Electronic Supplementary Information

Pd-Catalyzed cascade cyclization of *o*-alkynylanilines via C-H/C-N bond cleavage leading to dibenzo[*a,c*]carbazoles

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1. General Information

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm or TMS, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra were recorded on Bruker Avance II-400 (100.5 MHz) spectrometer with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line for $CDCl_3$ at 77 ppm. High-resolution mass spectra were recorded on a GC-TOF mass spectrometry. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~100 μm, KANTO Chemical Co.) and Silica gel 60 (Merck). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

All chemicals were purchased and used as received. The starting materials were prepared following the reported methods.[1-8] The starting substrates and products were determined by ^{1}H and ^{13}C NMR spectroscopy, and high-resolution mass spectrometry. The structures of products were also determined by comparison with the reported authentic samples.[9]

References

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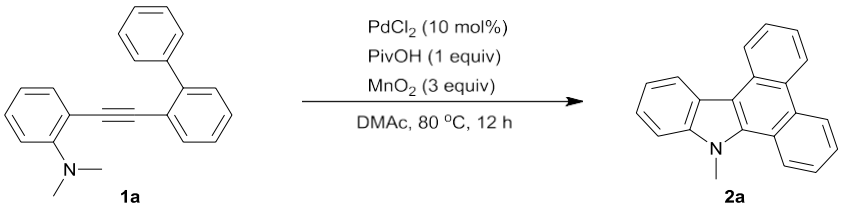
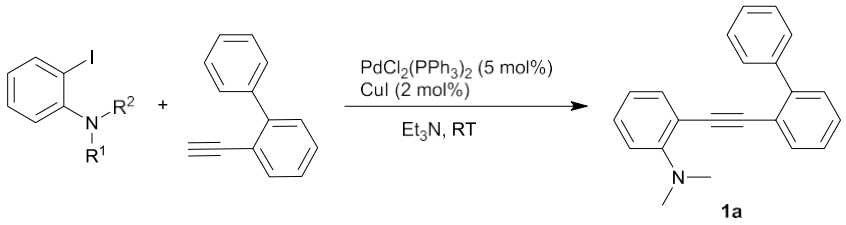
2. General Procedure for the Pd-catalyzed synthesis of dibenzo[*a,c*]carbazoles



To a mixture of 2-(biphenyl-2-ylethynyl)-*N*,*N*-dimethylaniline **1a** (89.2 mg, 0.3 mmol), $PaCl_2$ (5.3 mg, 10 mol%), MnO_2 (78 mg, 3 equiv), PivOH (30.6 mg, 1.0 equiv) was added anhydrous dimethylacetamide (DMAc, 1.5 mL, 0.2 M) under N_2 atmosphere. The reaction mixture was stirred vigorously at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was passed through a short silica pad using CH_2Cl_2 as an eluent. After concentration, the residue was purified by silica gel chromatography, affording the product **2a** as a brown solid (93%, 78.5 mg).

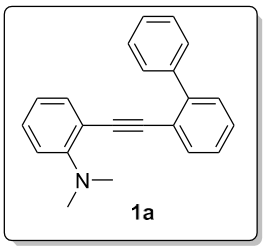
3. Representative synthetic method for biaryl-tethered *o*-alkynylanilines 1. The substrates **1** were prepared by Pd-catalyzed Sonogashira coupling of *o*-alkynylanilines with 2-halobiaryls. The *o*-alkynylanilines and 2-halobiaryls were prepared following the reported methods.[1-8]



Scheme 1. Synthesis of 2-(biphenyl-2-ylethynyl)-*N*,*N*-dimethylaniline **1a**.

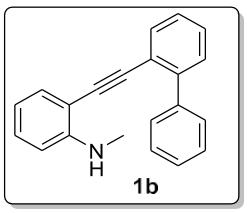
4. Characterization Data of 1-3

2-(Biphenyl-2-ylethynyl)-*N*,*N*-dimethylaniline (1a)



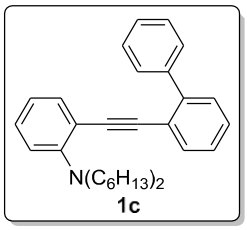
Brown oil (0.61 g, 93% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77-7.80 (m, 3H), 7.50-7.55 (m, 3H), 7.37-7.48 (m, 4H), 7.28 (t, J = 8.0 Hz, 1H), 6.90-6.95 (m, 2H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.3, 140.6, 134.2, 132.6, 129.4, 129.3, 129.0, 128.1, 127.8, 127.2, 126.9, 122.2, 120.1, 116.6, 115.0, 94.3, 91.6, 43.1; HRMS [m/z]: Calcd for $C_{22}H_{19}N$: 297.1517, Found: 297.1506.

2-(Biphenyl-2-ylethynyl)-*N*-methylaniline (1b)



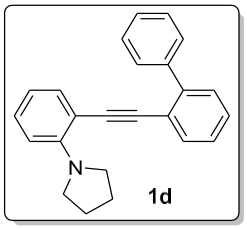
Brown oil (0.48 g, 50% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74-7.78 (m, 3H), 7.51-7.60 (m, 3H), 7.40-7.50 (m, 4H), 7.29 (d, J = 7.2 Hz, 1H), 6.72 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 4.22 (m, 1H), 2.74 (d, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 143.2, 141.1, 132.3, 131.8, 129.9, 129.3, 129.1, 128.1, 128.0, 127.4, 127.1, 122.0, 115.8, 108.6, 107.1, 94.7, 89.4, 29.9.; HRMS [m/z]: Calcd for $C_{21}H_{17}N$: 283.1361, Found: 283.1374.

2-(Biphenyl-2-ylethynyl)-*N*,*N*-dihexylaniline (1c)



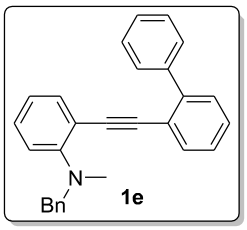
Brown oil (0.57 g, 62% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 8.0 Hz, 2H),7.63(d, J = 8.0 Hz, 1H), 7.41-7.46 (m, 3H), 7.37 (d, J = 8.0 Hz , 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.14-7.21 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.78 (t, J = 8.0 Hz, 1H), 3.20 (t, J = 8.0 Hz, 4H), 1.43-1.48 (m, 4H), 1.19-1.26 (m, 12H), 0.84 (t, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 143.3, 140.8, 134.4, 132.7, 129.5, 129.4, 128.6, 128.0, 127.9, 127.3, 126.9, 122.5, 119.9, 119.6, 116.5, 93.5, 92.2, 52.4, 31.7, 27.3, 26.9, 22.7, 14.0; HRMS [m/z]: Calcd for $C_{32}H_{39}N$: 437.3083, Found: 437.3094.

1-(2-(Biphenyl-2-ylethynyl)phenyl)pyrrolidine (1d)



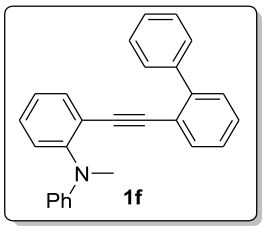
Yellow solid (0.54 g, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65-7.67 (m, 2H), 7.60-7.62 (m, 1H), 7.31-7.47 (m, 6H), 7.25-7.27 (m, 1H), 7.13-7.17 (m, 1H), 6.60-6.66 (m, 2H), 3.38 (t, J = 8.0 Hz, 4H), 1.80-1.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 143.1, 140.9, 135.3, 132.1, 129.5, 129.3, 129.2, 127.9, 127.7, 127.2, 127.0, 122.7, 116.5, 113.6, 108.4, 93.7, 92.0, 50.1, 25.7 ; HRMS [m/z]: Calcd for $C_{24}H_{21}N$: 323.1674, Found: 323.1664.

2-(Biphenyl-2-ylethynyl)-*N*-benzyl-*N*-methylaniline (1e)



Brown oil (0.19 g, 12% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69-7.72 (m, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.30-7.45 (m, 9H), 7.23-7.27 (m, 3H), 6.88-6.93 (m, 2H), 4.53 (s, 2H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 143.5, 140.7, 138.9, 134.4, 132.5, 129.4, 129.3, 129.1, 128.2, 128.04, 127.97, 127.8, 127.3, 126.8, 126.8, 122.1, 120.3, 117.7, 115.1, 94.6, 91.5, 59.6, 39.1; HRMS [m/z]: Calcd for $C_{28}H_{23}N$: 373.1830, Found: 373.1836.

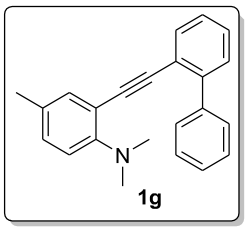
2-(Biphenyl-2-ylethynyl)-*N*-methyl-*N*-phenylaniline (1f)



Brown oil (0.95 g, 87% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54-7.56 (m, 2H), 7.31-7.35 (m, 3H), 7.25-7.30 (m, 5H), 7.22-7.23 (m, 1H), 7.17-7.21 (m, 3H), 7.09 (d, J = 7.5 Hz, 1H), 6.78 (t, J = 7.0 Hz, 1H), 6.69 (d, J = 8.5 Hz, 2H), 3.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1,

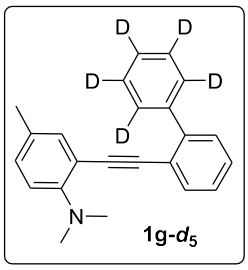
149.0, 143.4, 140.4, 133.9, 133.2, 129.3, 129.2, 128.7, 128.4, 127.8, 127.4, 127.3, 126.8, 124.9, 121.8, 121.6, 118.0, 115.0, 94.2, 90.0, 39.6; HRMS [m/z]: Calcd for $C_{27}H_{21}N$: 359.1674, Found: 359.1666.

2-(Biphenyl-2-ylethynyl)-*N*,*N*,4-trimethylaniline (1g)



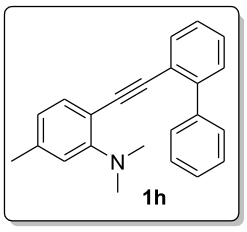
Brown oil (0.27 g, 11% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.70 (m, 3H), 7.32-7.47 (m, 6H), 7.09 (s, 1H), 7.03 (d, J = 8.0 Hz,1H), 6.79 (d, J = 8.0 Hz,1H), 2.78 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 143.5, 140.8, 134.5, 132.7, 129.8, 129.7, 129.44, 129.42, 128.1, 127.9, 127.2, 126.9, 122.3, 116.8, 115.4, 94.1, 91.6, 43.5, 20.2; HRMS [m/z]: Calcd for $C_{23}H_{21}N$: 311.1674, Found: 311.1680.

2-((Biphenyl-2-yl-2',3',4',5',6'-d_5)ethynyl)-*N*,*N*,4-trimethylaniline (1g-d_5)



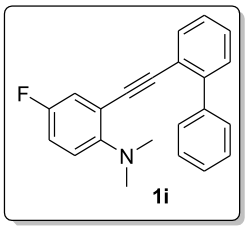
Brown oil (0.61 g, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 8.0 Hz, 1H), 7.39-7.44 (m, 2H), 7.32-7.37 (m, 1H), 7.08 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 2.78 (s, 6H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 143.4, 140.6, 134.5, 132.7, 129.8, 129.7, 129.4, 128.1, 126.9, 122.3, 116.8, 115.4, 94.1, 91.6, 43.5, 20.2; HRMS [m/z]: Calcd for $C_{23}H_{16}D_5N$: 316.1988, Found: 316.1978.

2-(Biphenyl-2-ylethynyl)-*N*,*N*,5-trimethylaniline (1h)



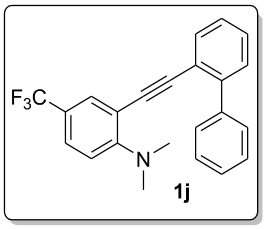
Brown oil (0.12 g, 20% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66-7.70 (m, 3H), 7.45 (t, J = 8.0 Hz, 2H), 7.31-7.42 (m, 4H), 7.16 (d, J = 8.0 Hz,1H), 6.67 (d, J = 12.0 Hz,2H), 2.82 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.2, 140.7, 139.1, 134.0, 132.5, 129.32, 129.28, 127.9, 127.8, 127.1, 126.8, 122.3, 121.0, 117.3, 112.1, 93.7, 91.8, 43.0, 21.7; HRMS [m/z]: Calcd for $C_{23}H_{21}N$: 311.1674, Found: 311.1665.

2-(Biphenyl-2-ylethynyl)-4-fluoro-*N*,*N*-dimethylaniline (1i)



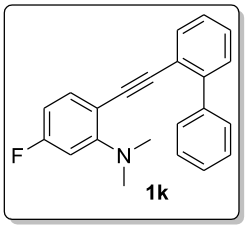
Brown solid (0.25 g, 81% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53-7.55 (m, 3H), 7.25-7.34 (m, 5H), 7.19-7.22 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.65-6.68 (m, 1H), 2.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.74 (d, J = 238.0 Hz), 151.1 (d, J = 2.0 Hz), 143.7, 140.6, 132.8, 129.5, 129.3, 128.5, 127.9, 127.4, 127.0, 121.7, 120.0 (d, J = 23.0 Hz), 118.0 (d, J = 8.0 Hz), 117.0 (d, J = 10.0 Hz), 115.7 (d, J = 22.0 Hz), 95.2, 90.2 (d, J = 2.0 Hz), 43.6; HRMS [m/z]: Calcd for $C_{22}H_{18}FN$: 315.1423, Found: 315.1429.

2-(Biphenyl-2-ylethynyl)-*N*,*N*-dimethyl-4-(trifluoromethyl)aniline (1j)



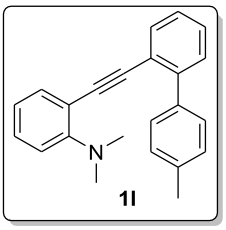
Light yellow solid (0.73 g, 95% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76-7.78 (m, 3H), 7.65 (s, 1H), 7.47-7.58 (m, 6H), 7.42-7.45 (m, 1H), 6.88 (d, J = 10.0 Hz,1H), 2.96 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 143.7, 140.6, 132.4, 131.7 (q, J = 3.8 Hz), 129.5, 128.6 (q, J = 275.0 Hz), 128.5, 127.9, 127.0, 125.7 (q, J = 3.8 Hz), 125.4, 123.3, 121.8, 121.0 (q, J = 32.5 Hz), 115.8, 113.0, 95.2, 90.8, 42.3; HRMS [m/z]: Calcd for $C_{23}H_{18}F_3N$: 365.1391, Found: 365.1396.

2-(Biphenyl-2-ylethynyl)-5-fluoro-*N*,*N*-dimethylaniline (1k)



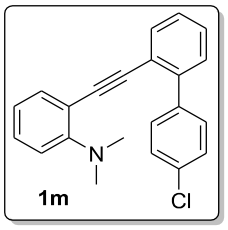
Brown oil (0.17 g, 57% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63-7.67 (m, 3H), 7.37-7.46 (m, 5H), 7.33 (d, J = 6.0 Hz,1H), 7.19 (t, J = 6.4 Hz, 1H), 6.49-6.53 (m, 2H), 2.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 247.0 Hz), 156.11 (d, J = 9.0 Hz), 143.4, 140.7, 135.6 (d, J = 10.0 Hz), 132.4, 129.5, 129.4, 128.2, 127.9, 127.3, 127.0, 122.2, 110.3 (d, J = 3.0 Hz), 106.7 (d, J = 22.0 Hz), 103.9 (d, J = 25.0 Hz), 93.9 (d, J = 1.0 Hz), 90.9, 42.8; HRMS [m/z]: Calcd for $C_{22}H_{18}FN$: 315.1423, Found: 315.1428.

***N*,*N*-Dimethyl-2-((4'-methyl-biphenyl-2-yl)ethynyl)aniline (1l)**



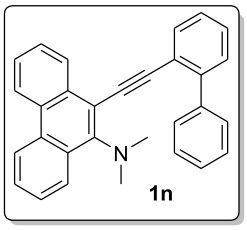
Brown oil (0.32 g, 90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.40-7.52 (m, 4H), 7.34-7.38 (m, 2H), 7.27-7.31 (m, 1H), 6.92-6.96 (m, 2H), 2.92 (s, 6H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.3, 137.8, 136.8, 134.2, 132.6, 129.4, 129.2, 129.0, 128.5, 128.1, 126.7, 122.1, 120.1, 116.6, 115.2, 94.5, 91.5, 43.1, 21.1; HRMS [m/z]: Calcd for $C_{23}H_{21}N$: 311.1674, Found: 311.1680.

2-((4'-Chloro-biphenyl-2-yl)ethynyl)-*N*,*N*-dimethylaniline (1m)



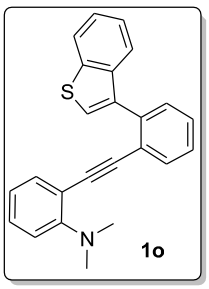
Yellow solid (0.34 g, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.33-7.43 (m, 5H), 7.29-7.31 (m, 1H), 7.21-7.26 (m, 1H), 6.85-6.90 (m, 2H), 2.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 142.1, 139.2, 134.2, 133.3, 132.8, 130.7, 129.3, 129.2, 128.2, 128.1, 127.3, 122.2, 120.3, 116.8, 115.0, 93.9, 92.1, 43.2; HRMS [m/z]: Calcd for $C_{22}H_{18}ClN$: 331.1128, Found: 331.1129.

10-(Biphenyl-2-ylethynyl)-*N*,*N*-dimethylphenanthren-9-amine (1n)



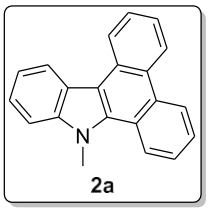
Yellow-green solid (0.23 g, 59% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.42-8.44 (m, 1H), 7.86-7.91 (m, 2H), 7.69-7.71 (m, 2H), 7.59-7.65 (m, 2H), 7.53-7.56 (m, 1H), 7.38-7.51 (m, 7H), 3.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 143.9, 141.1, 132.4, 132.2, 131.4, 131.2, 129.8, 129.4, 128.3, 128.2, 127.4, 127.3, 127.2, 126.9, 126.7, 126.3, 125.9, 125.4, 122.7, 122.6, 122.2, 114.5, 99.5, 89.8, 43.8; HRMS [m/z]: Calcd for $C_{30}H_{23}N$: 397.1830, Found: 397.1829.

2-((2-(Benzo[*b*]thiophen-3-yl)phenyl)ethynyl)-*N*,*N*-dimethylaniline (1o)



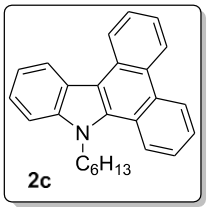
Brown oil (1.36 g, 96% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93-7.95 (m, 1H), 7.73-7.79 (m, 2H), 7.65 (s, 1H), 7.52-7.53 (m, 1H), 7.35-7.46 (m, 4H), 6.14-7.19 (m, 1H), 6.94-6.97 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.73-6.78 (m, 1H), 2.73 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 139.9, 138.5, 137.4, 136.3, 134.3, 132.6, 130.1, 129.0, 127.9, 127.4, 125.4, 124.2, 124.1, 123.7, 123.5, 122.5, 120.1, 116.6, 114.9, 94.0, 92.3, 43.1; HRMS [m/z]: Calcd for $C_{24}H_{19}NS$: 353.1238, Found: 353.1229.

9-Methyl-9*H*-dibenzo[*a*,*c*]carbazole (2a)



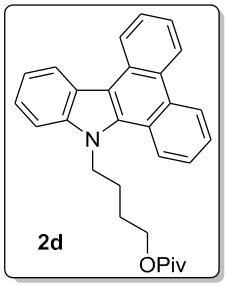
Brown solid (78.5 mg, 95% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.86 (d, J = 10.0 Hz, 1H), 8.82-8.84 (m, 1H), 8.75 (d, J = 10.0 Hz, 1H), 8.62-8.64 (m, 1H), 8.61 (d, J = 10.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.62-7.67 (m, 2H), 7.56-7.60 (m, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 4.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 134.6, 130.9, 129.9, 127.3, 126.9, 126.1, 125.6, 124.0, 123.9, 123.64, 123.56, 123.5, 123.42, 123.41, 122.8, 121.8, 120.3, 113.4, 109.5, 34.5; HRMS [m/z]: Calcd for $C_{21}H_{15}N$: 281.1192, Found: 281.1205.

9-Hexyl-9*H*-dibenzo[*a*,*c*]carbazole (2c)



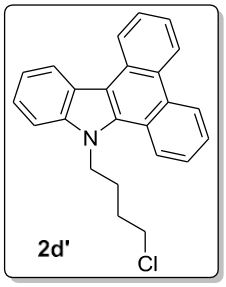
Brown solid (96.9 mg, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.95 (d, J = 8.0 Hz, 1H), 8.86-8.88 (m, 1H), 8.79 (d, J = 8.0 Hz, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.43-8.45 (m, 1H), 7.81 (t, J = 8.0 Hz, 1H), 7.67-7.69 (m, 2H), 7.58-7.64 (m, 2H), 7.54 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 4.63 (t, J = 8.0 Hz, 2H), 2.03-2.11 (m, 2H), 1.51-1.58 (m, 2H), 1.38-1.46 (m, 4H), 0.99 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 133.6, 130.8, 130.0, 127.2, 126.8, 126.2, 125.4, 124.1, 123.6, 123.52, 123.50, 123.48, 123.39, 123.35, 122.4, 121.8, 120.2, 113.6, 109.6, 46.1, 31.4, 29.8, 26.6, 22.6, 14.0; HRMS [m/z]: Calcd for $C_{26}H_{25}N$: 351.2017, Found: 351.1984.

4-(9*H*-Dibenzo[*a*,*c*]carbazol-9-yl)butyl pivalate (2d)



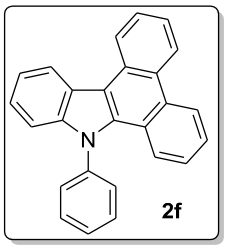
Brown liquid (87.1 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.90 (d, J = 8.0 Hz, 1H), 8.83-8.87 (m, 1H), 8.76 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 8.0 Hz, 1H), 8.40-8.42 (m, 1H), 7.77 (t, J = 8.0 Hz, 1H), 7.65-7.68 (m, 2H), 7.56-7.62 (m, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 4.72 (t, J = 8.0 Hz, 2H), 4.16 (t, J = 8.0 Hz, 2H), 2.11-2.19 (m, 2H), 1.78-1.85 (m, 2H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 140.4, 133.5, 130.9, 129.9, 127.3, 126.9, 126.4, 125.5, 124.2, 123.74, 123.65, 123.51, 123.47, 123.4, 122.2, 121.9, 120.4, 113.8, 109.5, 63.5, 45.7, 38.7, 27.1, 26.6, 26.1; HRMS [m/z]: Calcd for $C_{29}H_{29}NO_2$: 423.2198, Found: 423.2208.

9-(4-Chlorobutyl)-9*H*-dibenzo[*a*,*c*]carbazole (2d')



Yellow solid (11.0 mg, 10% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85-8.90 (m, 2H), 8.77 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.44 (t, J = 8.0 Hz, 1H), 7.77 (t, J = 8.0 Hz, 1H), 7.65-7.68 (m, 2H), 7.56-7.61 (m, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 4.74 (t, J = 8.0 Hz, 2H), 3.56 (t, J = 8.0 Hz, 2H), 2.19-2.27 (m,2H), 1.89-1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 133.6, 130.9, 129.9, 127.3, 127.0, 126.5, 125.6, 124.3, 123.9, 123.8, 123.6, 123.5, 123.4, 122.3, 122.0, 120.5, 113.9, 109.6, 45.5, 44.3, 29.8, 27.4; HRMS [m/z]: Calcd for $C_{24}H_{20}ClN$: 357.1284, Found: 357.1293.

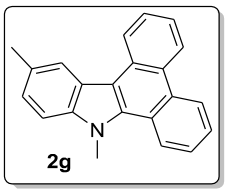
9-Phenyl-9*H*-dibenzo[*a*,*c*]carbazole (2f)



White solid (68.1 mg, 67% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (d, J = 8.0 Hz, 1H), 8.82 (d, J = 8.0 Hz, 2H), 8.67 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H), 7.62-7.70 (m, 4H), 7.53-7.59 (m, 3H), 7.38-7.50 (m, 3H), 7.29 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H) ; ^{13}C NMR

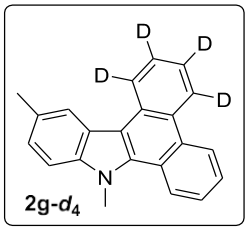
(100 MHz, $CDCl_3$) δ 142.1, 140.3, 134.5, 130.9, 130.2, 129.9, 129.1, 128.9, 127.4, 127.3, 125.9, 125.7, 124.00, 123.95, 123.82, 123.80, 123.5, 123.2, 121.7, 121.0, 114.2, 111.0; HRMS [m/z]: Calcd for $C_{26}H_{17}N$: 343.1361, Found: 343.1355.

9,12-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (2g)



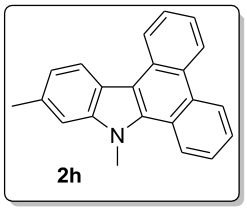
Light yellow solid (67.1 mg, 78% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.77 (d, J = 8.0 Hz, 2H), 8.68 (d, J = 8.0 Hz, 1H), 8.59 (t, J = 8.0 Hz, 1H), 8.30 (s, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.58-7.60 (m, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 4.14 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 139.2, 134.7, 130.7, 130.0, 129.6, 127.2, 126.7, 126.2, 125.5, 125.2, 124.0, 123.5, 123.43, 123.41, 123.36, 123.0, 121.5, 112.7, 109.3, 34.5, 21.5; HRMS [m/z]: Calcd for $C_{22}H_{17}N$: 295.1361, Found: 295.1369.

9,12-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole-1,2,3,4-*d*$_4$ (2g-*d*$_4$)



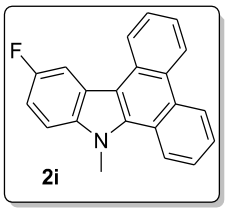
Light yellow solid (67.5 mg, 76% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.74-8.77 (m, 1H), 8.62-8.64 (m, 1H), 8.29 (s, 1H), 7.57-7.62 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 4.26 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 139.3, 134.8, 130.7, 129.9, 129.7, 126.7, 126.2, 125.6, 125.2, 124.0, 123.4, 123.0, 121.5, 112.8, 109.3, 34.6, 21.5; HRMS [m/z]: Calcd for $C_{22}H_{13}D_4N$: 299.1612, Found: 299.1620.

9,11-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (2h)



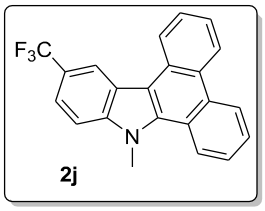
Gray-green solid (61.8 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.84-8.87 (m, 2H), 8.77 (d, J = 8.0 Hz, 1H), 8.68-8.70 (m, 1H), 8.48 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.65-7.68 (m, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.39 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 4.37 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 134.2, 133.6, 130.6, 129.8, 127.1, 126.8, 125.9, 125.2, 123.93, 123.88, 123.5, 123.4, 123.3, 122.6, 121.8, 121.4, 121.2, 113.3, 109.6, 34.3, 22.1; HRMS [m/z]: Calcd for $C_{22}H_{17}N$: 295.1361, Found: 295.1367.

12-Fluoro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (2i)



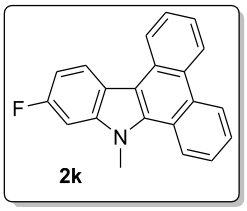
White solid (68.6 mg, 78% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.76-8.78 (m, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.56-8.59 (m, 2H), 8.13 (d, J = 10.4 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.61-7.67 (m, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.42-7.45 (m, 1H), 7.20 (t, J = 8.8 Hz, 1H), 4.21 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 157.9 (d,J = 233.0 Hz), 137.1, 135.6, 130.9, 129.4, 127.3, 126.6, 126.2, 125.9, 123.9, 123.7, 123.6, 123.4, 123.1, 123.0, 122.9, 112.6 (d, J = 5.0 Hz), 111.4 (d, J = 26.0 Hz), 110.1 (d, J = 9.0 Hz), 106.7 (d, J = 24.0 Hz), 34.5; HRMS [m/z]: Calcd for $C_{21}H_{14}FN$: 299.1110, Found: 299.1105.

9-Methyl-12-(trifluoromethyl)-9*H*-dibenzo[*a*,*c*]carbazole (2j)



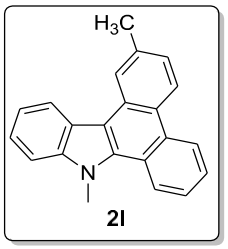
Brown solid (100.8 mg, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65-8.69 (m, 2H), 8.60 (t, J = 8.0 Hz, 2H), 8.40 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.53-7.64 (m, 4H), 7.43 (d, J = 8.0 Hz, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 135.4, 131.0, 127.5, 126.9, 126.8, 126.0, 124.6 (q, J = 292.0 Hz), 124.1, 124.0, 123.4, 123.2, 122.7, 122.6, 122.3, 122.0, 120.1 (q, J = 4.0 Hz), 119.0 (q, J = 4.0 Hz), 113.2, 109.4, 34.4.; HRMS [m/z]: Calcd for $C_{22}H_{14}F_3N$: 349.1078, Found: 349.1068.

11-Fluoro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (2k)



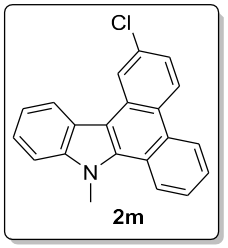
White solid (76.3 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.71 (d, J = 8.0 Hz, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.60 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.50-7.60 (m, 3H), 7.00-7.07 (m, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (d, J = 238.0 Hz), 141.0 (d, J = 11.0 Hz) 134.6, 130.3, 129.2, 127.1, 126.7, 125.9, 125.3, 123.8, 123.6, 123.34, 123.25, 123.1, 122.4, 122.3, 119.6, 112.9, 108.2 (d, J = 24.0 Hz), 95.8 (d, J = 27 Hz), 34.3; HRMS [m/z]: Calcd for $C_{21}H_{14}FN$: 299.1110, Found: 299.1105.

2,9-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (2l)



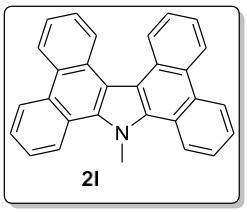
White solid (71.5 mg, 81% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.71 (d, J = 8.0 Hz,1H), 8.57 (t, J = 8.0 Hz, 3H), 8.45 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.42-7.49 (m, 3H), 7.38 (d, J = 8.0 Hz, 1H), 4.08 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.7, 134.5, 130.8, 129.9, 125.4, 125.2, 125.0, 124.5, 123.6, 123.3, 123.24, 123.23, 123.1, 122.6, 121.7, 119.9, 112.9, 109.3, 34.1, 22.0; HRMS [m/z]: Calcd for $C_{22}H_{17}N$: 295.1361, Found: 295.1365.

2-Chloro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (2m)



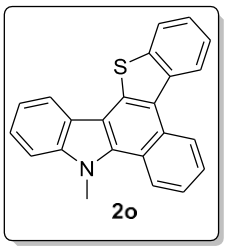
Light yellow solid (81.6 mg, 87% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24-8.44 (m, 5H), 7.29-7.49 (m, 6H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 134.4, 132.7, 130.4, 129.9, 125.9, 125.4, 124.7, 124.5, 123.5, 123.3, 123.2, 122.63, 122.56, 122.4, 121.2, 120.2, 111.8, 109.2, 33.9; HRMS [m/z]: Calcd for $C_{21}H_{14}ClN$: 315.0843, Found: 315.0816.

9-Methyl-9*H*-tetrabenzo[*a*,*c*,*g*,*i*]carbazole (2n)



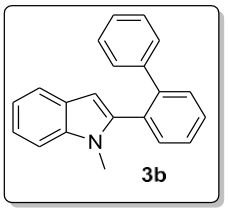
Off-white solid (100.0 mg, 87% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.00-9.02 (m, 2H), 8.88 (d, J = 8.0 Hz, 2H), 8.78-8.82 (m, 2H), 8.60 (d, J = 8.0 Hz, 2H), 7.70-7.79 (m, 4H), 7.63-7.69 (m, 4H), 4.65 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 137.5, 130.7, 128.7, 128.1, 126.4, 125.7, 125.6, 125.36, 124.43, 124.0, 123.73, 123.65, 123.0, 117.0, 41.4; HRMS [m/z]: Calcd for $C_{29}H_{19}N$: 381.1517, Found: 381.1516.

5-Methyl-5*H*-benzo[*a*]benzo[4,5]thieno[3,2-*c*]carbazole (2o)



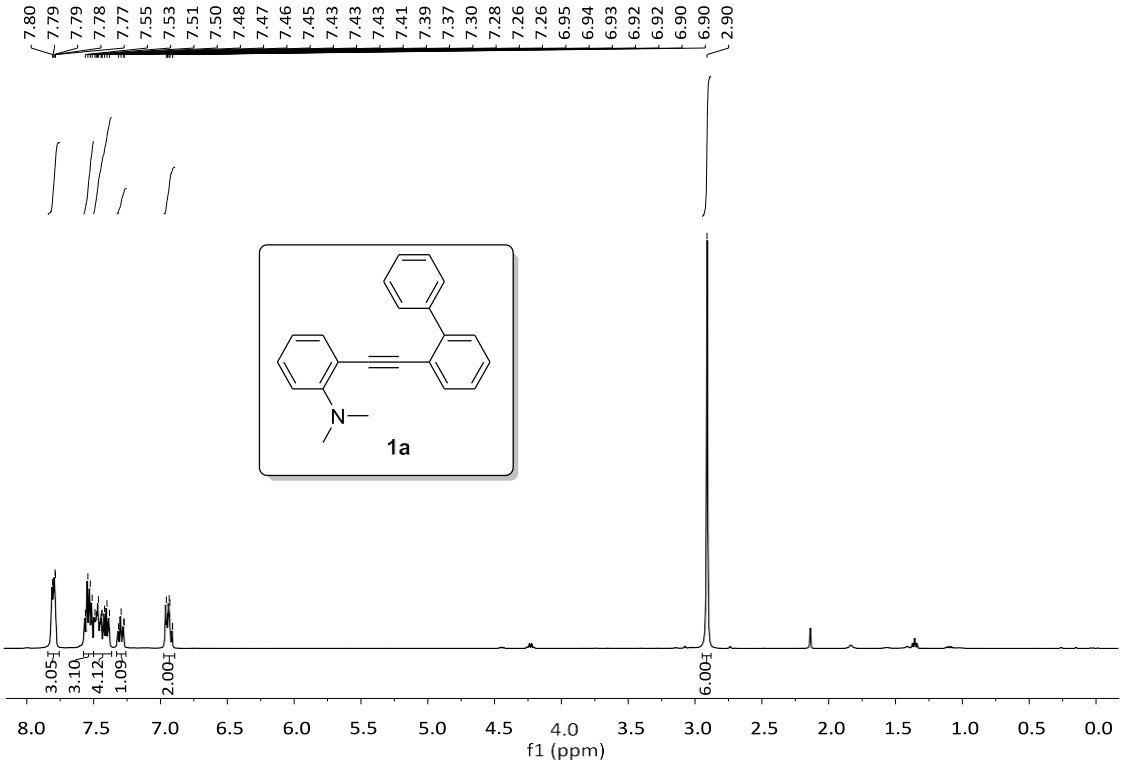
Light brown solid (64.4 mg, 67% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 9.12 (d, J = 10.0 Hz, 1H), 8.79 (d, J = 10.0 Hz, 2H), 8.28 (d, J = 10.0 Hz, 1H), 8.06 (d, J = 10.0 Hz, 1H), 7.72 (t, J = 10.0 Hz, 1H), 7.52-7.64 (m, 4H), 7.46 (t, J = 10.0 Hz, 1H), 7.41 (t, J = 10.0 Hz, 1H), 4.33 (s, 3H); ^{13}C NMR (500 MHz, CD_2Cl_2) δ 141.2, 139.2, 137.0, 135.4, 134.4, 130.7, 126.1, 125.3, 125.1, 124.7, 124.5, 124.3, 124.0, 123.7, 123.6, 123.2, 122.32, 122.26, 121.2, 120.6, 113.5, 109.7, 34.7; HRMS [m/z]: Calcd for $C_{23}H_{15}NS$: 337.0925, Found: 337.0936.

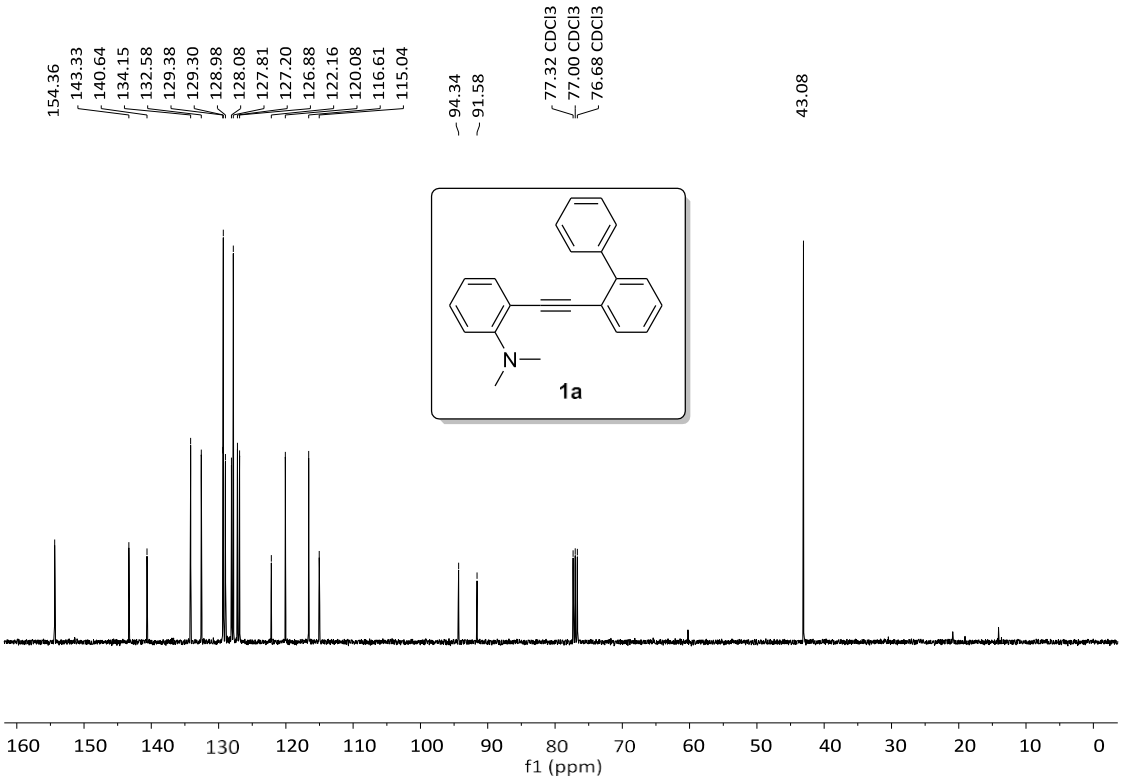
2-(Biphenyl-2-yl)-1-methyl-1*H*-indole (3b)

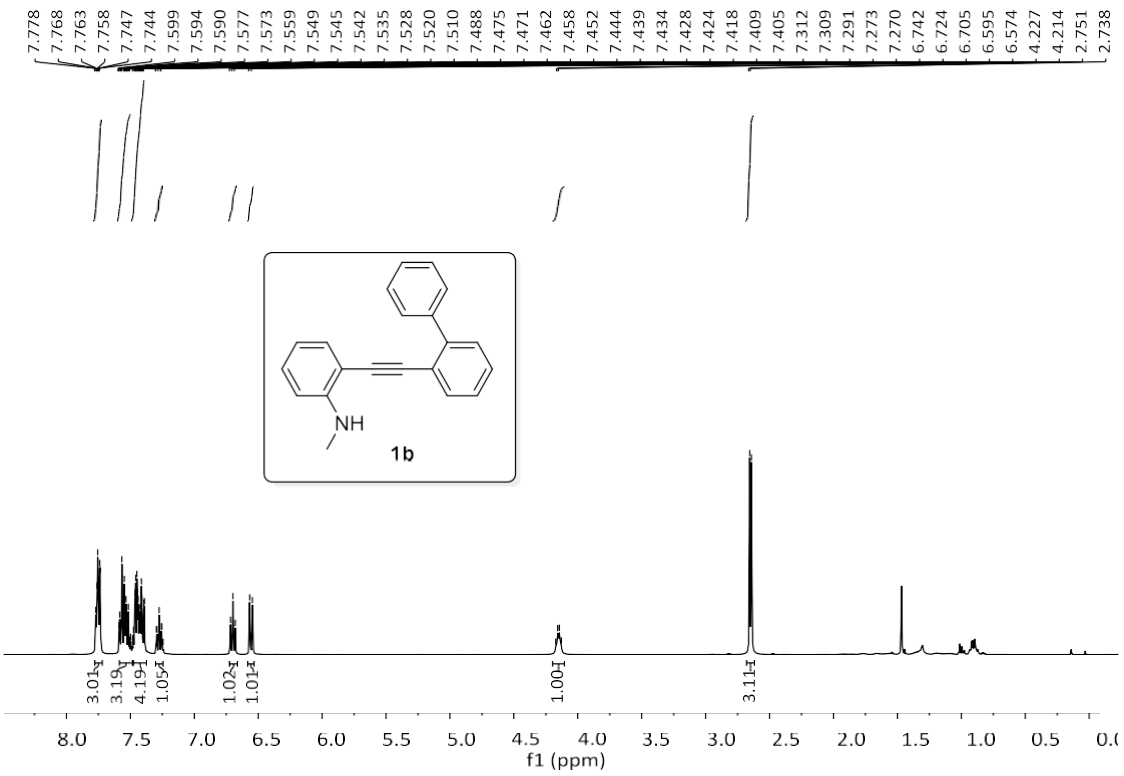


White solid (49.9 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, J = 8.0 Hz, 1H), 8.63-8.68 (m, 3H), 7.56 (d, J = 8.0 Hz, 1H), 7.22-7.35 (m, 8H), 6.66 (s, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.9, 140.7, 137.2, 132.4, 131.1, 130.1, 129.0, 128.8, 128.2, 128.0, 127.3, 126.9, 121.1, 120.2, 119.5, 109.3, 102.5, 30.3; HRMS [m/z]: Calcd for $C_{21}H_{17}N$: 283.1361, Found: 283.1380.

5. ^{1}H and ^{13}C NMR Spectra



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6.595
6.574
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NH
1b
3.01
3.19
4.19
1.05
1.02
1.01
1.00
3.11
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7.0
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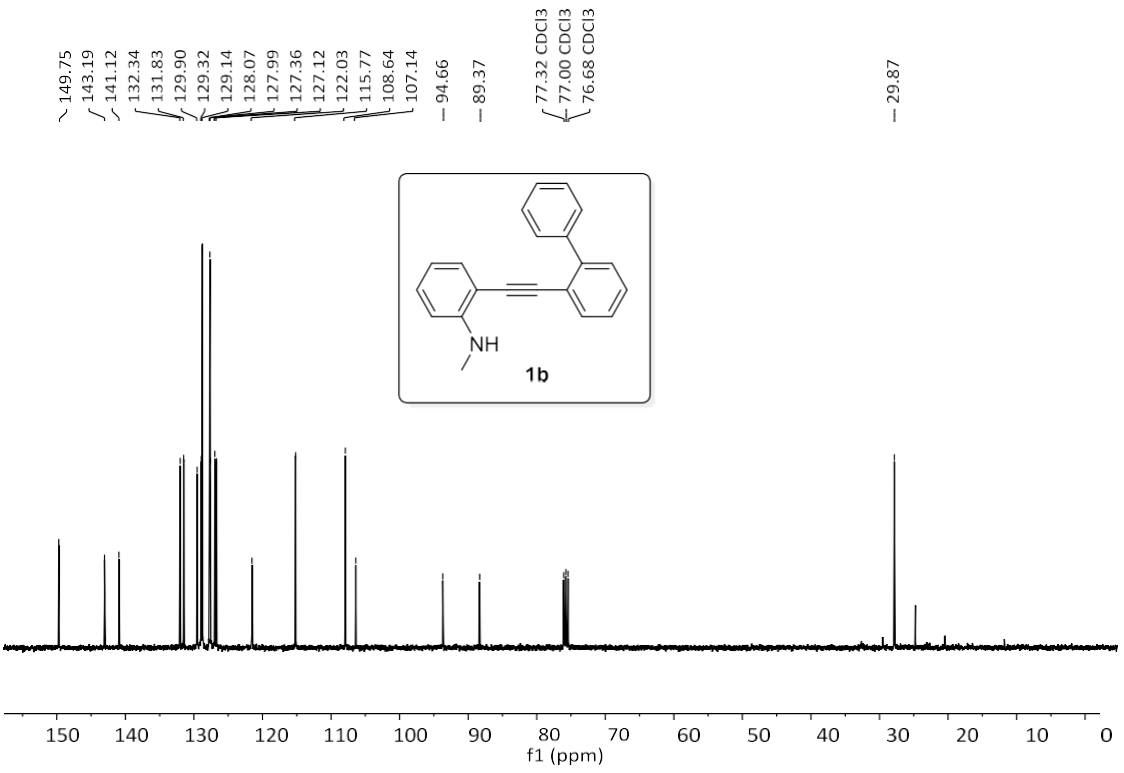
f1 (ppm)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77.00 CDCl3
76.68 CDCl3
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NH
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90
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70
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50
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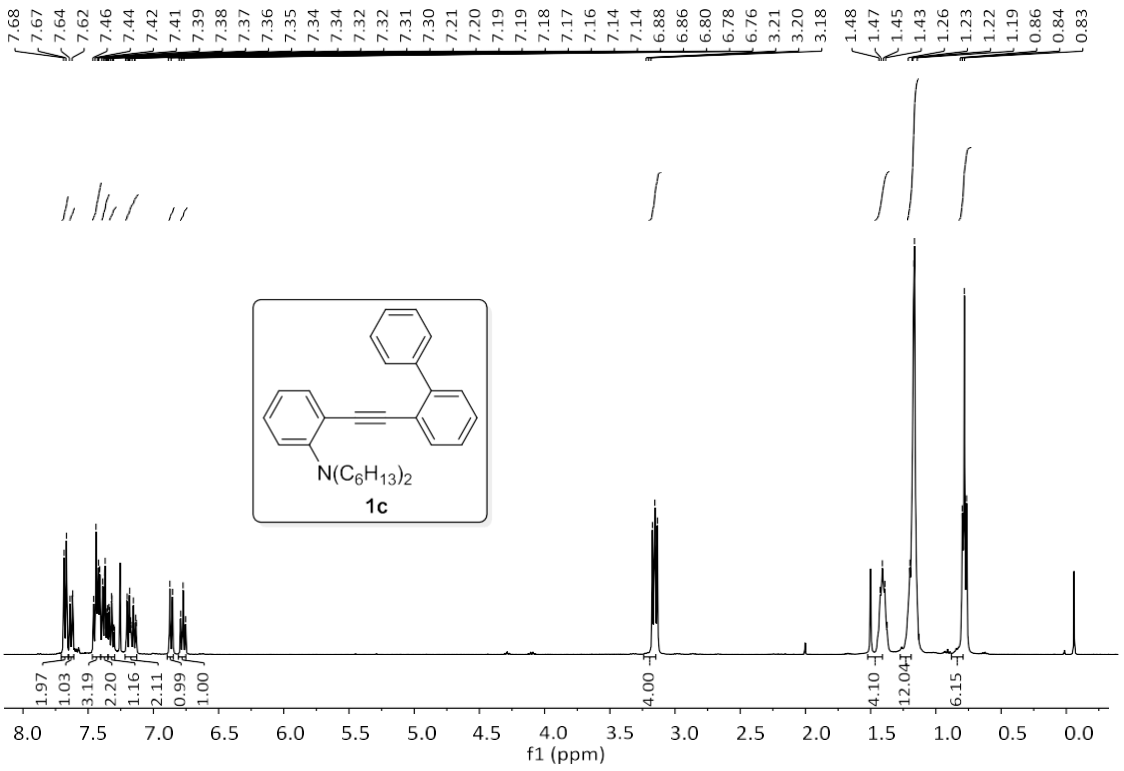
10
0
f1 (ppm)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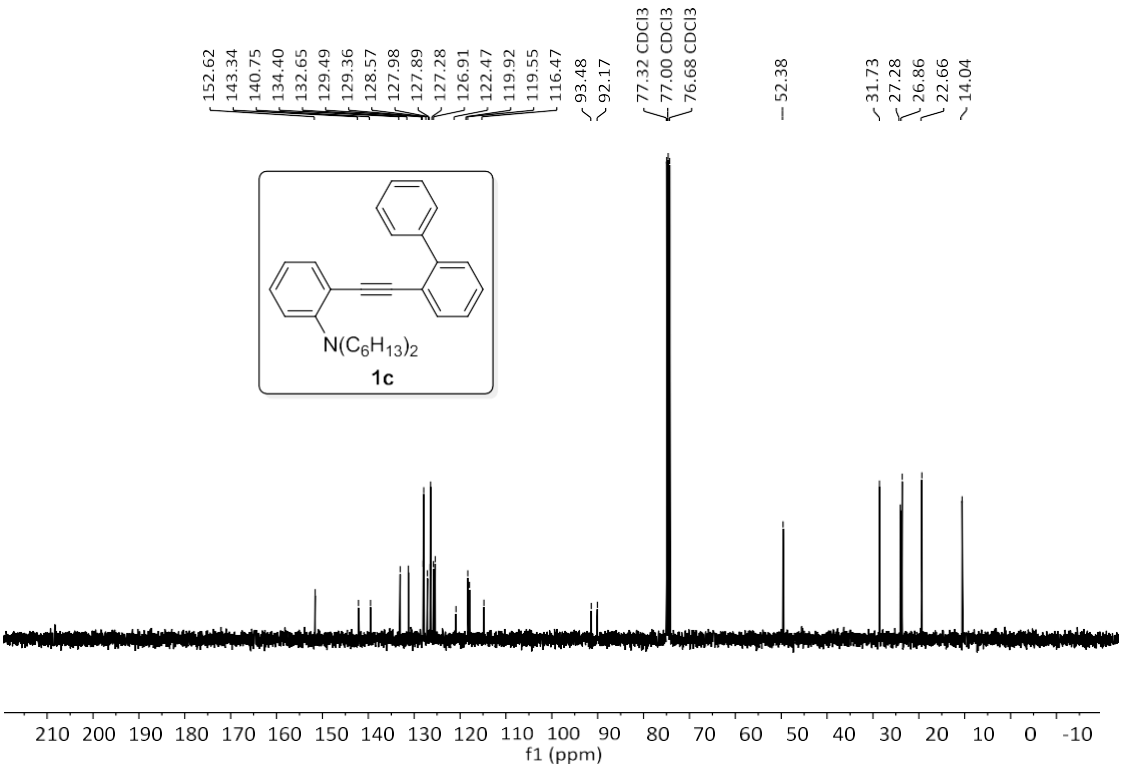
N(C6H13)2
1c
1.97 1.03 3.19 2.20 1.16 2.11 0.99 1.00 4.00 4.10 12.04 6.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.62 143.34 140.75 134.40 132.65 129.49 129.36 128.57 127.98 127.89 127.28 126.91 122.47 119.92 119.55 116.47 93.48 92.17 77.32 CDCl3 77.00 CDCl3 76.68 CDCl3 52.38 31.73 27.28 26.86 22.66 14.04
N(C6H13)2
1c
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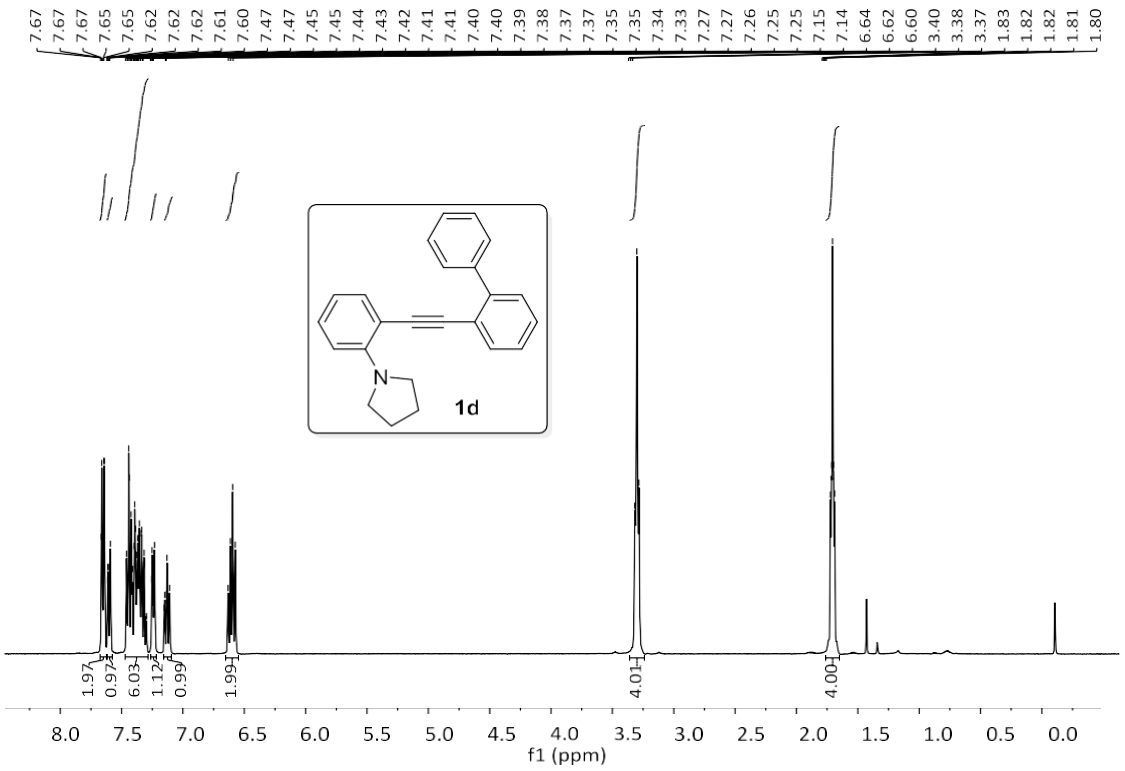
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1d
1.97 0.97 6.03 1.12 0.99 1.99 4.01 4.00
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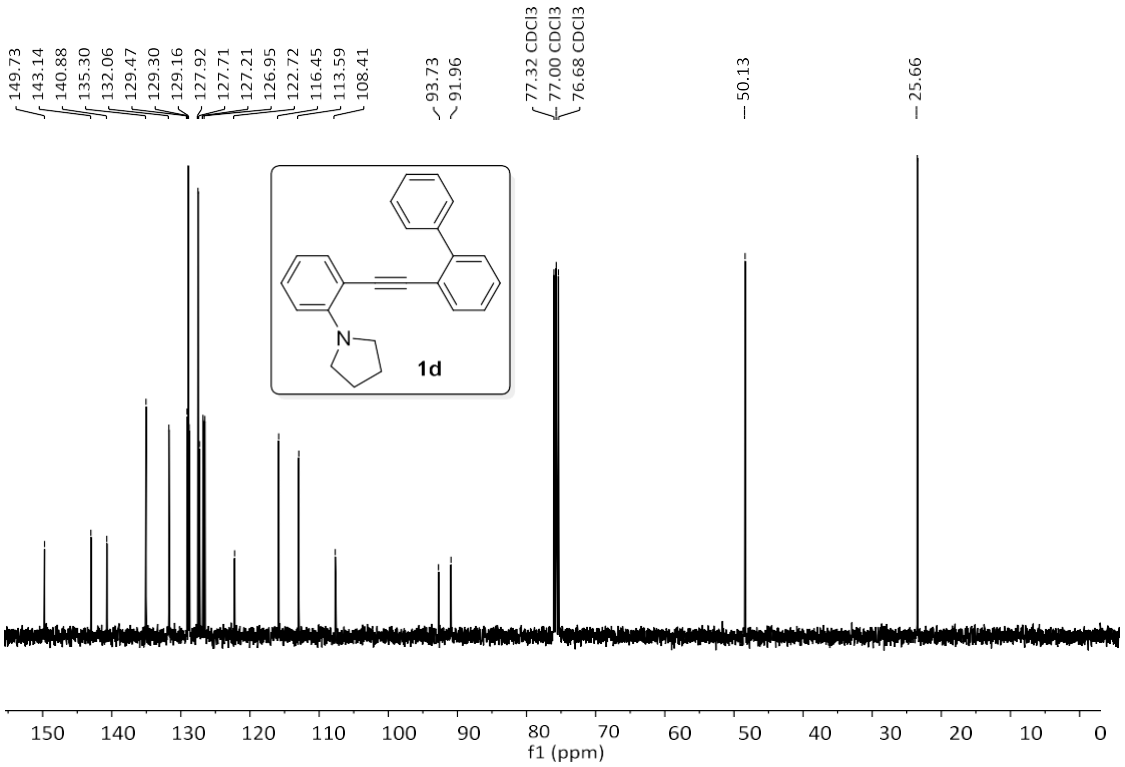
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93.73 91.96
77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
50.13
25.66
1d
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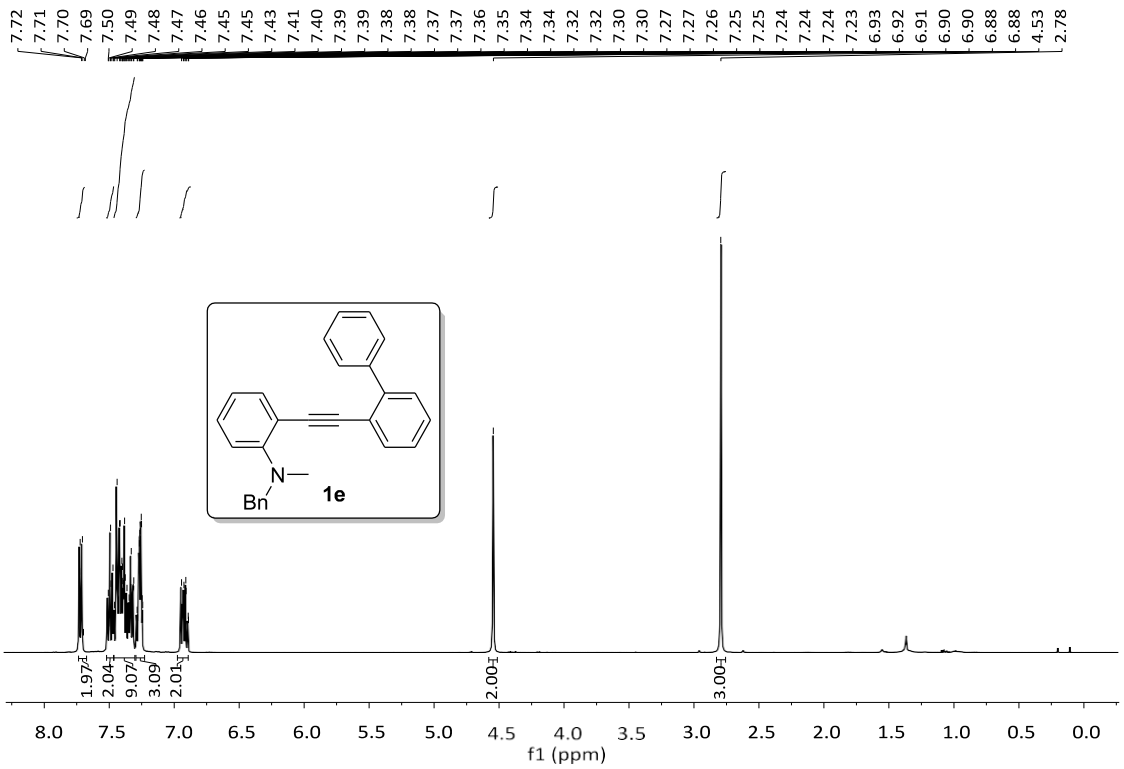
f1 (ppm)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1e
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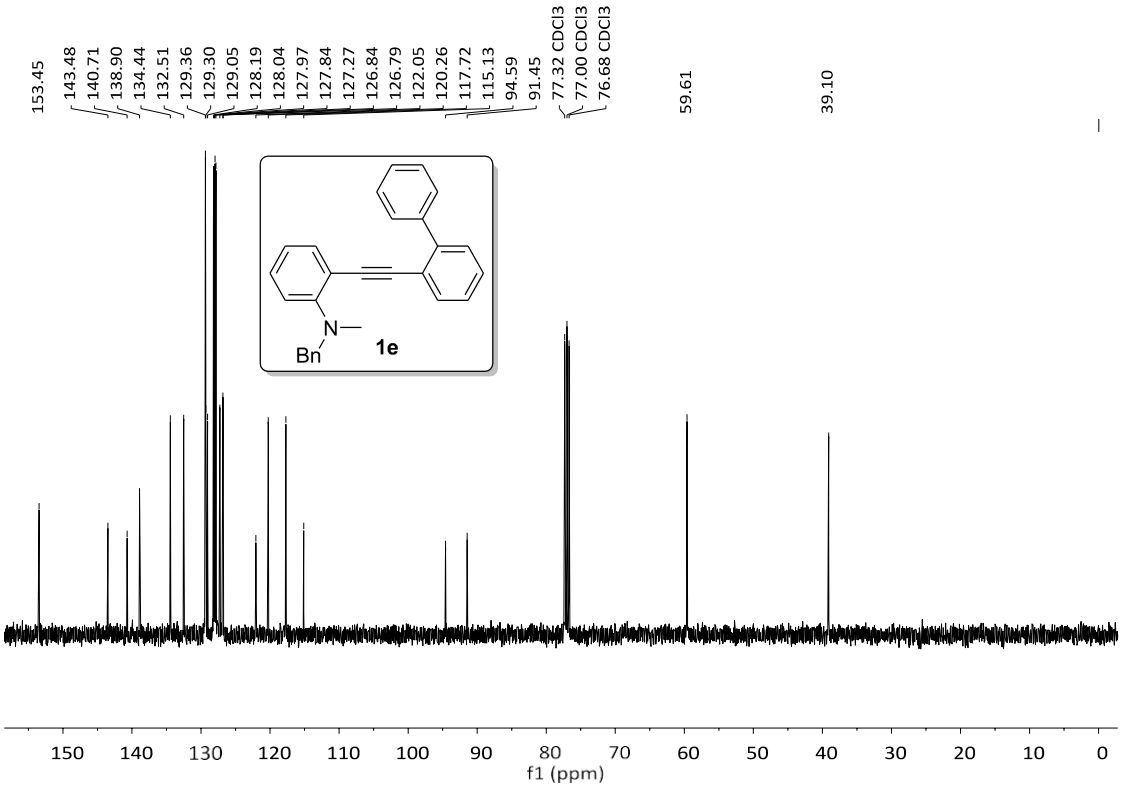
f1 (ppm)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1e
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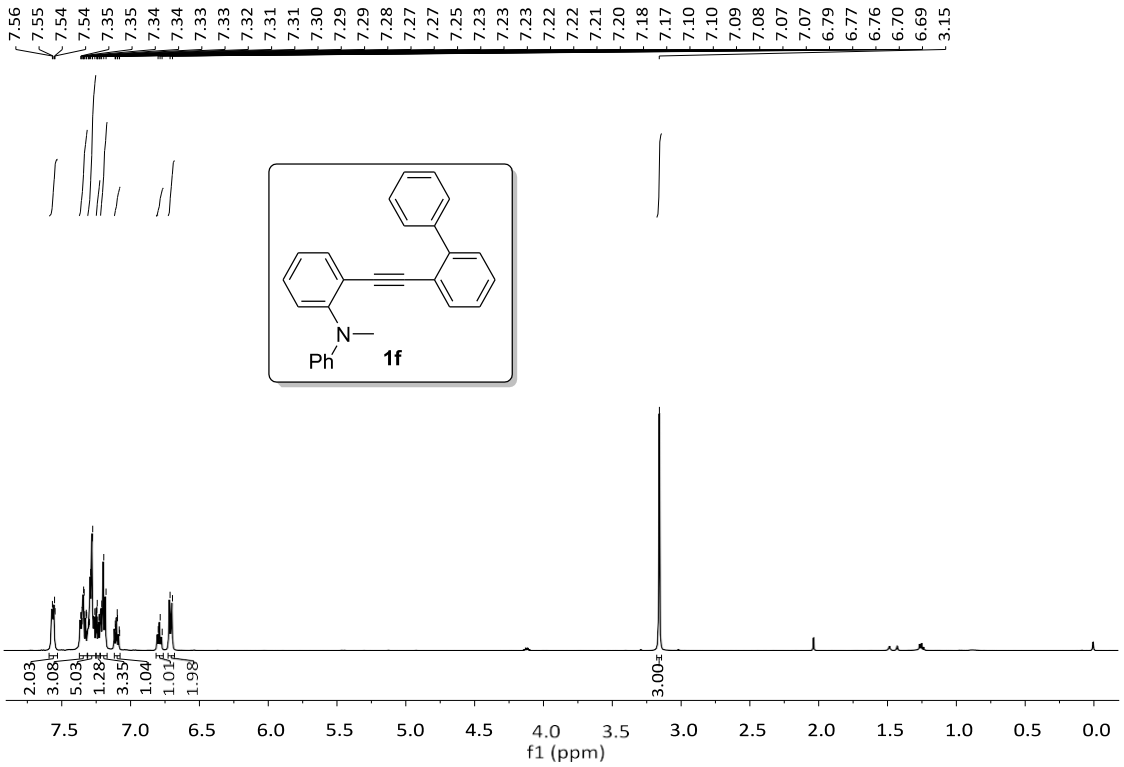
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N
Ph
1f
2.03 3.08 5.03 1.28 3.35 1.04 1.01 1.98 3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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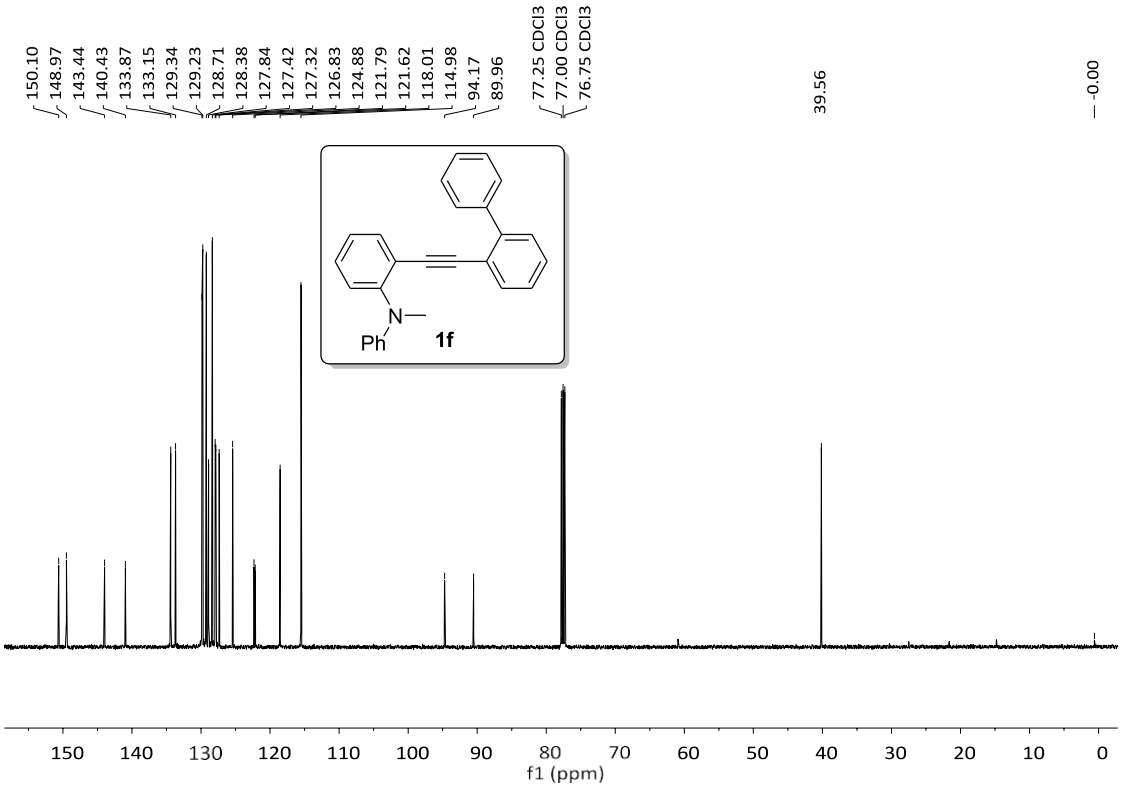
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77.25 CDCl3 77.00 CDCl3 76.75 CDCl3
39.56
-0.00
N
Ph
1f
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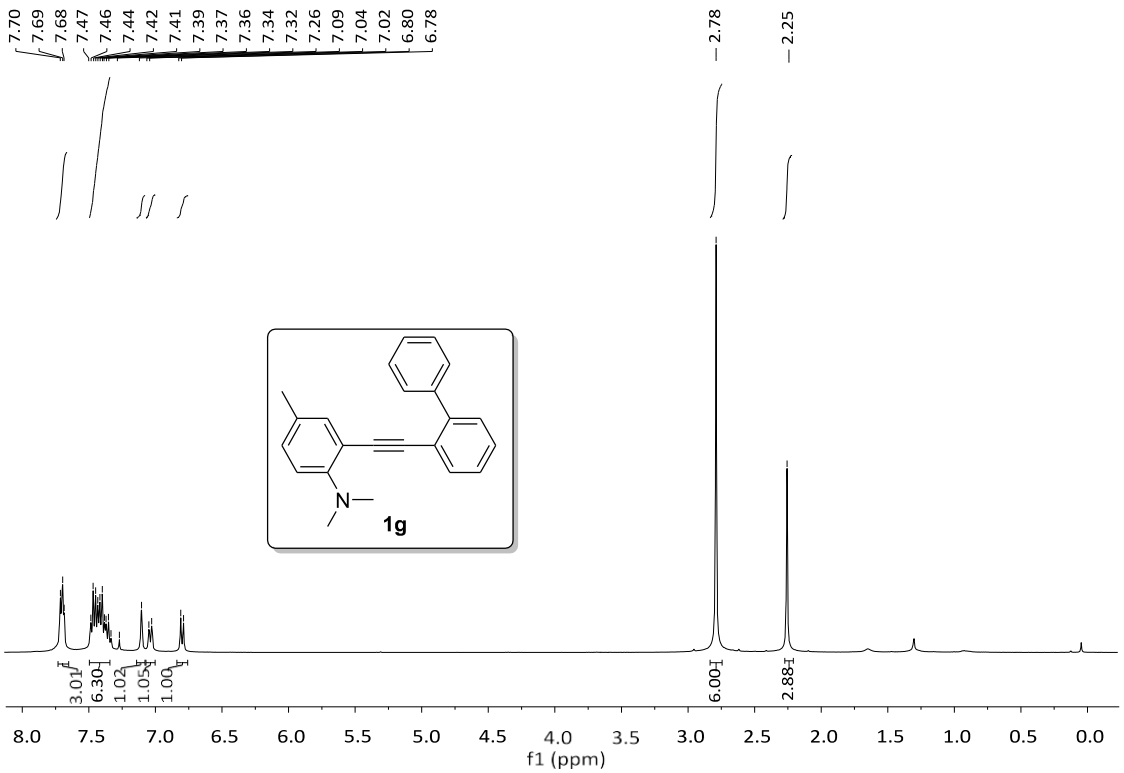
f1 (ppm)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7.04
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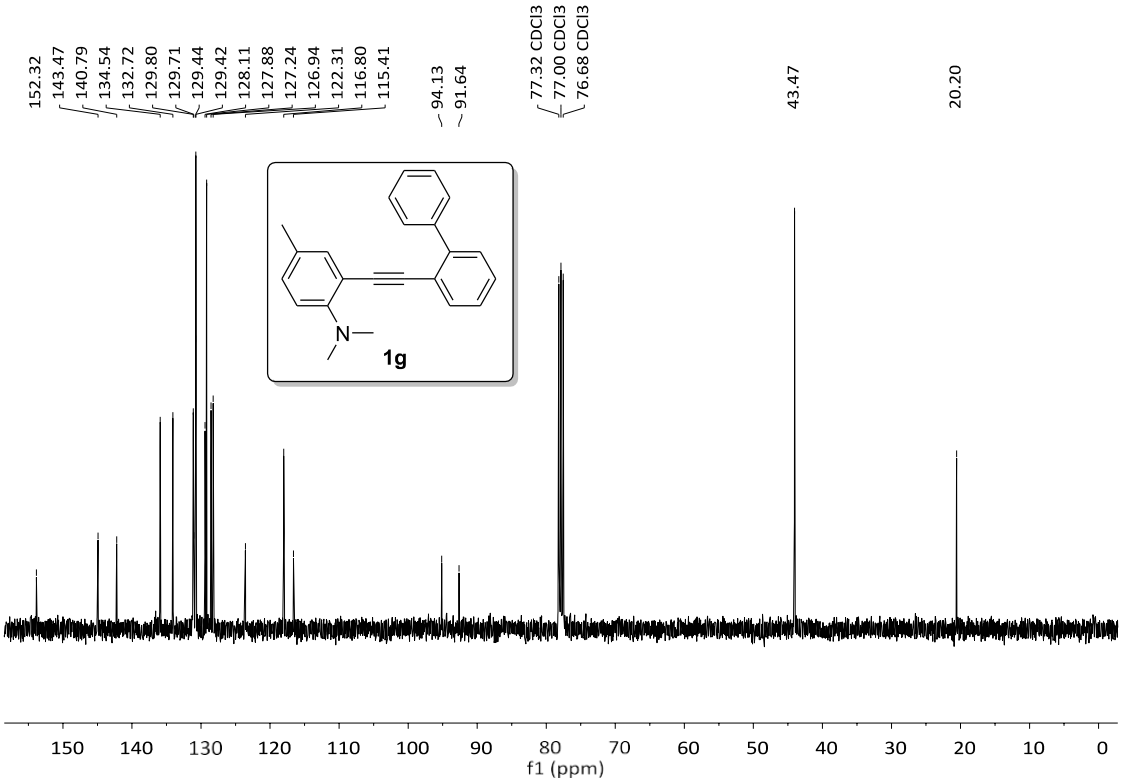
1.05
1.00
6.00
2.88
f1 (ppm)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116.80
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91.64
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
43.47
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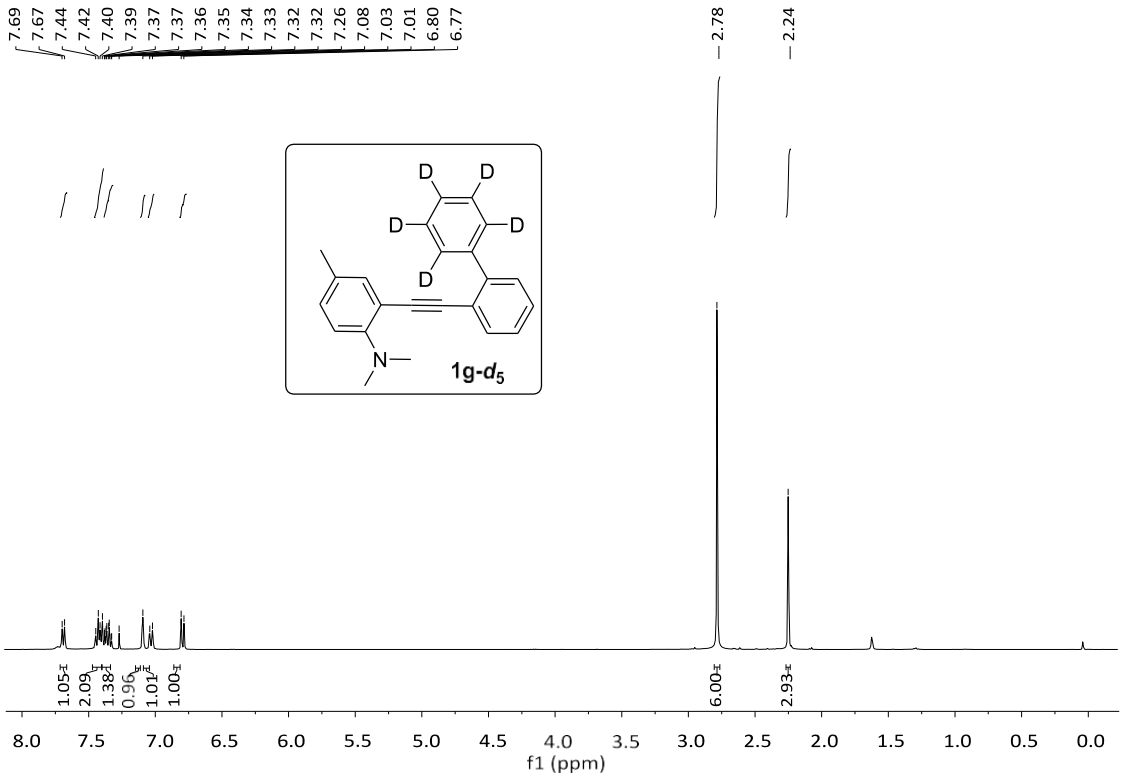
1g
f1 (ppm)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7.26
7.08
7.03
7.01
6.80
6.77
2.78
2.24
D
D
D
D
D
N
1g-d_5
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2.09
1.38
0.96
1.01
1.00
6.00
2.93
8.0
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7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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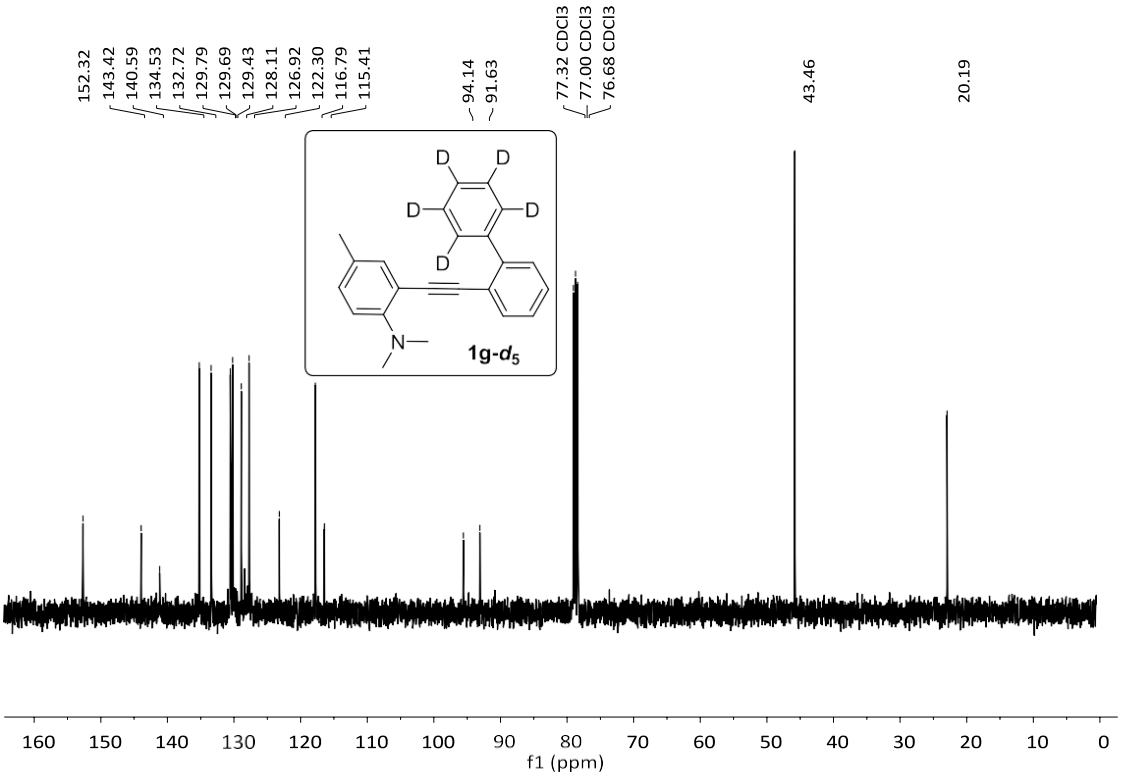
0.0
f1 (ppm)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115.41
94.14
91.63
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
43.46
20.19
D
D
D
D
D
N
1g-d_5
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100
90
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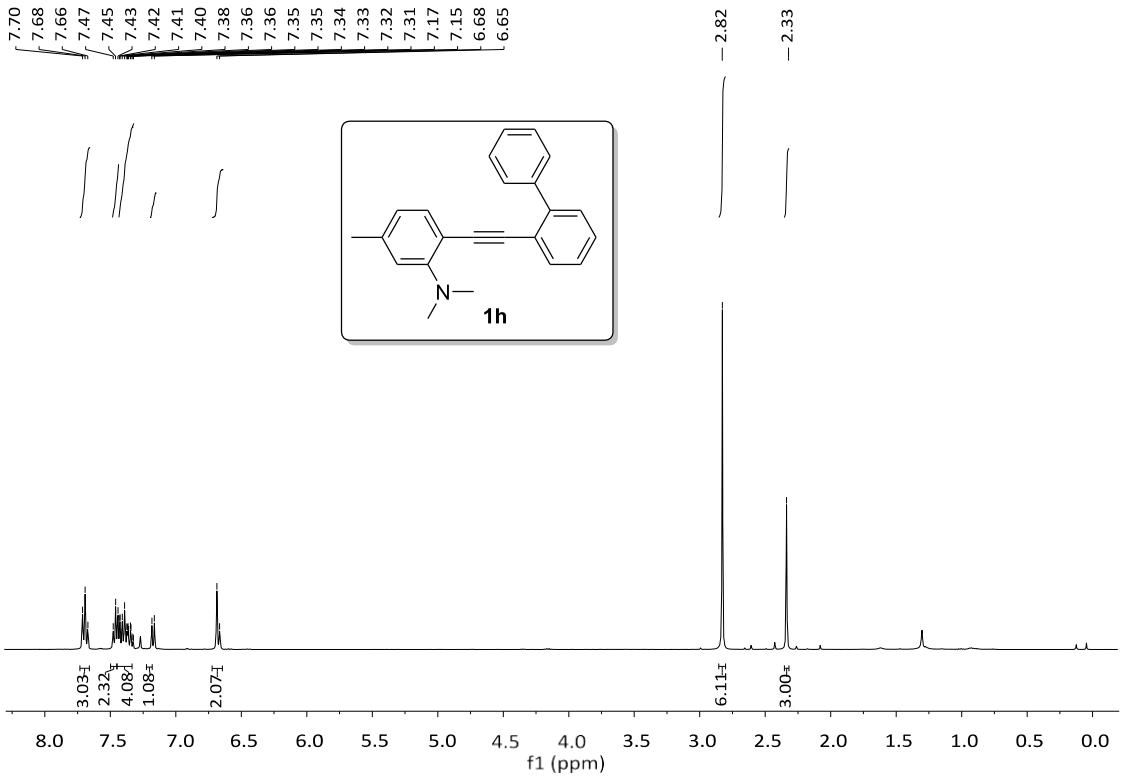
50
40
30
20
10
0
f1 (ppm)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7.35
7.34
7.33
7.32
7.31
7.17
7.15
6.68
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1h
3.03
2.32
4.08
1.08
2.07
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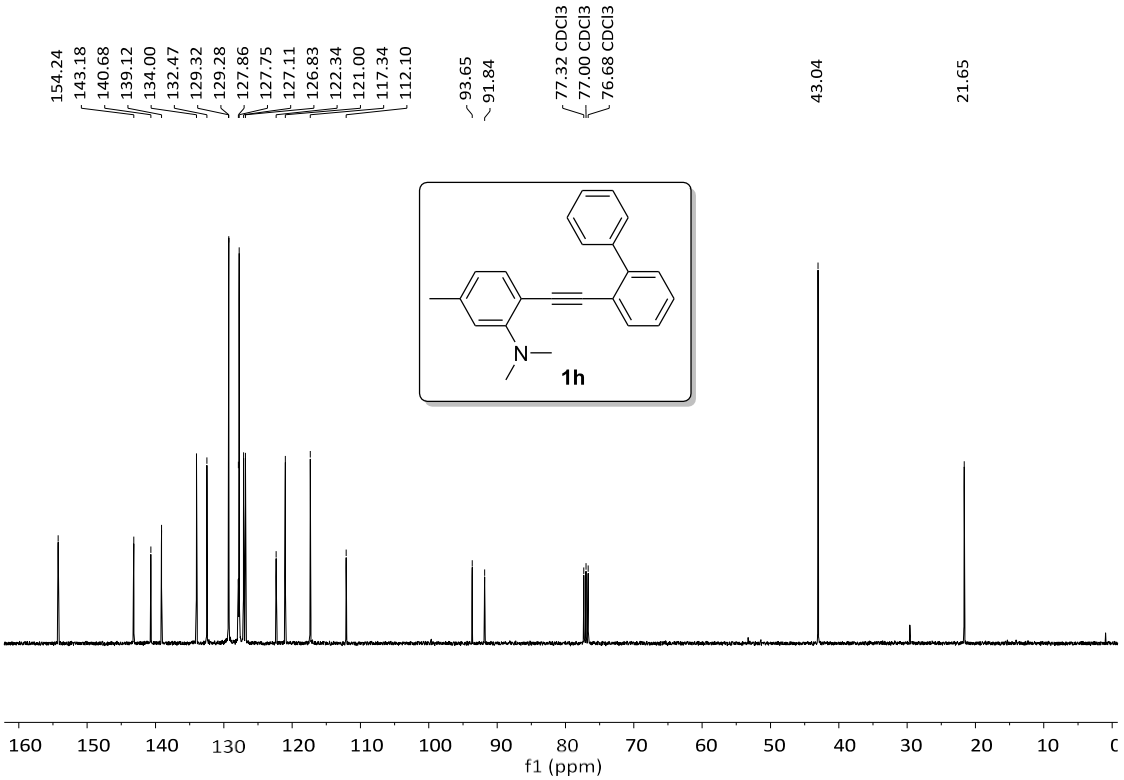
3.00
f1 (ppm)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121.00
117.34
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91.84
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77.00 CDCl3
76.68 CDCl3
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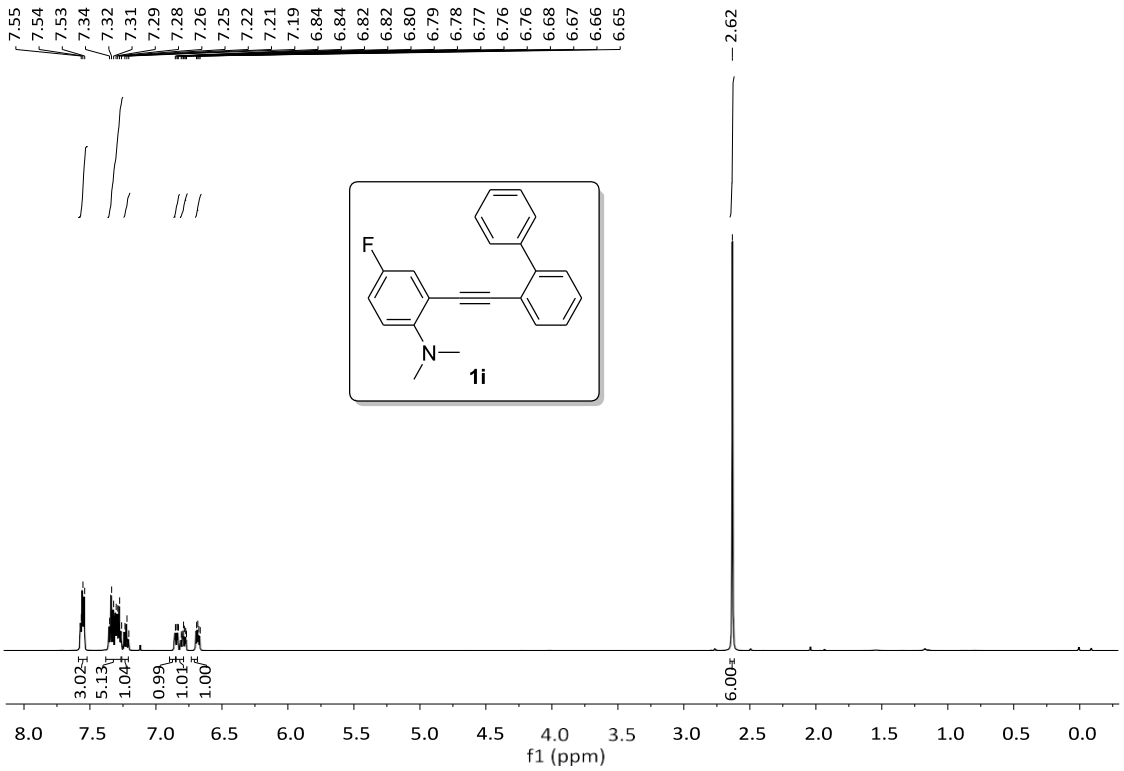
21.65
1h
f1 (ppm)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6.84
6.82
6.82
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6.76
6.76
6.68
6.67
6.66
6.65
2.62
F
N
1i
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5.13
1.04
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1.01
1.00
6.00
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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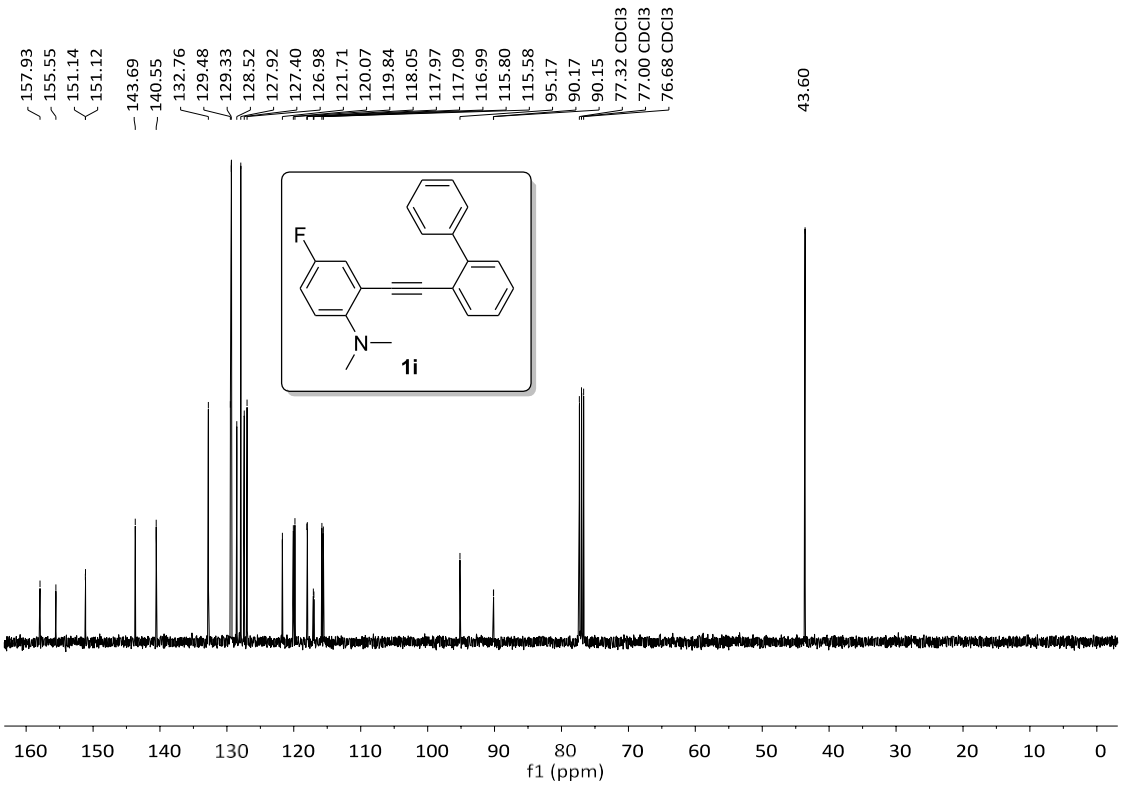
f1 (ppm)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120.07
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117.09
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90.17
90.15
77.32 CDCl3
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F
N
1i
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120
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90
80
70
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50
40
30
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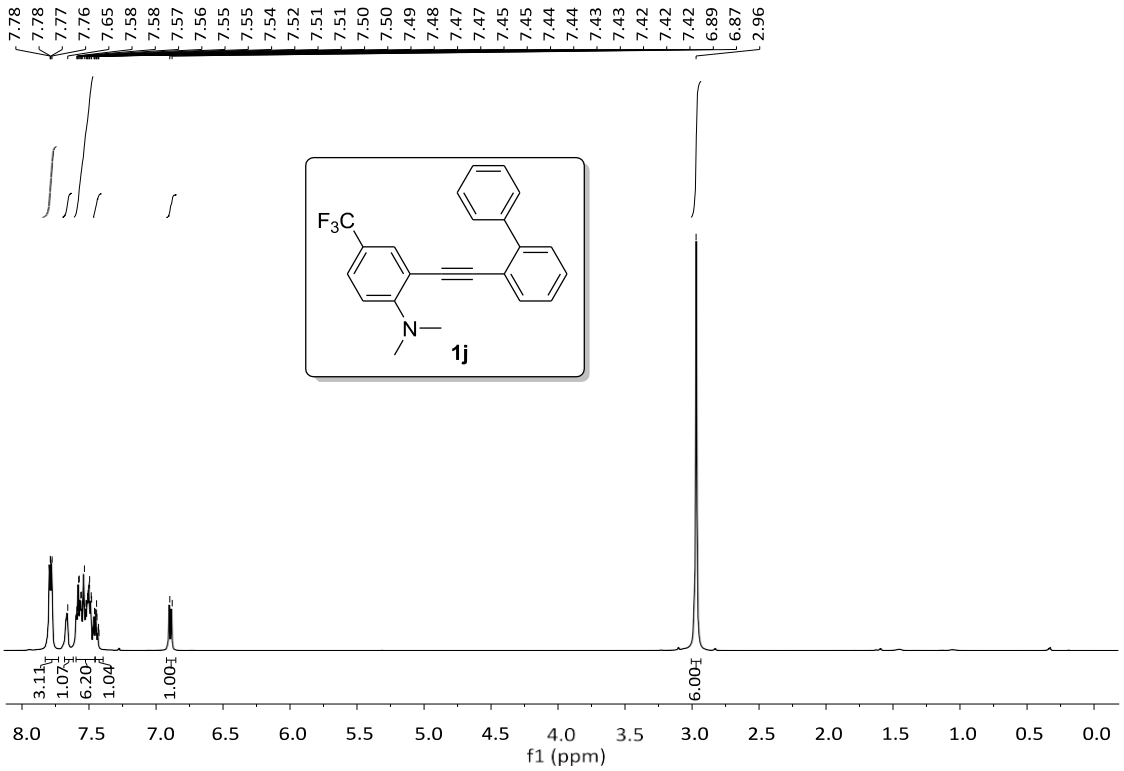
10
0
f1 (ppm)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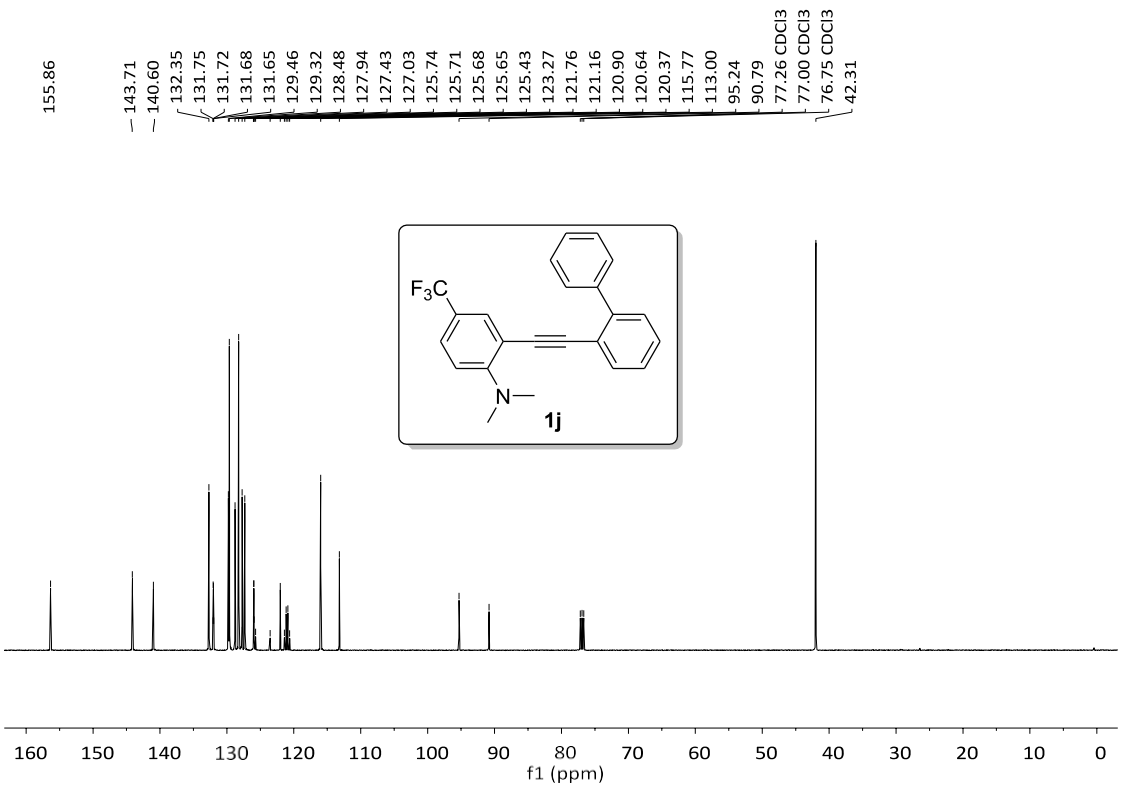
F3C
N
1j
3.11
1.07
6.20
1.04
1.00
6.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.71
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121.76
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90.79
77.26 CDCl3
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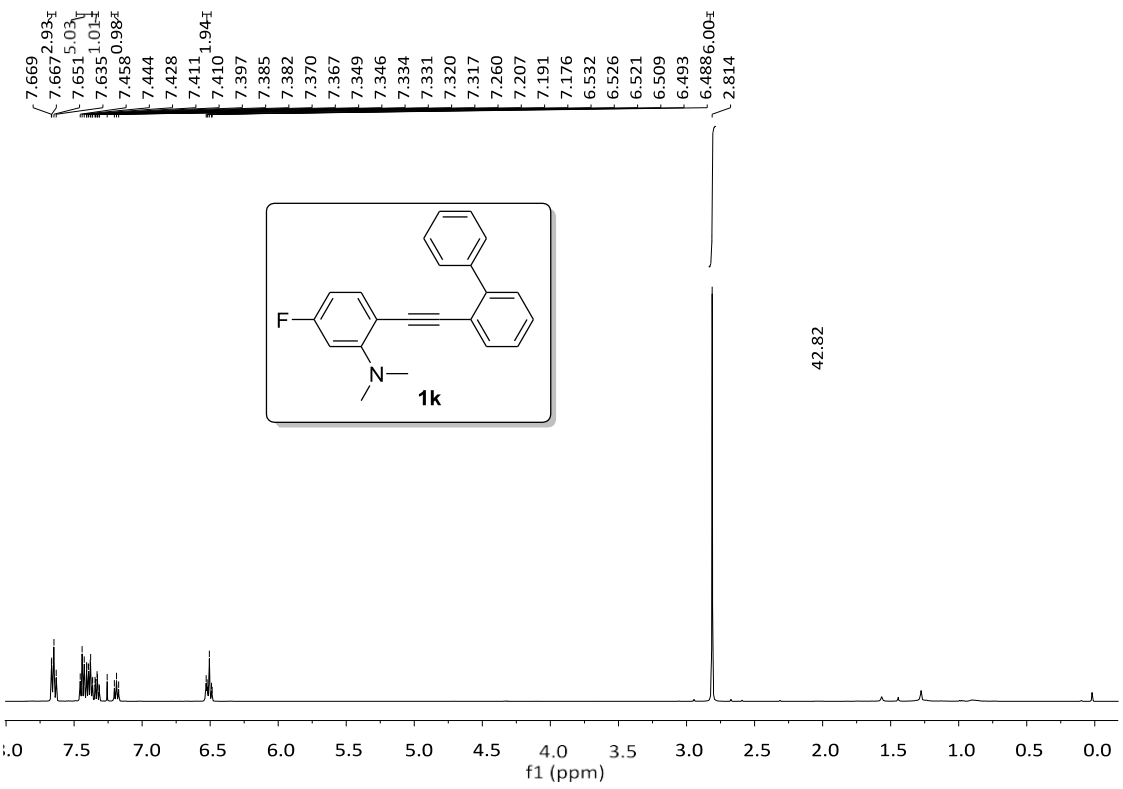
42.31
F3C
N
1j
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.176
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6.509
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2.93
5.03
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0.98
1.94
6.00
F
N
1k
42.82
7.5
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6.0
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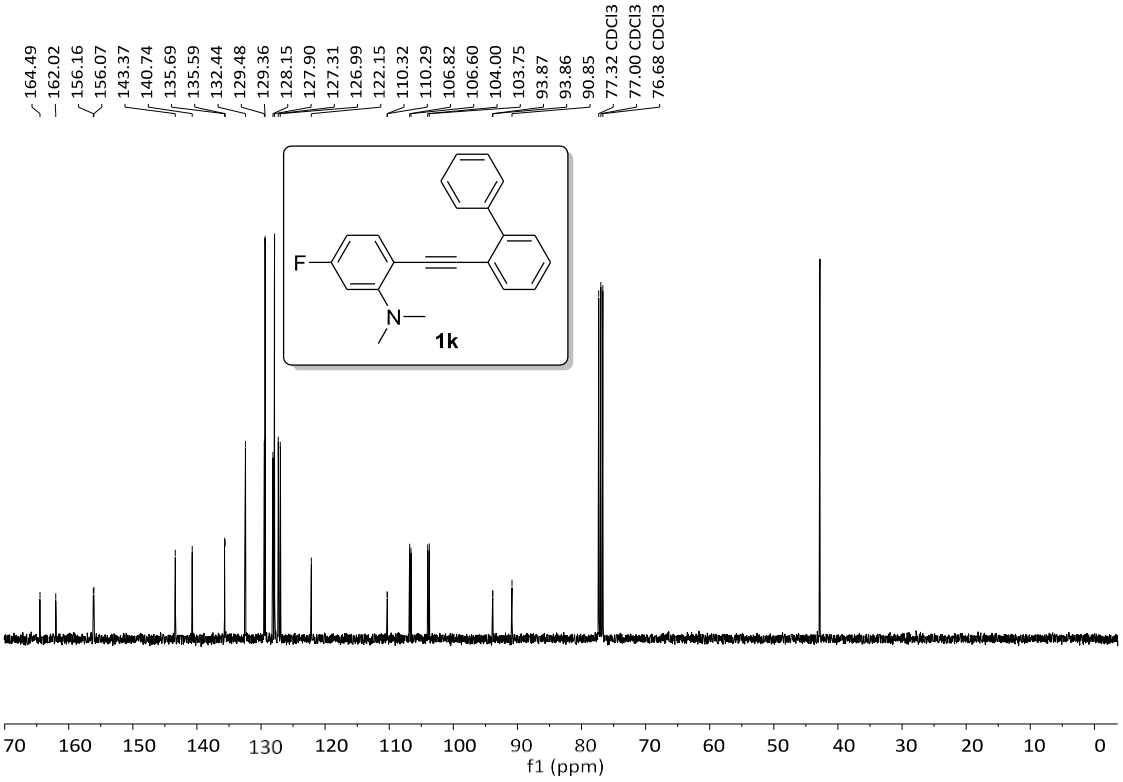
f1 (ppm)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127.31
126.99
122.15
110.32
110.29
106.82
106.60
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103.75
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93.86
90.85
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
F
N
1k
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50
40
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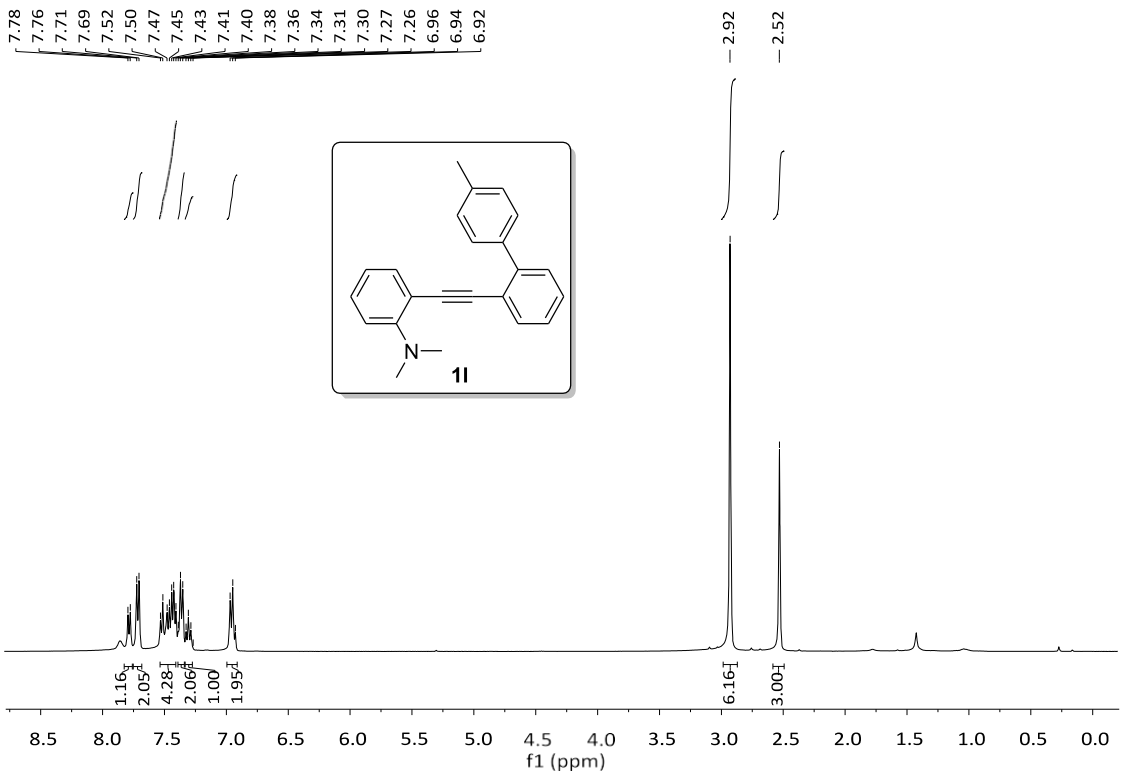
10
0
f1 (ppm)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7.34
7.31
7.30
7.27
7.26
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6.94
6.92
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1.95
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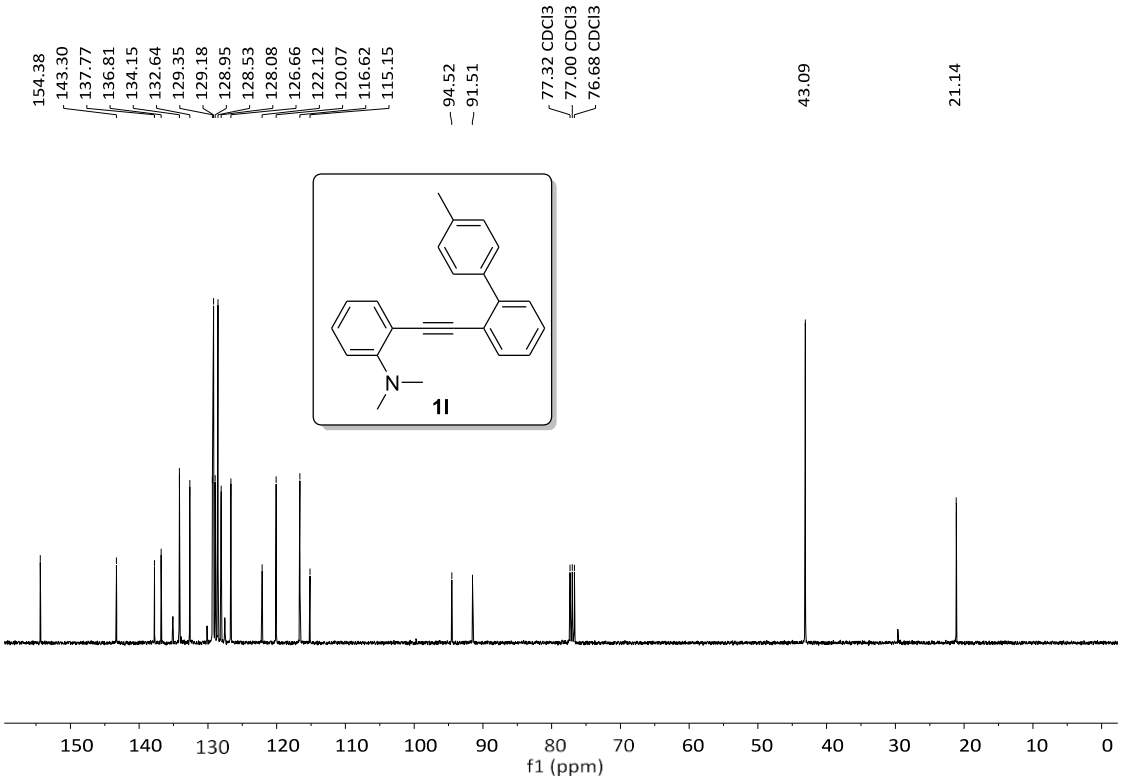
3.00
f1 (ppm)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91.51
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
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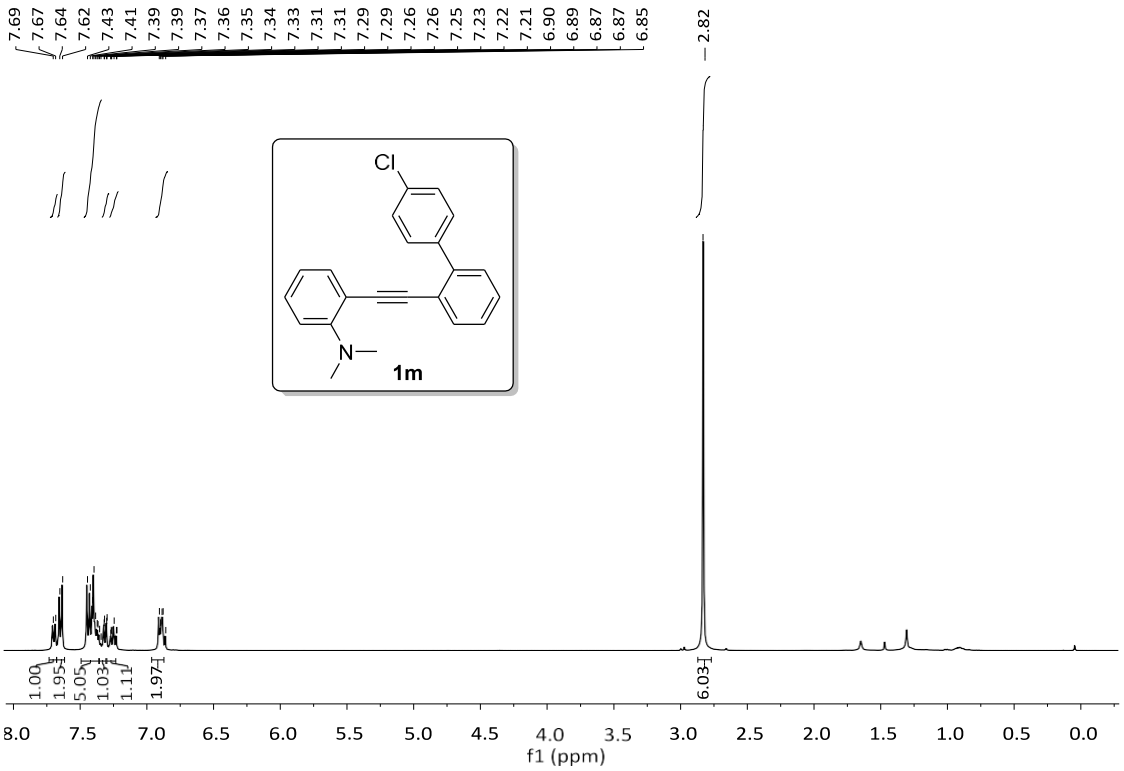
21.14
1l
f1 (ppm)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7.35
7.34
7.33
7.31
7.31
7.29
7.29
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7.26
7.25
7.23
7.22
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6.89
6.87
6.87
6.85
2.82
Cl
N
1m
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1.95
5.05
1.03
1.11
1.97
6.03
8.0
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7.0
6.5
6.0
5.5
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2.5
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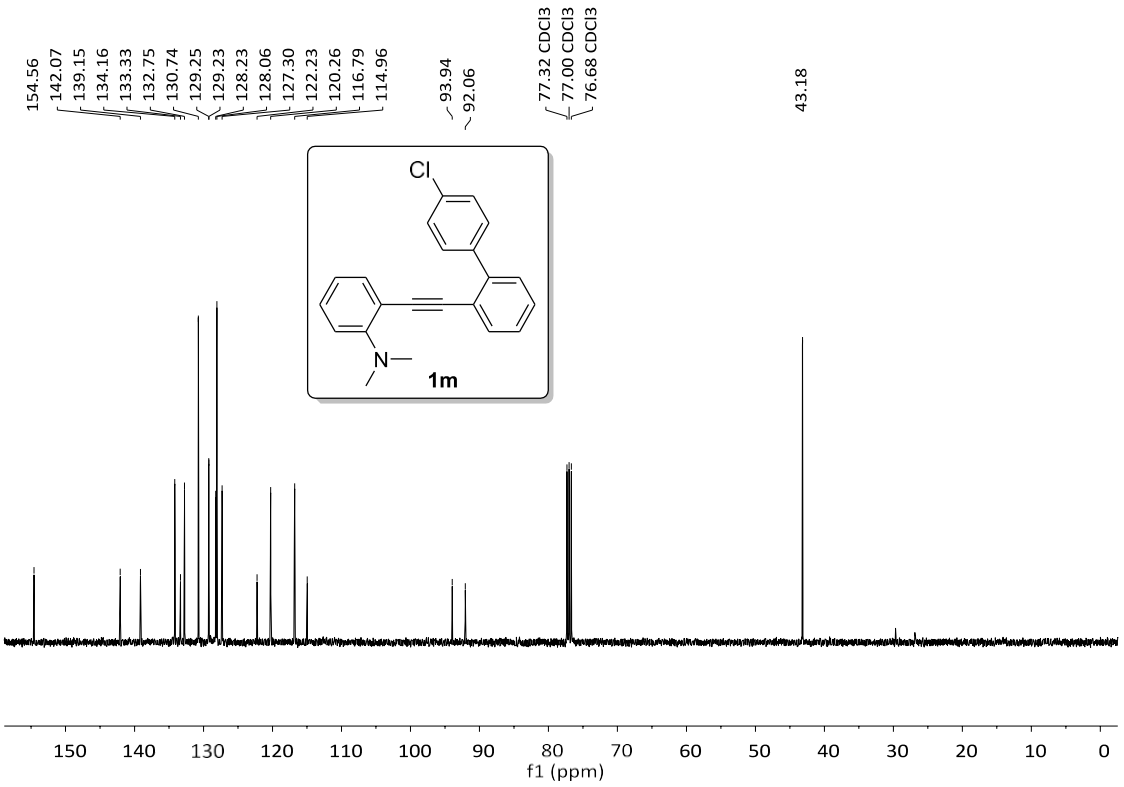
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116.79
114.96
93.94
92.06
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77.00 CDCl3
76.68 CDCl3
43.18
Cl
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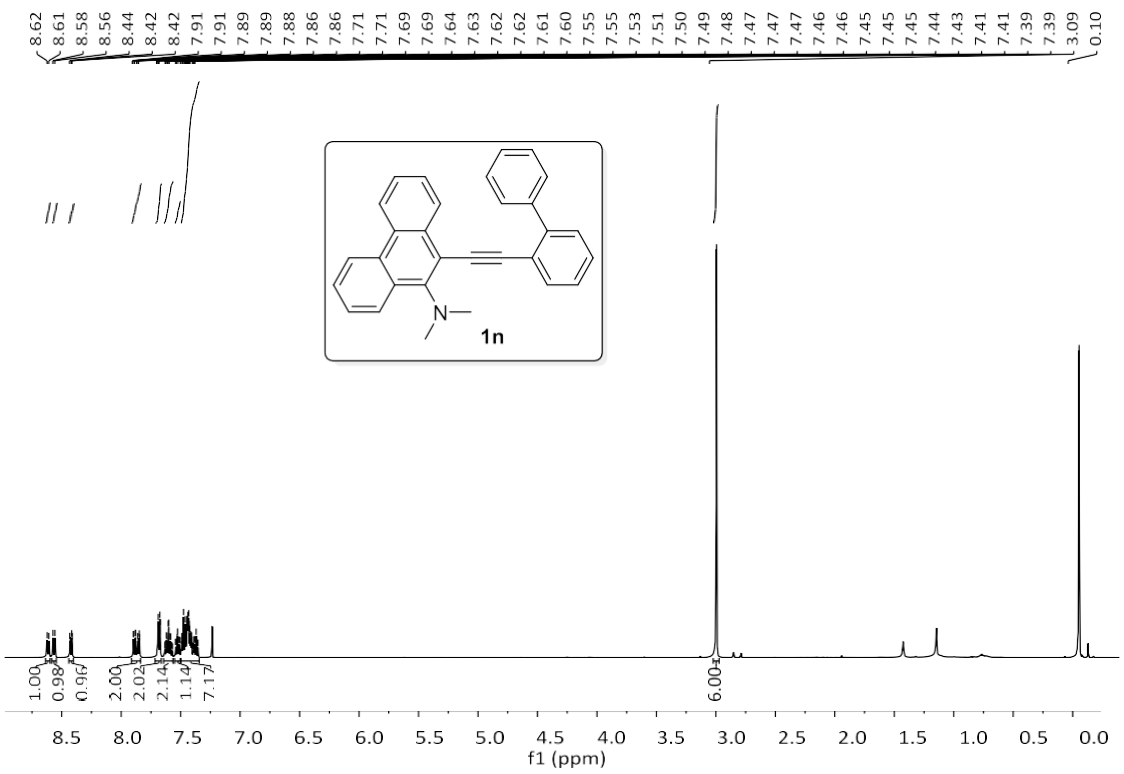
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7.69
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7.63
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7.45
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7.41
7.39
7.39
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1n
1.00
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2.00
2.02
2.14
1.14
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6.00
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6.5
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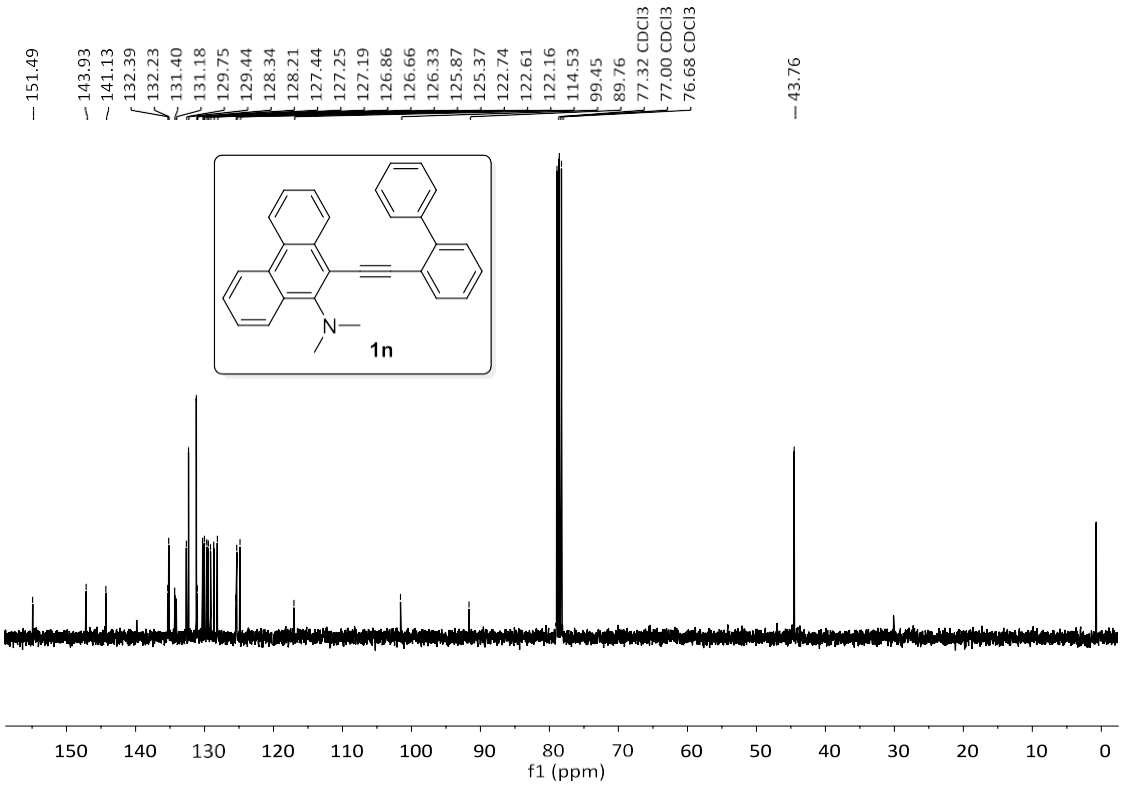
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127.19
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126.66
126.33
125.87
125.37
122.74
122.61
122.16
114.53
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89.76
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
43.76
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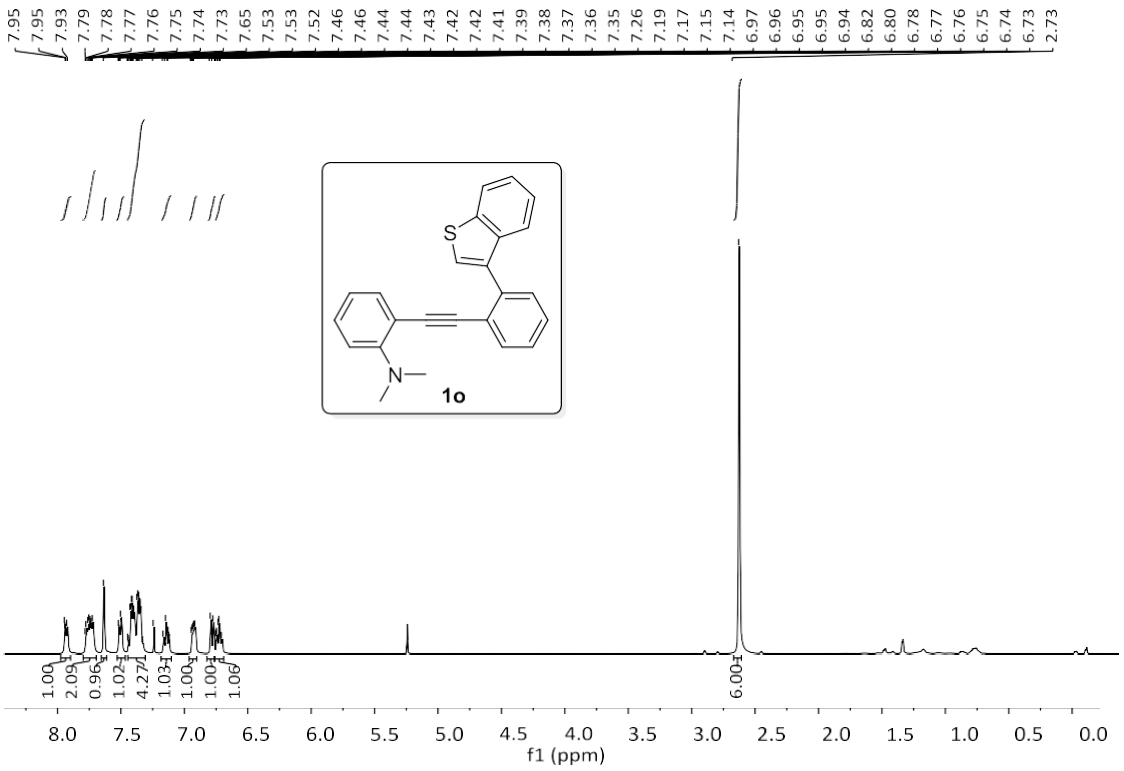
f1 (ppm)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S
N
1o
1.00 2.09 0.96 1.02 4.27 1.03 1.00 1.00 1.06 6.00
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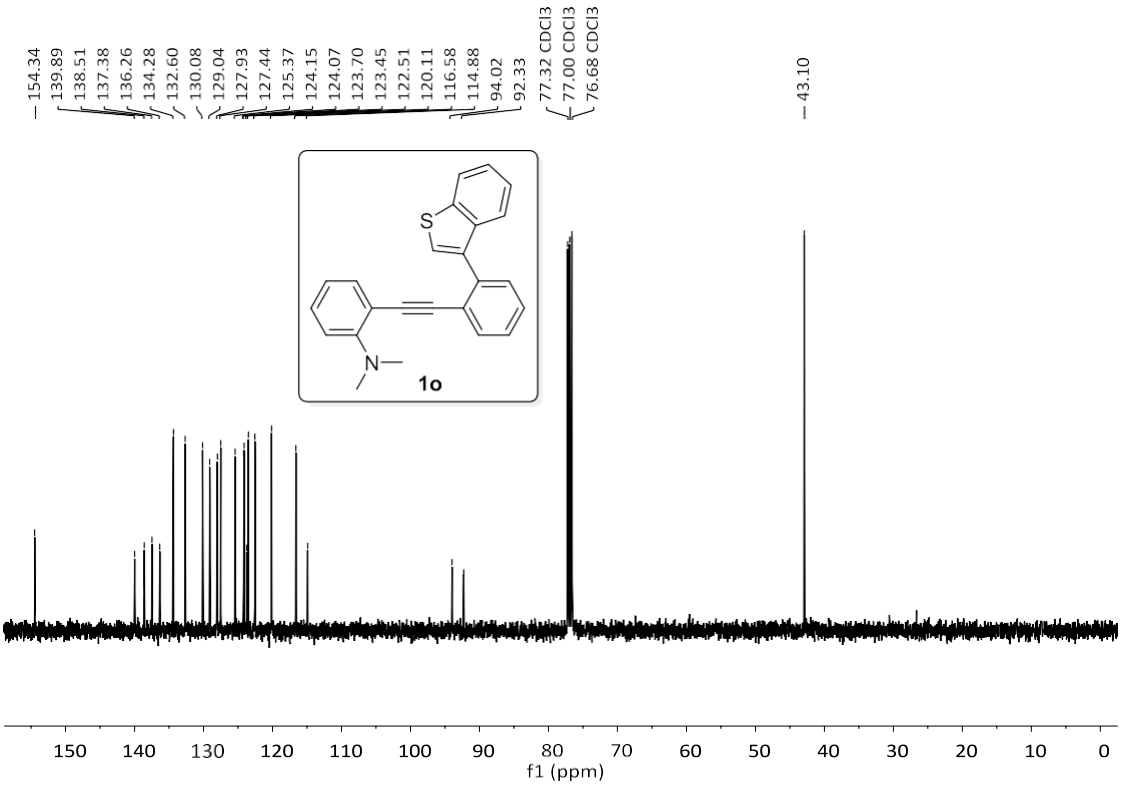
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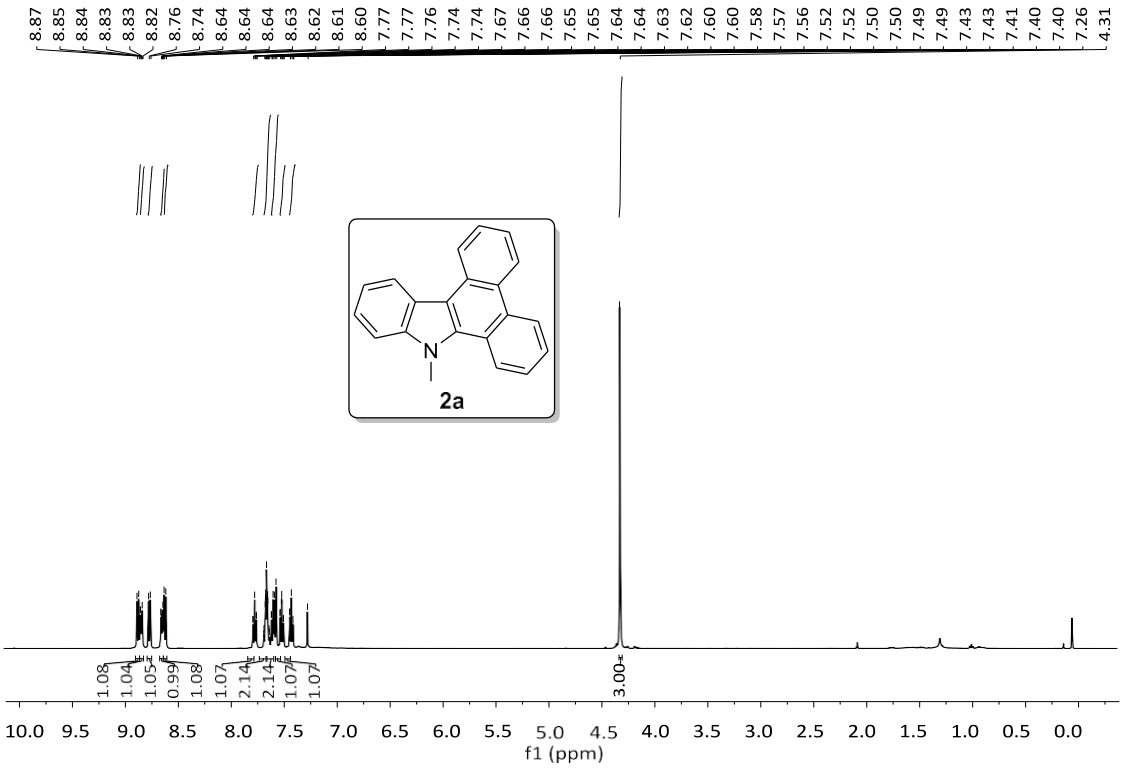
S
N
1o
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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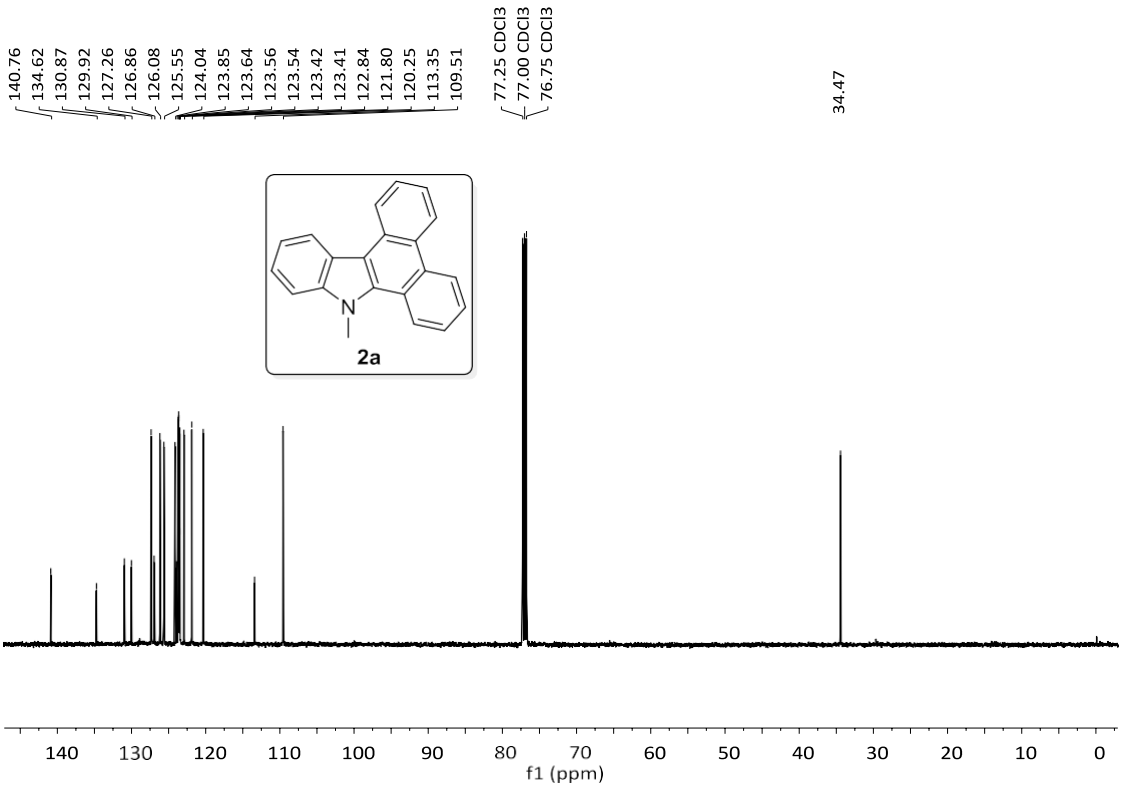
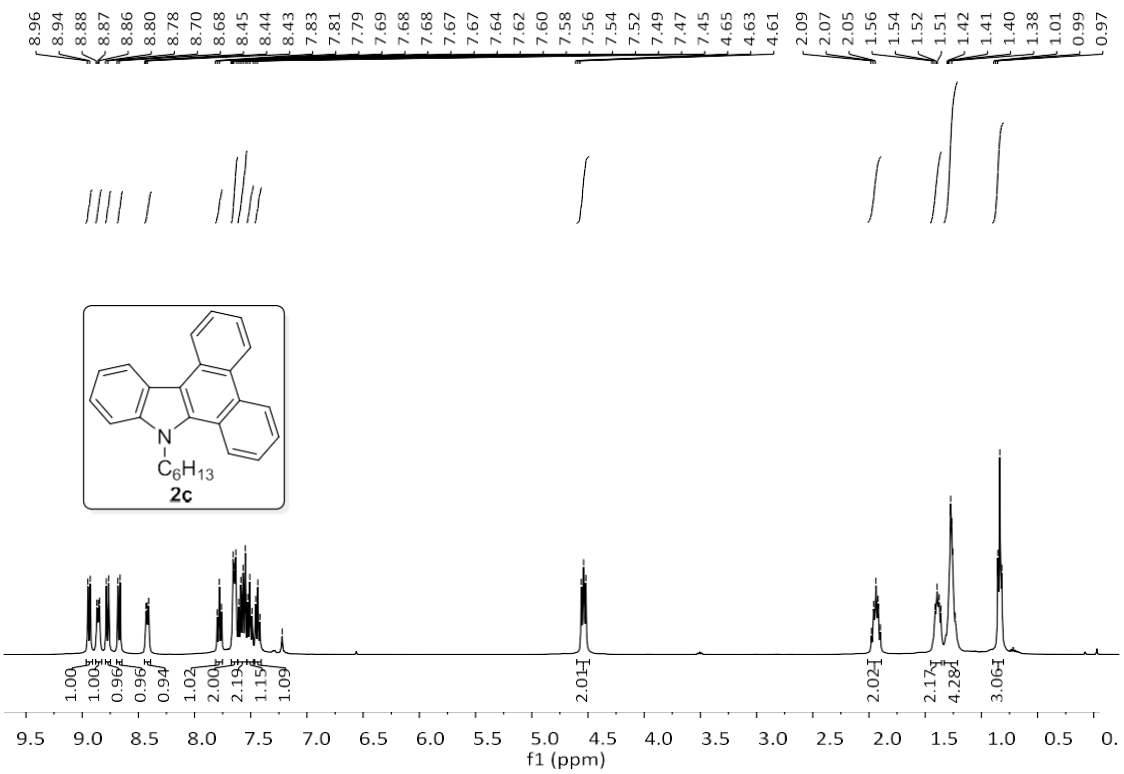
2a
1.08 1.04 1.05 0.99 1.08 1.07 2.14 2.14 1.07 1.07
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.76 134.62 130.87 129.92 127.26 126.86 126.08 125.55 124.04 123.85 123.64 123.56 123.54 123.42 123.41 122.84 121.80 120.25 113.35 109.51
77.25 CDCl3 77.00 CDCl3 76.75 CDCl3
34.47
2a
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.44
8.43
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7.79
7.69
7.68
7.68
7.67
7.67
7.64
7.62
7.60
7.58
7.56
7.54
7.52
7.49
7.47
7.45
4.65
4.63
4.61
2.09
2.07
2.05
1.56
1.54
1.52
1.51
1.42
1.41
1.40
1.38
1.01
0.99
0.97
N
C6H13
2c
1.00
1.00
0.96
0.96
0.94
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2.19
1.15
1.09
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2.02
2.17
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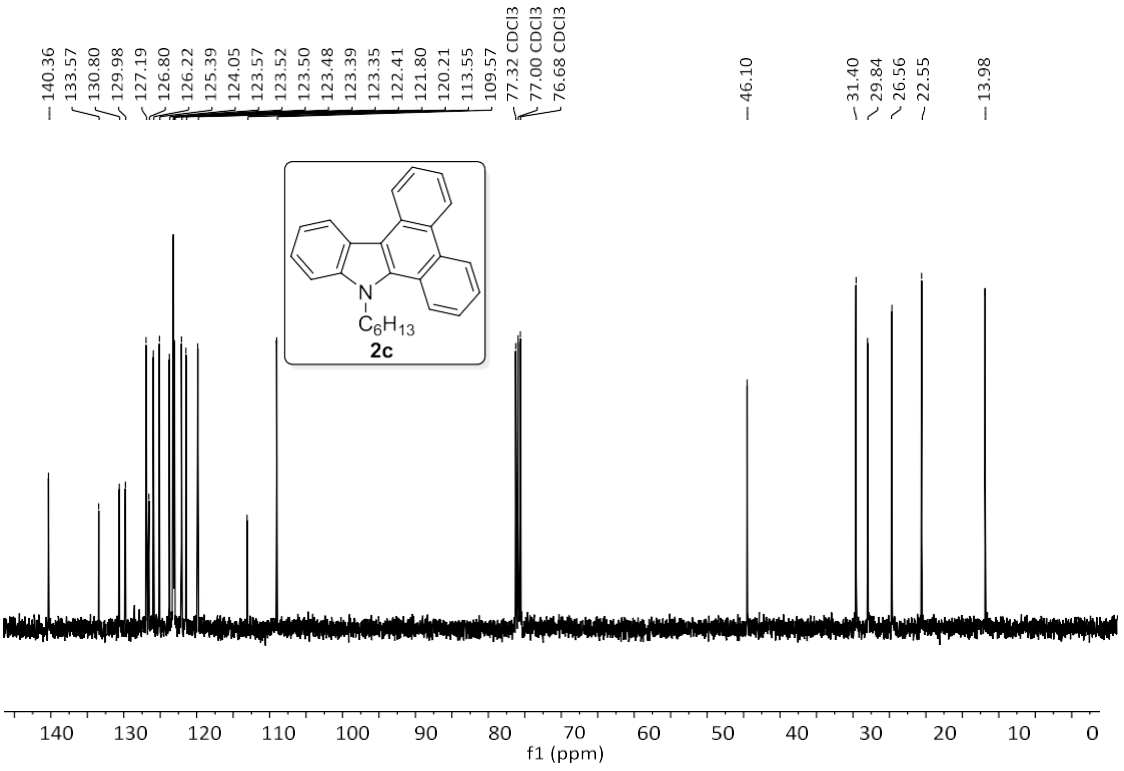
3.06
f1 (ppm)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123.39
123.35
122.41
121.80
120.21
113.55
109.57
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
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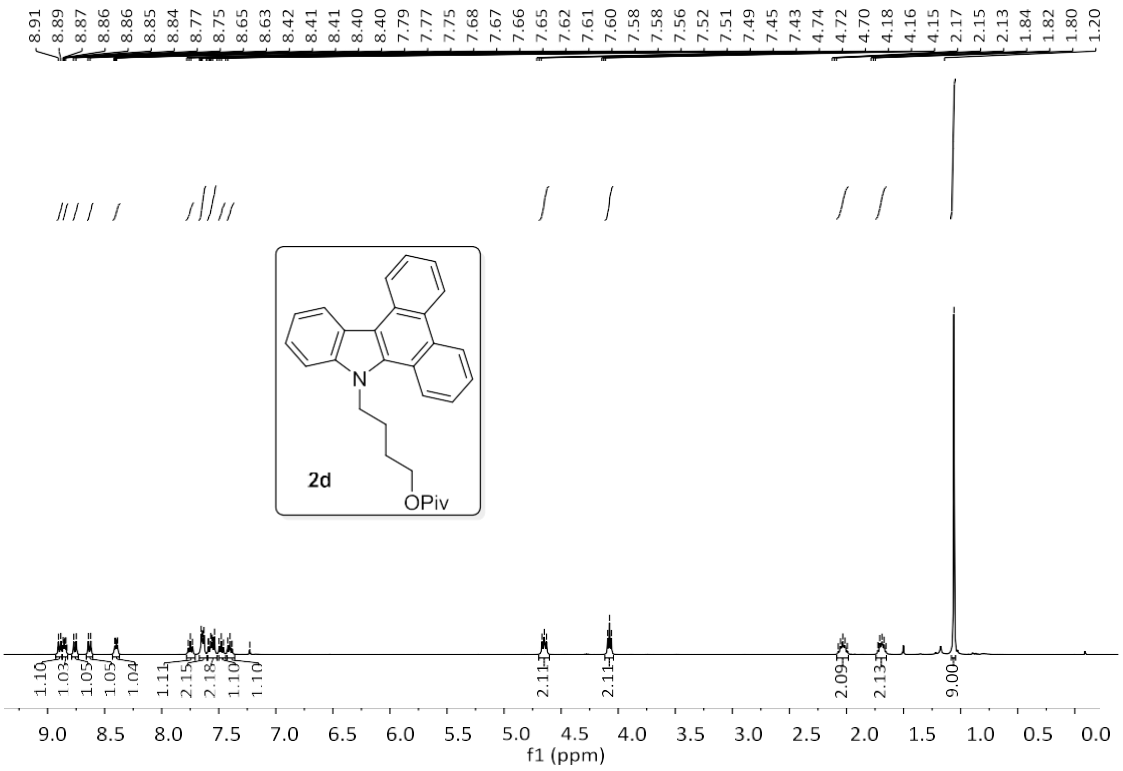
26.56
22.55
13.98
N
C6H13
2c
f1 (ppm)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2d
OPiv
1.10 1.03 1.05 1.05 1.04 1.11 2.15 2.18 1.10 1.10 2.11 2.11 2.09 2.13 9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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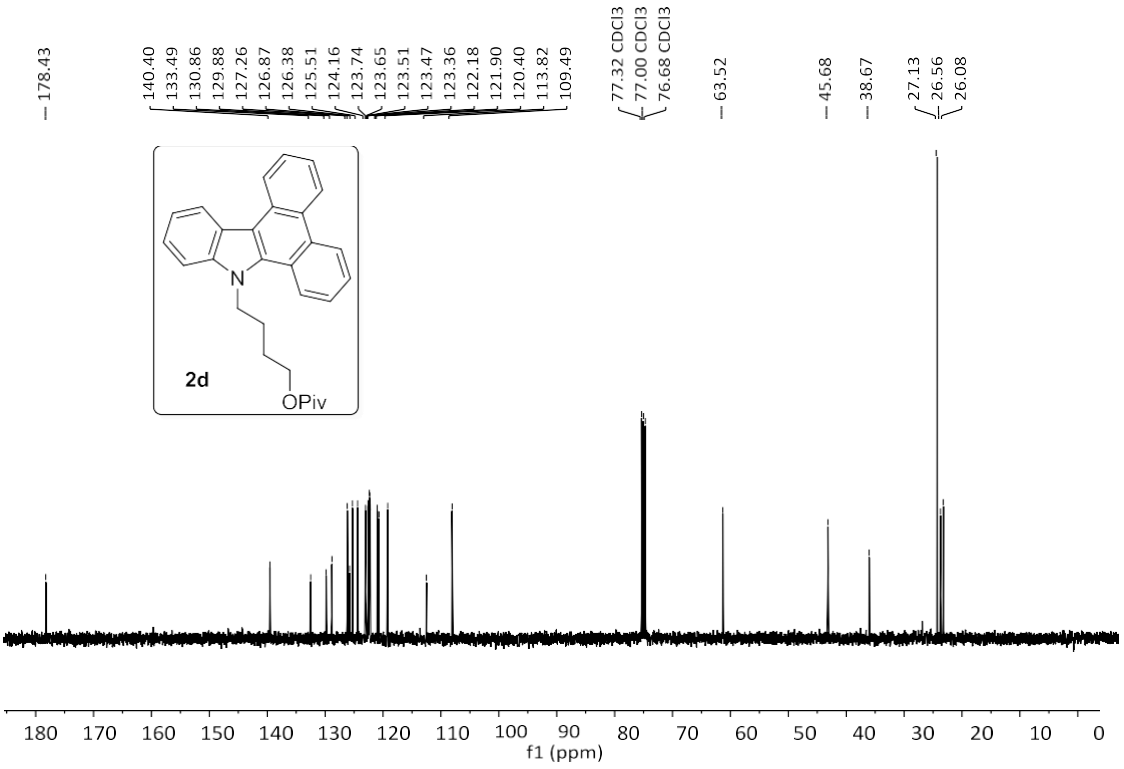
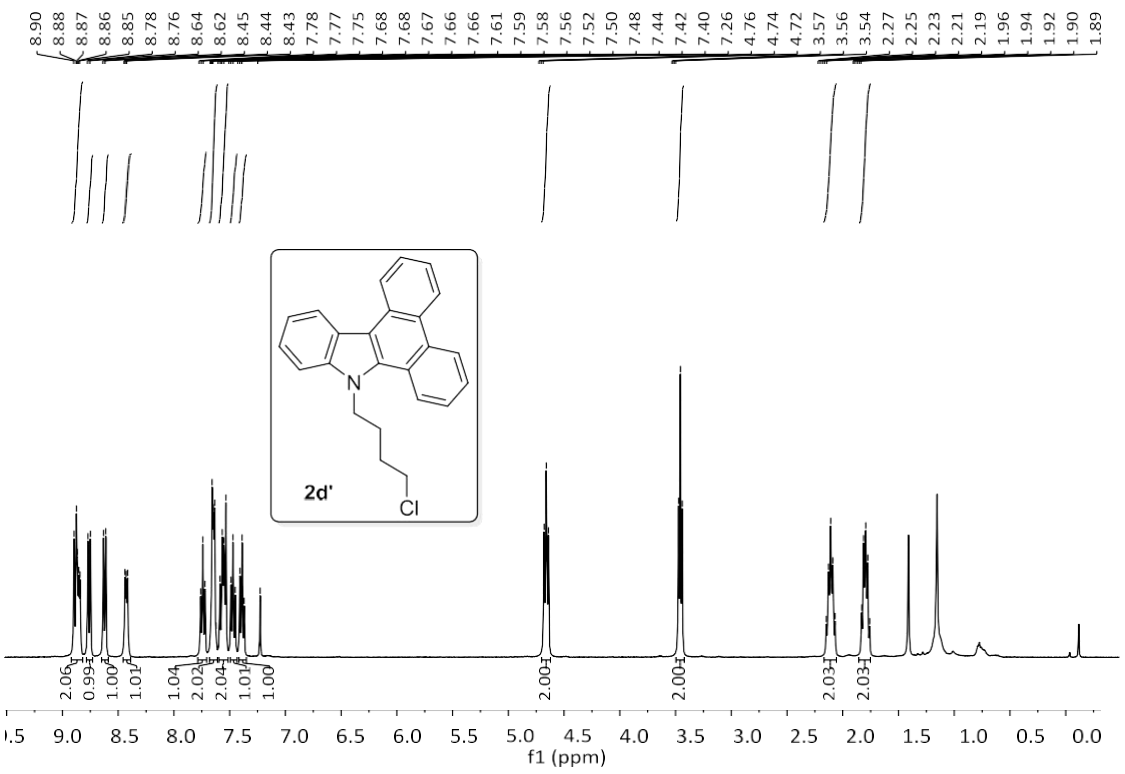

178.43
140.40 133.49 130.86 129.88 127.26 126.87 126.38 125.51 124.16 123.74 123.65 123.51 123.47 123.36 122.18 121.90 120.40 113.82 109.49
77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
63.52
45.68
38.67
27.13 26.56 26.08
2d
OPiv
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.56
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2.25
2.23
2.21
2.19
1.96
1.94
1.92
1.90
1.89
N
Cl
2d'
2.06
0.99
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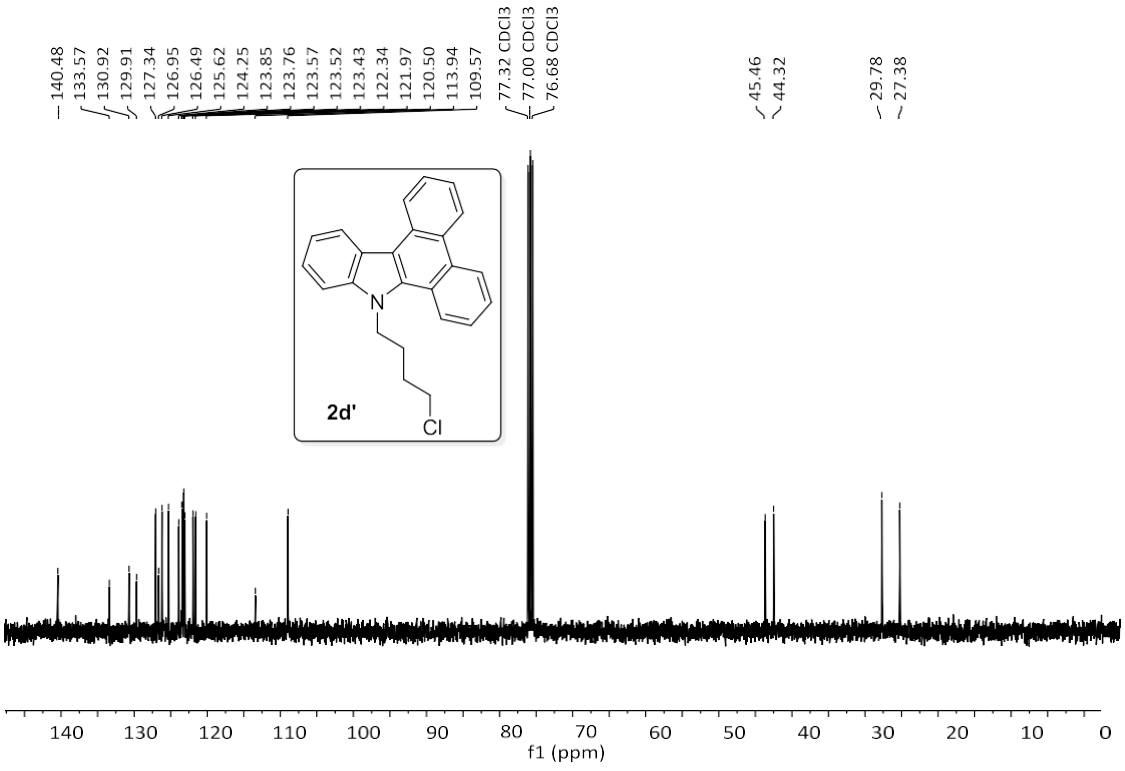
1.01
1.04
2.02
2.04
1.01
1.00
2.00
2.00
2.03
2.03
f1 (ppm)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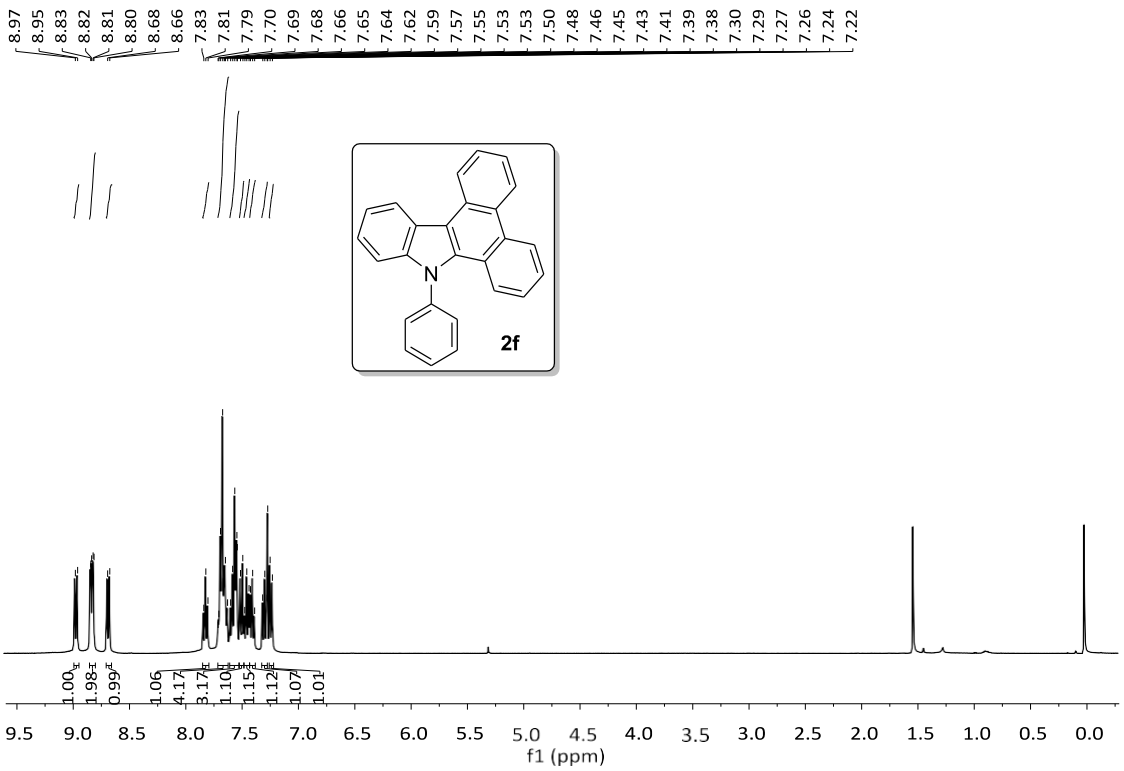
123.52
123.43
122.34
121.97
120.50
113.94
109.57
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
45.46
44.32
29.78
27.38
N
Cl
2d'
f1 (ppm)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7.43
7.41
7.39
7.38
7.30
7.29
7.27
7.26
7.24
7.22
2f
1.00
1.98
0.99
1.06
4.17
3.17
1.10
1.15
1.12
1.07
1.01
9.5 9.0 8.5 8.0 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
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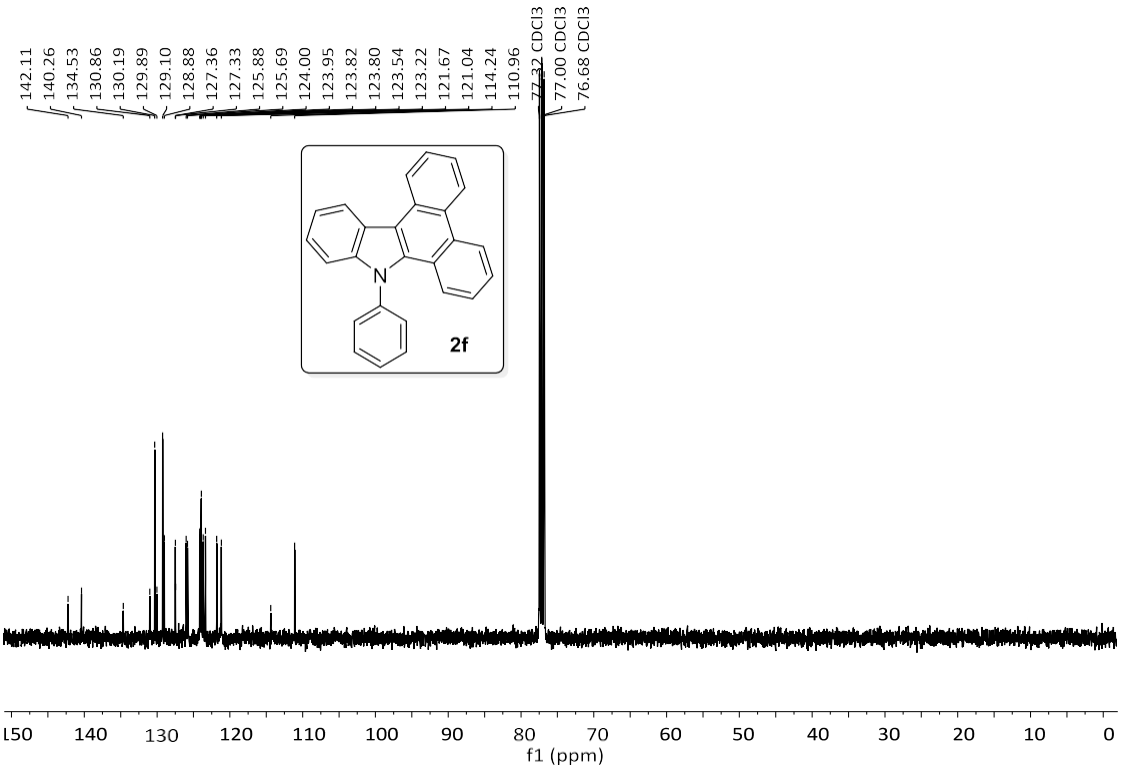
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125.88
125.69
124.00
123.95
123.82
123.80
123.54
123.22
121.67
121.04
114.24
110.96
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
2f
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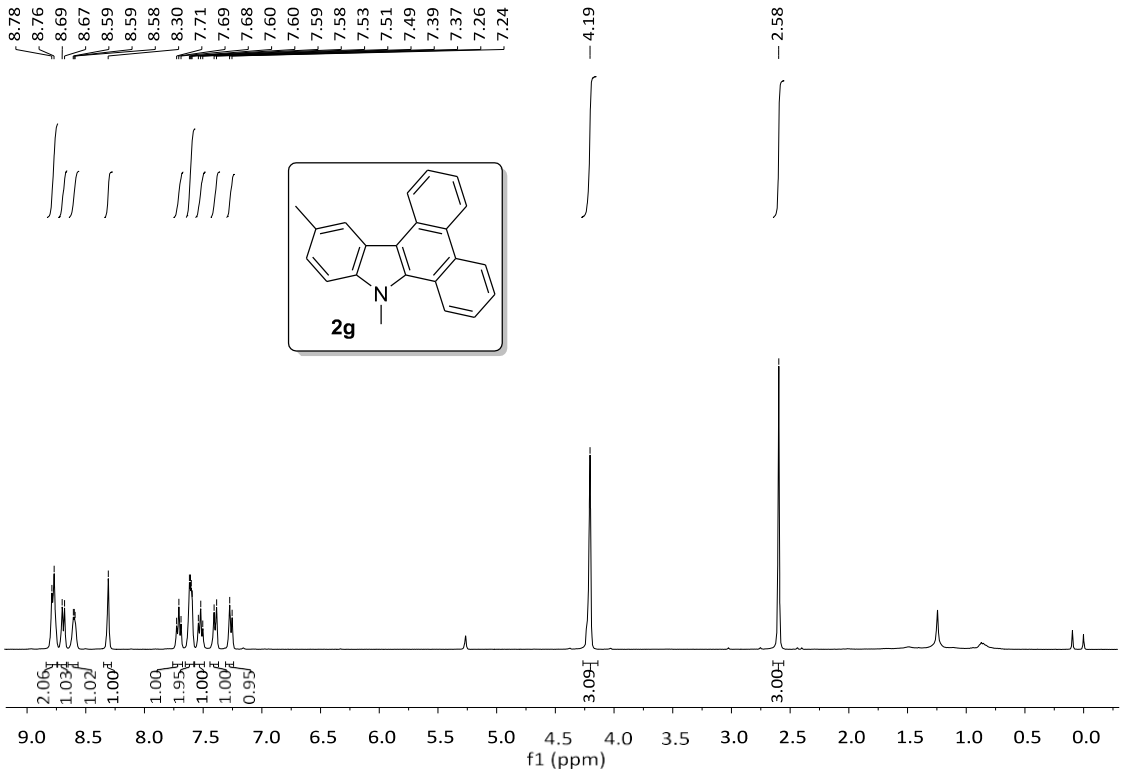
f1 (ppm)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7.60
7.60
7.59
7.58
7.53
7.51
7.49
7.39
7.37
7.26
7.24
4.19
2.58
2g
2.06
1.03
1.02
1.00
1.00
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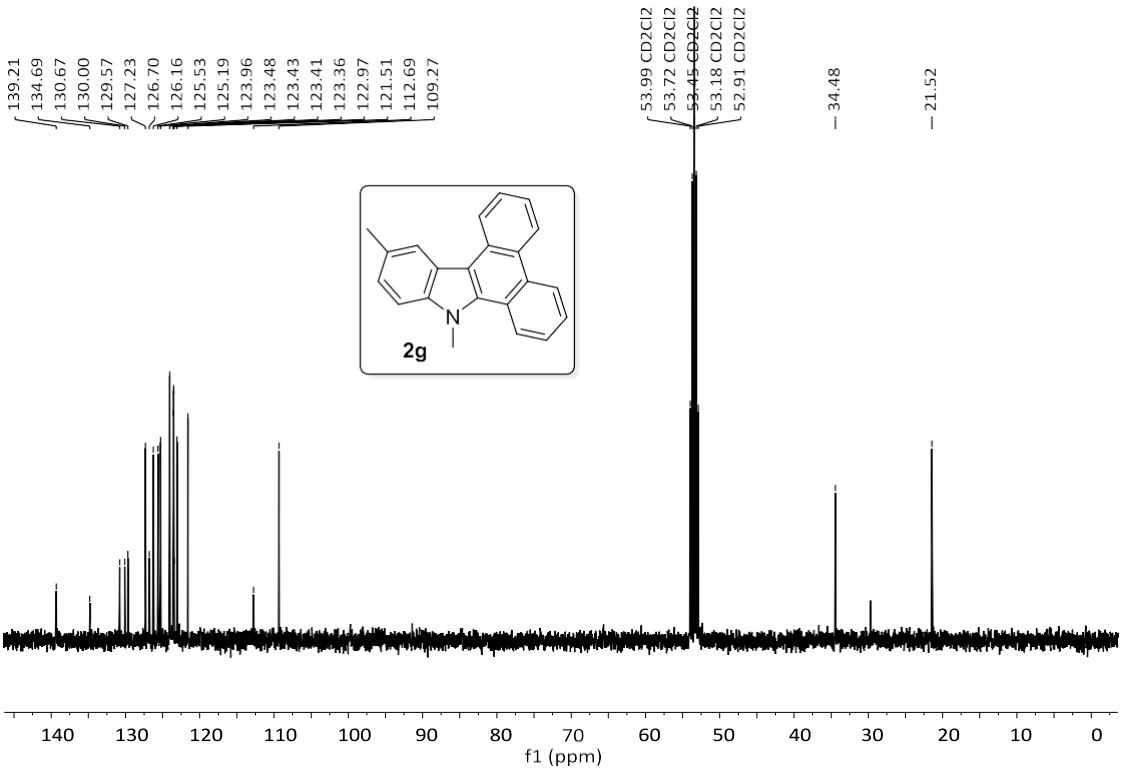
1.00
1.00
0.95
3.09
3.00
f1 (ppm)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123.43
123.41
123.36
122.97
121.51
112.69
109.27
53.99 CD2Cl2
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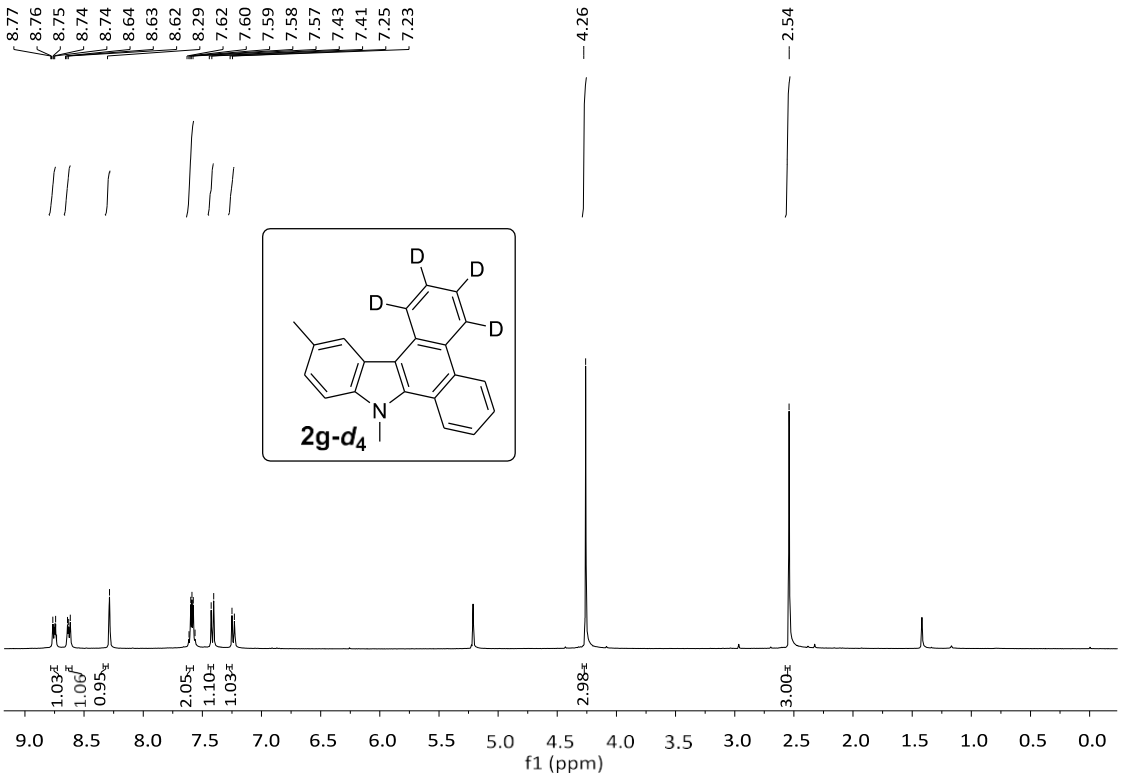
52.91 CD2Cl2
34.48
21.52
2g
f1 (ppm)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7.59
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7.43
7.41
7.25
7.23
4.26
2.54
D
D
D
D
N
2g-d_4
1.03
1.06
0.95
2.05
1.10
1.03
2.98
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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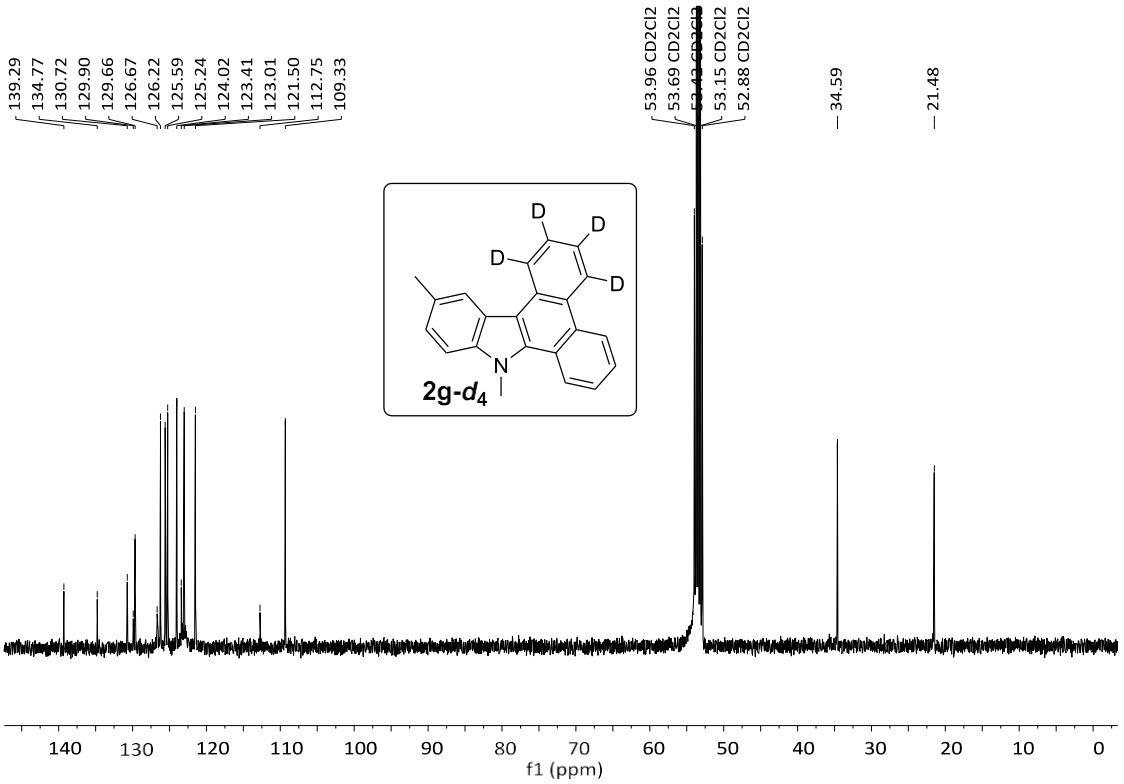
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123.01
121.50
112.75
109.33
53.96 CD2Cl2
53.69 CD2Cl2
53.42 CD2Cl2
53.15 CD2Cl2
52.88 CD2Cl2
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D
D
D
D
N
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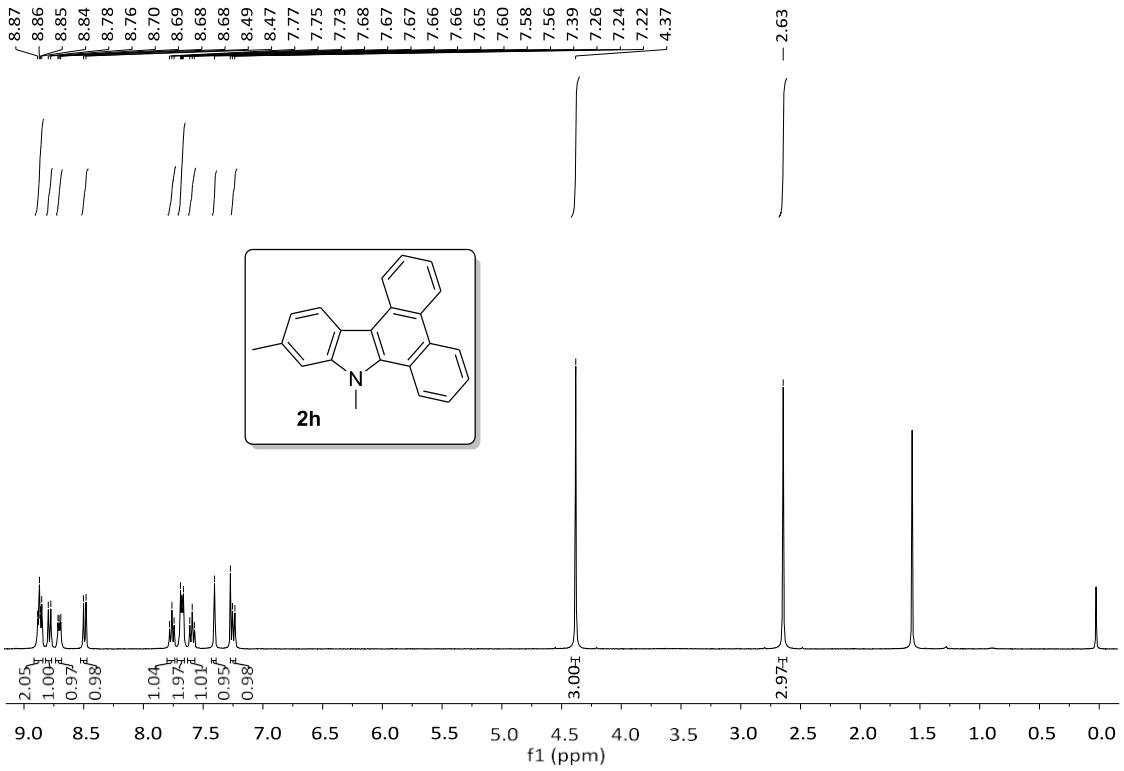
f1 (ppm)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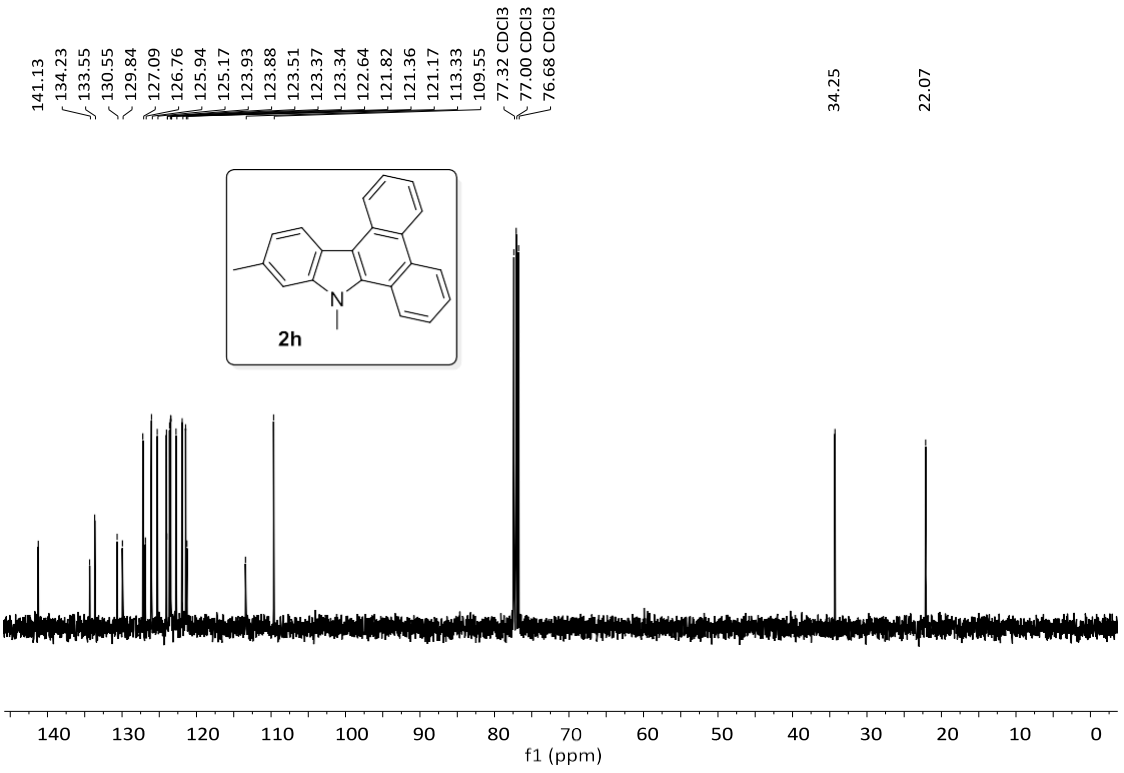
7.24
7.22
4.37
2.63
2h
2.05
1.00
0.97
0.98
1.04
1.97
1.01
0.95
0.98
3.00
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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123.88
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123.37
123.34
122.64
121.82
121.36
121.17
113.33
109.55
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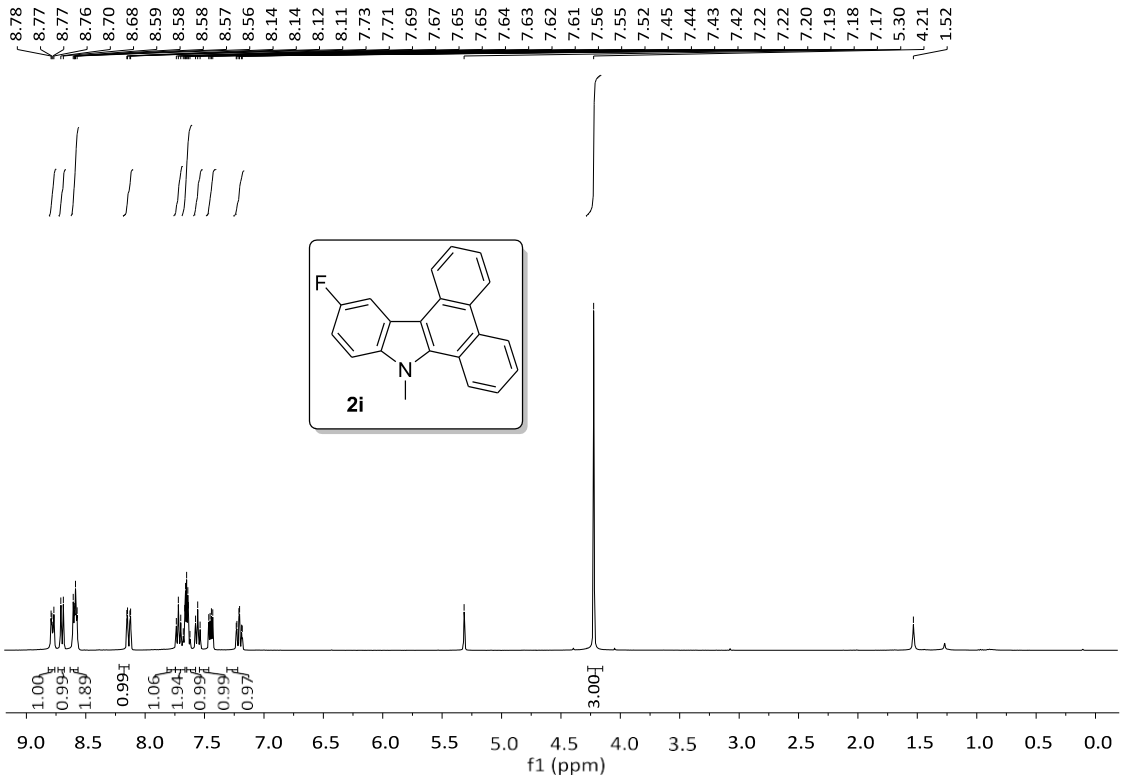
76.68 CDCl3
34.25
22.07
2h
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.18
7.17
5.30
4.21
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F
N
2i
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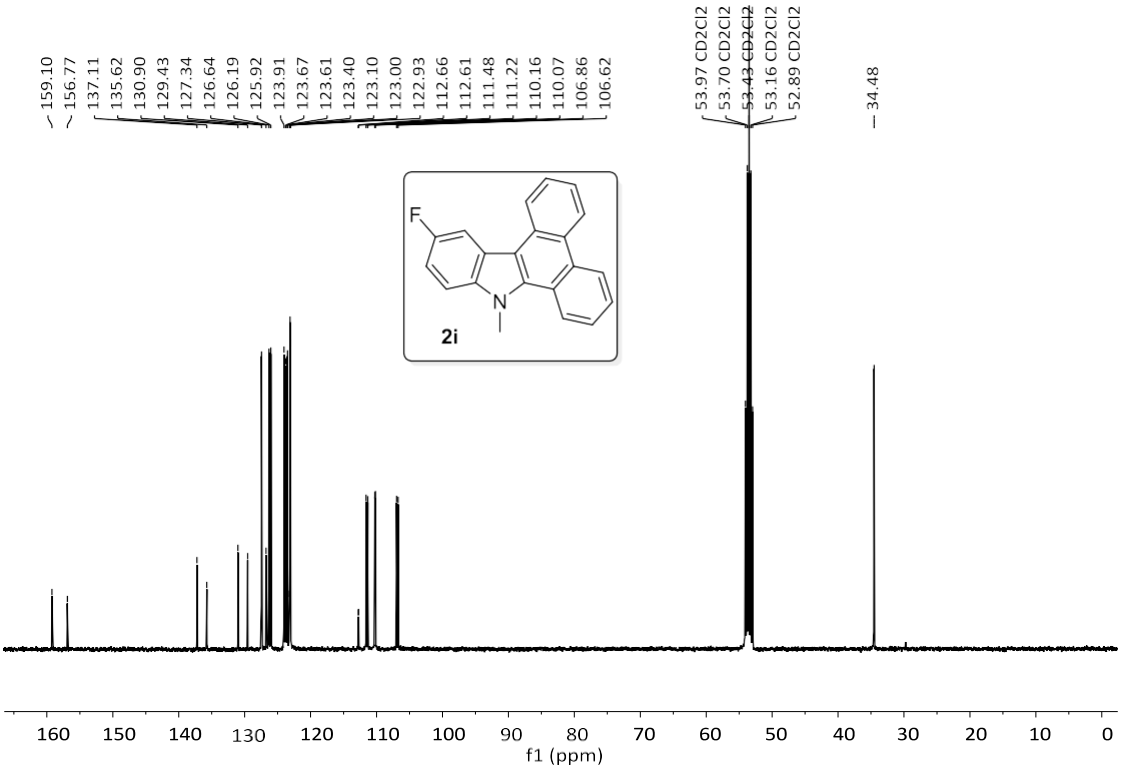
0.99
1.89
0.99
1.06
1.94
0.99
0.99
0.97
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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106.62
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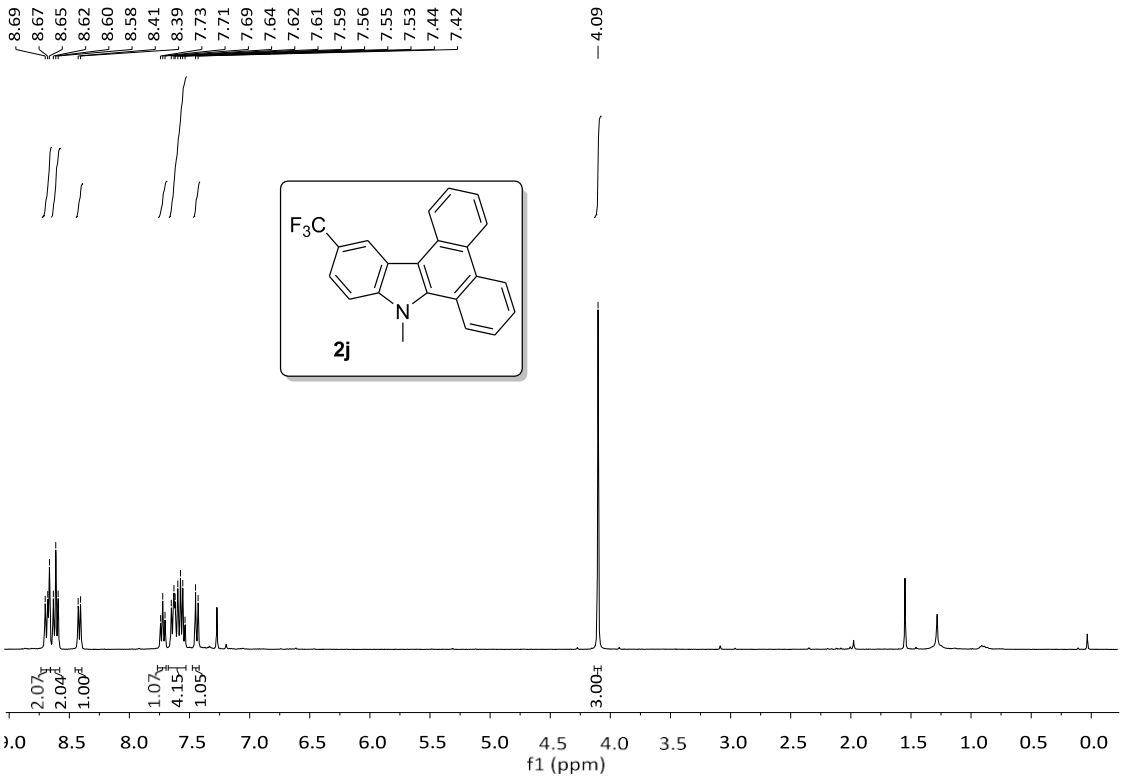
53.70 CD2Cl2
53.43 CD2Cl2
53.16 CD2Cl2
52.89 CD2Cl2
34.48
F
N
2i
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.61
7.59
7.56
7.55
7.53
7.44
7.42
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F3C
N
2j
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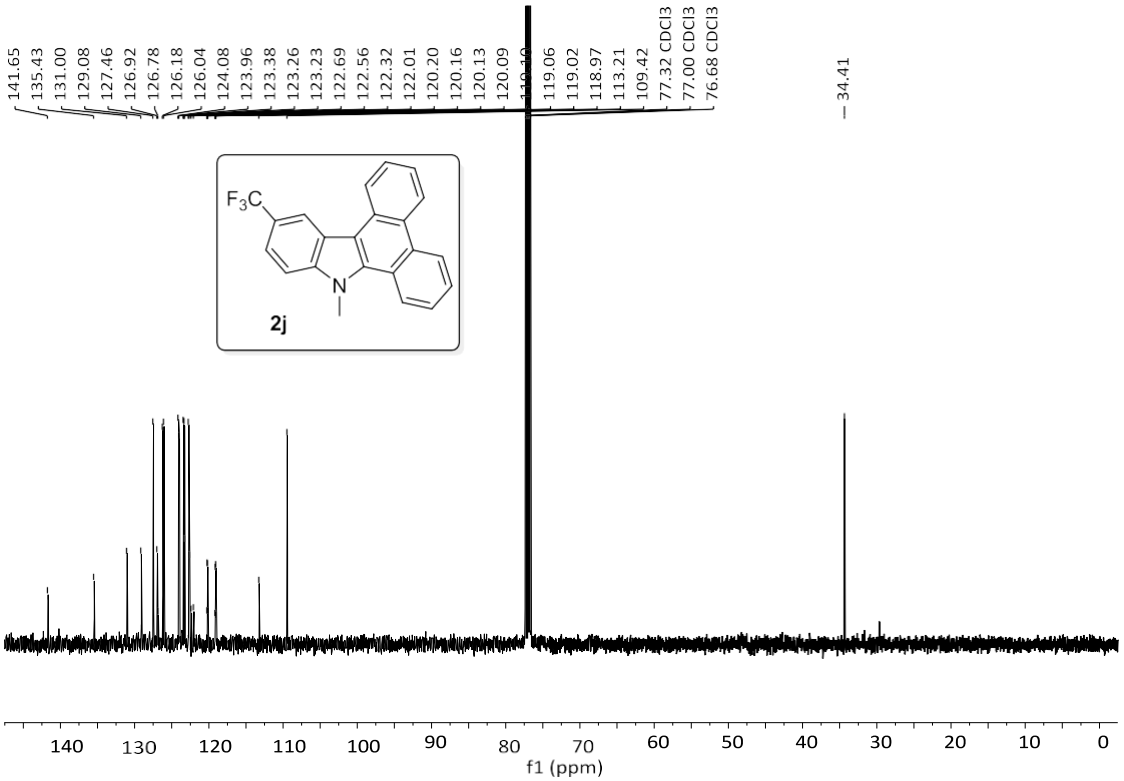
2.04
1.00
1.07
4.15
1.05
3.00
f1 (ppm)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124.08
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123.26
123.23
122.69
122.56
122.32
122.01
120.20
120.16
120.13
120.09
119.06
119.02
118.97
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77.32 CDCl3
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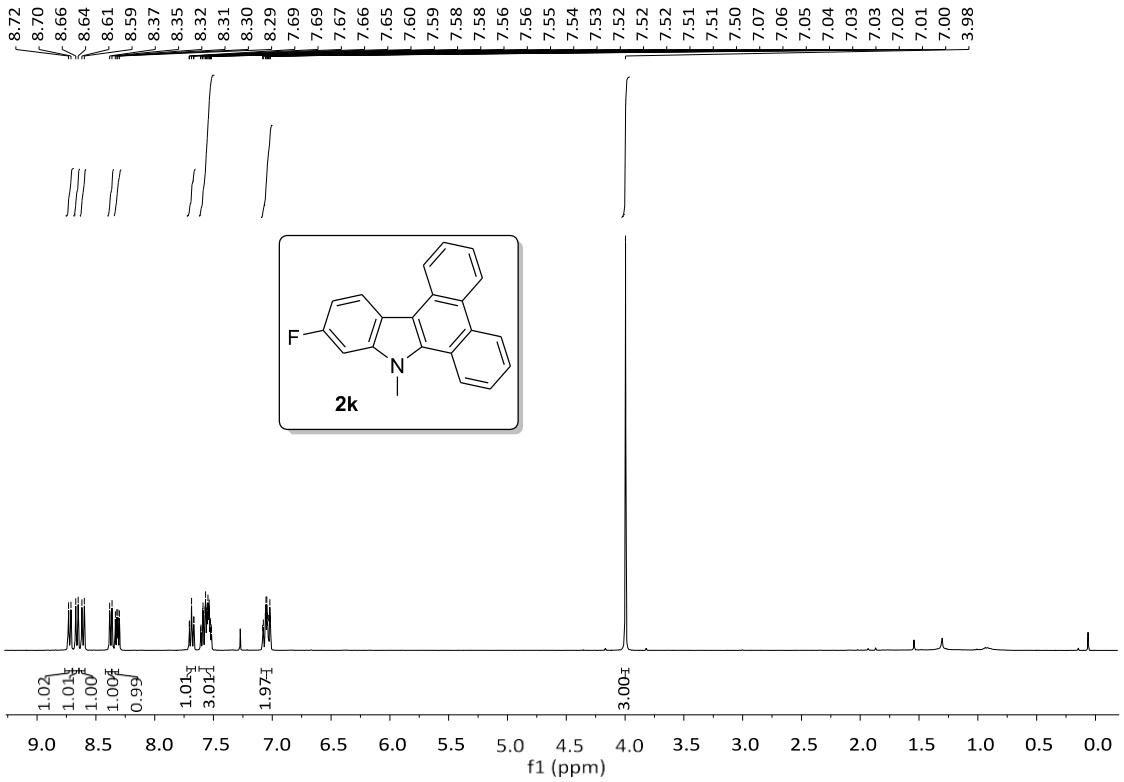
76.68 CDCl3
34.41
F3C
N
2j
f1 (ppm)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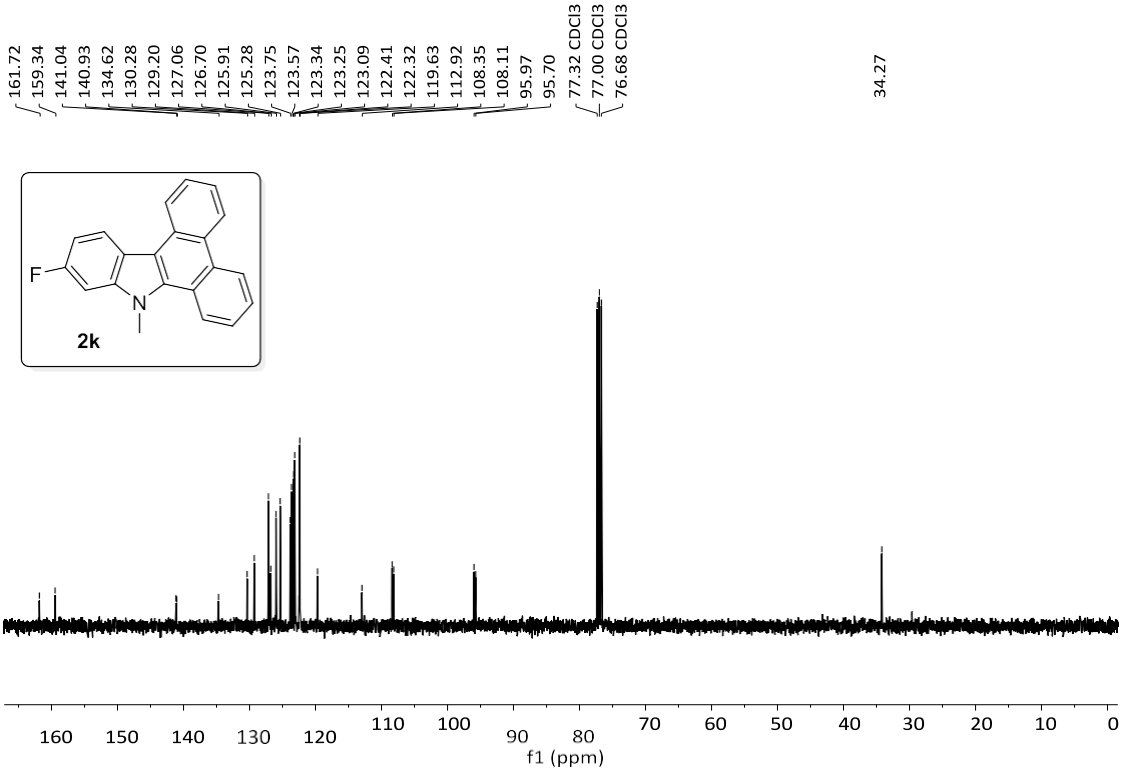
F
N
2k
1.02 1.01 1.00 1.00 0.99 1.01 3.01 1.97 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.72 159.34 141.04 140.93 134.62 130.28 129.20 127.06 126.70 125.91 125.28 123.75 123.57 123.34 123.25 123.09 122.41 122.32 119.63 112.92 108.35 108.11 95.97 95.70
77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
34.27
F
N
2k
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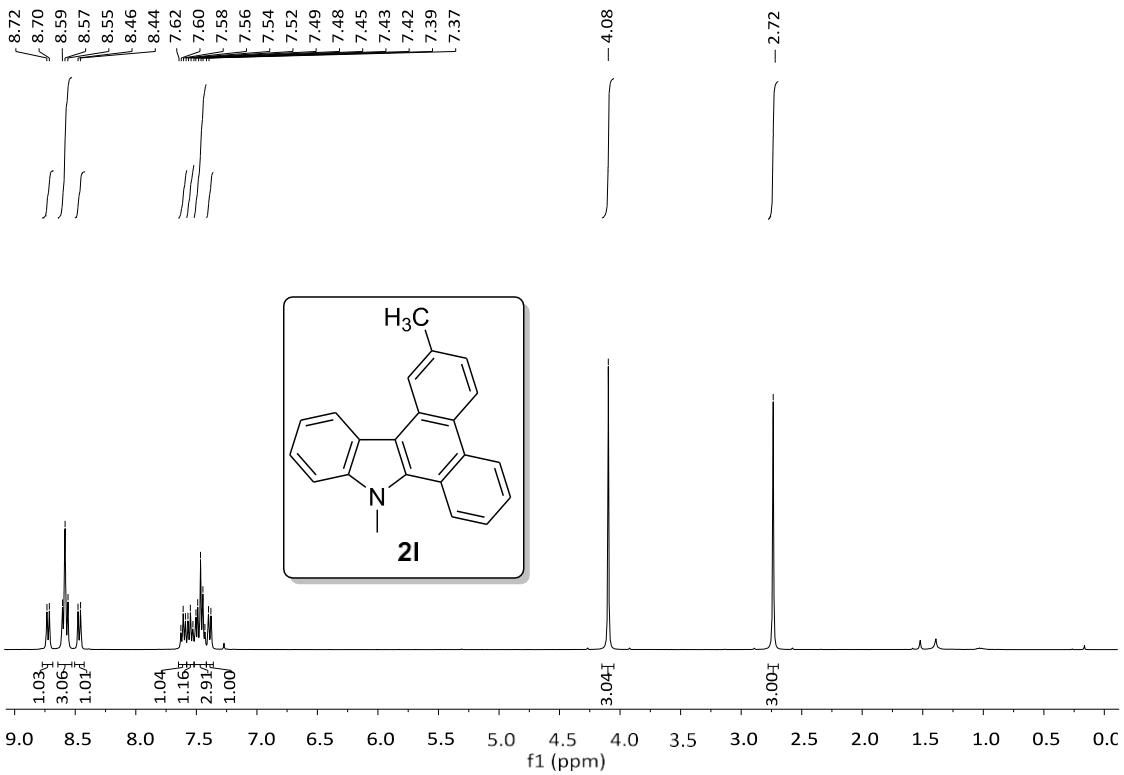
f1 (ppm)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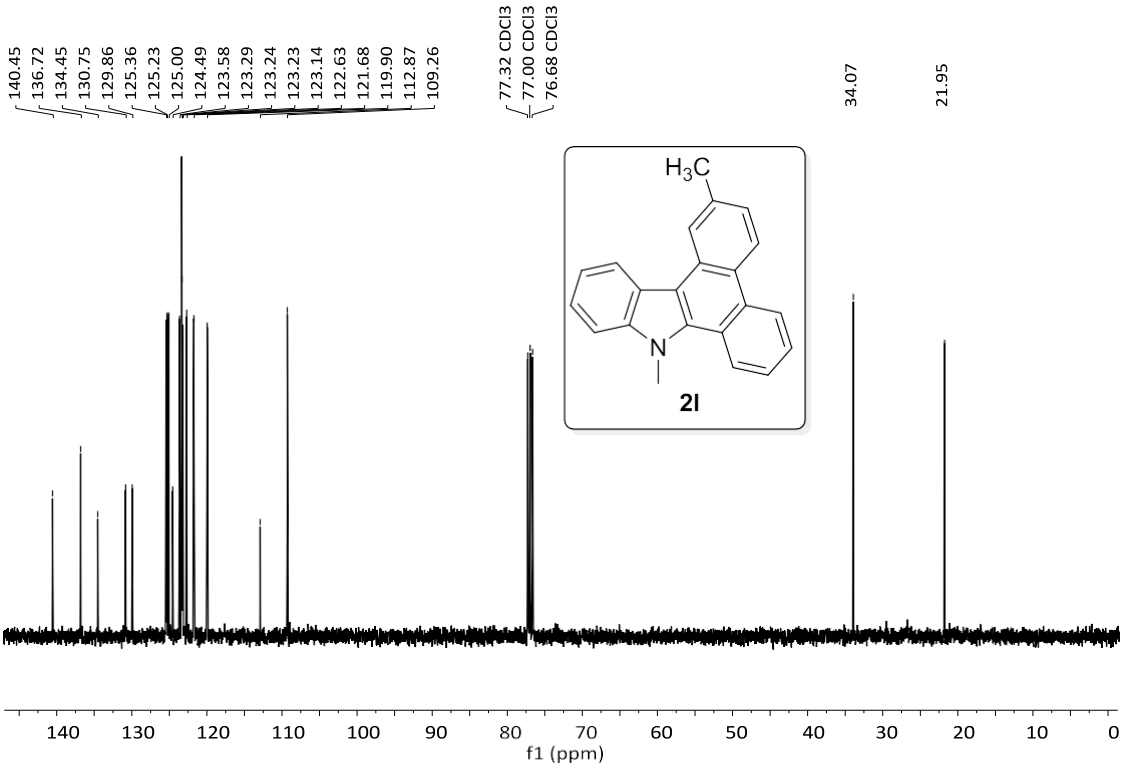
8.46
8.44
7.62
7.60
7.58
7.56
7.54
7.52
7.49
7.48
7.45
7.43
7.42
7.39
7.37
4.08
2.72
H3C
N
2l
1.03
3.06
1.01
1.04
1.16
2.91
1.00
3.04
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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123.58
123.29
123.24
123.23
123.14
122.63
121.68
119.90
112.87
109.26
77.32 CDCl3
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34.07
21.95
H3C
N
2l
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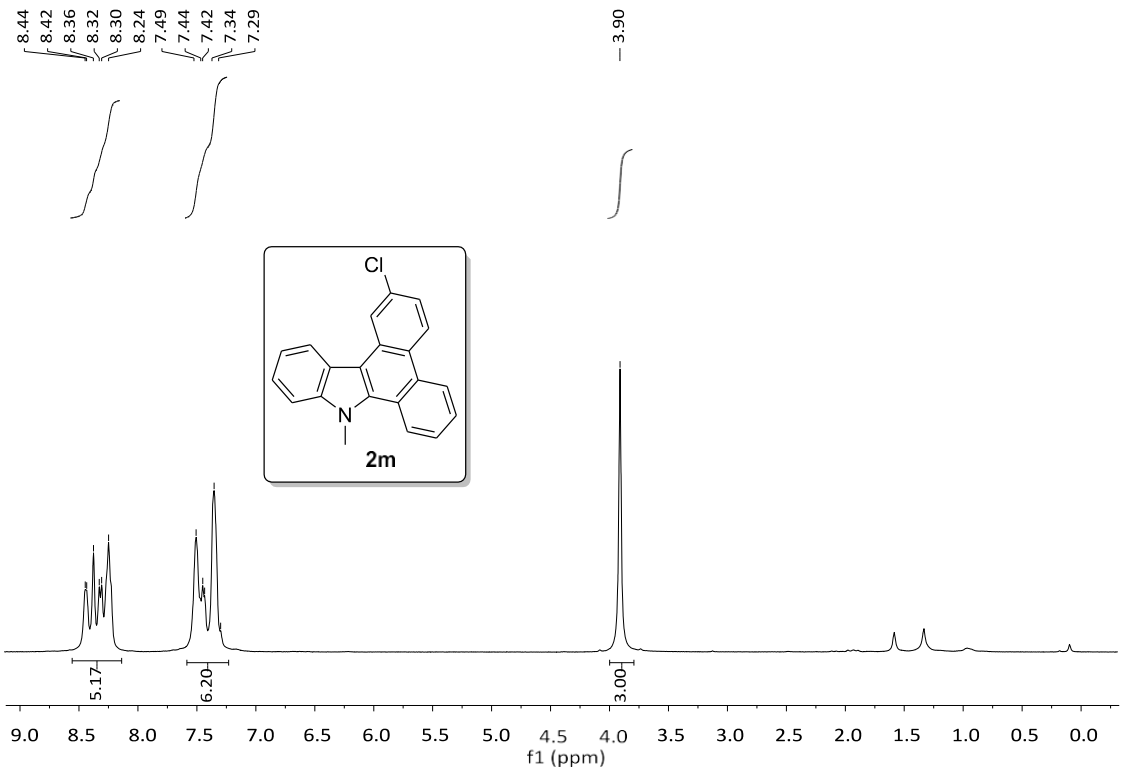
f1 (ppm)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8.36
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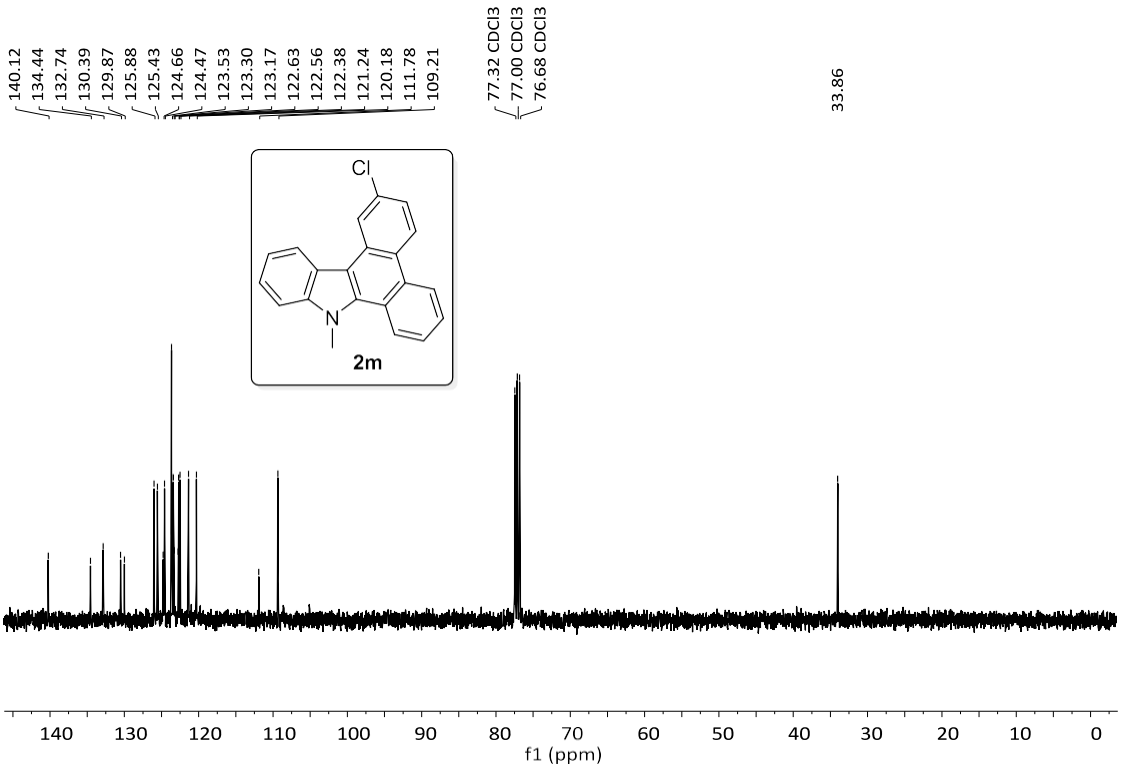
8.24
7.49
7.44
7.42
7.34
7.29
3.90
Cl
N
2m
5.17
6.20
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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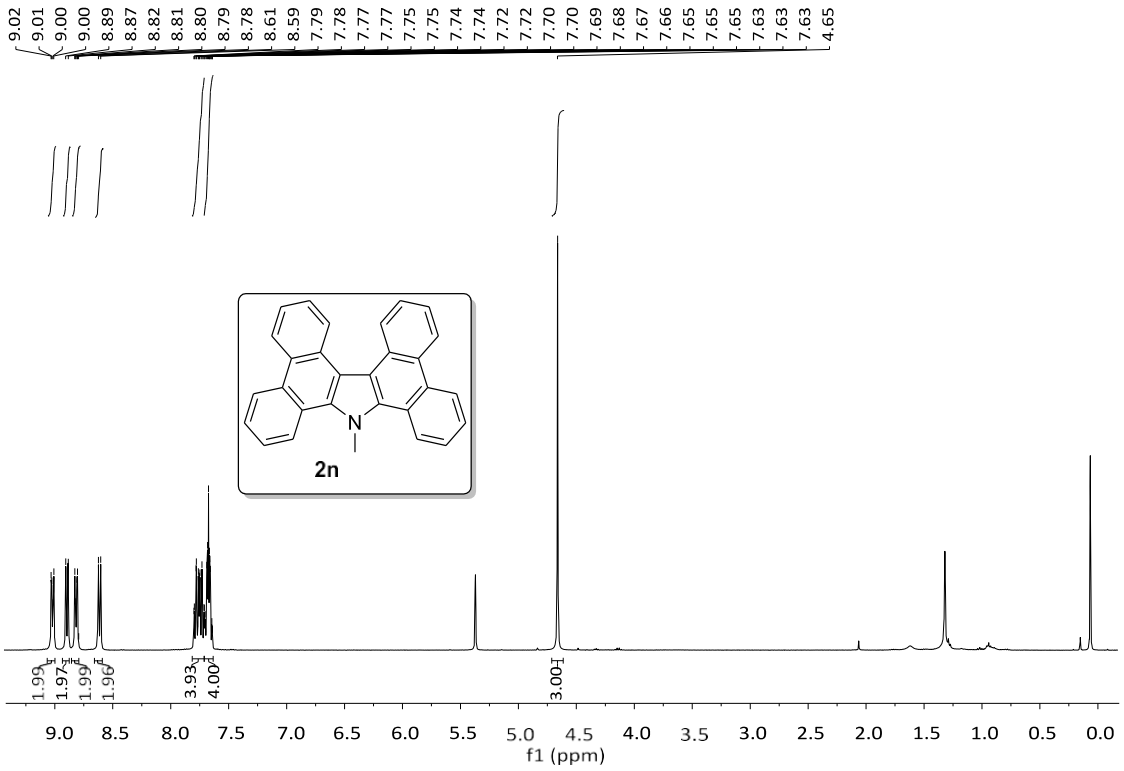
132.74
130.39
129.87
125.88
125.43
124.66
124.47
123.53
123.30
123.17
122.63
122.56
122.38
121.24
120.18
111.78
109.21
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
33.86
Cl
N
2m
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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9.00
9.00
8.89
8.87
8.82
8.81
8.80
8.79
8.78
8.61
8.59
7.79
7.78
7.77
7.77
7.75
7.75
7.74
7.74
7.72
7.72
7.70
7.70
7.69
7.68
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7.66
7.65
7.65
7.65
7.63
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7.63
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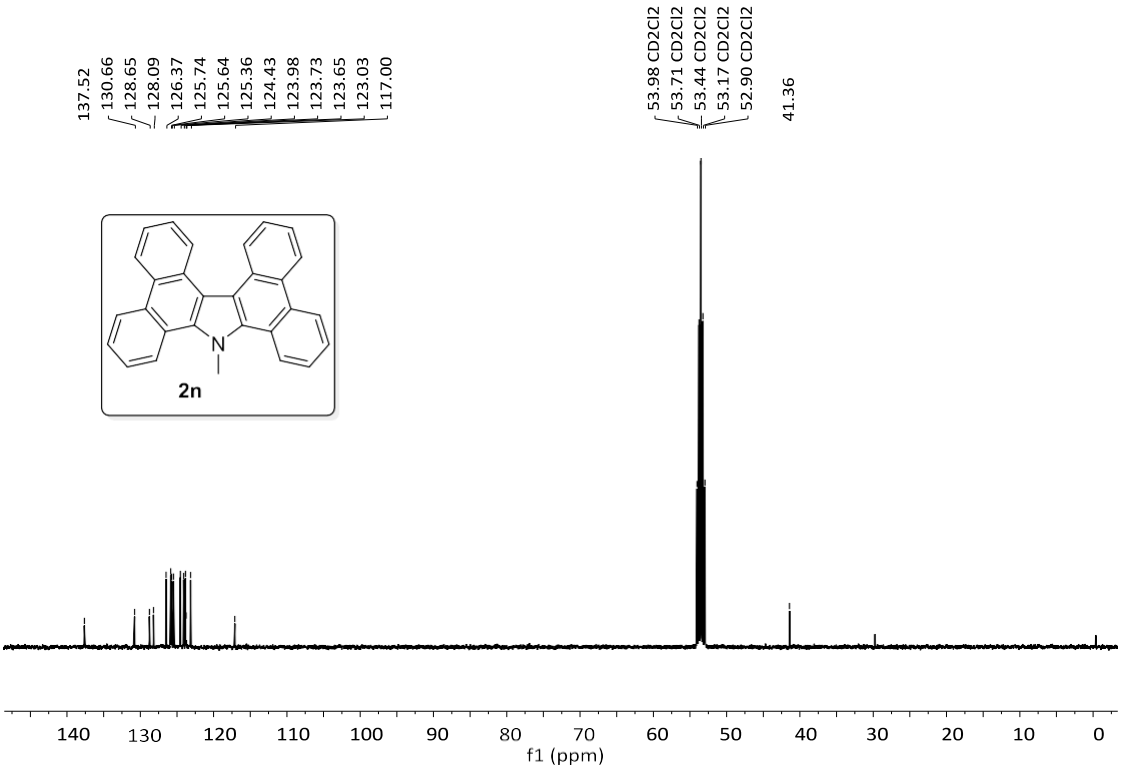
1.97
1.99
1.96
3.93
4.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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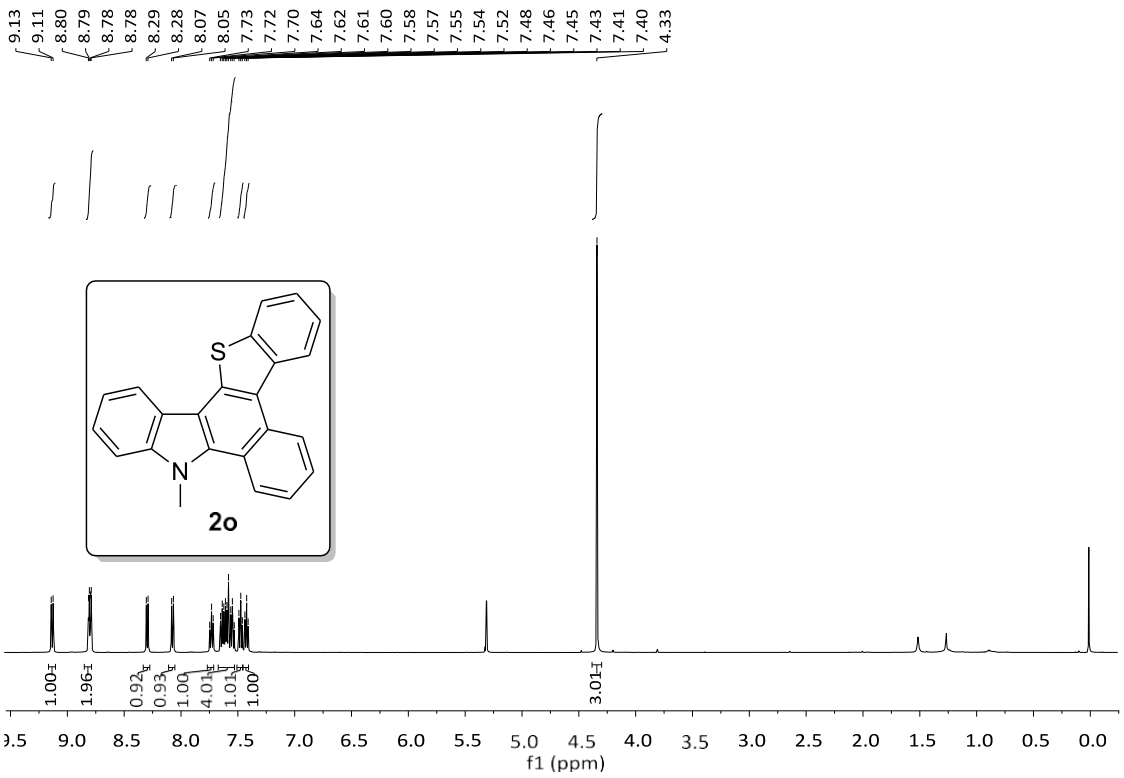
126.37
125.74
125.64
125.36
124.43
123.98
123.73
123.65
123.03
117.00
53.98 CD2Cl2
53.71 CD2Cl2
53.44 CD2Cl2
53.17 CD2Cl2
52.90 CD2Cl2
41.36
2n
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.78
8.29
8.28
8.07
8.05
7.73
7.72
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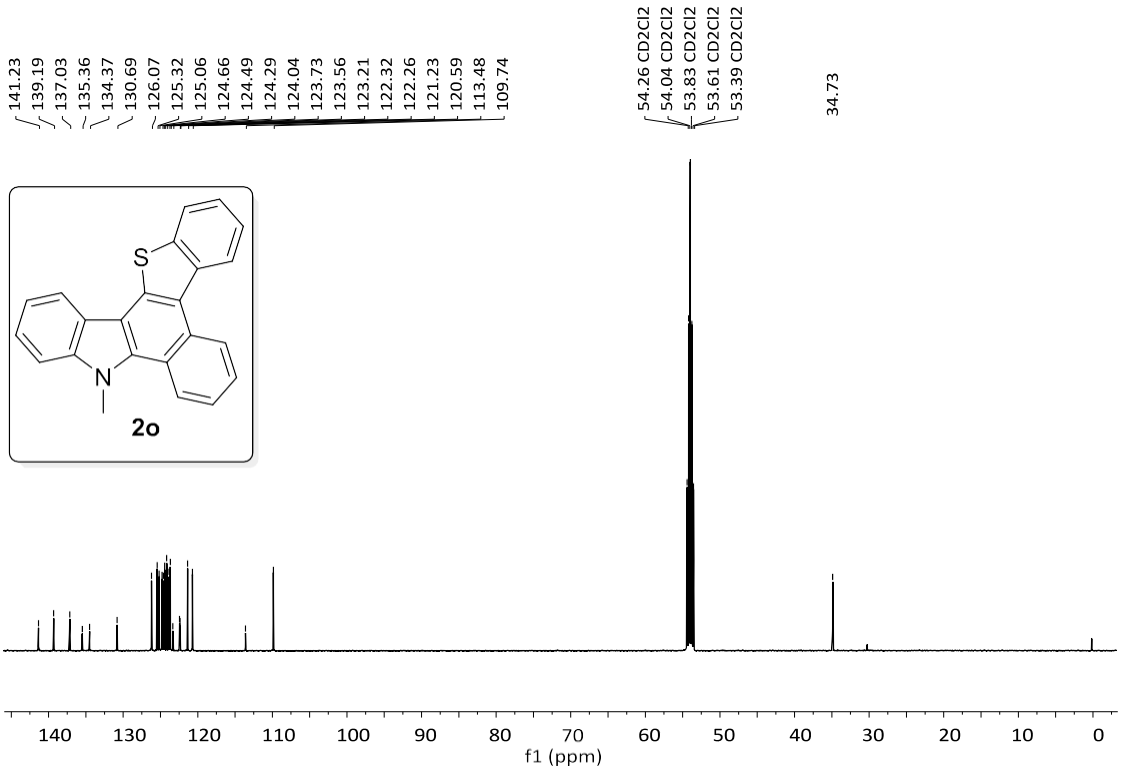
7.54
7.52
7.48
7.46
7.45
7.43
7.41
7.40
4.33
S
N
2o
1.00
1.96
0.92
0.93
1.00
4.01
1.01
1.00
3.01
f1 (ppm)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125.32
125.06
124.66
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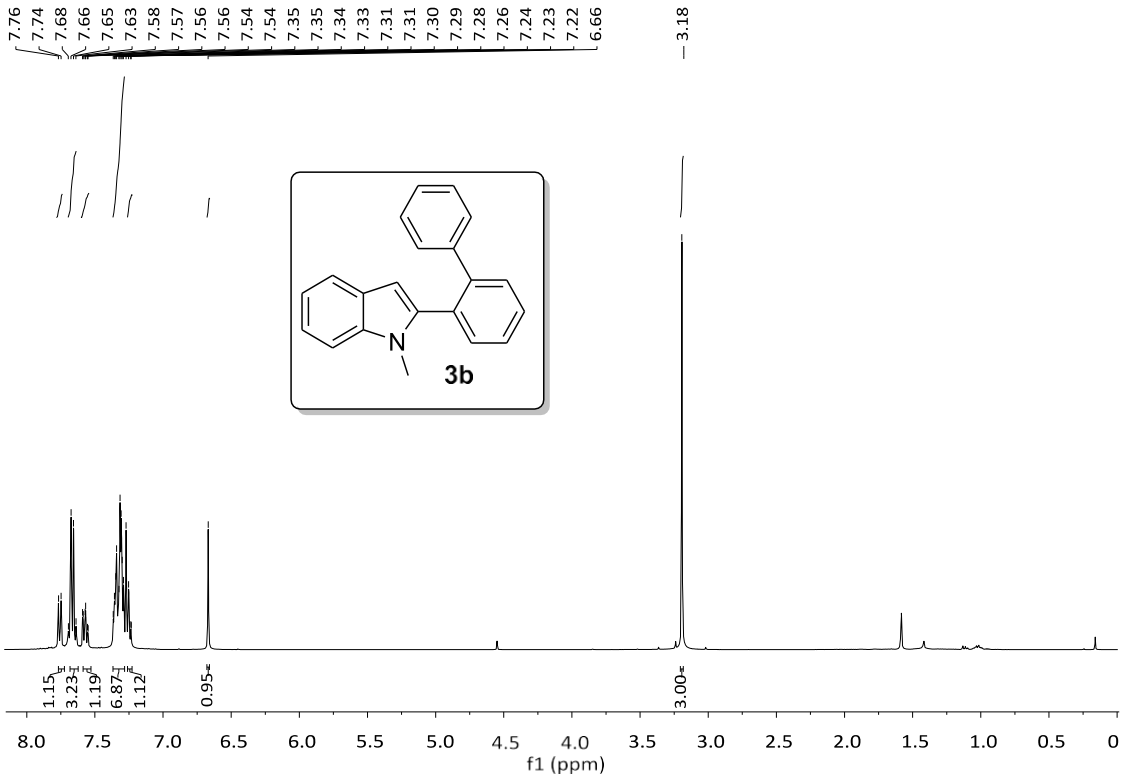
124.29
124.04
123.73
123.56
123.21
122.32
122.26
121.23
120.59
113.48
109.74
54.26 CD2Cl2
54.04 CD2Cl2
53.83 CD2Cl2
53.61 CD2Cl2
53.39 CD2Cl2
34.73
S
N
2o
f1 (ppm)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7.68
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7.65
7.63
7.58
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7.56
7.54
7.54
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7.26
7.24
7.23
7.22
6.66
3.18
3b
1.15
3.23
1.19
6.87
1.12
0.95
3.00
8.0
7.5
7.0
6.5
6.0
5.5
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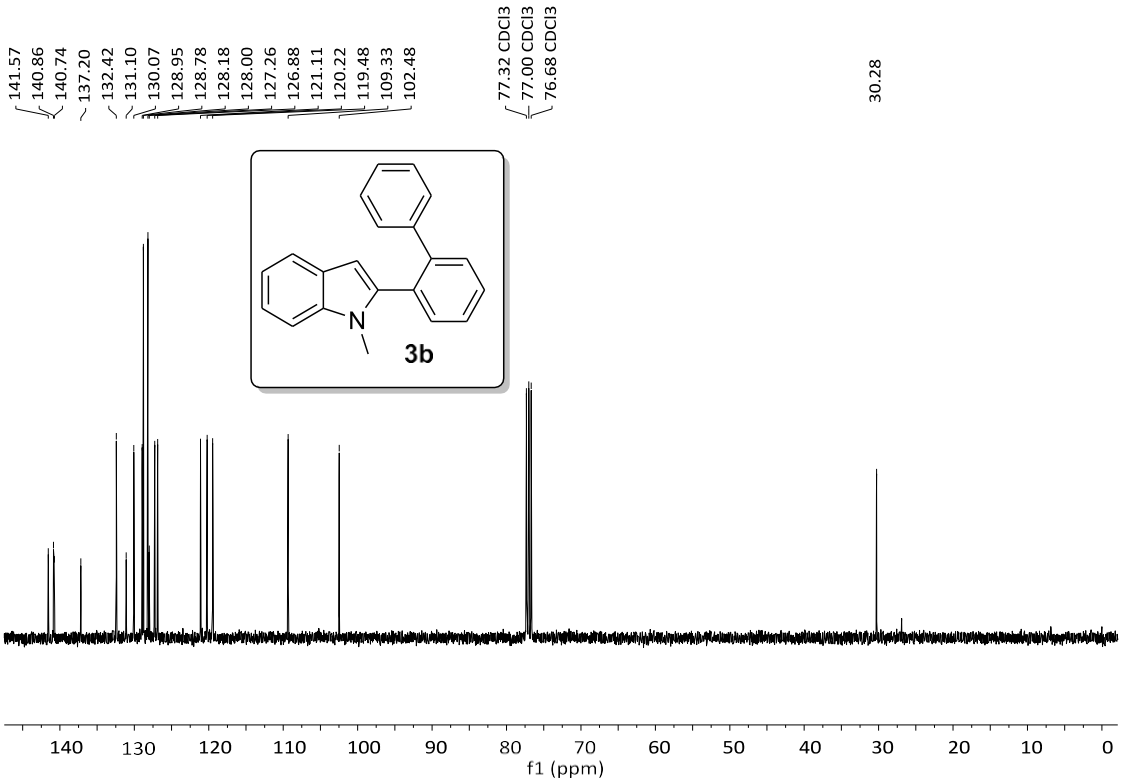
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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131.10
130.07
128.95
128.78
128.18
128.00
127.26
126.88
121.11
120.22
119.48
109.33
102.48
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
30.28
3b
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)