Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

1,1,2-Tribromoethyl arenes: a novel and highly efficient precursor for the synthesis of 1-bromoalkynes and α-bromoketones

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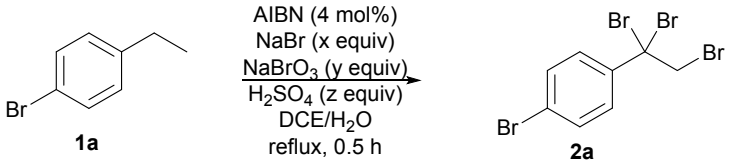
I. General remarks

NMR spectra were obtained on a Bruker AV-600 MHz spectrometer. The ^{1}H NMR (600 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (151 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

II. Optimization of tribromination of 1-bromo-4-ethylbenzene 1a

A 25-mL boiling flask-3-neck with a magnetic stir bar was charged with 1-bromo-4-ethylbenzene **1a** (3 mmol, 1 equiv), NaBr (x equiv), $NaBrO_3$ (y equiv), DCE and H_2O. The reaction mixture was heated to reflux. AIBN was added and then H_2SO_4 (z equiv) was added dropwise to the solution. The resulting mixture was stirred at reflux temperature for 0.5 h and monitored by TLC. Upon completion, the reaction mixture was cooled to rt and then quenched with 10 mL of saturated aqueous $NaHCO_3$. The resulting mixture was extracted with DCE (3x), and the combined organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product **2a**.

Table S1. Optimization of tribromination of 1-bromo-4-ethylbenzene **1a**[a]



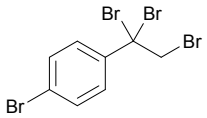
Entry	**1a**/x/y/z	AIBN(mol%)	DCE (mL)	H_2O (mL)	Yield (%)
1	1:2:1:1.5	4	5	0.5	83
2	1:2.2:1.1:1.65	4	5	0.5	85
3	1:2.3:1.15:1.75	4	5	0.5	84
4	1:2.4:1.2:1.8	4	5	0.5	85
5	1:2.2:1.1:1.65	4	3	0.5	83
6	1:2.2:1.1:1.65	4	9	0.5	85

7	**1:2.2:1.1:1.65**	**4**	**12**	**0.5**	**86**
8	1:2.2:1.1:1.65	4	12	0.8	84
9	1:2.2:1.1:1.65	4	12	1.0	81
10	1:2.2:1.1:1.65	4	12	0	76
11	1:2.2:1.1:1.65	8	12	0.5	85

[a]Yields of isolated products. AIBN = azobisisobutyronitrile, DCE = 1,2-dichloroethane.

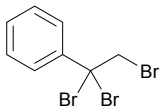
III. General procedure for tribromination of ethylbenzene derivatives

A 25-mL boiling flask-3-neck with a magnetic stir bar was charged with 1-bromo-4-ethylbenzene **1a** (3 mmol, 1 equiv), NaBr (2.2 equiv), $NaBrO_3$ (1.1 equiv), DCE and H_2O. The reaction mixture was heated to reflux. AIBN (20 mg, 4 mol%) was added and then H_2SO_4 (1.65 equiv) was added dropwise to the solution. The resulting mixture was stirred at reflux temperature for 0.5-2.5 h and monitored by TLC. Upon completion, the reaction mixture was cooled to rt and then quenched with 10 mL of saturated aqueous $NaHCO_3$. The resulting mixture was extracted with DCE (3x), and the combined organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product.



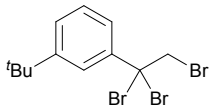
1-Bromo-4-(1,1,2-tribromoethyl)benzene (2a)

Following the general procedure, product was obtained as colorless oil (1.09 g, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 4.61 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 131.45, 128.9, 123.9, 63.1, 45.2.



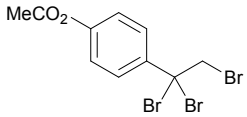
(1,1,2-Tribromoethyl)benzene (2b)

Following the general procedure, product was obtained as yellow oil (1.01 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 7.1 Hz, 1H), 4.66 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 129.5, 128.3, 127.1, 64.6, 45.5. GC-MS (EI): Calcd for $C_8H_7Br_2$ (M-Br): 262.9. Found: 262.9.



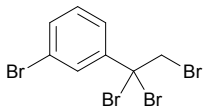
1-(*tert*-Butyl)-3-(1,1,2-tribromoethyl)benzene (2c)

Following the general procedure, product was obtained as colorless oil (1.2 g, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (t, J = 2.0 Hz, 1H), 7.59-7.58 (m, 1H), 7.40-7.38 (m, 1H), 7.32 (t, J = 7.8 Hz, 1H), 4.67 (s, 2H), 1.37 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3, 140.9, 128.1, 126.7, 124.6, 124.4, 65.6, 45.7, 35.0, 31.4.



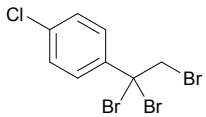
4-(1,1,2-Tribromoethyl)phenyl acetate (2d)

Following the general procedure, product was obtained as colorless oil (0.97 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.01 (m, 2H), 7.25-7.22 (m, 2H), 4.43 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.2, 168.8, 155.1, 131.6, 130.8, 122.3, 30.7, 21.3.



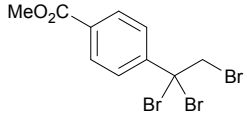
1-Bromo-3-(1,1,2-tribromoethyl)benzene (2e)

Following the general procedure, product was obtained as colorless oil (0.95 g, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (t, J = 2.0 Hz, 1H), 7.67 (dd, J = 8.1 Hz, 2.1 Hz, 1H), 7.49 (dd, J = 8.0 Hz, 2.2 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 4.60 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 132.8, 130.7, 129.9, 126.0, 122.5, 62.6, 45.4.



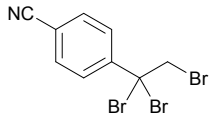
1-Chloro-4-(1,1,2-tribromoethyl)benzene (2f)

Following the general procedure, product was obtained as colorless oil (0.98 g, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 4.61 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.7, 135.6, 128.6, 128.4, 63.1, 45.2.



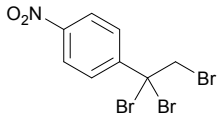
Methyl 4-(1,1,2-tribromoethyl)benzoate (2g)

Following the general procedure, product was obtained as a white solid (0.96 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.84 – 7.81 (m, 2H), 4.64 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 145.3, 131.0, 129.5, 127.3, 63.0, 52.3, 45.1.



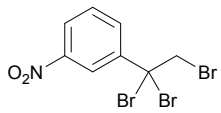
4-(1,1,2-Tribromoethyl)benzonitrile (2h)

Following the general procedure, product was obtained as a white solid (0.50 g, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 4.62 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 132.1, 128.1, 126.8, 117.7, 113.3, 61.6, 44.6. HRMS (ESI) calcd for $C_9H_6Br_3NNa$ $(M+Na)^+$ 387.7933, found 387.7943.



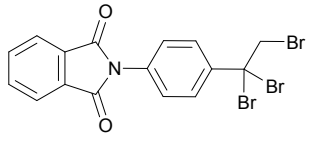
1-Nitro-4-(1,1,2-tribromoethyl)benzene (2i)

Following the general procedure, product was obtained as a yellow solid (0.52 g, 45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 – 8.23 (m, 2H), 7.95 – 7.93 (m, 2H), 4.64 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 147.3, 128.5, 123.4, 61.1, 44.6. GC-MS (EI): Calcd for $C_8H_6Br_2NO_2$ (M-Br): 307.9. Found: 307.9.



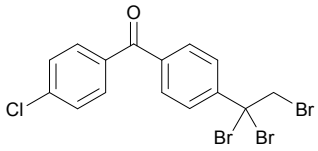
1-Nitro-3-(1,1,2-tribromoethyl)benzene (2j)

Following the general procedure, product was obtained as a yellow solid (0.70 g, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (t, J = 2.1 Hz, 1H), 8.23 (ddd, J = 8.2, 2.0, 0.7 Hz, 1H), 8.09 (ddd, J = 8.0, 2.0, 0.8 Hz, 1H), 7.61 (t, J = 8.1 Hz, 1H), 4.65 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 143.2, 133.1, 129.5, 124.3, 122.5, 61.1, 44.8.GC-MS (EI): Calcd for $C_8H_6Br_2NO_2$ (M-Br): 307.9. Found: 307.9.



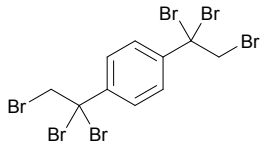
2-(4-(1,1,2-Tribromoethyl)phenyl)isoindoline-1,3-dione (2k)

Following the general procedure, product was obtained as a white solid (1.20 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, J = 5.4, 3.0 Hz, 2H), 7.91 – 7.88 (m, 2H), 7.81 (dd, J = 5.5, 3.0 Hz, 2H), 7.56 – 7.52 (m, 2H), 4.66 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 140.4, 134.6, 132.7, 131.5, 128.0, 125.6, 123.9, 63.4, 45.2. HRMS (ESI) calcd for $C_{16}H_{10}Br_3NNaO_2$ $(M+Na)^+$ 507.8160, found 507.8154.



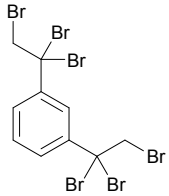
(4-Chlorophenyl)(4-(1,1,2-tribromoethyl)phenyl)methanone (2l)

Following the general procedure, product was obtained as a white solid (1.21 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 8.6 Hz, 2H), 7.78 (dd, J = 8.5, 6.9 Hz, 4H), 7.48 (d, J = 8.5 Hz, 2H), 4.67 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.2, 145.1, 139.3, 137.9, 135.2, 131.4, 129.7, 128.8, 127.4. HRMS (ESI) calcd for $C_{15}H_{10}Br_3ClNaO$ $(M+Na)^+$ 500.7859, found 500.7863.



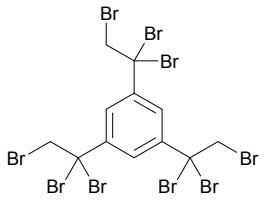
1,4-Bis(1,1,2-tribromoethyl)benzene (2m)

NaBr (4.4 equiv), $NaBrO_3$ (2.2 equiv) and H_2SO_4 (3.3 equiv) were used to afford the product as a white solid (1.64 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 4H), 4.62 (s, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 127.2, 62.8, 45.0.



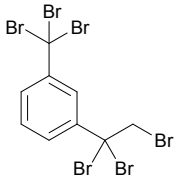
1,3-Bis(1,1,2-tribromoethyl)benzene (2n)

NaBr (4.4 equiv), $NaBrO_3$ (2.2 equiv) and H_2SO_4 (3.3 equiv) were used to afford the product as colorless oil (1.27 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (t, J = 2.0 Hz, 1H), 7.75 (dd, J = 8.0, 2.1 Hz, 2H), 7.42 (t, J = 8.0 Hz, 1H), 4.63 (s, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 128.3, 126.6, 63.2, 45.3.



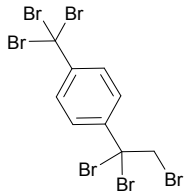
1,3,5-Tris(1,1,2-tribromoethyl)benzene (2o)

NaBr (6.6 equiv), $NaBrO_3$ (3.3 equiv), H_2SO_4 (4.4 equiv) and AIBN (6 mol%) were used to afford the product as colorless oil (2.35 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 3H), 4.62 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.6, 127.5, 62.1, 45.1.



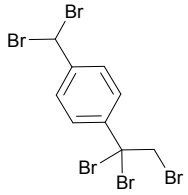
1-(1,1,2-Tribromoethyl)-3-(tribromomethyl)benzene (2p)

NaBr (4.4 equiv), $NaBrO_3$ (2.2 equiv) and H_2SO_4 (3.3 equiv) were used to afford the product as a white solid (1.26 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (t, J = 2.0 Hz, 1H), 8.00 (dd, J = 8.0, 1.5 Hz, 1H), 7.74 (dd, J = 8.0, 1.3 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 4.65 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 141.2, 128.8, 128.2, 127.4, 125.6, 62.8, 45.1, 34.6.



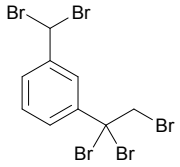
1-(1,1,2-Tribromoethyl)-4-(tribromomethyl)benzene (2q)

NaBr (4.4 equiv), $NaBrO_3$ (2.2 equiv) and H_2SO_4 (3.3 equiv) were used to afford the product as a white solid (1.28 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.79 – 7.76 (m, 2H), 4.64 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 142.7, 127.0, 126.5, 62.4, 44.9, 34.1.



1-(Dibromomethyl)-4-(1,1,2-tribromoethyl)benzene (2r)

NaBr (3.3 equiv), $NaBrO_3$ (1.65 equiv) and H_2SO_4 (2.5 equiv) were used to afford the product as yellow oil (1.17 g, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.60 – 7.57 (m, 2H), 6.65 (s, 1H), 4.63 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 142.4, 127.5, 126.5, 62.9, 45.1, 39.4.



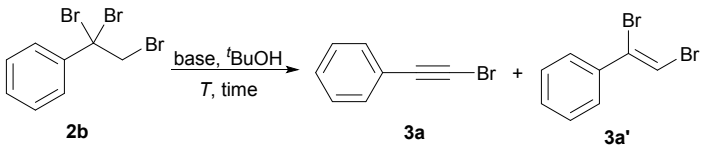
1-(Dibromomethyl)-3-(1,1,2-tribromoethyl)benzene (2s)

NaBr (3.3 equiv), $NaBrO_3$ (1.65 equiv) and H_2SO_4 (2.5 equiv) were used to afford the product as yellow oil (1.15 g, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (t, J = 1.9 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 6.67 (s, 1H), 4.63 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.9, 141.6, 128.8, 128.4, 127.8, 125.4, 63.1, 45.1, 39.8.

IV. Optimization of β-H elimination of 1,1,2-tribromoethyl arenes

A 25-mL round-bottom flask with a magnetic stir bar was charged with ^{t}BuOK and ^{t}BuOH. The mixture was stirred at rt for 5 min, and then (1,1,2-tribromoethyl)benzene **2b** (0.34g, 1.0 mmol) was added. The reaction mixture was stirred at 35 °C for 0.5 h and monitored by TLC. Upon completion, the reaction mixture was diluted with 10 mL of H_2O and extracted with EtOAc (3x). The combined organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product **3a**.

Table S2. Optimization of β-H elimination of (1,1,2-tribromoethyl)benzene **2b**[a]



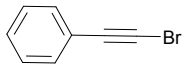
Entry	base	*T*	Time	Yield of **3a**	Yield of **3a'**
1	NaOH, 4.0 equiv	85 °C	10 h	0	91
2	KOH, 4.0 equiv	85 °C	10 h	0	93
3	NaH, 4.0 equiv	85 °C	10 h	0	0
4	^{t}BuOK, 4.0 equiv	85 °C	10 h	95	0
5	^{t}BuOK, 4.0 equiv	35 °C	10 h	95	0

6	^{t}BuOK, 4.0 equiv	35 ^{o}C	0.5 h	98	0
7	^{t}BuOK, 2.1 equiv	35 ^{o}C	0.5 h	98	0
8	^{t}BuOK, 2.0 equiv	35 ^{o}C	0.5 h	95	0
9[b]	**^{t}BuOK, 2.1 equiv**	**35 ^{o}C**	**0.5 h**	**98**	**0**

[a]1.0 mmol of **2b**, 5 mL of ^{t}BuOH was used. Yields of isolated products. [b]3 mL of ^{t}BuOH was used..

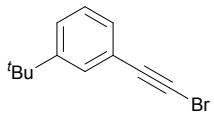
V. General procedure for the synthesis of 1-bromoalkynes

A 25-mL round-bottom flask with a magnetic stir bar was charged with ^{t}BuOK (0.24g, 2.1 mmol, 2.1 equiv) and ^{t}BuOH (3 mL). The mixture was stirred at rt for 5 min, and then (1,1,2-tribromoethyl)benzene derivative (1.0 mmol) was added. The reaction mixture was stirred at 35 ^{o}C for 0.5 h and monitored by TLC. Upon completion, the reaction mixture was diluted with 10 mL of H_2O and extracted with EtOAc (3x). The combined organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product.



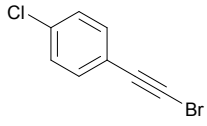
(Bromoethynyl)benzene (3a)[1]

Following the general procedure, product was obtained as a white solid (177 mg, 98%). ^{1}H NMR (600 MHz, CDCl3) δ 7.47 – 7.46 (m, 1H), 7.46 (t, J = 1.9 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.33 (dd, J = 2.2, 1.4 Hz, 1H), 7.32 (dd, J = 2.2, 1.5 Hz, 1H); ^{13}C NMR (151 MHz, CDCl3) δ 131.9, 128.6, 128.3, 122.6, 80.0, 49.7.



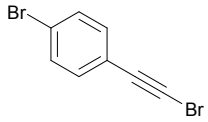
1-(Bromoethynyl)-3-(*tert*-butyl)benzene (3b)

Following the general procedure, product was obtained as colorless oil (182 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.45-7.43 (m, 1H), 7.34-7.29 (m, 2H), 1.37 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 129.2, 128.2, 126.1, 122.4, 80.7, 49.1, 34.8, 31.3. HRMS (ESI) calcd for $C_{12}H_{14}Br$ $(M+H)^+$ 237.0279, found 237.0274.



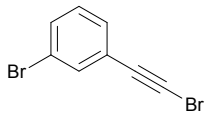
1-(Bromoethynyl)-4-chlorobenzene (3c)[1]

Following the general procedure, product was obtained as a white solid (211 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 133.1, 128.6, 121.1, 78.9, 51.0.



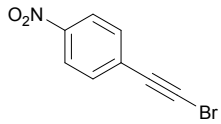
1-Bromo-4-(bromoethynyl)benzene (3d)[1]

Following the general procedure, product was obtained as a white solid (223 mg, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 133.1, 128.6, 121.1, 78.9, 51.0.



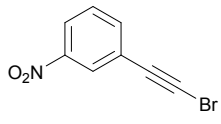
1-Bromo-3-(bromoethynyl)benzene (3e)[2]

Following the general procedure, product was obtained as a white solid (210 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (t, J = 1.7 Hz, 1H), 7.47 (ddd, J = 8.1, 1.8, 0.9 Hz, 1H), 7.37 (dd, J = 7.7, 1.0 Hz, 1H), 7.18 (t, J = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 131.8, 130.5, 129.7, 124.6, 122.0, 78.5, 51.6.



1-(Bromoethynyl)-4-nitrobenzene (3f)[1]

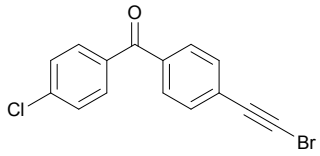
Following the general procedure, product was obtained as a yellow solid (215 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 7.7 Hz, 2H), 7.59 (d, J = 7.7 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 132.8, 129.4, 123.5, 78.4, 56.3.



1-(Bromoethynyl)-3-nitrobenzene (3g)[1]

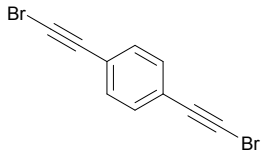
Following the general procedure, product was obtained as a yellow solid (192 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 – 8.28 (m, 1H), 8.19 (dd, J = 8.3, 1.3 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ

137.6, 129.4, 126.8, 124.4, 123.4, 77.7, 53.5.



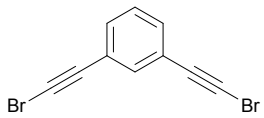
(4-(Bromoethynyl)phenyl)(4-chlorophenyl)methanone (3h)

Following the general procedure, product was obtained as a white solid (253 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 4H), 7.61 – 7.59 (m, 2H), 7.48 – 7.46 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.6, 139.1, 137.0, 135.4, 132.1, 131.3, 129.7, 128.7, 126.5, 82.6, 58.7. HRMS (ESI) calcd for $C_{15}H_9BrClO$ $(M+H)^+$ 318.9534, found 318.9520.



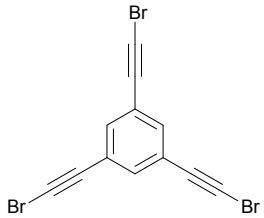
1,4-Bis(bromoethynyl)benzene (3i)[3]

^{t}BuOK (0.46 g, 4.1 mmol, 4.1 equiv) and ^{t}BuOH (6 mL) were used. The reaction mixture was stirred at 55 ^{o}C for 3 h to give the product as a white solid (247 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (s, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.8, 122.9, 79.5, 52.1.



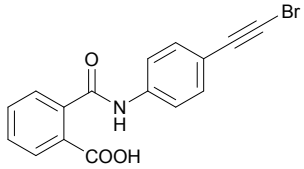
1,3-Bis(bromoethynyl)benzene (3j)[4]

^{t}BuOK (0.46 g, 4.1 mmol, 4.1 equiv) and ^{t}BuOH (6 mL) were used. The reaction mixture was stirred at 55 ^{o}C for 3 h to give the product as a white solid as colorless oil (244 mg, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.42 (dd, J = 7.8, 1.6 Hz, 2H), 7.27 (t, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.3, 132.1, 128.4, 123.1, 78.9, 50.9.



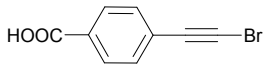
1,3,5-Tris(bromoethynyl)benzene (3k)[5]

^{t}BuOK (0.46 g, 4.1 mmol, 4.1 equiv) and ^{t}BuOH (6 mL) were used. The reaction mixture was stirred at 55 ^{o}C for 3 h to give the product as a white solid (317 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.2, 123.5, 78.1, 52.1.



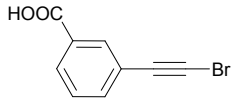
2-((4-(Bromoethynyl)phenyl)carbamoyl)benzoic acid (3l)

2-(4-(1,1,2-Tribromoethyl)phenyl)isoindoline-1,3-dione **2k** (0.49 g, 1.0 mmol) were used as the starting material to give the product as a white solid (292 mg, 85%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.09 (s, 1H), 10.54 (s, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.68 – 7.65 (m, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 168.0, 167.7, 140.6, 139.1, 132.8, 132.2, 130.2, 129.9, 128.1, 119.6, 116.6, 80.2, 51.9. HRMS (ESI) calcd for $C_{16}H_{10}BrNNaO_3$ $(M+Na)^+$ 365.9737, found 365.9736.



4-(Bromoethynyl)benzoic acid (3m)[6]

1-(Dibromomethyl)-4-(1,1,2-tribromoethyl)benzene **2r** (0.52 g, 1 mmol), ^{t}BuOK (0.39 g, 3.5 mmol, 3.5 equiv) and ^{t}BuOH (4 mL) were used. The reaction mixture was stirred at 65 ^{o}C for 5 h to give the product as a white solid (170 mg, 76%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.16 (s, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.1, 132.4, 131.4, 129.9, 126.6, 79.5, 56.6.



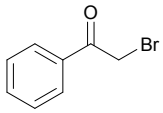
3-(Bromoethynyl)benzoic acid (3n)[7]

1-(1,1,2-Tribromoethyl)-3-(tribromomethyl)benzene **2p** (0.52 g, 1 mmol), ^{t}BuOK (0.45 g, 4.0 mmol, 4.0 equiv) and ^{t}BuOH (4 mL) were used. The reaction mixture was stirred at 65 ^{o}C for 15 h to give the product as a white solid (144 mg, 64%). ^{1}H NMR

(600 MHz, DMSO-d_6) δ 13.25 (s, 1H), 7.97 – 7.94 (m, 2H), 7.71 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 8.1 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.8, 136.2, 132.7, 131.8, 130.1, 129.6, 122.7, 79.2, 54.5.

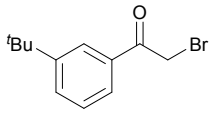
VI. General procedure for the synthesis of 2-bromoacetophenones

A 10-mL round-bottom flask with a magnetic stir bar was charged with(1,1,2-tribromoethyl)benzene **2b** (1.0 mmol) and 40% HBr (4 mL). The mixture was stirred at 105 ^{o}C for 10 h and monitored by TLC. Upon completion, the reaction mixture was cooled to rt, diluted with 10 mL of H_2O and extracted with EtOAc (3x). The combined organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give the product **4a**.



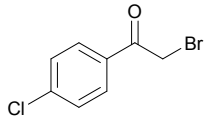
2-Bromoacetophenone (4a)[8]

Following the general procedure, product was obtained as a white solid (175 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.4, 1.2 Hz, 2H), 7.62 – 7.59 (m, 1H), 7.51 – 7.47 (m, 2H), 4.46 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.2, 133.8, 128.8, 30.9.



2-Bromo-3'-*tert*-butylacetophenone (4b)[9]

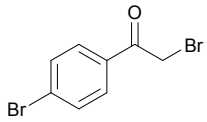
Following the general procedure, product was obtained as colorless oil (173 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 4.47 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.6, 152.0, 133.7, 131.1, 128.5, 126.2, 125.7, 34.8, 31.1



2-Bromo-4'-chloroacetophenone (4c)[8]

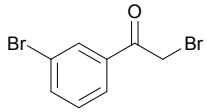
Following the general procedure, product was obtained as a white solid (173 mg, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.49 – 7.45 (m, 2H), 4.41

(s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.1, 140.5, 132.2, 130.3, 129.2, 30.3.



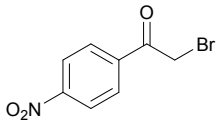
2,4'-Dibromoacetophenone (4d)[8]

Following the general procedure, product was obtained as a white solid (209 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (t, J = 1.7 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.73 (ddd, J = 8.0, 1.8, 0.9 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 4.41 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.9, 136.7, 135.6, 131.8, 130.3, 127.4, 123.1, 30.3.



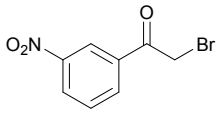
2,3'-Dibromoacetophenone (4e)[8]

Following the general procedure, product was obtained as a white solid (195 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (t, J = 1.7 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.73 (ddd, J = 8.0, 1.8, 0.9 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 4.41 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.9, 136.7, 135.6, 131.8, 130.3, 127.4, 123.1, 30.3.



2-Bromo-4'-nitroacetophenone (4f)[8]

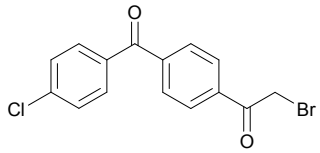
40% HBr (5 mL) was used. The mixture was stirred at reflux temperature for 3 h to afford a yellow solid (180 mg, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 2H), 8.17 – 8.14 (m, 2H), 4.46 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.8, 150.6, 138.3, 130.0, 124.0, 30.1.



2-Bromo-3'-nitroacetophenone (4g)[8]

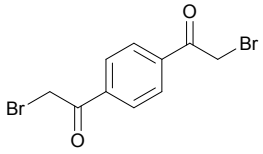
40% HBr (5 mL) was used. The mixture was stirred at reflux temperature for 3 h to afford a white solid (168 mg, 69%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (t, J = 1.9 Hz, 1H), 8.46 (ddd, J = 8.2, 2.2, 1.0 Hz, 1H), 8.34 – 8.31 (m, 1H), 7.73 (t, J = 8.0 Hz, 1H),

4.48 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.3, 148.4, 135.1, 134.4, 130.1, 128.1, 123.7, 29.9.



2-Bromo-1-(4-(4-chlorobenzoyl)phenyl)ethan-1-one (4h)

40% HBr (5 mL) was used. The mixture was stirred at reflux temperature for 3 h to afford a white solid (250 mg, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 4.48 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.4, 190.7, 141.6, 139.7, 136.5, 134.9, 131.4, 130.0, 128.9, 30.4. HRMS (ESI) calcd for $C_{15}H_{11}BrClO_2$ $(M+H)^+$ 336.96.15, found 336.96.25.



1,1'-(1,4-Phenylene)bis(2-bromoethan-1-one) (4i)[10]

40% HBr (5 mL) was used. The mixture was stirred at reflux temperature for 3 h to afford a yellow solid (269 mg, 84%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.13 (s, 4H), 5.01 (s, 4H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 191.9, 138.0, 129.4, 34.8.

VII. References

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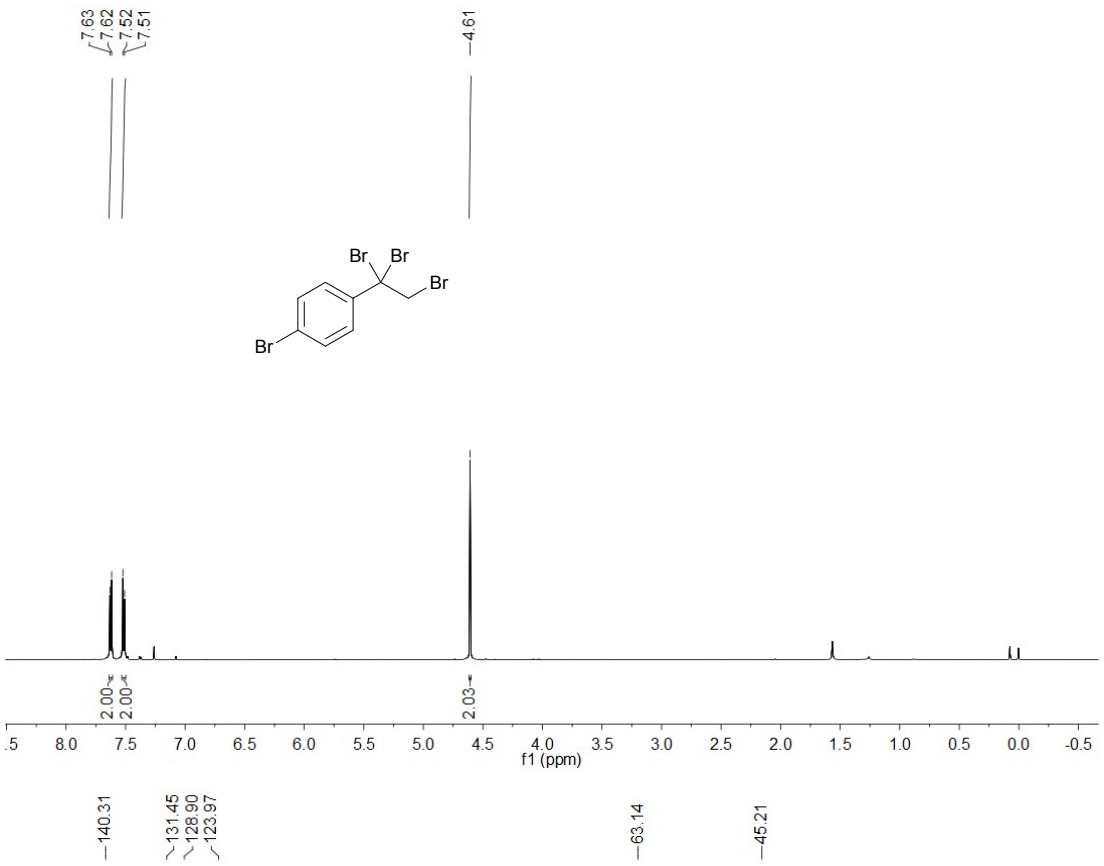
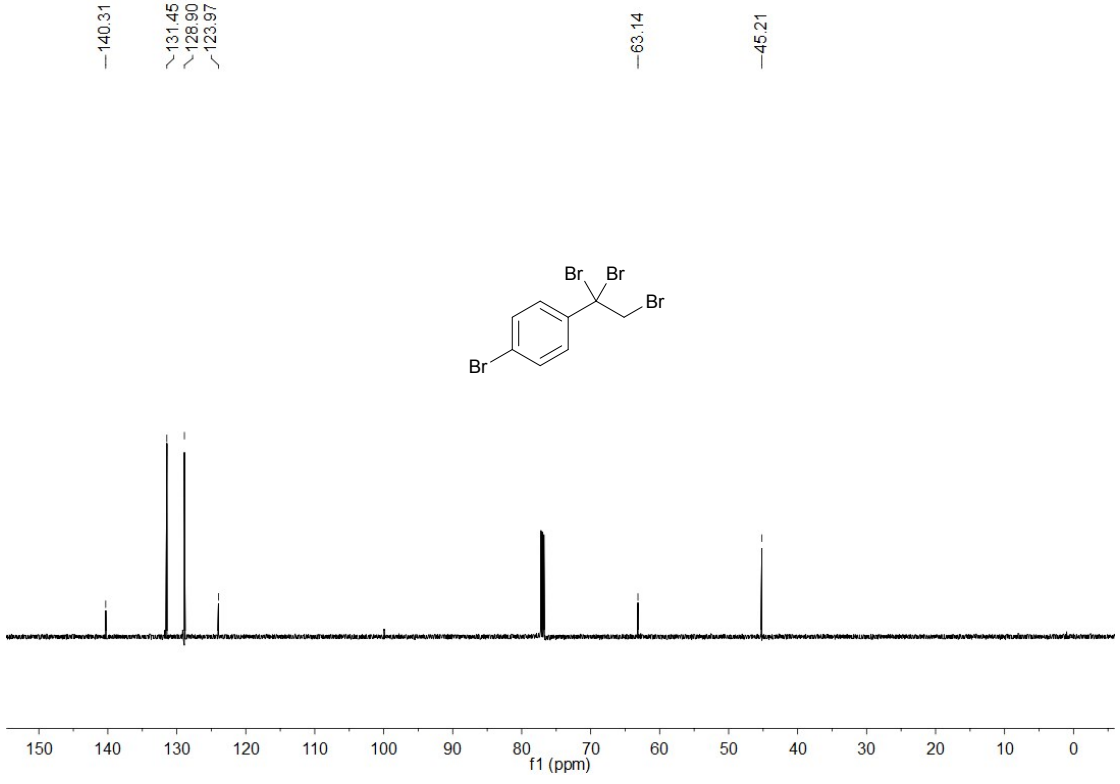
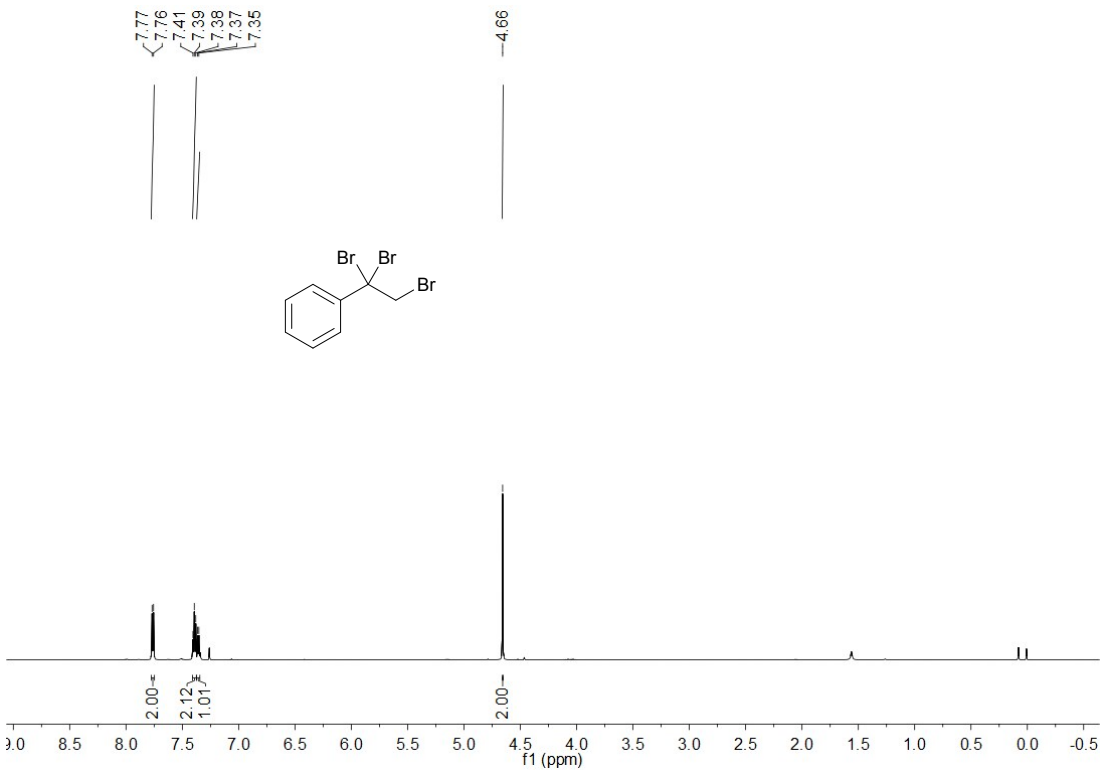
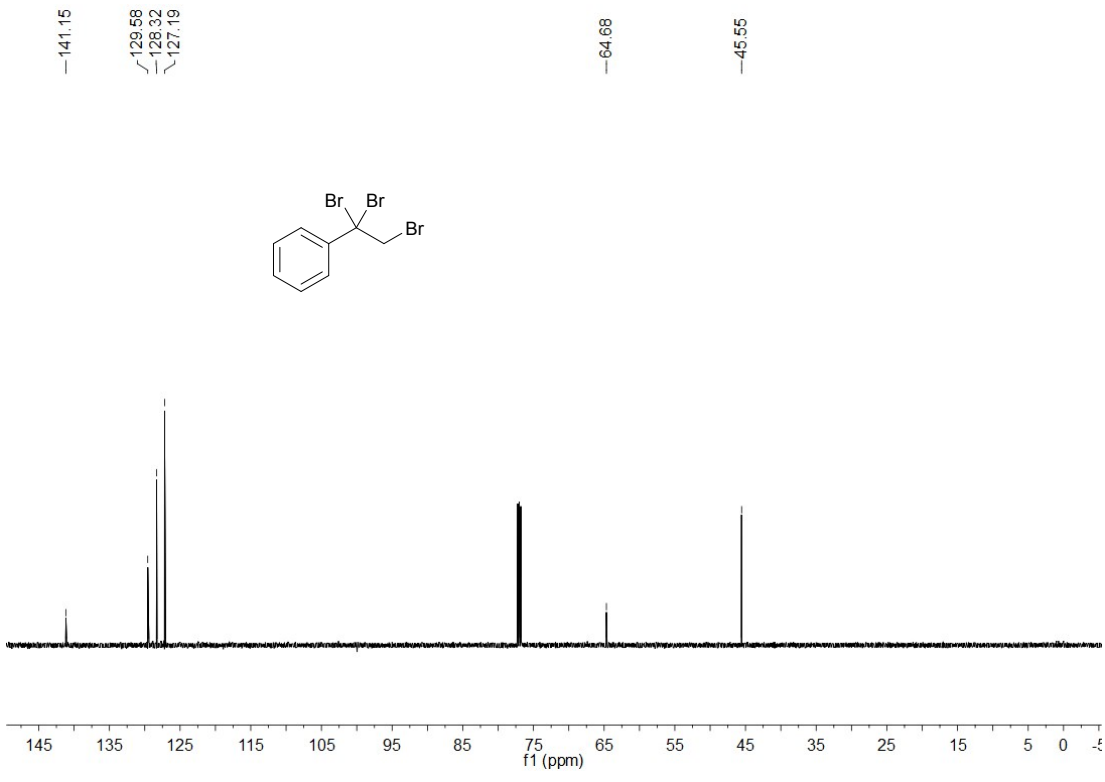
VIII. Copies of ^{1}H and ^{13}C NMR spectra

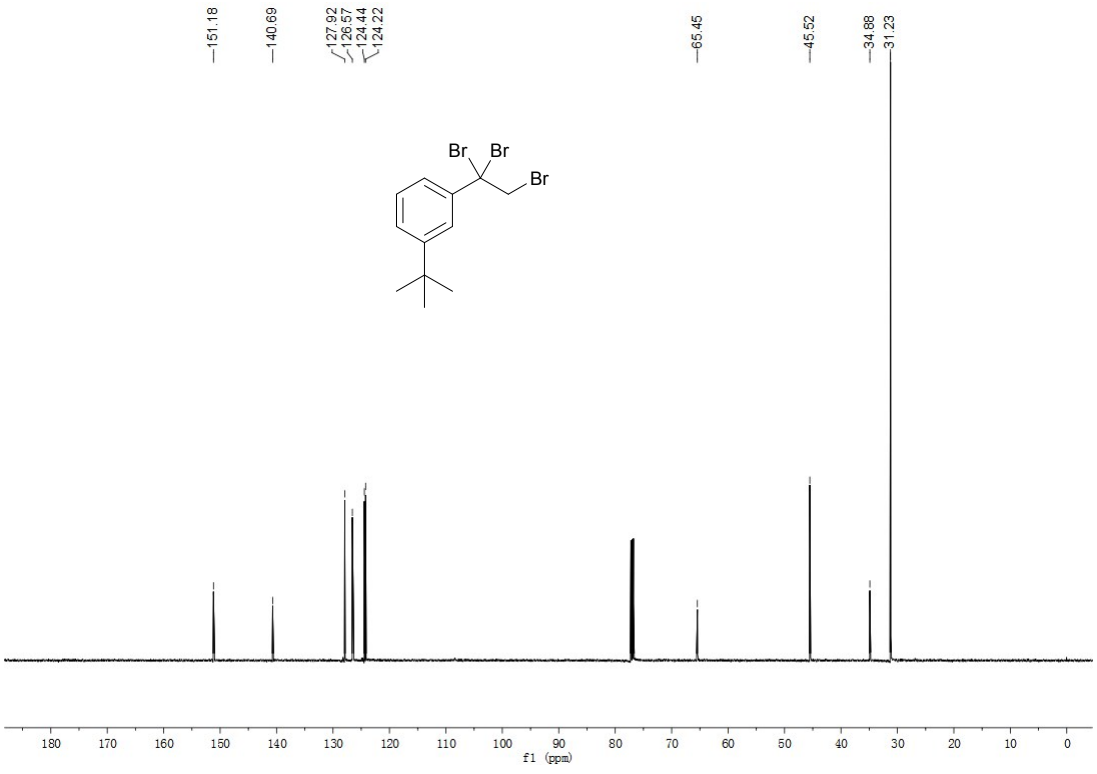

7.63
7.62
7.52
7.51
4.61
Br
Br
Br
Br
2.00
2.00
2.03
f1 (ppm)

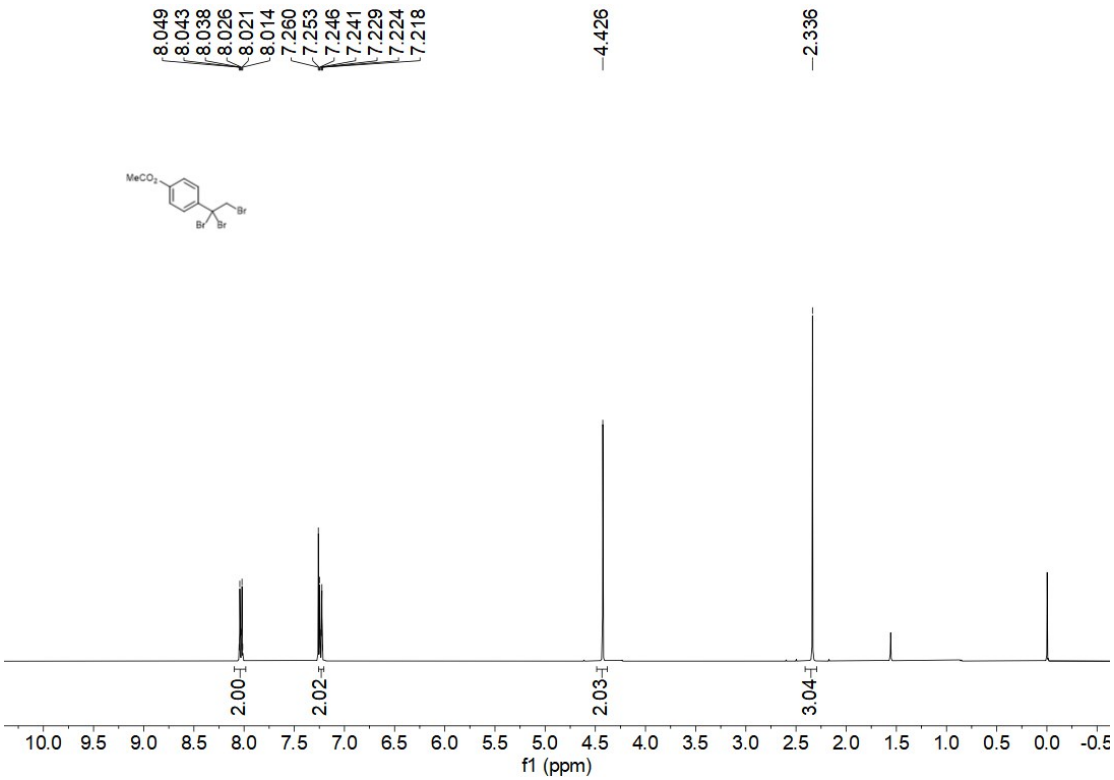

140.31
131.45
128.90
123.97
63.14
45.21
Br
Br
Br
Br
f1 (ppm)

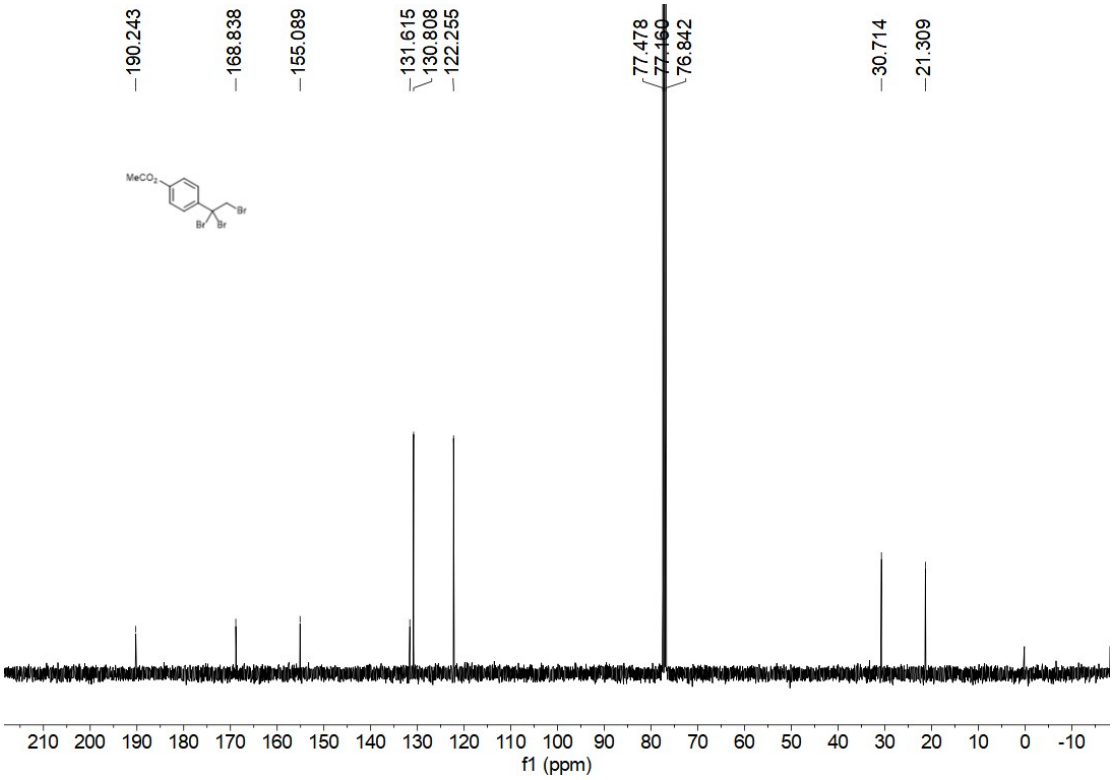

7.77
7.76
7.41
7.39
7.38
7.37
7.35
4.66
Br
Br
Br
2.00
2.12
1.01
2.00
f1 (ppm)

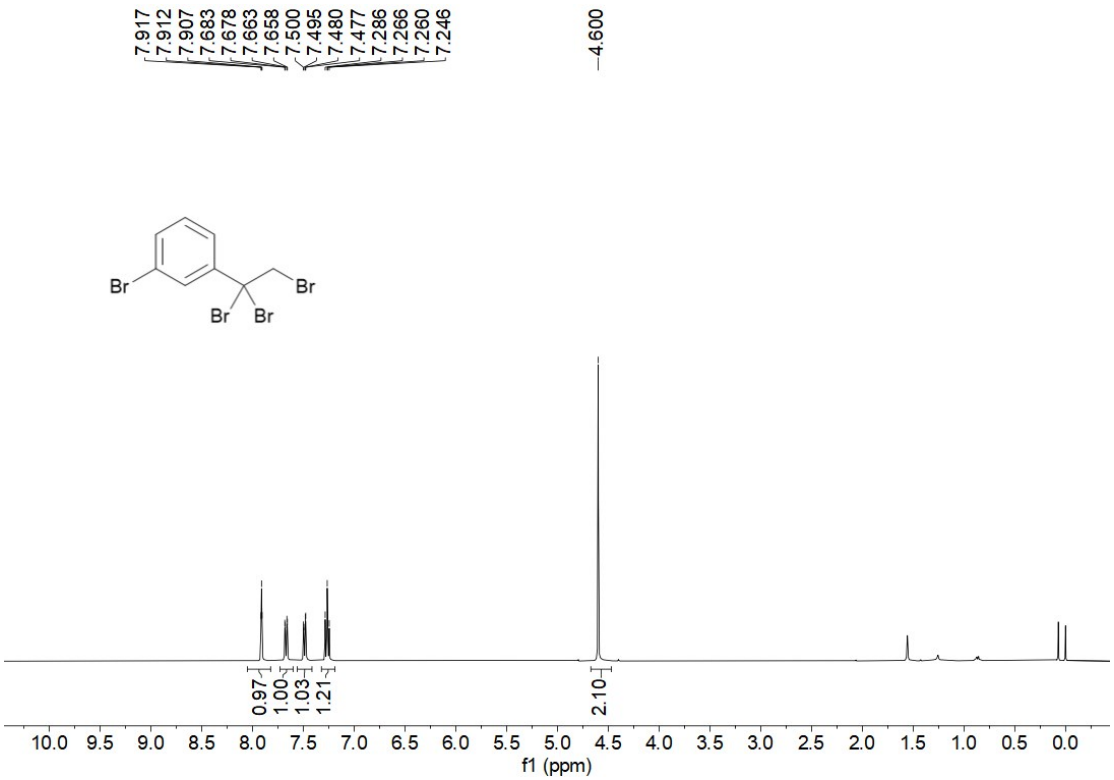

141.15
129.58
128.32
127.19
64.68
45.55
Br
Br
Br
f1 (ppm)

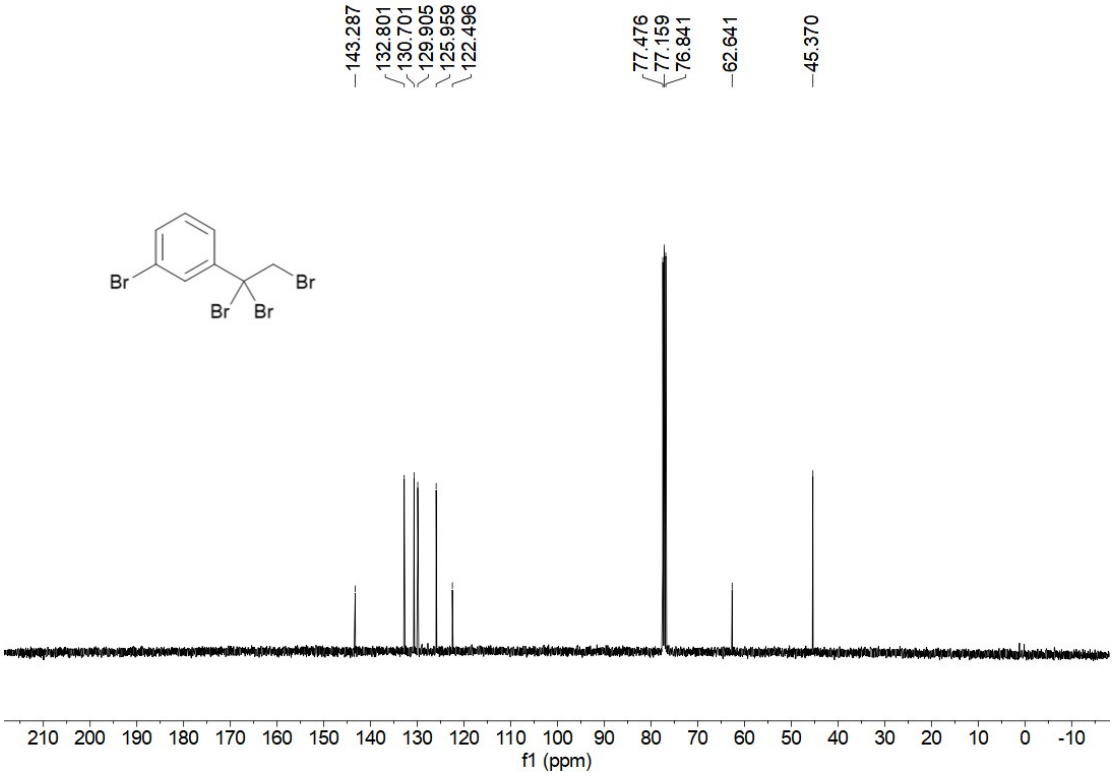

7.80
7.80
7.80
7.59
7.59
7.59
7.59
7.58
7.58
7.58
7.58
7.56
7.40
7.39
7.38
7.38
7.34
7.32
7.31
4.67
1.37
Br
Br
Br
1.00
1.00
1.02
1.05
2.03
9.06
f1 (ppm)

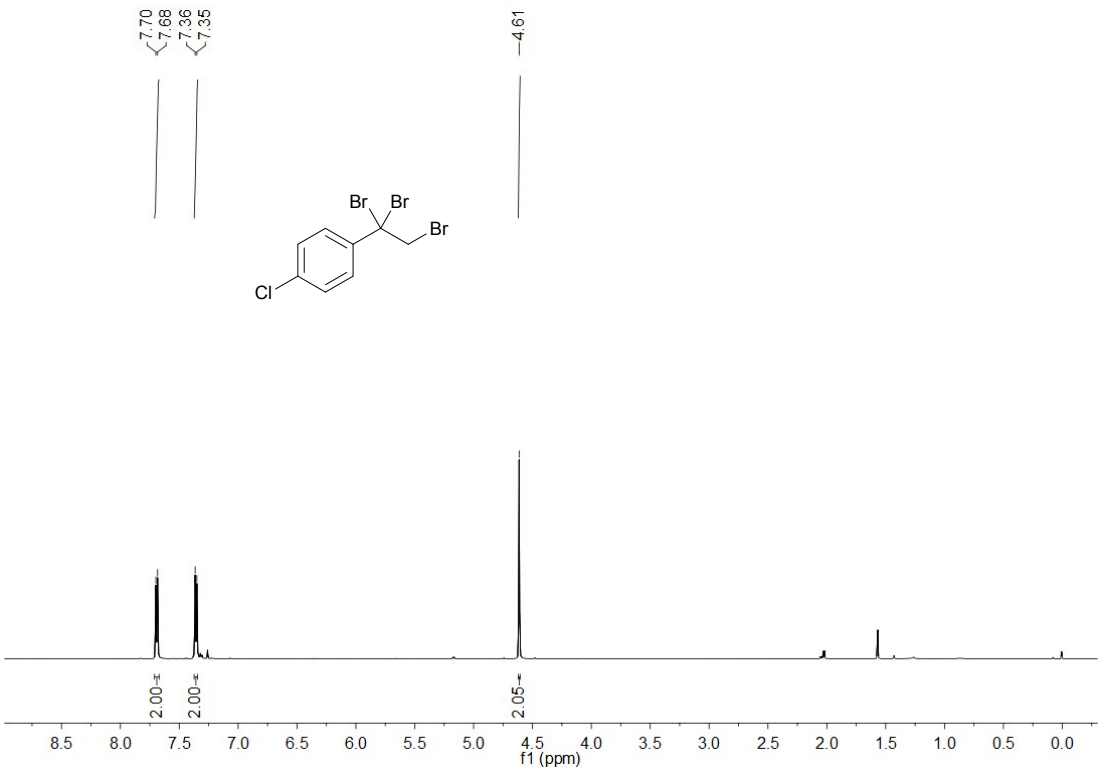

151.18
140.69
127.92
126.57
124.44
124.22
65.45
45.52
34.88
31.23
Br
Br
Br
f1 (ppm)

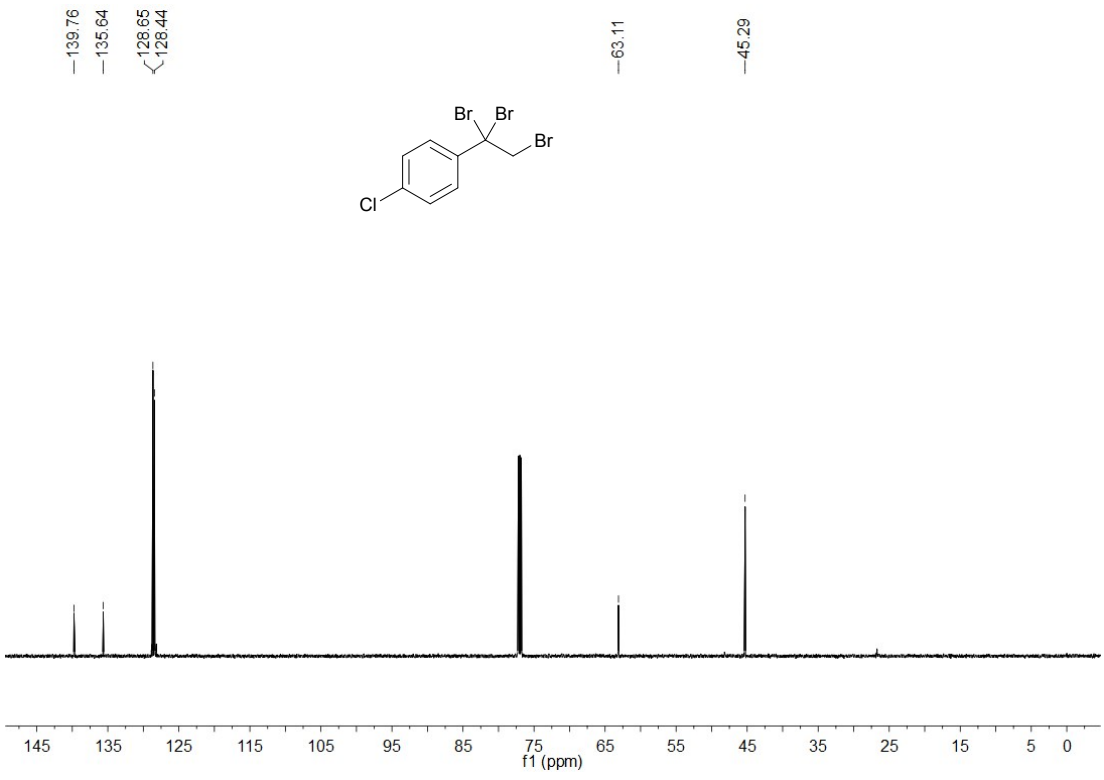

8.049
8.043
8.038
8.026
8.021
8.014
7.260
7.253
7.246
7.241
7.229
7.224
7.218
4.426
2.336
2.00
2.02
2.03
3.04
f1 (ppm)

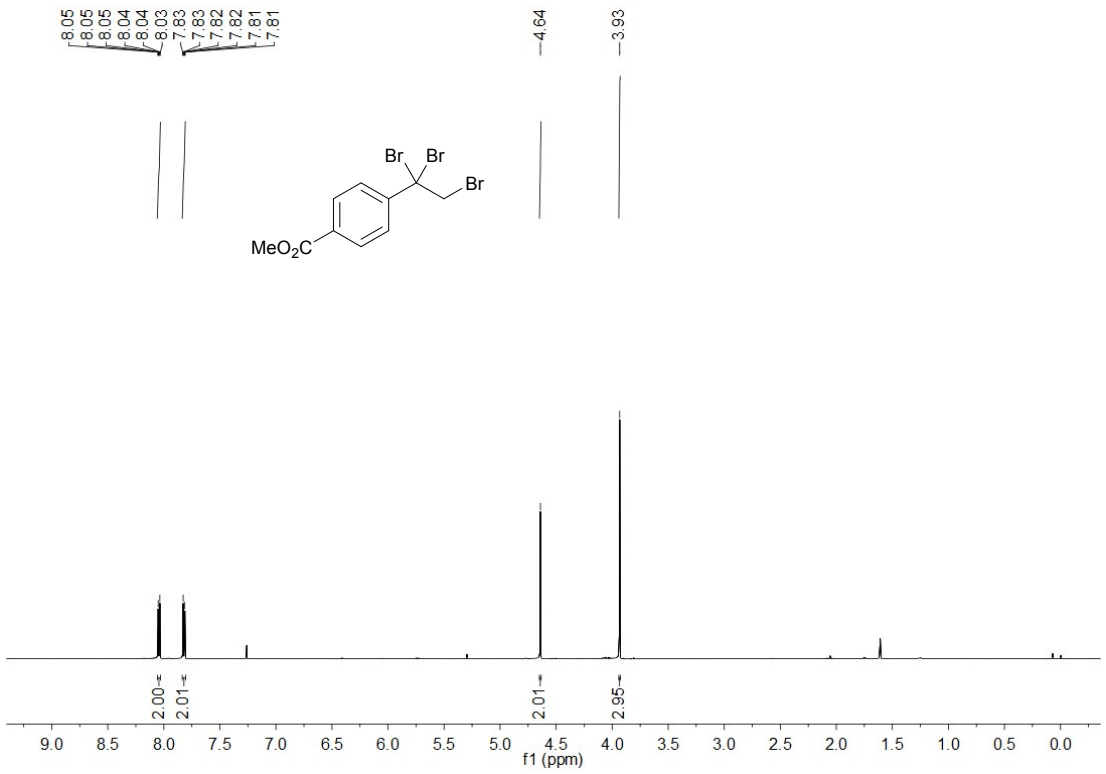

190.243
168.838
155.089
131.615
130.808
122.255
77.478
77.160
76.842
30.714
21.309
f1 (ppm)

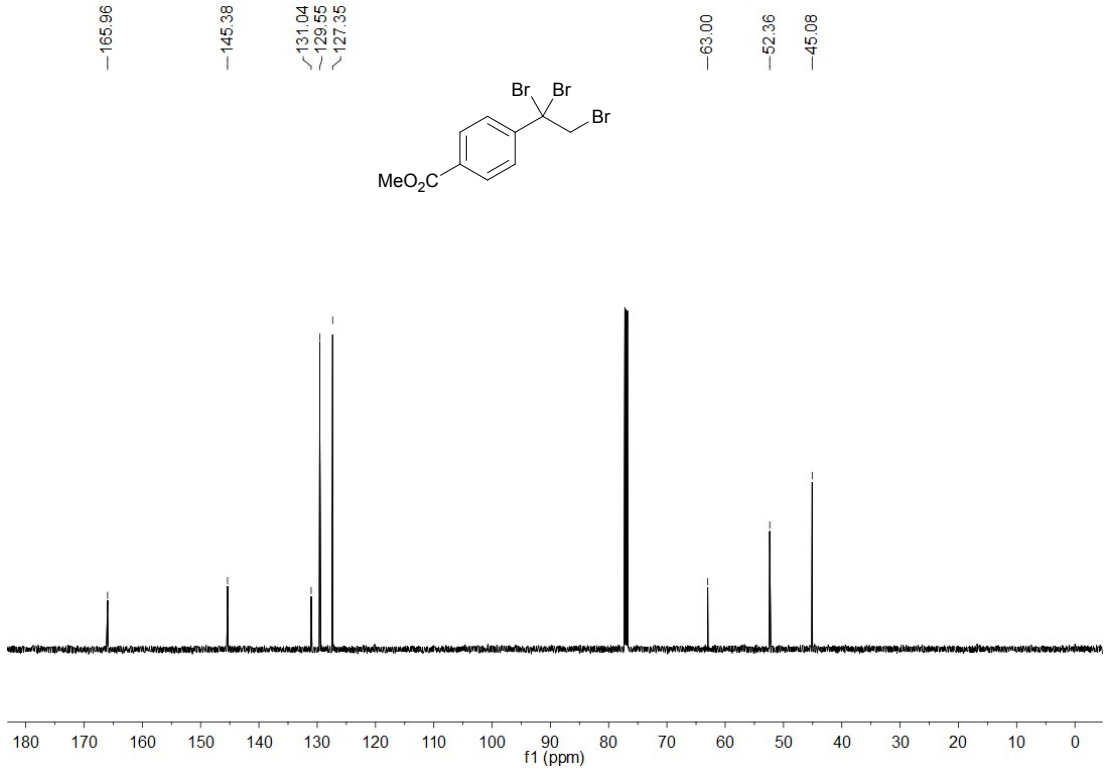

7.917
7.912
7.907
7.683
7.678
7.663
7.658
7.500
7.495
7.480
7.477
7.286
7.266
7.260
7.246
4.600
Br
Br
Br
Br
0.97
1.00
1.03
1.21
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

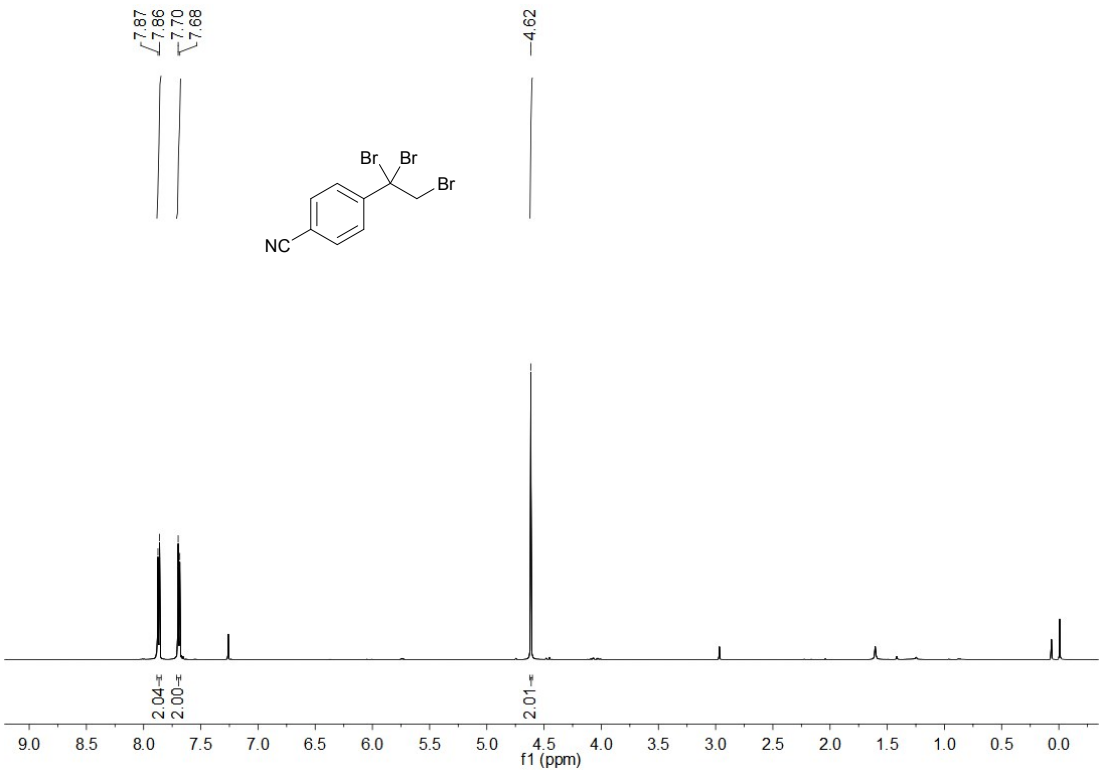

143.287
132.801
130.701
129.905
125.959
122.496
77.476
77.159
76.841
62.641
45.370
Br
Br
Br
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

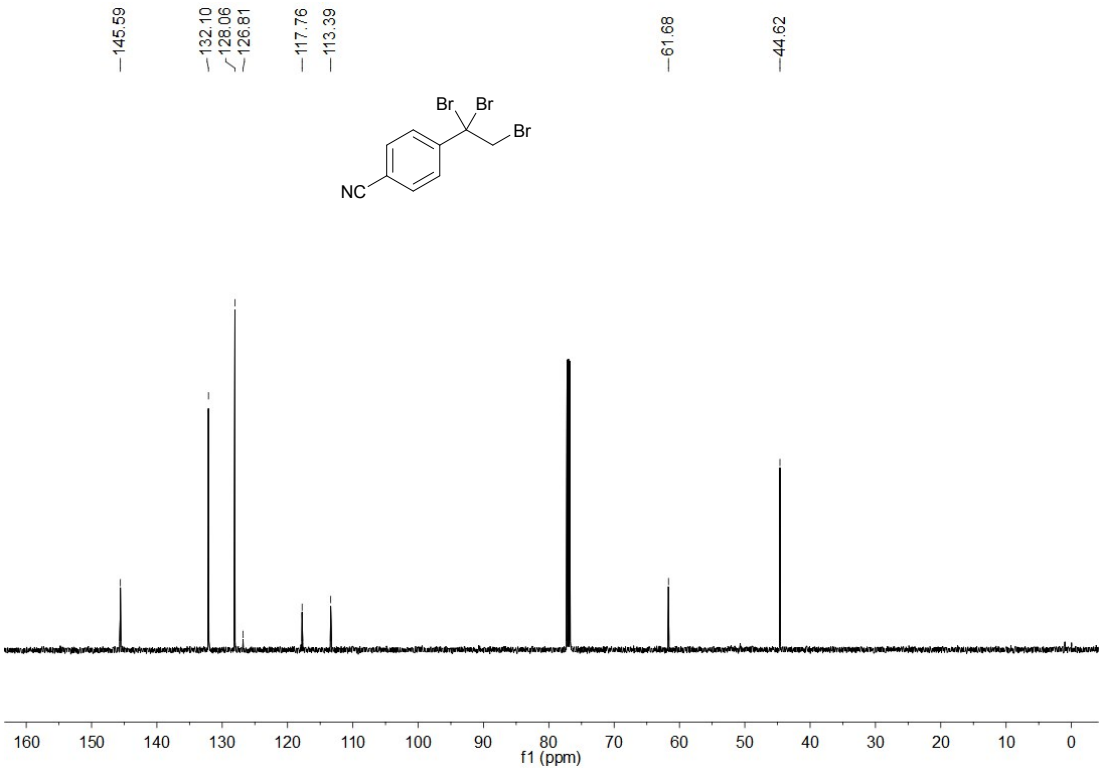

7.70
7.68
7.36
7.35
4.61
Br
Br
Br
Cl
2.00
2.00
2.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

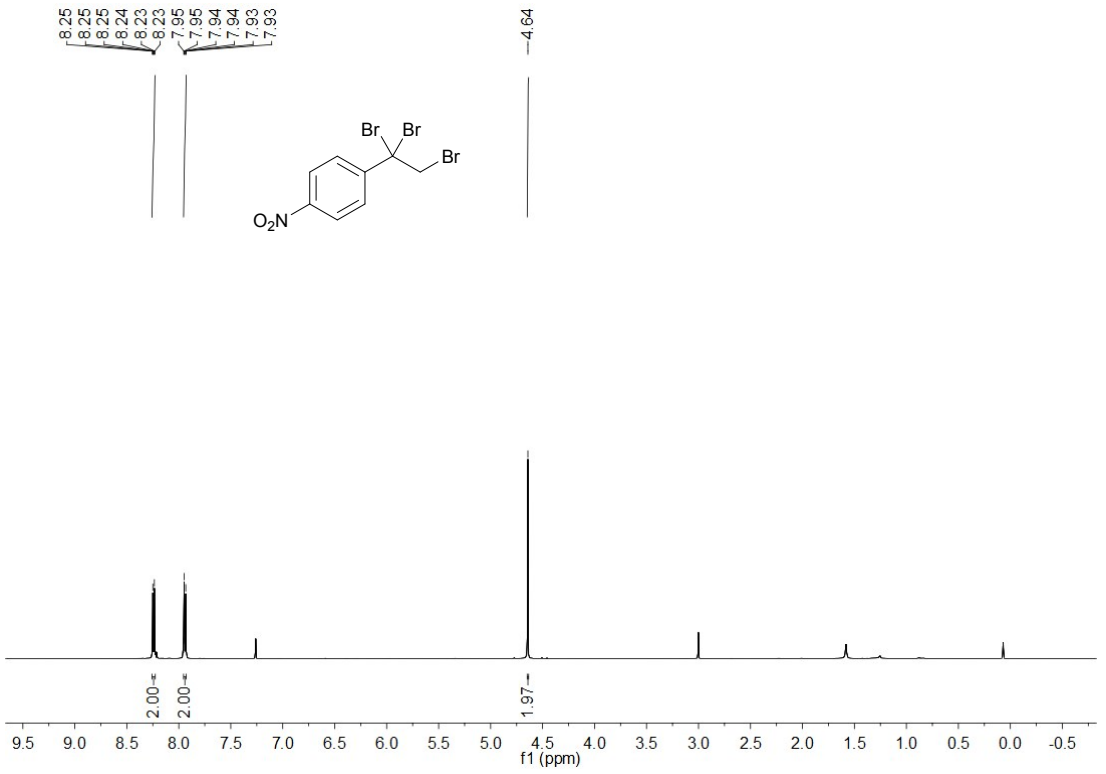

139.76
135.64
128.65
128.44
63.11
45.29
Br
Br
Br
Cl
145
135
125
115
105
95
85
75
65
55
45
35
25
15
5
0
f1 (ppm)

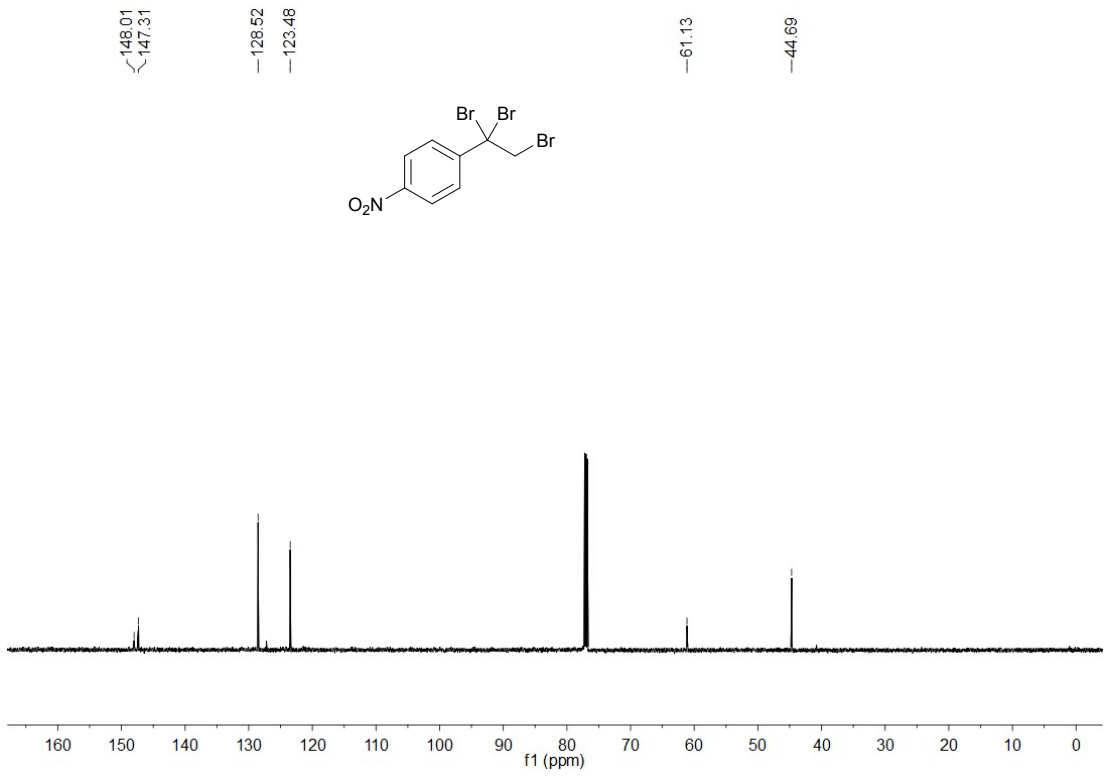

8.05
8.05
8.05
8.04
8.04
8.03
7.83
7.83
7.82
7.82
7.81
7.81
4.64
3.93
Br
Br
Br
MeO2C
2.00
2.01
2.01
2.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

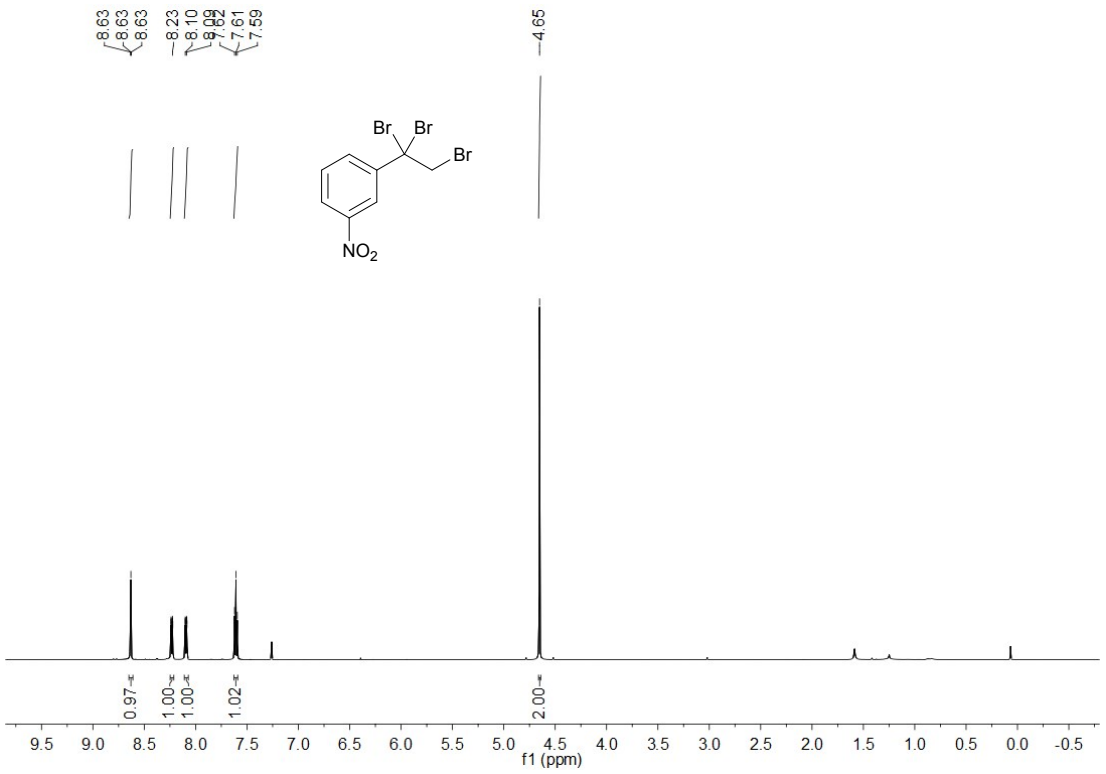

165.96
145.38
131.04
129.55
127.35
63.00
52.36
45.08
Br
Br
Br
MeO2C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

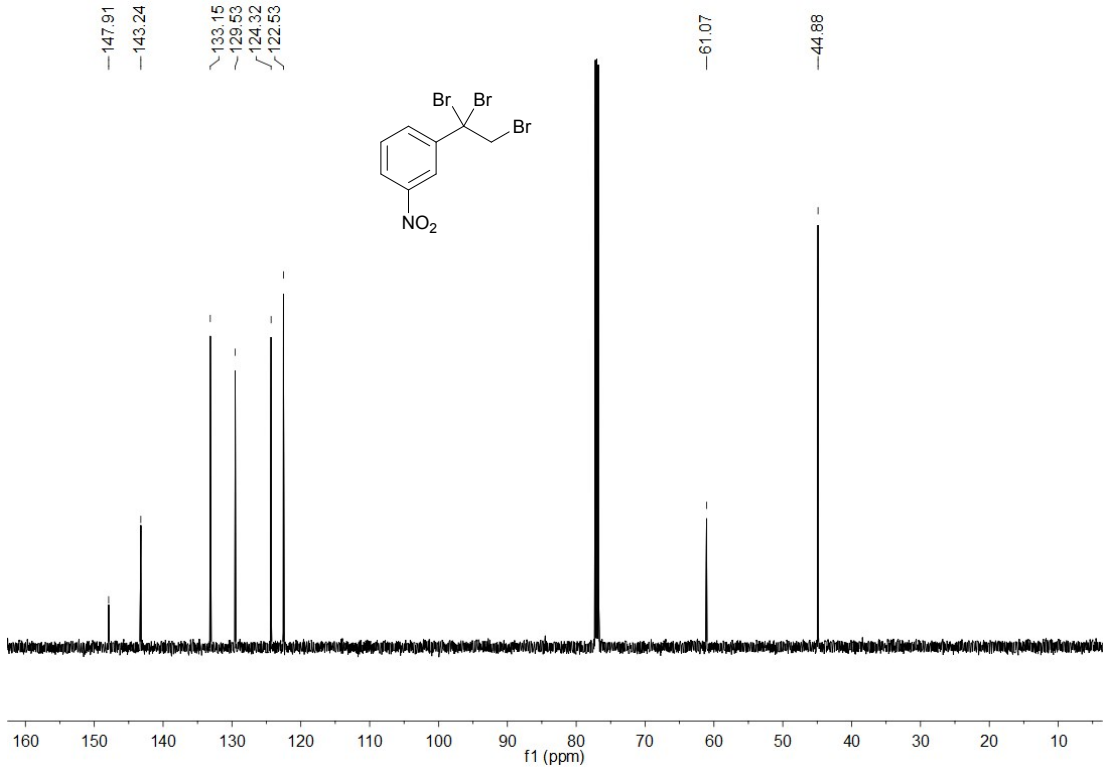

7.87
7.86
7.70
7.68
4.62
Br
Br
Br
NC
2.04
2.00
2.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

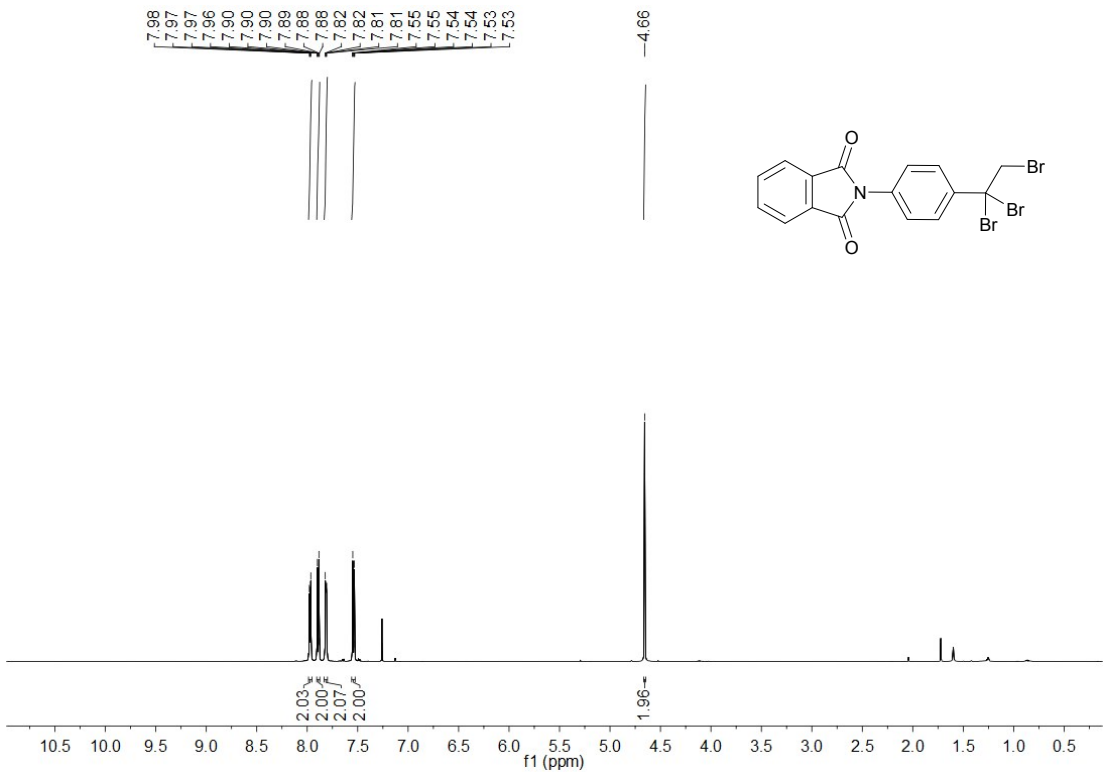

145.59
132.10
128.06
126.81
117.76
113.39
61.68
44.62
Br
Br
Br
NC
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

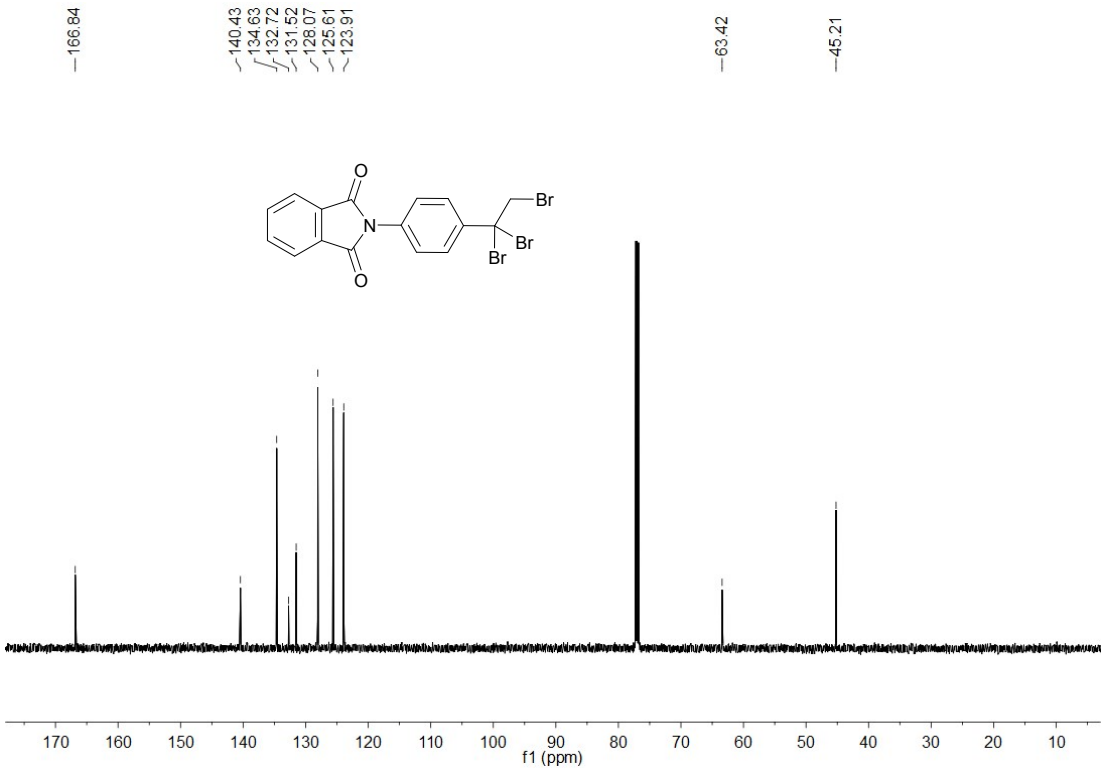

8.25
8.25
8.25
8.24
8.23
8.23
7.95
7.95
7.94
7.94
7.93
7.93
4.64
Br
Br
Br
O2N
2.00
2.00
1.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

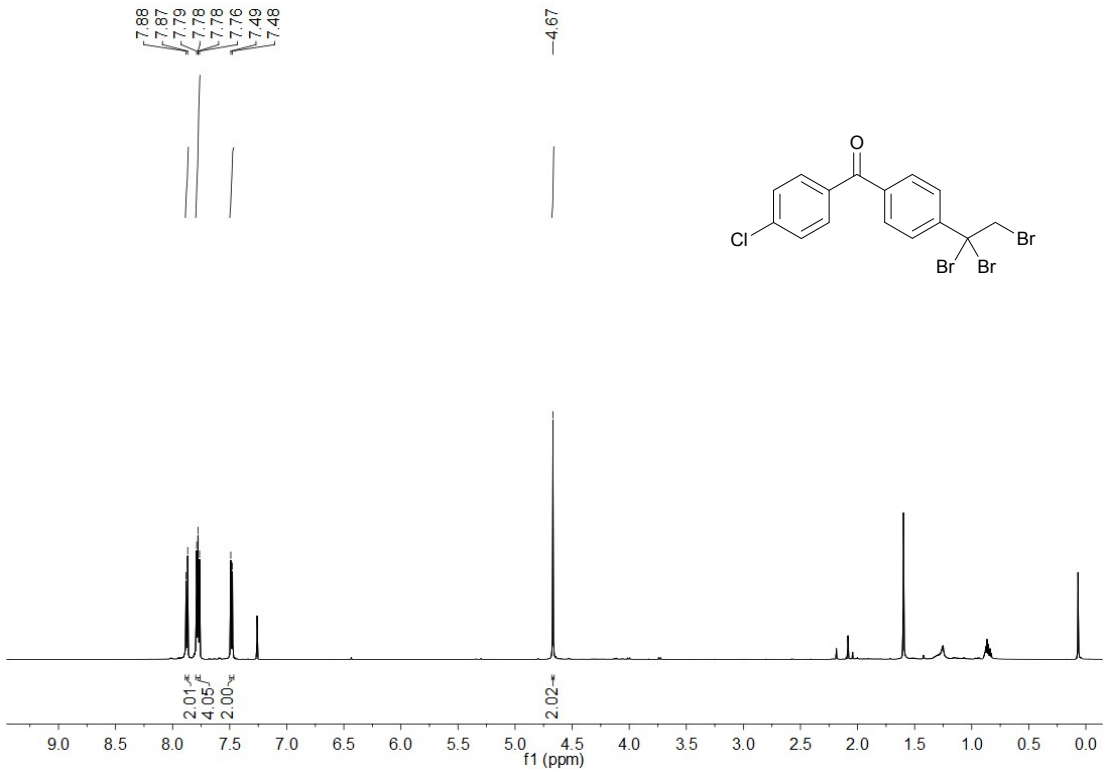

148.01
147.31
128.52
123.48
61.13
44.69
Br
Br
Br
O2N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

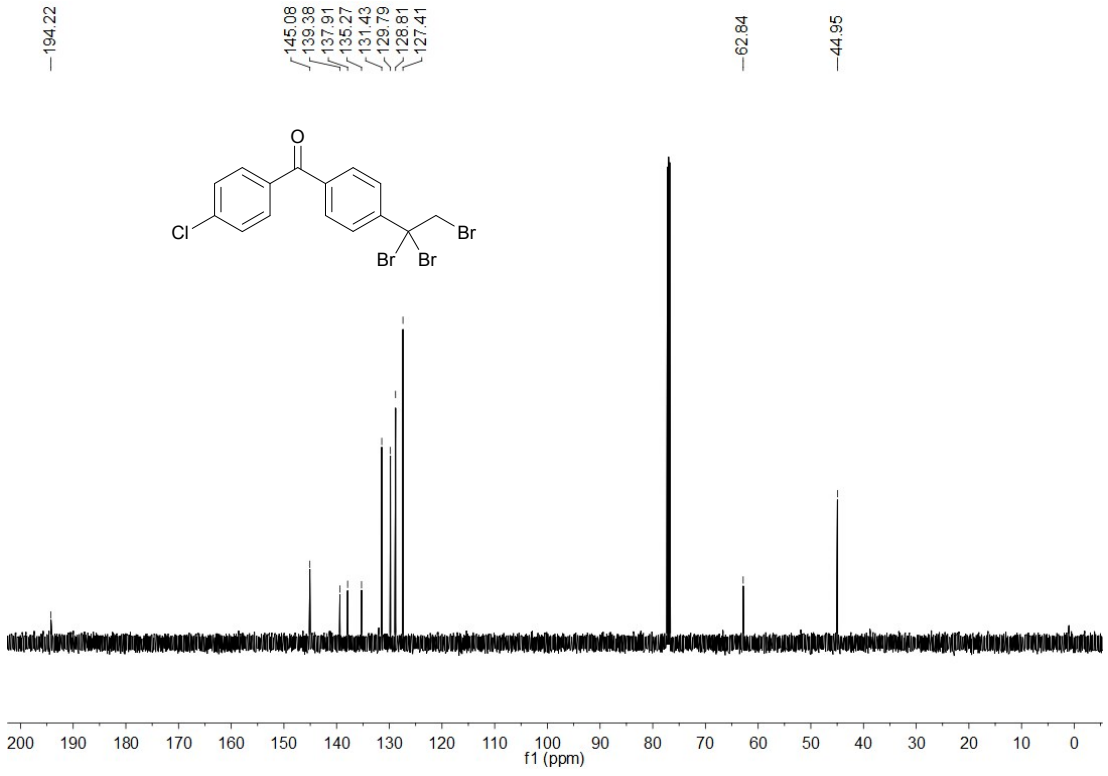

8.63
8.63
8.63
8.23
8.10
7.61
7.59
4.65
Br
Br
Br
NO2
0.97
1.00
1.00
1.02
2.00
f1 (ppm)

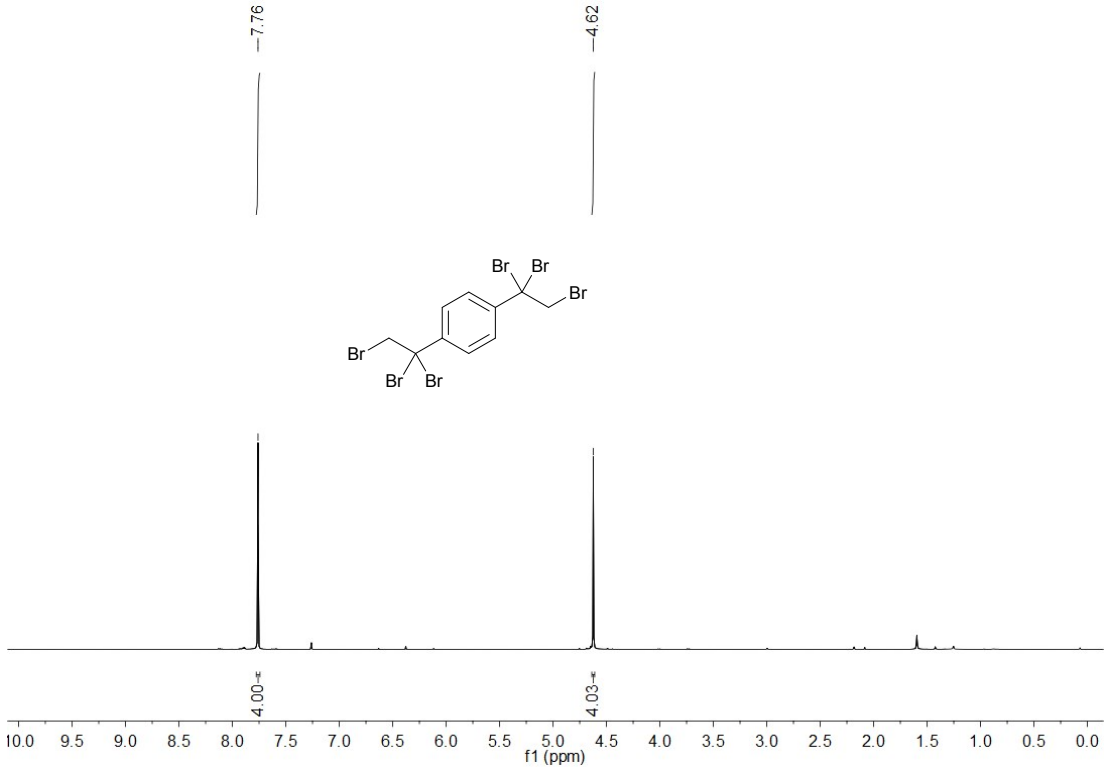

147.91
143.24
133.15
129.53
124.32
122.53
61.07
44.88
Br
Br
Br
NO2
f1 (ppm)

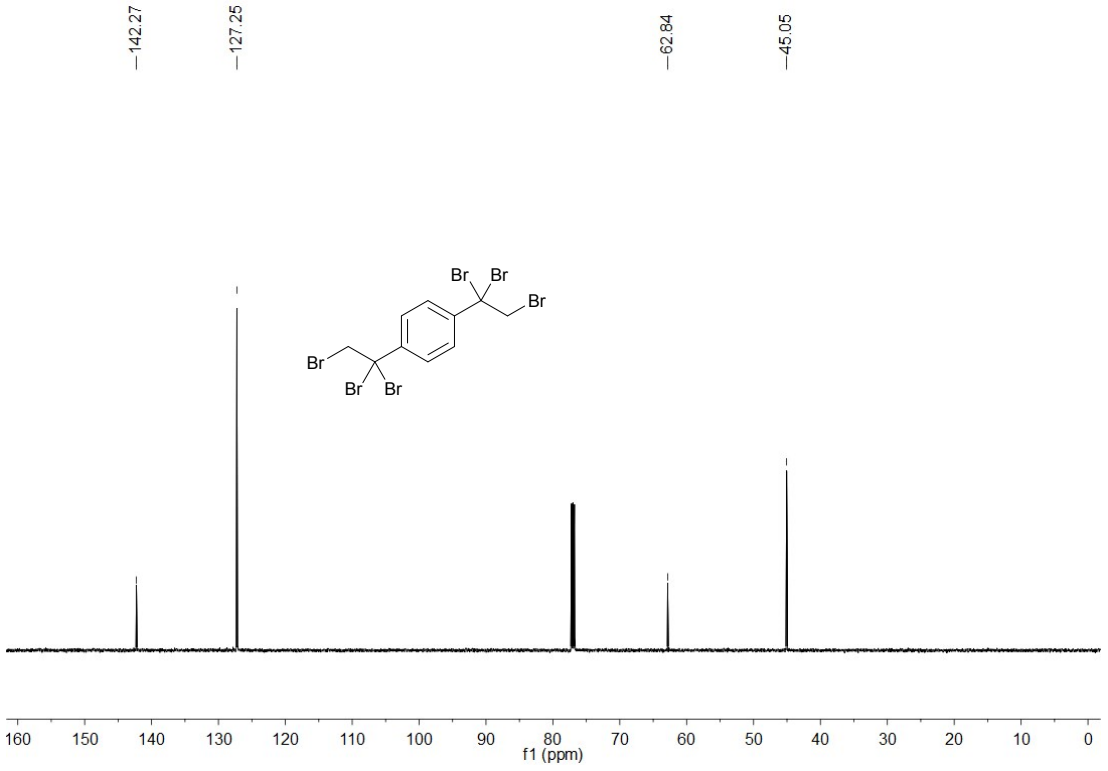

7.98
7.97
7.97
7.96
7.90
7.90
7.90
7.89
7.88
7.88
7.82
7.82
7.81
7.81
7.55
7.55
7.54
7.54
7.53
7.53
4.66
O
N
O
Br
Br
Br
2.03
2.00
2.07
2.00
1.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

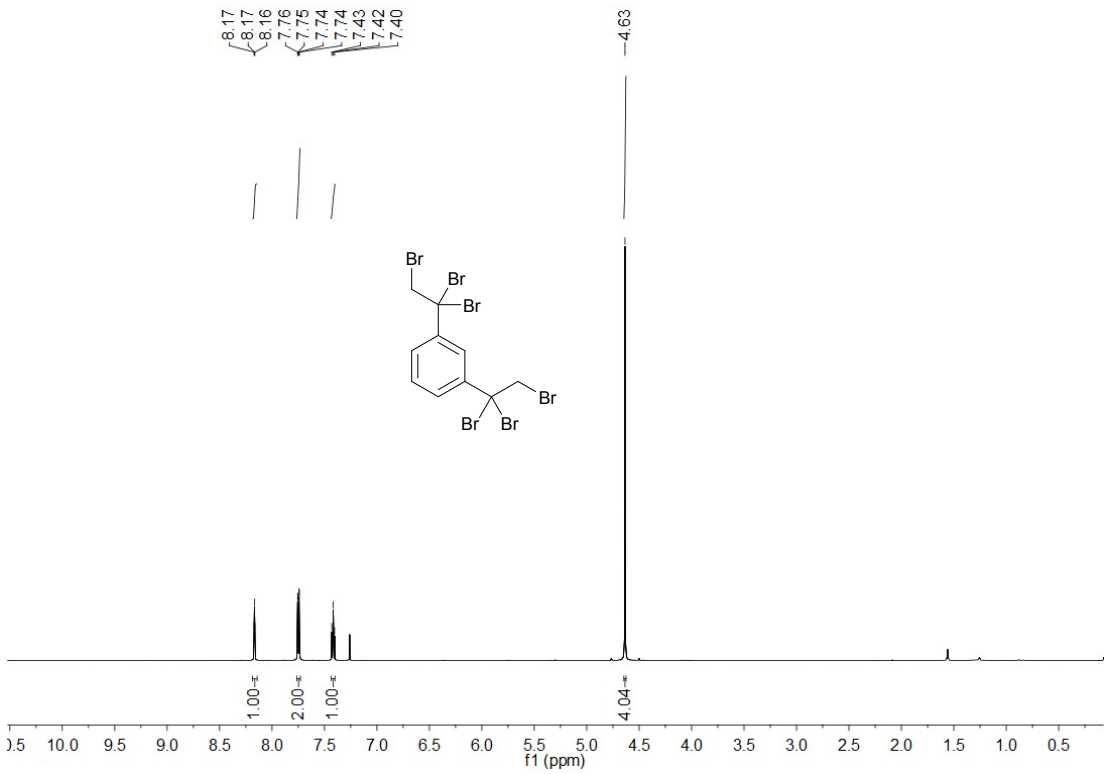

166.84
140.43
134.63
132.72
131.52
128.07
125.61
123.91
63.42
45.21
O
N
O
Br
Br
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

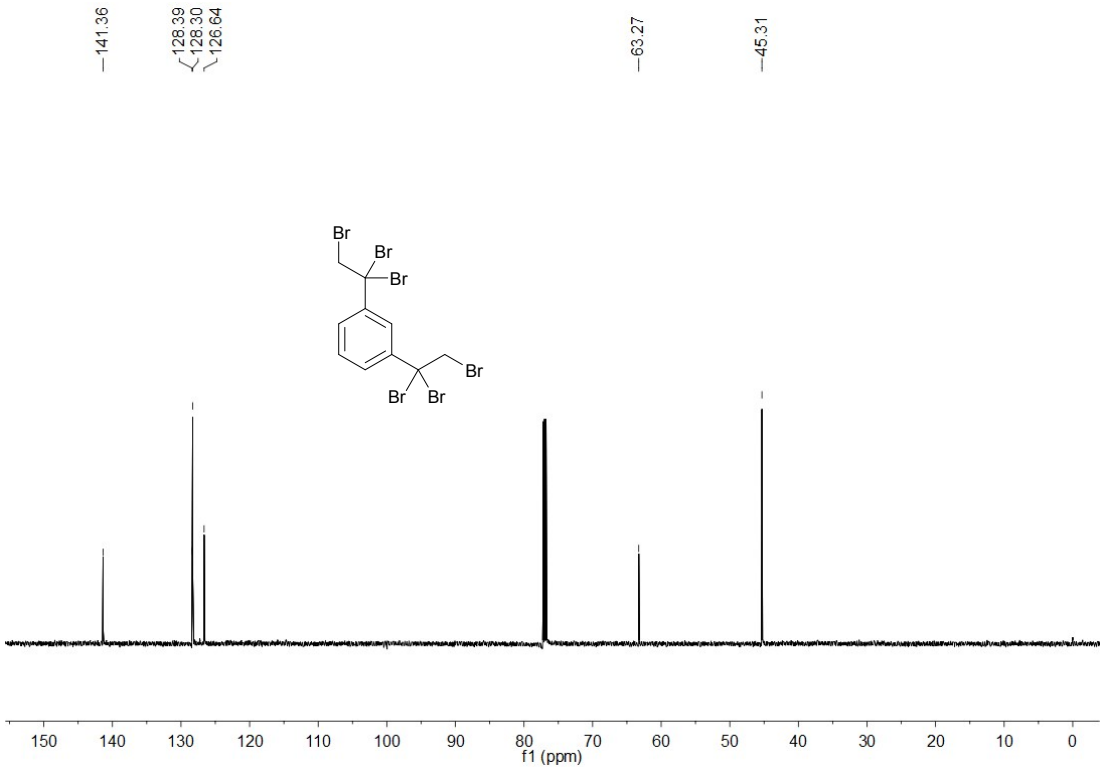

7.88
7.87
7.79
7.78
7.78
7.76
7.49
7.48
4.67
O
Cl
Br
Br
Br
2.01
4.05
2.00
2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.22
145.08
139.38
137.91
135.27
131.43
129.79
128.81
127.41
62.84
44.95
O
Cl
Br
Br
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.76
4.62
Br
Br
Br
Br
Br
Br
4.00
4.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.27
127.25
62.84
45.05
Br
Br
Br
Br
Br
Br
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.17
8.17
8.16
7.76
7.75
7.74
7.74
7.43
7.42
7.40
4.63
Br
Br
Br
Br
Br
Br
Br
1.00
2.00
1.00
4.04
f1 (ppm)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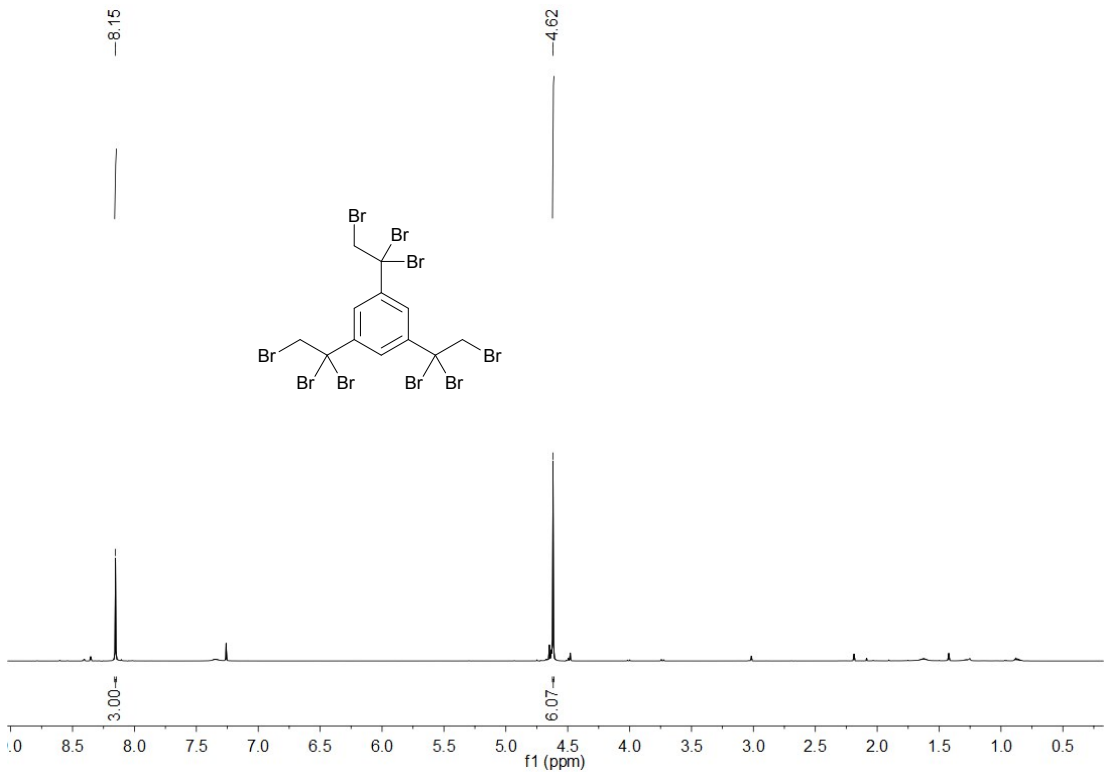
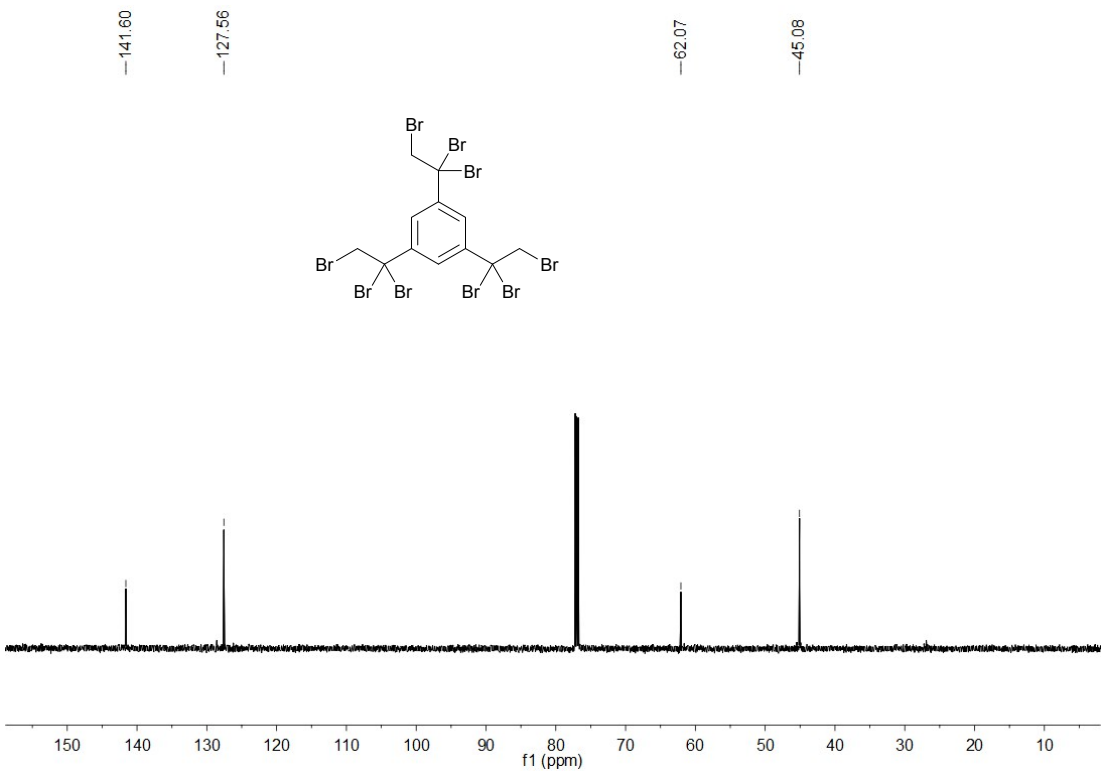
128.39
128.30
126.64
63.27
45.31
Br
Br
Br
Br
Br
Br
f1 (ppm)


8.15
4.62
Br
Br
Br
Br
Br
Br
Br
Br
Br
Br
Br
3.00
6.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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127.56
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45.08
Br
Br
Br
Br
Br
Br
Br
Br
Br
Br
Br
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140
130
120
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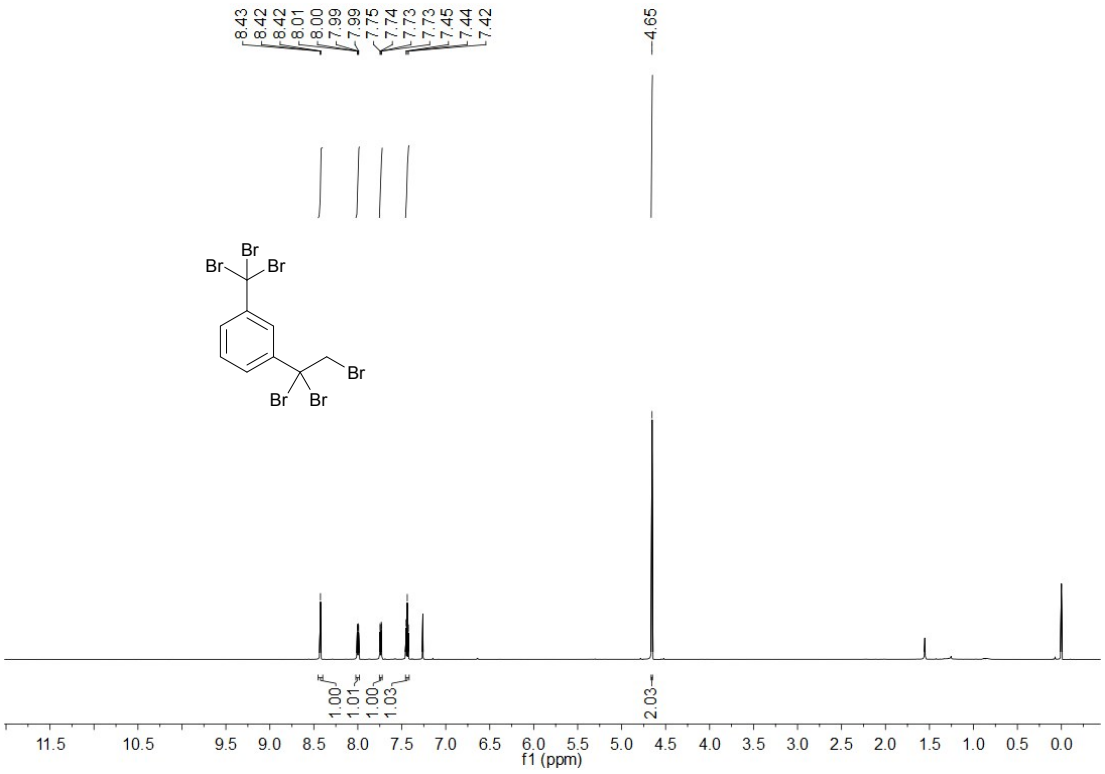
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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8.42
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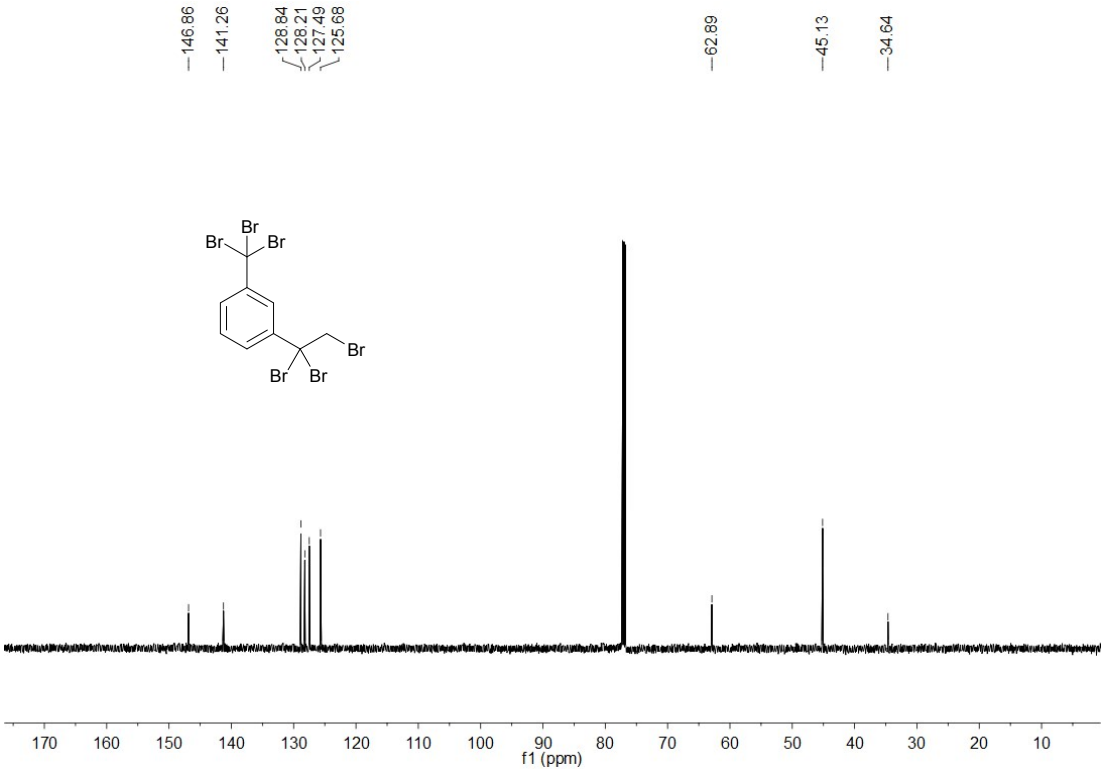
8.00
7.99
7.99
7.75
7.74
7.73
7.73
7.45
7.44
7.42
4.65
Br
Br
Br
Br
Br
Br
1.00
1.01
1.00
1.03
2.03
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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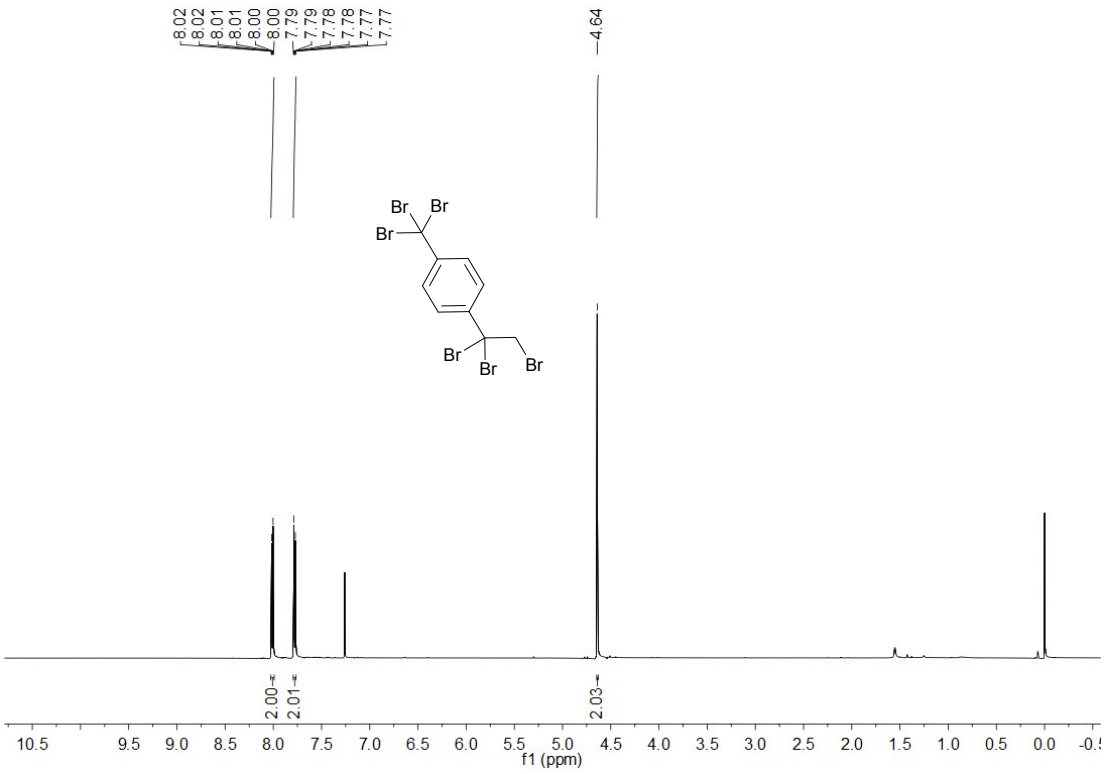
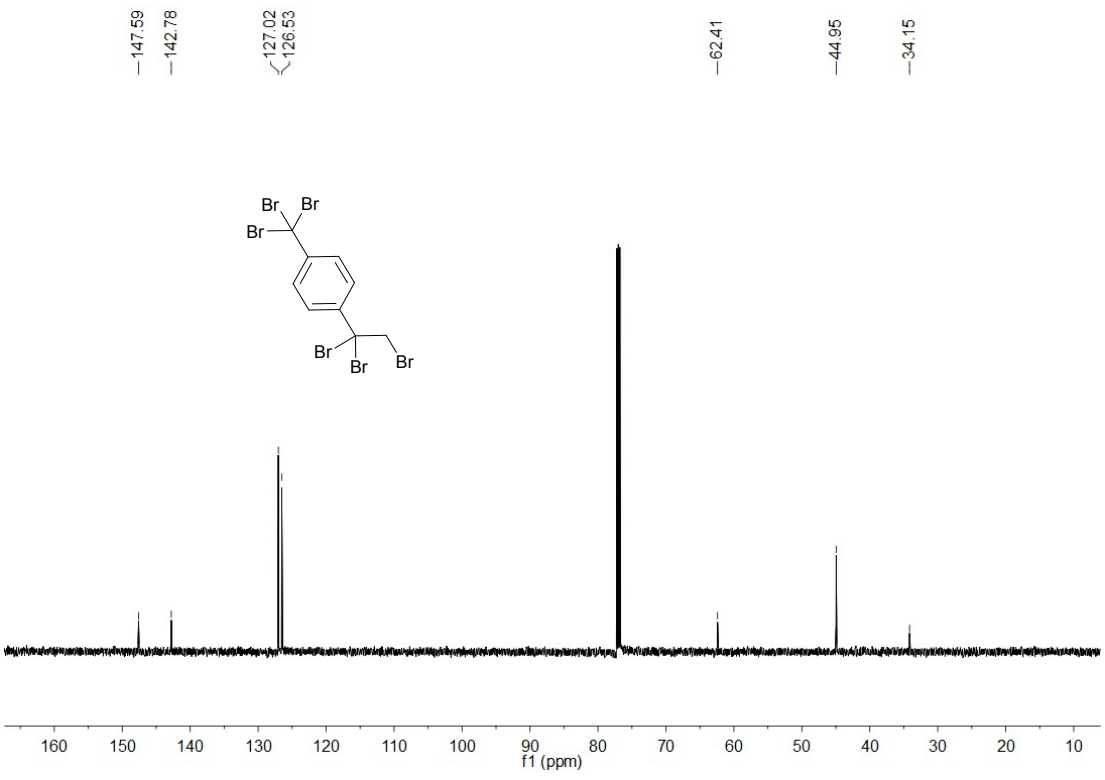
127.49
125.68
62.89
45.13
34.64
Br
Br
Br
Br
Br
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.02
8.02
8.01
8.01
8.00
8.00
7.79
7.79
7.78
7.78
7.77
7.77
4.64
Br
Br
Br
Br
Br
Br
2.00
2.01
2.03
f1 (ppm)


147.59
142.78
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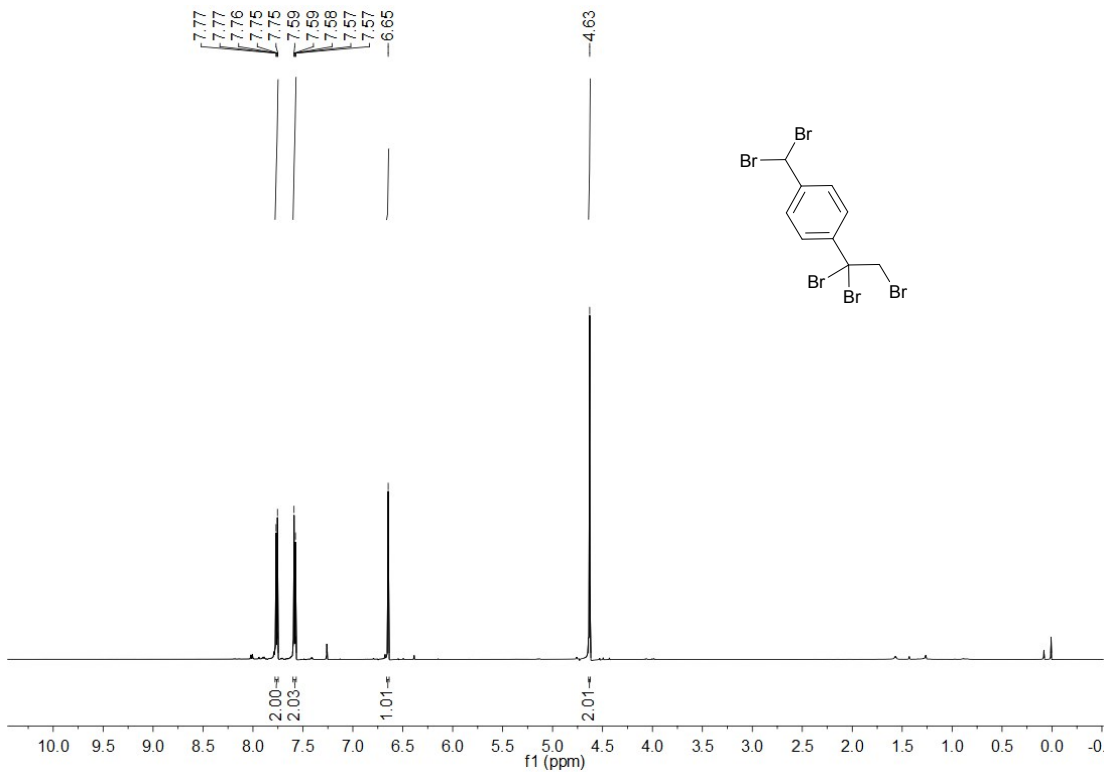
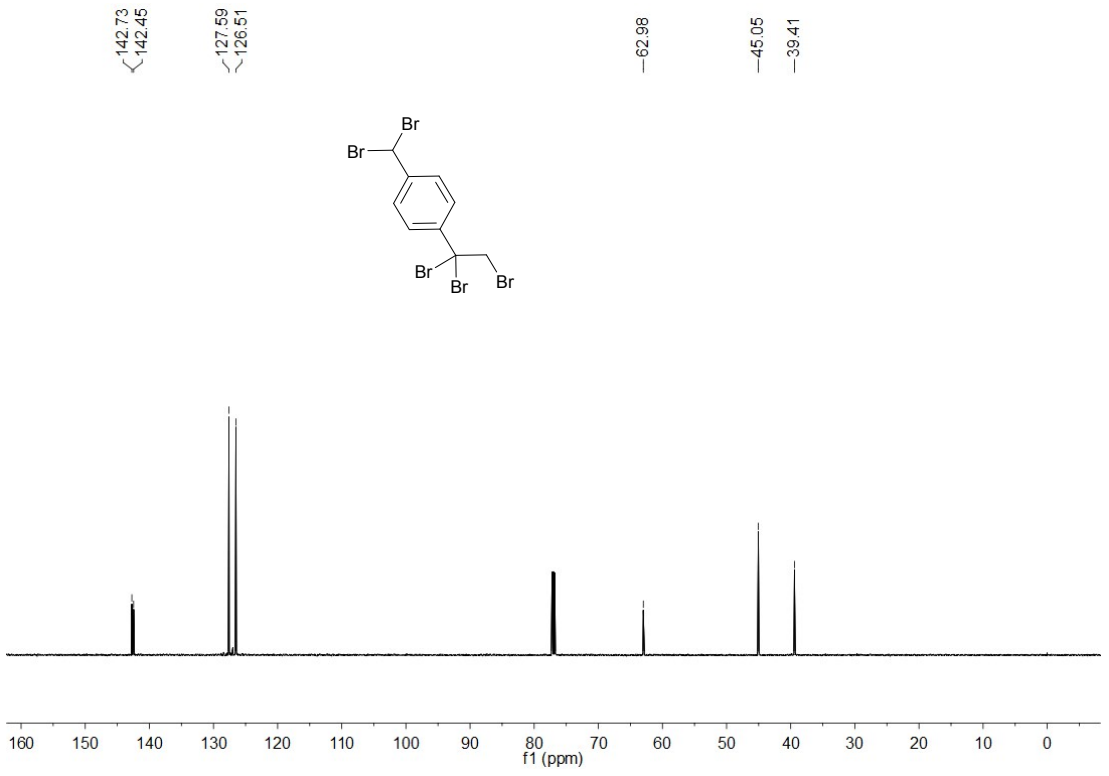
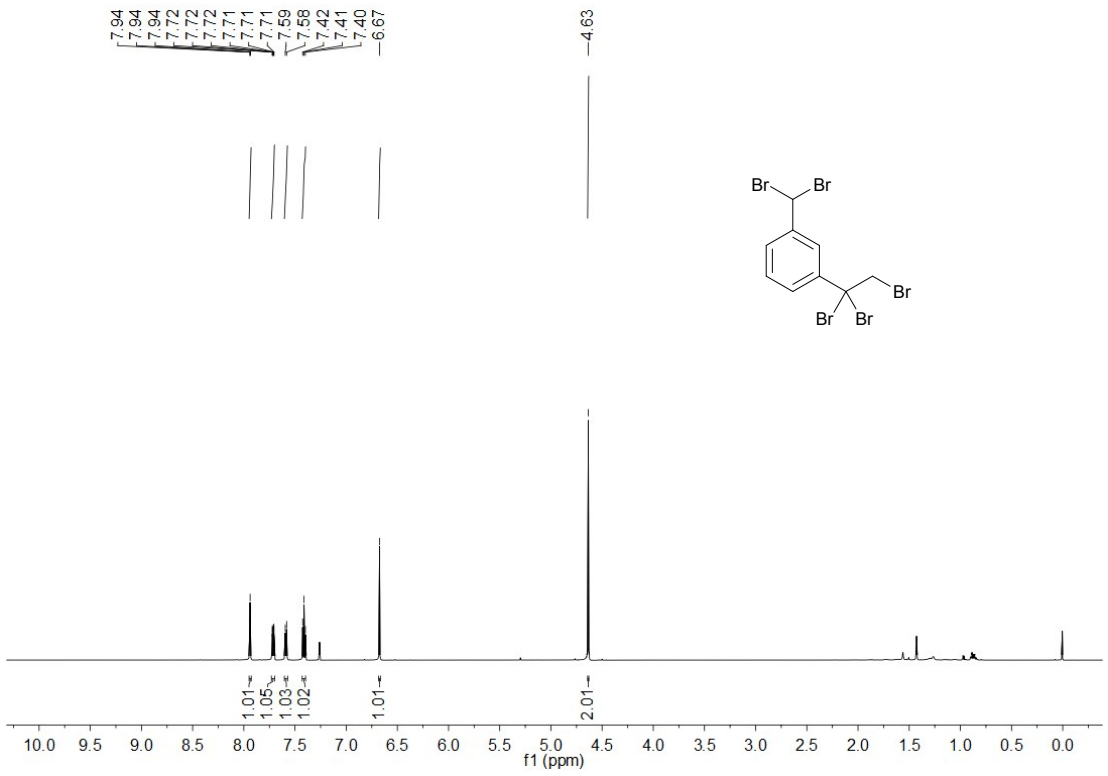
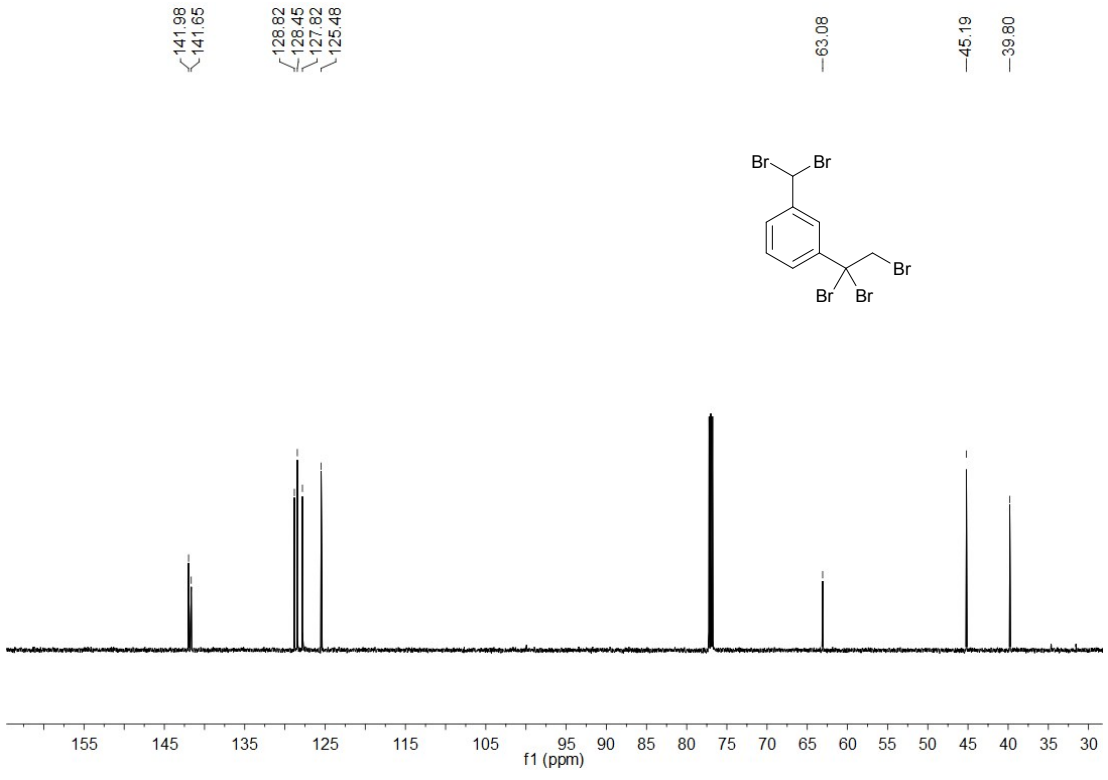
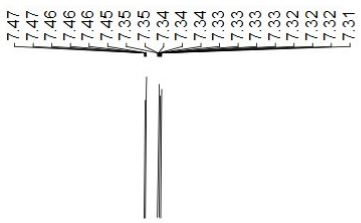
126.53
62.41
44.95
34.15
Br
Br
Br
Br
Br
Br
f1 (ppm)

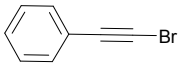

7.77
7.77
7.76
7.75
7.75
7.59
7.59
7.58
7.57
7.57
6.65
4.63
Br
Br
Br
Br
Br
2.00
2.03
1.01
2.01
f1 (ppm)

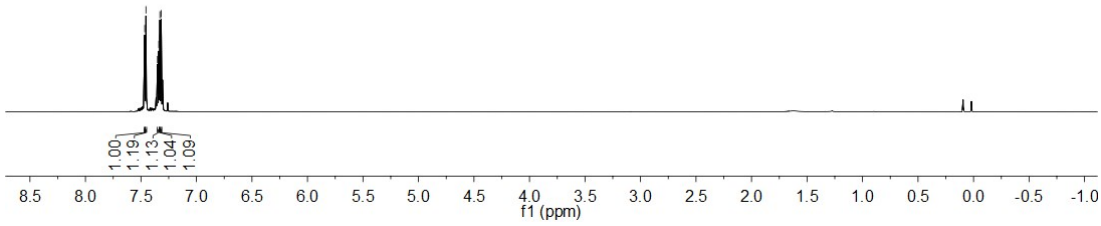

142.73
142.45
127.59
126.51
62.98
45.05
39.41
Br
Br
Br
Br
Br
f1 (ppm)


7.94
7.94
7.94
7.72
7.72
7.72
7.71
7.71
7.71
7.59
7.58
7.42
7.41
7.40
6.67
4.63
Br
Br
Br
Br
Br
1.01
1.05
1.03
1.02
1.01
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.98
141.65
128.82
128.45
127.82
125.48
63.08
45.19
39.80
Br
Br
Br
Br
Br
155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)


7.47
7.47
7.46
7.46
7.46
7.45
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.31

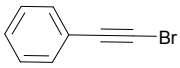

Br

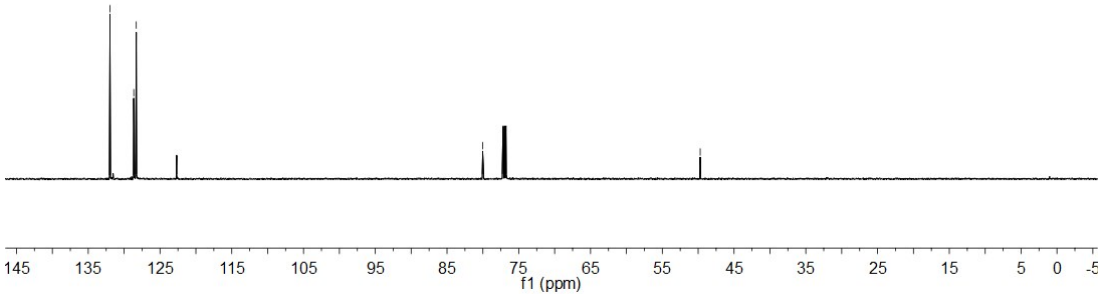

1.00
1.19
1.13
1.04
1.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

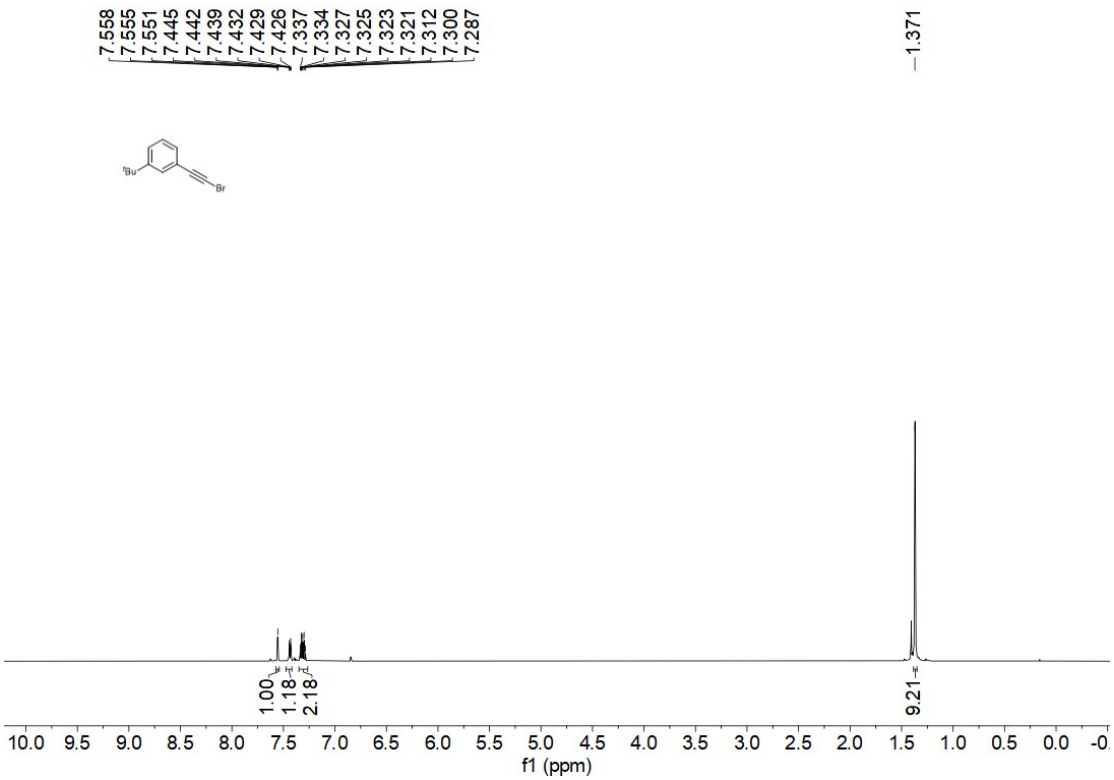

131.97
128.66
128.31

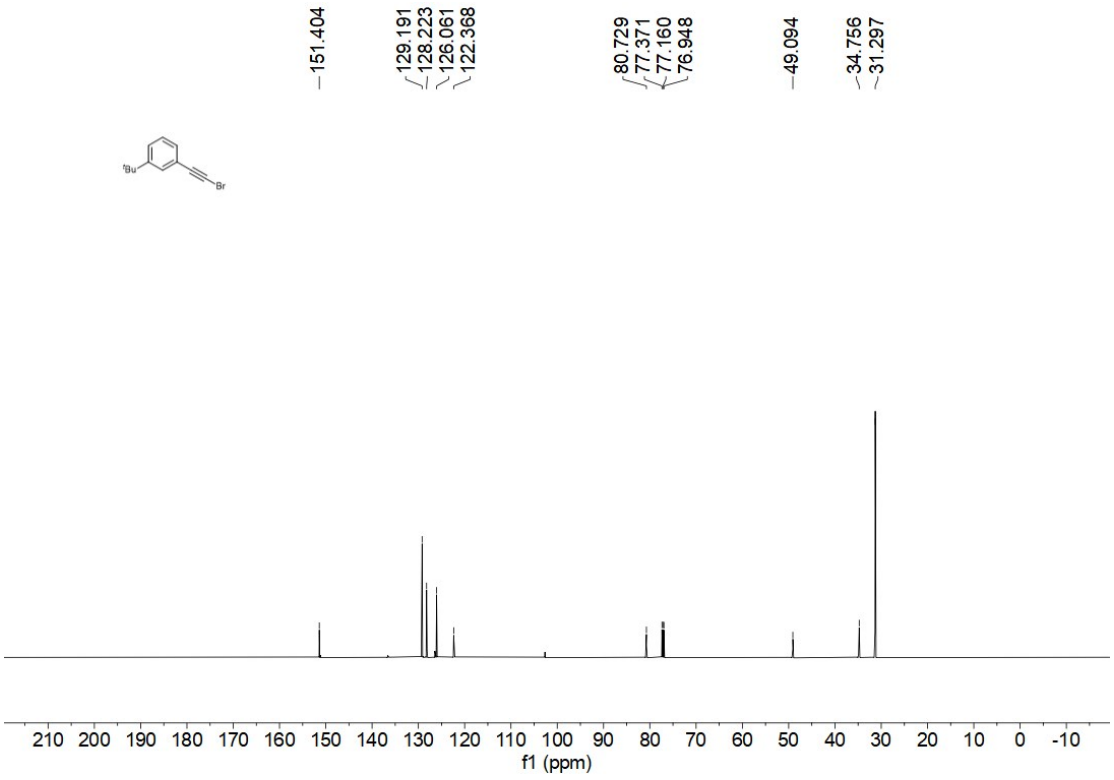

80.03

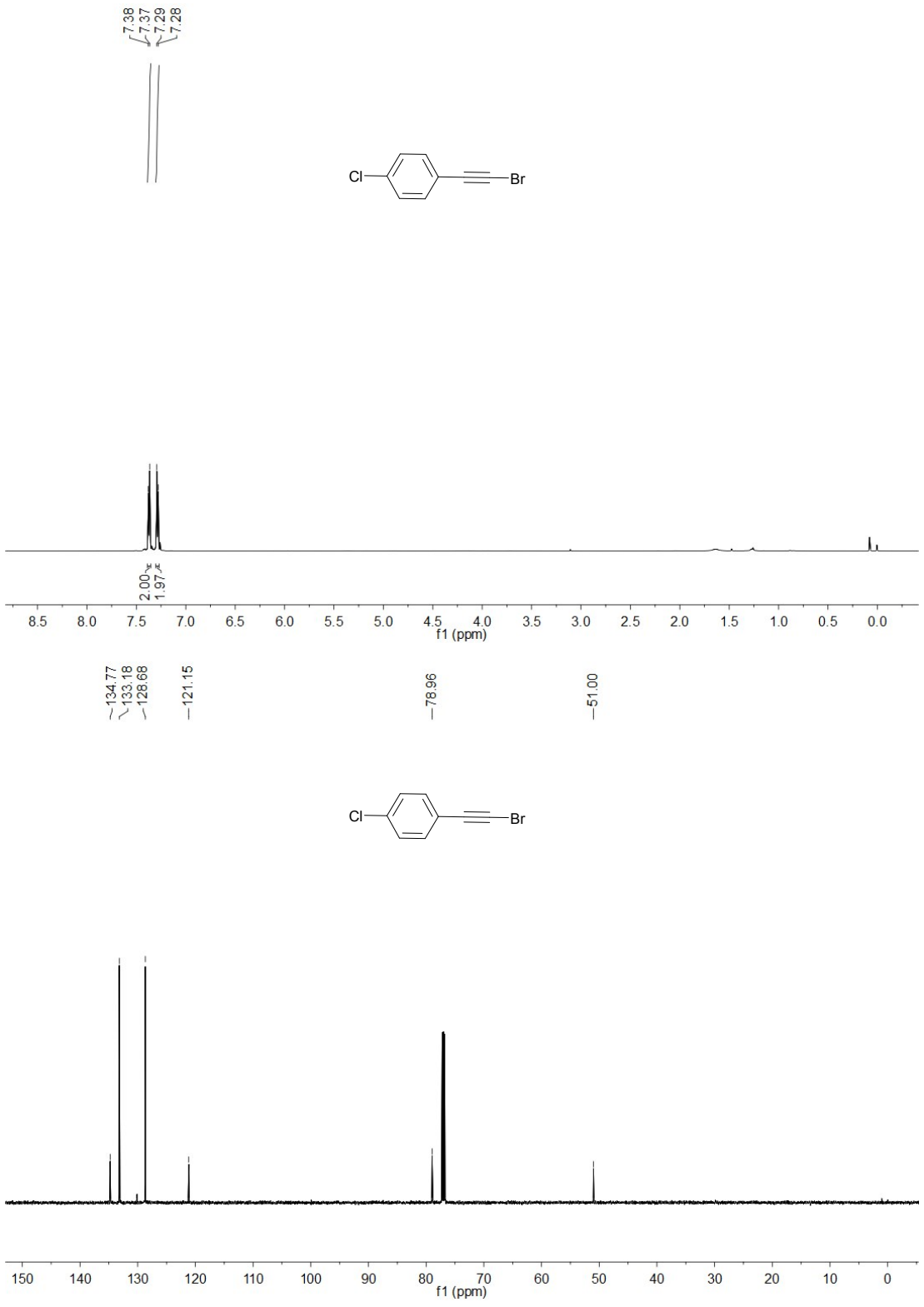

49.72

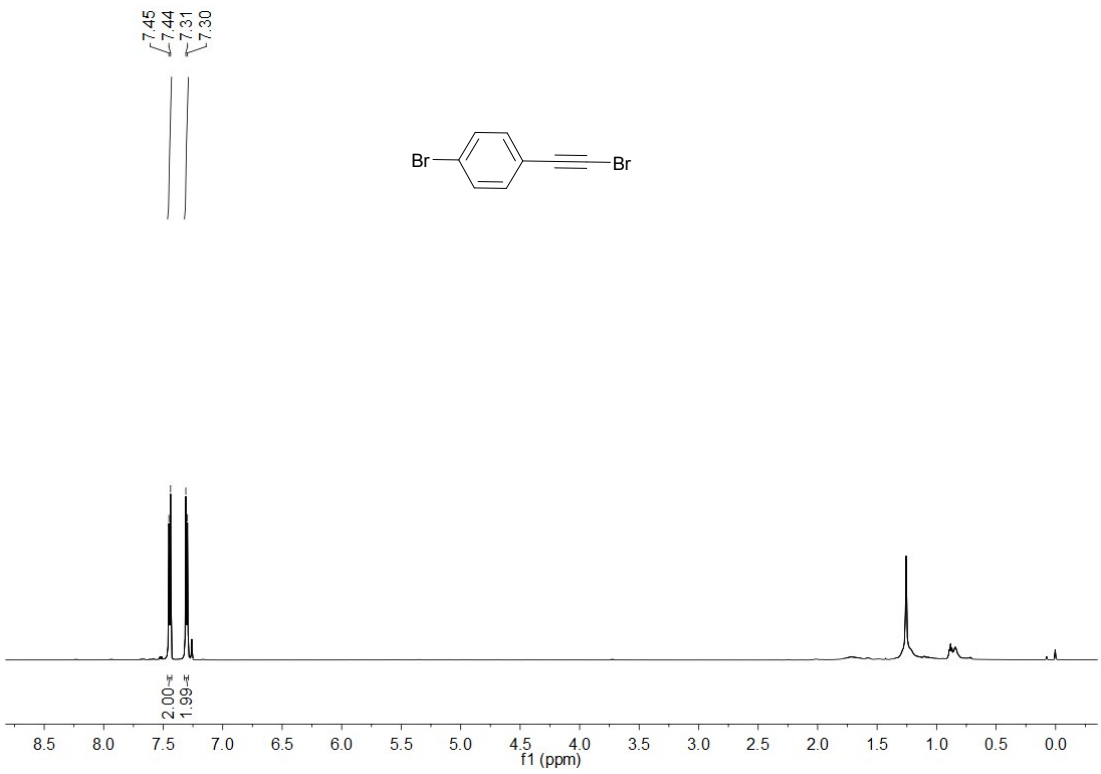

Br

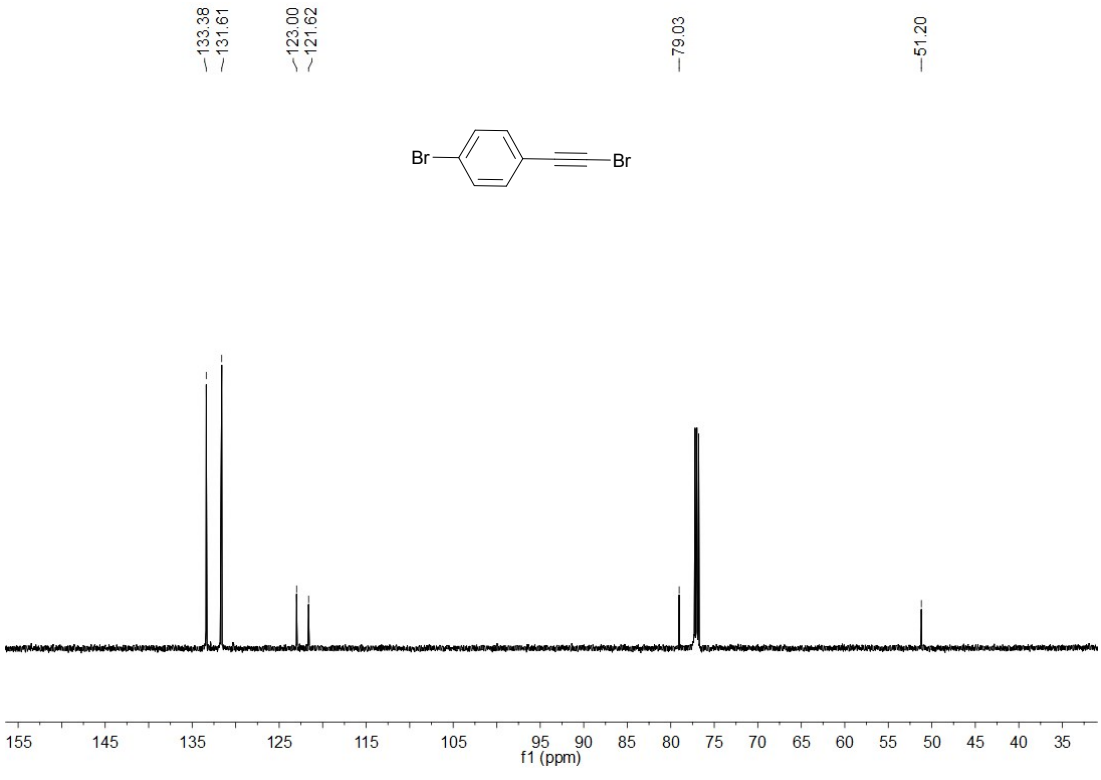

145
135
125
115
105
95
85
75
65
55
45
35
25
15
5
0
f1 (ppm)


7.558
7.555
7.551
7.445
7.442
7.439
7.432
7.429
7.426
7.337
7.334
7.327
7.325
7.323
7.321
7.312
7.300
7.287
1.371
tBu
Br
1.00
1.18
2.18
9.21
f1 (ppm)

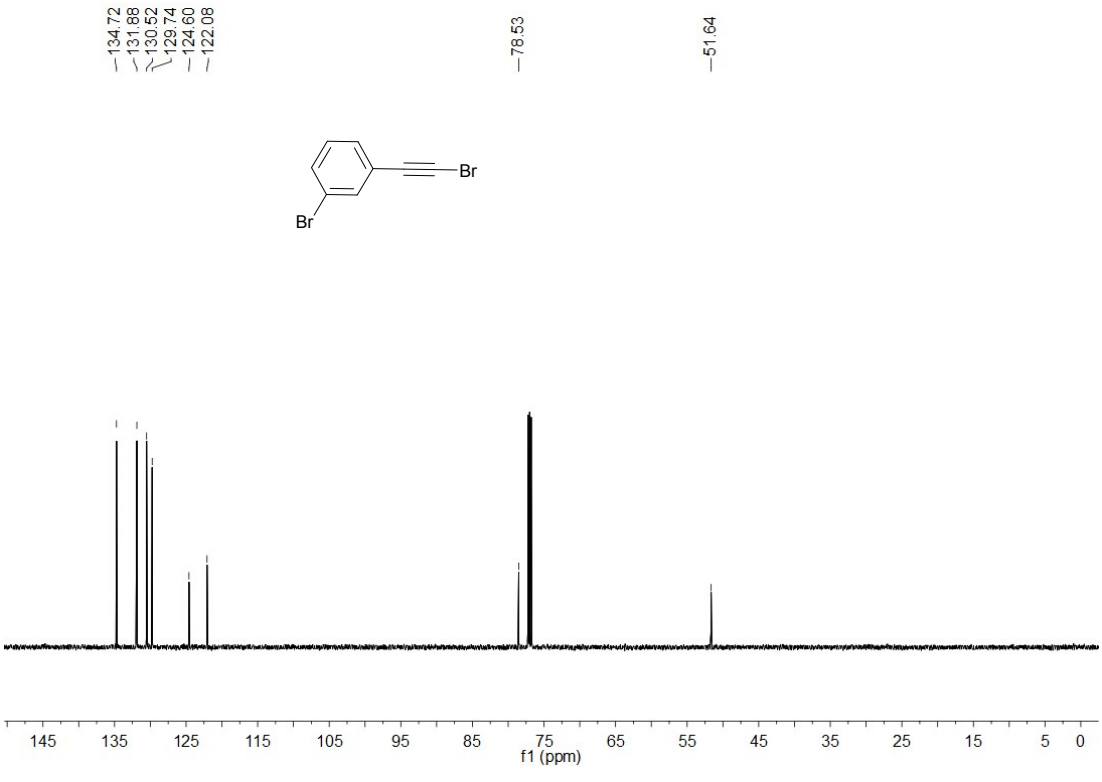

151.404
129.191
128.223
126.061
122.368
80.729
77.371
77.160
76.948
49.094
34.756
31.297
tBu
Br
f1 (ppm)

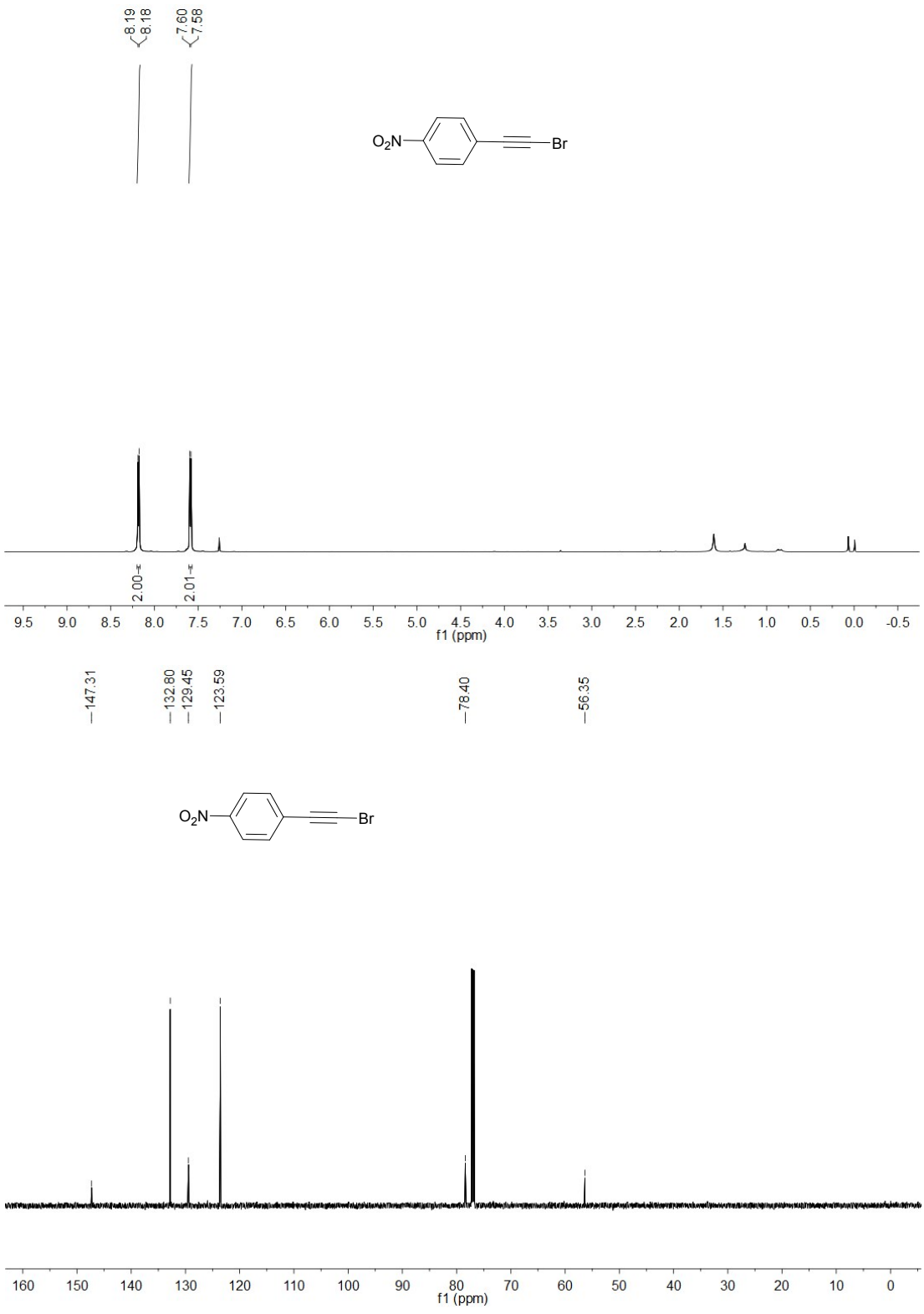

7.38
7.37
7.29
7.28
Cl
Br
2.00
1.97
f1 (ppm)
134.77
133.18
128.68
121.15
78.96
51.00
Cl
Br
f1 (ppm)

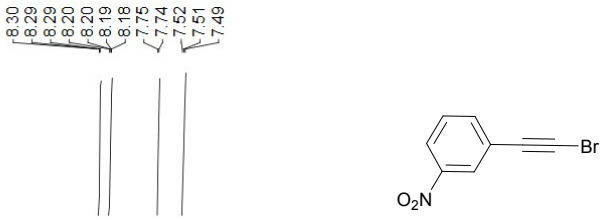

7.45
7.44
7.31
7.30
Br
Br
2.00
1.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

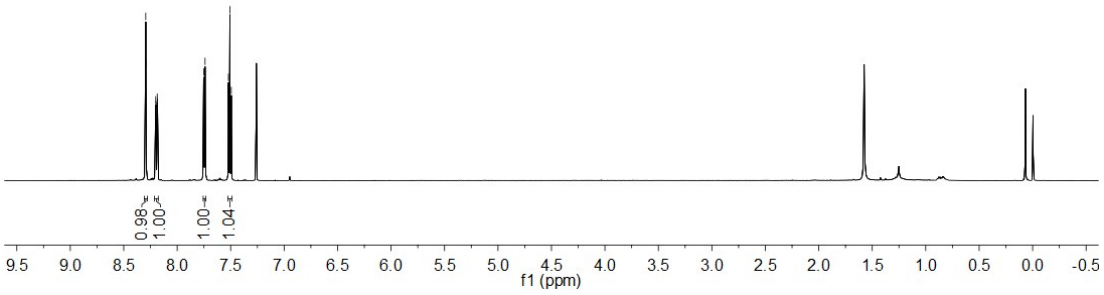

133.38
131.61
123.00
121.62
79.03
51.20
Br
Br
155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

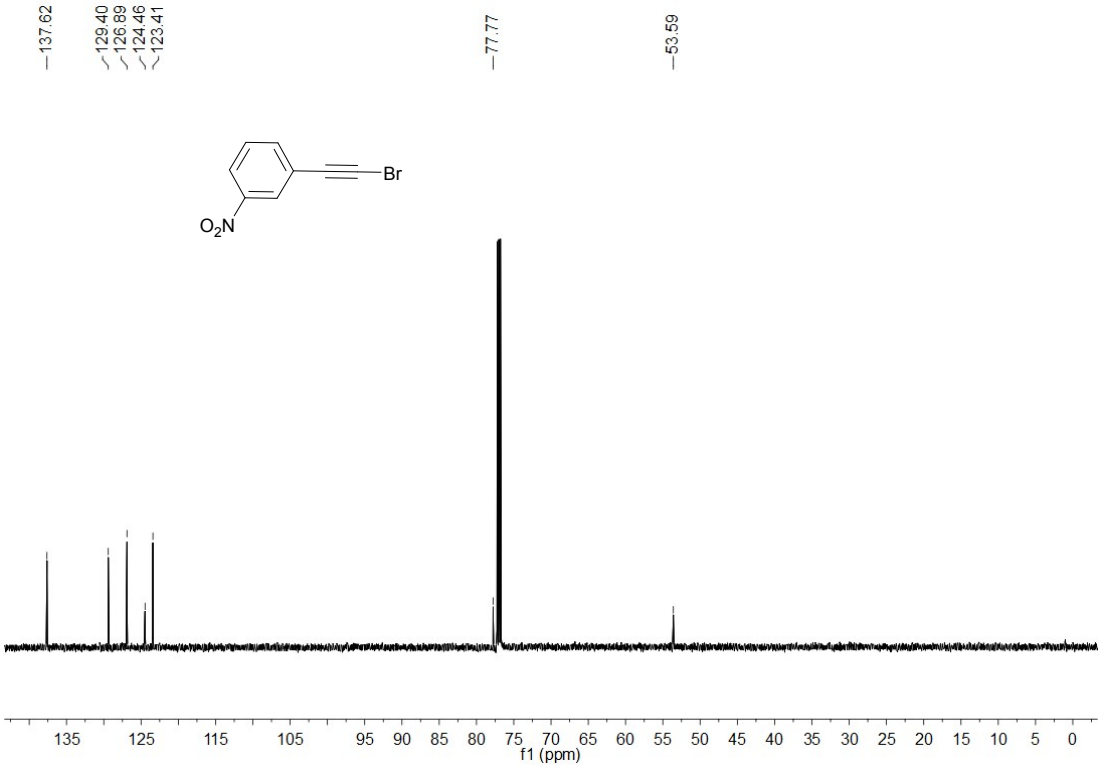

7.60
7.59
7.59
7.48
7.48
7.48
7.48
7.47
7.47
7.47
7.46
7.38
7.36
7.36
7.19
7.18
7.16
Br
Br
0.98
1.00
1.00
1.04
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

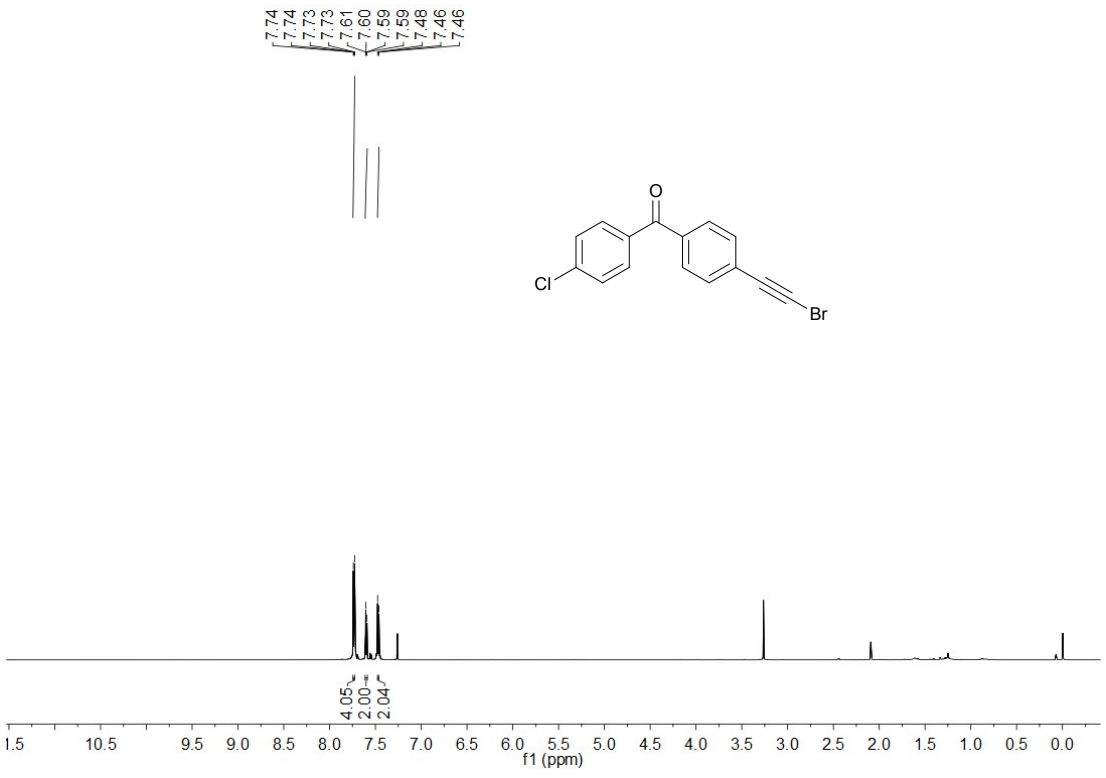

134.72
131.88
130.52
129.74
124.60
122.08
78.53
51.64
Br
Br
145
135
125
115
105
95
85
75
65
55
45
35
25
15
5
0
f1 (ppm)

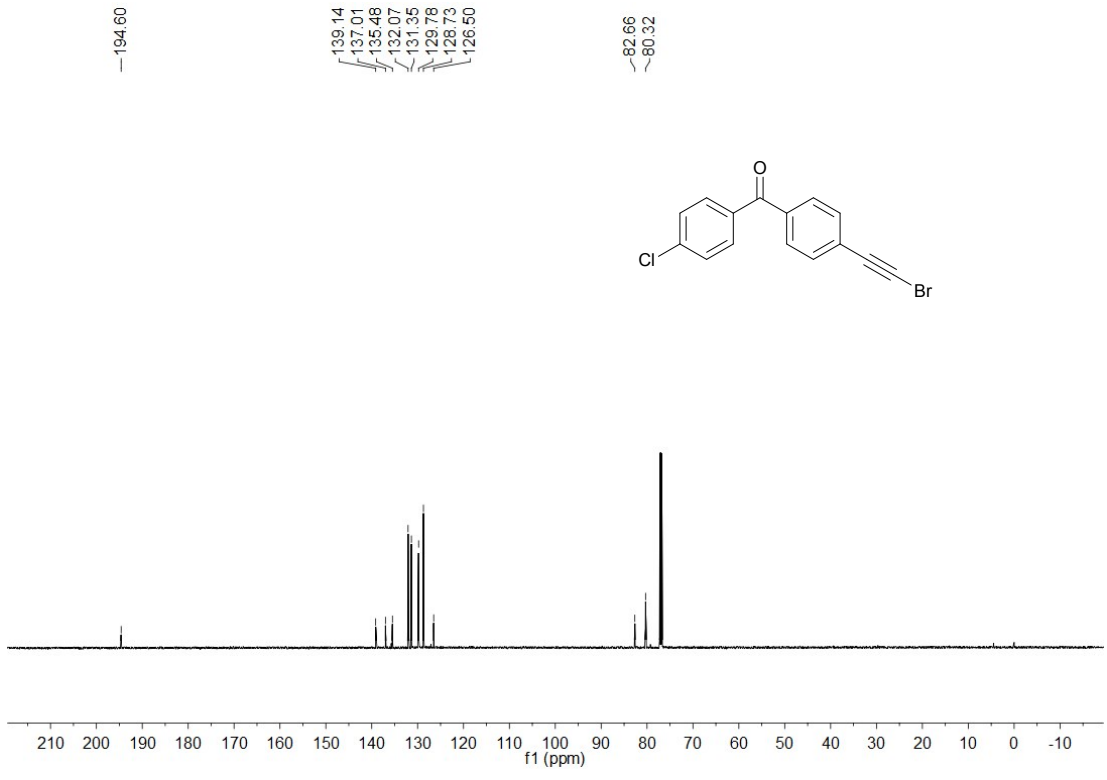

8.19
8.18
7.60
7.58
O2N
Br
2.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
147.31
132.80
129.45
123.59
78.40
56.35
O2N
Br
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

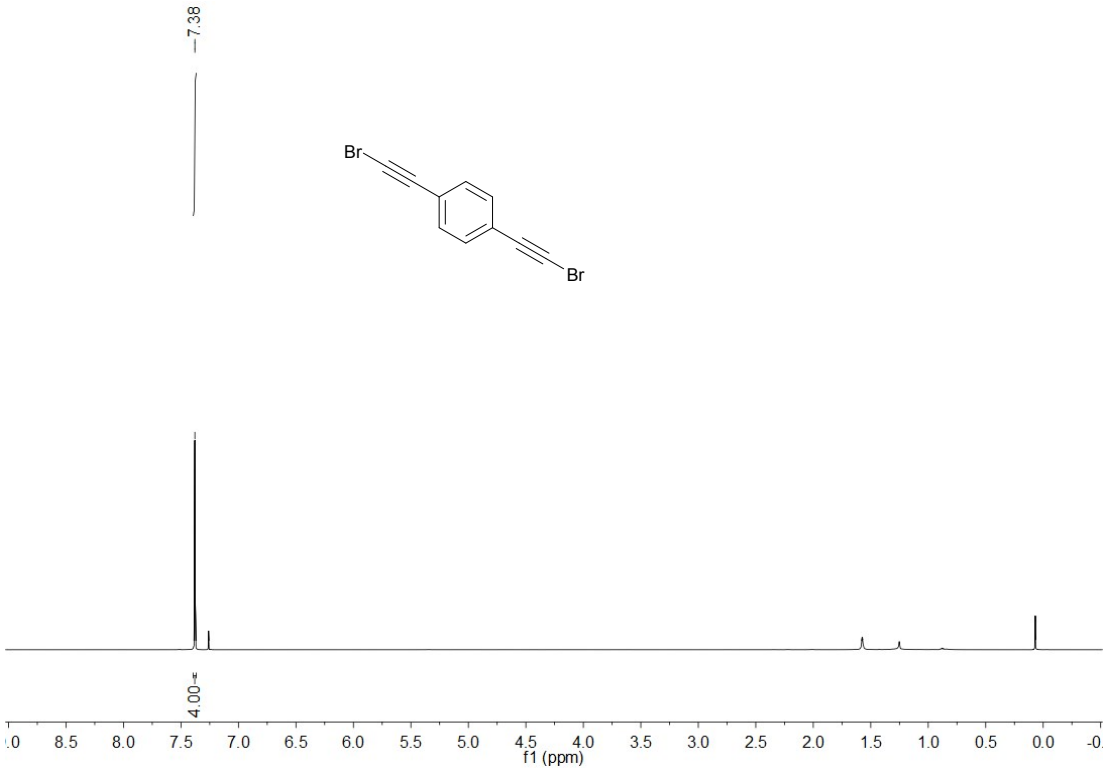

8.30
8.29
8.29
8.20
8.20
8.19
8.18
7.75
7.74
7.52
7.51
7.49
Br
O2N

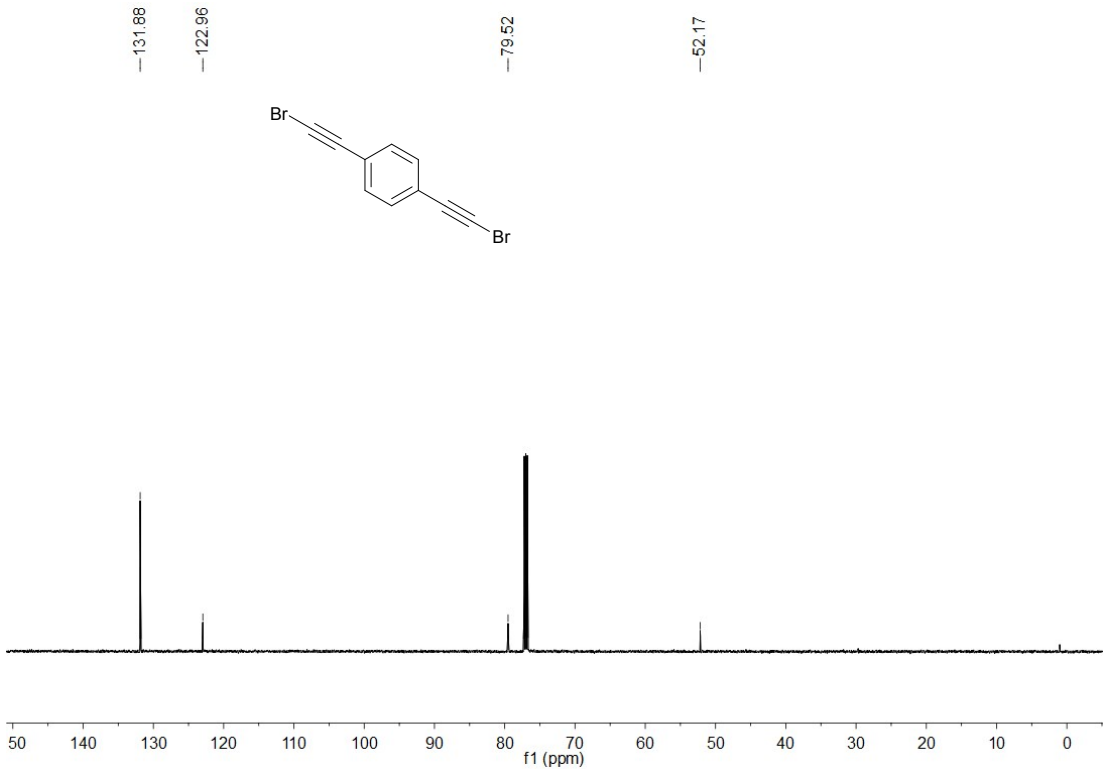

0.98
1.00
1.00
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

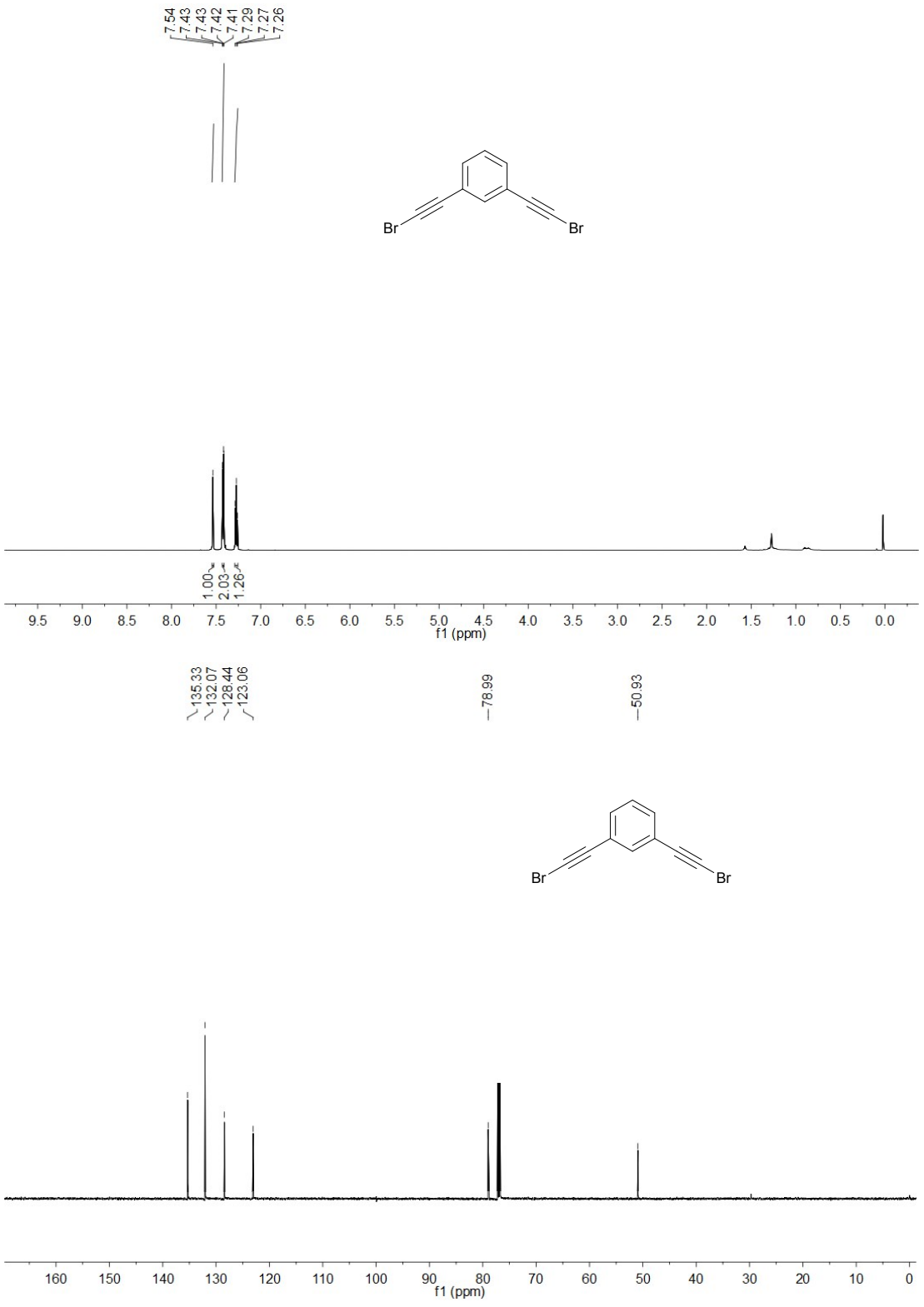

137.62
129.40
126.89
124.46
123.41
77.77
53.59
Br
O2N
135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

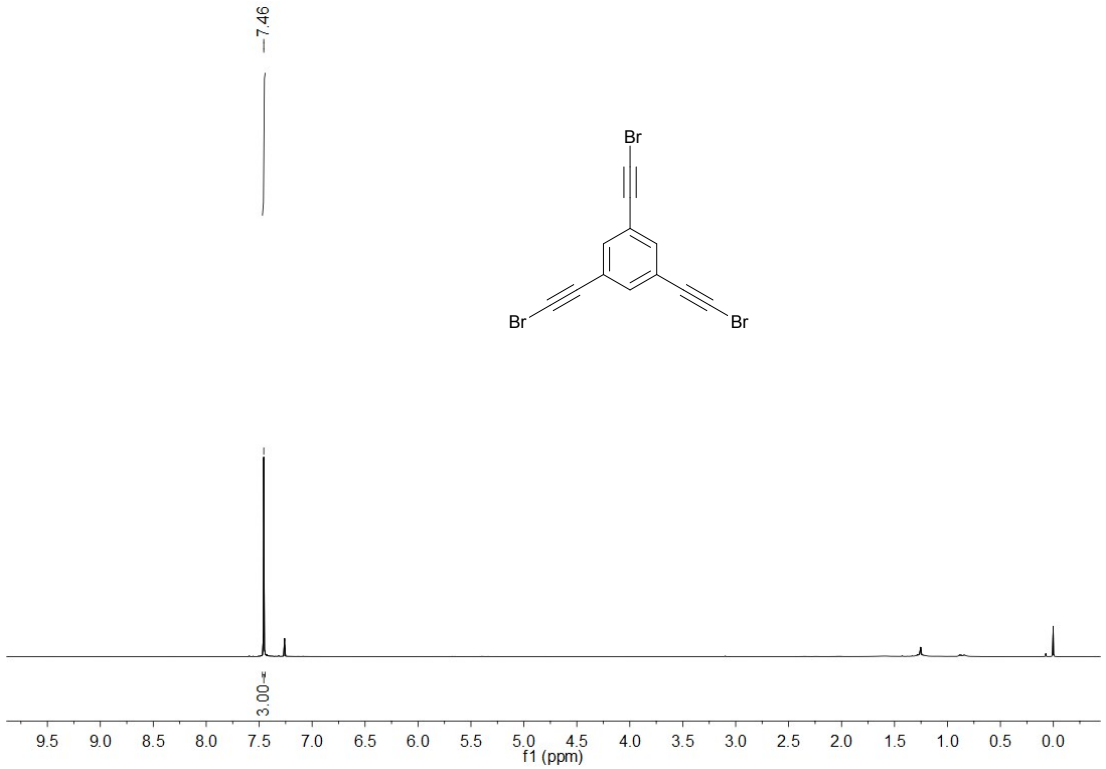

7.74
7.74
7.73
7.73
7.61
7.60
7.59
7.59
7.48
7.46
7.46
O
Cl
Br
4.05
2.00
2.04
f1 (ppm)

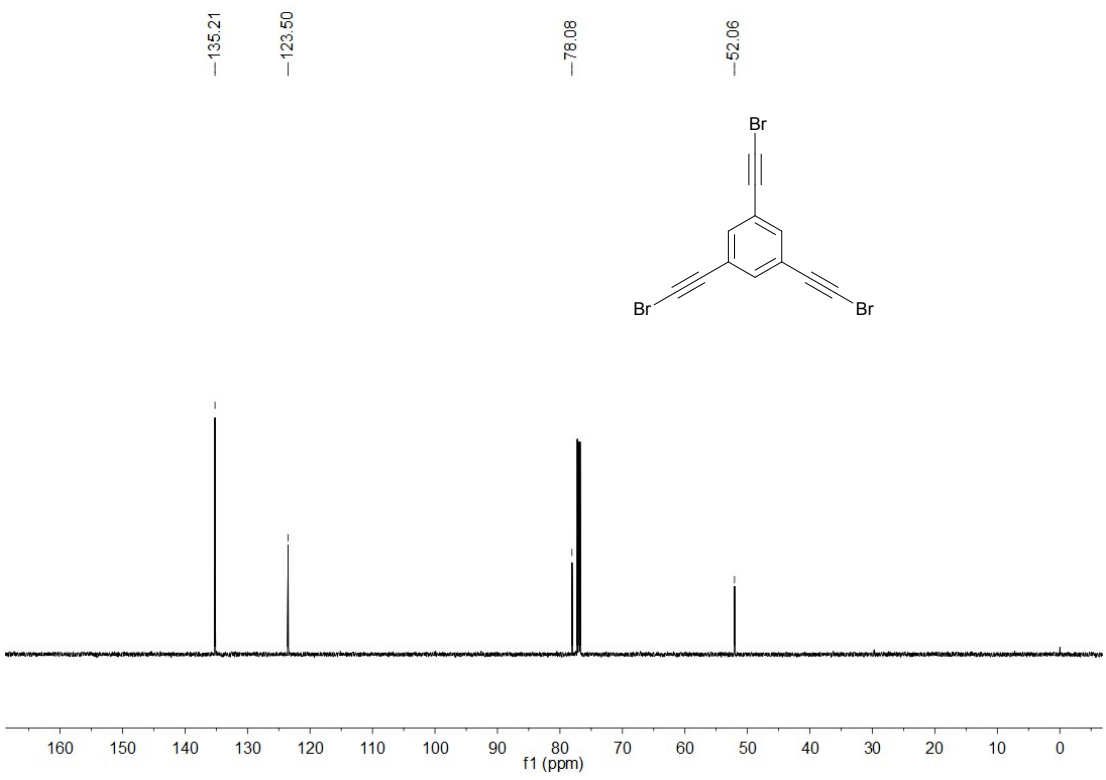

194.60
139.14
137.01
135.48
132.07
131.35
129.78
128.73
126.50
82.66
80.32
O
Cl
Br
f1 (ppm)

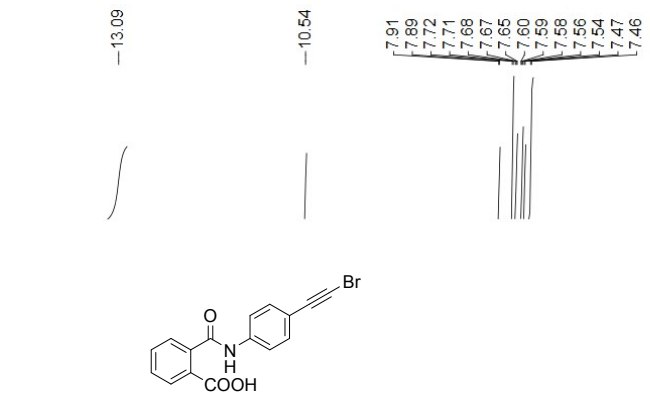

7.38
Br
Br
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

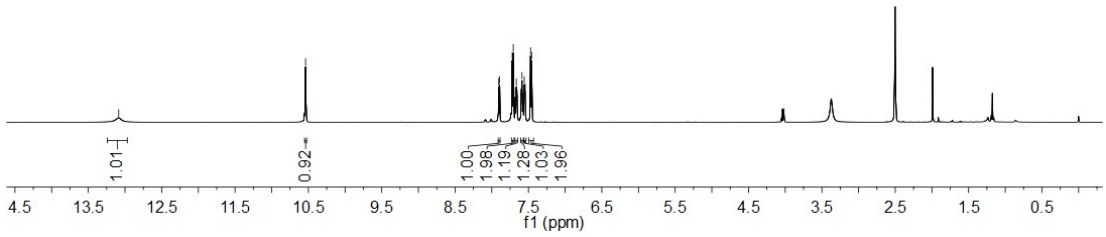

131.88
122.96
79.52
52.17
Br
Br
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

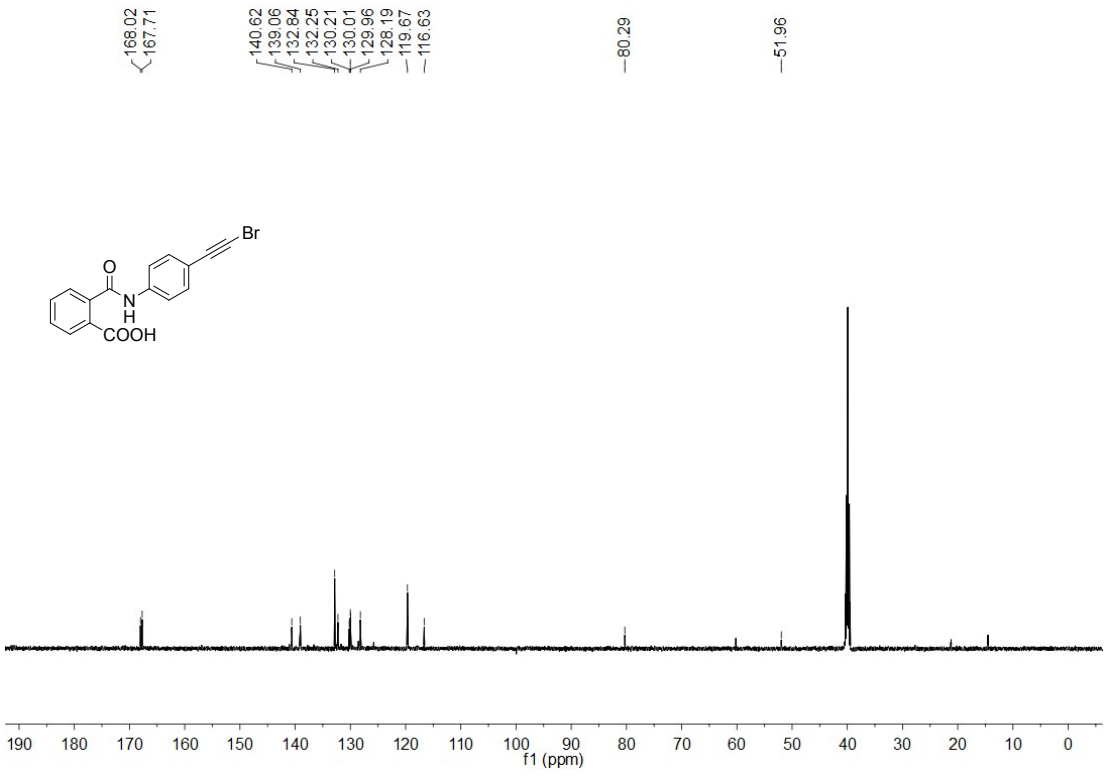

7.54
7.43
7.43
7.42
7.41
7.29
7.27
7.26
Br
Br
1.00
2.03
1.26
f1 (ppm)
135.33
132.07
128.44
123.06
78.99
50.93
Br
Br
f1 (ppm)

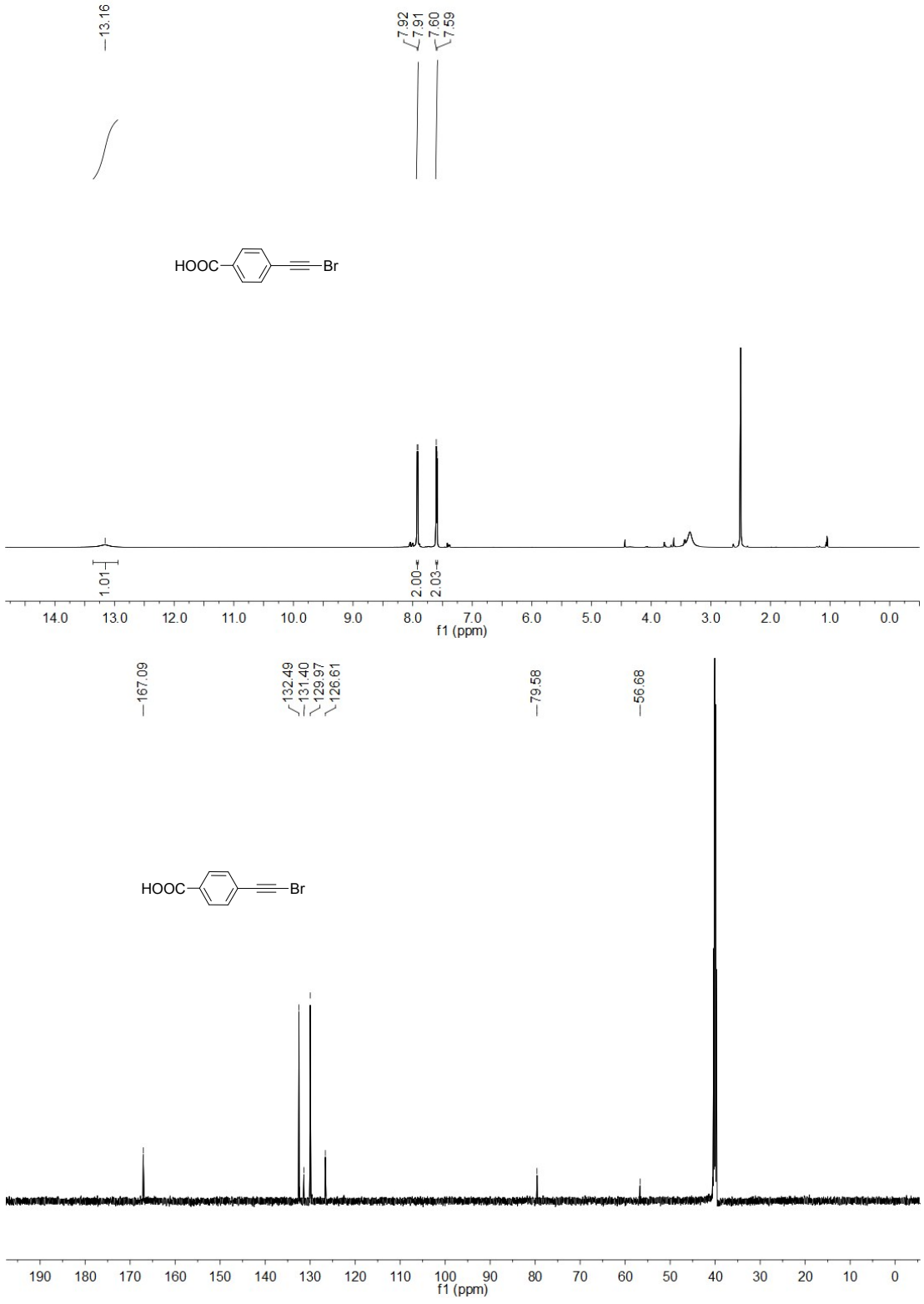

7.46
Br
Br
Br
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

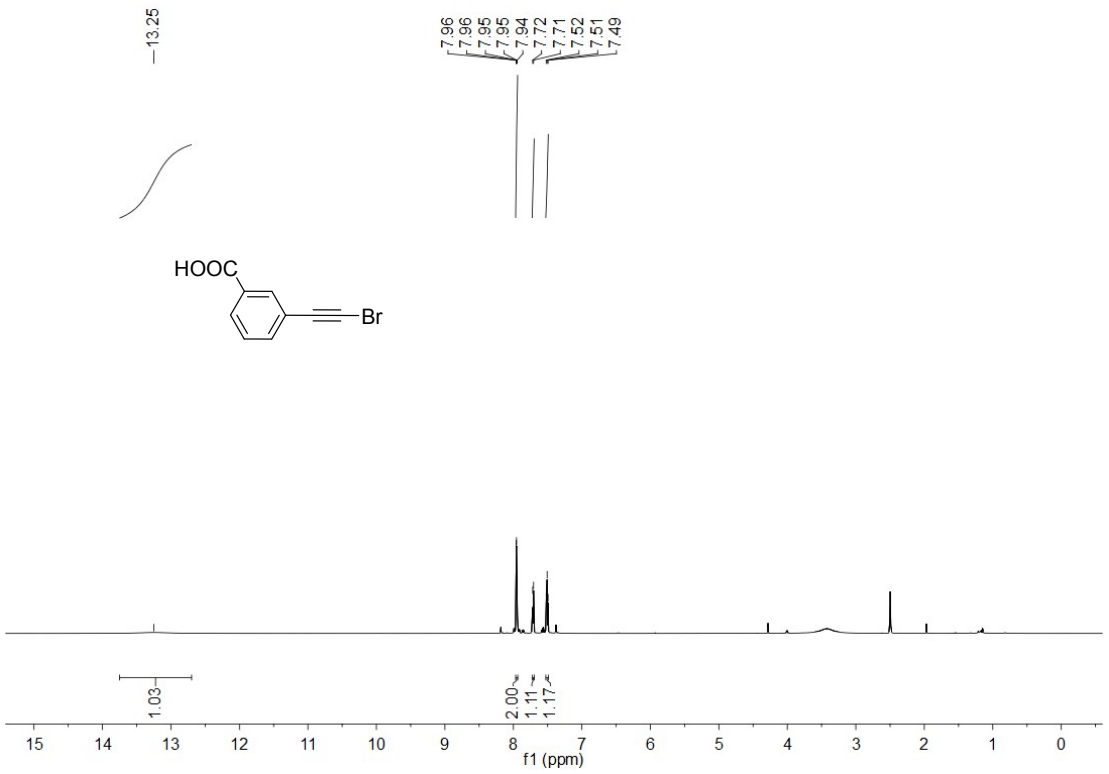

135.21
123.50
78.08
52.06
Br
Br
Br
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

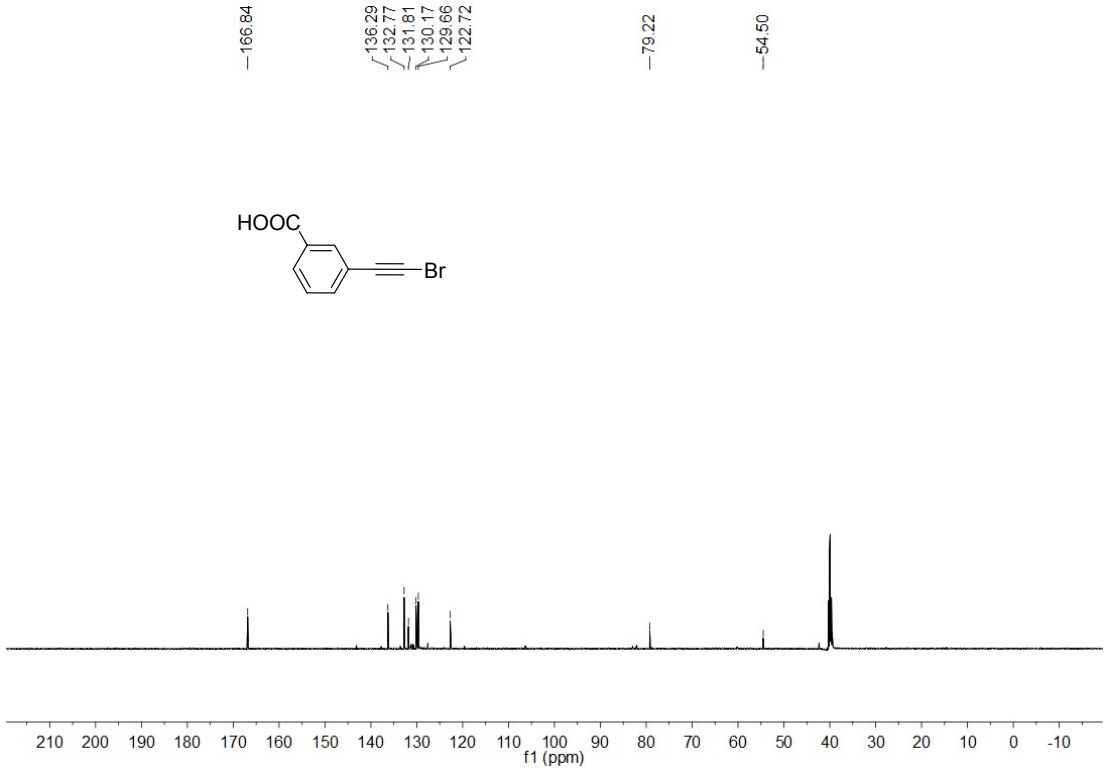

13.09
10.54
7.91
7.89
7.72
7.71
7.68
7.67
7.65
7.60
7.59
7.58
7.56
7.54
7.47
7.46
Br
O
N
H
COOH

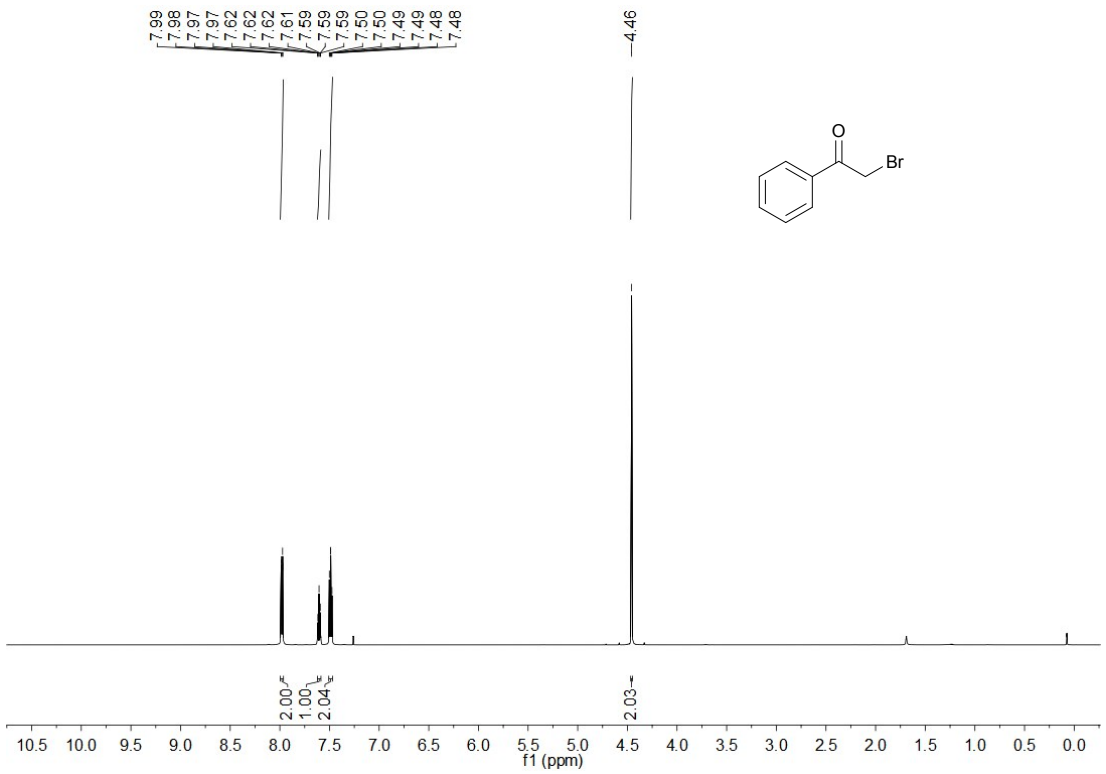

1.01
0.92
1.00
1.98
1.19
1.28
1.03
1.96
4.5
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

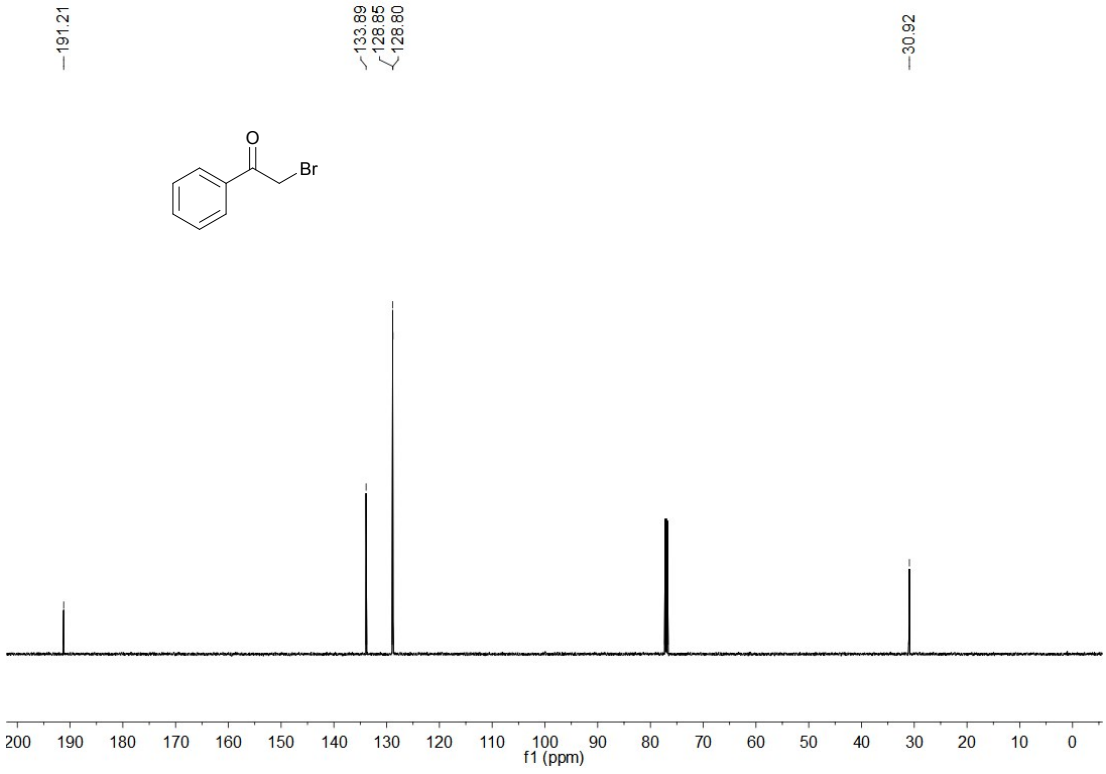

168.02
167.71
140.62
139.06
132.84
132.25
130.21
130.01
129.96
128.19
119.67
116.63
80.29
51.96
Br
O
N
H
COOH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

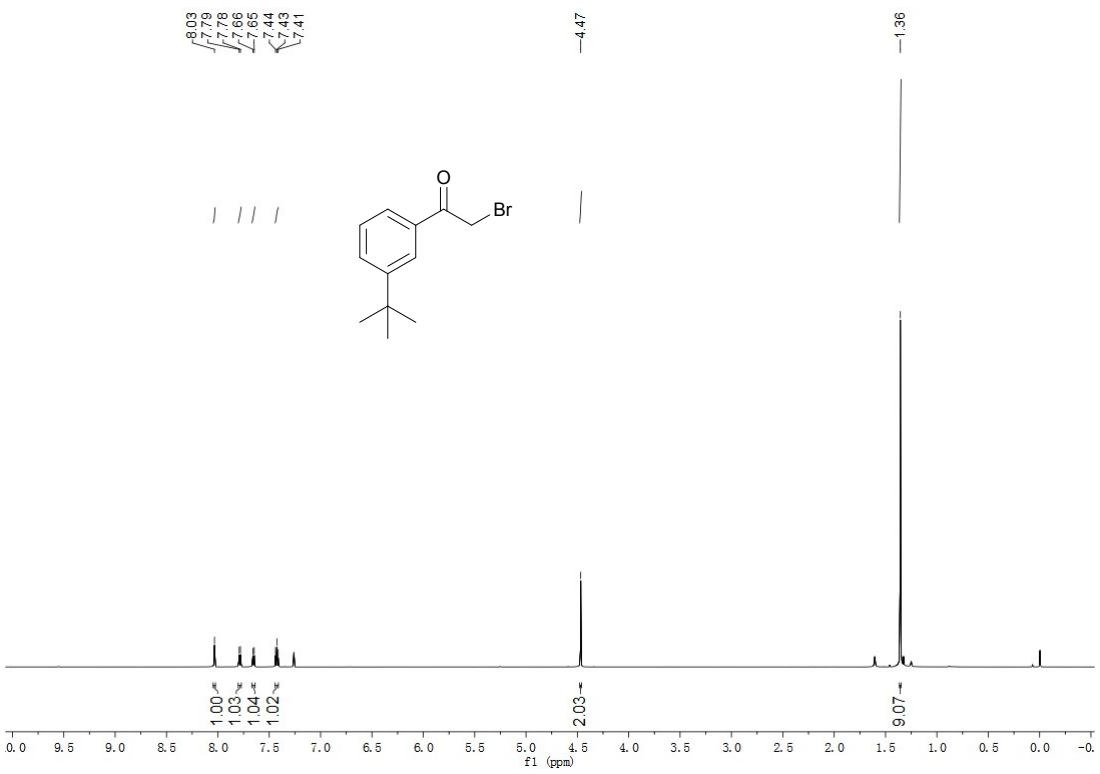

13.16
7.92
7.91
7.60
7.59
HOOC
Br
1.01
2.00
2.03
f1 (ppm)
167.09
132.49
131.40
129.97
126.61
79.58
56.68
HOOC
Br
f1 (ppm)

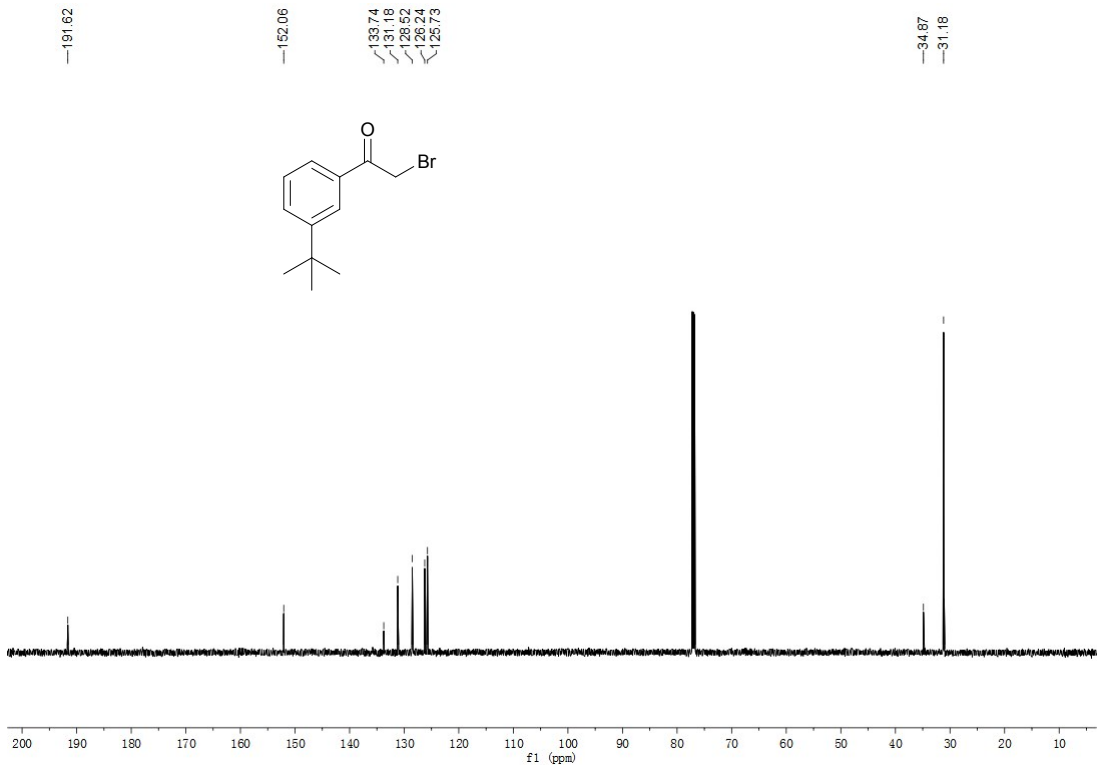

13.25
7.96
7.96
7.95
7.95
7.94
7.72
7.71
7.52
7.51
7.49
HOOC
Br
1.03
2.00
1.11
1.17
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

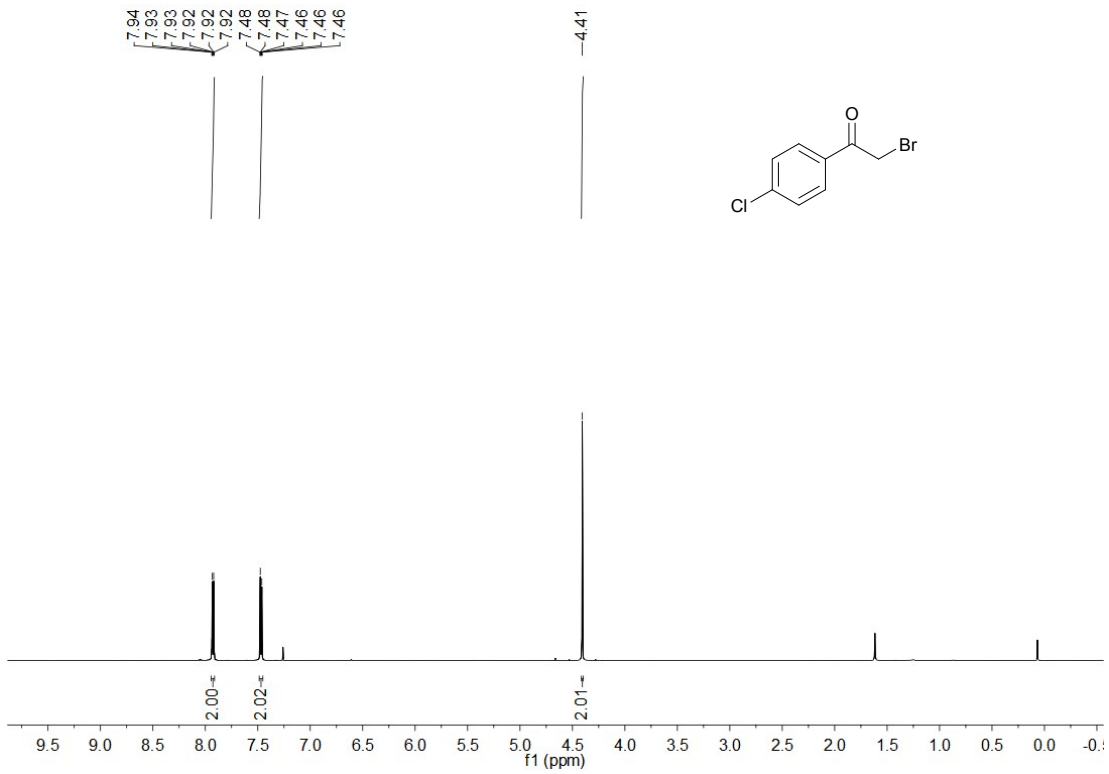

166.84
136.29
132.77
131.81
130.17
129.66
122.72
79.22
54.50
HOOC
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

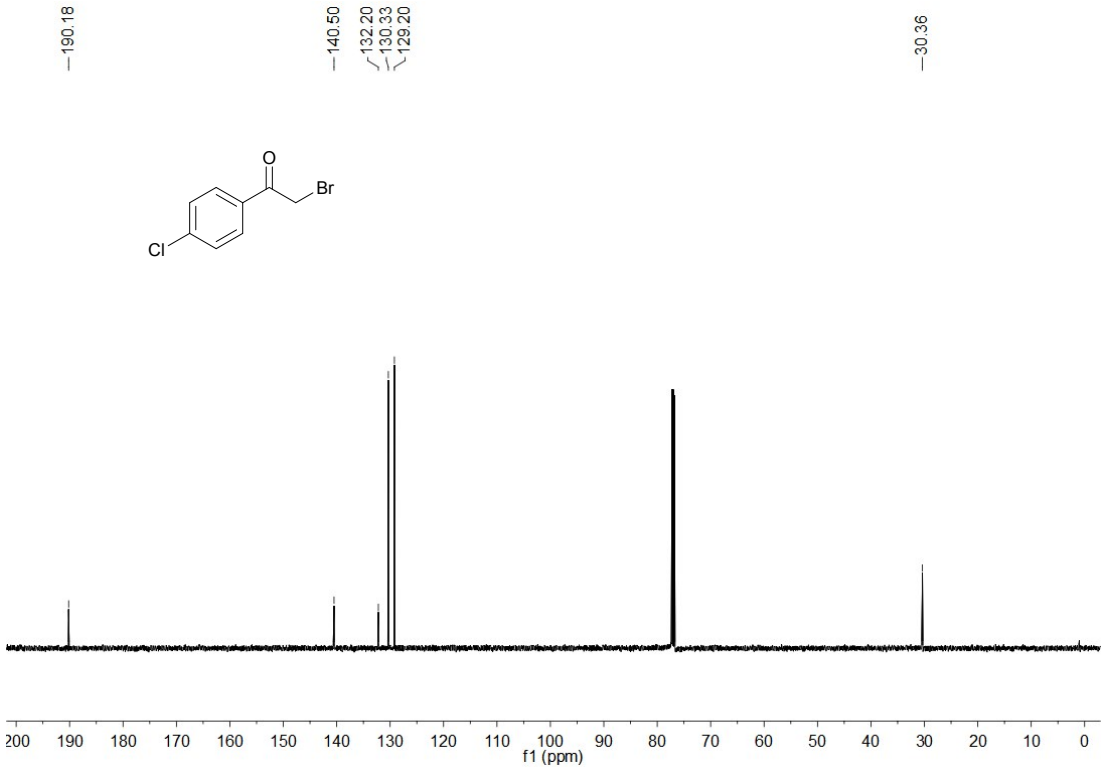

7.99
7.98
7.97
7.97
7.62
7.62
7.62
7.61
7.59
7.59
7.59
7.50
7.50
7.49
7.49
7.48
7.48
4.46
O
Br
2.00
1.00
2.04
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

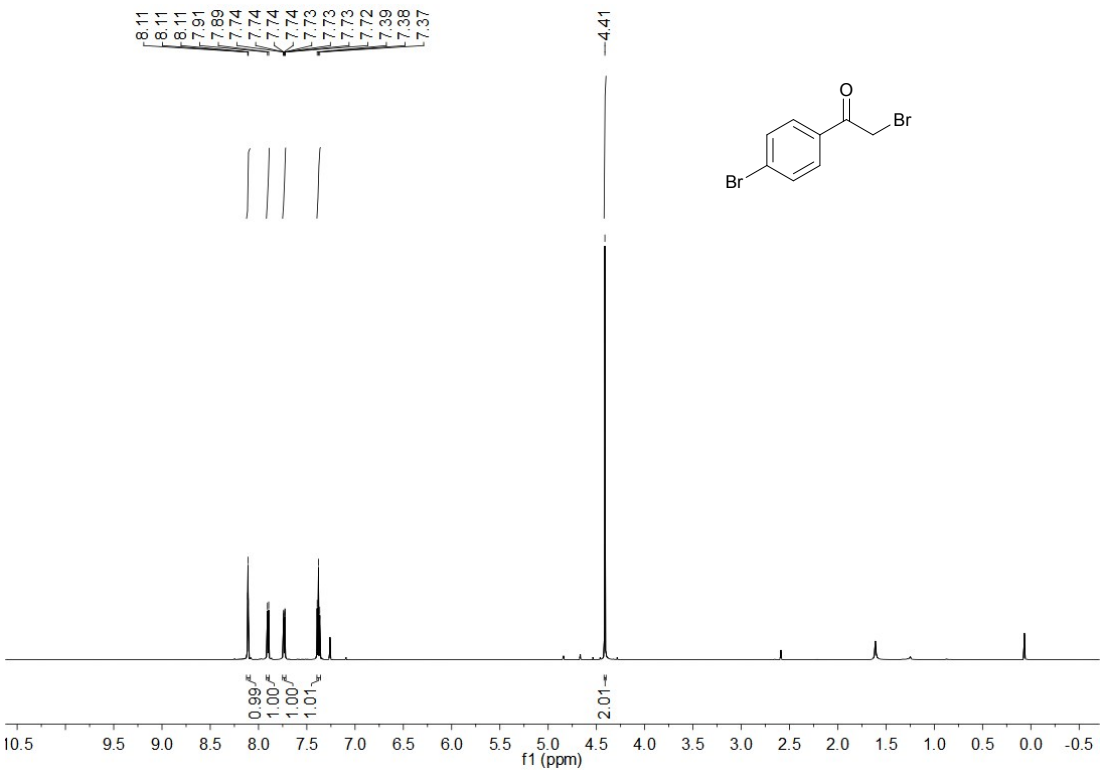

191.21
133.89
128.85
128.80
30.92
O
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

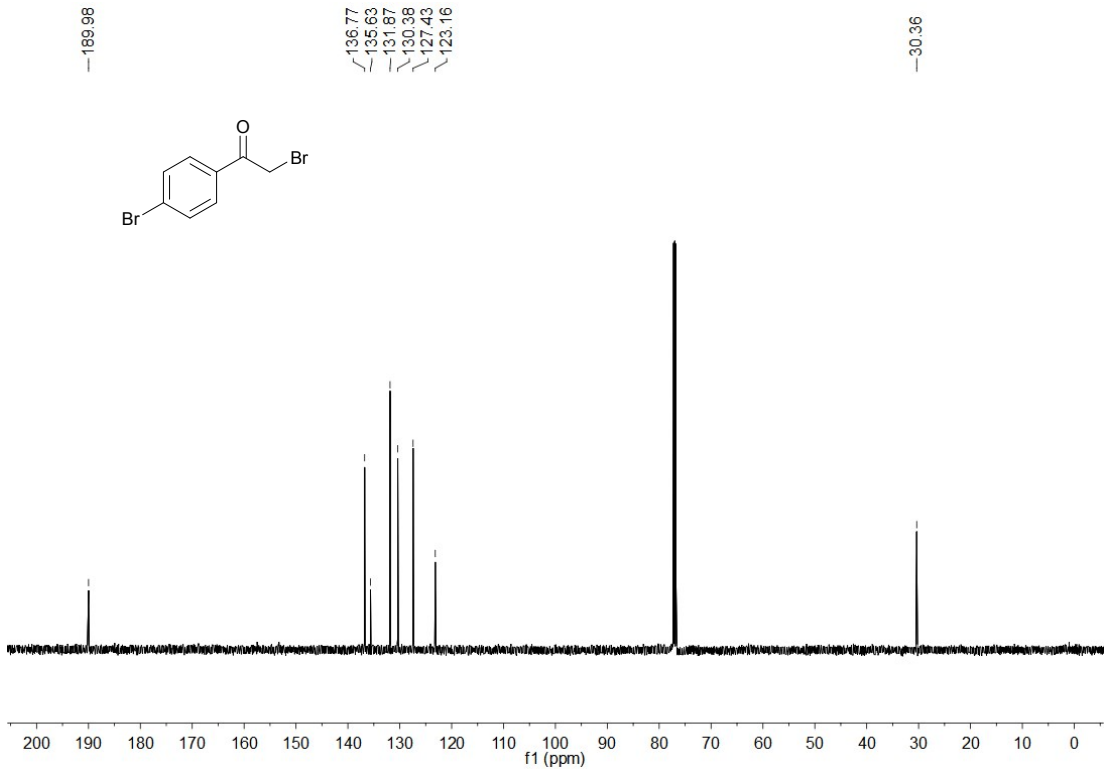

8.03
7.79
7.78
7.66
7.65
7.44
7.43
7.41
4.47
1.36
O
Br
1.00
1.03
1.04
1.02
2.03
9.07
f1 (ppm)

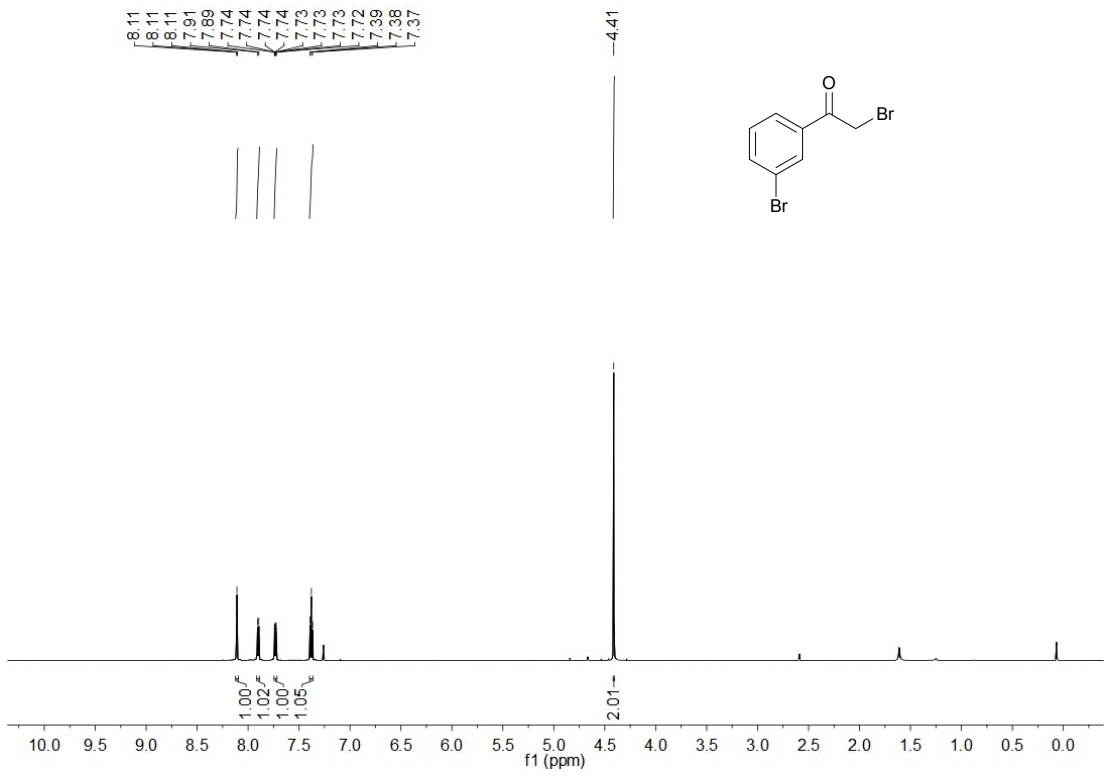

191.62
152.06
133.74
131.18
128.52
126.24
125.73
34.87
31.18
O
Br
f1 (ppm)

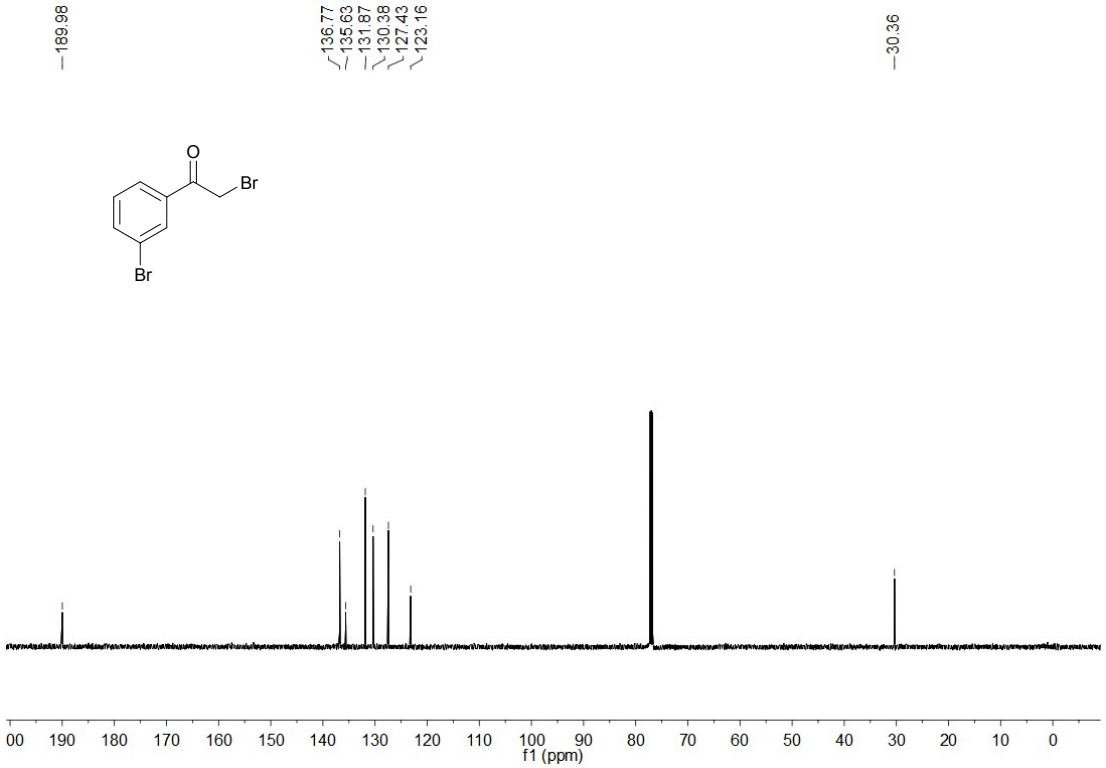

7.94
7.93
7.93
7.92
7.92
7.92
7.48
7.48
7.47
7.46
7.46
7.46
4.41
O
Br
Cl
2.00
2.02
2.01
f1 (ppm)

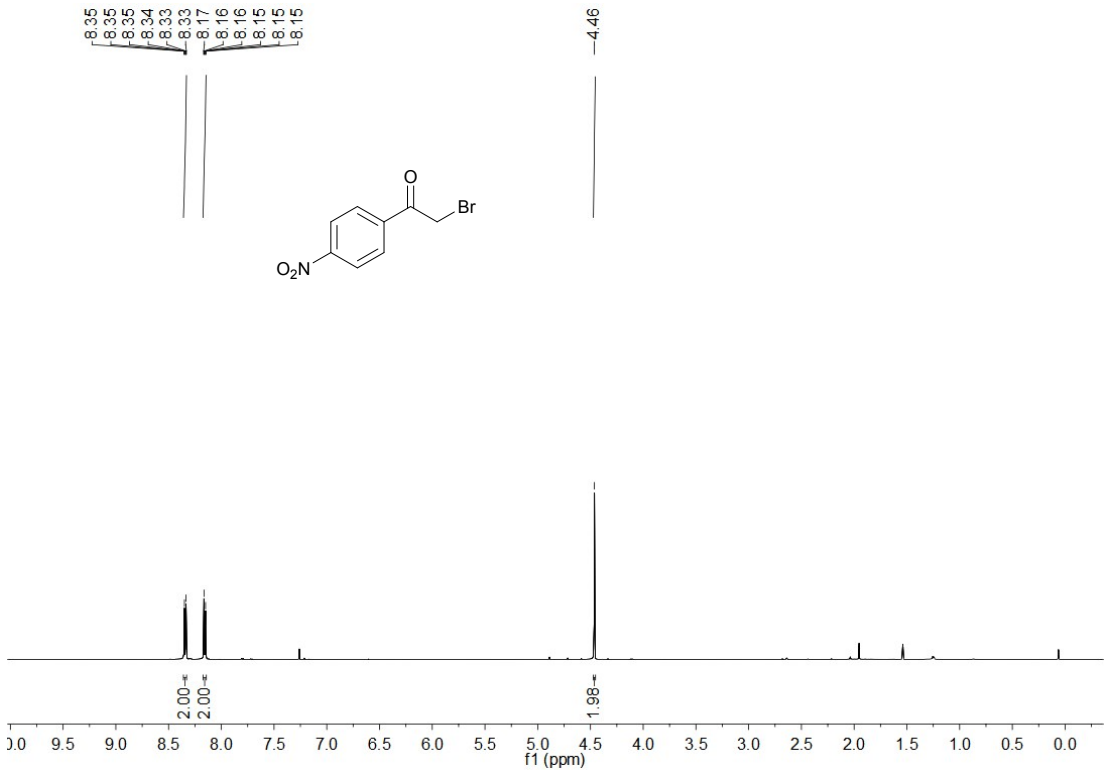

190.18
140.50
132.20
130.33
129.20
30.36
O
Br
Cl
f1 (ppm)

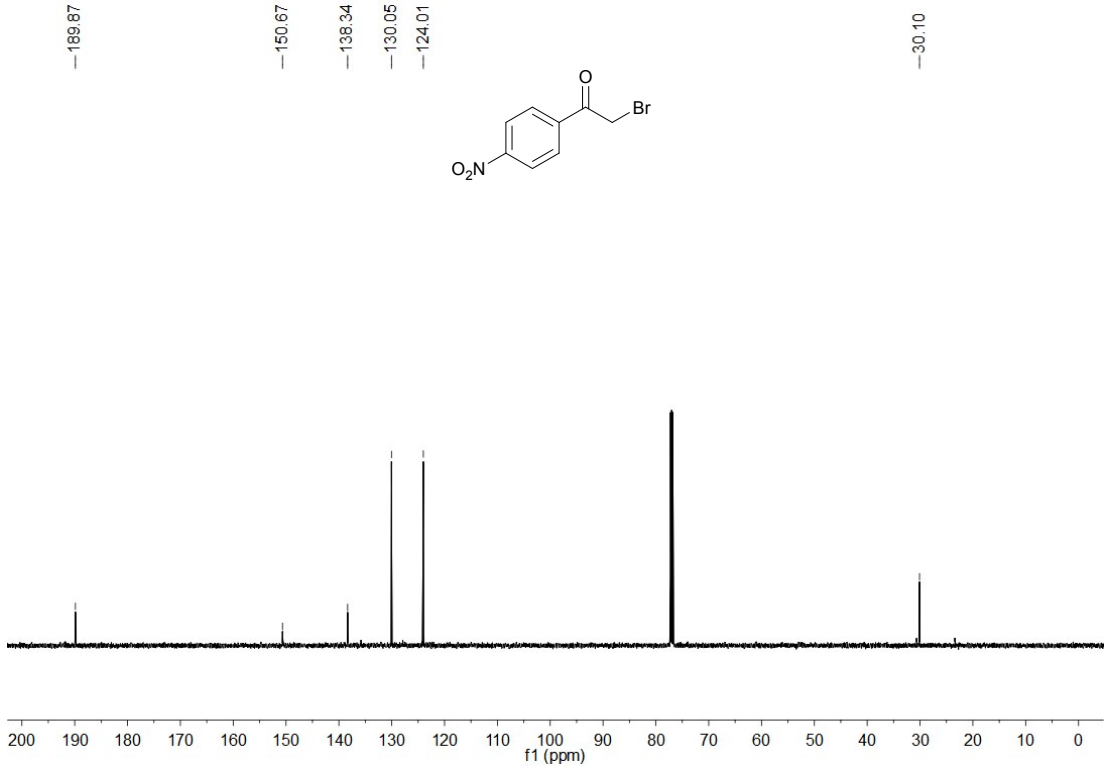

8.11
8.11
8.11
7.91
7.89
7.74
7.74
7.74
7.74
7.73
7.73
7.73
7.72
7.39
7.38
7.37
4.41
O
Br
Br
0.99
1.00
1.00
1.01
2.01
f1 (ppm)

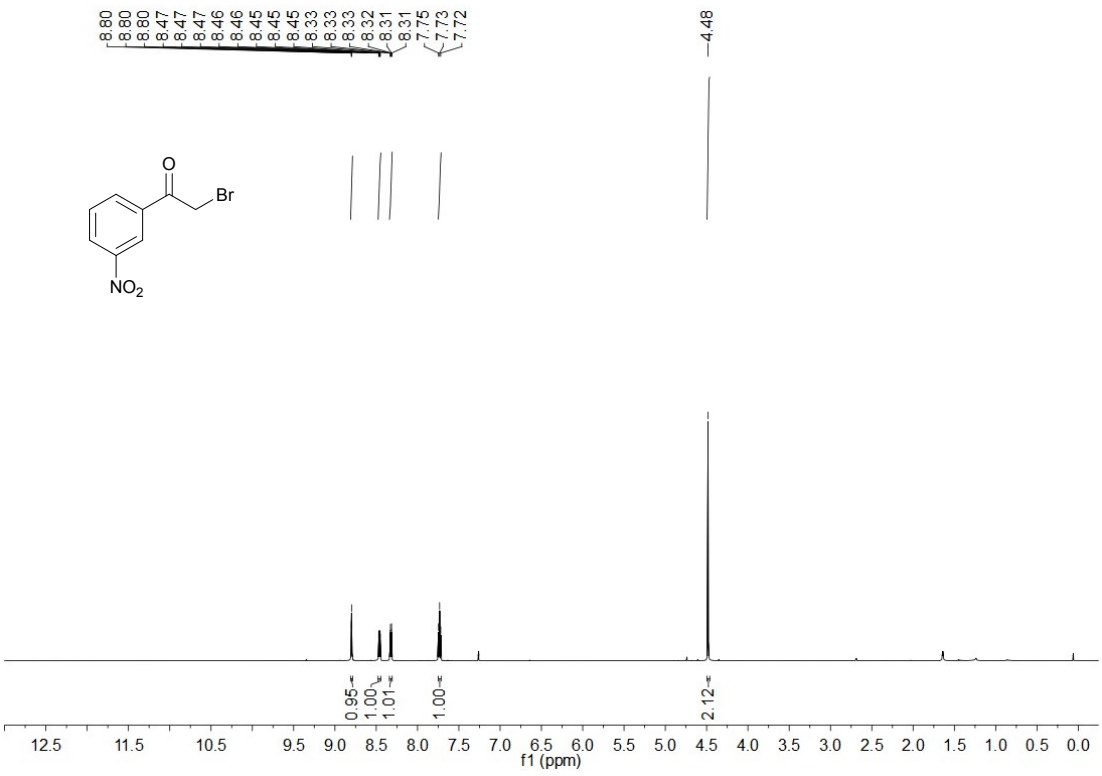

189.98
136.77
135.63
131.87
130.38
127.43
123.16
30.36
O
Br
Br
f1 (ppm)

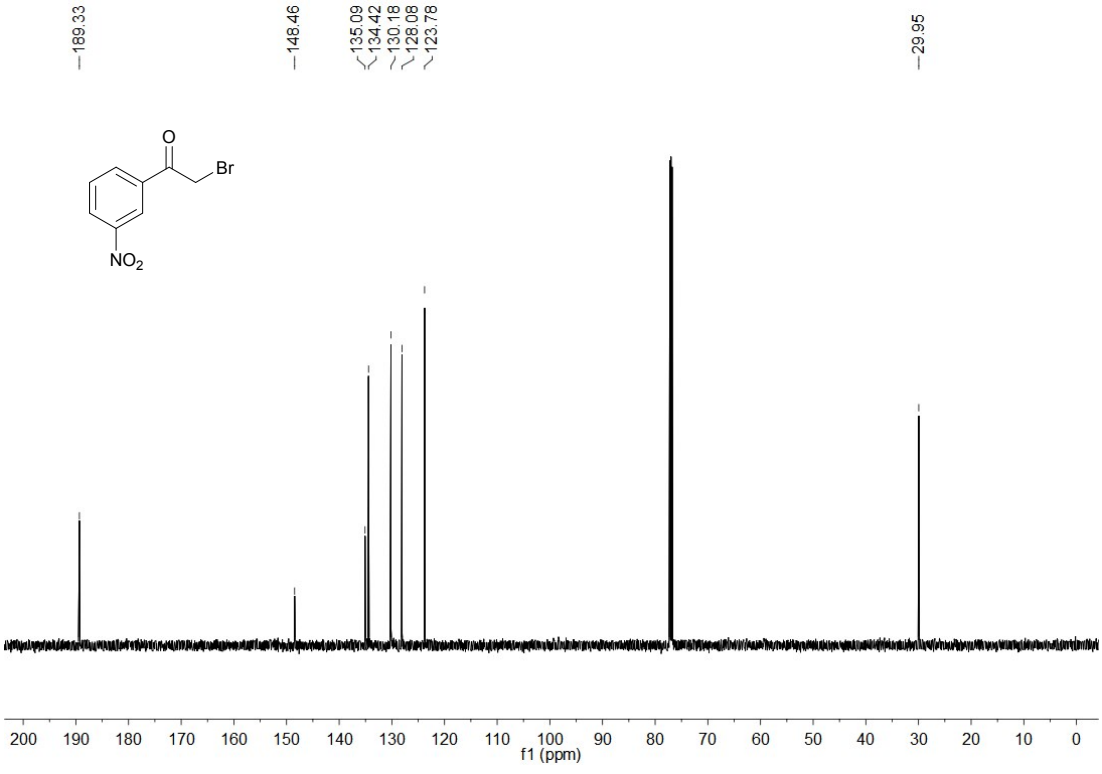

8.11
8.11
8.11
7.91
7.89
7.74
7.74
7.74
7.74
7.73
7.73
7.73
7.72
7.39
7.38
7.37
4.41
O
Br
Br
1.00
1.02
1.00
1.05
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

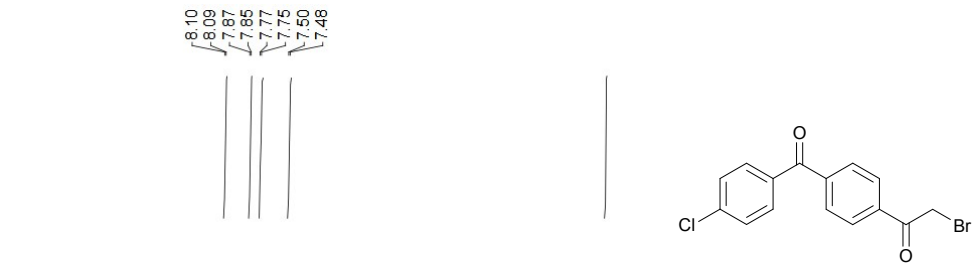

189.98
136.77
135.63
131.87
130.38
127.43
123.16
30.36
O
Br
Br
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

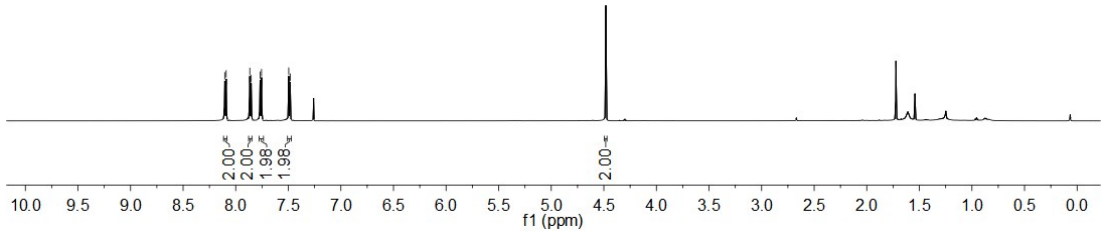

8.35
8.35
8.35
8.34
8.33
8.33
8.17
8.16
8.16
8.15
8.15
8.15
4.46
O
Br
O2N
2.00
2.00
1.98
f1 (ppm)

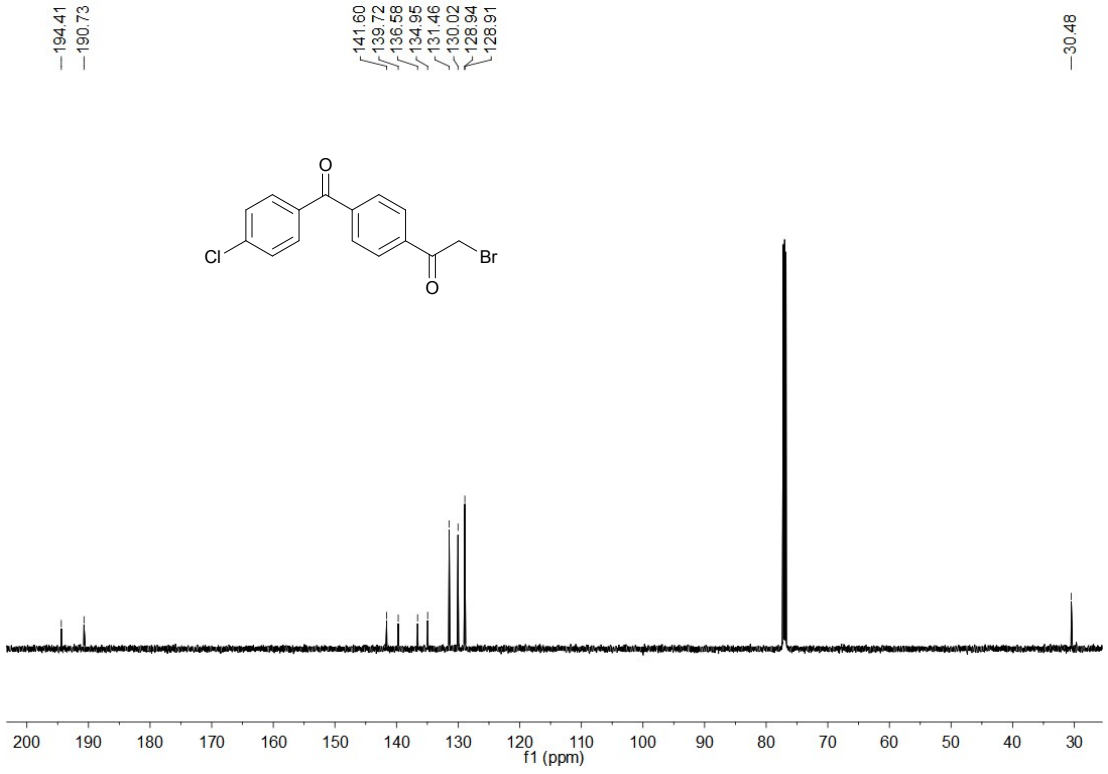

189.87
150.67
138.34
130.05
124.01
30.10
O
Br
O2N
f1 (ppm)

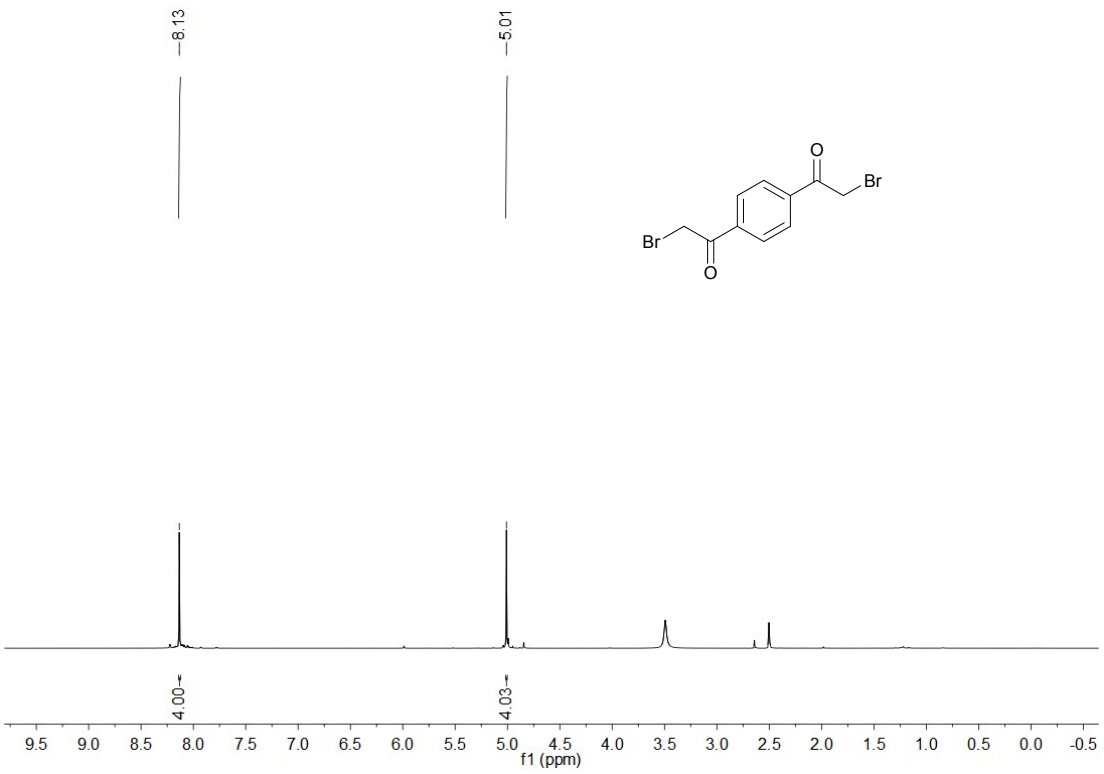

8.80
8.80
8.80
8.47
8.47
8.47
8.46
8.46
8.45
8.45
8.45
8.33
8.33
8.33
8.32
8.31
8.31
7.75
7.73
7.72
4.48
O
Br
NO2
0.95
1.00
1.01
1.00
2.12
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

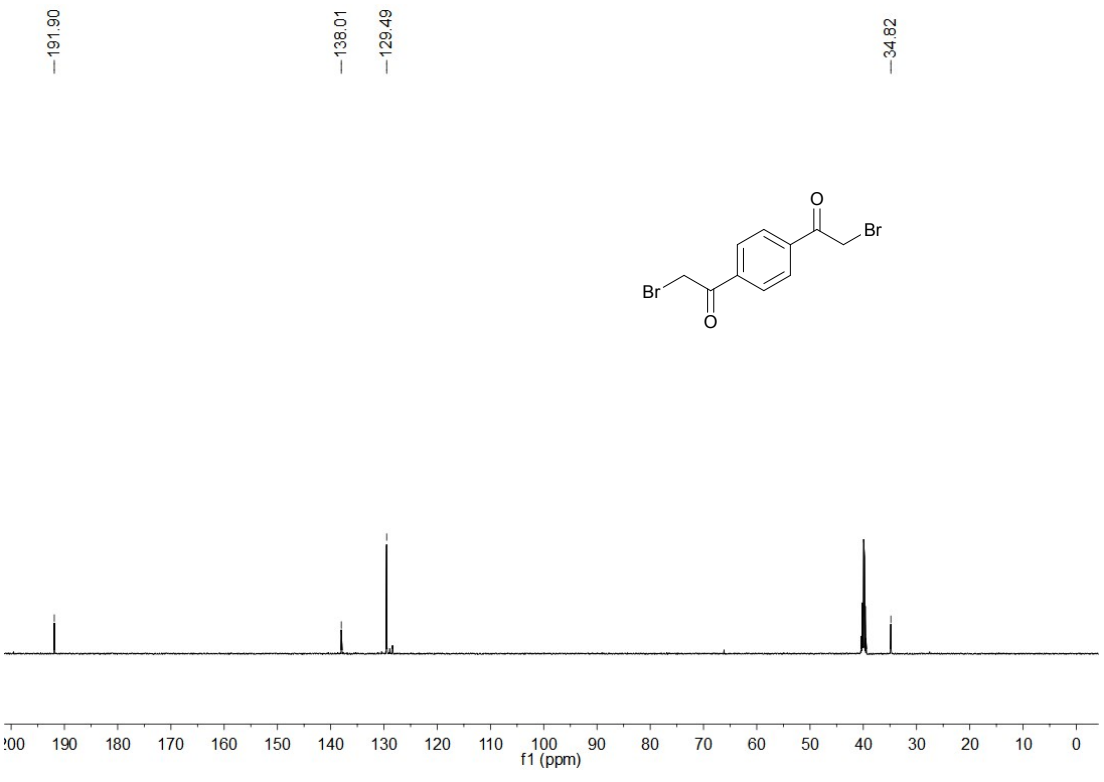

189.33
148.46
135.09
134.42
130.18
128.08
123.78
29.95
O
Br
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.10
8.09
7.87
7.85
7.77
7.75
7.50
7.48
O
Cl
Br
O


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


194.41
190.73
141.60
139.72
136.58
134.95
131.46
130.02
128.94
128.91
30.48
O
Cl
Br
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


8.13
5.01
O
Br
Br
O
4.00
4.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


191.90
138.01
129.49
34.82
O
Br
Br
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)