Electronic Supplementary Material (ESI) for Chemical Communications.

Dibrominated Addition and Substitution of Alkenes Catalyzed by $Mn_2(CO)_{10}$

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General Information

Unless stated otherwise, all reactions were carried out under air without N_2 protection. All solvents were directly used without any pretreatment. NMR spectras were recorded on a Bruker Avance III 400, or Ascend TM 500 spectrometer and were recorded in ppm (δ) downfield of TMS (δ = 0) in deuterated solvent. Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz. High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with ESI and APCI mode and Thermo Q Exactive GC spectrometer with EI mode unless otherwise stated. The mass spectra (MS) was obtained using a Shimadzu LCMS-2020 mass spectrometer with ESI mode.

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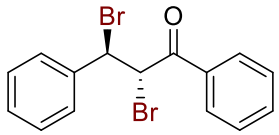
General procedure for the dibromination reaction with olefin.

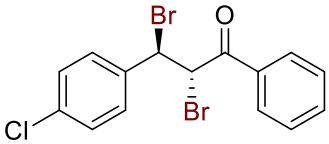
To a 25ml Schlenk tube was added olefin (**1a-1x, 3a-3k, and 5a-5h**) (0.2 mmol) and NBS (88.5 mg, 0.5 mmol) and $Mn_2(CO)_{10}$ (3.9mg, 0.05 eq), then 2 ml DCE was added. The mixture was stirred at 110℃ until the olefin was disappeared (monitored by TLC). Then the mixture was filtered through a Celite pad, evaporated the solvent for crude ^{1}H-NMR (confirmed the dr). The residue was purified by silica gel column chromatography PE/EA (100:1, v/v) to afford product (**2a-2w, 4a-4k, and 6a-6h**).

Characterization data of products.



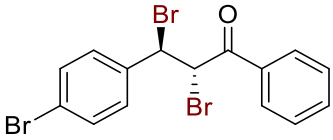
(*trans*)-2,3-dibromo-1,3-diphenylpropan-1-one **(Rac)-2a**[s1]

White solid, 91% yield, 18:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.05 (m, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.60 – 7.47 (m, 4H), 7.46 – 7.34 (m, 3H), 5.83 (d, *J* = 11.2 Hz, 1H), 5.65 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 138.3, 134.5, 134.2, 129.3, 129.0, 128.9, 128.9, 128.4, 49.8, 46.9.



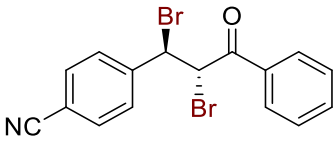
(*trans*)-2,3-dibromo-3-(4-chlorophenyl)-1-phenylpropan-1-one **(Rac)-2b**[s2]

White solid, 91% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.71 – 7.64 (m, 1H), 7.60 – 7.52 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 5.77 (d, *J* = 11.2 Hz, 1H), 5.62 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 136.9, 135.2, 134.3, 134.3, 129.7, 129.2, 129.0, 128.9, 48.7, 46.6.



(*trans*)-2,3-dibromo-3-(4-bromophenyl)-1-phenylpropan-1-one **(Rac)-2c**[s8]

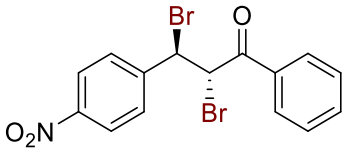
White solid, 93% yield, >20:1 dr, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 4H), 7.40 (d, *J* = 8.5 Hz, 2H), 5.76 (d, *J* = 11.5 Hz, 1H), 5.60 (d, *J* = 11.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.9, 137.4, 134.3, 134.3, 132.1, 123.0, 129.0, 128.9, 123.3, 48.7, 46.5. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{15}H_{11}OBr_3Na$: 466.8252. Found: 466.8233.



4-((*trans*)-1,2-dibromo-3-oxo-3-phenylpropyl)benzonitrile **(Rac)-2d**[s3]

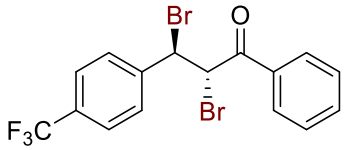
White solid, 95% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 5.75 (d, *J* = 11.2 Hz, 1H), 5.64 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 143.3, 134.5, 134.1, 132.7, 129.2, 129.1, 128.9, 118.2, 113.1, 47.7, 45.9. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{16}H_{11}Br_2NO$:

413.9100. Found: 413.9119.



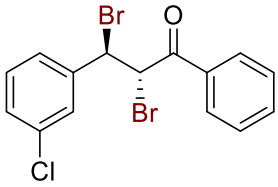
(*trans*)-2,3-dibromo-3-(4-nitrophenyl)-1-phenylpropan-1-one **(Rac)-2e**[s3]

White solid, 92% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.70 (dd, *J* = 10.8, 8.0 Hz, 3H), 7.57 (t, *J* = 7.6 Hz, 2H), 5.78 (d, *J* = 11.2 Hz, 1H), 5.70 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 148.4, 145.2, 134.5, 134.0, 129.5, 129.1, 129.0, 124.2, 47.2, 45.9.



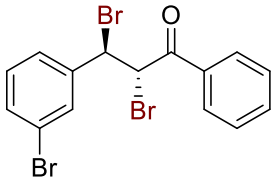
(*trans*)-2,3-dibromo-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one **(Rac)-2f**

White solid, 80% yield, 17:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.69 (m, 5H), 7.59 (t, *J* = 7.6 Hz, 2H), 5.82 (d, *J* = 11.2 Hz, 1H), 5.69 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 142.2, 134.4, 134.2, 131.3 (d, *J* = 32.7 Hz), 129.1, 128.9, 128.9, 125.9 (q, *J* = 3.5 Hz), 123.8 (q, *J* = 272.3 Hz), 48.1, 46.3. ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.75. HRMS (EI) m/z $[M-Br]^+$: Calcd for $C_{16}H_{11}OBrF_3$: 354.9939. Found: 354.9938.



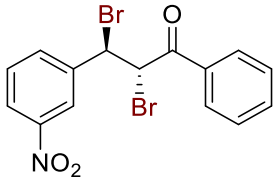
(*trans*)-2,3-dibromo-3-(3-chlorophenyl)-1-phenylpropan-1-one **(Rac)-2g**

White solid, 84% yield, 14:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.55 (m, 3H), 7.39 (m, 3H), 5.76 (d, *J* = 11.2 Hz, 1H), 5.59 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 140.2, 134.7, 134.3, 134.3, 130.1, 129.5, 129.1, 129.0, 128.5, 126.7, 48.4, 46.5. HRMS (ESI) m/z $[M+Na]^+$: Calcd for: $C_{15}H_{11}Br_2ClONa$ 422.8757. Found: 422.8757.



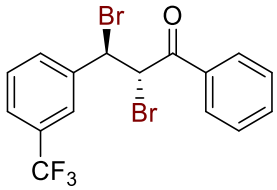
(*trans*)-2,3-dibromo-3-(3-bromophenyl)-1-phenylpropan-1-one **(Rac)-2h**

White solid, 91% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.68 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.42 (m, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 5.75 (d, *J* = 11.2 Hz, 1H), 5.57 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 140.5, 134.3, 134.2, 132.4, 131.4, 130.4, 129.1, 129.0, 127.2, 122.8, 48.4, 46.5. HRMS (ESI) m/z $[M+Na]^+$: Calcd for: $C_{15}H_{11}OBr_3Na$ 466.8252. Found: 466.8234.



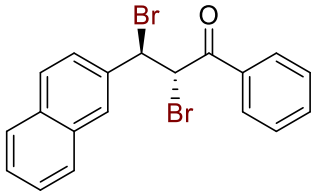
(*trans*)-2,3-dibromo-3-(3-nitrophenyl)-1-phenylpropan-1-one **(Rac)-2i**[s4]

White solid, 97% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 6.8 Hz, 1H), 7.60 (dt, *J* = 18.4, 7.6 Hz, 3H), 5.81 (d, *J* = 11.2 Hz, 1H), 5.72 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 148.5, 140.6, 134.5, 134.5, 134.1, 129.9, 129.1, 129.0, 124.1, 123.4, 47.5, 46.2. HRMS (ESI) m/z $[M+Na]^+$: Calcd for: $C_{15}H_{11}NO_3Br_2Na$ 433.8998. Found: 433.9007.



(*trans*)-2,3-dibromo-1-phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one **(Rac)-2j**

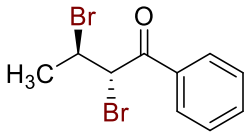
White solid, 85% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.81 (s, 1H), 7.76 – 7.65 (m, 3H), 7.59 (t, *J* = 7.6 Hz, 3H), 5.82 (d, *J* = 11.2 Hz, 1H), 5.70 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 139.4, 134.4, 134.2, 131.4 (d, *J* = 32.9 Hz), 131.5, 129.5, 129.1, 129.0, 126.1 (q, *J* =7.6 Hz), 125.2 (q, *J* = 7.6, Hz), 123.7 (d, *J* = 272.7 Hz). 48.3, 46.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.64. HRMS (EI) m/z $[M-Br]^+$: Calcd for $C_{16}H_{11}OBrF_3$: 354.9939. Found: 354.9940.



(*trans*)-2,3-dibromo-3-(naphthalen-2-yl)-1-phenylpropan-1-one **(Rac)-2k**[s5]

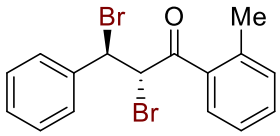
White solid, 83% yield, 8:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.09 (m, 2H), 7.96 (d, *J* = 1.2 Hz,

1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.71 – 7.62 (m, 2H), 7.55 (m , 4H), 5.96 (d, *J* = 11.2 Hz, 1H), 5.85 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 135.3, 134.5, 134.3, 133.6, 132.9, 129.1, 129.1, 129.0, 128.3, 128.2, 127.8, 127.1, 126.8, 124.9, 50.4, 46.7. HRMS (ESI) m/z $[M+Na]^+$: Calcd for: $C_{19}H_{14}Br_2ONa$ 438.9304. Found: 438.9306.



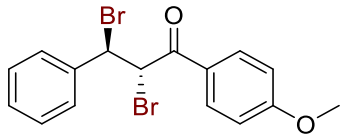
(*trans*)-2,3-dibromo-1-phenylbutan-1-one **(Rac)-2l**[s6]

Colorless oil, 83% yield, 8:1 dr, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 5.38 (d, *J* = 10.5 Hz, 1H), 4.75 (dq, *J* = 10.5, 6.5 Hz, 1H), 2.03 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.4, 134.3, 134.1, 129.0, 128.9, 49.4, 44.9, 24.4.



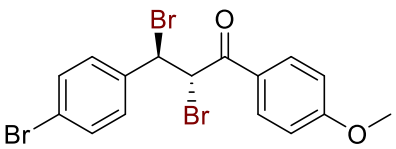
(*trans*)-2,3-dibromo-3-phenyl-1-(*o*-tolyl)propan-1-one **(Rac)-2m**[s7]

White solid, 81% yield, 17:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.30 (m, 8H), 5.68 (d, *J* = 11.2 Hz, 1H), 5.60 (d, *J* = 11.2 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.73, 138.92, 137.08, 134.56, 131.40, 131.12, 128.29, 127.85, 127.32, 127.14, 124.76, 49.25, 48.96, 19.90. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{16}H_{14}Br_2ONa$: 402.9304. Found: 402.9311.



(*trans*)-2,3-dibromo-1-(4-methoxyphenyl)-3-phenylpropan-1-one **(Rac)-2n**[s2]

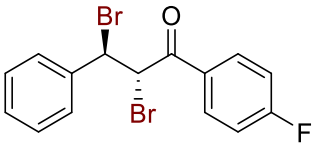
White solid, 85% yield, 15:1 dr, (5 mmol scale: 84% yield, 12:1 dr) ^{1}H NMR (400 MHz, CDCl3) δ 8.09 (d, J = 8.8 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.47 – 7.32 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.80 (d, *J* = 12.0 Hz, 1H), 5.65 (d, *J* = 12.0 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 164.5, 138.5, 131.4, 129.3, 128.9, 128.4, 127.2, 114.3, 55.7, 50.0, 46.8.



(*trans*)-2,3-dibromo-3-(4-bromophenyl)-1-(4-methoxyphenyl)propan-1-one **(Rac)-2o**

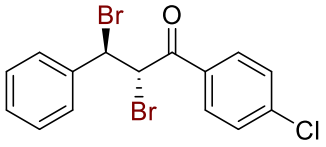
White solid, 87% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* =

8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.73 (d, *J* = 11.2 Hz, 1H), 5.60 (d, *J* = 11.2 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.33, 164.53, 137.57, 132.06, 131.38, 130.00, 127.08, 123.24, 114.32, 77.33, 77.02, 76.70, 55.66, 48.95, 46.45. HRMS (APCI) m/z $[M+H]^+$: Calcd for $C_{16}H_{14}Br_3O_2$: 474.8538 Found: 474.8532.



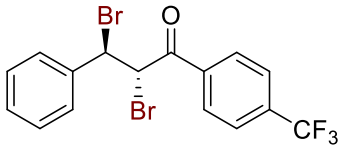
(*trans*)-2,3-dibromo-1-(4-fluorophenyl)-3-phenylpropan-1-one **(Rac)-2p**[s8]

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.44 (dd, *J* = 11.0, 4.5Hz, 2H), 7.39 (ddd, *J* = 7.0, 3.5, 1.0 Hz, 1H), 7.26 – 7.19 (m, 2H), 5.78 (dd, *J* = 11.0, 2.0 Hz, 1H), 5.63 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 166.4 (d, *J* = 257.2 Hz), 138.1, 131.7 (d, *J* = 9.6 Hz), 130.8 (d, *J* = 3.0 Hz), 129.4, 128.9, 128.4,116.3 (d, *J* = 22.1 Hz), 49.7, 46.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -102.76.



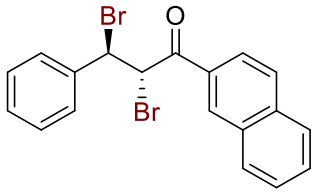
(*trans*)-2,3-dibromo-1-(4-chlorophenyl)-3-phenylpropan-1-one **(Rac)-2q**[s2]

White solid, 92% yield, >20:1 dr, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.52 (dd, *J* = 8.0, 4.0 Hz, 4H), 7.48 – 7.32 (m, 3H), 5.76 (d, *J* = 11.0 Hz, 1H), 5.63 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 140.8, 138.0, 132.7, 130.3, 129.4, 128.9, 128.3, 49.7, 46.8.



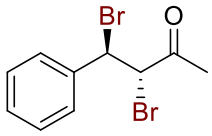
(*trans*)-2,3-dibromo-3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one **(Rac)-2r**

White solid, 86% yield, 15:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.49 (m, 2H), 7.48 – 7.36 (m, 3H), 5.79 (d, *J* = 11.2 Hz, 1H), 5.63 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 137.8, 137.2, 135.3 (q, *J* = 32.6 Hz), 129.5, 129.3, 129.0, 128.3, 126.1 (q, *J* = 3.5 Hz), 123.4 (q, *J* = 272.9 Hz), 49.5, 46.9. ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.25. HRMS (EI) m/z $[M-Br]^+$: Calcd for $C_{16}H_{11}OBrF_3$: 354.9939. Found: 354.9938.



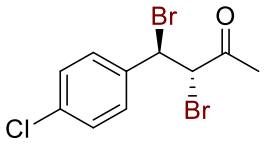
(*trans*)-2,3-dibromo-1-(naphthalen-2-yl)-3-phenylpropan-1-one **(Rac)-2s**[s9]

White solid, 83% yield, 10:1 dr, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.60 (dd, *J* = 15.2, 7.2 Hz, 3H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 6.00 (d, *J* = 11.2 Hz, 1H), 5.71 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 138.3, 136.1, 132.5, 131.8, 130.8, 129.9, 129.4, 129.2, 129.1, 128.9, 128.5, 127.9, 127.2, 124.2, 50.0, 47.0.



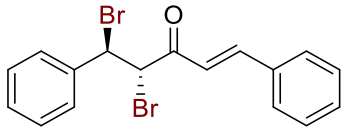
(*trans*)-3,4-dibromo-4-phenylbutan-2-one **(Rac)-2t**[s1]

White solid, 92% yield, >20:1 dr, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 5H), 5.32 (d, *J* = 11.5 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 137.8, 129.4, 128.9, 128.1, 52.8, 49.5, 27.0.



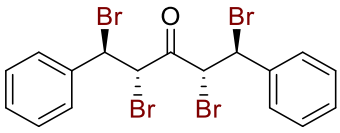
(*trans*)-3,4-dibromo-4-(4-chlorophenyl)butan-2-one **(Rac)-2u**[s16]

White solid, 94% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 5.29 (d, *J* = 11.2 Hz, 1H), 4.87 (d, *J* = 11.2 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 136.4, 135.2, 129.5, 129.2, 52.4, 48.4, 27.2.



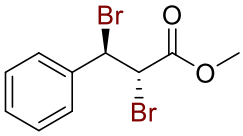
(*trans*,*E*)-4,5-dibromo-1,5-diphenylpent-1-en-3-one **(Rac)-2v**[s10]

White solid, 85% yield, >20:1 dr, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.5Hz, 1H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.50 – 7.35 (m, 9H), 6.98 (d, *J* = 15.5 Hz, 1H), 5.50 (d, *J* = 11.5 Hz, 1H),5.23 (d, *J* = 11.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.9, 146.1, 138.2, 134.0, 131.3, 129.3, 129.1, 128.9, 128.8, 128.3, 122.1, 51.6, 49.5. HRMS (ESI) m/z $[M+Na]^+$: Calcd for: $C_{17}H_{14}OBr_2Na$ 414.9304. Found: 414.9302.



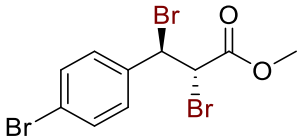
(*trans*,*trans*)-1,2,4,5-tetrabromo-1,5-diphenylpentan-3-one **(Rac)-2w**

White solid, 83% yield, >20:1 dr,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.36 (m, 10H), 5.52 (d, *J* = 11.2 Hz, 2H), 5.40 (d, *J* = 11.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 138.3, 129.3, 128.9, 128.2, 50.2, 47.4. HRMS (ESI) m/z $[M+Na]^+$: Calcd for: $C_{17}H_{14}OBr_4Na$ 572.7670. Found: 572.7659.



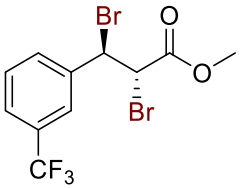
methyl (*trans*)-2,3-dibromo-3-phenylpropanoate **(Rac)-4a**[s1]

White solid, 89% yield, 17:1 dr, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.30 (m, 5H), 5.34 (d, *J* = 11.5 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 137.6, 129.4, 128.9, 128.1, 53.5, 50.6, 46.7.



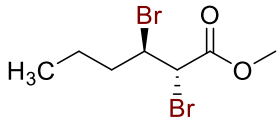
methyl (*trans*)-2,3-dibromo-3-(4-bromophenyl)propanoate **(Rac)-4b**[s1]

White solid, 94% yield, 19:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.25 (d,*J* = 8.4 Hz, 2H), 5.29 (d, *J* = 11.6 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 136.7, 132.2, 129.7, 123.5, 53.5, 49.6, 46.4.



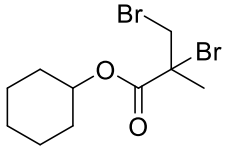
methyl (*trans*)-2,3-dibromo-3-(3-(trifluoromethyl)phenyl)propanoate **(Rac)-4c**

Colorless oil, 85% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 5.37 (d, *J* = 11.6 Hz, 1H), 4.82 (d, *J* = 11.6 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 138.7, 131.4, 131.4 (q, *J* = 32.8 Hz), 129.6, 126.2 (q, *J* = 3.6 Hz), 125.0 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.1 Hz), 53.6, 49.1, 46.3. ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.77. HRMS (EI) m/z $[M-F]^+$: Calcd for $C_{11}H_9O_2Br_2F_2$: 368.8931. Found: 368.8932. HRMS (EI) m/z $[M-Br]^+$: Calcd for $C_{11}H_9O_2Br_2F_2$: 308.9732. Found: 308.9734.



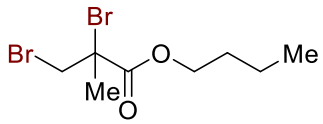
methyl (*trans*)-2,3-dibromohexanoate **(Rac)-4d**

Colorless oil, 73% yield, 12:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 (m, 2H), 3.83 (s, 3H), 2.21 (m, 1H), 1.81 (m, 1H), 1.63 (m, 1H), 1.51 (m, 1H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 53.2, 52.5, 47.7, 37.1, 19.7, 13.3. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_7H_{12}Br_2O_2Na$: 308.9096. Found: 308.9082.



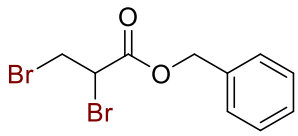
cyclohexyl 2,3-dibromo-2-methylpropanoate **(Rac)-4e**

Colorless oil, 89% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.02 – 4.83 (m, 1H), 4.24 (d, *J* = 9.5 Hz, 1H), 3.73 (d, *J* = 9.5 Hz, 1H), 2.03 (s, 3H), 1.85 (m, 2H), 1.75 (m, 2H), 1.60 – 1.49 (m, 3H), 1.40 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 74.8, 56.0, 38.3, 30.9, 26.3, 25.3, 23.3. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{10}H_{16}O_2Br_2Na$: 348.9409. Found: 348.9403.



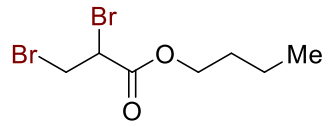
butyl 2,3-dibromo-2-methylpropanoate**(Rac)-4f**

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (dt, *J* = 6.4, 2.4 Hz, 3H), 3.75 (d, *J* = 9.8 Hz, 1H), 2.05 (s, 3H), 1.70 (dt, *J* = 13.2, 6.4 Hz, 2H), 1.46 (dq, *J* = 14.8, 7.2 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 66.4, 55.6, 38.3, 30.4, 26.4, 19.1, 13.7.



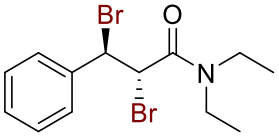
benzyl 2,3-dibromopropanoate **(Rac)-4g**[s1]

Colorless oil, 89% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 5H), 5.26 (s, 2H), 4.48 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.94 (dd, *J* = 11.2, 9.6 Hz, 1H), 3.68 (dd, *J* = 9.6, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 134.7, 128.7, 128.3, 128.3, 68.2, 41.0, 29.6.



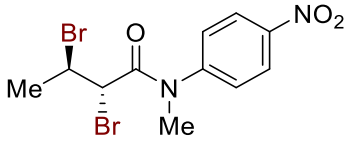
butyl 2,3-dibromopropanoate **(Rac)-4h**[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.94 (dd, *J* = 11.2, 9.6 Hz, 1H), 3.69 (dd, *J* = 9.8, 4.4 Hz, 1H), 1.74 – 1.64 (m, 2H), 1.51 – 1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 66.3, 41.2, 30.4, 29.7, 18.9, 13.6, 13.6.



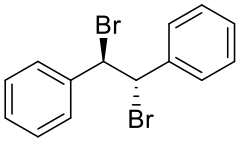
(*trans*)-2,3-dibromo-*N*,*N*-diethyl-3-phenylpropanamide **(Rac)-4i**

White solid, 88% yield, 14:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.42 – 7.31 (m, 3H), 5.61 (d, *J* = 11.2 Hz, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 3.65 – 3.50 (m, 2H), 3.44 (tt, *J* = 14.8, 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.26 – 1.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 138.5, 129.2, 128.8, 128.3, 77.3, 77.0, 76.7, 52.2, 44.9, 42.7, 41.8, 14.7, 12.4. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{13}H_{17}NOBr_2Na$: 383.9569. Found: 383.9565.



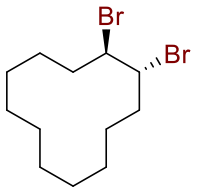
(*trans*)-2,3-dibromo-*N*-methyl-*N*-(4-nitrophenyl)butanamide **(Rac)-4j**

White solid, 87% yield, 13:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.64 (dq, *J* = 13.2, 6.4 Hz, 1H), 4.18 (d, *J* = 10.8 Hz, 1H), 3.37 (s, 3H), 1.79 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 148.2, 147.4, 128.6, 125.6, 47.4, 47.1, 38.1, 23.8. HRMS (ESI) m/z $[M+Na]^+$: Calcd for: $C_{11}H_{12}N_2O_3Br_2Na$ 400.9107. Found: 400.9108.



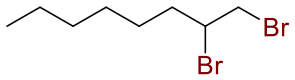
(*trans*)-1,2-dibromo-1,2-diphenylethane **(Rac)-4k**[s1]

White solid, 87% yield, >20:1 dr (*trans*-stilbene used); 91% yield, >20:1 dr (*cis*-stilbene used), ^{1}H NMR (400 MHz, DMSO) δ 7.70 (d, *J* = 7.2 Hz, 4H), 7.43 (t, *J* = 7.2 Hz, 4H), 7.36 (t, *J* = 7.2 Hz, 2H), 6.15 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 141.2, 129.2, 129.0, 128.6, 56.2.



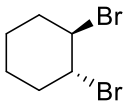
(trans)-1,2-dibromocyclododecane **(Rac)-4l**[s15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 – 4.29 (m, 2H), 2.24 – 2.12 (m, 2H), 1.98 (m, 2H), 1.64 – 1.55 (m, 2H), 1.53 – 1.44 (m, 2H), 1.43 – 1.27 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.0, 36.2, 24.7, 23.4, 23.2, 22.6.



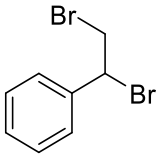
succinimide **(Rac)-4m**[s15]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (ddd, *J* = 13.5, 9.5, 4.0 Hz, 1H), 3.85 (dd, *J* = 10.0, 4.5Hz, 1H), 3.63 (t, *J* = 10.0 Hz, 1H), 2.23 – 2.04 (m, 1H), 1.78 (dtd, *J* = 14.5, 9.5, 4.5 Hz, 1H), 1.65 – 1.52 (m, 1H), 1.50 – 1.38 (m, 1H), 1.39 – 1.23 (m, 6H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 53.2, 36.4, 36.1, 31.6, 28.5, 26.7, 22.6, 14.1.



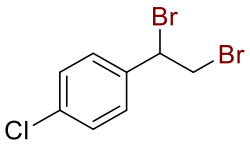
(*trans*)-1,2-dibromocyclohexane **(Rac)-4n**[s1]

Colorless oil, 83% yield, >20:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 2H), 2.50 – 2.40 (m, 2H), 1.95 – 1.77 (m, 4H), 1.56 – 1.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 32.0, 22.4.



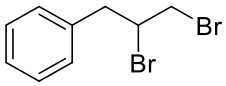
(1,2-dibromoethyl)benzene **(Rac)-4o**[s1]

White solid, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 5.15 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.15 – 3.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 129.2, 128.9, 127.7, 50.9, 35.0.



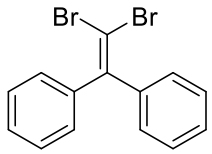
1-chloro-4-(1,2-dibromoethyl)benzene **(Rac)-4p**[s15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.28 (m, 4H), 5.14 (dd, *J* = 11.0, 5.1 Hz, 1H), 4.14 – 3.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 135.0, 129.1, 129.1, 49.6, 34.7.



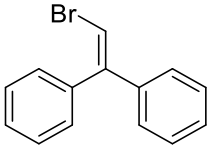
(2,3-dibromopropyl)benzene **(Rac)-4q**[S15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 4.39 (tt, *J* = 8.8, 4.4 Hz, 1H), 3.85 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.73 – 3.61 (m, 1H), 3.53 (dd, *J* = 14.4, 4.8 Hz, 1H), 3.16 (dd, *J* = 14.4, 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 129.5, 128.5, 127.2, 52.5, 42.0, 36.1.



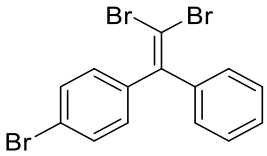
(2,2-dibromoethene-1,1-diyl)dibenzene **6a**[s15]

White solid, 95% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 141.4, 128.8, 128.4, 128.0, 90.3.



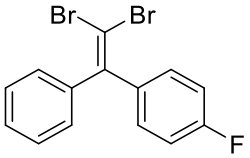
(2-bromoethene-1,1-diyl)dibenzene **6b**[s15]

White solid, 99% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 8H), 7.23 – 7.16 (m, 2H), 6.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 140.8, 139.2, 129.7, 128.5, 128.3, 128.2, 128.1, 127.7, 105.3.



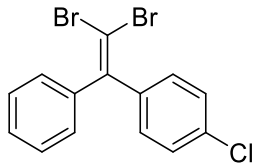
1-bromo-4-(2,2-dibromo-1-phenylvinyl)benzene **6c**

White solid, 82% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 140.9, 140.2, 131.6, 130.5, 128.8, 128.5, 128.2, 122.2, 90.8.



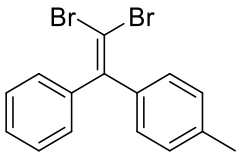
1-(2,2-dibromo-1-phenylvinyl)-4-fluorobenzene **6d**[s11]

Colorless oil, 85% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 7H), 7.02 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ162.2 (d, *J* = 248.3 Hz), 146.8, 141.2, 137.2 (d, *J* = 3.5 Hz), 130.7 (d, *J* = 8.2 Hz), 128.8, 128.4, 128.1, 115.5, 90.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -113.09.



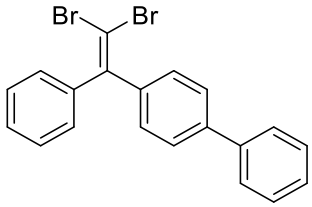
1-chloro-4-(2,2-dibromo-1-phenylvinyl)benzene **6e**

White solid, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 141.0, 139.7, 134.0, 130.2, 128.8, 128.6, 128.4, 128.2, 90.8. HRMS (EI) m/z $[M]^{\cdot+}$: Calcd for $C_{14}H_9Br_2Cl$: 369.8754. Found: 369.8756.



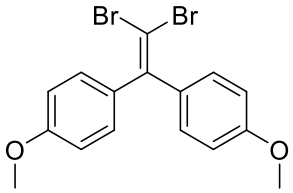
1-(2,2-dibromo-1-phenylvinyl)-4-methylbenzene **6f**

White solid, 60% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 5H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 141.6, 138.5, 137.9, 129.0, 128.8, 128.7, 128.3, 127.9, 89.8, 21.3. HRMS (EI) m/z $[M]^{\cdot+}$: Calcd for $C_{15}H_{12}Br_2$: 349.9300. Found: 349.9300.



4-(2,2-dibromo-1-phenylvinyl)-1,1'-biphenyl **6g**[s12]

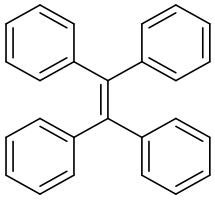
White solid, 90% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.28 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 141.5, 140.8, 140.4, 140.2, 129.3, 128.8, 128.8, 128.4, 128.1, 127.6, 127.1, 127.0, 90.3.



4,4'-(2,2-dibromoethene-1,1-diyl)bis(methoxybenzene) **6h**[s13]

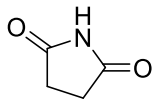
White solid, 87%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 4H), 6.85 (d, *J* = 8.0 Hz, 4H),

3.80 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 147.0, 133.9, 130.4, 113.6, 88.5, 55.3. HRMS (EI) m/z $[M]^{\cdot+}$: Calcd for $C_{16}H_{14}O_2Br_2$: 395.9355. Found: 395.9354.



1,1,2,2-tetraphenylethene **7a**[s14]

Light yellow solid, 85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 12H), 7.08 (dd, *J* = 7.2, 2.4 Hz, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 140.9, 131.3, 127.6, 126.3.



succinimide

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 2.77 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 29.6.

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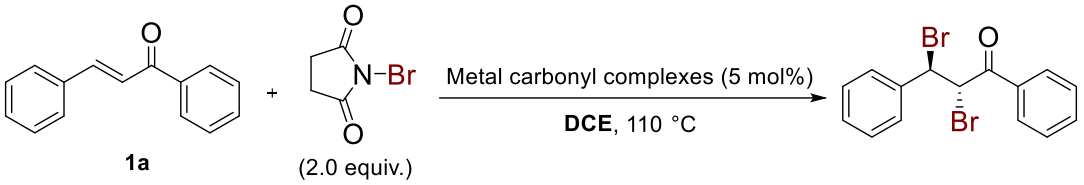
Optimization of the Reaction Conditions

Table S1. Optimization of catalysts.[a]



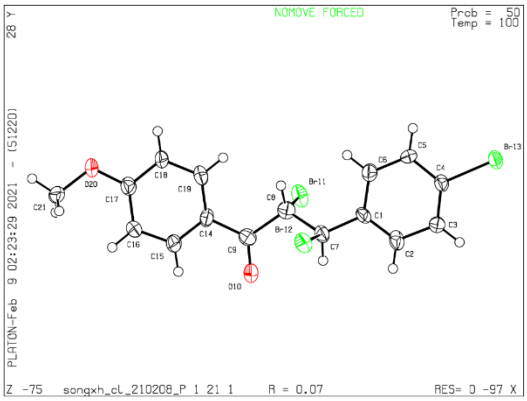
1a (2.0 equiv.) **(Rac)-2a**

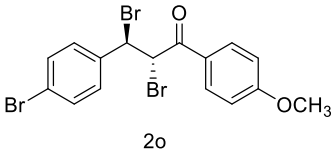
Entry	Metal carbonyl complexes	Yield%[a]	dr[b]
1	$Mn_2(CO)_8Br$	71	10:1
2	$Re_2(CO)_{10}$	58	5:1
3	$Ru_3(CO)_{12}$	49	6:1
4	$Mn(CO)_5Br$	66	14:1
5	$CpMn(CO)_3$	28	-
6	$Co_2(CO)_8$	63	12:1
7	$Mn_2(CO)_{10}$	78	18:1

[a]Reaction conditions: 1a (0.2 mmol), NBS (0.4 mmol), catalyst (5 mol%), 110 °C, solvent (1 ml), air. [b]Isolated yield. [c]The dr was determined by crude NMR spectra.

The Single Crystal X-ray Diffraction Study of 2o

To ascertain the structural correctness of these products, a crystallizing form of **2o** was obtained and the structure was undisputedly confirmed by single crystal X-ray analysis.





2o

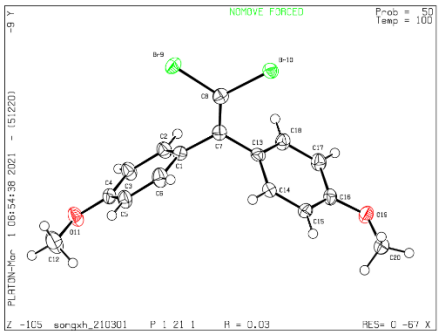
Fig. S1 X-ray single crystal structure of **2o**, CCDC: 2082644.

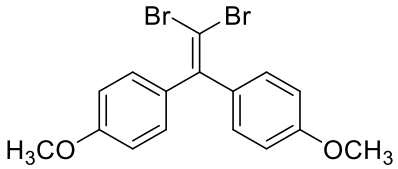
Empirical formula	$C_{16}H_{13}Br_3O_2$
Formula weight	476.99
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.5472(2)
b/Å	7.8195(4)
c/Å	18.3327(7)
α/°	90
β/°	94.308(4)
γ/°	90
Volume/Å^3	792.96(6)
Z	2
ρ_{calc}mg/mm^3	1.998
μ/mm^{-1}	9.447
F(000)	460.0
Crystal size/mm^3	0.25 × 0.2 × 0.1
2Θ range for data collection	4.834 to 153.692°
Index ranges	$-6 \le h \le 6$, $-9 \le k \le 9$, $-23 \le l \le 23$
Reflections collected	16382

Independent reflections	3232[R(int) = 0.1869]
Data/restraints/parameters	3232/1/181
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0697, wR_2 = 0.1568
Final R indexes [all data]	R_1 = 0.0934, wR_2 = 0.1783
Largest diff. peak/hole / e $Å^{-3}$	1.01/-1.63
Flack parameter	-0.08(6)

The Single Crystal X-ray Diffraction Study of 6h

To ascertain the structural correctness of these products, a crystallizing form of **6h** was obtained and the structure was undisputedly confirmed by single crystal X-ray analysis.





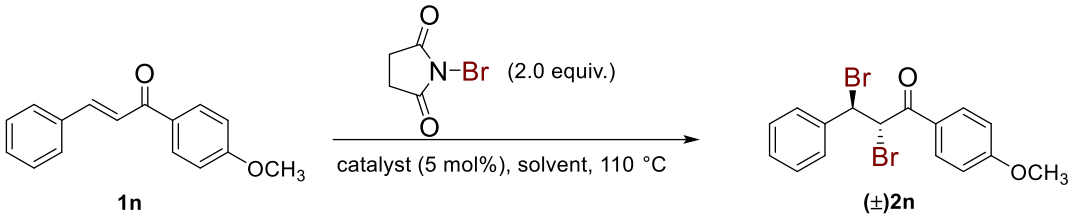
6h

Fig. S2 X-ray single crystal structure of **6h**, CCDC: 2082642.

Identification code	songxh_210301
Empirical formula	$C_{16}H_{14}Br_2O_2$
Formula weight	398.09
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.96300(10)
b/Å	6.03520(10)
c/Å	16.0210(2)
α /°	90
β /°	93.6370(10)
γ /°	90
Volume/$Å^3$	768.391(19)
Z	2
ρ_{calc}g/cm^3	1.721

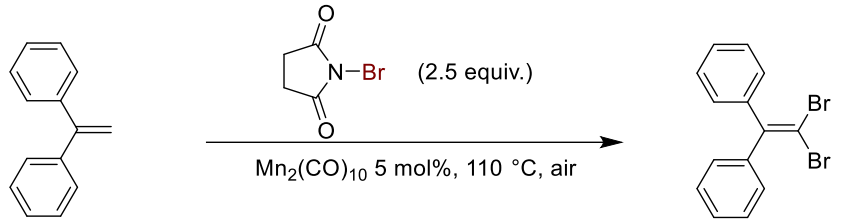
μ /mm^{-1}	6.678
F(000)	392.0
Crystal size/mm^3	0.1 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.528 to 154.082
Index ranges	-9 ⩽ h ⩽ 9, -7 ⩽ k ⩽ 7, -20 ⩽ l ⩽ 18
Reflections collected	15800
Independent reflections	3060 [R_{int} = 0.0519, R_{sigma} = 0.0321]
Data/restraints/parameters	3060/1/183
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0673
Final R indexes [all data]	R_1 = 0.0286, wR_2 = 0.0676
Largest diff. peak/hole / e Å^{-3}	0.46/-0.47
Flack parameter	-0.04(2)

Gram-scale Synthesis



1n **(±)2n**

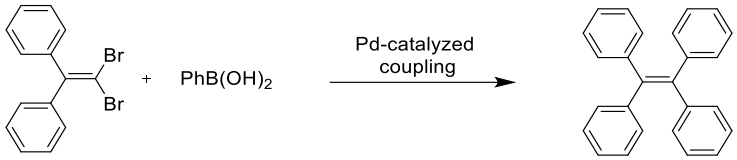
To a 50 ml Schlenk tube was added olefin (**1n**) (1.19 g, 5 mmol), NBS (2.22 g, 1.25 mmol), $Mn_2(CO)_{10}$ (79 mg, 4 mol%), then 20 ml DCE was added. The mixture was stirred at 110 ℃ for 12 hours. (Monitored by TLC). After cooling down to room temperature, the mixture was filtered through a Celite pad, evaporated the solvent for crude ^{1}H-NMR. The crude residue was separated by column chromatography on a silica gel column using PE/EA (100/1, v/v) as eluent, the desired product **2n** was obtained in 84% yield, 12:1 dr (1.67g).



5a **6a**

To a 50 ml Schlenk tube was added olefin (**5a**) (0.72 g, 4 mmol), NBS (1.77 g, 1.00 mmol), $Mn_2(CO)_{10}$ (78 mg, 5 mol%), then 20 ml DCE was added. The mixture was stirred at 110 ℃ for 36 hours (monitored by TLC). After cooling down to room temperature, the mixture was filtered through a Celite pad, evaporated the solvent. The crude residue was separated by column chromatography on a silica gel column using PE/EA (100/1, v/v) as eluent, the desired product **6a** was obtained in 95% yield (1.29 g).

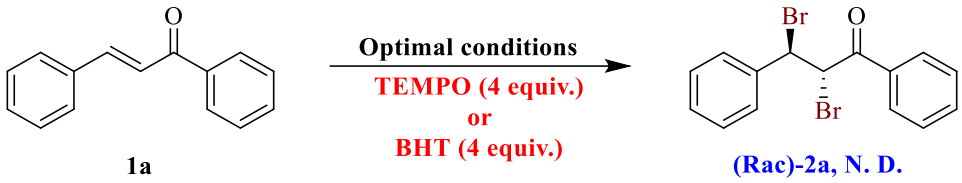
Synthesis of 1,1,2,2-teraphenylethene (TPE)



To a two-neck flask (100 ml), 1,1-dibromo-2,2-diphenylene (**6a**) (0.67 g, 2 mmol), boronic acid (2) (0.31 g, 2.5 mmol), $Pd(PPh_3)_4$ (115 mg, 0.1 mmol), tetrabutylammonium hydrogen sulfate (68 mg, 0.2 mmol), K_2CO_3 (828 mg, 6 mmol) in toluene (40 ml) were added and heated to 90 ℃ and stirred under nitrogen overnight. After cooling down to room temperature, the organic layer was separated and the water layer was extracted with dichloromethane (DCM). The combined organic solution was dried with Na_2SO_4. After filtration, evaporated the solvent, the crude residue was separated by column chromatography on a silica gel column using DCM/PE (1/9, v/v) as eluent, the desired product **7a** was obtained in 85% yield (0.56 g).

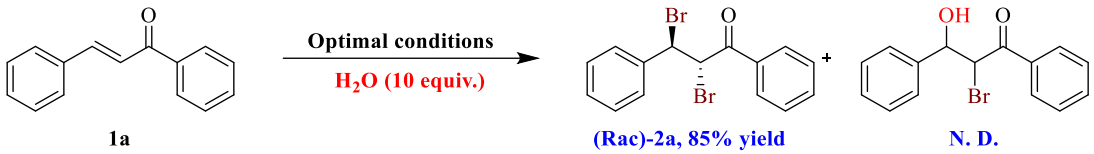
Controlled experiments

(a)



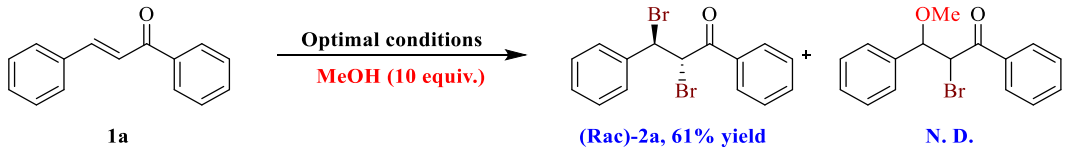
To a 25 ml Schlenk tube was added olefin (**1a**) (0.2 mmol), NBS (0.5 mmol), $Mn_2(CO)_{10}$ (5 mol%) and TEMPO or BHT (0.8 mmol), then 2 ml DCE was added. The mixture was stirred at 110 ℃ for 12 hours. After cooling down to room temperature, the mixture was filtered through a Celite pad, evaporated the solvent for crude ^1H NMR. No desired product was obtained.

(b)



To a 25 ml Schlenk tube was added olefin (**1a**) (0.2 mmol), NBS (0.5 mmol), $Mn_2(CO)_{10}$ (5 mol%) and H_2O (18 mg, 10.0 eq.), then 2 ml DCE was added. The mixture was stirred at 110 ℃ for 12 hours. (monitored by TLC). After cooling down to room temperature, the mixture was filtered through a Celite pad and evaporated the solvent. The crude residue was separated by column chromatography on a silica gel column using PE/EA (100/1, v/v) as eluent, to give the dibromination proceeded smoothly without any other byproducts, the desired product **2a** was obtained in 85% yield.

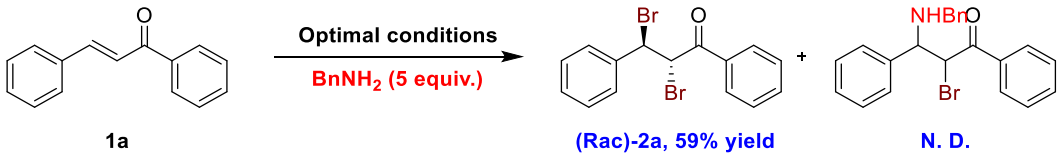
(c)



To a 25 ml Schlenk tube was added olefin (**1a**) (0.2 mmol), NBS (0.5 mmol), $Mn_2(CO)_{10}$ (5 mol%) and MeOH (32 mg, 10.0 eq.), then 2 ml DCE was added. The mixture was stirred at 110 ℃ for 12 hours. (monitored by TLC). After cooling down to room temperature, the mixture was filtered through a Celite pad and evaporated the solvent. The crude residue was separated by column chromatography on a silica gel column using PE/EA (100/1, v/v) as eluent, to give the dibromination proceeded smoothly without

any other byproducts, the desired product **2a** was obtained in 61% yield.

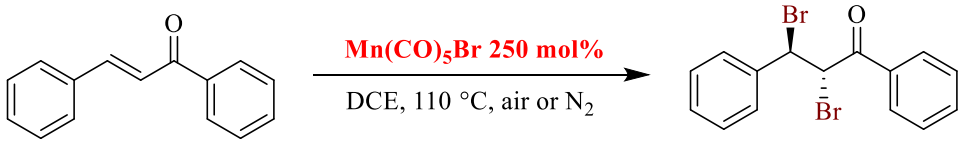
(d)



1a **(Rac)-2a, 59% yield** **N. D.**

To a 25 ml Schlenk tube was added olefin (**1a**) (0.2 mmol), NBS (0.5 mmol), $Mn_2(CO)_{10}$ (5 mol%) and $BnNH_2$(107 mg, 10.0 eq.), then 2 ml DCE was added. The mixture was stirred at 110 ℃ for 12 hours. (monitored by TLC). After cooling down to room temperature, the mixture was filtered through a Celite pad and evaporated the solvent. The crude residue was separated by column chromatography on a silica gel column using PE/EA (100/1, v/v) as eluent, to give the dibromination proceeded smoothly without any other byproducts, the desired product **2a** was obtained in 61% yield.

(e)

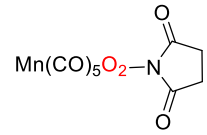


1a **No reaction**

To a 25 ml Schlenk tube was added olefin (**1a**) (0.2 mmol) and 250% $Mn(CO)_5Br$, then 2 ml DCE was added. The mixture was stirred at 110 ℃ for 12 hours. (monitored by TLC). After cooling down to room temperature, the mixture was filtered through a Celite pad, evaporated the solvent for crude ^1H NMR. No reaction was happened.

The mass spectra of intermediate (B) and (D).

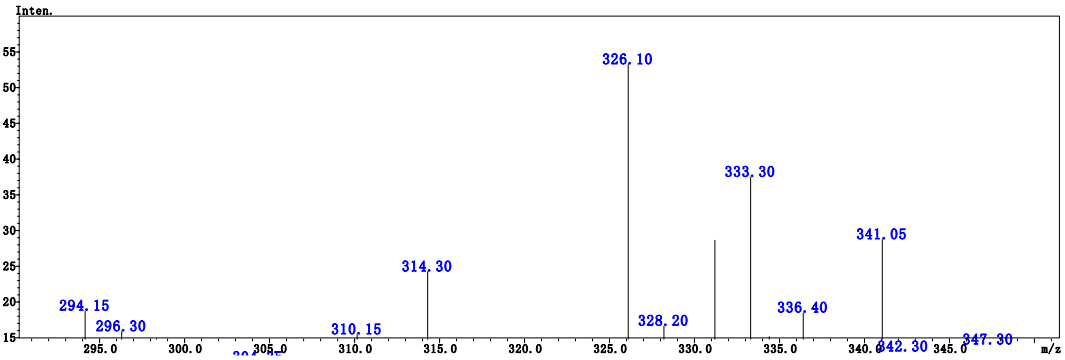
To a 25 ml Schlenk tube was added olefin (**1a**) (0.2 mmol), NBS (0.5 mmol) and $Mn_2(CO)_{10}$ (0.2 mmol), then 2 ml DCE was added. The mixture was stirred at 110℃ for 1 hours. Then the solution was filtered for crude mass spectra detected. The intermediate (**B**) and (**D**) molecular weight was found (see Fig. S1).

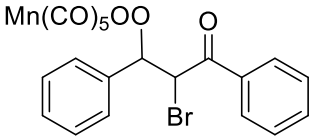


(C)

Calcd m/z $[M+H]^+$: 325.93

Found : 326.10





Calcd m/z $[M+H]^+$: 513.91

Found : 513.90

Calcd m/z $[M+Na]^+$: 536.90

Found : 537.30

Calcd m/z $[M+K]^+$: 552.87

Found : 553.10

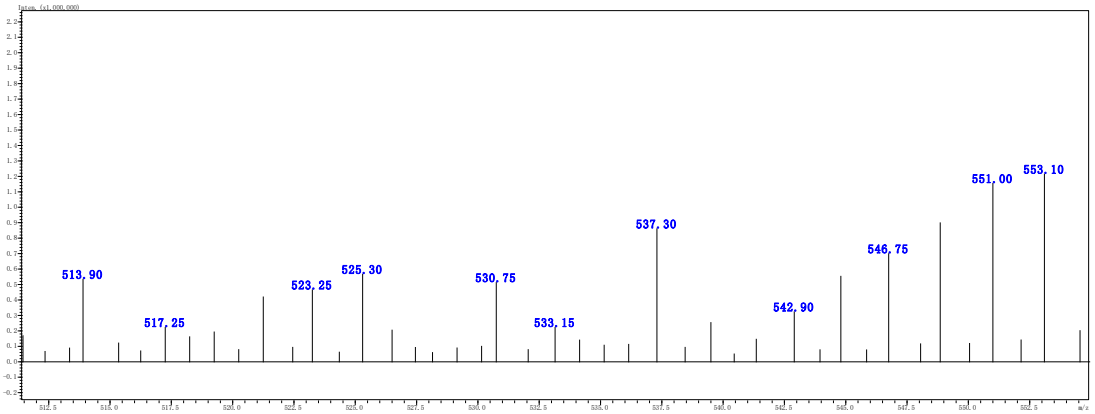


Fig S1. The mass spectra of intermediate (B) and (D).

Proposed mechanism for Dibrominated Addition of Alkenes (Fig. S2)

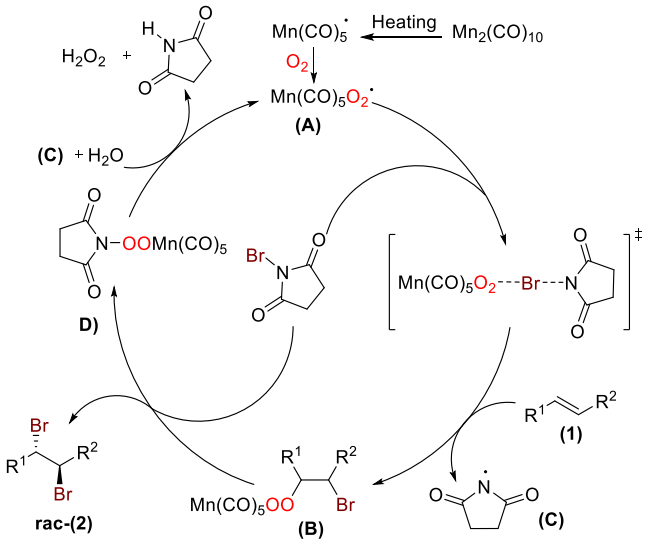


Fig. S2

Proposed mechanism for Dibrominated Substitution of Alkenes (Fig. S3)

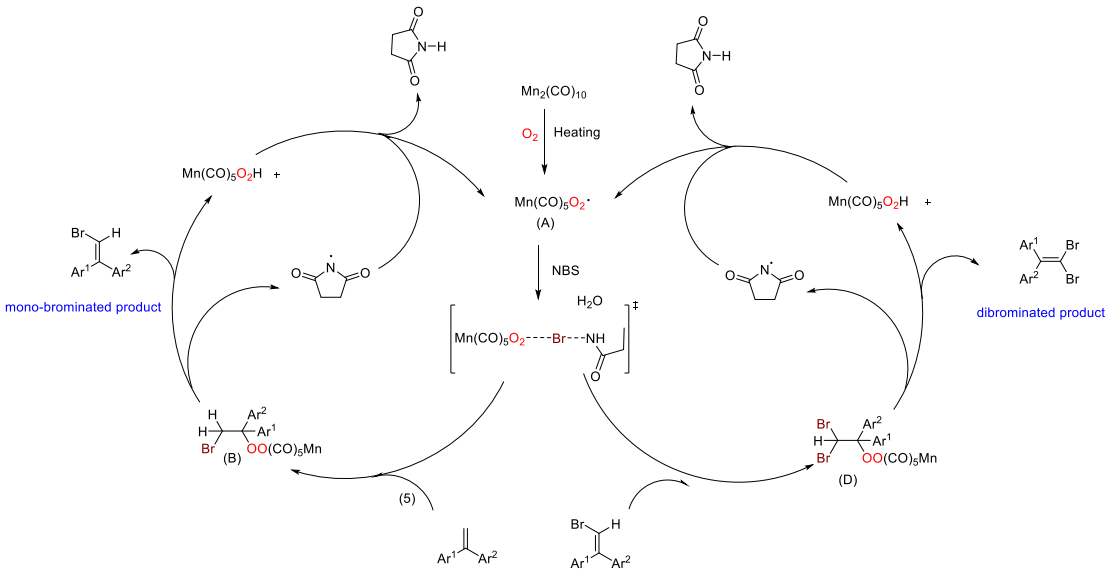
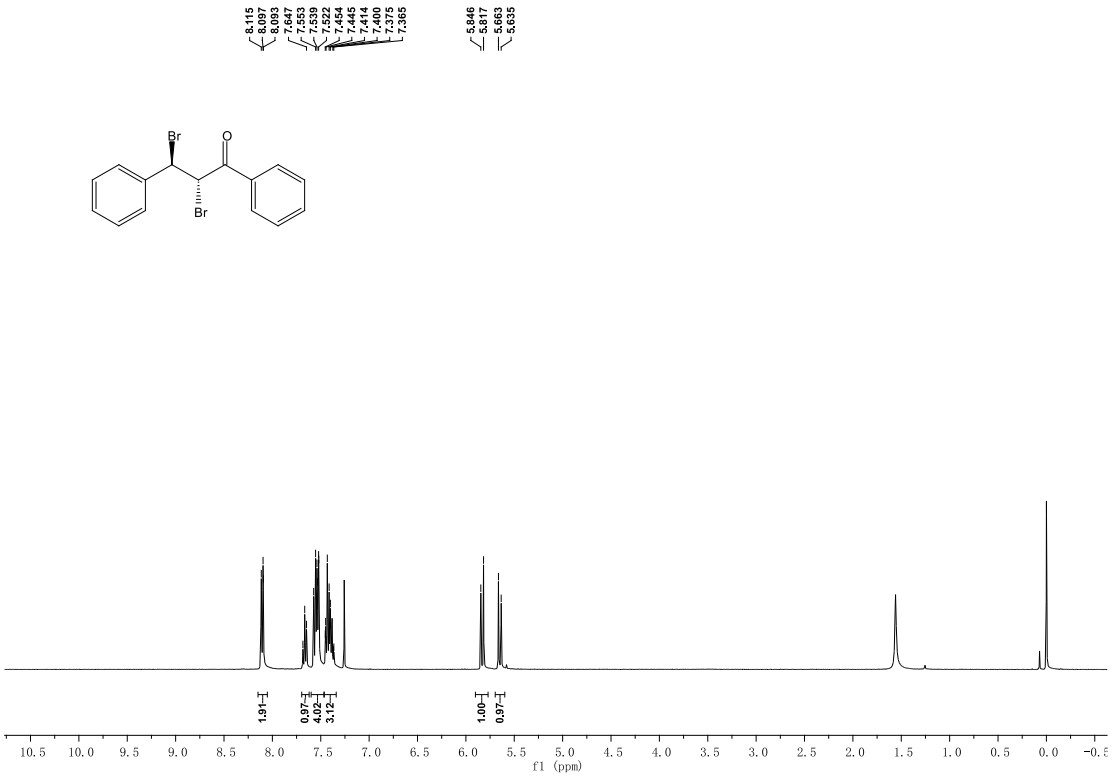


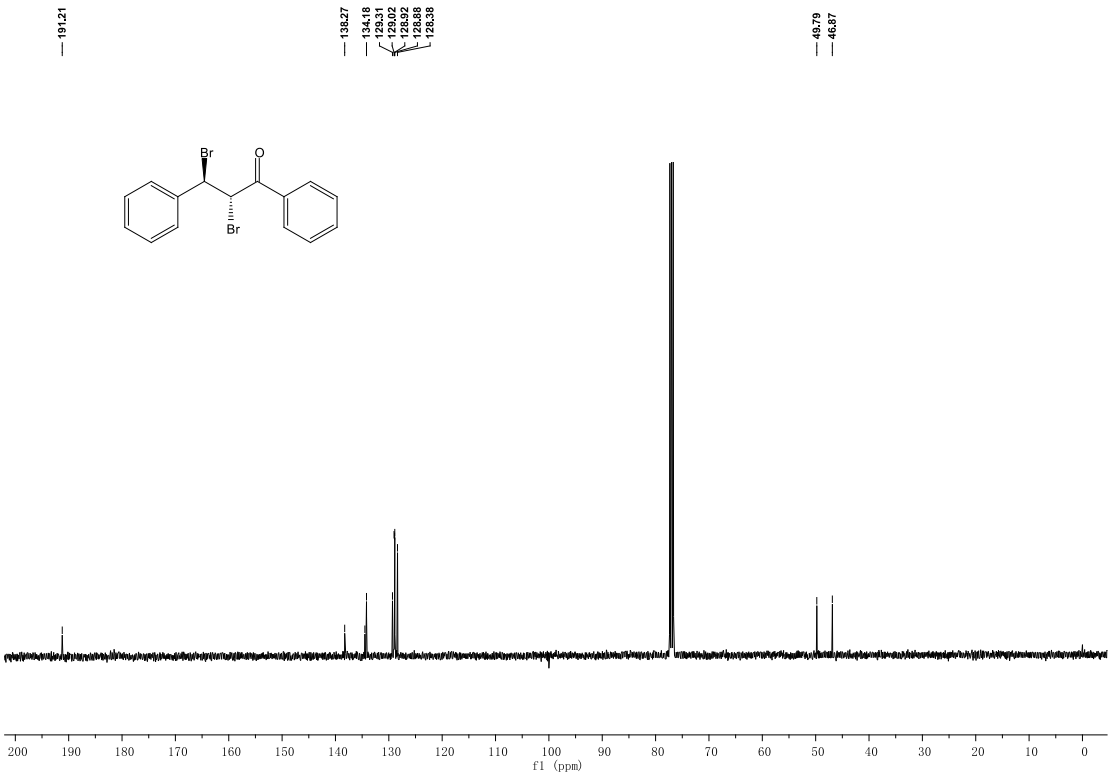
Fig. S3

NMR spectra

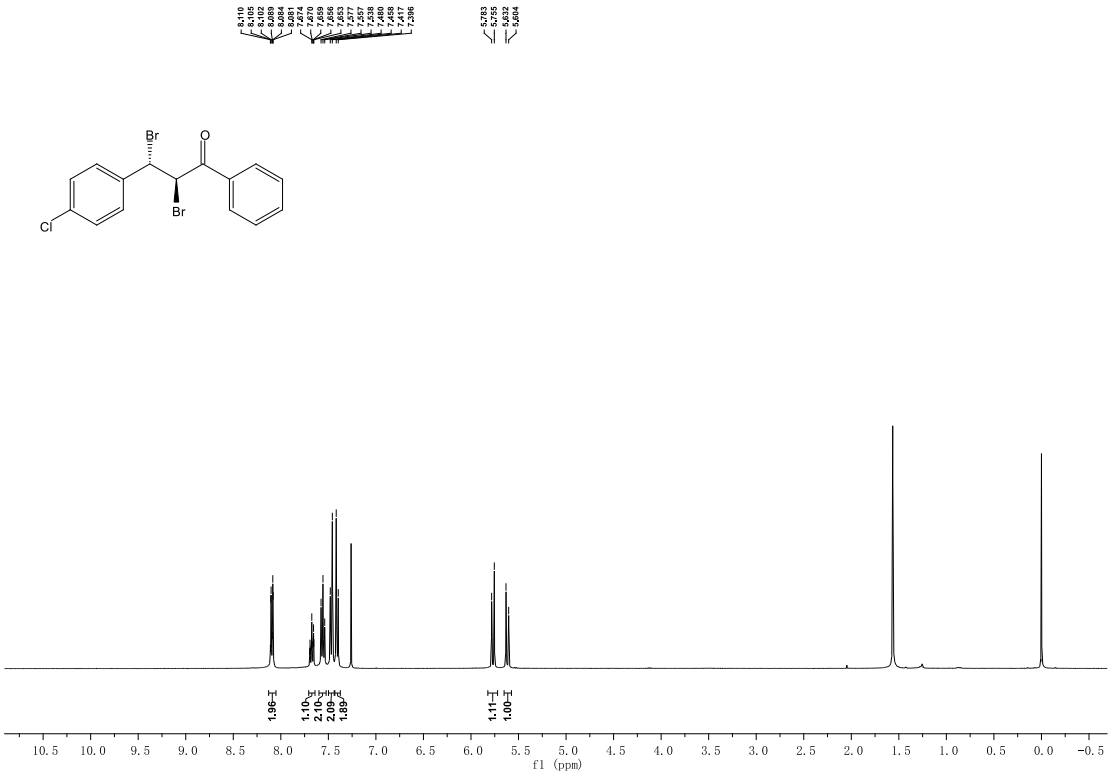
2a ^{1}H NMR



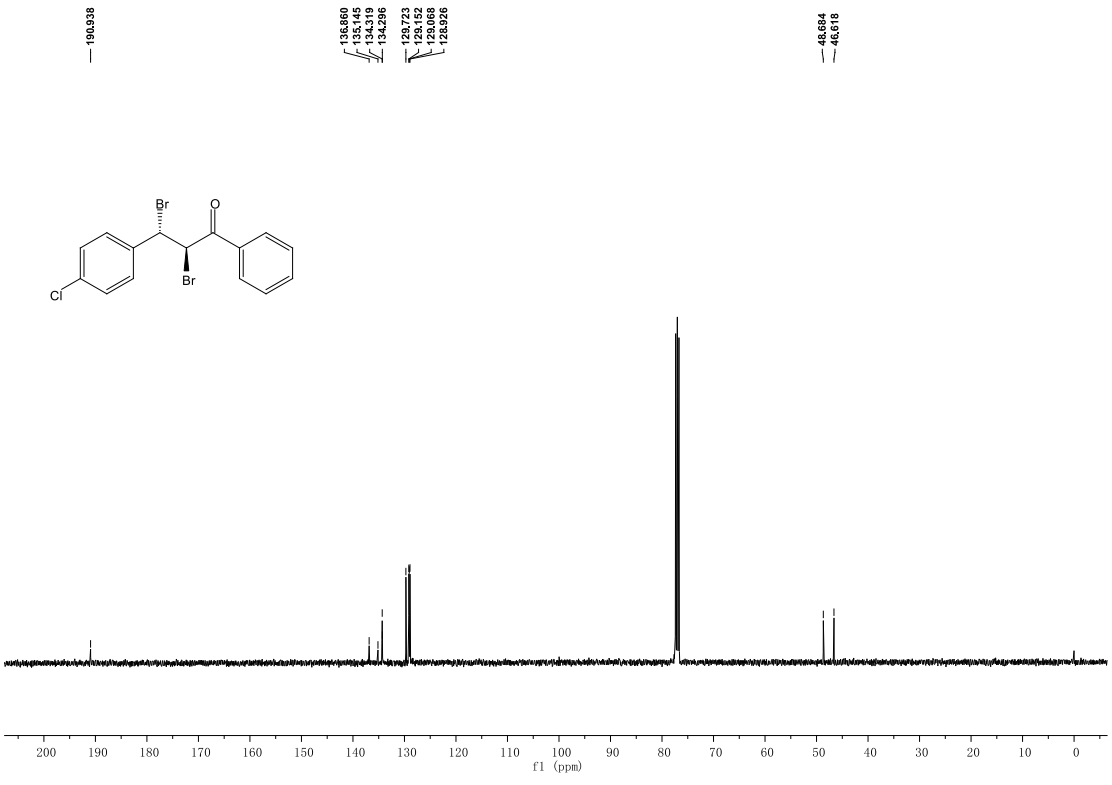
2a ^{13}C NMR



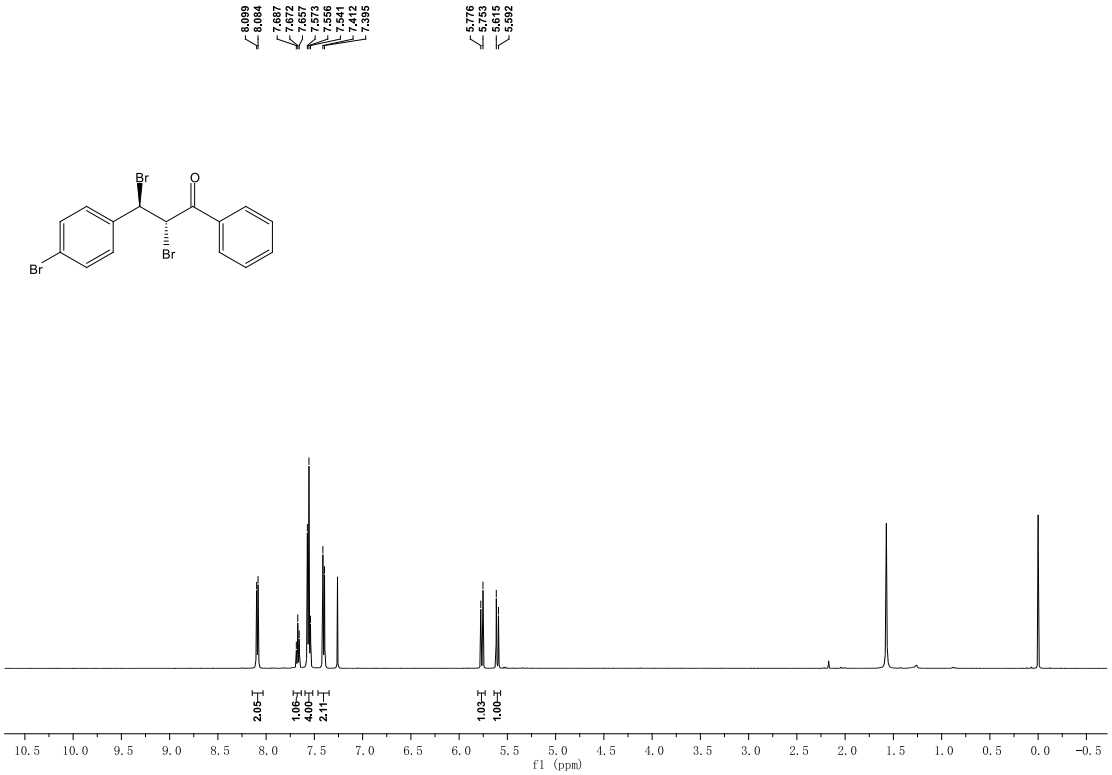
2b ^{1}H NMR



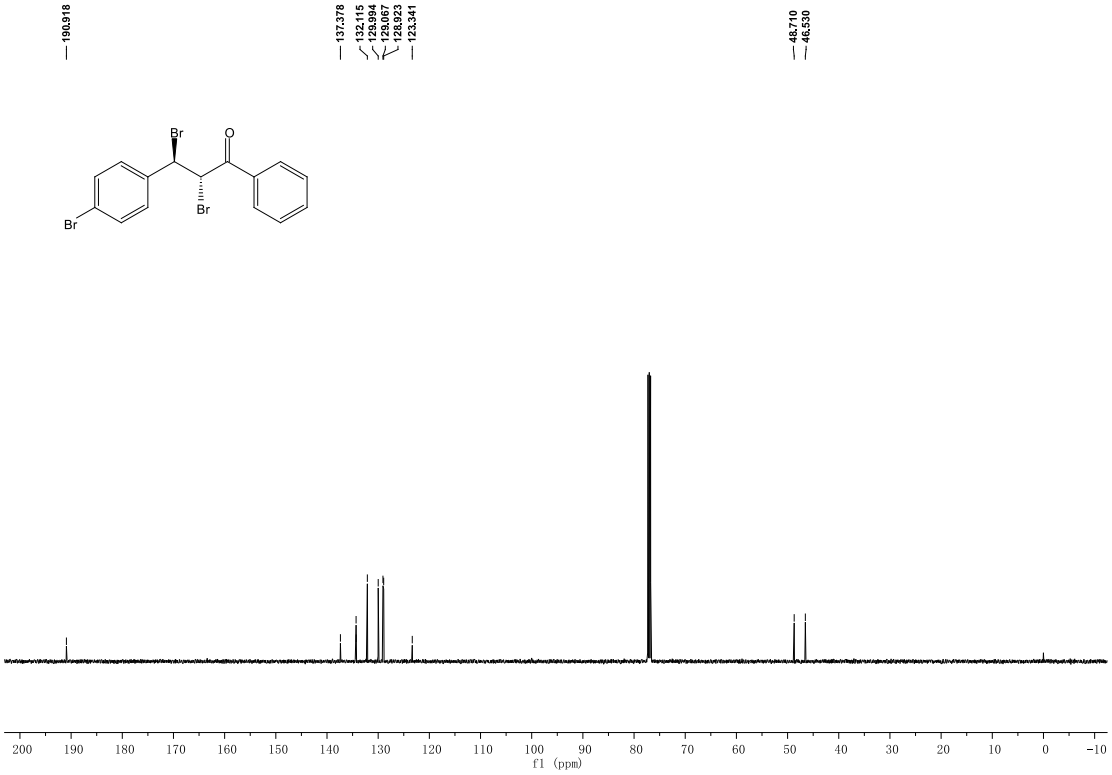
2b ^{13}C NMR



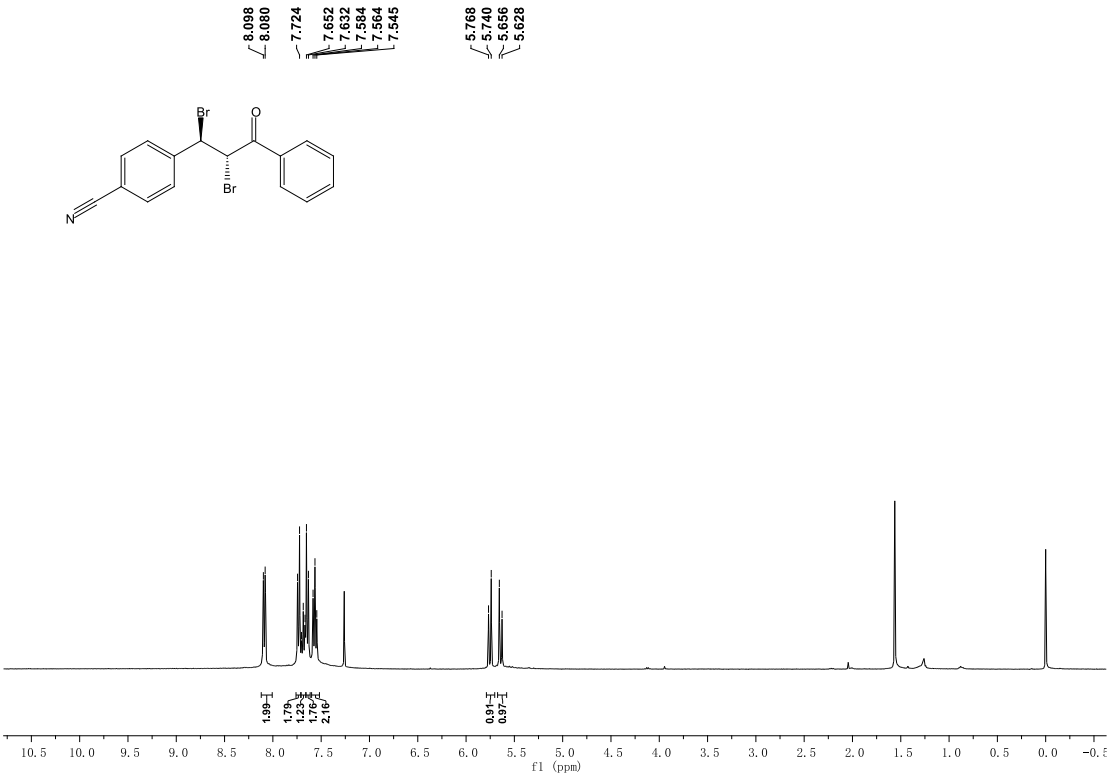
2c ^{1}H NMR



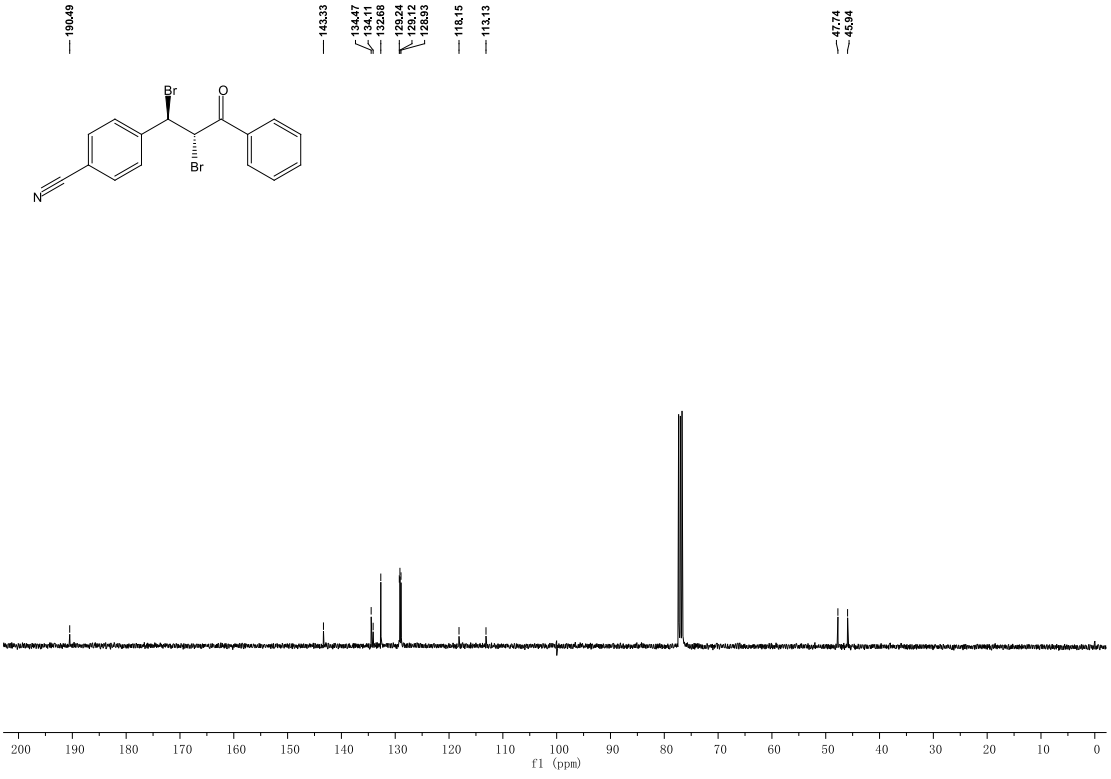
2c ^{13}C NMR



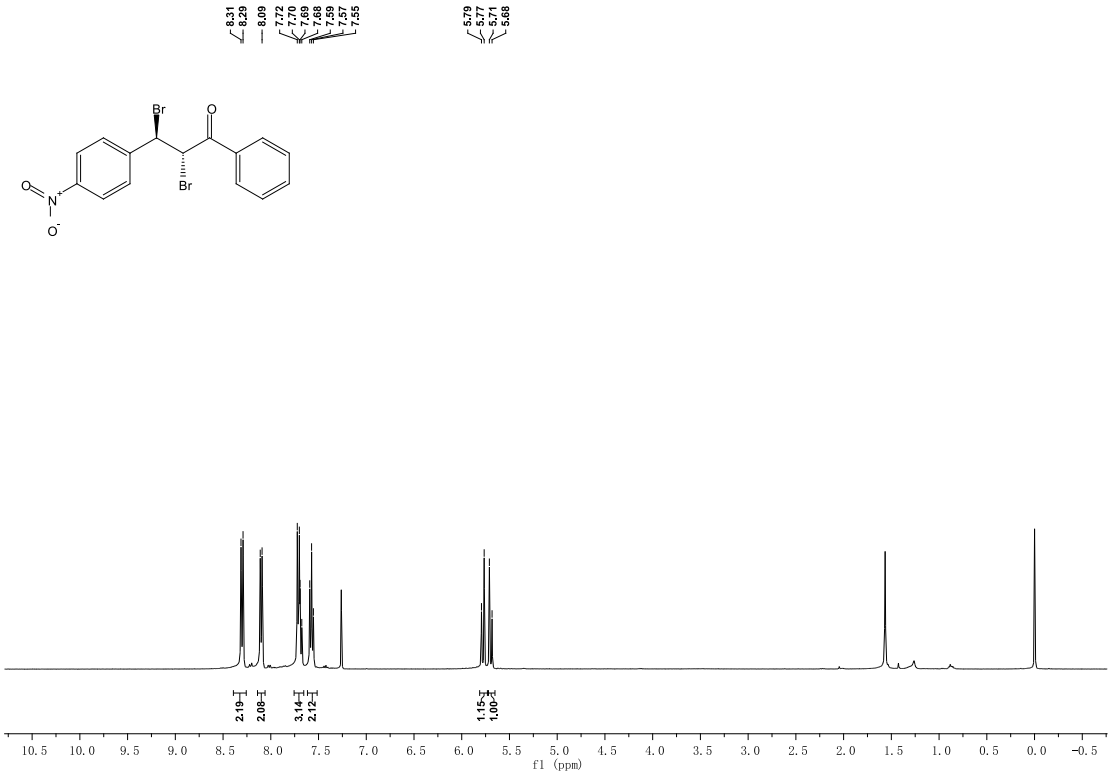
2d ^{1}H NMR



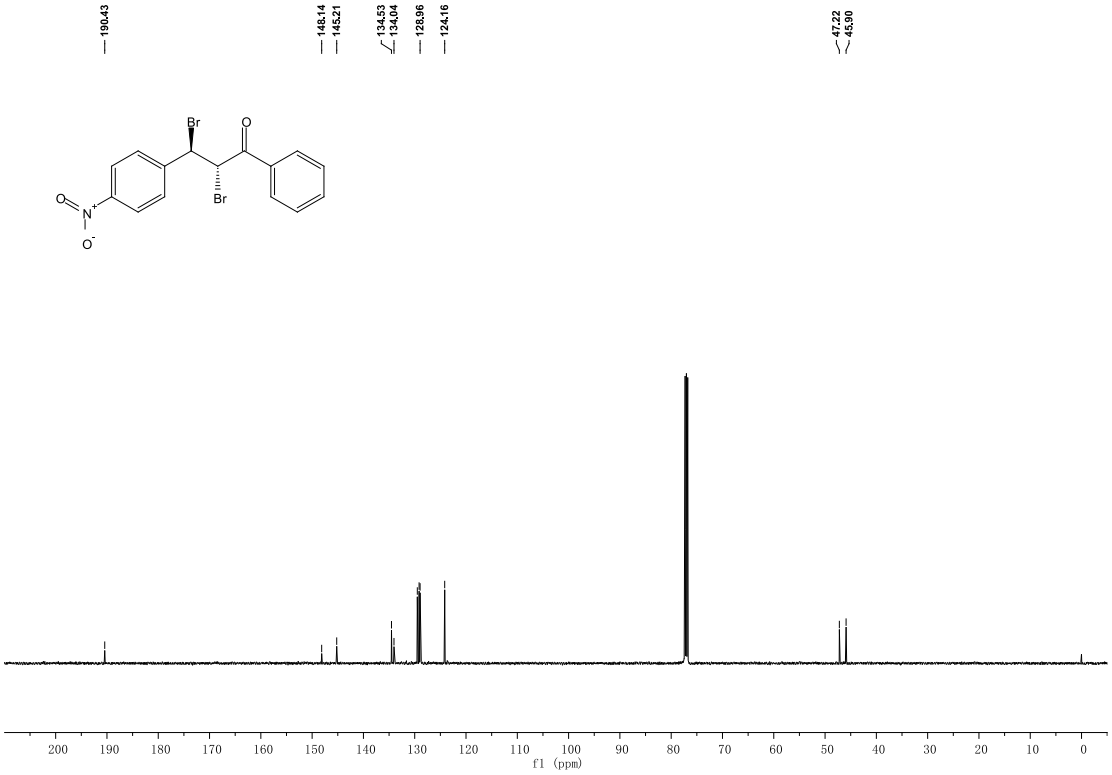
2d ^{13}C NMR



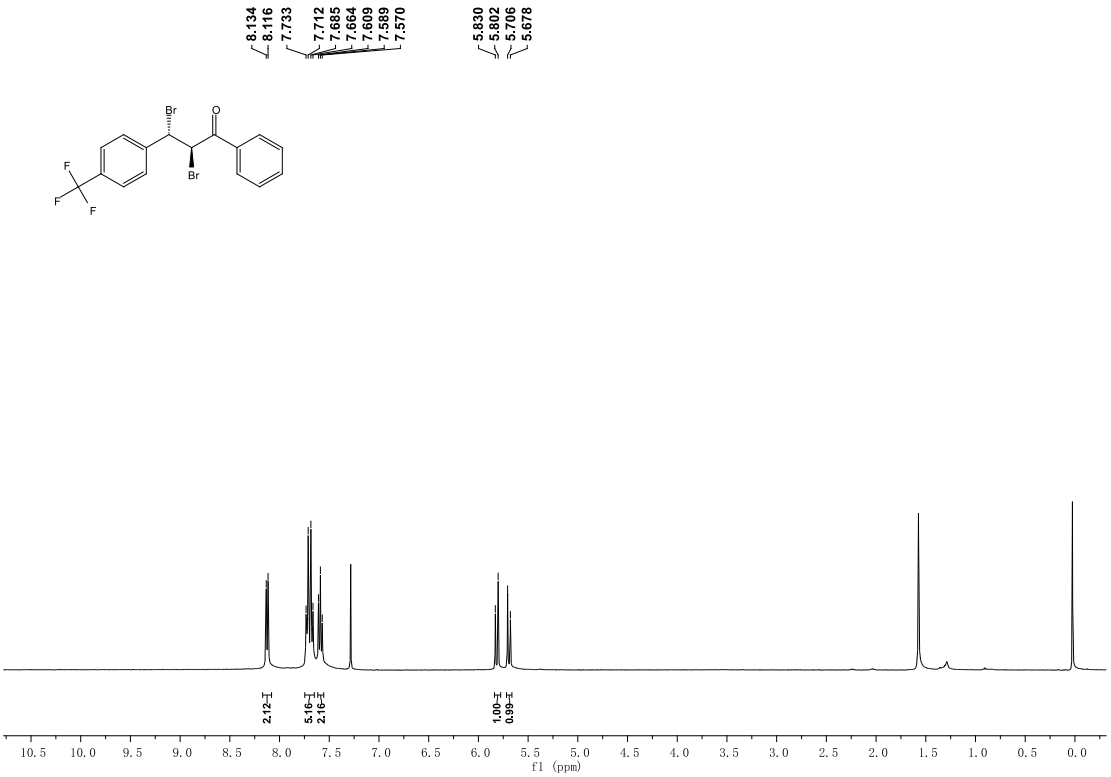
2e ^{1}H NMR



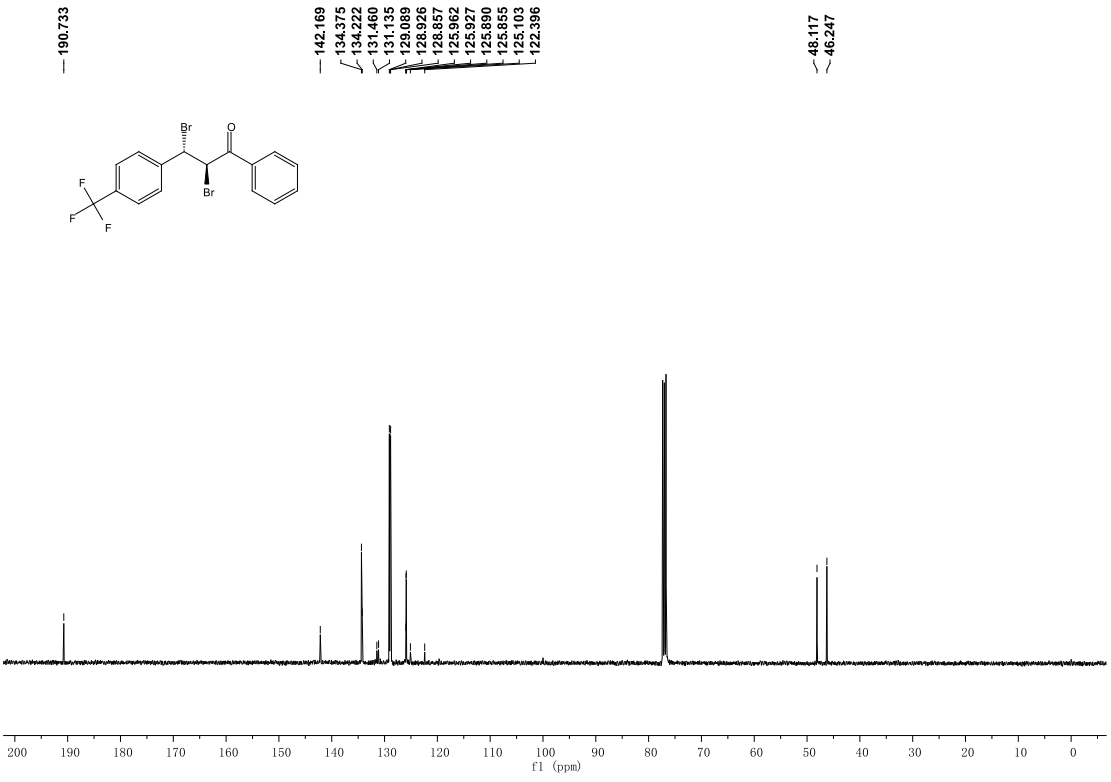
2e ^{13}C NMR



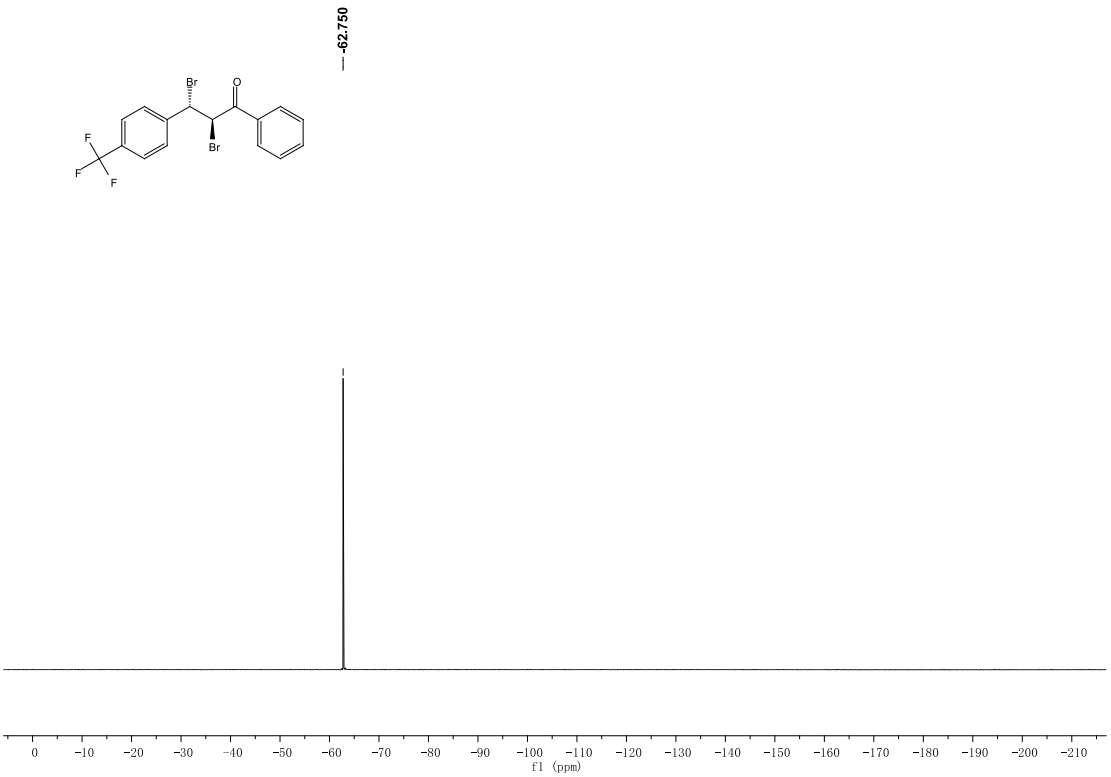
2f ^{1}H NMR



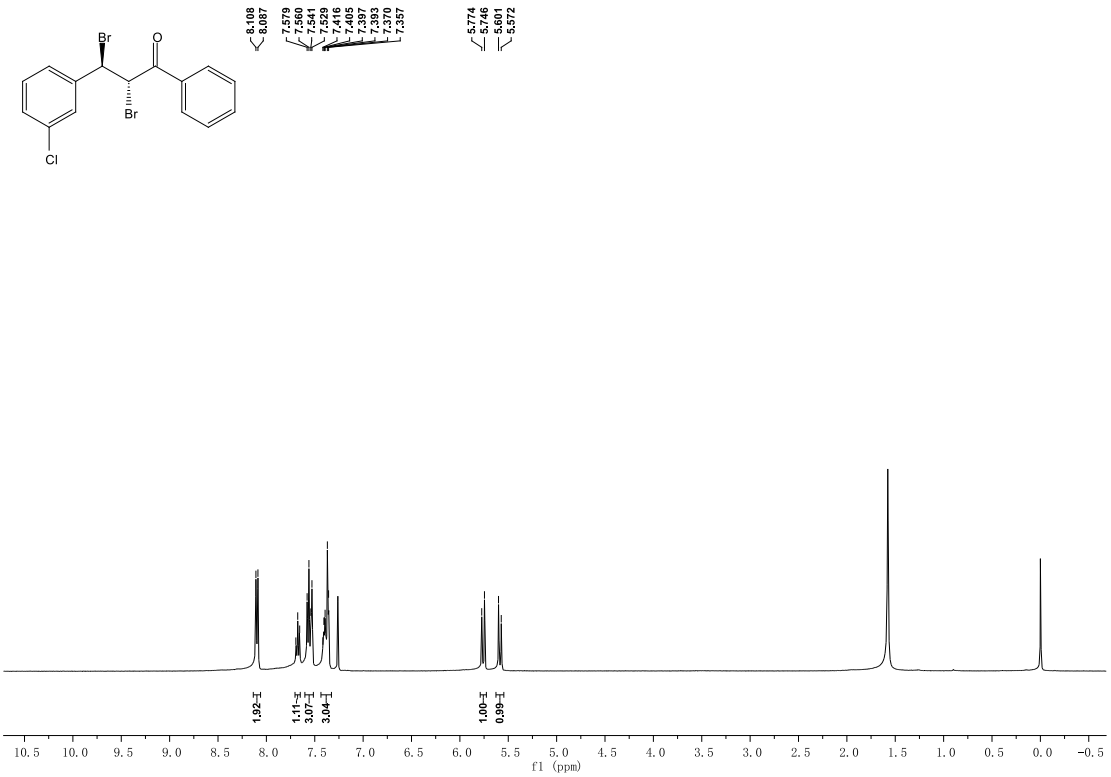
2f ^{13}C NMR



2f ^{19}F NMR



2g ^{1}H NMR



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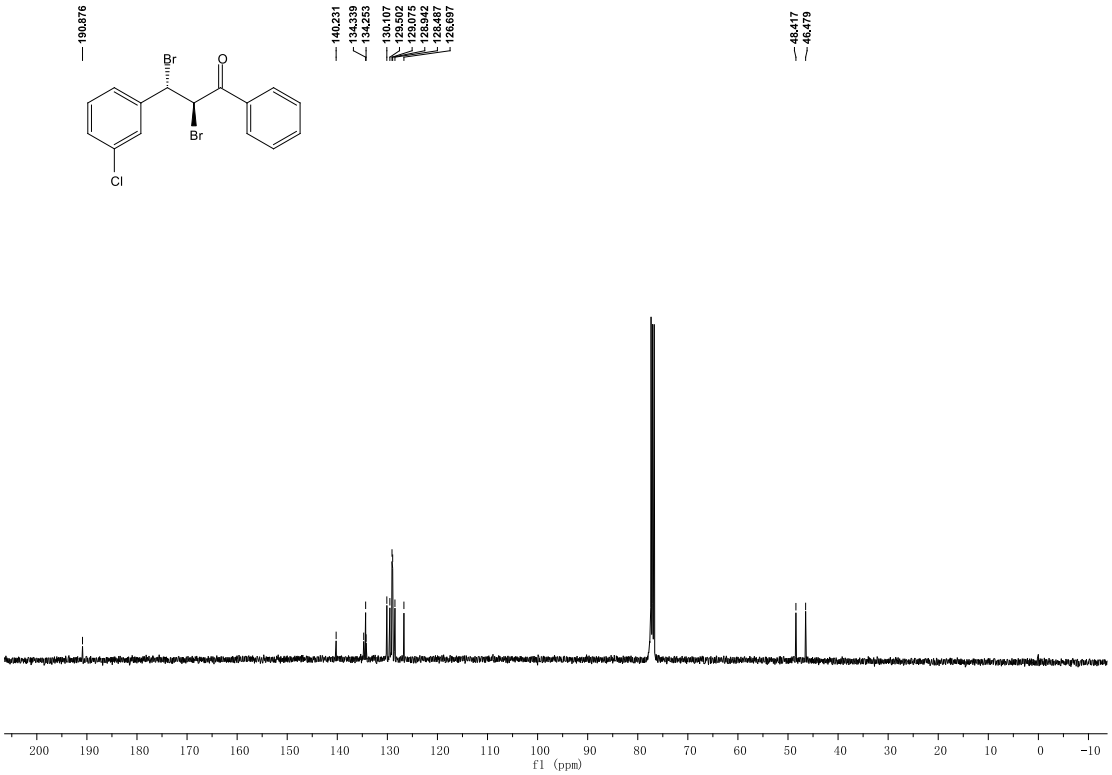
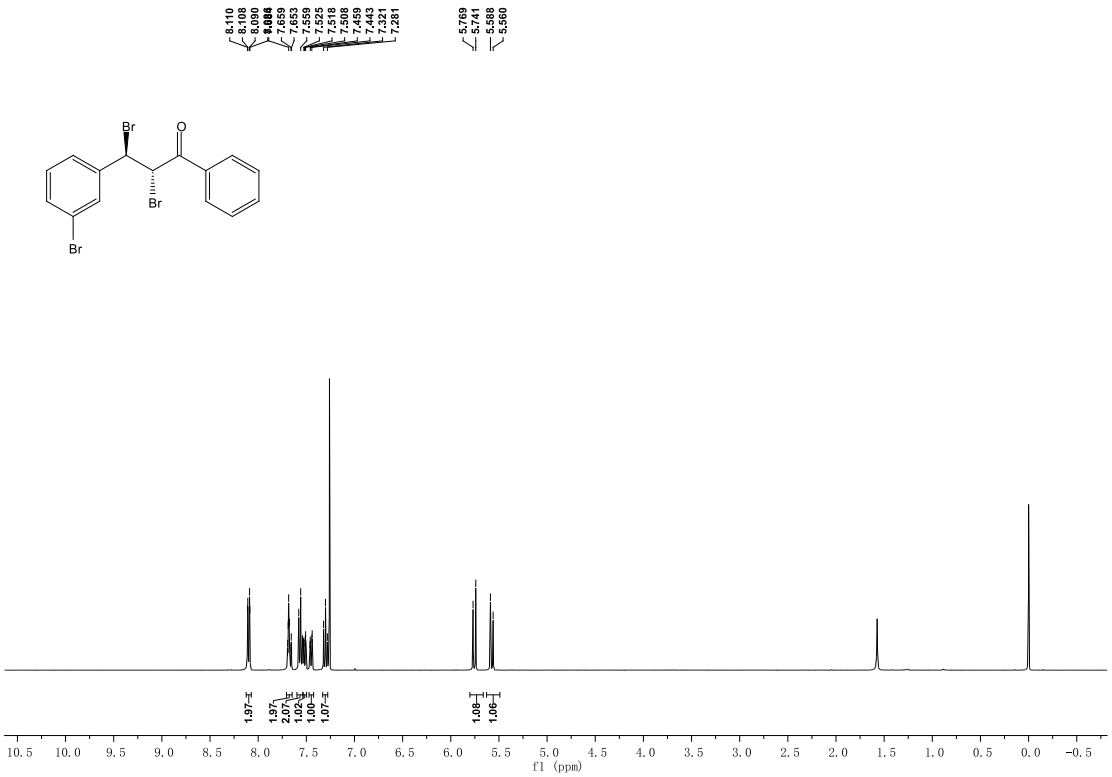
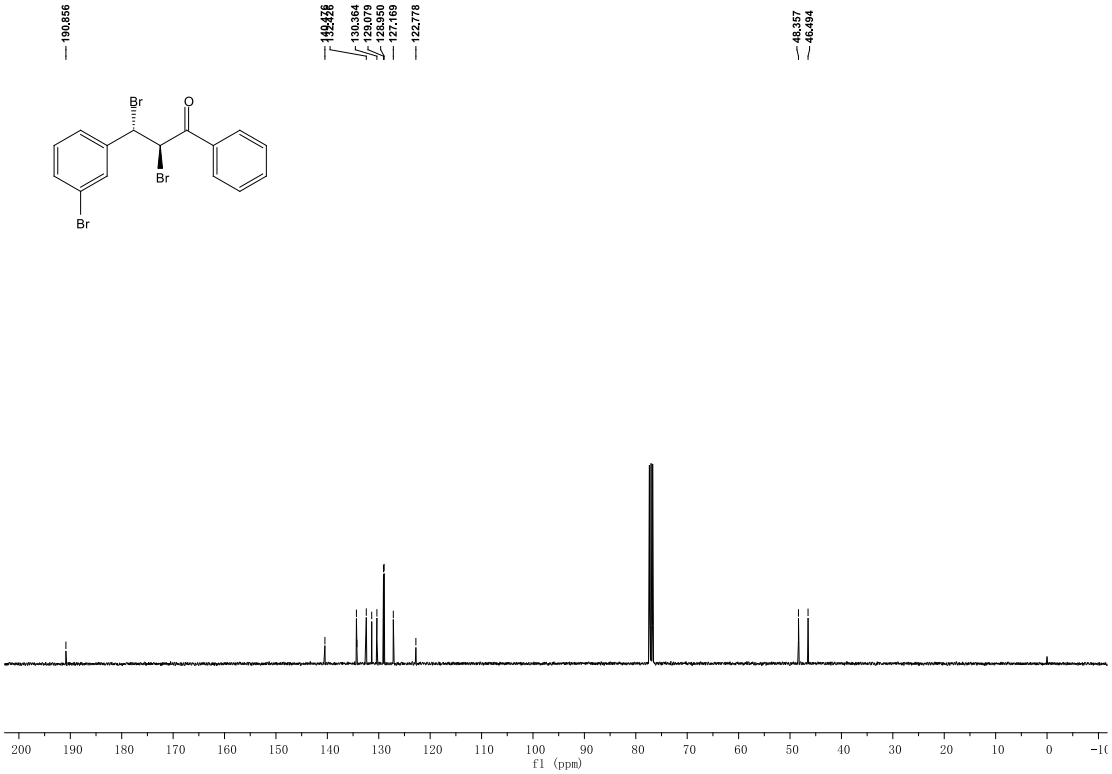


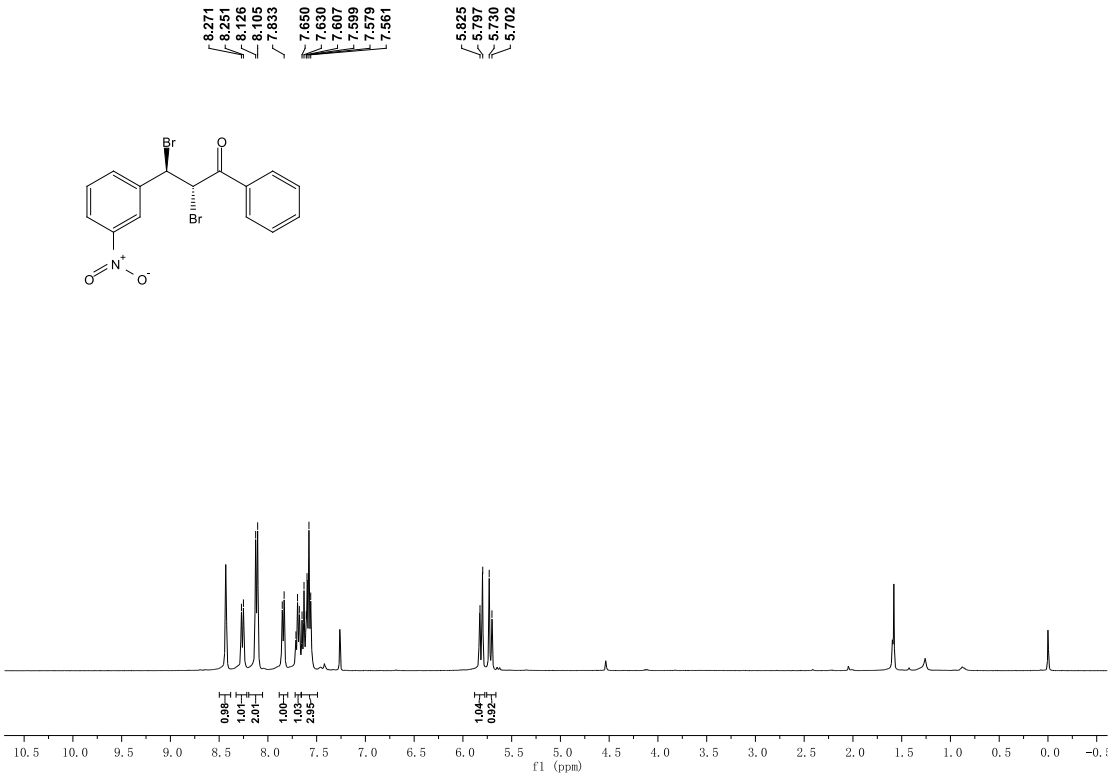
2h ^{1}H NMR



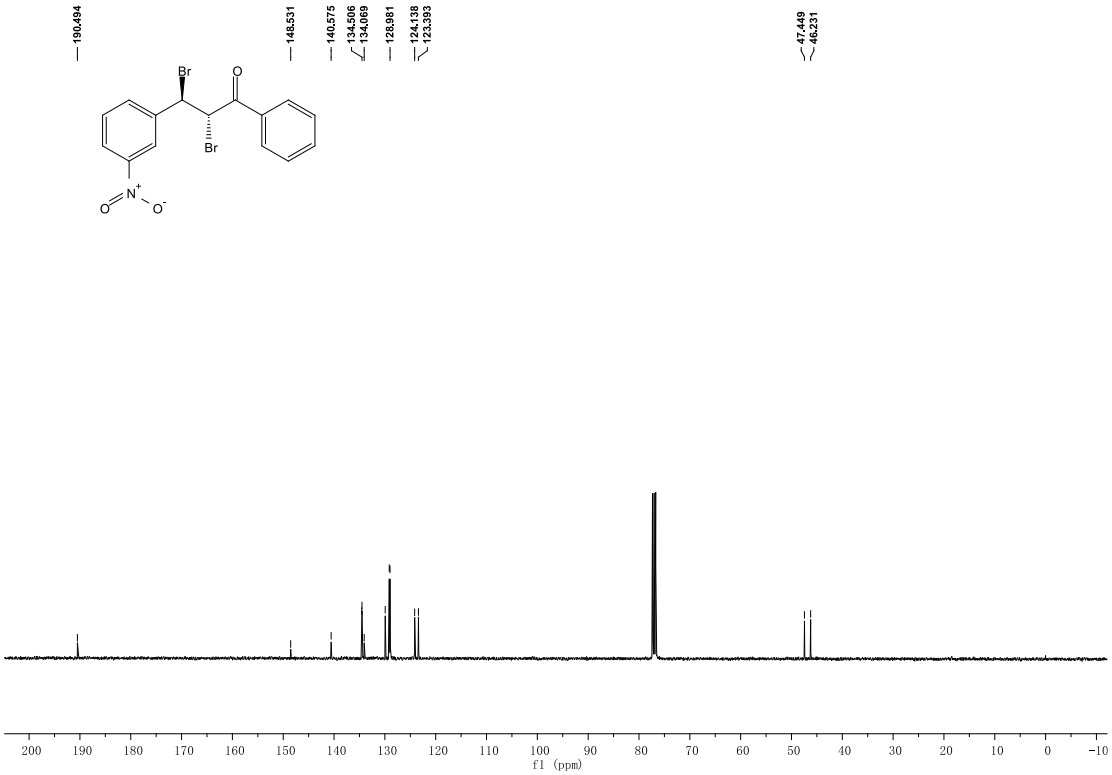
2h ^{13}C NMR



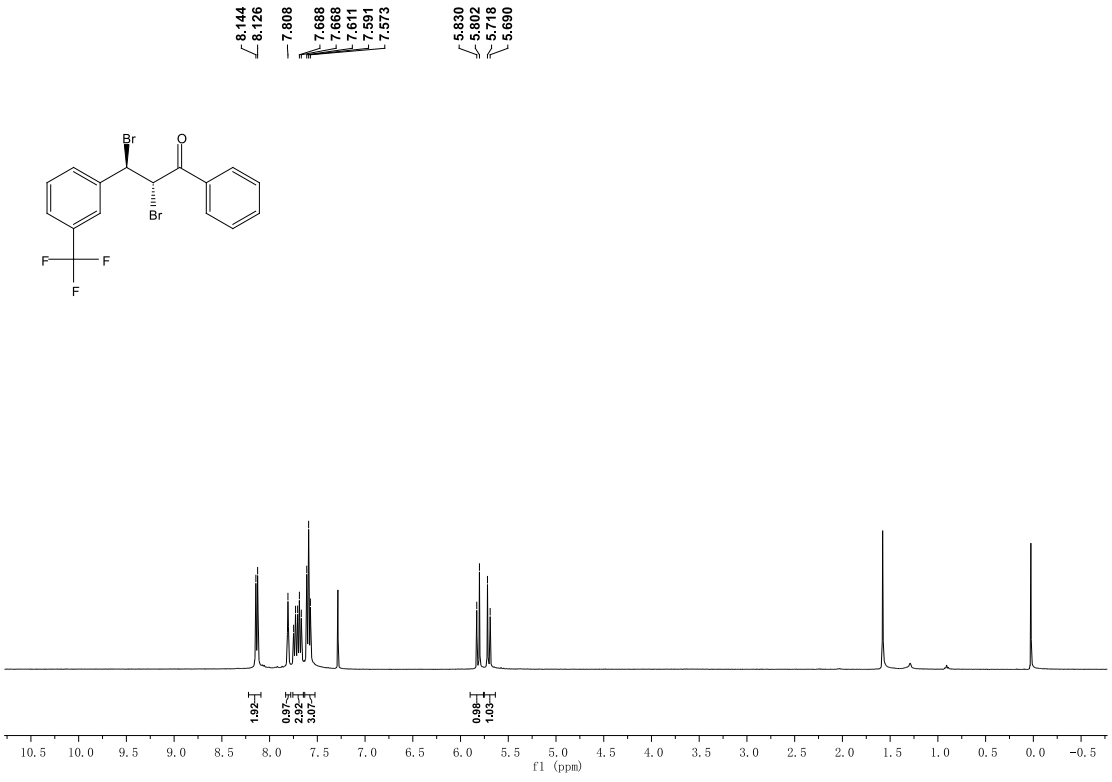
2i ^{1}H NMR



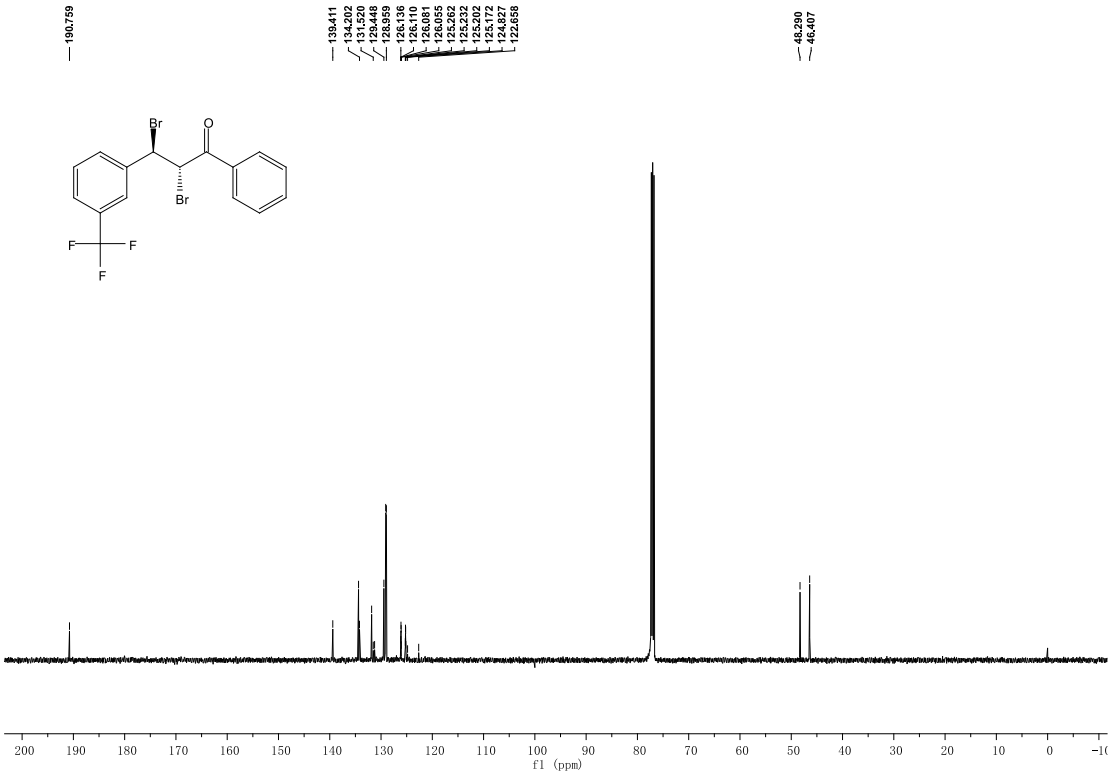
2i ^{13}C NMR



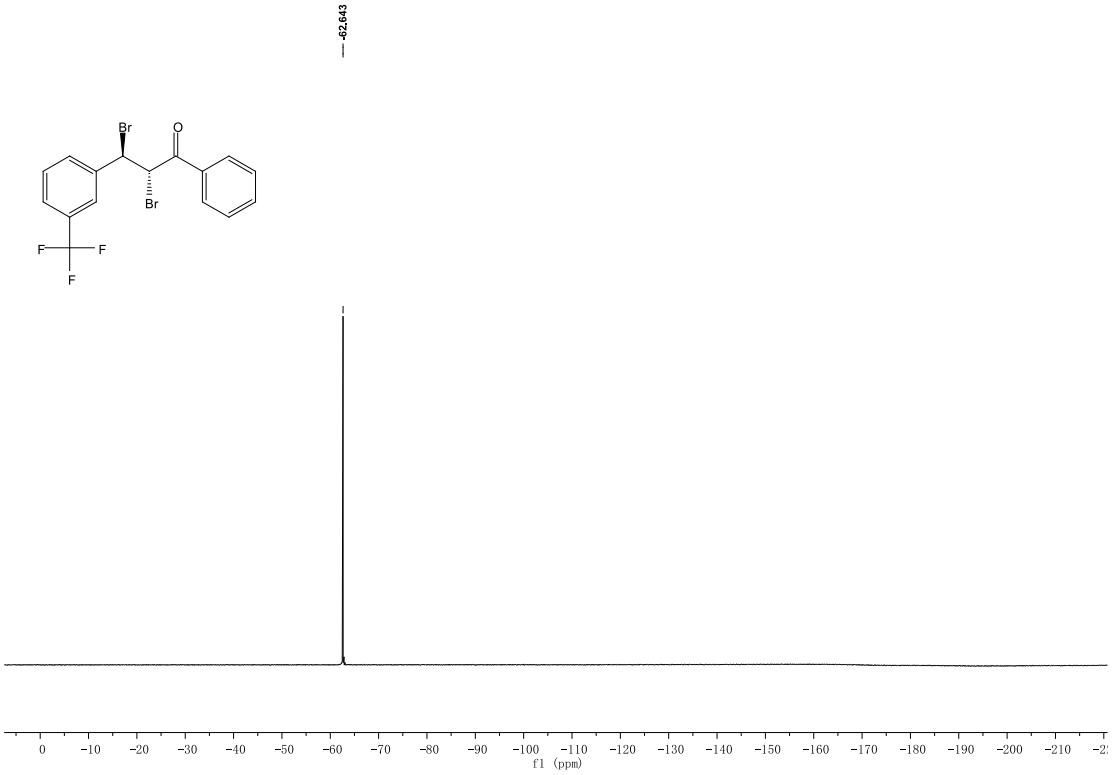
2j ^{1}H NMR



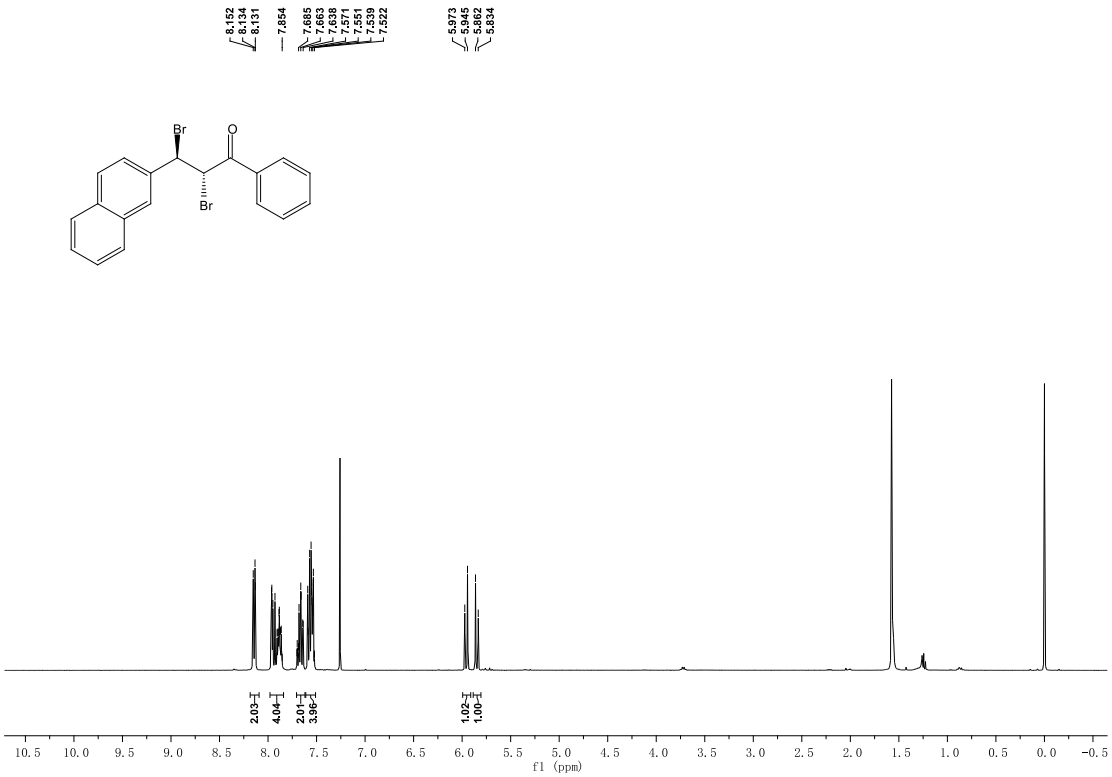
2j ^{13}C NMR



2j ^{19}F NMR



2k ^{1}H NMR



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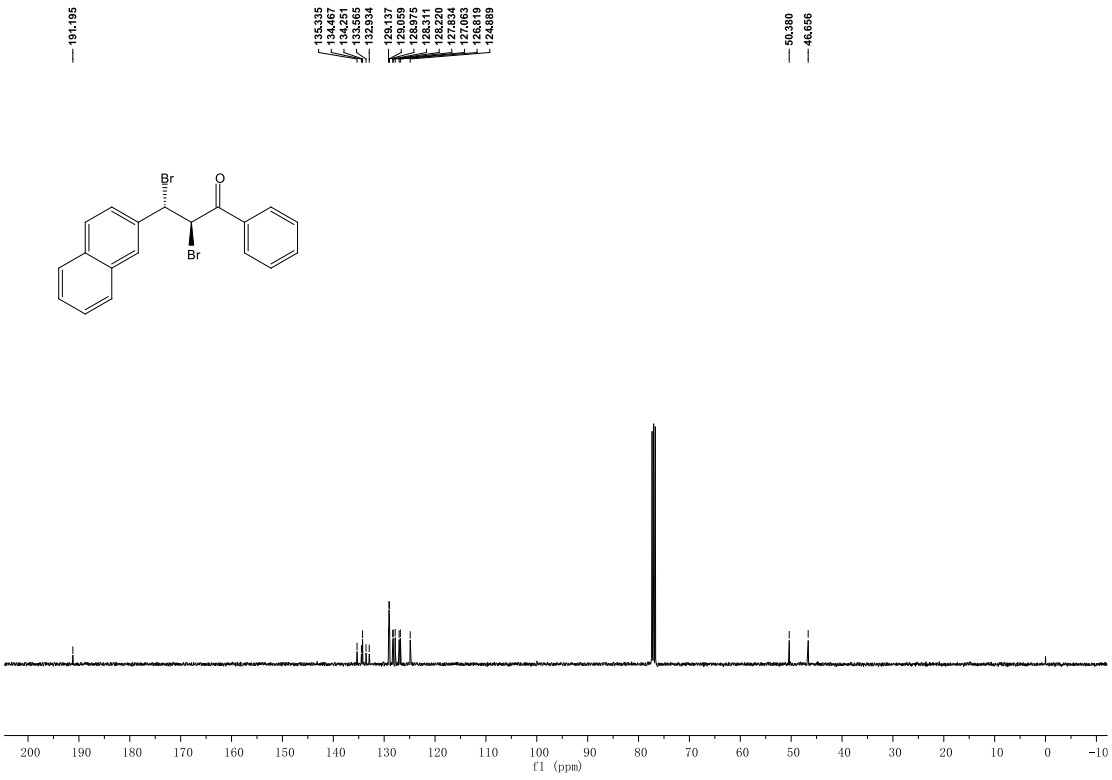
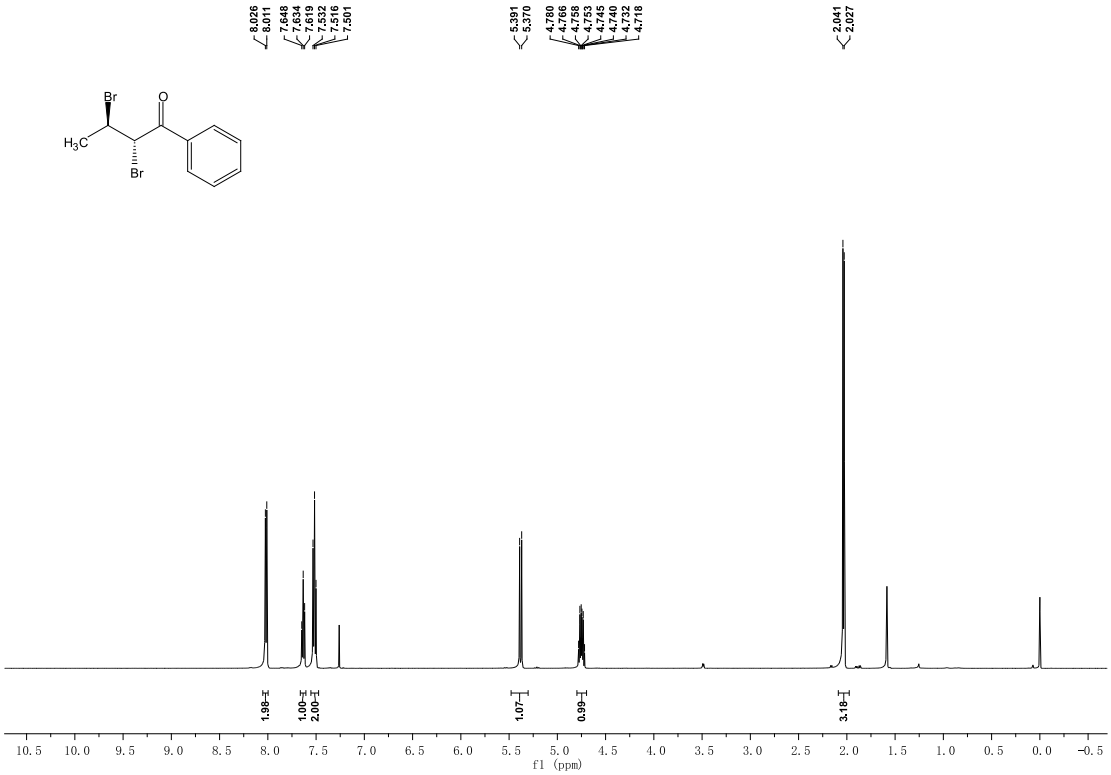
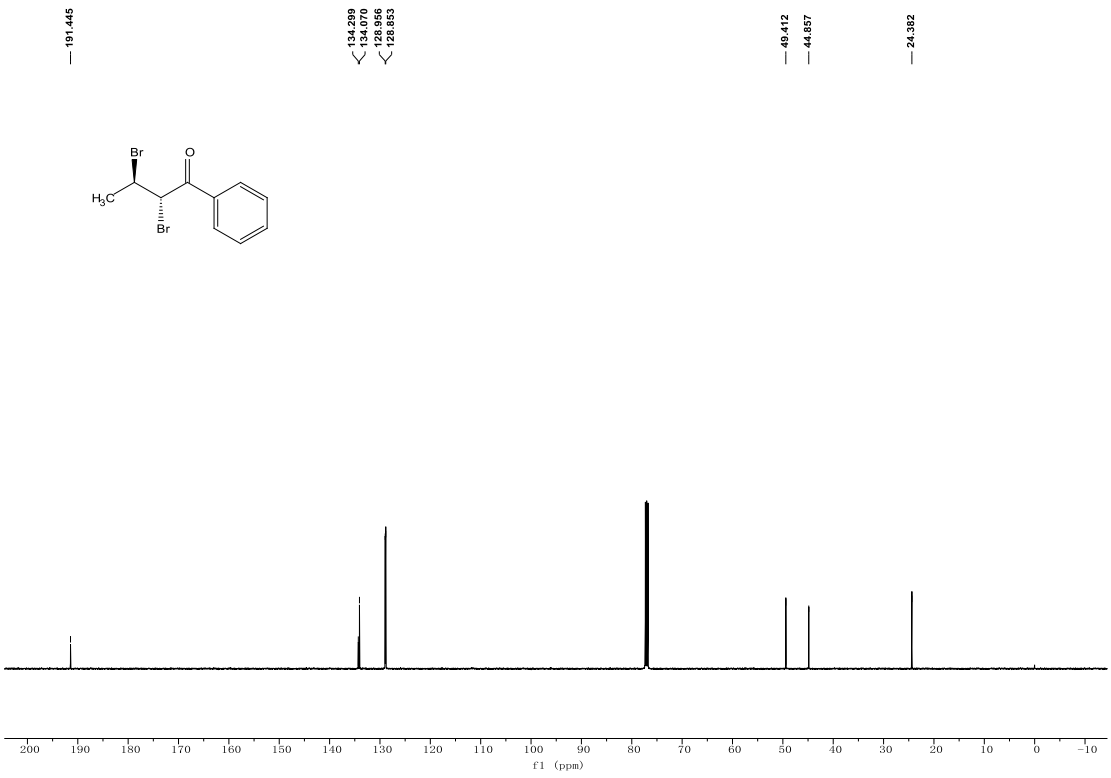


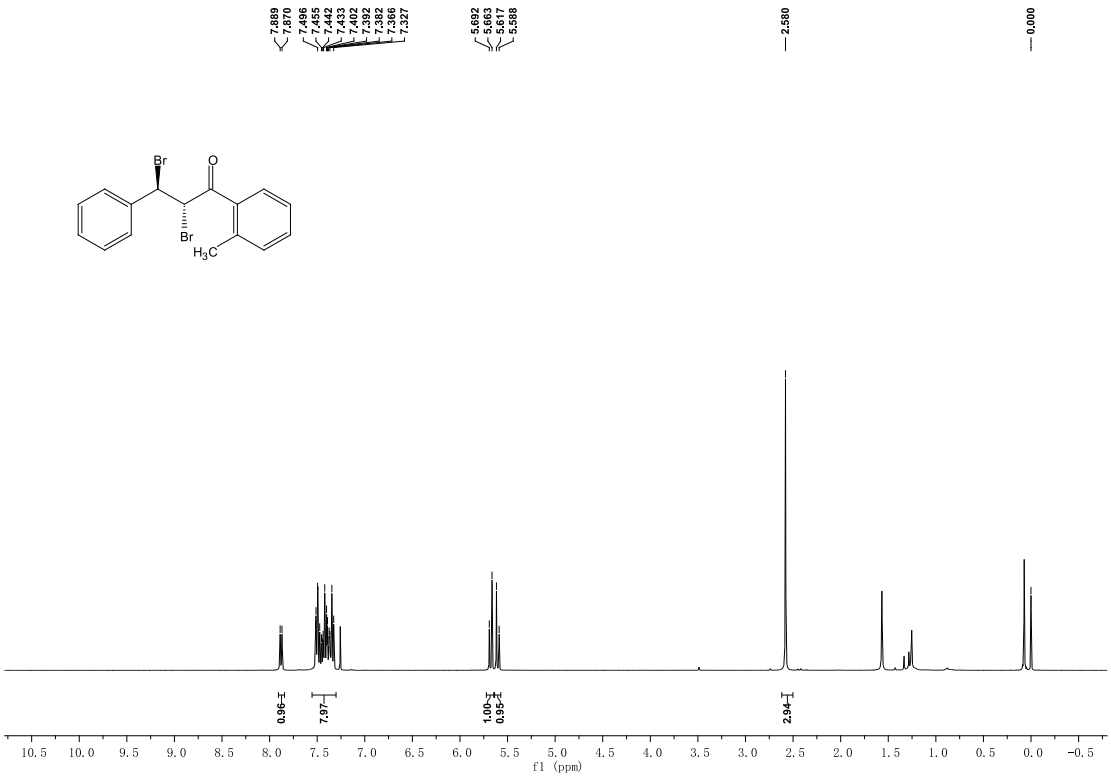
2l ^{1}H NMR



2l ^{1}C NMR



2m ^{1}H NMR



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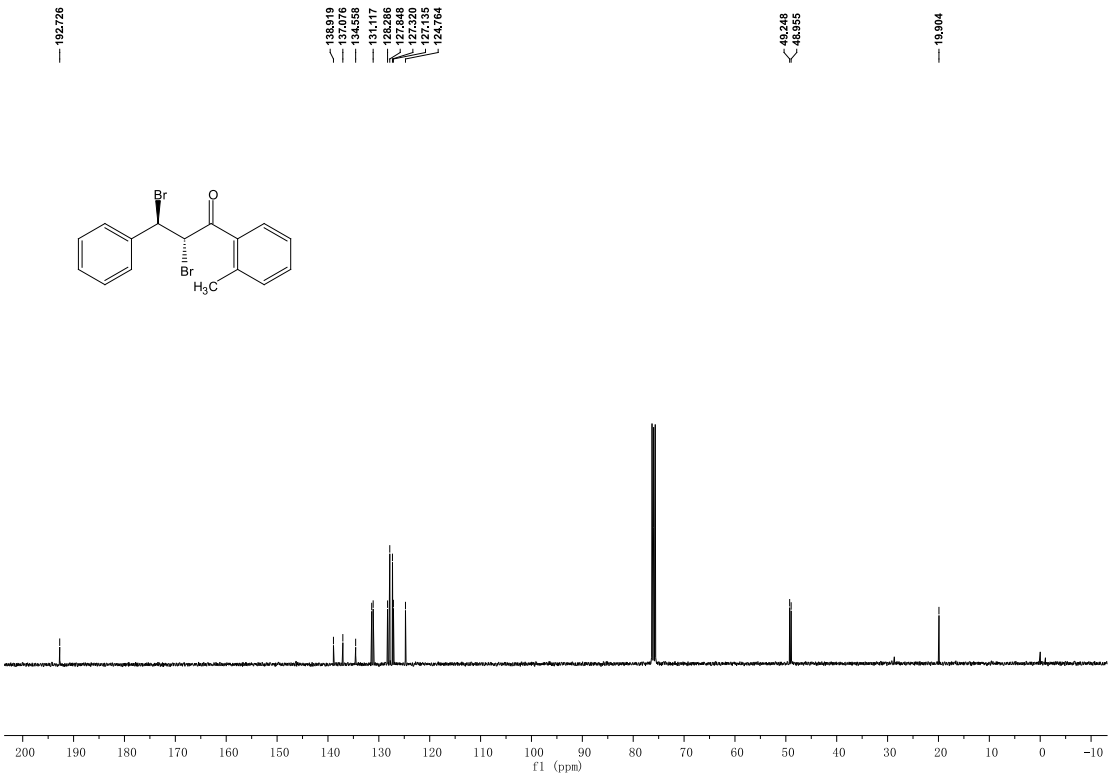

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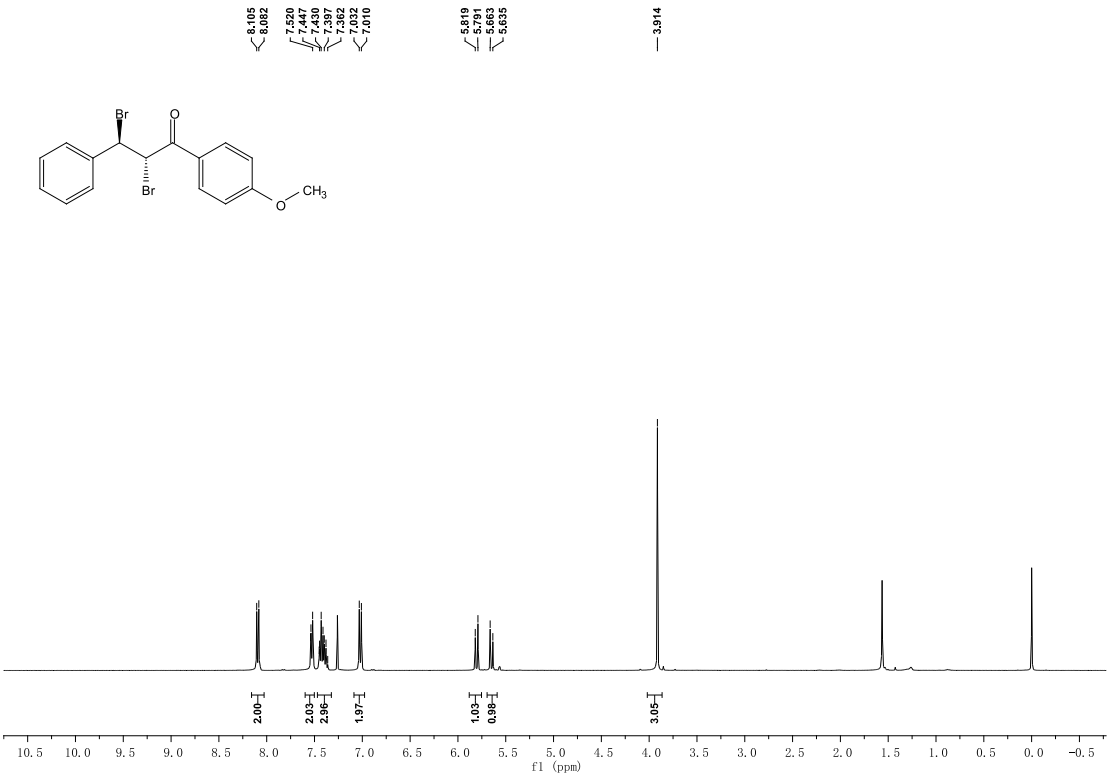

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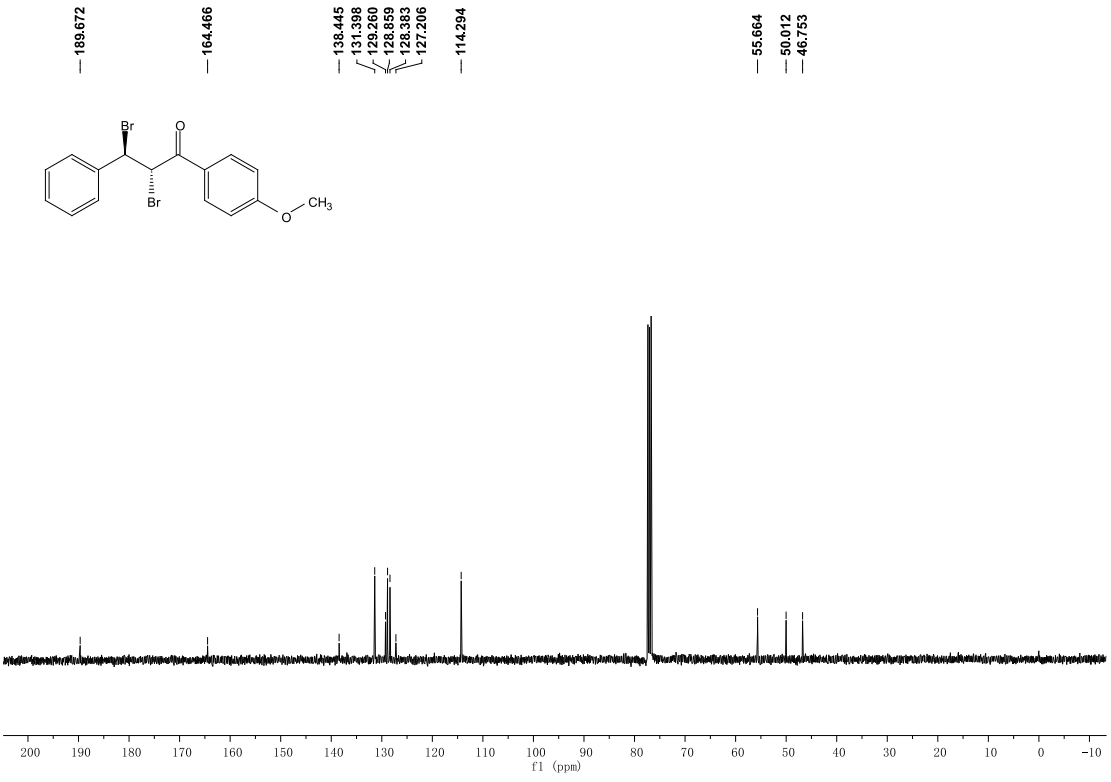
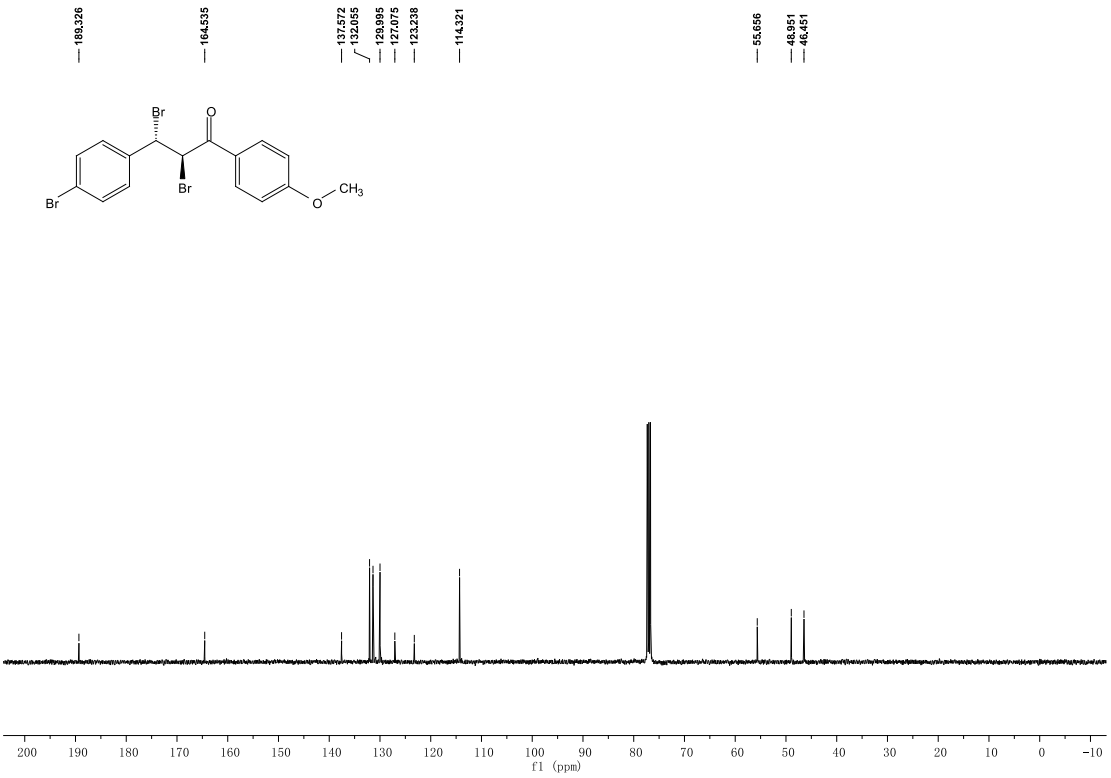
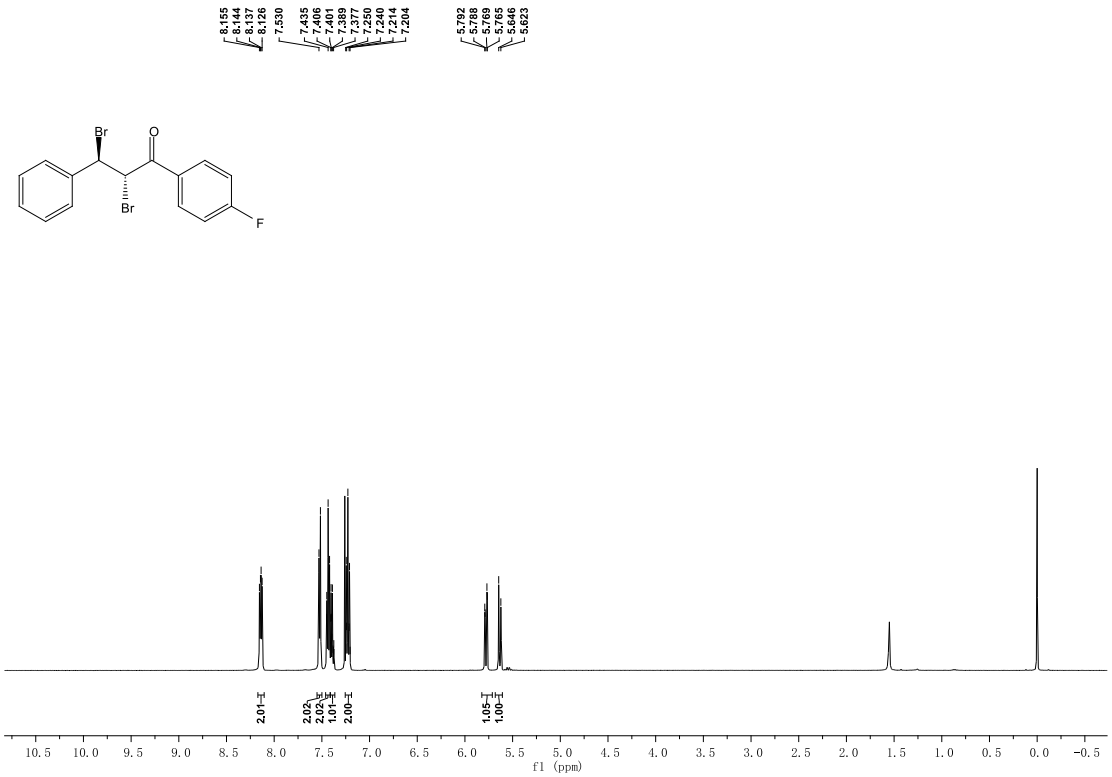


2o ^{1}H NMR

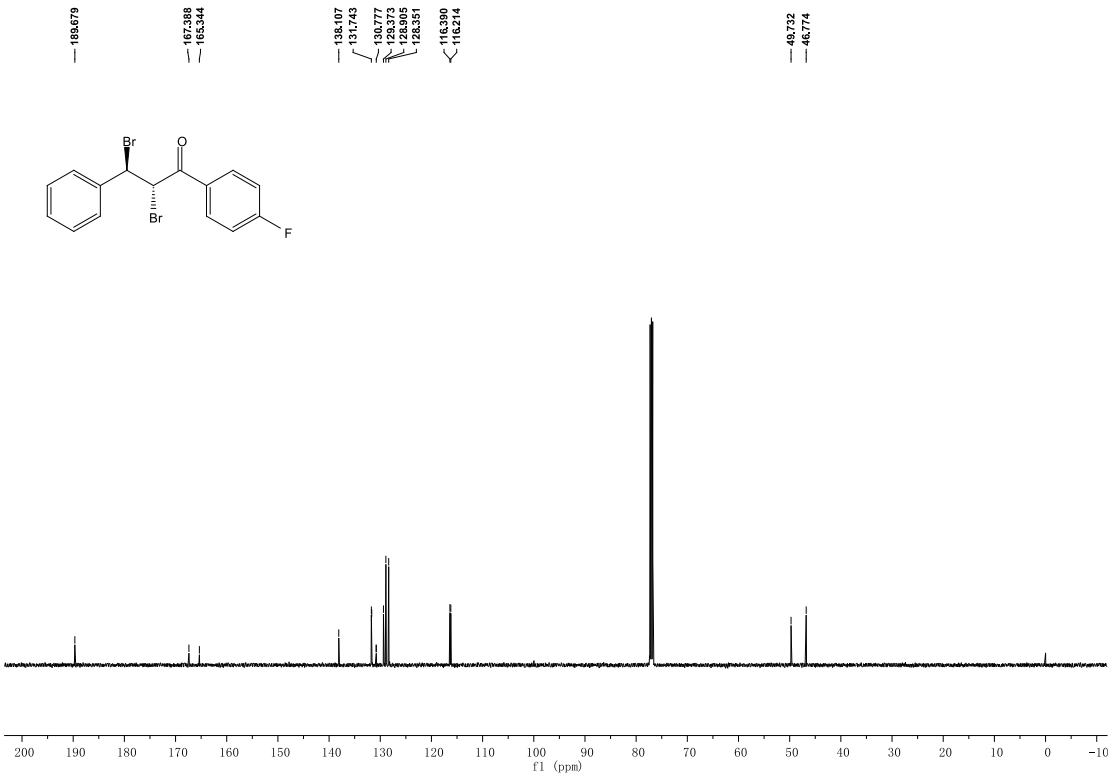
2o ^{13}C NMR



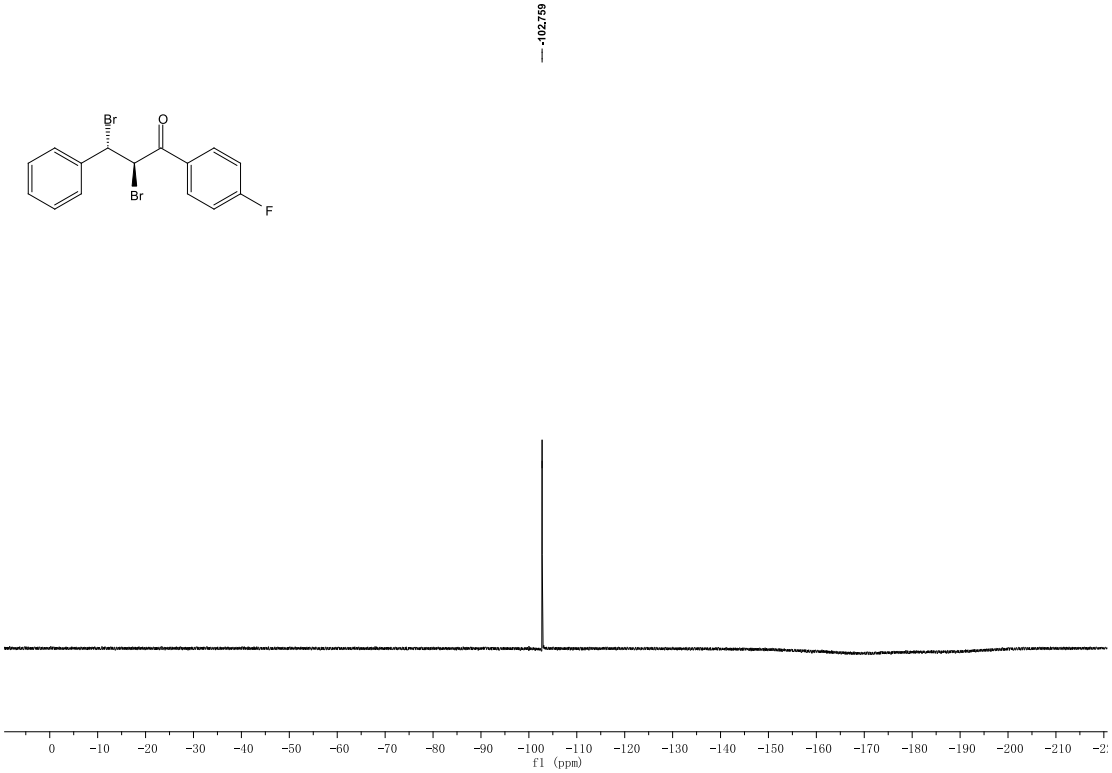
2p ^{1}H NMR



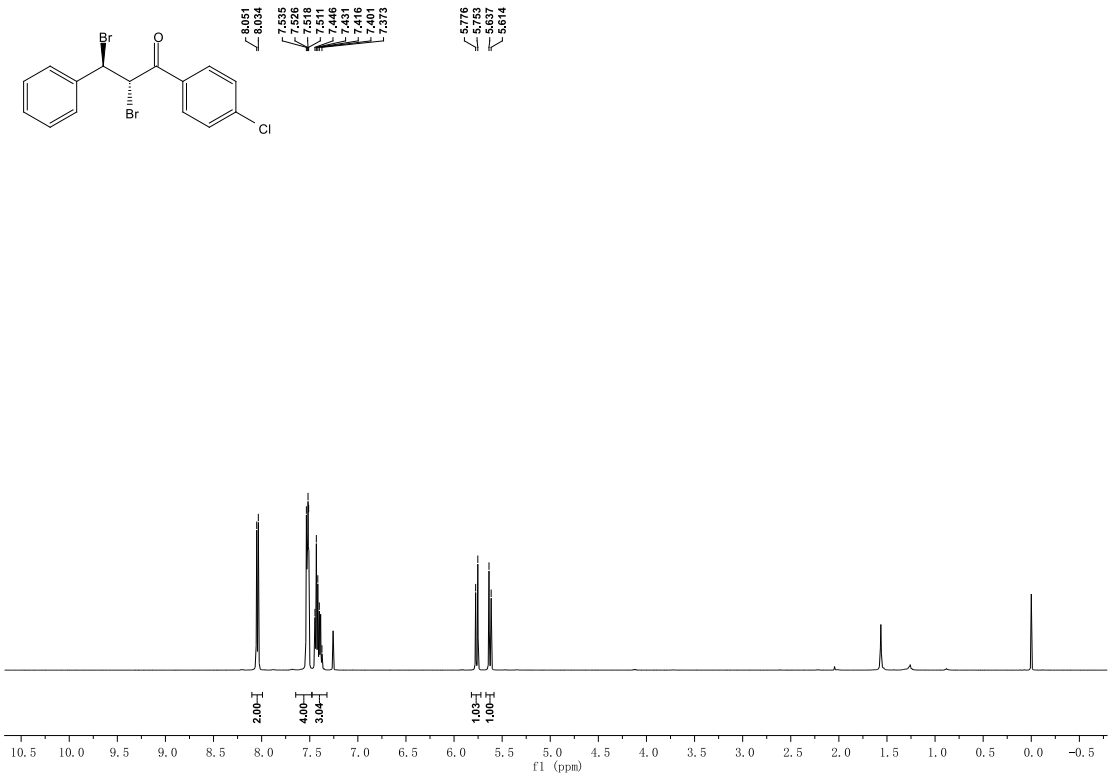
2p ^{13}C NMR



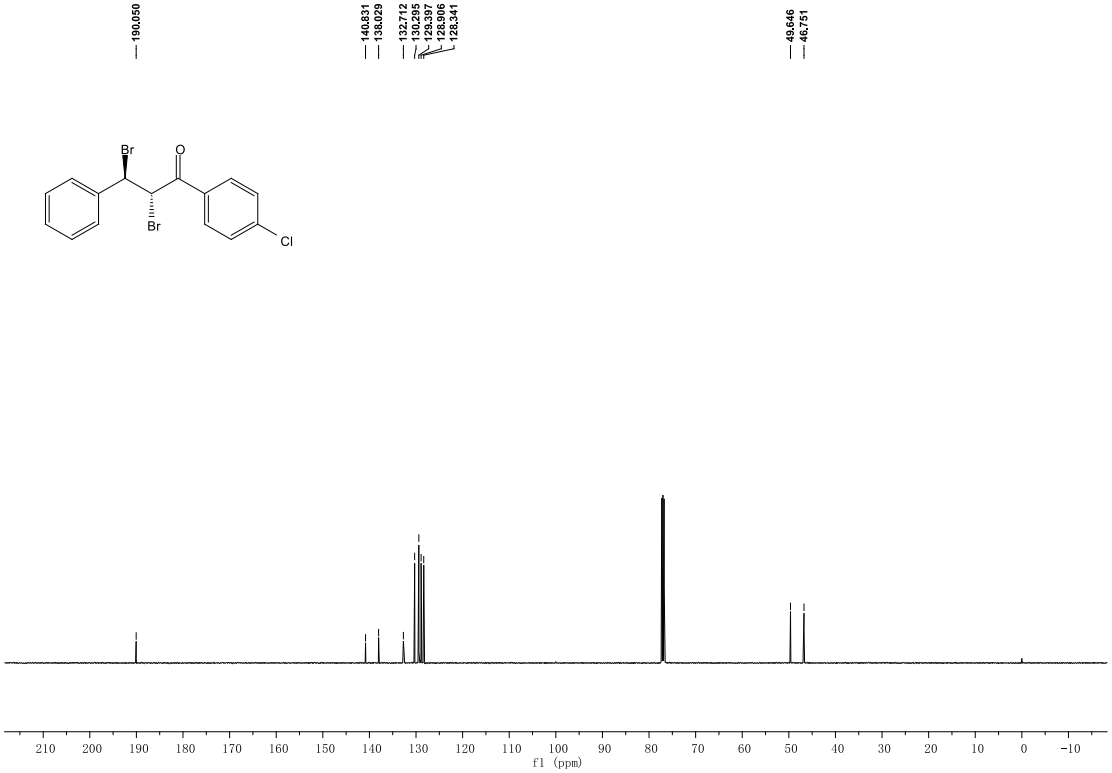
2p ^{19}F NMR



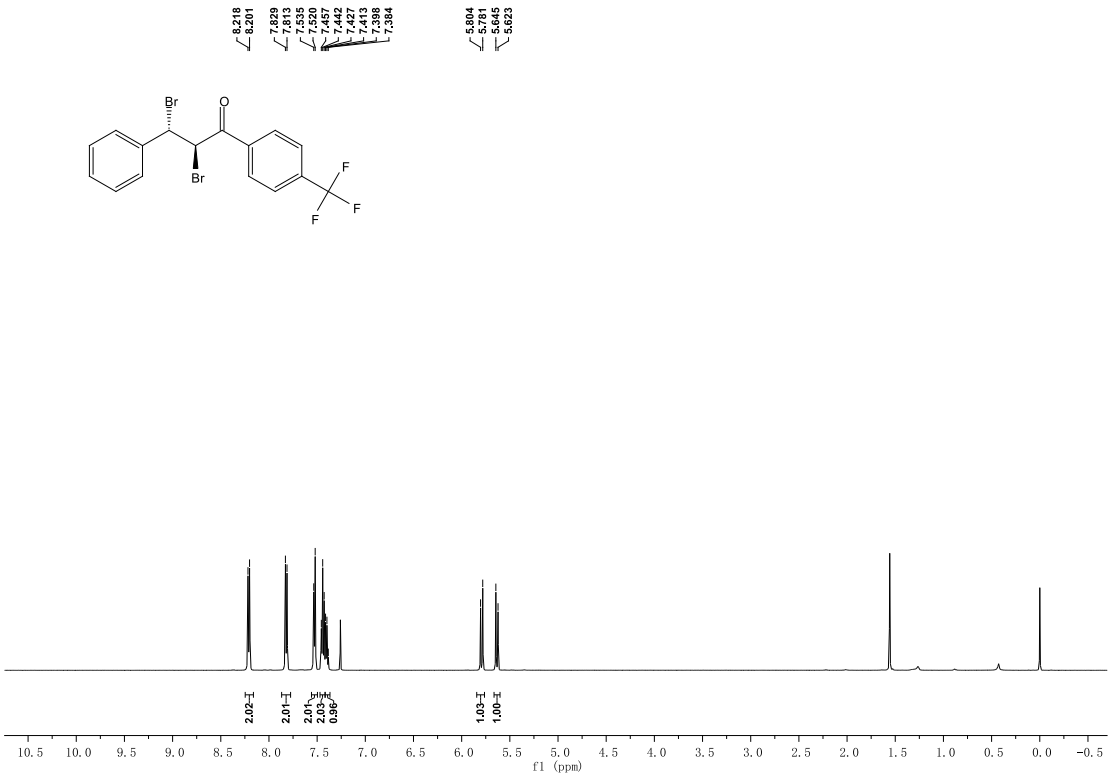
2q ^{1}H NMR



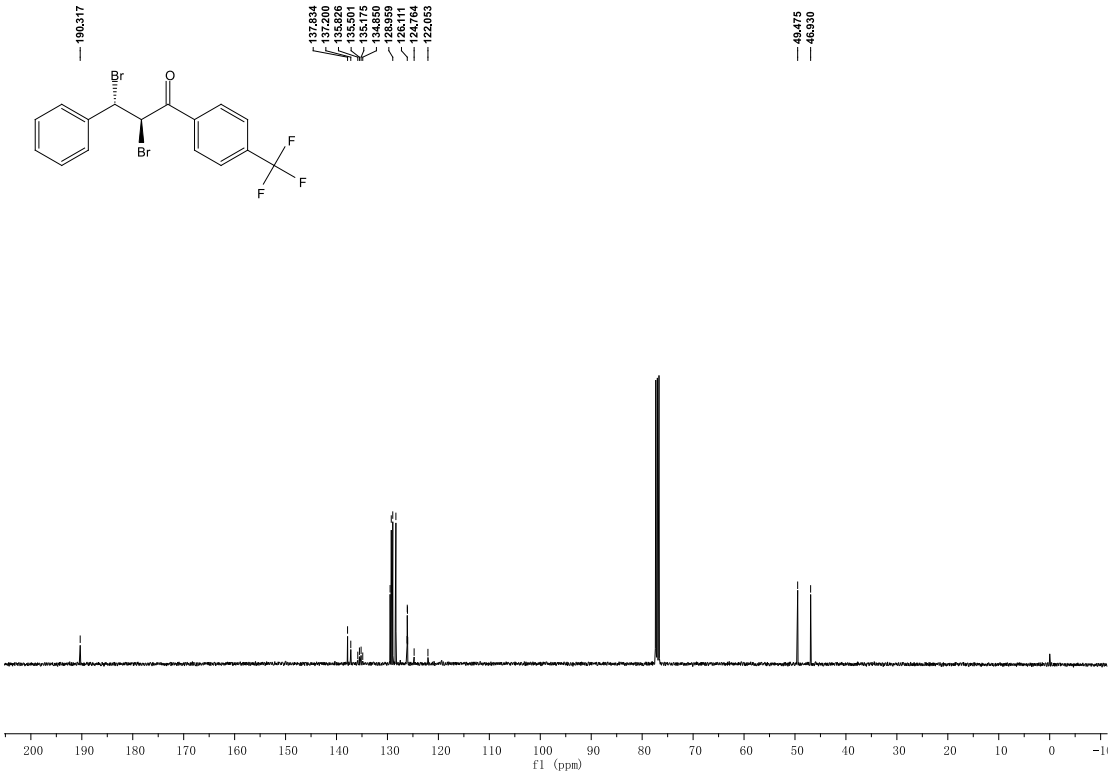
2q ^{13}C NMR



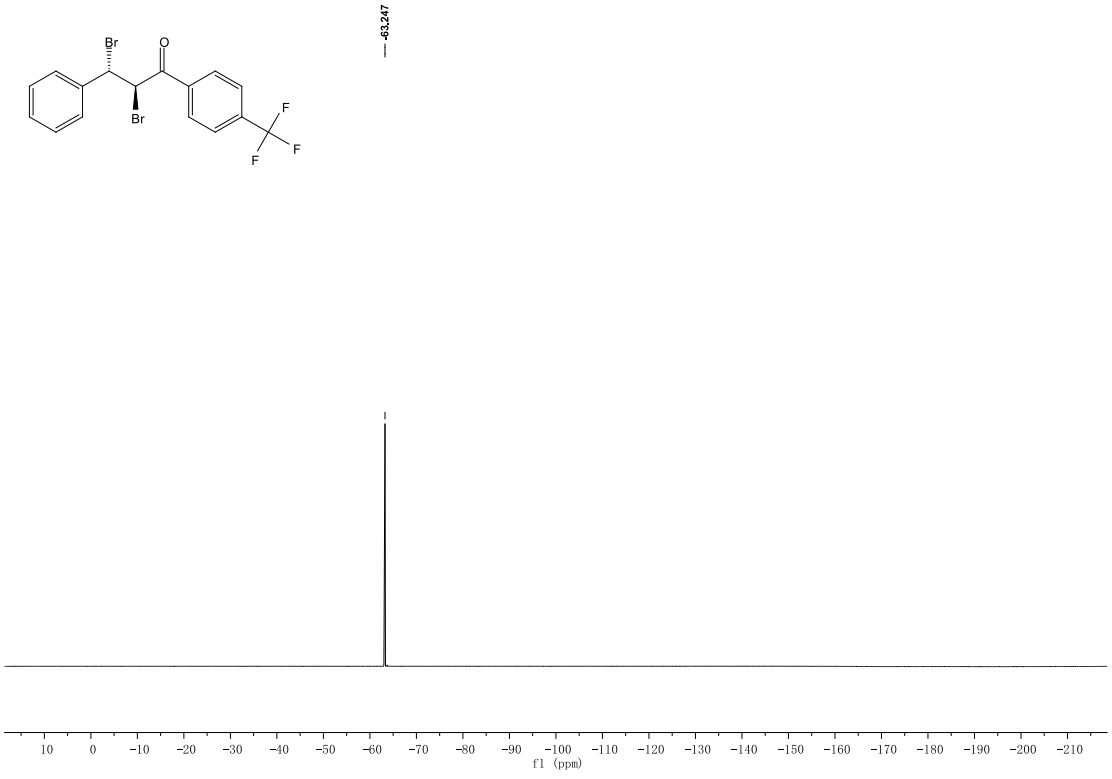
2r ^{1}H NMR



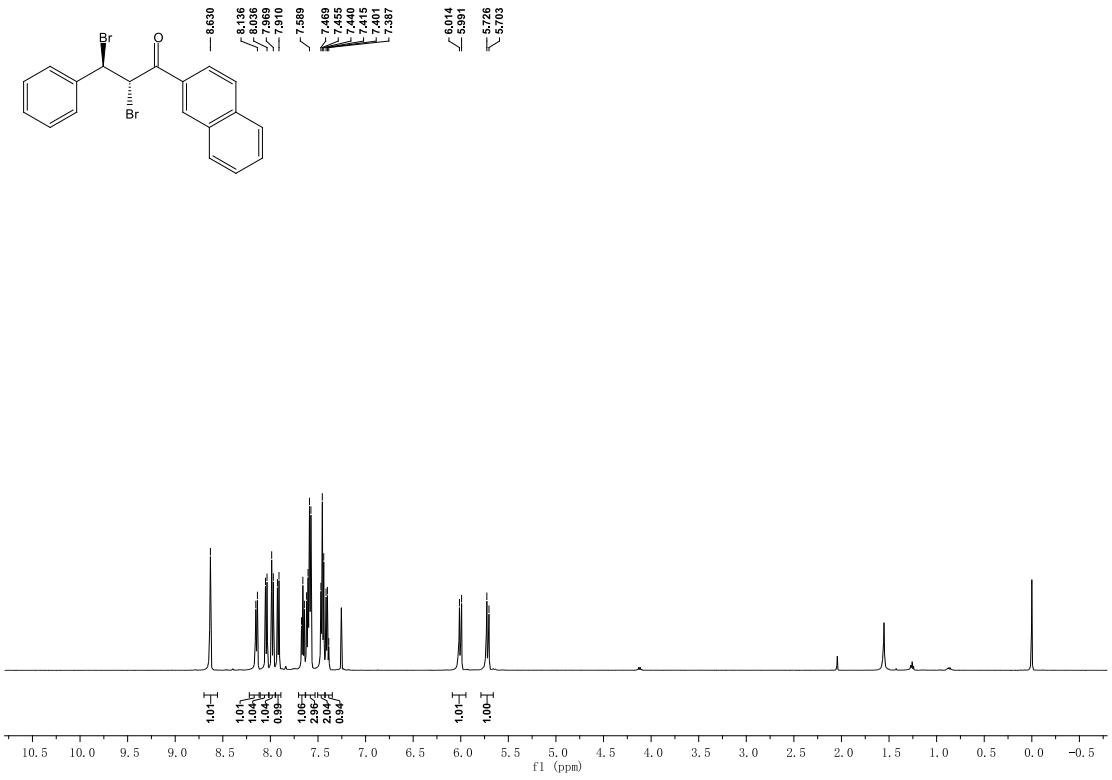
2r ^{13}C NMR



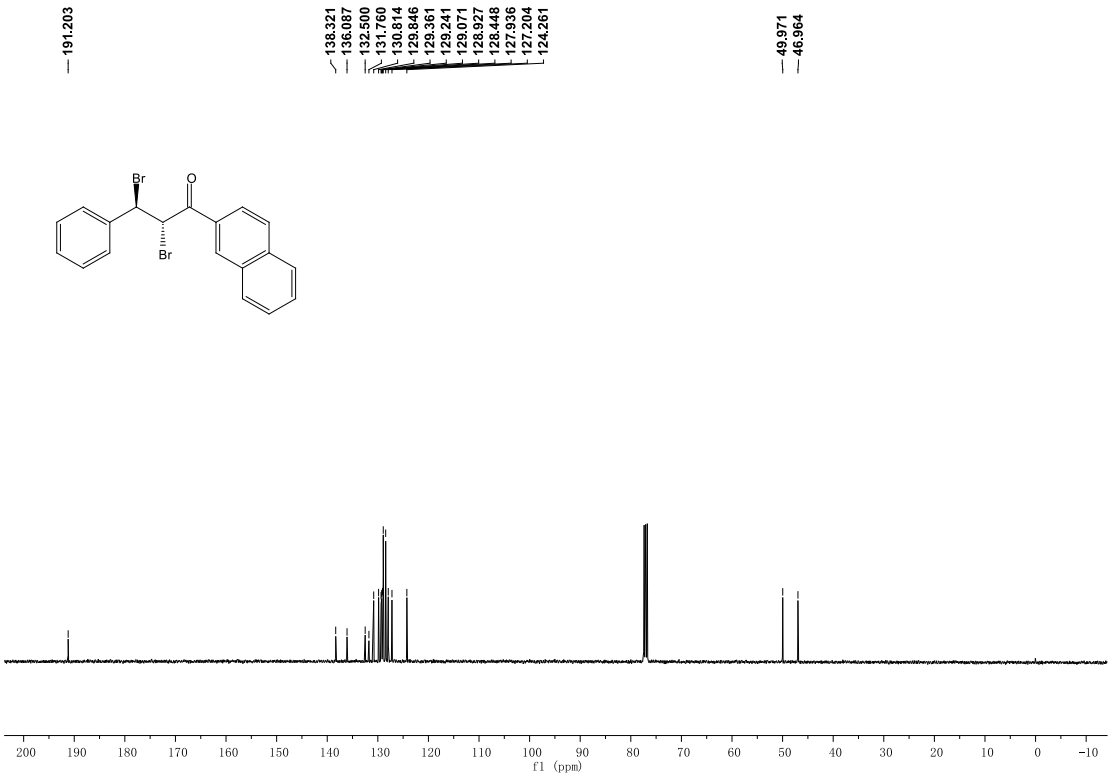
2r ^{19}F NMR



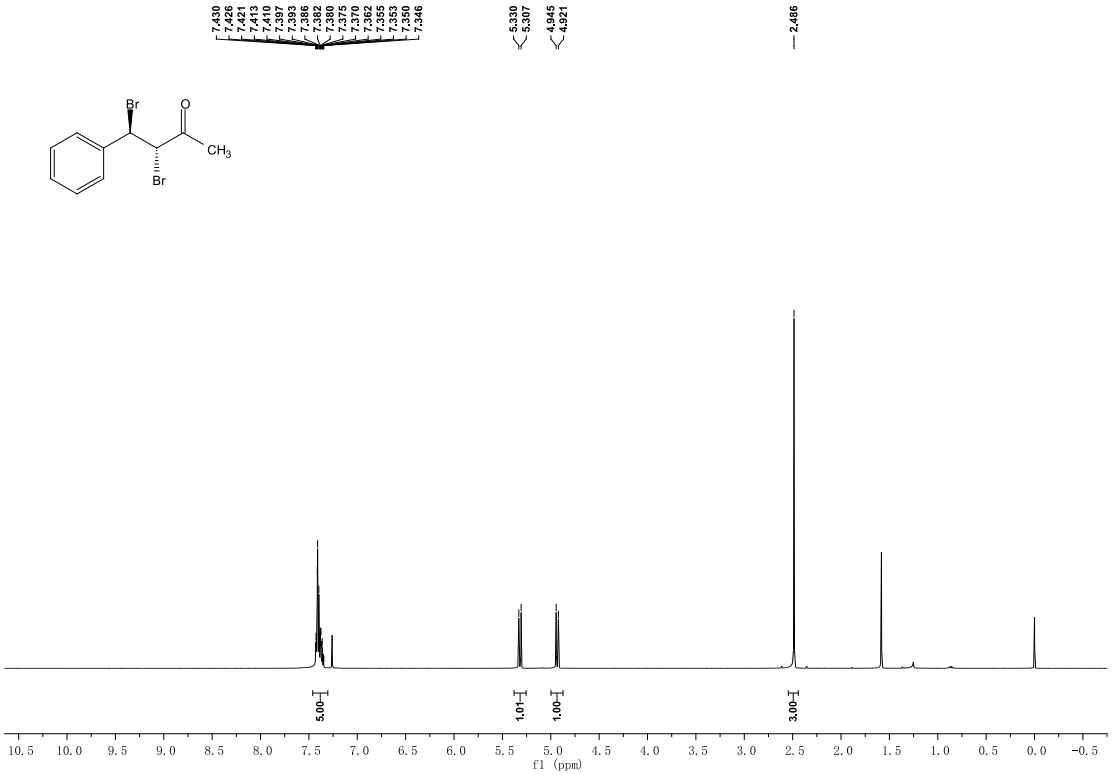
2s ^{1}H NMR



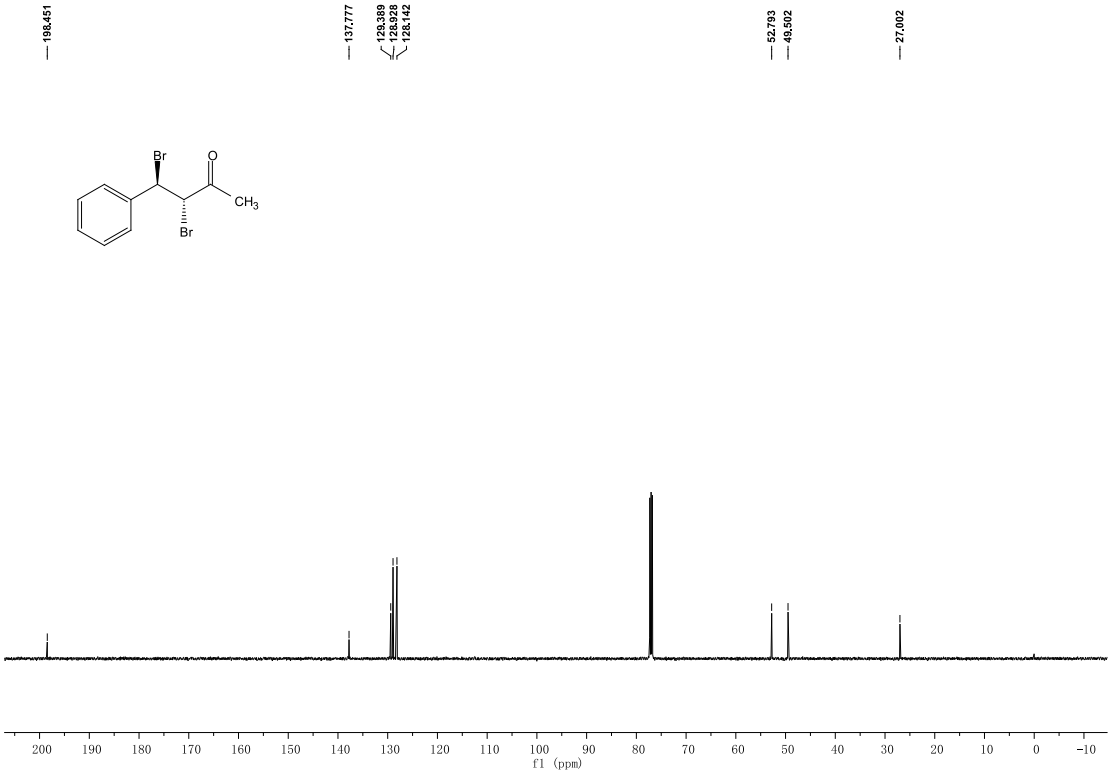
2s ^{13}C NMR



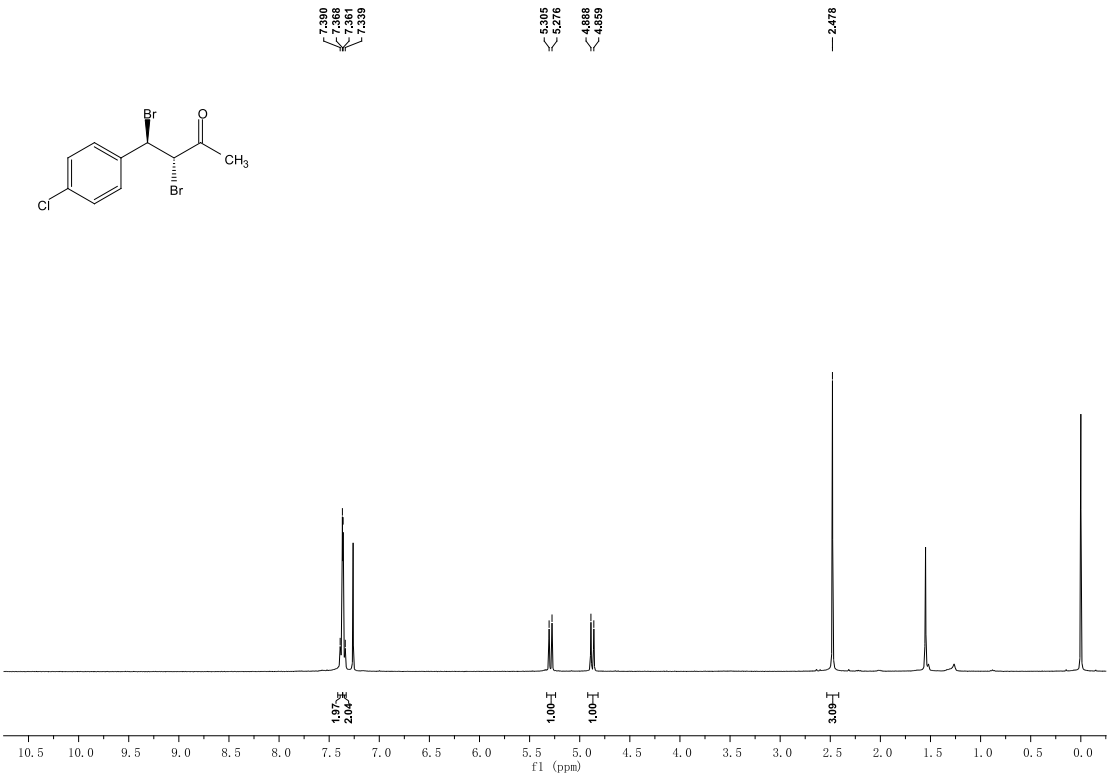
2t ^{1}H NMR



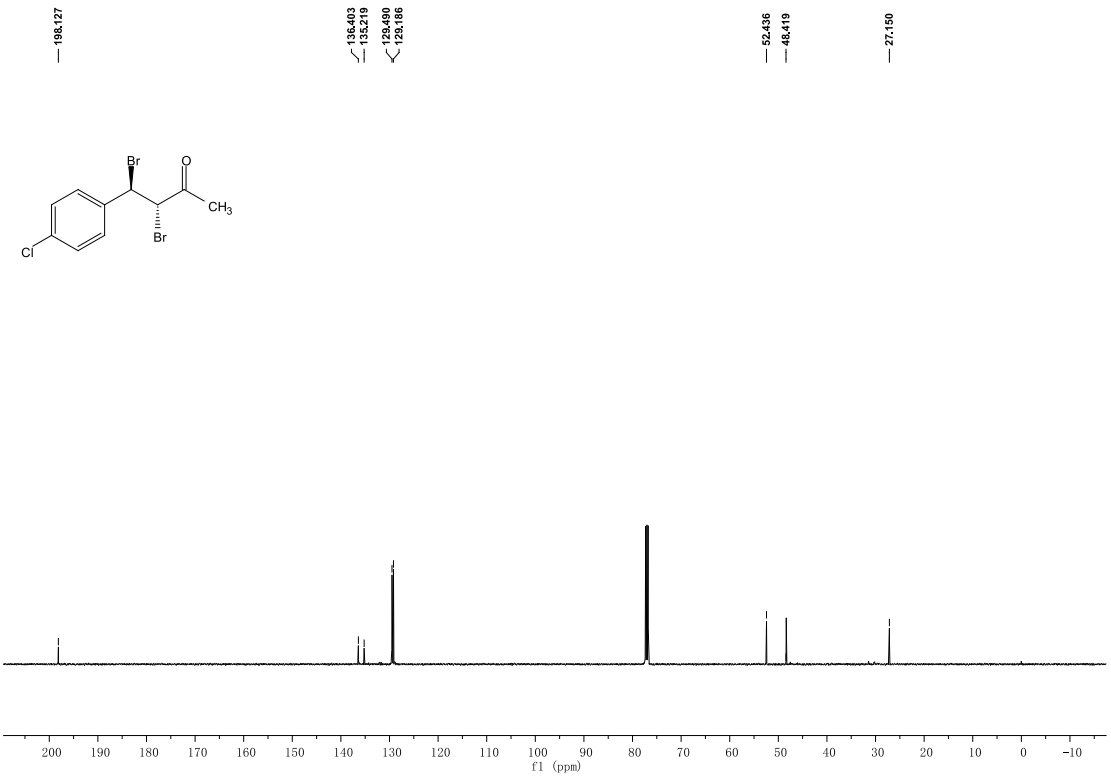
2t ^{1}H NMR



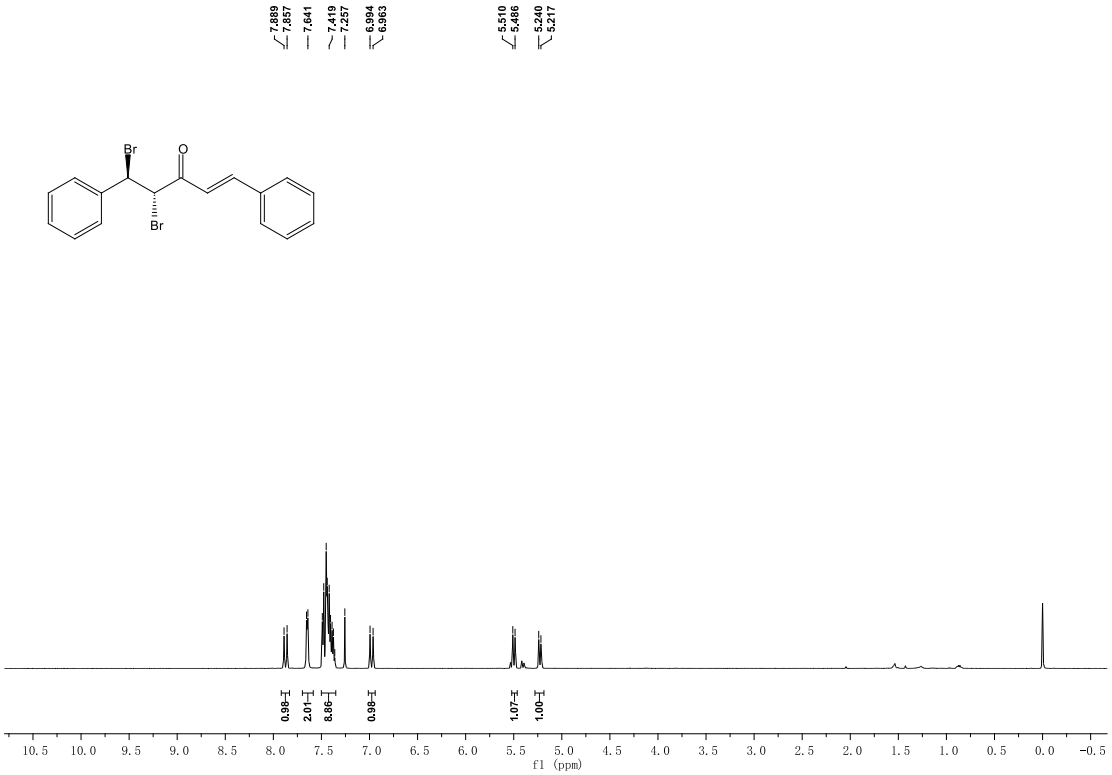
2u ^{1}H NMR



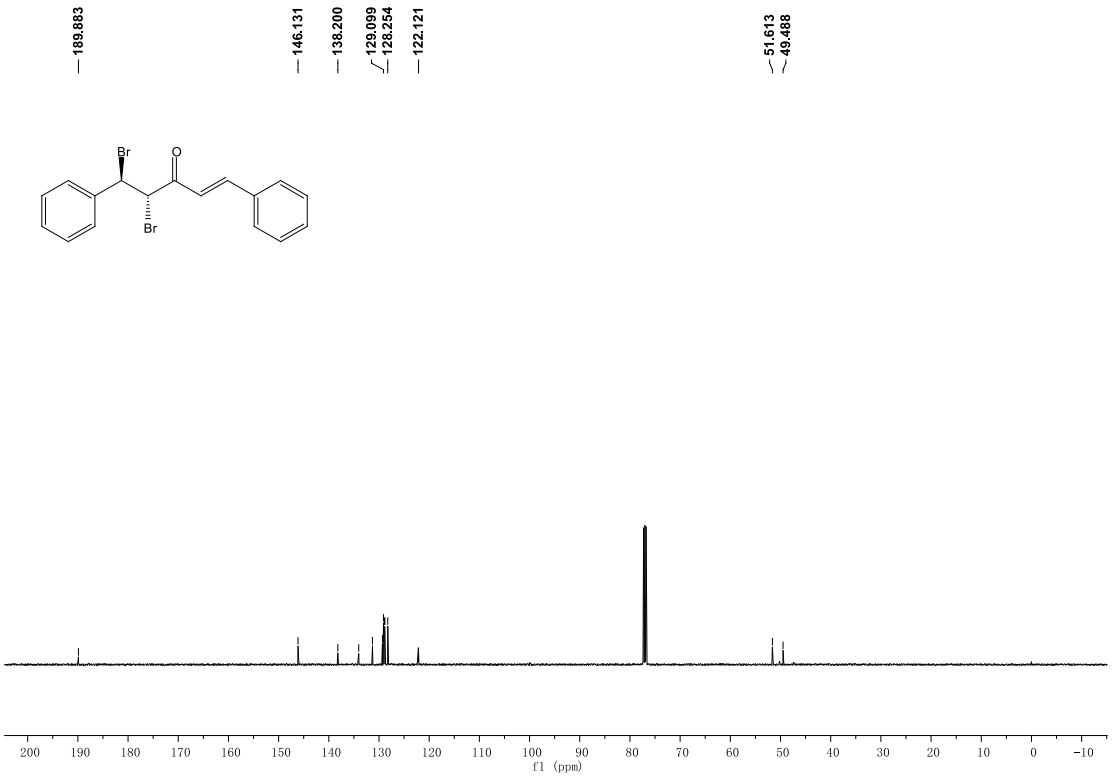
2u ^{13}C NMR



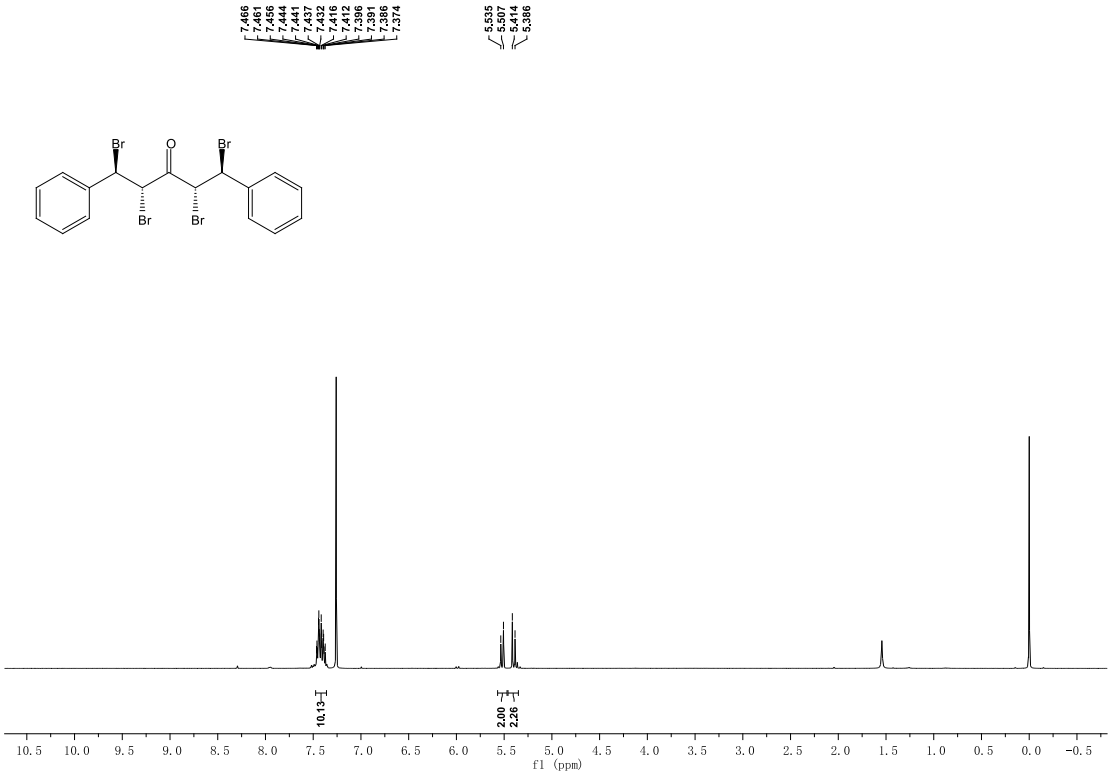
2v ^{1}H NMR



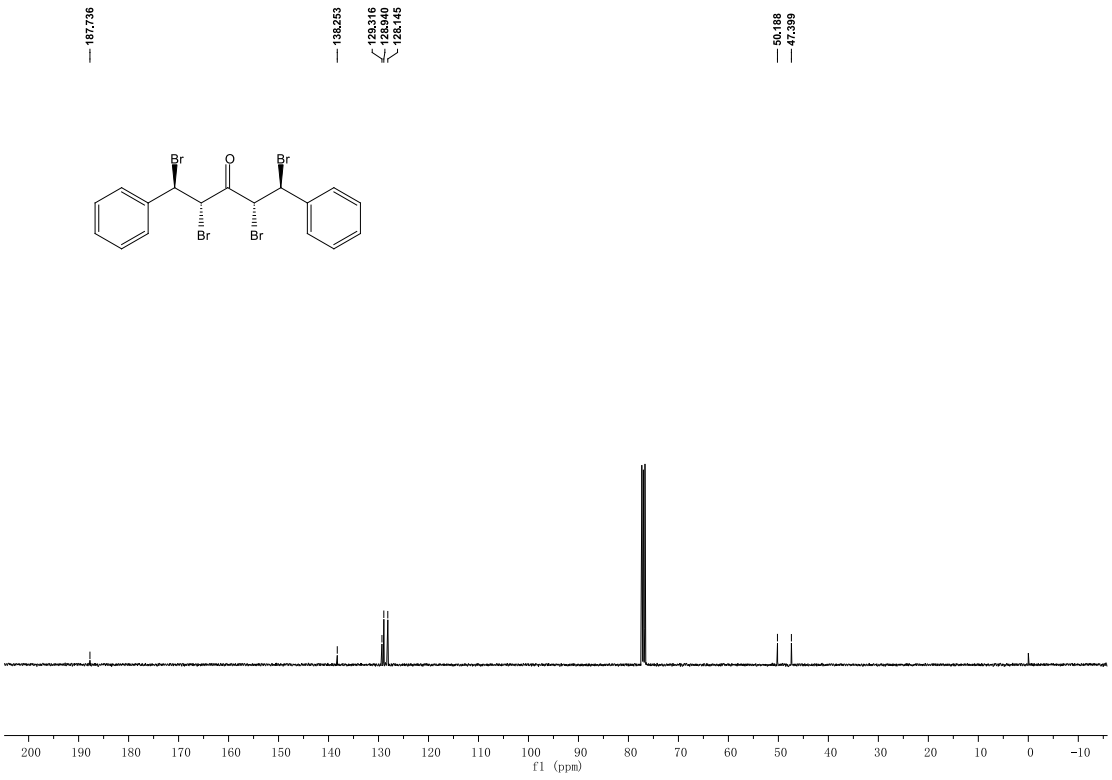
2v ^{13}C NMR



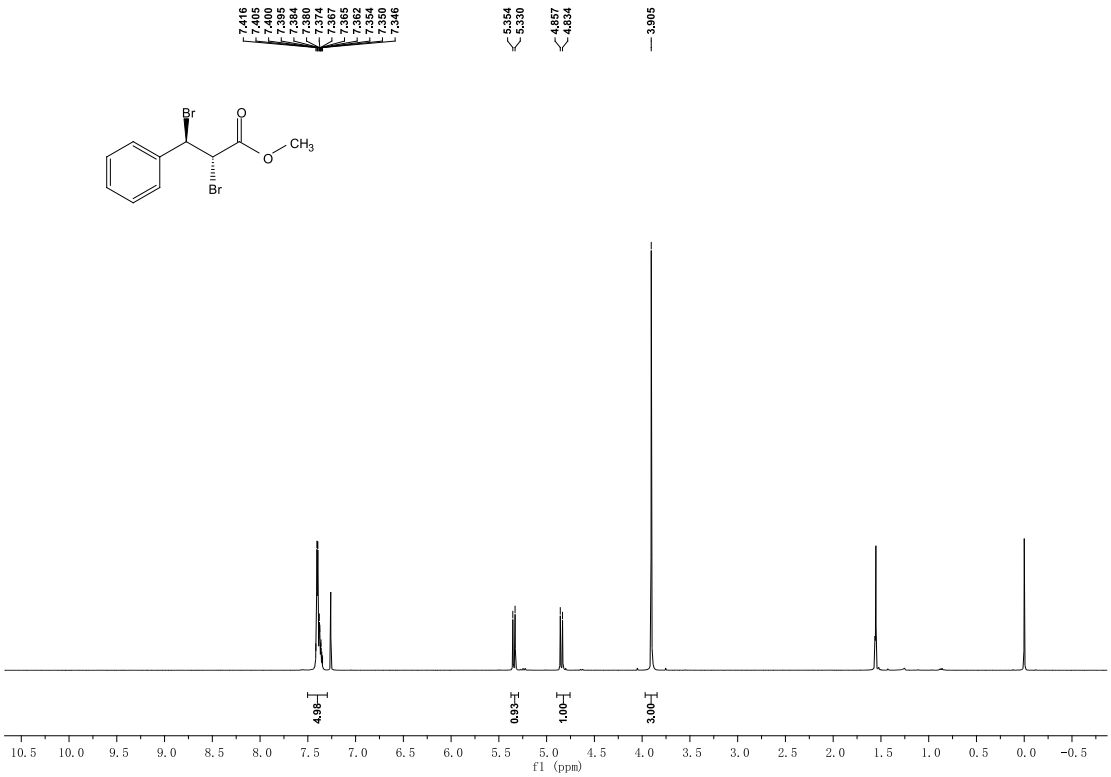
2w ^{1}H NMR



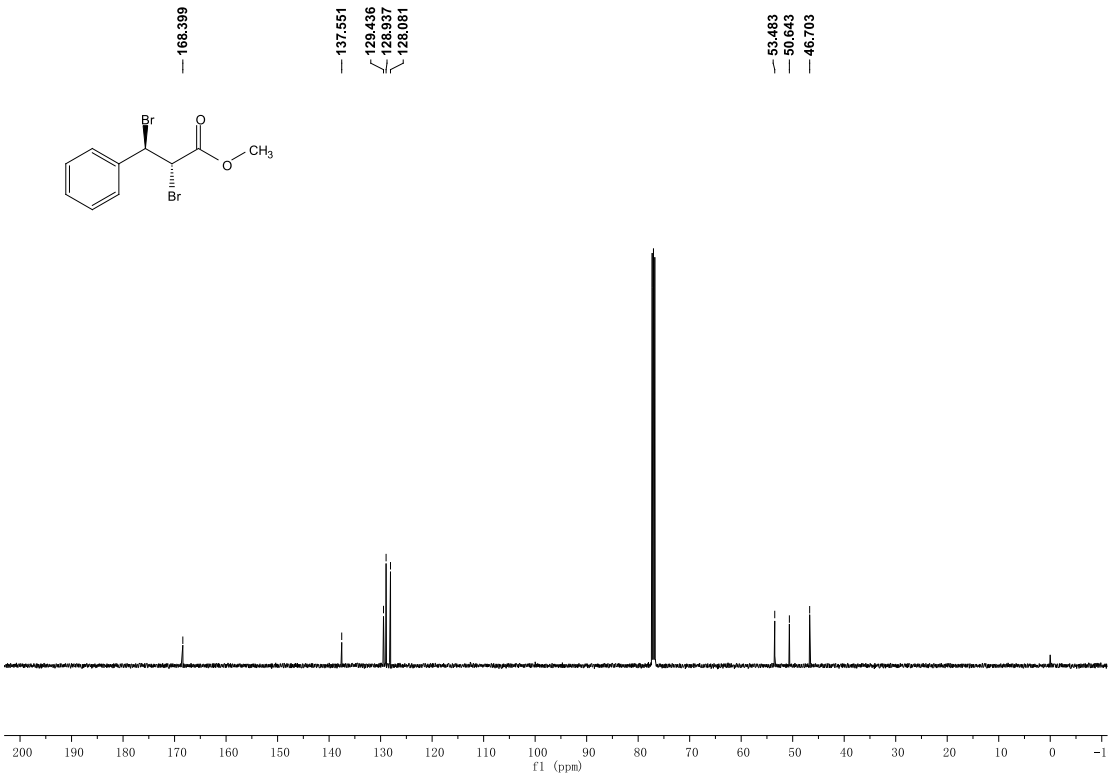
2w ^{13}C NMR



4a ^{1}H NMR



4a ^{13}C NMR



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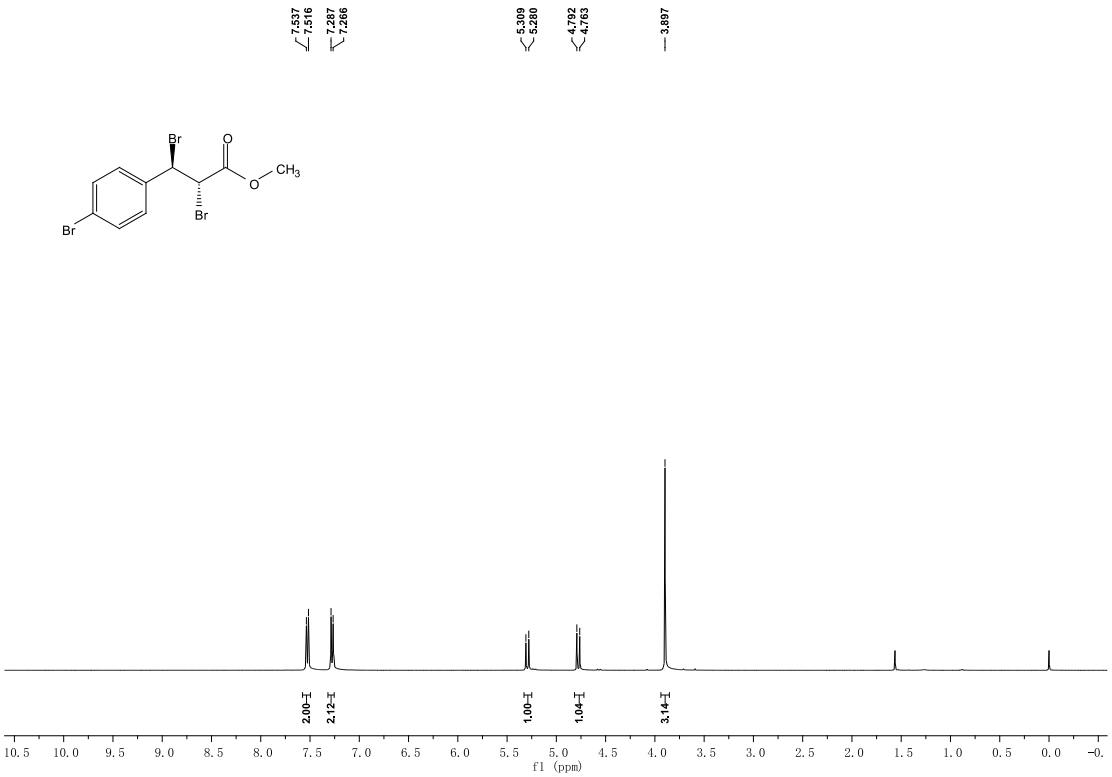

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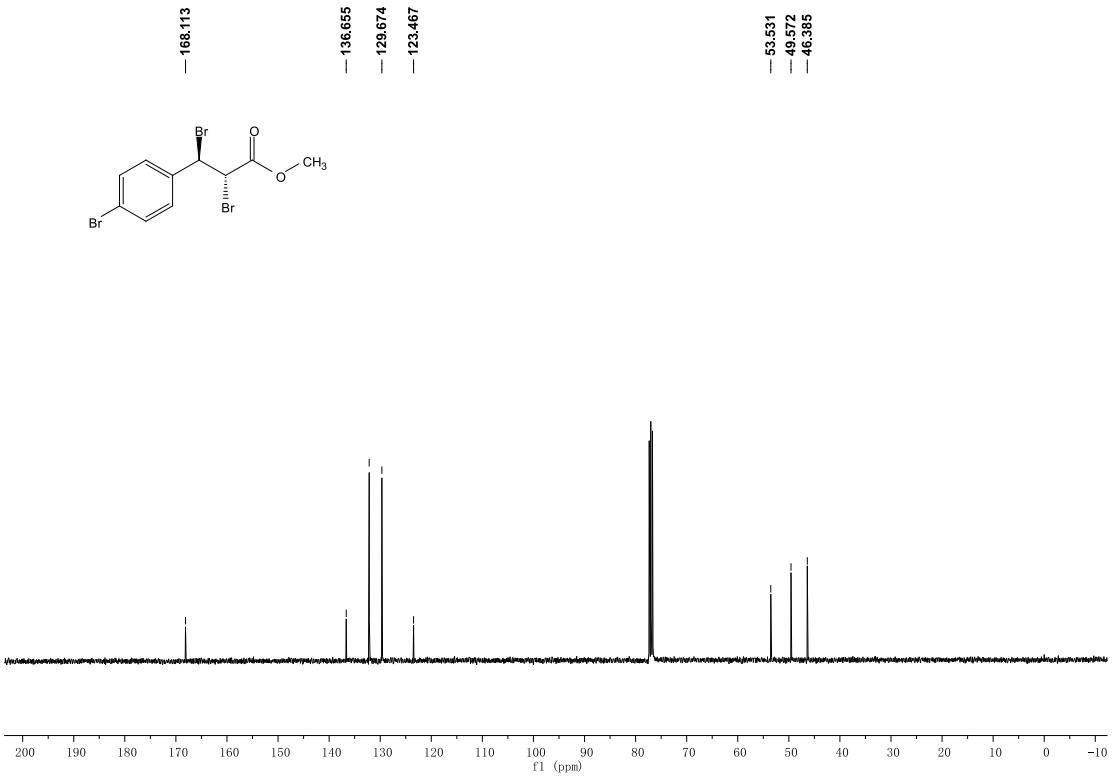

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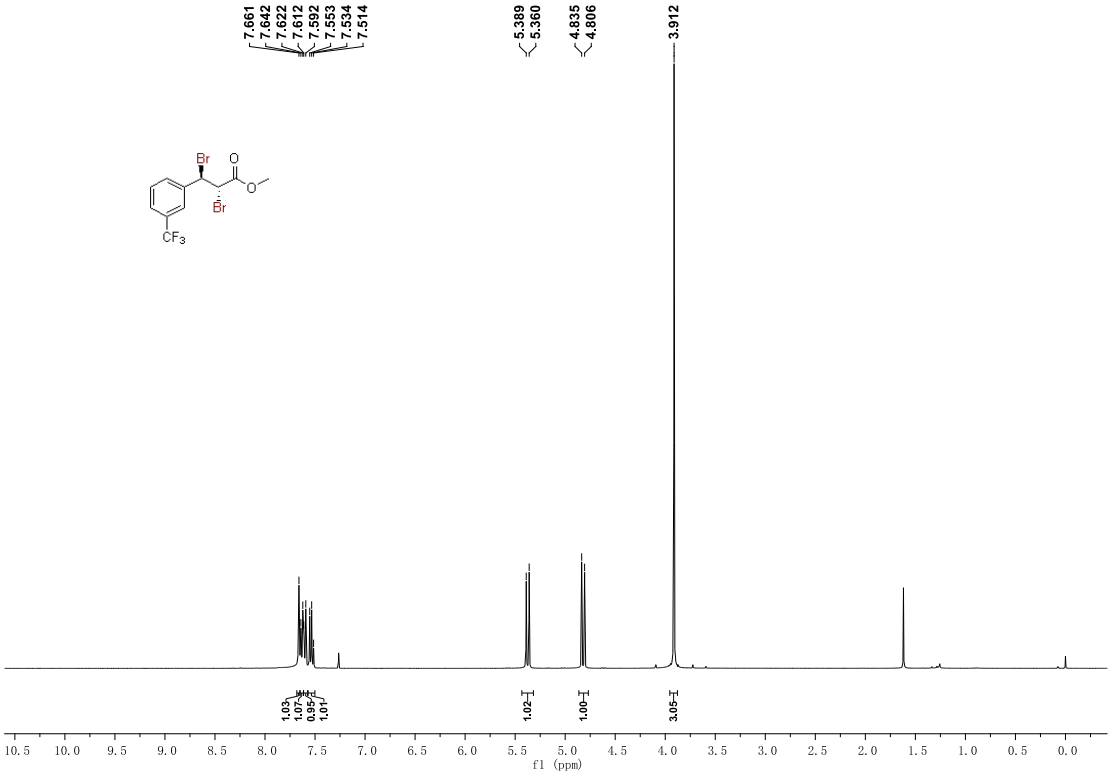

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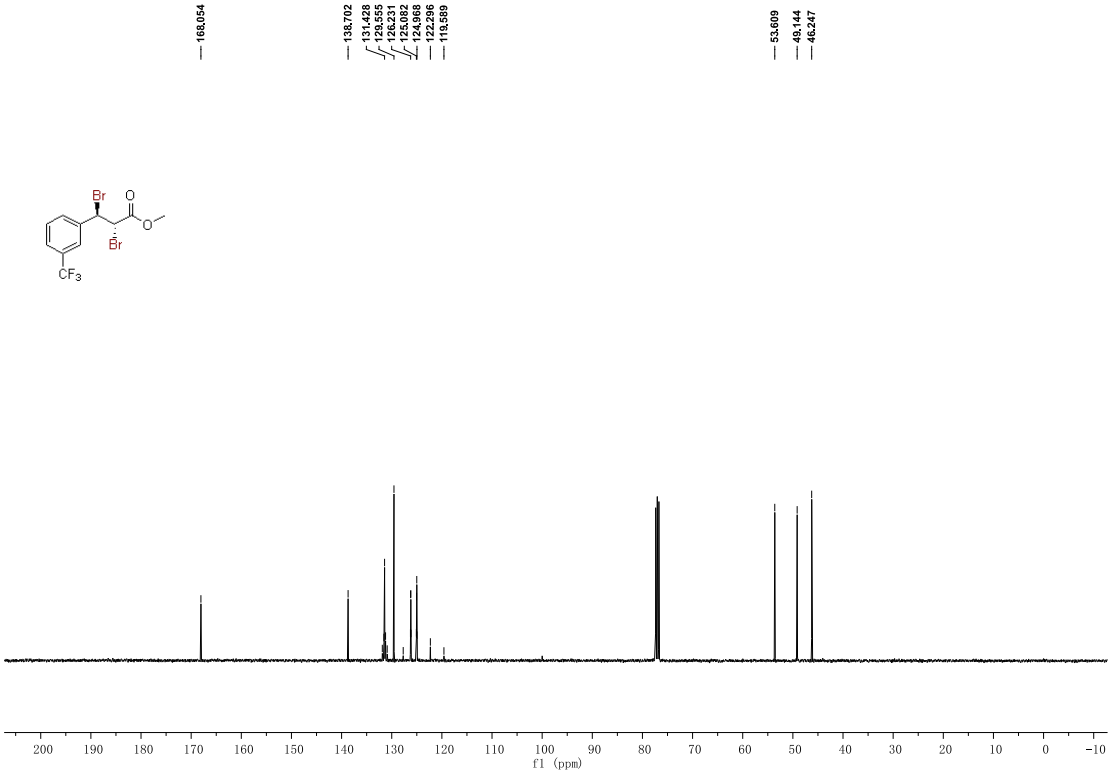

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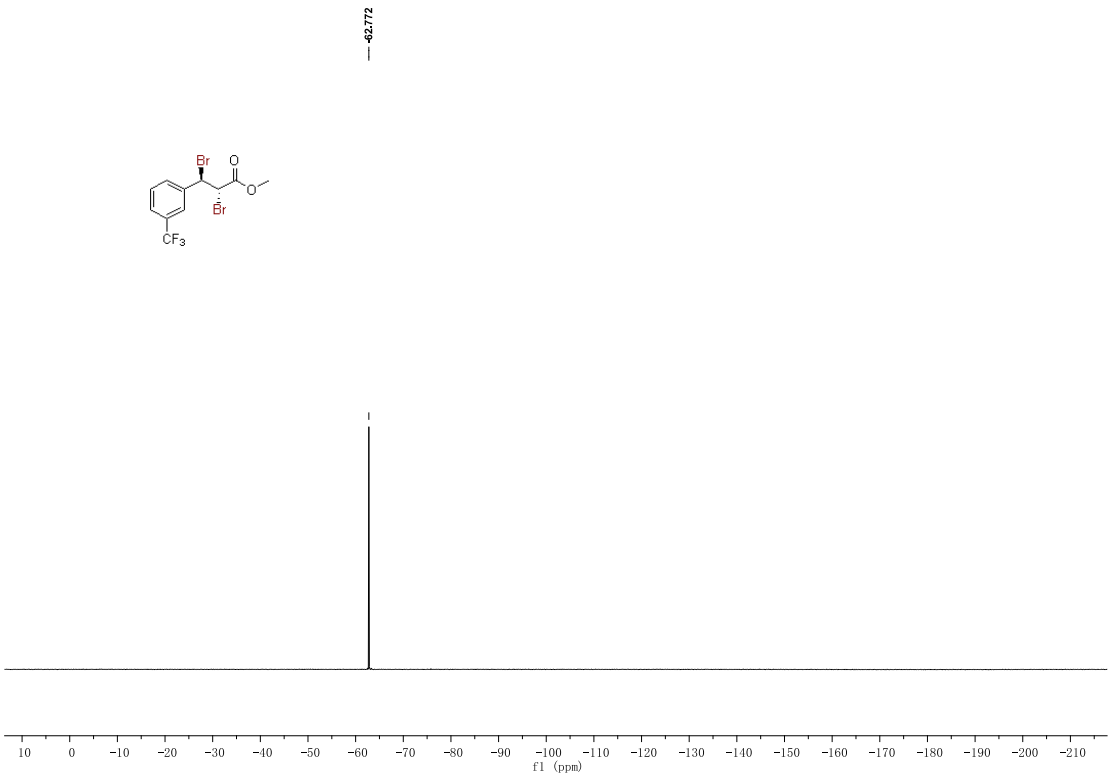

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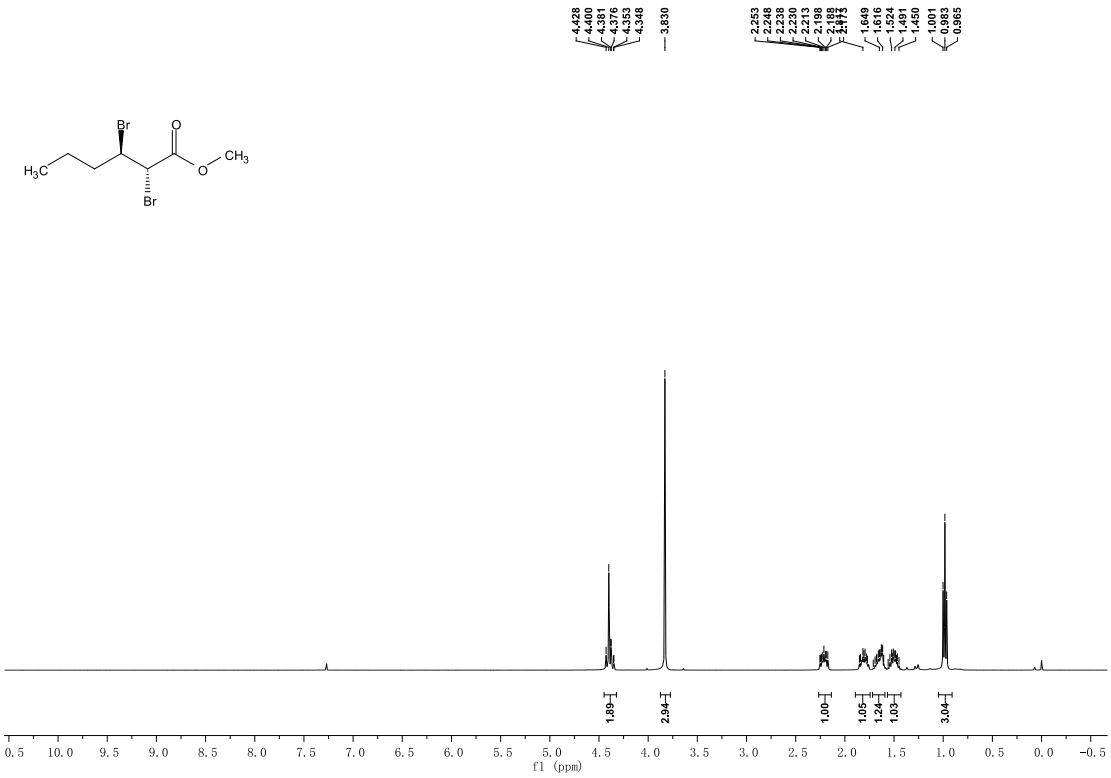

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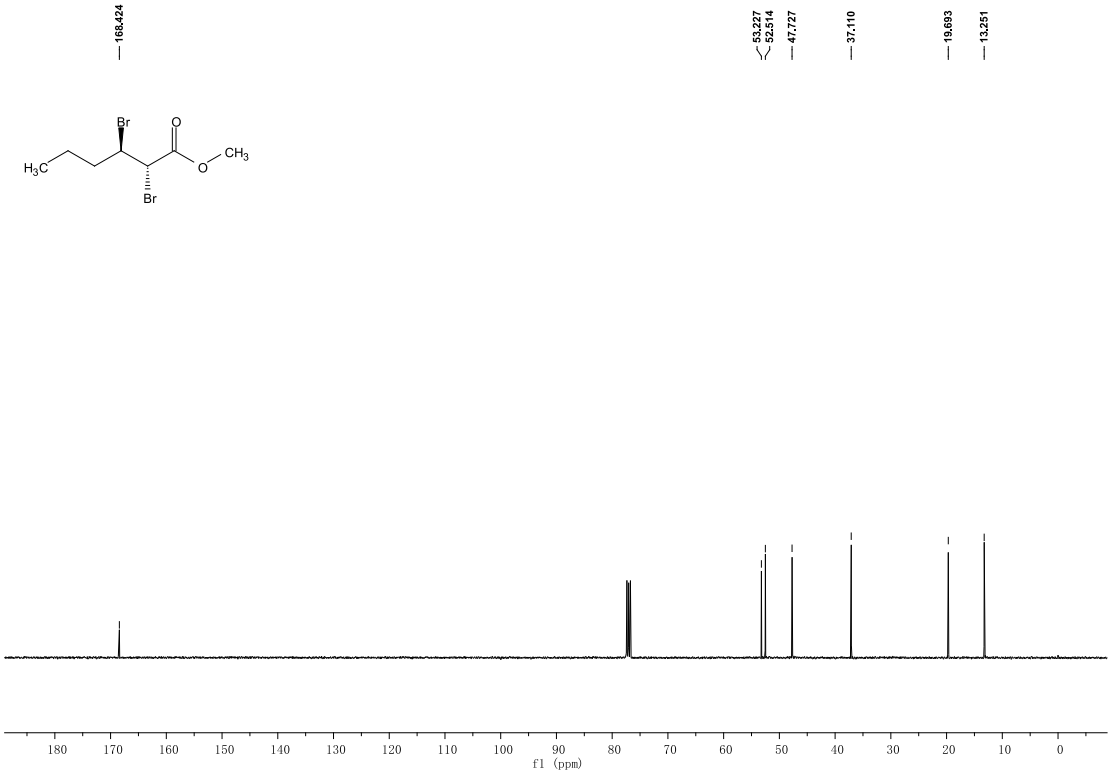

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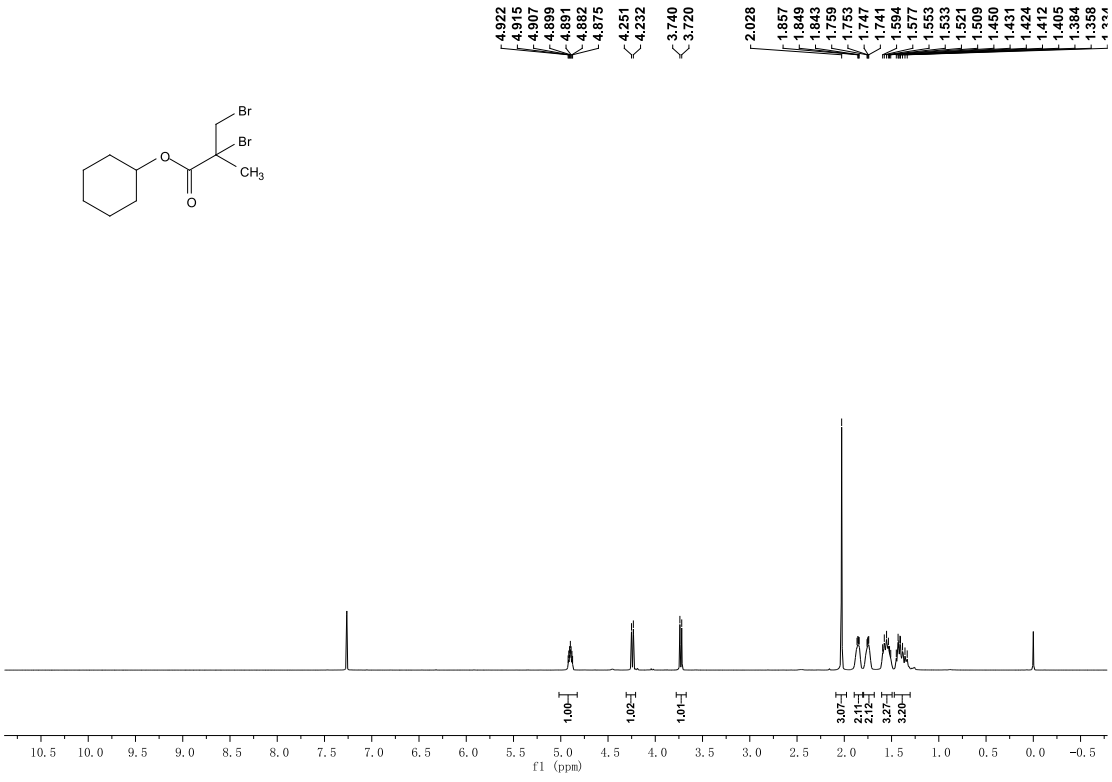

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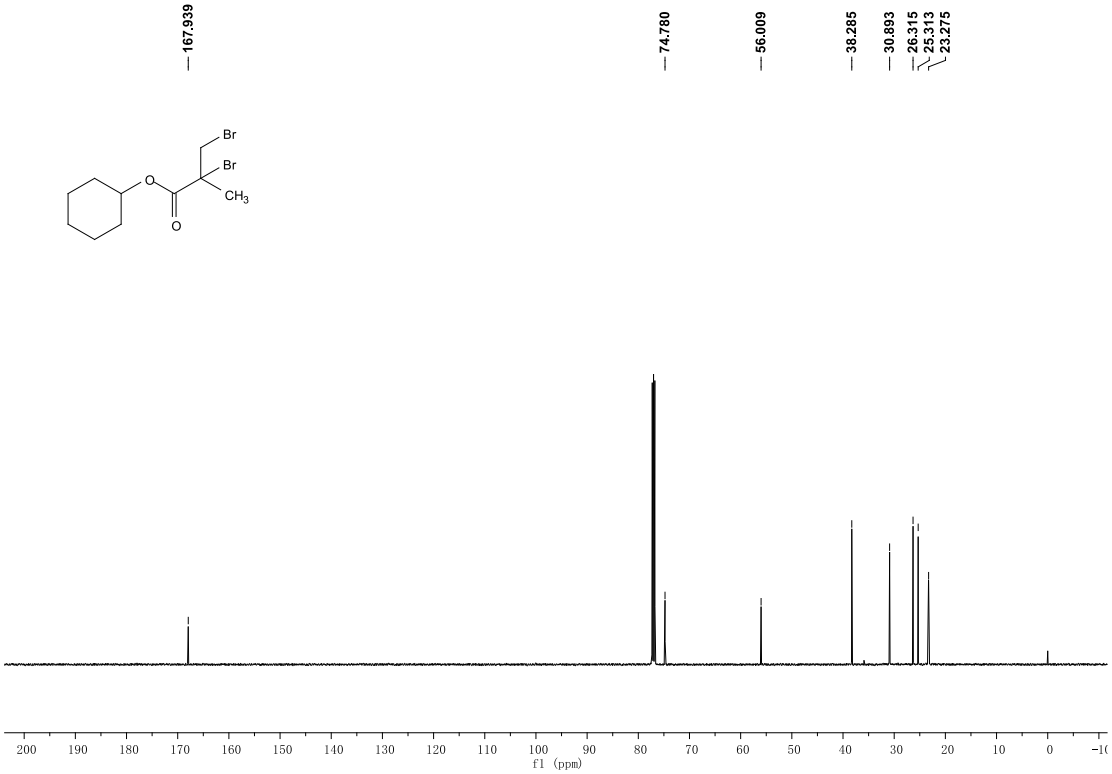

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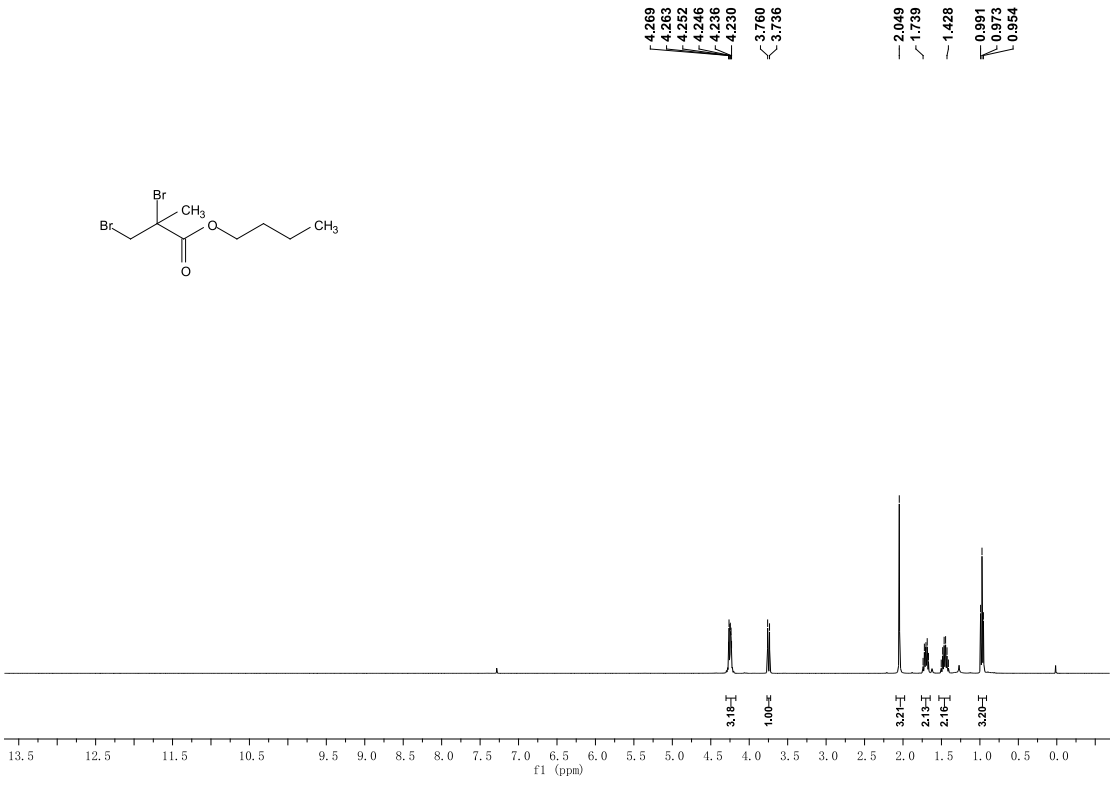

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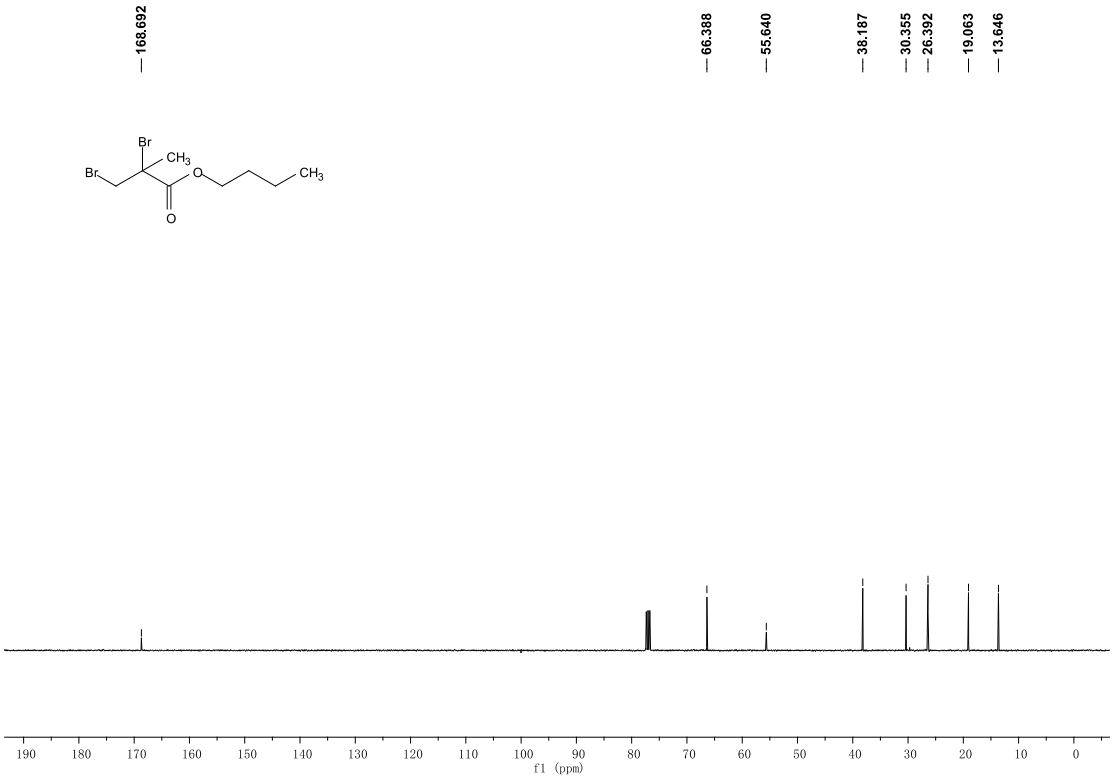

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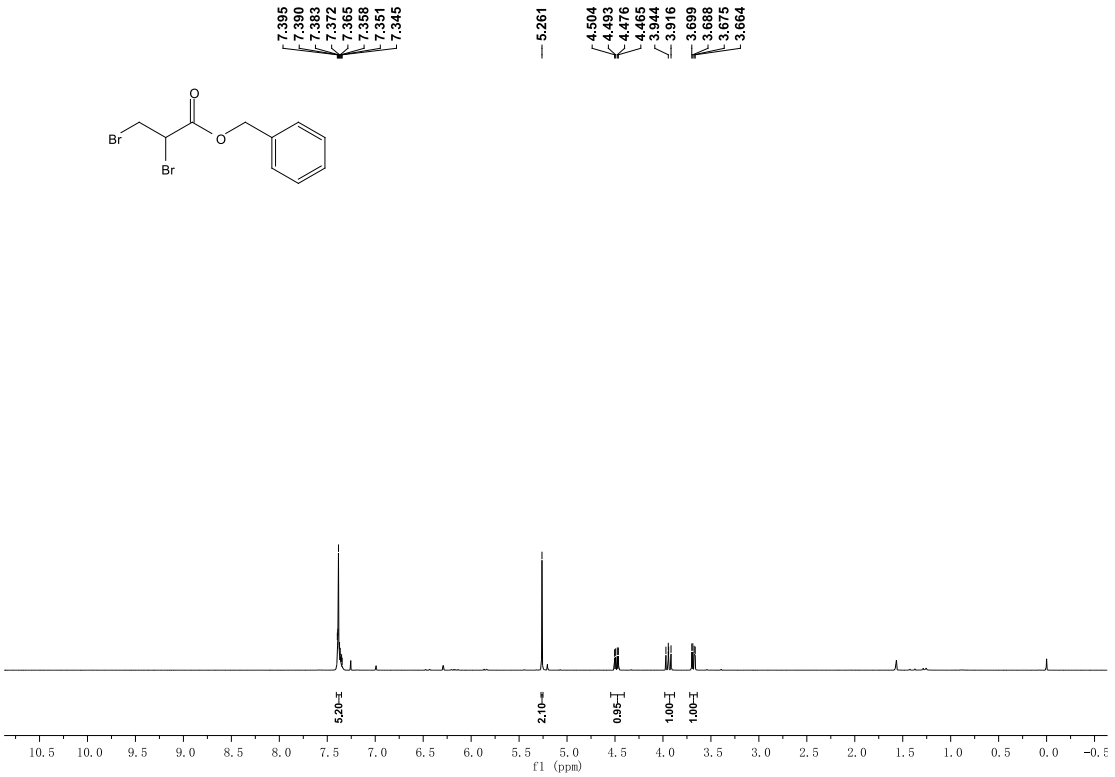

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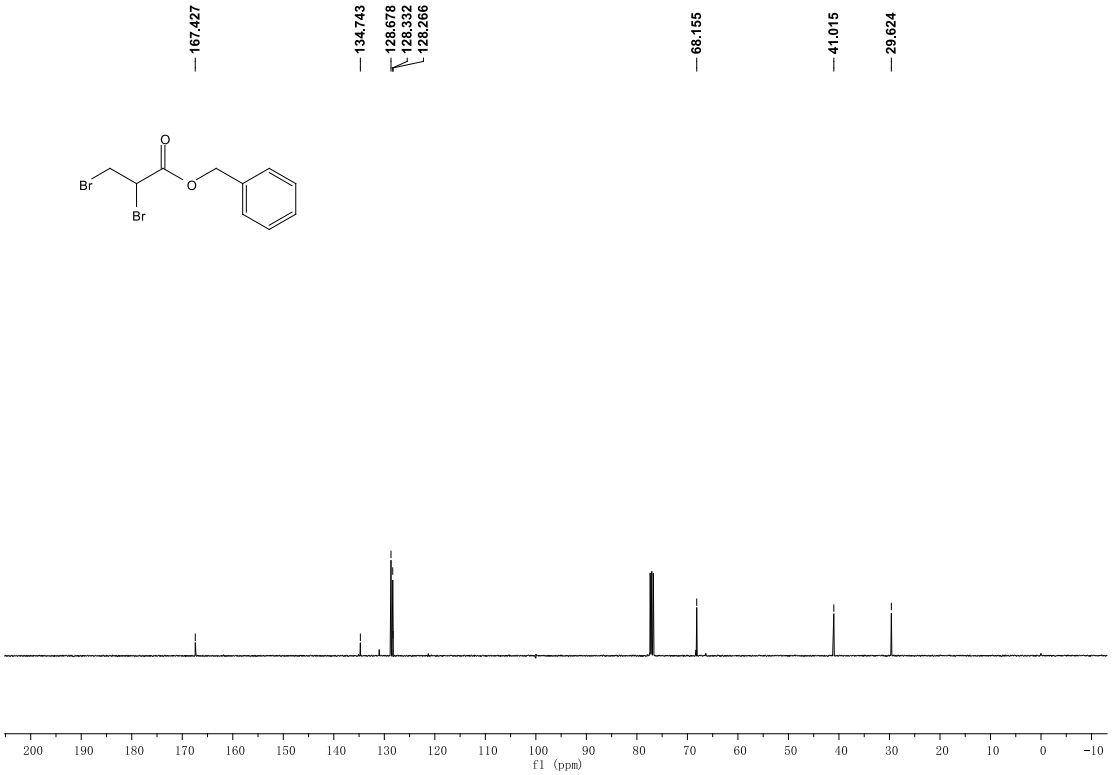
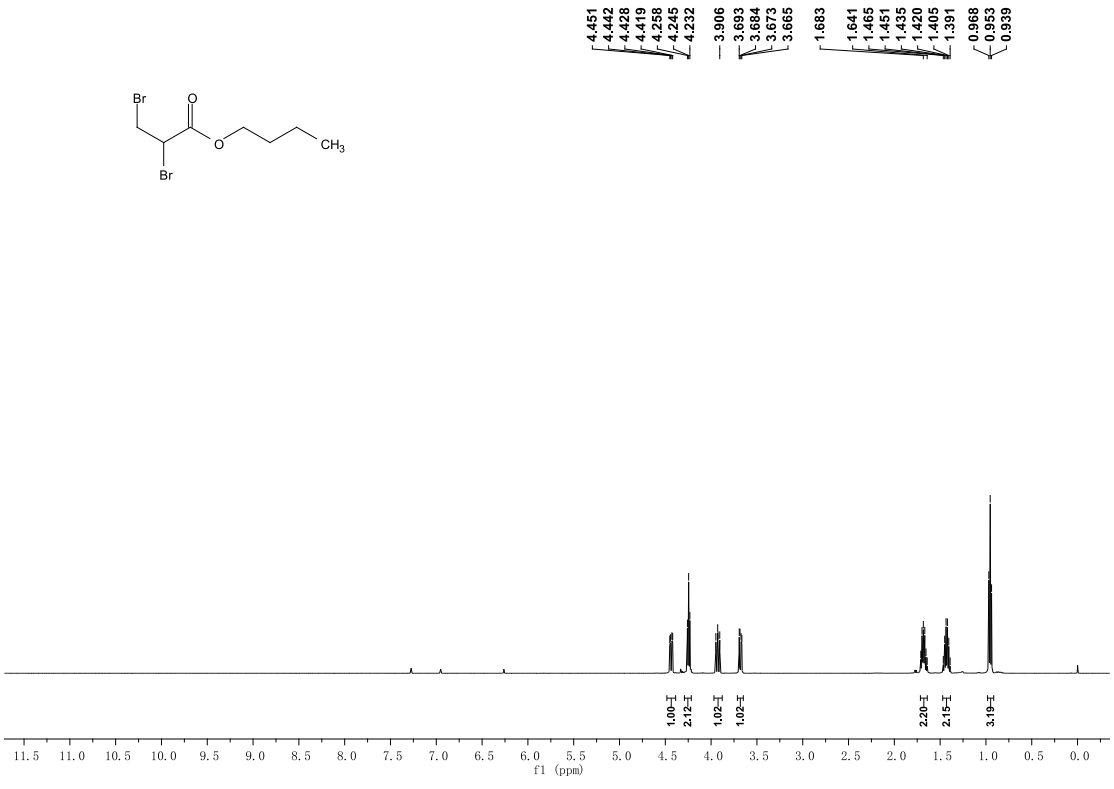


4h ^{1}HNMR



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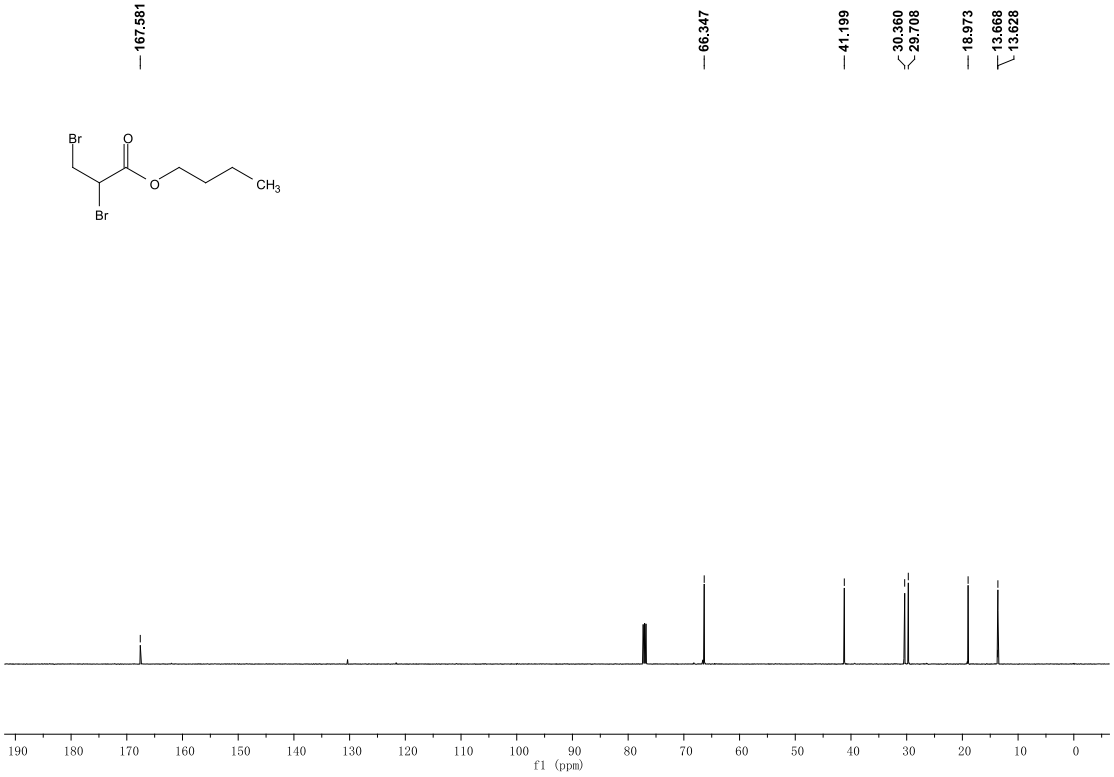

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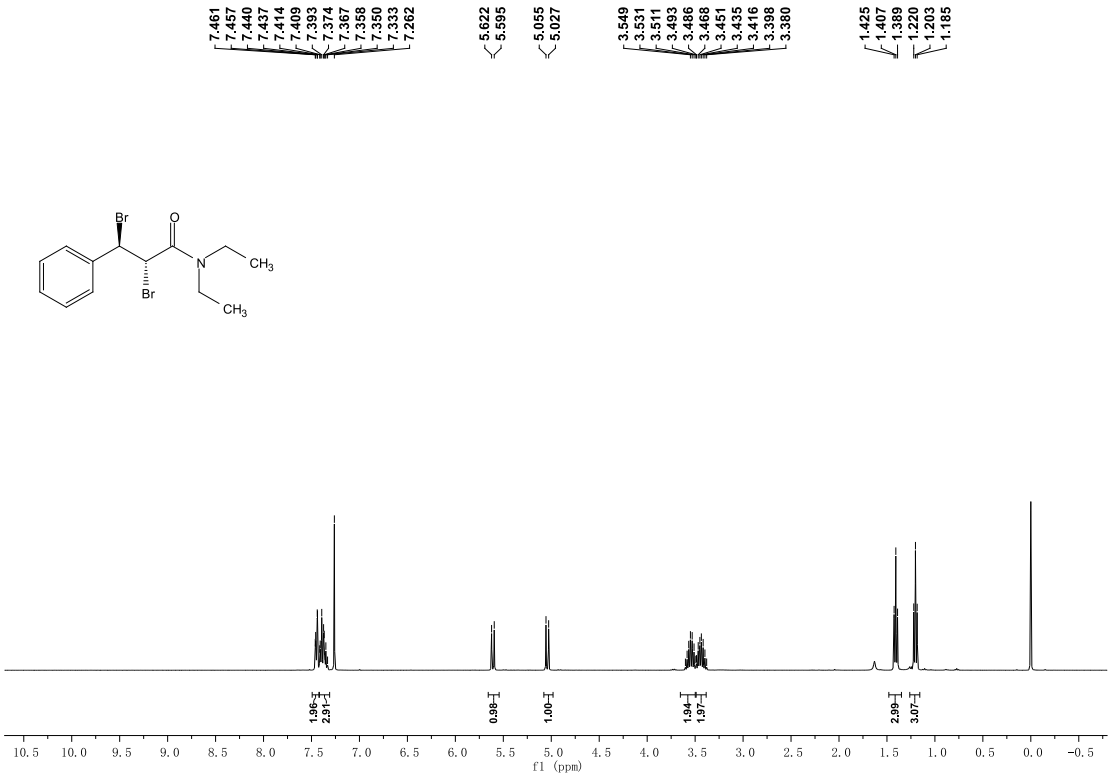

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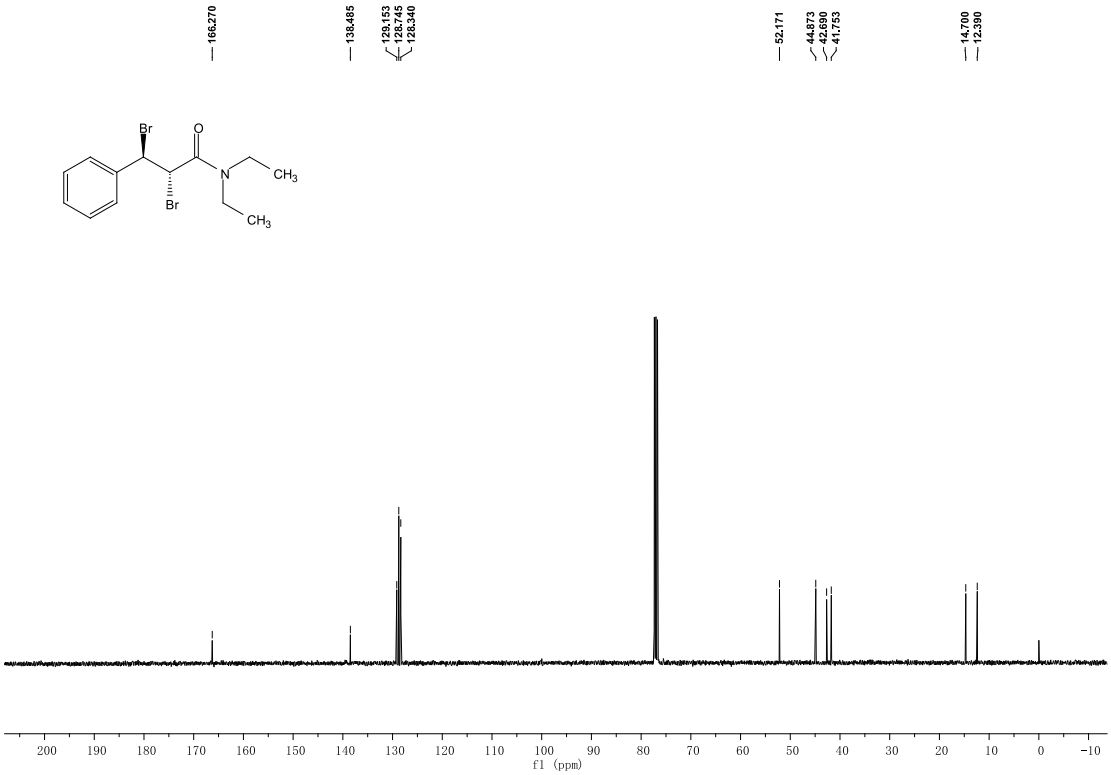

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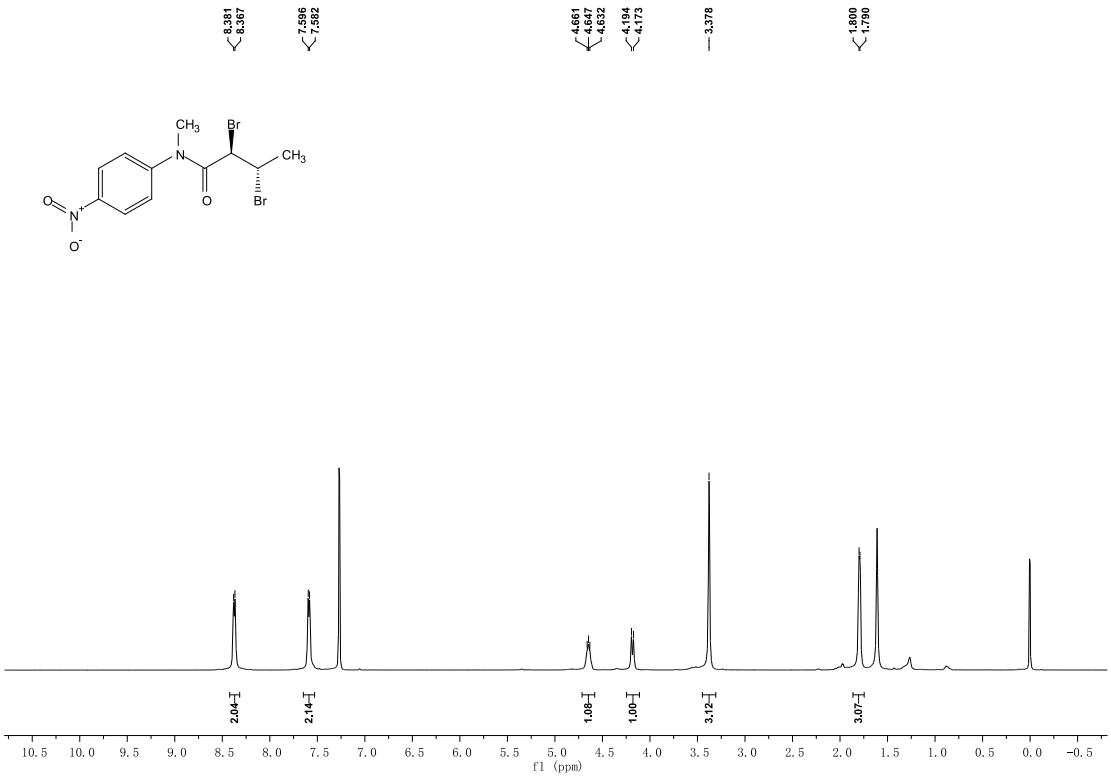

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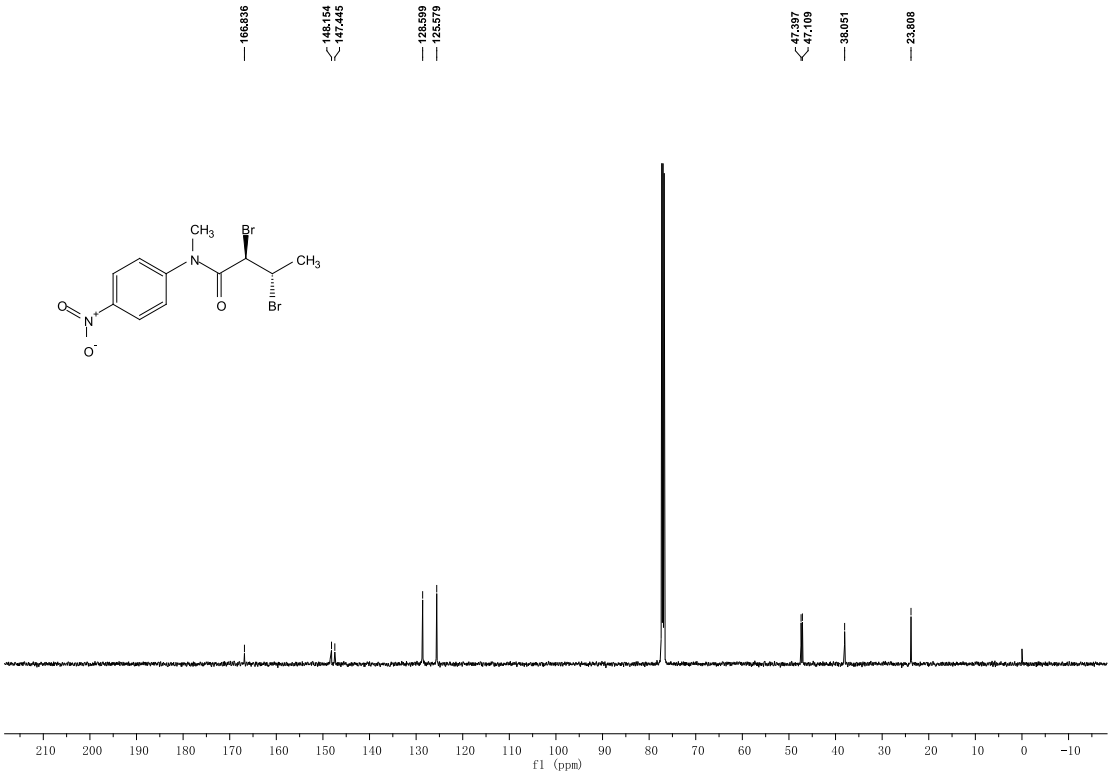

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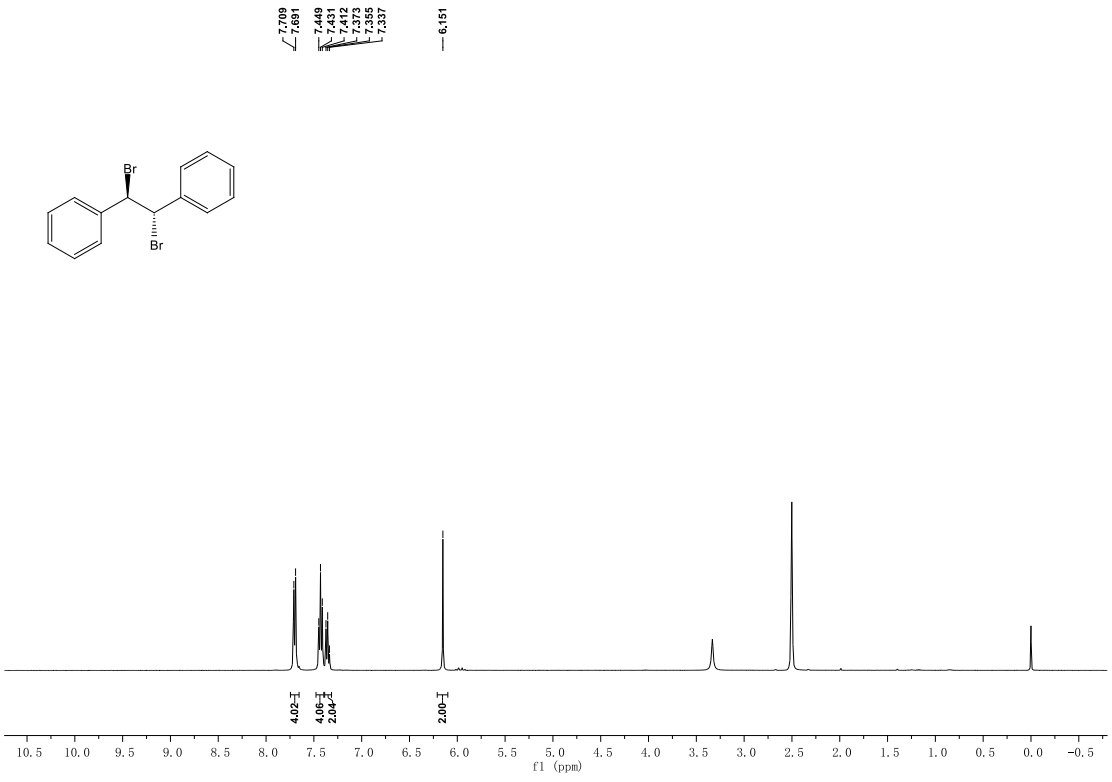

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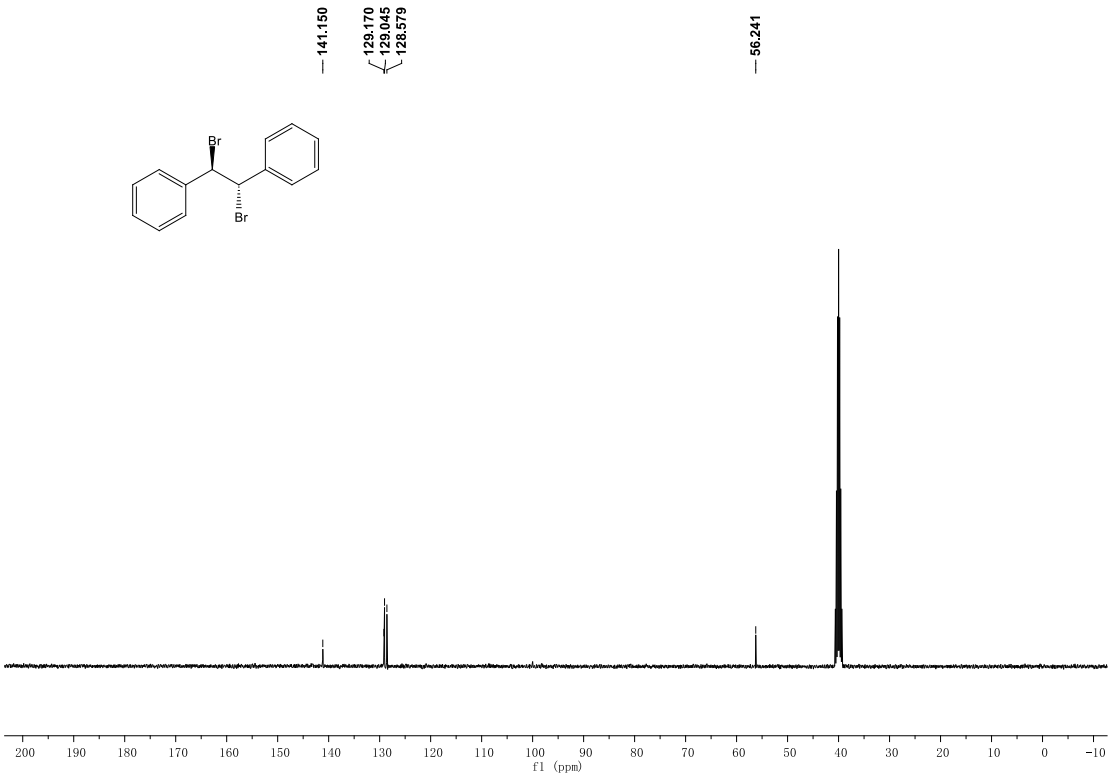

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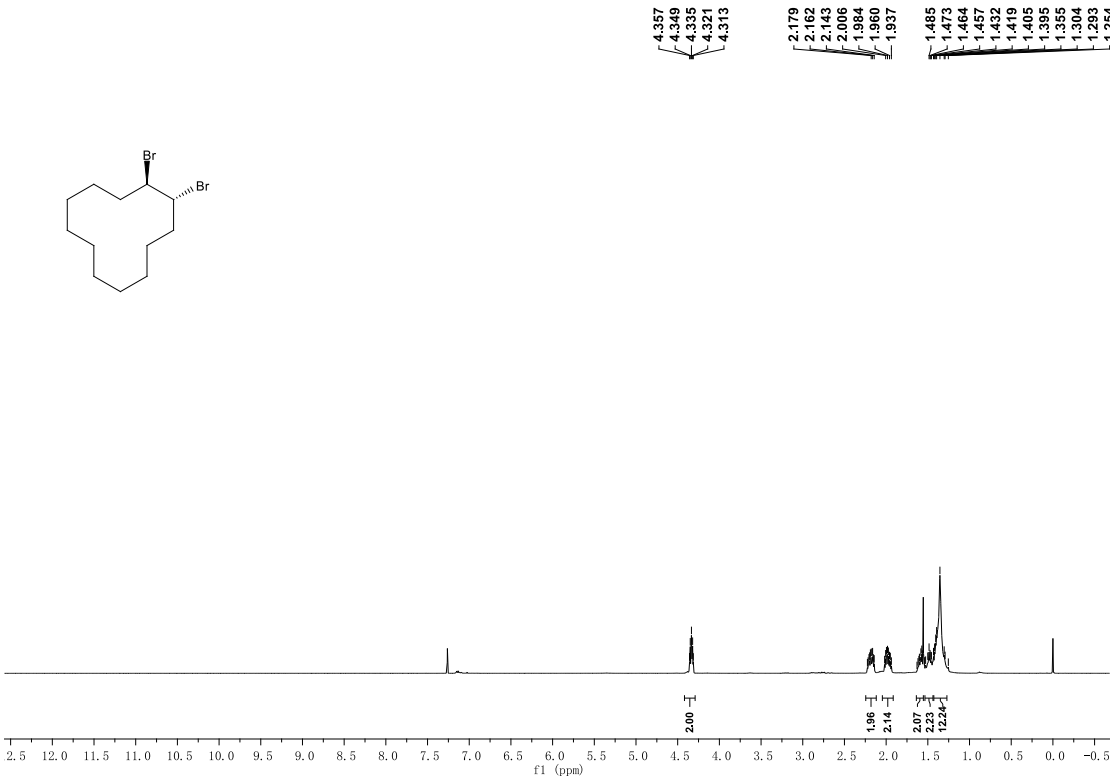

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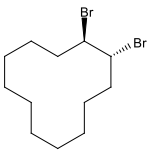
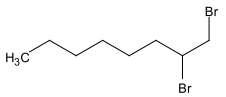
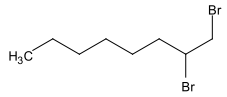


4m ^{1}HNMR

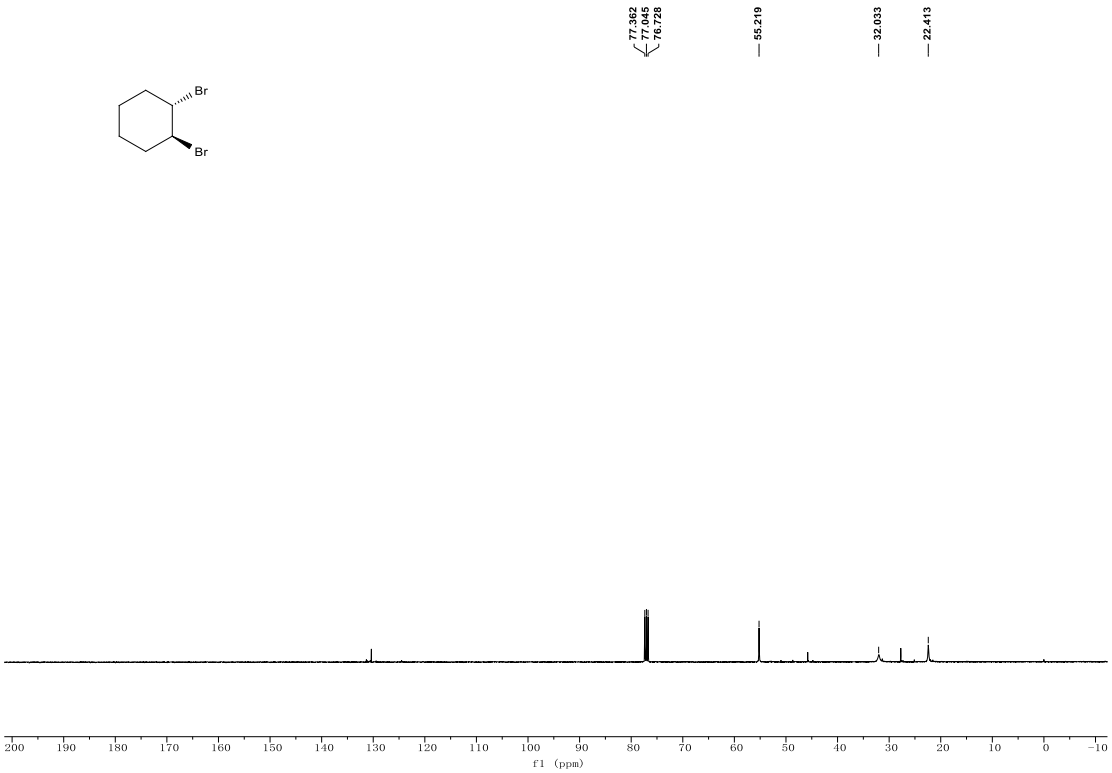


4m ^{13}CNMR



4n ^{1}H NMR

4n ^{13}C NMR



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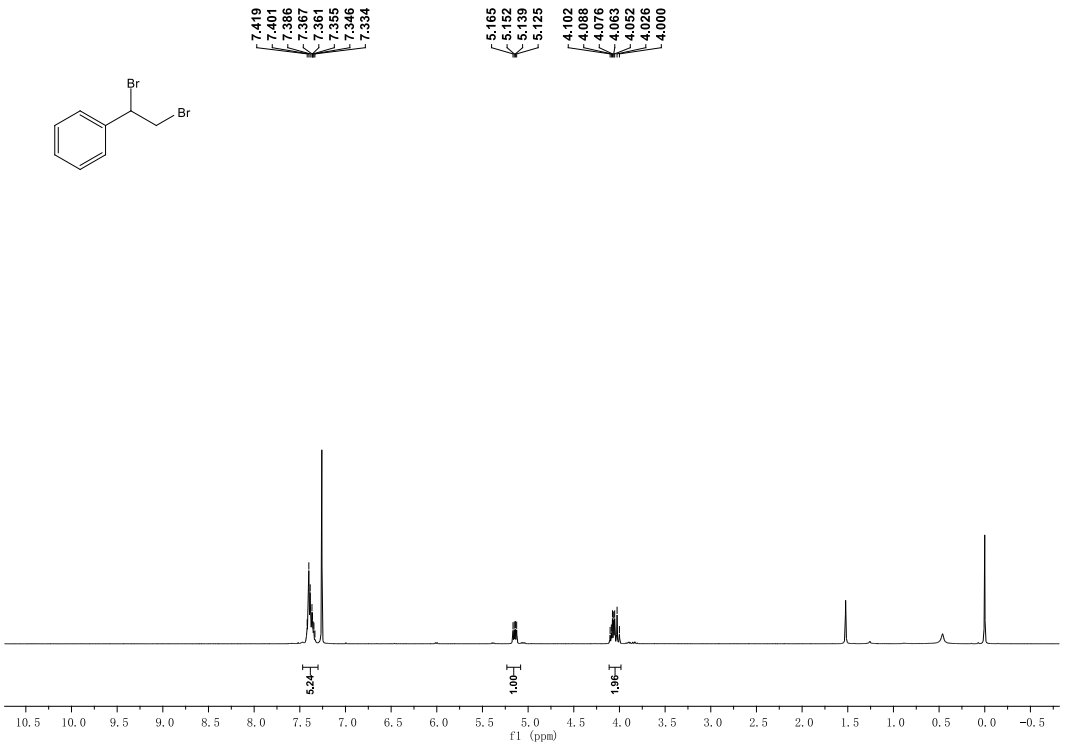

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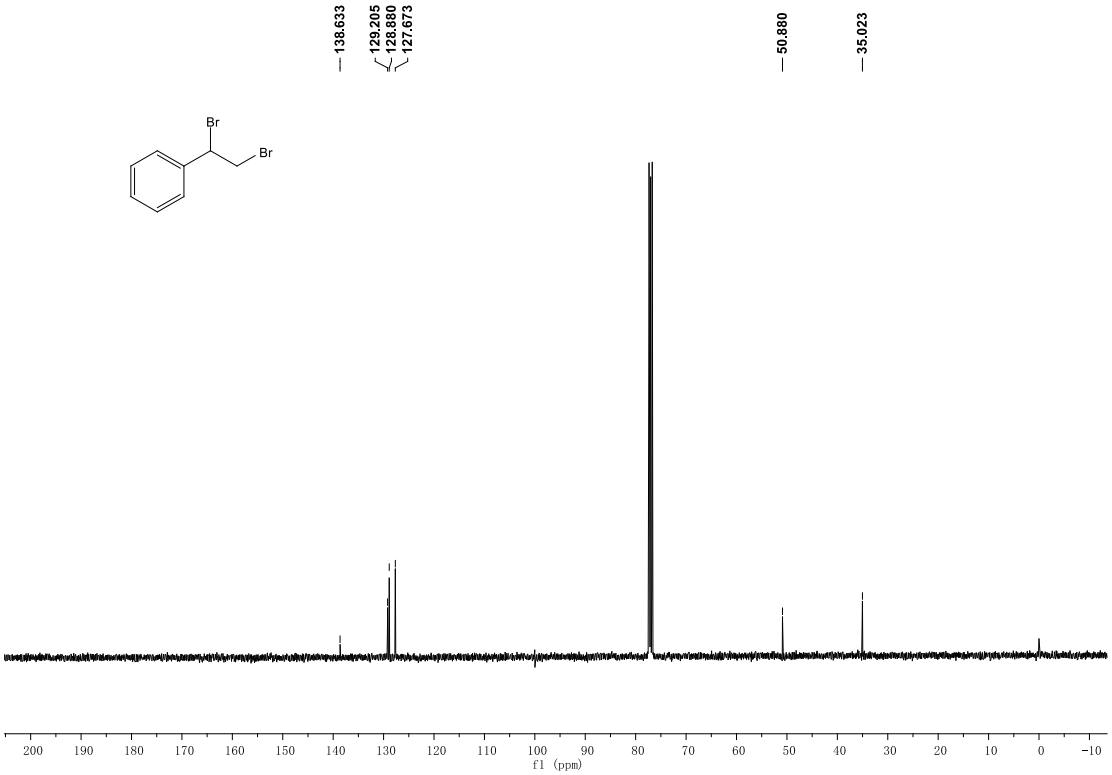

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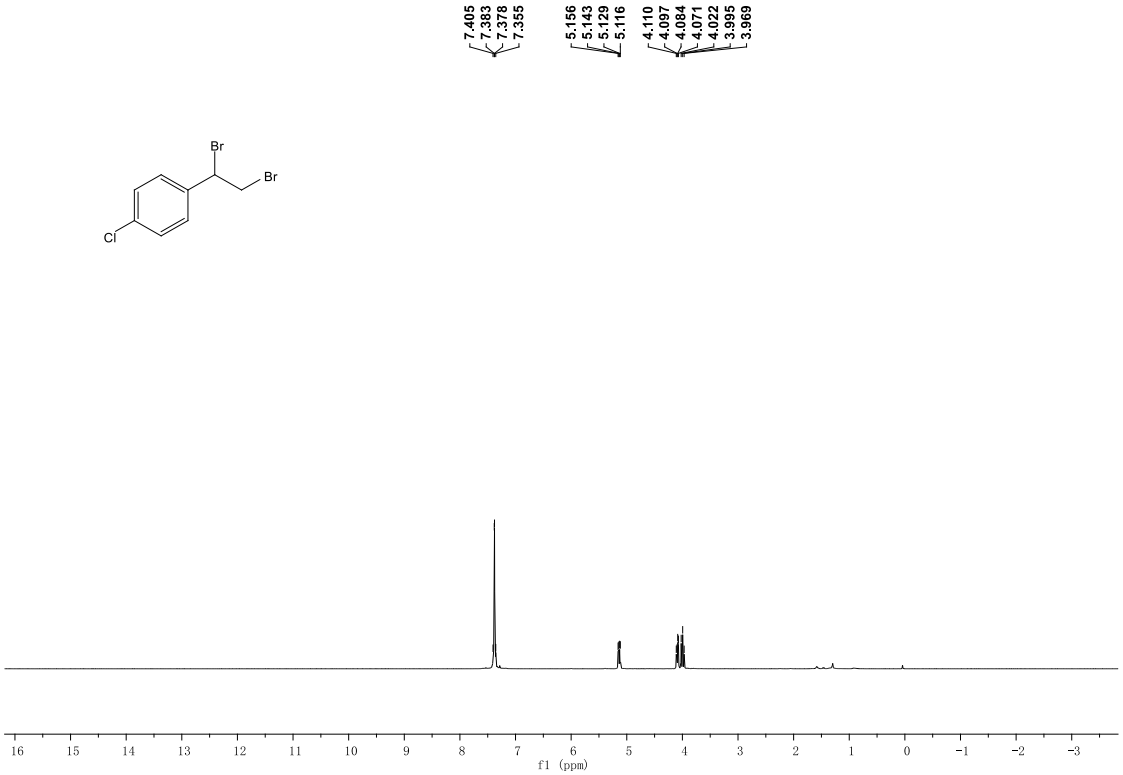

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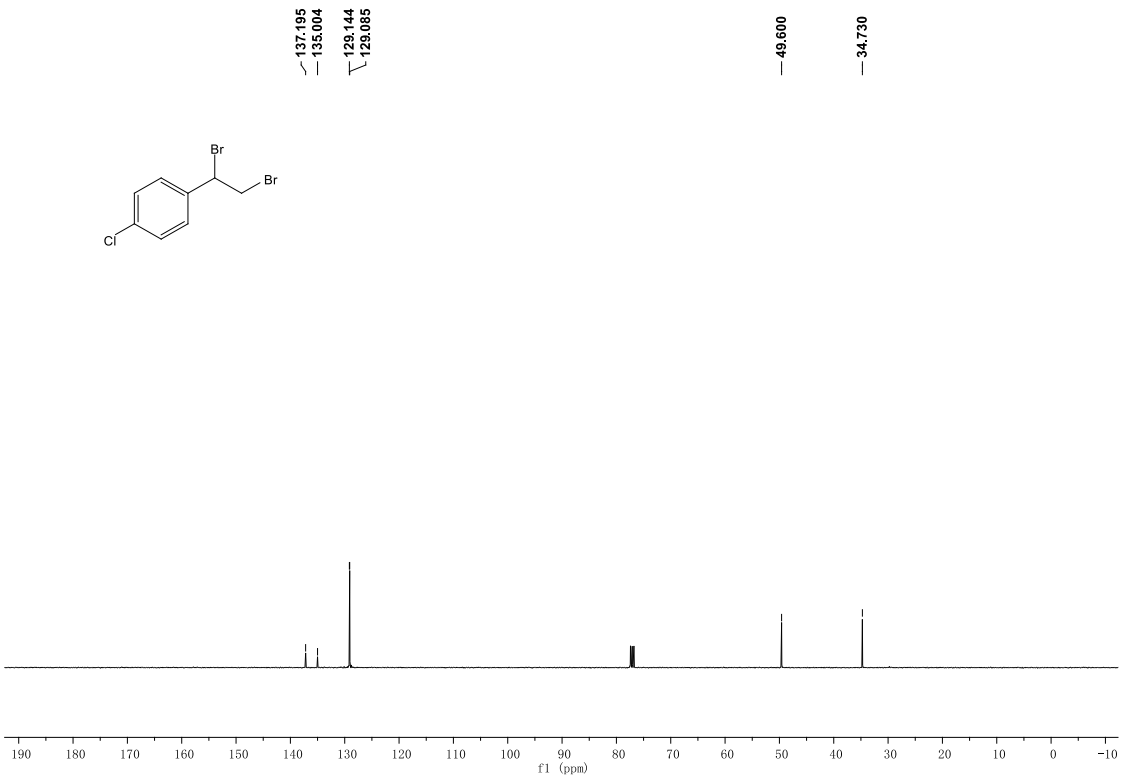

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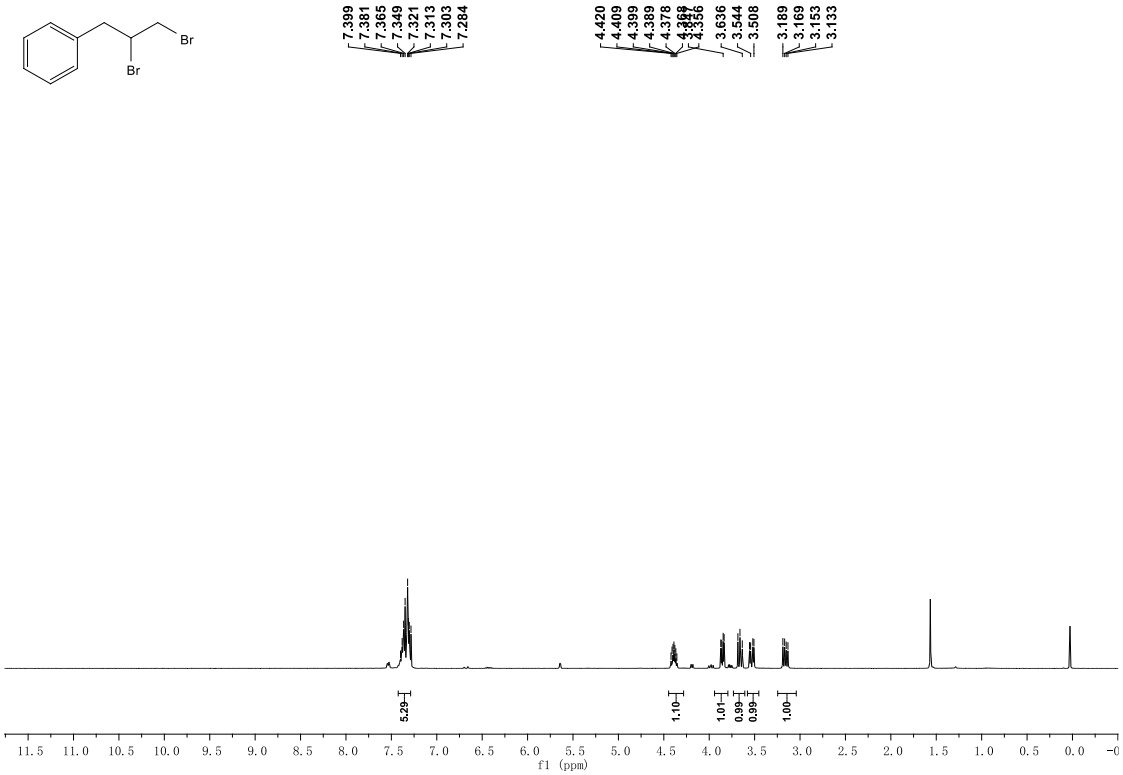

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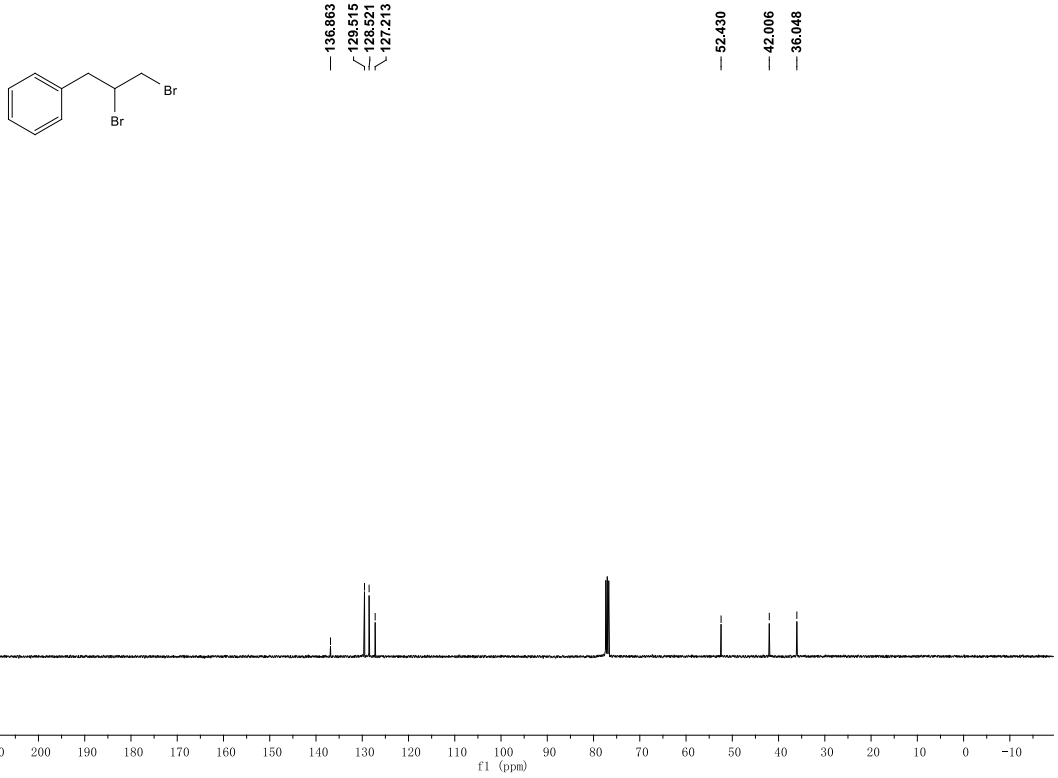
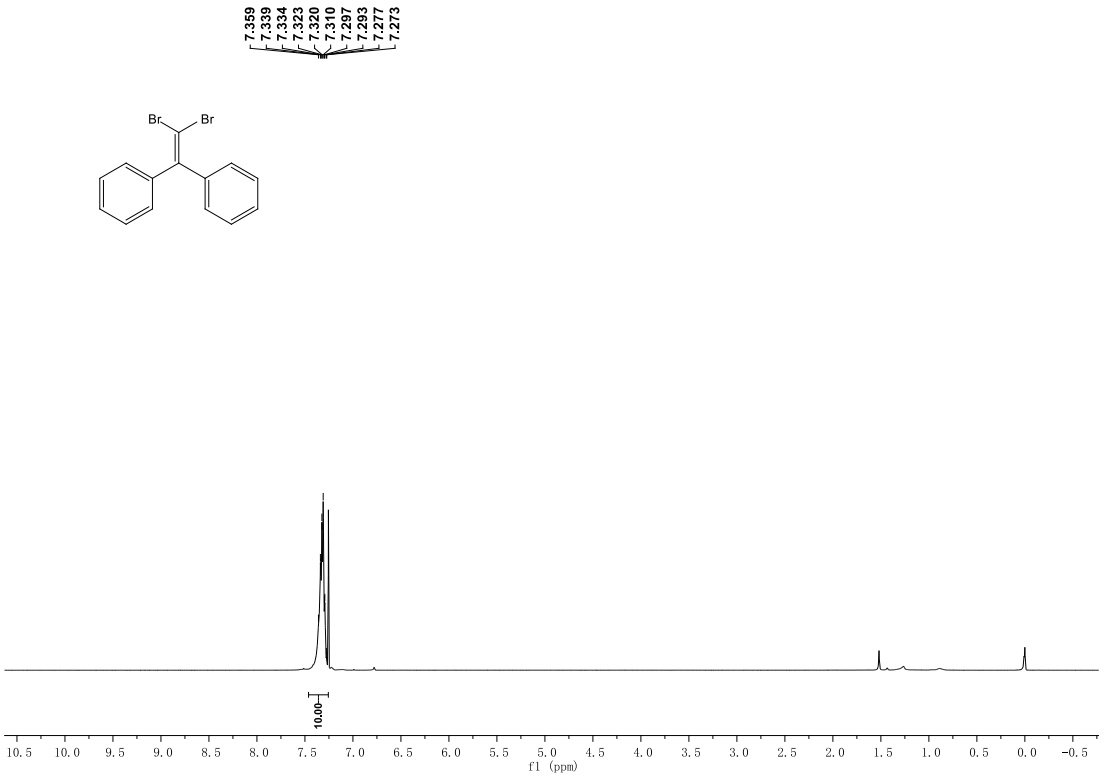
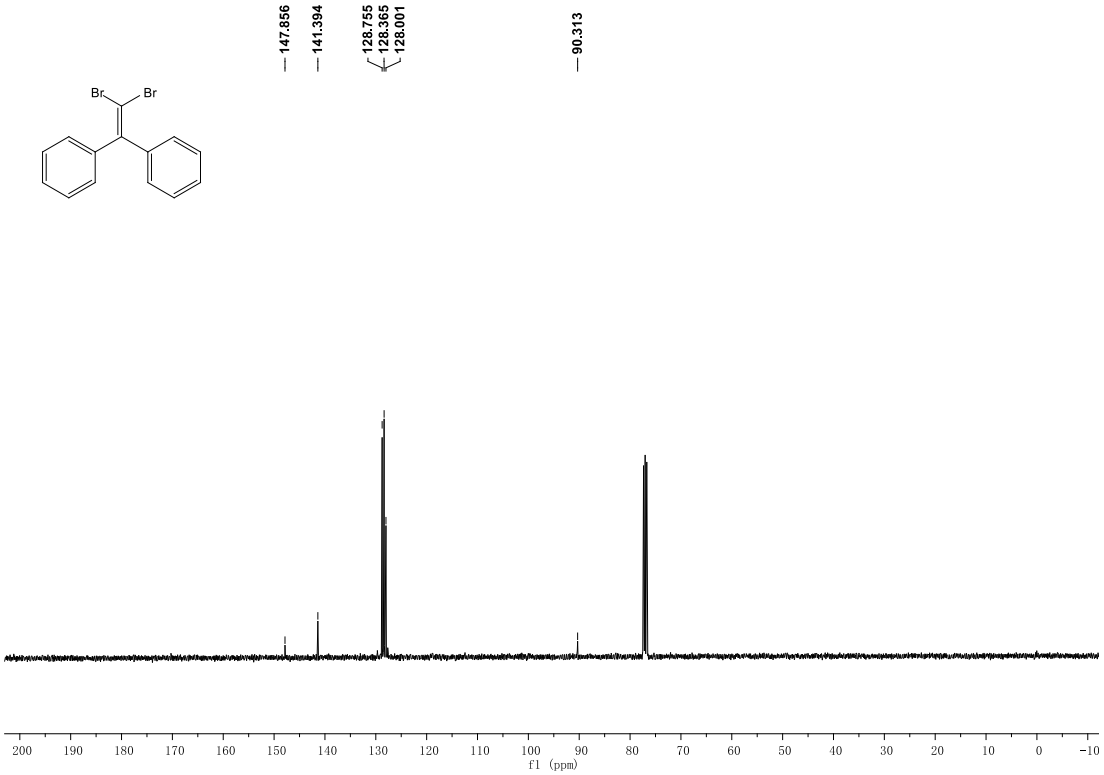


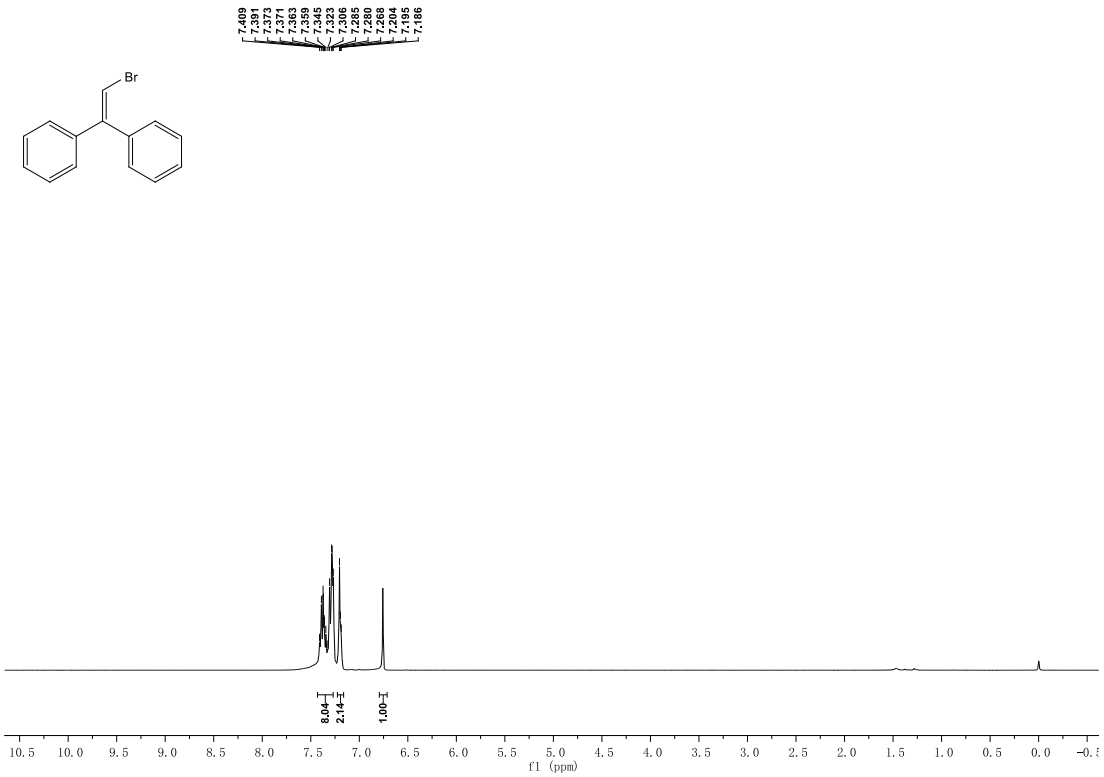
6a ^{1}H NMR



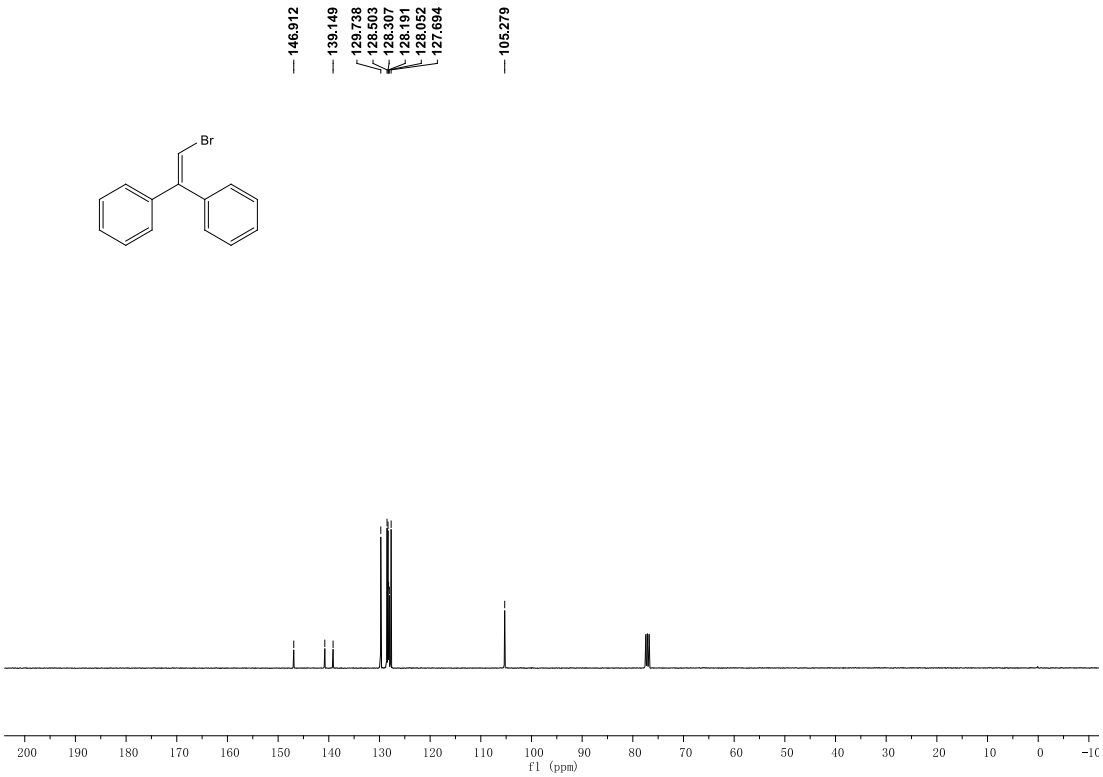
6a ^{13}C NMR



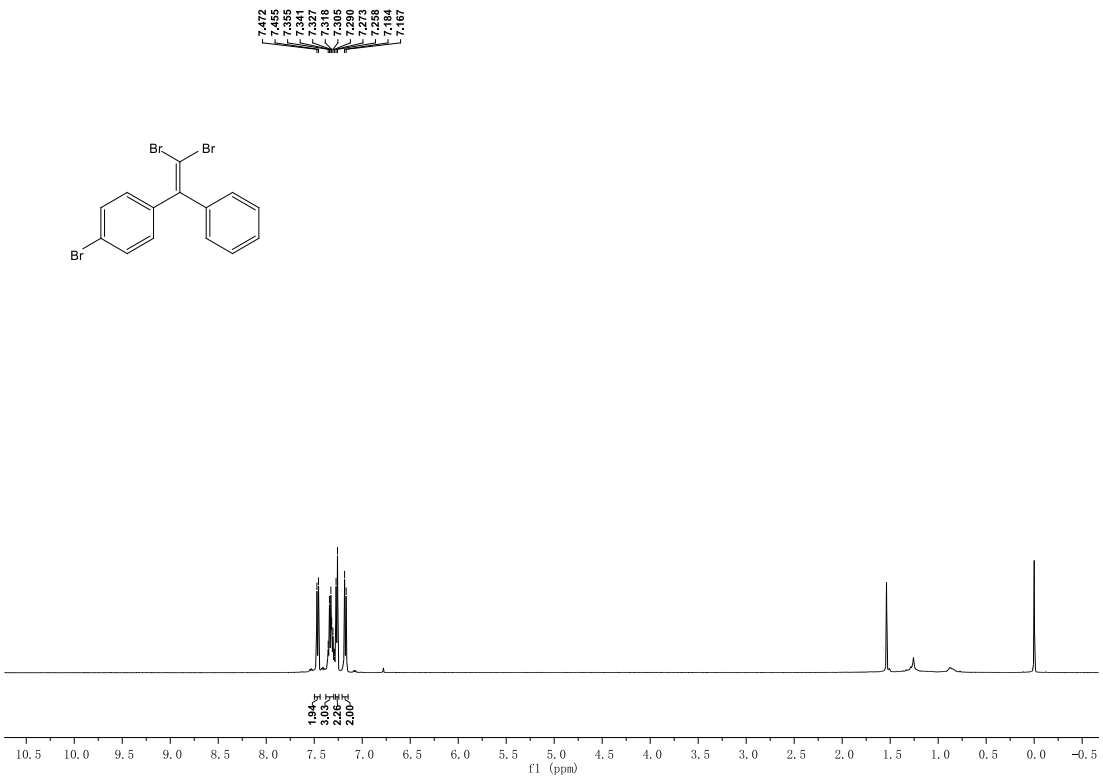
6b ^{1}H NMR



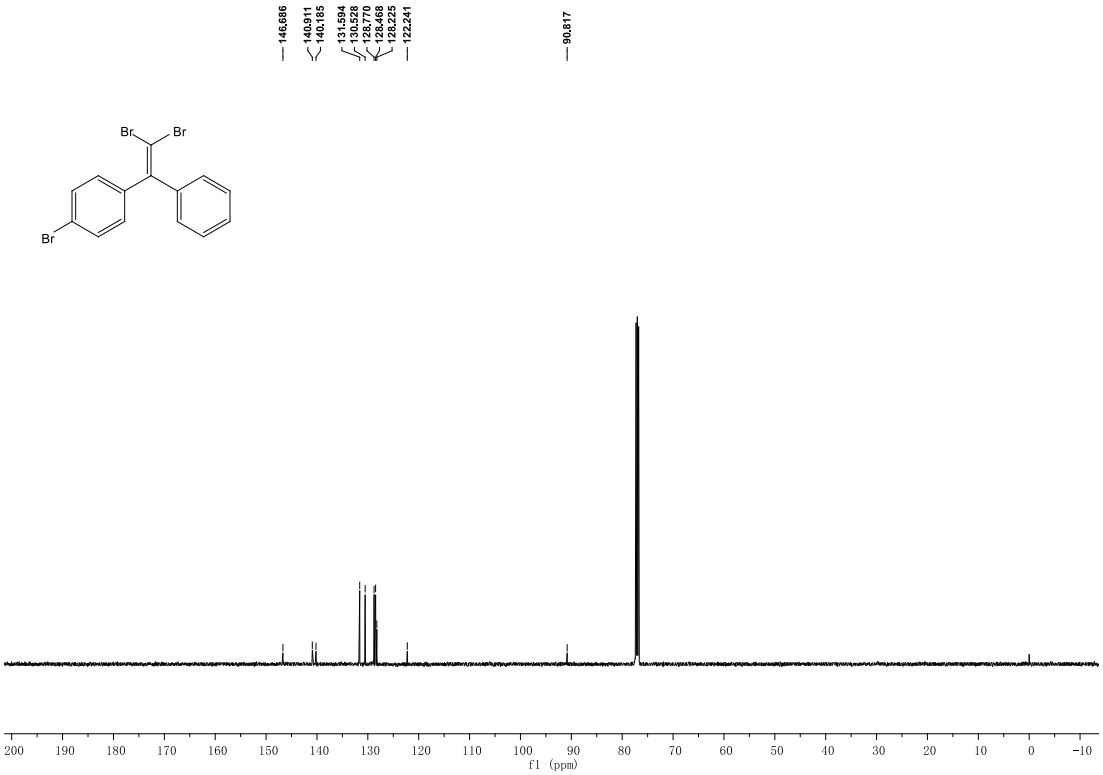
6b ^{13}C NMR



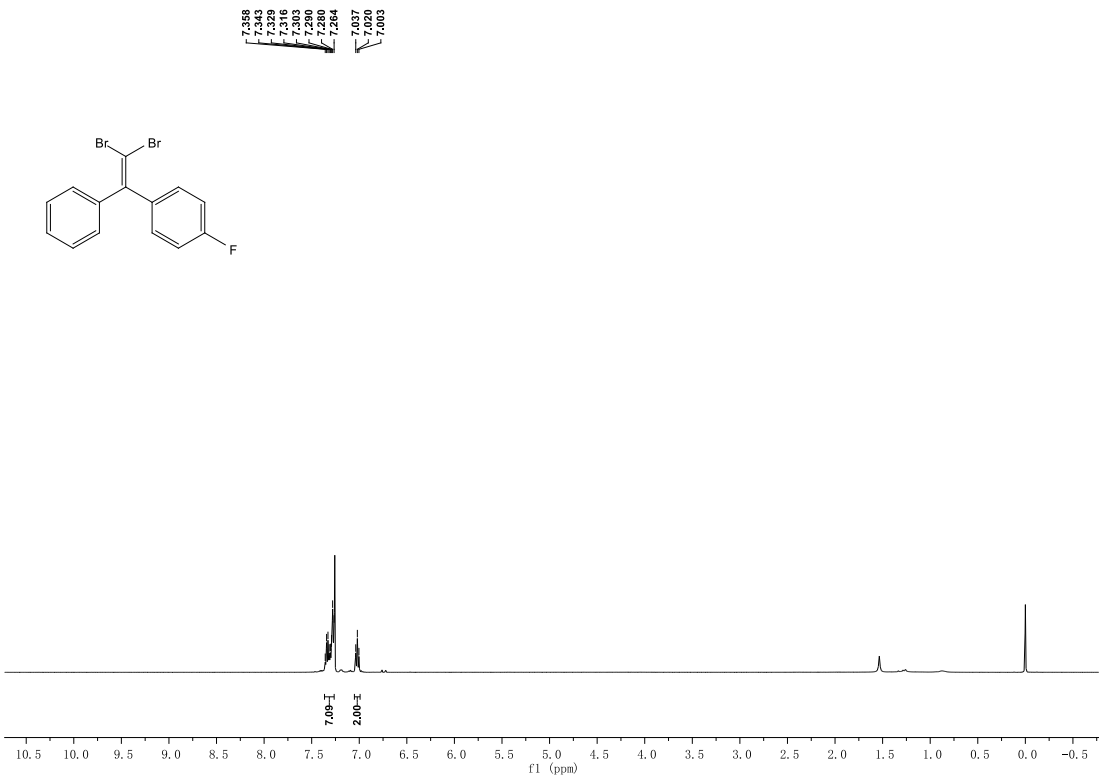
6c ^{1}H NMR



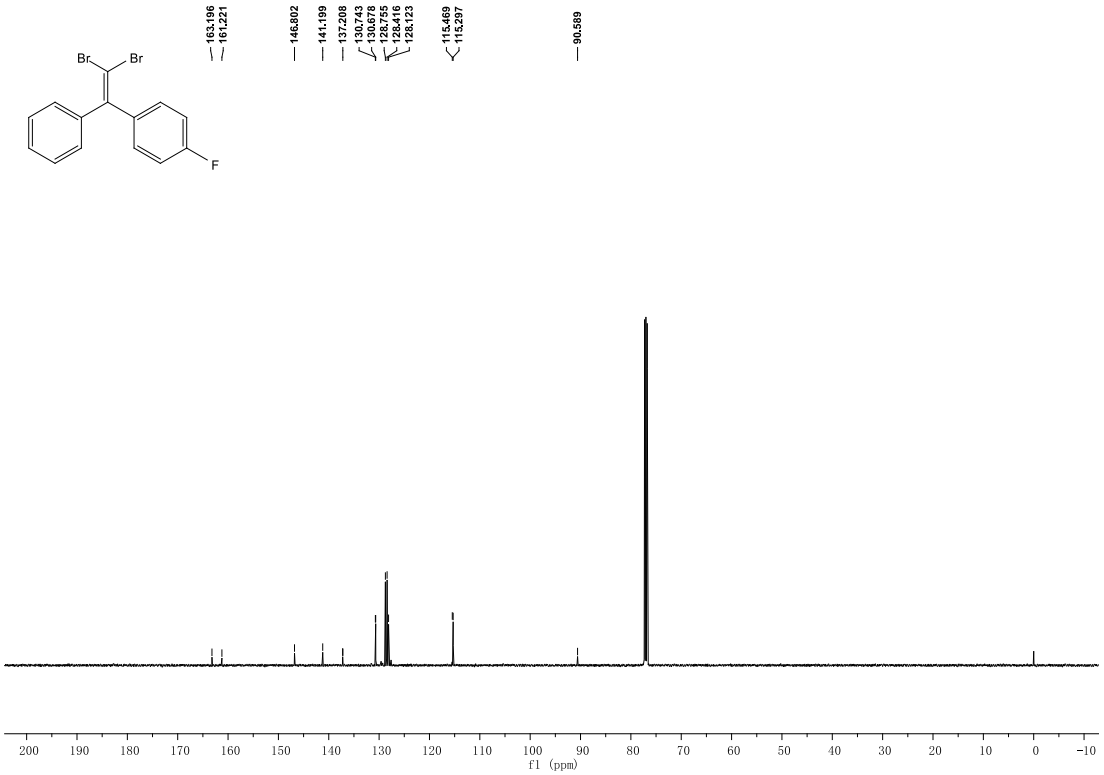
6c ^{13}C NMR



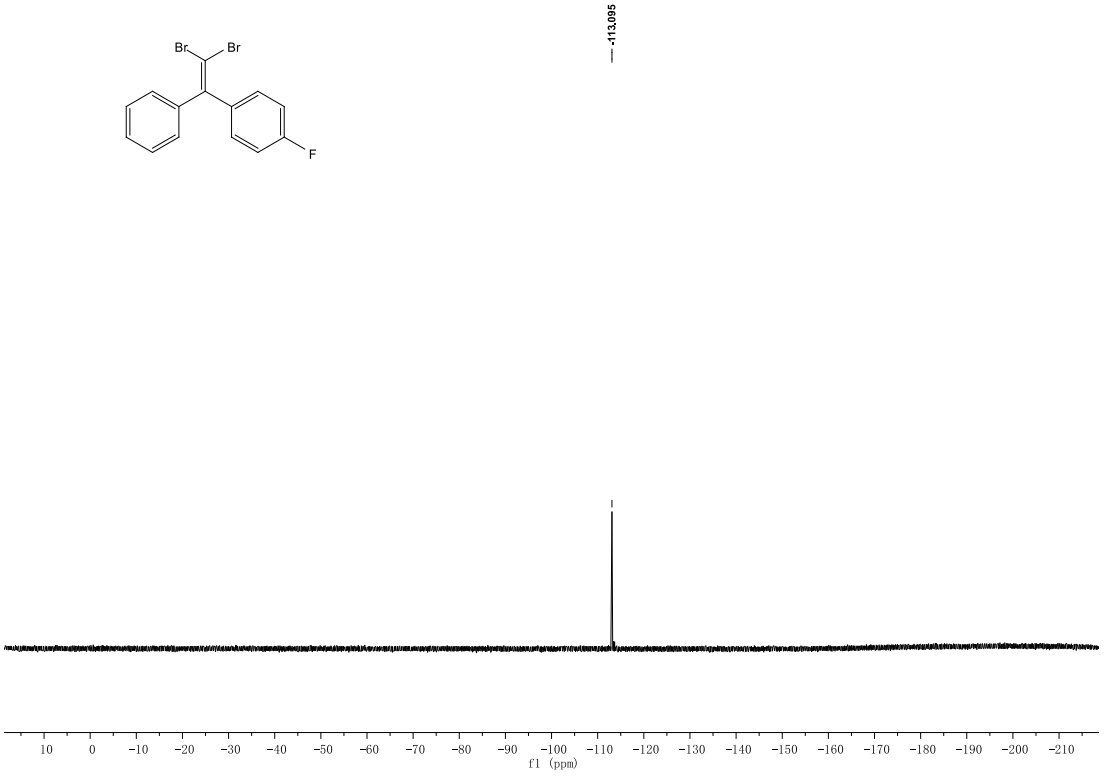
6d ^{1}H NMR



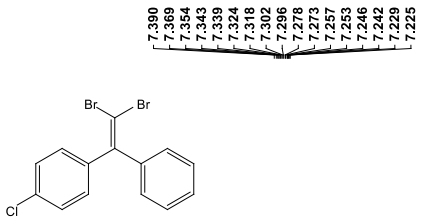
6d ^{13}C NMR

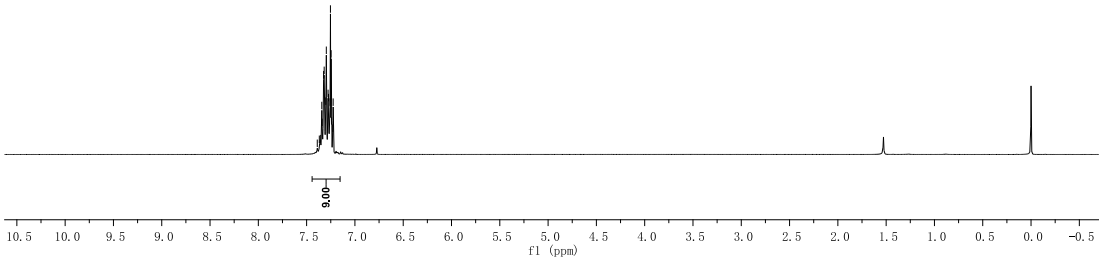


6d ^{19}F NMR



6e ^{1}H NMR





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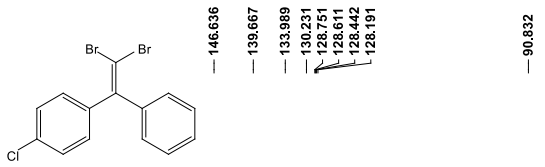

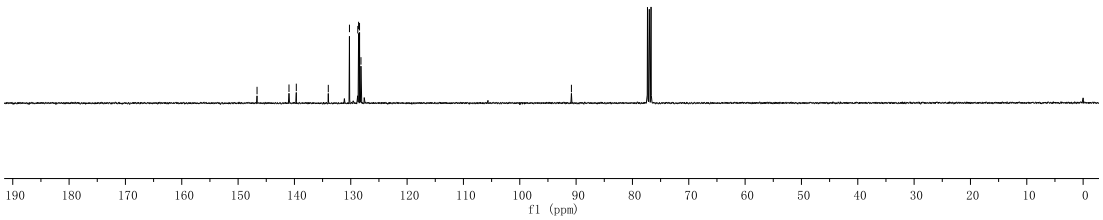

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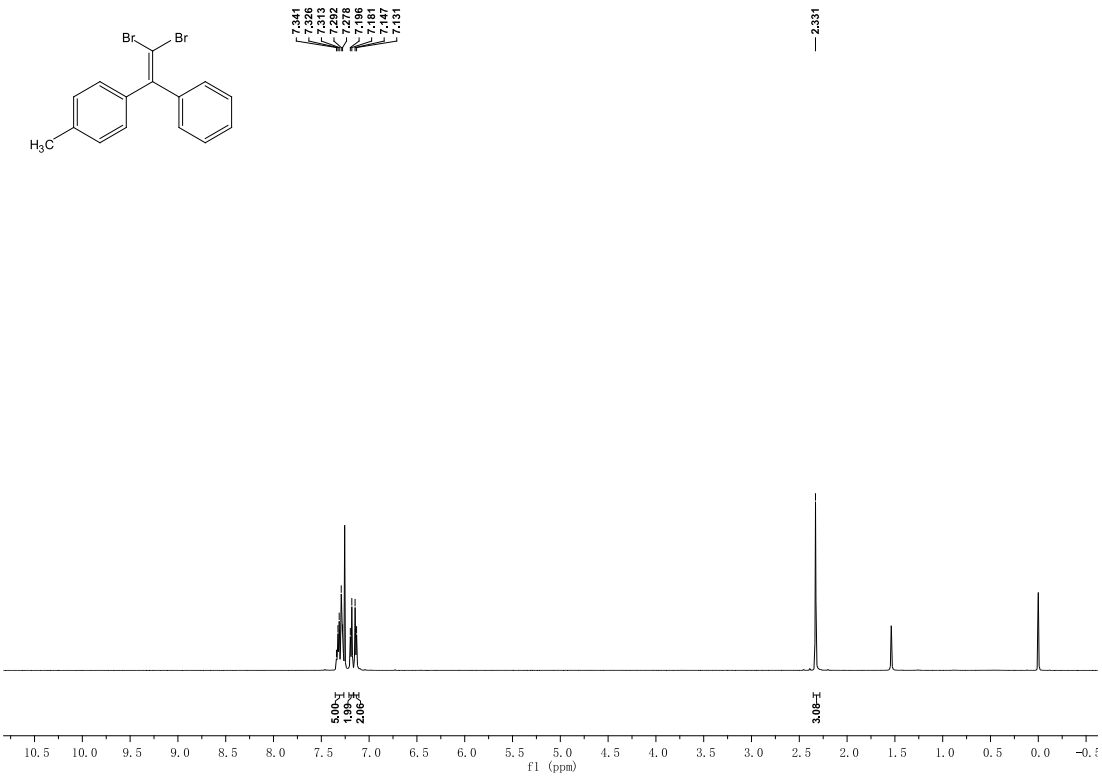
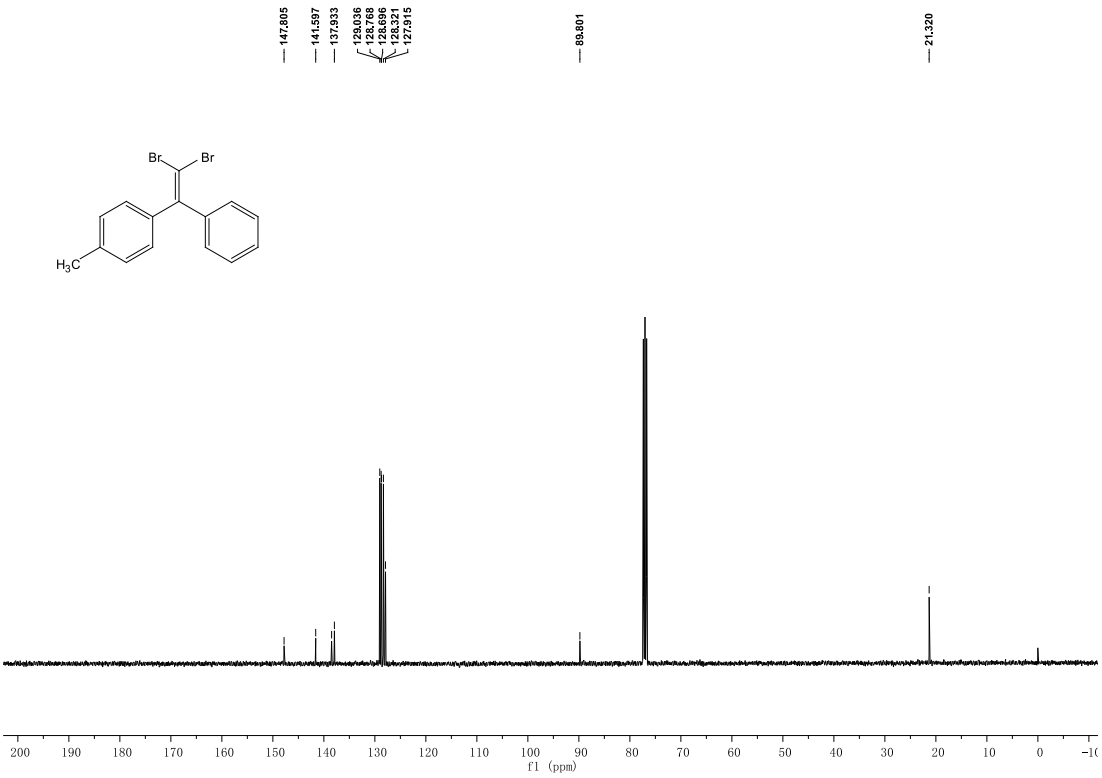
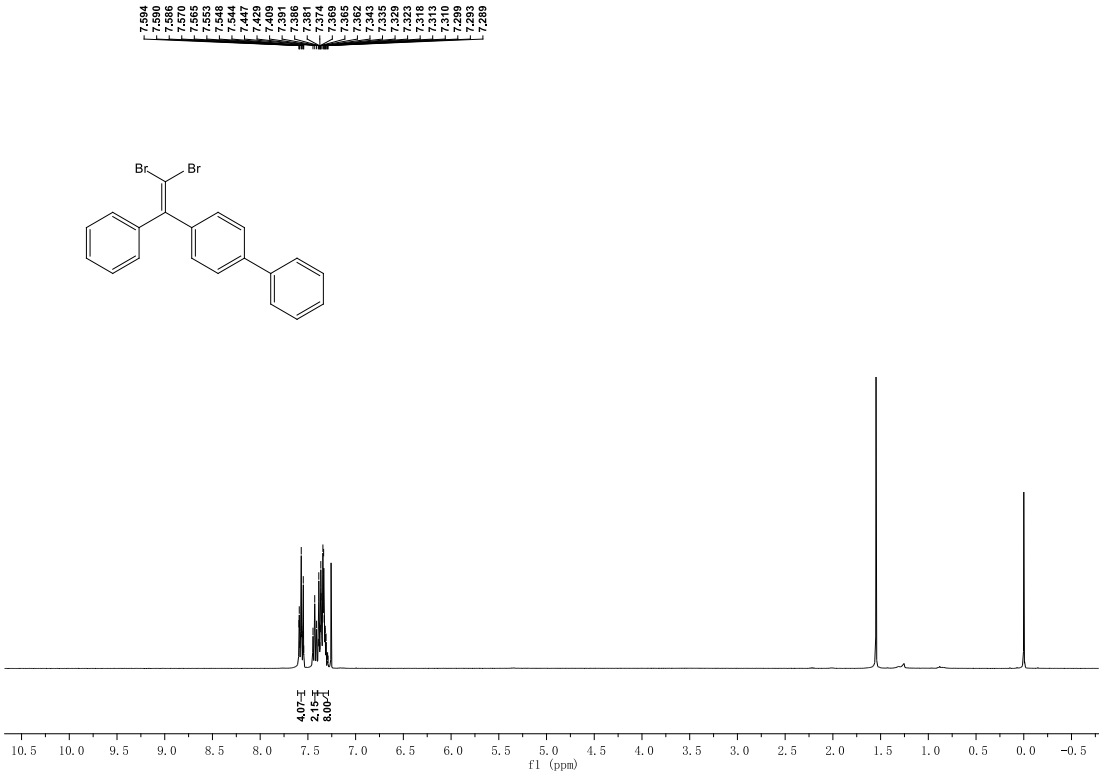


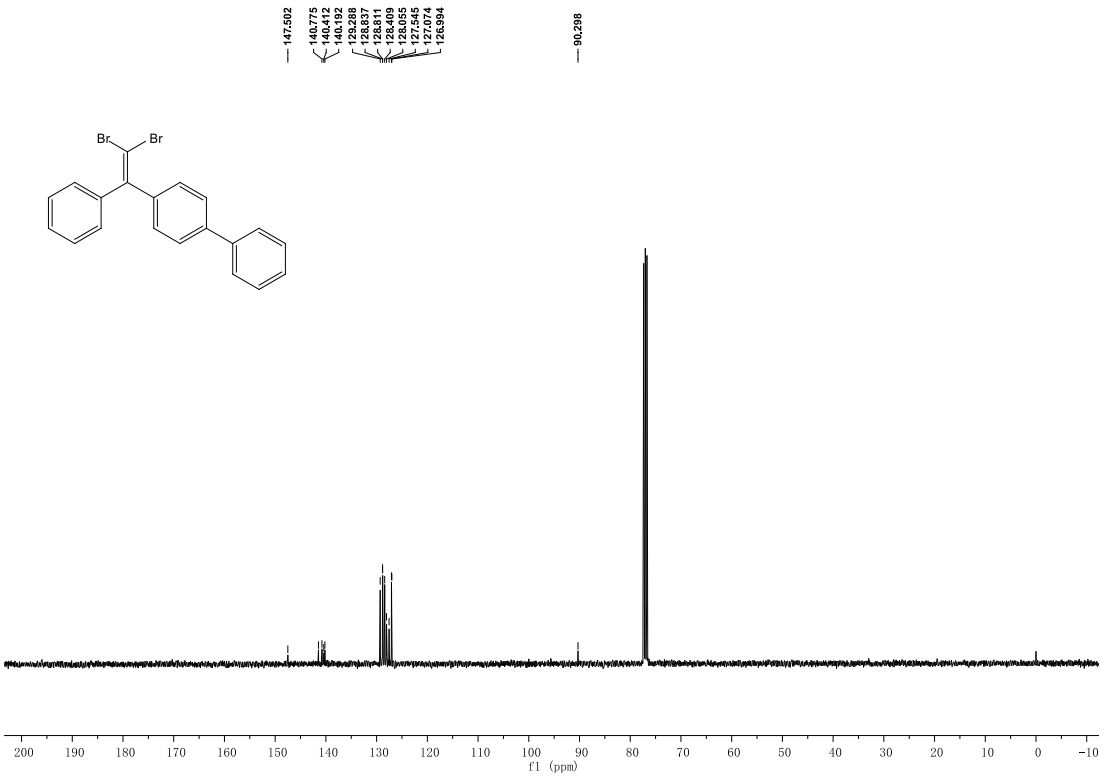
6f ^{13}C NMR



6g ^{1}H NMR



6g ^{13}C NMR



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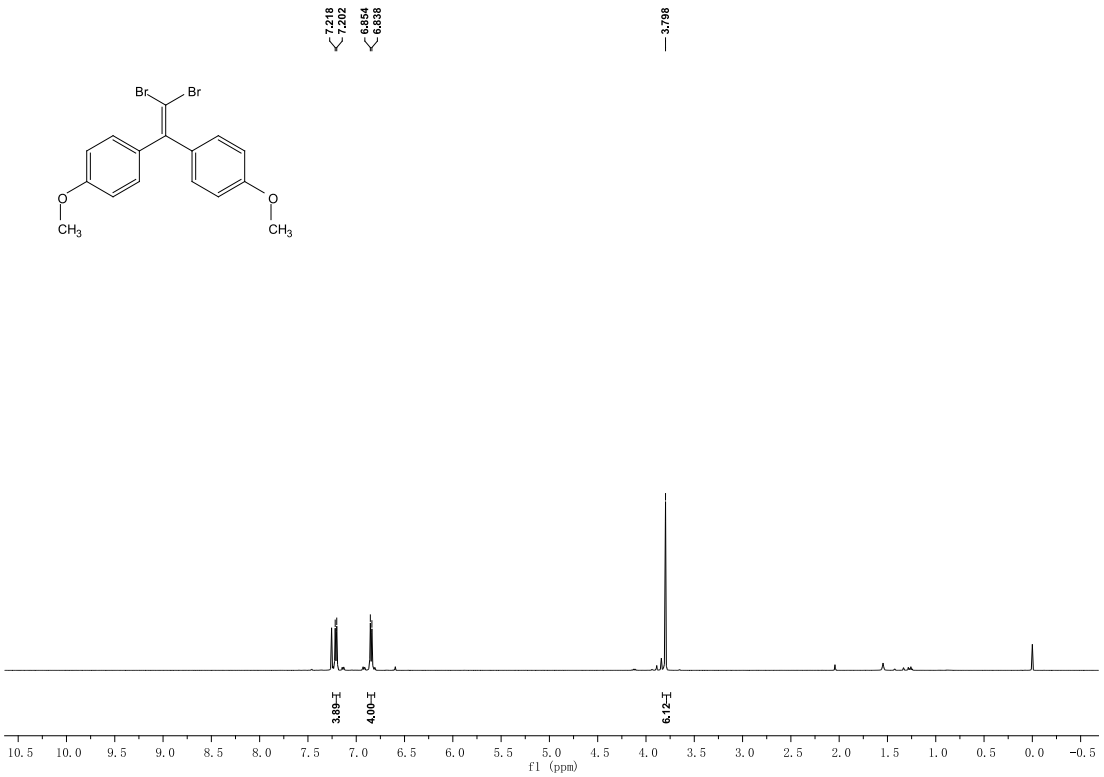
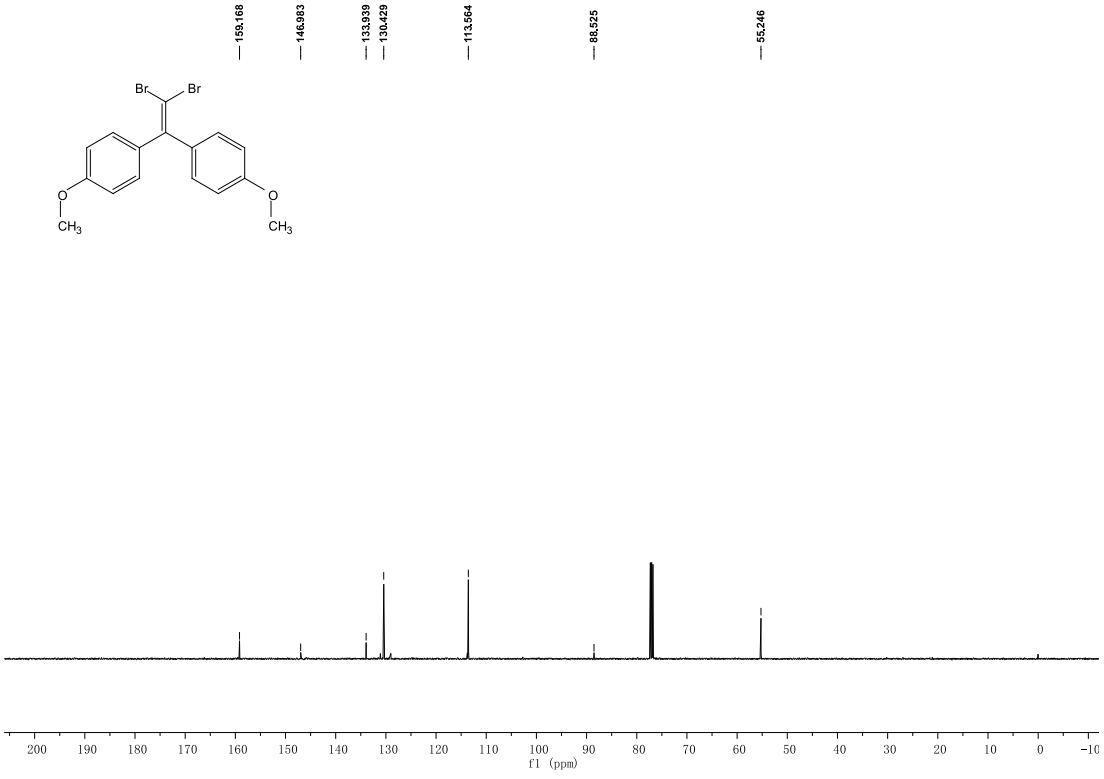
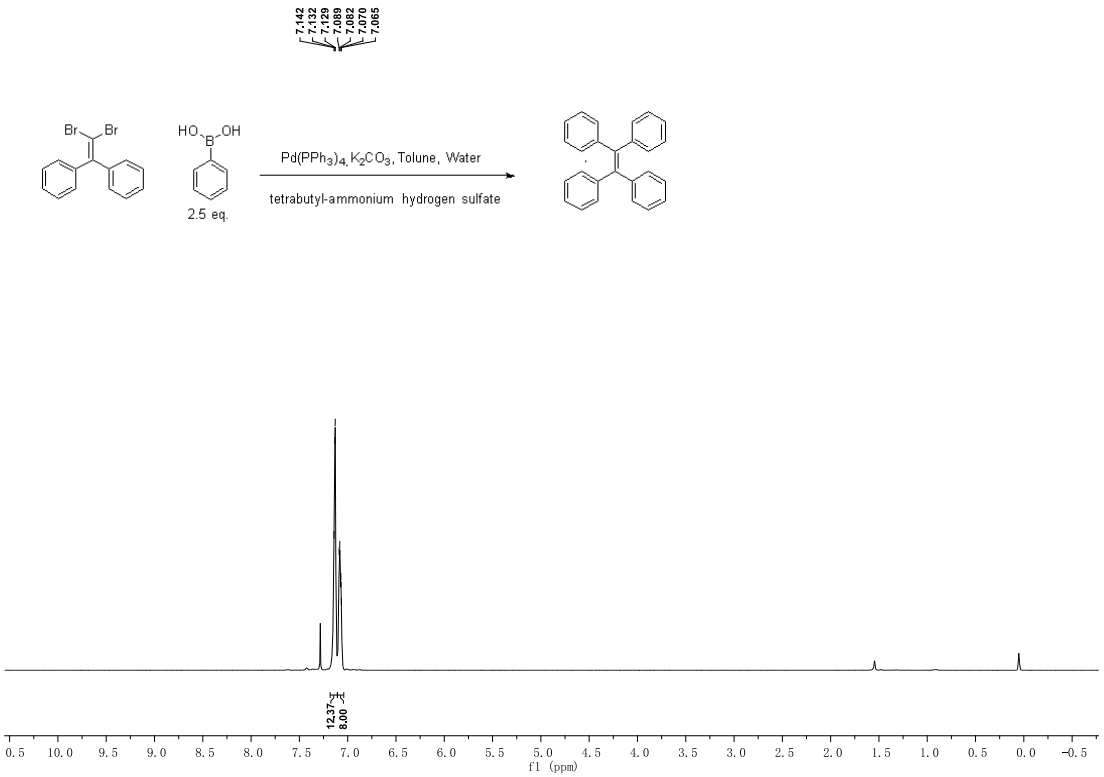


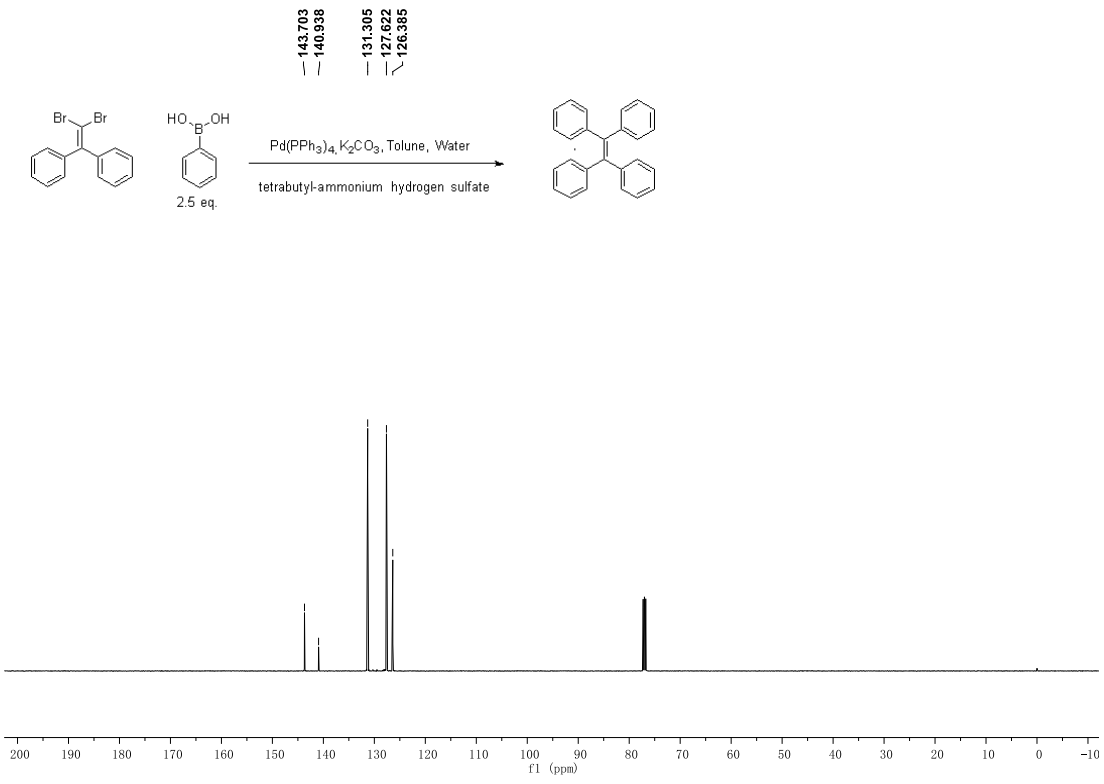
6h ^{13}C NMR



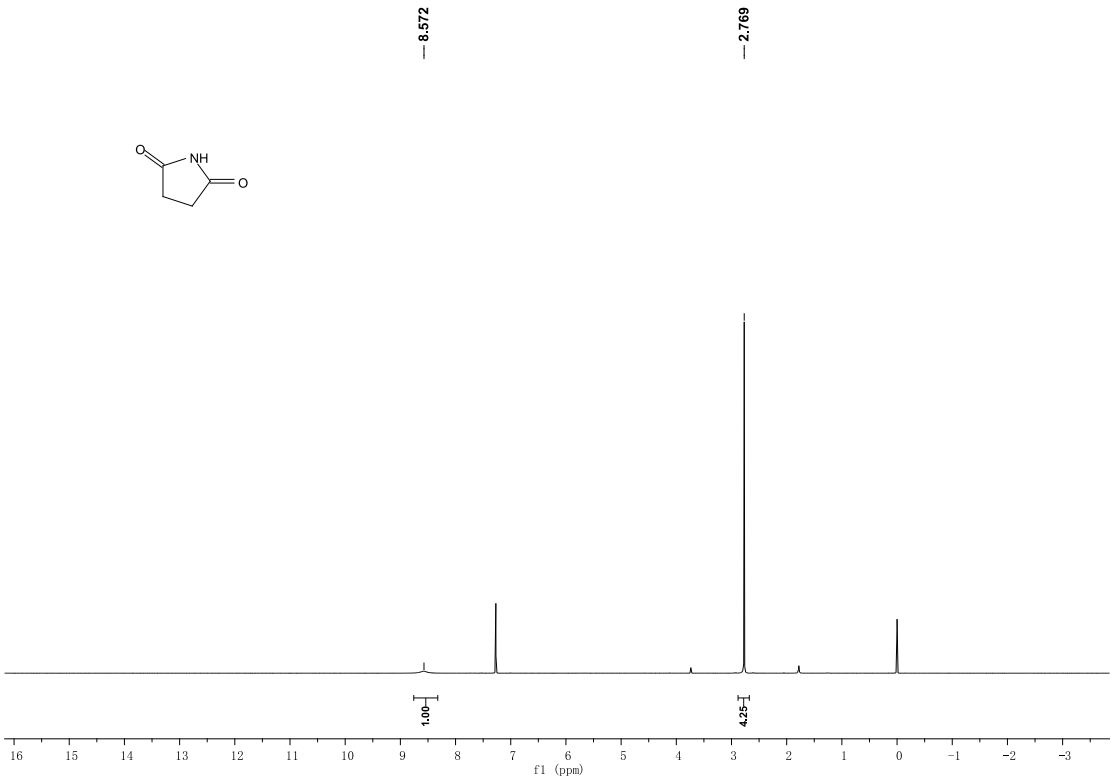
7a ^{1}H NMR



7a ^{13}C NMR



Succinimide ^{1}H NMR



Succinimide ^{13}C NMR