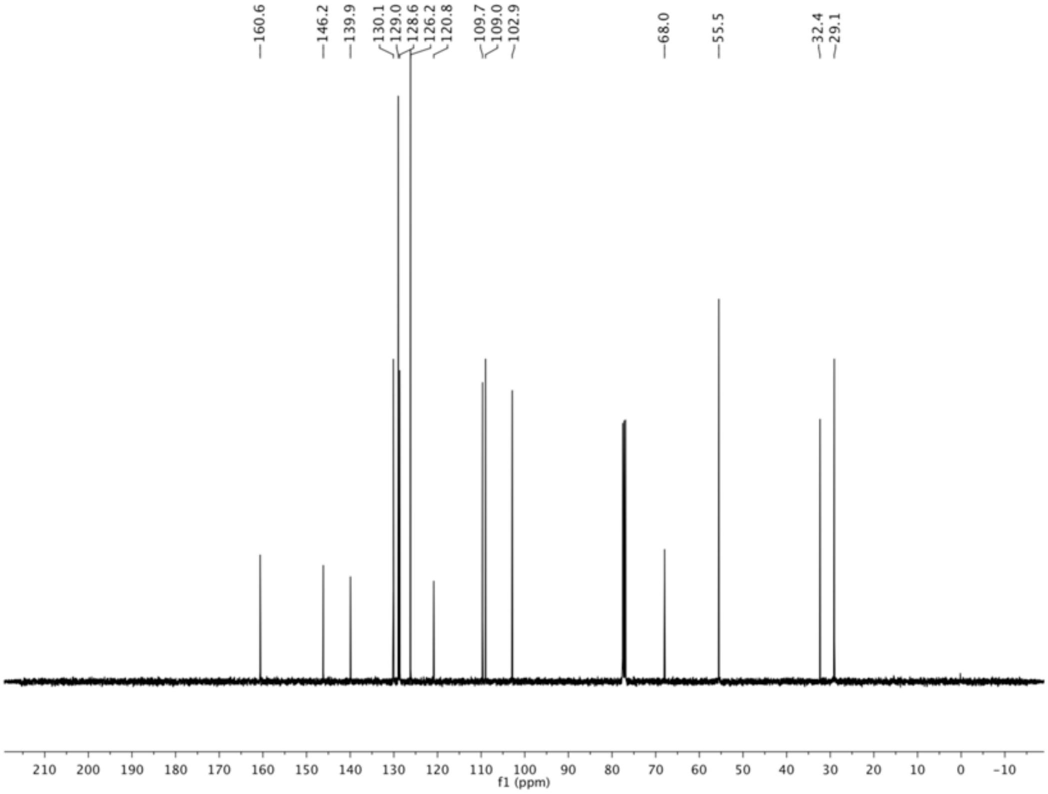
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.0
128.6
126.2
120.8
109.7
109.0
102.9
68.0
55.5
32.4
29.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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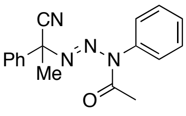
60
50
40
30
20
10
0
-10
f1 (ppm)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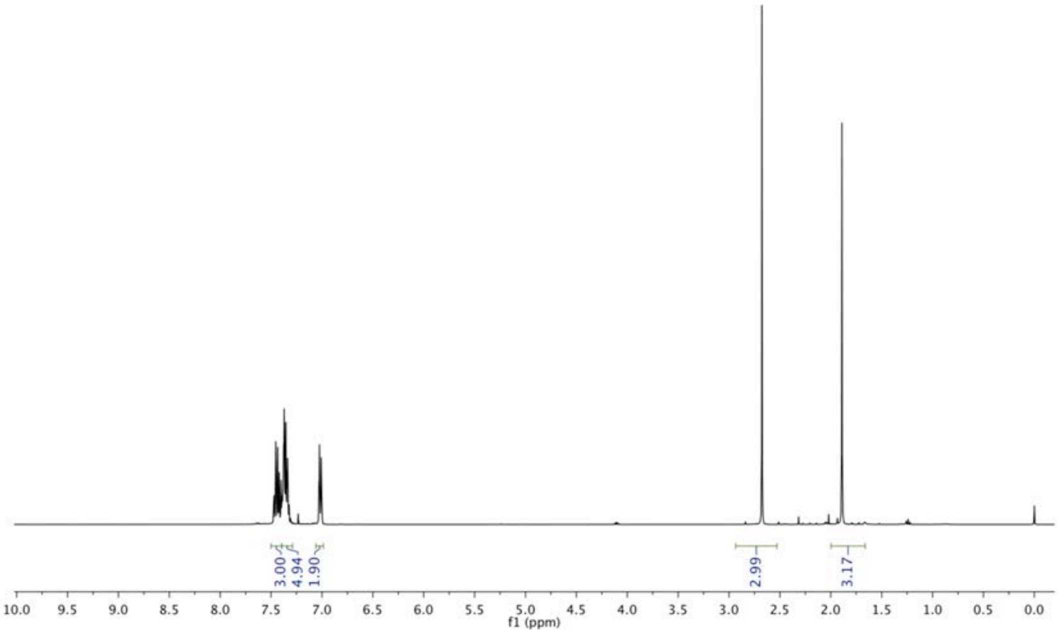
Ph
Me
N
N
N
O

2j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9.0
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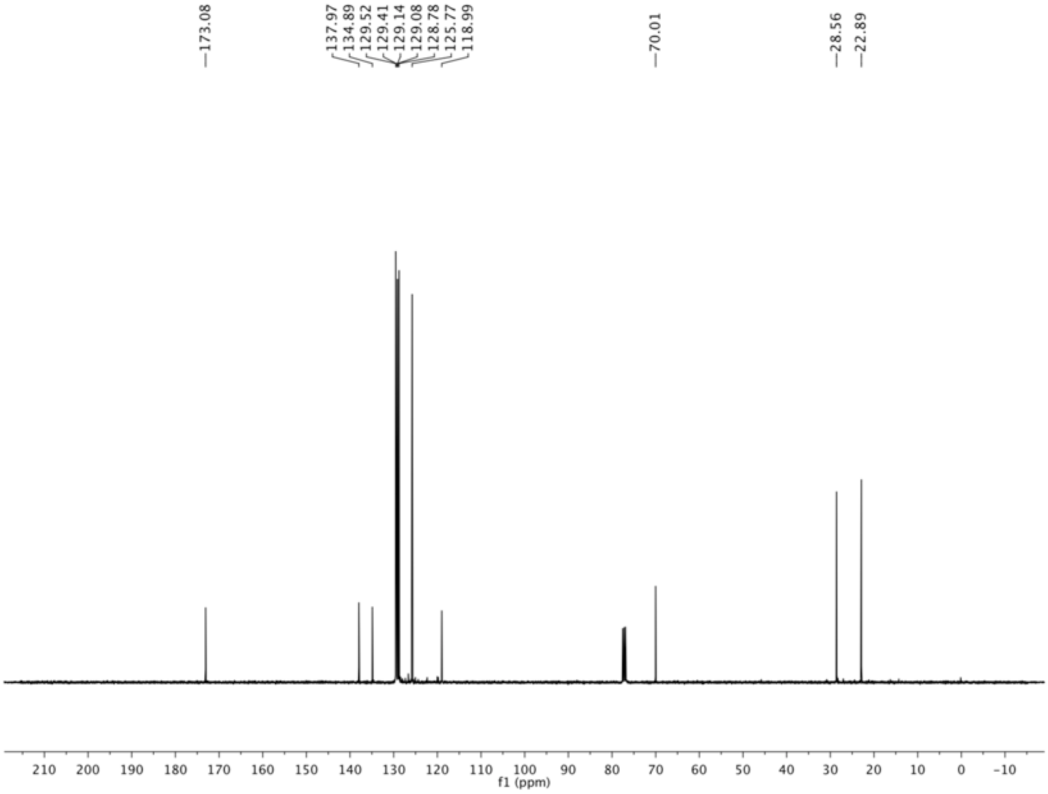
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.08
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129.52
129.41
129.14
129.08
128.78
125.77
118.99
70.01
28.56
22.89
210
200
190
180
170
160
150
140
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120
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100
90
80
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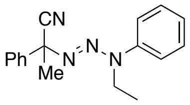
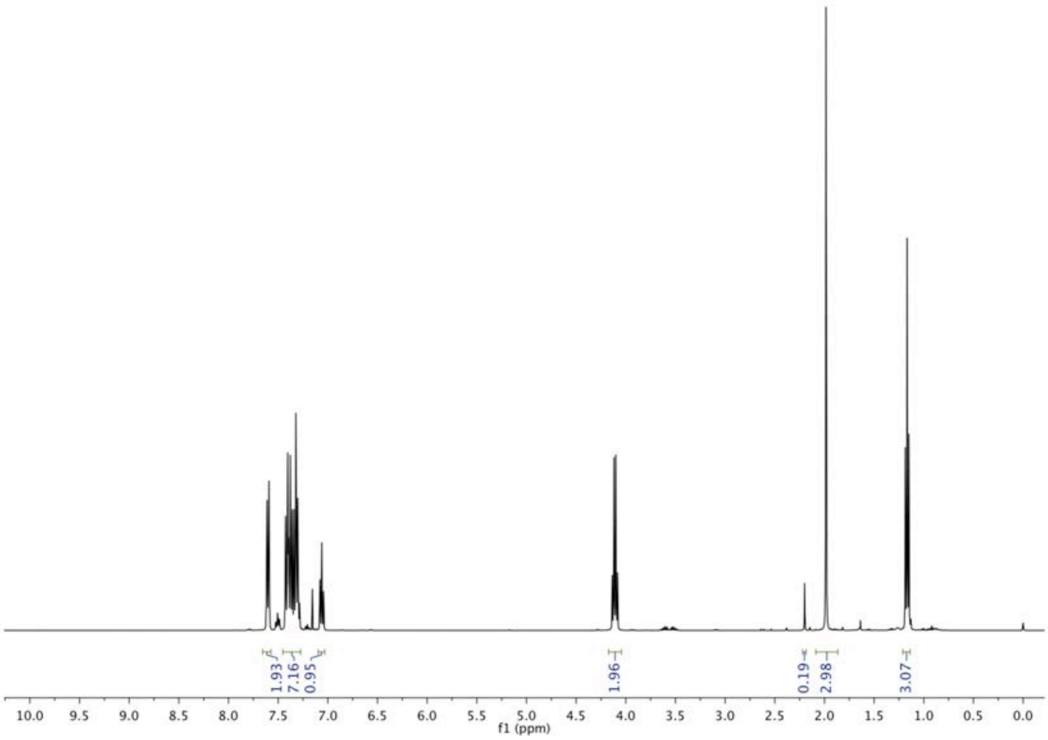
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
N
N
N
Me

2k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9.0
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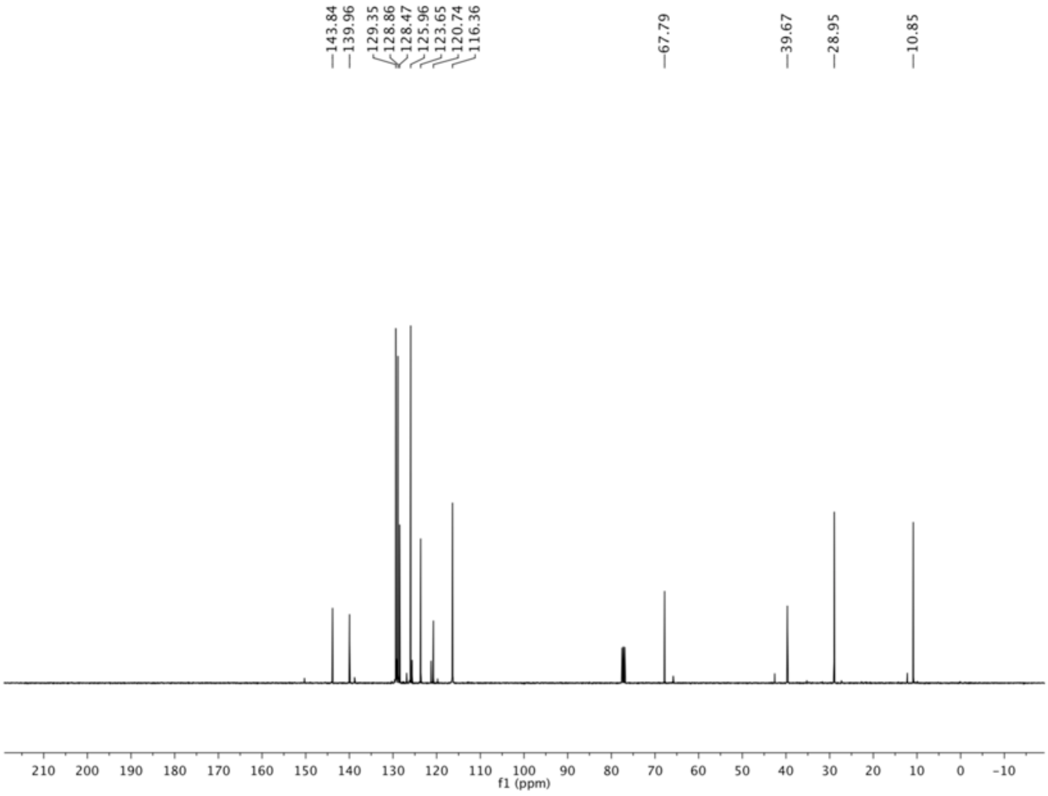
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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120.74
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67.79
39.67
28.95
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210
200
190
180
170
160
150
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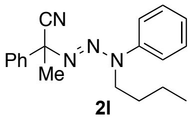
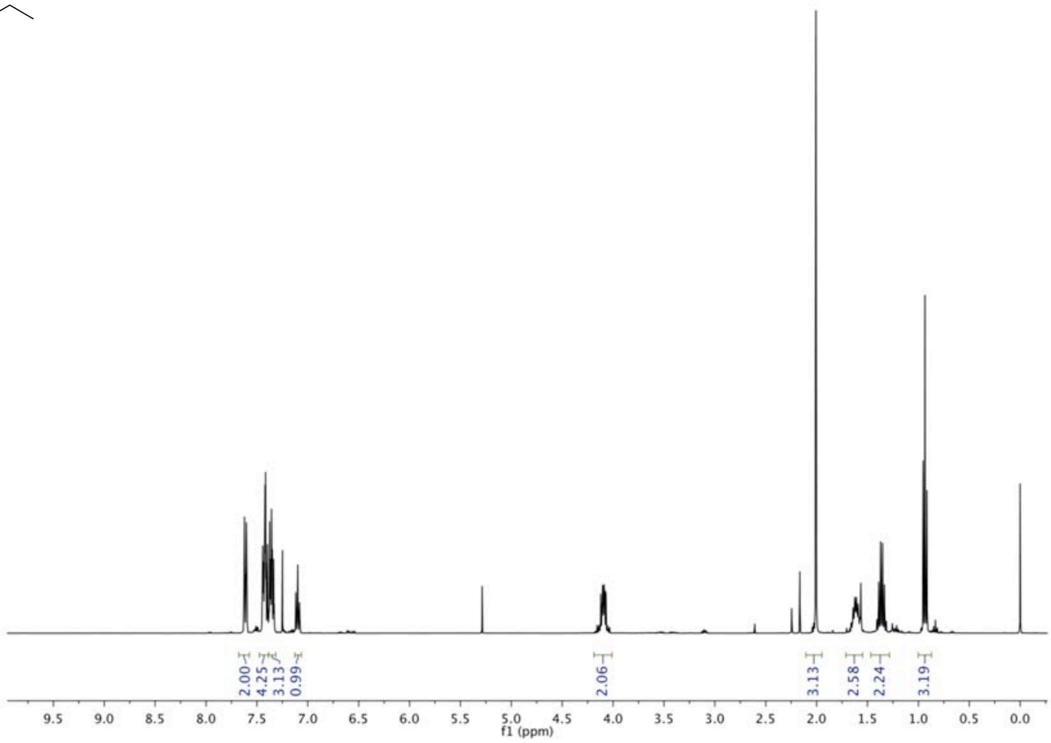
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
N
N

2l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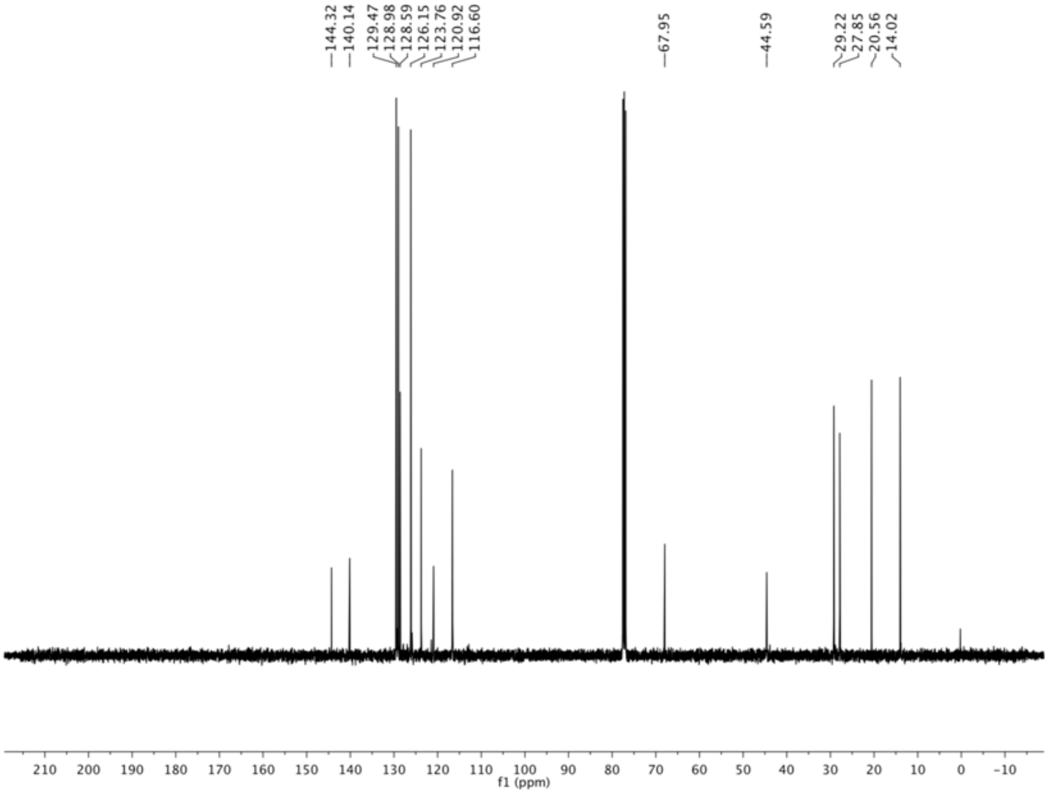
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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126.15
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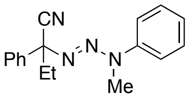
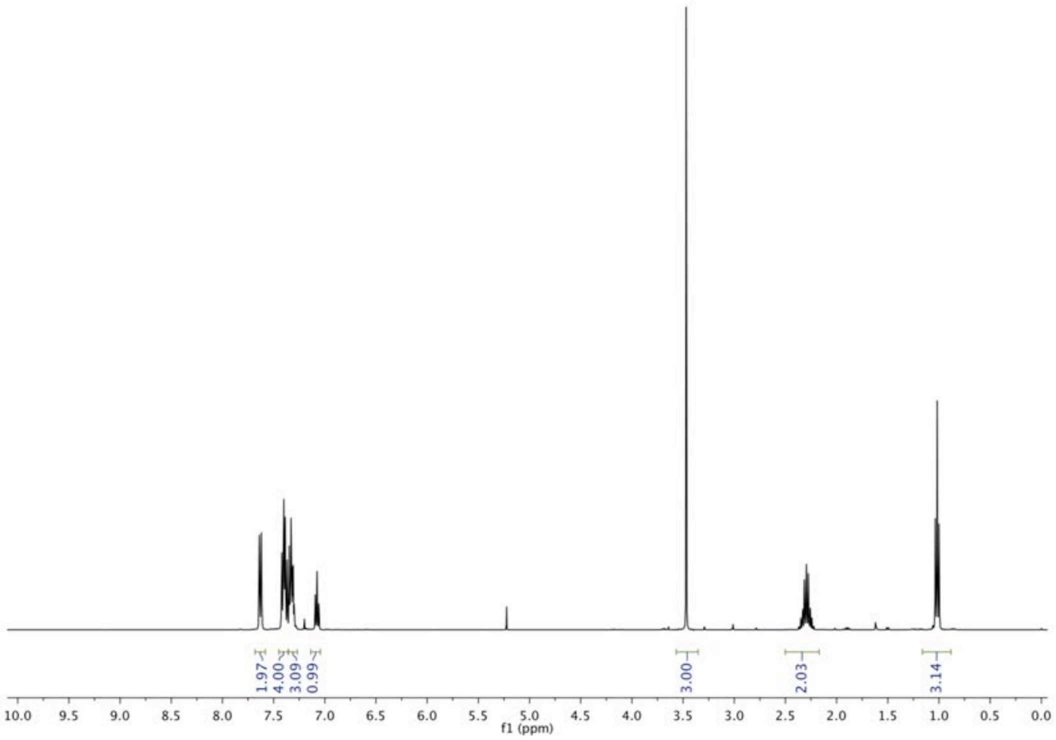
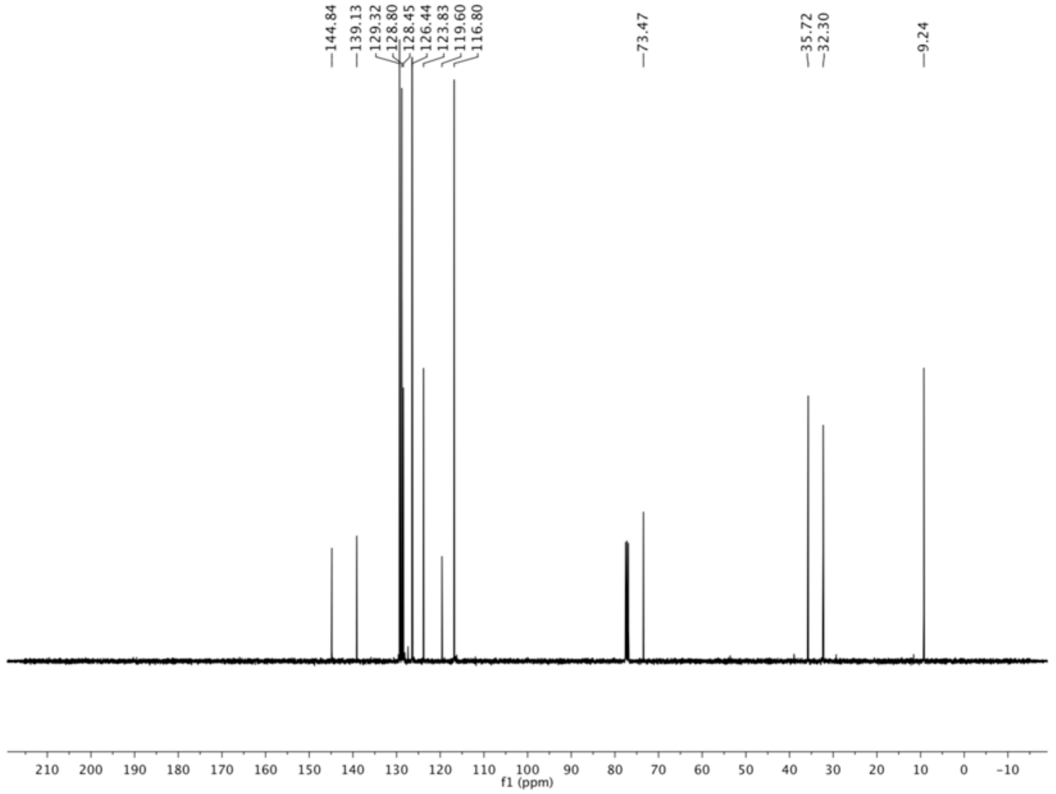
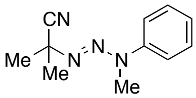
120.92
116.60
67.95
44.59
29.22
27.85
20.56
14.02
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
N
N
N
Et
Me

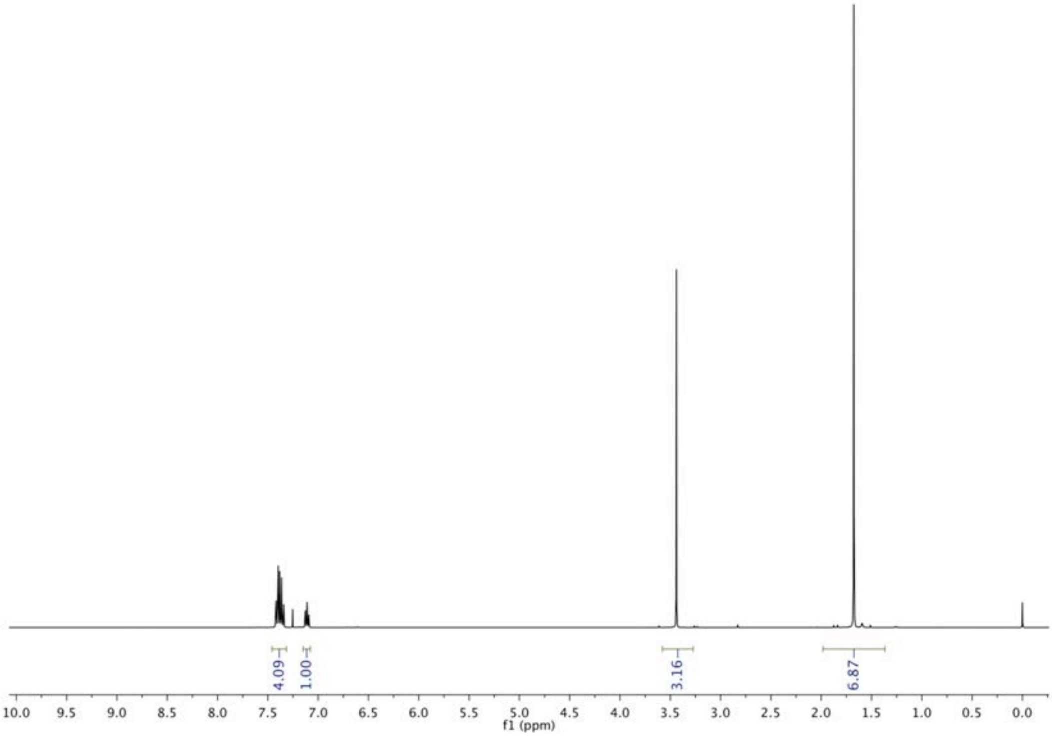
2m

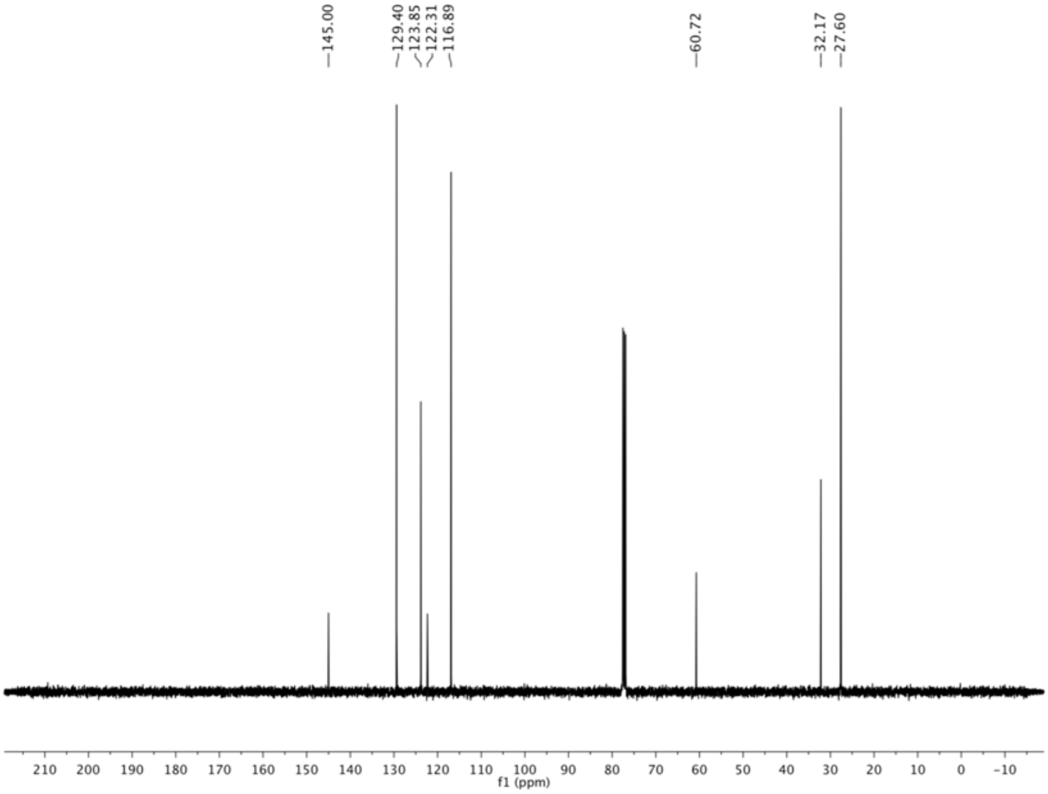

1.97
4.00
3.09
0.99
3.00
2.03
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

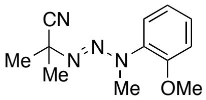

144.84
139.13
129.32
128.80
128.45
126.44
123.83
119.60
116.80
73.47
35.72
32.30
9.24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Me
Me
N
N
N
Me

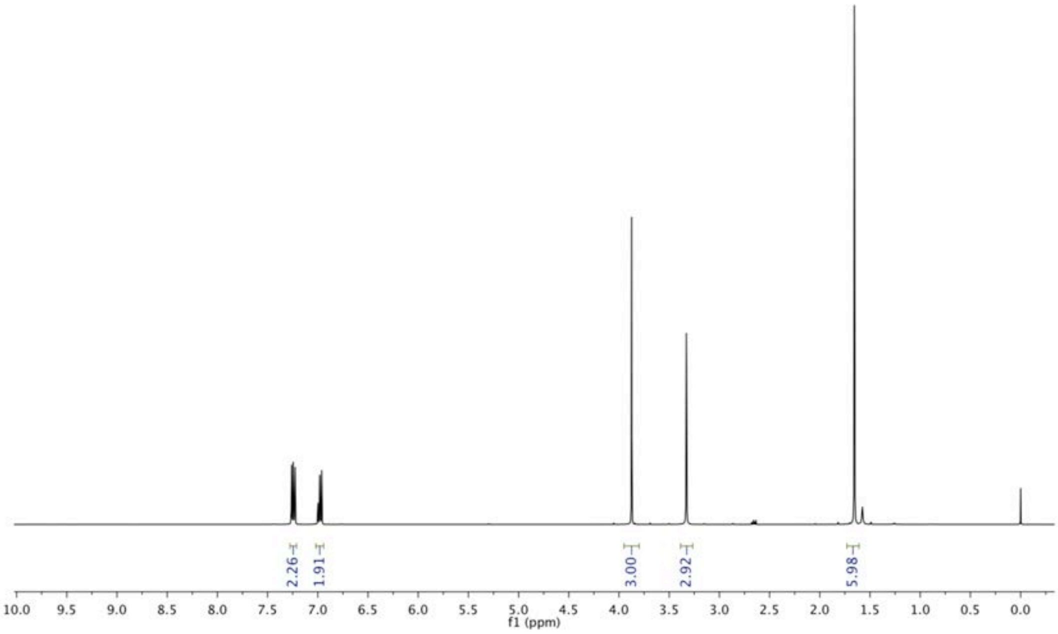
2n

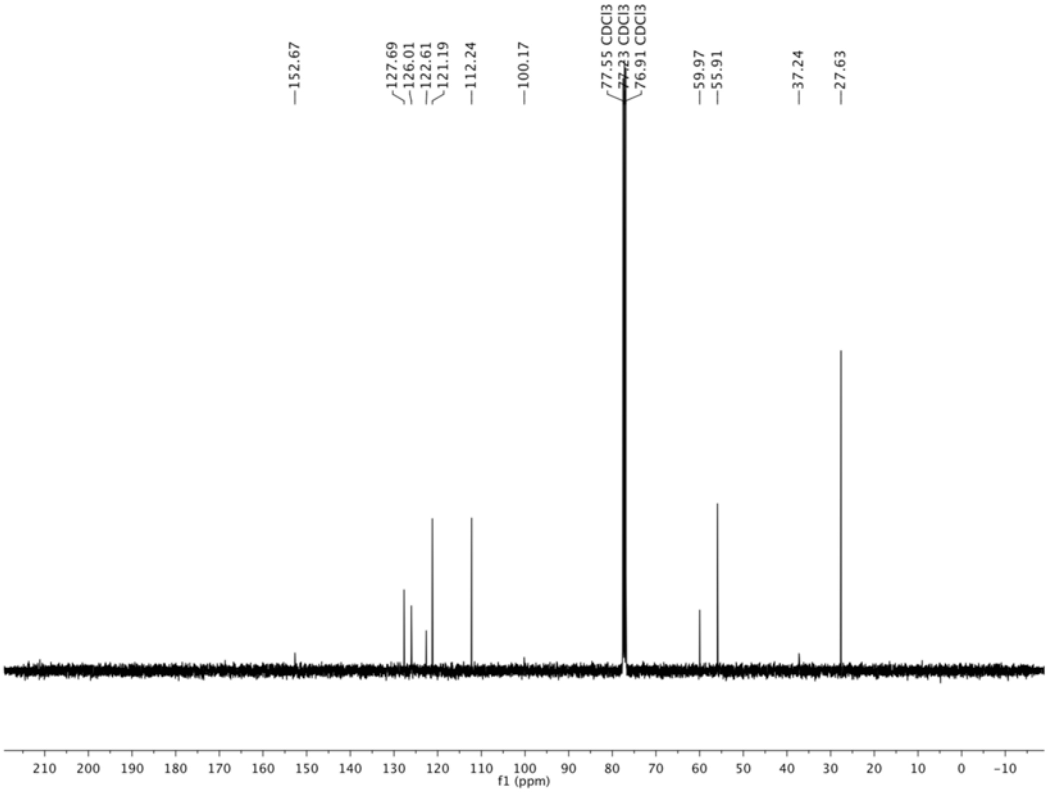

4.09
1.00
3.16
6.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

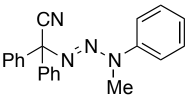

145.00
129.40
123.85
122.31
116.89
60.72
32.17
27.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CN
Me
Me
N
N
N
Me
OMe

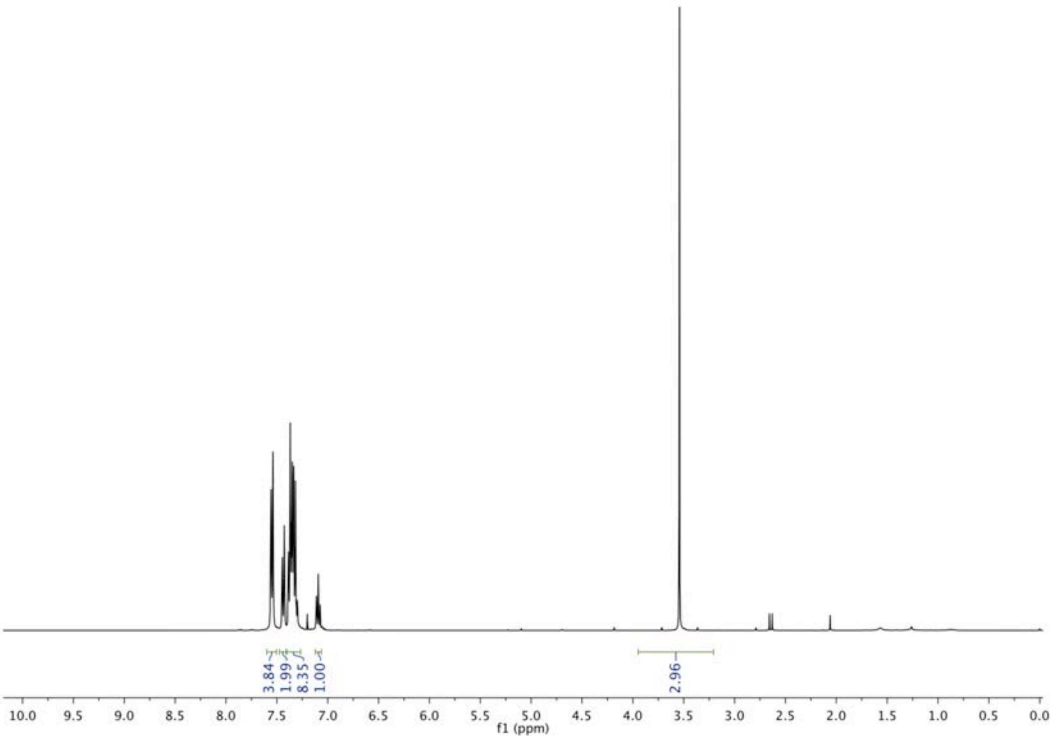
2o

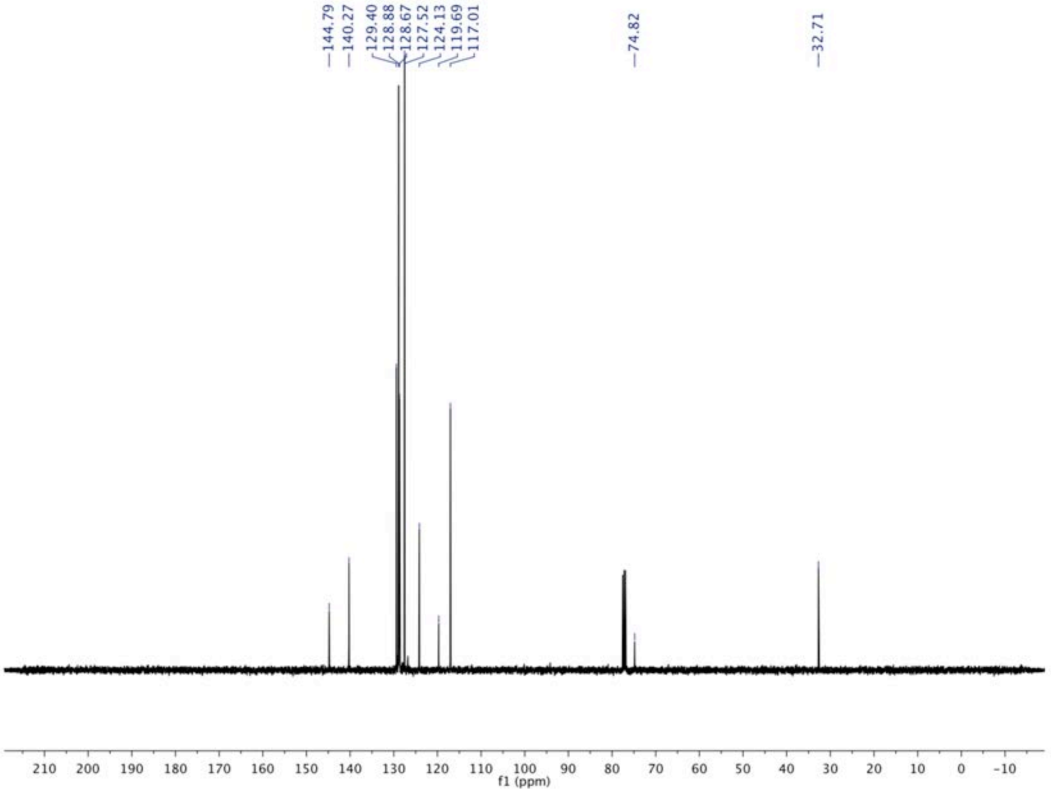

2.26
1.91
3.00
2.92
5.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

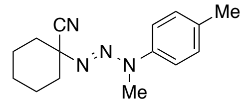

152.67
127.69
126.01
122.61
121.19
112.24
100.17
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
59.97
55.91
37.24
27.63
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Ph
N
N
N
Me

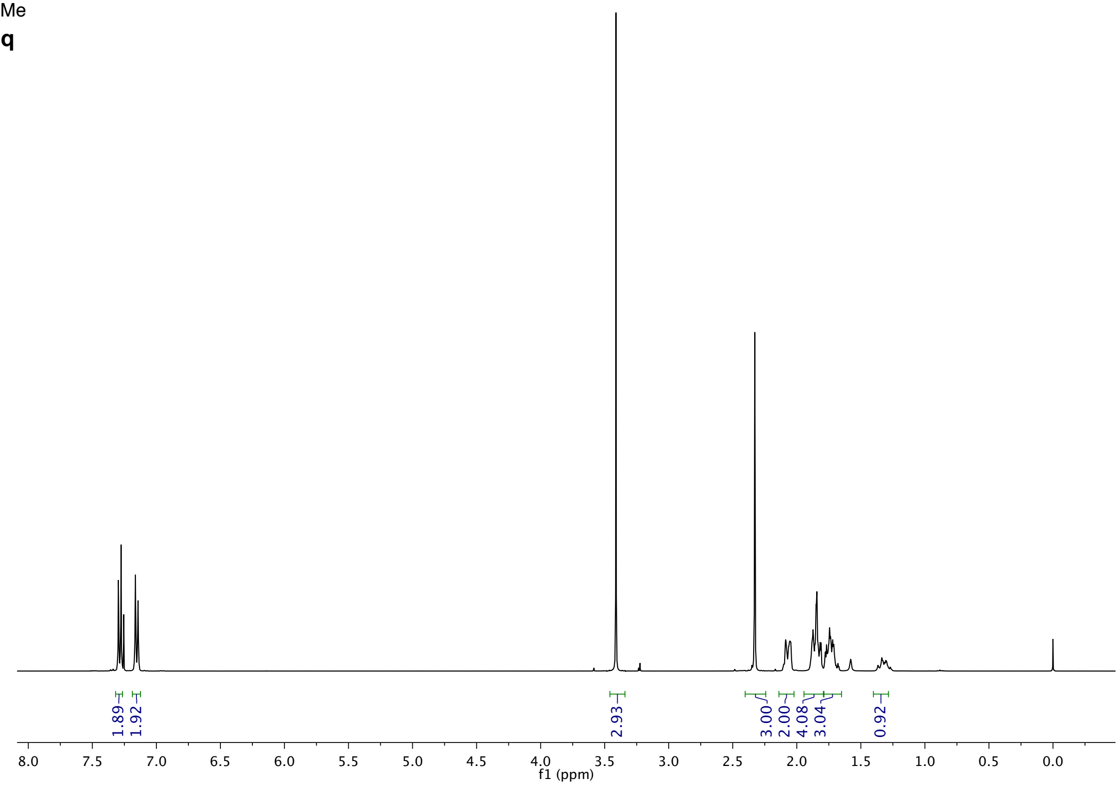
2p

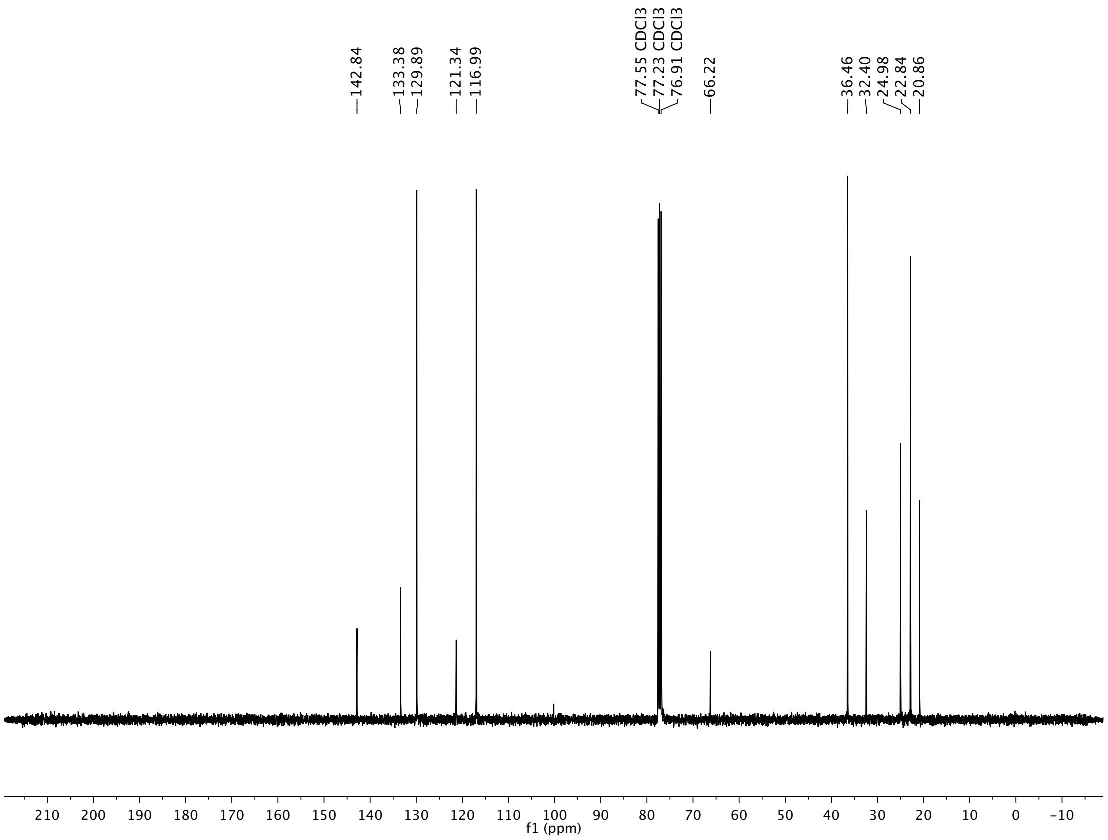

3.84
1.99
8.35
1.00
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

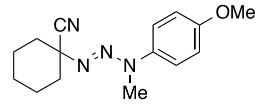

144.79
140.27
129.40
128.88
128.67
127.52
124.13
119.69
117.01
74.82
32.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
N
N
N
Me
Me

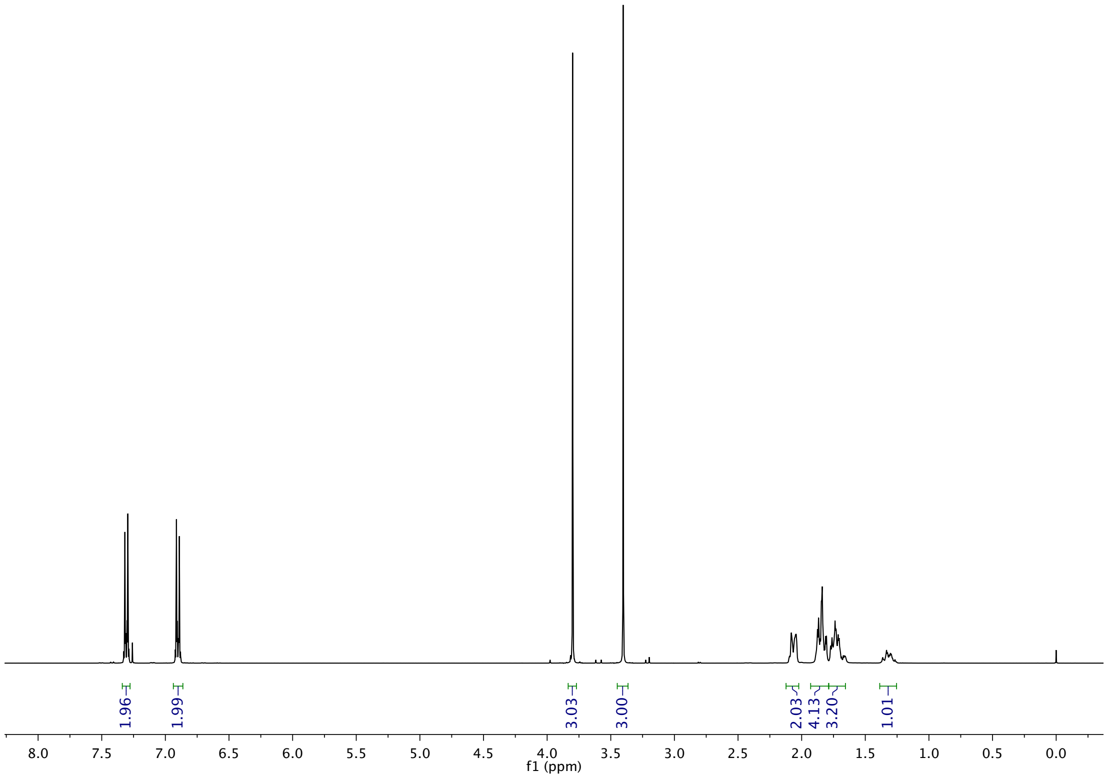
2q

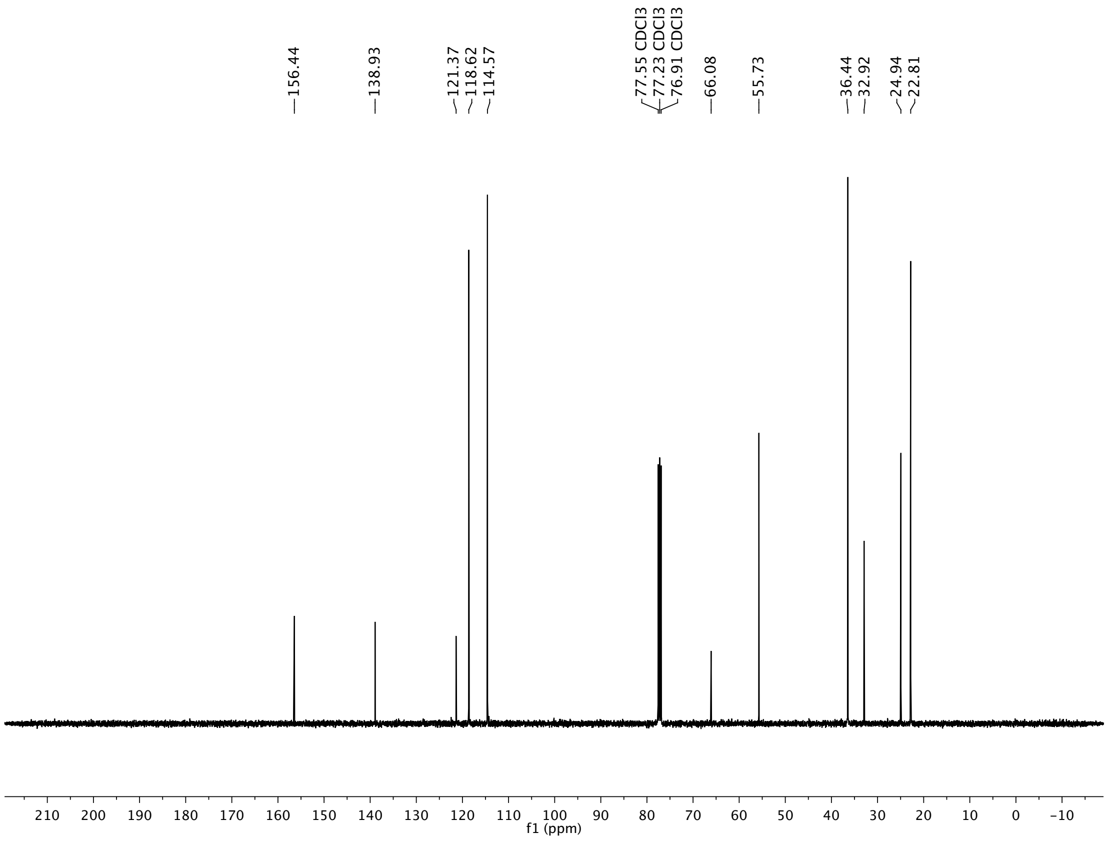

1.89
1.92
2.93
3.00
2.00
4.08
3.04
0.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

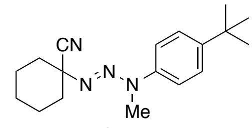

142.84
133.38
129.89
121.34
116.99
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
66.22
36.46
32.40
24.98
22.84
20.86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
OMe
N
N
N
Me

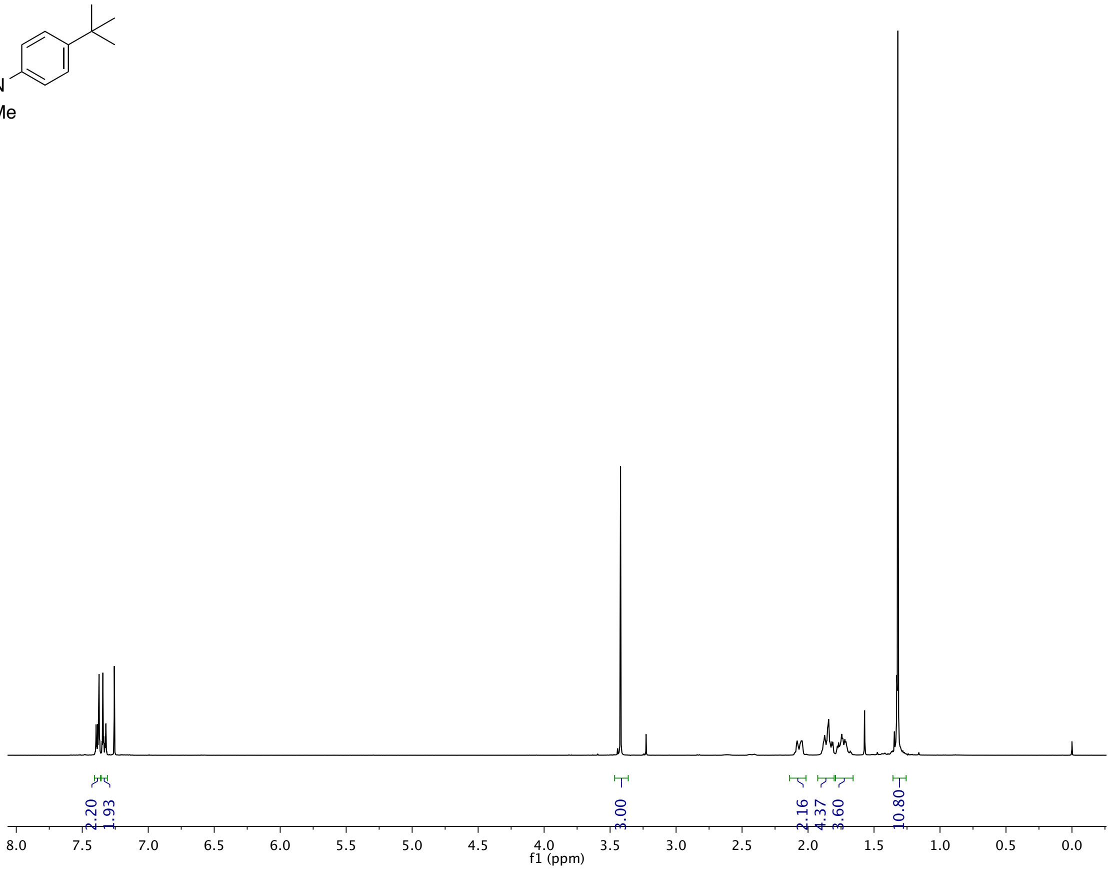
2r

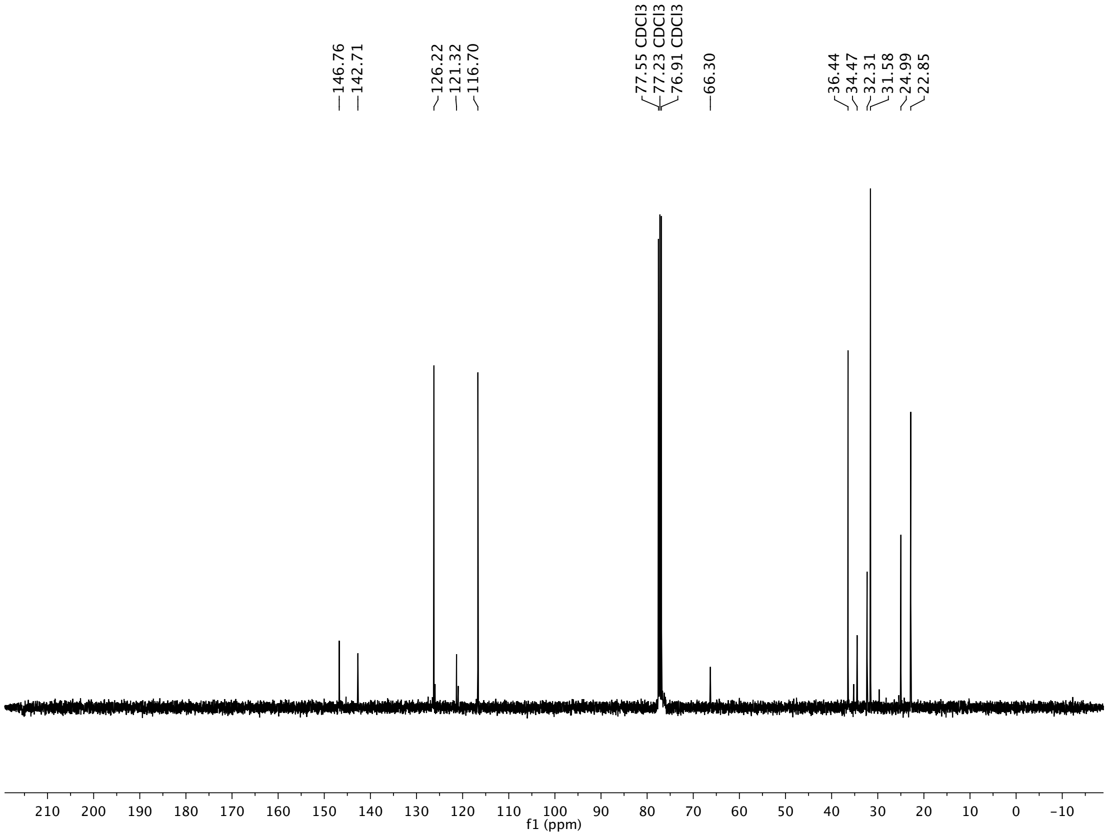

1.96
1.99
3.03
3.00
2.03
4.13
3.20
1.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

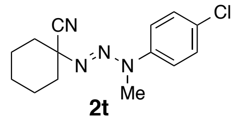

156.44
138.93
121.37
118.62
114.57
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
66.08
55.73
36.44
32.92
24.94
22.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
N
N
N
Me

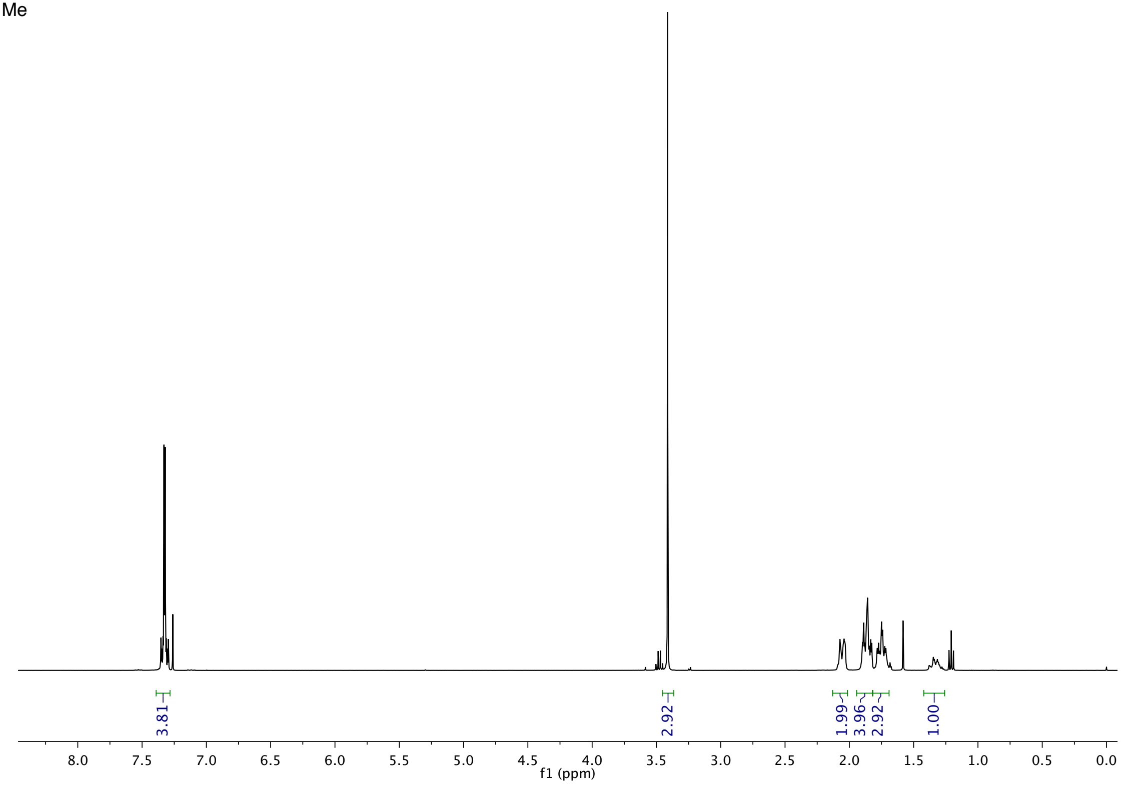
2s

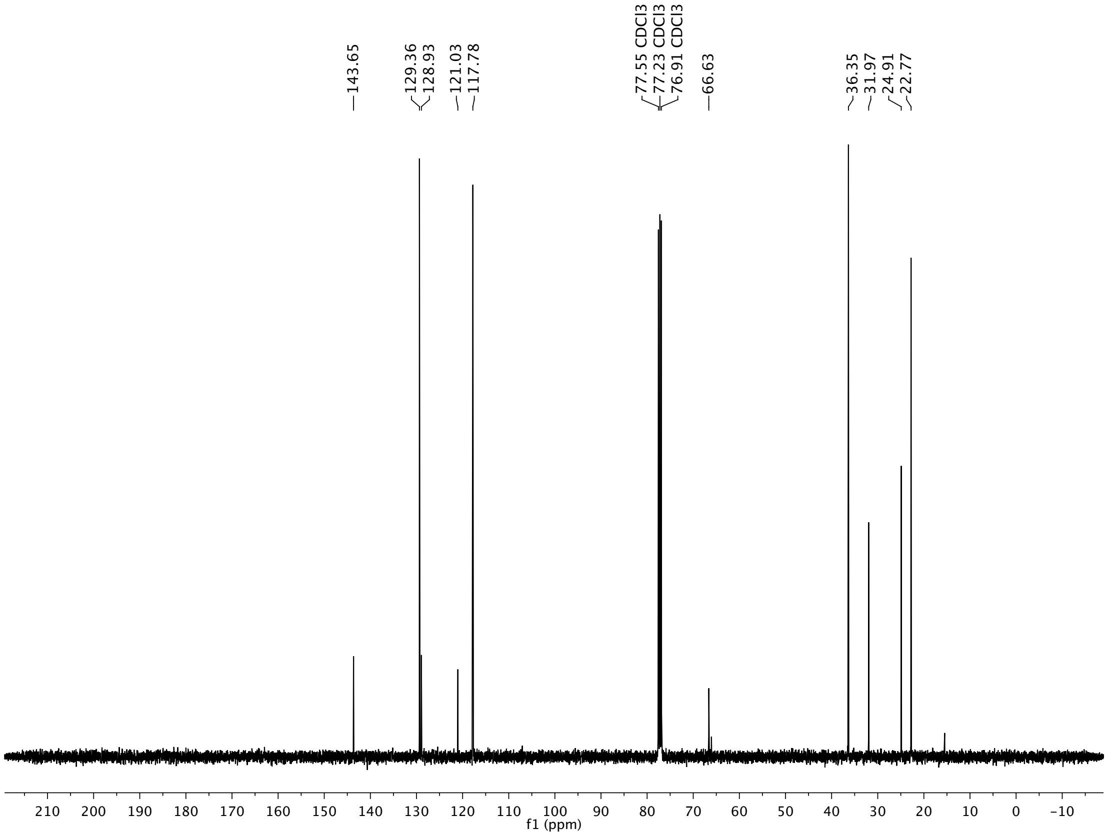

2.20
1.93
3.00
2.16
4.37
3.60
10.80
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

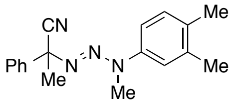

146.76
142.71
126.22
121.32
116.70
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
66.30
36.44
34.47
32.31
31.58
24.99
22.85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
N
N
N
Cl
Me

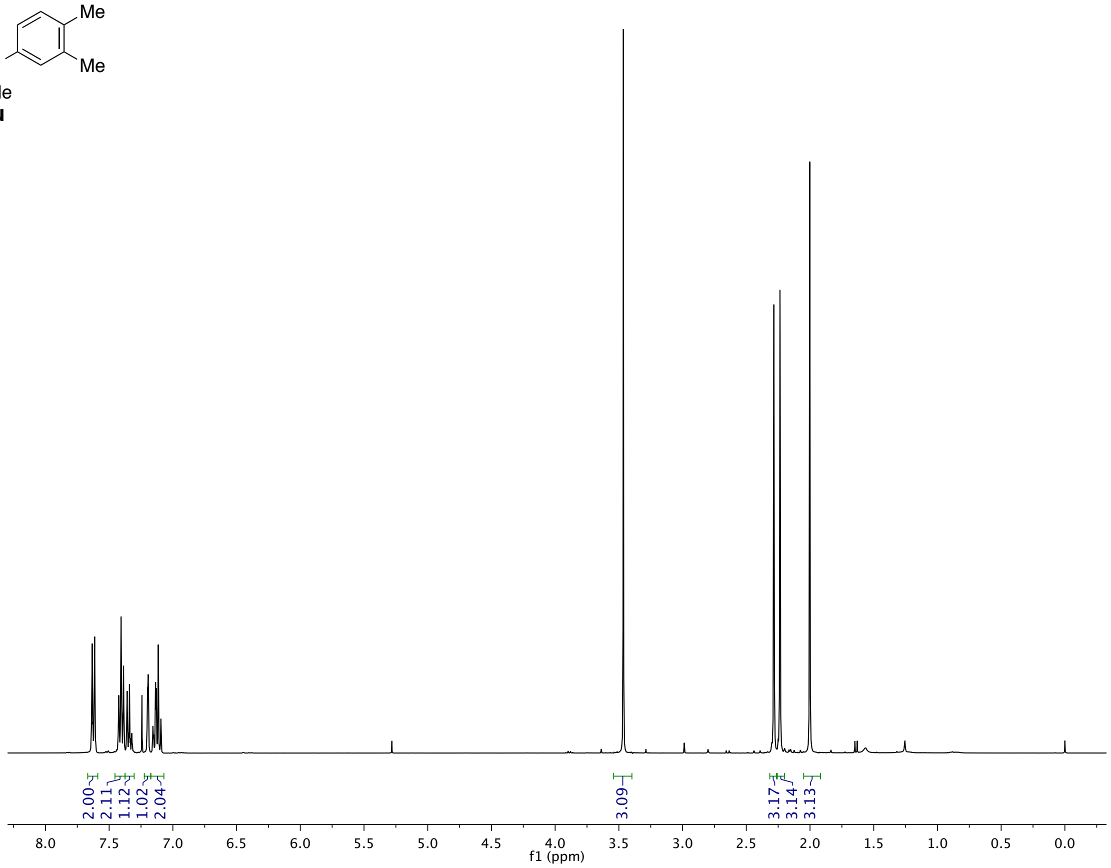
2t

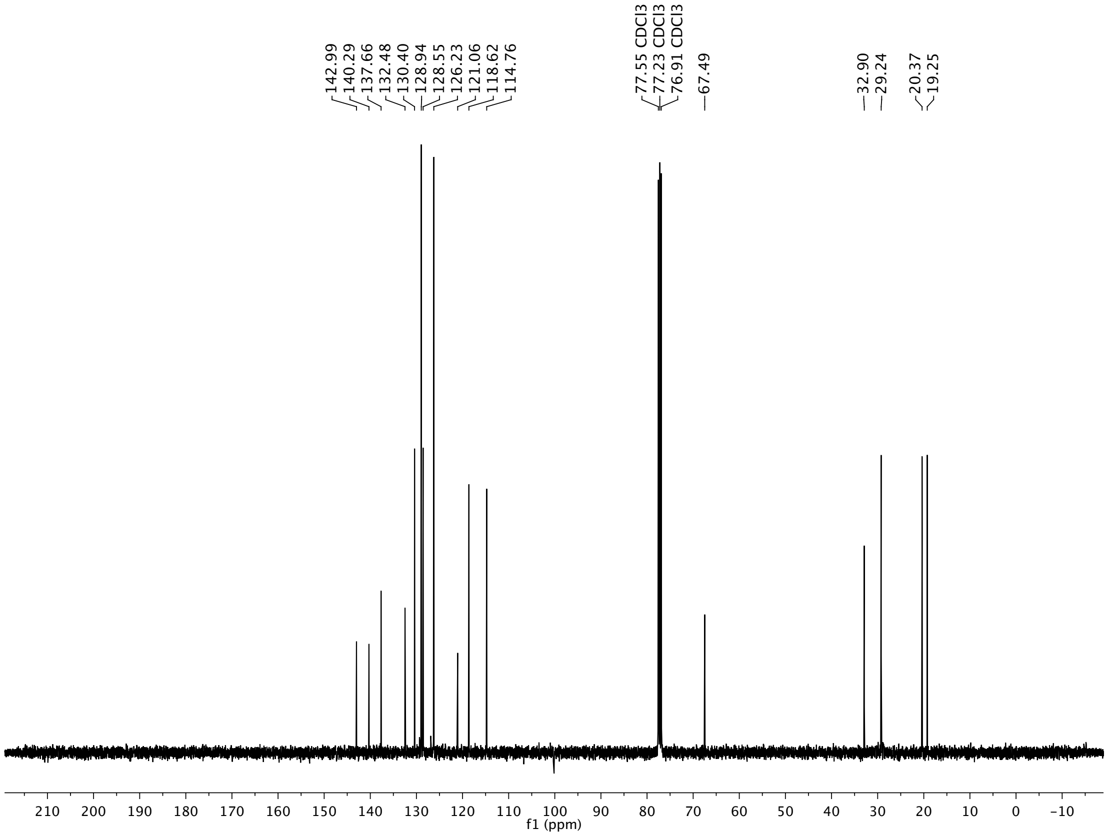

3.81
2.92
1.99
3.96
2.92
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

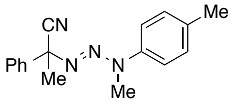

143.65
129.36
128.93
121.03
117.78
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
66.63
36.35
31.97
24.91
22.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
N
N
Me
Me
Me

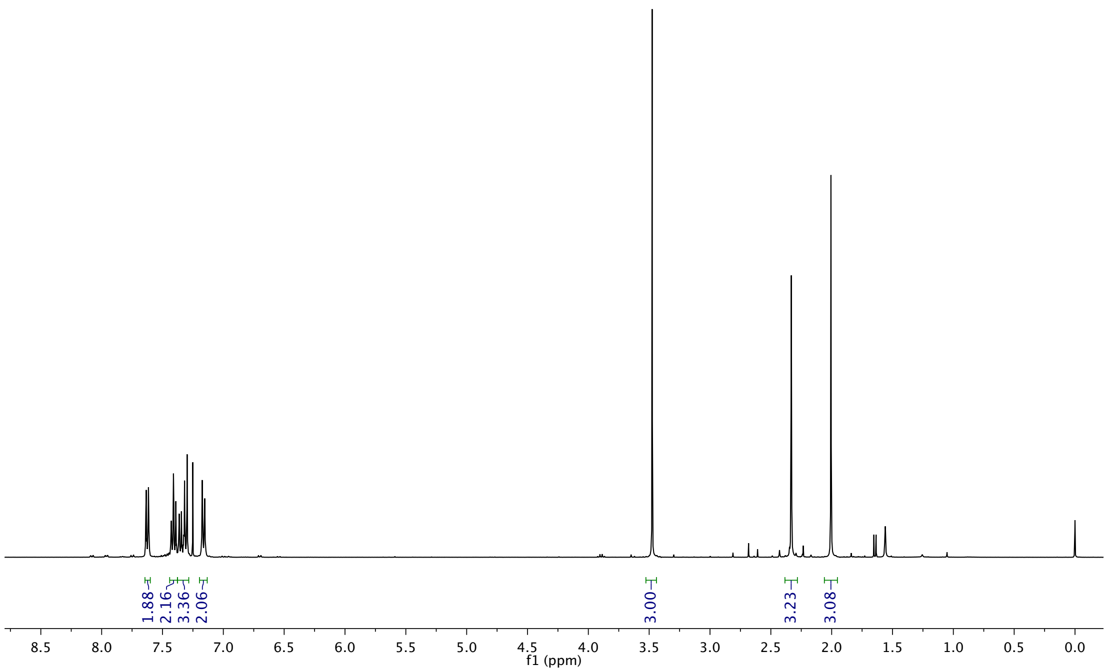
2u

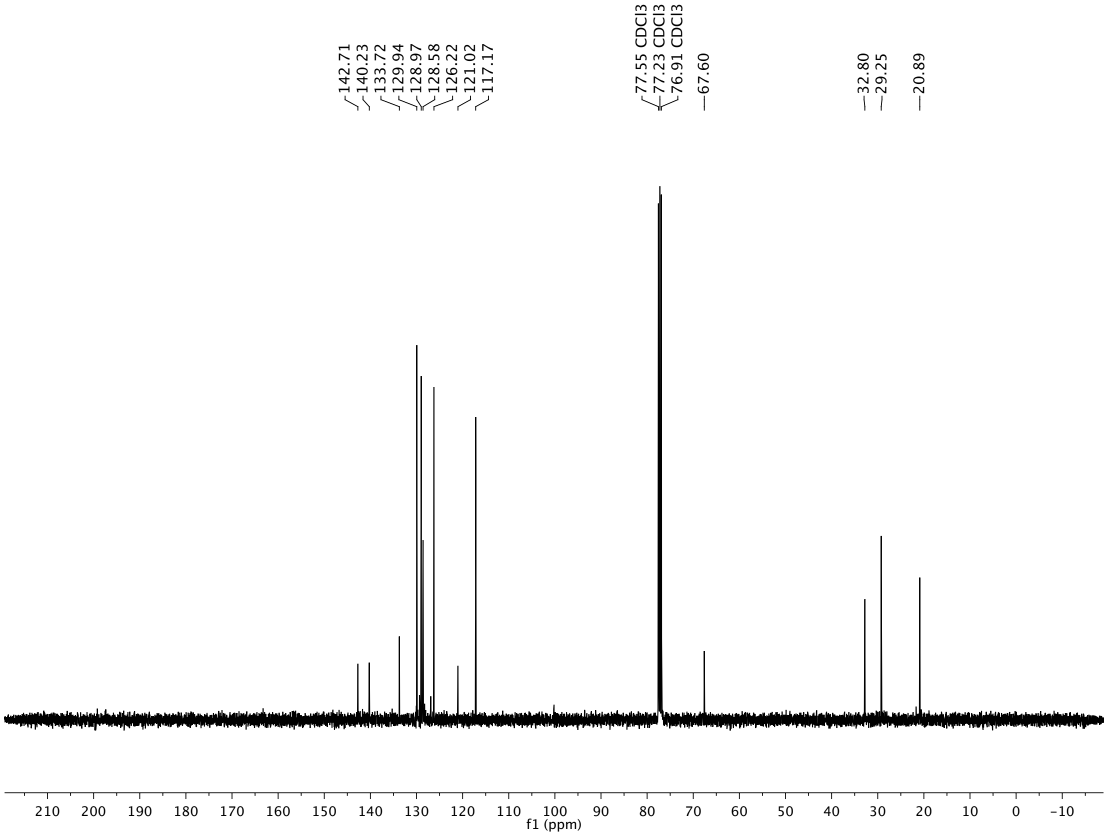

2.00
2.11
1.12
1.02
2.04
3.09
3.17
3.14
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

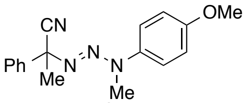

142.99
140.29
137.66
132.48
130.40
128.94
128.55
126.23
121.06
118.62
114.76
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
67.49
32.90
29.24
20.37
19.25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
N
N
Me
Me

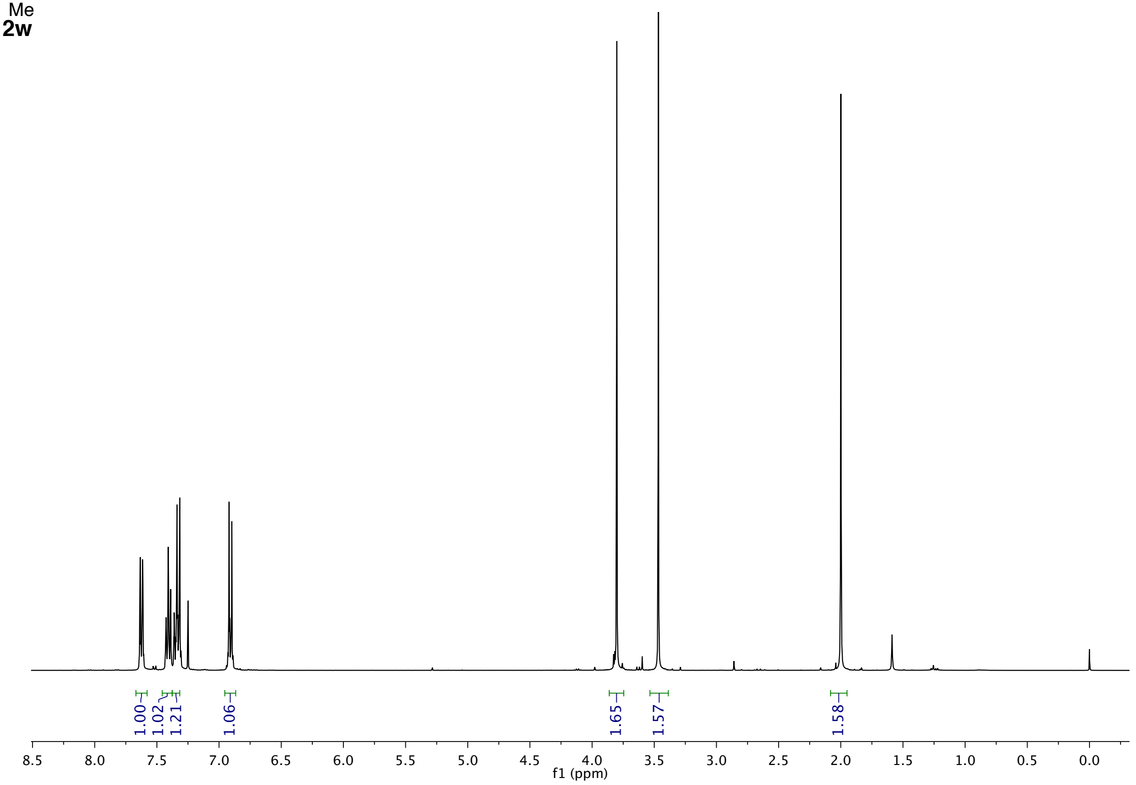
2v

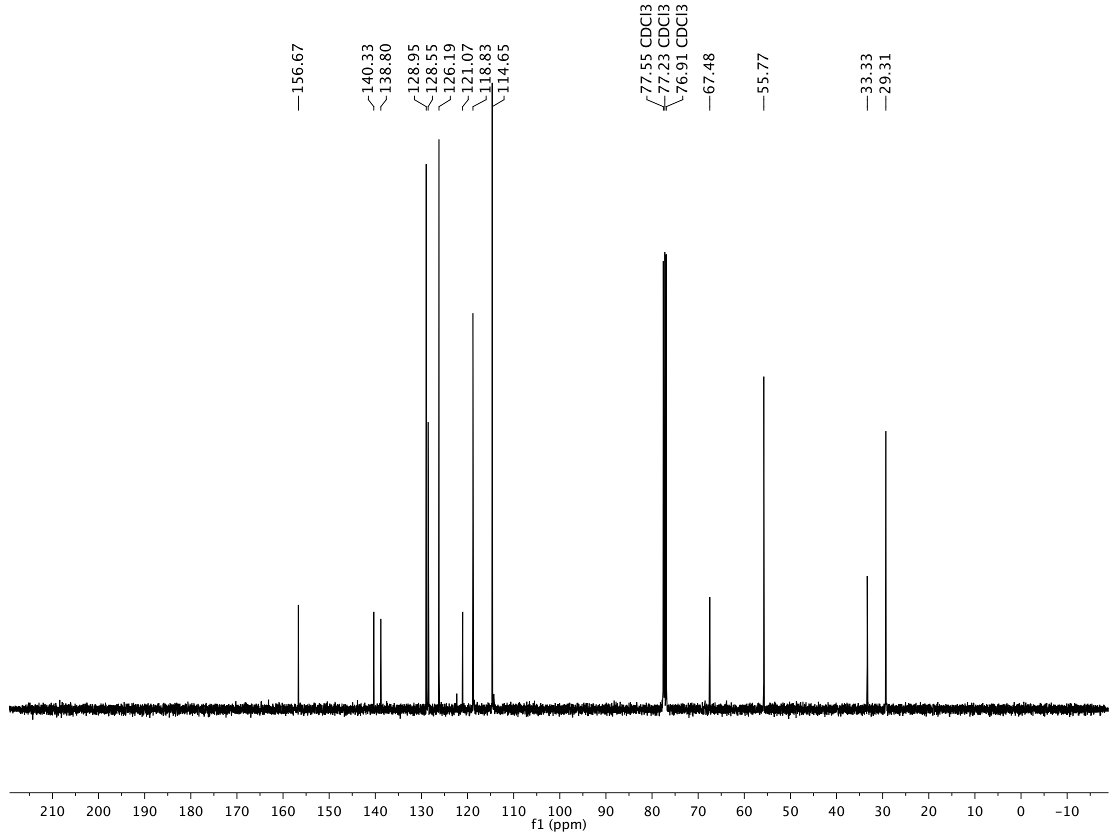

1.88
2.16
3.36
2.06
3.00
3.23
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

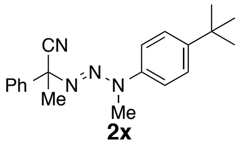

142.71
140.23
133.72
129.94
128.97
128.58
126.22
121.02
117.17
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
67.60
32.80
29.25
20.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


CN
OMe
Ph
Me
N
N
N
Me

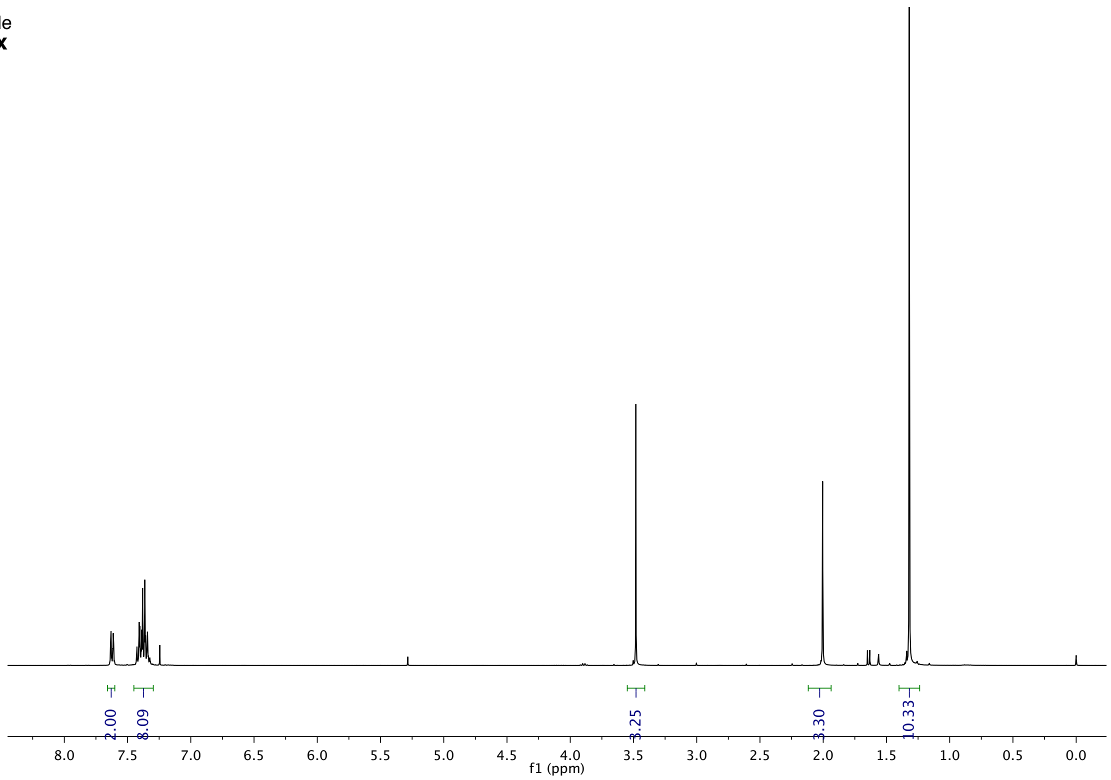
2w

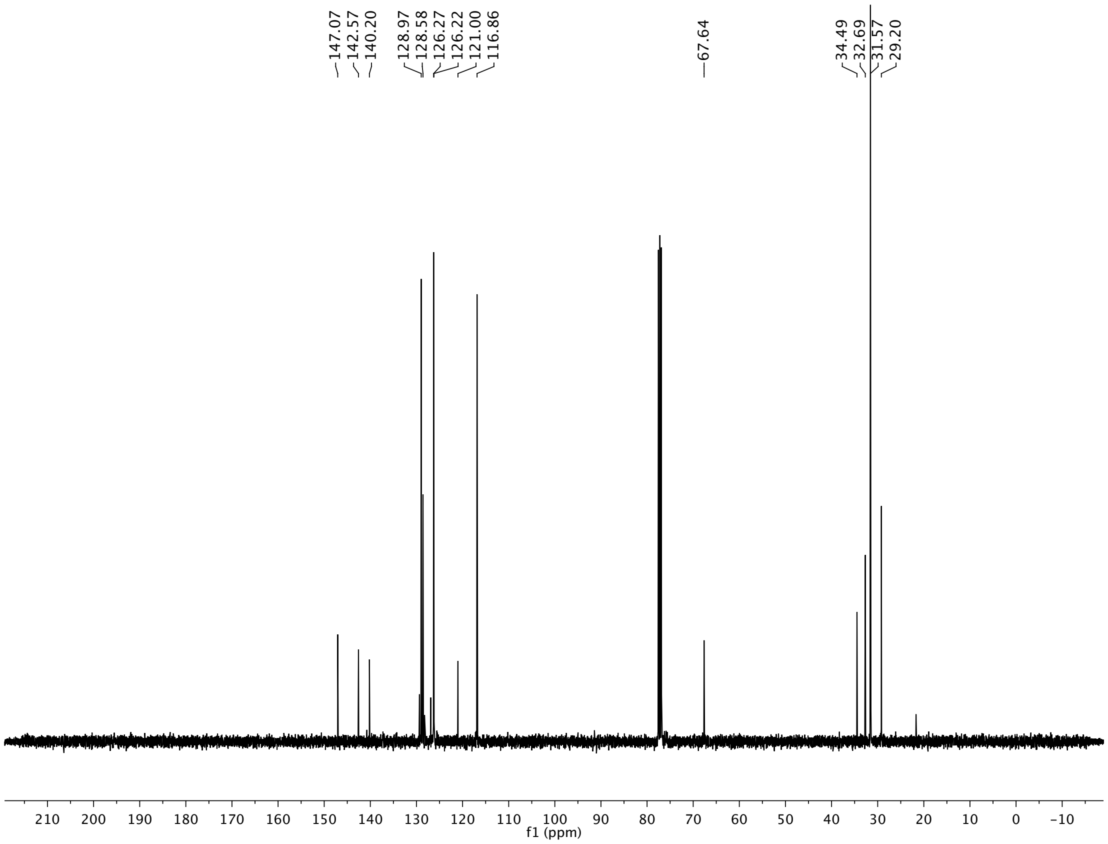

1.00
1.02
1.21
1.06
1.65
1.57
1.58
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

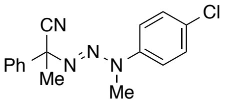

156.67
140.33
138.80
128.95
128.55
126.19
121.07
118.83
114.65
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
67.48
55.77
33.33
29.31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
N
N
N
Me
Me

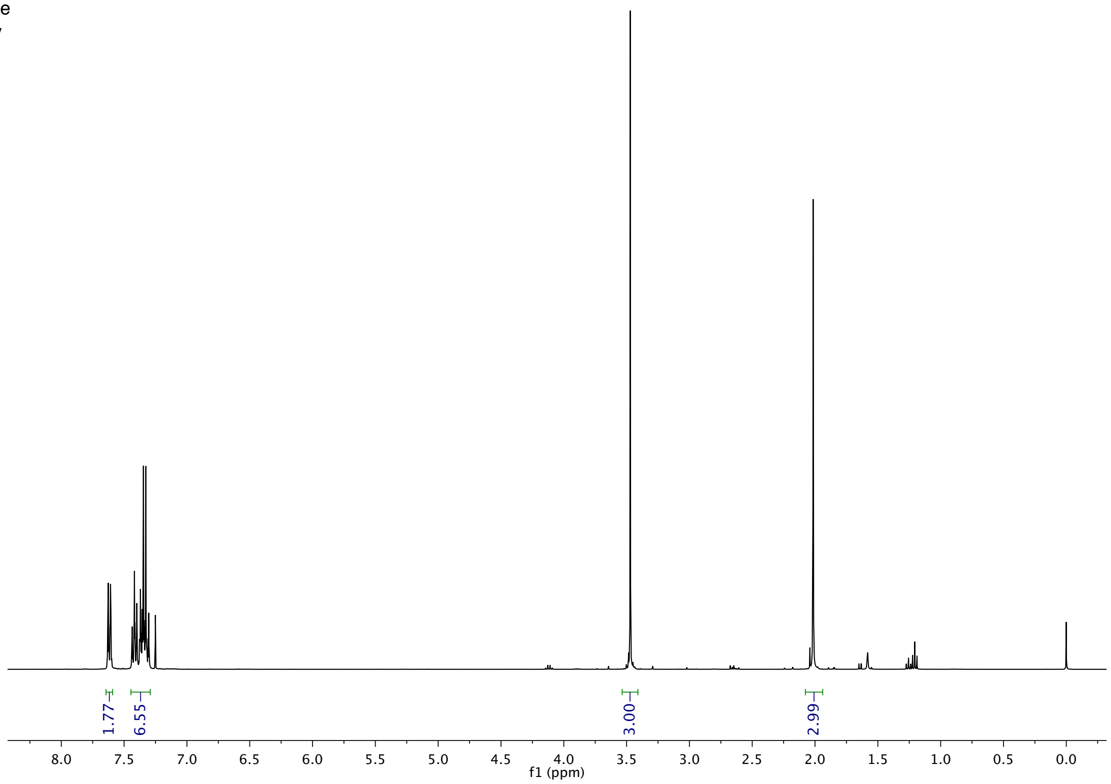
2x

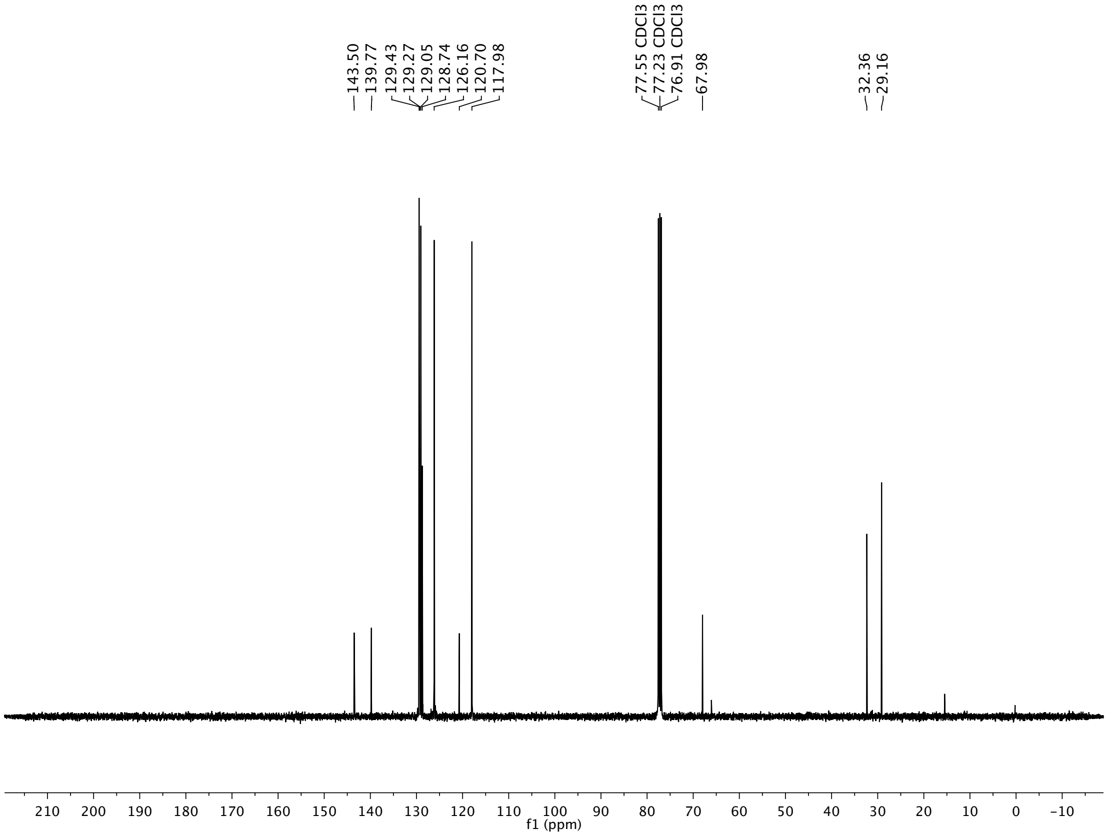

2.00
8.09
3.25
3.30
10.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

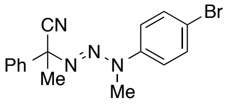

147.07
142.57
140.20
128.97
128.58
126.27
126.22
121.00
116.86
67.64
34.49
32.69
31.57
29.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Cl
Ph
N
N
N
Me
Me

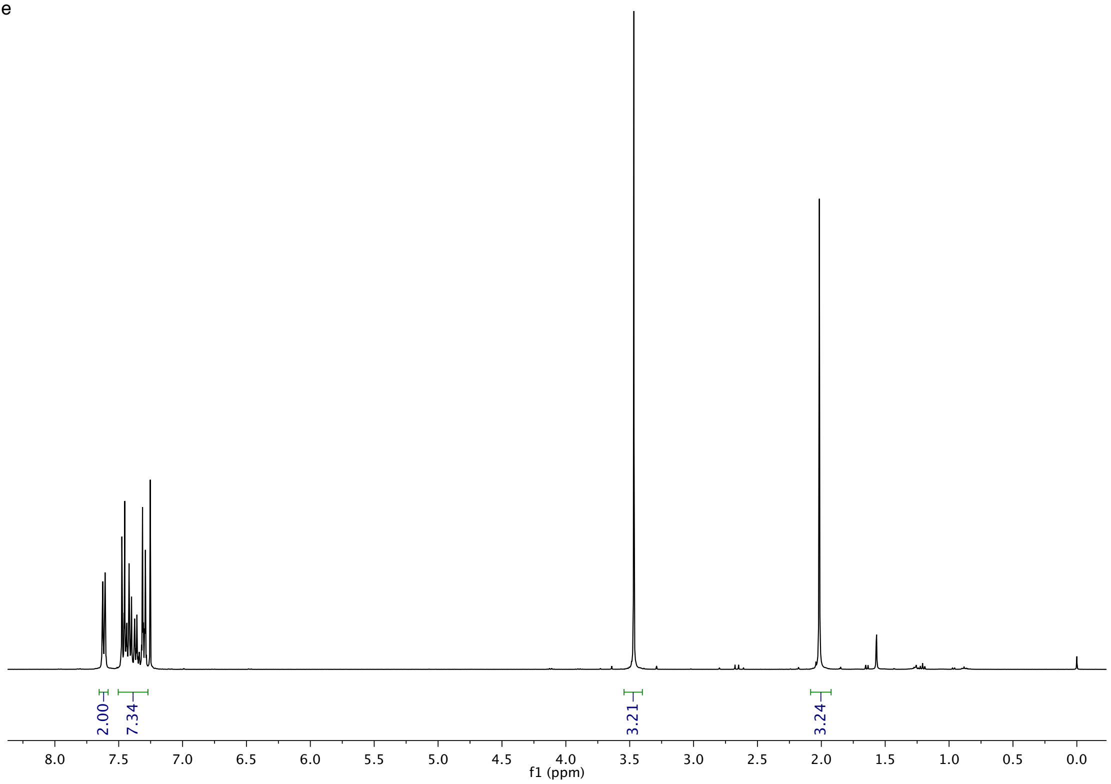
2y

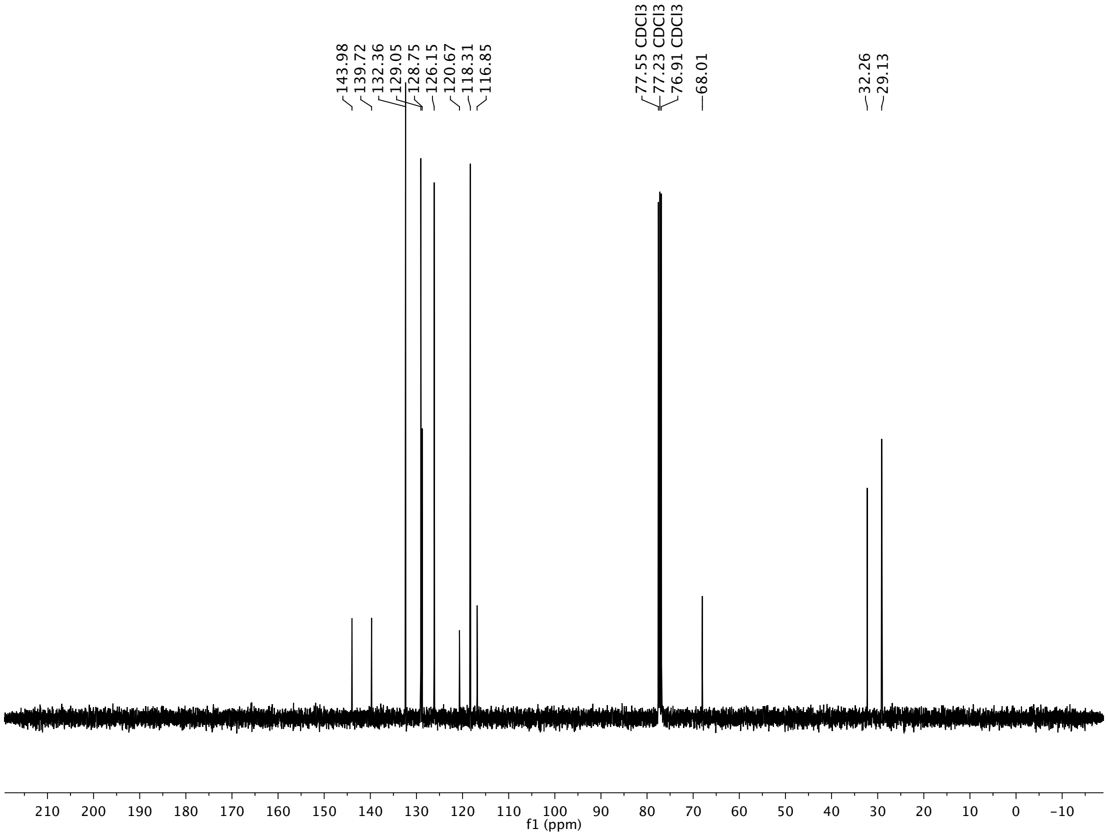

1.77
6.55
3.00
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

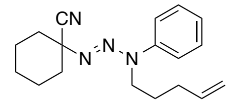

143.50
139.77
129.43
129.27
129.05
128.74
126.16
120.70
117.98
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
67.98
32.36
29.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
N
N
N
Me
Me
Br

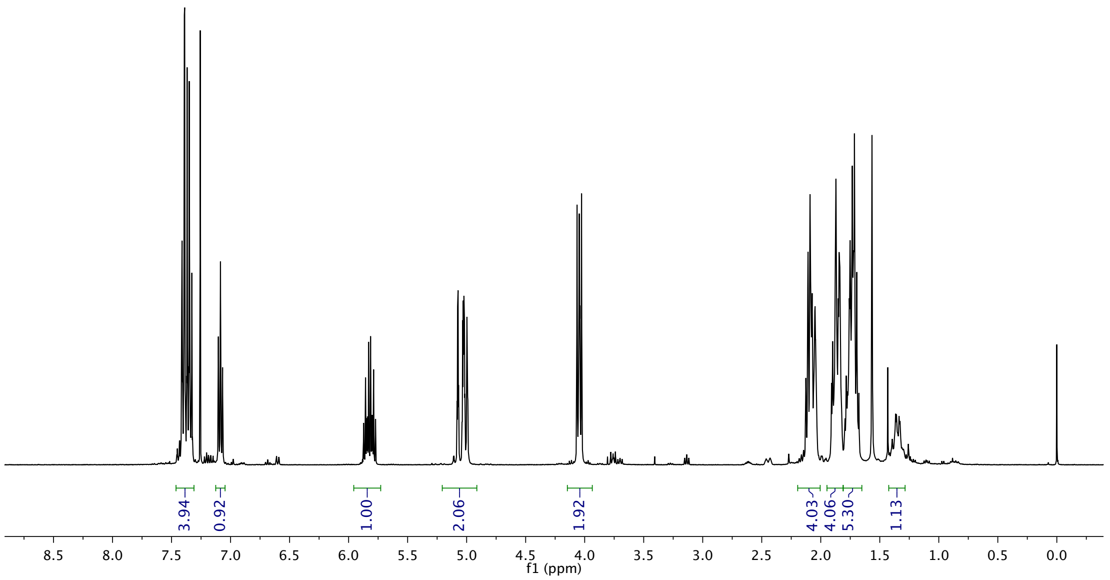
2z

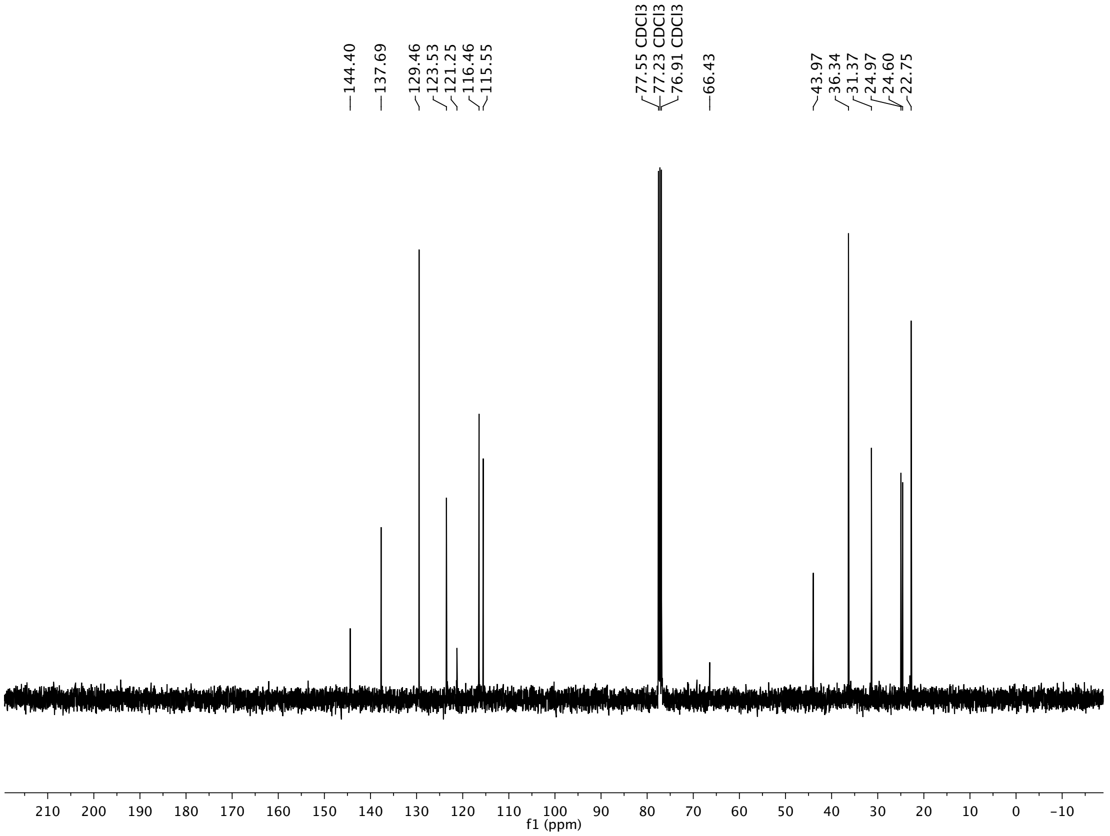

2.00
7.34
3.21
3.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

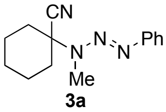

143.98
139.72
132.36
129.05
128.75
126.15
120.67
118.31
116.85
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
68.01
32.26
29.13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


CN
N
N
N

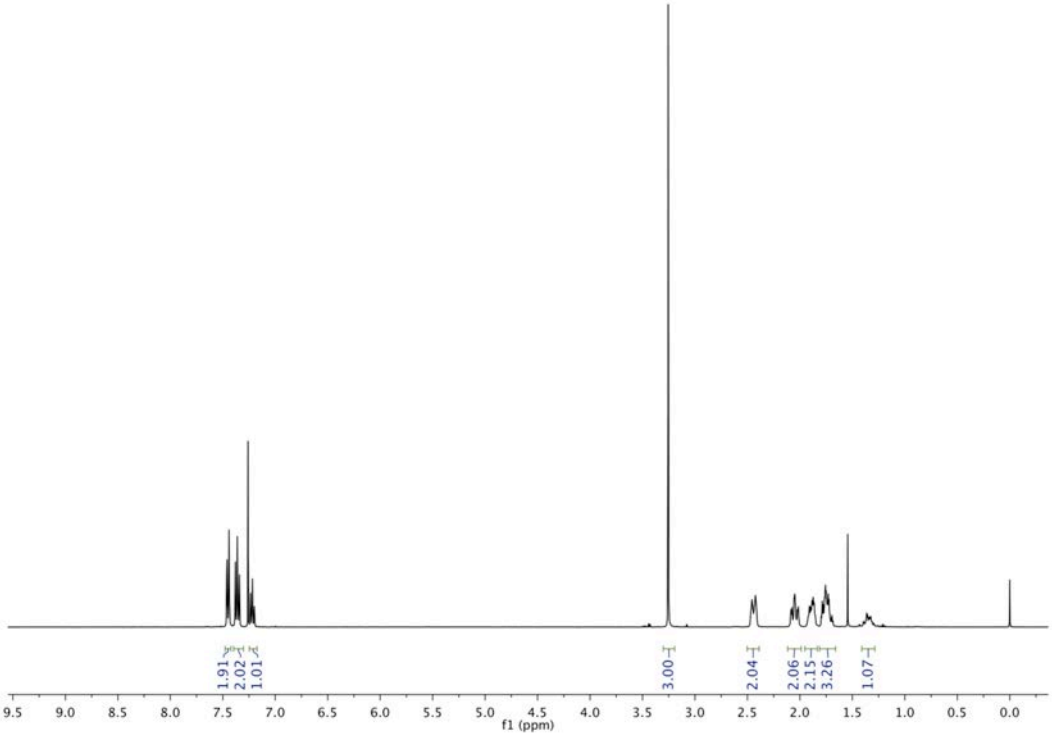
2aa

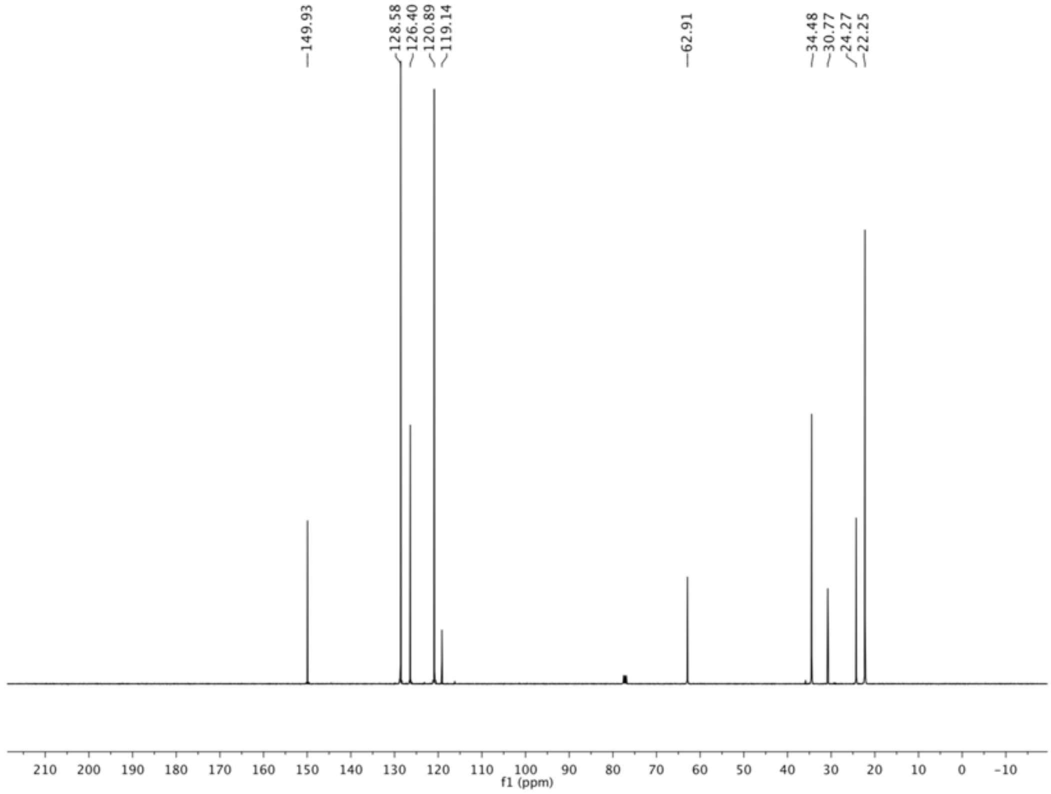

3.94
0.92
1.00
2.06
1.92
4.03
4.06
5.30
1.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

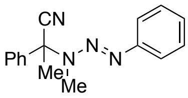

144.40
137.69
129.46
123.53
121.25
116.46
115.55
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
66.43
43.97
36.34
31.37
24.97
24.60
22.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
N
N
N
Ph
Me

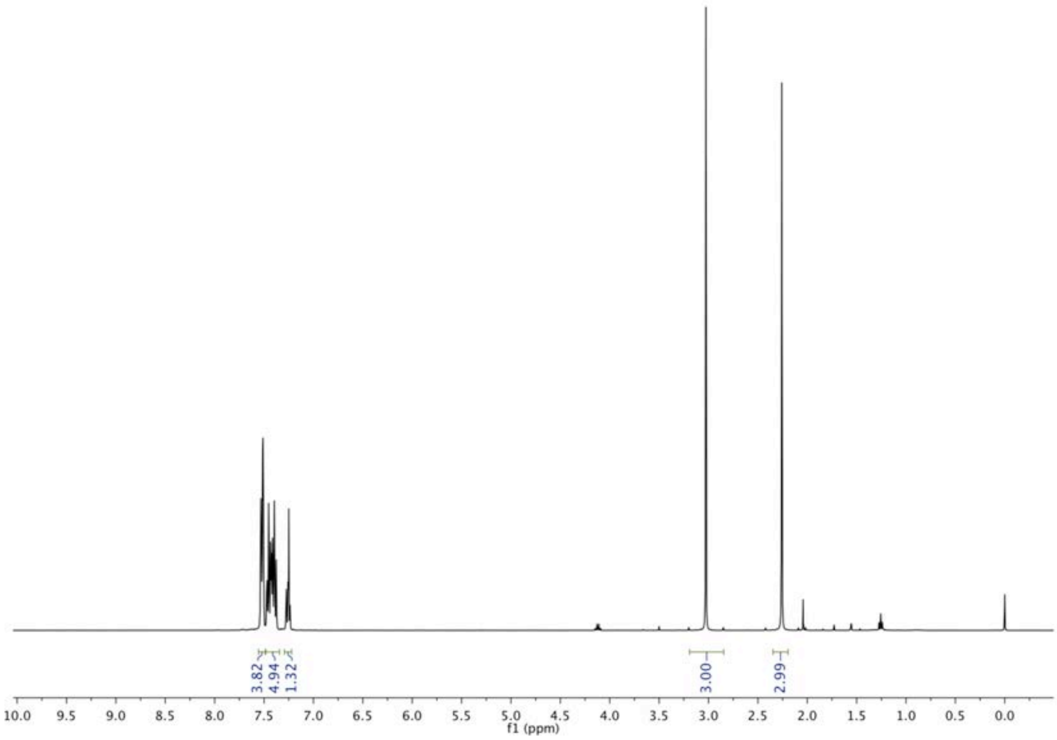
3a

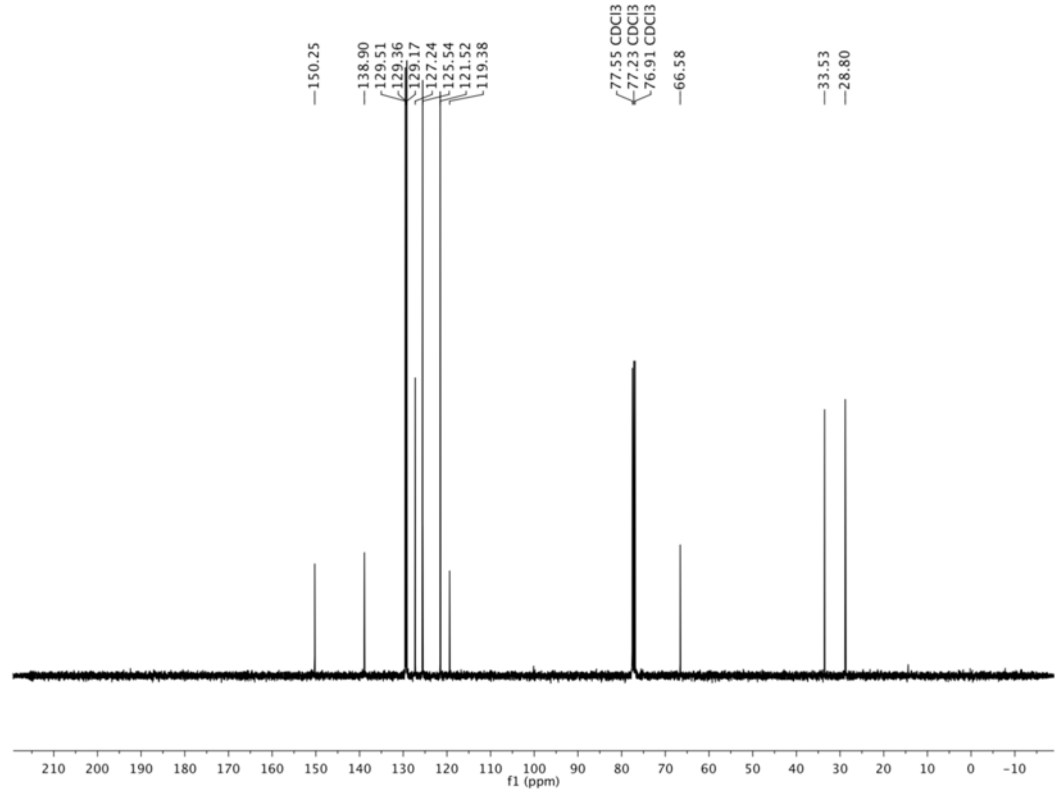

1.91
2.02
1.01
3.00
2.04
2.06
2.15
3.26
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

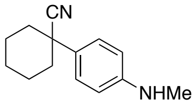

149.93
128.58
126.40
120.89
119.14
62.91
34.48
30.77
24.27
22.25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
N
N
N
Me
Me

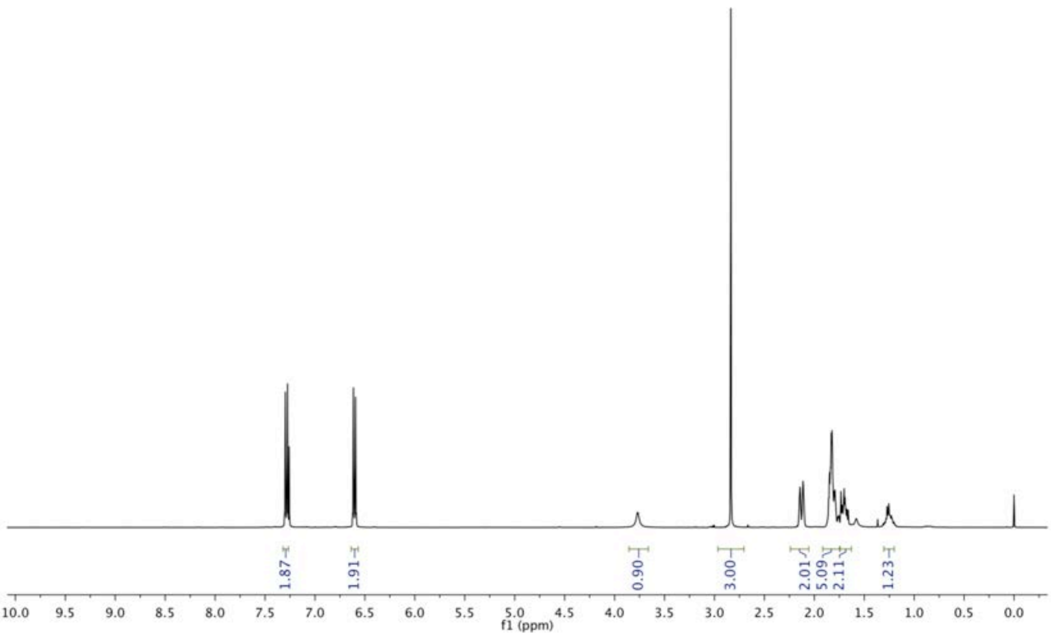
3b

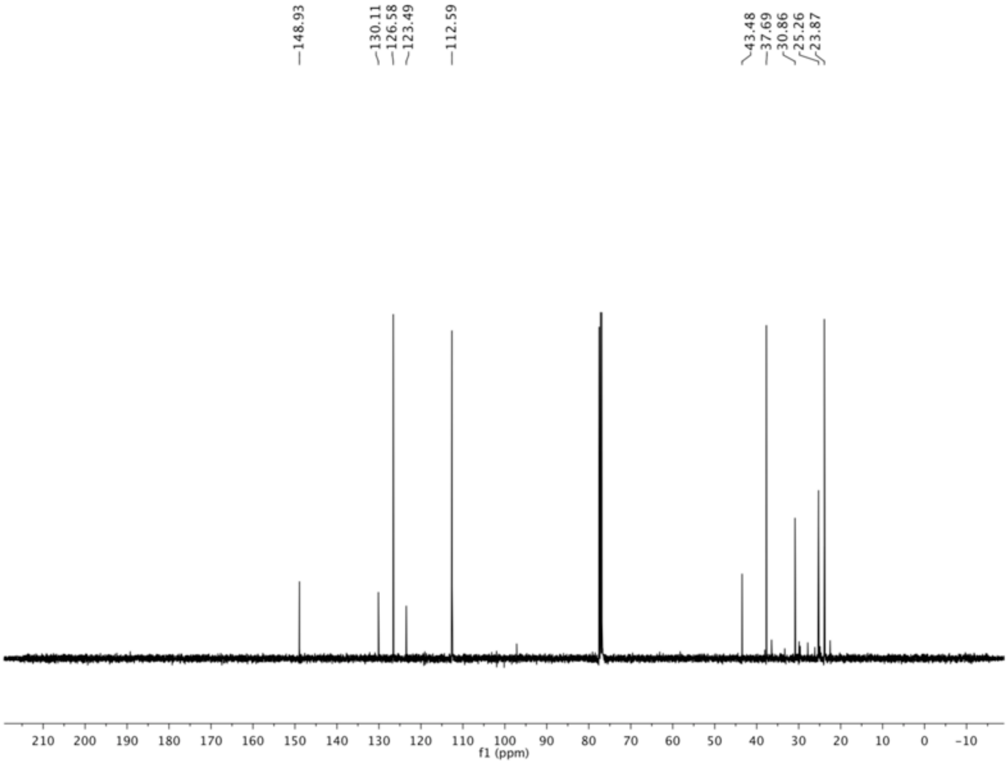

3.82
4.94
1.32
3.00
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

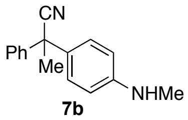

150.25
138.90
129.51
129.36
129.17
127.24
125.54
121.52
119.38
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
66.58
33.53
28.80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
NHMe

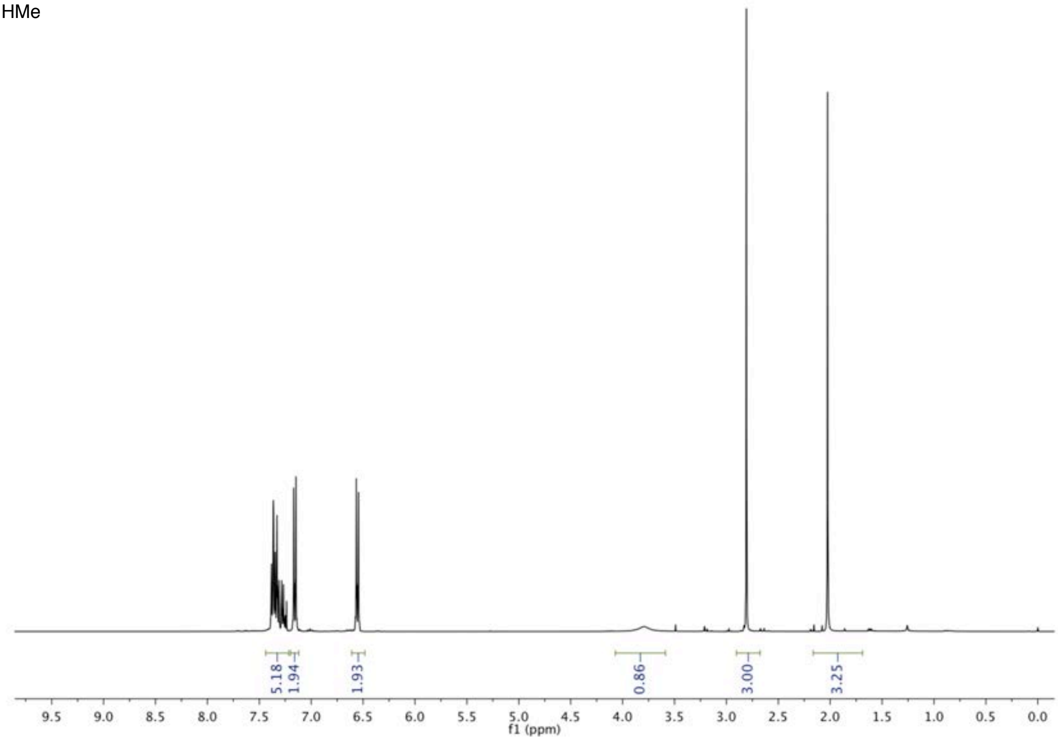
7a

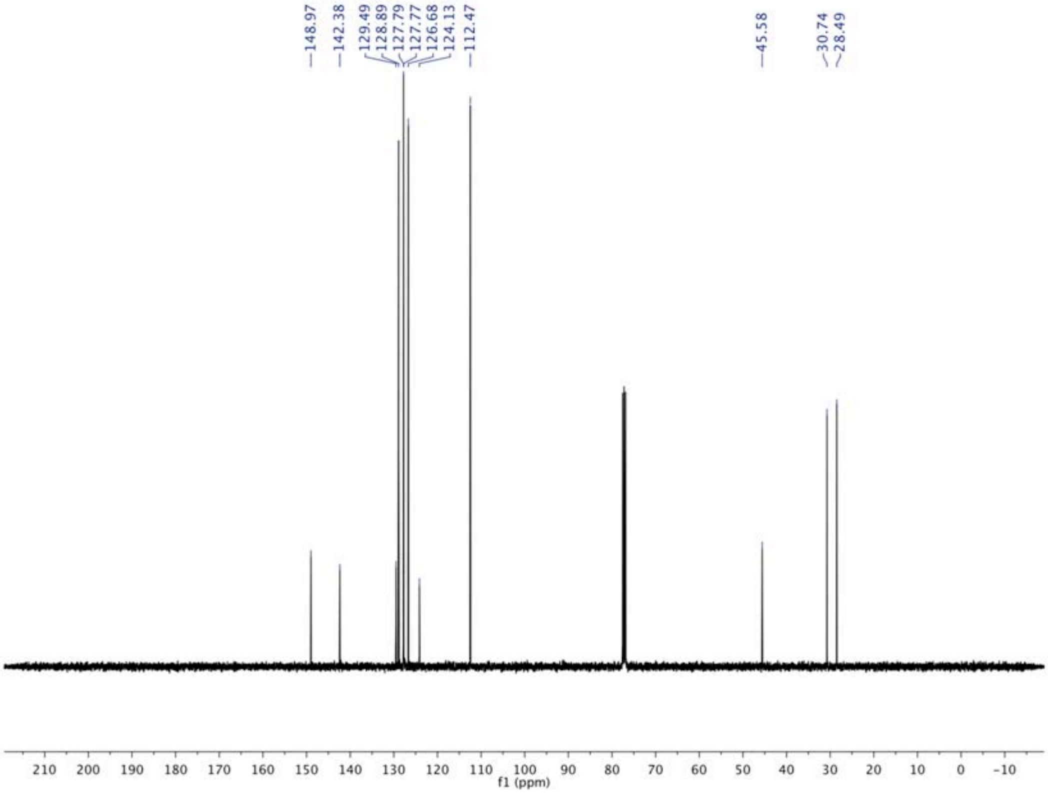

1.87
1.91
0.90
3.00
2.01
5.09
2.11
1.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

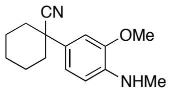

148.93
130.11
126.58
123.49
112.59
43.48
37.69
30.86
25.26
23.87
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
NHMe

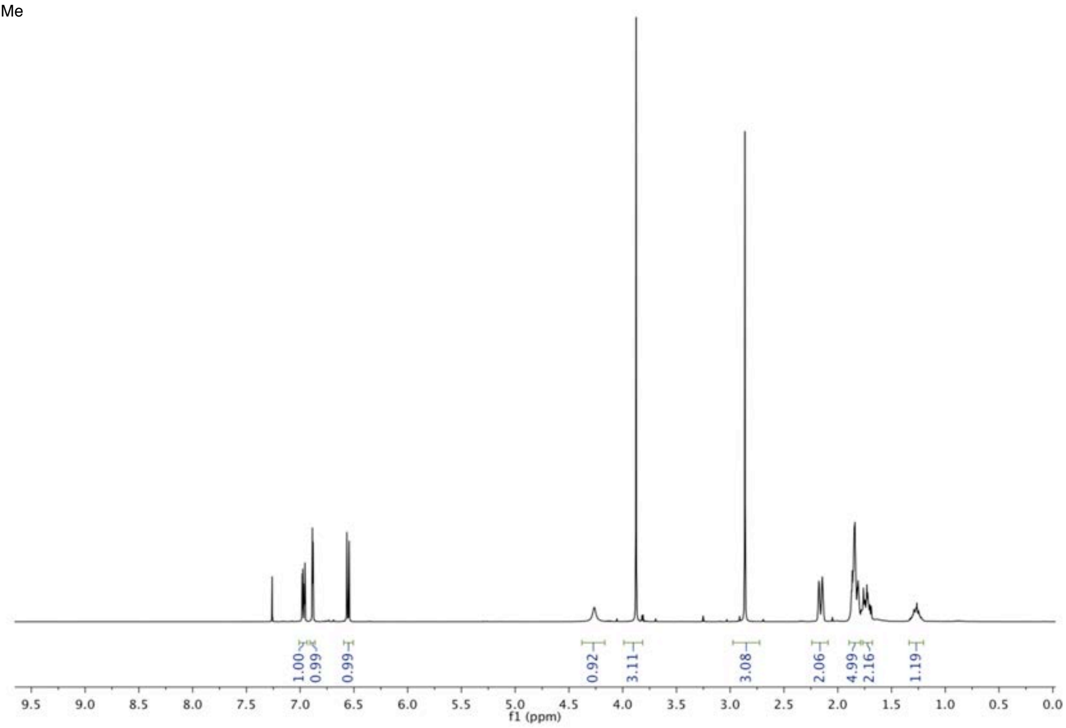
7b

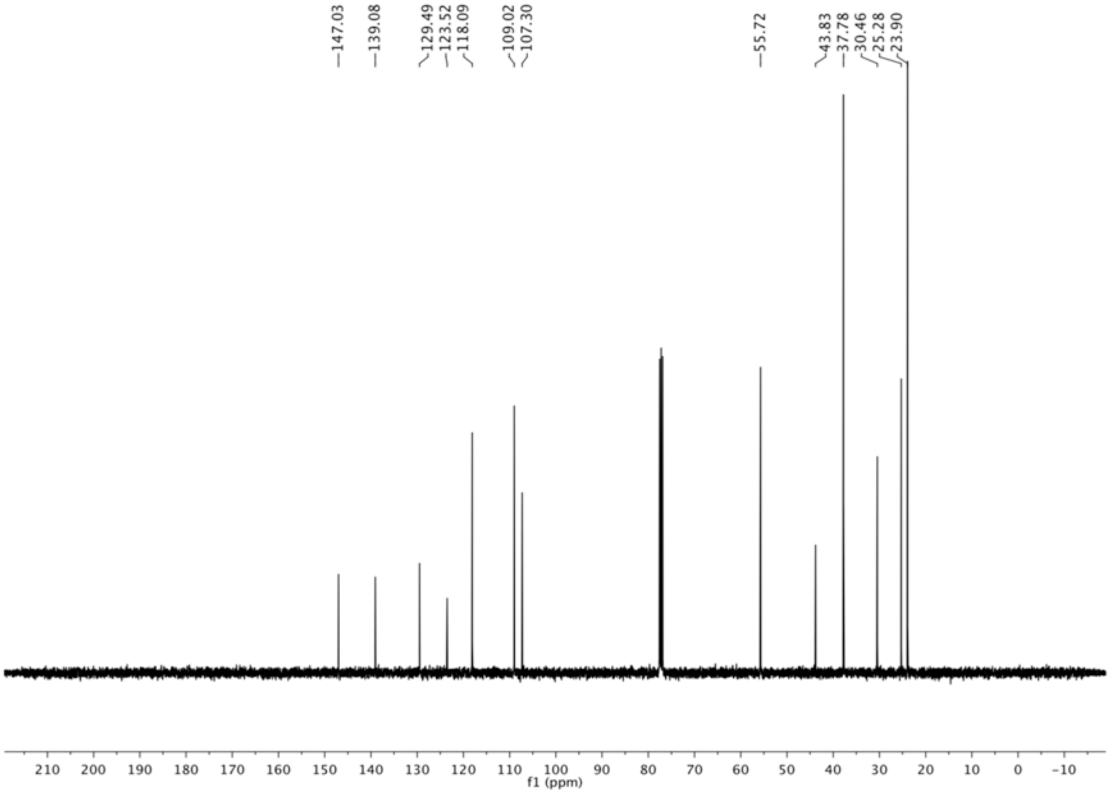

5.18
1.94
1.93
0.86
3.00
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

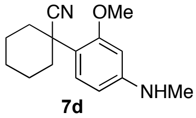

148.97
142.38
129.49
128.89
127.79
127.77
126.68
124.13
112.47
45.58
30.74
28.49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
OMe
NHMe

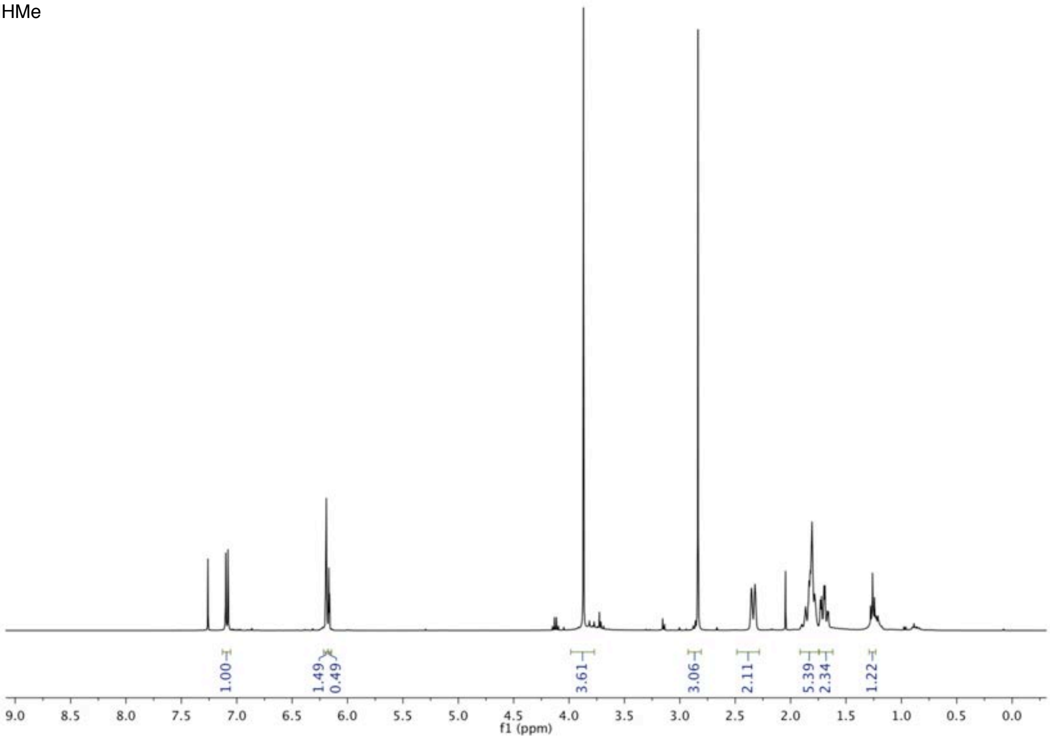
7c

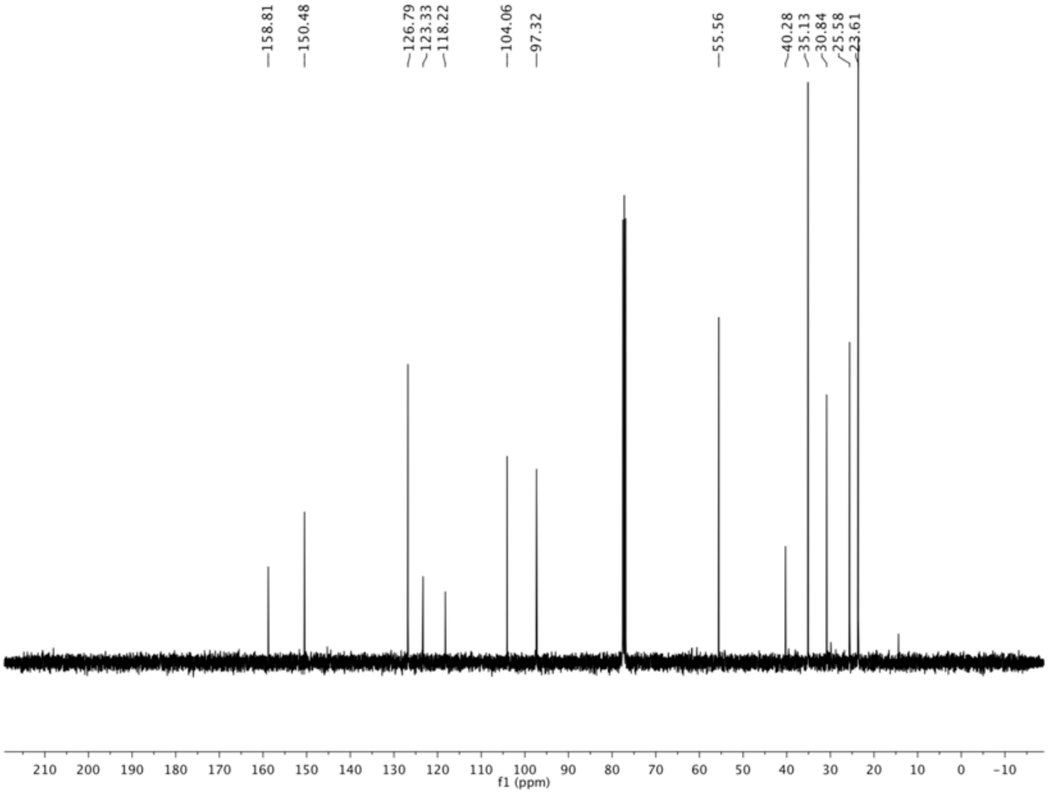

1.00
0.99
0.99
0.92
3.11
3.08
2.06
4.99
2.16
1.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

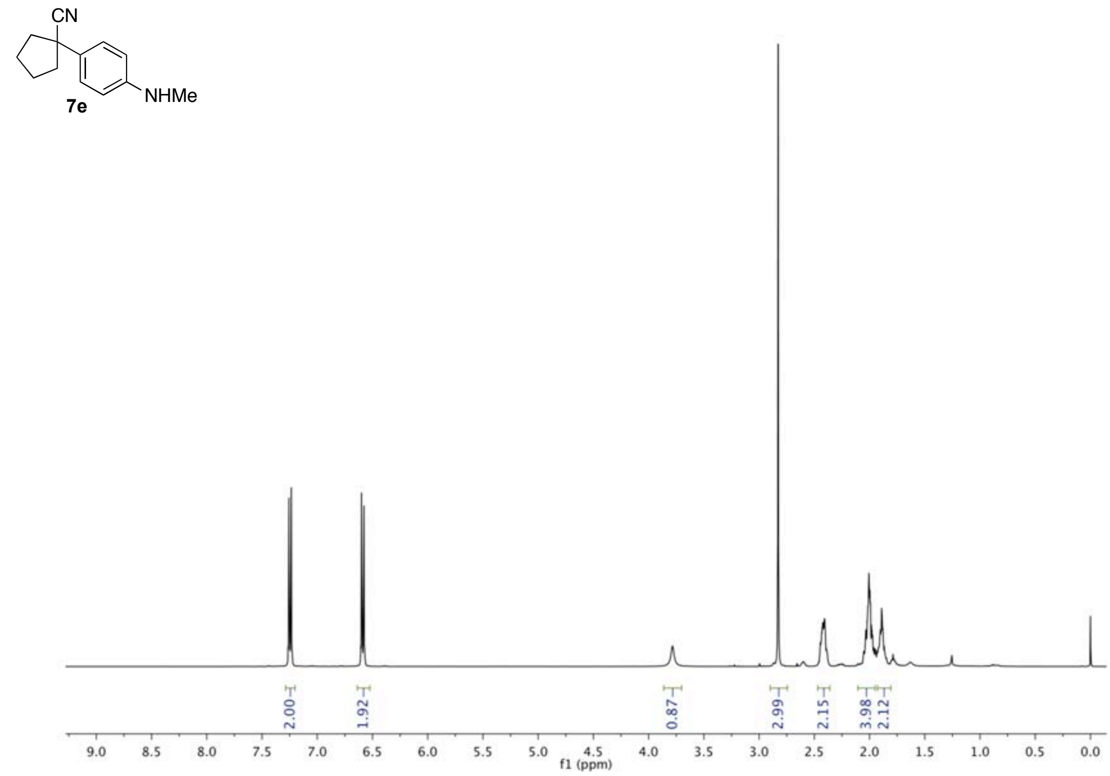

147.03
139.08
129.49
123.52
118.09
109.02
107.30
55.72
43.83
37.78
30.46
25.28
23.90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
OMe
NHMe

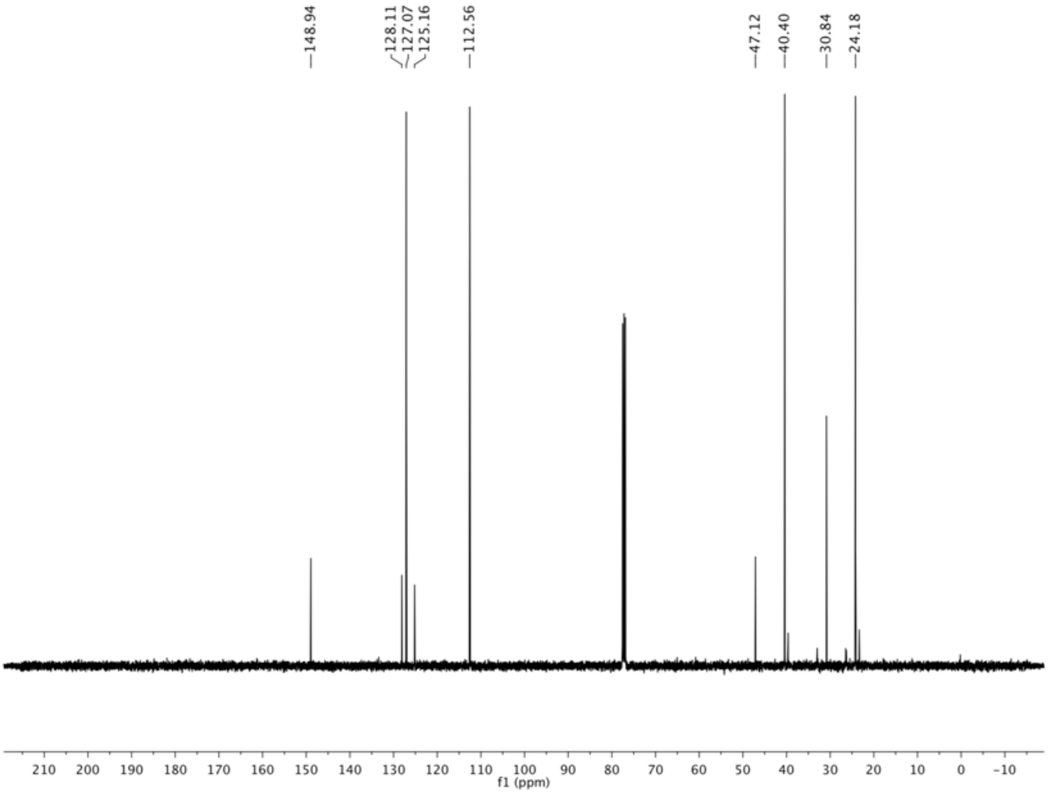
7d

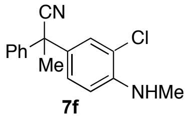

1.00
1.49
0.49
3.61
3.06
2.11
5.39
2.34
1.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.81
150.48
126.79
123.33
118.22
104.06
97.32
55.56
40.28
35.13
30.84
25.58
23.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

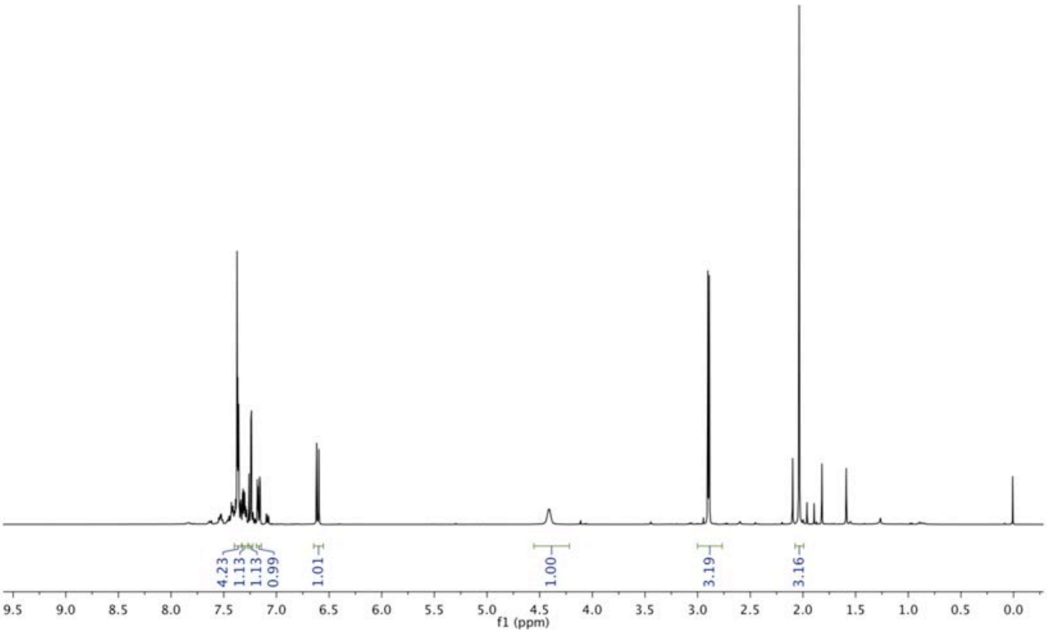

CN
NHMe
2.00
1.92
0.87
2.99
2.15
3.98
2.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

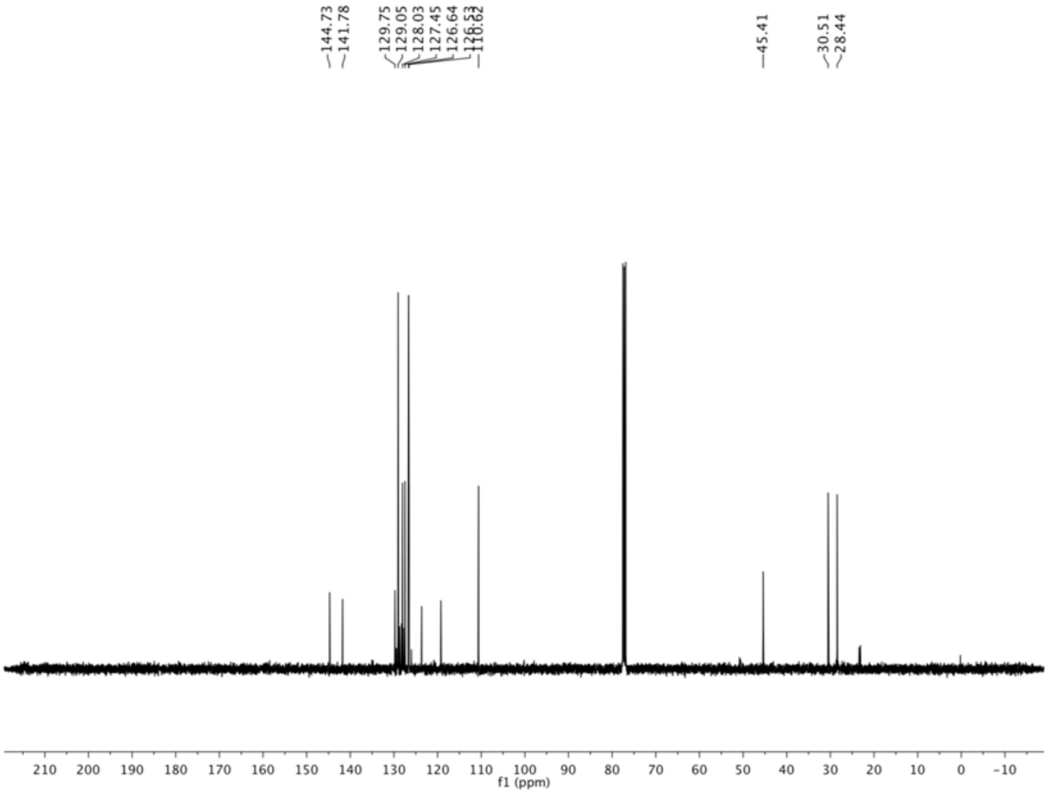
7e

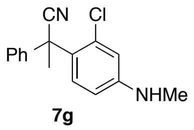

148.94
128.11
127.07
125.16
112.56
47.12
40.40
30.84
24.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CN
Ph
Me
Cl
NHMe

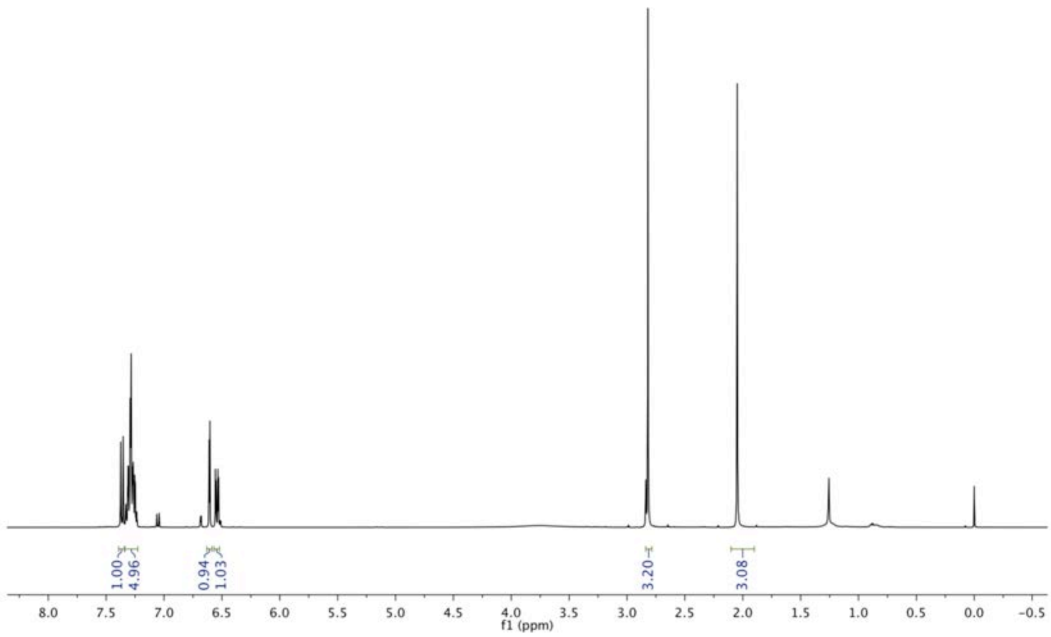
7f

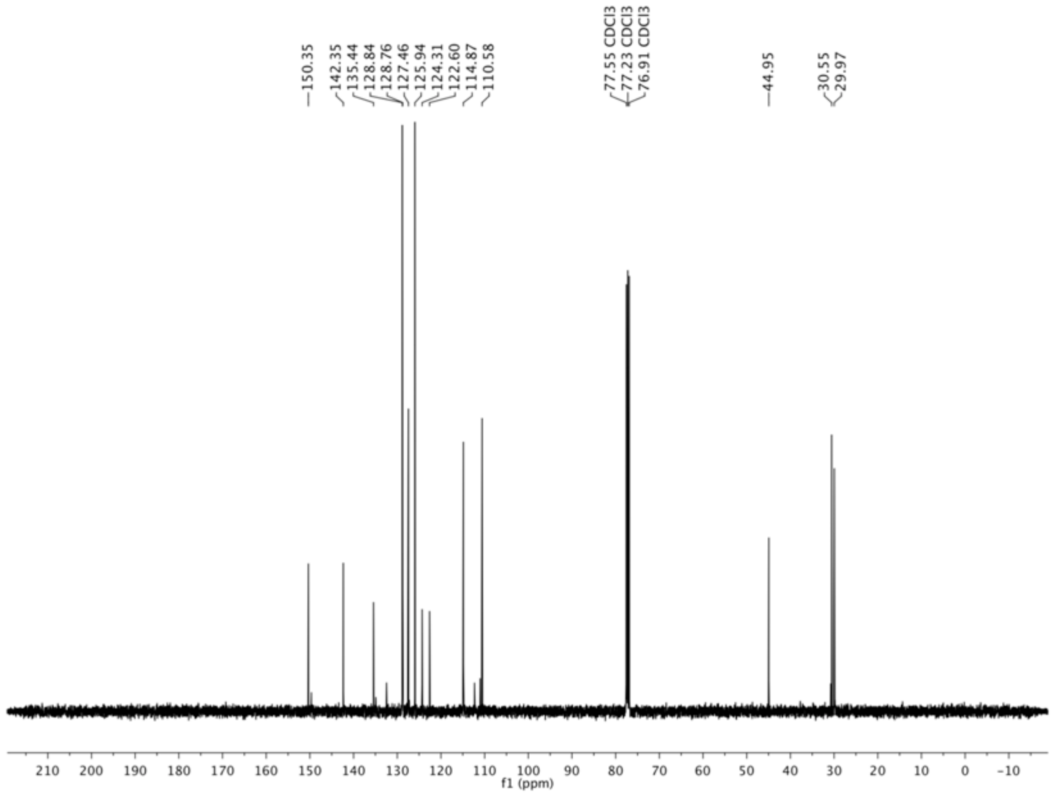

4.23
1.13
1.13
0.99
1.01
1.00
3.19
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

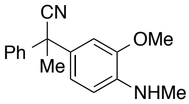

144.73
141.78
129.75
129.05
128.03
127.45
126.64
126.53
110.62
45.41
30.51
28.44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Cl
Ph
NHMe

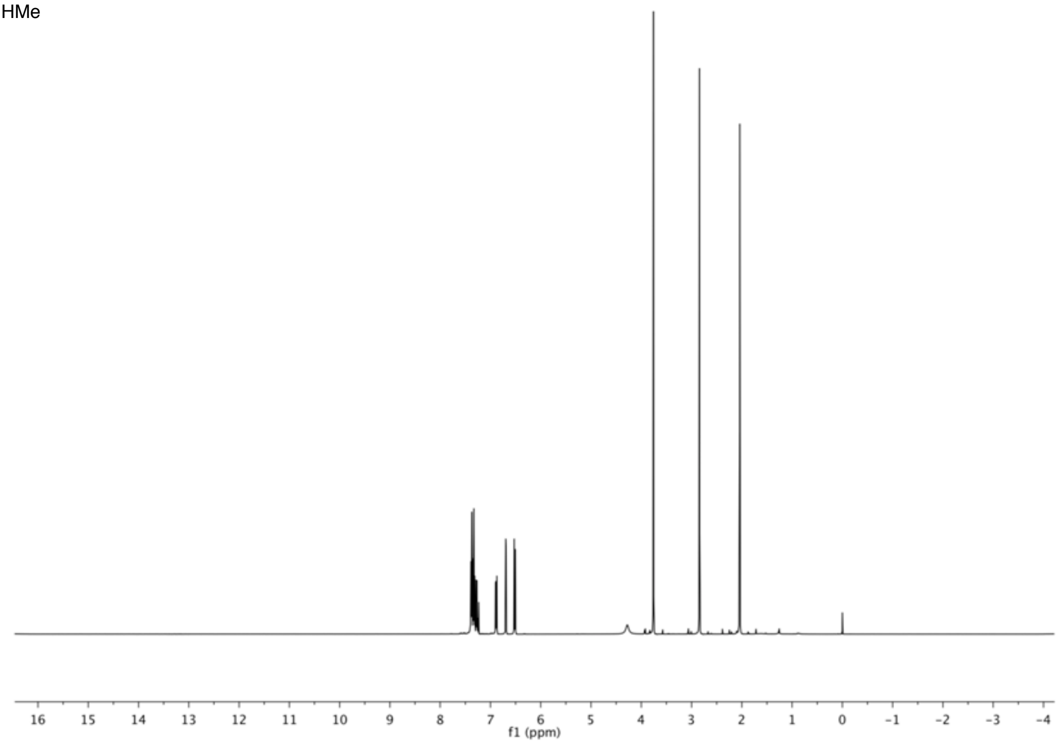
7g

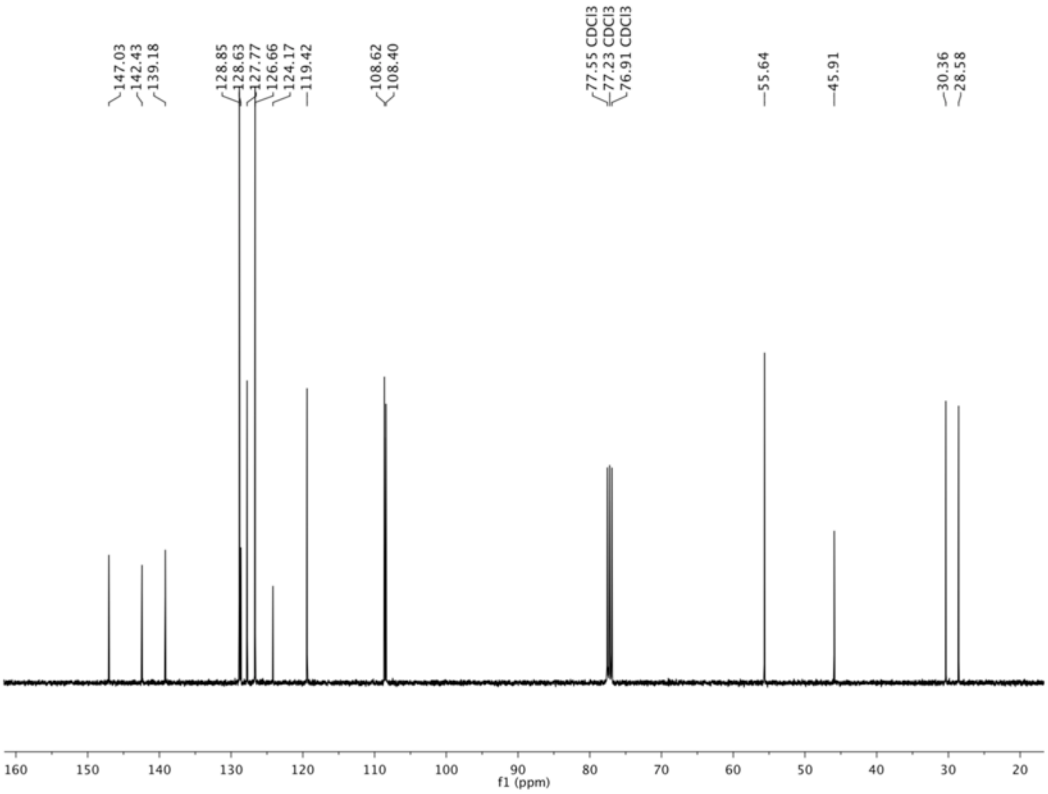

1.00
4.96
0.94
1.03
3.20
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

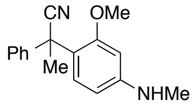

150.35
142.35
135.44
128.84
128.76
127.46
125.94
124.31
122.60
114.87
110.58
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
44.95
30.55
29.97
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
OMe
NHMe

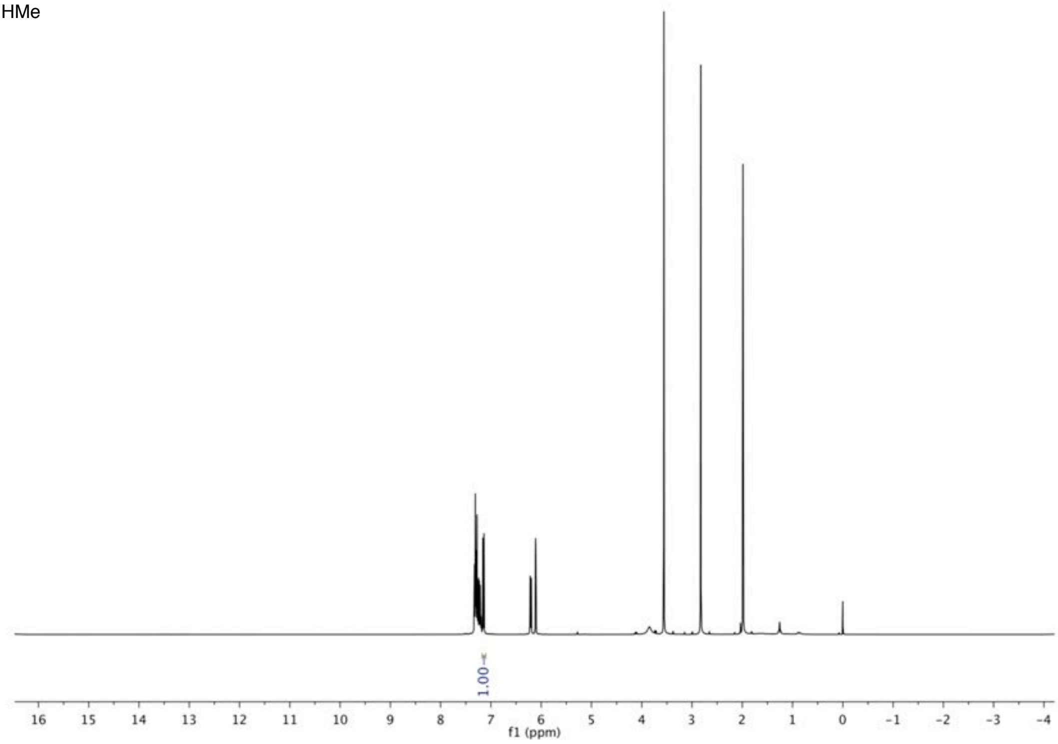
7h

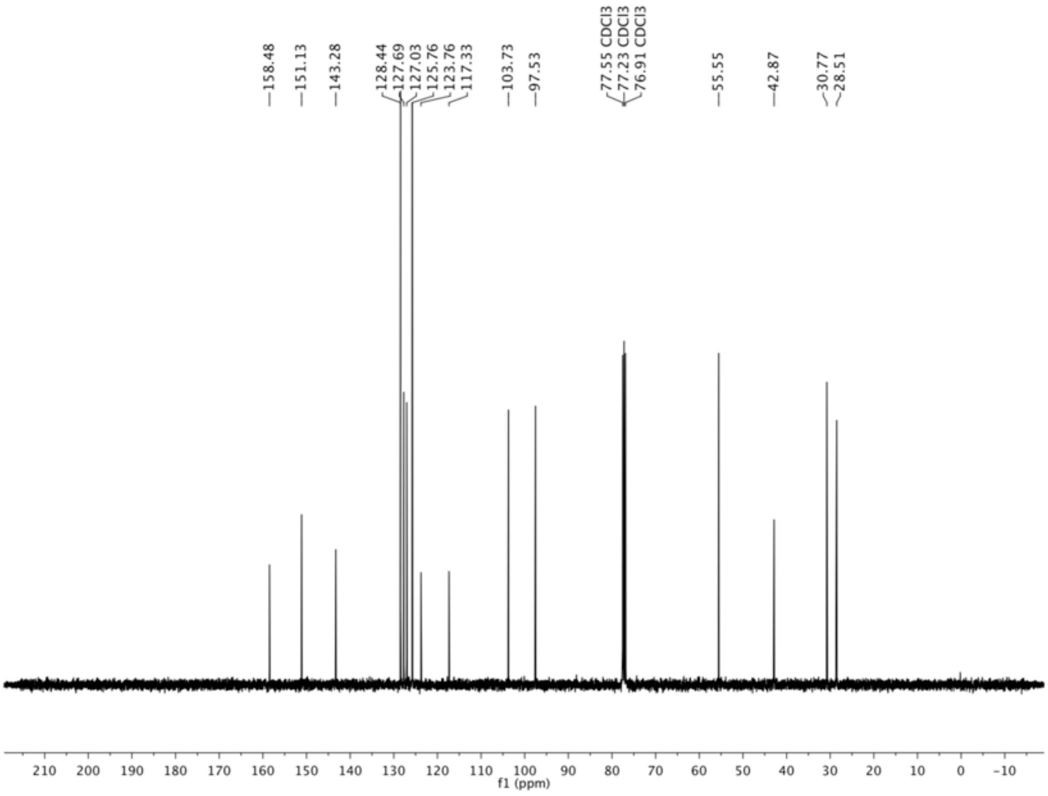

16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

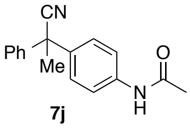

147.03
142.43
139.18
128.85
128.63
127.77
126.66
124.17
119.42
108.62
108.40
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
55.64
45.91
30.36
28.58
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


CN
OMe
Ph
Me
NHMe

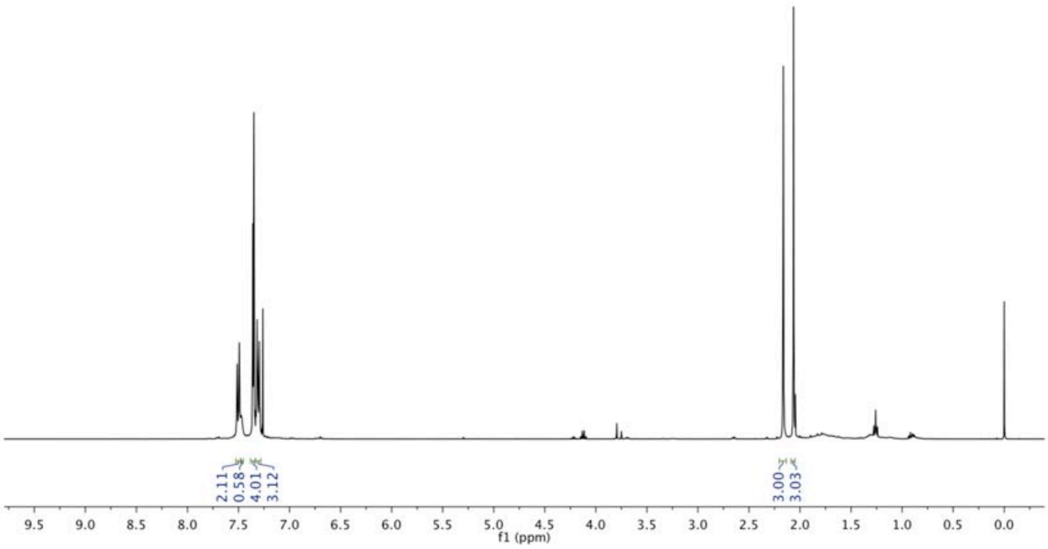
7i

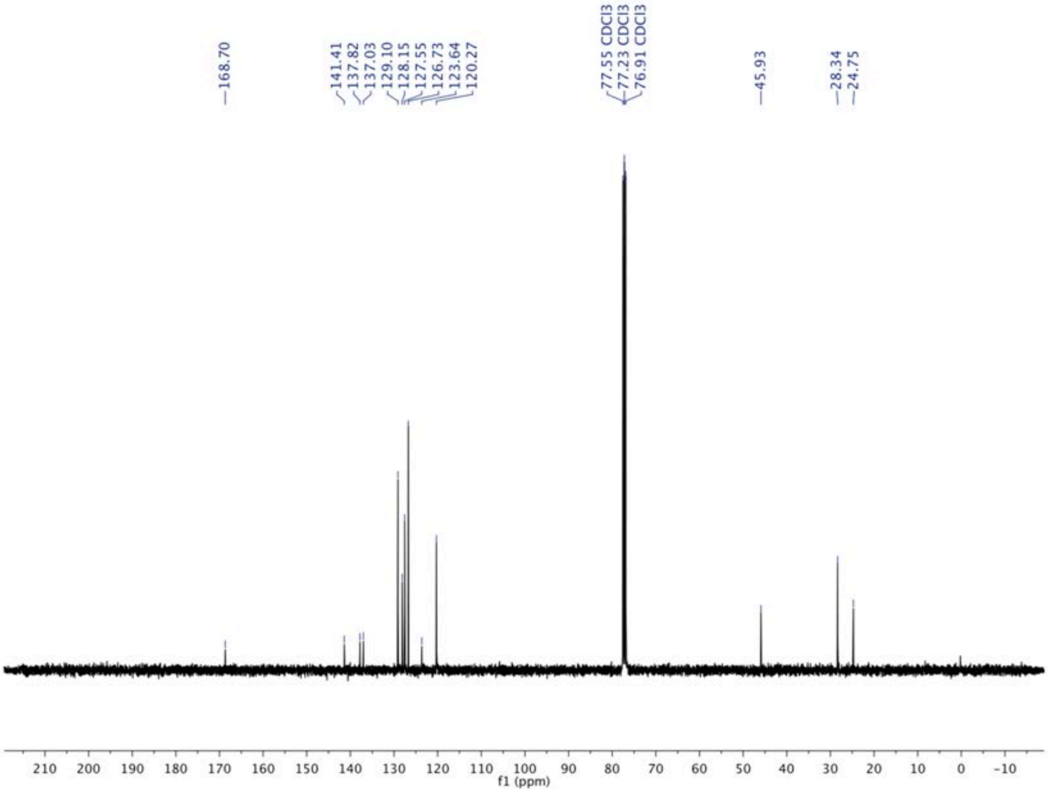

1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

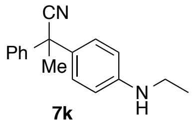

158.48
151.13
143.28
128.44
127.69
127.03
125.76
123.76
117.33
103.73
97.53
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
55.55
42.87
30.77
28.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
O
N
H

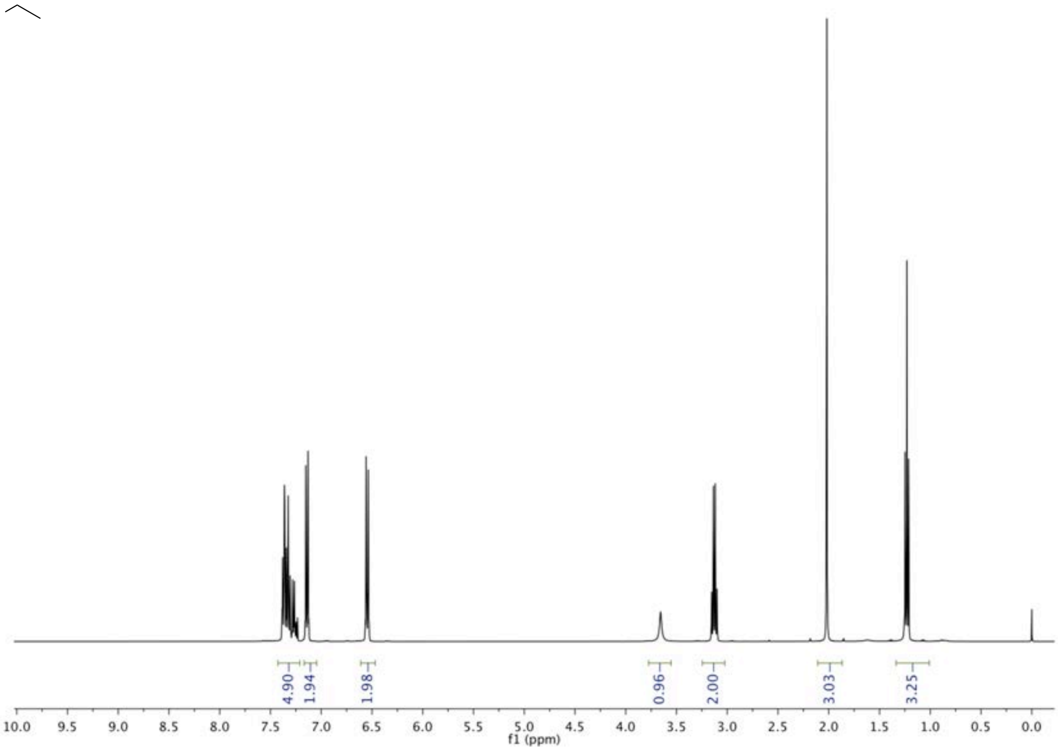
7j

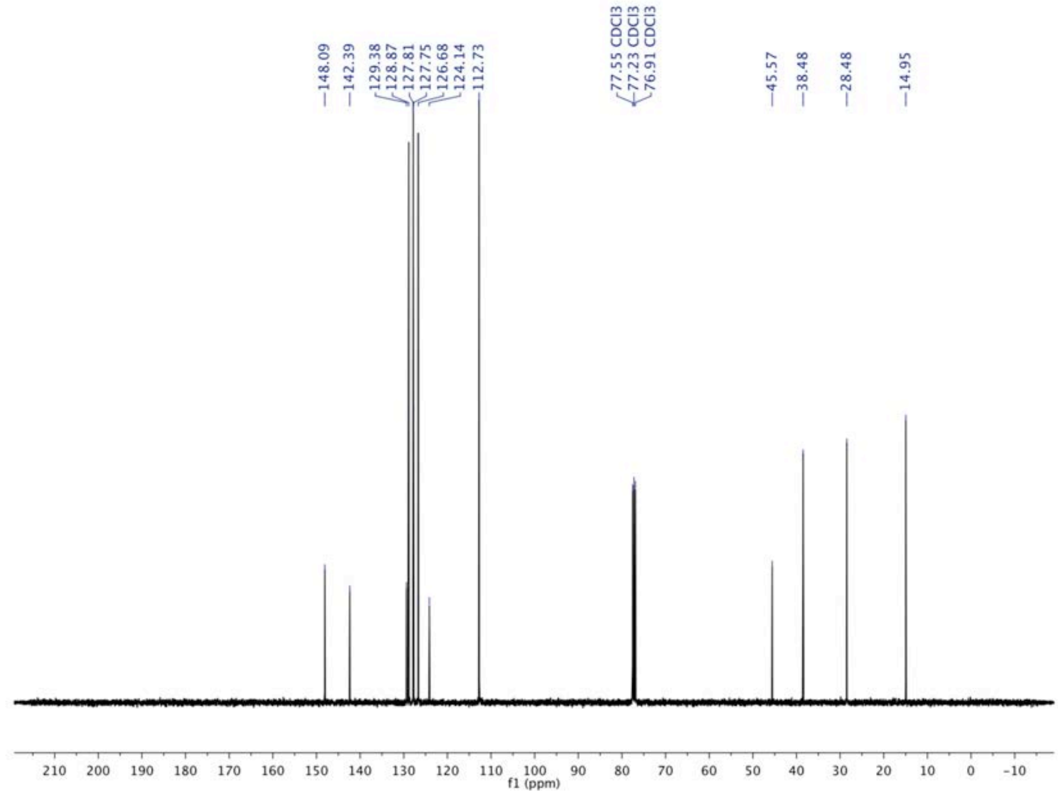

2.11
0.58
4.01
3.12
3.00
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

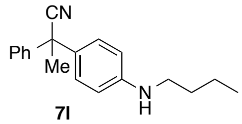

168.70
141.41
137.82
137.03
129.10
128.15
127.55
126.73
123.64
120.27
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
45.93
28.34
24.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
H

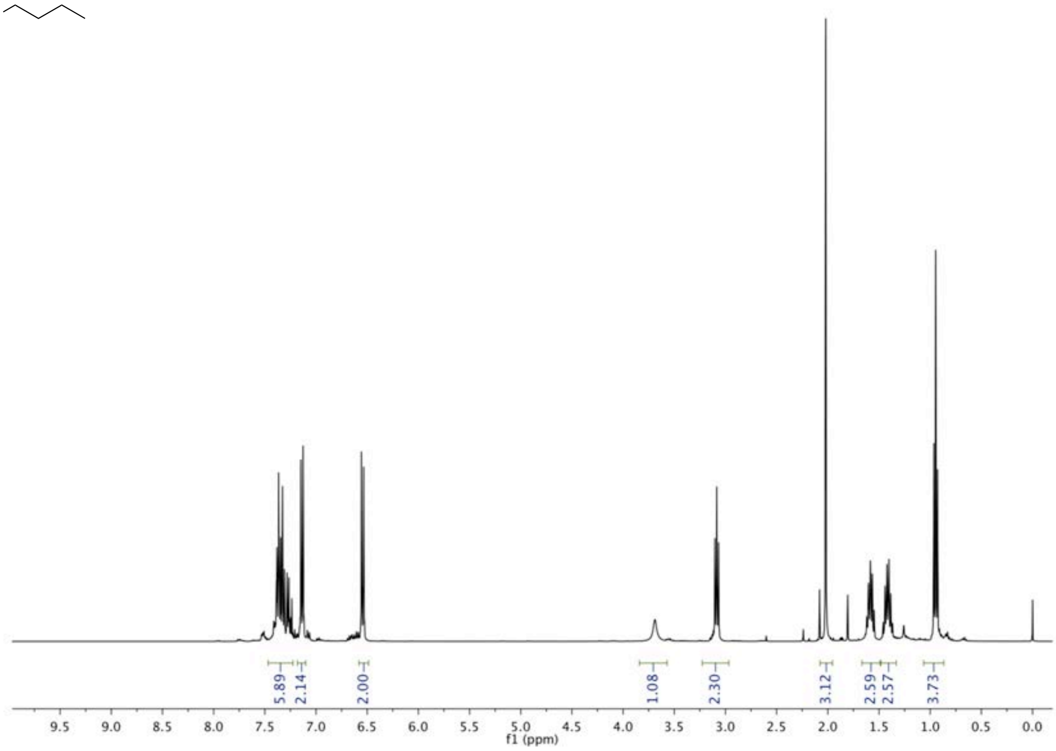
7k

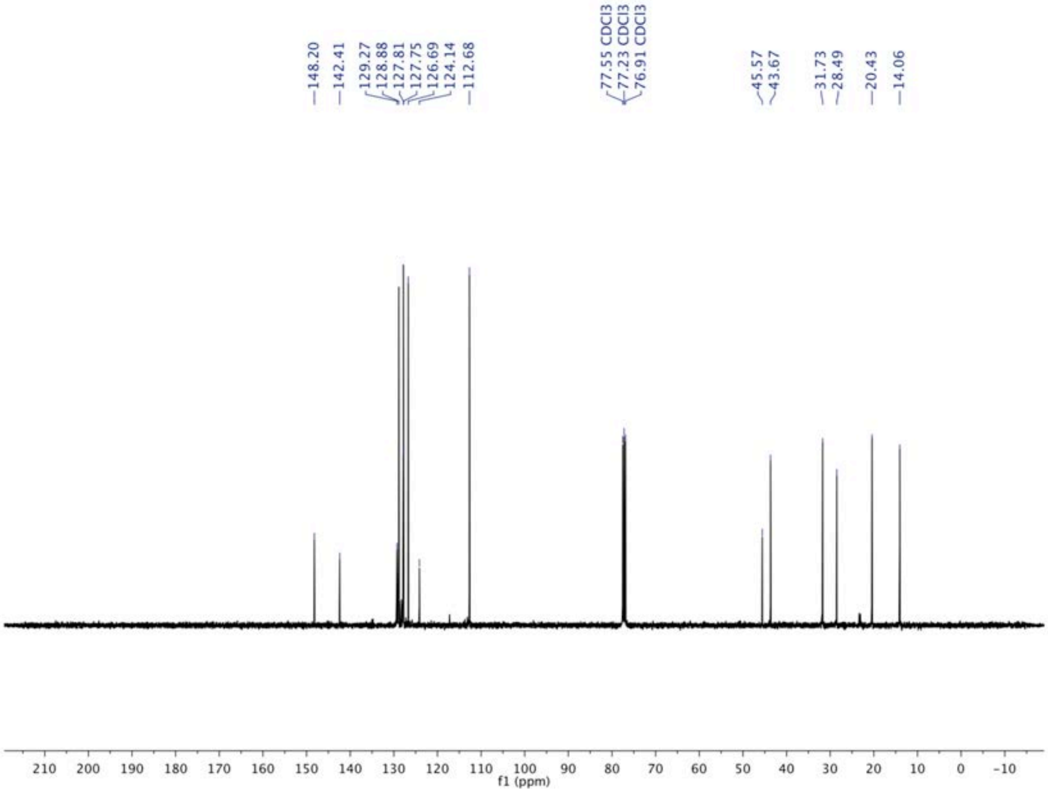

4.90
1.94
1.98
0.96
2.00
3.03
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

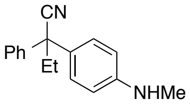

148.09
142.39
129.38
128.87
127.81
127.75
126.68
124.14
112.73
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
45.57
38.48
28.48
14.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Me
N
H

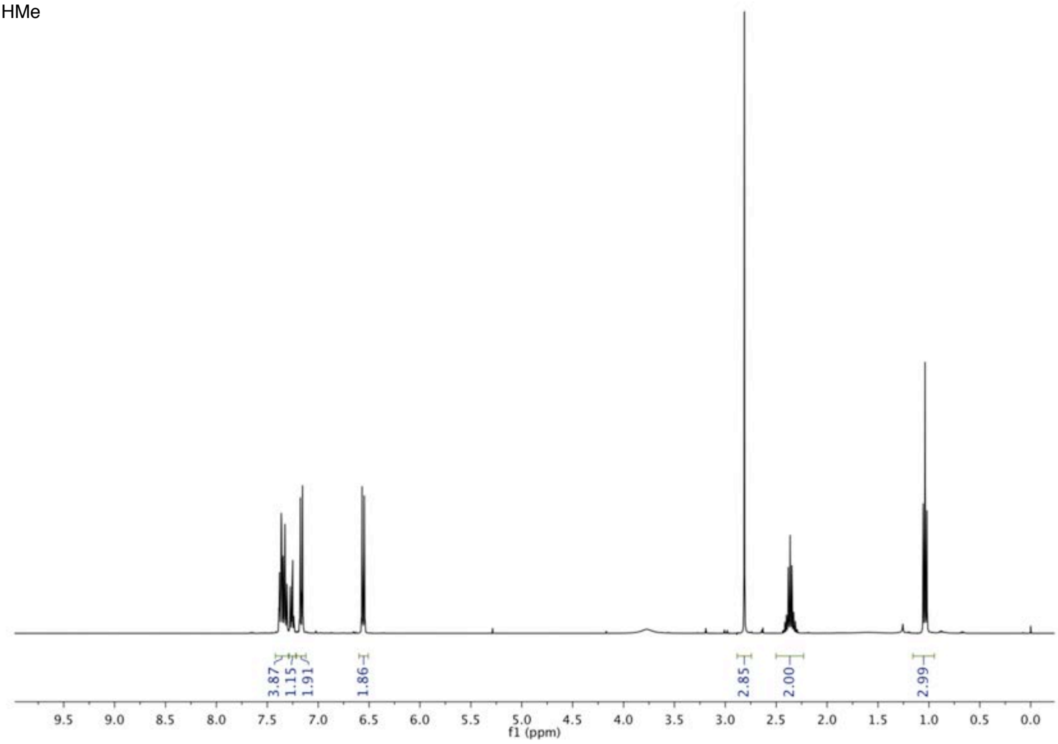
7l

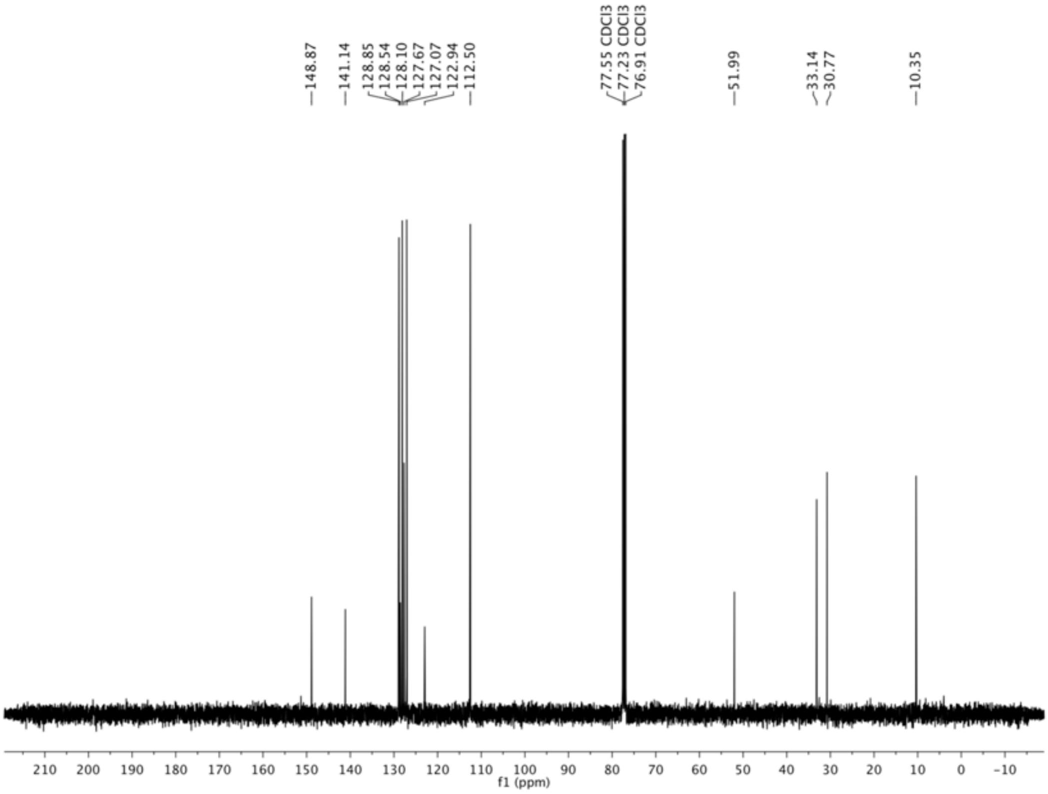

5.89
2.14
2.00
1.08
2.30
3.12
2.59
2.57
3.73
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

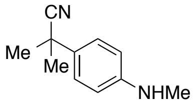

148.20
142.41
129.27
128.88
127.81
127.75
126.69
124.14
112.68
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
45.57
43.67
31.73
28.49
20.43
14.06
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Et
NHMe

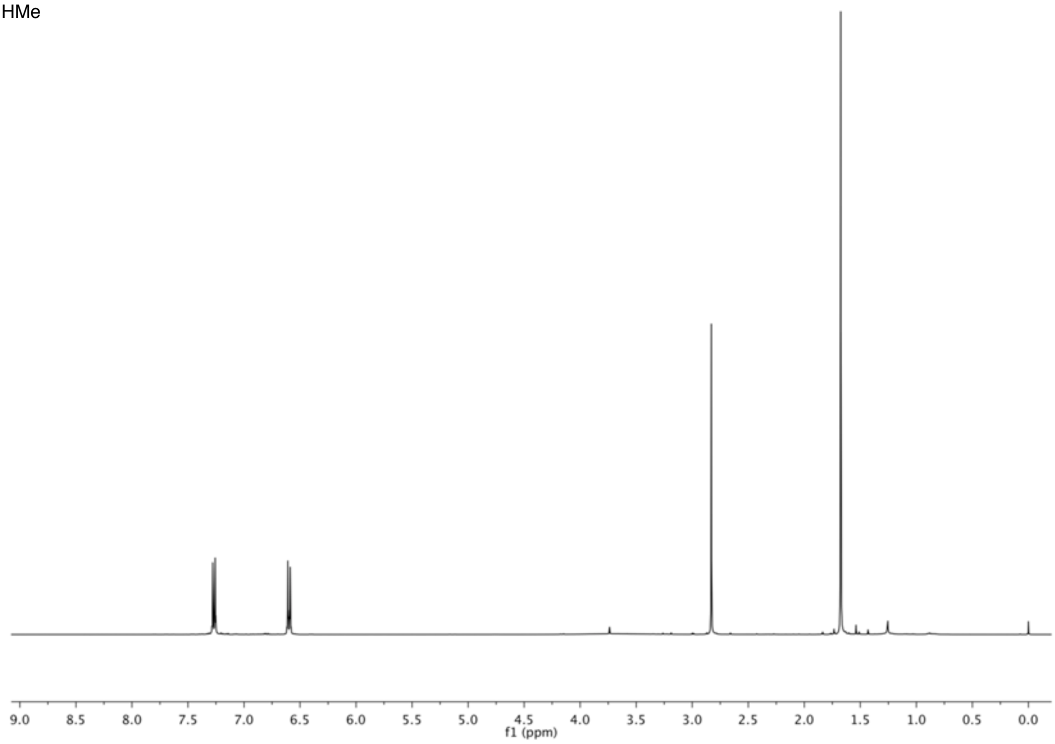
7m

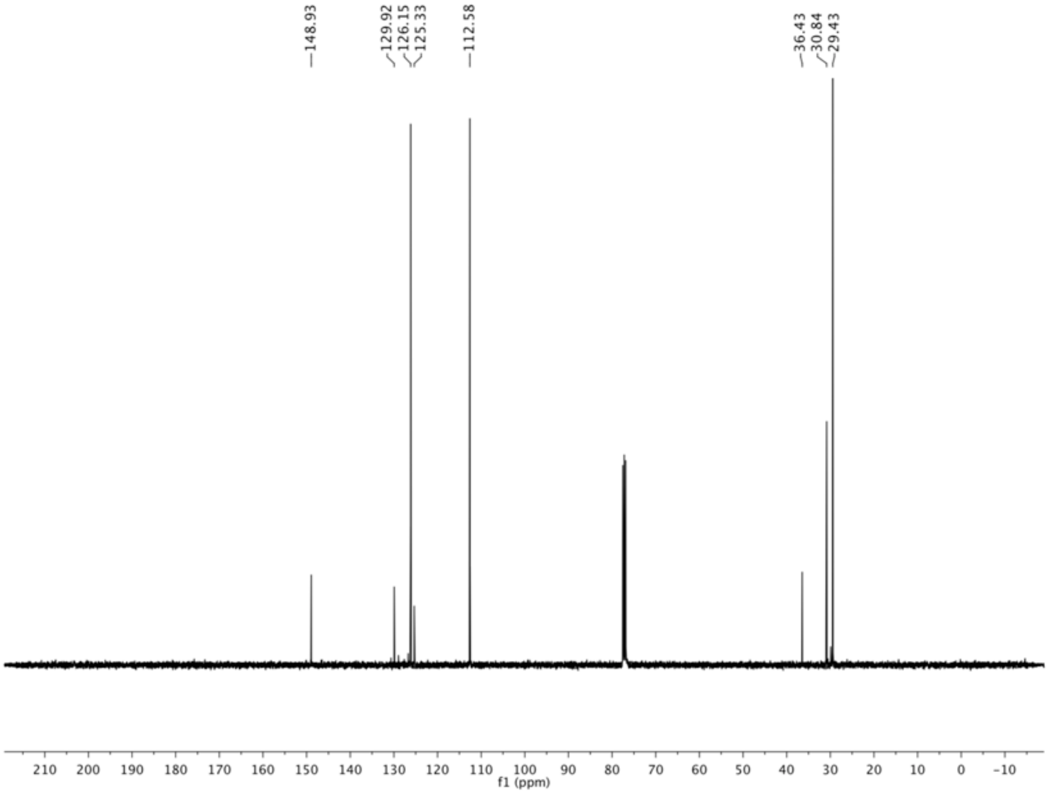

3.87
1.15
1.91
1.86
2.85
2.00
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

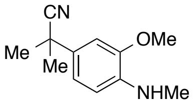

148.87
141.14
128.85
128.54
128.10
127.67
127.07
122.94
112.50
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
51.99
33.14
30.77
10.35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


CN
Me
Me
NHMe

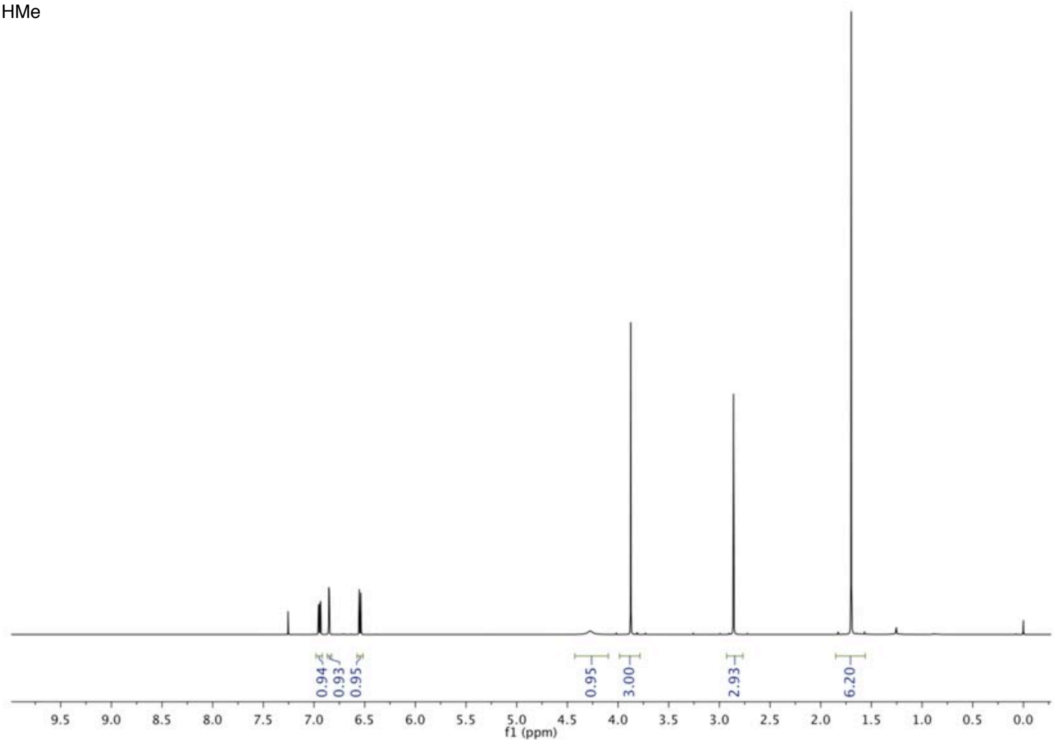
7n

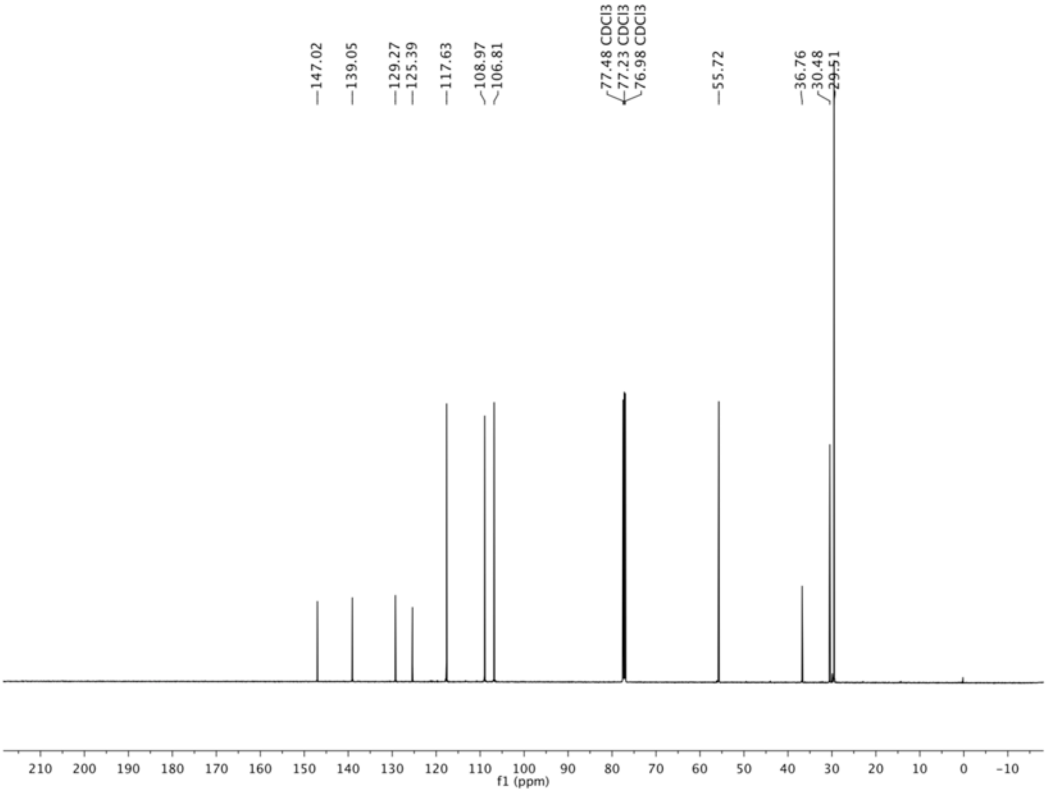

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

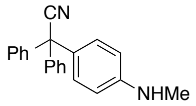

148.93
129.92
126.15
125.33
112.58
36.43
30.84
29.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Me
Me
OMe
NHMe

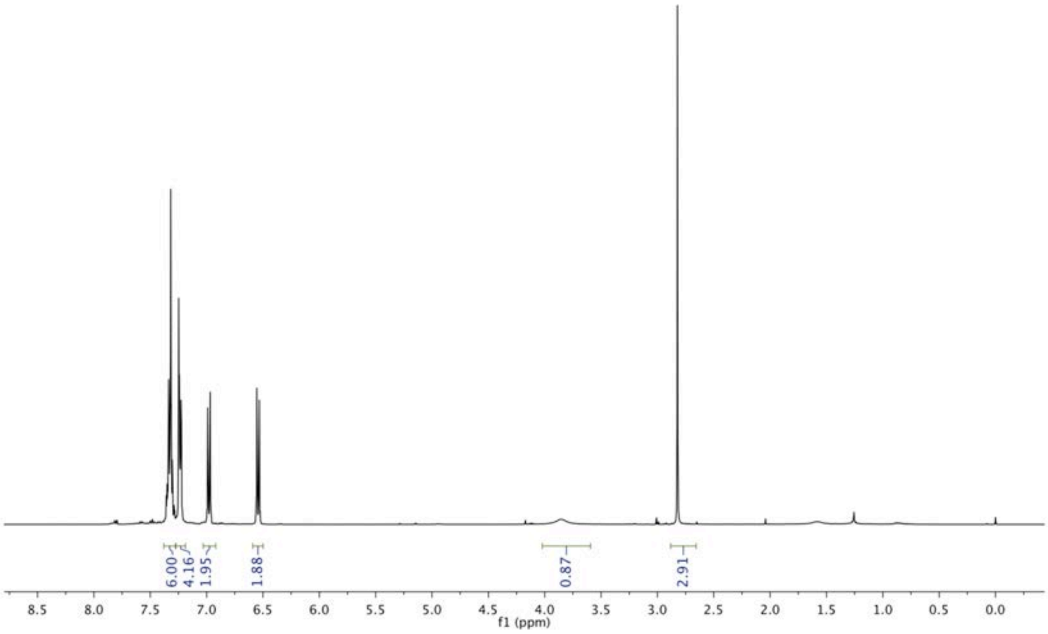
7o

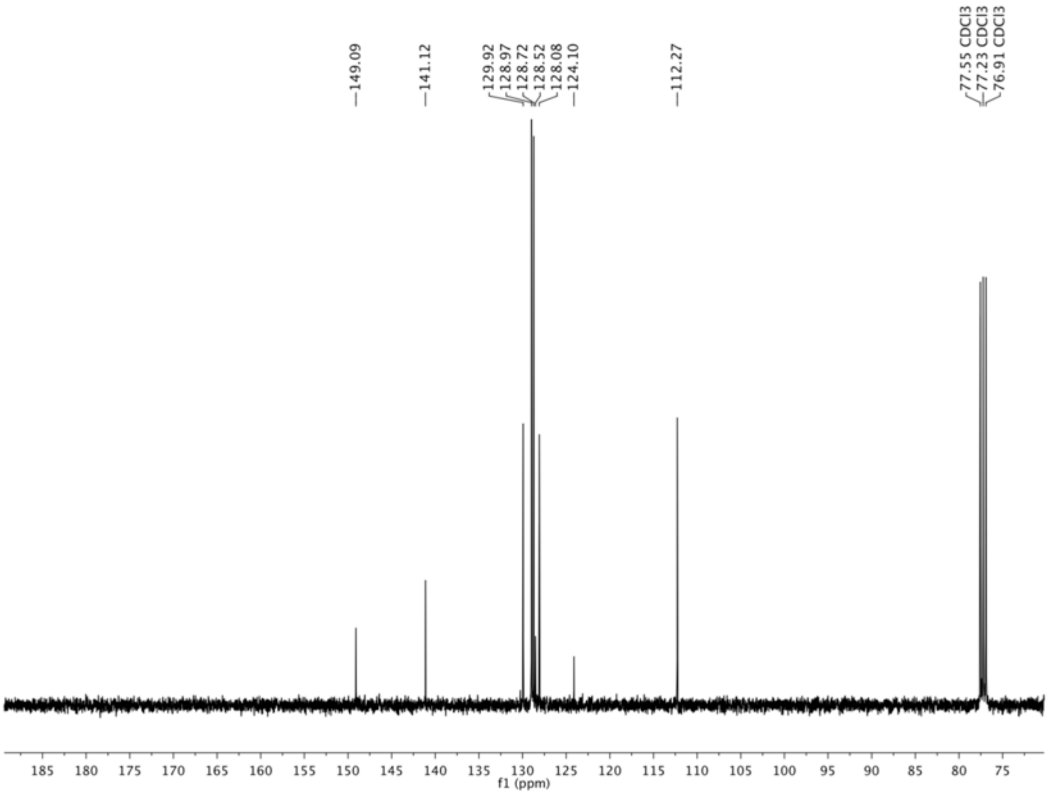

0.94
0.93
0.95
0.95
3.00
2.93
6.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.02
139.05
129.27
125.39
117.63
108.97
106.81
77.48 CDCl3
77.23 CDCl3
76.98 CDCl3
55.72
36.76
30.48
29.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CN
Ph
Ph
NHMe

7p


6.00
4.16
1.95
1.88
0.87
2.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.09
141.12
129.92
128.97
128.72
128.52
128.08
124.10
112.27
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
185
180
175
170
165
160
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150
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135
130
125
120
115
110
105
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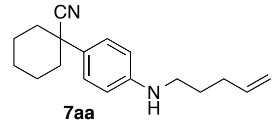
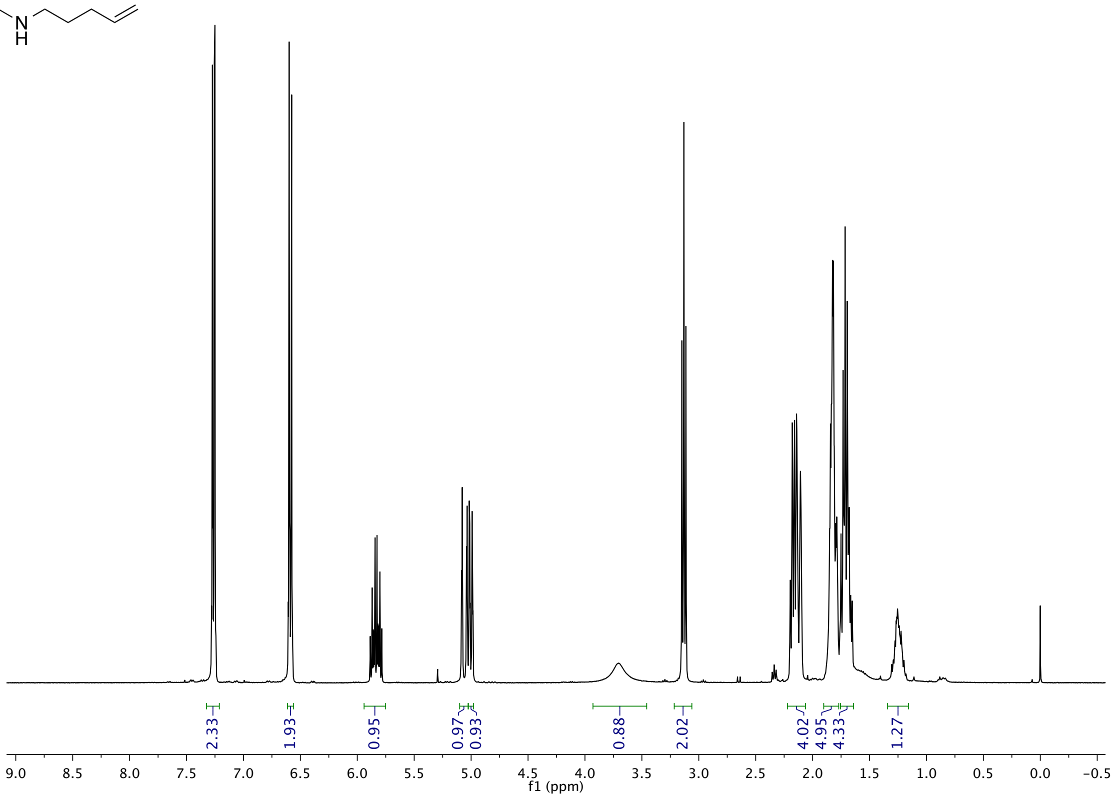
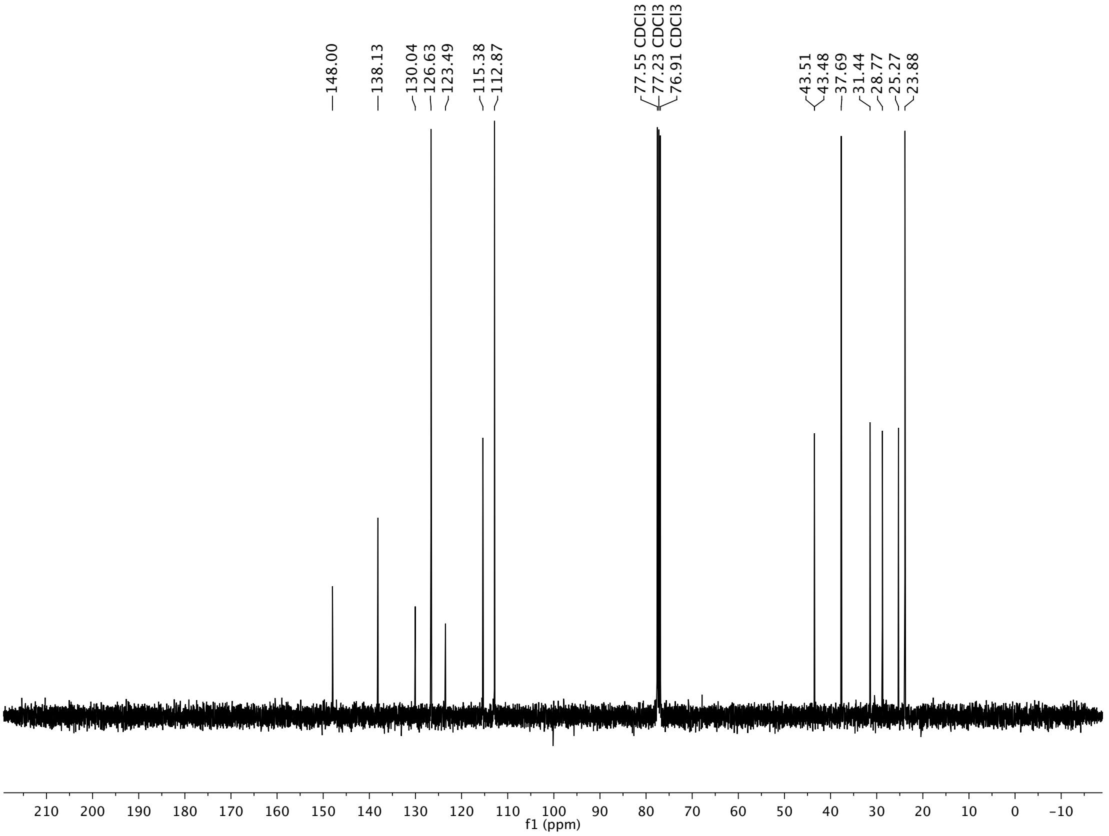
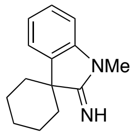
95
90
85
80
75
f1 (ppm)


CN
N
H

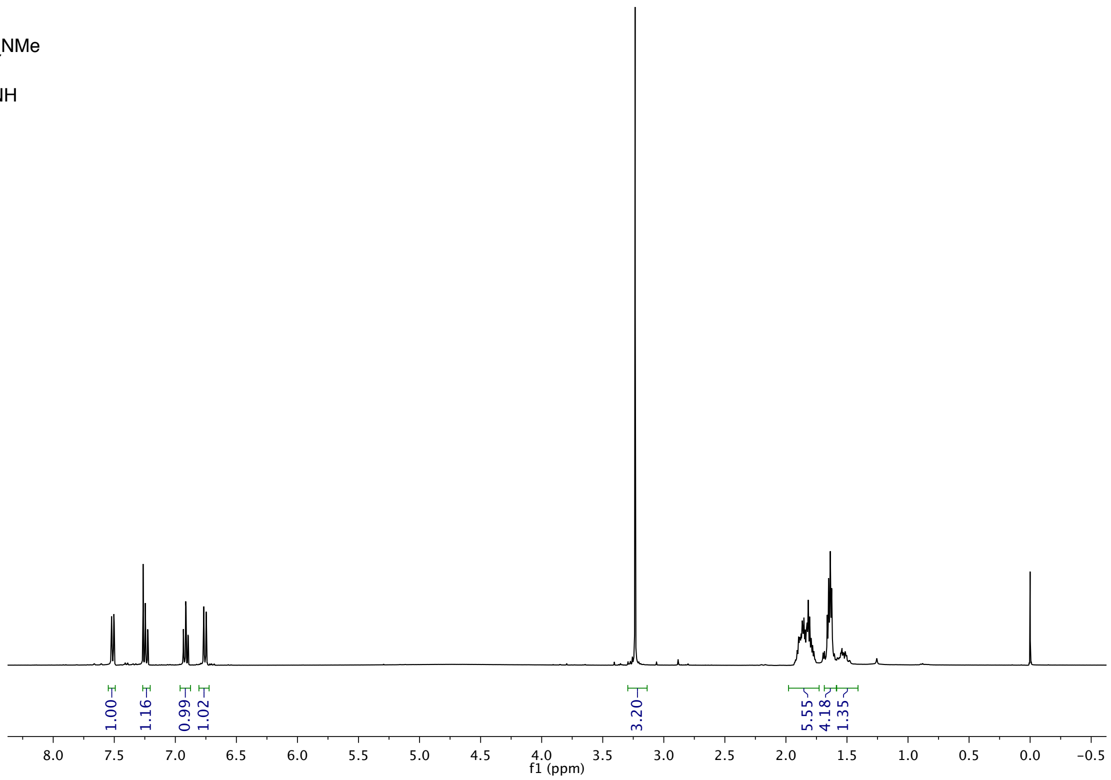
7aa

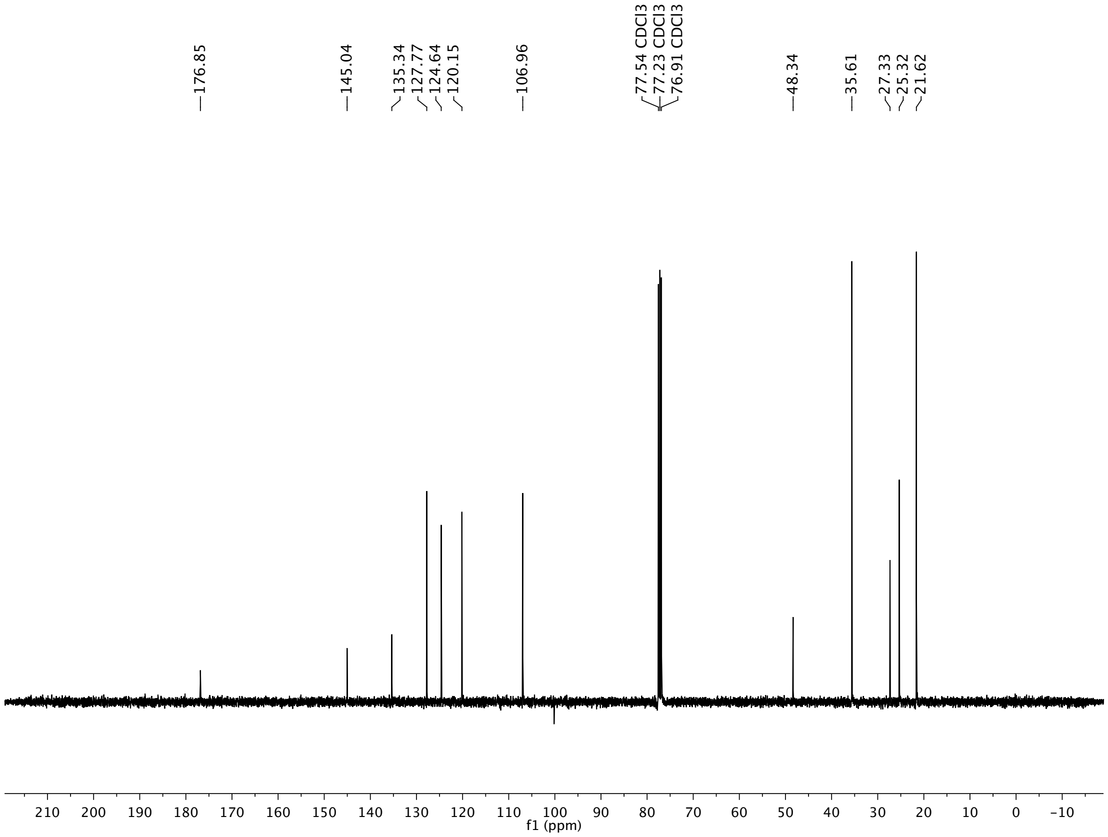

2.33
1.93
0.95
0.97
0.93
0.88
2.02
4.02
4.95
4.33
1.27
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

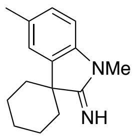

148.00
138.13
130.04
126.63
123.49
115.38
112.87
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
43.51
43.48
37.69
31.44
28.77
25.27
23.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


NMe
NH

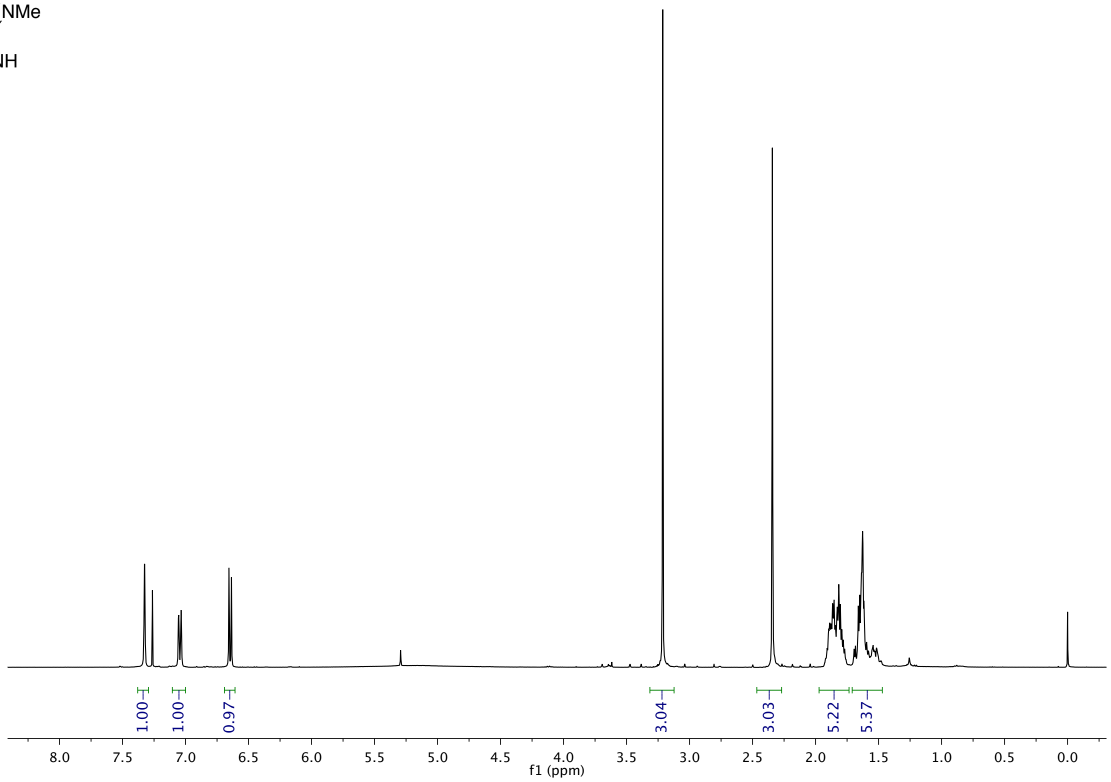
8a

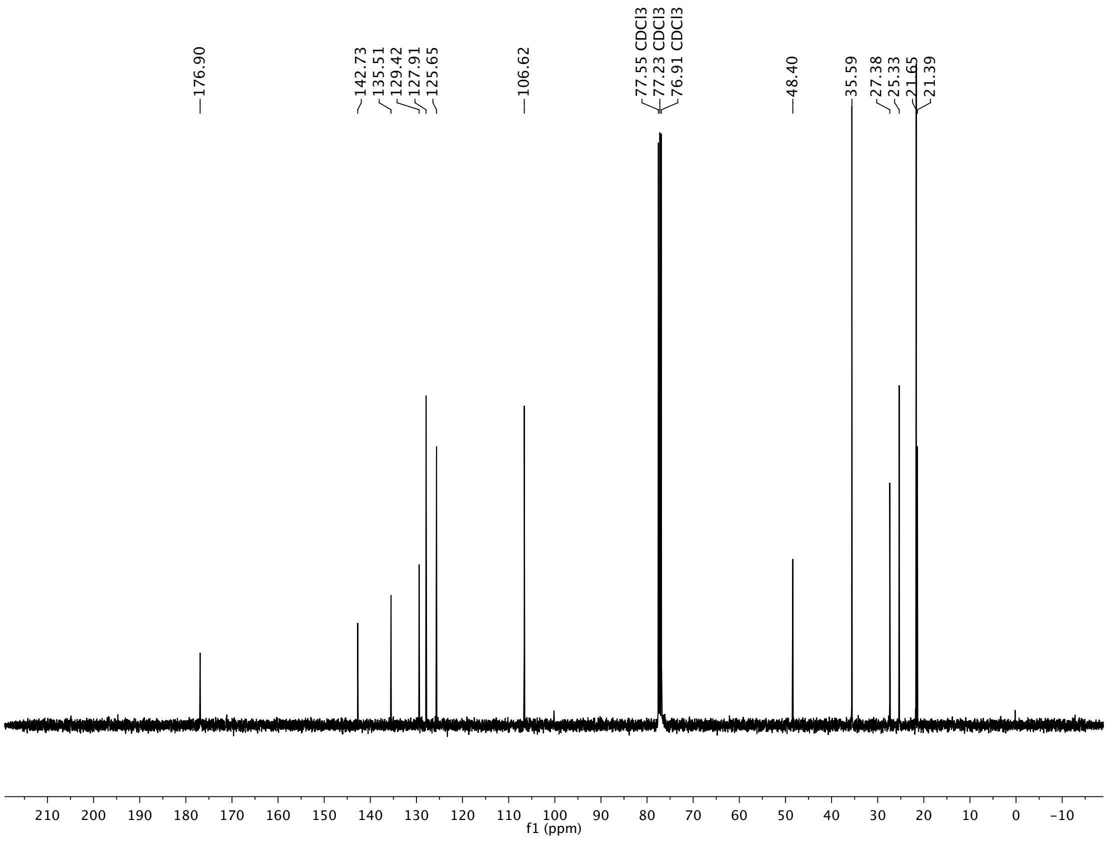

1.00
1.16
0.99
1.02
3.20
5.55
4.18
1.35
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

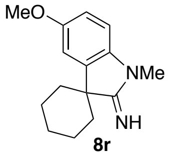

176.85
145.04
135.34
127.77
124.64
120.15
106.96
77.54 CDCl3
77.23 CDCl3
76.91 CDCl3
48.34
35.61
27.33
25.32
21.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


NMe
NH

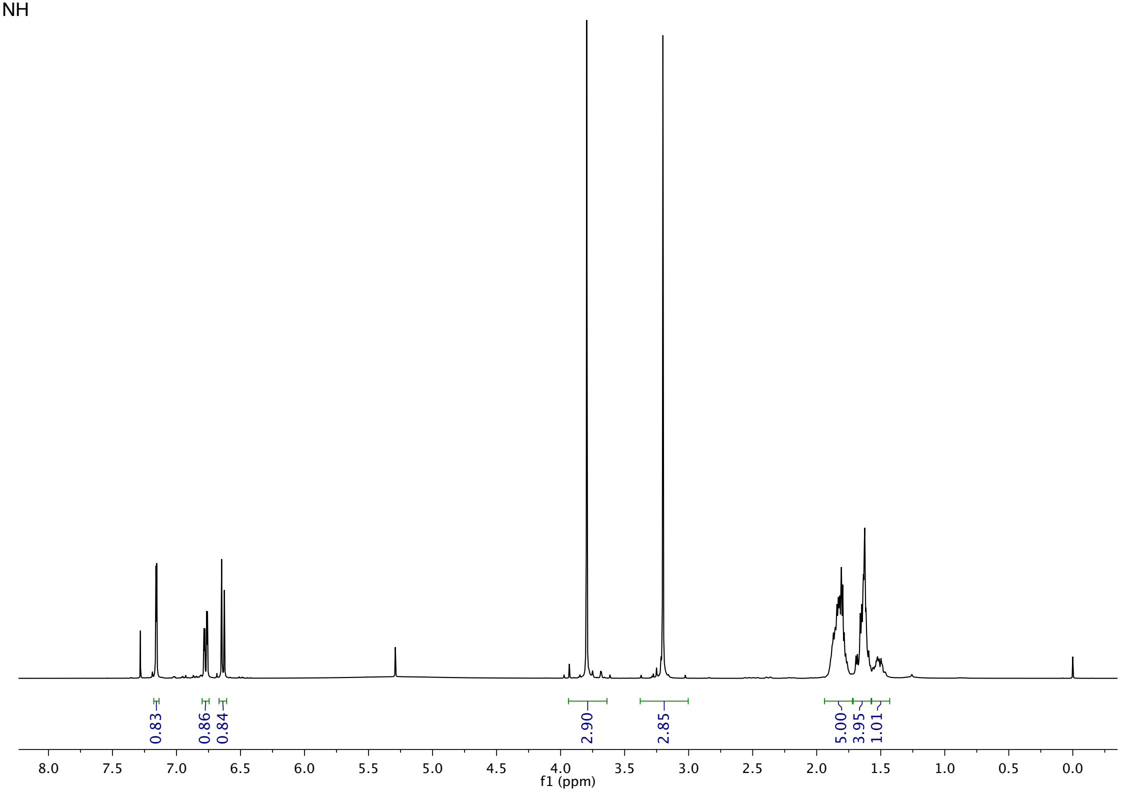
8q

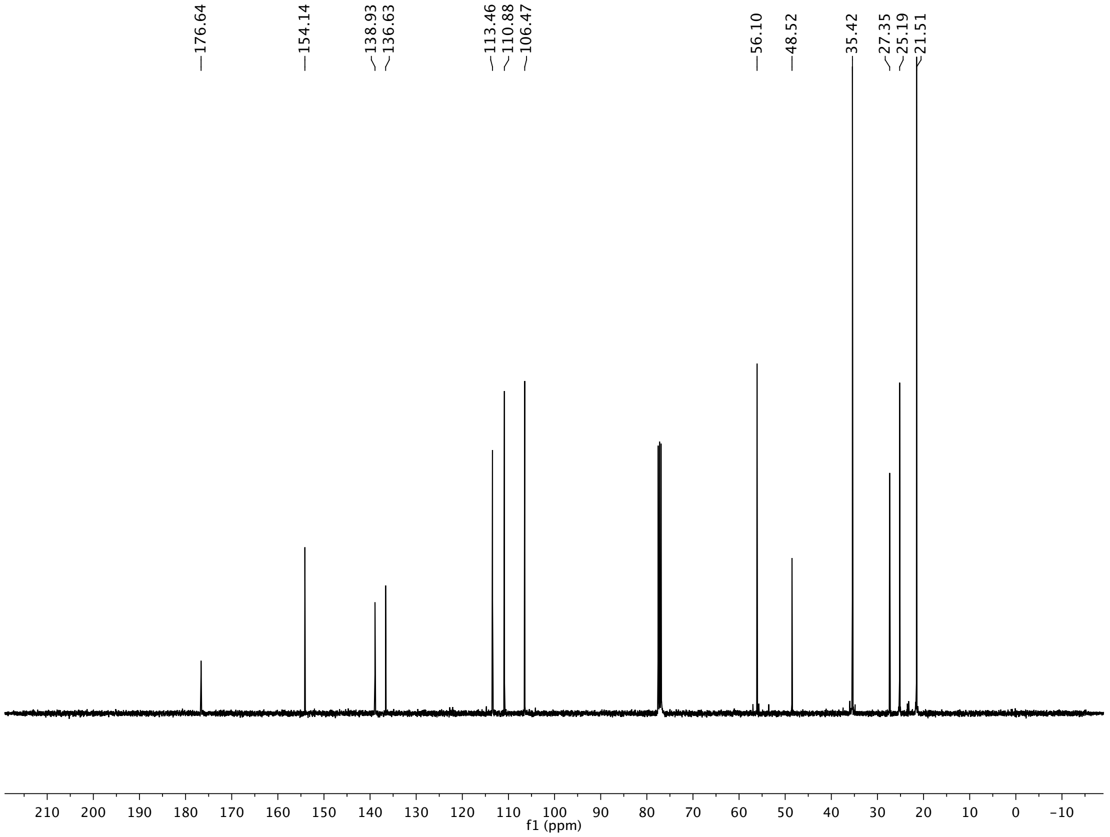

1.00
1.00
0.97
3.04
3.03
5.22
5.37
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

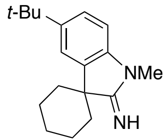

176.90
142.73
135.51
129.42
127.91
125.65
106.62
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
48.40
35.59
27.38
25.33
21.65
21.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
NMe
NH

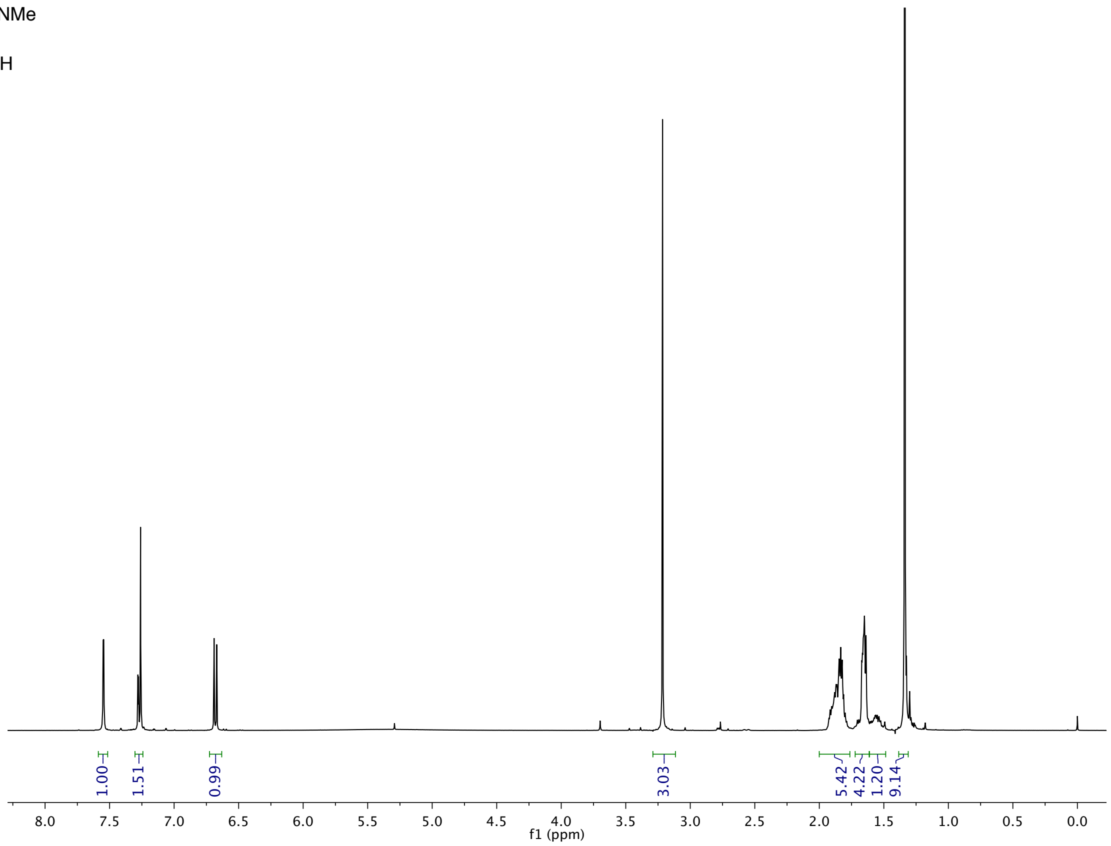
8r

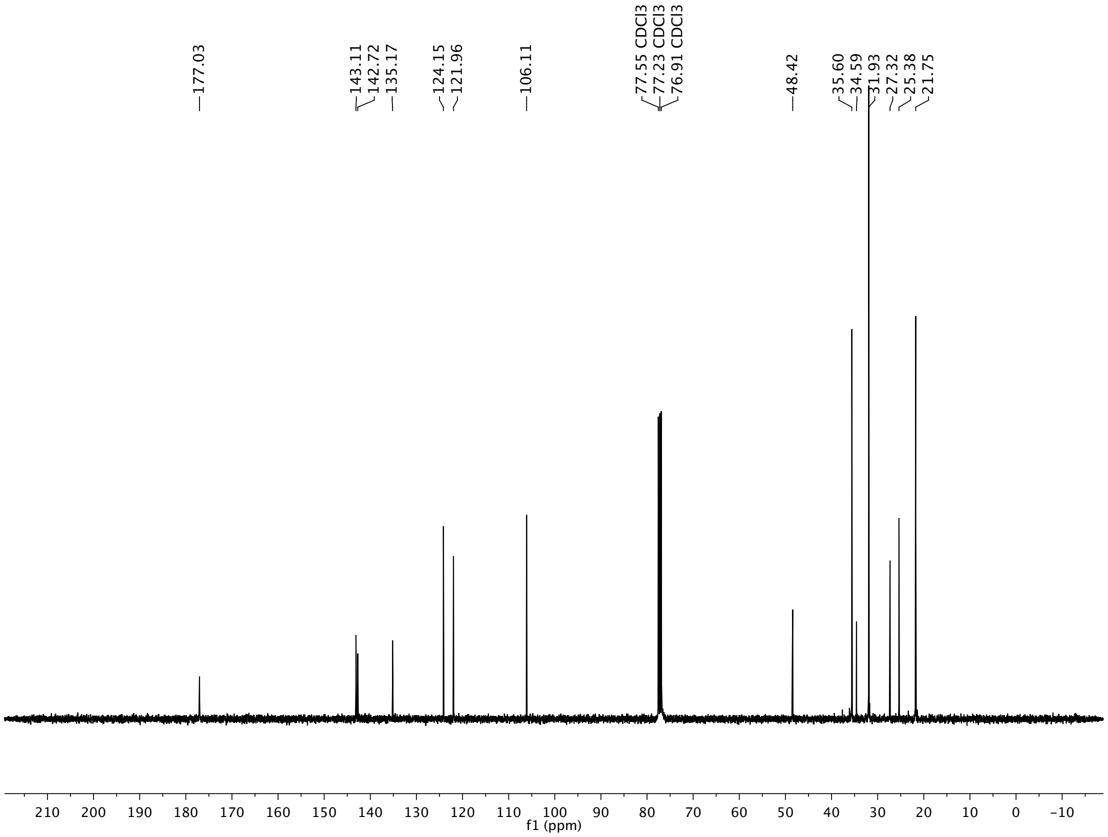

0.83
0.86
0.84
2.90
2.85
5.00
3.95
1.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

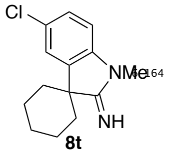

176.64
154.14
138.93
136.63
113.46
110.88
106.47
56.10
48.52
35.42
27.35
25.19
21.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


t-Bu
NMe
NH

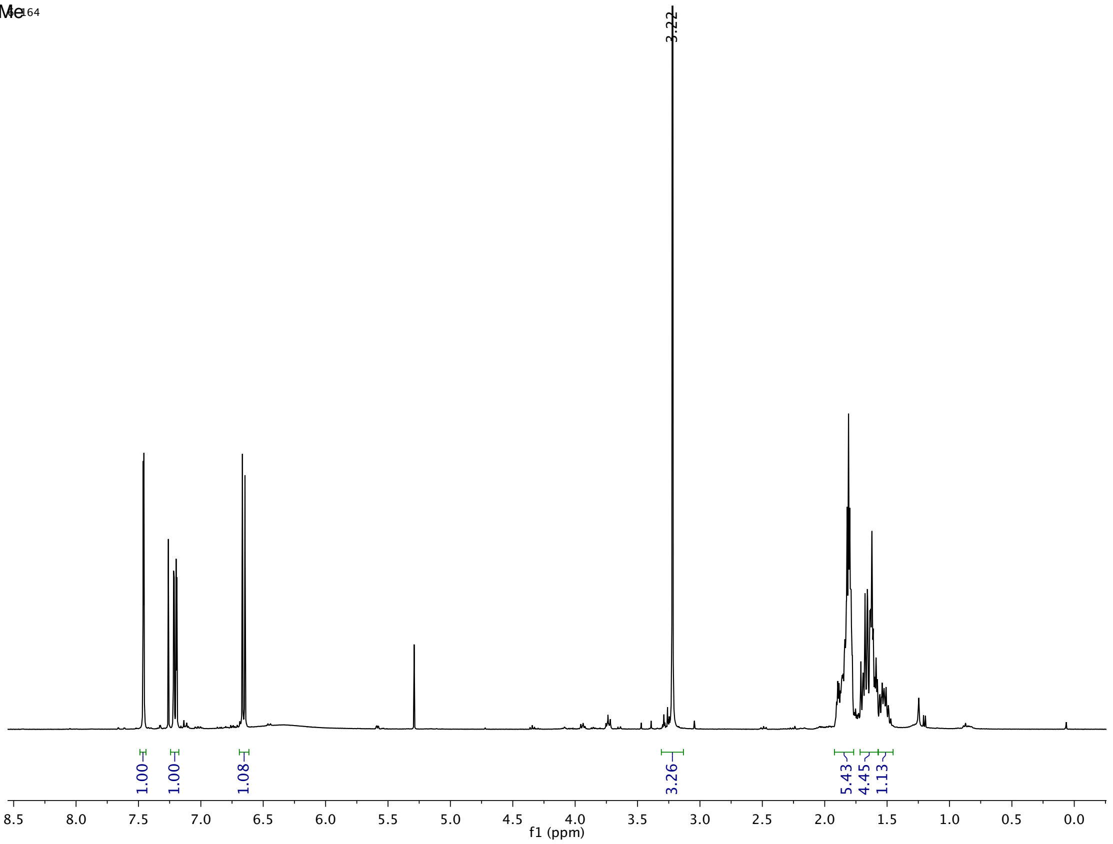
8s

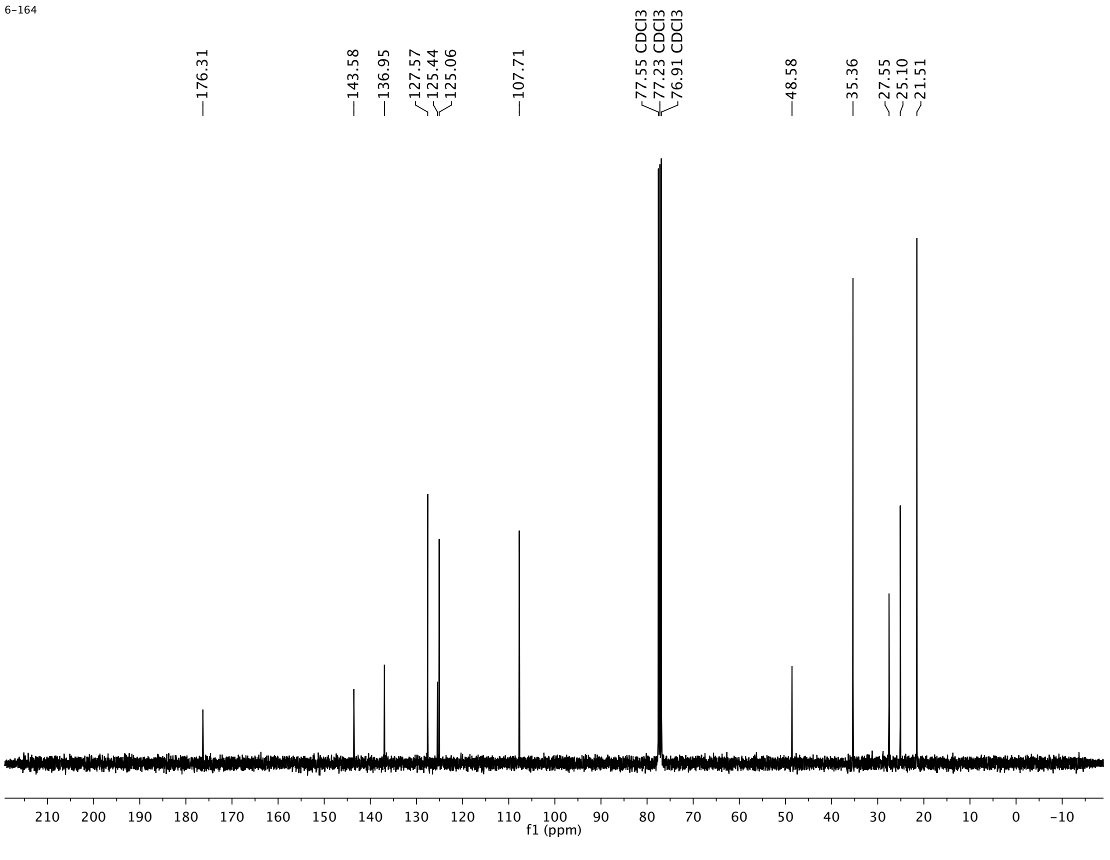

1.00
1.51
0.99
3.03
5.42
4.22
1.20
9.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

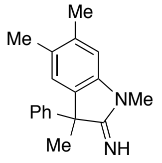

177.03
143.11
142.72
135.17
124.15
121.96
106.11
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
48.42
35.60
34.59
31.93
27.32
25.38
21.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
NMe
NH

8t

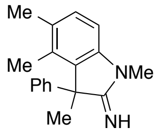

6-164
3.22
1.00
1.00
1.08
3.26
5.43
4.45
1.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


6-164
176.31
143.58
136.95
127.57
125.44
125.06
107.71
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
48.58
35.36
27.55
25.10
21.51
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

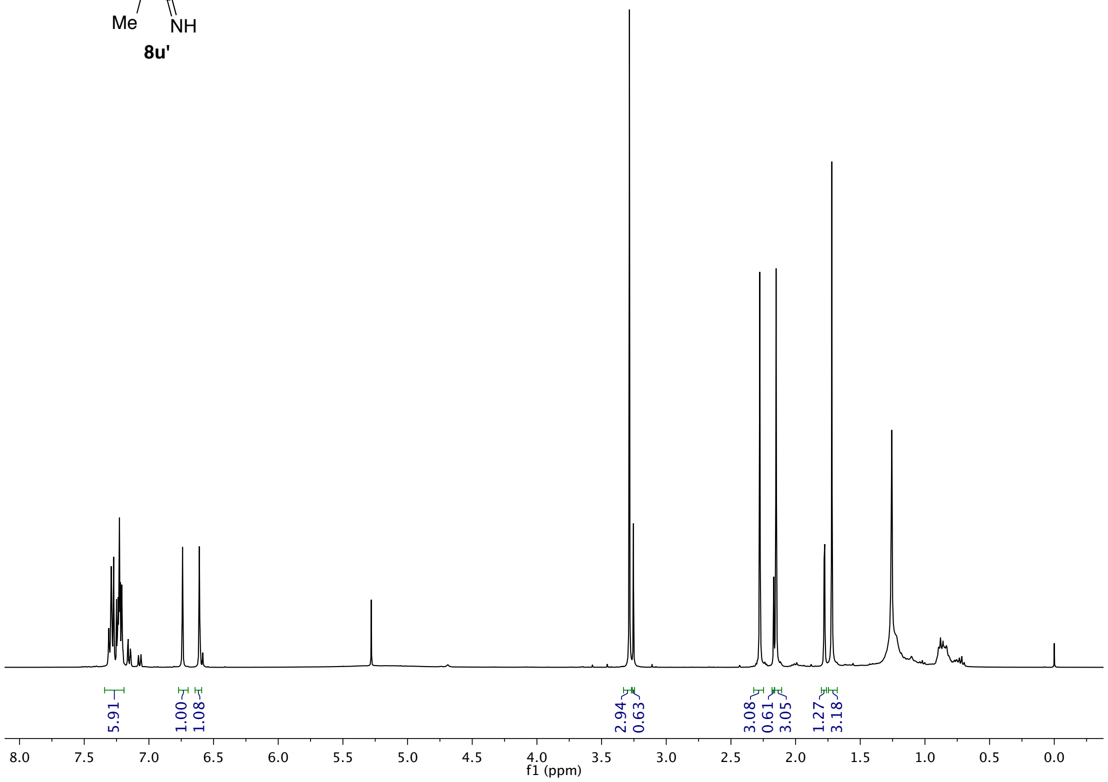

Me
Me
NMe
Ph
Me
NH

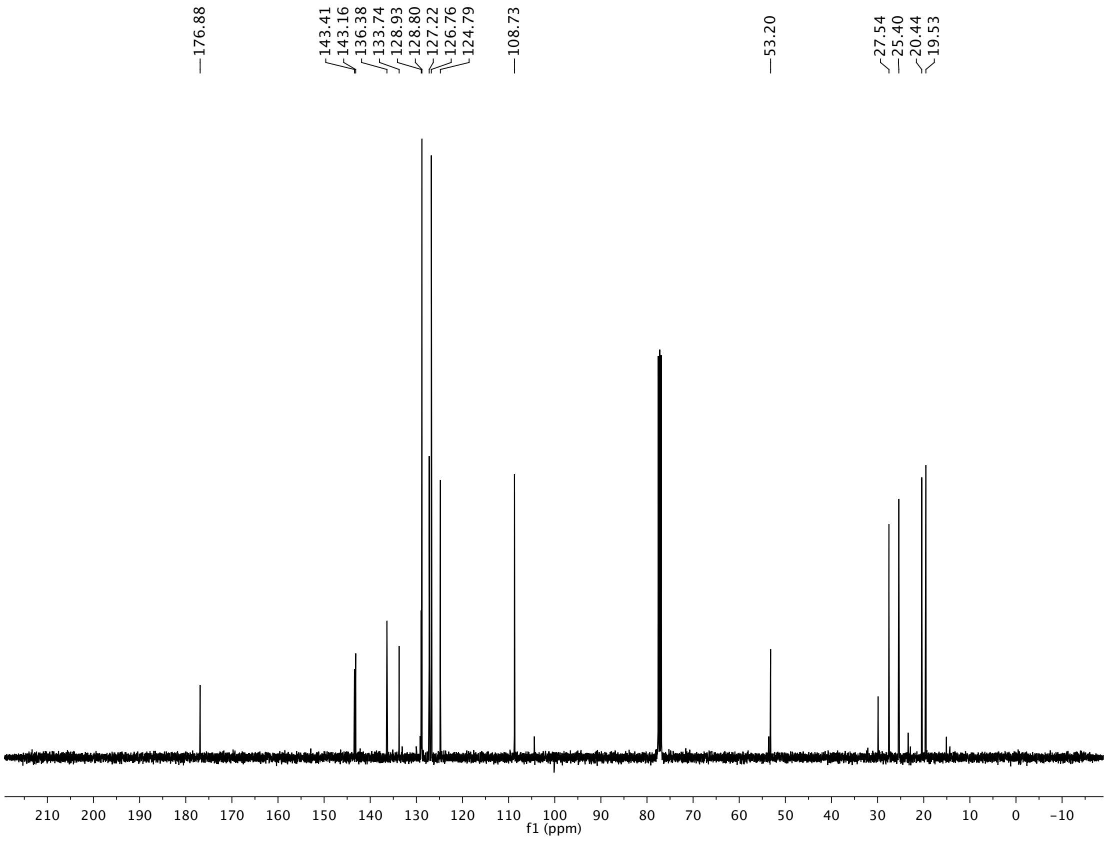
8u

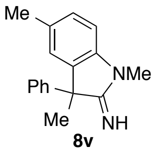
+


Me
Me
NMe
Ph
Me
NH

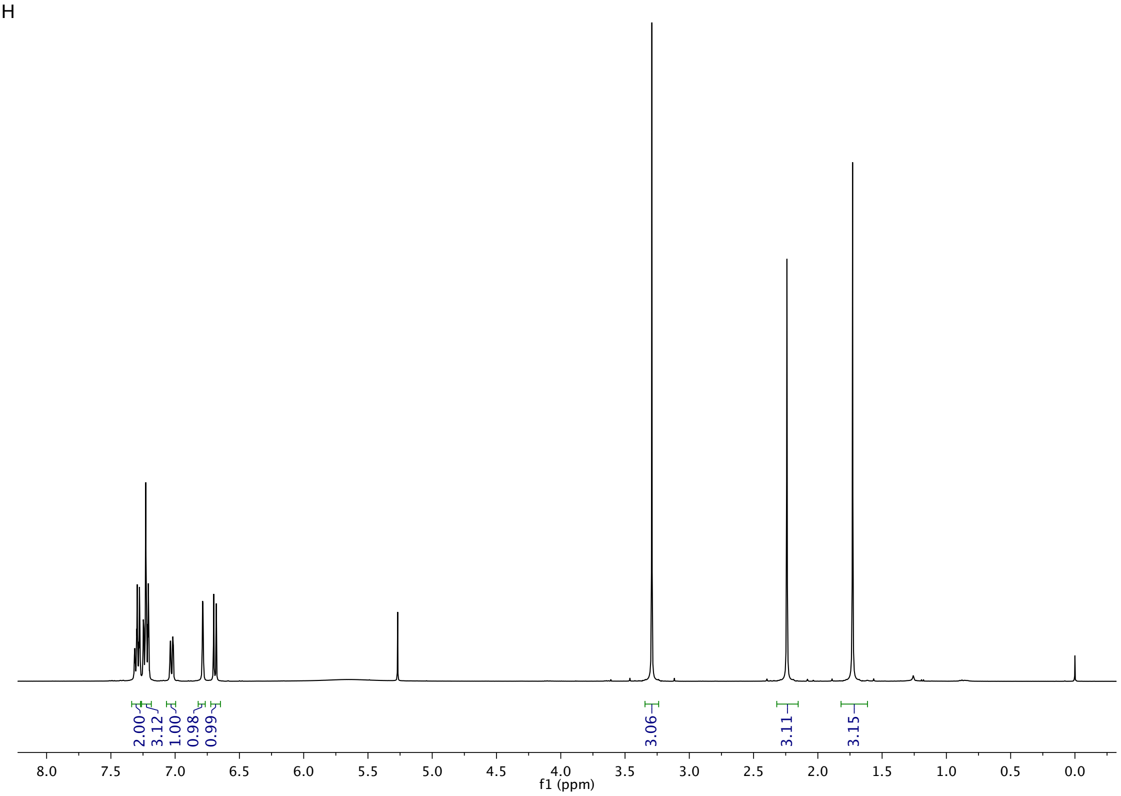
8u'

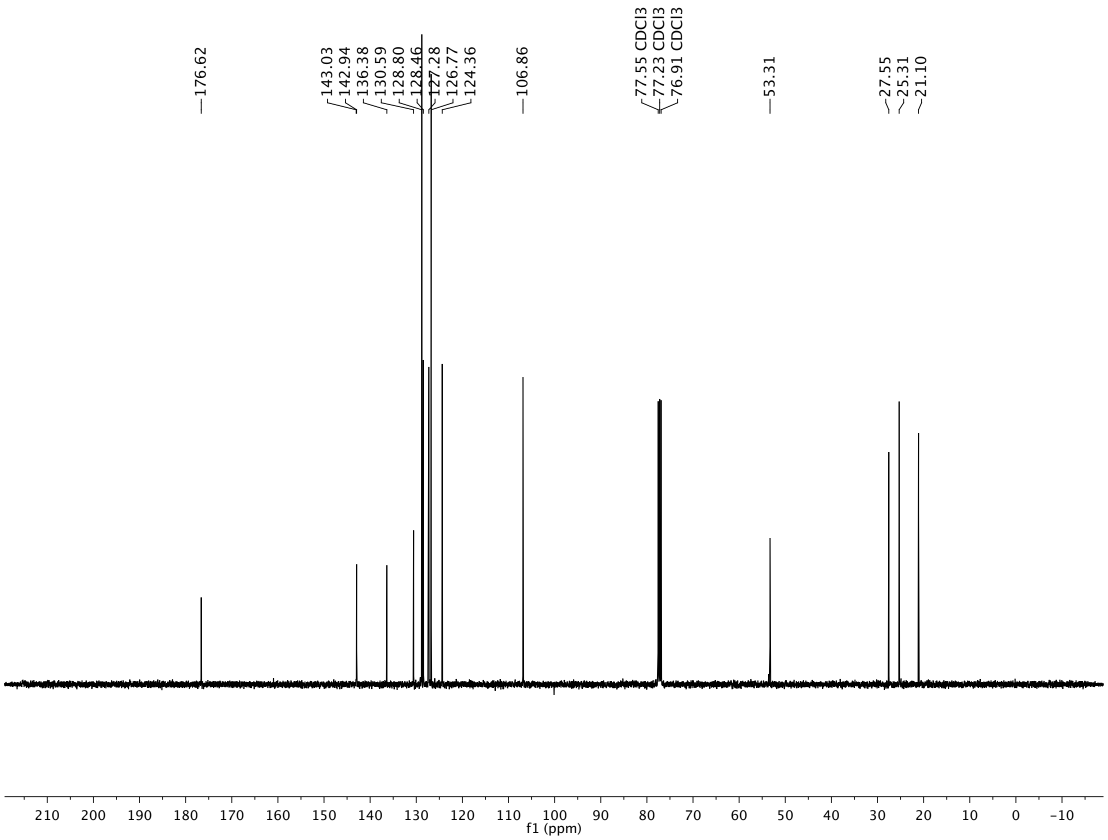

5.91
1.00
1.08
2.94
0.63
3.08
0.61
3.05
1.27
3.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

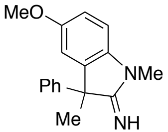

176.88
143.41
143.16
136.38
133.74
128.93
128.80
127.22
126.76
124.79
108.73
53.20
27.54
25.40
20.44
19.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
NMe
Ph
Me
NH

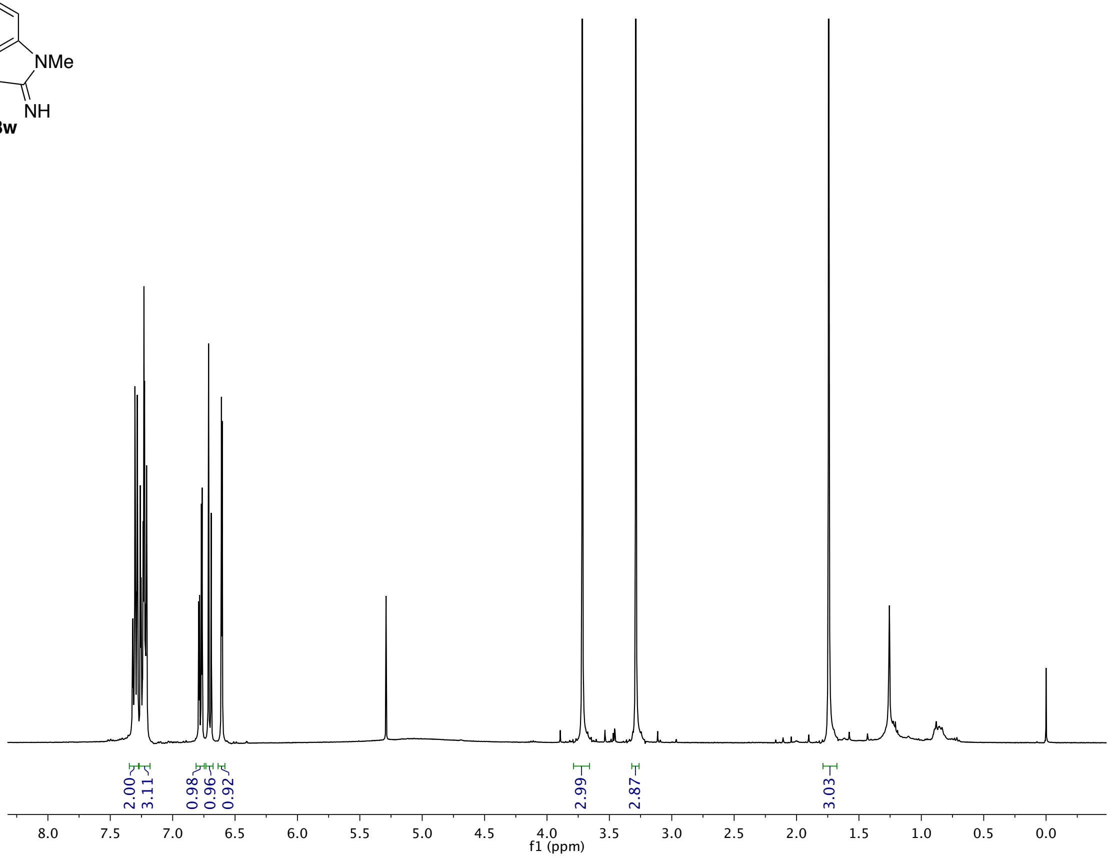
8v

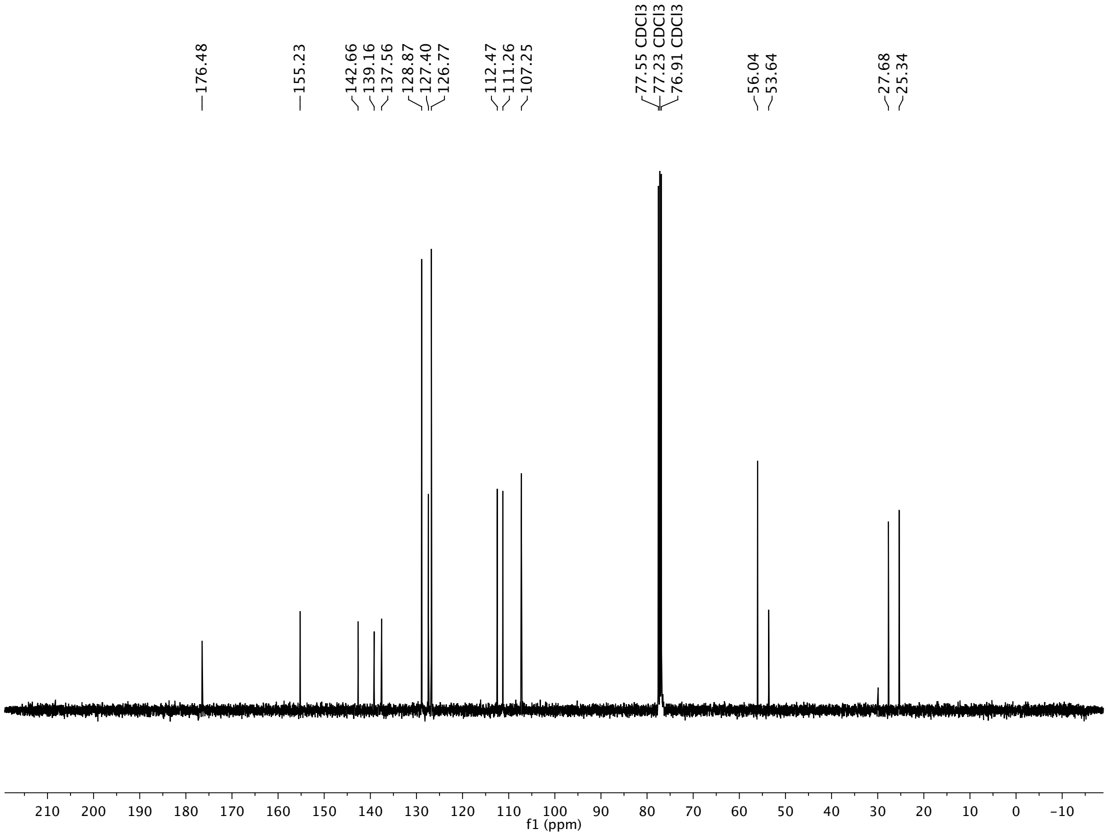

2.00
3.12
1.00
0.98
0.99
3.06
3.11
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

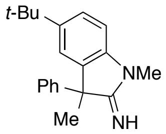

176.62
143.03
142.94
136.38
130.59
128.80
128.46
127.28
126.77
124.36
106.86
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
53.31
27.55
25.31
21.10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
NMe
Ph
Me
NH

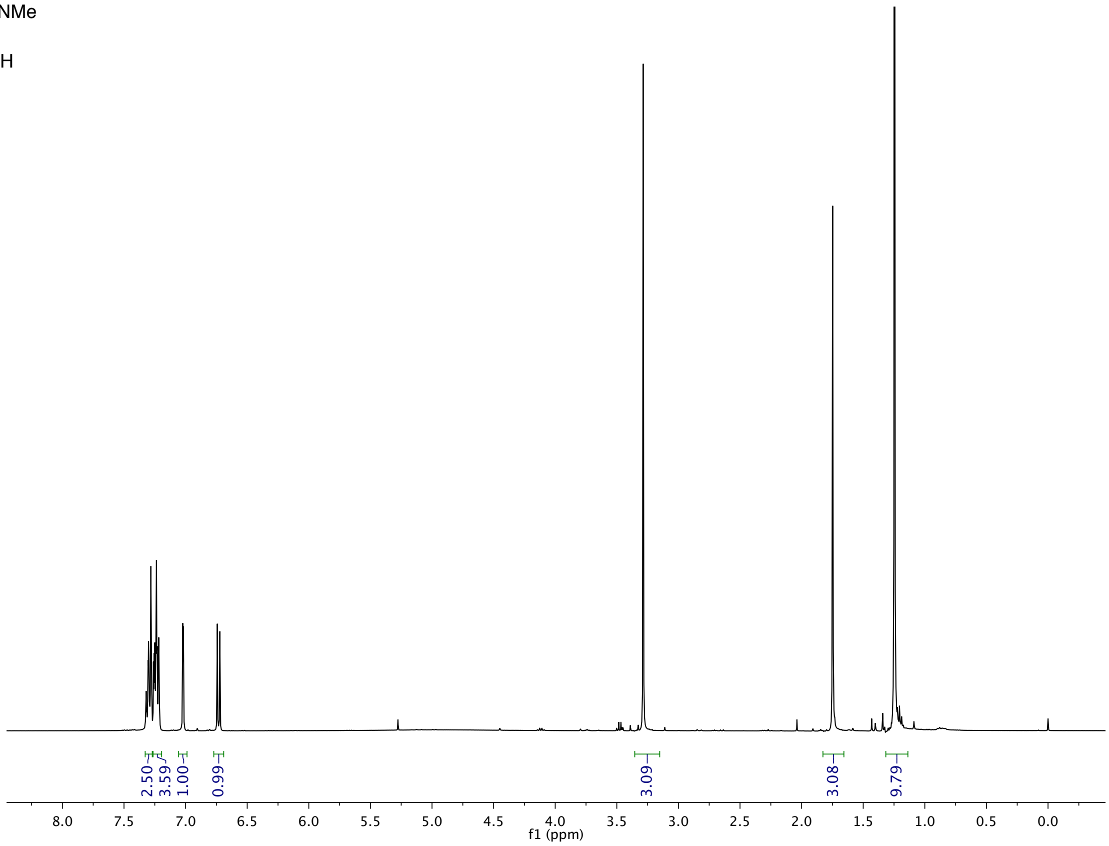
8w

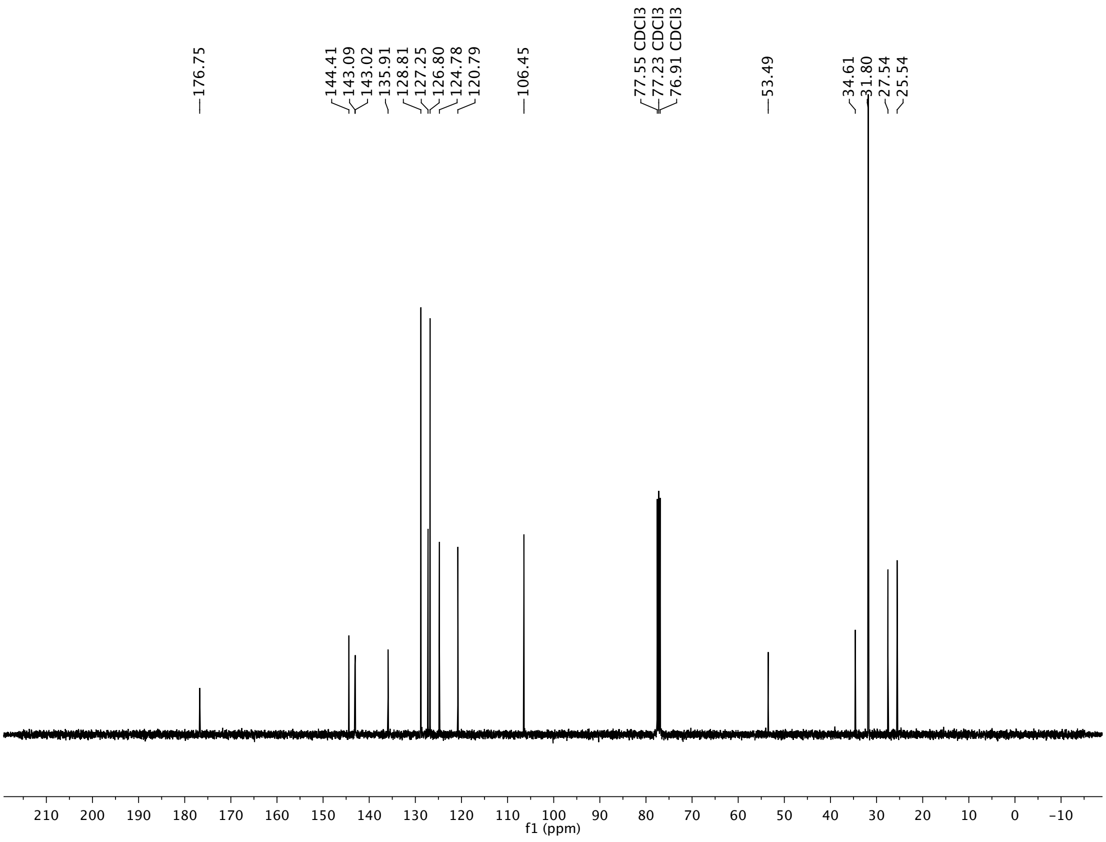

2.00
3.11
0.98
0.96
0.92
2.99
2.87
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

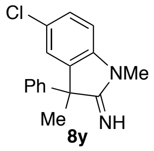

176.48
155.23
142.66
139.16
137.56
128.87
127.40
126.77
112.47
111.26
107.25
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
56.04
53.64
27.68
25.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


t-Bu
NMe
Ph
Me
NH

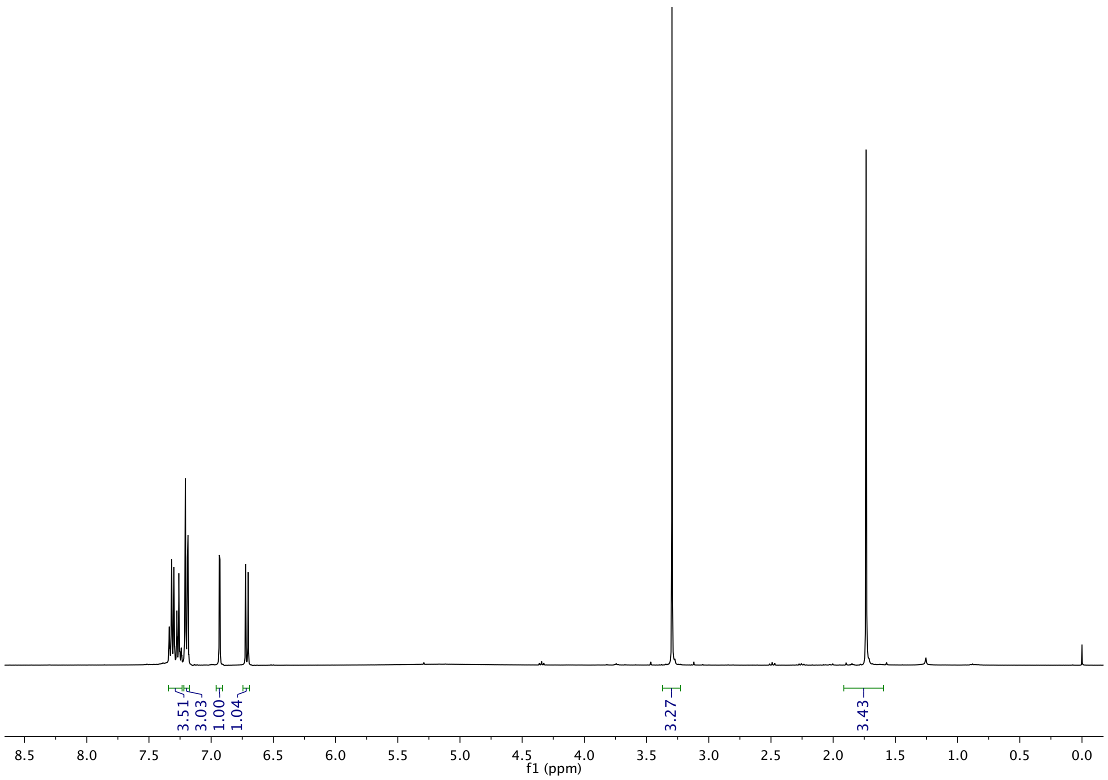
8x

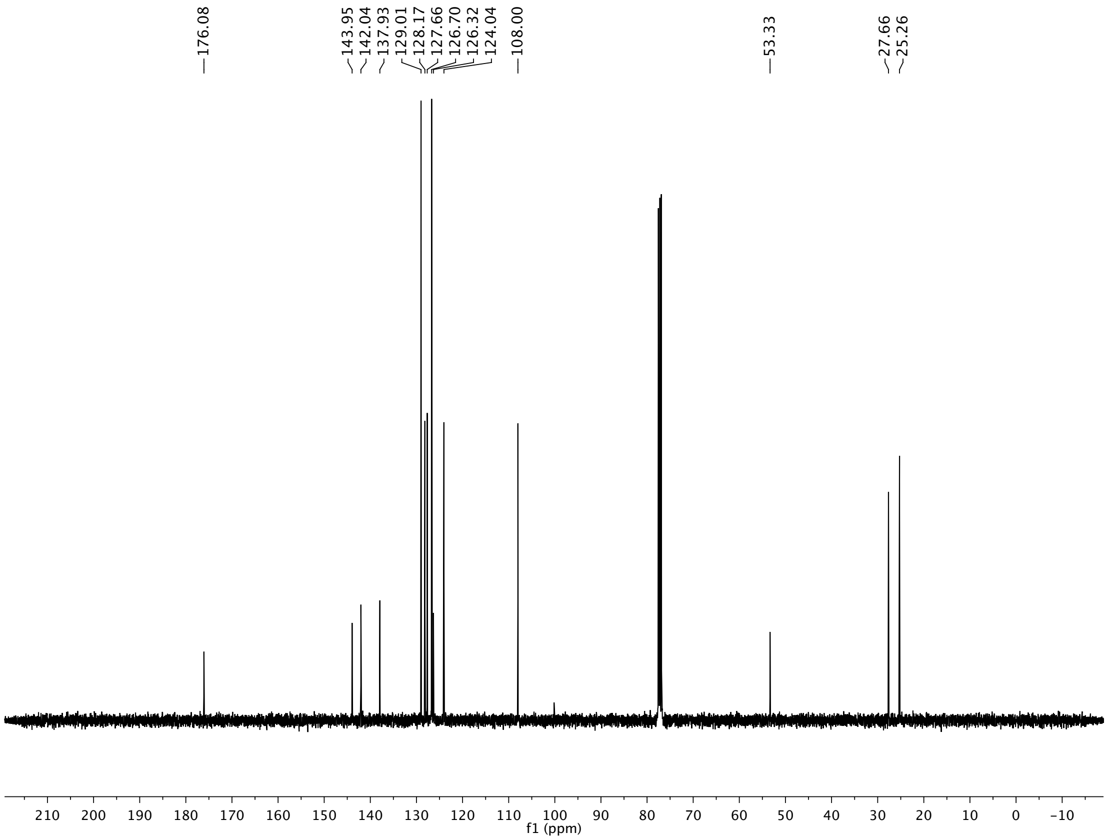

2.50
3.59
1.00
0.99
3.09
3.08
9.79
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

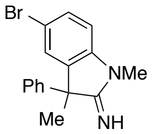

176.75
144.41
143.09
143.02
135.91
128.81
127.25
126.80
124.78
120.79
106.45
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
53.49
34.61
31.80
27.54
25.54
210
200
190
180
170
160
150
140
130
120
110
100
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
-10


Cl
NMe
Ph
Me
NH

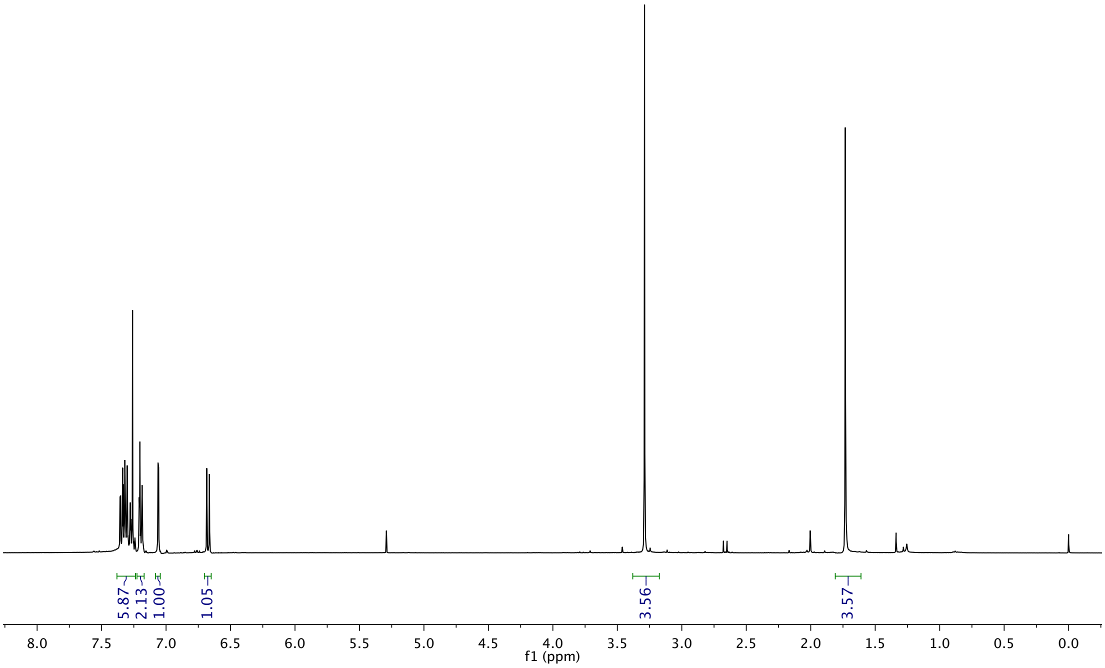
8y

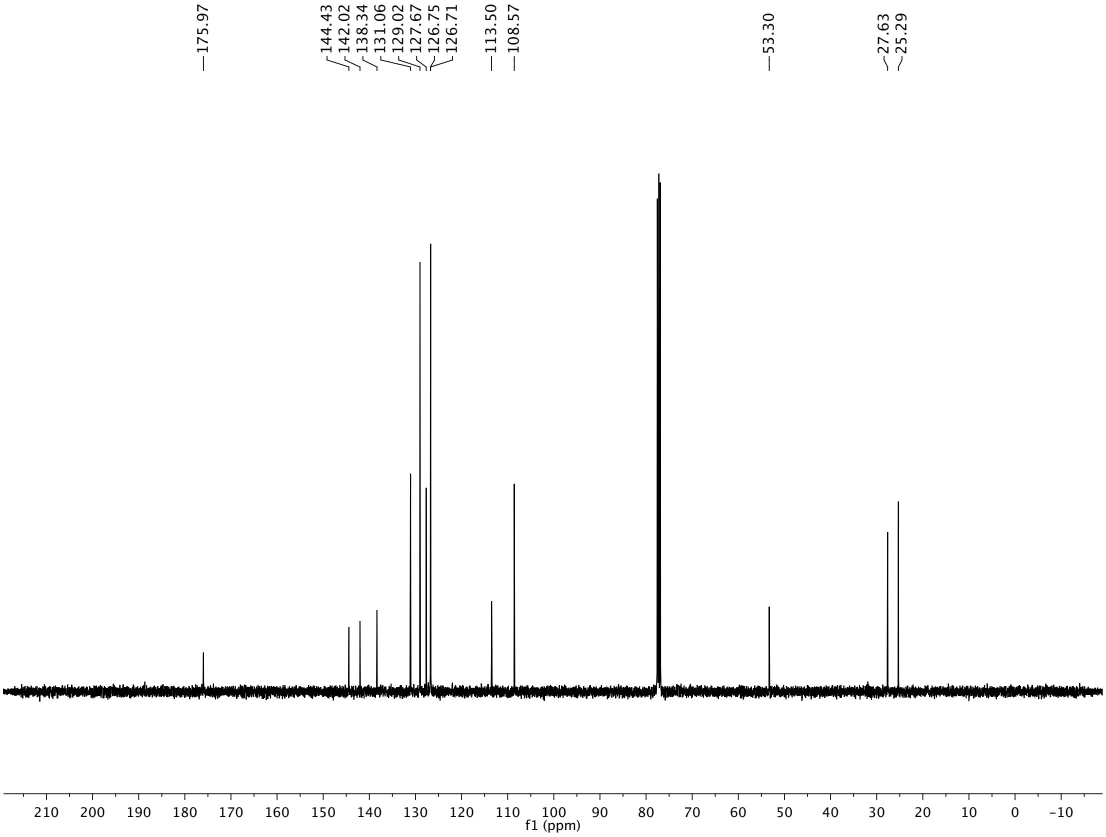

3.51
3.03
1.00
1.04
3.27
3.43
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

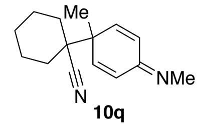

176.08
143.95
142.04
137.93
129.01
128.17
127.66
126.70
126.32
124.04
108.00
53.33
27.66
25.26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Br
NMe
Ph
Me
NH

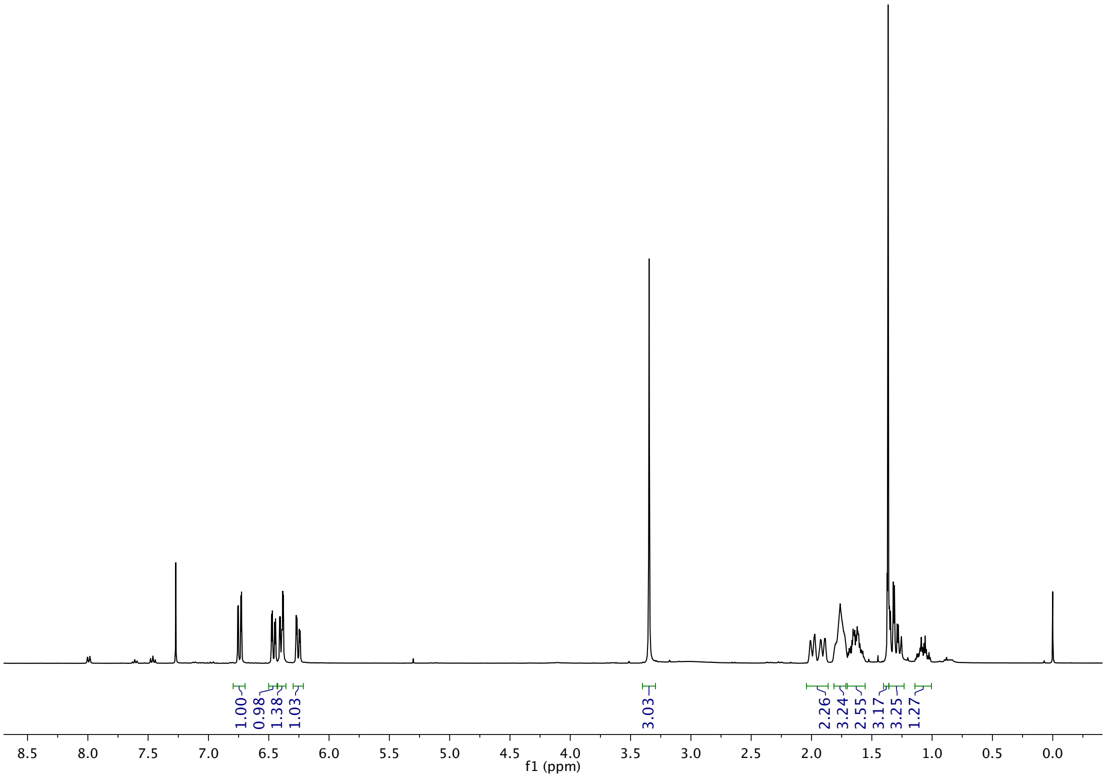
8z

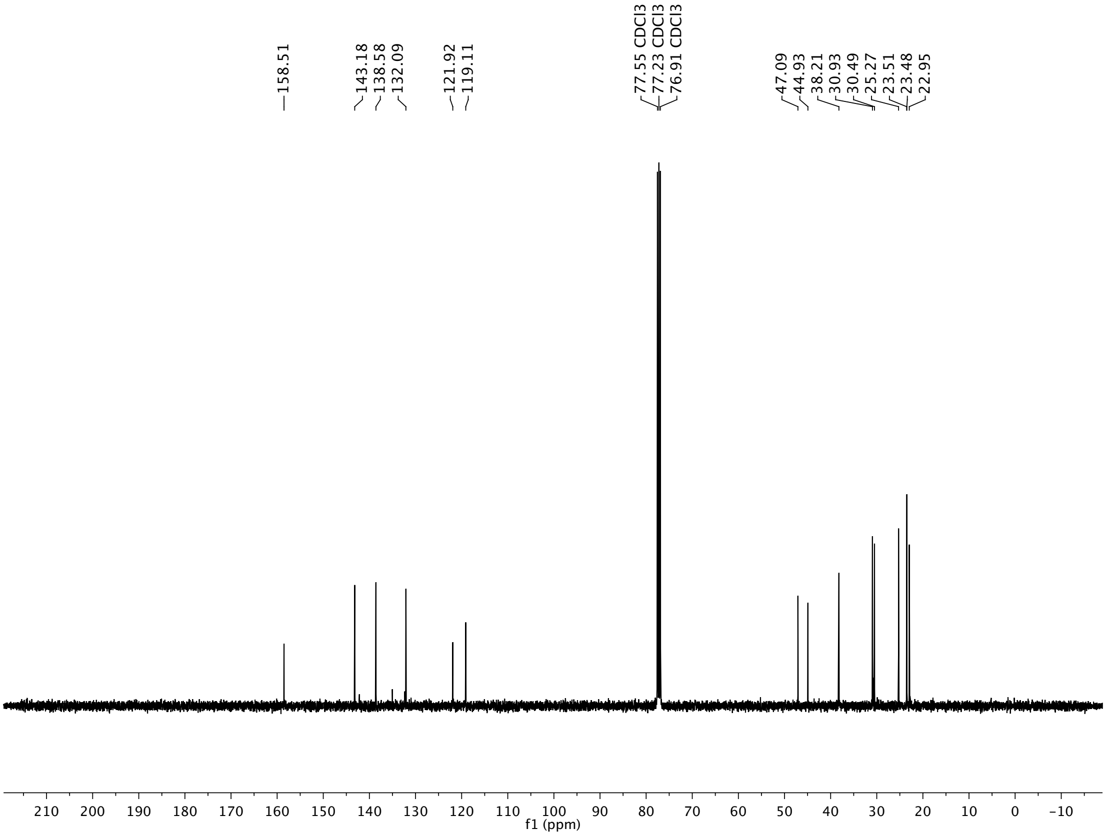

5.87
2.13
1.00
1.05
3.56
3.57
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

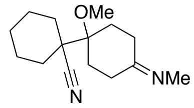

175.97
144.43
142.02
138.34
131.06
129.02
127.67
126.75
126.71
113.50
108.57
53.30
27.63
25.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
NMe
N

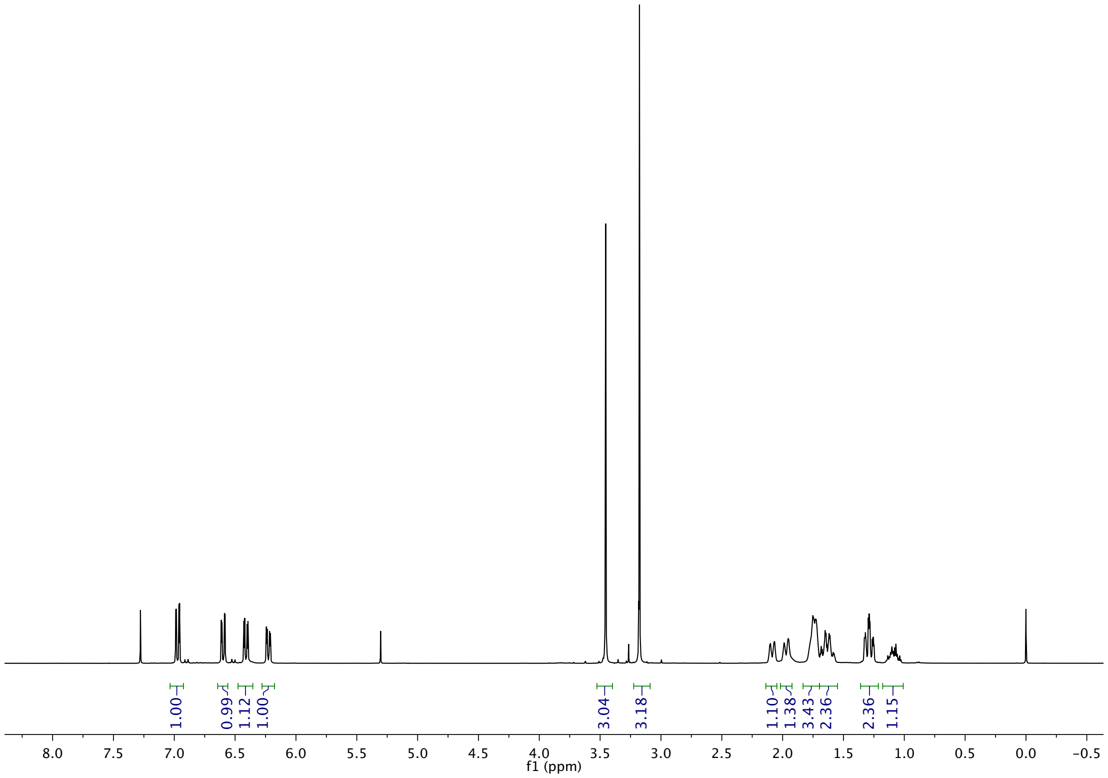
10q

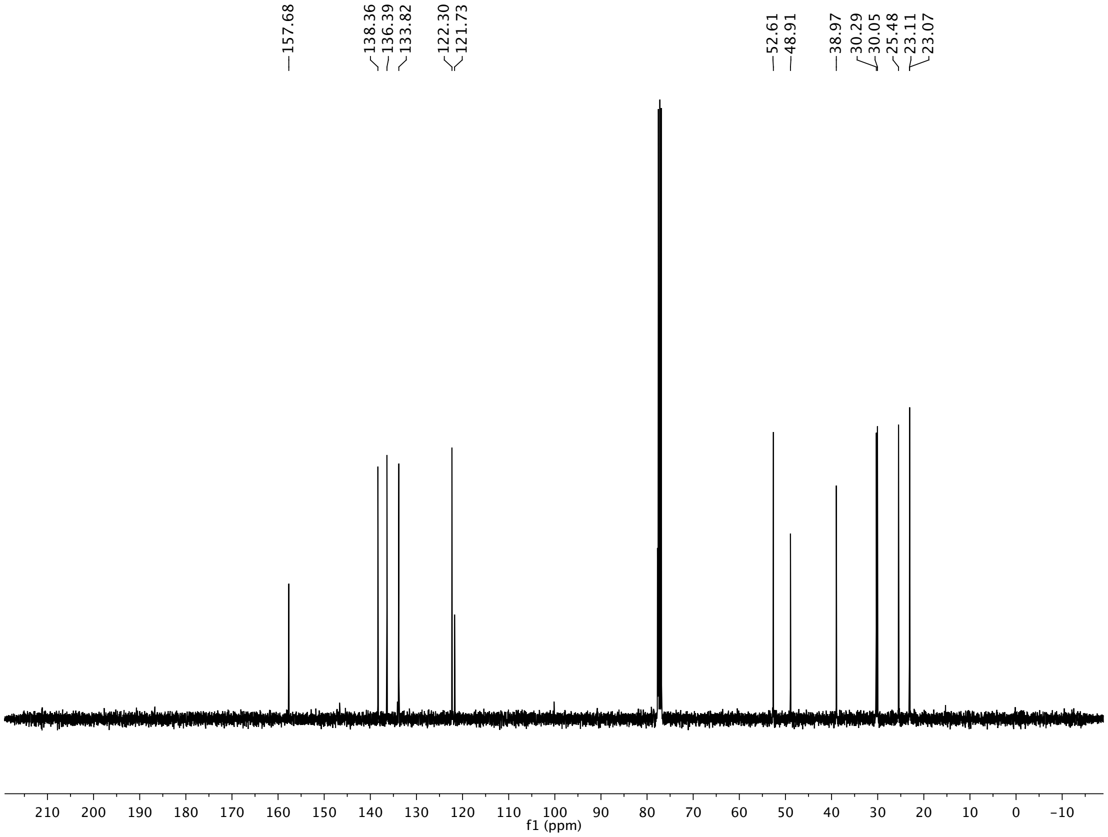

1.00
0.98
1.38
1.03
3.03
2.26
3.24
2.55
3.17
3.25
1.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.51
143.18
138.58
132.09
121.92
119.11
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
47.09
44.93
38.21
30.93
30.49
25.27
23.51
23.48
22.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OMe
NMe
N

10r


1.00
0.99
1.12
1.00
3.04
3.18
1.10
1.38
3.43
2.36
2.36
1.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


157.68
138.36
136.39
133.82
122.30
121.73
52.61
48.91
38.97
30.29
30.05
25.48
23.11
23.07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)