Supporting Information

Bromination of 1,1-diarylethylenes with bromoethane

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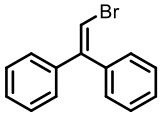
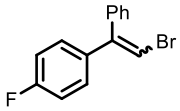
1. General Information

All reactions were carried out under N_2 atmosphere with dry solvents in flame-dried glassware unless otherwise noted. Bromoethane was purchased from commercial sources and used as received. Flash chromatographic separations were carried out on 200-300 mesh silica gel. Reactions were monitored by TLC or GC analysis of reaction aliquots. GC analyses were performed on an Agilent 7890 Gas Chromatography using a HP-5 capillary column (30 m × 0.32 mm, 0.5 μm film). ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker AVANCE III spectrometer and calibrated using residual undeuterated solvent ($CDCl_3$ at 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectrometry (HRMS) was recorded on a QTOF mass analyzer with electrospray ionization (ESI) through a Aglient 6550 iFunnel Q-TOF and Bruker Daltonics-micrOTOF-QII.

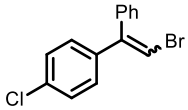
2. Representative procedure and characterization of 2a-2u.



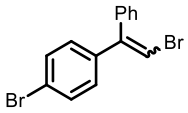
(2-Bromoethene-1,1-diyl)dibenzene (**2a**).[1] ***Representative Procedure I.*** A mixture of 1,1-diphenylethylene (**1a**) (88 μL, 0.5 mmol), bromoethane (45 μL, 0.6 mmol) in DMSO (1.0 mL) was stirred at 110 ºC (oil bath) for 5 hrs under N_2 atmosphere. The reaction was quenched with ethyl acetate and water, and then extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (petroleum ether) to give the desired product **2a** as white solid (116 mg, 90% yield). Melting Point: 49 – 50 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.45 – 7.37 (m, 5H), 7.33 – 7.31 (m, 2H), 6.88 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.94, 140.82, 139.18, 129.77 (2C), 128.54 (2C), 128.34 (2C), 128.22, 128.08, 127.73 (2C), 105.33.



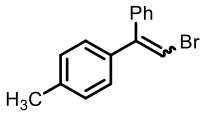
1-(2-Bromo-1-phenylvinyl)-4-fluorobenzene (**2b**)**.**[2] The title compound was prepared according to Representative Procedure I except that 1-fluoro-4-(1-phenylvinyl)benzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (126 mg, 91% yield); *Z*/*E* isomer ratio: 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 1.5H), 7.40 – 7.37 (m, 3.5H), 7.31 – 7.23 (m, 2H), 7.22 – 7.13 (m, 1H), 7.08 – 7.04(m, 1H), 6.85 (s, 0.5H), 6.81 (s, 0.5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.81 (d, J = 30.7 Hz), 161.35 (d, J = 30.0 Hz), 146.00, 145.92, 140.69, 138.99, 136.98 (d, J = 3.3 Hz), 135.01 (d, J = 3.4 Hz), 131.66 (d, J = 8.1 Hz), 129.71, 129.41 (d, J = 8.2 Hz), 128.61, 128.43, 128.38, 128.24, 127.72, 115.54 (d, J = 10.0 Hz), 115.32 (d, J = 9.9 Hz), 105.57, 105.08; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.14, -113.36.



1-(2-Bromo-1-phenylvinyl)-4-chlorobenzene (**2c**)**.**[1] The title compound was prepared according to Representative Procedure I except that 1-chloro-4-(1-phenylvinyl)benzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (128 mg, 88% yield); *Z*/*E* isomer ratio: 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.36 (m, 5H), 7.28 – 7.26 (m, 1H), 7.22 – 7.20 (m, 1H), 6.85 (s, 0.5H), 6.85 (s, 0.5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.58, 145.83, 140.40, 139.24, 138.70, 137.50, 134.20, 134.02, 134.23, 129.69, 128.94, 128.72, 128.63, 128.45, 128.43, 128.29, 127.70, 105.84, 105.79.

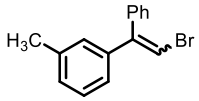


1-(2-Bromo-1-phenylvinyl)-4-bromobenzene (2d).[3] The title compound was prepared according to Representative Procedure I except that 1-bromine-4-(1-phenylvinyl)benzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (151 mg, 90% yield); *Z*/*E* isomer ratio: 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.53 – 7.45 (m, 2H), 7.40 – 7.36 (m, 3H), 7.31 – 7.25 (m, 2H), 7.18 – 7.13 (m, 1H), 6.86 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.85, 140.29, 139.67, 138.59, 137.96, 131.66, 131.57, 131.51, 129.68, 129.23, 128.62, 128.44, 128.29, 127.68, 122.41, 122.27, 105.90, 105.78.

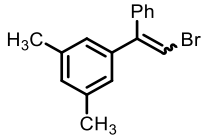


1-(2-Bromo-1-phenylvinyl)-4-methylbenzene (2e).[4] The title compound was prepared according to Representative Procedure I except that 1-methyl-4-(1-phenylvinyl)benzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (126 mg, 93% yield); *Z*/*E* isomer ratio: 1.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.41 (m, 4H), 7.41 – 7.34 (m, 3H), 7.29 – 7.23 (m, 2H), 6.90 – 6.88 (m, 1H), 2.55 (s, 1.2H), 2.48 (s, 1.8H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.83, 146.76, 141.02, 139.31, 138.06, 138.00, 137.79, 136.18, 129.74, 129.68, 129.20,

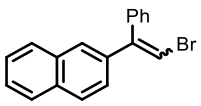
129.00, 128.45, 128.26, 128.12, ,127.96, 127.76, 127.58, 104.91, 104.45, 21.44, 21.24.



1-(2-Bromo-1-phenylvinyl)-3-methylbenzene (2f).[3] The title compound was prepared according to Representative Procedure I except that 1-methyl-3-(1-phenylvinyl)benzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (134 mg, 98% yield); *Z*/*E* isomer ratio: 1.1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.11 (m, 9H), 6.91 (s, 1H), 2.52 (s, 1.4H), 2.46 (s, 1.6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.04, 147.00, 140.85, 140.79, 139.24, 139.09, 138.08, 137.90, 130.22, 129.74, 128.99, 128.81, 128.39, 128.35, 128.27, 128.20, 128.13, 127.99, 127.67, 126.84, 124.95, 105.16, 105.12, 21.53, 21.47.

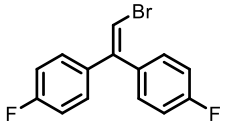


1-(2-Bromo-1-phenylvinyl)-3,5-dimethylbenzene (2g). The title compound was prepared according to Representative Procedure I except that 1,3-dimethyl-5-(1-phenylvinyl)benzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (142 mg, 99% yield); *Z*/*E* isomer ratio: 1.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.09 (m, 8H), 7.05 (s, 0.6H), 6.60 (s, 0.4H), 2.49 (s, 1.8H), 2.48 (s, 1.2H), 2.27 (s, 1.8H), 2.15 (s, 1.2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.63, 146.40, 141.02, 139.30, 138.71, 138.53, 135.38, 135.29, 133.21, 132.86, 130.84, 130.52, 130.24, 129.83, 129.35, 128.99, 128.89, 128.67, 128.09, 128.02, 127.94, 126.62, 106.51, 105.33, 21.10, 20.95, 19.79, 19.03. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{16}Br^+$ 287.0430; Found 287.0441.

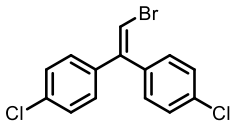


2-(2-Bromo-1-phenylvinyl)naphthalene (2h).[1] The title compound was prepared according to Representative Procedure I except that 2-(1-phenylvinyl)naphthalene was

used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (130 mg, 84% yield); *Z*/*E* isomer ratio: 1.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.78 (m, 3.5H), 7.74 (s, 0.6H), 7.63 – 7.30 (m, 8.1H), 6.99 (s, 0.6H), 6.94 (s, 0.4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.90, 140.82, 139.12, 138.14, 136.60, 133.29, 133.04, 132.98, 129.89, 129.17, 128.58, 128.41, 128.35, 128.30, 128.18, 128.16, 127.97, 127.84, 127.70, 127.53, 127.14, 126.55, 126.49, 126.32, 126.35, 105.78, 105.67.

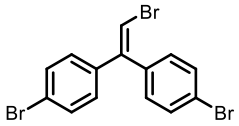


4,4'-(2-Bromoethene-1,1-diyl)bis(fluorobenzene) (2i).[1] The title compound was prepared according to Representative Procedure I except that 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (144 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 7.18 – 7.11 (m, 2H), 7.07 – 7.00 (m, 2H), 6.76 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.91 (d, J = 32.2 Hz), 161.44 (d, J = 31.6 Hz), 145.01, 136.88 (d, J = 3.4 Hz), 134.84 (d, J = 3.5 Hz), 131.64 (d, J = 8.2 Hz, 2C), 129.44 (d, J = 8.2 Hz, 2C), 115.66 (d, J = 9.7 Hz, 2C), 115.44 (d, J = 9.6 Hz, 2C), 105.32; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.89, -113.14.

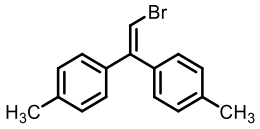


4,4'-(2-Bromoethene-1,1-diyl)bis(chlorobenzene) (2j).[1] The title compound was prepared according to Representative Procedure I except that 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (160 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.6 Hz,

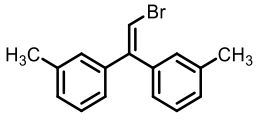
2H), 6.84 (s, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.74, 138.81, 137.00, 134.44, 134.26, 131.14 (2C), 128.91 (2C), 128.82 (2C), 128.75 (2C), 106.31.



4,4'-(2-Bromoethene-1,1-diyl)bis(bromobenzene) (2k).[5] The title compound was prepared according to Representative Procedure I except that 4,4'-(ethene-1,1-diyl)bis(bromobenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (185 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.80 (s, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.87, 139.21, 137.44, 131.81 (2C), 131.74 (2C), 131.46 (2C), 129.23 (2C), 122.71, 122.56, 106.35.

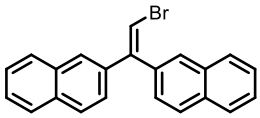


4,4'-(2-Bromoethene-1,1-diyl)bis(methylbenzene) (2l).[1] The title compound was prepared according to Representative Procedure I except that 4,4'-(ethene-1,1-diyl)bis(methylbenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (141 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.32 – 7.21 (m, 4H), 6.87 (s, 1H), 2.56 (s, 3H), 2.50 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 146.68, 138.24, 137.97, 137.69, 136.32, 129.67 (2C), 129.16 (2C), 128.96 (2C), 127.65 (2C), 104.06, 21.43, 21.23.

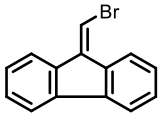


3,3'-(2-Bromoethene-1,1-diyl)bis(methylbenzene) (2m).[5] The title compound was prepared according to Representative Procedure I except that 3,3'-(ethene-1,1-diyl)bis(methylbenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title

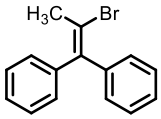
compound as colorless oil (140 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 1H), 7.33 – 7.22 (m, 5H), 7.21 – 7.10 (m, 2H), 6.86 (s, 1H), 2.50 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.17, 140.90, 139.20, 138.08, 137.87, 130.23, 128.96, 128.78, 128.38, 128.33, 128.17, 126.86, 124.96, 104.97, 21.55, 21.49.



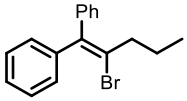
2,2'-(2-Bromoethene-1,1-diyl)dinaphthalene (2n). The title compound was prepared according to Representative Procedure I except that 2,2'-(ethene-1,1-diyl)dinaphthalene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (156 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.74 (m, 7H), 7.70 (s, 1H), 7.59 – 7.45 (m, 5H), 7.41 (d, J = 8.6 Hz, 1H), 7.02 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.95, 138.23, 136.63, 133.35, 133.30, 133.13, 133.10, 129.35, 128.40, 128.39, 128.25, 128.07, 127.93, 127.75, 127.66, 127.34, 126.63, 126.58, 126.39, 125.48, 106.08. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{16}Br^+$ 359.0430; Found 359.0414.



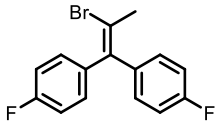
9-(Bromomethylene)-9H-fluorene (2o).[6] The title compound was prepared according to Representative Procedure I except that 9-methylene-9H-fluorene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (100 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.33 (t, J = 7.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.54, 139.25, 138.93, 138.48, 136.69, 129.55, 128.76, 127.38, 127.33, 125.81, 120.28, 119.96, 119.91, 105.94.



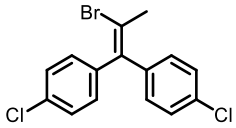
(2-Bromoprop-1-ene-1,1-diyl)dibenzene (2p).[4] The title compound was prepared according to Representative Procedure I except that prop-1-ene-1,1-diyldibenzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (86 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.01 (m, 10H), 2.57 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.30, 141.82, 140.80, 129.30 (2C), 129.21 (2C), 128.39 (2C), 128.09 (2C), 127.32, 127.23, 121.24, 27.51.



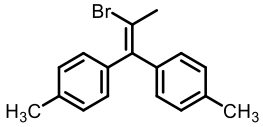
(2-Bromopent-1-ene-1,1-diyl)dibenzene (2q).[8] The title compound was prepared according to Representative Procedure I except that pent-1-ene-1,1-diyldibenzene was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (98 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 10H), 2.59 (t, J = 8 Hz, 2H), 1.88 – 1.63 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.47, 142.11, 141.24, 129.21 (2C), 128.95 (2C), 128.49 (2C), 128.17, 128.14 (2C), 127.29, 127.21, 40.42, 22.41, 13.23.



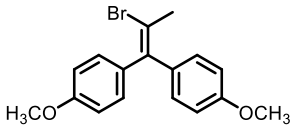
4,4'-(2-Bromoprop-1-ene-1,1-diyl)bis(fluorobenzene) (2r).[7] The title compound was prepared according to Representative Procedure I except that 4,4'-(prop-1-ene-1,1-diyl)bis(fluorobenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (104 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (m, 2H), 7.03 (m, 2H), 6.92 – 6.85 (m, 4H), 2.31 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.19 (d, J = 8.5 Hz), 160.74 (d, J = 7.9 Hz), 139.77, 138.99 (d, J = 3.4 Hz), 136.52 (d, J = 3.5 Hz), 131.17 (d, J = 8.1 Hz, 2C), 130.97 (d, J = 8.1 Hz, 2C), 121.85, 115.48 (d, J = 21.4 Hz, 2C), 115.15 (d, J = 21.5 Hz, 2C), 27.54; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.09, -114.23.



4,4'-(2-Bromoprop-1-ene-1,1-diyl)bis(chlorobenzene) (2s).[4] The title compound was prepared according to Representative Procedure I except that 4,4'-(prop-1-ene-1,1-diyl)bis(chlorobenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (124 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.18 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.55, 138.77, 133.59, 133.41, 130.86 (2C), 130.67 (2C), 128.78 (2C), 128.50 (2C), 122.38, 27.61.



4,4'-(2-Bromoprop-1-ene-1,1-diyl)bis(methylbenzene) (2t).[4] The title compound was prepared according to Representative Procedure I except that 4,4'-(prop-1-ene-1,1-diyl)bis(methylbenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (104 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 7.01 (m, 4H), 7.01 – 6.94 (m, 4H), 2.33 (s, 3H), 2.22 (s, 3H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.57, 140.61, 138.08, 136.97, 129.24 (2C), 129.16(2C), 129.04 (2C), 128.77 (2C), 120.55, 27.57, 21.39, 21.29.



4,4'-(2-Bromoprop-1-ene-1,1-diyl)bis(methoxybenzene) (2u).[4] The title compound was prepared according to Representative Procedure I except that 4,4'-(prop-1-ene-1,1-diyl)bis(methoxybenzene) was used instead of 1,1-diphenylethylene. The crude product was purified by silica gel column chromatography (petroleum ether) to give the title compound as colorless oil (129 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 4H), 6.70 (d, J = 8.8 Hz, 2H), 3.74 – 3.47 (m, 6H),

2.31 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 158.62, 158.49, 140.75, 135.86, 133.32, 130.68 (2C), 130.50 (2C), 119.96, 113.57 (2C), 113.21 (2C), 55.18, 55.10, 27.60.

3 References

1. Zhang, G.; Bai, R.-X.; Li, C.-H.; Feng, C.-G.; Lin, G.-Q. *Tetrahedron* **2019**, *75*, 1658.

2. Chang, M.-Y.; Tai, H.-Y.; Tsai, C.-Y.; Chuang, Y.-J.; Lin, Y.-T. *Tetrahedron Lett.* **2014**, *55*, 6482.

3. Pei, C.; Yang, Z.; Koenigs, R. M. *Org. Lett*. **2020**, 22, 7300.

4. Suarez, A. R.; Mazzieri, M. R. *J. Org. Chem.* **1987**, *52*, 1145.

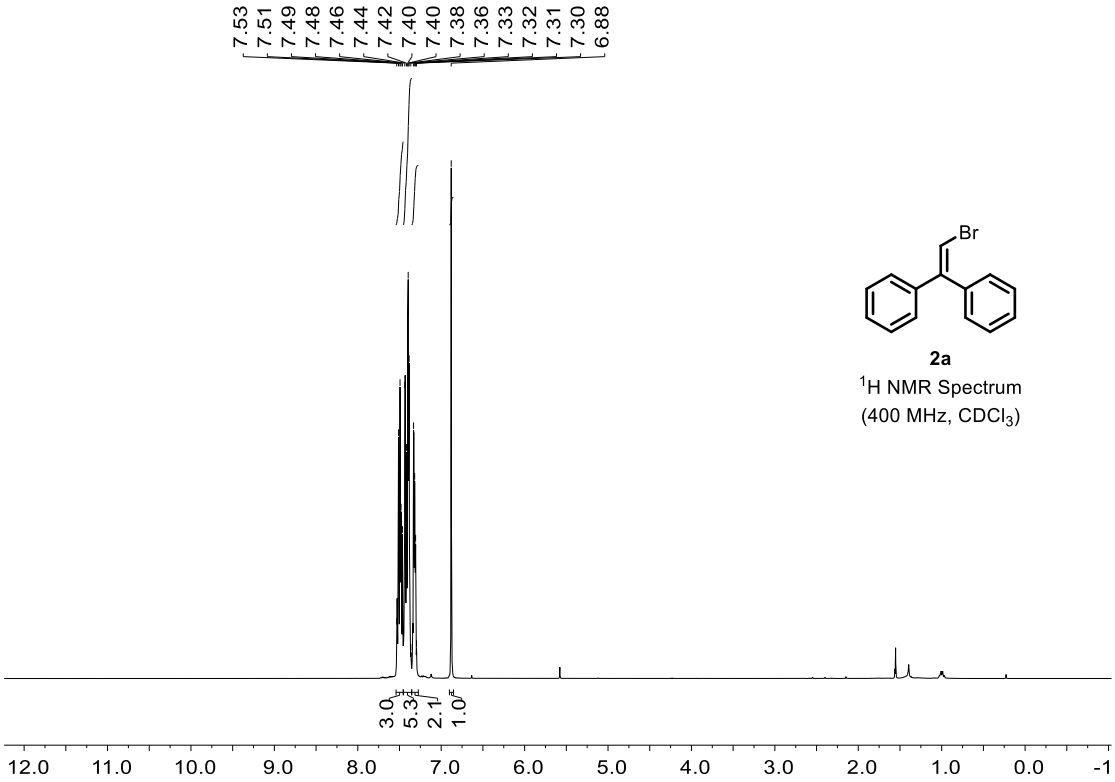
5. Hao, T.-T.; Liang, H.-R.; Ou-Yang, Y.-H.; Yin, C.-Z.; Zheng, X.-L.; Yuan, M.-L.; Li, R.-X.; Fu, H.-Y.; Chen, H. *J. Org. Chem*. **2018**, *83*, 4441.

6. Paul, G. C; Gajewski, J. J. S*ynthesis* **1997**, *1997*, 524.

7. Ken, S.; Tohru K.; Takenobu, N.; Yoji, H.; Toshimitsu, H. Preparation of 2,2-(diaryl)vinylphosphine compounds, palladium catalyst thereof, and a process for producing arylamine, diaryl, or arylalkyne with the catalyst. Eur. Pat. Appl. 1167372, Jan 2, 2002.

8. Lothar, L.; Edgar, J. 2-Alkyl-1,1-diaryl-3-amino-1-propenes. Ger. Offen. DD63372, Aug 20, 1968

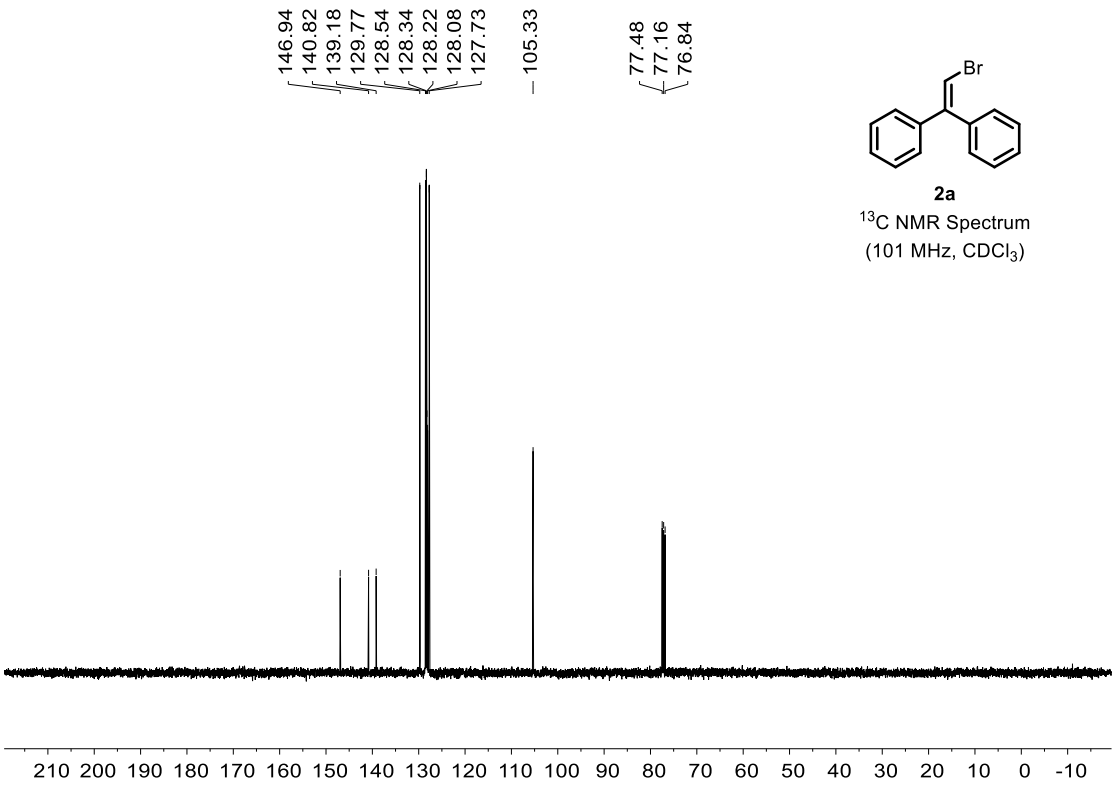
4. ^{1}H NMR and ^{13}C NMR Spectra



2a

^{1}H NMR Spectrum

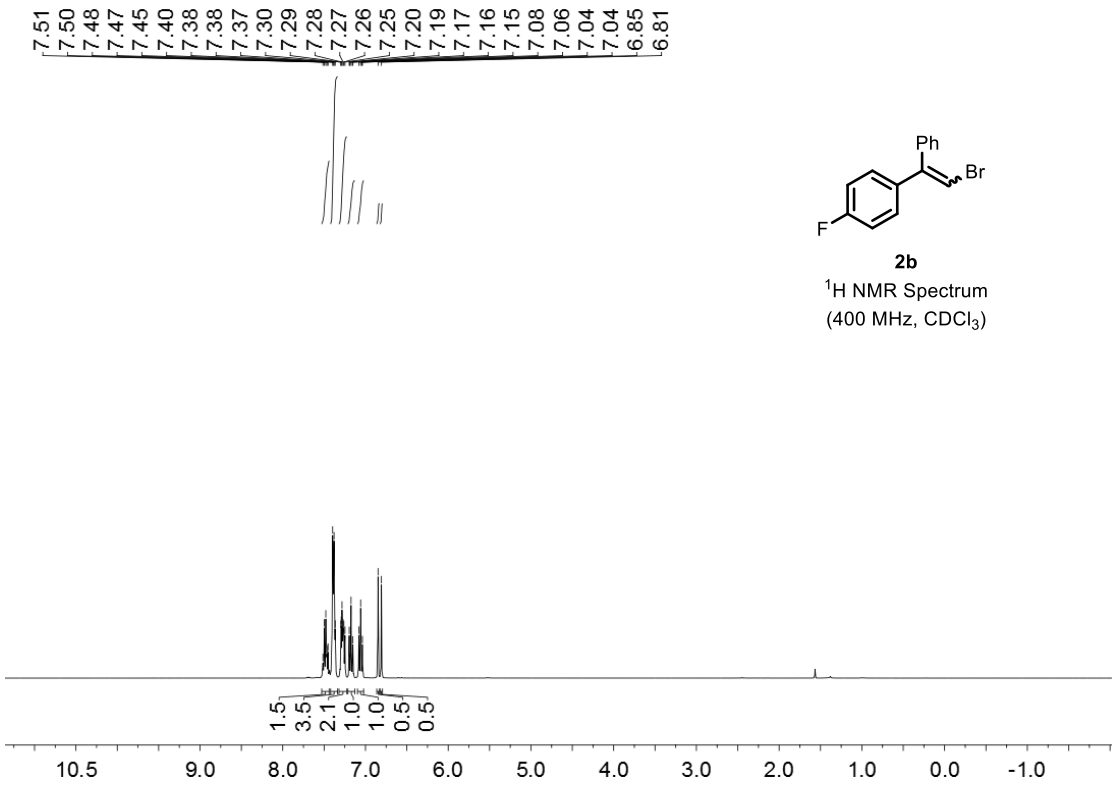
(400 MHz, $CDCl_3$)



2a

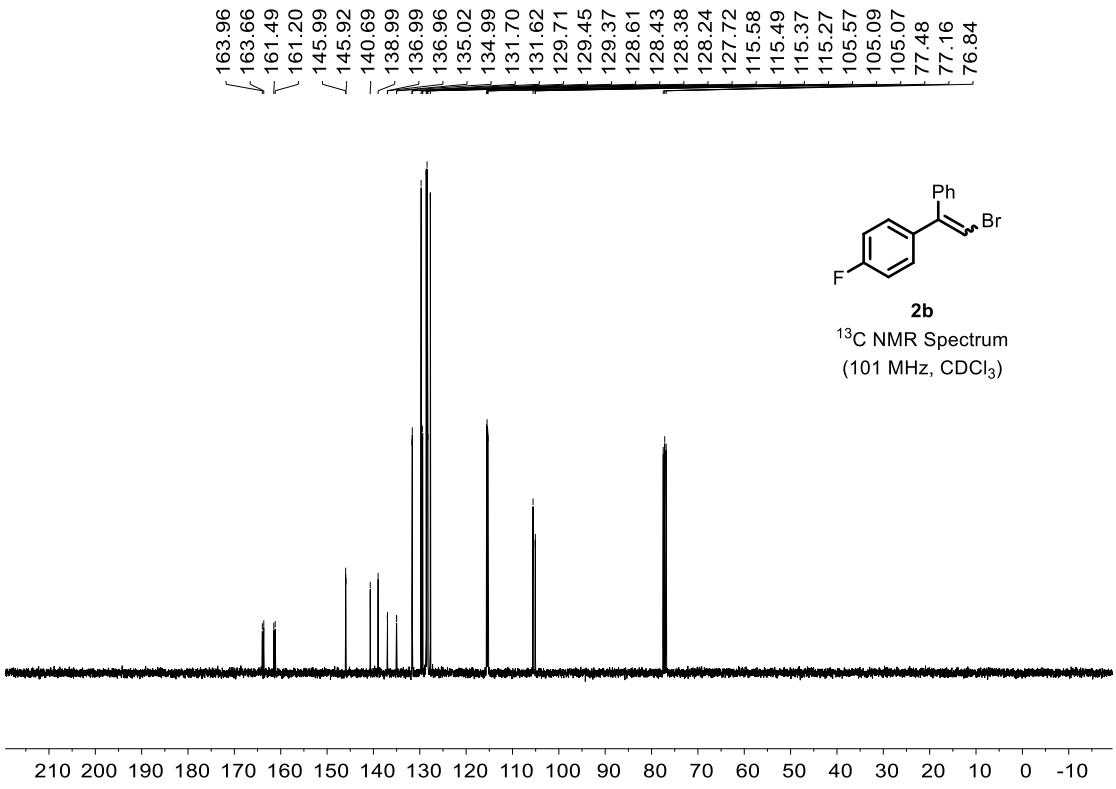
^{13}C NMR Spectrum

(101 MHz, $CDCl_3$)



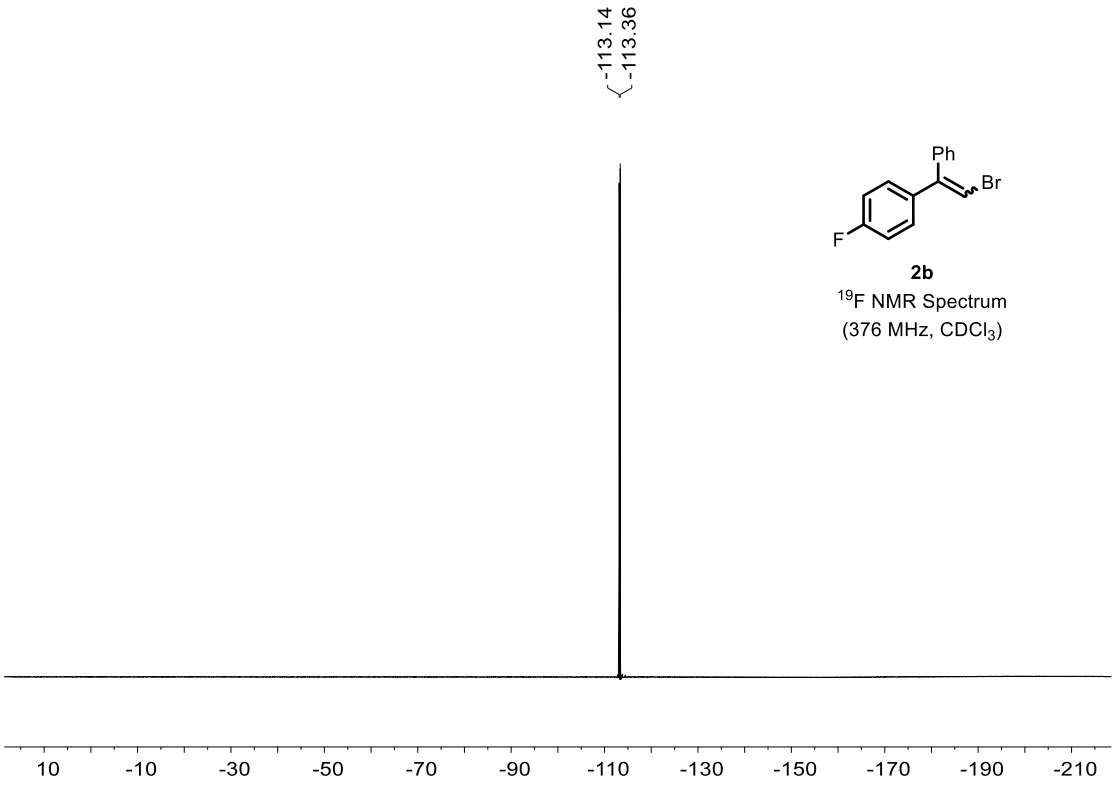
2b

^{1}H NMR Spectrum
(400 MHz, $CDCl_3$)



2b

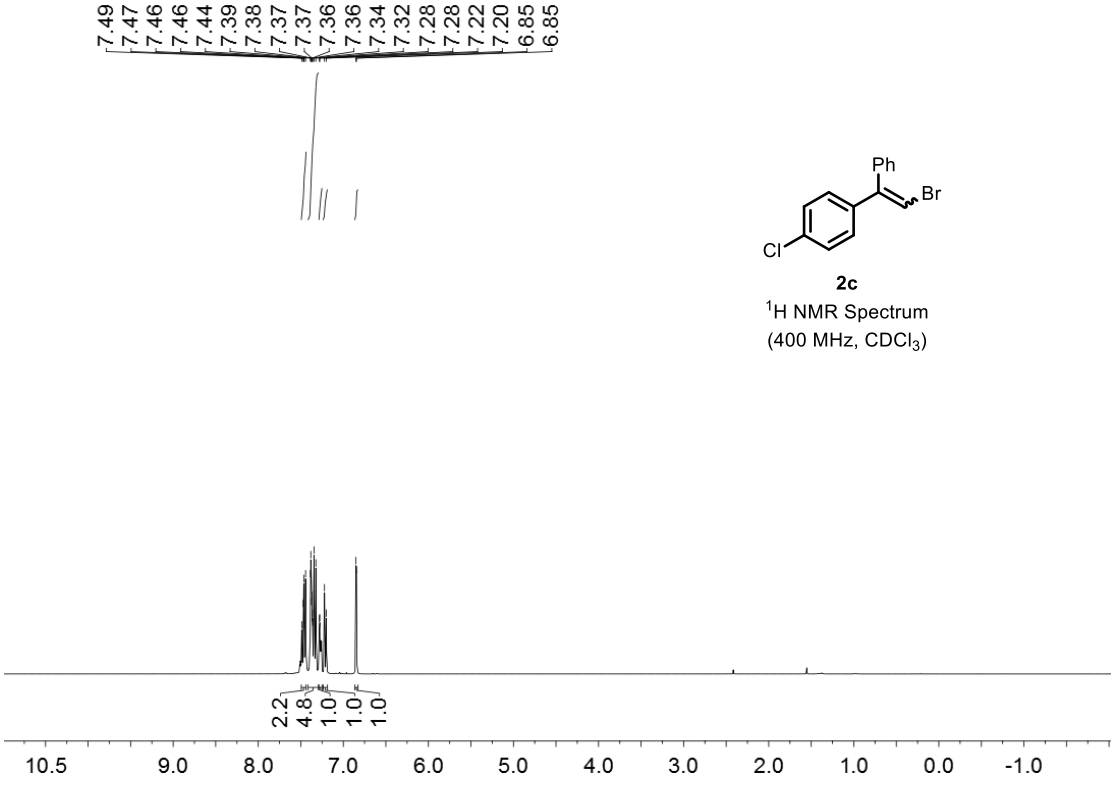
^{13}C NMR Spectrum
(101 MHz, $CDCl_3$)



2b

^{19}F NMR Spectrum

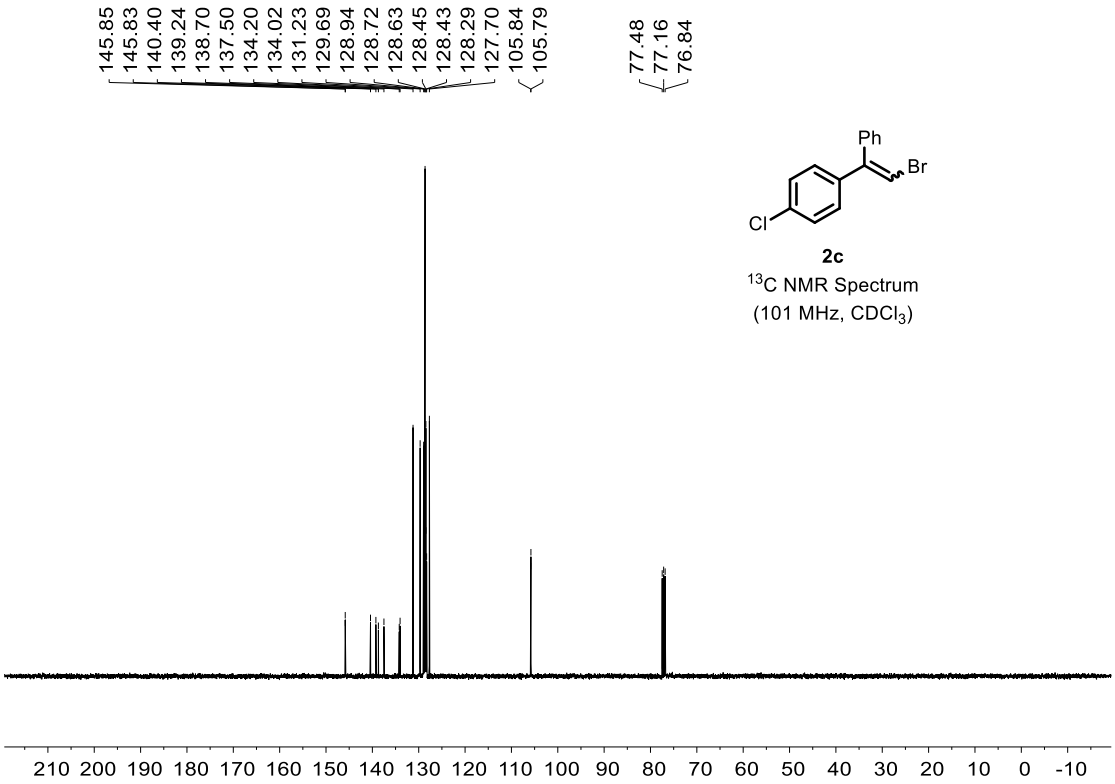
(376 MHz, $CDCl_3$)



2c

^{1}H NMR Spectrum

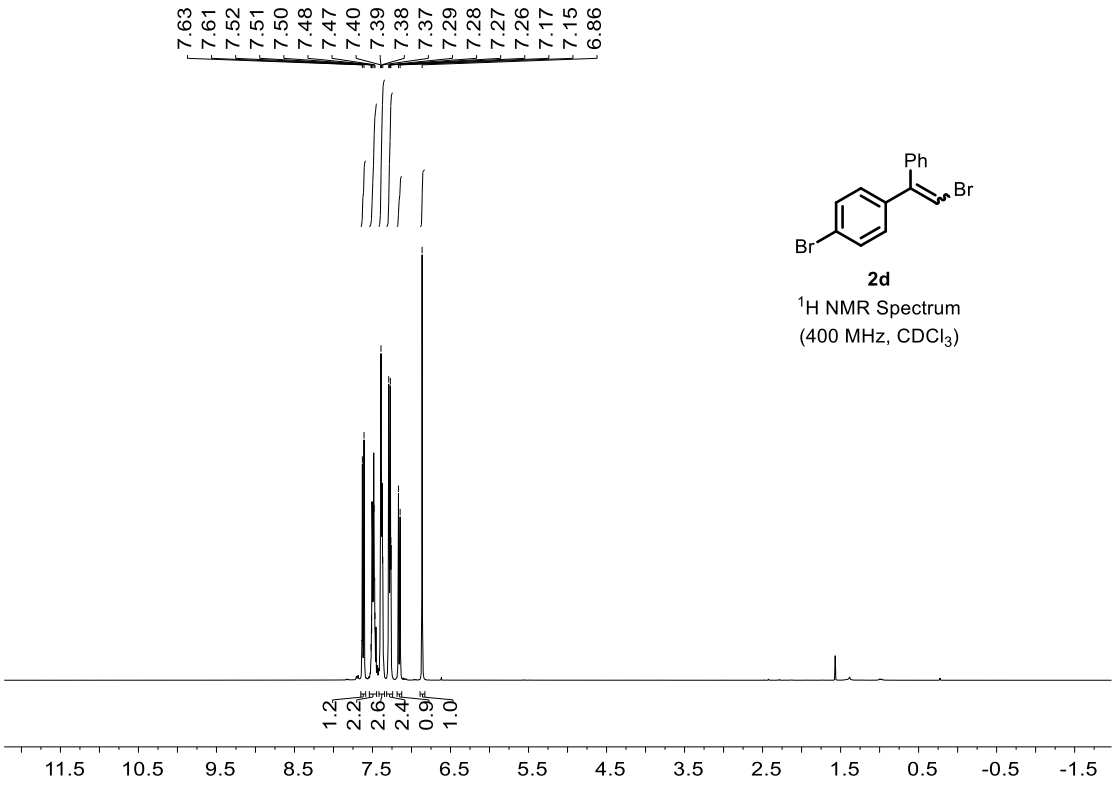
(400 MHz, $CDCl_3$)



2c

^{13}C NMR Spectrum

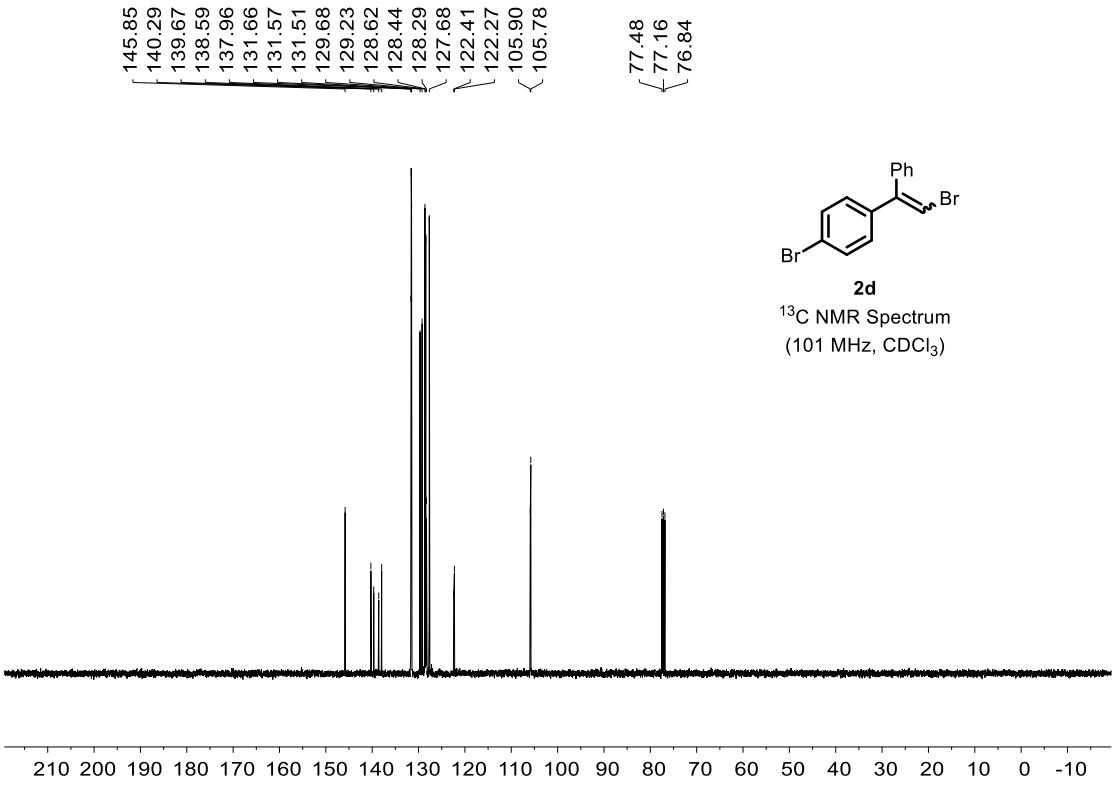
(101 MHz, $CDCl_3$)



2d

^{1}H NMR Spectrum

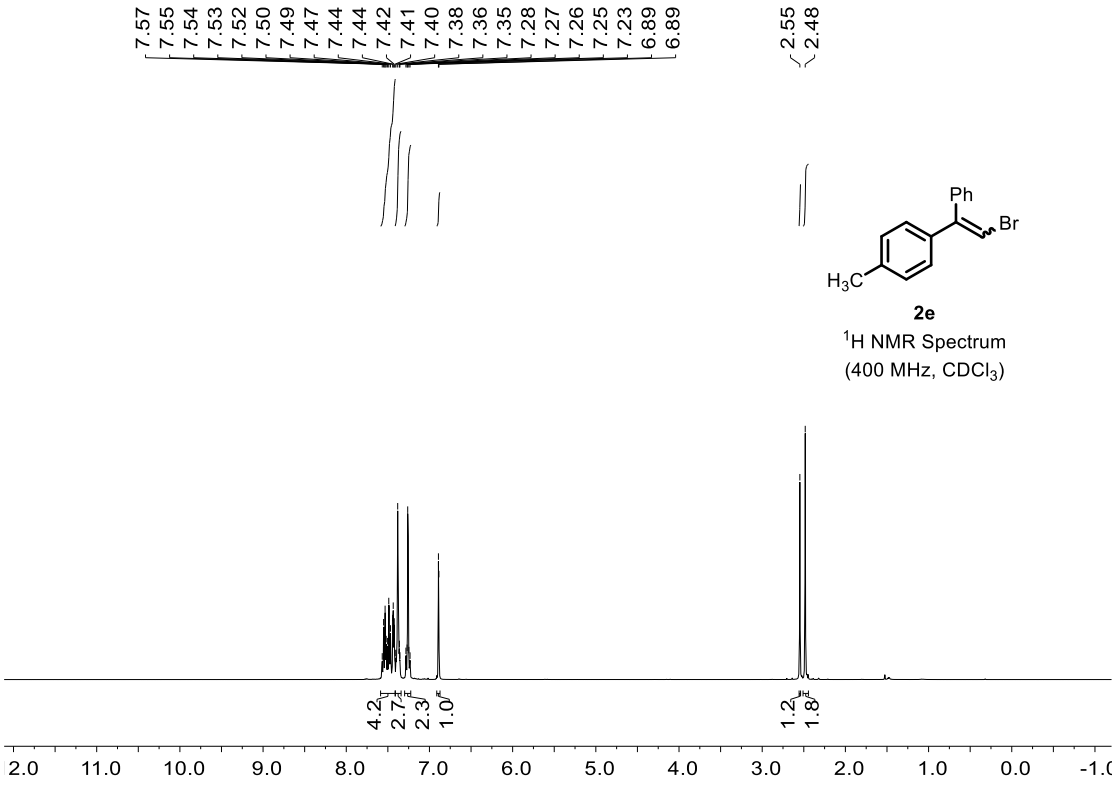
(400 MHz, $CDCl_3$)



2d

^{13}C NMR Spectrum

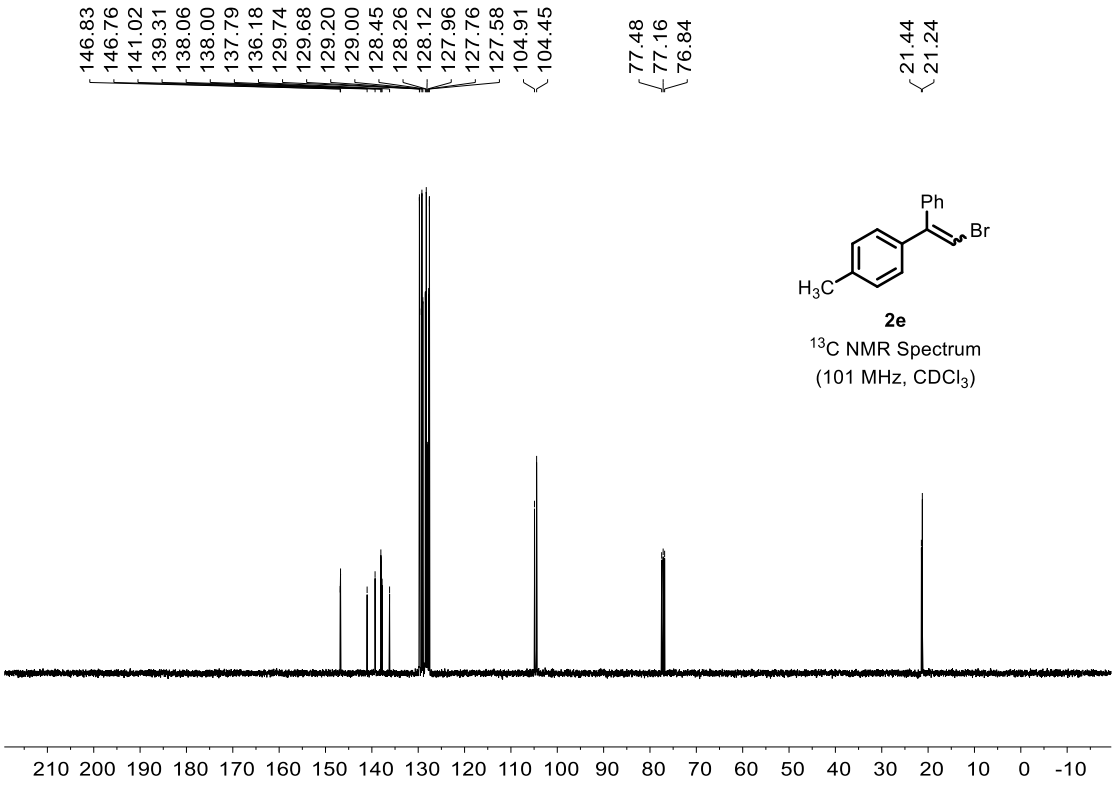
(101 MHz, $CDCl_3$)



2e

^{1}H NMR Spectrum

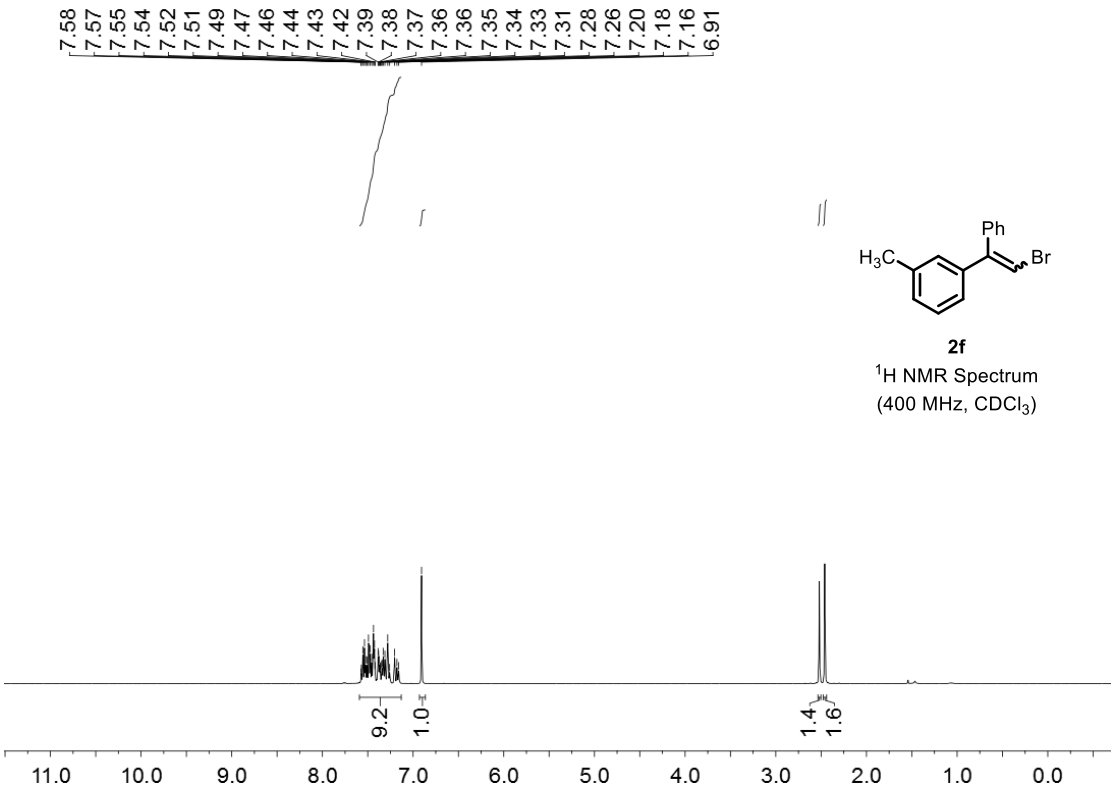
(400 MHz, $CDCl_3$)



2e

^{13}C NMR Spectrum

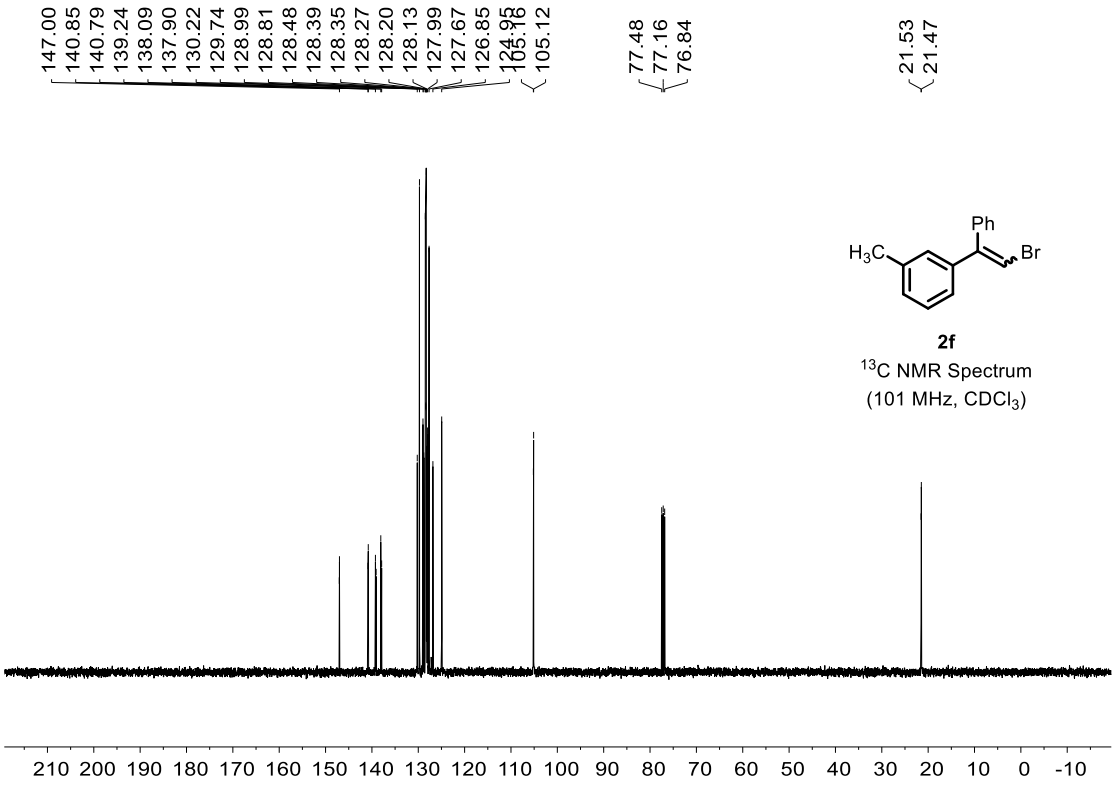
(101 MHz, $CDCl_3$)



2f

^{1}H NMR Spectrum

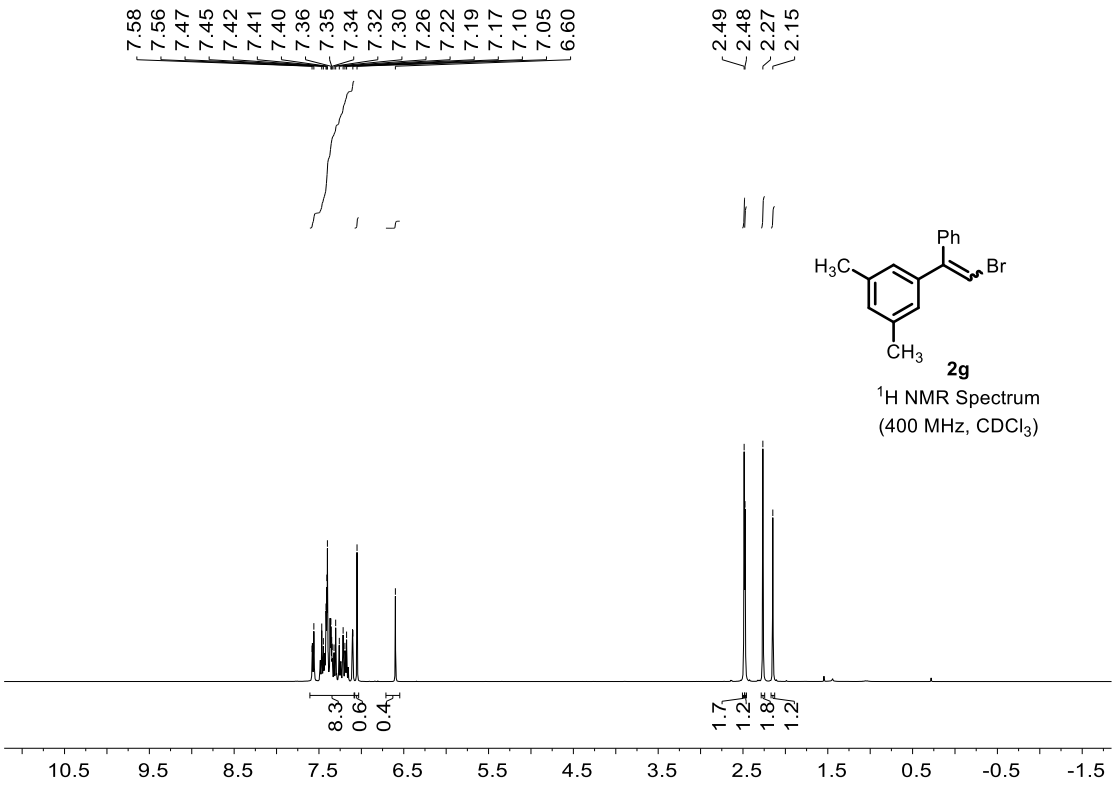
(400 MHz, $CDCl_3$)



2f

^{13}C NMR Spectrum

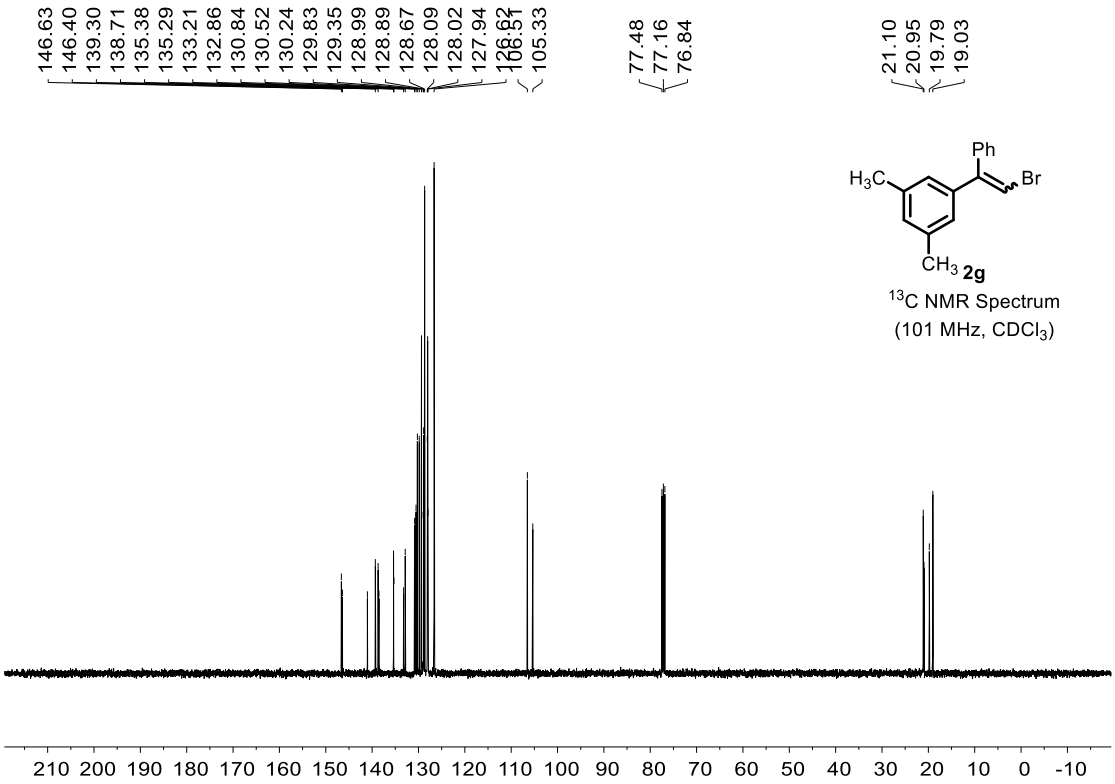
(101 MHz, $CDCl_3$)

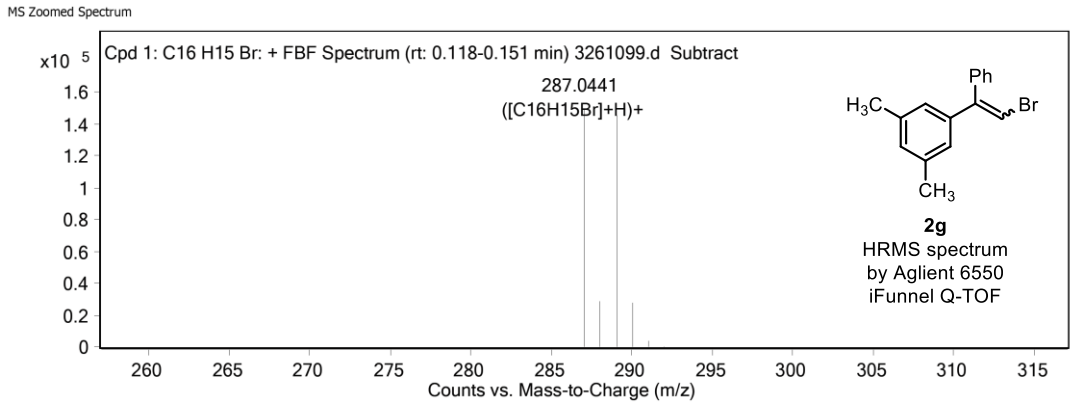


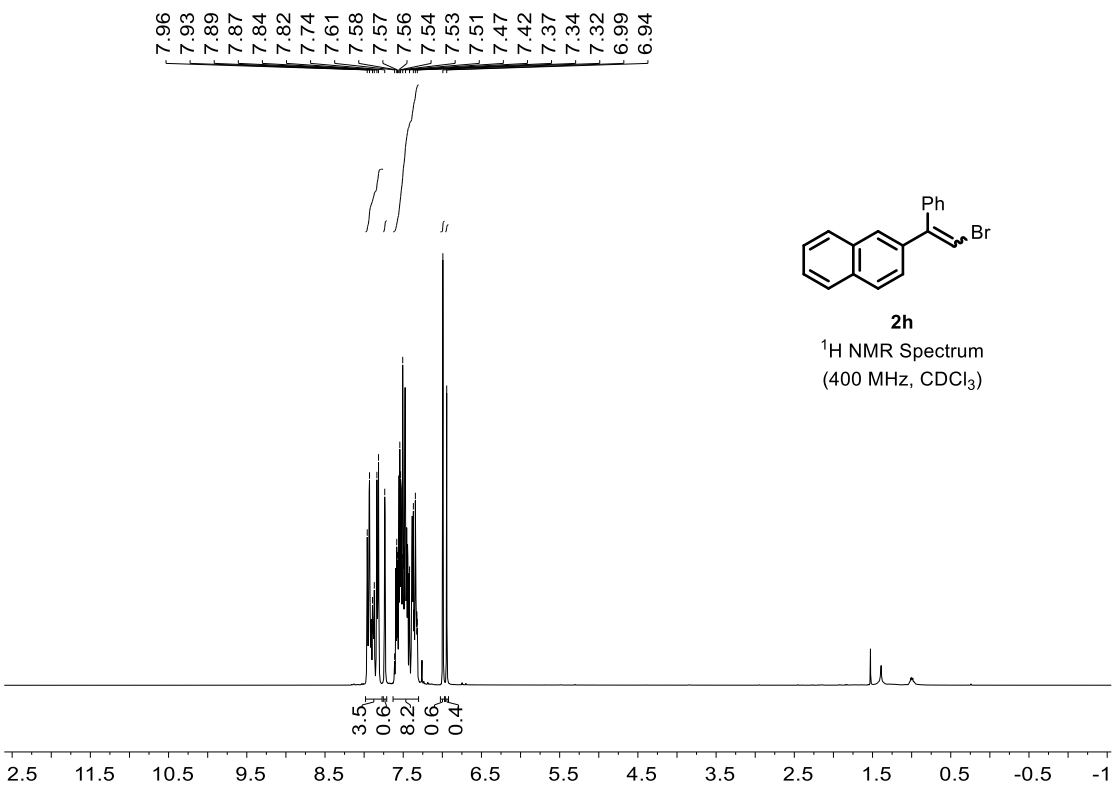
2g

^{1}H NMR Spectrum

(400 MHz, $CDCl_3$)


146.63
146.40
139.30
138.71
135.38
135.29
133.21
132.86
130.84
130.52
130.24
129.83
129.35
128.99
128.89
128.67
128.09
128.02
127.94
126.62
126.51
105.33
77.48
77.16
76.84
21.10
20.95
19.79
19.03
Ph
H3C
Br
CH3
2g
13C NMR Spectrum
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

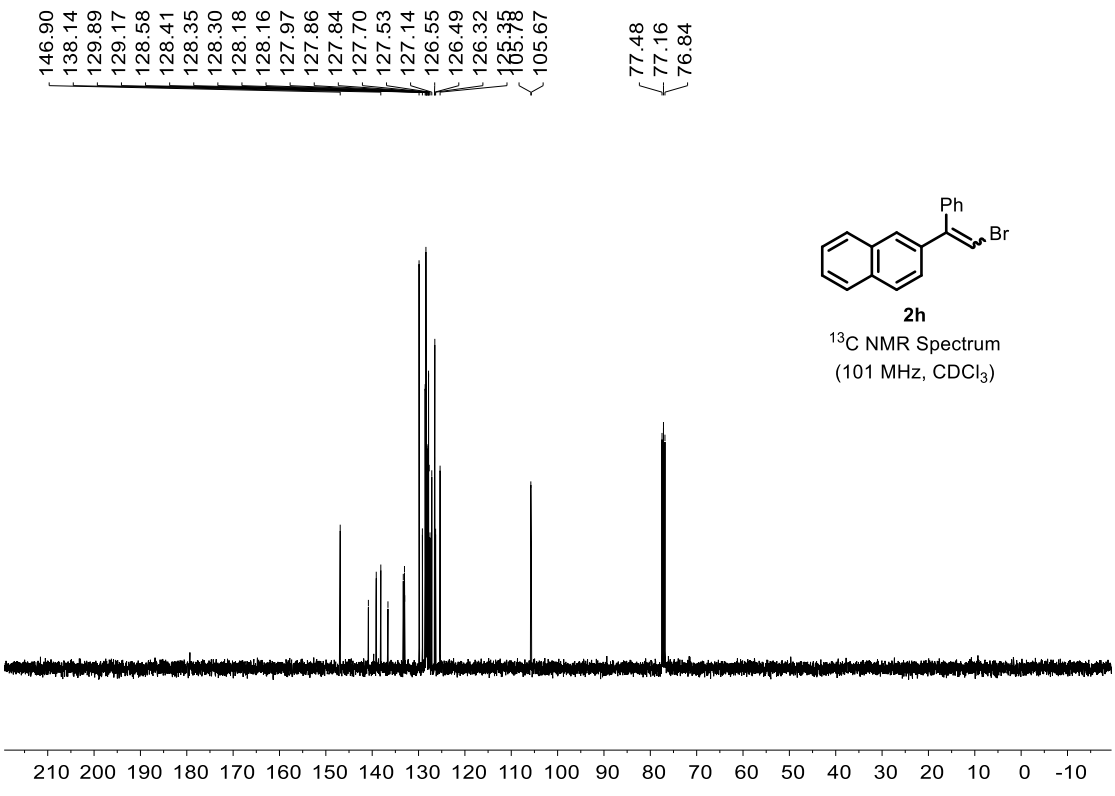

MS Zoomed Spectrum
Cpd 1: C16 H15 Br: + FBF Spectrum (rt: 0.118-0.151 min) 3261099.d Subtract
x10 5
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
287.0441
([C16H15Br]+H)+
Ph
H3C
Br
CH3
2g
HRMS spectrum
by Aglient 6550
iFunnel Q-TOF
260 265 270 275 280 285 290 295 300 305 310 315
Counts vs. Mass-to-Charge (m/z)



2h

^{1}H NMR Spectrum

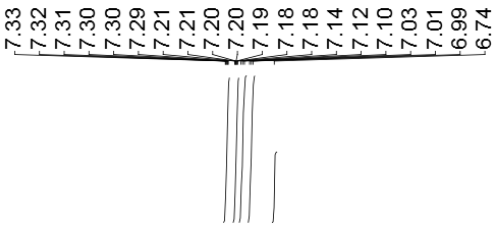
(400 MHz, $CDCl_3$)

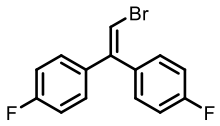


2h

^{13}C NMR Spectrum

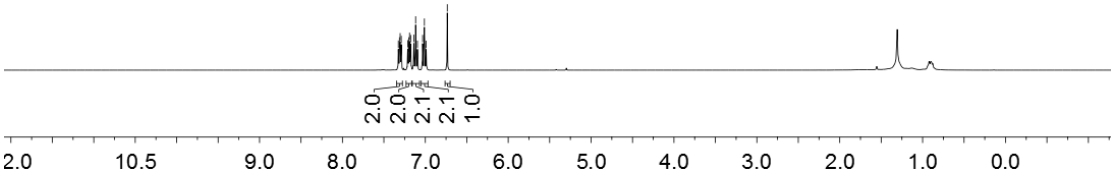
(101 MHz, $CDCl_3$)

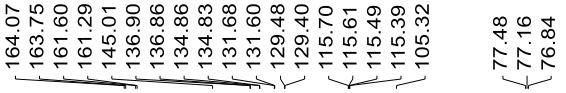


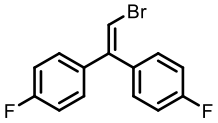


2i

^{1}H NMR Spectrum
(400 MHz, $CDCl_3$)

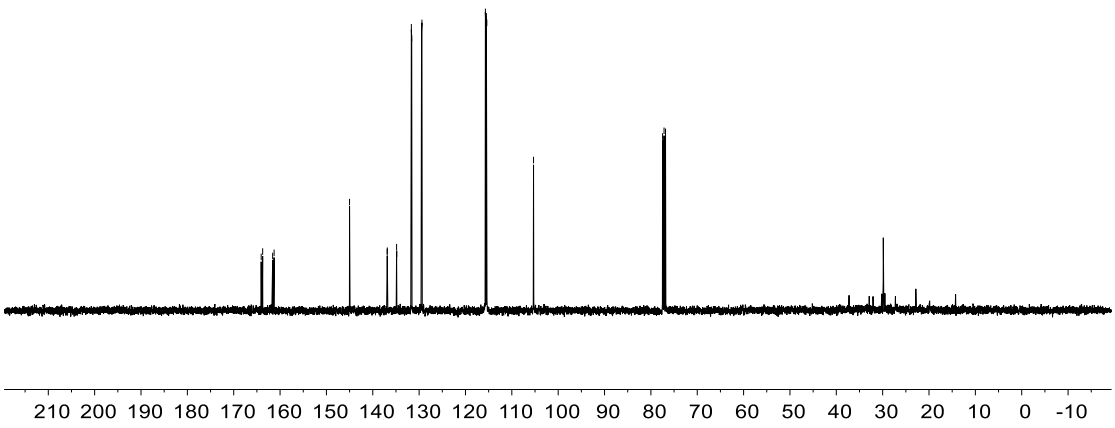


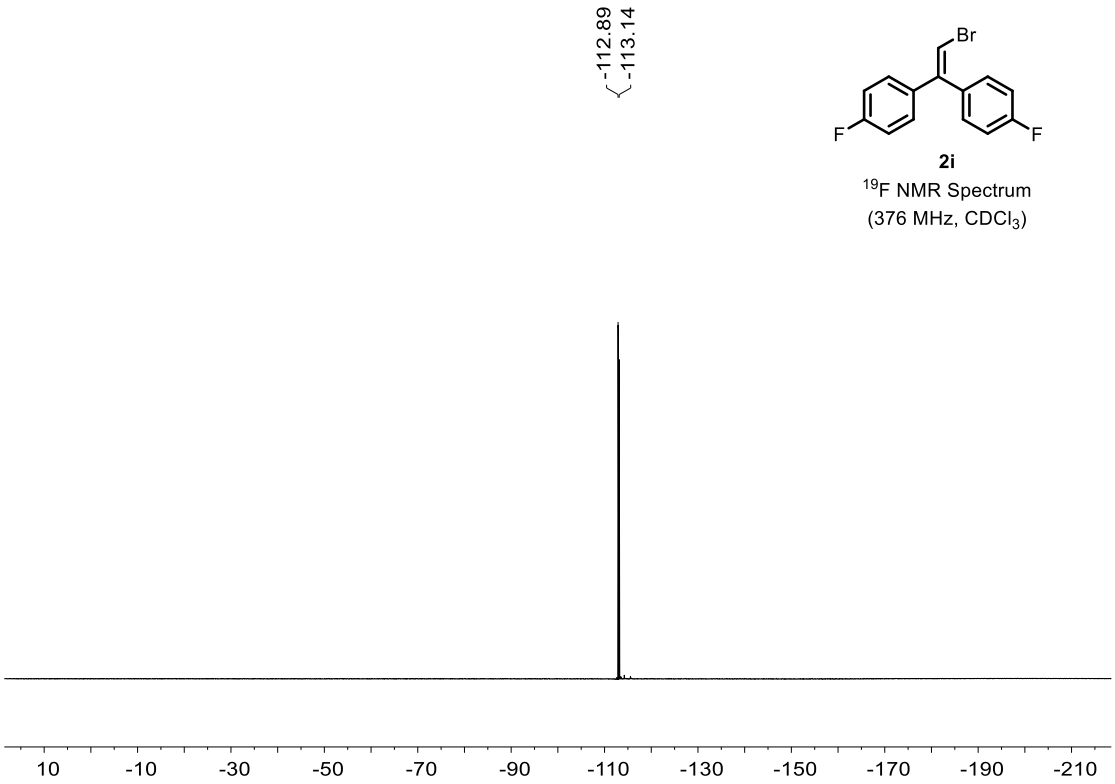




2i

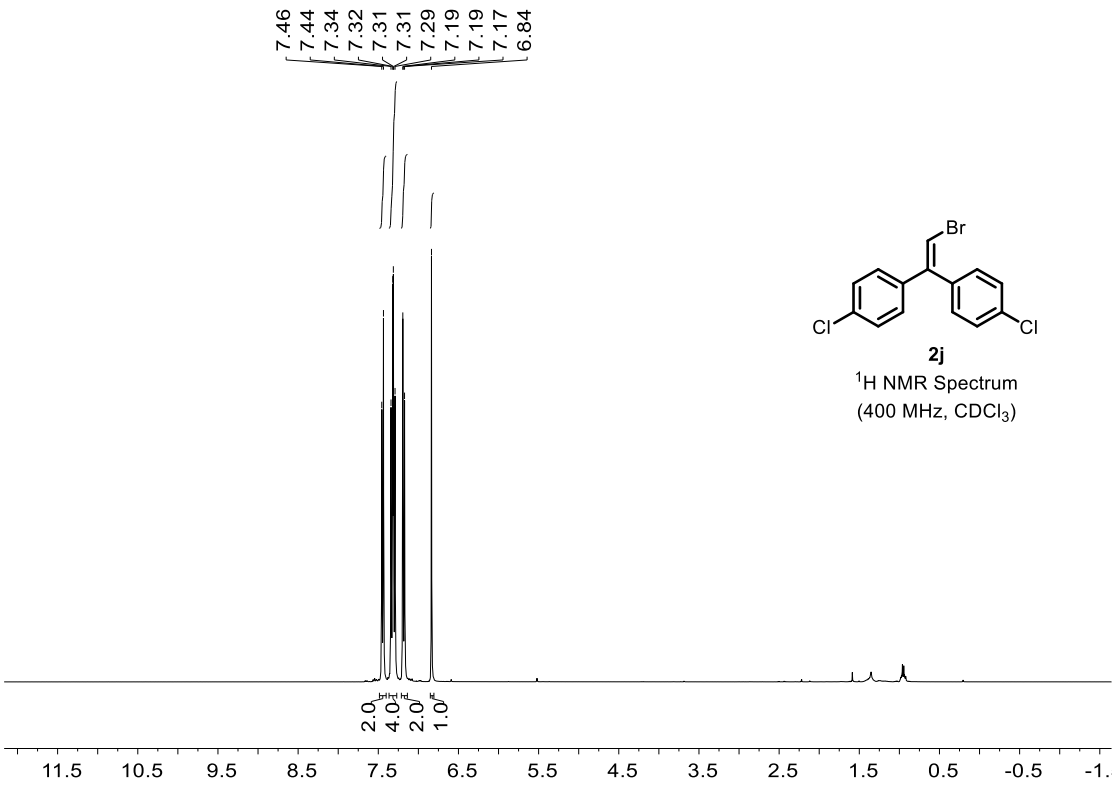
^{13}C NMR Spectrum
(101 MHz, $CDCl_3$)





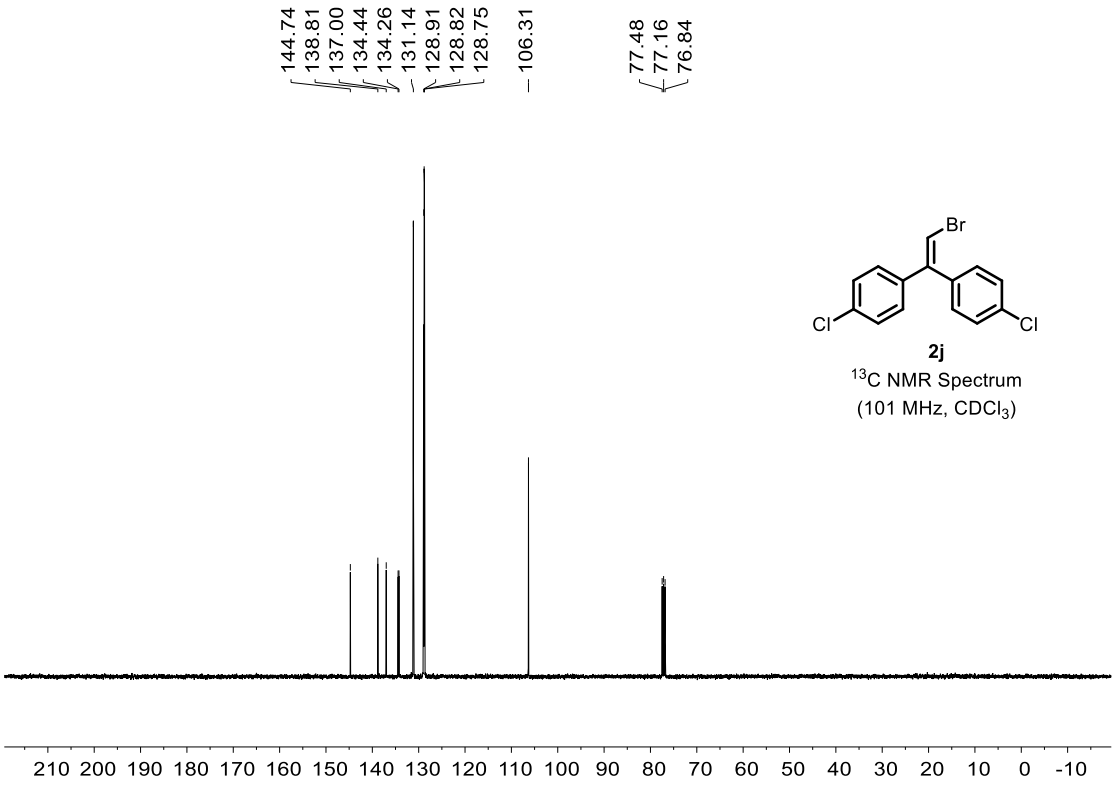
2i

^{19}F NMR Spectrum
(376 MHz, $CDCl_3$)



2j

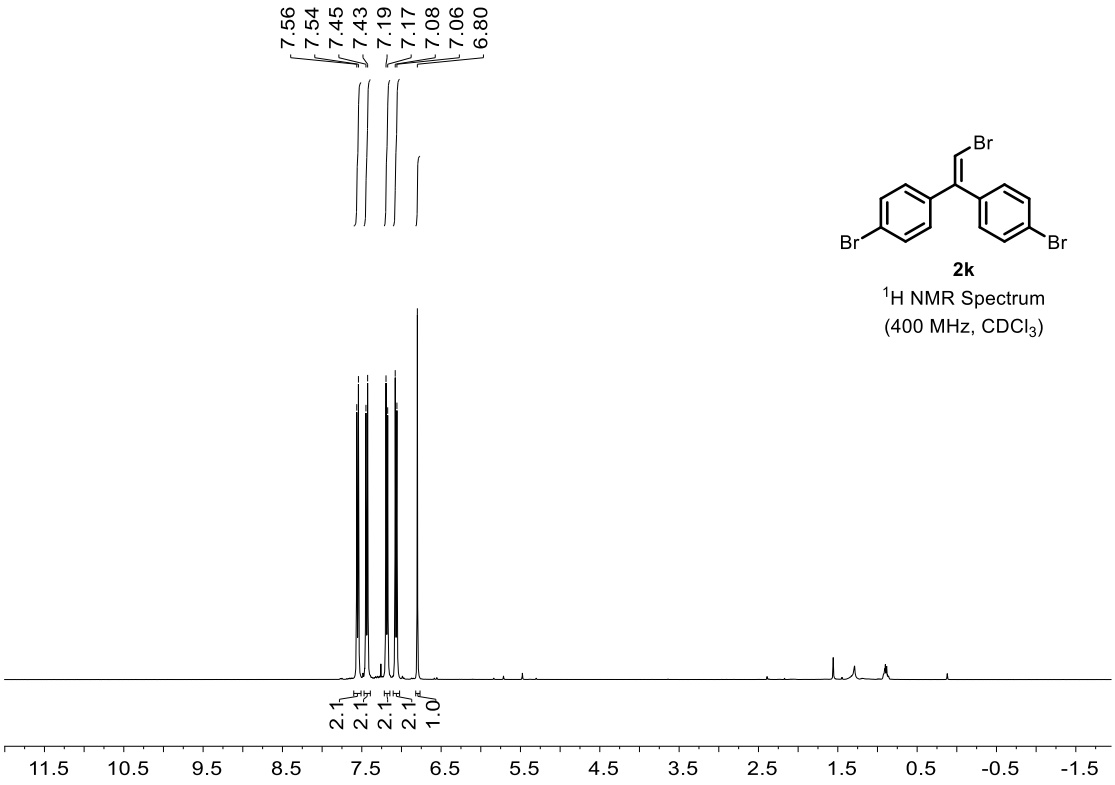
^{1}H NMR Spectrum
(400 MHz, $CDCl_3$)



2j

^{13}C NMR Spectrum

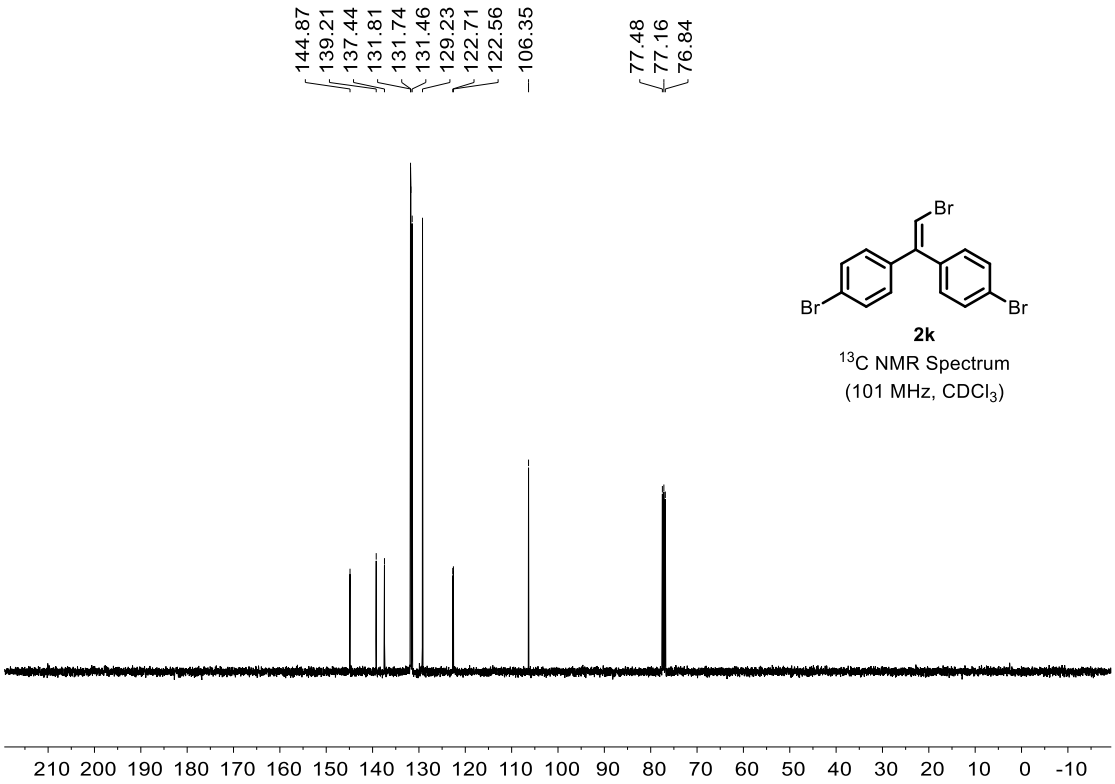
(101 MHz, $CDCl_3$)



2k

^{1}H NMR Spectrum

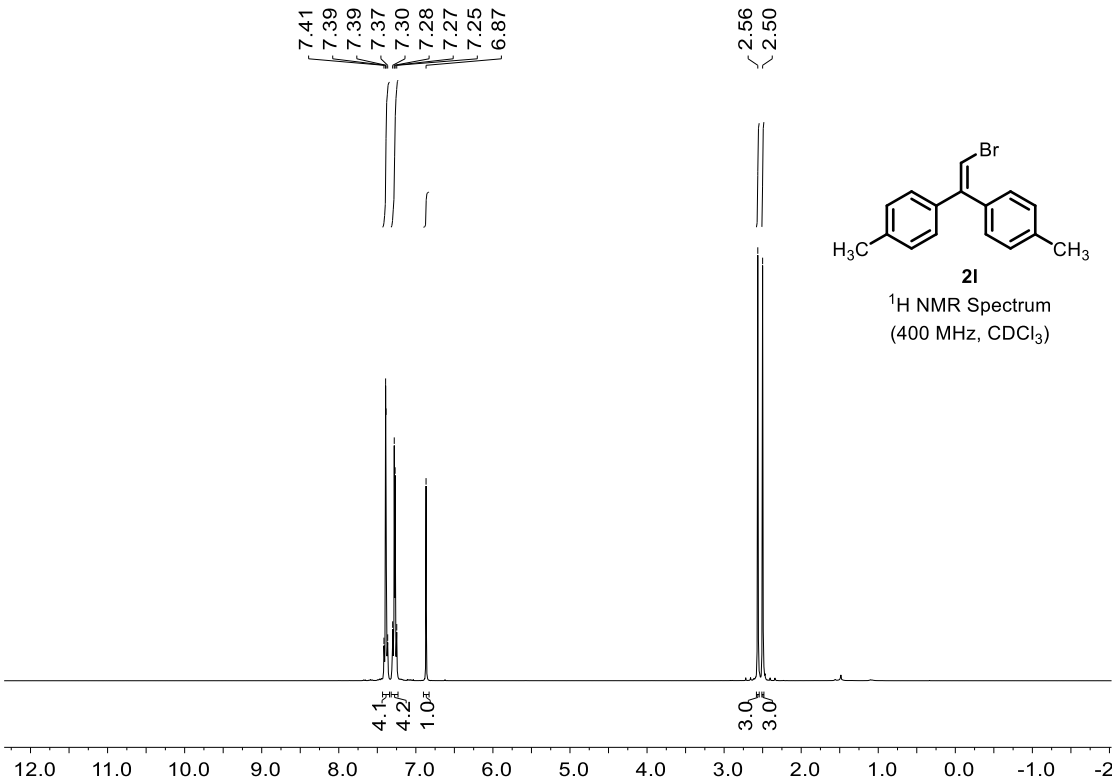
(400 MHz, $CDCl_3$)



2k

^{13}C NMR Spectrum

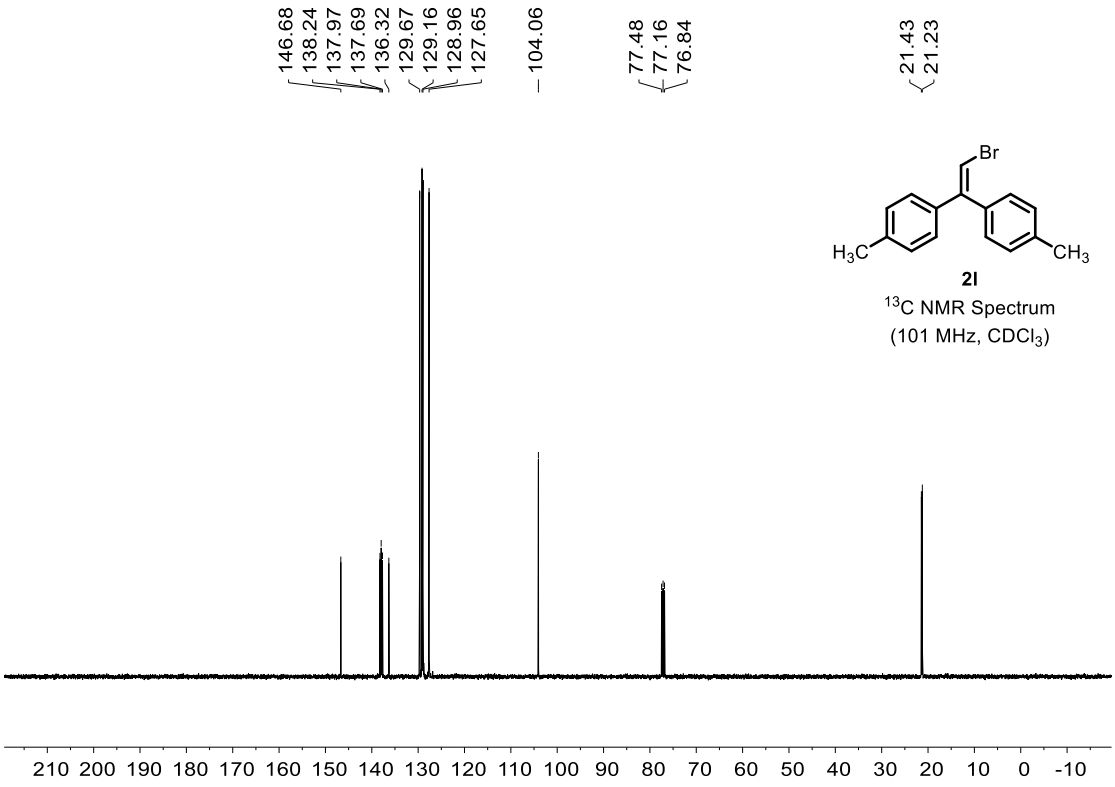
(101 MHz, $CDCl_3$)



2l

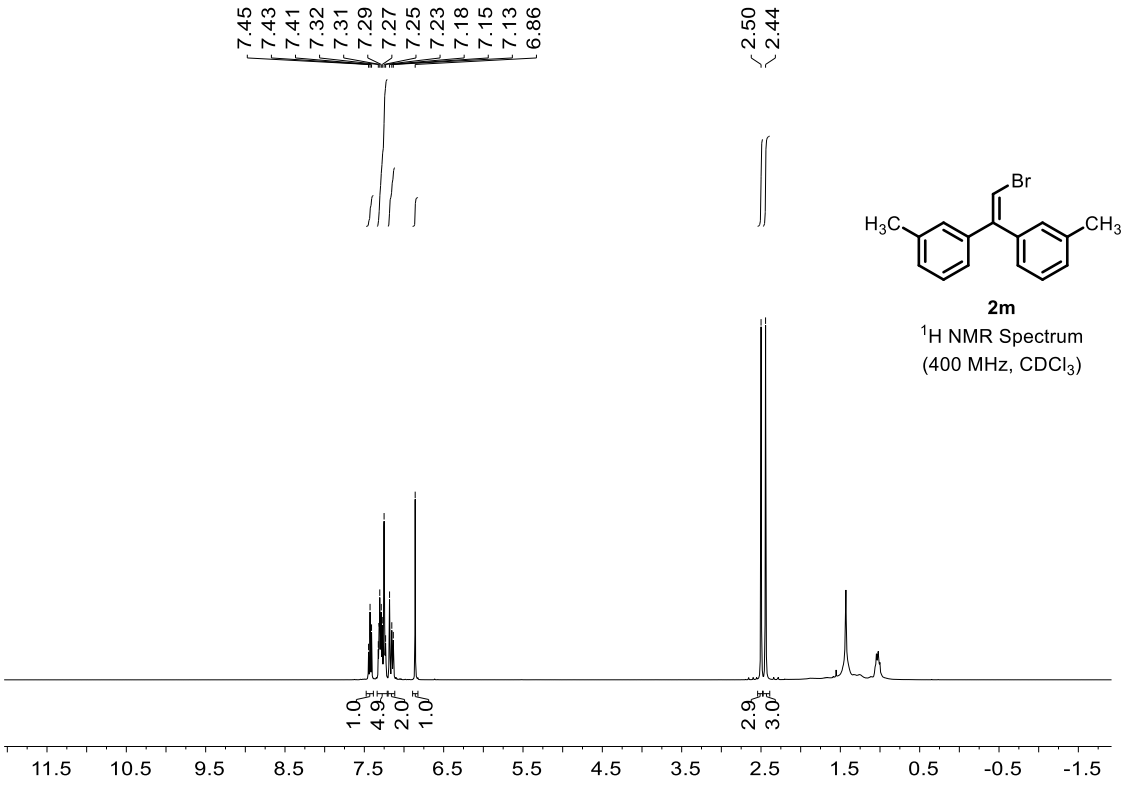
^{1}H NMR Spectrum

(400 MHz, $CDCl_3$)



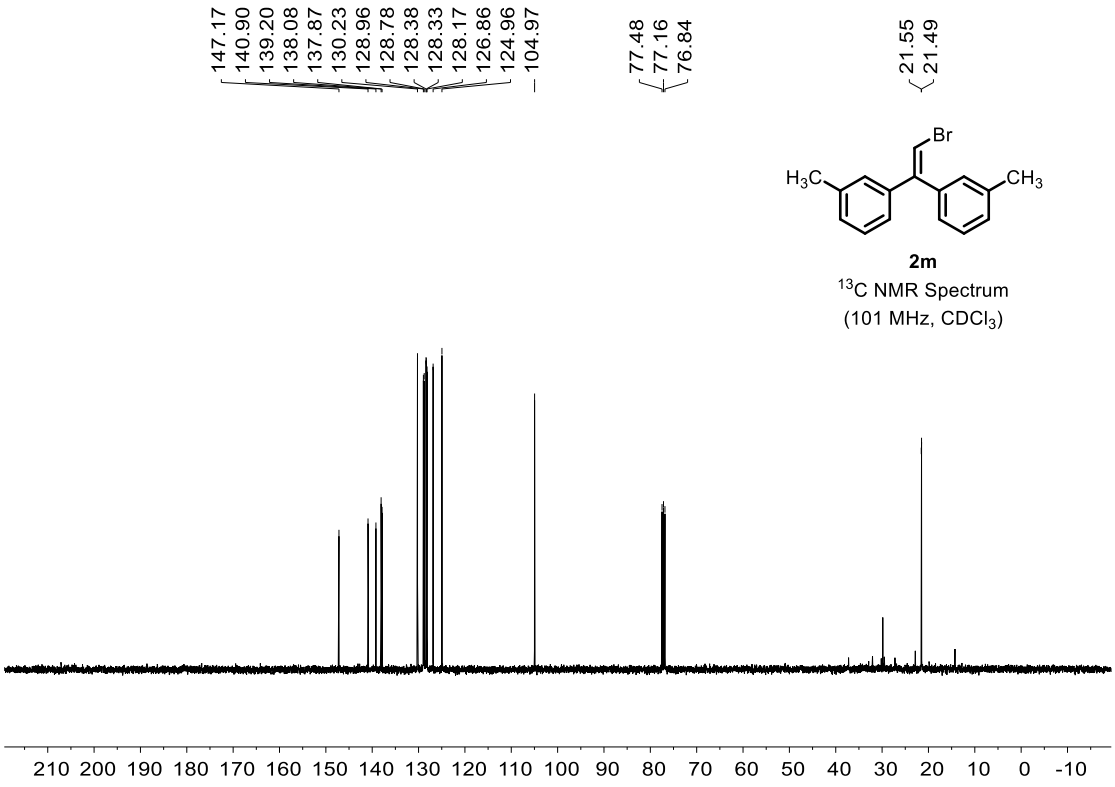
2l

^{13}C NMR Spectrum
(101 MHz, $CDCl_3$)



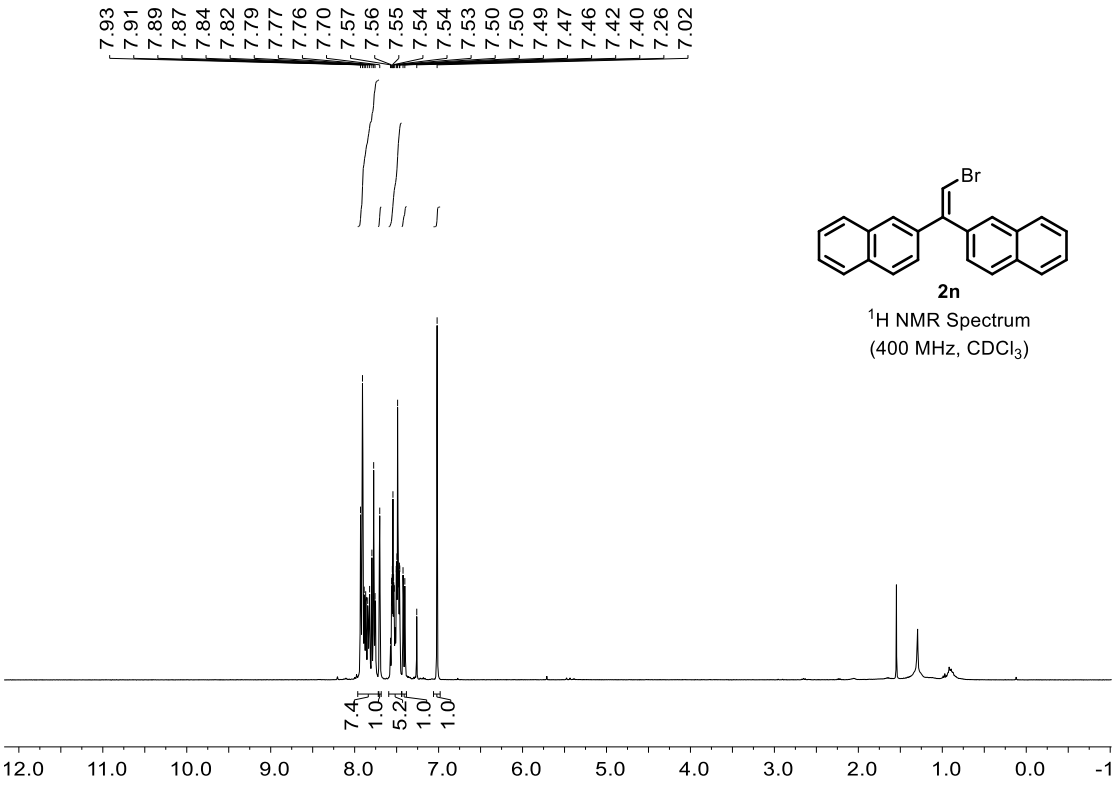
2m

^{1}H NMR Spectrum
(400 MHz, $CDCl_3$)



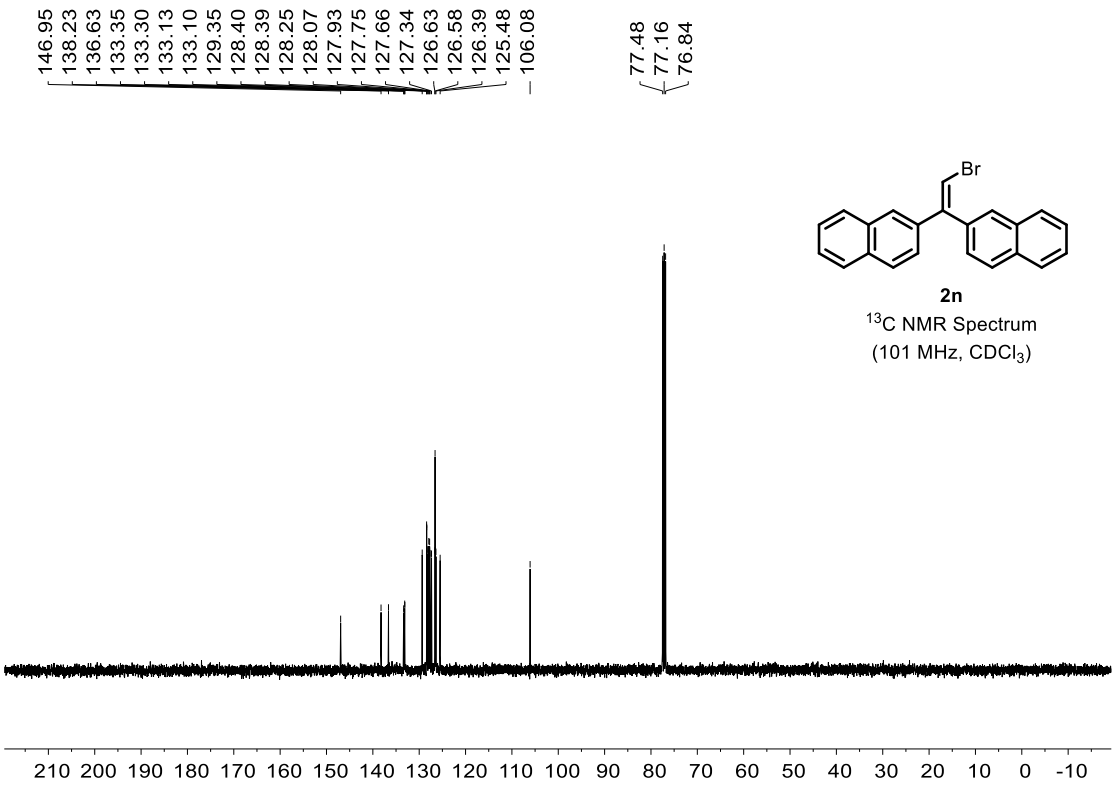
2m

^{13}C NMR Spectrum
(101 MHz, $CDCl_3$)



2n

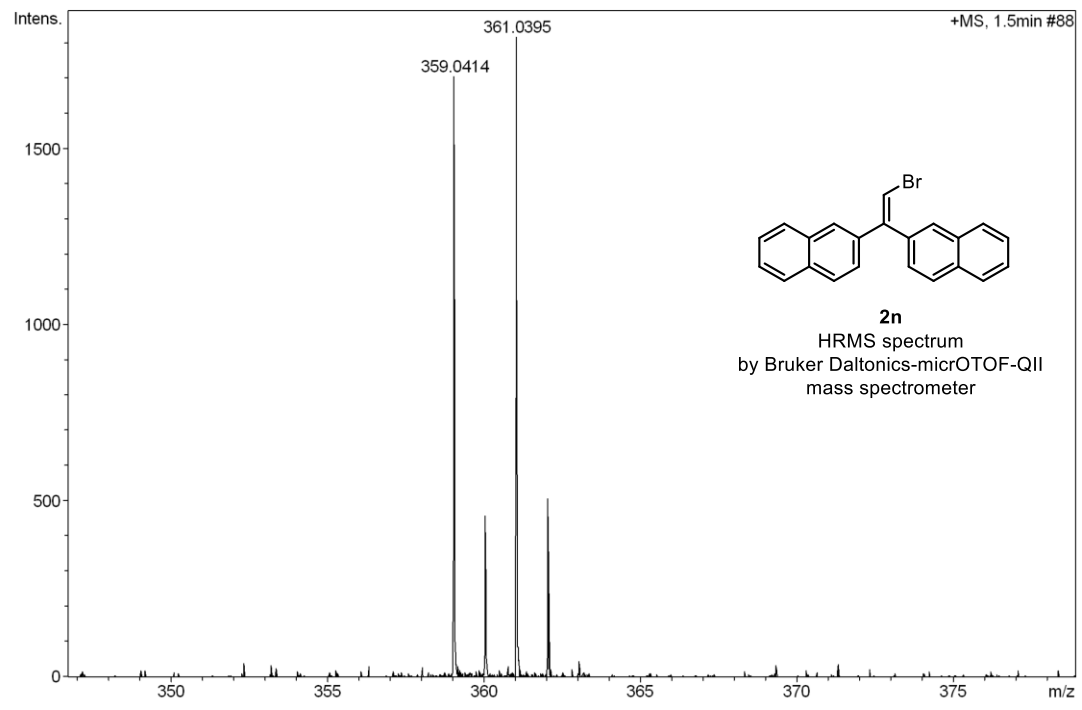
^{1}H NMR Spectrum
(400 MHz, $CDCl_3$)



2n

^{13}C NMR Spectrum

(101 MHz, $CDCl_3$)

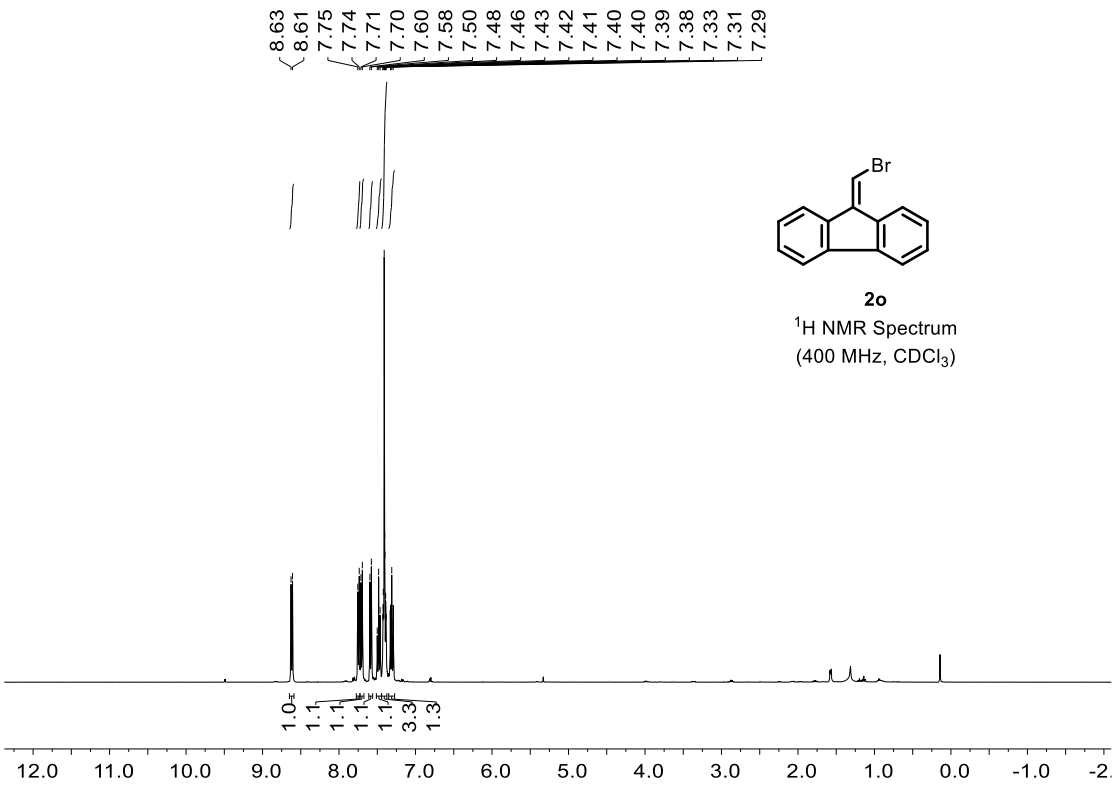


2n

HRMS spectrum

by Bruker Daltonics-micrOTOF-QII

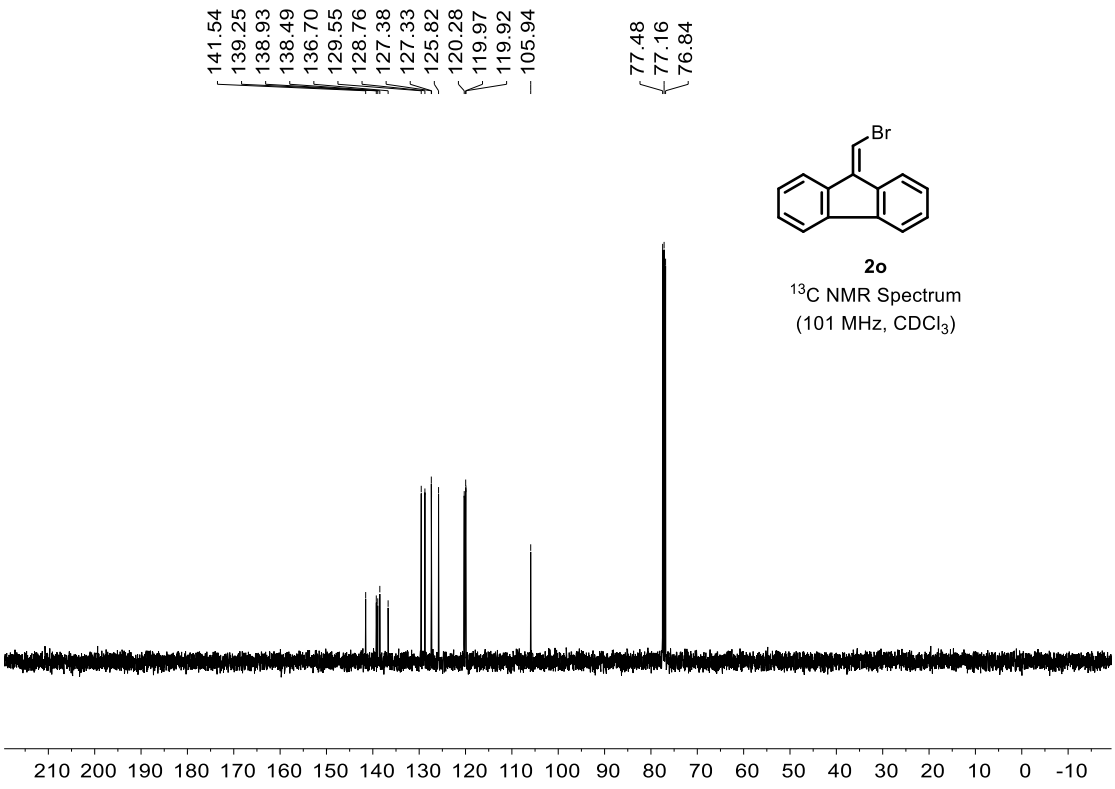
mass spectrometer



2o

^{1}H NMR Spectrum

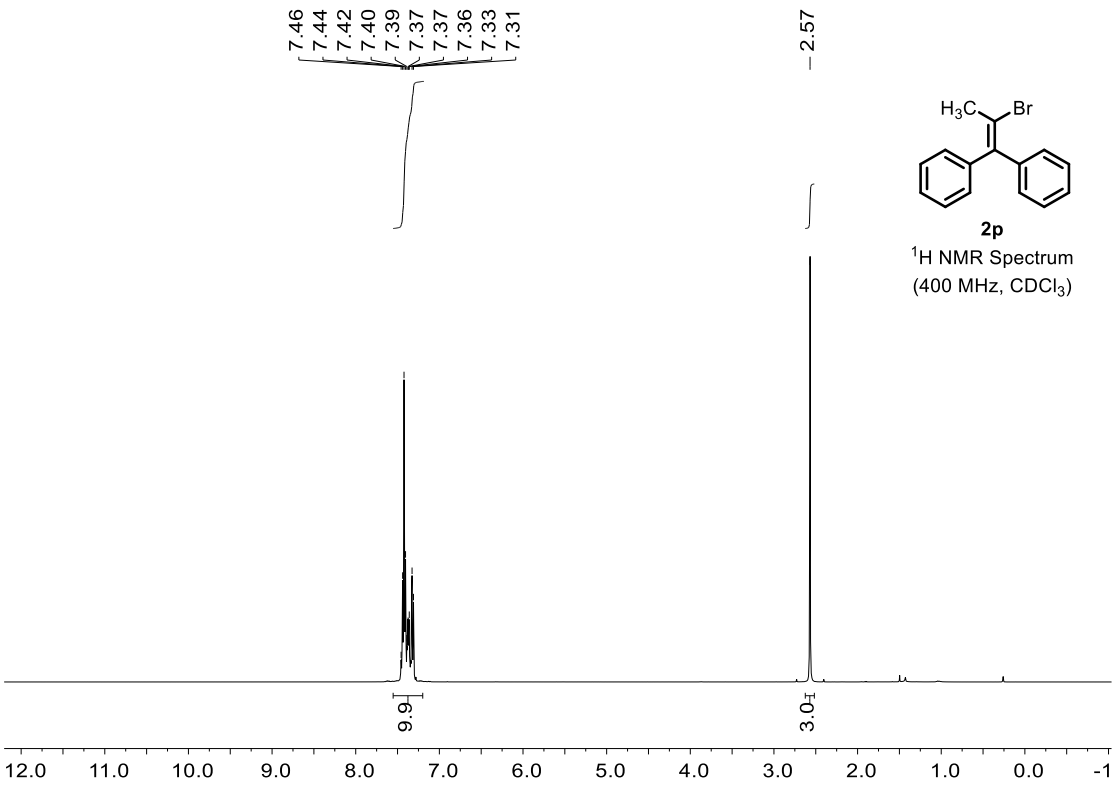
(400 MHz, $CDCl_3$)

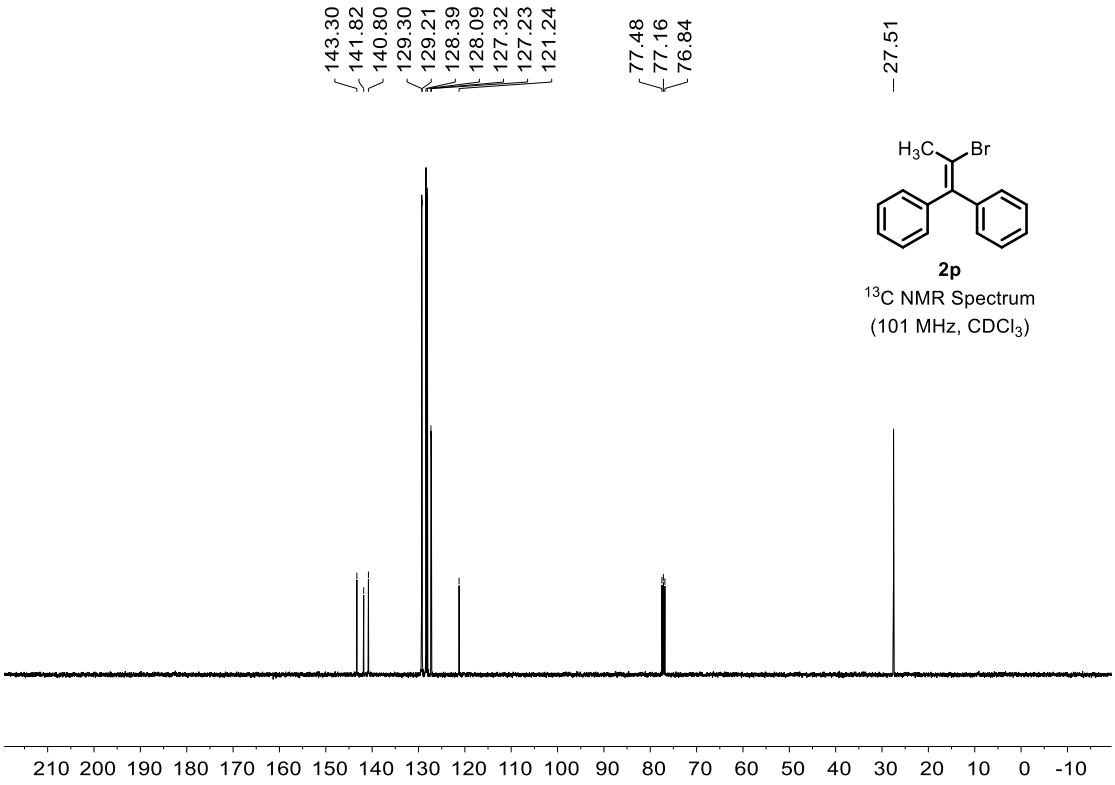


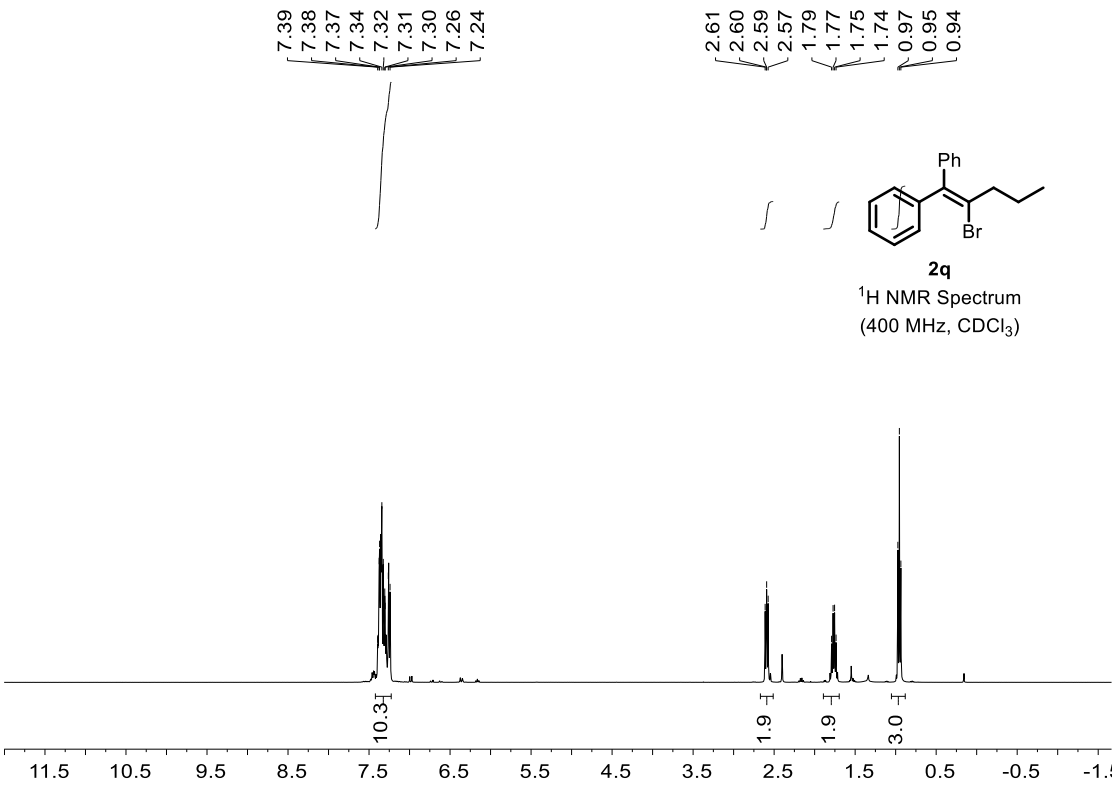
2o

^{13}C NMR Spectrum

(101 MHz, $CDCl_3$)

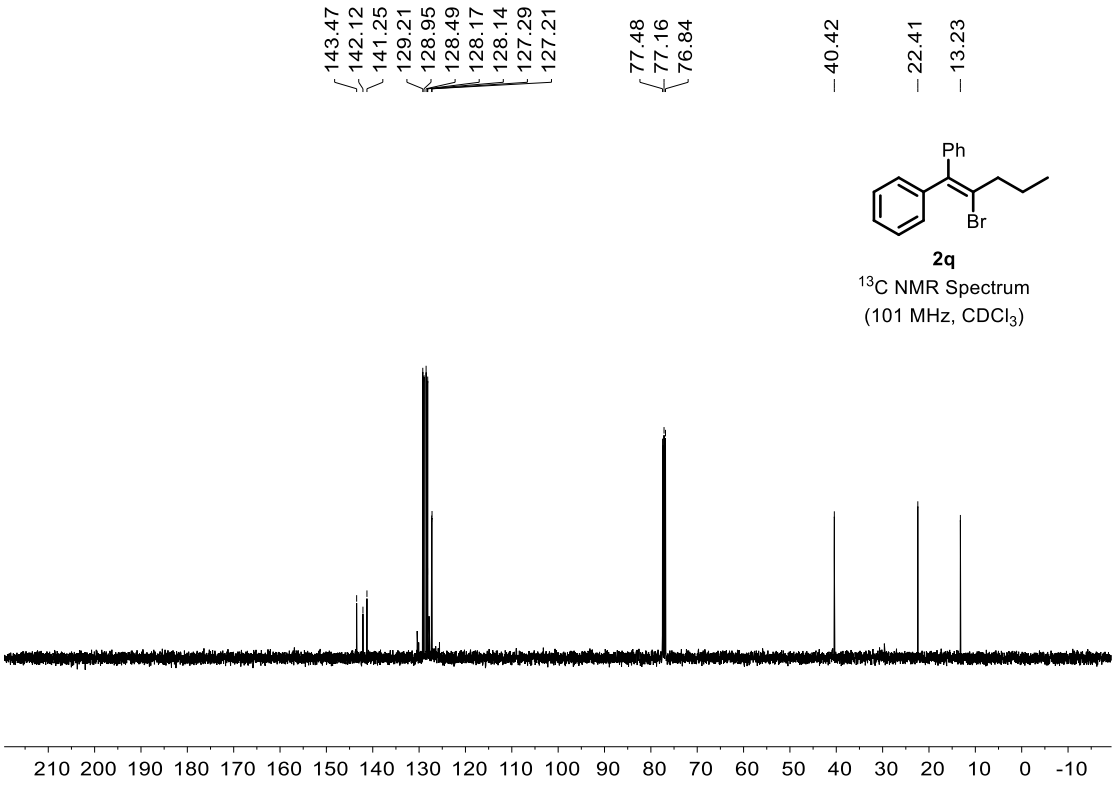

7.46
7.44
7.42
7.40
7.39
7.37
7.37
7.36
7.33
7.31
2.57
H3C
Br
2p
1H NMR Spectrum
(400 MHz, CDCl3)
9.9
3.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1


143.30
141.82
140.80
129.30
129.21
128.39
128.09
127.32
127.23
121.24
77.48
77.16
76.84
27.51
H3C
Br
2p
13C NMR Spectrum
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



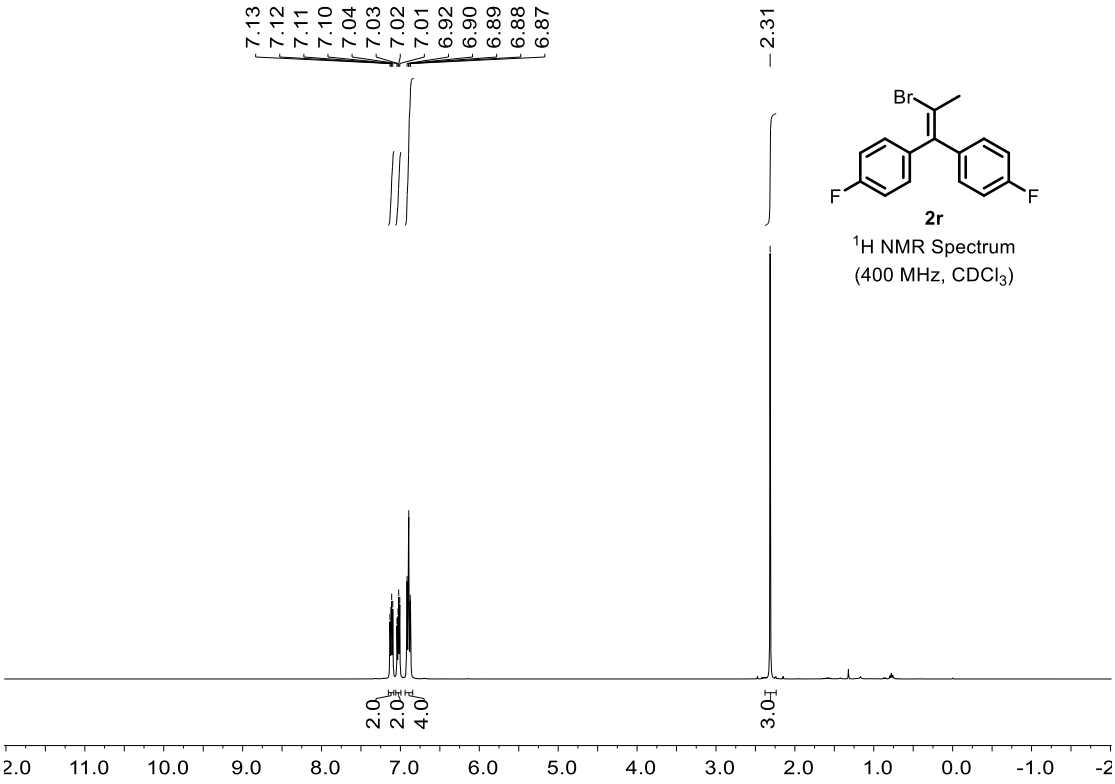
2q

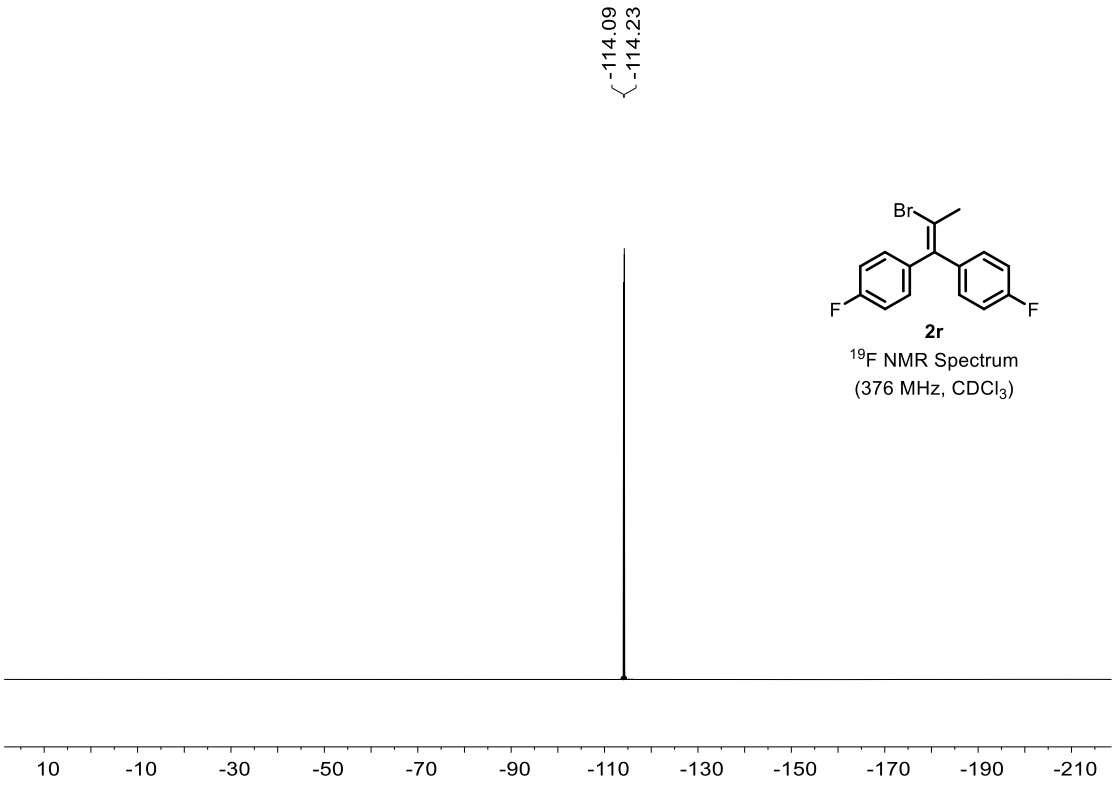
^{1}H NMR Spectrum
(400 MHz, $CDCl_3$)

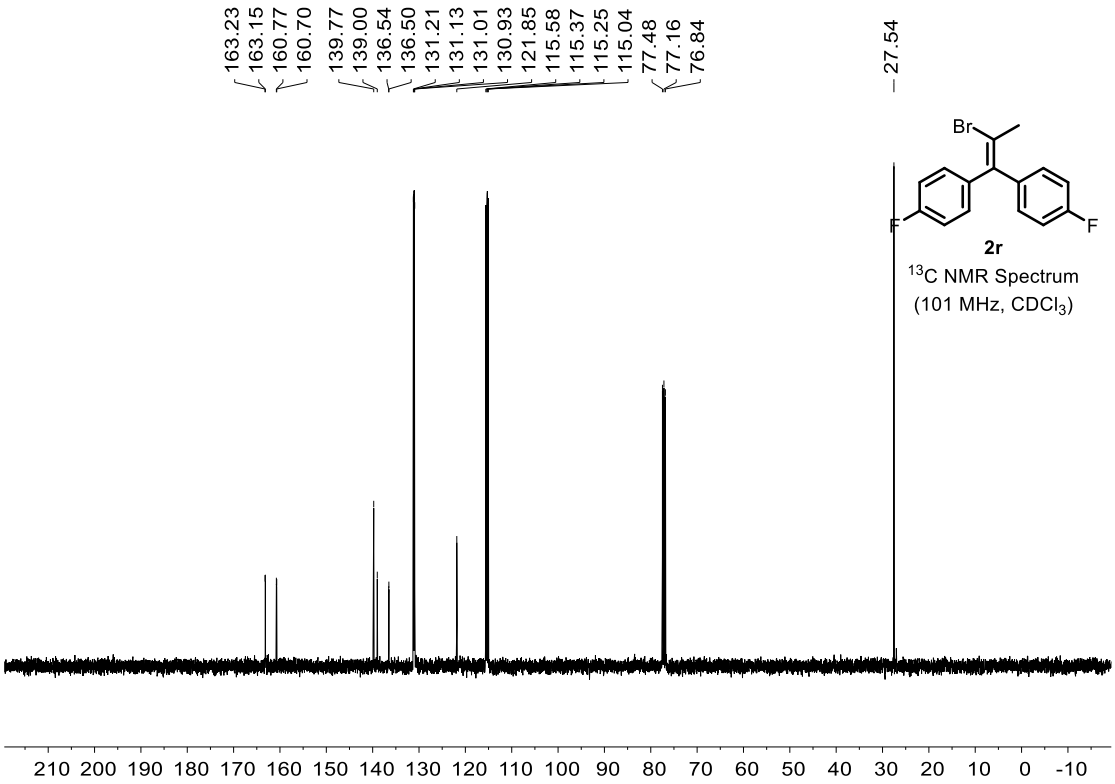


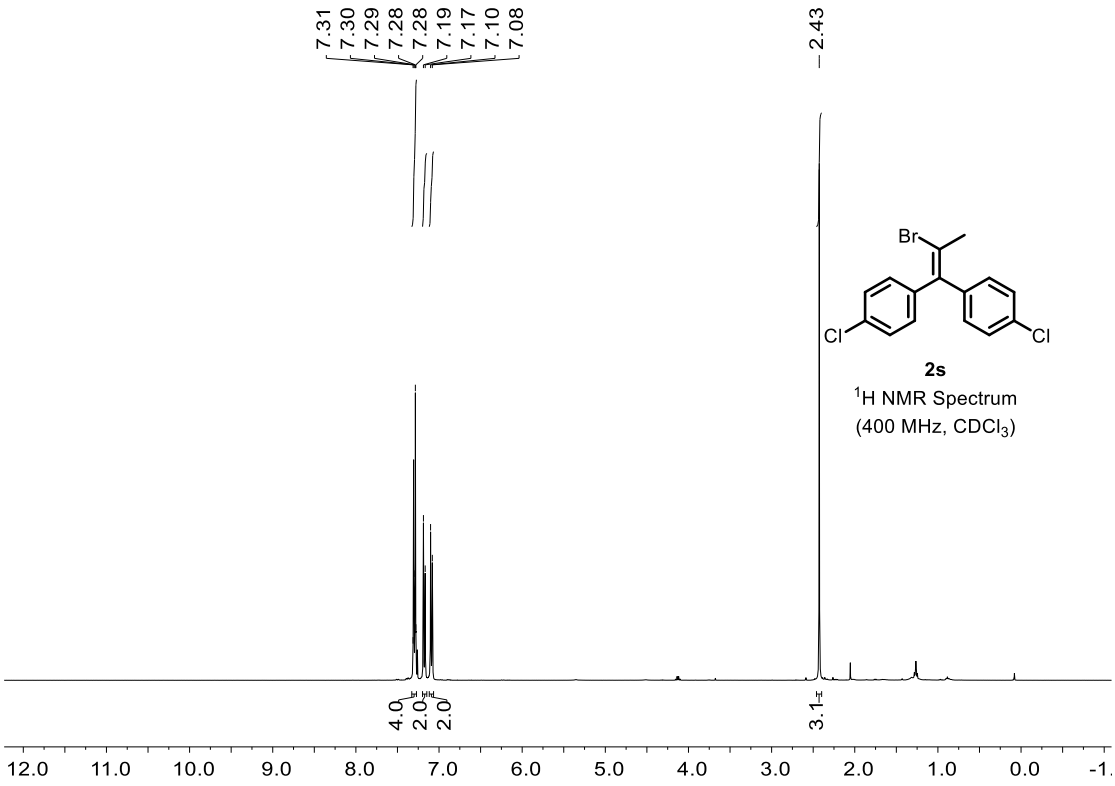
2q

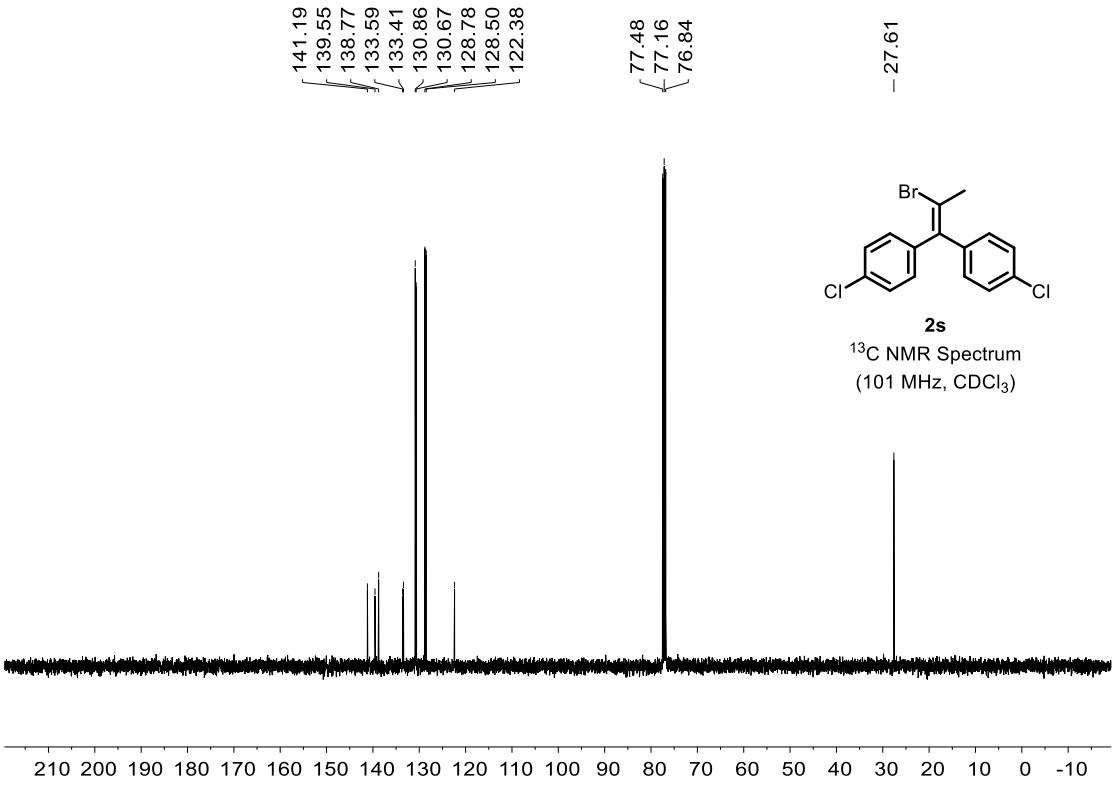
^{13}C NMR Spectrum
(101 MHz, $CDCl_3$)


7.13
7.12
7.11
7.10
7.04
7.03
7.02
7.01
6.92
6.90
6.89
6.88
6.87
2.31
Br
F
F
2r
1H NMR Spectrum
(400 MHz, CDCl3)
2.0
2.0
4.0
3.0
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2


-114.09
-114.23
Br
F
F
2r
19F NMR Spectrum
(376 MHz, CDCl3)
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210


163.23
163.15
160.77
160.70
139.77
139.00
136.54
136.50
131.21
131.13
131.01
130.93
121.85
115.58
115.37
115.25
115.04
77.48
77.16
76.84
27.54
Br
F
F
2r
13C NMR Spectrum
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

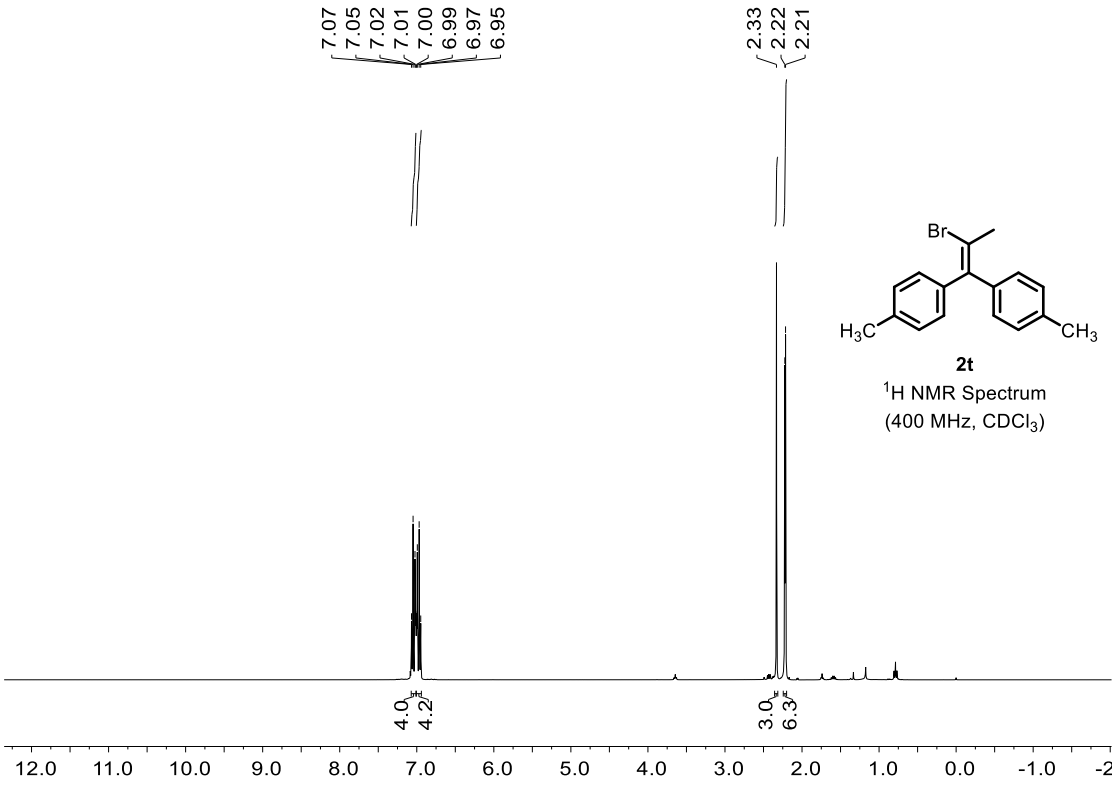

7.31
7.30
7.29
7.28
7.28
7.19
7.17
7.10
7.08
2.43
Br
Cl
Cl
2s
1H NMR Spectrum
(400 MHz, CDCl3)
4.0
2.0
2.0
3.1
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0



2s

^{13}C NMR Spectrum

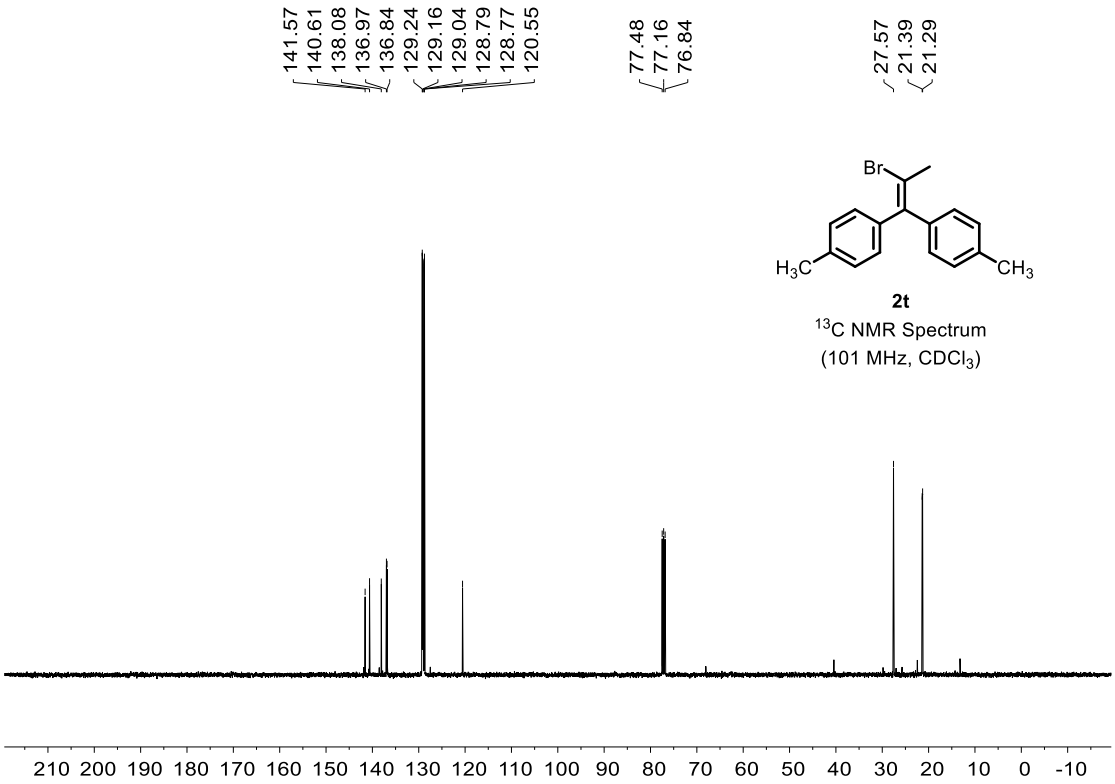
(101 MHz, $CDCl_3$)



2t

^{1}H NMR Spectrum

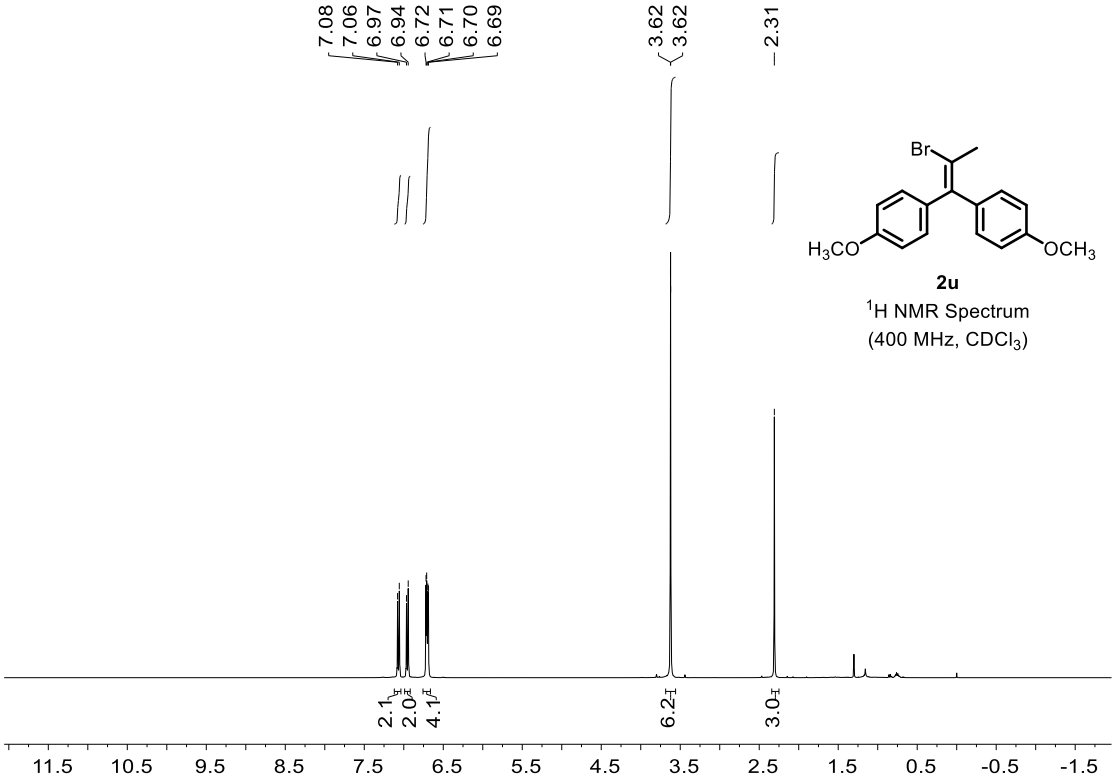
(400 MHz, $CDCl_3$)



2t

^{13}C NMR Spectrum

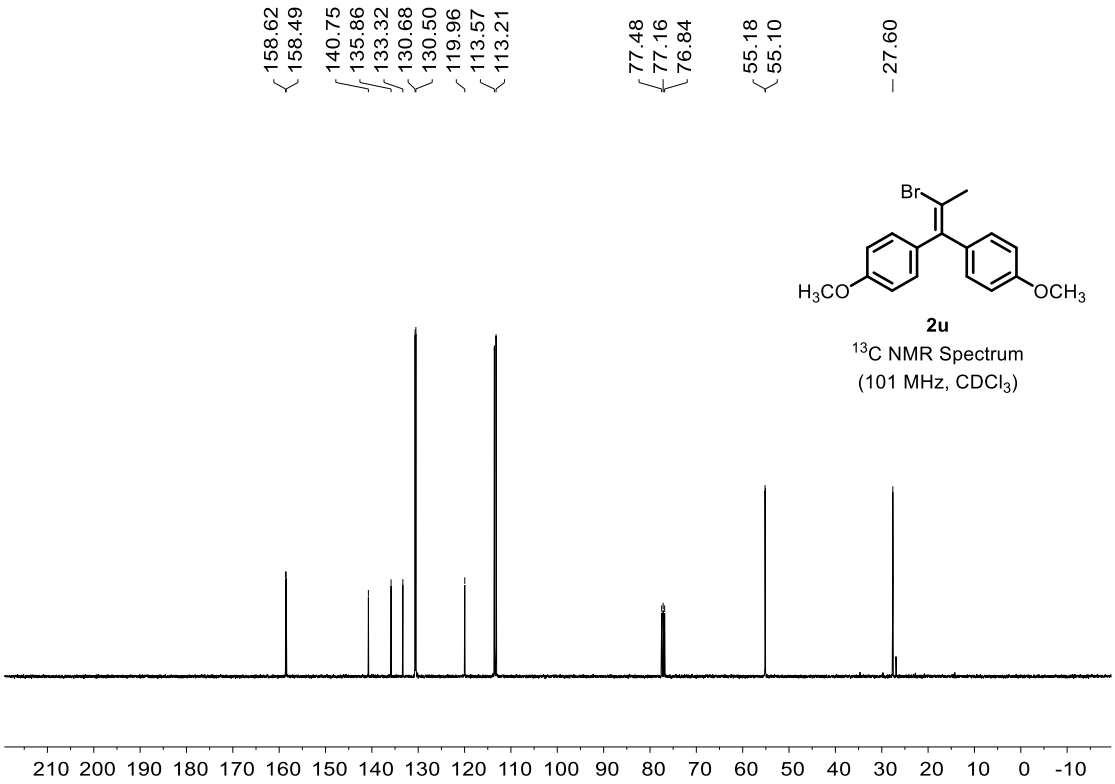
(101 MHz, $CDCl_3$)



2u

^{1}H NMR Spectrum

(400 MHz, $CDCl_3$)


158.62
158.49
140.75
135.86
133.32
130.68
130.50
119.96
113.57
113.21
77.48
77.16
76.84
55.18
55.10
27.60
Br
H3CO
OCH3
2u
13C NMR Spectrum
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10