Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information:

Stereoselective Synthesis of (*Z*/*E*)-1,2-Dibromoalkenes from Terminal Alkynes

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1. General

Unless noted otherwise, commercially available chemicals were used without further purification. Flash chromatography was performed with silica gel (200-300 mesh). Oil bath served as the heat source. NMR spectra were acquired on Bruker 400 MHz (^{1}H at 400 MHz, ^{13}C at 101 MHz) or Jeol 400 MHz (^{1}H at 400 MHz, ^{13}C at 101 MHz). Unless otherwise noted, all spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, $\delta = 0.00$ ppm) and are referenced to residual solvent ($CDCl_3$, $\delta = 7.26$ ppm (^{1}H) and 77.16 ppm (^{13}C)). Coupling constants were reported in Hertz (Hz). Data for 1H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), an integration). Infrared (IR) data were acquired on a Bruker Invenio-R FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were acquired on a BrukerDaltonics S2 MicroTof-Q II mass spectrometer. X-ray crystal structure analyses were measured on Bruker Smart APEXIICCD instrument using Ga-Kα radiation. The structures were solved and refined using the SHELXTL software package.

2. Experimental section

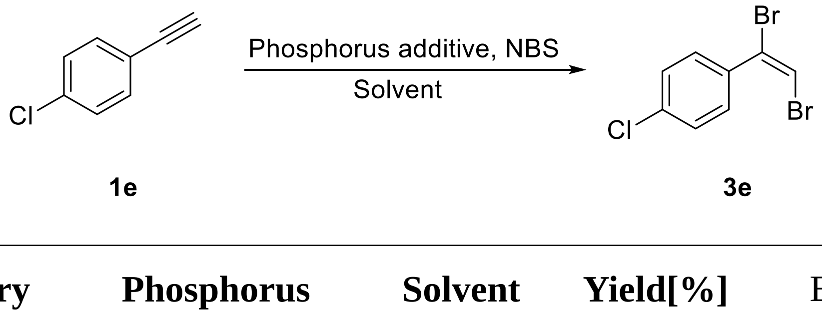
2.1 Synthesis of (*Z*)-1,2-Dibromoalkenes

To a mixture of $AgNO_3$ (10 mol%), NBS (2 equiv) and CH_3SO_3H (10 mol%) in 1,4-dioxane (0.2 mL) was added terminal alkyne (**1**, 0.2 mmol). The reaction mixture was without stirred at room temperature for 8 h. After removal of the solvents with a rotary evaporator, the residue was purified by column chromatography.

2.2 Synthesis of (*E*)-1,2-Dibromoalkenes

To a mixture of PPh_3 (0.2 mmol) and terminal alkyne (**1**, 0.2 mmol) in CH_2Cl_2 (0.4 mL) was added NBS (0.4 mmol). The reaction mixture was stirred at room temperature for 6 h. After removal of the solvents with a rotary evaporator, the residue was purified by column chromatography.

Table s1. Reaction Optimization[a]

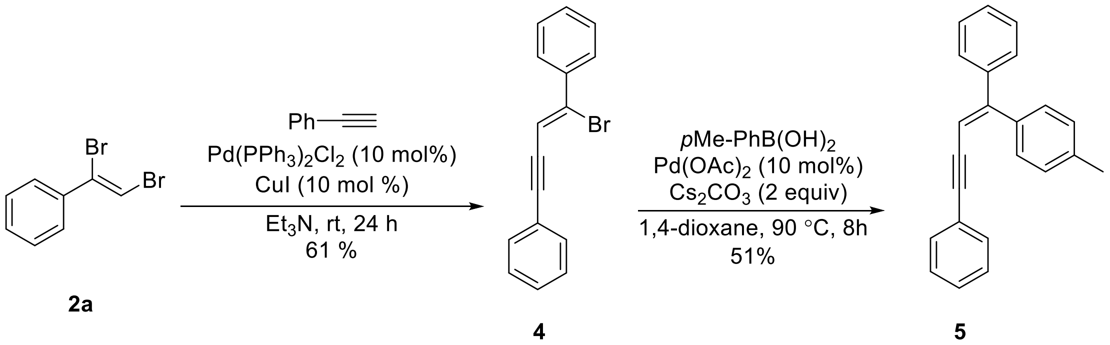


Entry	Phosphorus additive	Solvent	Yield[%]	E/Z
1	$OPPh_3$	1,4-Dioxane	trace	-

2	$P(OPh)_3$	1,4-Dioxane	66%	14:1
3	PPh_3	1,4-Dioxane	76%	20:1
4	PPh_3	CH_3OH	56%	15:1
5	PPh_3	C_2H_5OH	62%	18:1
6	PPh_3	*n*-Propanol	62%	20:1
7	PPh_3	*i*-Propanol	62%	20:1
8	PPh_3	THF	61%	18:1
9	PPh_3	CH_2Cl_2	76%	20:1
10	PPh_3	$CHCl_3$	74%	20:1
11[b]	PPh_3	CH_2Cl_2	48%	1:1

[a] Reaction conditions: **1e** (0.2 mmol), **phosphorus additive** (0.2 mmol), NBS (0.4 mmol) in **solvent** (0.4 mL) at room temperature for 6 h; [b] Using phosphorus additive (0.1 mmol).

2.3 Application of this method[1]



Step 1: To a mixture of $Pd(PPh_3)_2Cl_2$ (14.0 mg), CuI (3.8 mg,), Et_3N (1 mL) and **2a** (52.4 mg, 0.2 mmol) was slowly added phenylacetylene (27 μL, 0.25 mmol). After stirring overnight at room temperature under Ar,

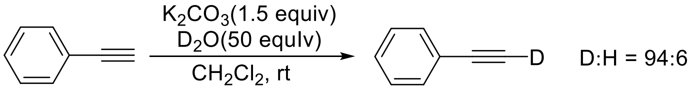
the reaction mixture was quenched with water, extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Column chromatography on silica gel (petroleum ether) gave 34.5 mg (yield: 61%) of **4** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.57 – 7.55 (m, 2H), 7.43 – 7.37 (m, 6H), 6.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 135.2, 131.8 (2C), 129.7, 128.8, 128.6 (2C), 128.5 (2C), 127.6 (2C), 123.2, 111.4, 97.4, 88.1. HRMS (ESI): Calcd for $C_{16}H_{11}{}^{79}BrNa$ 304.9936, Found 304.9941; Calcd for $C_{16}H_{11}{}^{81}BrNa$ 306.9916, Found 306.9929. IR: 3056, 2921, 2850, 1807, 1647, 1598, 1485, 1442, 1278, 1214, 753, 687, 591, 529 cm^{-1}.

Step 2: To a mixture of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (26.2 mg, 0.1 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol) and *p*-tolylboronic acid (33.9 mg, 0.25 mmol) was added a solution of **4** (56.6 mg, 0.2 mmol) in 1 mL of dry 1,4-dioxane. After stirring overnight at 90 °C under argon, the reaction mixture was quenched with water, extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Column chromatography on silica gel (petroleum ether) gave 29.4 mg (yield: 51%) of compound **5**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.35 – 7.31 (s, 7H), 7.30 – 7.26 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.18 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 141.9, 138.2, 136.4, 131.5 (2C), 130.3 (2C), 128.6 (2C), 128.4(5C), 128.3

(2C), 128.1, 123.9, 106.7, 93.6, 89.5, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{18}Na$ 317.1301; Found 317.1299. IR: 3054, 3025, 2920, 1647, 1598, 1511, 1444, 1156, 915, 823, 755, 690 cm^{-1}.

3. General procedure for the mechanistic experiments

3.1 Preparation of (ethynyl-d)benzene[2]



A flame dried 10mL round bottomed flask was charged with phenylacetylene (**1a**, 0.1 mL, 1 mmol) and potassium carbonate (207 mg, 1.5 mmol) in dry CH_2Cl_2 (2mL). This was allowed to stir under an atmosphere of Ar for 30 minutes. To this D_2O (500 μL, 50 equiv) was added and left to stir for 1 hour. After removal of the solvents with a rotary evaporator, the residue was purified by column chromatography. Subsequent NMR analysis showed the alkyne had been deuterated.

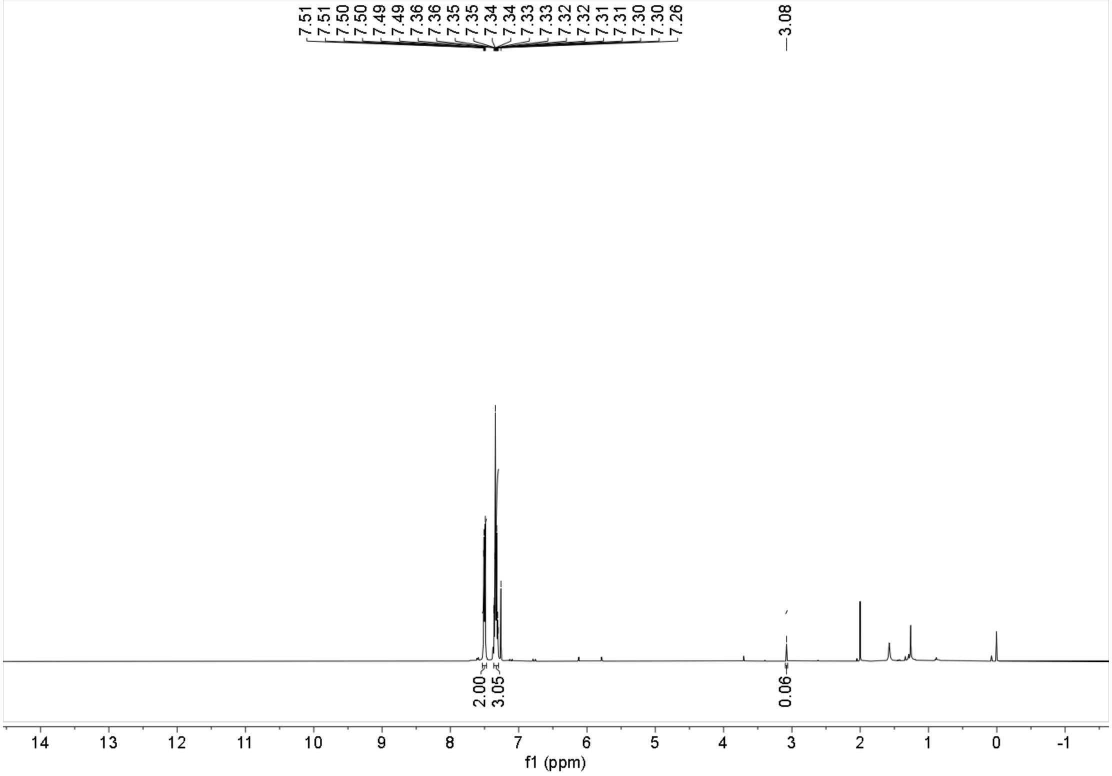
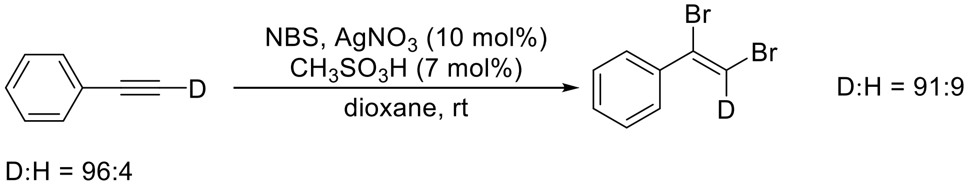


Figure S1 ^{1}H NMR spectrum of (ethynyl-*d*)benzene

3.2 H/D exchange experiment



To a mixture of $AgNO_3$ (10 mol%), NBS (2 equiv) and CH_3SO_3H (5 mol%) in 1,4-Dioxane (0.4 mL) was added (ethynyl-*d*)benzene (0.2 mmol). The reaction mixture was without stirred at room temperature for 8 h. After removal of the solvents with a rotary evaporator, the residue was purified by column chromatography.

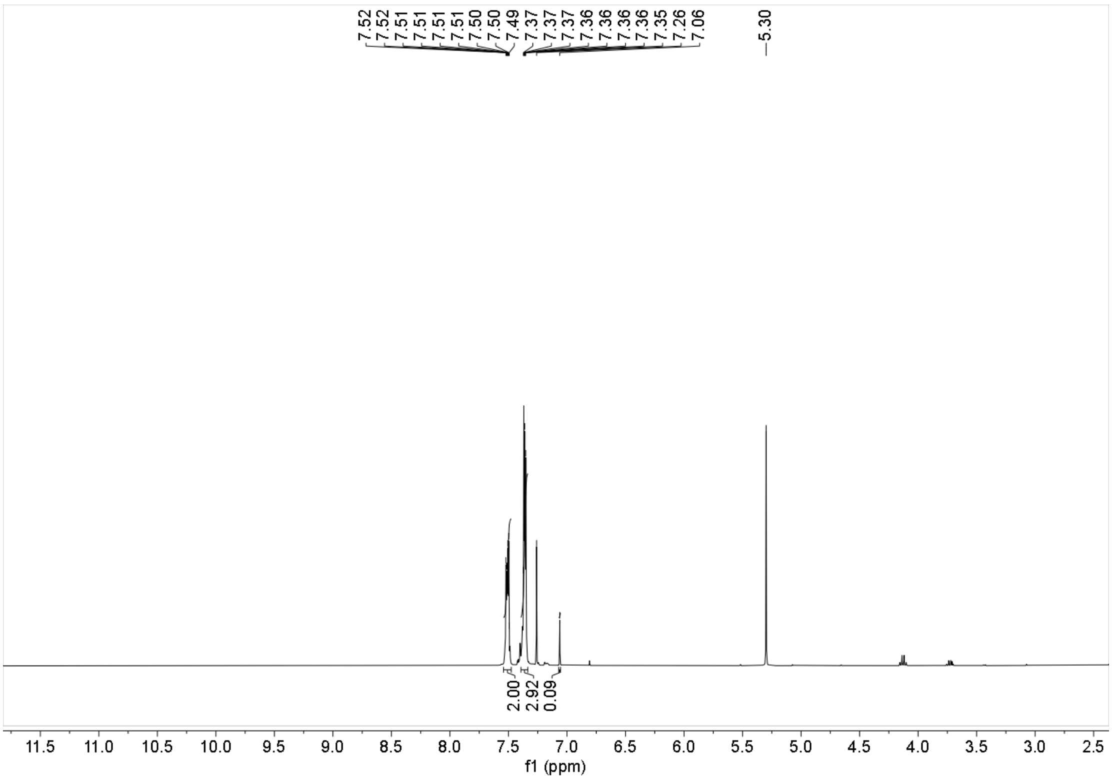
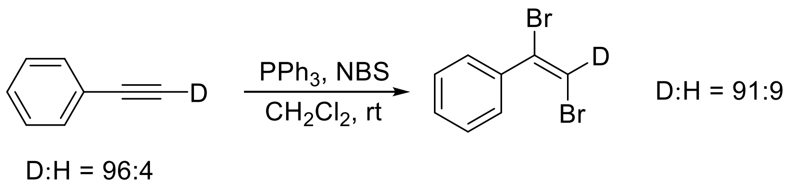


Figure S2 ^{1}H NMR spectrum of (*Z*)-(1,2-dibromovinyl-2-d)benzene



To a mixture of PPh$_3$ (2 equiv) and NBS (2 equiv) in CH$_2$Cl$_2$ (0.6 mL) was added (ethynyl-*d*)benzene (0.2 mmol). The reaction mixture was without stirred at room temperature for 6 h. After removal of the solvents with a rotary evaporator, the residue was purified by column chromatography.

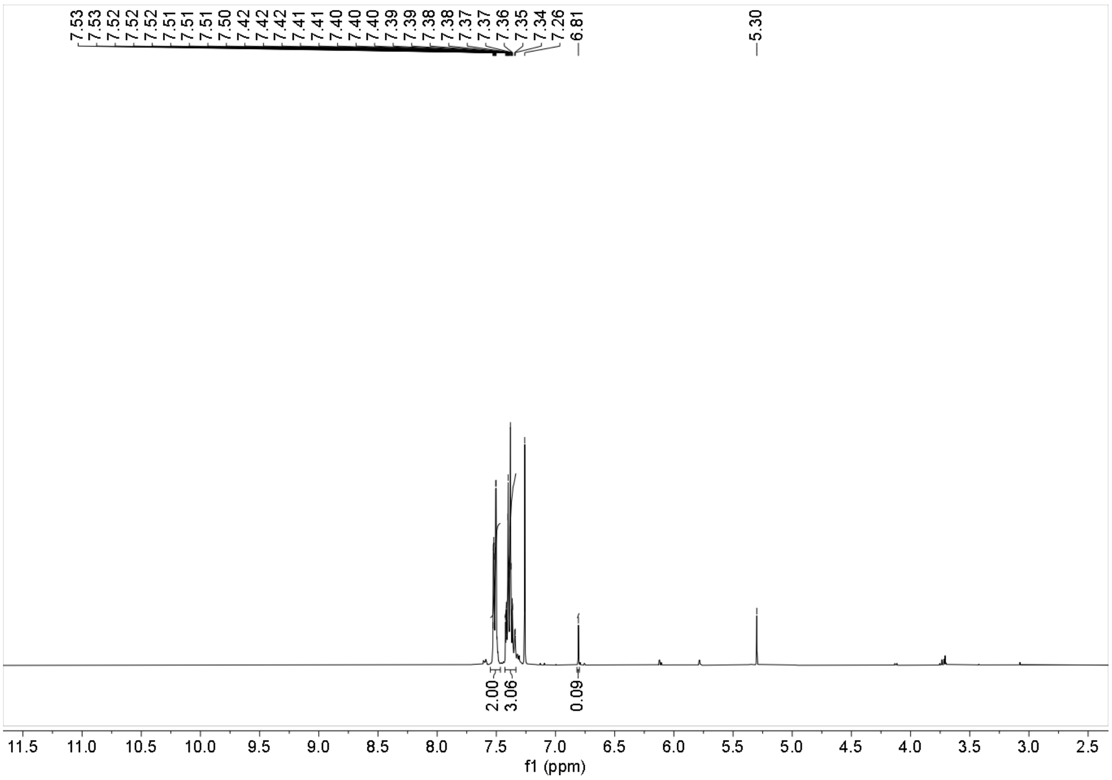


Figure S3 ^{1}H NMR spectrum of (*E*)-(1,2-dibromovinyl-2-d)benzene

3.3 NMR Investigations[3]

To further verify our proposed mechanism, We studied the interaction of NBS and CH$_3$SO$_3$H by using NMR spectroscopy. Figure **S4-3** shows that the peak marked with H corresponded to the CH$_2$ signal of NBS, located at 2.96 ppm in $CDCl_3$. Figure **S4-2** shows that the peak marked with H corresponded to the CH_3 signal of CH_3SO_3H, located at 3.16 ppm in $CDCl_3$. When NBS and CH_3SO_3H are added to $CDCl_3$ (Figure **S4-1**), There was a downfield shift of the methylene group of NBS from 2.96 to 2.98 ppm and a upfield shift of the methyl group of CH_3SO_3H from 3.16 to 3.10 ppm.

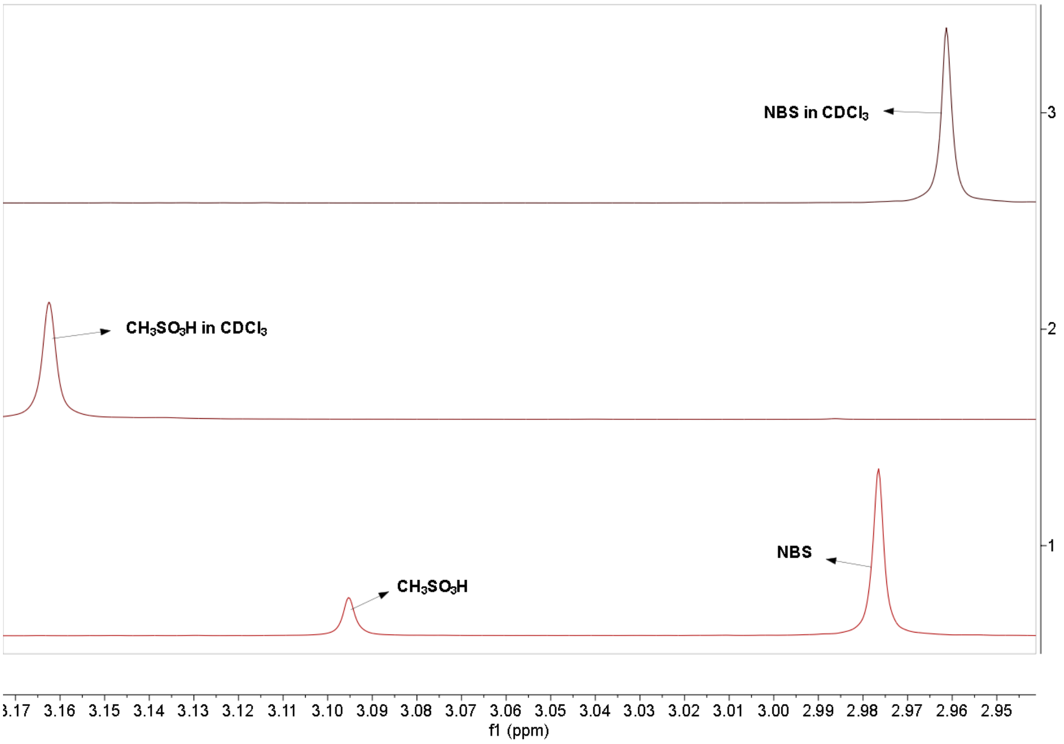
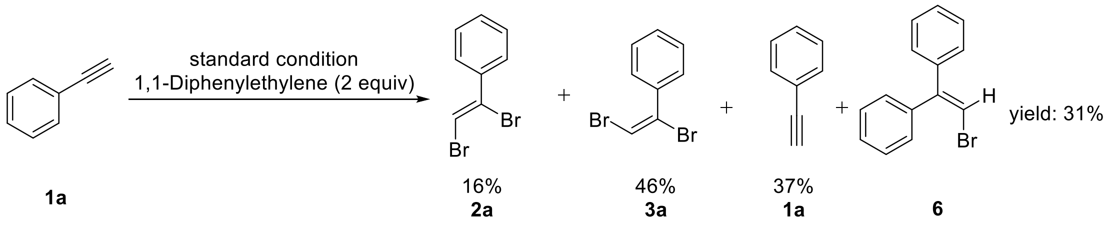


Figure S4 NMR Investigations
(1-3) ^{1}H NMR spectra of (1) NBS and CH_3SO_3H in $CDCl_3$; (2) only CH_3SO_3H in $CDCl_3$; (3) only NBS in $CDCl_3$.

3.4 radical experiment



To a mixture of $AgNO_3$ (10 mol%), NBS (2 equiv), 1,1-Diphenylethylene(2 equiv) and CH_3SO_3H (5 mol%) in 1,4-dioxane (0.2 mL) was added phenylacetylene (**1a**, 0.2 mmol) The reaction mixture was without stirred at room temperature for 8 h. After removal of the solvent with a rotary evaporator, column chromatography on silica gel (petroleum ether) gave 16.1 mg (yield: 31%) of compound **6**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 3H), 7.35 – 7.27 (m, 5H), 7.25 – 7.19 (m, 2H), 6.79 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 140.8, 139.2, 129.8 (2C), 128.6 (2C), 128.4 (2C), 128.3, 128.1, 127.8 (2C), 105.3. HRMS (ESI): Calcd for $C_{14}H_{11}{}^{79}BrNa$ 280.9936, Found 280.9935; Calcd for $C_{14}H_{11}{}^{81}BrNa$ 282.9916, Found 282.9927. IR: 3057, 2922, 1886, 1808, 1590, 1494, 1442, 1218, 1075, 933, 762, 739, 694, 611 cm^{-1}.

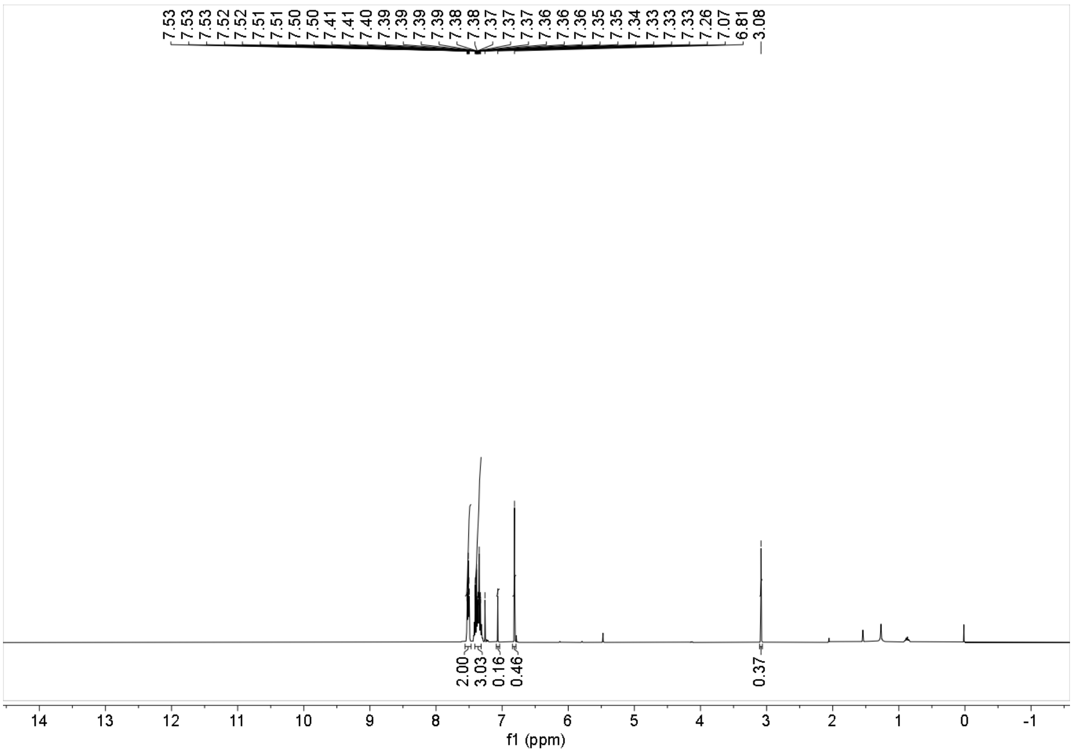
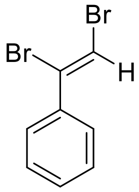
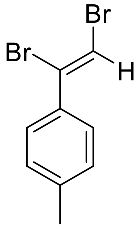


Figure S5 radical experiment

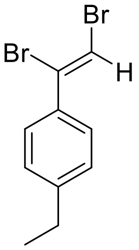
4. Characterization datas for compounds



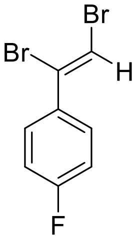
(*Z*)-(1,2-dibromovinyl)benzene (2a)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (37.2 mg, 71% yield). Eluant: petroleum ether (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.06 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 131.3, 129.5, 128.7 (2C), 127.8 (2C), 109.0. IR: 3061, 2922, 1951, 1586, 1570, 1488, 1443, 1225, 1210, 888, 787, 762, 736, 691 cm^{-1}.



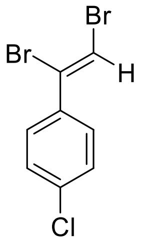
(*Z*)-1-(1,2-dibromovinyl)-4-methylbenzene (2b)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as light yellow liquid (41.9 mg, 76% yield). Eluant: petroleum ether (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 135.9, 131.4, 129.4 (2C), 127.7 (2C), 108.1, 21.4. IR: 3061, 2921, 2851, 2361, 1699, 1609, 1507, 1276, 1225, 1185, 890, 822, 767, 751 cm^{-1}.



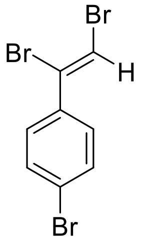
(*Z*)-1-(1,2-dibromovinyl)-4-ethylbenzene (2c) Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (35.4 mg, 61% yield). Eluant: petroleum ether (R_f = 0.7). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.40 (m, 2H), 7.21 – 7.16 (m, 2H), 7.01 (s, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 146.0, 136.0, 131.4, 128.2 (2C), 127.8 (2C), 108.1, 77.5, 77.16, 76.8, 28.7, 15.5. HRMS (EI): Calcd for $C_{10}H_{10}{}^{79}Br_2$ 287.9144, Found 287.9155; Calcd for $C_{10}H_{10}{}^{79}Br^{81}Br$ 289.9129, Found 289.9135; Calcd for $C_{10}H_{10}{}^{81}Br_2$ 291.9108, Found 291.9116. IR: 3188, 3063, 3027, 2962, 2851, 1505, 1458, 1411, 1377, 892, 836, 765, 751, 721 cm^{-1}.



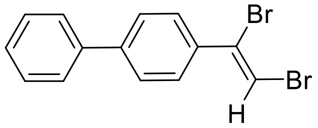
(*Z*)-1-(1,2-dibromovinyl)-4-fluorobenzene (2d)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (38.6 mg, 69% yield). Eluant: petroleum ether (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.08 – 7.02 (m, 2H), 7.01 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (C-F, J_{C-F} = 250.3 Hz), 134.8 (C-F, J_{C-F} = 3.1 Hz), 130.0, 129.7 (C-F, J_{C-F} = 8.4 Hz), 115.7 (C-F, J_{C-F} = 22.0 Hz), 108.9 (C-F, J_{C-F} = 1.6 Hz). IR: 3059, 2924, 2852, 2367, 2353, 2045, 1963, 1601, 1505, 1405, 1235, 1160, 839, 807 cm^{-1}.



(*Z*)-1-chloro-4-(1,2-dibromovinyl)benzene (2e)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (46.2 mg, 78% yield). Eluant: petroleum ether (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.07 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 135.6, 130.0, 129.1 (2C), 128.9 (2C), 109.6. IR: 2955, 2918, 2870, 2850, 1736, 1647, 1492, 1466, 1378, 1191, 1018, 908, 851, 763 cm^{-1}.

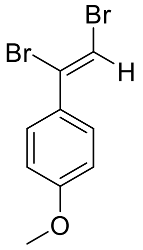


(*Z*)-1-bromo-4-(1,2-dibromovinyl)benzene (**2f**)**[4]** Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (51.8 mg, 76% yield). Eluant: petroleum ether (R_f = 0.7).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.40 – 7.35 (m, 2H), 7.08 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 131.9 (2C), 130.0, 129.3 (2C), 123.8, 109.7. IR: 3059, 2924, 2852, 2355, 2325, 2250, 2155, 1988, 1578, 1479, 1393, 1210, 889, 828, 758 cm^{-1}.

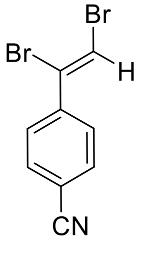


(*Z*)-4-(1,2-dibromovinyl)-1,1'-biphenyl (**2g**) Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (48.6 mg, 72% yield). m. p. = 108 - 109 °C. Eluant: petroleum ether (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 6H), 7.49 – 7.45 (m, 2H), 7.41 – 7.37 (m, 1H), 7.12 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.1, 137.4, 131.0, 129.0 (2C), 128.3 (2C), 128.0, 127.3 (2C), 127.2 (2C), 108.9. HRMS (EI): Calcd for $C_{14}H_{10}{}^{79}Br_2$ 335.9144, Found 335.9151; Calcd for $C_{14}H_{10}{}^{79}Br^{81}Br$ 337.9129, Found 337.9134; Calcd for $C_{14}H_{10}{}^{81}Br_2$ 339.9108, Found

339.9111. IR: 3064, 3033, 2924, 2853, 1573, 1845, 1403, 1202, 1134, 1005, 894, 839, 758, 689 cm^{-1}.

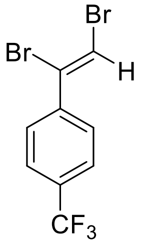


(*Z*)-1-(1,2-dibromovinyl)-4-methoxybenzene (**2h**)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (23.3 mg, 40% yield). Eluant: petroleum ether (R_f = 0.2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 6.94 (s, 1H), 6.91 – 6.84 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 131.2, 131.0, 129.2 (2C), 114.0 (2C), 107.2, 55.6. IR: 3081, 3003, 2929, 2836, 1603, 1575, 1503, 1460, 1440, 1293, 1248, 1173,1030, 831 cm^{-1}.

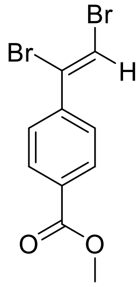


(*Z*)-4-(1,2-dibromovinyl)benzonitrile (2i) Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (40.7 mg, 71% yield). m. p. = 84-85 °C. Eluant: ethyl acetate/petroleum ether (1:30, R_f = 0.40). ^{1}H NMR (400 MHz,

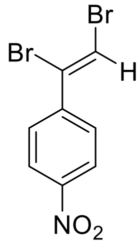
$CDCl_3$) δ 7.67 – 7.60 (m, 4H), 7.24 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 132.5 (2C), 129.2, 128.4 (2C), 118.2, 113.1, 112.3. HRMS (ESI) m/z: Calcd for $C_9H_6N_1{}^{79}Br_2$ 285.8862; Found 285.8872; Calcd for $C_9H_6N_1{}^{79}Br_2$ 287.8841, Found 287.8844; Calcd for $C_9H_6N_1{}^{79}Br_2$ 289.8821; Found 285.8824. IR: 3062, 2921, 2852, 2223, 1604, 1580, 1556, 1499, 1405, 1216, 897, 845, 779 cm^{-1}.



(*Z*)-1-(1,2-dibromovinyl)-4-(trifluoromethyl)benzene (2j)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (44.8 mg, 83% yield). Eluant: petroleum ether ($R_f = 0.50$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 4H), 7.18 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8 (C-F, $J_{C\text{-}F}$ = 1.4 Hz), 131.4 (C-F, $J_{C\text{-}F}$ = 32.9 Hz), 131.0, 129.7, 128.2, 125.0 (C-F, $J_{C\text{-}F}$ = 3.8 Hz), 123.87 (C-F, $J_{C\text{-}F}$ = 272.3 Hz), 111.2. IR: 3063, 2926, 2854, 1679, 1618, 1406, 1323, 1228, 1169, 1128, 1068, 1017, 845,781 cm^{-1}.

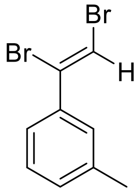


Methyl (*Z*)-4-(1,2-dibromovinyl)benzoate (2k)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (45.4 mg, 71% yield). Eluant: ethyl acetate/petroleum ether (1:30, R_f = 0.40). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.60 – 7.54 (m, 2H), 7.19 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 142.4, 130.9, 130.2, 129.9 (2C), 127.8 (2C), 111.1, 52.4. IR: 3068, 2950, 2924, 1715, 1606, 1583, 1561, 1433, 1406, 1279, 1221, 1187, 750, 696 cm^{-1}.

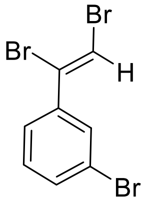


(*Z*)-1-(1,2-dibromovinyl)-4-nitrobenzene (2l)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (41.7 mg, 68% yield). Eluant: ethyl acetate/petroleum ether (1:30, R_f = 0.20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.29 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 144.2, 128.8, 128.7 (2C), 124.0 (2C), 112.9.

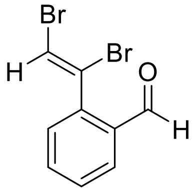
IR: 3067, 2924, 2851, 1602, 1592, 1570, 1515, 1344, 1317, 1112, 900, 857, 846, 742 cm^{-1}.



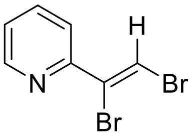
(*Z*)-1-(1,2-dibromovinyl)-3-methylbenzene (2m)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (41.4 mg, 75% yield). Eluant: petroleum ether (R_f = 0.60). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.6, 138.5, 131.4, 130.3, 128.6, 128.5, 125.0, 108.7, 21.5. IR: 3064, 2955, 2919, 2850, 1736, 1646, 1603, 1464, 1378, 1257, 1214, 1180, 908, 768, 612 cm^{-1}.



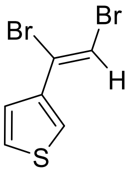
(*Z*)-1-bromo-3-(1,2-dibromovinyl)benzene (2n) Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (51.8 mg, 74% yield). Eluant: petroleum ether (R_f = 0.60). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, *J* = 1.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.10 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 140.4, 132.5, 130.8, 130.2, 129.4, 126.5, 122.7, 110.4. HRMS (EI): Calcd for $C_8H_5{}^{79}Br_3$ 337.7941, Found 337.7936; Calcd for $C_8H_5{}^{79}Br_2{}^{81}Br$ 339.7921, Found 337.7922; Calcd for $C_8H_5{}^{79}Br{}^{81}Br_2$ 341.7900, Found 341.7902; Calcd for $C_8H_5{}^{81}Br_3$ 343.7880, Found 343.7879. IR: 3062, 2954, 2923, 2852, 1590, 1557, 1470 1410, 1210, 1074, 914, 822, 766, 673 cm^{-1}.



(*Z*)-2-(1,2-dibromovinyl)benzaldehyde (2o) Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (38.8 mg, 67% yield). m. p. = 84 – 85 °C. Eluant: ethyl acetate/petroleum ether (1:50, R_f = 0.30). ^1H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.02 – 7.93 (m, 1H), 7.69 – 7.65 (m, 1H), 7.59 – 7.50 (m, 1H), 7.38 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.01 (s, 1H). ^{13}C NMR (101 MHz,) δ 190.4, 140.6, 134.5, 132.4, 130.2, 130.0, 128.6, 116.7, 107.9. HRMS (ESI): Calcd for $C_9H_6Br_2ONa$ 310.8678, Found 310.8668; Calcd for $C_9H_6Br_2ONa$ 312.8657, Found 312.8654; Calcd for $C_9H_6Br_2ONa$ 314.8637, Found 314.8624. IR: 2984, 2363, 1735, 1447, 1373, 1300, 1235, 1097, 1043, 938, 918, 847, 786, 736 cm^{-1}.

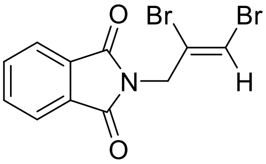


(*Z*)-2-(1,2-dibromovinyl)pyridine (2p) Prepared according to general procedure and purified by flash column chromatography to afford the product as light yellow liquid (26.8 mg, 51% yield). Eluant: ethyl acetate/petroleum ether (1:10, R_f = 0.20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.52 (m, 1H), 8.04 (s, 1H), 7.78 – 7.71 (m, 2H), 7.26 – 7.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 149.4, 137.5, 129.9, 123.7, 122.8, 115.0. HRMS (ESI): Calcd for $C_7H_5{}^{79}Br_2NNa$ 283.8681, Found 283.8671; Calcd for $C_7H_5{}^{79}Br^{81}BrNNa$ 285.8660, Found 285.8650; Calcd for $C_7H_5{}^{81}Br_2NNa$ 287.8640, Found 287.8626. IR: 3054, 2924, 2853, 2363, 1733, 1589, 1559, 1459, 1429, 1376, 1264, 1051, 770, 734 cm^{-1}.

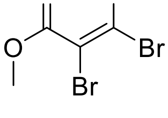


(*Z*)-3-(1,2-dibromovinyl)thiophene (2q) Prepared according to general procedure and purified by flash column chromatography to afford the product as yellow liquid (25.7 mg, 48% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 3.1, 1.3 Hz, 1H), 7.34 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.21 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.14 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 126.8, 125.5, 125.3 (2C), 108.2. HRMS (EI): Calcd for $C_6H_4{}^{79}Br_2S$ 265.8395, Found 265.8398; Calcd for $C_6H_4{}^{79}Br^{81}BrS$ 267.8380, Found 267.8376; Calcd for $C_6H_4{}^{81}Br_2S$

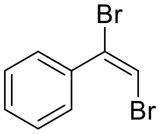
269.8360, Found 269.8355. IR: 3108, 3060, 2953, 2922, 1731, 1676, 1511, 1238, 1224, 1087, 958, 877, 846, 805 cm^{-1}.



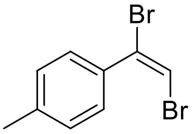
(*Z*)-2-(2,3-dibromoallyl)isoindoline-1,3-dione (2r) Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (21.3 mg, 31% yield). m. p. = 65 – 66 °C. Eluant: ethyl acetate/petroleum ether (1:20, R_f = 0.30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.70 (s, 1H), 4.74 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 134.4 (2C), 132.0, 123.8 (2C), 119.9, 106.4, 41.7. HRMS (ESI): Calcd for $C_{11}H_7{}^{79}Br_2NO_2Na$ 365.8736; Found 365.8735; Calcd for $C_{11}H_7{}^{79}Br^{81}BrNO_2Na$ 367.8715; Found 367.8723; Calcd for $C_{11}H_7{}^{81}Br_2NO_2Na$ 369.8695; Found 369.8698. IR: 3084, 2924, 2852, 1774, 1714, 1613, 1467, 1417, 1388, 1342, 1114, 1027, 924, 727, 705 cm^{-1}.



Methyl (*Z*)-2,3-dibromoacrylate (2s)[5] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (34.6 mg, 71% yield). Eluant: ethyl acetate/petroleum ether (1:30, R_f = 0.20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 127.0, 122.3, 53.9. IR: 3072, 2954, 2923, 2852, 1775, 1719, 1570, 1435, 1419, 1255, 1215, 1082, 934, 736 cm^{-1}.

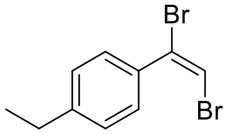


(*E*)-(1,2-dibromovinyl)benzene (3a)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (45.7 mg, 88% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.44 – 7.36 (m, 3H), 6.81 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 129.5, 129.3 (2C), 128.4 (2C), 121.4, 103.2. IR: 3083, 2955, 2922, 2852, 2363, 2343, 1733, 1541, 1489, 1459, 1445, 1377, 1264, 694 cm^{-1}.

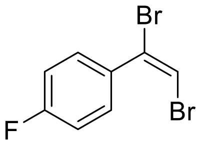


(*E*)-1-(1,2-dibromovinyl)-4-methylbenzene (3b)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as light yellow liquid (43.2 mg, 79% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39

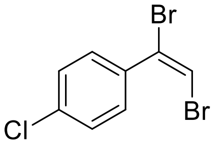
(m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 134.3, 129.2 (2C), 129.1 (2C), 121.7, 102.6, 21.6. IR: 3557, 3190, 2910, 2850, 2342, 2331, 2164, 1655, 1634, 1470, 1422, 1245, 748, 689 cm^{-1}.



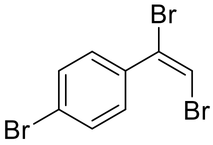
(*E*)-1-(1,2-dibromovinyl)-4-ethylbenzene (3c) Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (39.7 mg, 69% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.25 – 7.21 (m, 2H), 6.77 (s, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 134.4, 129.3 (2C), 127.9 (2C), 121.8, 102.5, 28.9, 15.3. HRMS (EI): Calcd for $C_{10}H_{10}{}^{79}Br_2$ 287.9144, Found 287.9150; Calcd for $C_{10}H_{10}{}^{79}Br^{81}Br$ 289.9129, Found 289.9129; Calcd for $C_{10}H_{10}{}^{81}Br_2$ 291.9108, Found 291.9110. IR: 3083, 3027, 2963, 2924, 2870, 2364, 1737, 1668, 1610, 1503, 1460, 1264, 876, 740 cm^{-1}.



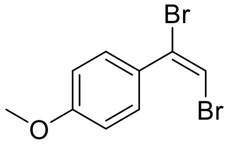
(*E*)-1-(1,2-dibromovinyl)-4-fluorobenzene (3d)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (43.7 mg, 76% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 6.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 250.2 Hz), 132.7 (d, *J* = 3.6 Hz), 131.0 (d, *J* = 8.5 Hz), 119.9, 115.1 (d, *J* = 22.0 Hz), 103.2. IR: 3352, 2954, 2922, 2852, 2365, 2356, 1974, 1736, 1663, 1602, 1460, 1264, 739, 705 cm^{-1}.



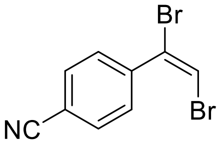
(*E*)-1-chloro-4-(1,2-dibromovinyl)benzene (3e)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (44.6 mg, 76% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 6.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 135.5, 130.7 (2C), 128.7 (2C), 120.2, 103.9. IR: 3082, 2954, 2923, 2364, 1907, 1587, 1485, 1397, 1262, 1165, 1091, 1015, 875, 828, 688 cm^{-1}.



(*E*)-1-bromo-4-(1,2-dibromovinyl)benzene (3f)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (49.9 mg, 74% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.42 – 7.35 (m, 2H), 6.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 131.7, 130.9, 123.8, 120.2, 103.9. IR: 3081, 2954, 2921 2850, 1902, 1582, 1480, 1394, 1260, 1162, 1102, 1072, 1012, 873, 823 cm^{-1}.

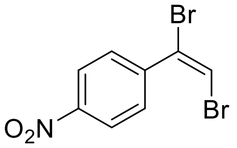


(*E*)-1-(1,2-dibromovinyl)-4-methoxybenzene (3g)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as light yellow liquid (34.2 mg, 59% yield). Eluant: petroleum ether (R_f = 0.20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 6.93 – 6.88 (m, 2H), 6.74 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 130.9, 129.3, 121.6, 113.7, 102.1, 55.5. IR: 3080 3303, 2954, 2921, 1890, 1602, 1503, 1297, 1248, 1160, 1030, 873, 830, 687 cm^{-1}.

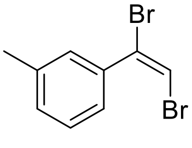


(*E*)-4-(1,2-dibromovinyl)benzonitrile (3h)[6] Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (34.7 mg, 61% yield). Eluant: ethyl acetate/petroleum ether (1:30, R_f = 0.30). ^{1}H NMR (400 MHz, $CDCl_3$) δ

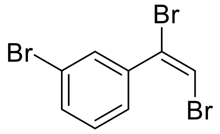
7.70 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 6.91 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 141.6, 132.3 (2C), 130.1 (2C), 118.9, 118.3, 113.2, 105.5. IR: 3078, 2955, 2961, 2850, 2231, 1646, 1497, 1400, 1276, 1159, 883, 839, 693, 611 cm^{-1}.



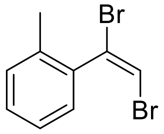
(*E*)-1-(1,2-dibromovinyl)-4-nitrobenzene (3i)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as white solid (33.7 mg, 55% yield). Eluant: ethyl acetate/petroleum ether (1:20, R$_f$ = 0.20). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 6.95 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.0, 143.4, 130.5 (2C), 123.8 (2C), 118.5, 105.9. IR: 3079, 2955, 2919, 2850, 2357, 1646, 1519, 1469, 1164, 1107, 1014, 961, 857, 840, 752, 697 cm^{-1}.



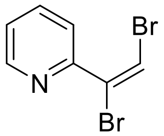
(*E*)-1-(1,2-dibromovinyl)-3-methylbenzene (3j)[4] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (42.7 mg, 78% yield). Eluant: petroleum ether (R$_f$ = 0.80). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.27 (m, 3H), 7.20 – 7.16 (m, 1H), 6.78 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.1, 130.4, 129.8, 128.3, 126.3, 121.7, 102.9, 21.5. IR: 3083, 2963, 2925, 2870, 2364, 1737, 1667, 1503, 1460, 1412, 1264, 1161, 876, 833, 740 cm^{-1}



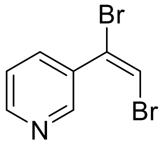
(*E*)-1-bromo-3-(1,2-dibromovinyl)benzene (3k)[6] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (53.8 mg, 79% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 1H), 7.50 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.29 – 7.25 (m, 1H), 6.84 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 132.6, 132.2, 130.0, 128.0, 123.0, 119.5, 104.5. IR: 3357, 2920, 2850, 2363, 2342, 2331, 1869, 1655, 1634, 1471, 1245, 1052, 748, 689 cm^{-1}.



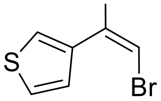
(*E*)-1-(1,2-dibromovinyl)-2-methylbenzene (3l)[6] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (34.7 mg, 63% yield). Eluant: petroleum ether (R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 4H), 6.81 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.2, 136.0, 130.5, 129.6, 128.7, 126.3, 121.1, 105.3, 19.3 cm^{-1}.



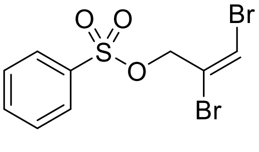
(*E*)-2-(1,2-dibromovinyl)pyridine (3m) Prepared according to general procedure and purified by flash column chromatography to afford the product as light yellow liquid (32.1 mg, 61% yield). Eluant: ethyl acetate/petroleum ether (1:10, R$_f$ = 0.20). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (d, *J* = 4.0 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.61 – 7.57 (m, 1H), 7.32 – 7.26 (m, 1H), 6.97 (dd, *J* = 3.9, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.4, 149.9, 136.5, 124.7, 124.0, 120.9, 105.2. HRMS (ESI): Calcd for $C_7H_5{}^{79}Br_2NNa$ 283.8681, Found 283.8666; Calcd for $C_7H_5{}^{79}Br^{81}BrNNa$ 285.8660, Found 285.8659; Calcd for $C_7H_5{}^{81}Br_2NNa$ 287.8640, Found 287.8635. IR: 3082, 2954, 2923, 2851, 2364, 1587, 1486, 1397, 1262, 1165, 1091, 1015, 828, 688 cm^{-1}.



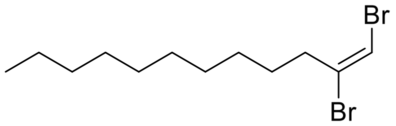
(*E*)-3-(1,2-dibromovinyl)pyridine (3n) Prepared according to general procedure and purified by flash column chromatography to afford the product as light yellow liquid (33.6 mg, 64% yield). Eluant: ethyl acetate/petroleum ether (1:10, R_f = 0.20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.67 (m, 2H), 7.87 – 7.78 (m, 1H), 7.34 (dd, *J* = 7.9, 5.0 Hz, 1H), 6.91 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 150.0, 136.8 (2C), 123.3, 117.8, 105.4. HRMS (ESI):Calcd for $C_7H_5{}^{79}Br_2NNa$ 283.8681, Found 283.8676; Calcd for $C_7H_5{}^{79}Br^{81}BrNNa$ 285.8660, Found 285.8651; Calcd for $C_7H_5{}^{81}Br_2NNa$ 287.8640, Found 287.8640. IR: 3081, 2954, 2921, 2850, 1582, 1480, 1394, 1260, 1072, 1012, 873, 823, 787, 726, 560 cm^{-1}.



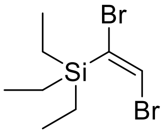
(*E*)-3-(1,2-dibromovinyl)thiophene (3o)[6] Prepared according to general procedure and purified by flash column chromatography to afford the product as brown liquid (34.8 mg, 65% yield). Eluant: petroleum ether (R_f = 0.90). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.48 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.33 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.75 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 128.6, 128.2, 125.3, 116.4, 102.0. IR: 3080, 2954, 2921, 1890, 1602, 1503, 1297, 1248, 1160, 1112, 1030, 873, 830, 687 cm^{-1}.



(*E*)-2,3-dibromoallyl benzenesulfonate (3p) Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (45.6 mg, 57% yield). Eluant: ethyl acetate/petroleum ether (1:10, R_f = 0.20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 7.73 – 7.65 (m, 1H), 7.62 – 7.53 (m, 2H), 6.66 (s, 1H), 4.92 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 134.3, 129.4 (2C), 128.3 (2C), 117.1, 109.8, 69.7. HRMS (ESI): Calcd for $C_9H_8{}^{79}Br_2SO_3Na$ 376.8453, Found 376.8461; Calcd for $C_9H_8{}^{79}Br^{81}BrSO_3Na$ 378.8433, Found 378.8370; Calcd for $C_9H_8{}^{81}Br_2SO_3Na$ 380.8412, Found 380.8355. IR: 3371, 3083, 2925, 2363, 1585, 1448, 1362, 1276, 1186, 1126, 952, 752, 686 cm^{-1}.



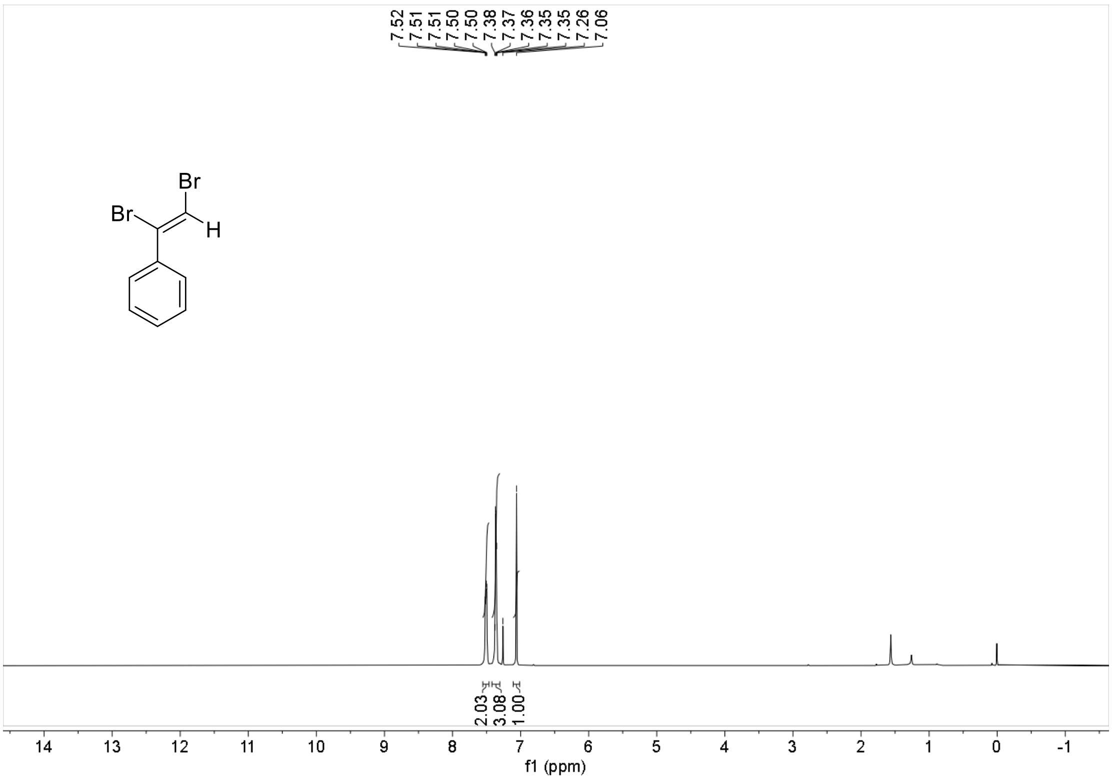
(*E*)-1,2-dibromododec-1-ene (3q)[7] Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (42.4 mg, 65% yield). Eluant: petroleum ether (R_f = 0.90). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 1H), 2.59 (t, *J* = 7.4 Hz, 2H), 1.59 – 1.55 (m, 2H), 1.34 – 1.27 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.2, 102.4, 37.0, 32.0, 29.7, 29.6, 29.5 (2C), 28.5, 27.2, 22.8, 14.3. IR: 3089, 2953, 2922, 2853, 1553, 1464, 1377, 1263, 1189, 1122, 1072, 851, 778 cm^{-1}.



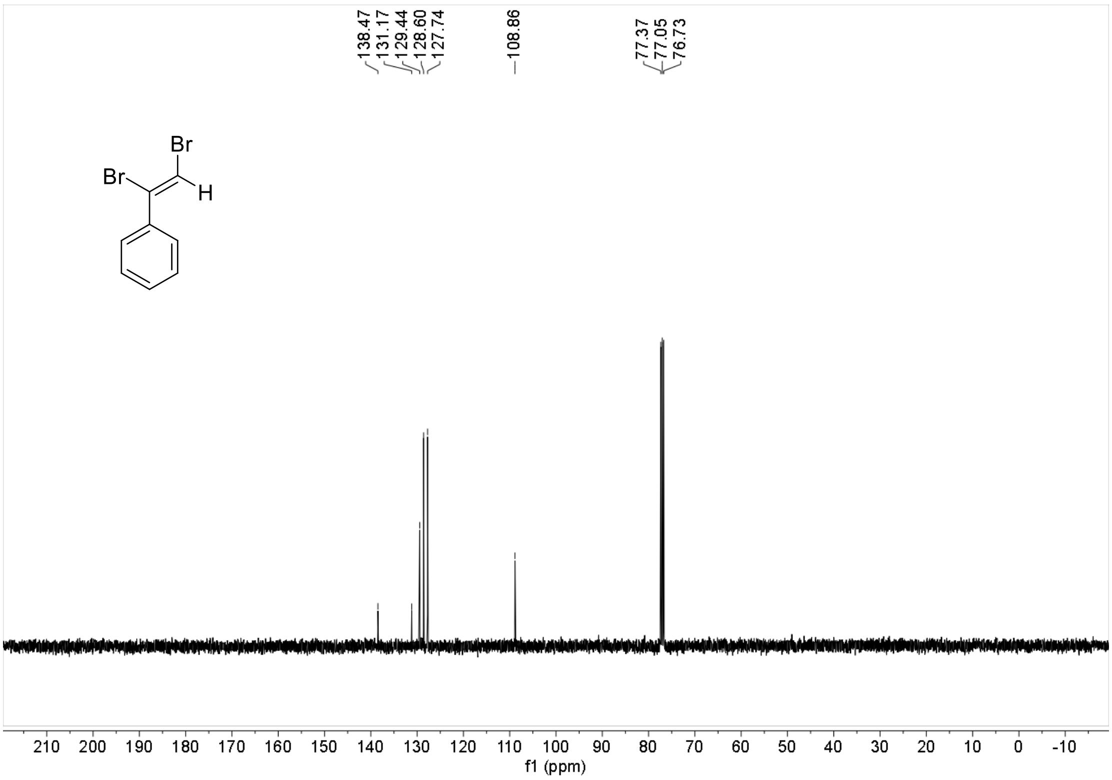
(*E*)-(1,2-dibromovinyl)triethylsilane (3r) Prepared according to general procedure and purified by flash column chromatography to afford the product as colorless liquid (41.1 mg, 69% yield). Eluant: petroleum ether (R_f = 0.90). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 1.03 – 0.99 (m, 9H), 0.91 – 0.86 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 126.4, 115.3, 7.3, 4.1. HRMS (EI): Calcd for $C_8H_{16}{}^{79}Br_2Si$ 297.9388, Found 297.9383; Calcd for $C_8H_{16}{}^{79}Br^{81}BrSi$ 299.9368, Found 299.9363; Calcd for $C_8H_{16}{}^{81}Br_2Si$ 301.9347, Found 301.9336. IR: 2955, 2921, 2875, 2364, 1545, 1462, 1414, 1378, 1237, 1082, 1003, 801, 736, 697 cm^{-1}.

5. NMR spectra

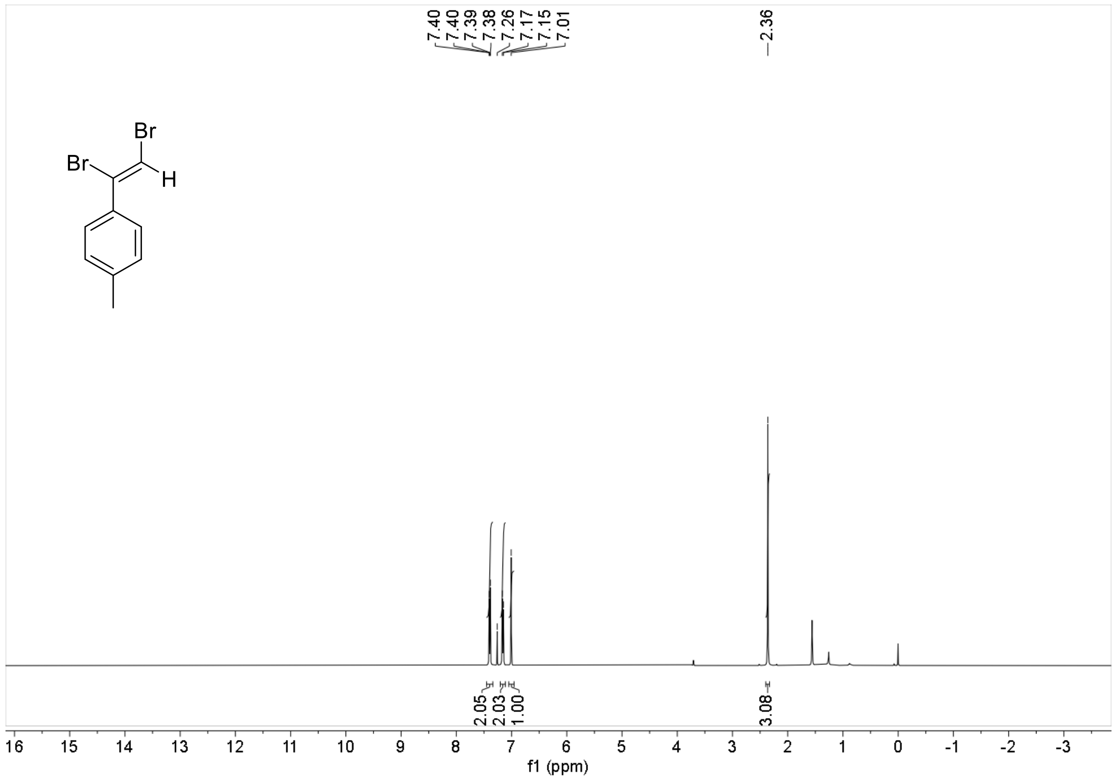
^{1}H NMR spectrum of compound **2a** (400 MHz, $CDCl_3$)



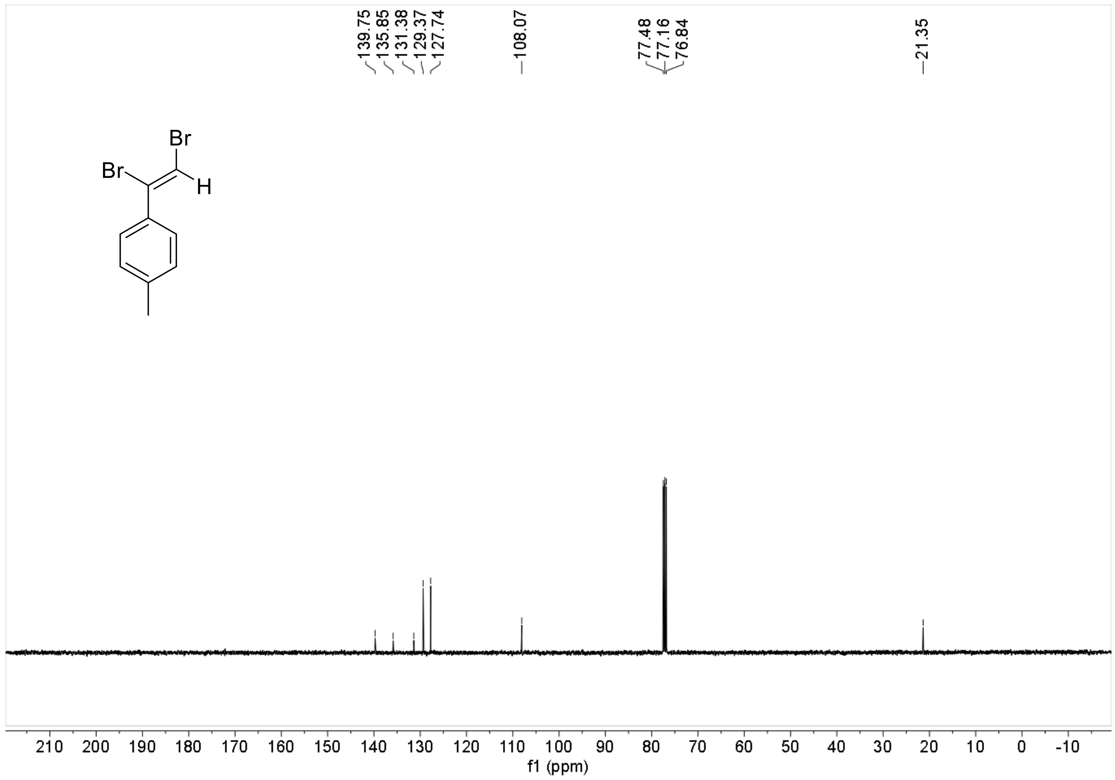
^{13}C NMR spectrum of compound **2a** (101 MHz, $CDCl_3$)



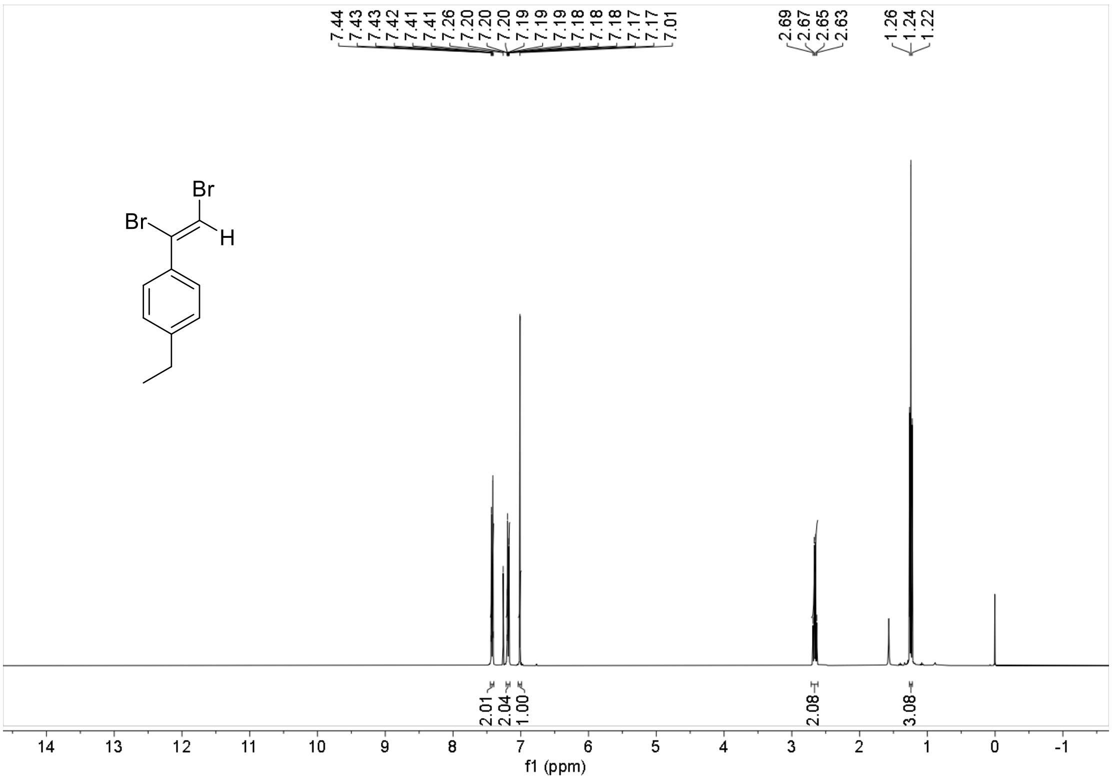
^{1}H NMR spectrum of compound **2b** (400 MHz, $CDCl_3$)



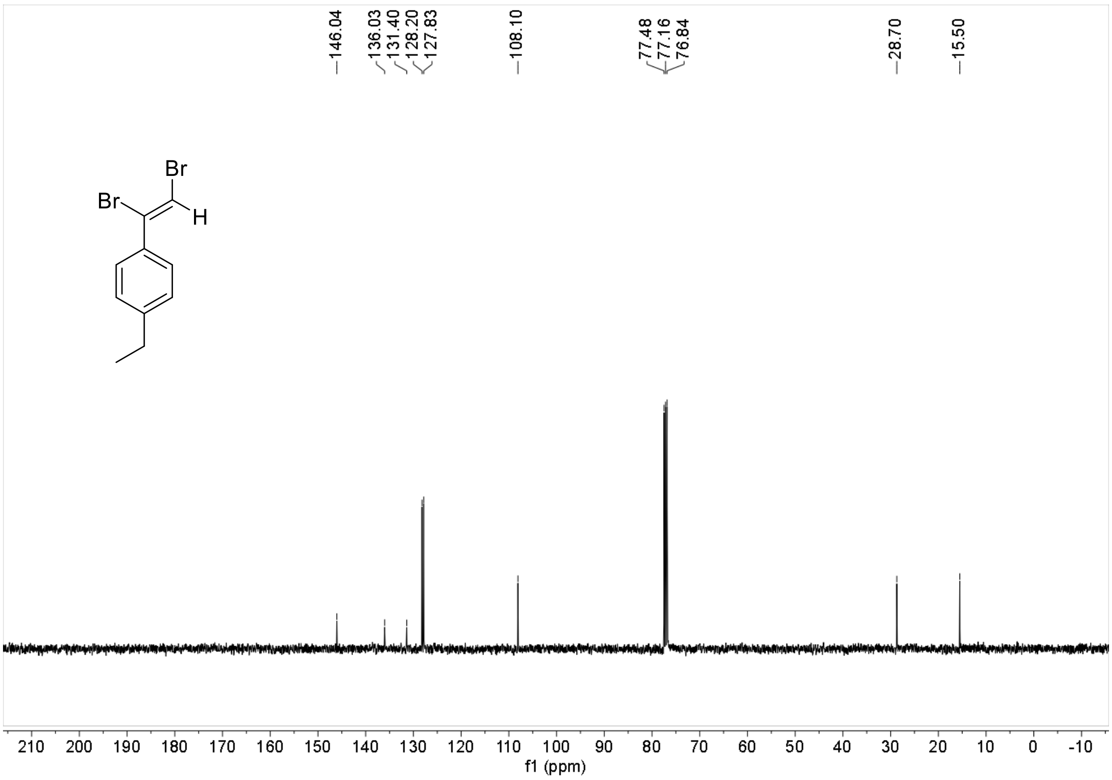
^{13}C NMR spectrum of compound **2b** (101 MHz, $CDCl_3$)



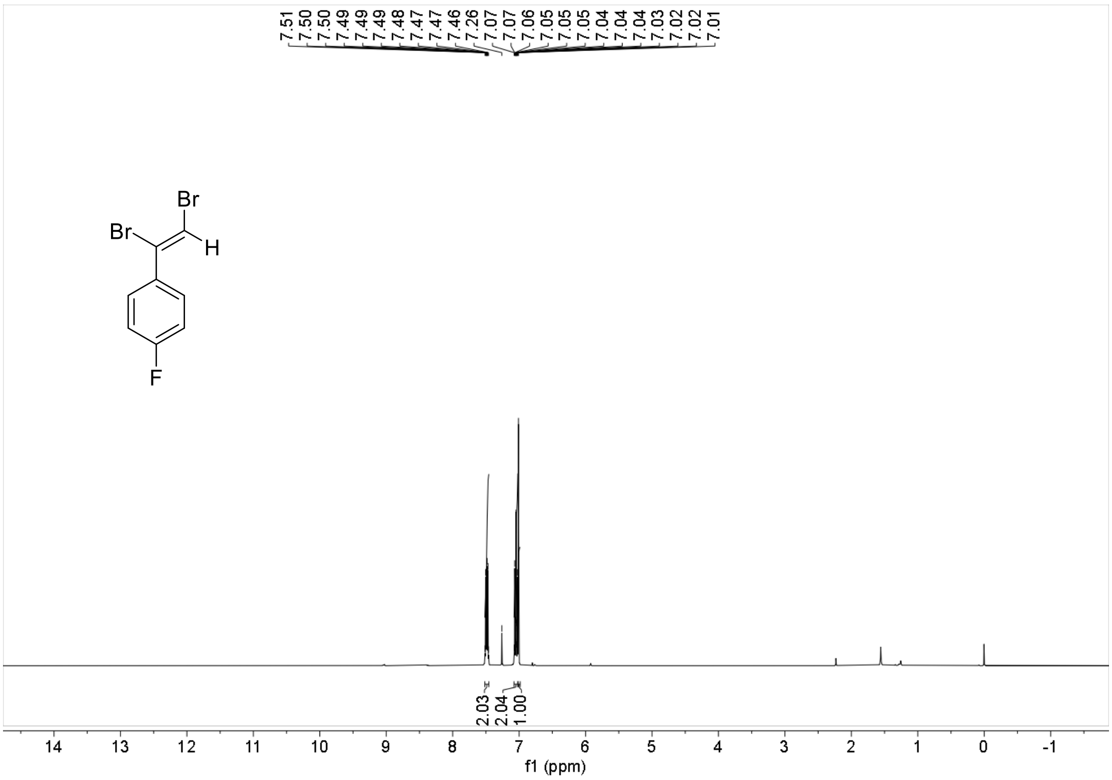
^{1}H NMR spectrum of compound **2c** (400 MHz, $CDCl_3$)



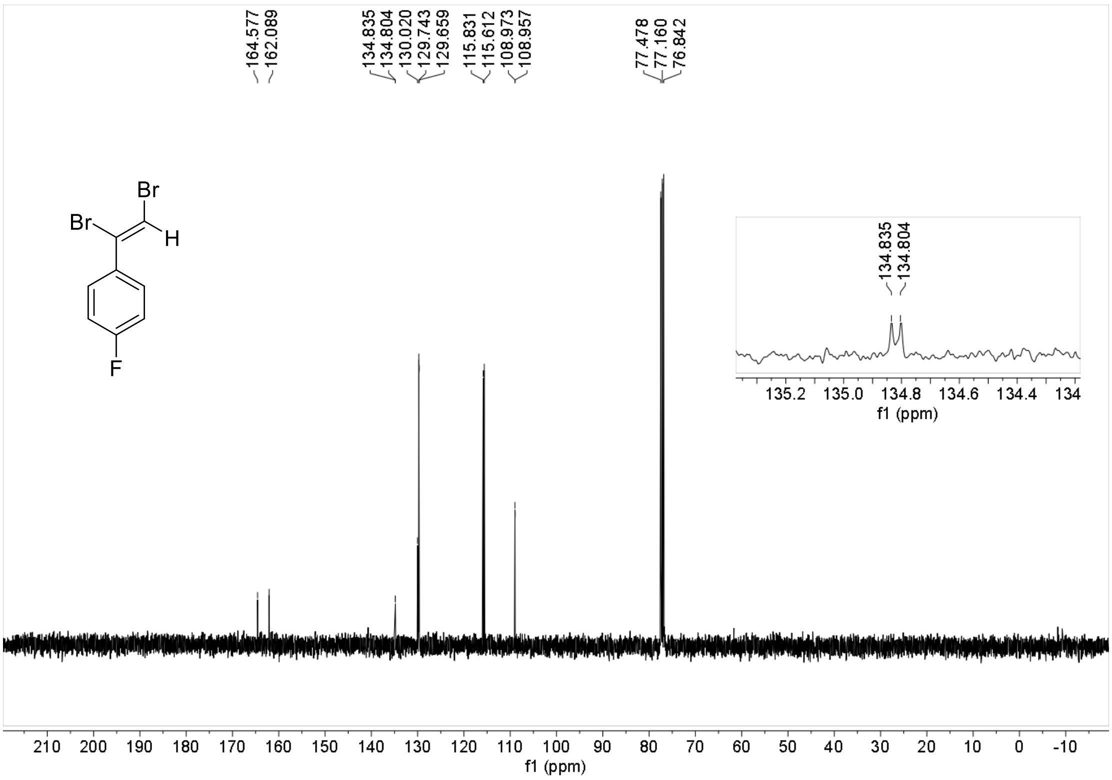
^{13}C NMR spectrum of compound **2c** (101 MHz, $CDCl_3$)



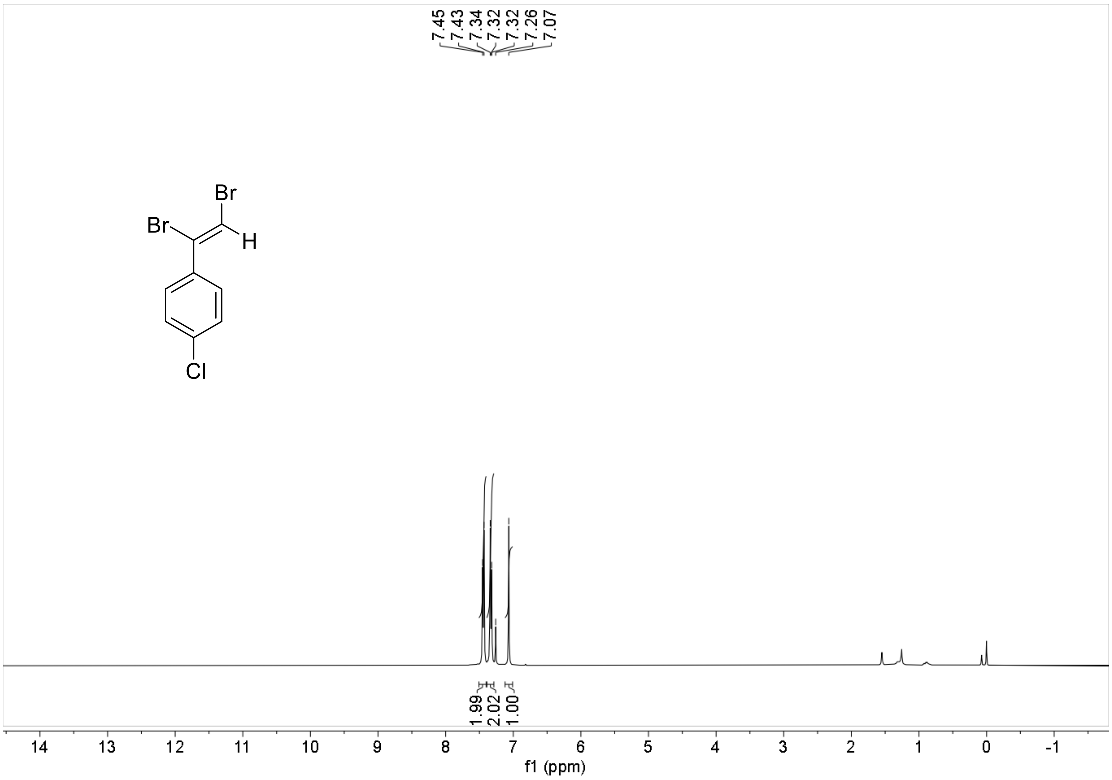
^{1}H NMR spectrum of compound **2d** (400 MHz, CDCl$_3$)



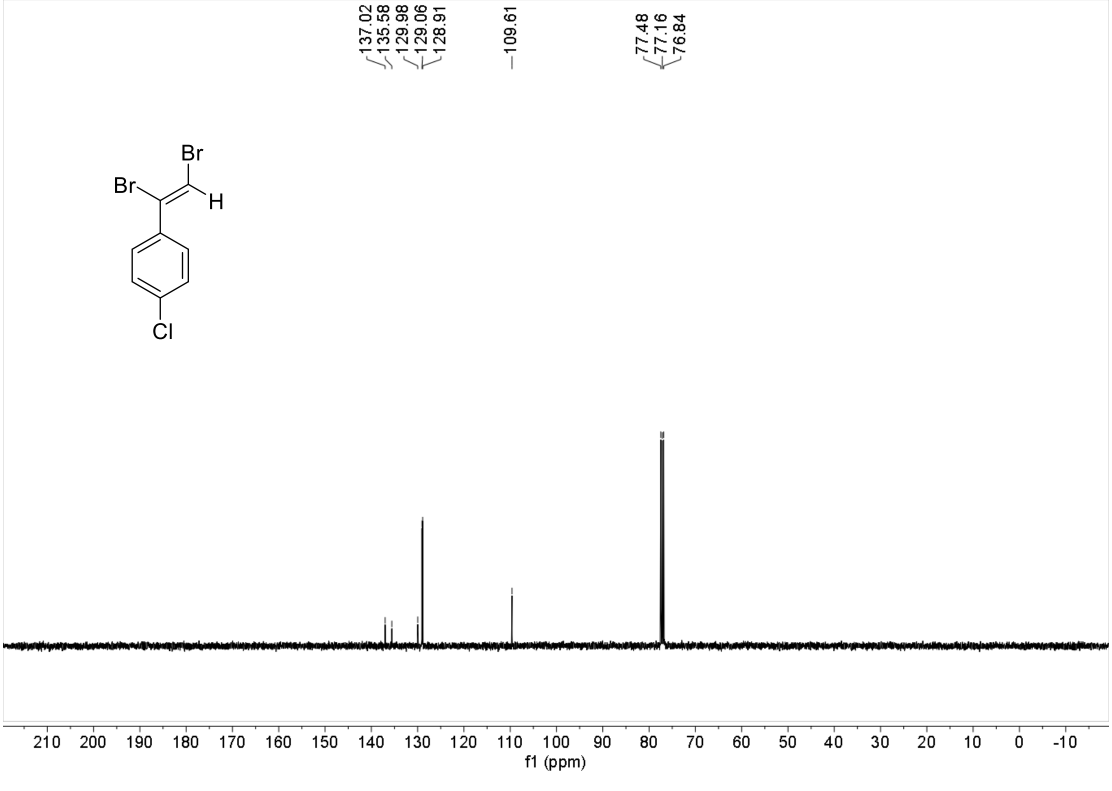
^{13}C NMR spectrum of compound **2d** (101 MHz, CDCl$_3$)



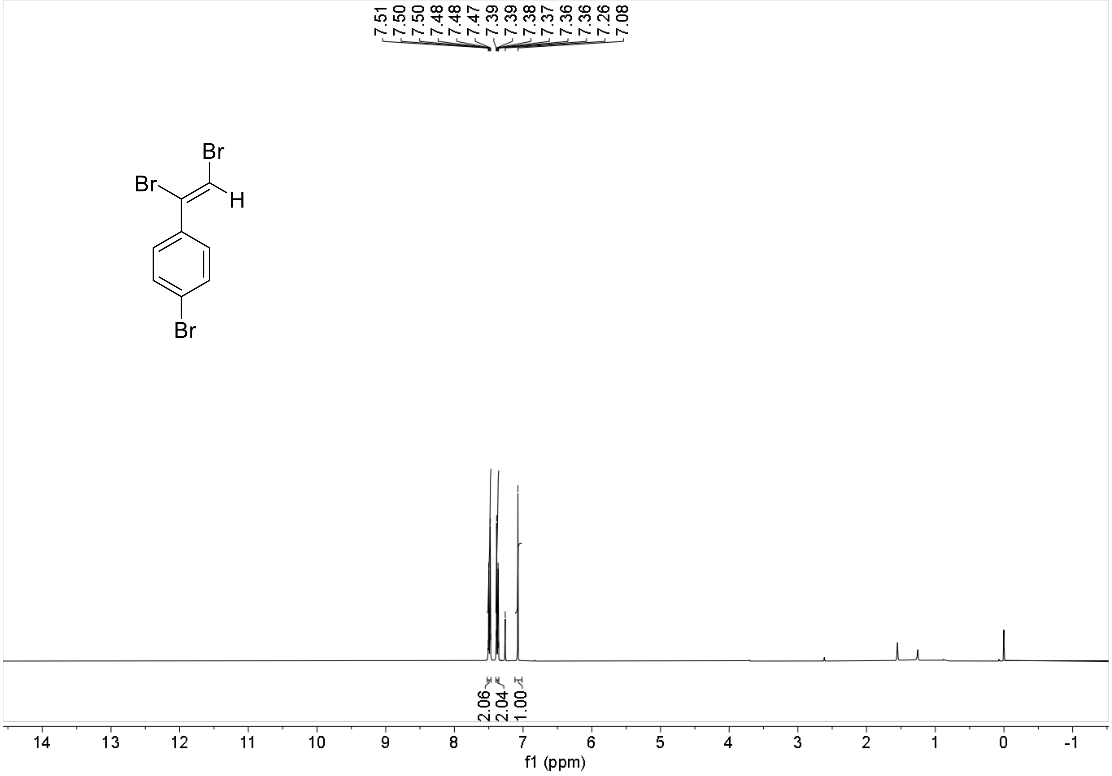
^{1}H NMR spectrum of compound **2e** (400 MHz, $CDCl_3$)



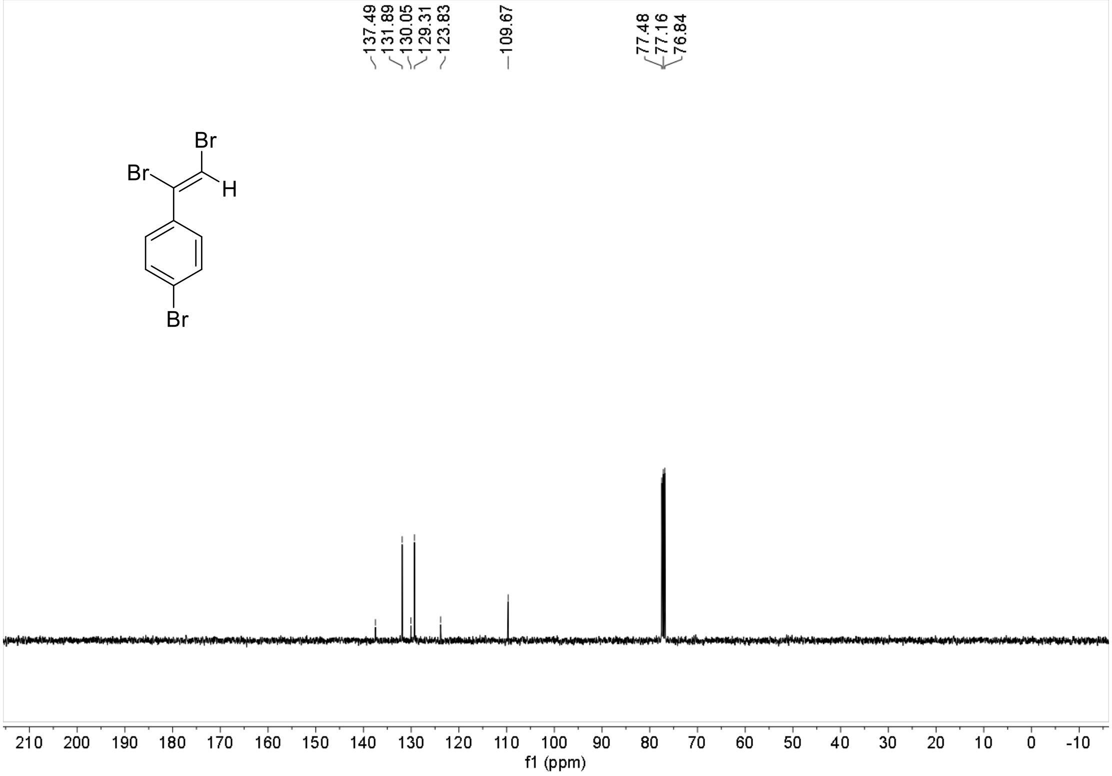
^{13}C NMR spectrum of compound **2e** (101 MHz, $CDCl_3$)



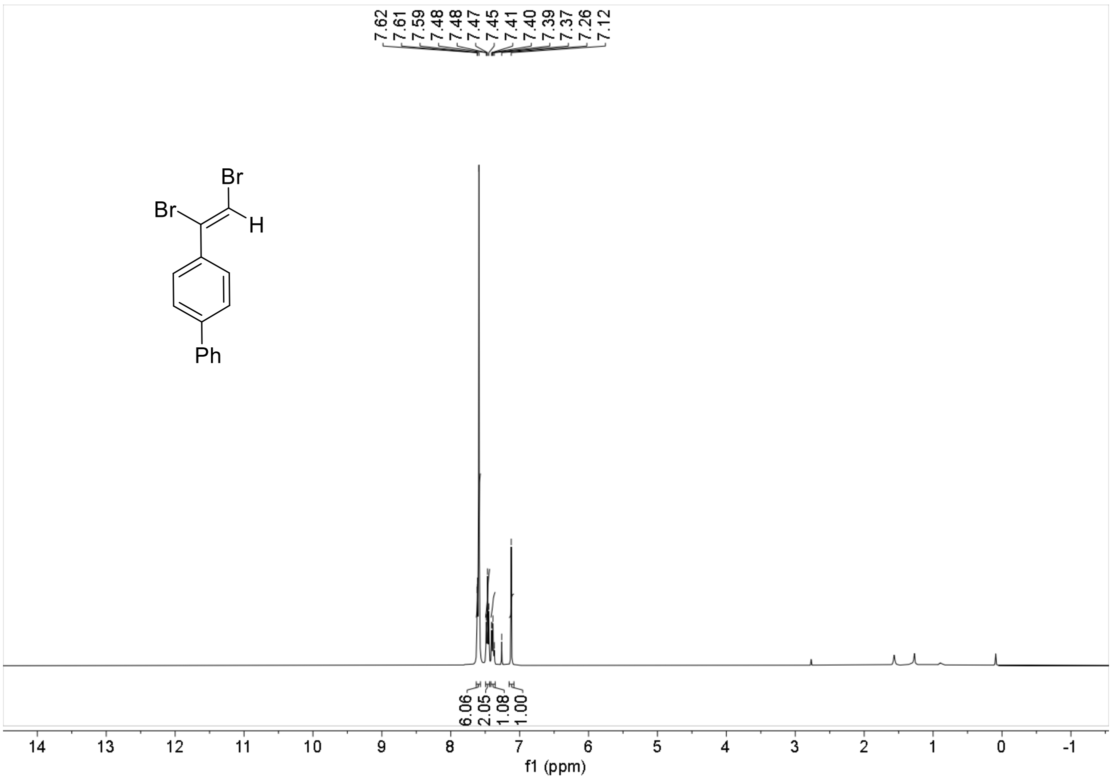
^{1}H NMR spectrum of compound **2f** (400 MHz, $CDCl_3$)



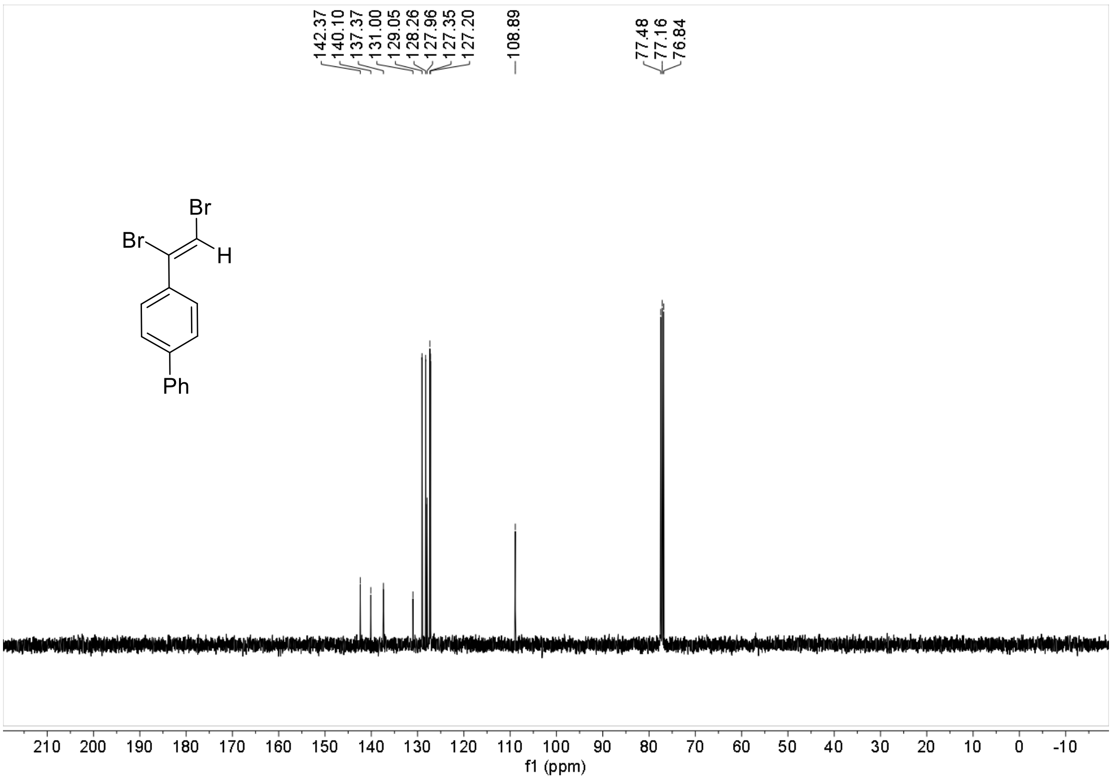
^{13}C NMR spectrum of compound **2f** (101 MHz, $CDCl_3$)



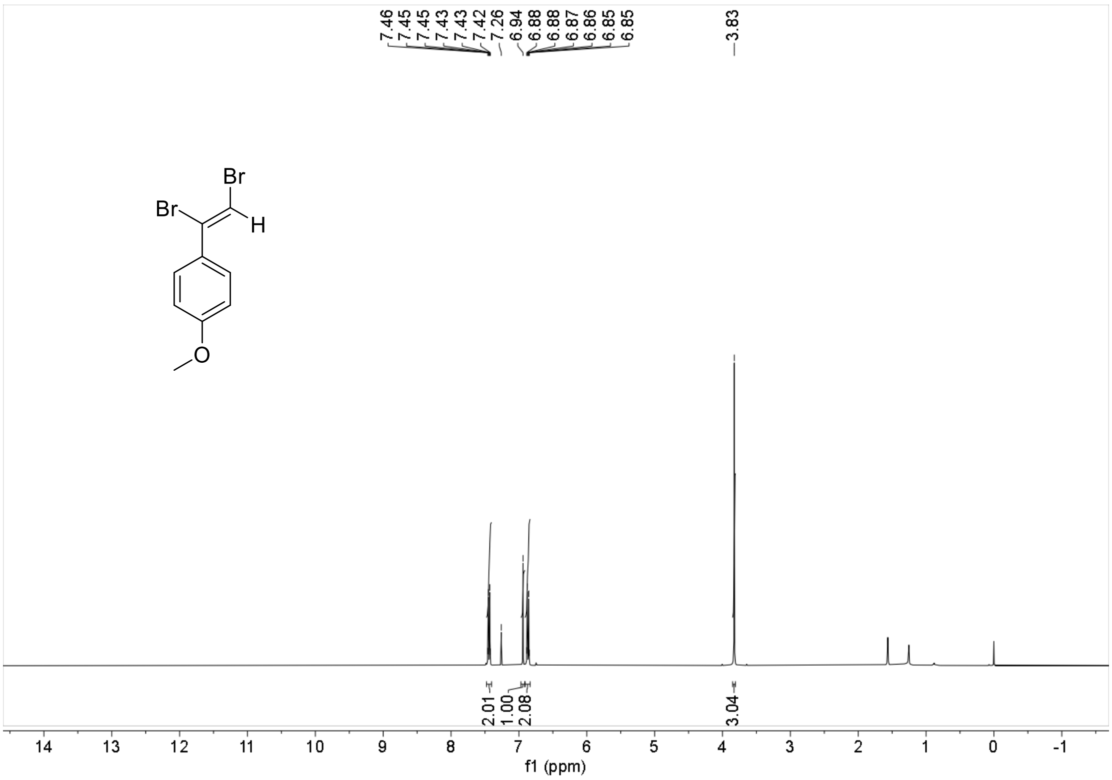
^{1}H NMR spectrum of compound **2g** (400 MHz, $CDCl_3$)



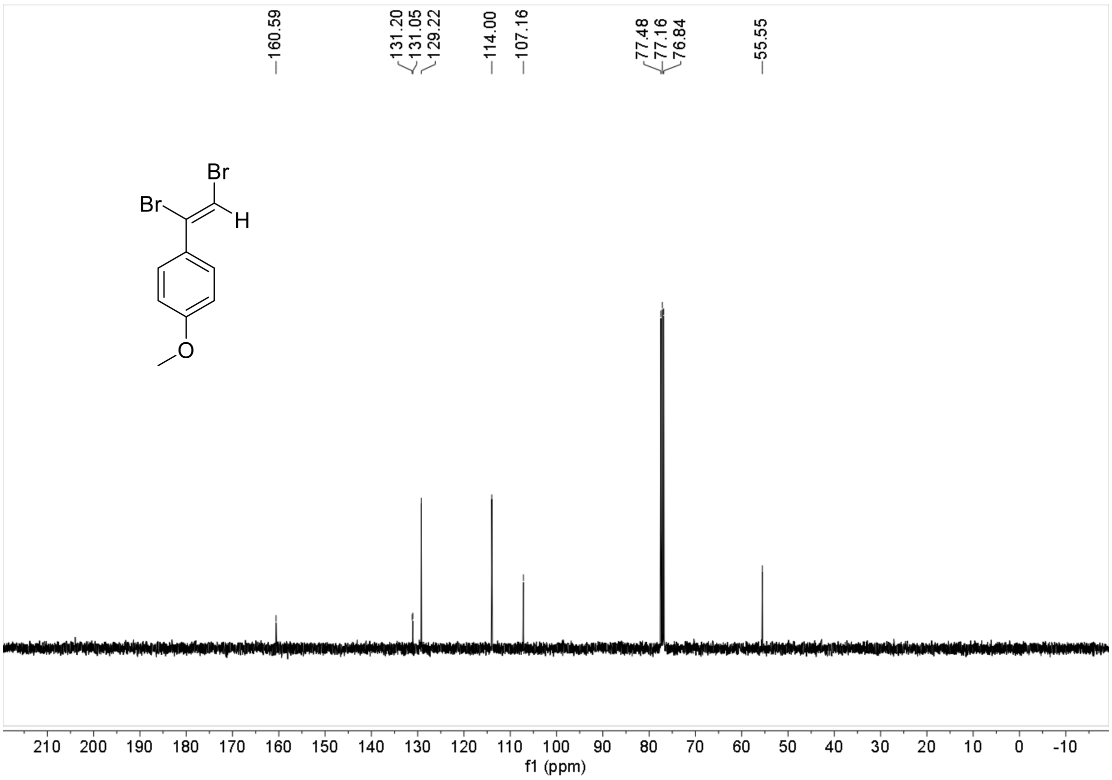
^{13}C NMR spectrum of compound **2g** (101 MHz, $CDCl_3$)



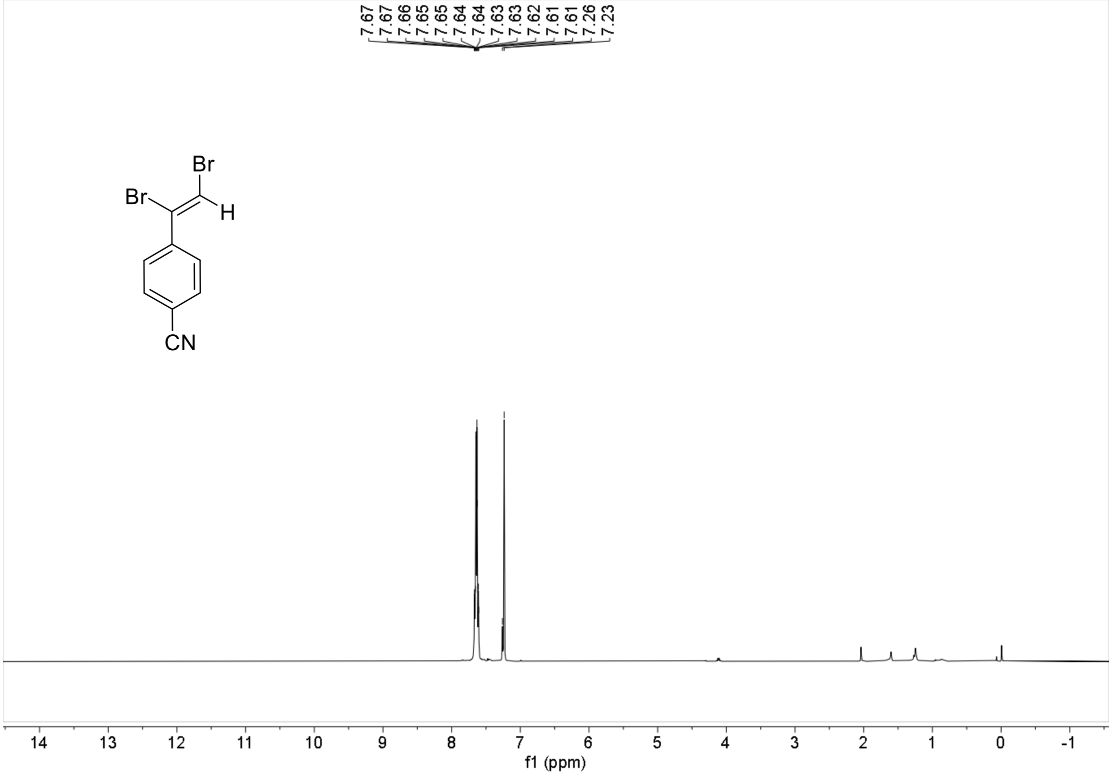
^{1}H NMR spectrum of compound **2h** (400 MHz, $CDCl_3$)



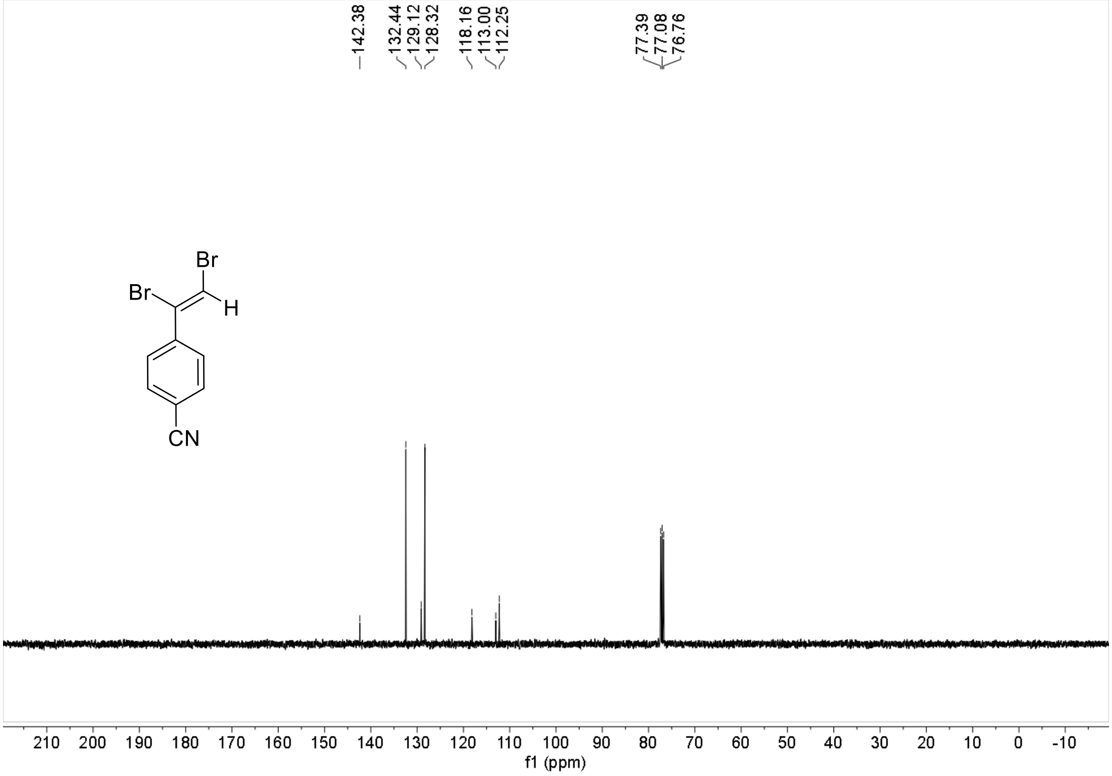
^{13}C NMR spectrum of compound **2h** (101 MHz, $CDCl_3$)



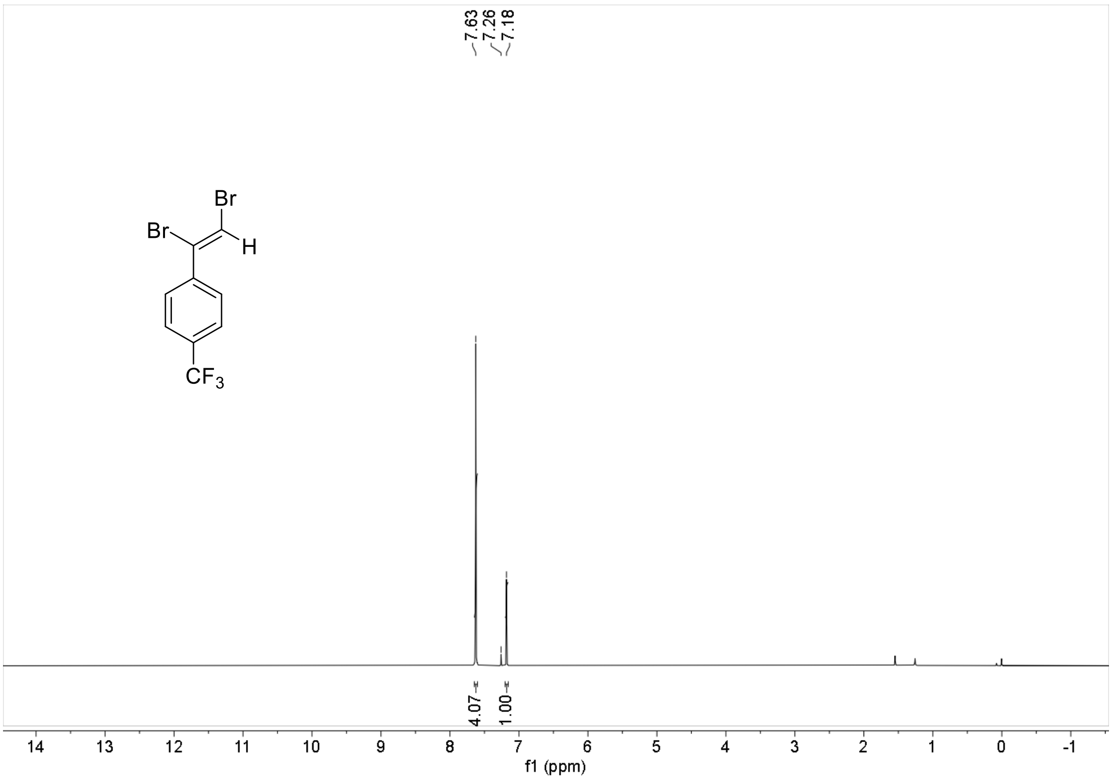
^{1}H NMR spectrum of compound **2i** (400 MHz, $CDCl_3$)



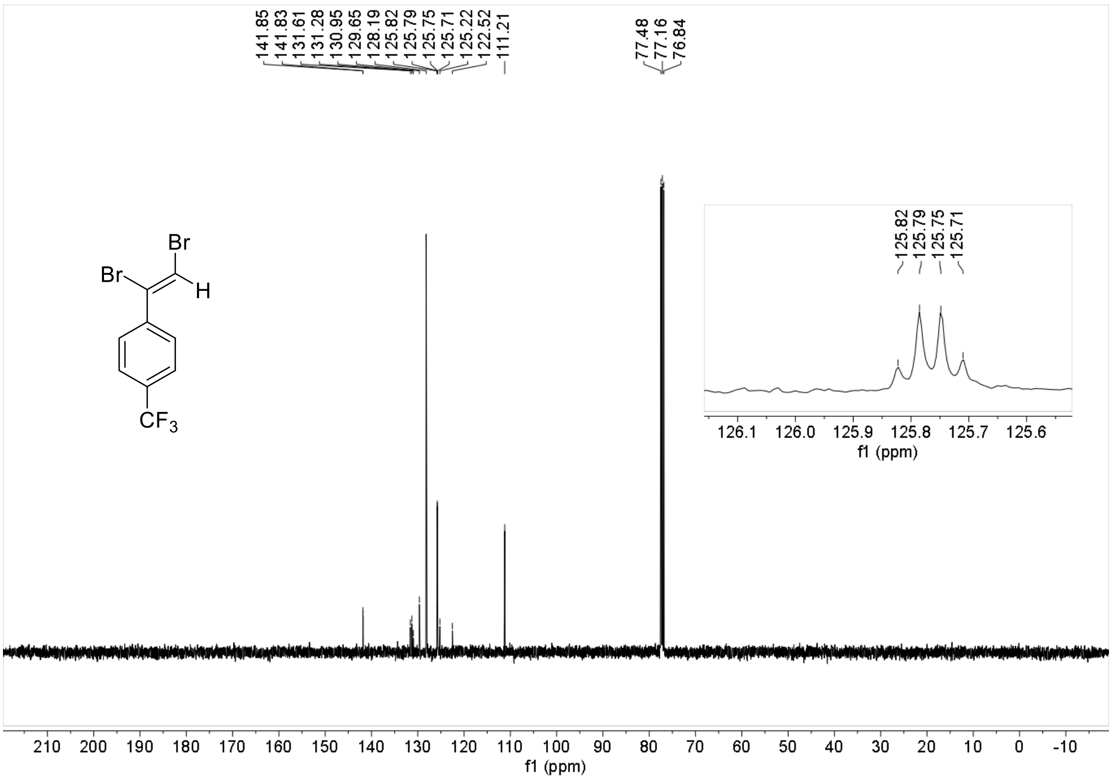
^{13}C NMR spectrum of compound **2i** (101 MHz, $CDCl_3$)



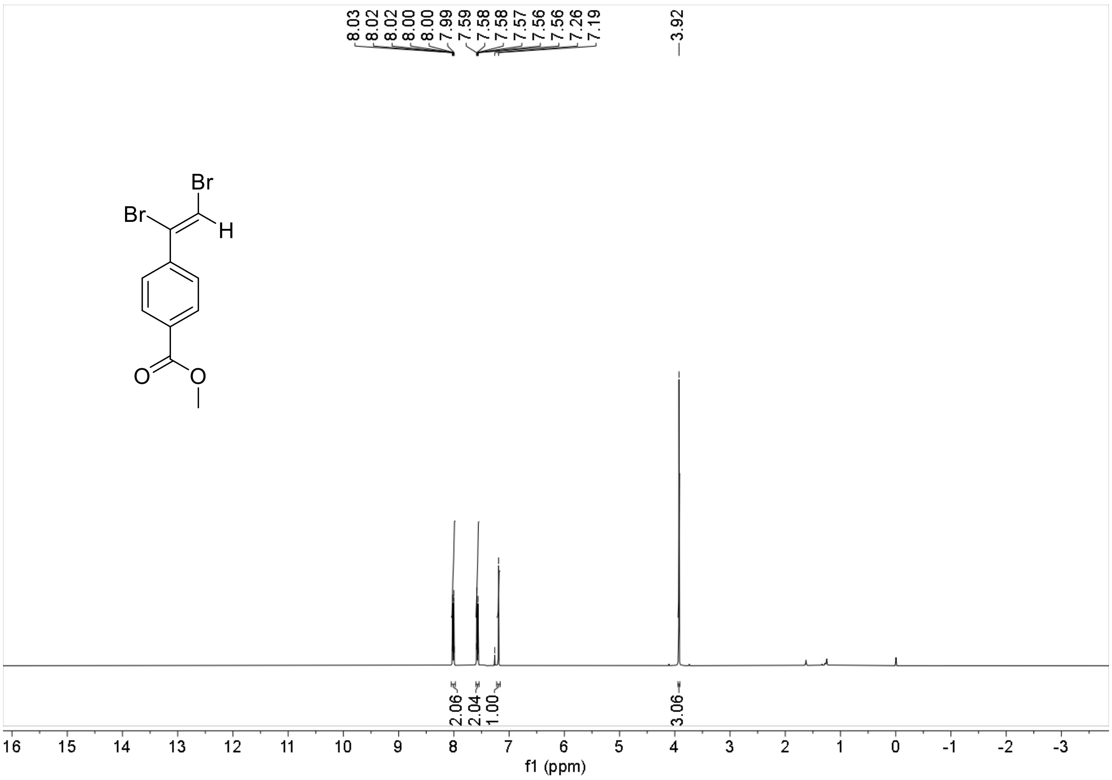
^{1}H NMR spectrum of compound **2j** (400 MHz, CDCl$_3$)



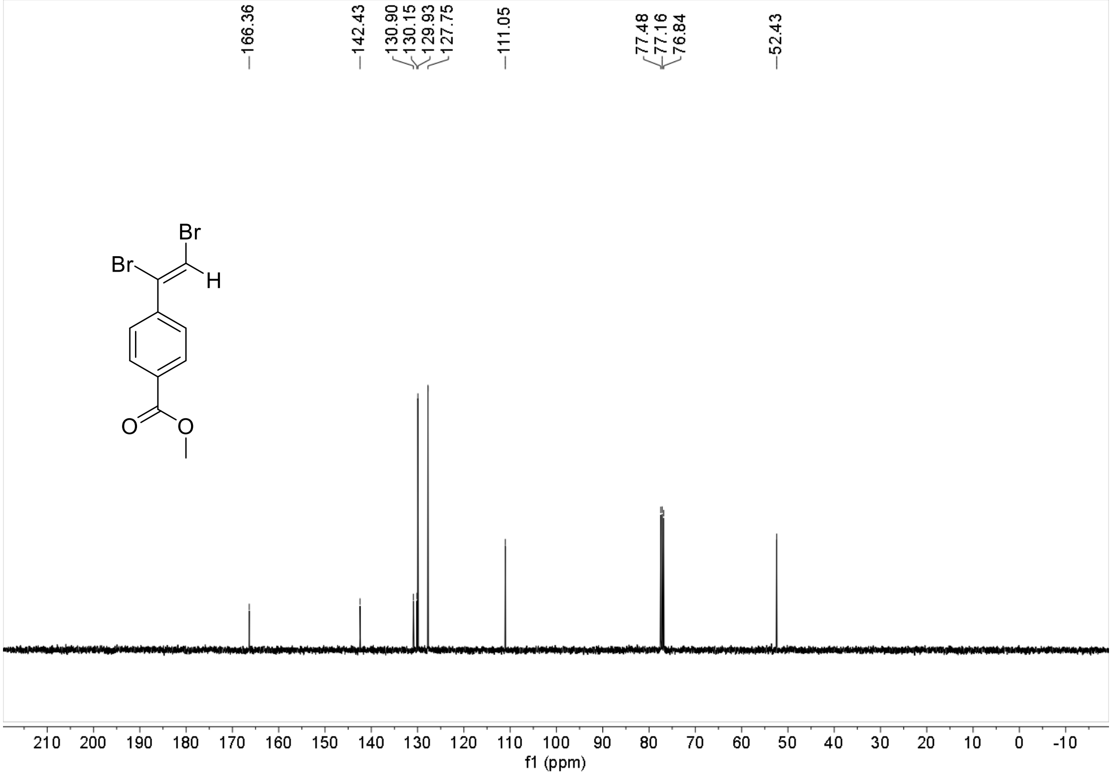
^{13}C NMR spectrum of compound **2j** (101 MHz, CDCl$_3$)



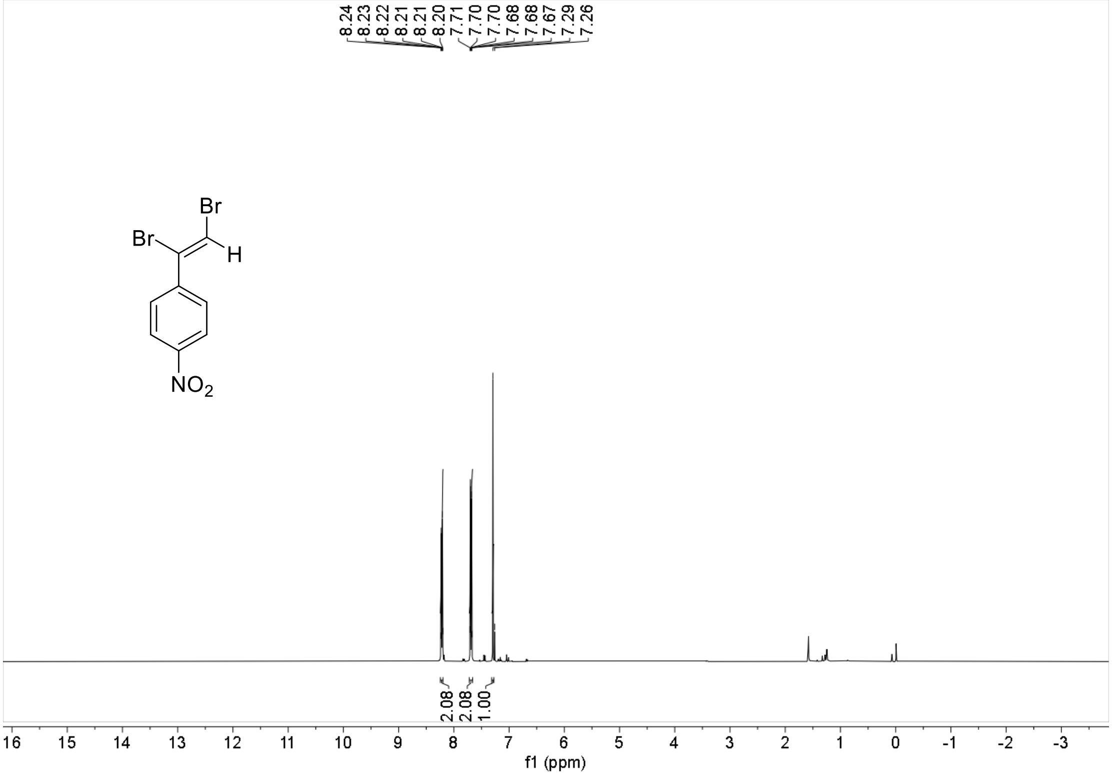
^{1}H NMR spectrum of compound **2k** (400 MHz, $CDCl_3$)



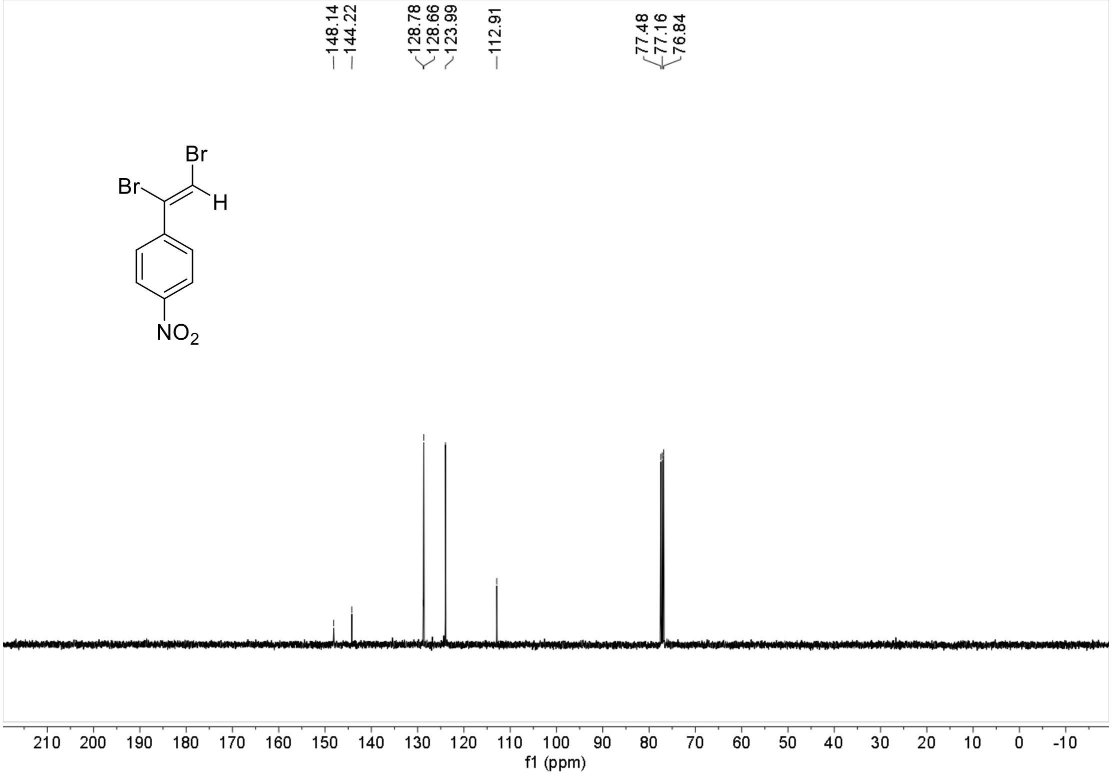
^{13}C NMR spectrum of compound **2k** (101 MHz, $CDCl_3$)



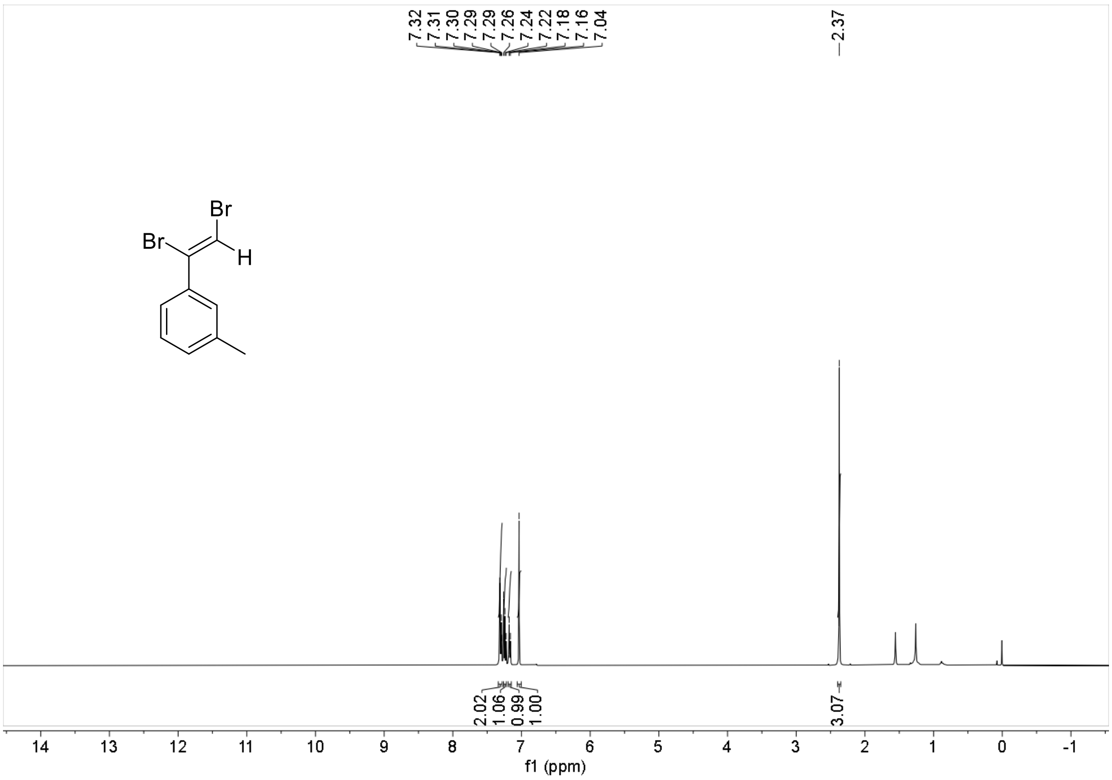
^{1}H NMR spectrum of compound **2l** (400 MHz, $CDCl_3$)



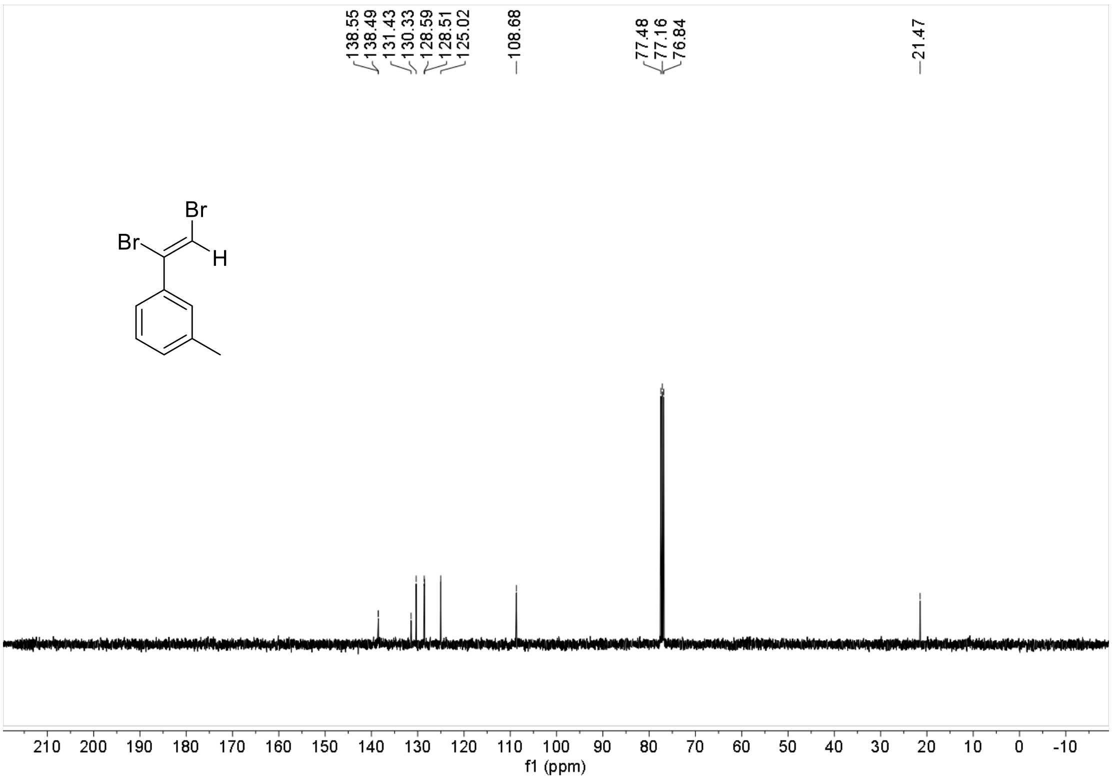
^{13}C NMR spectrum of compound **2l** (101 MHz, $CDCl_3$)



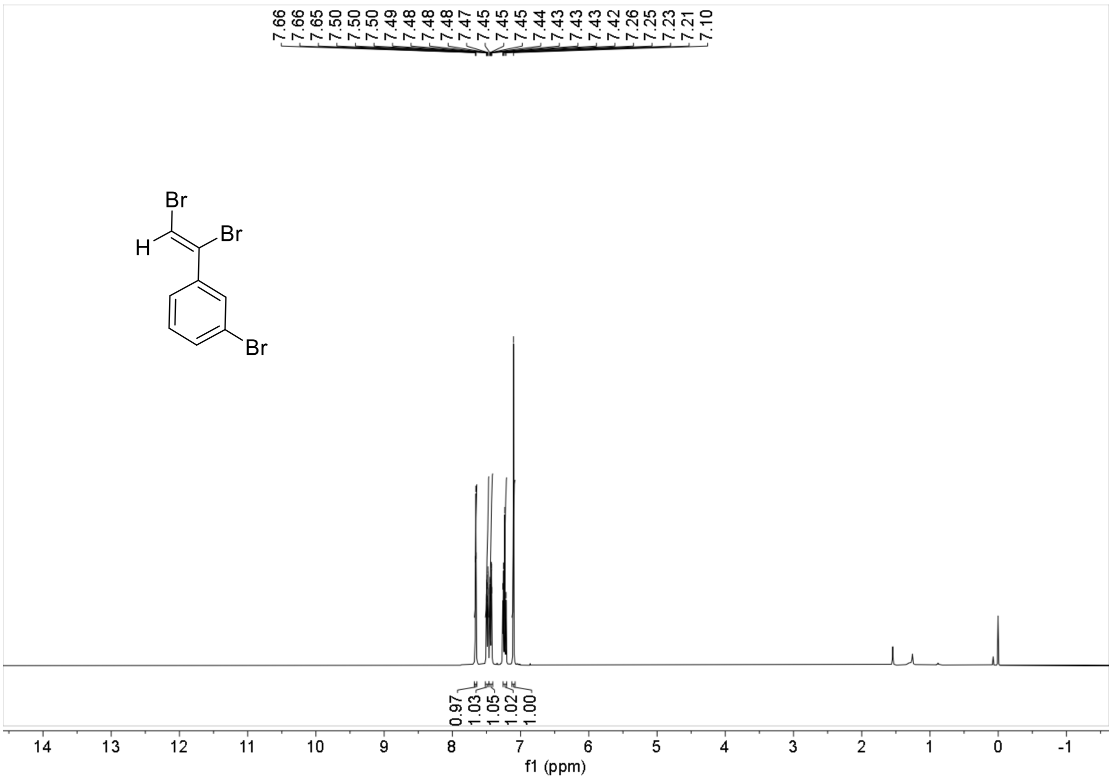
^{1}H NMR spectrum of compound **2m** (400 MHz, $CDCl_3$)



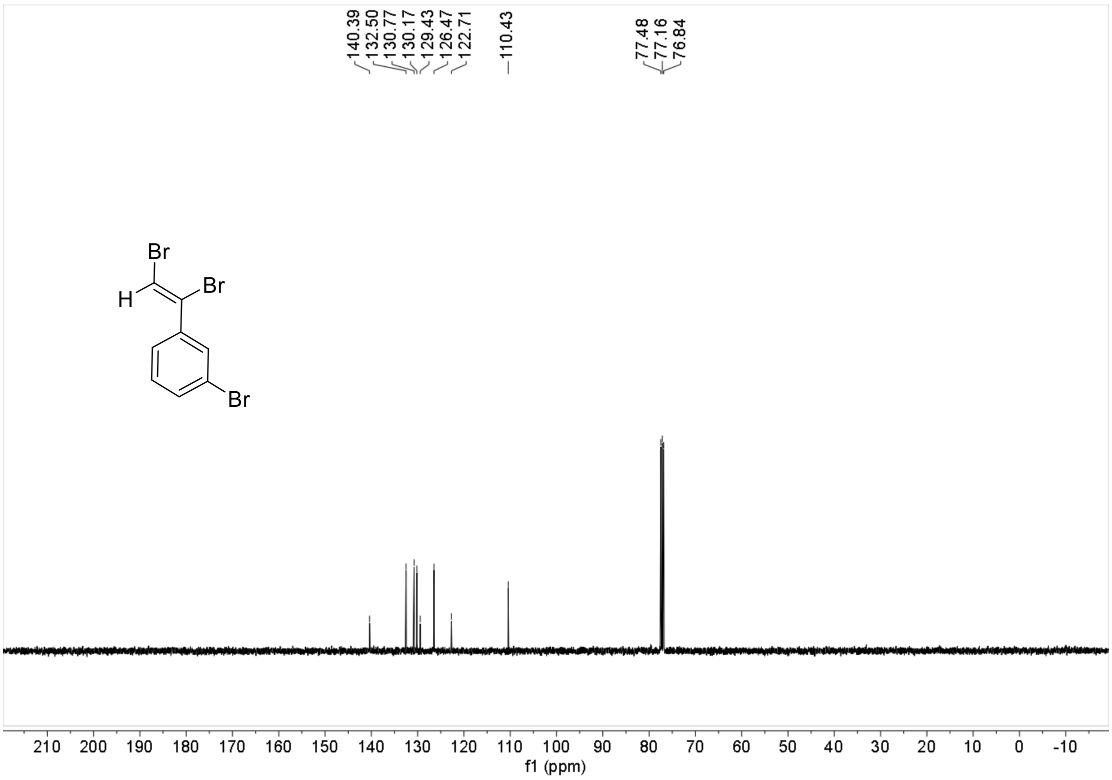
^{13}C NMR spectrum of compound **2m** (101 MHz, $CDCl_3$)



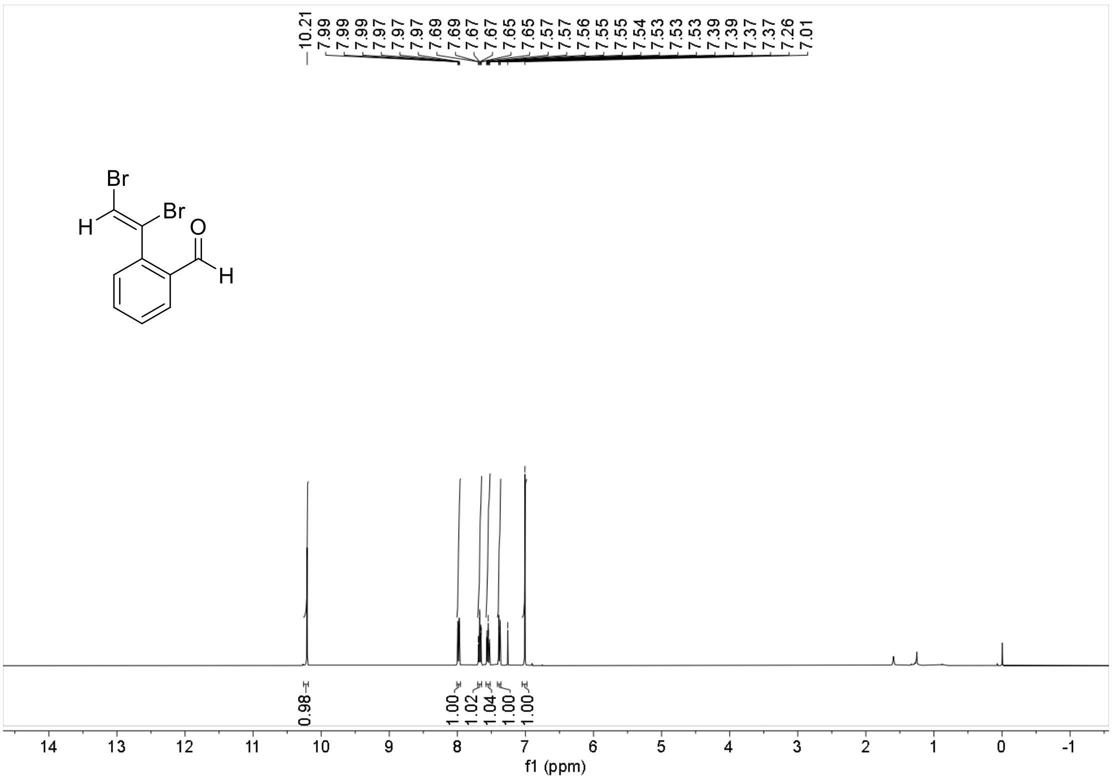
^{1}H NMR spectrum of compound **2n** (400 MHz, $CDCl_3$)



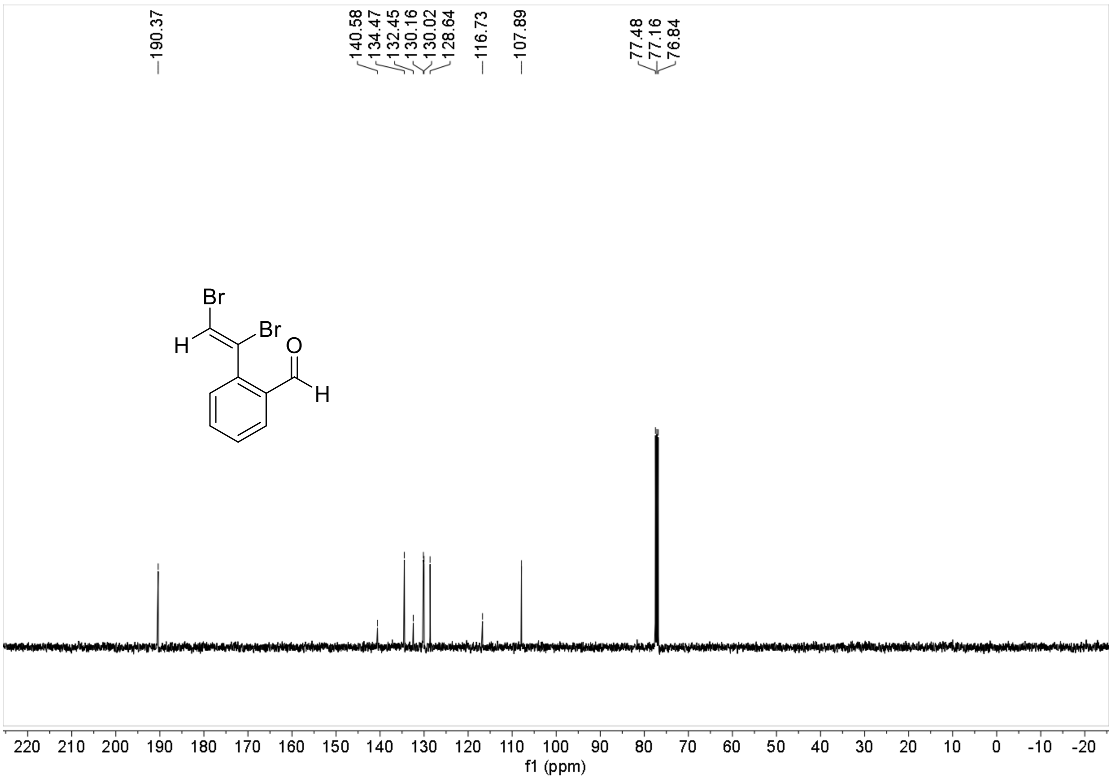
^{13}C NMR spectrum of compound **2n** (101 MHz, $CDCl_3$)



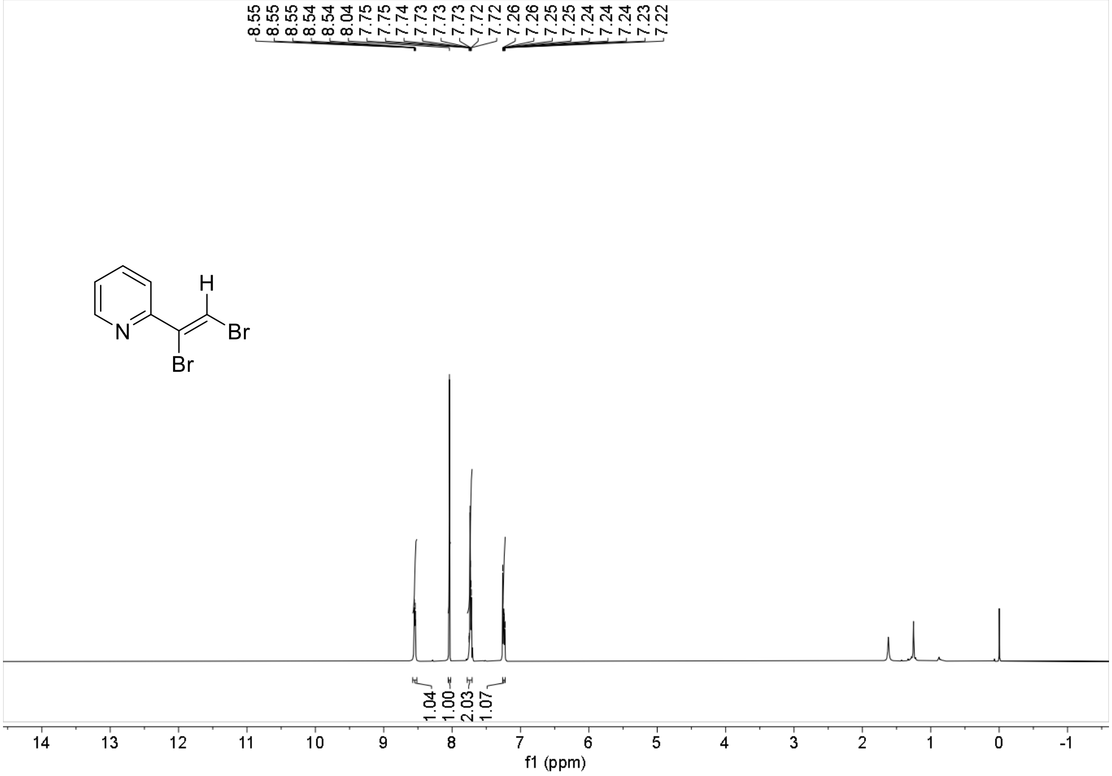
^{1}H NMR spectrum of compound **2o** (400 MHz, $CDCl_3$)



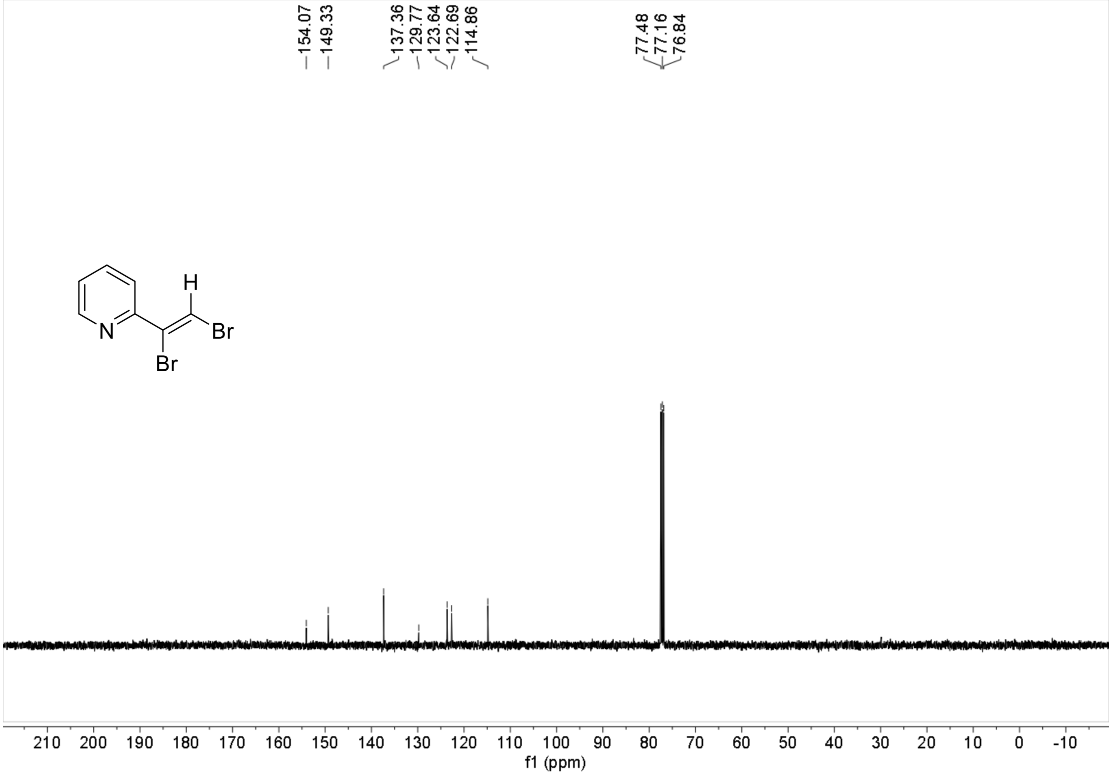
^{13}C NMR spectrum of compound **2o** (101 MHz, $CDCl_3$)



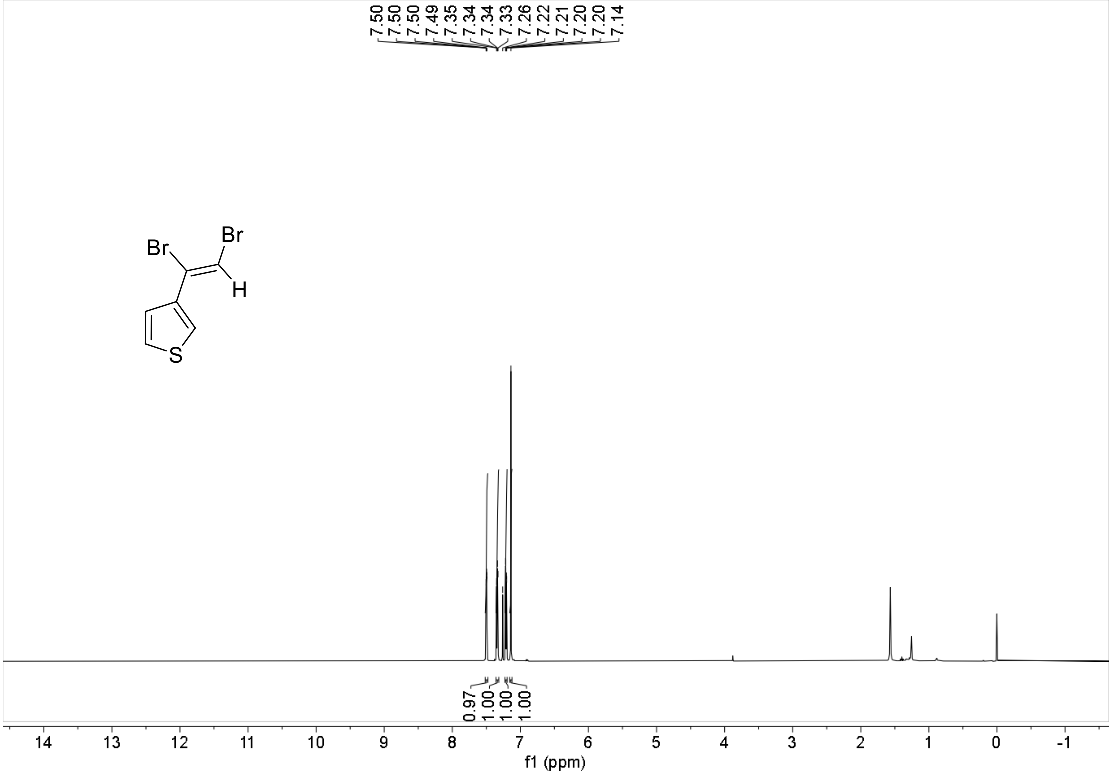
^{1}H NMR spectrum of compound **2p** (400 MHz, $CDCl_3$)



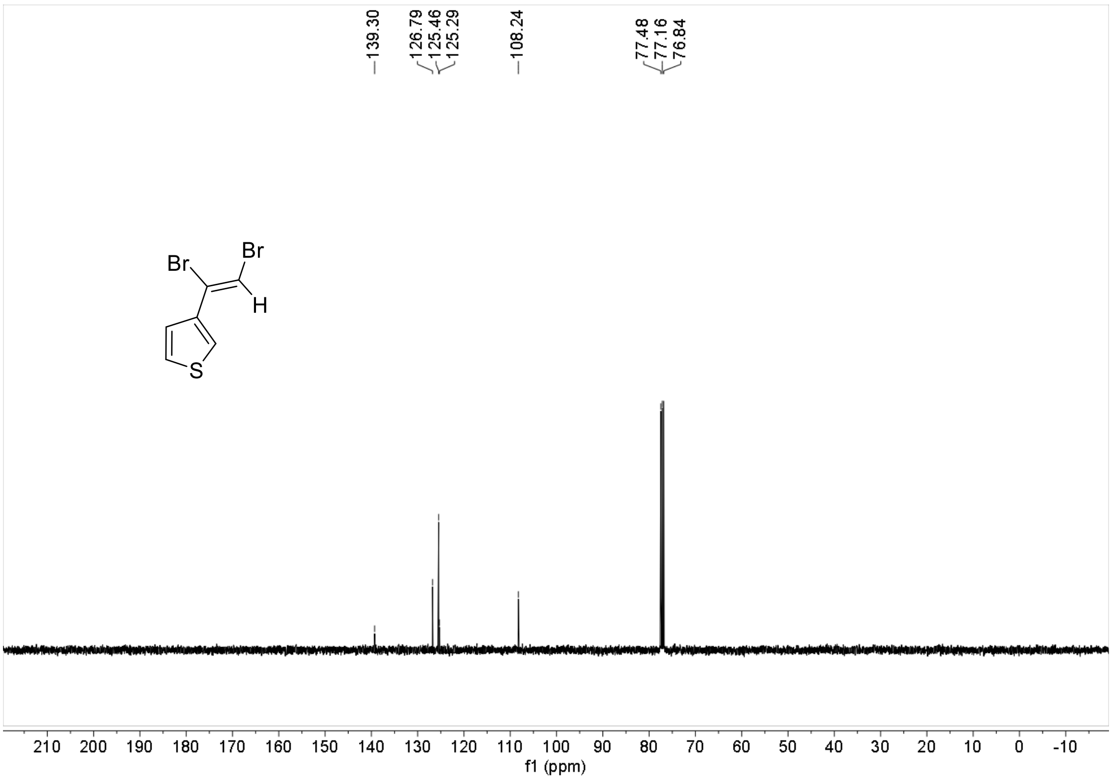
^{13}C NMR spectrum of compound **2p** (101 MHz, $CDCl_3$)



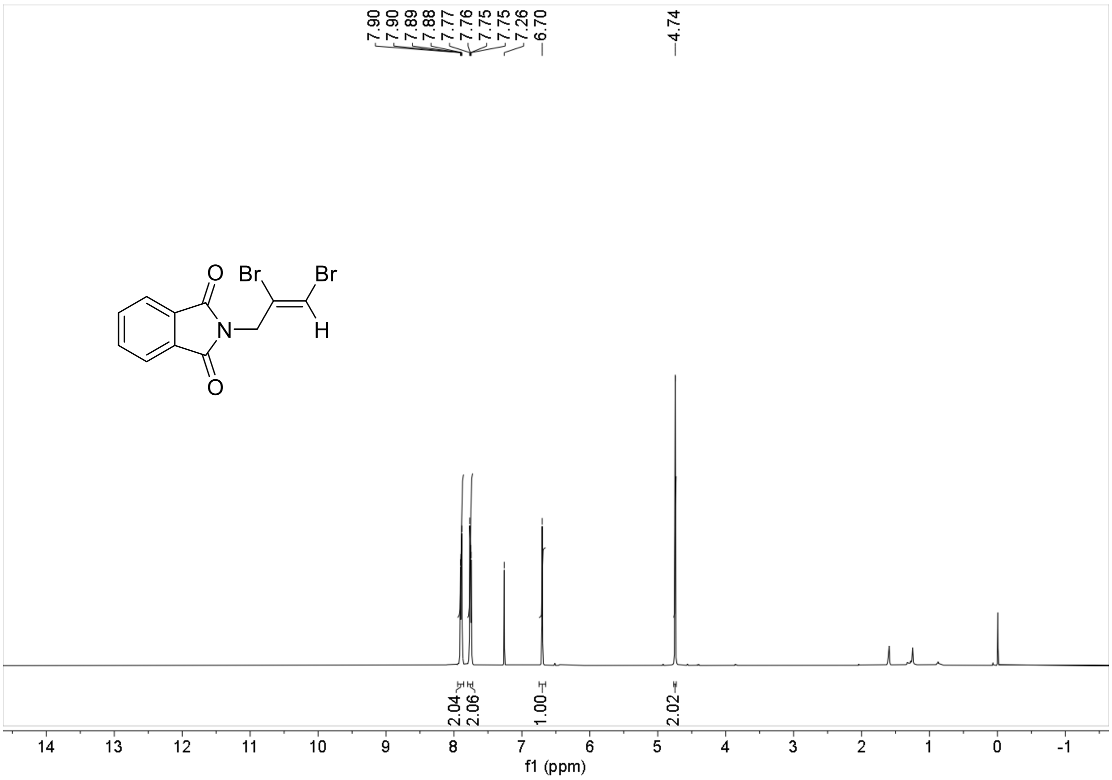
^{1}H NMR spectrum of compound **2q** (400 MHz, CDCl$_3$)



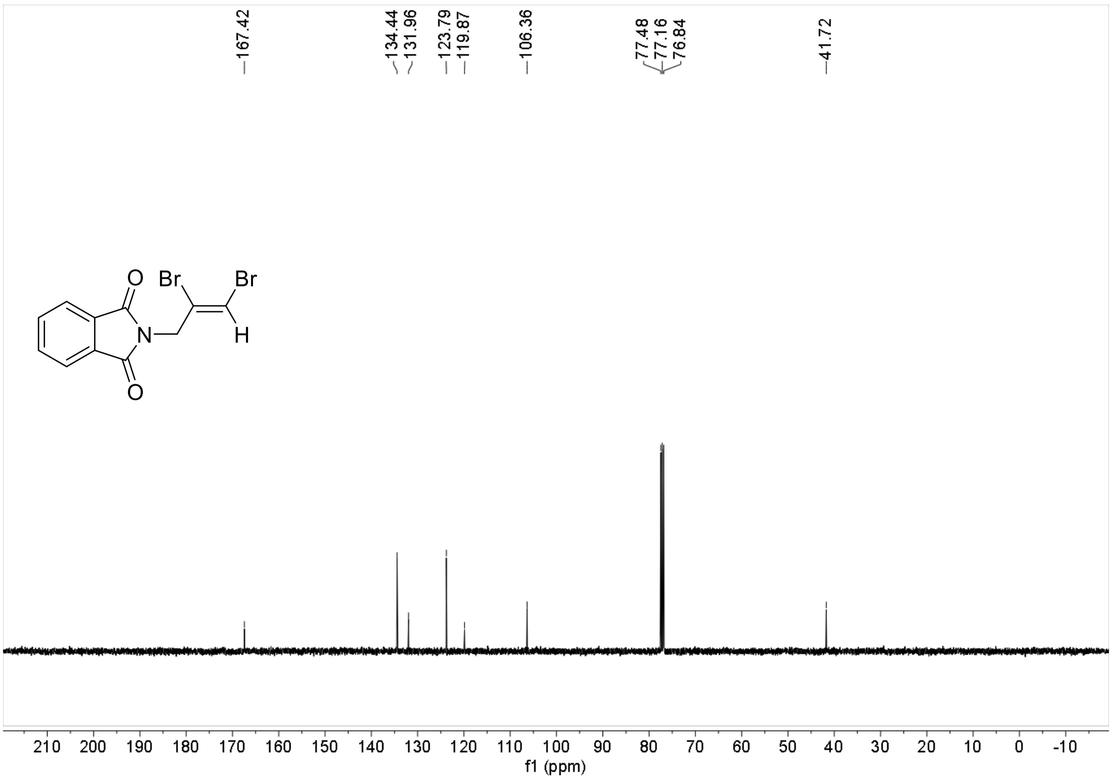
^{13}C NMR spectrum of compound **2q** (101 MHz, CDCl$_3$)



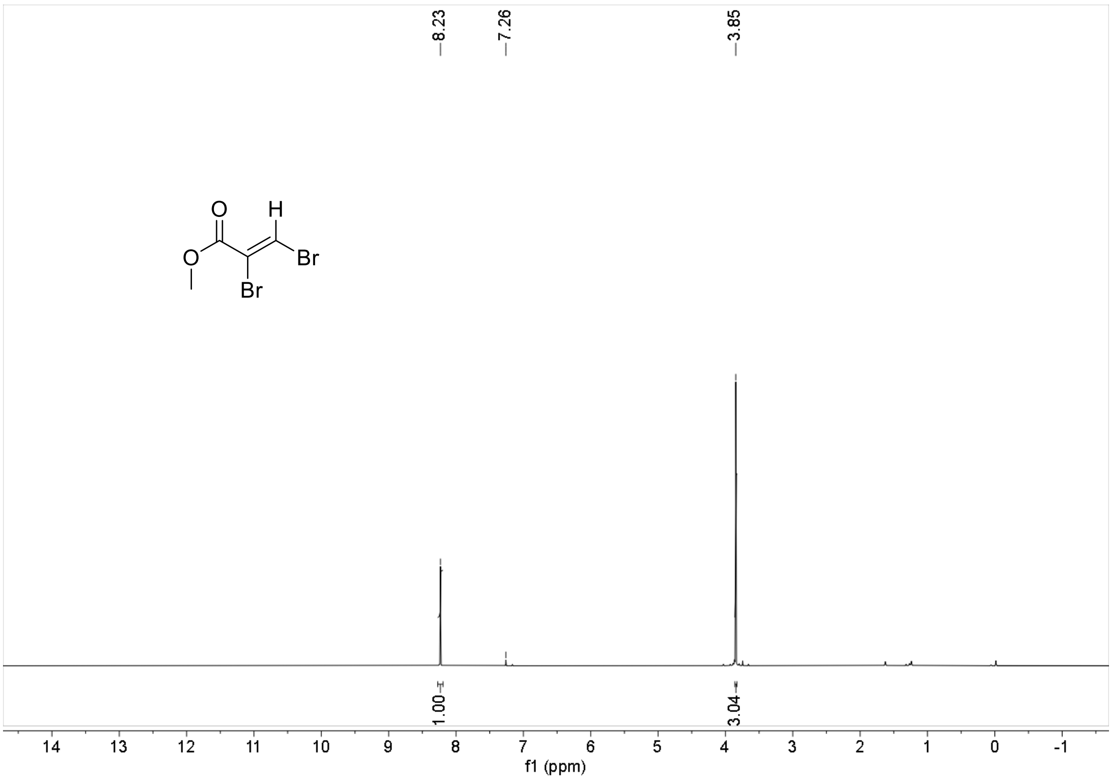
^{1}H NMR spectrum of compound **2r** (400 MHz, $CDCl_3$)



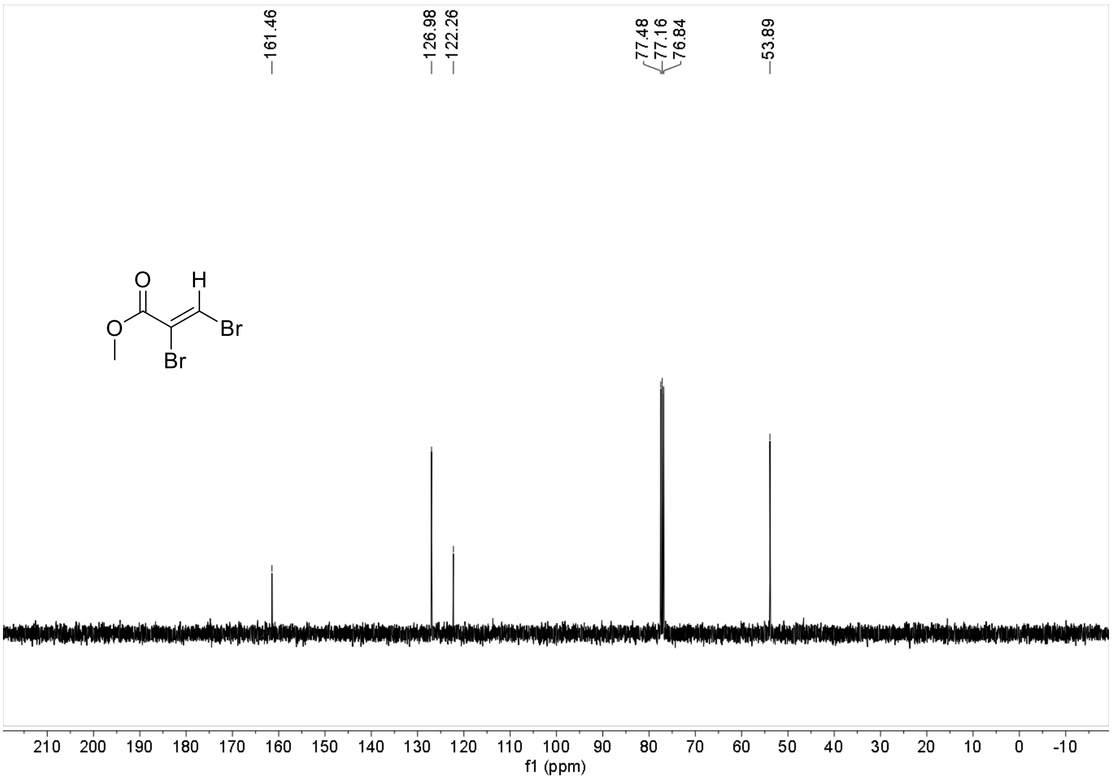
^{13}C NMR spectrum of compound **2r** (101 MHz, $CDCl_3$)



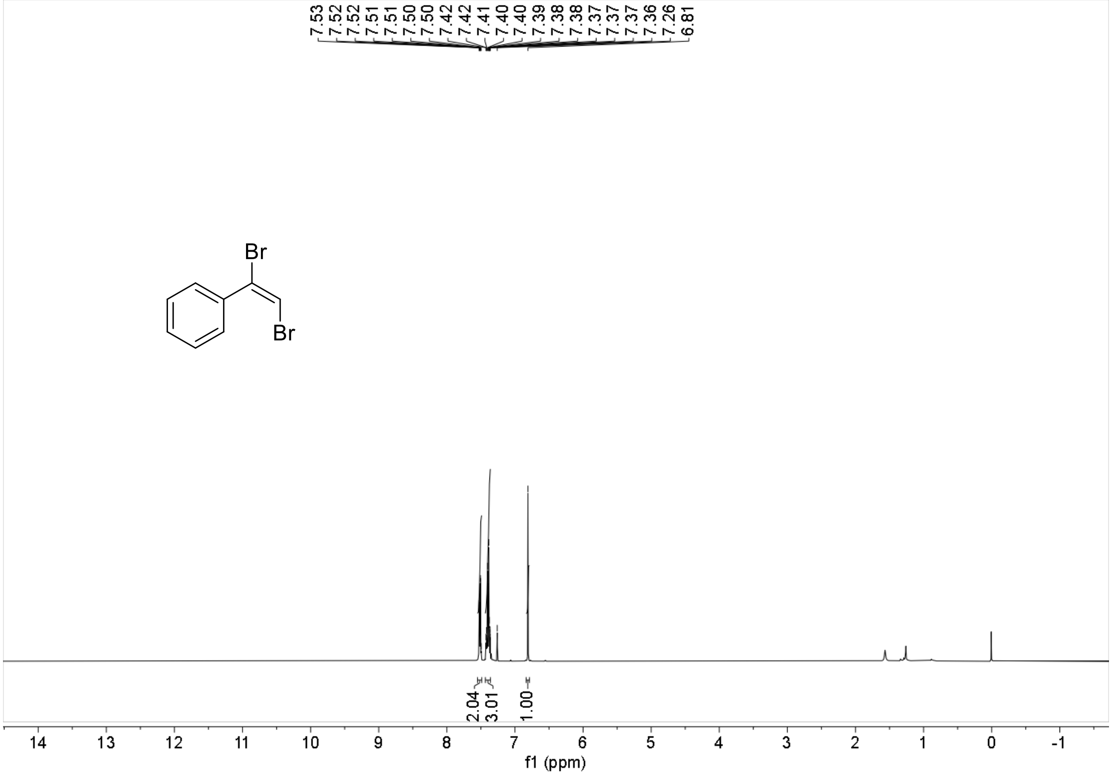
^{1}H NMR spectrum of compound **2s** (400 MHz, $CDCl_3$)



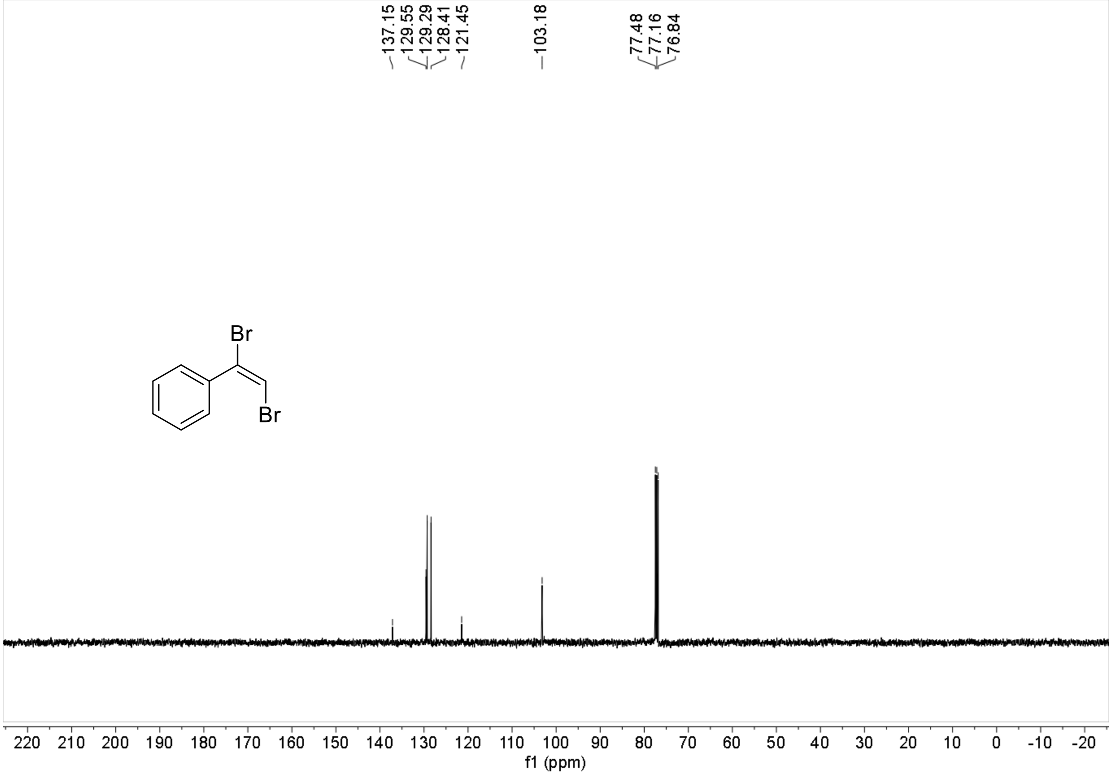
^{13}C NMR spectrum of compound **2s** (101 MHz, $CDCl_3$)



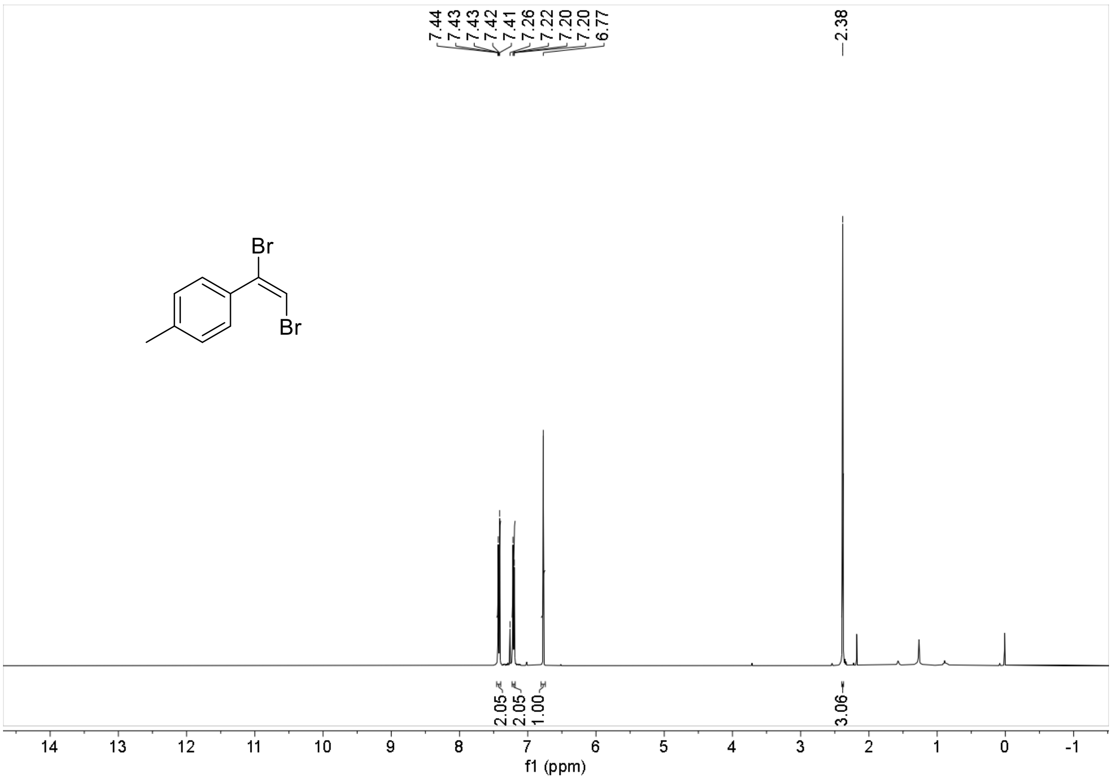
^{1}H NMR spectrum of compound **3a** (400 MHz, $CDCl_3$)



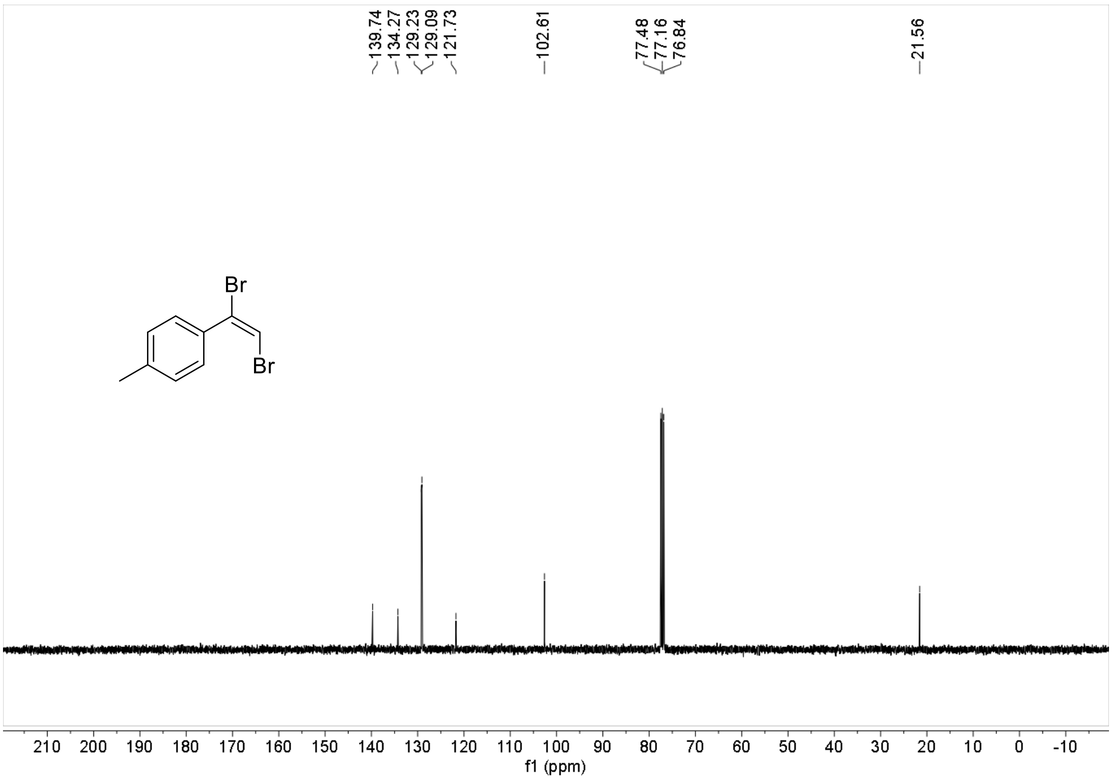
^{13}C NMR spectrum of compound **3a** (101 MHz, $CDCl_3$)



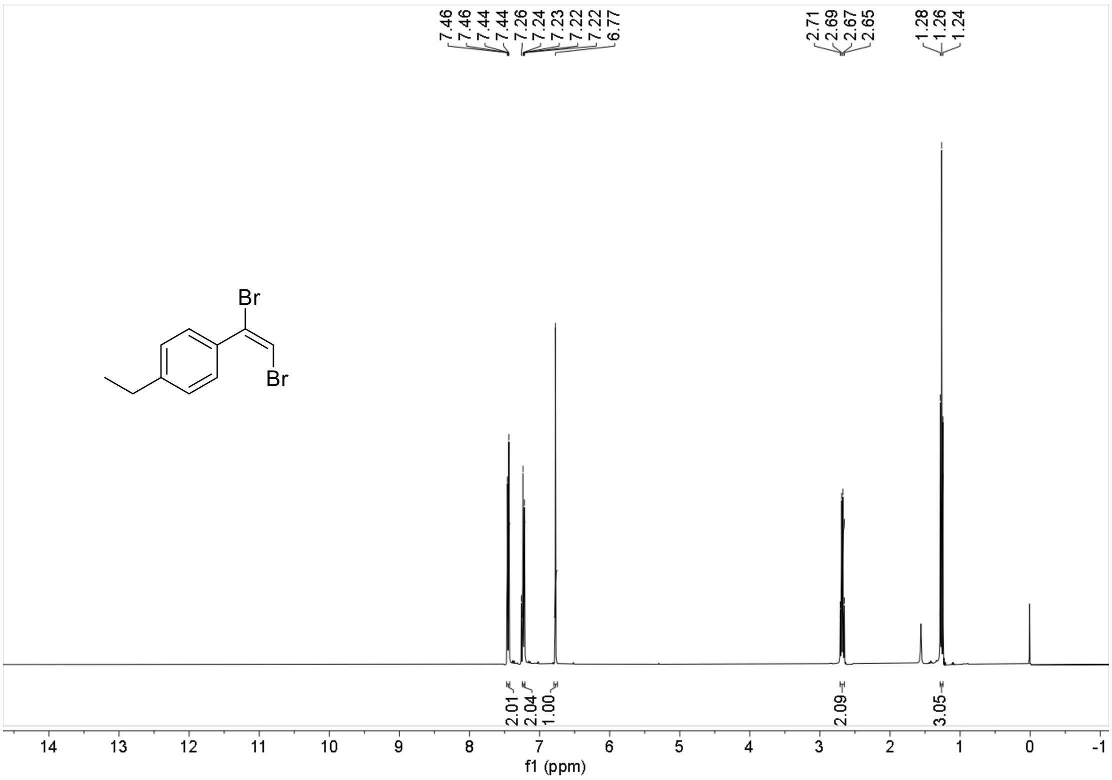
^{1}H NMR spectrum of compound **3b** (400 MHz, CDCl$_3$)



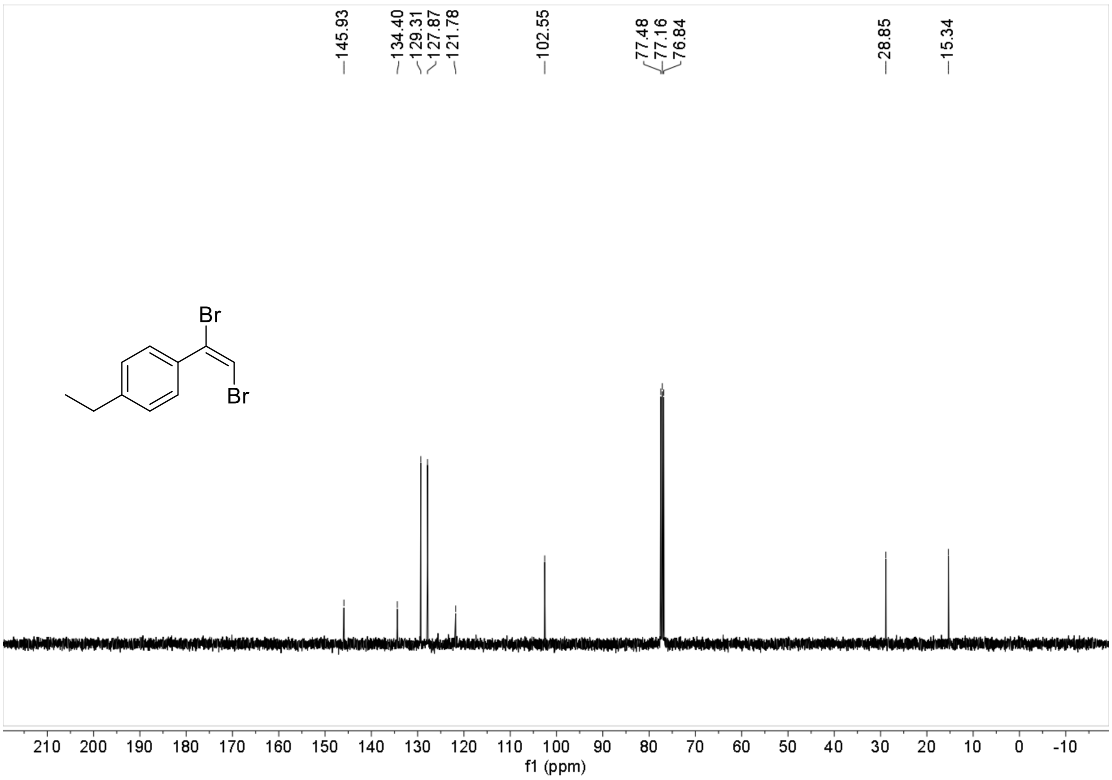
^{13}C NMR spectrum of compound **3b** (101 MHz, CDCl$_3$)



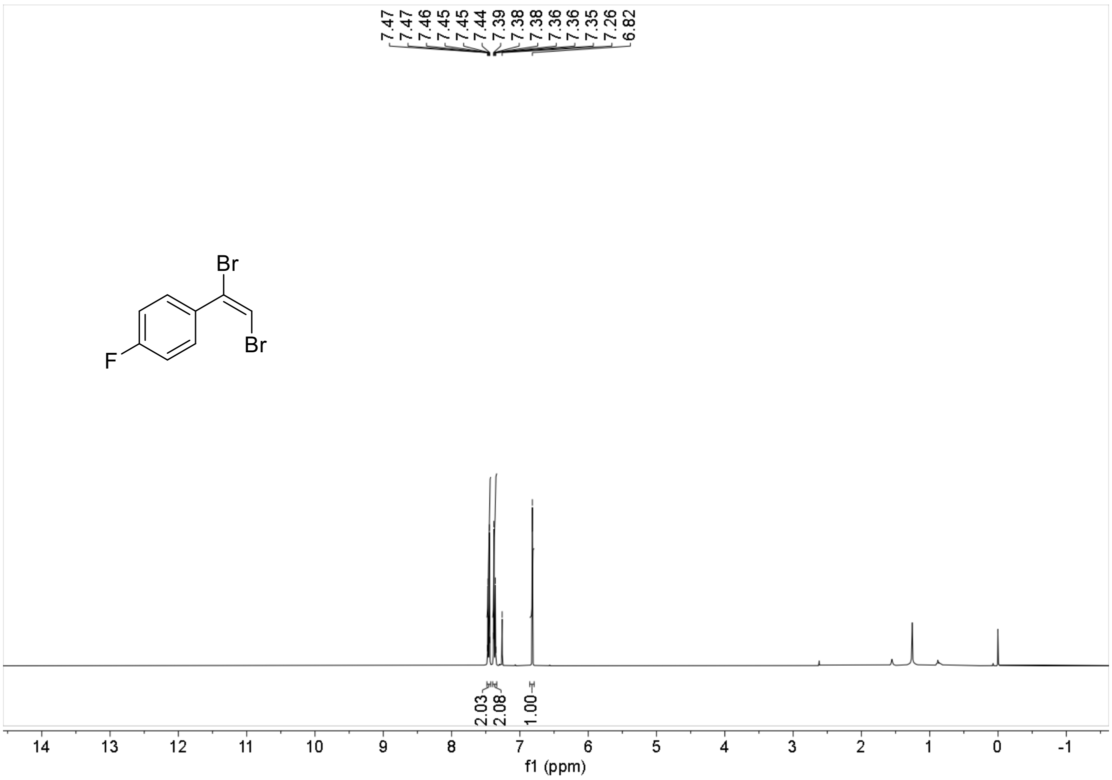
^{1}H NMR spectrum of compound **3c** (400 MHz, $CDCl_3$)



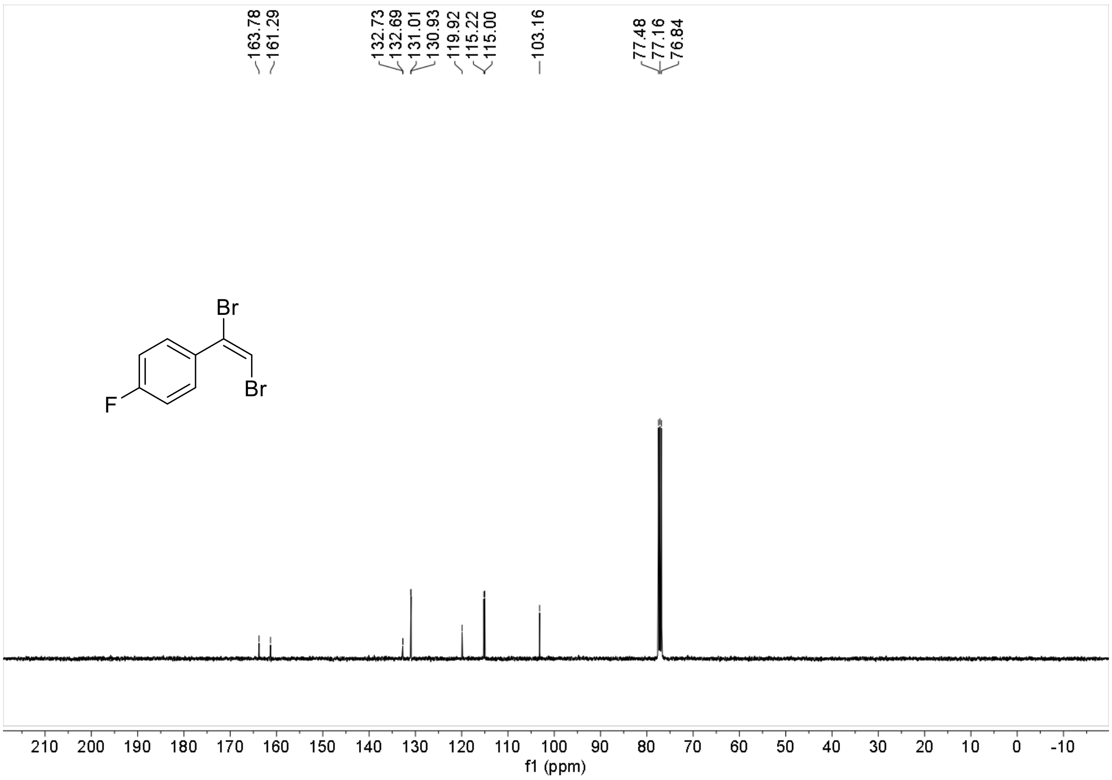
^{13}C NMR spectrum of compound **3c** (101 MHz, $CDCl_3$)



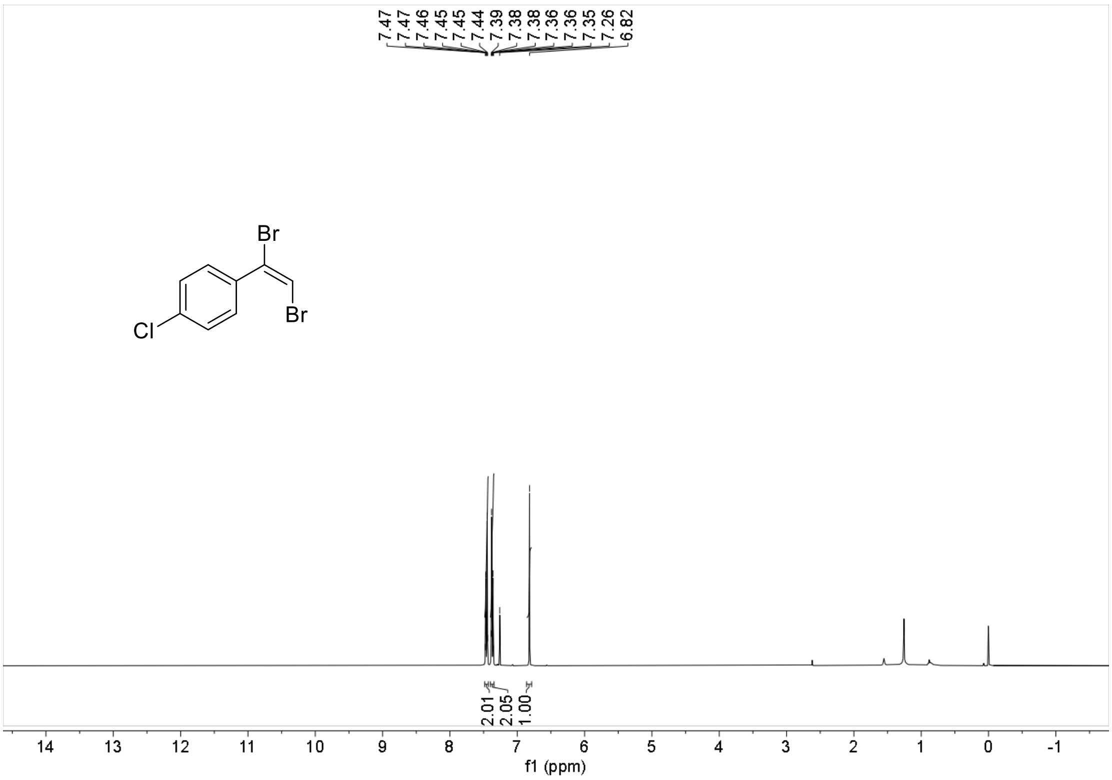
^{1}H NMR spectrum of compound **3d** (400 MHz, $CDCl_3$)



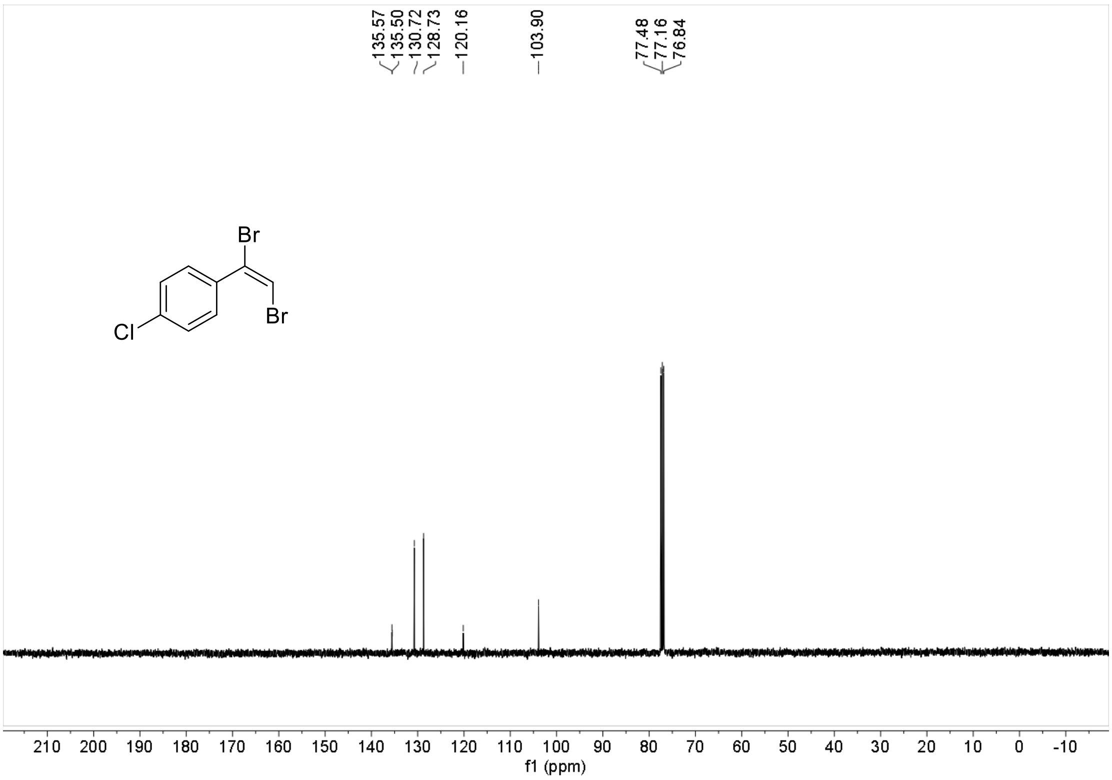
^{13}C NMR spectrum of compound **3d** (101 MHz, $CDCl_3$)



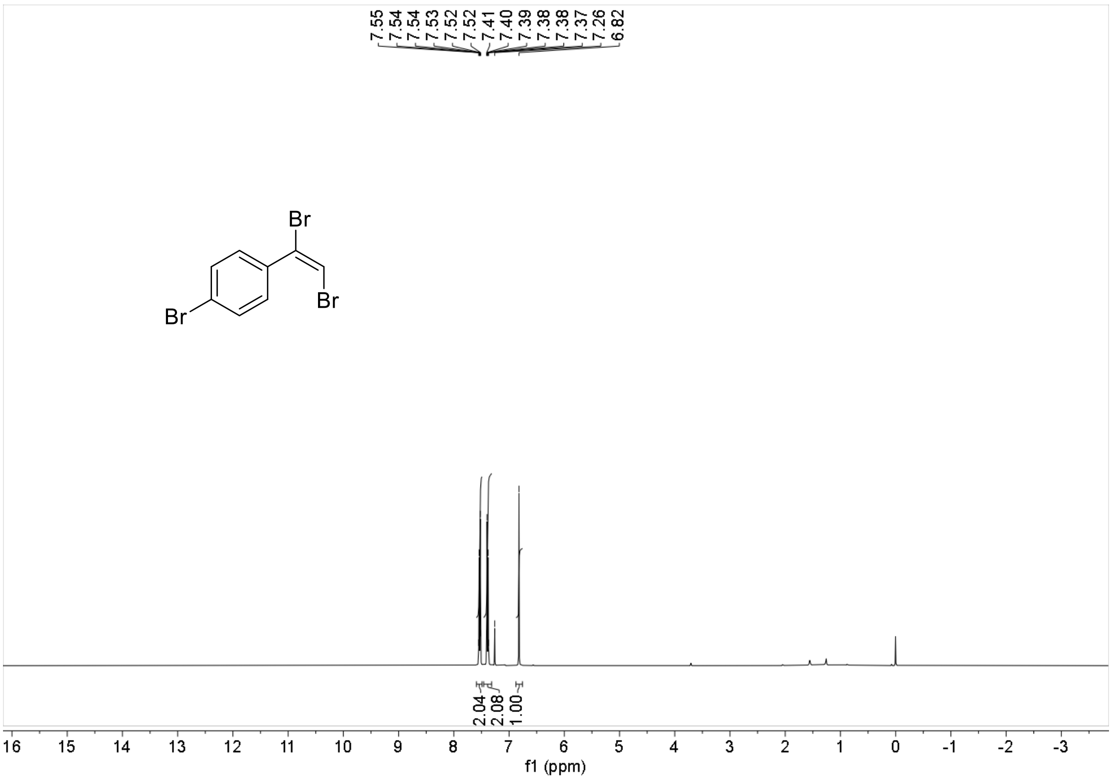
^{1}H NMR spectrum of compound **3e** (400 MHz, CDCl$_3$)



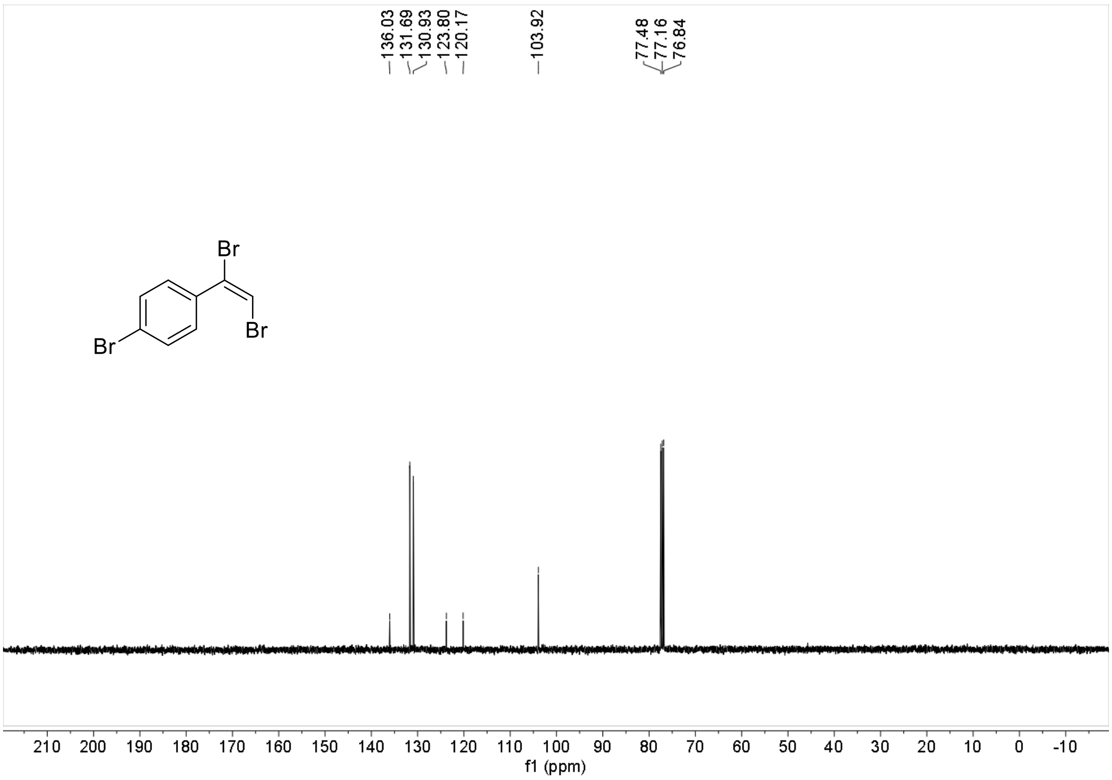
^{13}C NMR spectrum of compound **3e** (101 MHz, CDCl$_3$)



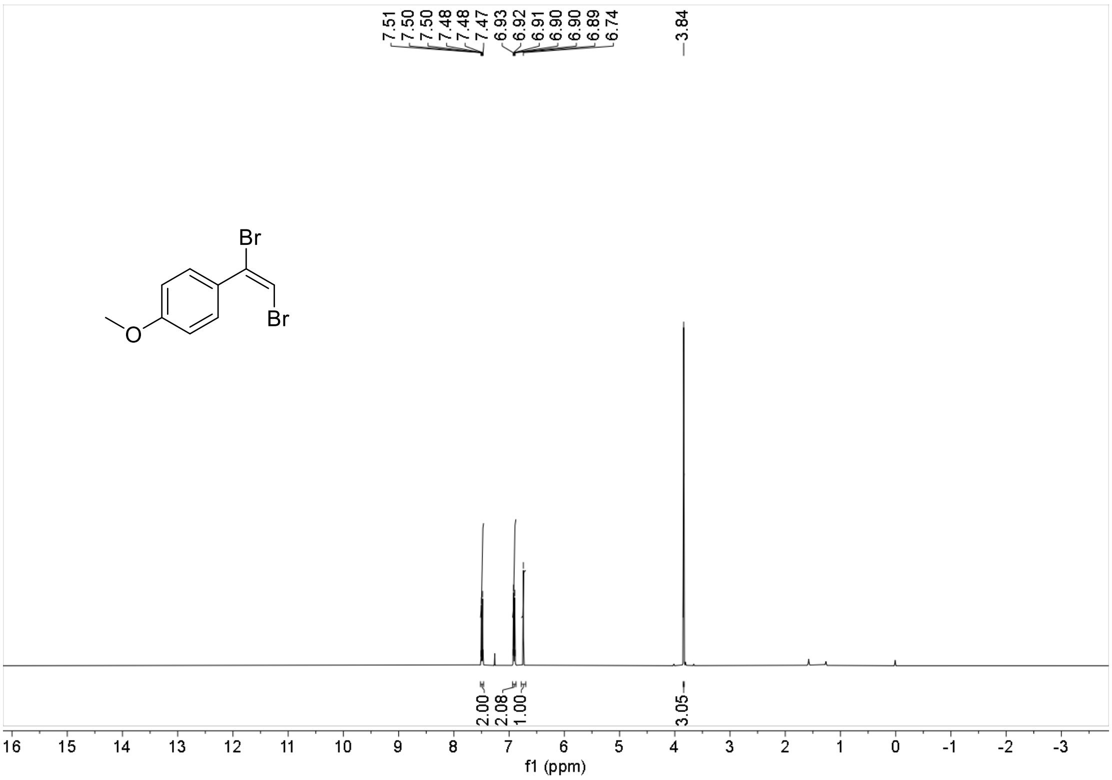
^{1}H NMR spectrum of compound **3f** (400 MHz, $CDCl_3$)



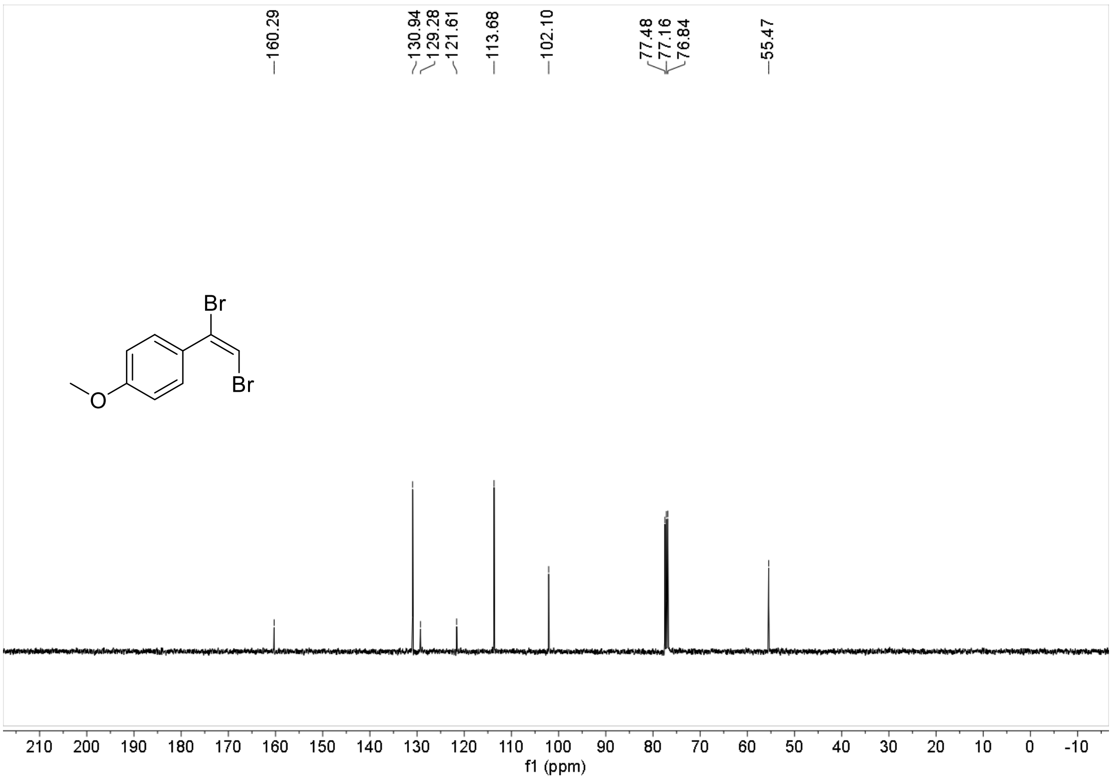
^{13}C NMR spectrum of compound **3f** (101 MHz, $CDCl_3$)



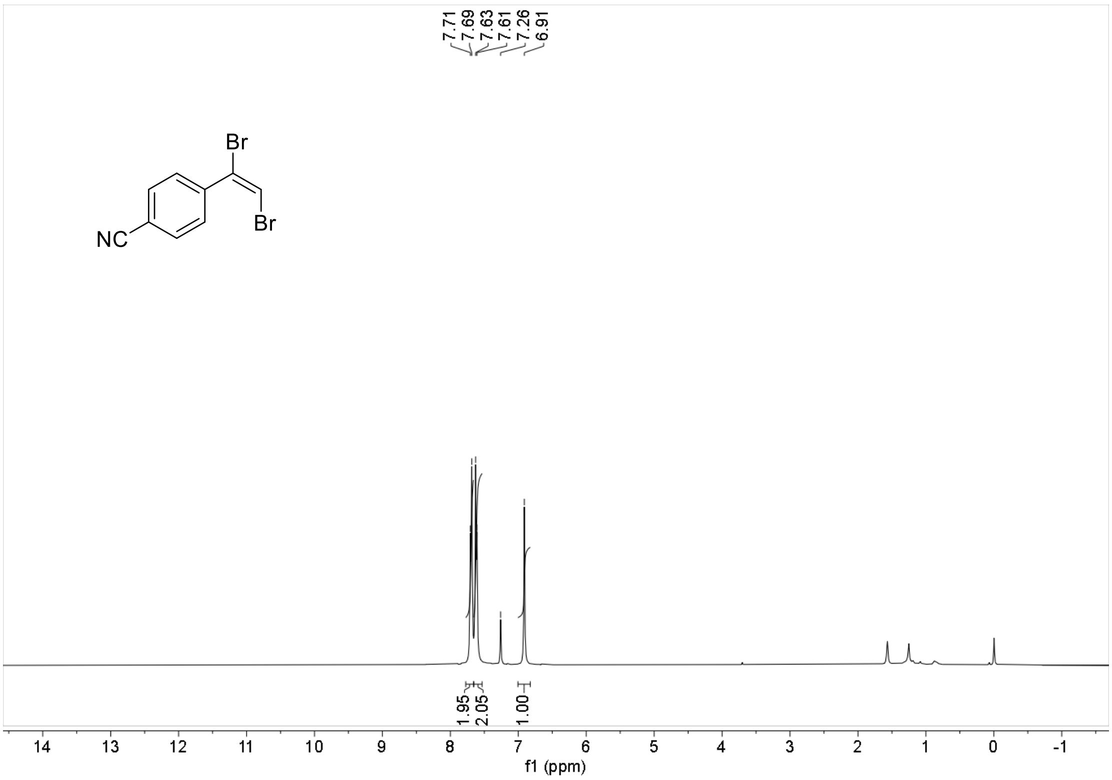
^{1}H NMR spectrum of compound **3g** (400 MHz, $CDCl_3$)



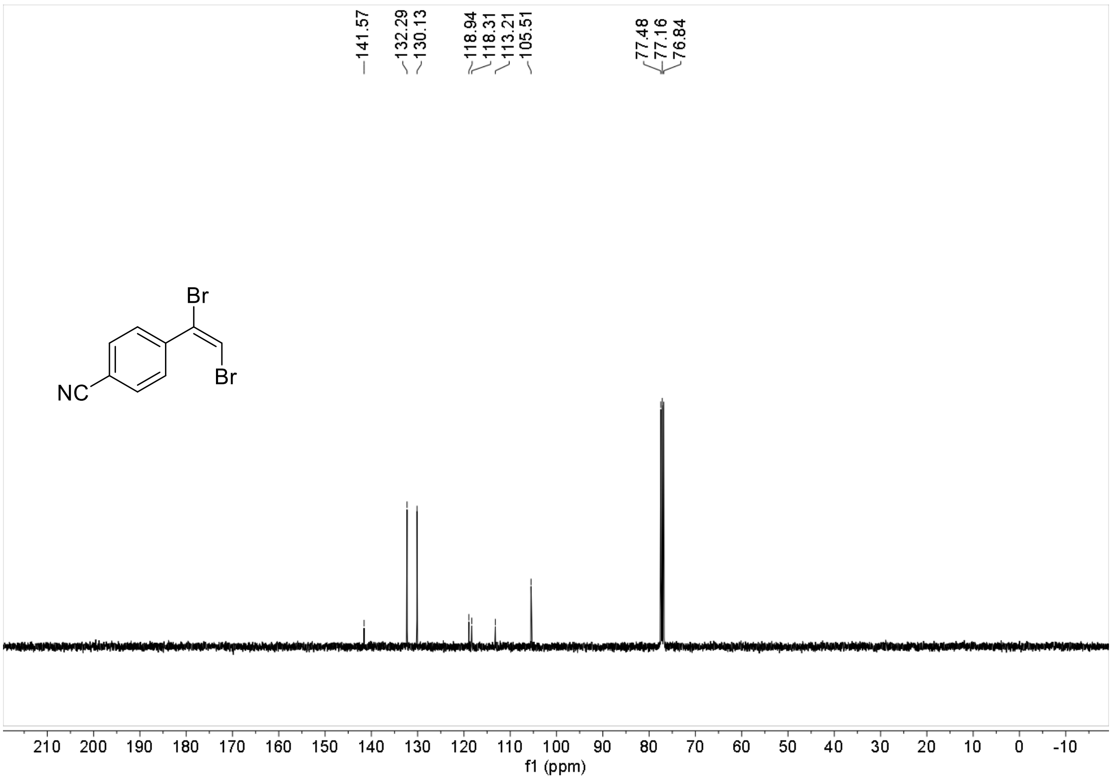
^{13}C NMR spectrum of compound **3g** (101 MHz, $CDCl_3$)



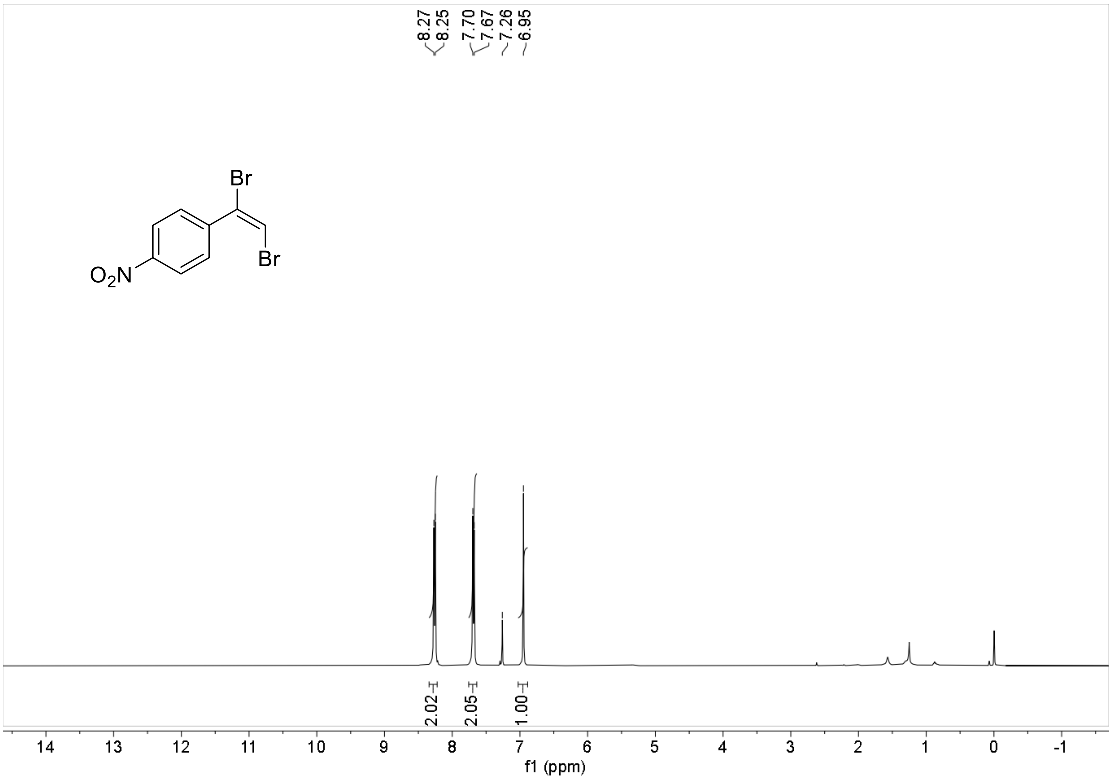
^{1}H NMR spectrum of compound **3h** (400 MHz, CDCl$_3$)



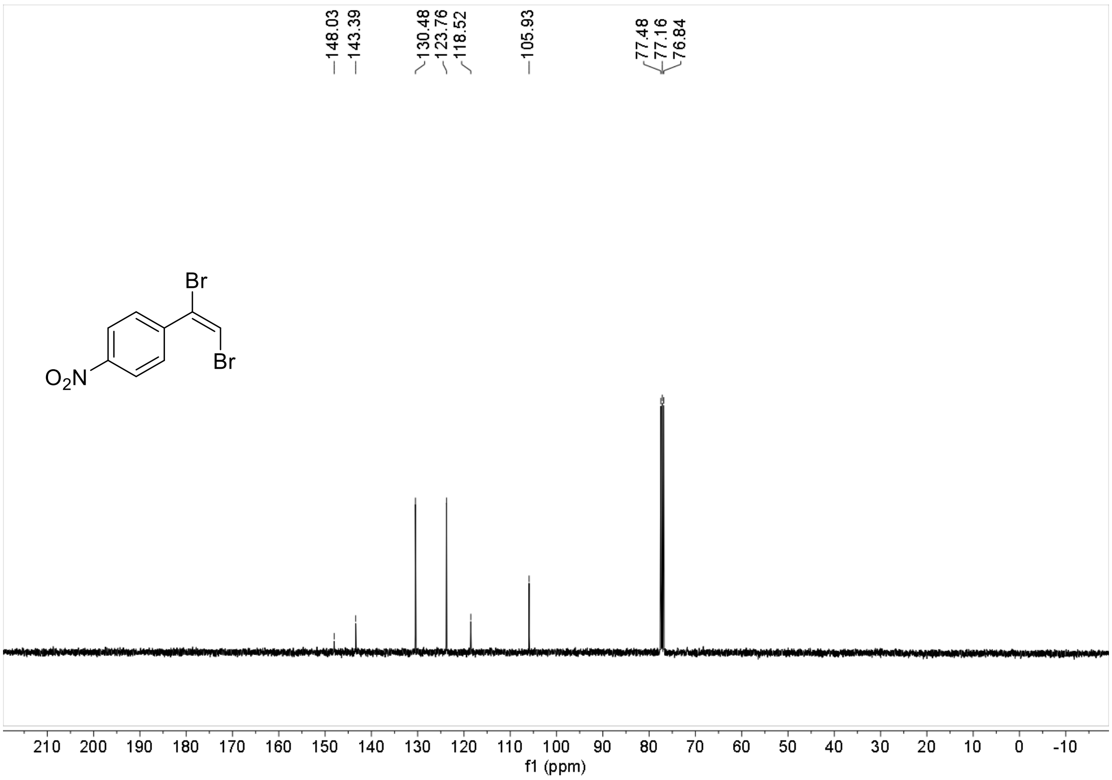
^{13}C NMR spectrum of compound **3h** (101 MHz, CDCl$_3$)



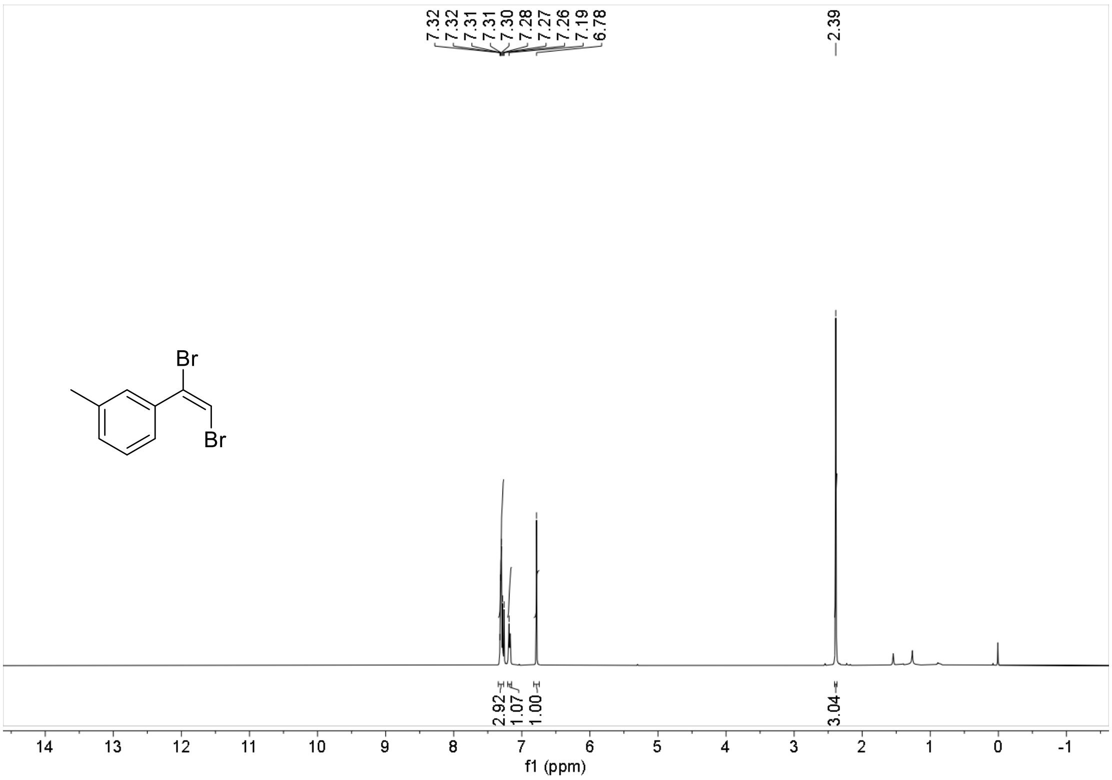
^{1}H NMR spectrum of compound **3i** (400 MHz, $CDCl_3$)



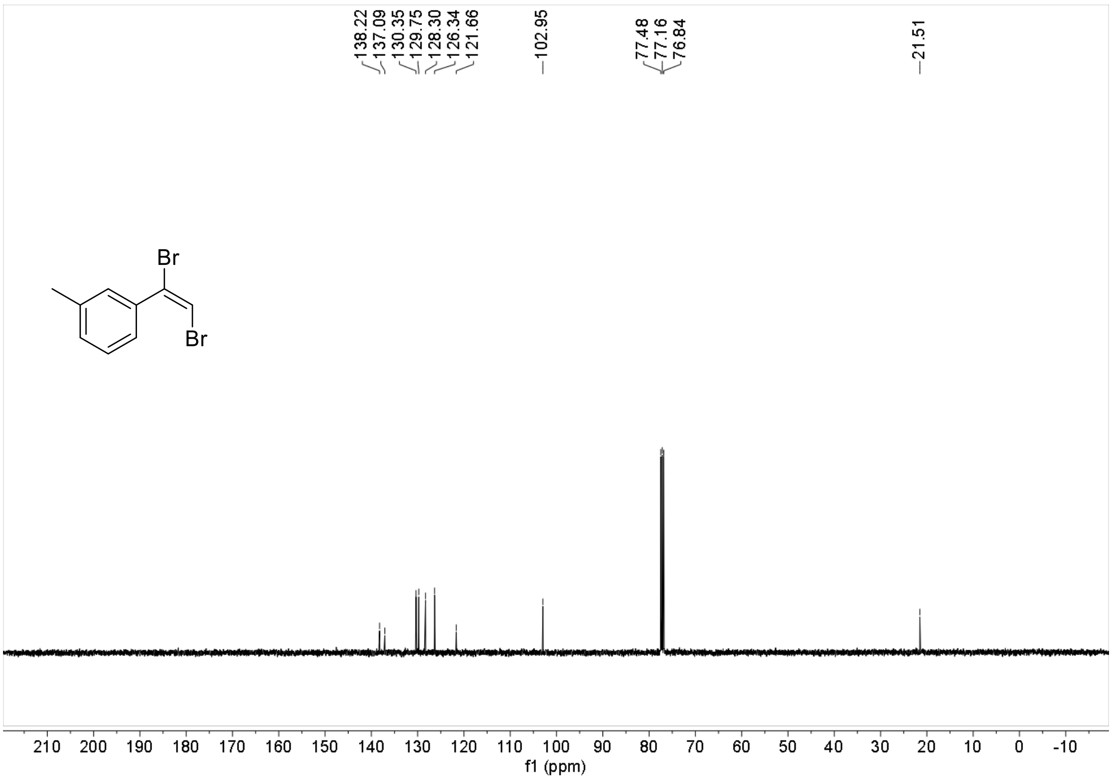
^{13}C NMR spectrum of compound **3i** (101 MHz, $CDCl_3$)



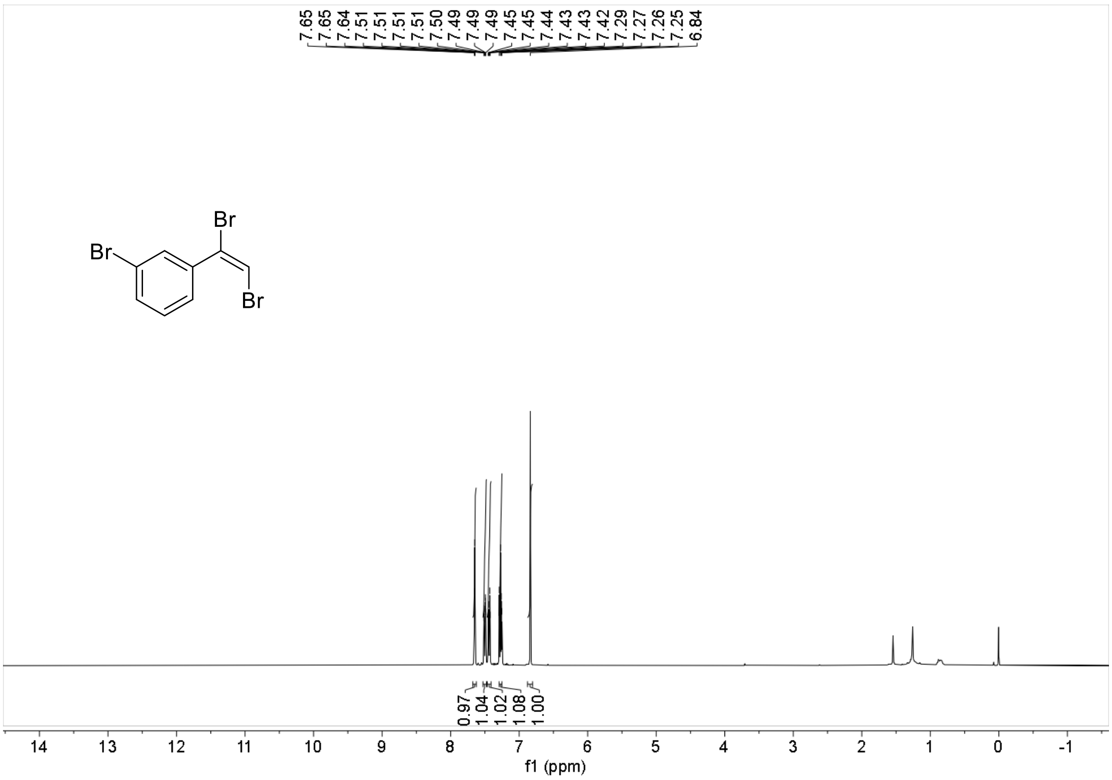
^{1}H NMR spectrum of compound **3j** (400 MHz, $CDCl_3$)



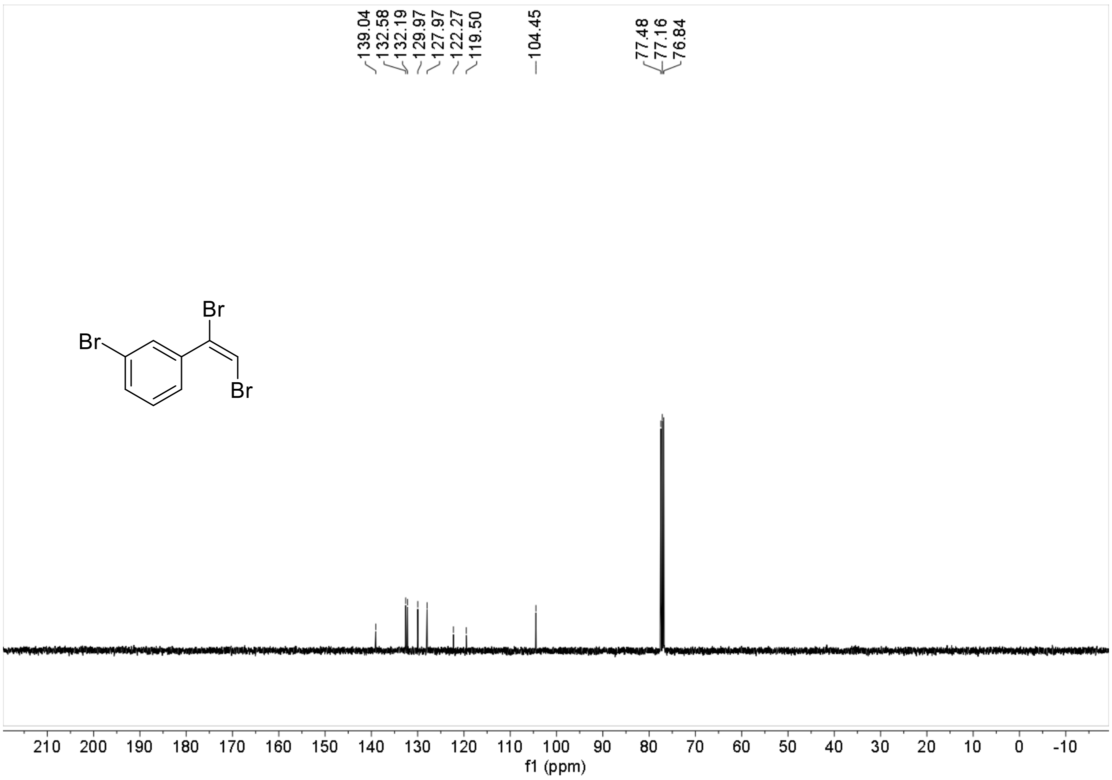
^{13}C NMR spectrum of compound **3j** (101 MHz, $CDCl_3$)



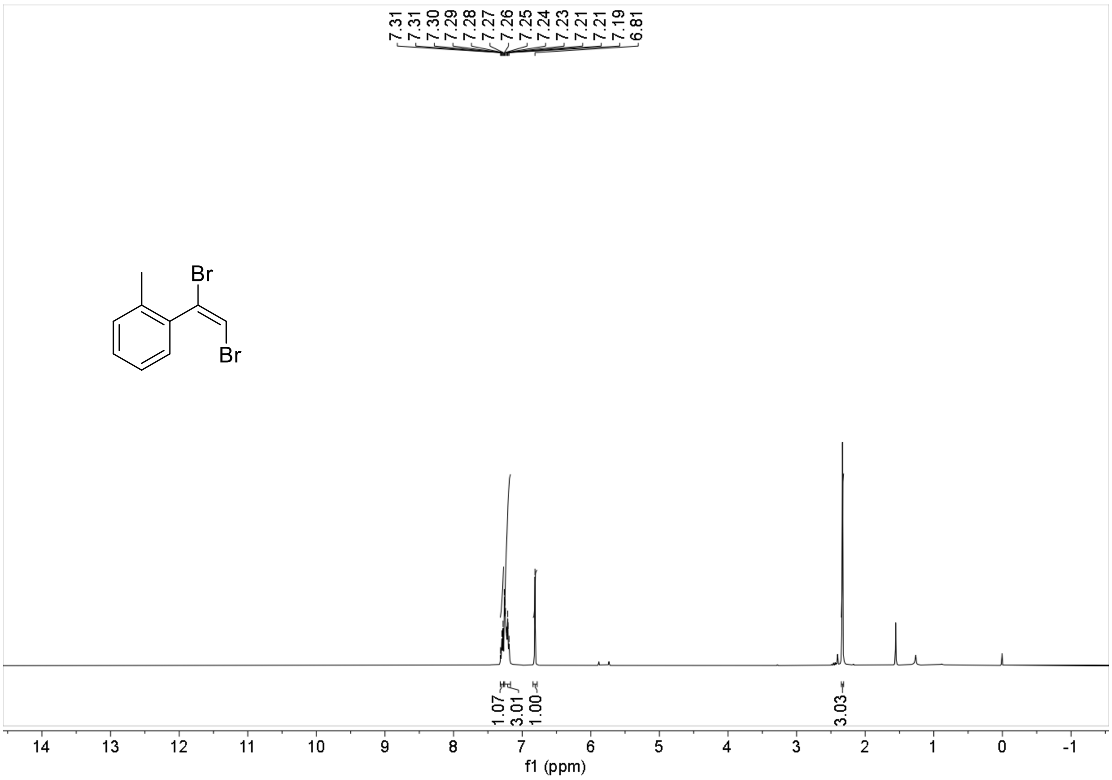
^{1}H NMR spectrum of compound **3k** (400 MHz, $CDCl_3$)



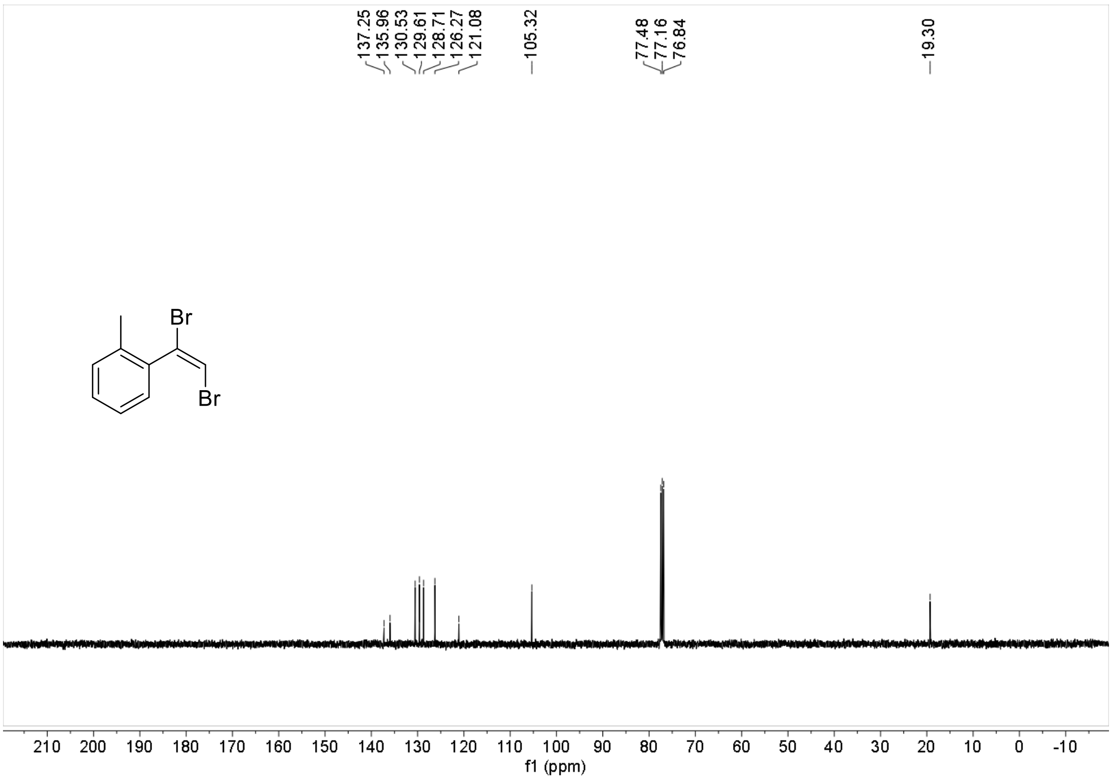
^{13}C NMR spectrum of compound **3k** (101 MHz, $CDCl_3$)



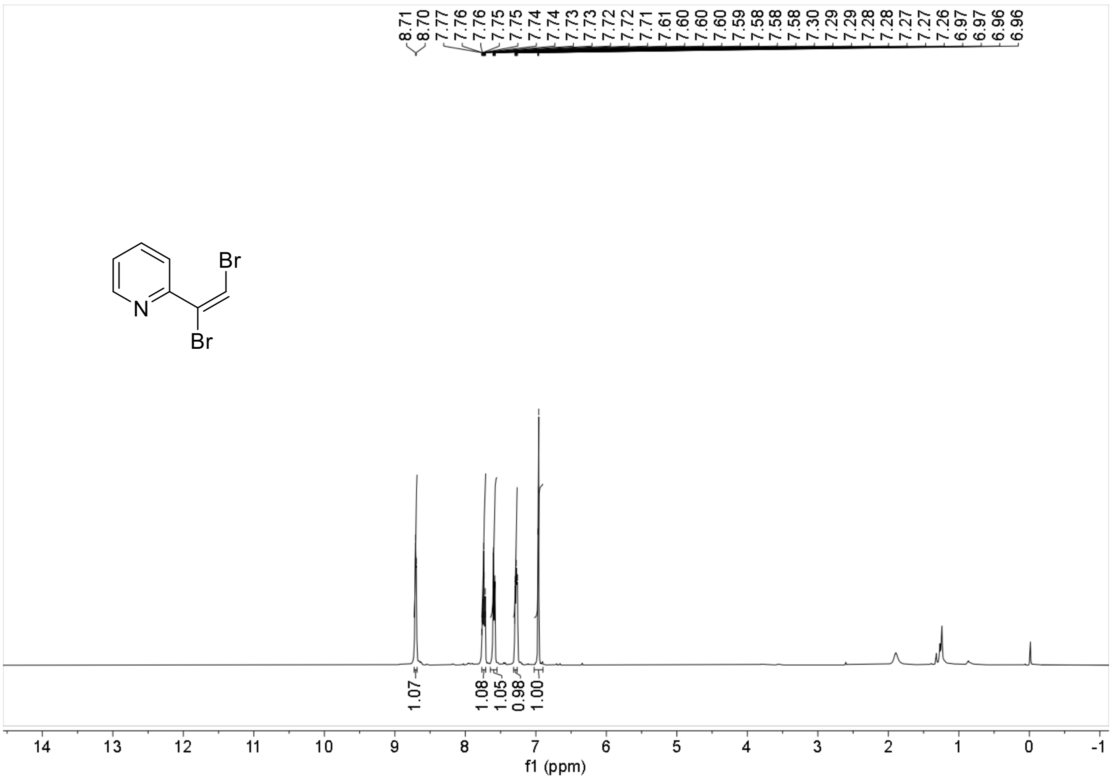
^{1}H NMR spectrum of compound **3l** (400 MHz, $CDCl_3$)



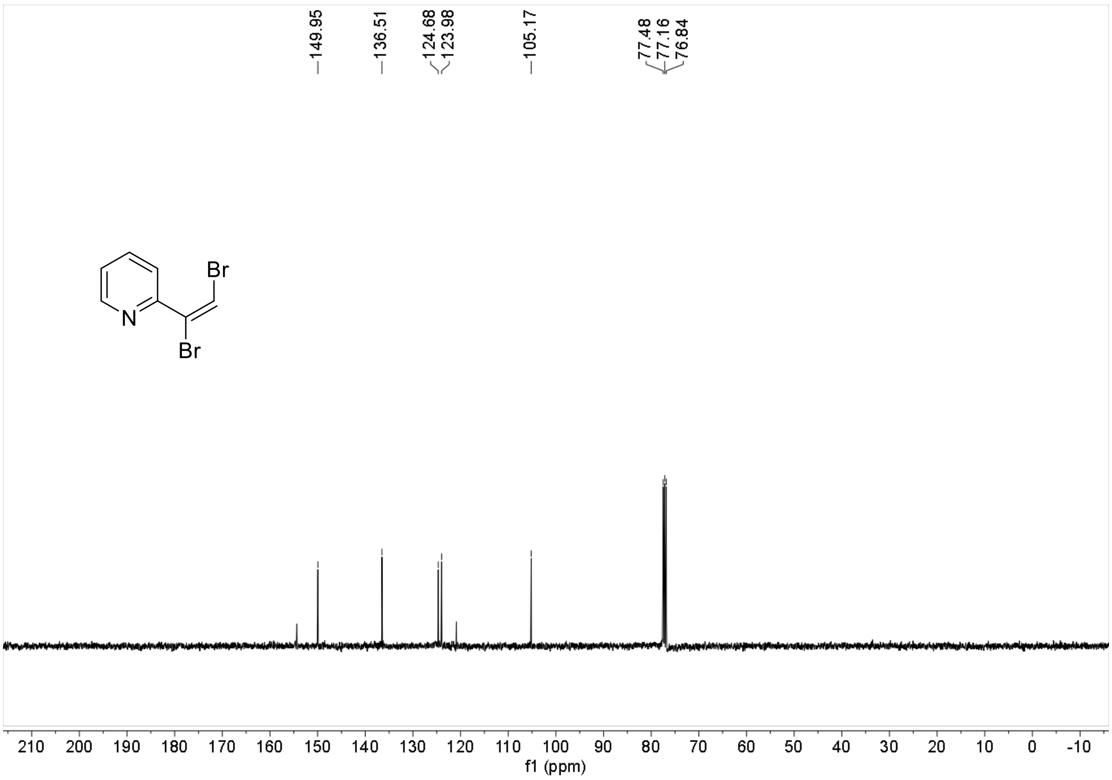
^{13}C NMR spectrum of compound **3l** (101 MHz, $CDCl_3$)



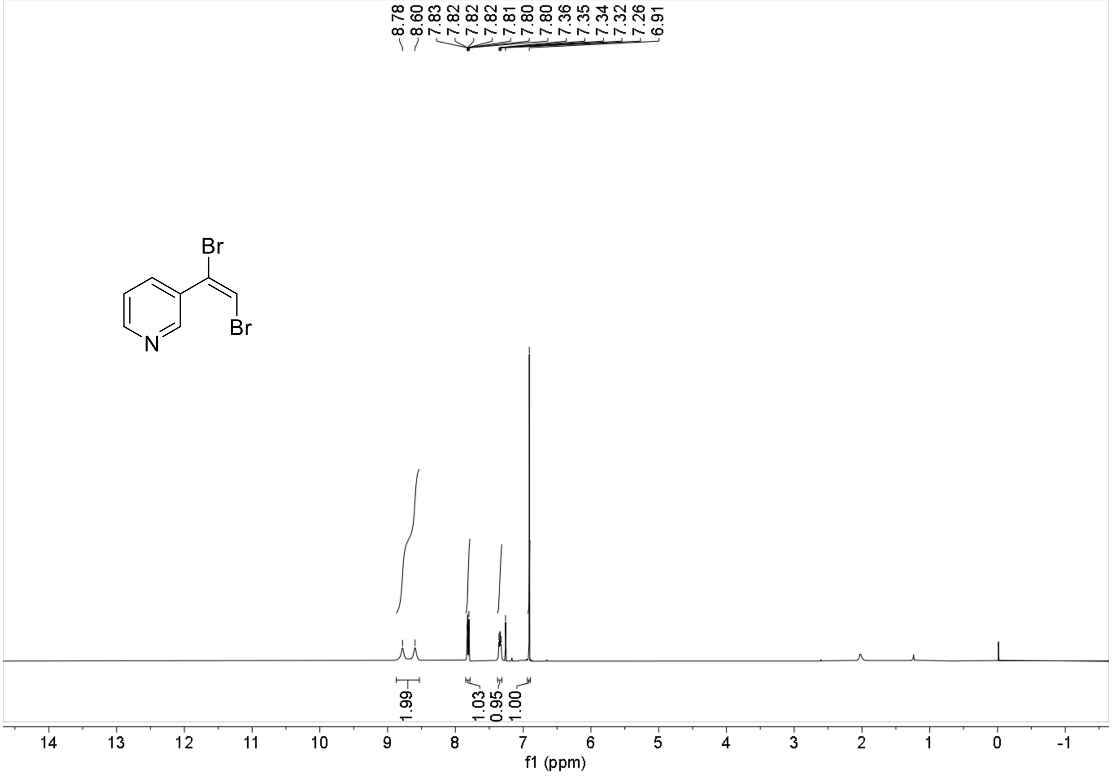
^{1}H NMR spectrum of compound **3m**(400 MHz, $CDCl_3$)



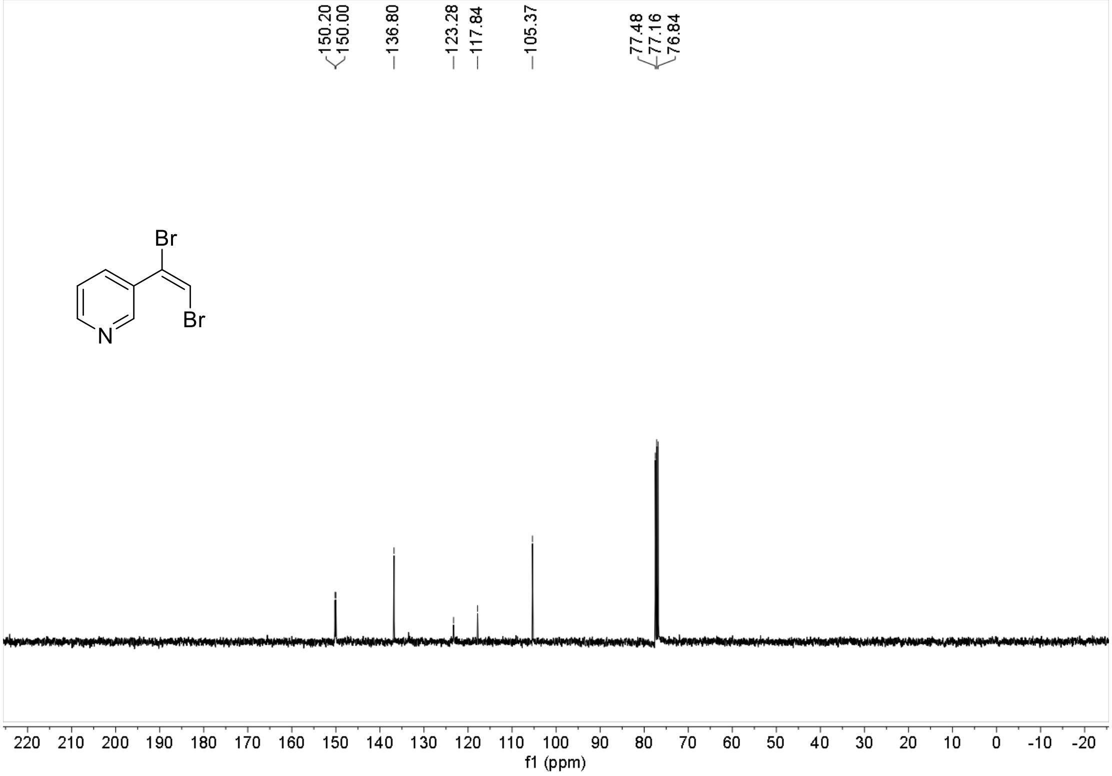
^{13}C NMR spectrum of compound **3m** (101 MHz, $CDCl_3$)



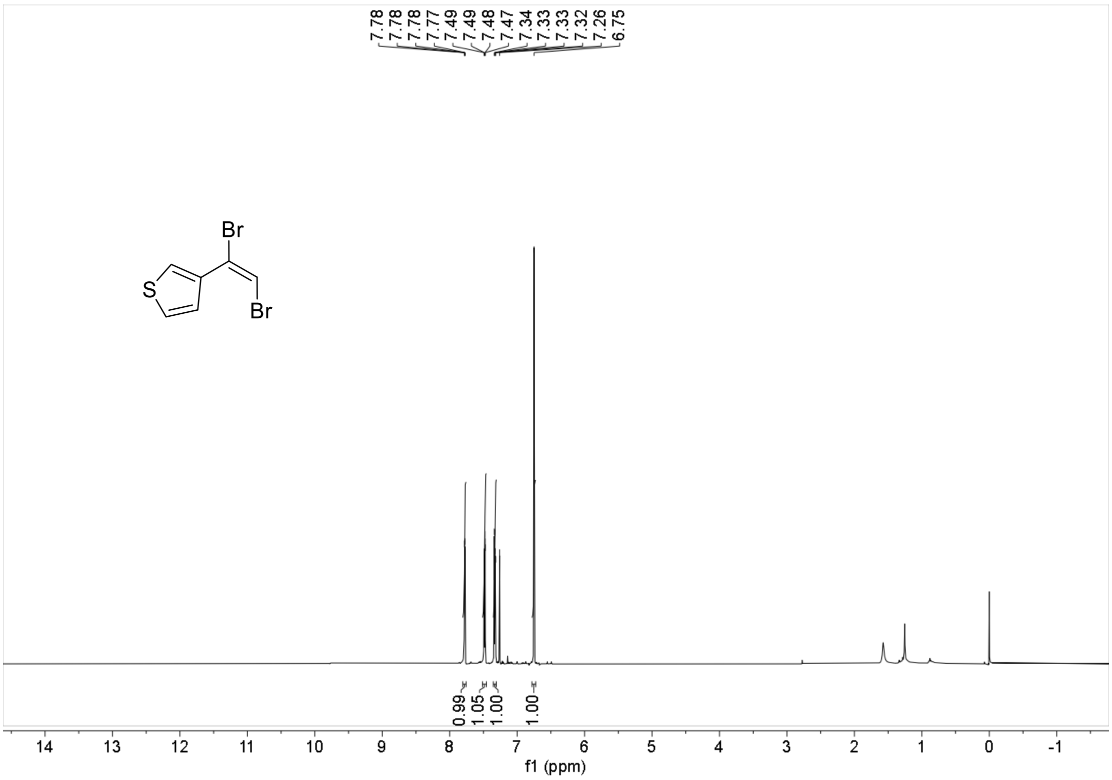
^{1}H NMR spectrum of compound **3n** (400 MHz, $CDCl_3$)



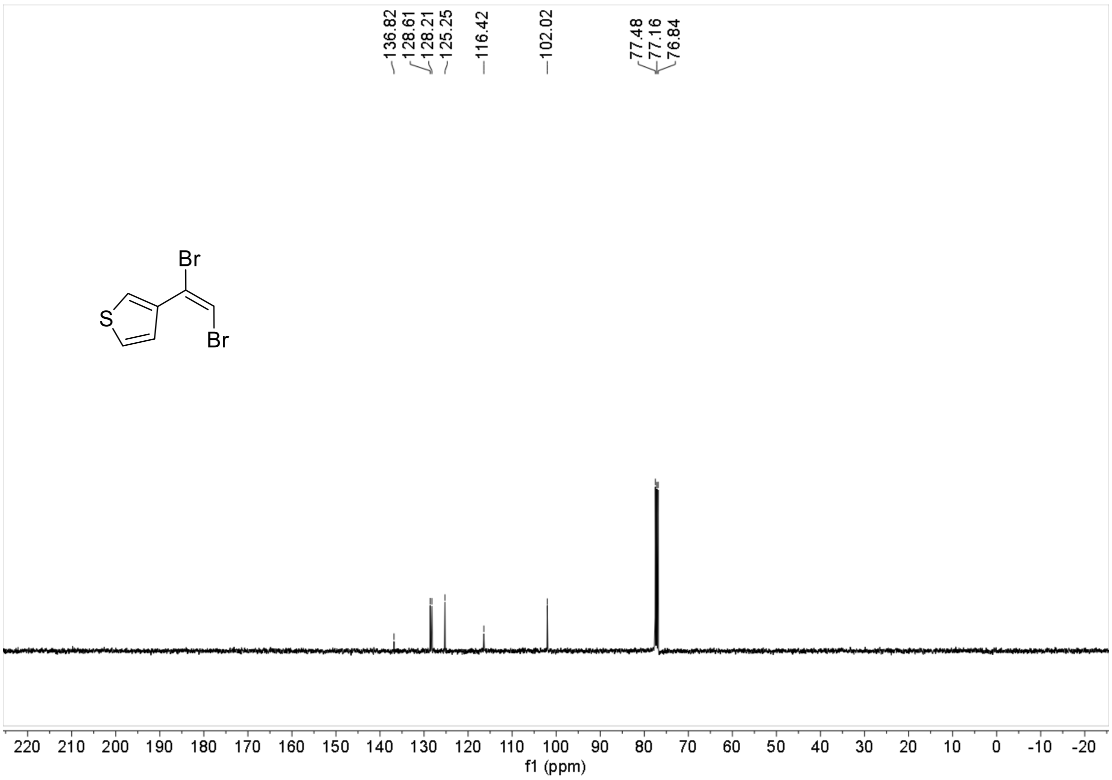
^{13}C NMR spectrum of compound **3n** (101 MHz, $CDCl_3$)



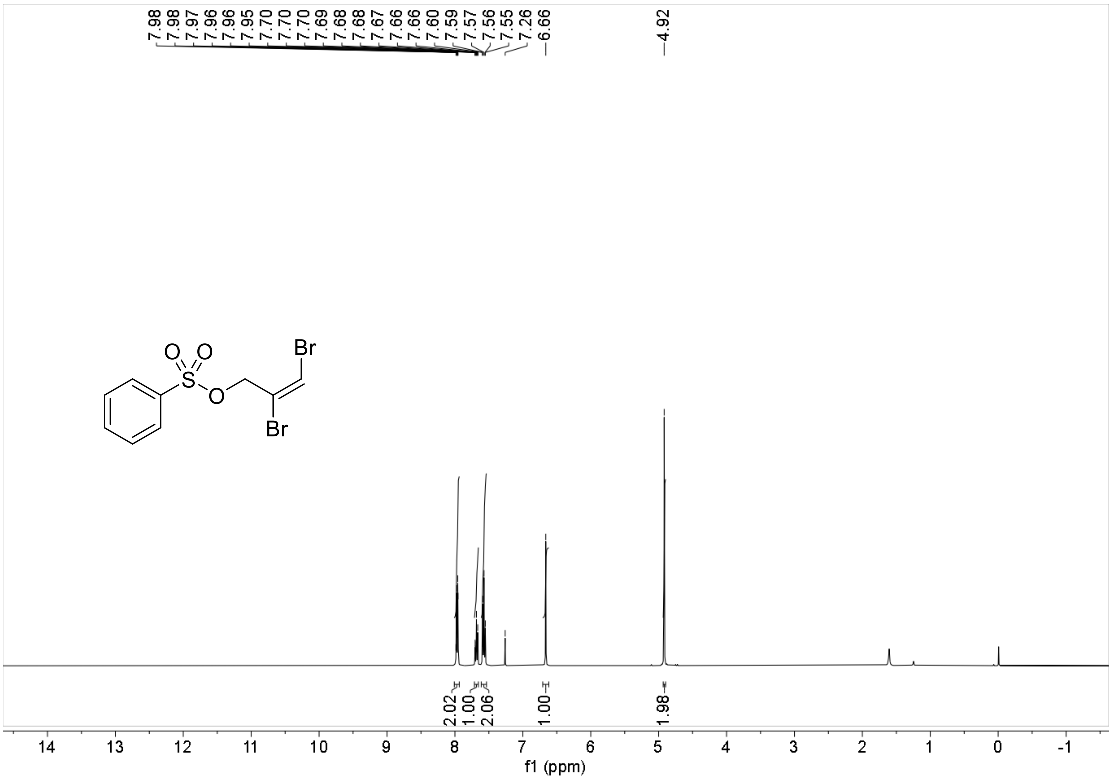
^{1}H NMR spectrum of compound **3o** (400 MHz, $CDCl_3$)



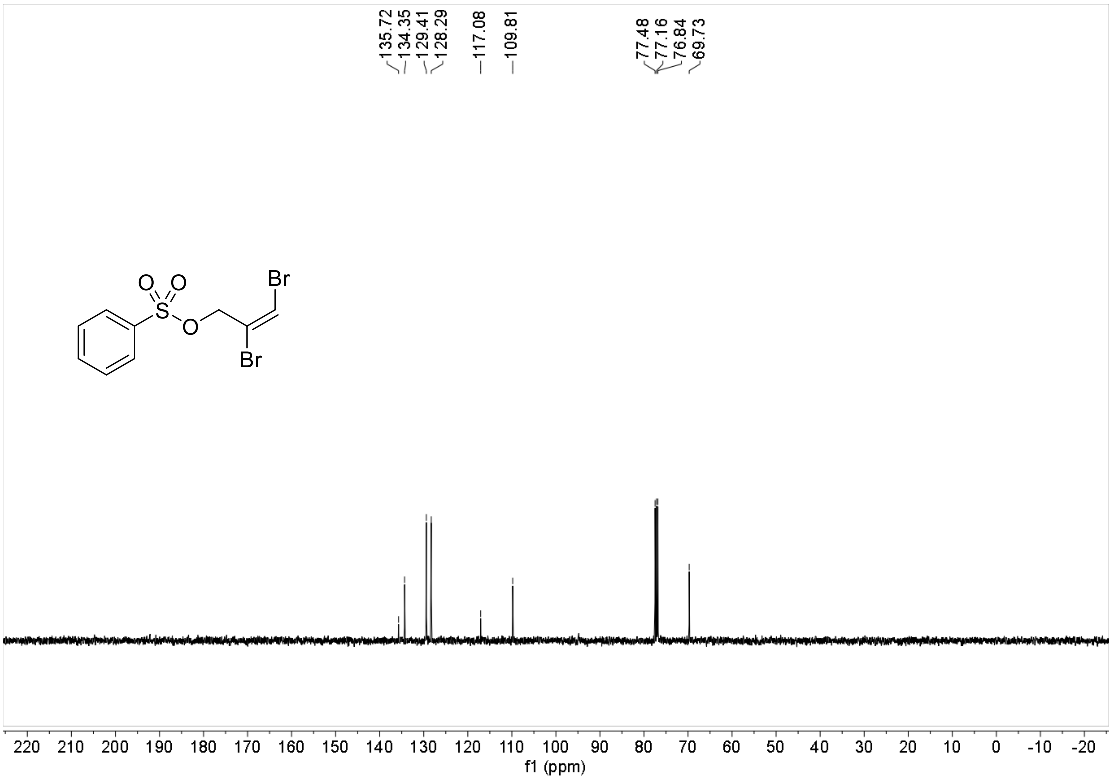
^{13}C NMR spectrum of compound **3o** (101 MHz, $CDCl_3$)



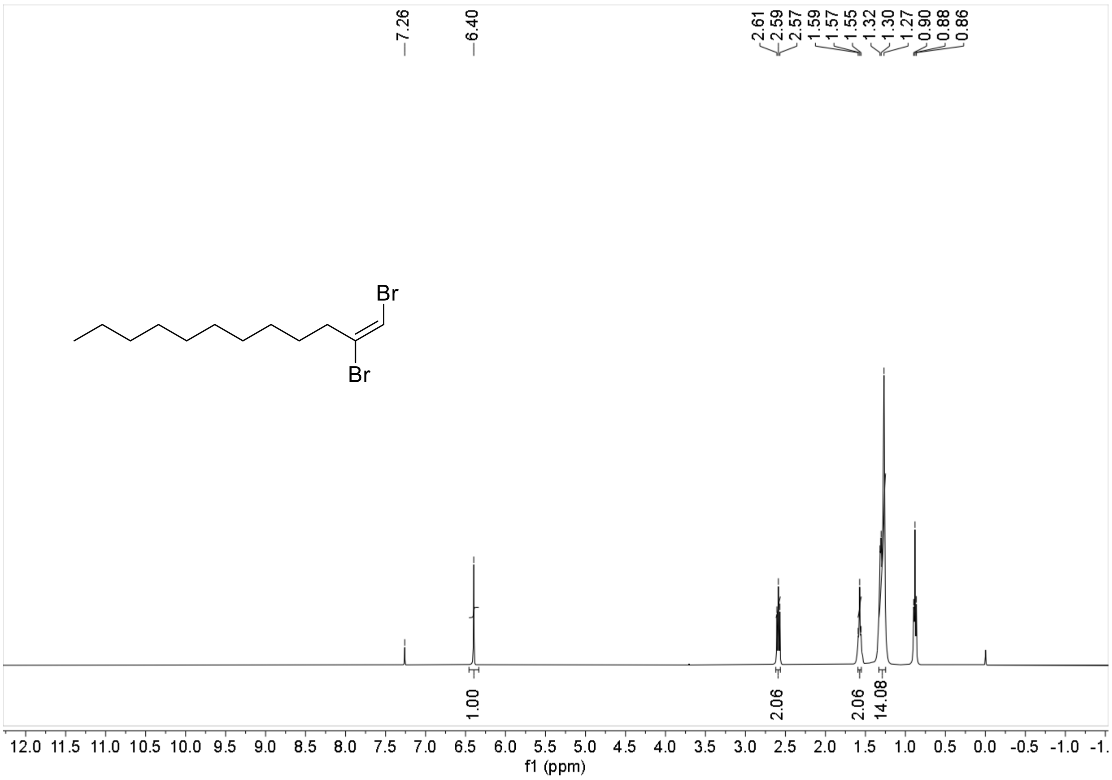
^{1}H NMR spectrum of compound **3p** (400 MHz, $CDCl_3$)



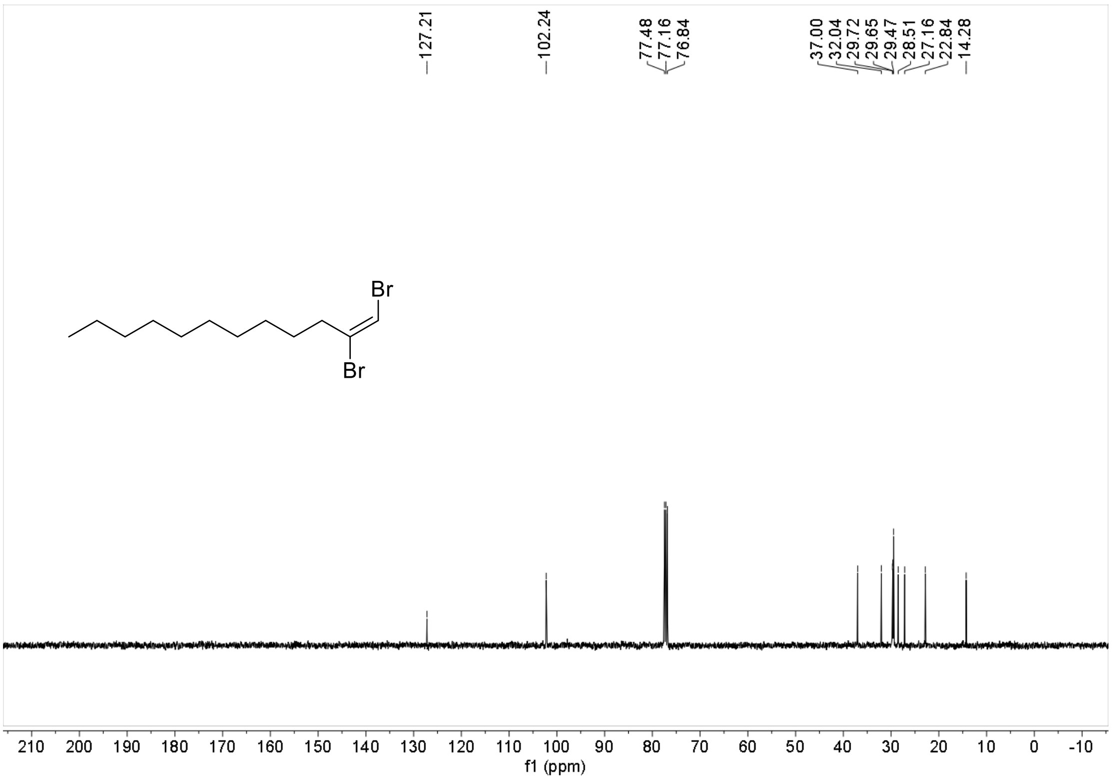
^{13}C NMR spectrum of compound **3p** (101 MHz, $CDCl_3$)



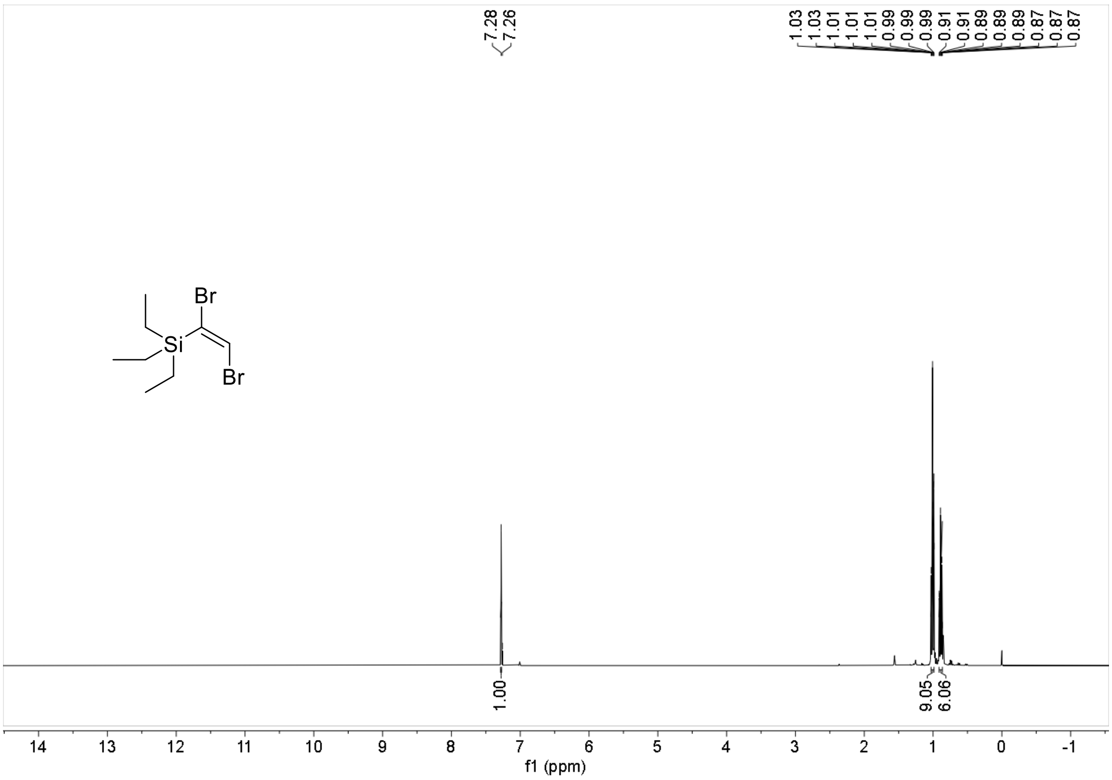
^{1}H NMR spectrum of compound **3q** (400 MHz, $CDCl_3$)



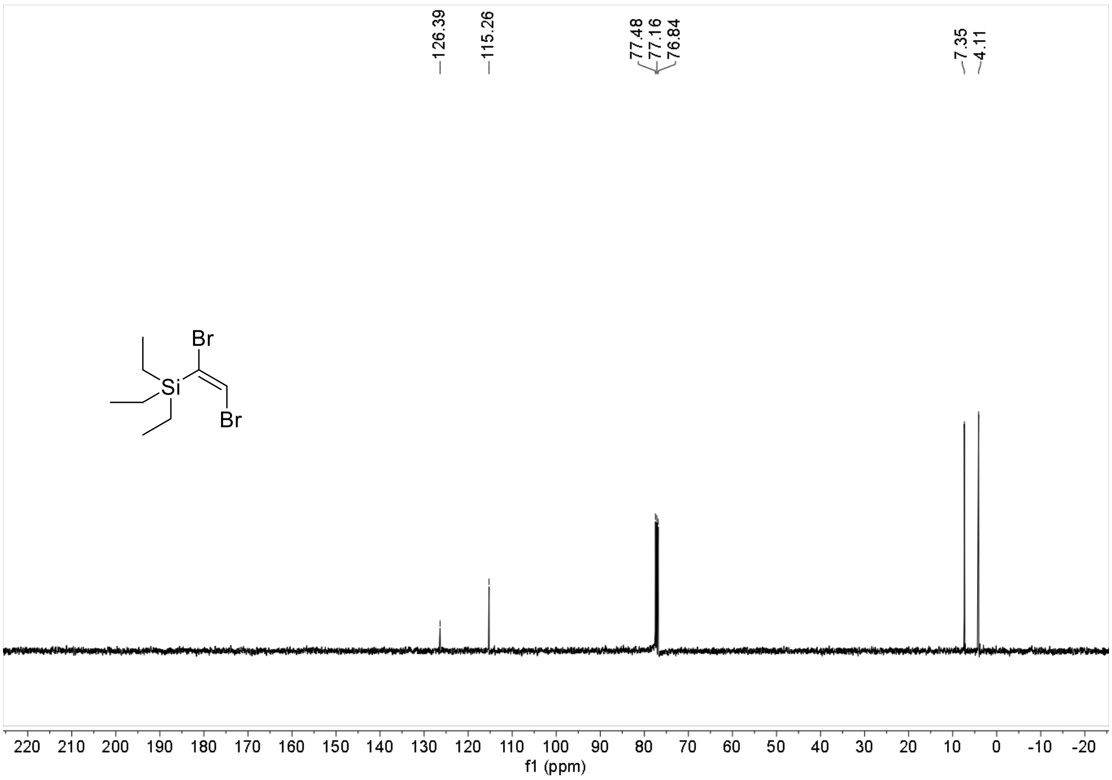
^{13}C NMR spectrum of compound **3q** (101 MHz, $CDCl_3$)



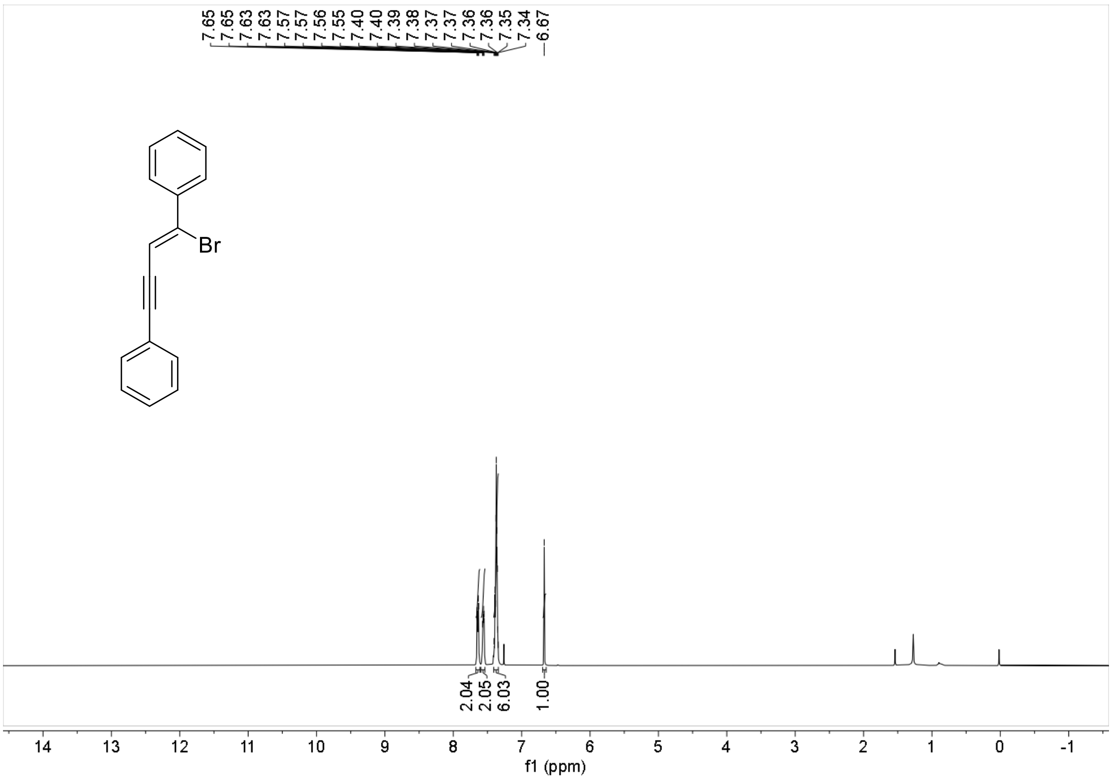
^{1}H NMR spectrum of compound **3r** (400 MHz, $CDCl_3$)



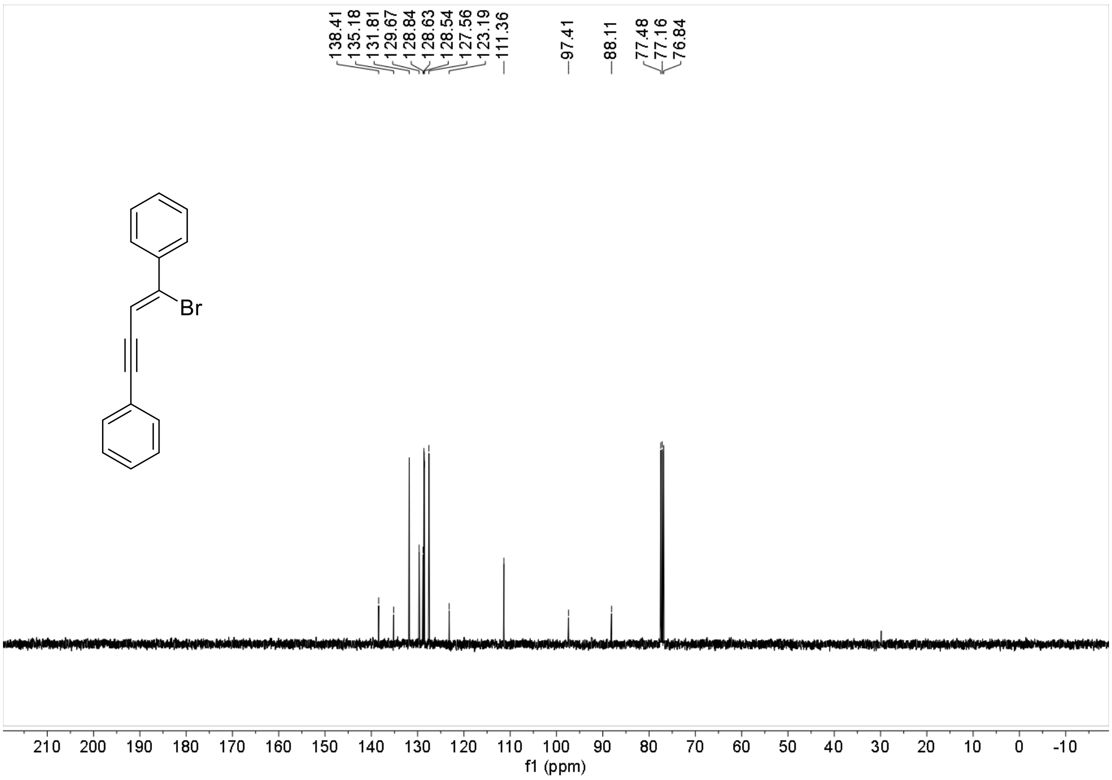
^{13}C NMR spectrum of compound **3r** (101 MHz, $CDCl_3$)



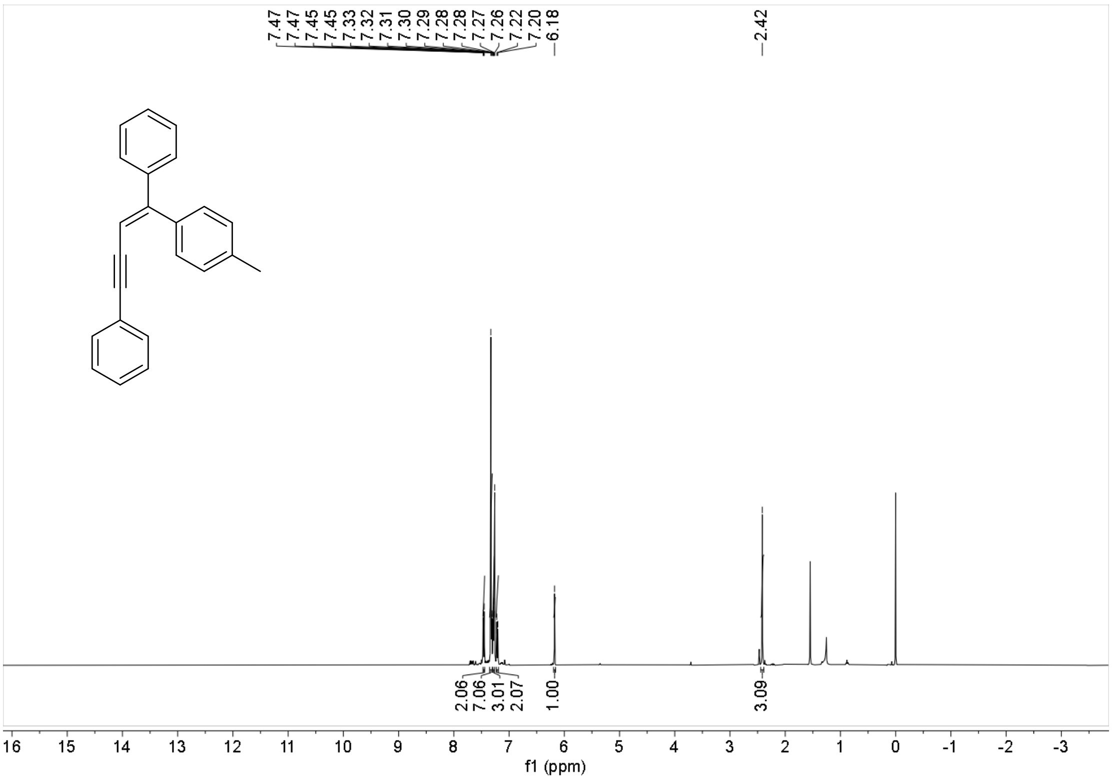
^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$)



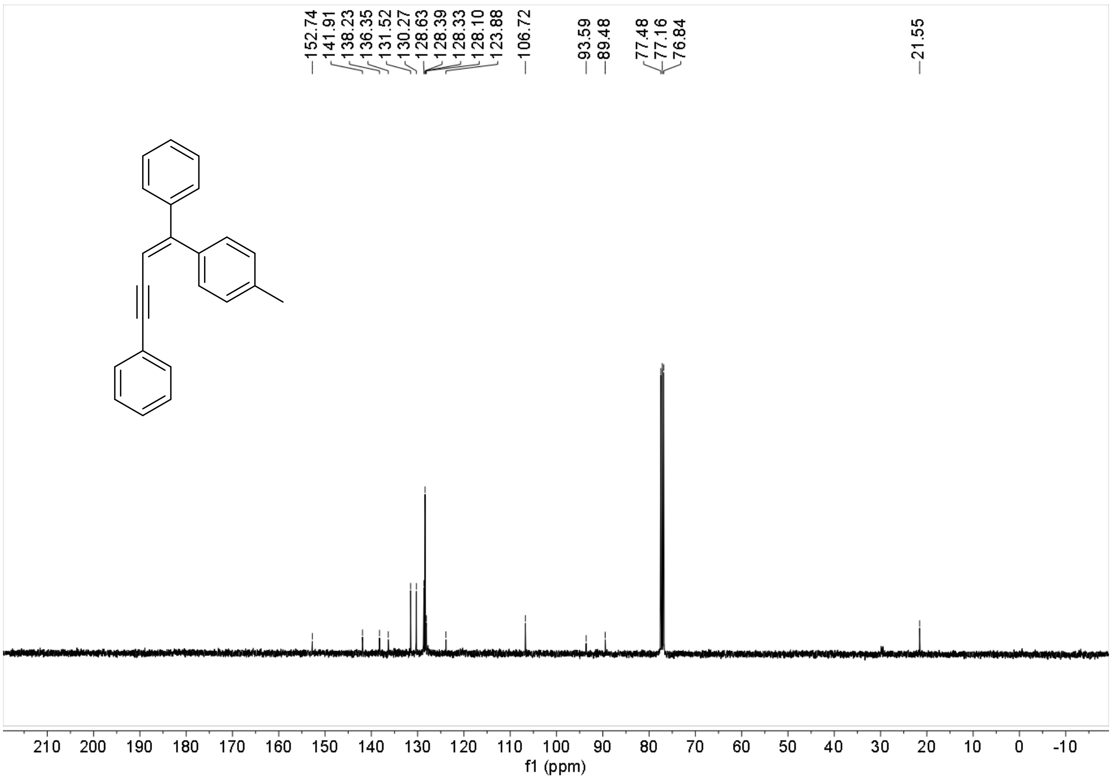
^{13}C NMR spectrum of compound **4** (101 MHz, $CDCl_3$)



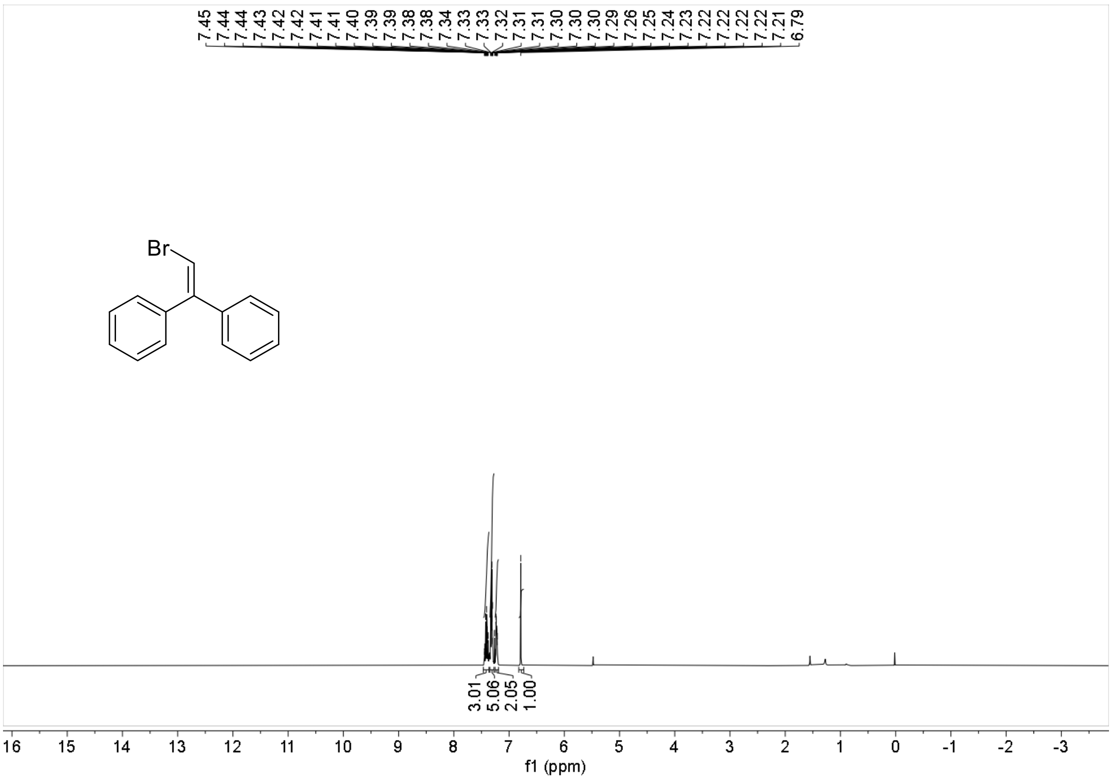
^{1}H NMR spectrum of compound **5** (400 MHz, CDCl$_3$)



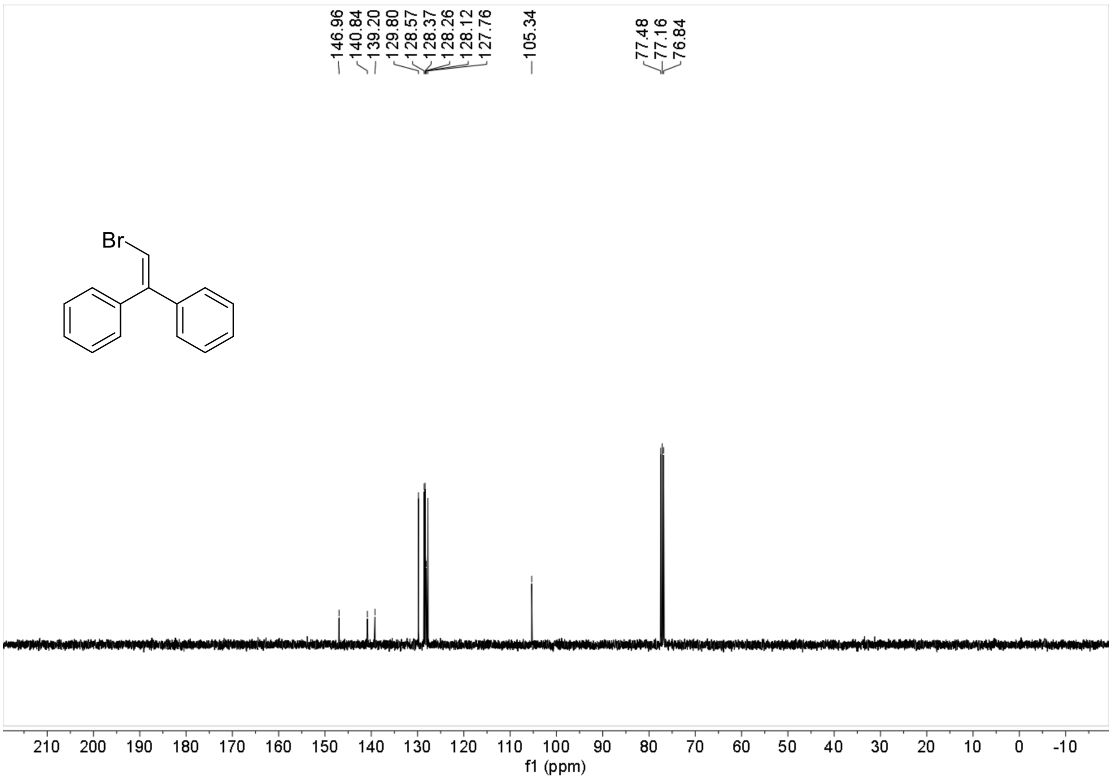
^{13}C NMR spectrum of compound **5** (101 MHz, CDCl$_3$)



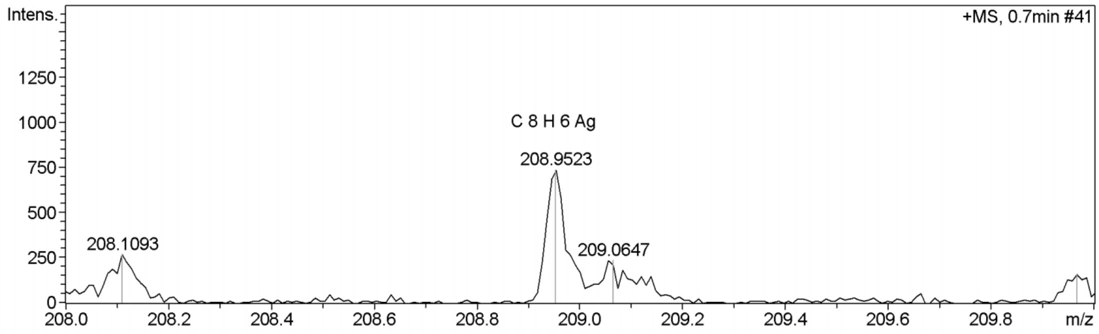
^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **6** (101 MHz, $CDCl_3$)

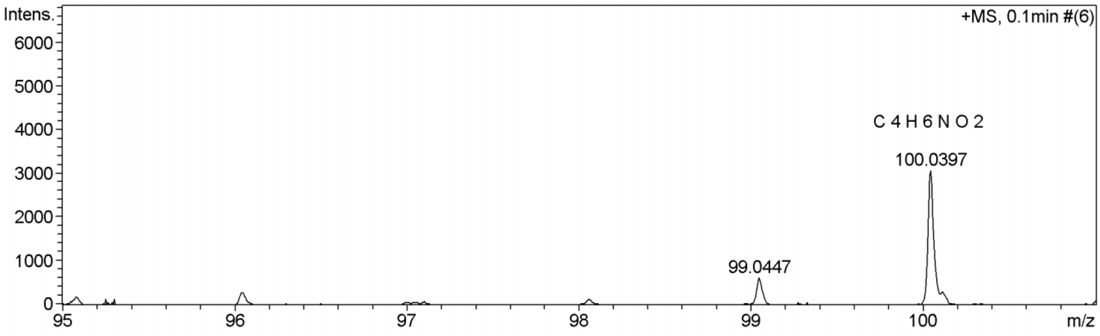


6 HRMS spectra



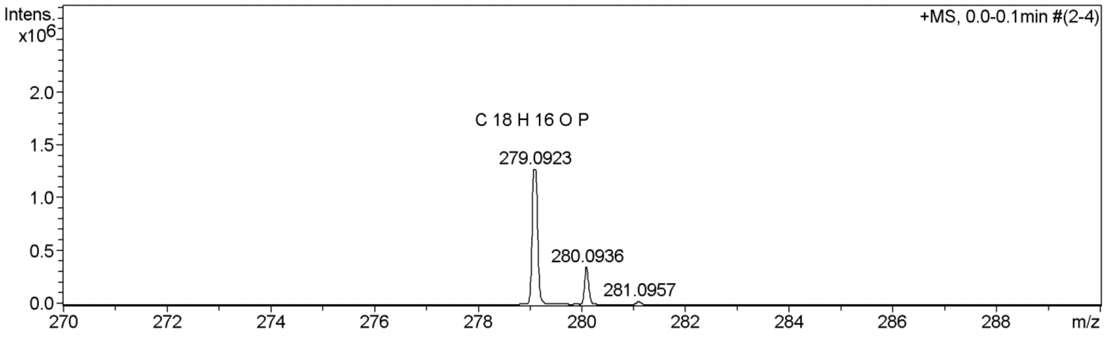
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
208.9523	1	C 8 H 6 Ag	100.00	208.9515	-0.8	-3.8	105.9	5.5	even	ok
	2	C 4 H 7 Ag N O 2	0.00	207.9522	-17.2	-82.9	767.1	1.5	even	ok
	3	C 3 H 5 Ag N 3 O	0.00	205.9478	0.0	0.0	795.9	2.5	even	ok

HRMS spectrum of compound **C**



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
100.0397	1	C 4 H 6 N O 2	100.00	100.0393	-0.4	-3.9	300.6	2.5	even	ok

HRMS spectrum of succinimide



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¡¥Conf	N-Rule
279.0923	1	C 18 H 16 O P	100.00	279.0933	1.0	3.8	47.3	11.5	even	ok
	2	C 13 H 16 N 2 O 3 P	9.14	279.0893	-3.0	-10.7	74.3	7.5	even	ok
	3	C 11 H 21 O 4 P 2	16.93	279.0910	-1.3	-4.7	91.1	2.5	even	ok
	4	C 10 H 22 N 2 O P 3	12.07	279.0939	1.7	6.0	93.4	2.5	even	ok

HRMS spectrum of compound triphenylphosphine oxide

7. X-Ray crystallographic data

The single crystal for compound **2l** were prepared from a mixture solvent of dichloromethane and petroleum ether (v/v = 1:2). The data were collected on a Bruker Smart APEXIICCD instrument using Ga-Kα radiation (λ = 1.34139Å) at 100 K. The crystal structures were solved and refined using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in the riding model and refined with isotropic thermal parameters. The crystallographic data have already been deposited at the Cambridge Crystallographic Data Centre. CCDC numbers: 2235710 (**2l**)

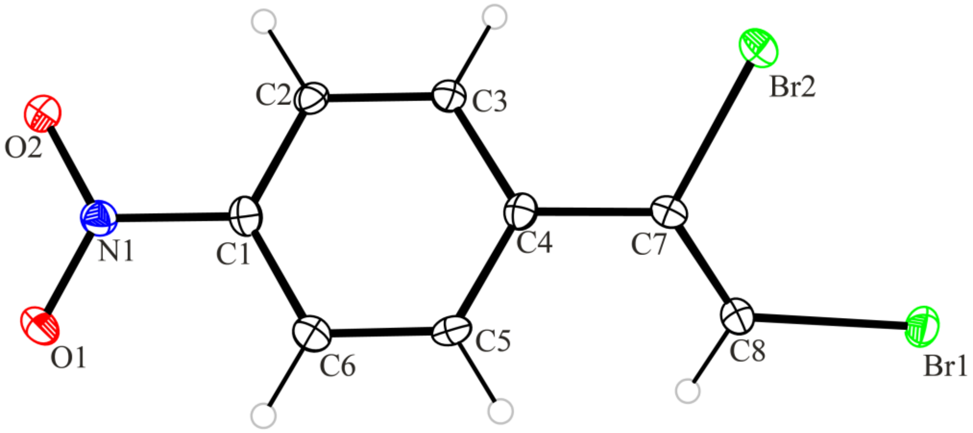


Figure S4 X-ray derived ORTEP of **2l** with thermal ellipsoids shown at the 30% probability level

Table S2. Crystal data and structure refinement for **2l**

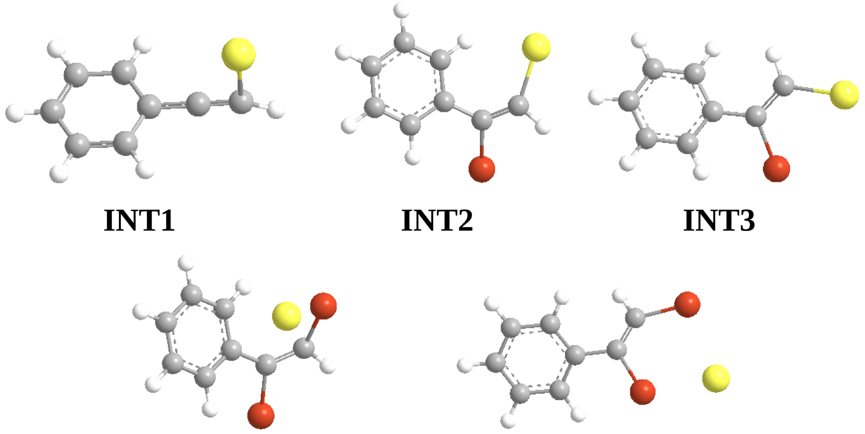
Identification code	**2l**
Empirical formula	C8H5Br2NO2

Formula weight	306.95
Temperature/K	100.0 K
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.4516(5)
b/Å	12.1323(7)
c/Å	9.7322(6)
α/°	90
β/°	110.762(2)
γ/°	90
Volume/Å3	933.11(10)
Z	4
ρcalcg/cm^3	2.185
μ/mm^{-1}	7.132
F(000)	584
Crystal size/mm^3	0.25 x 0.24 x 0.23
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	4.868 to 54.928
Index ranges	$-6 \le h \le 10$, $-13 \le k \le 14$, $-1 \le l \le 11$
Reflections collected	8511
Independent reflections	1774 [Rint = 0.0459, Rsigma = 0.0350]
Data/restraints/parameters	1774 / 0 / 118

Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	$R_1 = 0.0368$, $wR_2 = 0.0898$
Final R indexes [all data]	$R_1 = 0.0466$, $wR_2 = 0.0958$
Largest diff. peak/hole/ e Å^{-3}	0.823 / -1.023

8. computational details

Geometry optimization and free energy corrections were computed at density functional B3LYP/Def2-SVP level of theory with dispersion corrections.[8-12] Solvation effects in 1,4-dioxane were accounted by the implicit solvation model IEFPCM.[13] The electronic energies were further improved by single-point calculations on the aforementioned geometries at M06/Def2-TZVP level with dispersion corrections.[14, 15] Solvation model is SMD (solvent = 1,4-dioxane).[16] All computations were performed with G16 program.[17]


INT1 INT2 INT3

INT4 INT5

Figure S5. DFT optimized structures of key intermediates

Table S3. Single point energies *E* and free energies corrections Δ*G* (in hartree) for all optimized species at 298.15 K.

species	*E*	Δ*G*
INT1	-455.118830767	0.073927
INT2	-3029.15791737	0.072476

INT3	-3029.15893052	0.072792
INT4	-5603.28485943	0.074064
INT5	-5603.29562509	0.073926
2a	5456.44561561	0.076493
3a	-5456.44398289	0.076214

Table S4. Optimized Cartesian coordinates of the species.

15

INT1

C	3.84681400	0.20121800	-0.54780000
C	3.17143200	1.28282400	0.03196200
C	1.90385800	1.10127700	0.57420000
C	1.29895000	-0.17670000	0.52770500
C	1.98762500	-1.26495800	-0.05643500
C	3.25832900	-1.06912400	-0.58753700
H	4.84214200	0.35041900	-0.97160200
H	3.63929800	2.26848200	0.06109300
H	1.36816400	1.93234700	1.03576700
H	1.51732000	-2.24927400	-0.08206400
H	3.79529700	-1.90674100	-1.03590700
C	0.00590000	-0.36703700	1.07789000
C	-1.13140600	-0.52741700	1.54540400
H	-1.83504500	-0.78268800	2.32891400

Ag	-2.11438700	0.11291400	-0.35592600

16

INT2

C	2.04188100	-3.28611200	-0.01683500
C	0.74577400	-3.03066900	-0.48391200
C	0.24534000	-1.73609700	-0.46558600
C	1.03570500	-0.66039600	0.02223300
C	2.35340700	-0.93572900	0.46849200
C	2.84172800	-2.23391600	0.45722200
H	2.43624100	-4.30427600	-0.03384100
H	0.13913900	-3.84301700	-0.88793700
H	-0.73338000	-1.52803700	-0.90053100
H	2.96876500	-0.12279000	0.85516700
H	3.84945900	-2.43699100	0.82355800
C	0.49334300	0.68433700	0.10222300
C	-0.80683900	1.02561700	0.35512500
H	-1.01075600	2.02461600	0.76104500
Ag	-2.57157100	-0.07603500	0.04951600
Br	1.70035200	2.13776900	-0.15938500

16

INT3

C	-4.54243200	0.77355800	0.21992400
C	-4.00144700	-0.43128400	0.69798900
C	-2.64482300	-0.68400600	0.56711900
C	-1.79309200	0.26825100	-0.05102700
C	-2.35593300	1.49065100	-0.51770400
C	-3.71522500	1.73015200	-0.38775800
H	-5.61278900	0.96562800	0.32054900
H	-4.64773200	-1.16835200	1.17731000
H	-2.22318300	-1.61261500	0.95239800
H	-1.72599800	2.22360400	-1.02140500
H	-4.14253200	2.65830600	-0.77091200
C	-0.37091100	0.03087200	-0.20806000
C	0.59255200	1.00378100	-0.27907800
H	0.28858800	2.01880500	-0.56532300
Ag	2.61801300	0.68098400	0.18204200
Br	0.22871200	-1.77667000	-0.25420100

17

INT4

C	-3.88061200	1.41164700	-0.93445800

C	-2.62374300	1.94730800	-1.23992600
C	-1.46706200	1.31333700	-0.79865500
C	-1.54498600	0.11732500	-0.05055000
C	-2.81777500	-0.42464700	0.22796500
C	-3.97232100	0.22656900	-0.19952300
H	-4.78693100	1.91460400	-1.27789900
H	-2.54566700	2.86361200	-1.82800400
H	-0.49792600	1.74365900	-1.05101400
H	-2.90070300	-1.34960700	0.79843900
H	-4.94903300	-0.19839900	0.03886900
C	-0.33476800	-0.53587300	0.45494000
C	0.84219300	0.03899000	0.89798500
H	1.56968100	-0.58247700	1.42644300
Ag	1.82636500	-0.20599400	-1.20539600
Br	-0.39867900	-2.44308100	0.65136900
Br	1.05770400	1.89229200	1.30291900

17

INT5

C	-5.21031600	-0.03714000	-0.34285900
C	-4.64073800	1.09398300	0.24815300
C	-3.25723200	1.18394900	0.39945200

C	-2.42614700	0.14199500	-0.05569300
C	-3.00769500	-0.99935700	-0.63823200
C	-4.39124100	-1.08352400	-0.78113100
H	-6.29427800	-0.10874100	-0.45399800
H	-5.27647200	1.90588300	0.60708600
H	-2.81820600	2.05406100	0.89085600
H	-2.37557900	-1.81818900	-0.98621000
H	-4.83384000	-1.97088600	-1.23805900
C	-0.96391300	0.29191400	0.06167800
C	-0.32522100	1.44053600	-0.19788000
H	-0.87478900	2.29746700	-0.58942000
Br	1.51059200	1.85365300	0.02746500
Ag	2.47497200	-0.72262400	-0.30492000
Br	-0.03960700	-1.29909300	0.65653600

16

product-**2a**

C	-4.27229300	-0.70158300	0.07664800
C	-3.42043700	-1.61924600	-0.54402700
C	-2.04421100	-1.38948800	-0.57684900
C	-1.49541100	-0.23962600	0.02157500
C	-2.36326900	0.68391400	0.63157100

C	-3.73798500	0.45114900	0.66131300
H	-5.35011300	-0.87837700	0.09597000
H	-3.82954500	-2.51369800	-1.01949800
H	-1.38828800	-2.09458000	-1.09076500
H	-1.95233300	1.58598800	1.08753300
H	-4.39696600	1.17592700	1.14491200
C	-0.02873000	-0.03862400	0.02021900
C	0.83607700	-1.05129700	0.19340600
H	0.46847500	-2.05847400	0.39351700
Br	2.71314800	-0.94153300	0.14640800
Br	0.58989000	1.74759100	-0.24683100

16

product-**3a**

C	-2.38781000	2.82759200	0.00720200
C	-1.34779100	2.69884900	0.93181900
C	-0.56031700	1.54650500	0.94717500
C	-0.80689700	0.50609100	0.03513900
C	-1.86522800	0.63632000	-0.88066800
C	-2.64425300	1.79283000	-0.89844600
H	-3.00281300	3.73047200	-0.00402600
H	-1.14952300	3.49788100	1.64988400

H	0.24681900	1.44555900	1.67382300
H	-2.07350000	-0.17583700	-1.57973100
H	-3.45814800	1.88572300	-1.62113000
C	0.03621300	-0.70636900	0.04922800
C	1.37142100	-0.80310600	0.00922100
H	1.89501600	-1.75758600	0.05221600
Br	2.54122900	0.67590100	-0.18145400
Br	-0.91922600	-2.37928700	0.14216700

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