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Promotion of Appel-Type Reactions by N-Heterocyclic Carbenes

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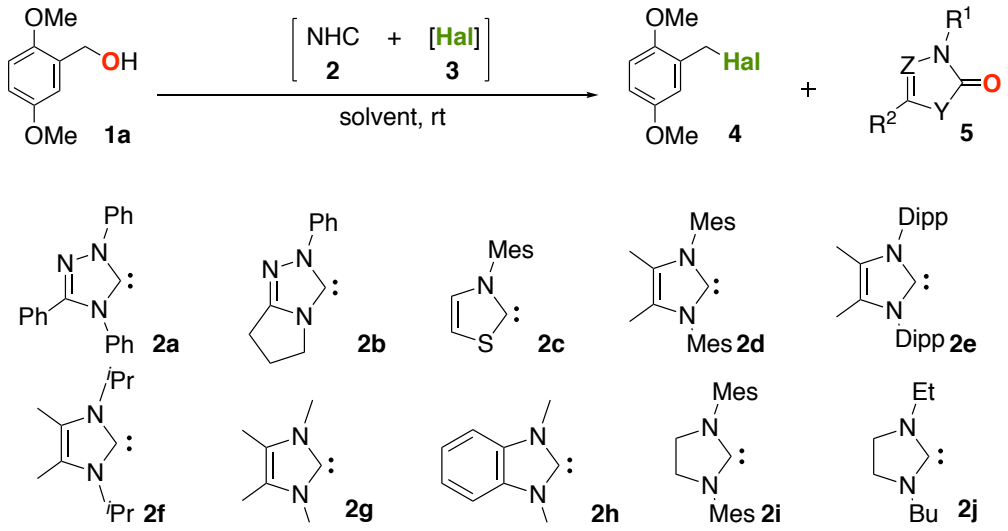
General methods

Reactions, unless otherwise stated, were conducted under a positive pressure of dry nitrogen in oven-dried glassware. Toluene, acetonitrile, hexane, CH_2Cl_2, tetrahydrofuran (THF), and ethyl acetate were dried with an SPS apparatus. Commercially available reagents were used as purchased unless otherwise noted. Analytical thin layer chromatography was performed using silica gel plates percolated with silica gel 60 F_{254} (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvents used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using either a Bruker Avance III 400 (400.13 MHz, ^{1}H; 100.6 MHz, ^{13}C; BBFO probe or Prodigy cryoprobe), a Varian Mercury 300 (300.13 MHz, ^{1}H), a Varian Inova 400 (400.13 MHz, ^{1}H; 100.6 MHz, ^{13}C), or a Varian Inova 600 (600.13 MHz, ^{1}H; 150.0 MHz, ^{13}C). Data is expressed in parts per million (ppm) downfield shift from tetramethyl), 5.27 ppm for dichloromethane, 1.94 ppm for acetonitrile, and 2.09 ppm for the toluene methyl group) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). ^{13}C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.2 ppm for the central peak of deuterated chloroform).

Table S1. Optimization of NHC-promoted Appel-type reactions



Entry[a]	NHC	[**Hal**] **3**	Solvent	Time	Yield[b] (%)
1	**2a**	CCl_4	DCM	18 h	26
2	**2a**	CBr_4	DCM	6 h	44
3	**2a**	NBS	DCM	6 h	78
4	**2a**	NBS	toluene	6 h	46
5	**2a**	NBS	MeCN	6 h	69
6	**2a**	NBS	THF	6 h	76
7	**2b**	NBS	DCM	6 h	59
8-1	**2c**	NBS/CBr_4	DCM	6 h	28/23
8-2	**2d**	NBS/CBr_4	DCM	6 h	21/traces
8-3	**2e**	NBS/CBr_4	DCM	6 h	26/traces
8-4	**2f**	NBS/CBr_4	DCM	6 h	41/26
8-5	**2g**	NBS/CBr_4	DCM	6 h	32/22
8-6	**2h**	NBS/CBr_4	DCM	6 h	28/21
8-7	**2i**	NBS/CBr_4	DCM	6 h	34/24
8-8	**2j**	NBS/CBr_4	DCM	6 h	32/29
9	**2a**	Br_2	DCM	6 h	67
10	**2a**	$BrCH(CO_2Et)_2$	DCM	6 h	40
11	**2a**	NCS	DCM	6 h	53
12	**2a**	CCl_3CCl_3	DCM	6 h	16

13	**2a**	$CCl_3C(=O)CCl_3$	DCM	6 h	19
14	**2a**	I_2	DCM	6 h	69
15	**2a**	NIS	DCM	6 h	55
16	**-**	all **3**	DCM	48 h	traces

[a] Reaction conditions: NHC **2** (1.2 mmol, freshly prepared from the corresponding azolium salt **2.H**$^+$ and KHMDS, see general procedure below), halide source **3** (1.2 equiv),[16] alcohol **1a** (1.0 equiv) in 10 mL solvent at rt for the indicaded time. [b] Yield of isolated **4** after column chromatography.

General procedure for the halogenation reaction of alcohols with NHCs as stoichiometric reagent (Table 1)

To a solution of potassium bis(trimethylsilyl)amide (1.2 mmol, 1.2 equiv from 0.5M solution in CH_2Cl_2), azolium salt **2.H**$^+$ (1.2 mmol, 1.2 equiv) was added and the reaction mixture was stirred at room temperature for 20 min. Halide source **3** (1.2 mmol, 1.2 equiv) in 5 mL of CH_2Cl_2 were added. After stirring for another 20 min at room temperature, alcohol substrate **1** (1.0 mmol, 1.0 equiv) was added. The resulting suspension was stirred until TLC showed the complete conversion of the alcohol starting material or no longer showed any further reaction progress (typically 6-18 hours). Subsequently the reaction mixture was concentrated under reduced pressure and the resulting residues were purified by flash column chromatography (silica-gel, hexanes/ethyl acetate).

General procedure for the halogenation reaction of alcohols with NHCs as stoichiometric reagent (Scheme 1)

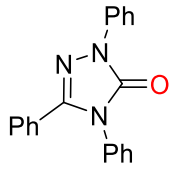
To a solution of potassium bis(trimethylsilyl)amide (1.2 mmol, 1.2 equiv from 0.5M solution in CH_2Cl_2), triazolium salt **2a.H**$^+$ (1.2 mmol, 1.2 equiv) was added and the reaction mixture was stirred at room temperature for 20 min. NXS **3** (1.2 mmol, 1.2 equiv) in 5 mL of CH_2Cl_2 were added. After stirring for another 20 min at room temperature, alcohol substrate **1** (1.0 mmol, 1.0 equiv) was added and the resulting suspension was stirred for 6 hours. Subsequently the reaction mixture was concentrated under reduced pressure and the resulting residues were purified by flash column chromatography (silica-gel, hexanes/ethyl acetate).

General procedure for the catalytic halogenation reaction of alcohols with oxalyl halide and NHC-oxide 5a catalyst (Scheme 3)

In round bottom flask loaded with a stirrer bar under argon atmosphere was added a solution of NHC-oxide **5a** (0.1 mmol, 0.1 equiv) and alcohol substrate **1** (1.0 mmol, 1 equiv) in dry DCM (10 mL). A solution of oxalyl chloride or bromide (1.2 mmol, 1.2 equiv) in dry DCM (5 mL) was added drop-wise by syringe pump over 10 h. The reaction mixture was stirred for another 6 hours then concentrated under reduced pressure. The resulting residues were purified by flash chromatography (silica-gel, hexanes/ethyl acetate).

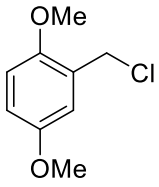
Characterization data of products

1,3,4-Triphenyl-1H-1,2,4-triazol-5(4*H*)-one[1] (5a)



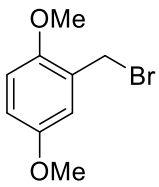
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.12 (m, 2H), 7.54-7.29 (m, 13H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 145.7, 138.4, 134.0, 130.7, 129.8, 129.4, 129.3, 128.9, 128.4, 127.9, 126.9, 125.8, 120.5, 119.1 ppm.

2,5-Dimethoxybenzyl chloride[2] (4a): Prepared according to the general procedure from 2,5-methoxybenzyl alcohol and N-chlorosuccinimide to yield the title compound as a white solid (152 mg, 82% yield).



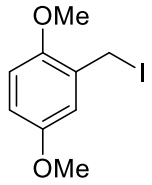
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 1.9 Hz, 1H), 6.85-6.82 (m, 2H), 4.63 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 151.8, 127.1, 116.5, 115.2, 112.3, 56.3, 55.9, 29.1 ppm.

2,5-Dimethoxybenzyl bromide[2] (4b): Prepared according to the general procedure from 2,5-dimethoxybenzyl alcohol and N-bromosuccinimide to yield the title compound as a white solid (182 mg, 78% yield).



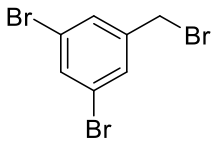
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, J = 0.9 Hz, 1H), 6.77-6.72 (m, 2H), 4.71(s, 2H), 3.78 (two coincident singles, 6H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.5, 130.8, 113.7, 112.0, 110.7, 59.7, 55.8 ppm.

2,5-Dimethoxybenzyl iodide[2] (4c): Prepared according to the general procedure from 2,5-methoxybenzyl alcohol and iodine to yield the title compound as a white solid (130 mg, 69% yield).



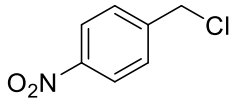
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (m, 1H), 6.81-6.74 (m, 2H), 4.45 (s, 2H), 3.87 (s, 3H), 3.76 (s, 3H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 151.8, 127.1, 116.5, 115.2, 112.3, 56.3, 55.9, 29.1 ppm.

1,3-Dibromo-5-(bromomethyl) benzene[2] (4d): Prepared according to the general procedure from 3,5-dibromobenzyl alcohol and N-bromosuccinimide to yield the title compound as a white solid (174 mg, 54% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J = 1.7 Hz, 1H), 7.47 (d, J = 1.7 Hz, 2H), 4.36 (s, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 134.3, 131.0, 123.3, 31.0 ppm.

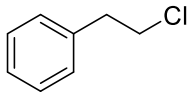
4-Nitrobenzyl chloride[4] (4e): Prepared according to the general procedure from 4-methoxybenzyl alcohol and N-chlorosuccinimide to yield the title compound as a white solid (126 mg, 74% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 2.4, 8.8 Hz, 2H), 7.56 (dd, J = 2.4, 8.8 Hz, 2H), 4.64 (s, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 144.4, 129.4, 124.0, 44.6 ppm.

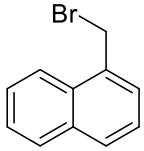
2-Phenylethylchloride[2] (4f): Prepared according to the general procedure B from 2-phenylethan-1-ol and N-chlorosuccinimide to yield the title compound as a colorless oil (101 mg, 73% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 3.82 (t, J = 6.7 Hz, 2H), 2.88 (t, J = 6.7 Hz, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 128.9, 128.4, 126.3, 63.4, 39.0 ppm.

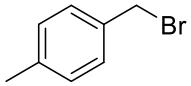
1-(Bromomethyl) naphthalene[11] (4g): Prepared according to the general procedure from 1-naphthalenemethanol and N-bromosuccinimide to yield the title compound as a white powder (198 mg, 89% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.81 (m, 4H), 7.52-7.48 (m, 3H), 4.67 (s, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.3, 133.2, 128.9, 128.1, 128.0, 127.8, 126.9, 126.7, 126.6, 34.2 ppm.

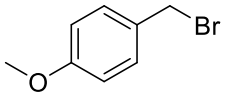
4-Methylbenzylbromide[2] (4h): Prepared according to the general procedure from 4-methylbenzyl alcohol and N-bromosuccinimide to yield the title compound as a yellowish liquid (142.4 mg, 78% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 4.50 (s, 2H), 2.37 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.9, 129.6, 129.1, 33.9, 21.3 ppm

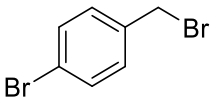
4-Methoxybenzyl bromide[4] (4i): Prepared according to the general procedure from 4-methoxybenzyl alcohol and N-bromosuccinimide to yield the title compound as a colorless oil (144 mg, 71% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.52 (s, 2H), 2.38 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.9, 129.6, 129.1, 33.9, 21.3 ppm.

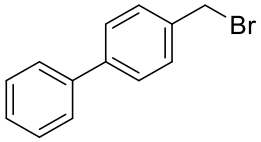
4-Bromobenzylbromide[2] (4j): Prepared according to the general procedure from 4-bromobenzyl alcohol and N-bromosuccinimide to yield the title compound as a yellowish oil (171mg, 79% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.30-7.27 (m, 2H), 4.46 (s, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.0, 130.7, 122.5, 32.5 ppm.

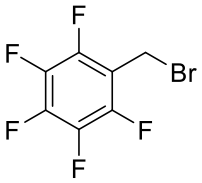
4-Bromomethyl-biphenyl[3] **(4k):** Prepared according to the general procedure from 2-biphenylmethanol and N-bromosuccinimide to yield the title compound as a colorless oil (168 mg, 68% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 4H), 7.49-7.42 (m, 4H) 7.36 (m, 1H), 4.56 (s, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.7, 139.9, 128.8, 127.5, 127.4, 127.1, 65.1 ppm.

2,3,4,5,6-Pentafluorobenzyl bromide[4] **(4l):** Prepared according to the general procedure from 2,3,4,5,6-pentafluorobenzyl alcohol and N-bromosuccinimide to yield the title compound as a colorless oil (122 mg, 53% yield).

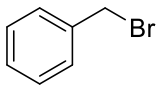


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (t, J = 1.4 Hz, 2H) ppm;

^{19}F NMR (376.5 MHz, $CDCl_3$) δ -142.4 (dd, J = 8.4, 6.3 Hz, 2F), -152.9 (t, J = 20.3 Hz, 1F), -161.3-161.4 (m, 2F) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6-142.0 (m, Ar–C), 141.9-138.0 (m, Ar–C), 137.9-135.3 (m, Ar–C), 111.5-111.1 (m, Ar–C), 15.1 (s, $BrCH_2$) ppm.

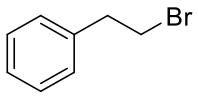
Benzyl bromide[2] **(4m):** Prepared according to the general procedure from benzyl alcohol and N-bromosuccinimide to yield the title compound as a colorless oil (138 mg, 80% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.35 (m, 5H), 4.56 (s, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 129.0, 128.7, 128.3, 33.6 ppm

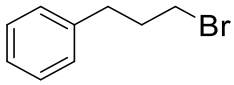
2-Phenylethylbromide[2] (4n): Prepared according to the general procedure from 2-phenylethan-1-ol and N-bromosuccinimide to yield the title compound as a colorless oil (120 mg, 64% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.22 (m, 5H), 3.59 (t, J = 7.5 Hz, 2H), 2.18 (t, J = 7.5 Hz, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 128.8, 128.7, 127.0, 39.5, 33.0 ppm.

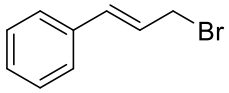
(3-Bromopropyl)benzene[5] (4o): Prepared according to the general procedure from 3-phenylpropanol and N-bromosuccinimide to yield the title compound as a colorless oil (120 mg, 60% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.32-7.28 (m, 3H), 3.46 (t, J = 6.6 Hz, 2H), 2.89-2.84 (m, 2H), 2.28-2.21 (m, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 128.7, 128.6, 126.3, 34.3, 34.1, 33.2 ppm.

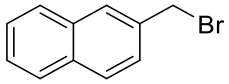
Cinnamyl bromide[6] (4p): Prepared according to the general procedure from cinnamyl alcohol and N-bromosuccinimide to yield the title compound as a light-yellow powder (170 mg, 85% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.25 (m, 5H), 6.67 (d, J = 15.9 Hz, 1H), 6.45-6.37 (m, 1H), 1.18 (dd, J = 7.8, 1.0 Hz, 2H) ppm;

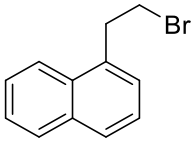
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 130.1, 128.9, 128.5, 127.4, 126.4, 63.4 ppm.

2-(Bromomethyl) naphthalene[7] (4q): Prepared according to the general procedure from 2-naphthalenemethanol N-bromosuccinimide to yield the title compound as a yellow liquid (198 mg, 91% yield).



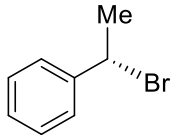
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 1H), 7.90-7.85 (m, 2H), 7.63-7.61 (m, 1H), 7.56-7.52 (m, 2H), 7.43-7.41 (m, 1H), 5.06 (s, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 133.1, 131.2, 129.9, 128.9, 127.8, 126.8, 126.2, 125.4, 123.7, 44.6 ppm.

1-(2-Bromoethyl) naphthalene[7] (4r): Prepared according to the general procedure from 1-naphthylethanol and N-bromosuccinimide to yield the title compound as a cloudy, viscous yellow liquid (180 mg, 76% yield).



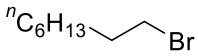
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 1H), 7.87 (dd, J = 1.5, 6.0Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.56-7.37 (m, 4H), 3.94 (t, J = 7.7, 7.3 Hz, 2H), 3.36 (t, J = 7.6, 7.3 Hz, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 134.1, 132.2, 129.0, 127.5, 127.3, 126.2, 125.8, 125.6, 123.8, 63.2, 36.4 ppm.

(*S*)-(1-Bromoethyl) benzene[8] (4s): Prepared according to the general procedure from (*R*)-1-phenylethanol 98% ee and N-bromosuccinimide to yield the title compound as a colorless liquid (105 mg, 68% yield).



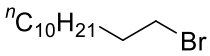
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.39-7.28 (m, 3H), 5.25 (q, J = 6.9 Hz, 1H), 2.08 (d, J = 6.9 Hz, 3H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 128.7, 128.4, 126.9, 49.6, 26.9 ppm.
$[\alpha]_D^{20}$ = -37.4 ° (0.1 g in 10 mL chloroform, literature value = -40.6 °); ee = 92%.

1-Bromooctane[2] (4u): Prepared according to the general procedure from 1-octanol and N-bromosuccinimide to yield the title compound as a colorless oil (153 mg, 76% yield).



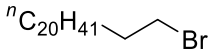
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (t, J = 6.7 Hz, 2H), 1.80-1.72 (m, 2H), 1.45-1.38 (m, 2H), 1.31-1.27 (m, 8H), 0.88 (t, J = 6.7, 7.1 Hz, 3H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 45.2, 32.8, 31.9, 29.2, 29.0, 27.0, 22.7, 14.2 ppm.

1-Bromododecane[2] (4v): Prepared according to the general procedure from 1-dodecanol and N-bromosuccinimide to yield the title compound as a colorless oil (177 mg, 72% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (t, J = 6.8 Hz, 2H), 1.89-1.81 (m, 2H), 1.42 (p, J = 7.0, 7.3 Hz, 2H), 1.35-1.26 (m, 16H), 0.88 (t, J = 6.87, 7.0 Hz, 3H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2, 33.0, 32.0, 29.7, 29.6, 29.5, 29.4, 28.9, 28.3, 22.8, 14.2 ppm.

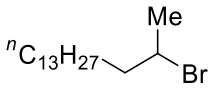
1-Bromodocosane[9] (4w): Prepared according to the general procedure from docosanol and N-bromosuccinimide to yield the title compound as a crystalline light brown solid (300 mg, 77% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (t, J = 6.9 Hz, 2H), 1.89-1.81 (m, 2H), 1.44-1.38 (m, 2H), 1.35-1.25 (m, 36H), 0.90 (t, J = 6.5, 7.0 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2, 33.0, 32.0, 29.9-29.8 (m), 29.7, 29.6, 29.5, 28.9, 28.4, 22.9, 14.2 ppm.

2-Bromohexadecane[10] **(4x):** Prepared according to the general procedure from 2-hexadecanol and N-bromosuccinimide to yield the title compound as a colourless oil (200 mg, 66% yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (t, J = 7.2 Hz, 3H), 1.86-1.79 (m, 2H), 1.39-1.20 (m, 26H), 0.87 (t, J = 6.6, 6.9 Hz, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 33.7, 32.1, 30.7, 30.6, 30.6, 29.8, 29.7, 29.6, 29.5, 28.7 ppm.

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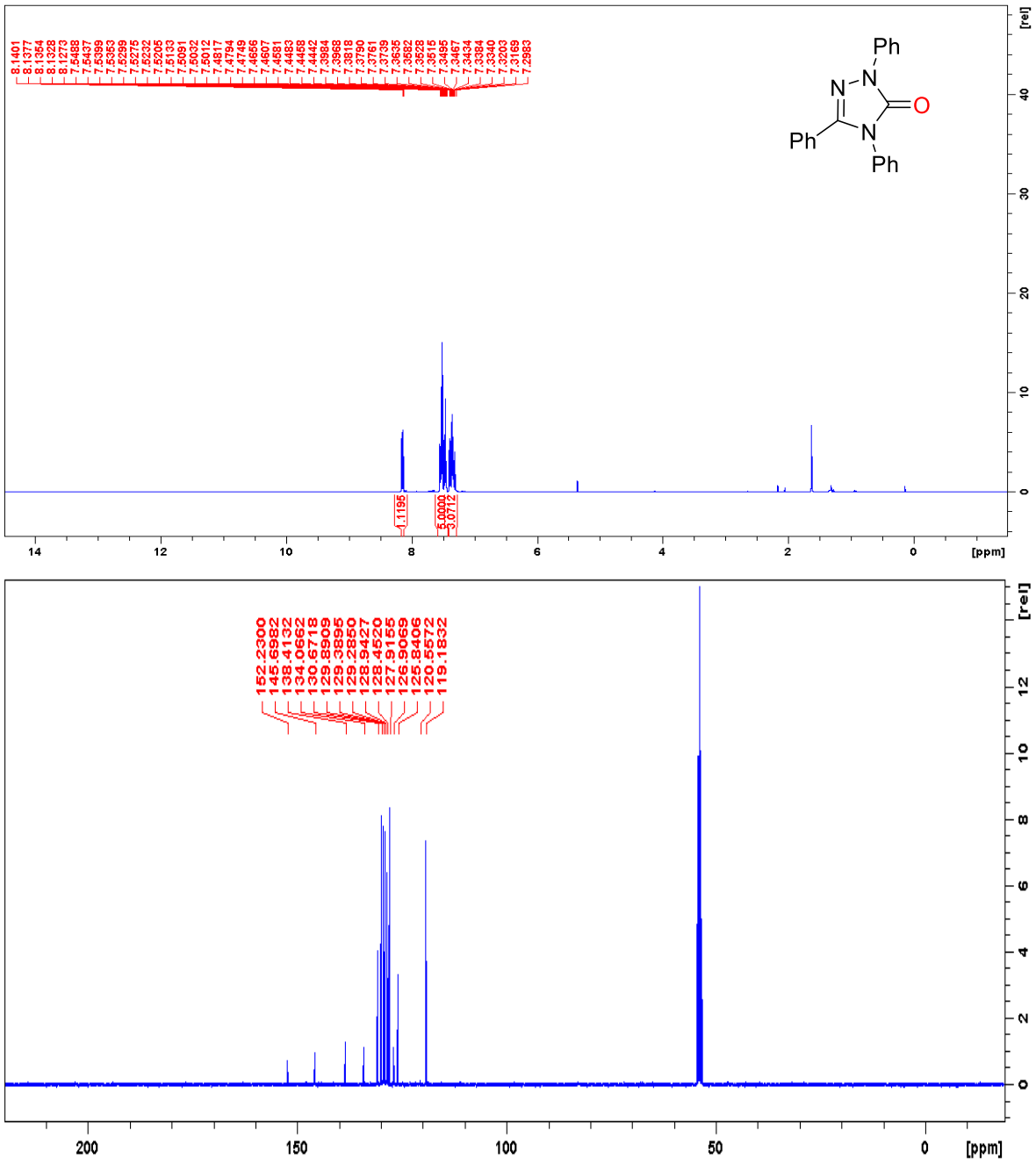
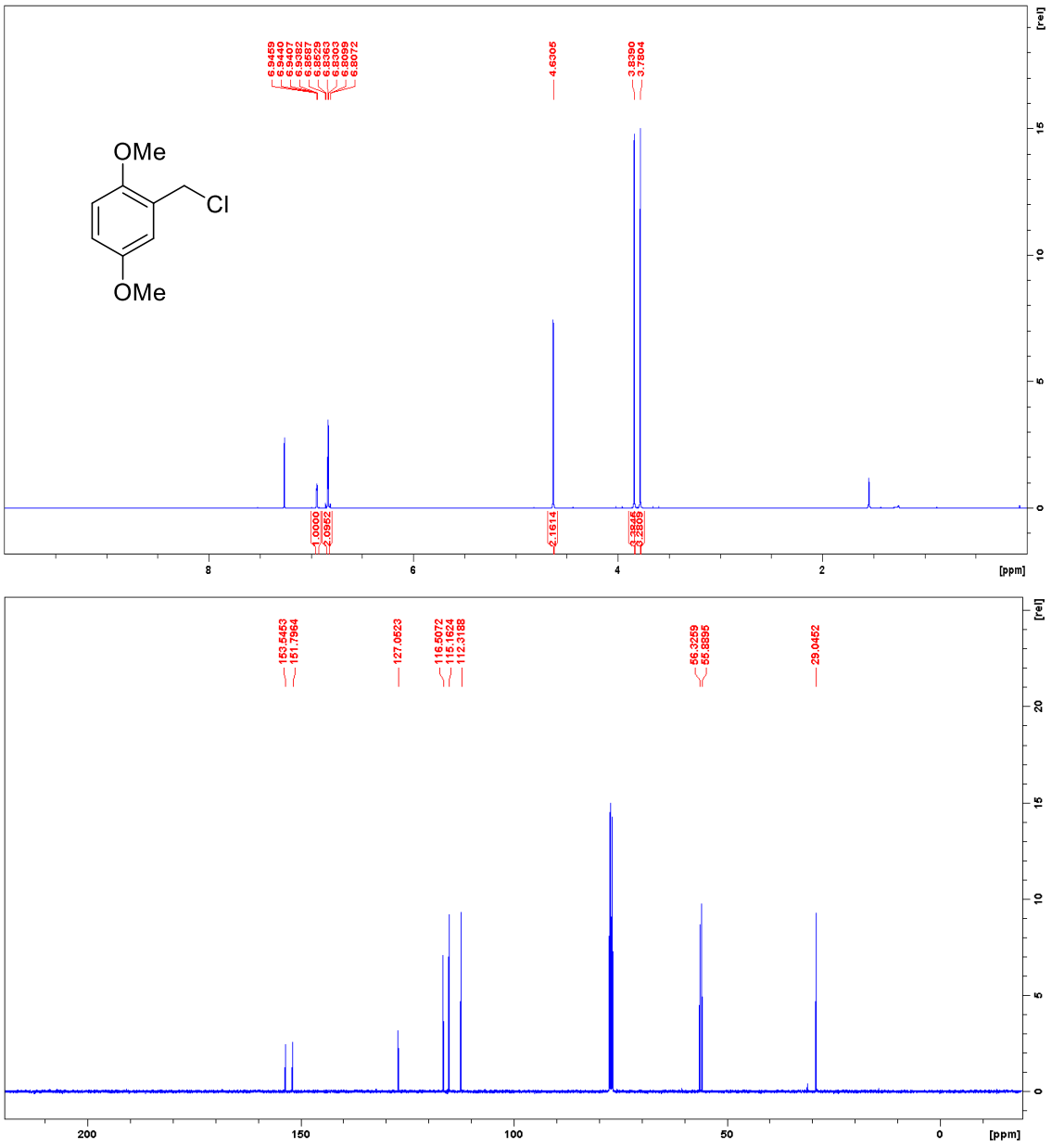
NMR Spectra

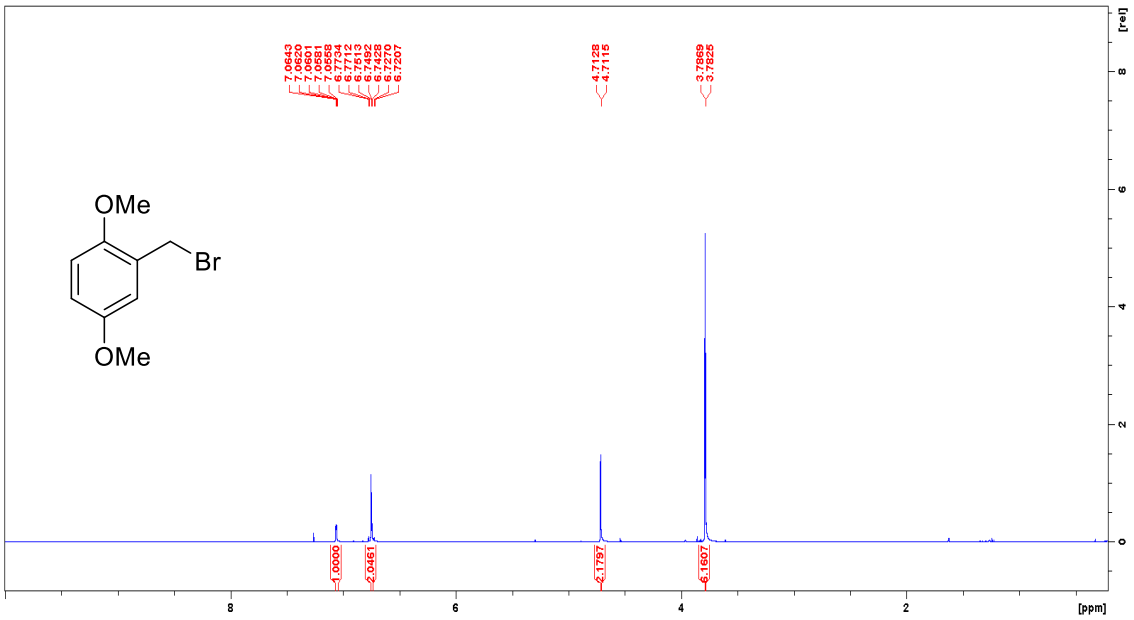
1,3,4-Triphenyl-1H-1,2,4-triazol-5(4*H*)-one (**5a**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, CD_2Cl_2).**

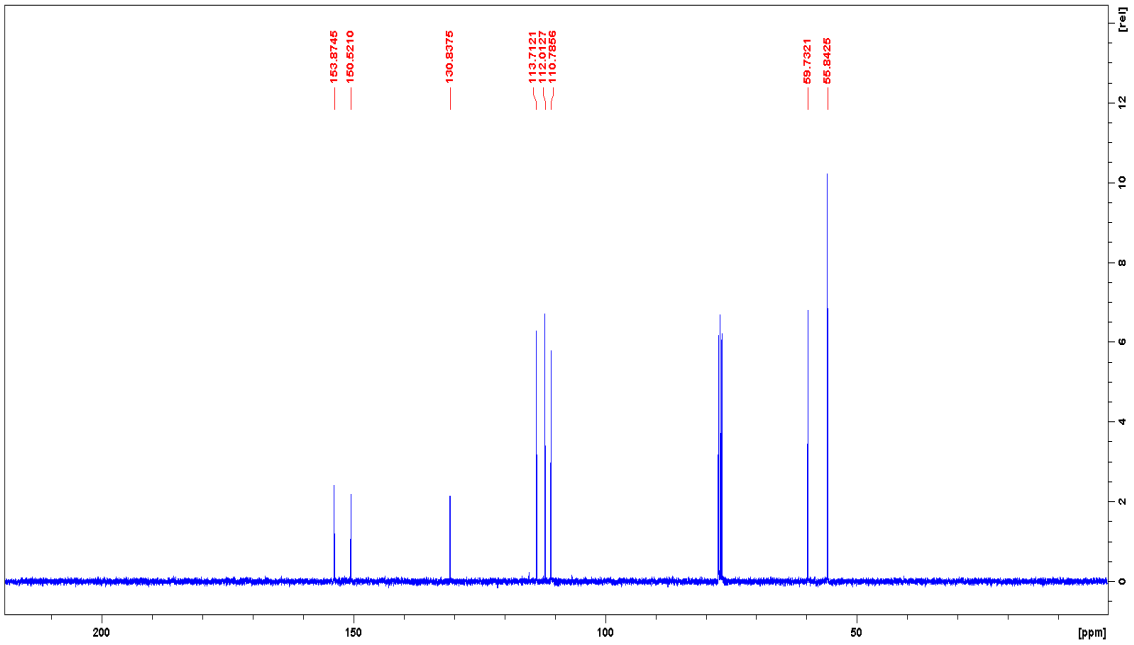


2,5-Dimethoxybenzyl chloride (**4a**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

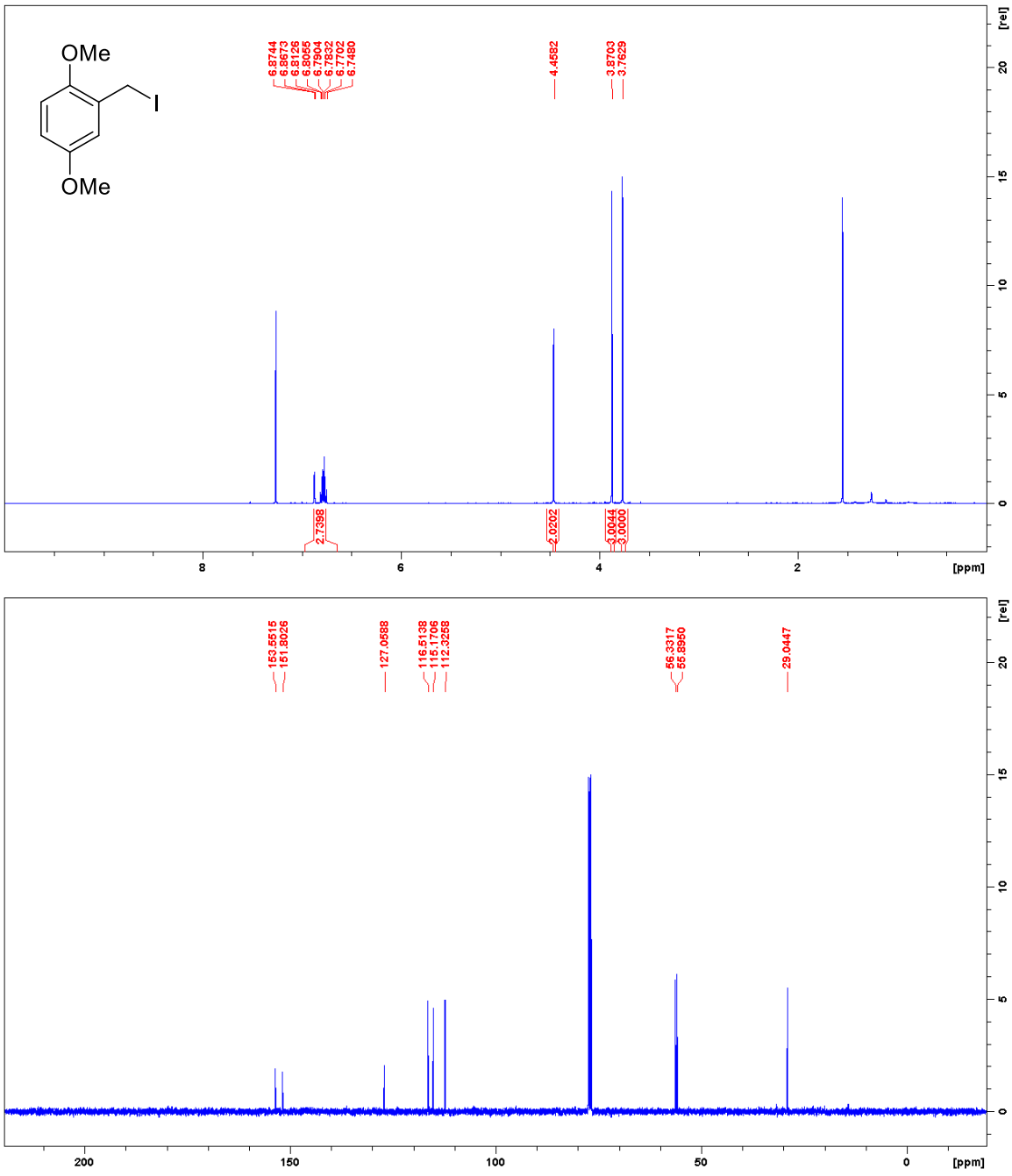


2,5-Dimethoxybenzyl bromide (**4b**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

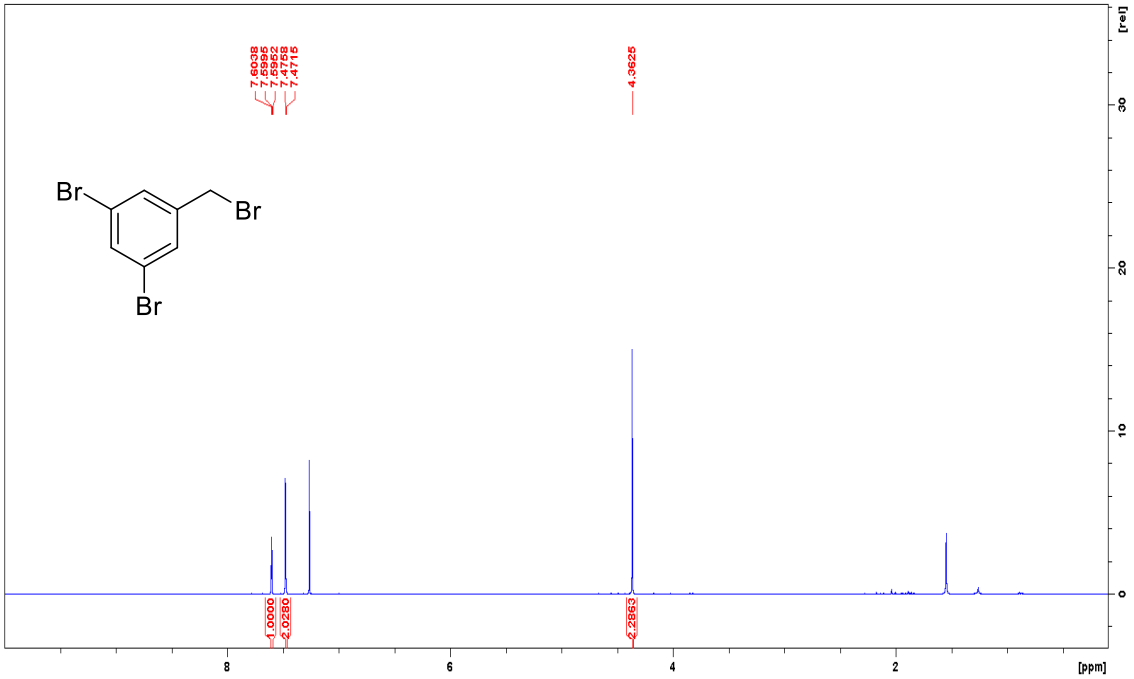


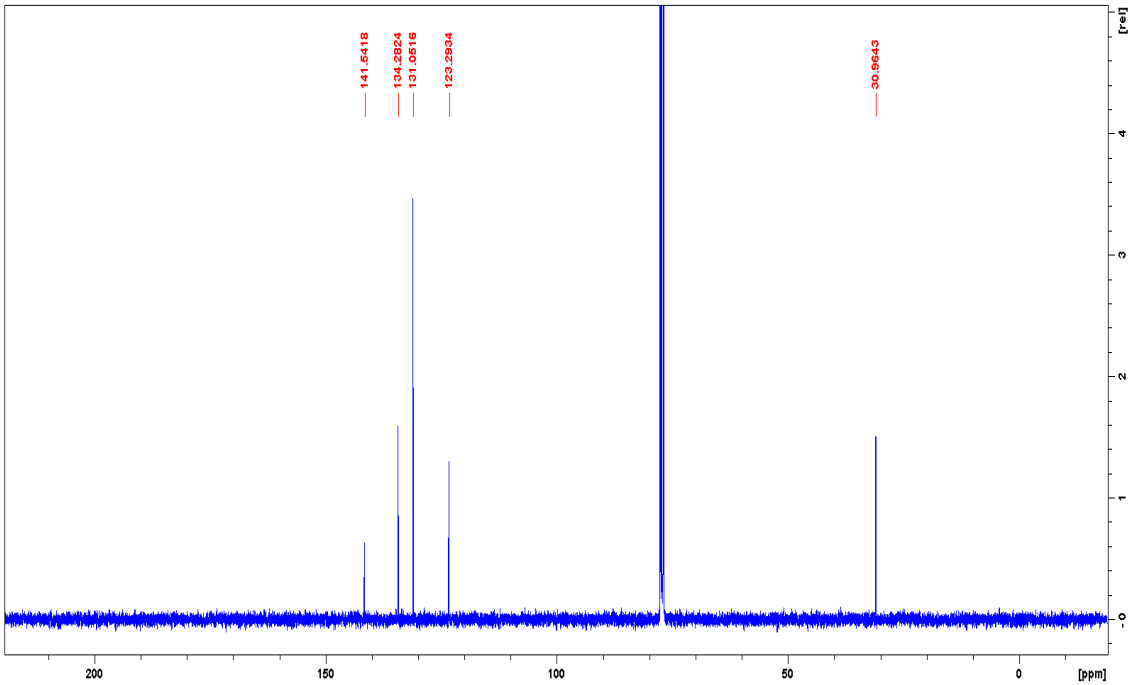


2,5-Dimethoxybenzyl iodide (**4c**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

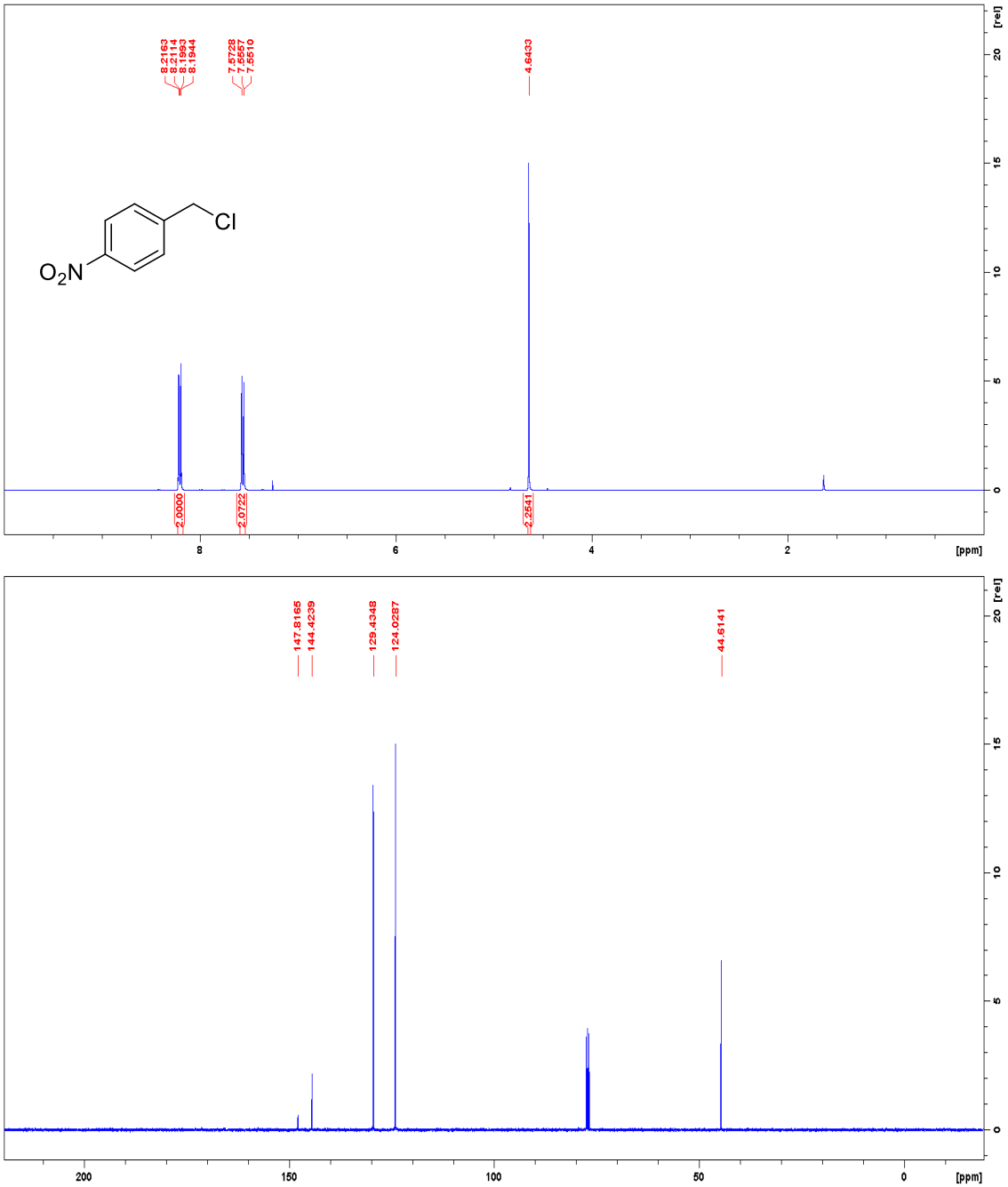


3,5-Dibromobenzyl bromide (**4d**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

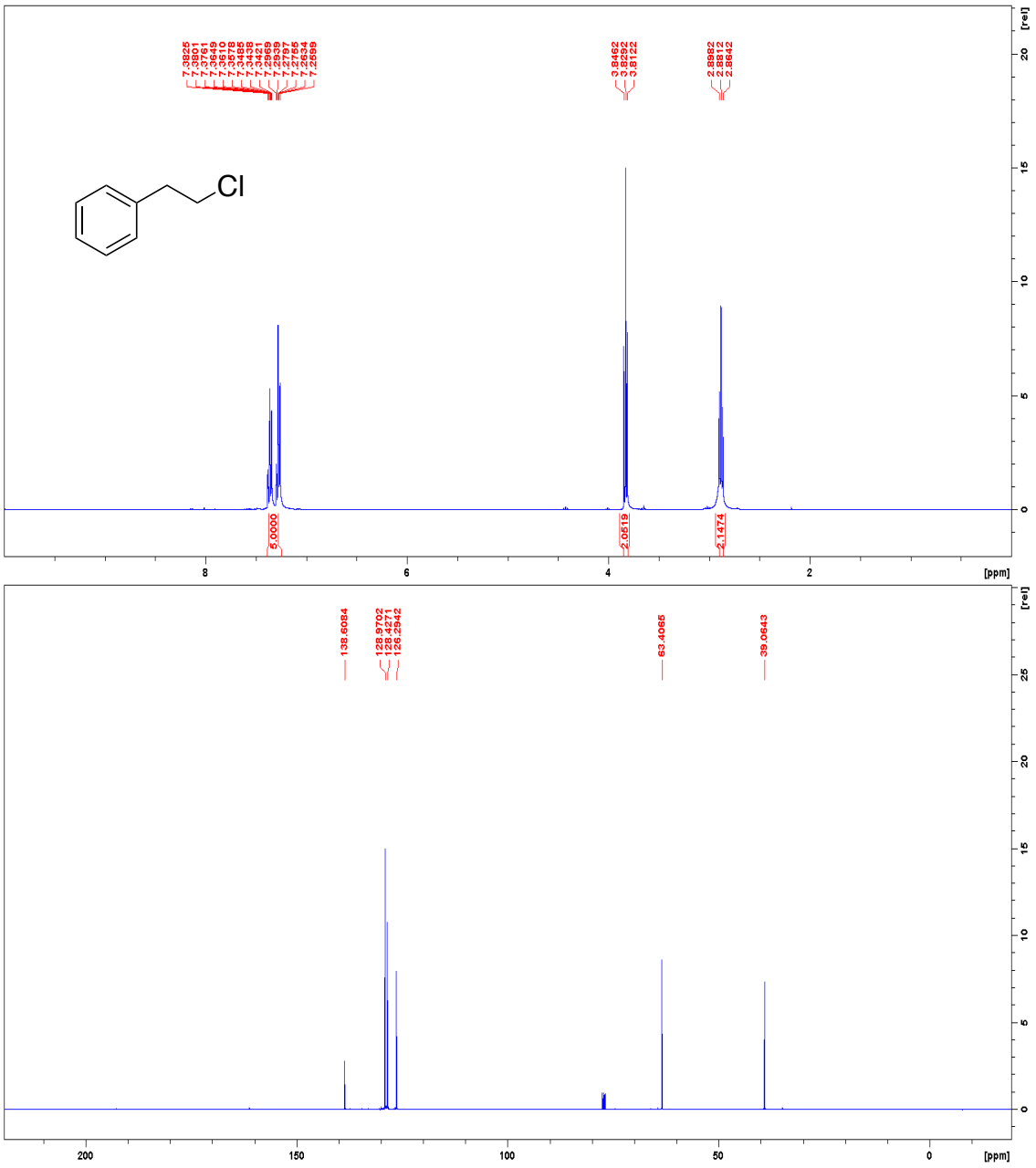




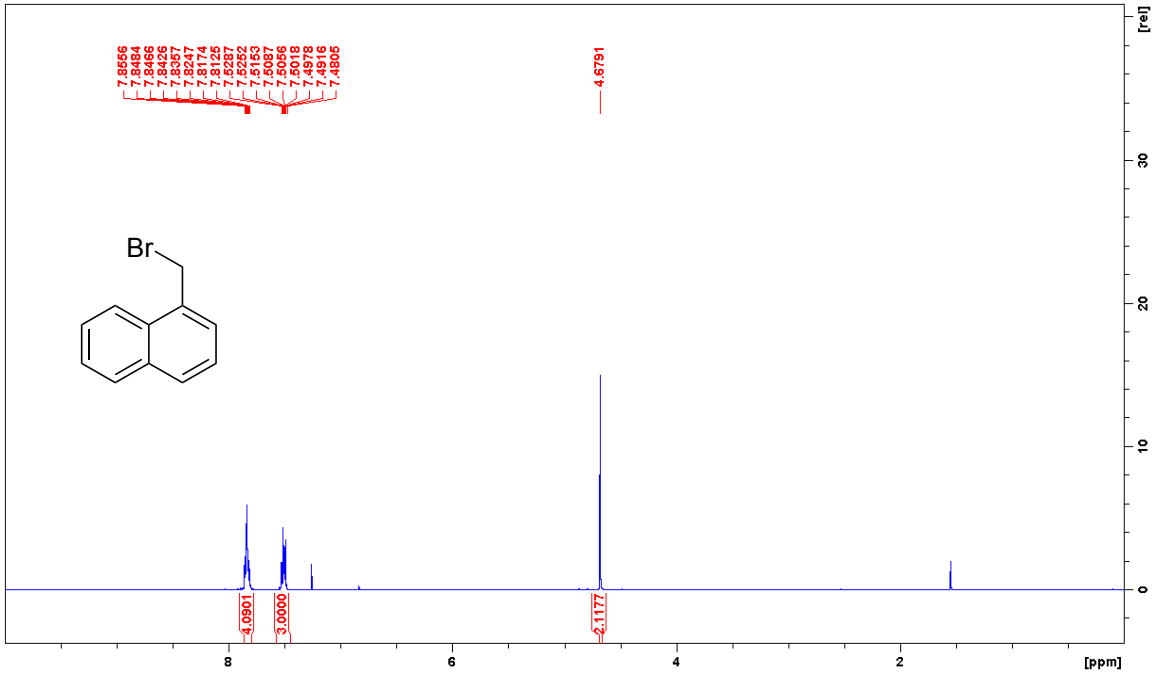
4-Nitrobenzyl chloride (**4e**);^{1}H NMR **(400 MHz, $CDCl_3$),**^{13}C NMR **(100 MHz, $CDCl_3$).**

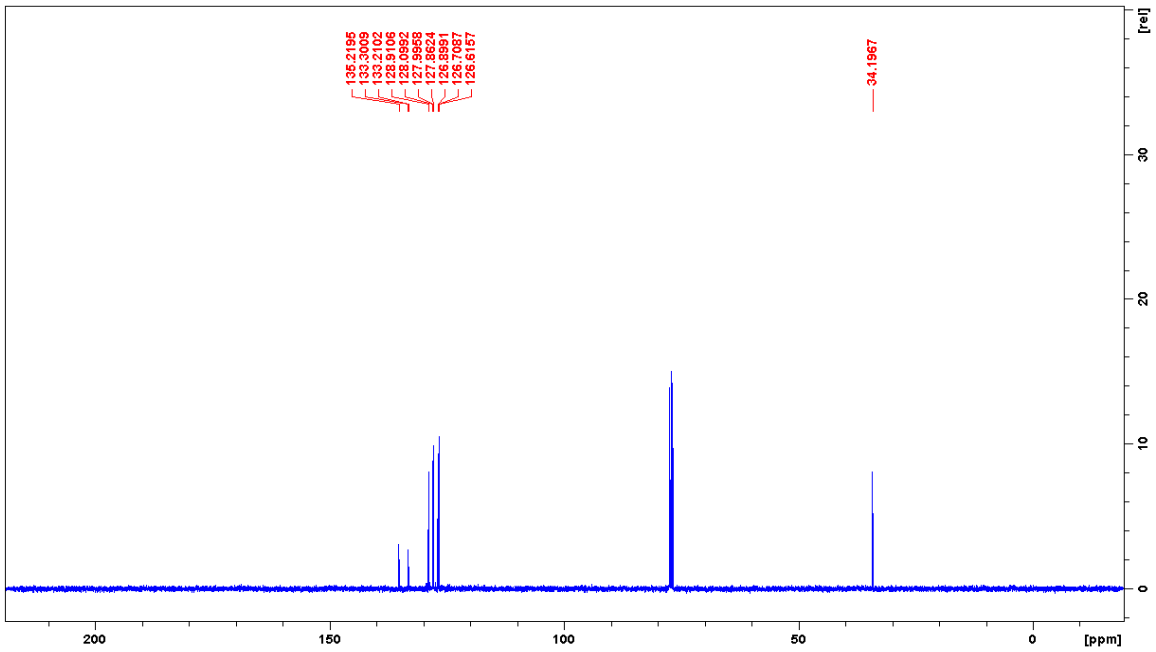


2-Phenylethylchloride (**4f**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

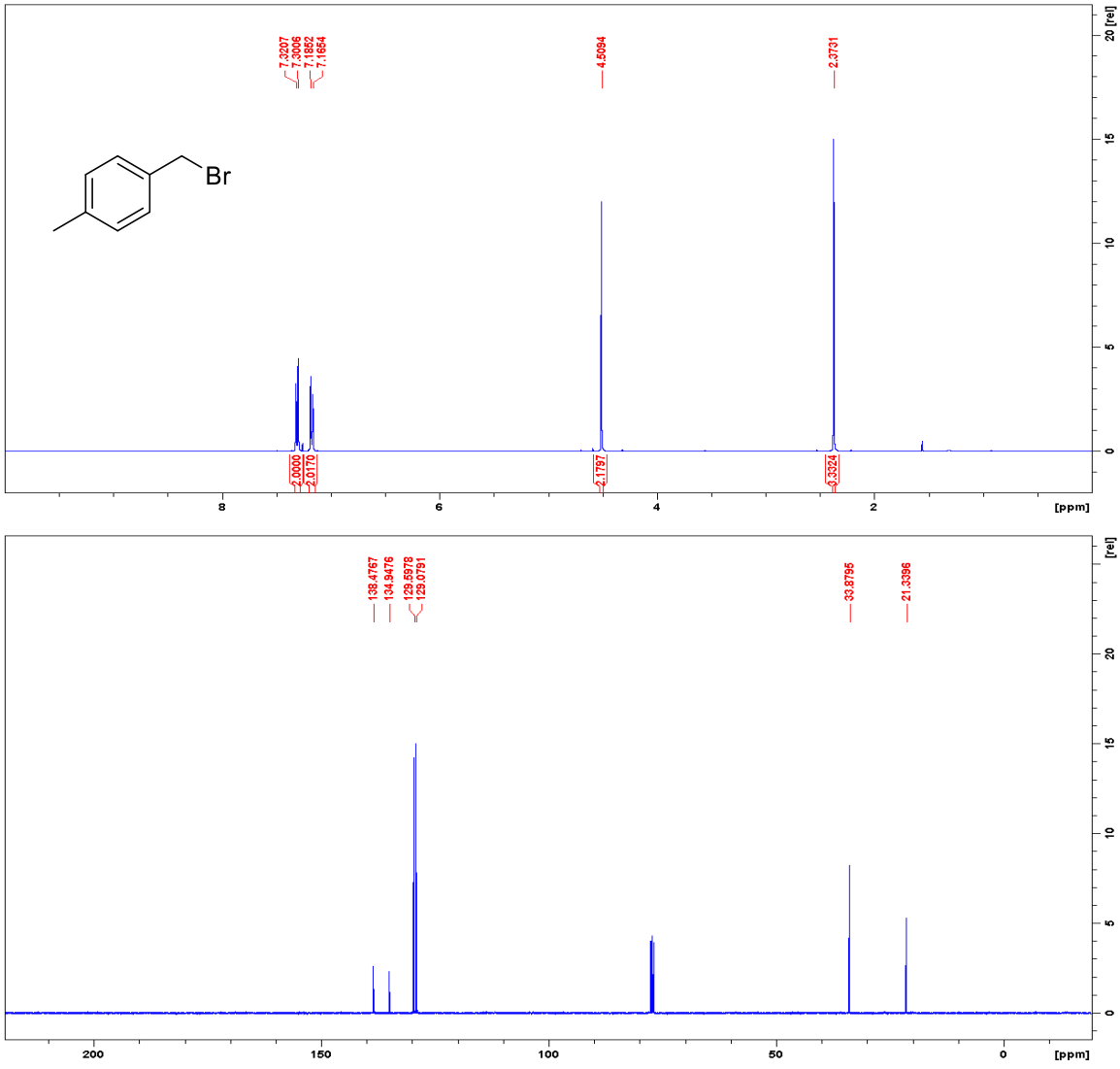


1-(Bromomethyl)naphthalene (**4g**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

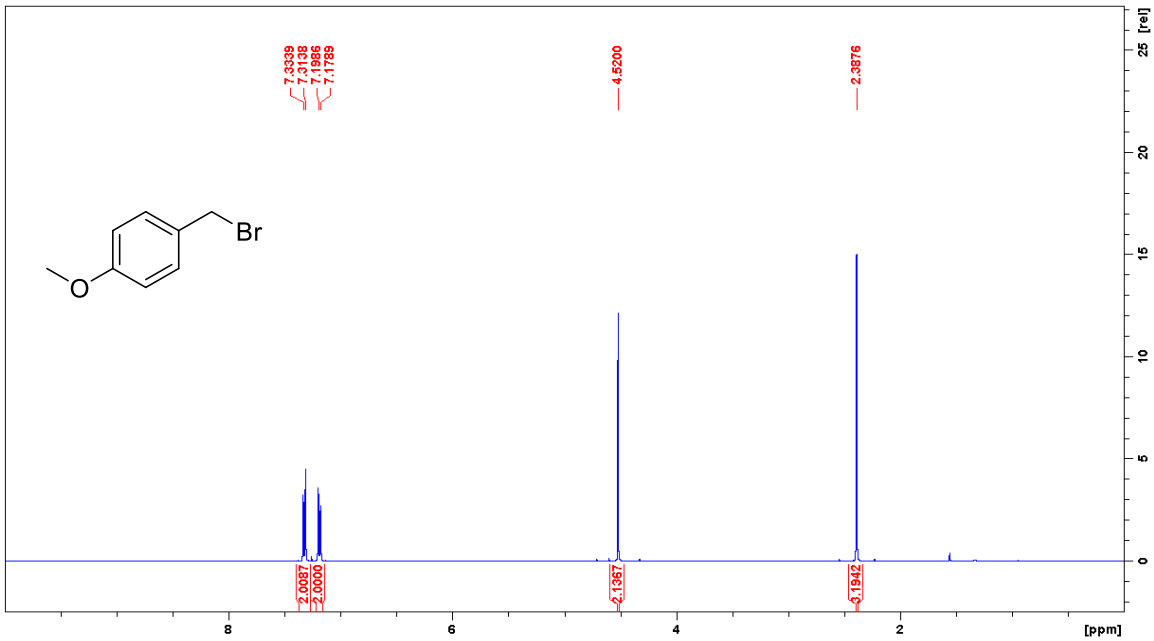


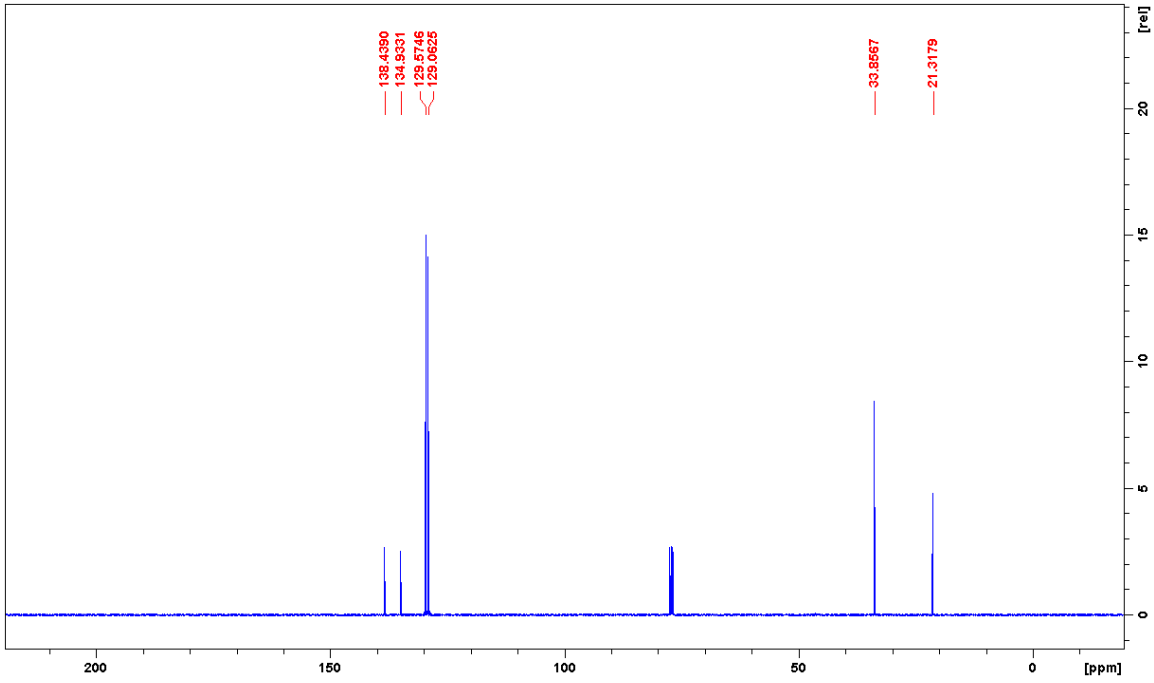


4-Methylbenzylbromide (**4h**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

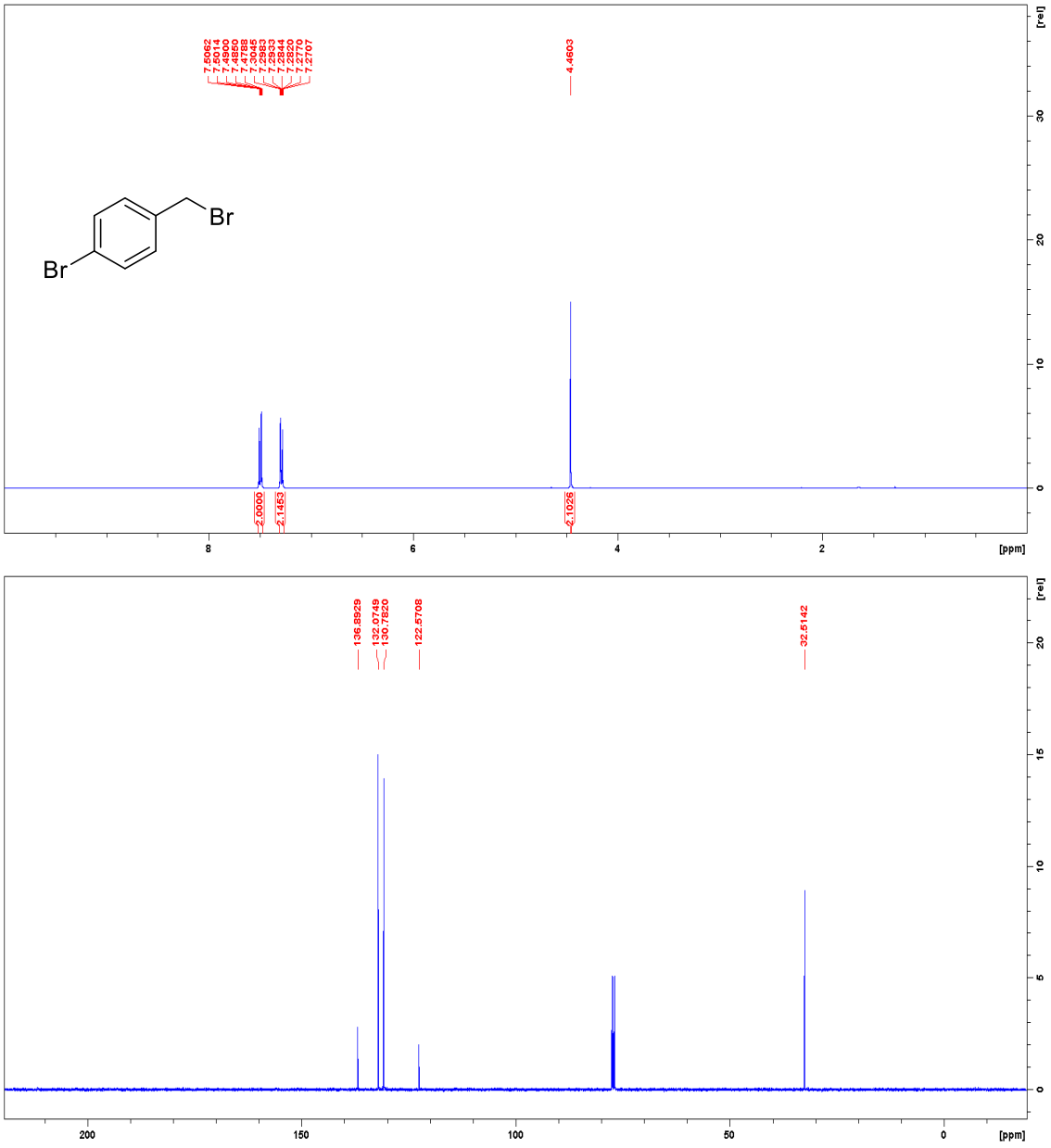


4-Methoxybenzyl bromide (**4i**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

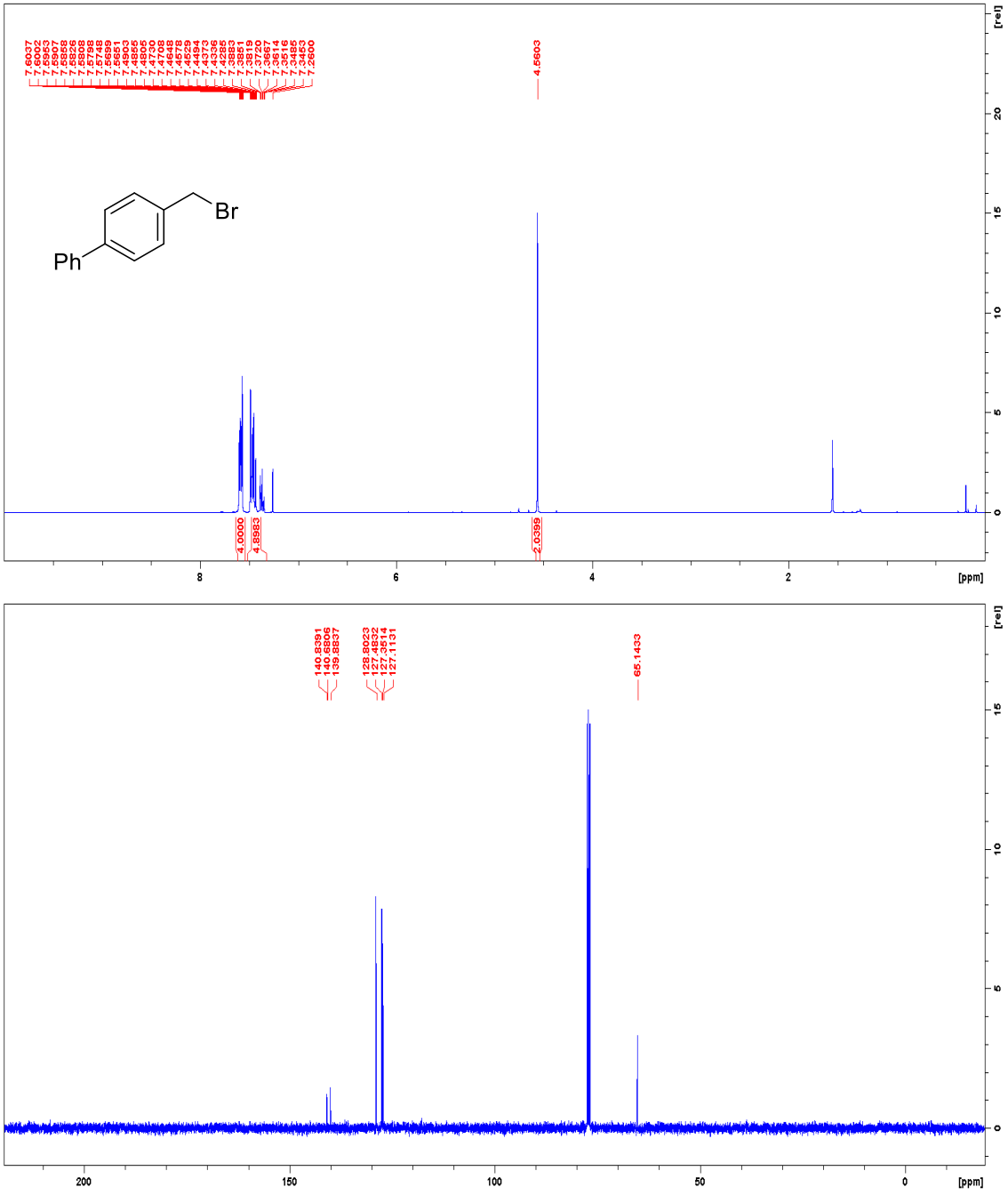




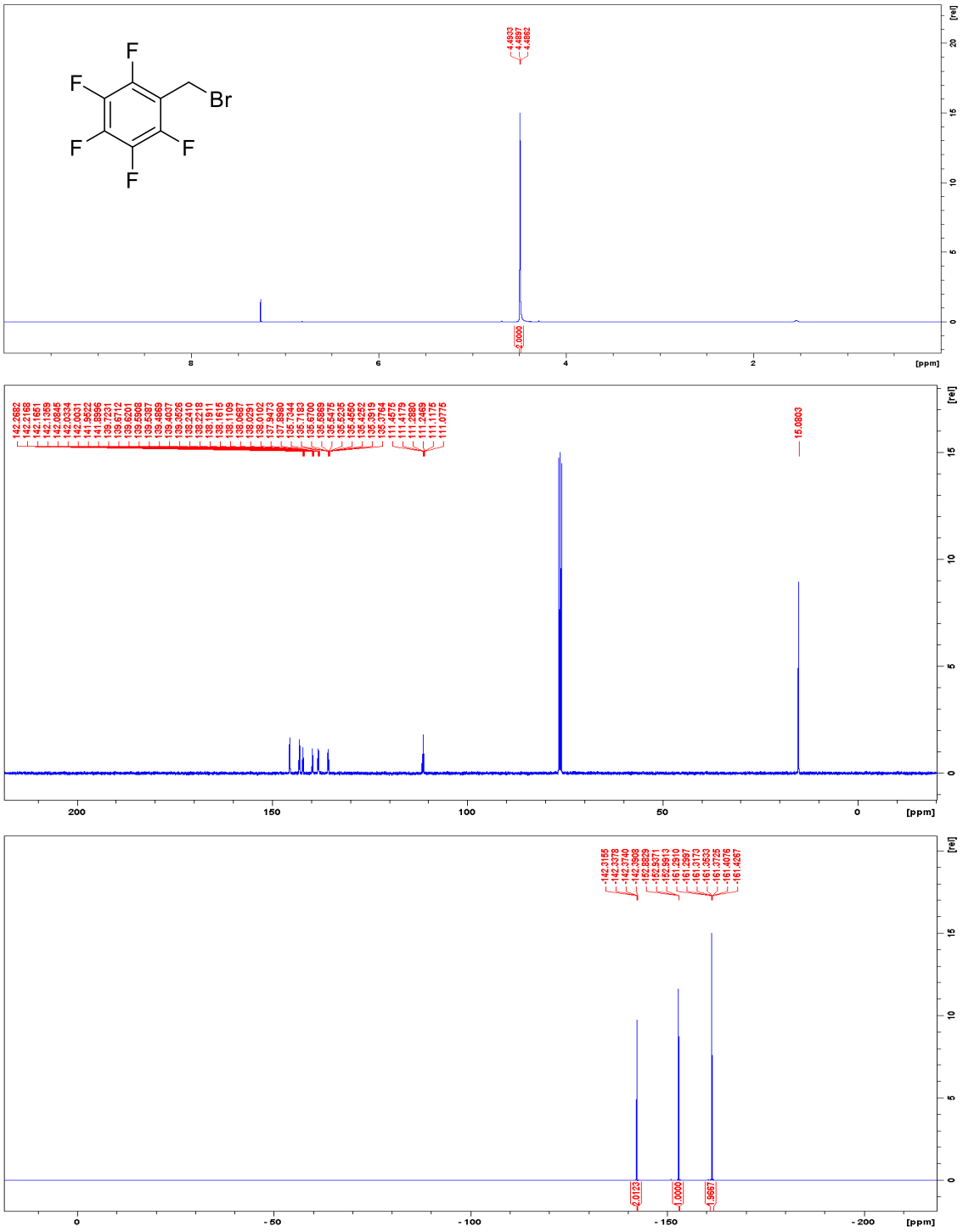
4-Bromobenzyl bromide (**4j**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



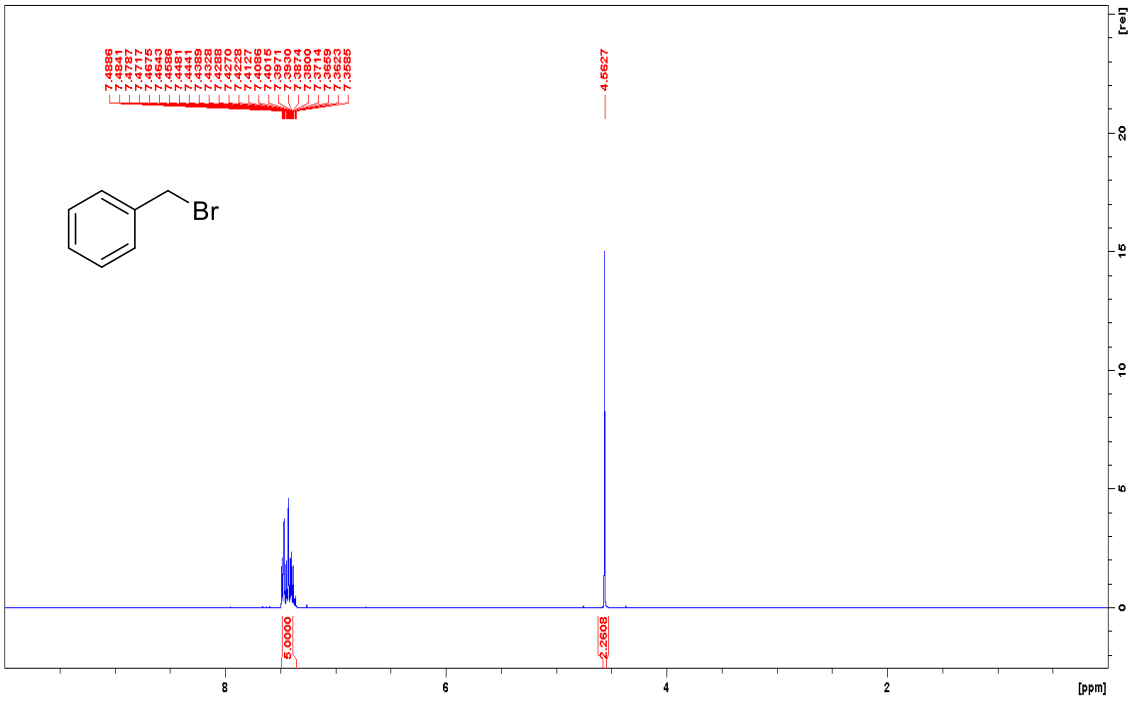
4-Bromomethyl biphenyl (**4k**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

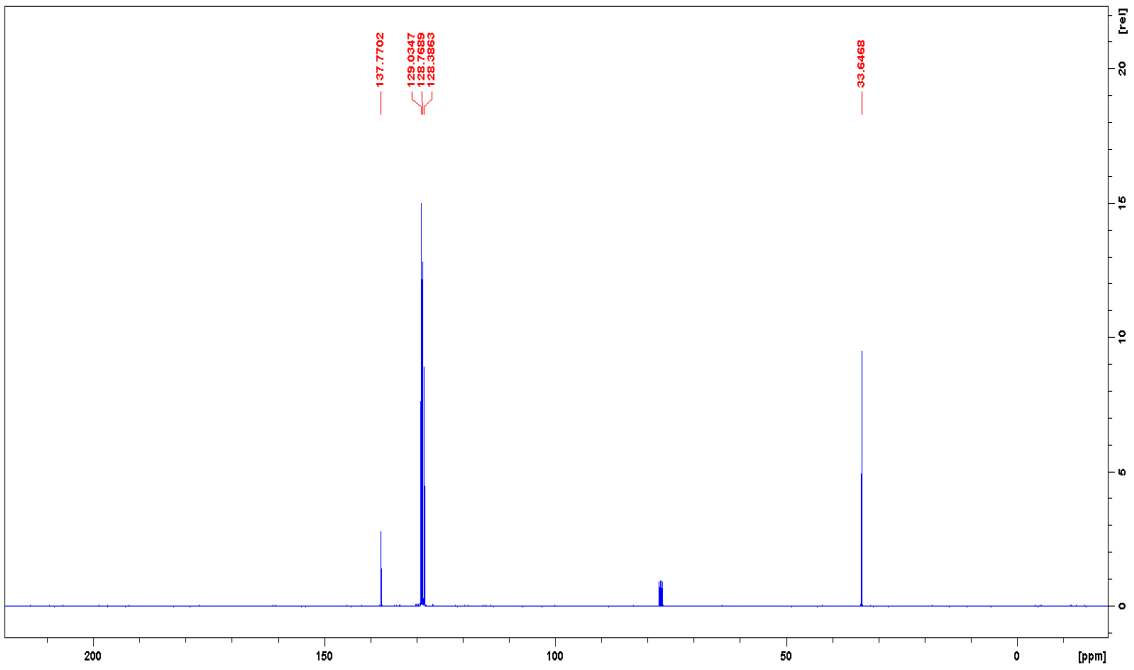


2,3,4,5,6-Pentafluorobenzyl bromide (**4l**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$),** ^{19}F NMR **(400 MHz, $CDCl_3$).**

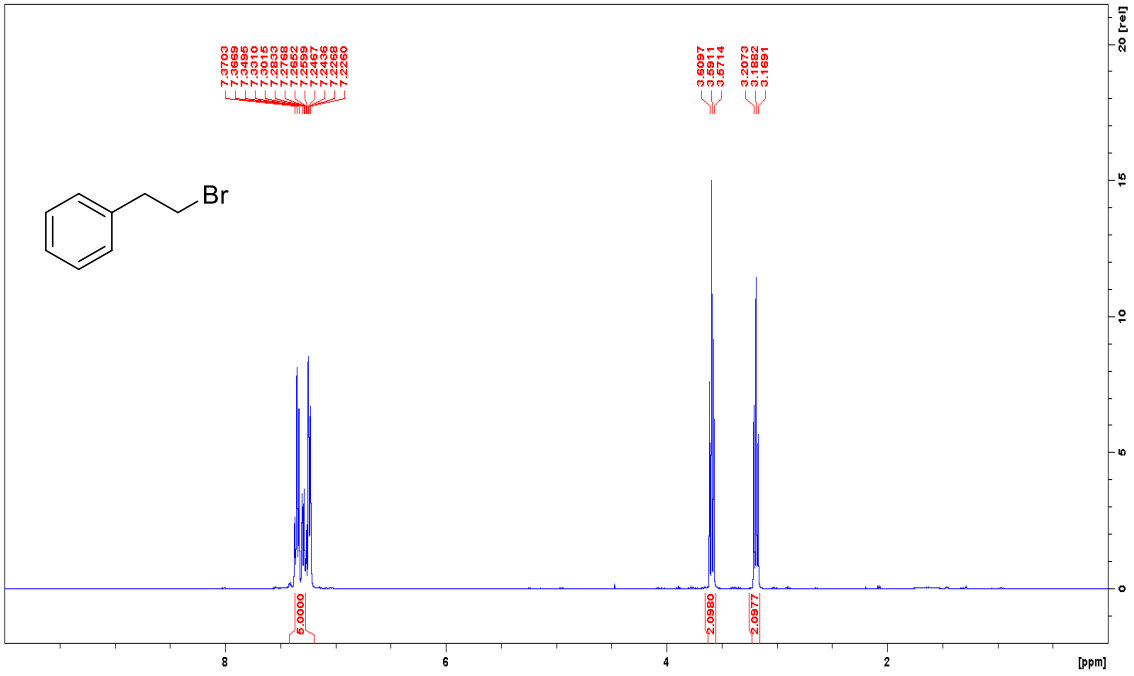


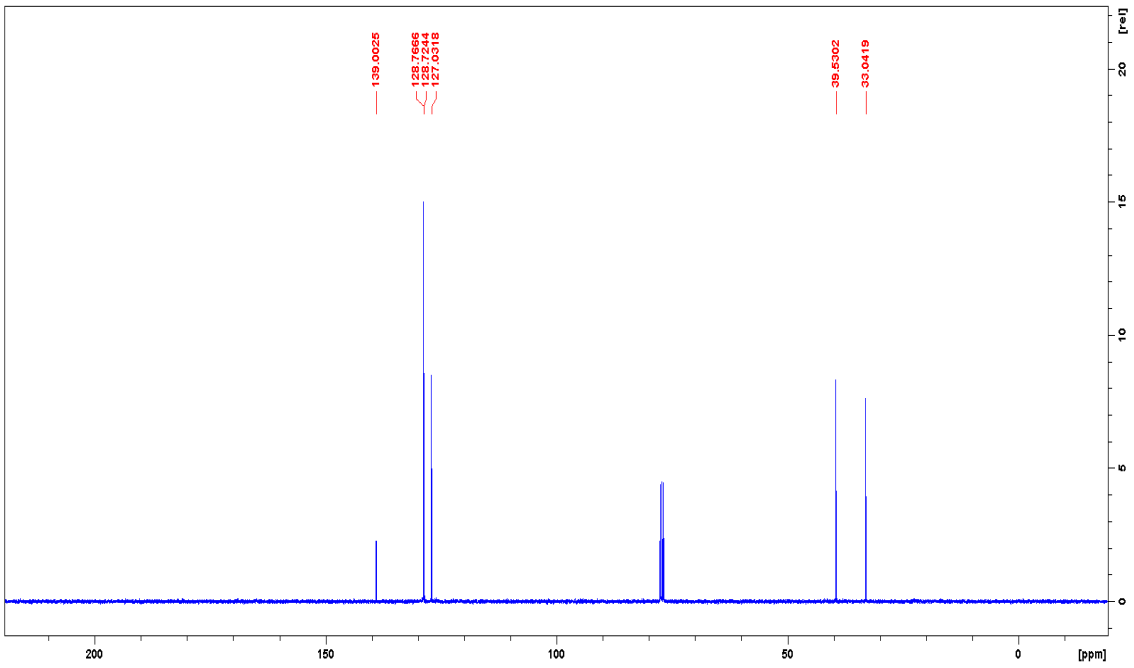
Benzyl bromide (**4m**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



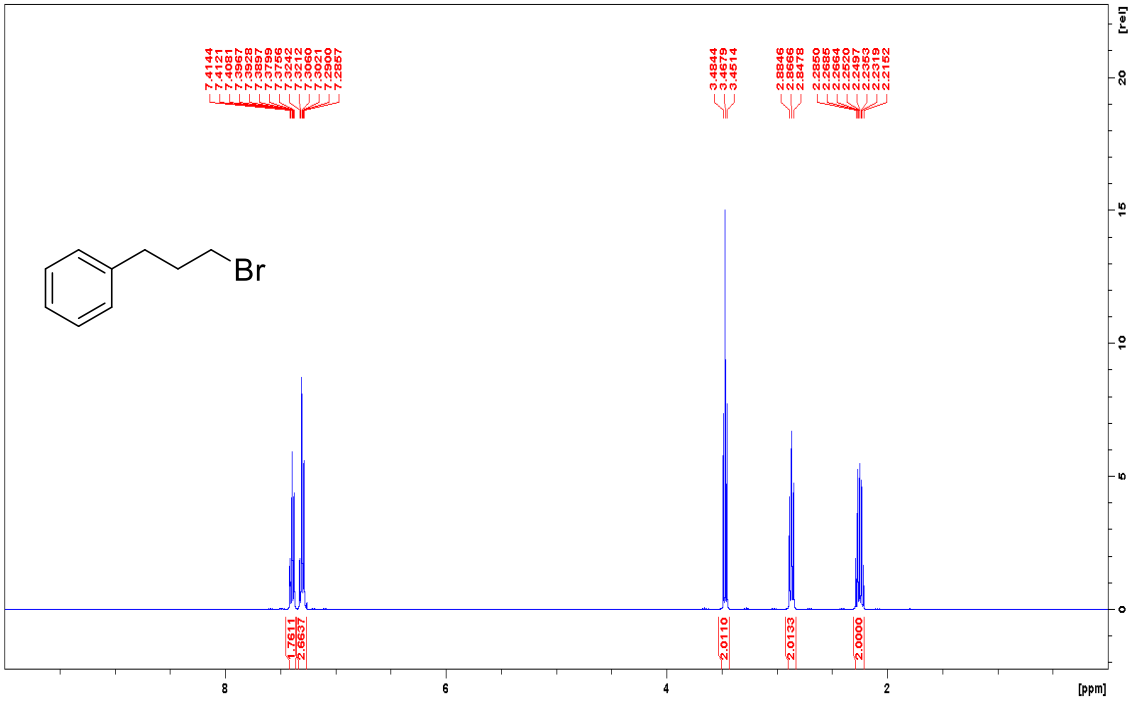


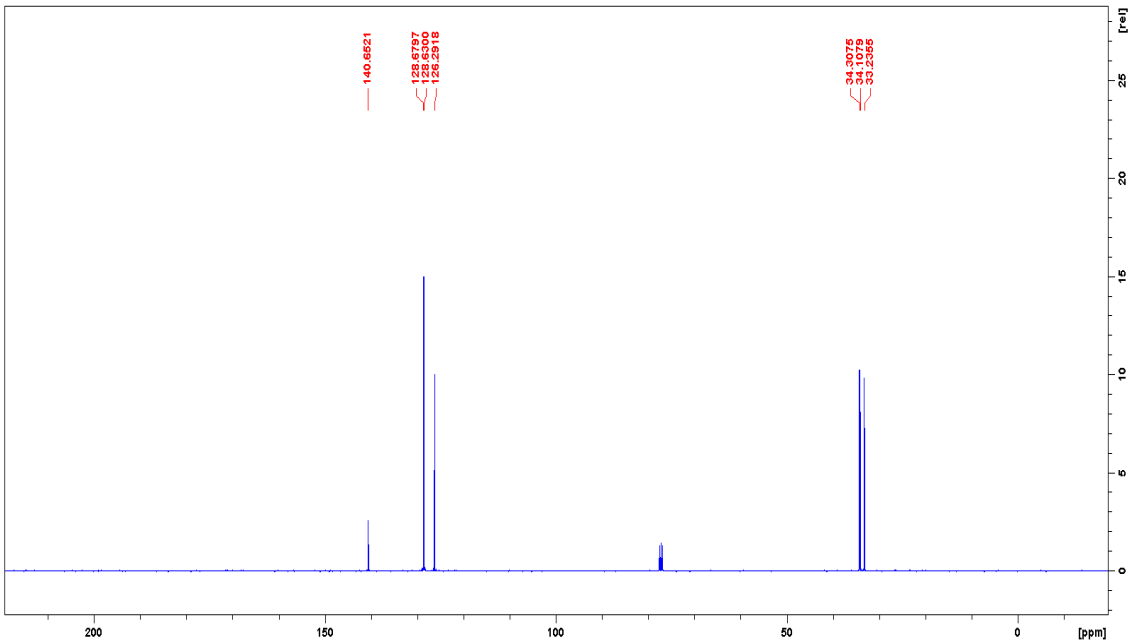
2-Phenylethylbromide (**4n**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



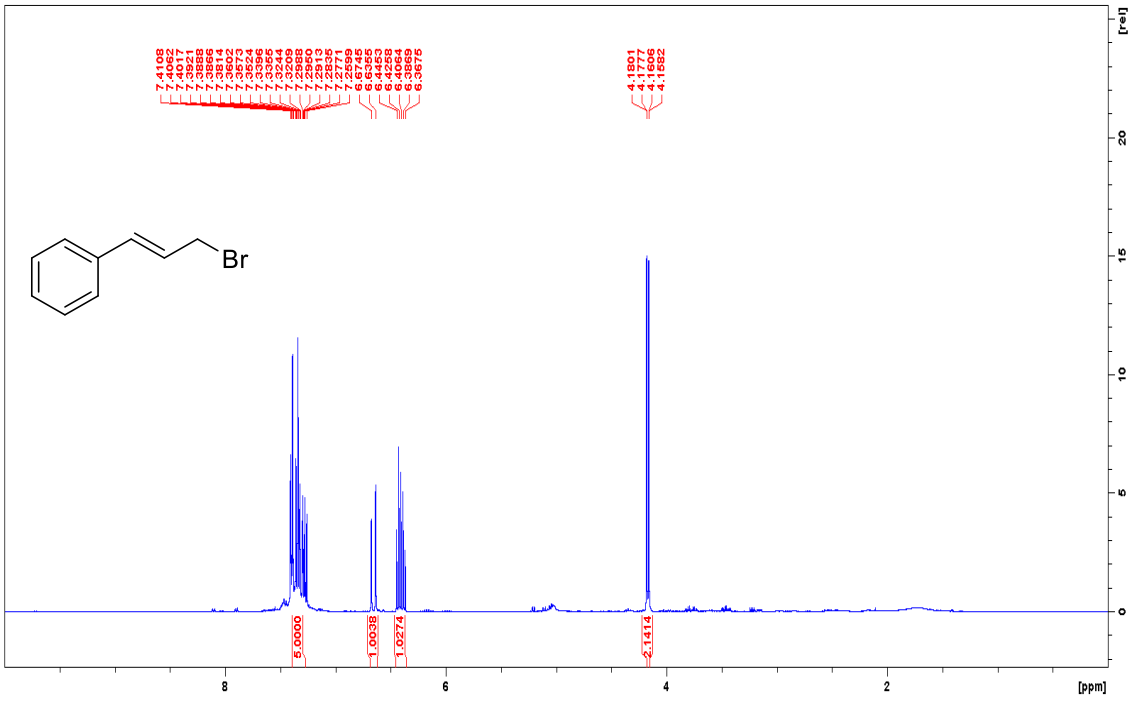


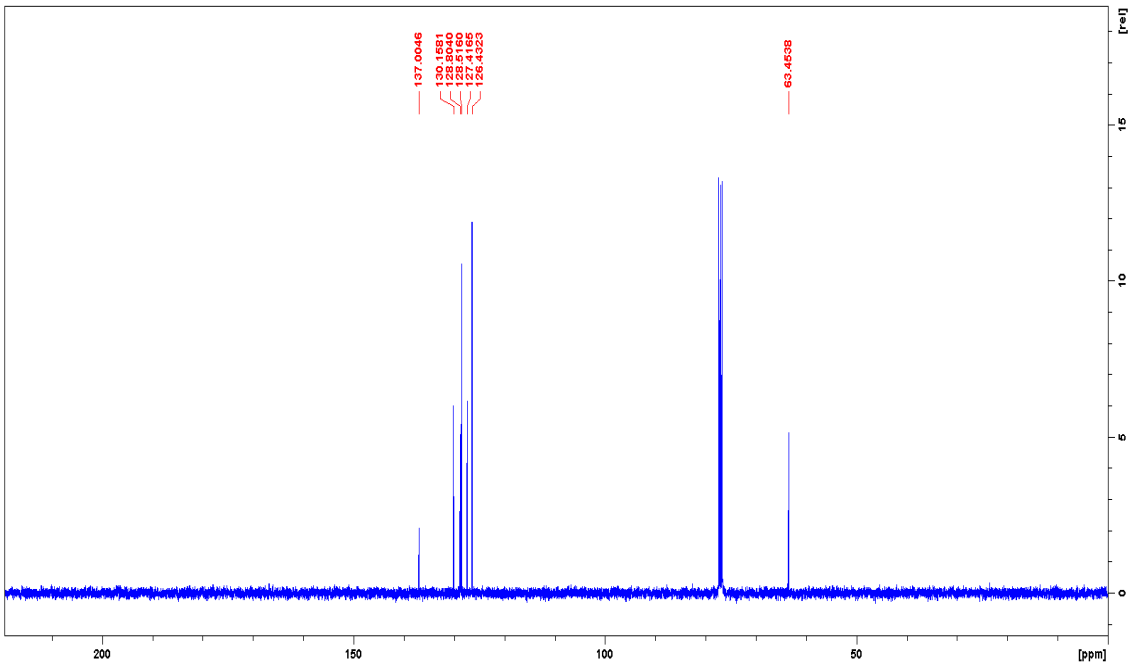
(3-Bromopropyl)benzene (**4o**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



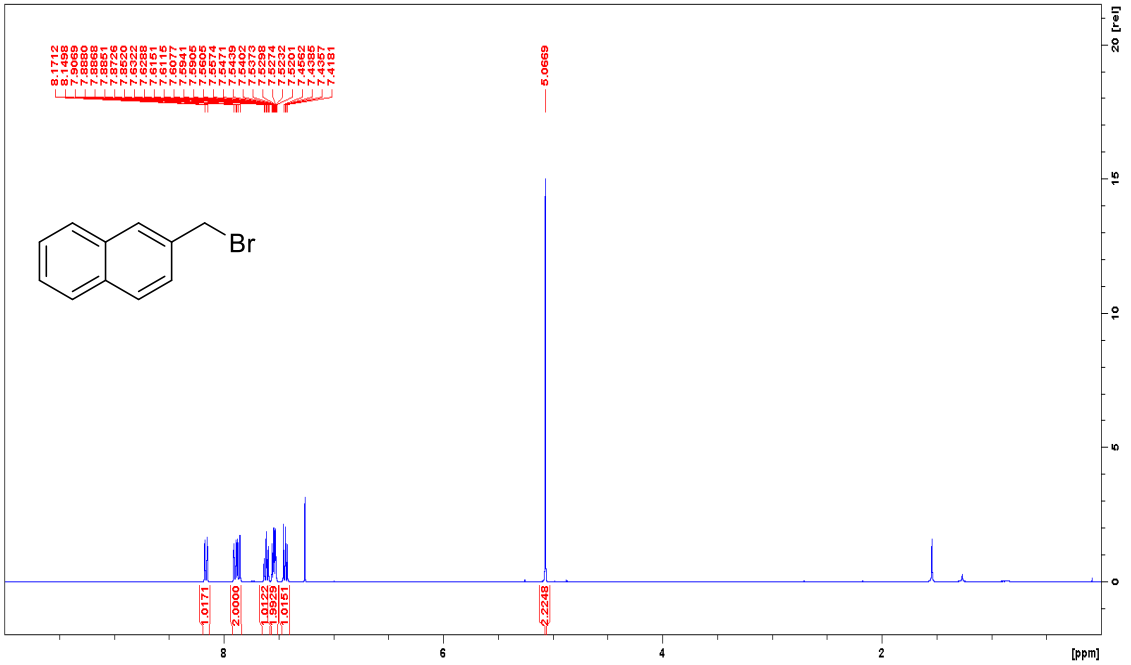


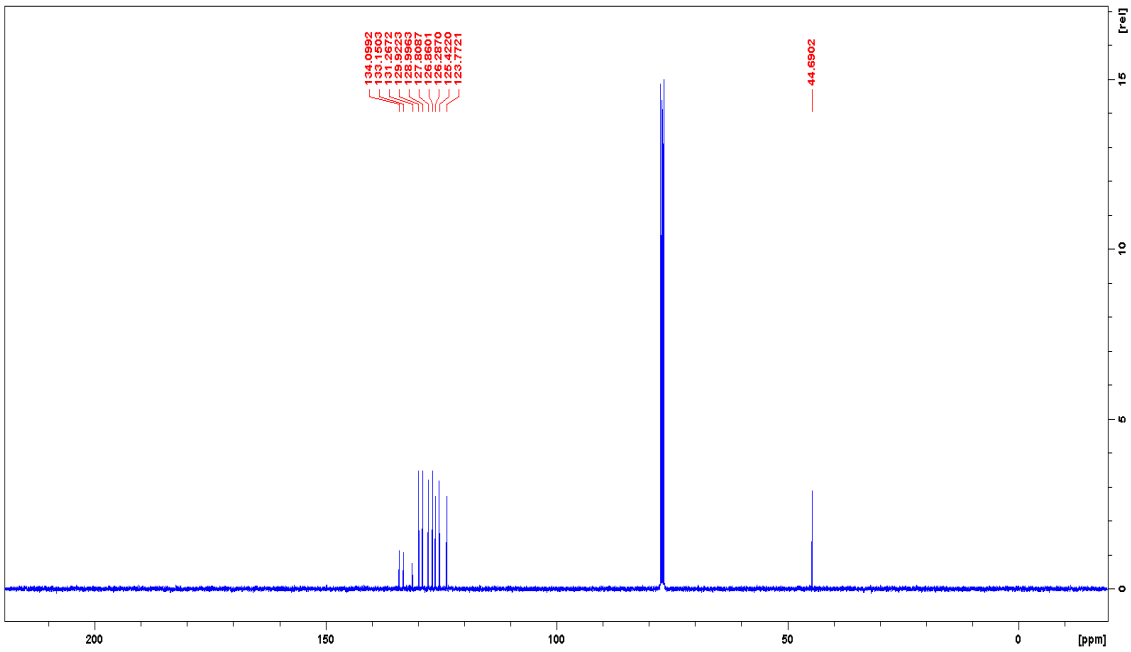
Cinnamyl bromide (**4p**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



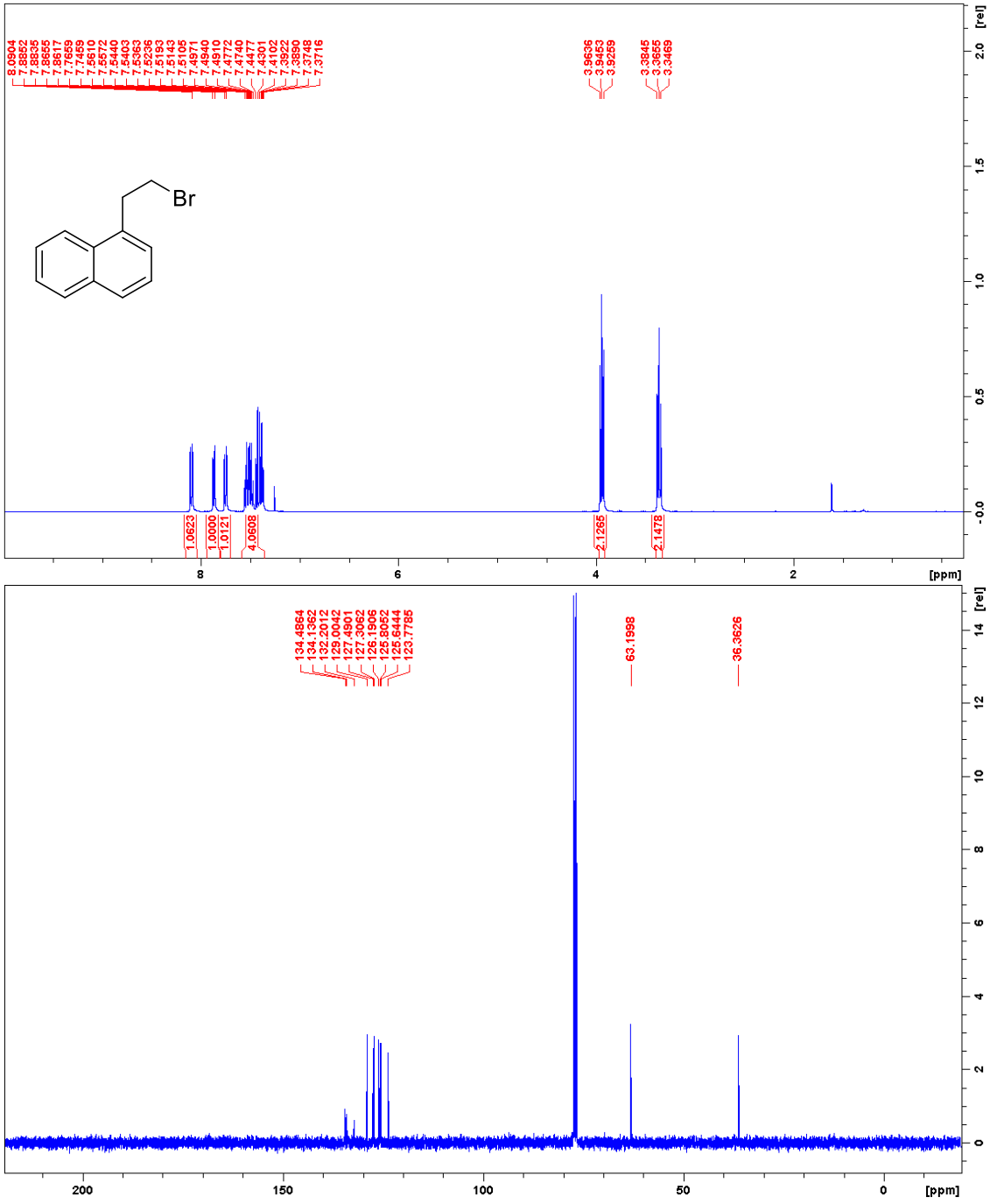


2-(Bromomethyl) naphthalene (**4q**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

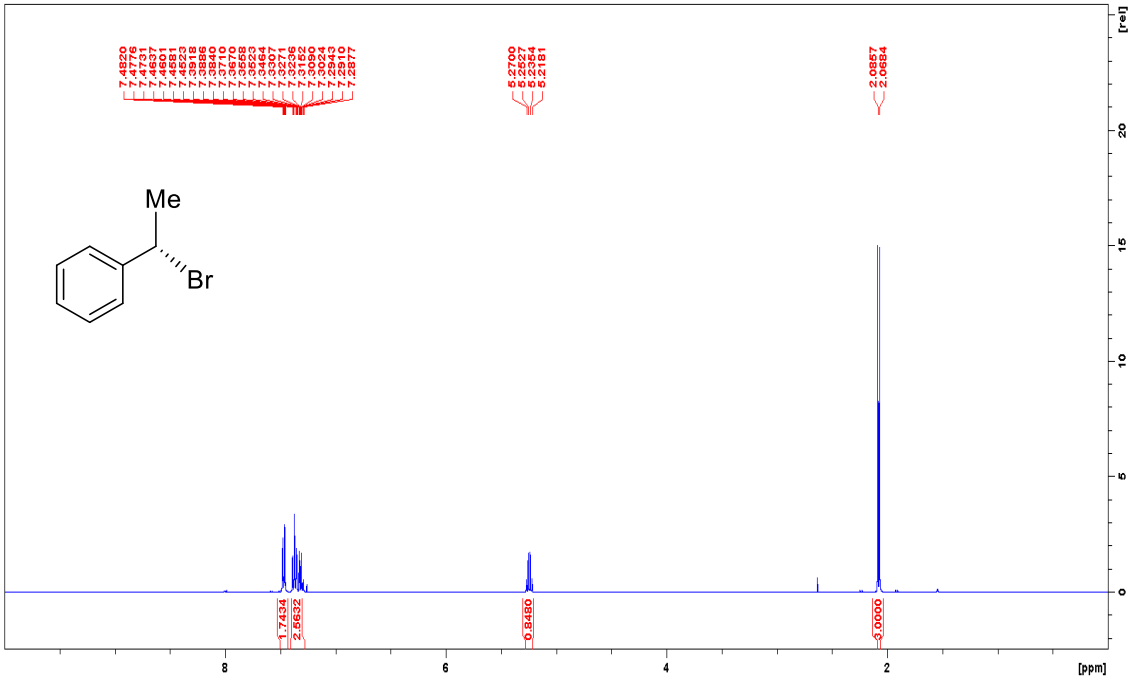


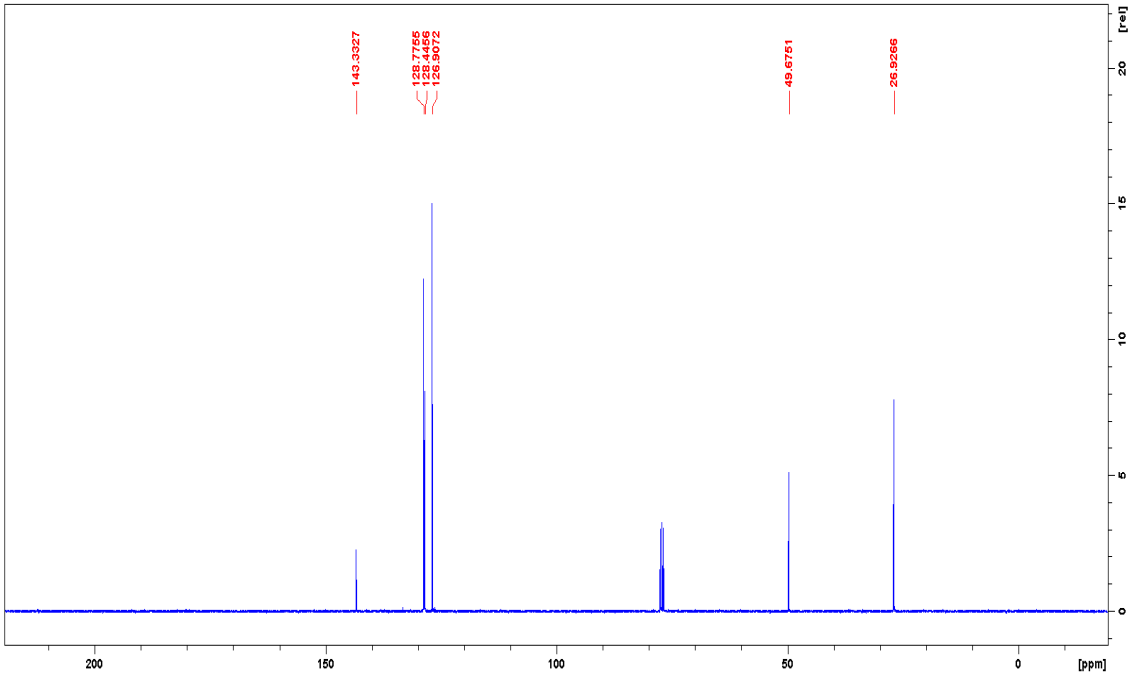


1-(2-Bromoethyl) naphthalene (**4r**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

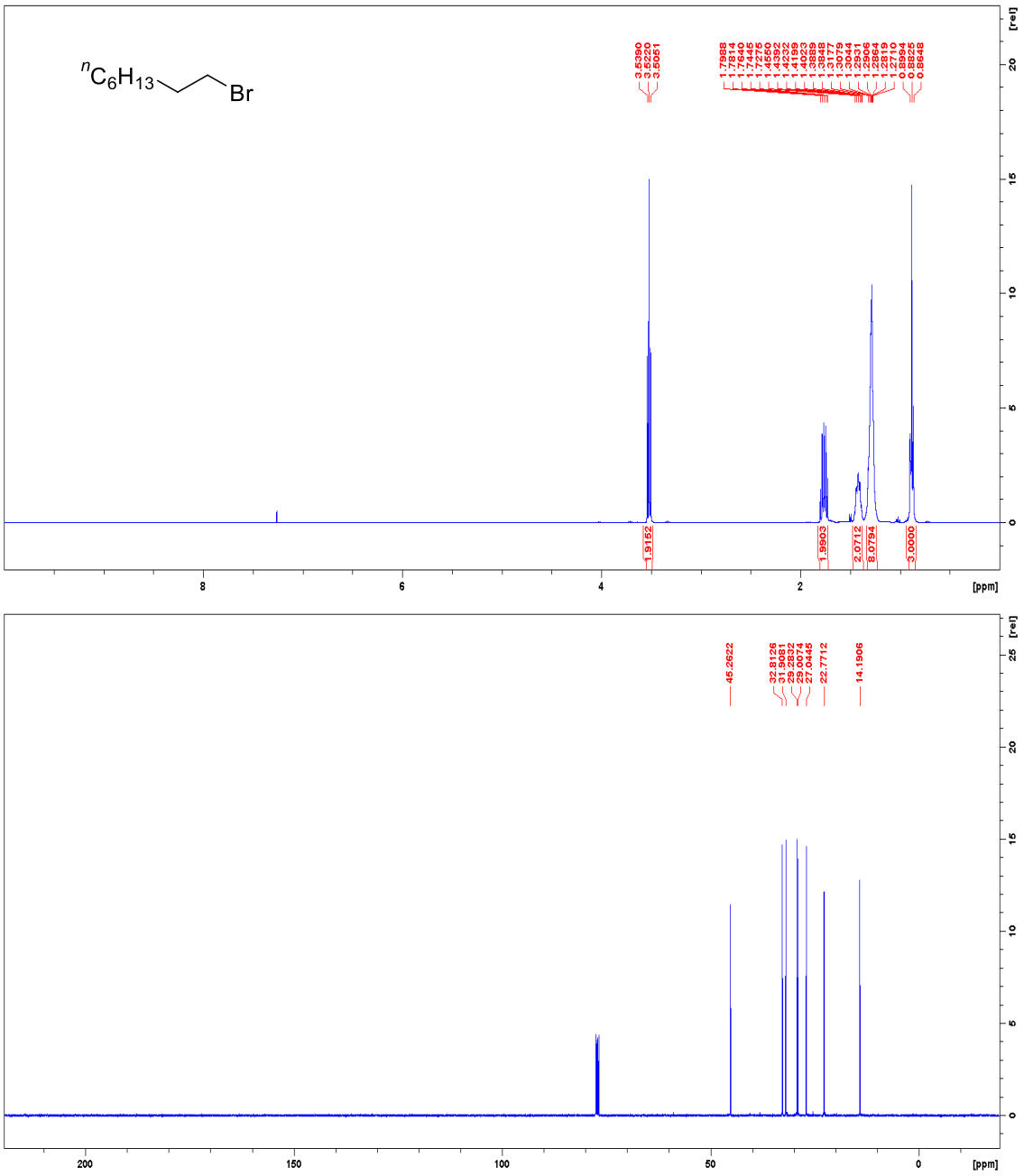


(1-Bromoethyl)benzene (**4s**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**

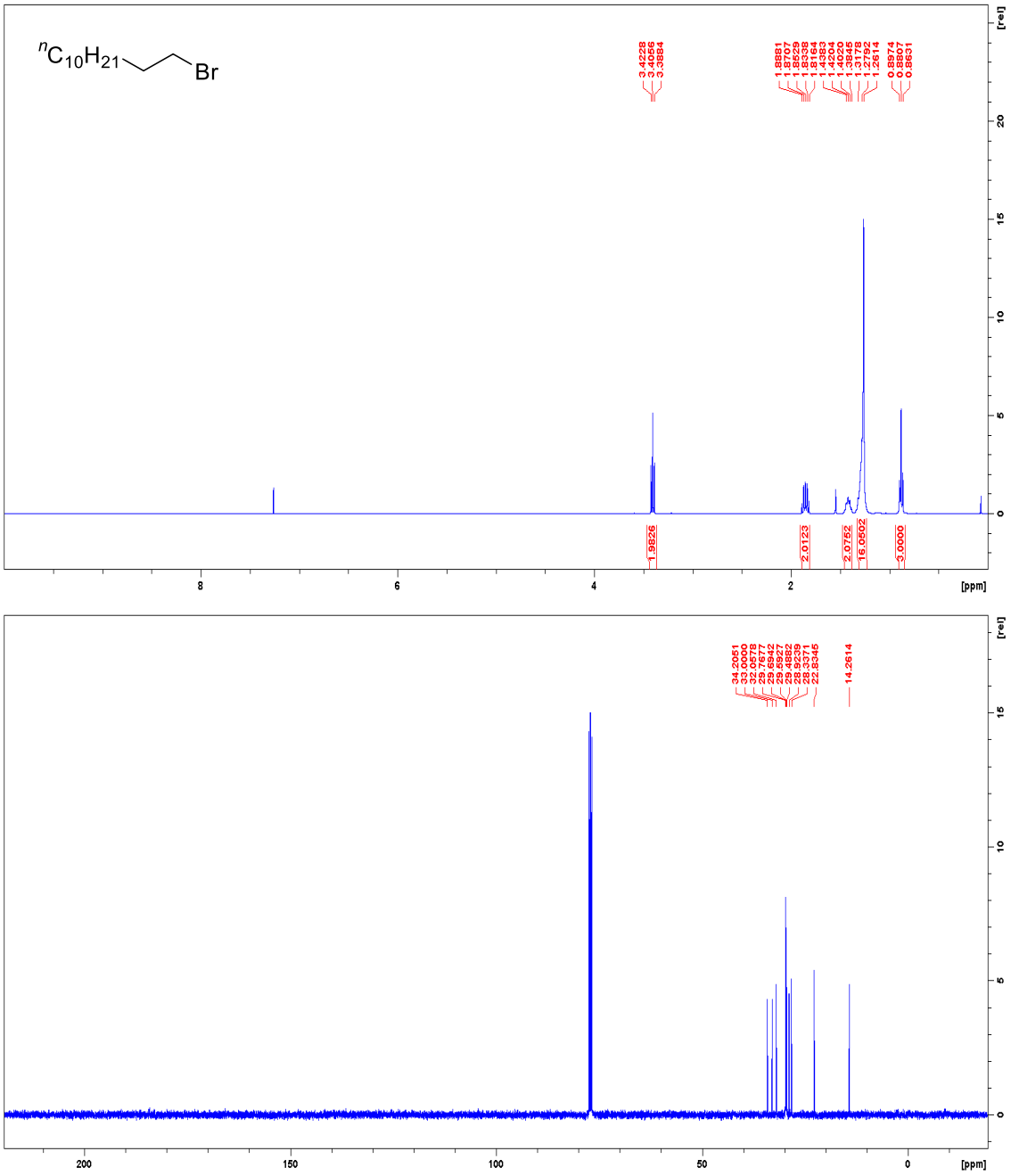




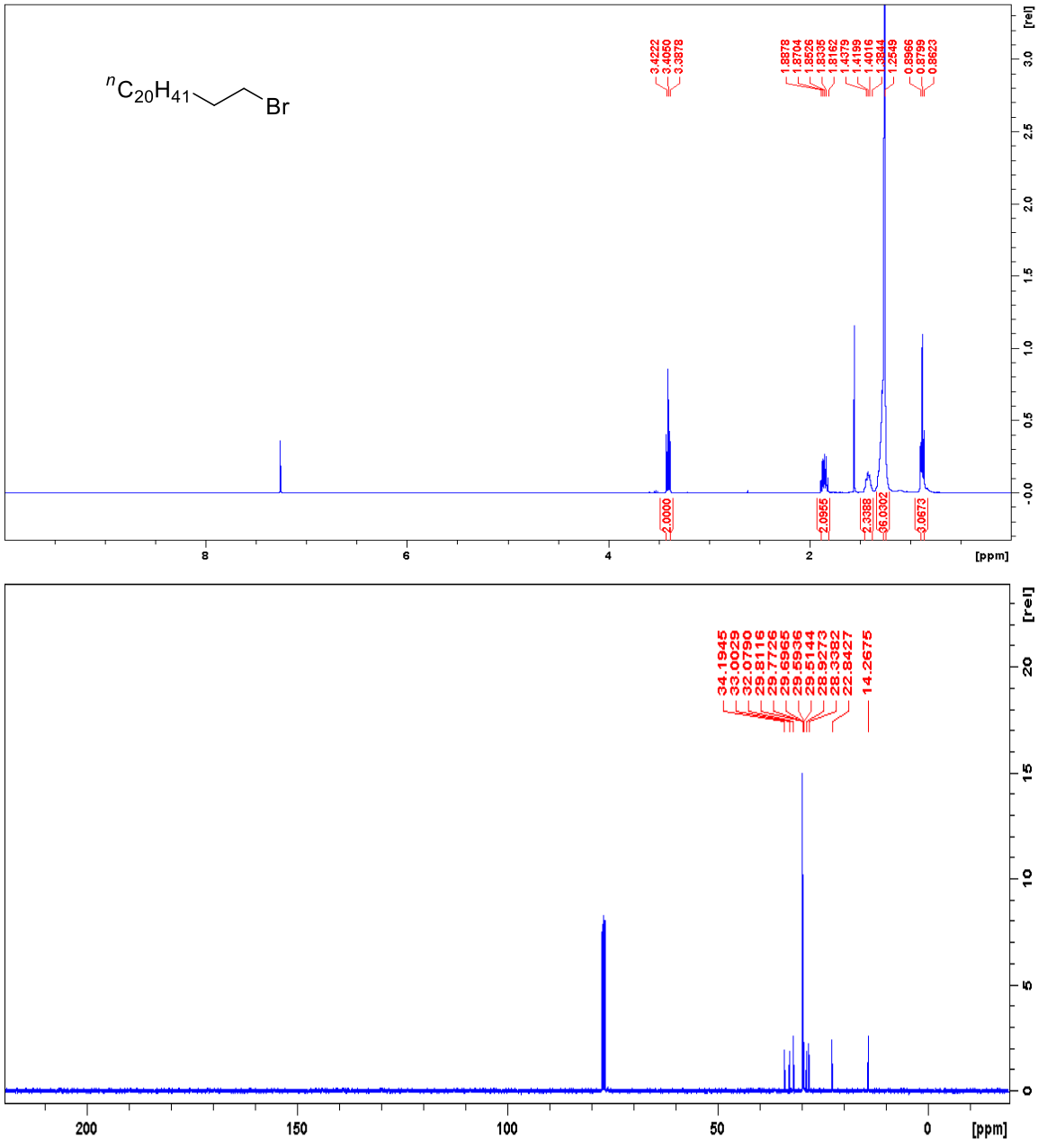
1-Bromooctane (**4u**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



1-Bromododecane (**4v**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



1-Bromodocosane (**4w**); ^{1}H NMR **(400 MHz, $CDCl_3$),** ^{13}C NMR **(100 MHz, $CDCl_3$).**



2-Bromohexadecane (**4x**);^{1}H NMR **(400 MHz, $CDCl_3$),**^{13}C NMR **(100 MHz, $CDCl_3$)**