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SUPPORTING INFORMATION

Simple metal salts supported on Montmorillonite as recyclable catalysts for intramolecular hydroalkoxylation of double bonds in conventional and VOC exempt solvents

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Experimental Section

1. Materials and Methods.

^{1}H NMR and ^{13}C NMR spectra were recorded on BRUCKER AC 200 (200 MHz). ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to $CDCl_3$ at 77.16 ppm.

Column chromatography was carried out on silica gel (spherical, neutral, 63-200 um, Geduran Si 60, Merck KGaA).

GC-TCD analysis were carried out using a Shimadzu QP2010 plus gas chromatograph, under the following operation conditions: vector gas, He; injector temperature, 250 °C; detector temperature, 210 °C at 60 mA; split ratio, 1/20; total flow, 22,5 mL/min; Phenomenex Zebron ZB5MS column, polydimethylsiloxane (10 m, inside diameter 0.10 mm, film thickness 0.10 μm); temperature program, 80-200 °C at 10 °C/min and 200 °C for 8 min.

GC/MS analysis were performed by using a Shimadzu QP2010 gas chromatograph (conditions: carrier gas, He; injector and detector temperatures, 250 °C; injected volume, 0.5 μL; split ratio, 1/100; (pressure, 180 kPa); SLB-5ms capillary column (thickness: 0.25 mm, length: 30 m, inside diameter: 0.25 mm); temperature program, 60-250 °C at 2 °C/min, and 250 °C, coupled to a mass selective detector. Mass spectra were obtained by electron ionisation at 70 eV, m/z 35-400, source temperature 250 °C; only the most abundant ions are given.

High resolution mass spectrometry (HRMS) was performed at ERINI platform (Grasse, FRANCE) using a Waters APGC coupled with a Waters Xevo G2 QTOF spectrometer.

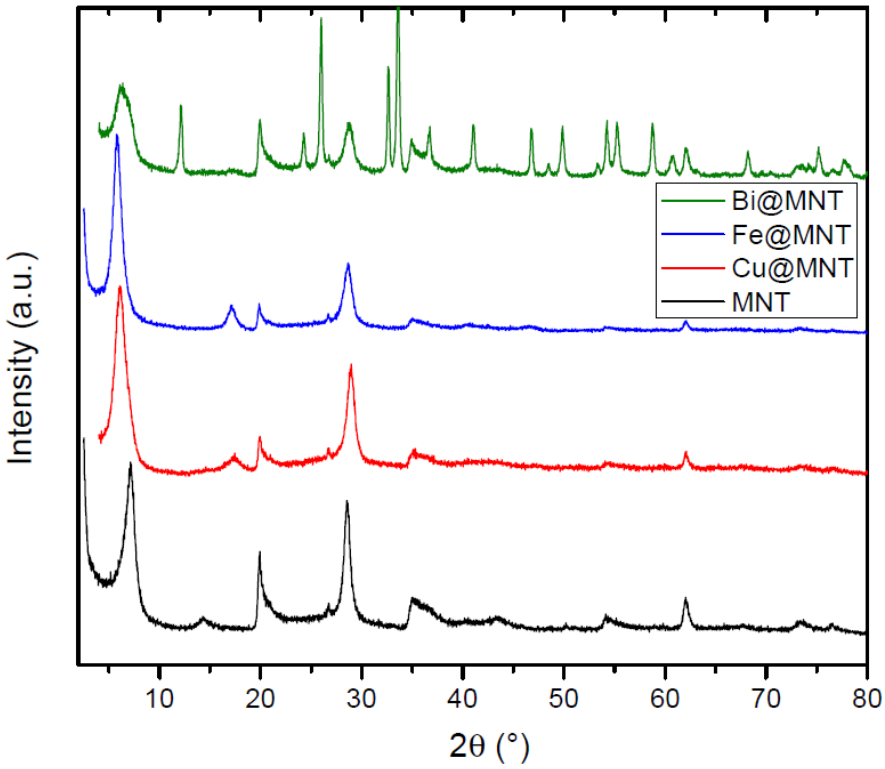
Reactions were performed in a Carousel 12 Plus parallel synthesiser purchased from Radley.

2. General procedure for cyclisation of unsaturated alcohols.

In a Schlenk tube, substrate (1 mmol), Fe-MMT (5 mol% of metal, 100 mg of material) and DMC (2 ml) are introduced and the tube tightly closed with a PTFE cap. The mixture is stirred at the desired temperature and the reaction monitored by TLC or GC-TCD. After completion, the mixture is filtered through a cotton wool pad. The filter was rinsed thoroughly with diethyl ether and the solution was concentrated at reduced pressure affording the crude cyclic ether which was purified by flash chromatography over silica gel (petroleum ether/Et_2O).

3. Catalyst characterization

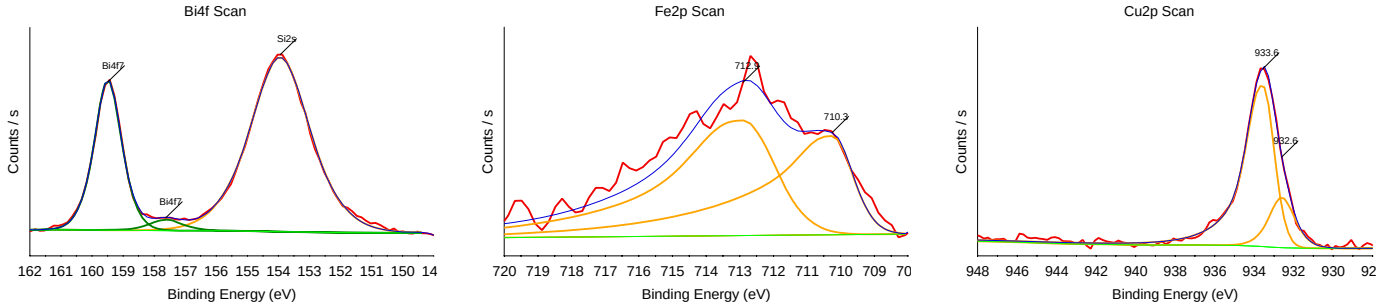
- XRD analysis



Sample name	Obs max first peak	BASAL DISTANCE d(obsmax) Å	2θ	sinθ	BASAL DISTANCE d(calc) Å	FWHM
MMT	7,2	12,26776	7,11	0,06200665	12,20981904	1,029
Fe@MMT	5,9	14,96759	5,826	0,05084569	14,88995517	0,93
Bi@MMT	6,371	13,86	6,365	0,05551655	13,63719566	1,738
Cu@MMT	6,18	14,29006	6,17	0,053817	14,0678596	1,214

The XRD spectrum of Bi-MMT clearly shows the presence of BiOCl within the matrix.[1]

- XPS analysis with deconvolution

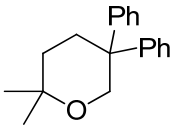


Name	Peak BE	FWHM eV	Area (P) CPS.eV	**At. %**	Type
Bi4f7	157.65	1.32	1140.32	**0.04**	Bi^{0}
Bi4f7	159.67	1.08	13238.96	**0.51**	Bi^{3+}

Name	Peak BE	FWHM eV	Area (P) CPS.eV	**At. %**	Type
Fe2p3	710.25	2.76	2626.06	0.27	Fe^{2+}
Fe2p3	712.90	3.36	3513.45	0.36	Fe^{3+}

Name	Peak BE	FWHM eV	Area (P) CPS.eV	**At. %**	Type
Cu2p3	932.60	1.54	1901.90	**0.09**	Cu^{0}
Cu2p3	933.56	1.72	7953.16	**0.40**	Cu^{2+}

4. Final Product Characterization



1b

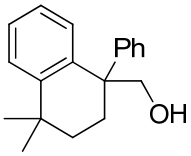
2,2-dimethyl-5,5-diphenyltetrahydro-2H-pyran (**1b**). The title compound was obtained from cyclisation of **1a** (1 mmol). Final product was isolated by column chromatography (silica gel) eluting with petroleum ether : diethylether = 90 : 10 as colourless crystalline solid (0.86 mmol, 86%). Spectral data matched literature reference.[2]

R_f = 0.64 (Cyclohexane, EtOAc = 4/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.37-7.10 (m, 10H), 4.06 (s, 2H), 2.50-2.33 (m, 2H), 1.40 (dd, J = 7.3, 5.0 Hz, 1H), 1.23 (s, 6H).

^{13}C NMR ($CDCl_3$, 50 MHz): 146.54, 128.21, 128.02, 126.05, 71.32, 69.06, 45.96, 32.65, 30.91, 26.46.

MS (EI; 70 eV) 266(5) $[M]^{+}$, 236(15), 180(100), 165(36), 152 (4); 129(2), 115(13), 103(4), 91(14), 73(8), 65(3), 43(10), 41(5).



1b'

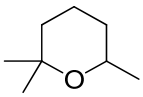
(4,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)methanol (**1b'**). Isolated by column chromatography (silica gel) eluting with petroleum ether : diethylether = 90 : 10.

R_f = 0.40 (Cyclohexane, EtOAc = 4/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.47 (d, J = 7.8 Hz, 1H), 7.33-7.11 (m, 6H), 7.10-6.98 (m, 2H), 4.28-4.02 (m, 2H), 2.58-2.28 (m, 1H), 1.94 (dt, J = 9.2, 4.2 Hz, 1H), 1.54 (dd, J = 6.7, 5.4 Hz, 2H), 1.46 (s, 1H), 1.33 (s, 3H), 1.30 (s, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): 148.28, 147.66, 137.81, 128.39, 128.18, 127.90, 127.42, 126.96, 126.14, 125.99, 69.83, 49.66, 34.38, 34.21, 32.16, 31.94, 31.36.

MS (EI; 70 eV) 266(0) $[M]^+$, 248(2), 233(1), 219(1), 205(4), 197(52), 180(7), 165(11), 157(7), 152 (4), 142(4), 129(5), 119(9), 155(10), 105(100), 91(100), 77(25), 65(8), 51 (5), 41(17).



2b

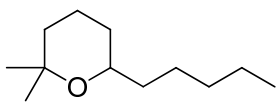
2,2,6-trimethyltetrahydro-2H-pyran (**2b**).[3] The title compound was obtained from cyclisation of **2a** (1 mmol) in deuterated dimethylcarbonate. The reaction was run to completion under TLC and GC monitoring. NMR analyses were carried out on samples directly taken from the reaction medium by using benzene as internal standard (calculated yield = 98%).

R_f = 0.53 (Cyclohexane, EtOAc = 9/1)

^{1}H NMR (DMC-d_6, 200 MHz): δ 3.78-3.54 (m, 1H), 1.75 – 1.53 (m, 2H), 1.52-1.25 (m, 4H), 1.17 (s, 3H), 1.13(s, 3H), 1.04 (d, J = 6.1 Hz, 3H).

^{13}C NMR (DMC-d_6, 50 MHz): δ 71.64, 66.65, 36.43, 33.99, 31.84, 22.53, 21.67, 20.59.

MS (EI; 70 eV) 128(0) $[M]^+$, 113(47), 95(7), 70(10), 59(100), 56(36), 43(80).



3b

2,2-dimethyl-6-pentyltetrahydro-2H-pyran (**3b**). The title compound was obtained from cyclisation of **3a** (1 mmol). Final product was isolated by column chromatography (silica gel) eluting with petroleum ether : diethylether = 95 : 5 as colourless liquid (0.89 mmol, 89%). Spectral data matched literature reference.

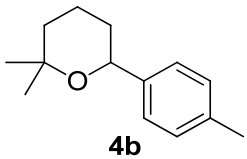
R_f = 0.79 (Cyclohexane, EtOAc = 9/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.50-3.41 (m, 1H), 1.67-0.94 (m, 14H), 1.19 (s, 3H), 1.17 (s, 3H), 0.87 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 71.57, 70.46, 37.10, 36.45, 32.10, 31.66, 25.39, 22.79, 22.13, 20.28, 14.22.

MS (EI; 70 eV) 184(0) $[M]^{+}$, 169(16), 151 (4), 126(3), 113(63), 99 (15), 95(61), 83(15), 69(38), 59(100), 56(72), 43(57).

HRMS calculated for $C_{12}H_{23}O$ $(M-H)^{+}$: 183,1749; found: 183,1743. $|\Delta|$= 3.3 ppm.



4b

2,2-dimethyl-6-(*p*-tolyl)tetrahydro-2H-pyran (**4b**). The title compound was obtained from cyclisation of **4a** (1 mmol). Final product was isolated by column chromatography (silica gel) eluting with petroleum ether: diethylether = 98 : 2 as colourless liquid (0.38 mmol, 38%).

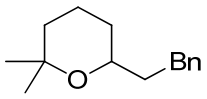
R_f = 0.67 (Cyclohexane, EtOAc = 9/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.25 (d, J = 8 Hz, 2H), 7.12 (d, J = 8 Hz, 2H), 4.55 (dd, J = 11.5, 1.9 Hz, 1H), 2.31 (s, 3H), 1.82-1.41 (m, 6H), 1.30 (s, 3H), 1.29 (s, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 141.33, 136.76, 129.04, 126.15, 72.90, 72.42, 36.19, 34.21, 32.13, 22.07, 21.24, 20.61.

MS (EI; 70 eV) 204(14) $[M]^{+}$, 189(5), 146 (25), 131(15), 121(100), 105 (5), 91(19), 84(4), 77(6), 69(6), 56(31), 43(11).

HRMS calculated for $C_{14}H_{19}O$ $(M-H)^{+}$: 203,1436; found: 203,1436. $|\Delta|$= 0.0 ppm.



5b

2,2-dimethyl-6-(2-phenylethyl)-tetrahydro-2H-pyran (**5b**). The title compound was obtained from cyclisation of **5a** (1 mmol). Final product was isolated by column chromatography (silica gel) eluting with petroleum ether: diethylether = 9 : 1 as colourless liquid (0.89 mmol, 89%).

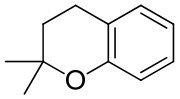
R_f = 0.64 (Cyclohexane, EtOAc = 9/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.43-7.01 (m, 5H), 3.66-3.30 (m, 1H), 2.89-2.46 (m, 2H), 1.90-0.99 (m, 8H), 1.23 (s, 3H), 1.17 (s, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 142.64, 128.62, 128.23, 125.60, 77.80, 77.16, 76.53, 71.62, 69.19, 38.49, 36.39, 32.05, 31.76, 22.07, 20.18.

MS (EI; 70 eV) 218(12) $[M]^{+}$, 185(6), 157 (7), 140(25), 129(14), 113(34), 104(36), 91(100), 69(22), 56(14), 43(29).

HRMS calculated for $C_{15}H_{23}O$ $(M+H)^{+}$: 219,1749; found: 203,1751. $|\Delta|$ = 0.9 ppm.



6b

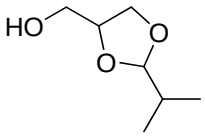
2,2-dimethylchroman (**6b**). The title compound was obtained from cyclisation of **6a** (1 mmol). Final product was isolated by column chromatography (silica gel) eluting with petroleum ether: diethylether = 9 : 1 as colourless liquid (0.63 mmol, 63%). Spectral data matched literature reference.[4]

R_f = 0.52 (Cyclohexane, EtOAc = 4/1)

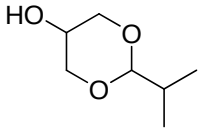
^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.16-6.94 (m, 2H), 6.86-6.76 (m, 2H), 2.78 (t, J = 6.8 Hz, 2H), 2.78 (t, J = 6.8 Hz, 2H), 1.34 (s, 6H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.11, 129.56, 127.36, 121.02, 119.71, 117.36, 74.19, 32.93, 27.01, 22.58.

MS (EI; 70 eV) 162(36) $[M]^{+}$, 147(40), 133(9), 119(18), 113(10), 107(100), 91(22), 77(25), 65(6), 51(13), 41(11).



7c



7d

cis,*trans*-(2-Isopropyl-1,3-dioxolan-4-yl)methanol (**7c**) and *cis*,*trans*-2-isopropyl-1,3-dioxan-5-ol (**7d**). The title compounds were obtained from cyclisation of **7a** (1 mmol). Final products were isolated as 1/1 mixture of stereoisomers (*cis*,*trans*-**7c** and *cis*,*trans*-**7d**, colourless oil) by column chromatography (silica gel) eluting with petroleum ether : diethylether with gradient elution from 4:1 to 10:0 (isolated yields: 51 and 31% respectively). Spectral data matched literature reference.[5]

R_f = 0.71 (Cyclohexane, EtOAc = 1/1) [*cis*,*trans*-**7c**]

R_f = 0.79 (Cyclohexane, EtOAc = 1/1) [*cis*,*trans*-**7d**]

[*cis*,*trans*-**7c**] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.75 (d, J = 4.7 Hz, 1H), 4.66 (d, J = 4.6 Hz, 1H), 4.32-4.02 (m, 3H), 4.00-3.16 (m, 7H), 2.04 (*br* s, 2H), 1.94-1.70 (m, 2H), 0.97 (d, J = 5.6 Hz, 6H), 0.94 (d, J = 6.6 Hz, 6H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 108.79, 108.65, 76.52, 76.29, 66.80, 66.55, 63.52, 62.76, 32.30, 31.85, 16.99, 16.95, 16.89, 16.80.

MS (EI; 70 eV) 146(0) $[M]^{+}$, 145(1), 115(3), 103(82), 97(7), 86(2), 71(5), 69(2), 57(100), 55(31), 43(24), 41(15). (I stereoisomer)

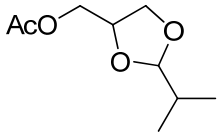
MS (EI; 70 eV) 146(0) $[M]^{+}$, 145(2), 115(4), 103(80), 97(10), 86(1), 71(6), 69(3), 57(100), 55(31), 43(26), 41(16). (II stereoisomer)

[*cis*,*trans*-**7d**] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.27 (d, J = 5 Hz, 1H), 4.20 (d, J = 5 Hz, 1H), 4.13 (t, J = 4.6 Hz, 2H), 4.01 (d, J = 11.2 Hz, 1H), 3.93-3.76 (m, 3H), 3.86 (d, J = 11.2 Hz, 1H), 3.54-3.45 (m, 1H), 3.36 (d, J = 10.9 Hz, 1H), 3.31 (d, J = 10.2 Hz, 1H), 2.02 (*br* s, 2H), 1.91-1.66 (m, 2H), 0.94 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.8 Hz, 6H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 106.35, 105.69, 71.88, 71.70, 64.28, 61.61, 32.82, 32.35, 17.31, 16.94.

MS (EI; 70 eV) 146(0) $[M]^{+}$, 145(1), 116(1), 103(100), 73(53), 57(63), 55(31), 43(42), 41(15). (I stereoisomer)

MS (EI; 70 eV) 146(0) $[M]^{+}$, 145(1), 116(2), 103(100), 73(54), 57(64), 55(33), 43(46), 41(17). (II stereoisomer)



8c

(2-isopropyl-1,3-dioxolan-4-yl)-methyl acetate (**8c**). The title compounds were obtained from cyclisation of **8a** (1 mmol). Final product was isolated as mixture of stereoisomers (±-**8c**, colourless oil) by column chromatography (silica gel) eluting with 9:1 petroleum ether : diethylether (isolated yield: 59%).

R_f = 0.52 (Cyclohexane, EtOAc = 4/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.73 (d, J = 4.6 Hz, 1H), 4.66 (d, J = 4.4 Hz, 1H), 4.37-4.18 (m, 2H), 4.17-3.98 (m, 3H), 3.91 (dd, J= 8.3, 6.9 Hz, 1H), 3.74 (dd, J= 8.3, 4.9 Hz, 1H), 3.58 (dd, J= 8.4, 6.7 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.94-1.67 (m, 2H), 0.97-0.88 (m, 12H).

^{13}C NMR ($CDCl_3$, 50 MHz): 170.89, 170.84, 109.02, 108.51, 73.70, 73.53, 67.27, 67.19, 64.72, 64.30, 32.06, 31.77, 20.89, 20.86, 16.93, 16.87, 16.59, 16.55.

MS (EI; 70 eV) 188(0) $[M]^{+}$, 187(0), 145(43), 115(1), 97(4), 86(1), 71(3), 61(4), 57(18), 43(100), 41(7). (I stereoisomer)

MS (EI; 70 eV) 188(0) $[M]^{+}$, 187(1), 145(46), 115(2), 97(45), 86(1), 71(4), 69(2), 57(19), 43(100), 41(7). (II stereoisomer)

HRMS calculated for $C_9H_{15}O_4$ $(M-H)^{+}$: 187,0970; found: 187,0967. $|\Delta|$= 1.6 ppm.

9b

2-Pentyltetrahydro-2H-pyran (THP-ether) and 2-hexyltetrahydrofuran (THF-ether) (**9b**). The title compounds were obtained from cyclisation of **9a** (1 mmol). Final products were isolated by column chromatography (silica gel) eluting with petroleum ether : diethylether = 95 : 5 as colourless liquids (isolated yields: 2 and 62% respectively). Spectral data matched literature reference.[6]

R_f = 0.64 (Cyclohexane, EtOAc = 9/1) [THP-ether/**9b**]

R_f = 0.52 (Cyclohexane, EtOAc = 9/1) [THF-ether/**9b**]

[THP-ether/**9b**] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.01-3.88 (m, 1H), 3.40 (td J= 10.9, 3.6 Hz, 1H), 3.29-3.08 (m, 1H), 2.17-1.04 (m, 14H), 0.87 (t, J = 6.5 Hz, 3H).

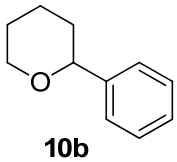
^{13}C NMR ($CDCl_3$, 50 MHz): δ 78.08, 68.63, 36.78, 32.12, 32.09, 26.40, 25.36, 23.76, 22.77, 14.19.

MS (EI; 70 eV) 156(1) $[M]^+$, 138 (1), 95 (1), 85(100), 67(16), 57(15), 43(21), 41(24).

[THF-ether/**9b**] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.97-3.59 (m, 3H), 2.08-1.69 (m, 3H), 1.69-1.03 (m, 11H), 0.86 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 79.59, 67.70, 35.89, 31.97, 31.51, 29.55, 26.50, 25.84, 22.73, 14.19.

MS (EI; 70 eV) 156(1) $[M]^+$, 138 (1), 96 (1), 81(1), 71(100), 55(6), 43(31), 41(31).



10b

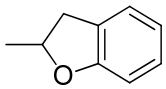
2-Phenyltetrahydro-2H-pyran (**10b**). The title compound was obtained from cyclisation of **10a** (1 mmol). Final product was isolated by column chromatography (silica gel) eluting with petroleum ether: diethylether = 98 : 2 as colourless liquid (0.97 mmol, 97%). Spectral data matched literature reference.[7]

R_f = 0.33 (Cyclohexane, EtOAc = 9/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.39-7.15 (m, 5H), 4.36-4.24 (m, 1H), 4.12 (dd, J = 11.4, 3.5 Hz, 1H), 3.76-3.46 (m, 1H), 2.01-1.46 (m, 6H).

^{13}C NMR ($CDCl_3$, 50 MHz): 143.45, 128.38, 127.38, 125.95, 80.26, 69.11, 34.14, 26.02, 24.14.

MS (EI; 70 eV) 162(54) $[M]^+$, 161 (46), 144(2), 133(4), 129(4), 115 (6), 105 (100), 91(29), 77(45), 65(8), 55(26), 51(19), 41(31).



11c

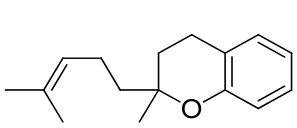
2-Methyl-2,3-dihydrobenzofuran (**11c**). The title compound was obtained from cyclisation of **11a** (1 mmol). Final product was isolated by column chromatography (silica gel) eluting with petroleum ether: diethylether = 9 : 1 as a colorless liquid (0.31 mmol, 31%). Spectral data matched literature reference.[8]

R_f = 0.69 (Cyclohexane, EtOAc = 4/1)

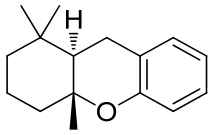
^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.23-7.05 (m, 2H), 6.85 (dd, J = 7.4, 0.9 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 4.93 (ddq, J = 8.7, 7.7, 6.2 Hz, 1H), 3.32 (dd, J = 15.4, 8.8 Hz, 1H), 2.82 (dd, J = 15.4, 7.7 Hz, 1H), 1.48 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.63, 128.07, 127.15, 125.08, 120.28, 109.44, 76.52, 37.25, 21.88.

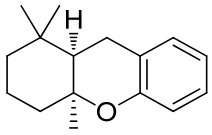
MS (EI; 70 eV) 134(100) $[M]^{+}$, 133(42), 119(66), 115(27), 113(34), 119(11), 107(100), 91(22), 77(25), 65(6), 51(13), 41(11).



12b



trans-**12b'**



cis-**12b'**

2-Methyl-2-(4-methylpent-3-en-1-yl)chroman (**12b**) and *cis*,*trans*-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene (**12b'**). The title compounds were obtained from cyclisation of **12a** (1 mmol). Final products were isolated as single isomer (*cis*-**12b'**, white crystals) or as mixture of isomers (**12b**, *trans*-**12b'**, colourless oil) by column chromatography (silica gel) eluting with petroleum ether : diethylether with gradient elution from 10:0 to 9:1 (isolated yields: 13 and 65% respectively). Spectral data matched literature reference.[9]

R_f = 0.80 (Cyclohexane, EtOAc = 95/5) [*cis*-**12b'**]

R_f = 0.66 (Cyclohexane, EtOAc = 95/5) [**12b**, *trans*-**12b'**]

[*cis*-**12b'**] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.05 (d, J = 7.1 Hz, 2H), 6.88-6.69 (m, 2H), 3.05 (dd, J = 17.7, 7.9 Hz, 1H), 2.76 (d, J = 17.7 Hz, 1H), 2.08-1.20 (m, 7H), 1.21 (s, 3H), 0.97 (s, 3H), 0.65 (s, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.64, 129.04, 126.81, 122.18, 119.94, 117.23, 75.36, 44.58, 41.80, 39.71, 34.12, 32.41, 27.16, 23.74, 21.54, 18.23.

MS (EI; 70 eV) 230(31) $[M]^{+}$, 214(4), 187(2), 173(1), 159(11), 145(17), 123(100), 107(39), 91(10), 81(30), 77(10), 67(12), 55(10), 43(9), 41(18).

[*trans*-**12b'**] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.09 (d, J = 7.1 Hz, 2H), 6.81-6.72 (m, 2H), 2.73 (dd, J = 16.2, 6.7 Hz, 1H), 2.57 (d, J = 16.4 Hz, 1H), 2.17-1.16 (m, 7H), 1.23 (s, 3H), 1.04 (s, 3H), 0.94 (s, 3H).

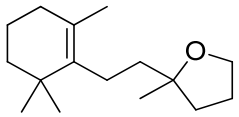
^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.38, 129.75, 127.23, 122.72, 119.74, 117.15, 76.29, 48.19, 41.63, 40.13, 33.49, 32.22, 23.37, 20.80, 19.96, 19.91.

MS (EI; 70 eV) 230(54) $[M]^{+}$, 215(14), 187(10), 173(3), 159(26), 145(37), 123(100), 107(92), 91(21), 81(31), 77(17), 67(13), 55(18), 43(14), 41(32).

[**12b**] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.06 (d, J = 7.3 Hz, 2H), 6.88-6.70 (m, 2H), 5.17-5.06 (m, 1H), 2.82-2.52 (m, 2H), 2.08-1.39 (m, 6H), 1.72 (s, 3H), 1.64 (s, 3H), 1.34 (s, 3H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.09, 129.50, 127.33, 124.38, 121.22, 119.64 117.41, 76.02, 39.66, 31.06, 25.80, 24.37, 22.40, 22.24, 17.71.

MS (EI; 70 eV) 230(52) $[M]^{+}$, 215(2), 187(20), 174(17), 161(27), 147(48), 133(20), 123(59), 107(94), 91(40), 81(40), 69(74), 55(16), 41(100).



13b

2-Methyl-2-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl)tetrahydrofuran (**13b**). The title compound was obtained from cyclisation of **13a** (1 mmol). Final product were isolated as a complex mixture of isomers, **13b** being the major isomer, by column chromatography (silica gel) eluting with petroleum ether : diethylether = 9 : 1 as colorless liquid (0.71 mmol, 71%). Spectral data matched literature reference.[10]

R_f = 0.76 (Cyclohexane, EtOAc = 4/1)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.97-3.68 (m, 1H), 2.17-1.33 (m, 14H), 1.59 (s, 1H), 1.21 (s, 1H), 0.98 (s, 1H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 137.12, 126.90, 82.88, 67.20, 41.13, 40.05, 36.83, 35.22, 32.92, 28.78, 26.24, 25.48, 23.63, 19.84, 19.69.

MS (EI; 70 eV) 236(2) $[M]^{+}$, 221(2), 203(2), 177(4), 161(2), 149(2), 136(18), 123(15), 121(25), 107(15), 95(17), 93(17), 85(100), 81(14), 69(9), 67(10), 55(14), 43(52), 41(24).

5. References

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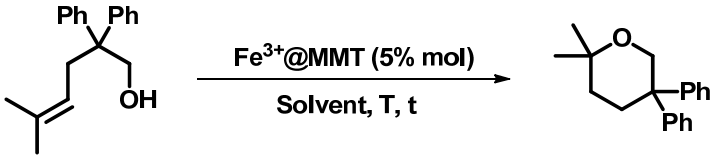
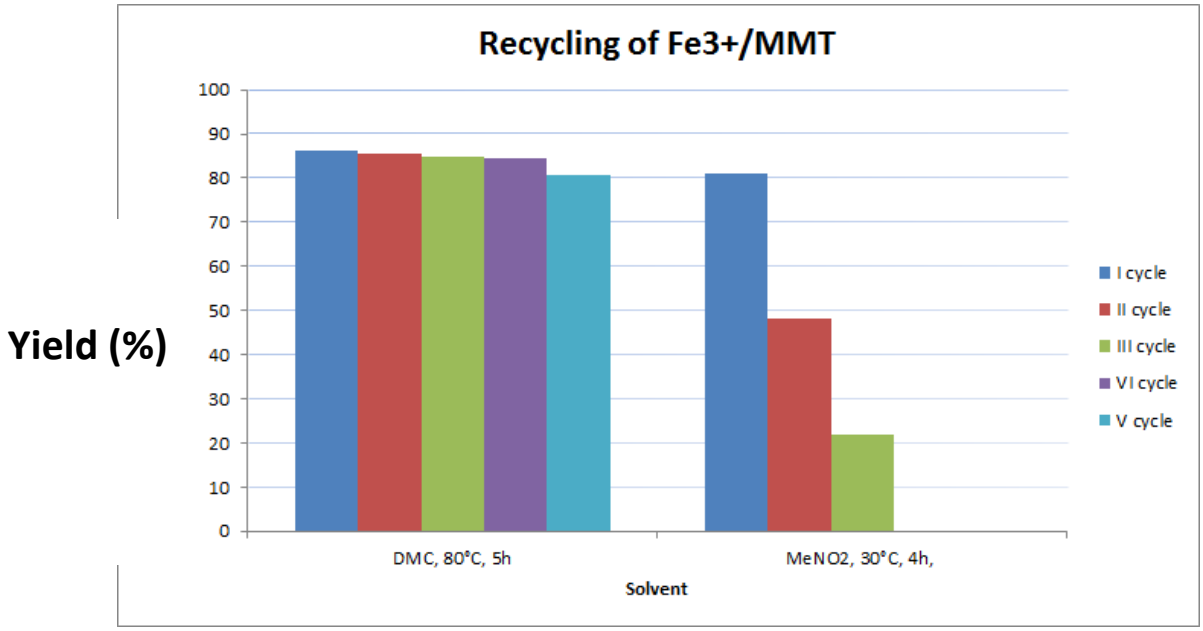
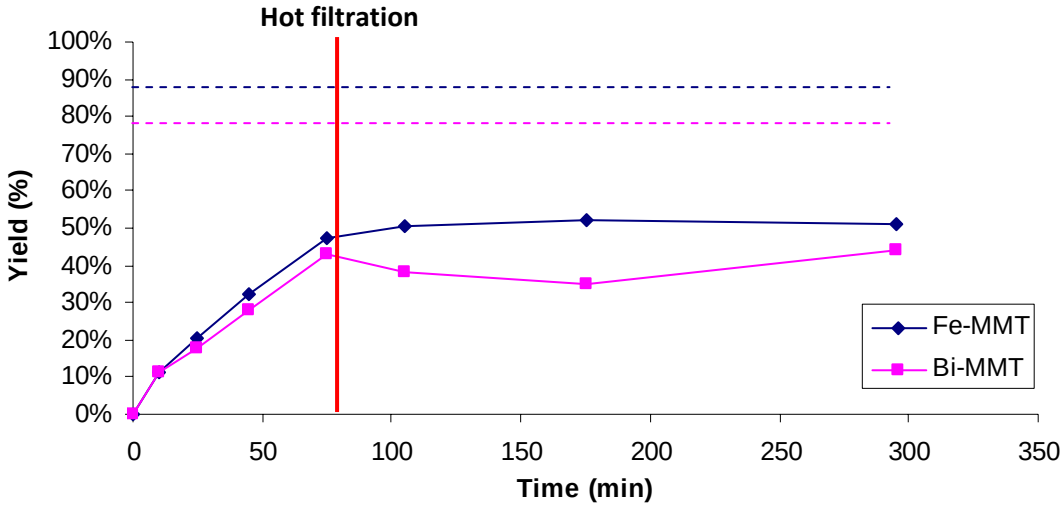
6. Recycling studies





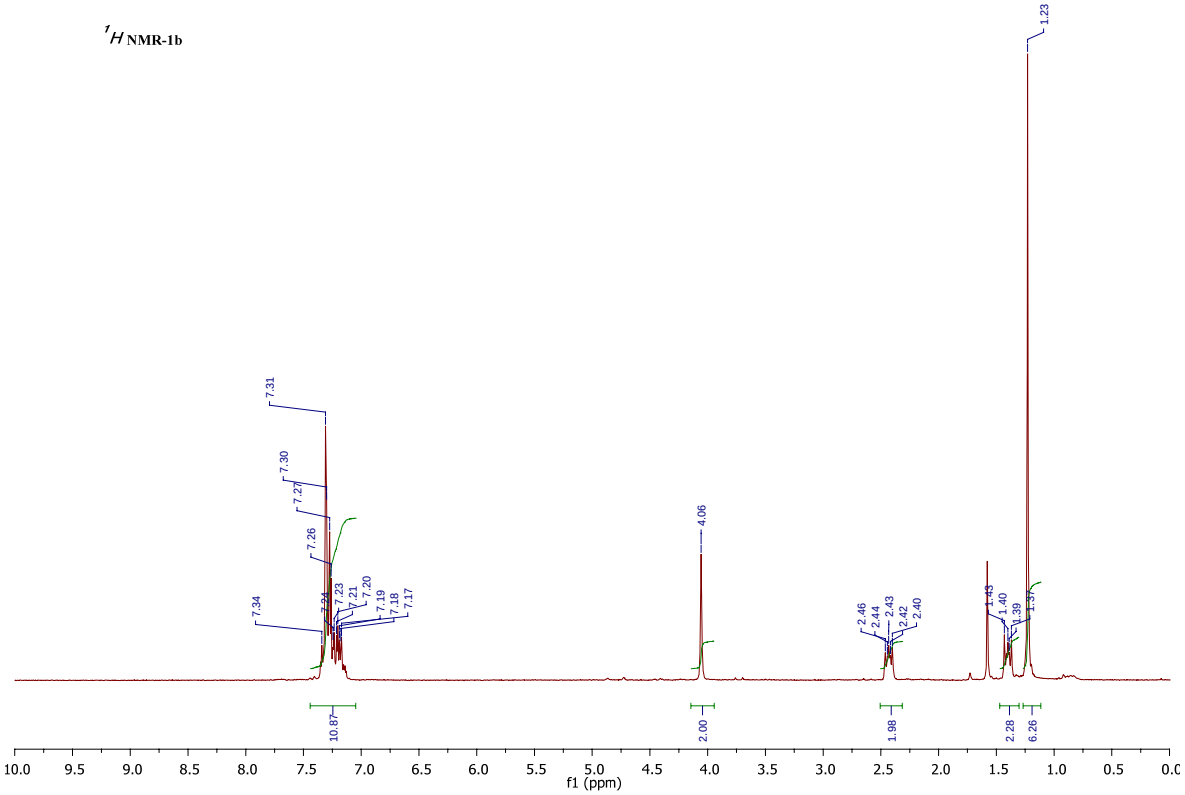
7. Hot filtration experiment



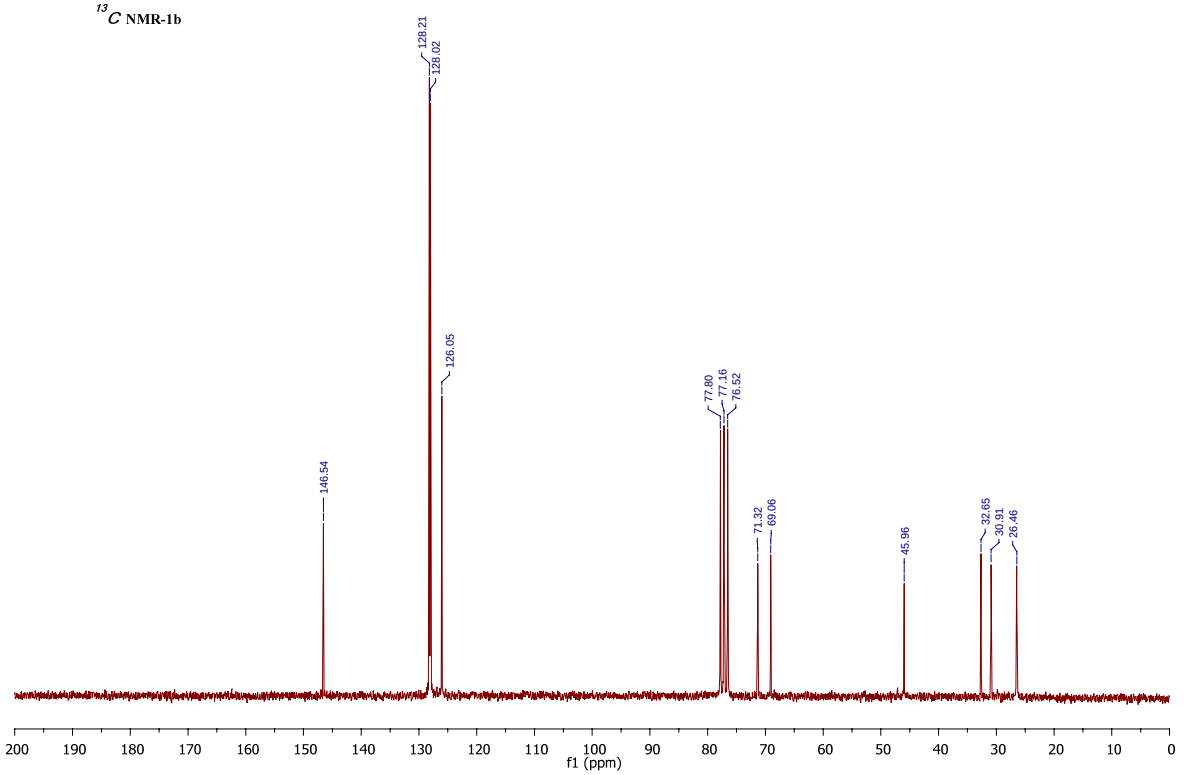
In dashed lines are the expected yields for each system at completion of the reaction. Filtration performed at 80 °C over porosity 4 fritted glass.

8. NMR spectra

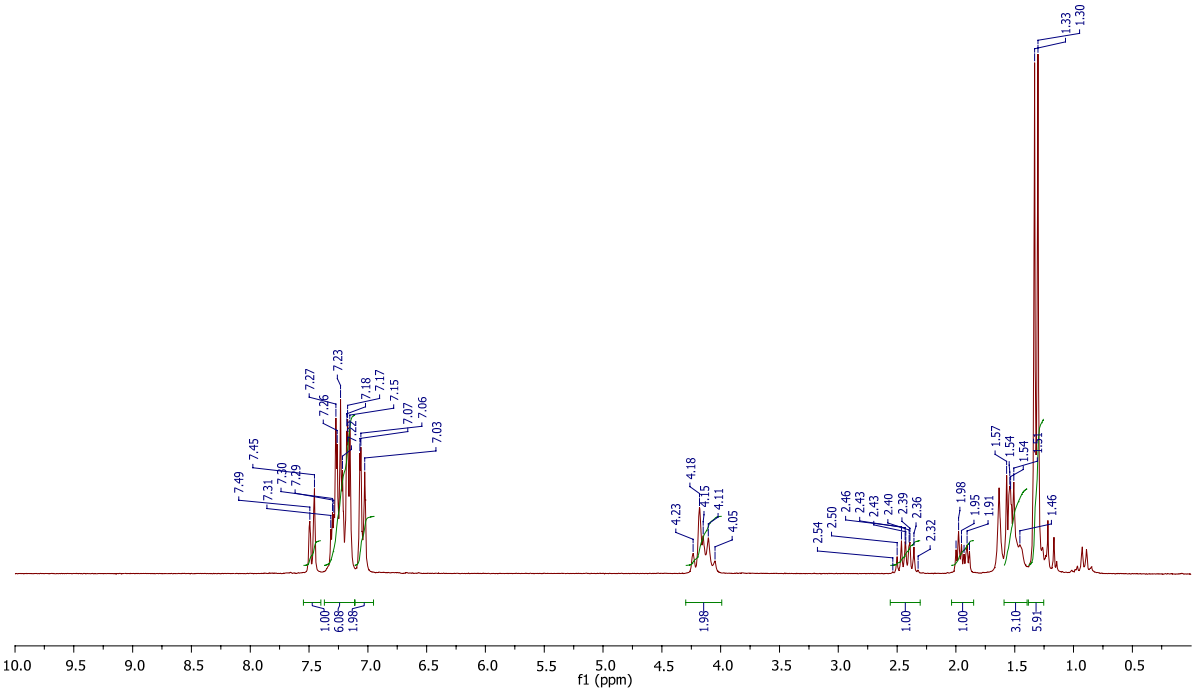
^{1}H NMR-1b



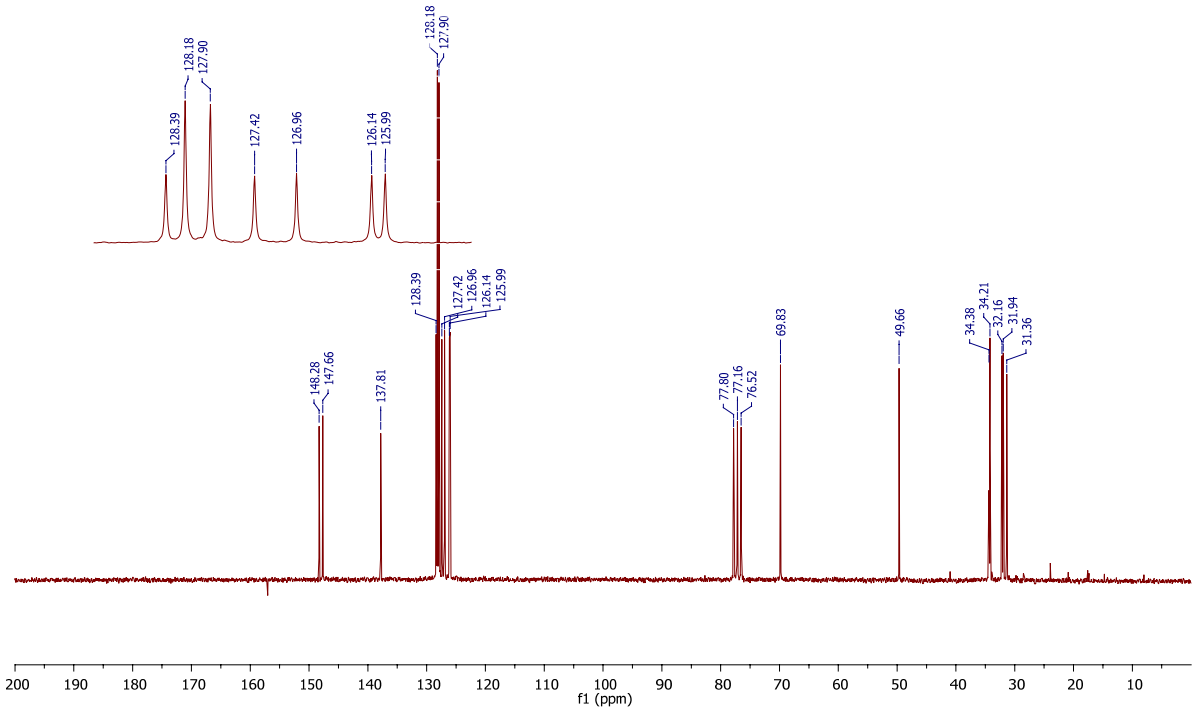
^{13}C NMR-1b



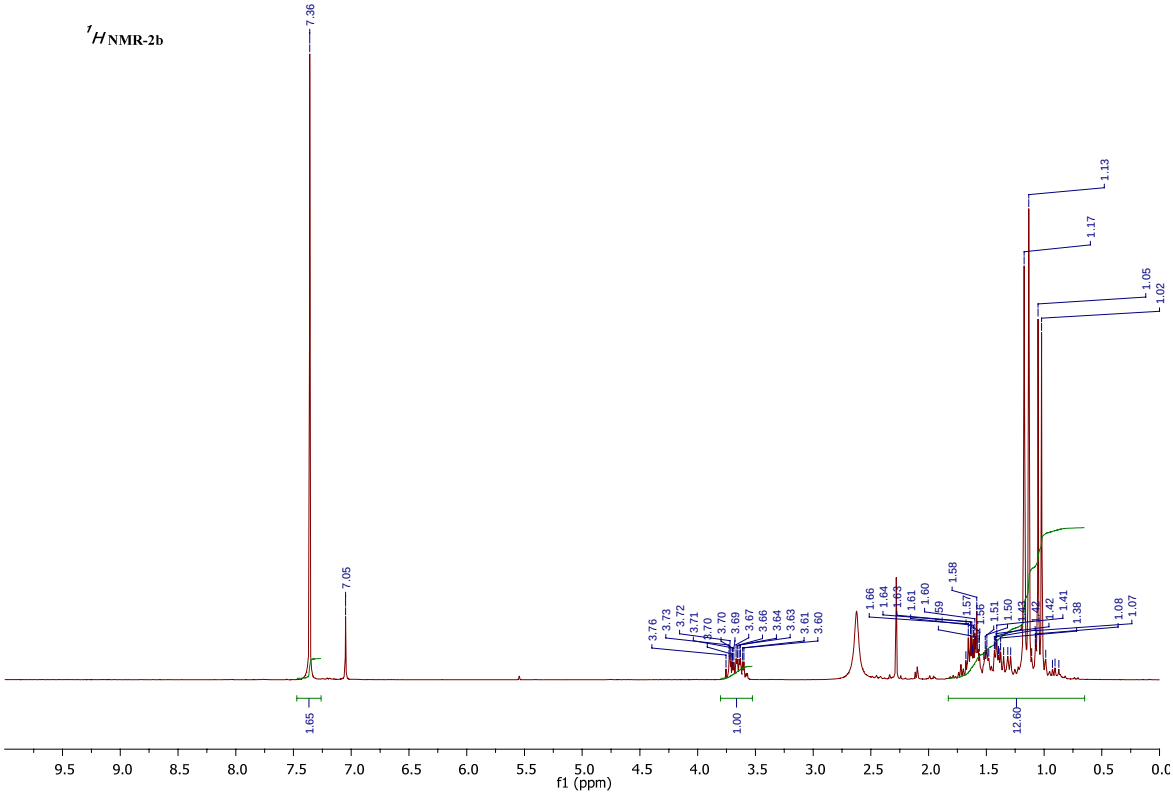
^{1}H NMR-1b'



^{13}C NMR-1b'



^{1}H NMR-2b



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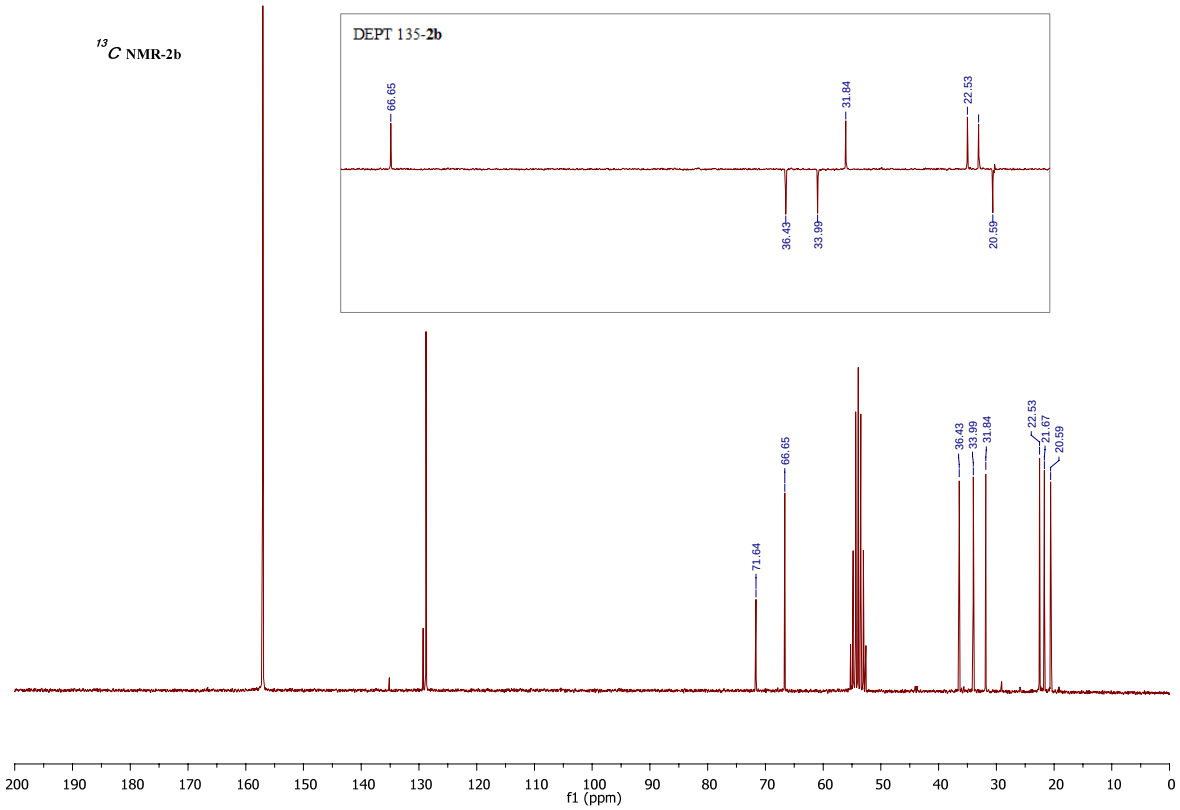
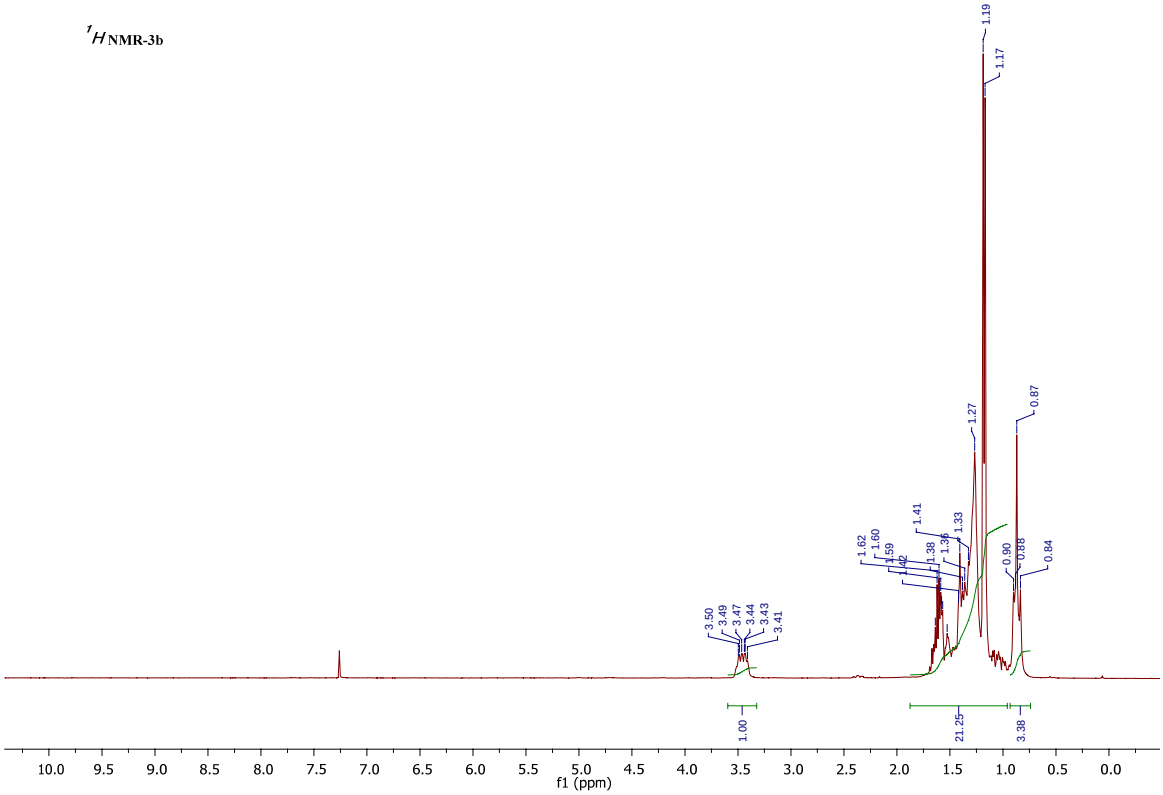
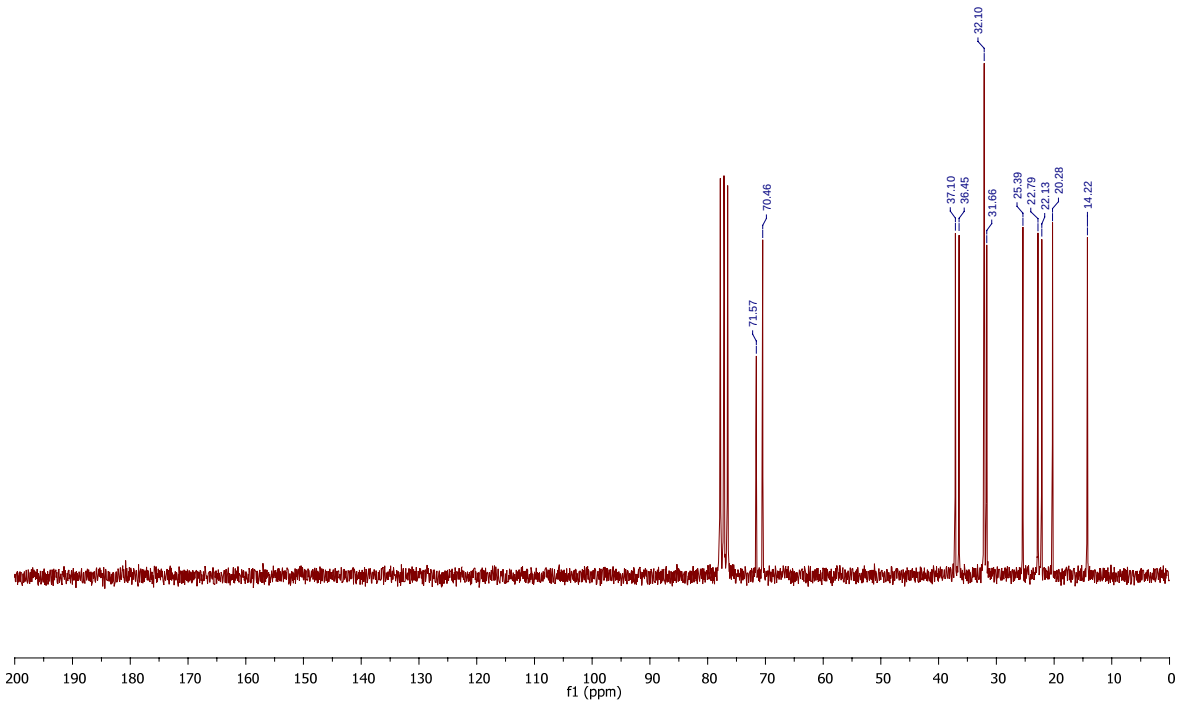


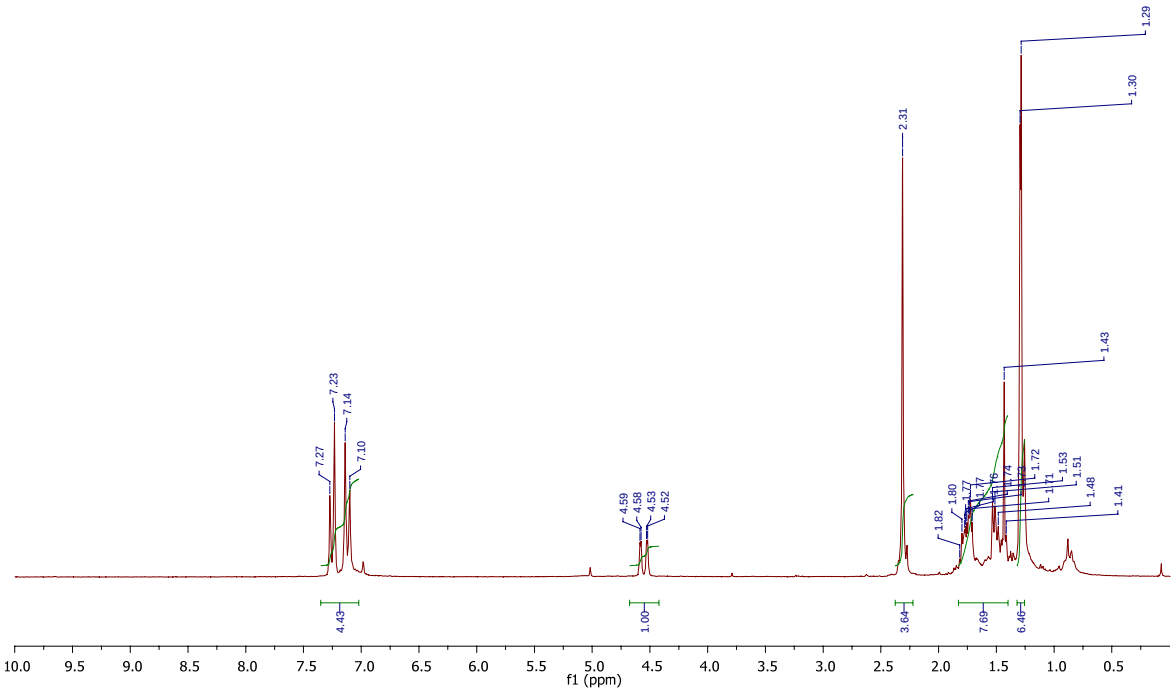
^{1}H NMR-3b



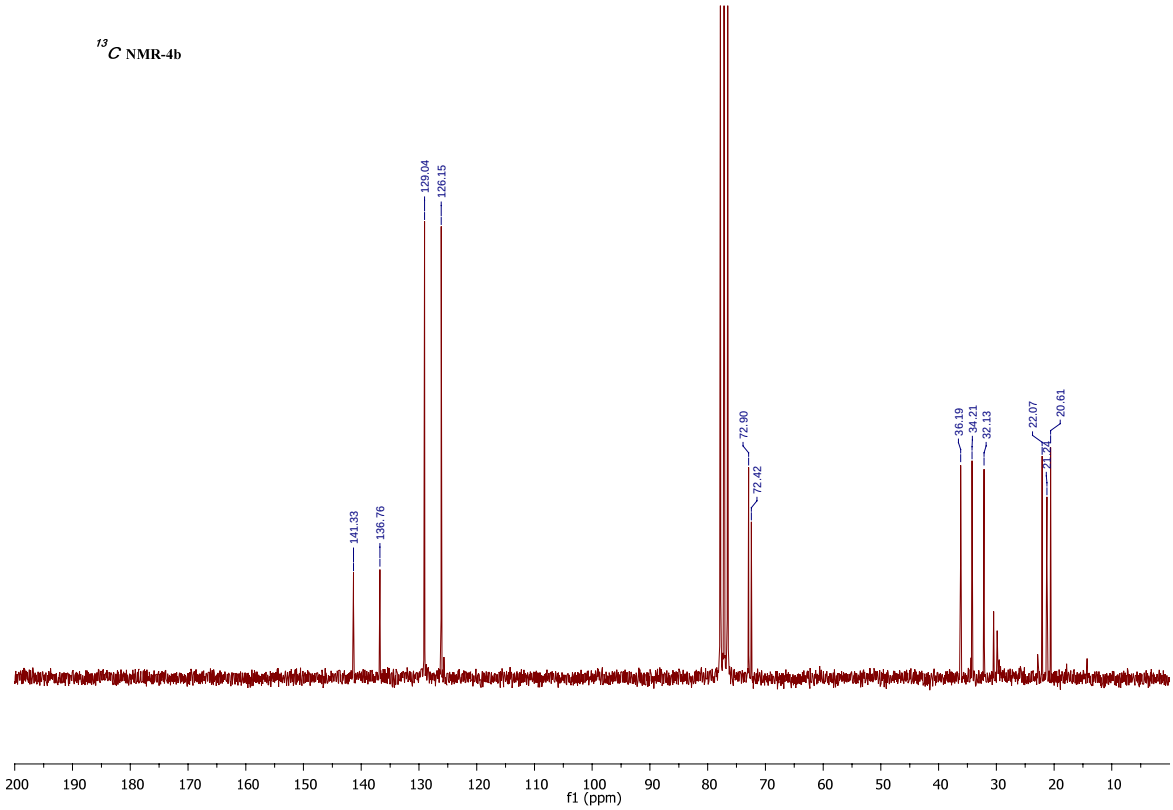
^{13}C NMR-3b



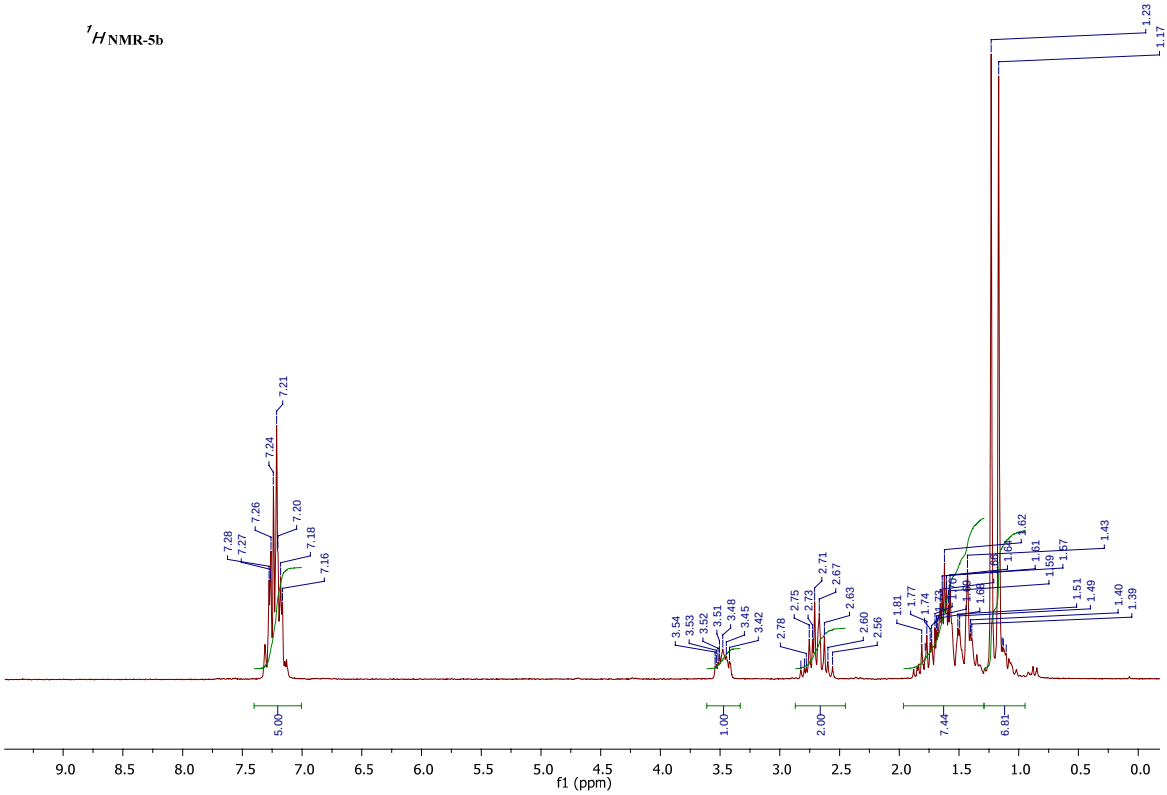
^{1}H NMR-4b



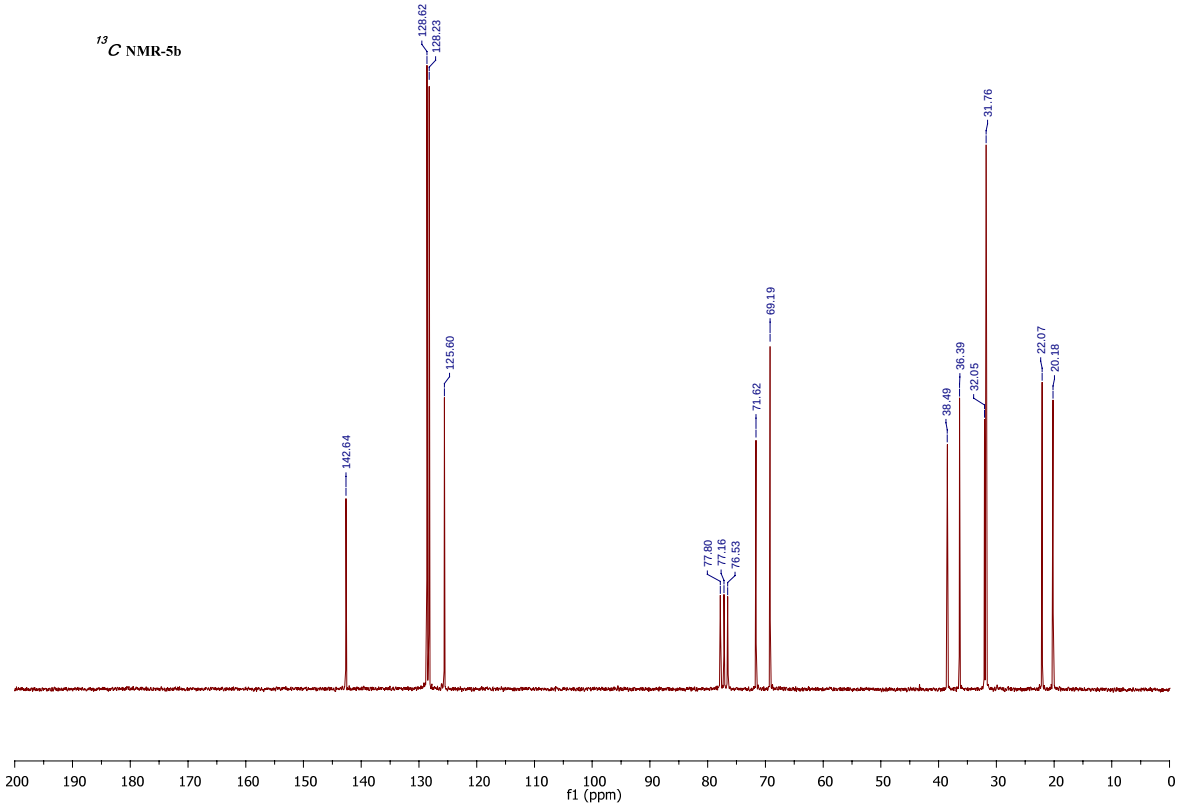
^{13}C NMR-4b



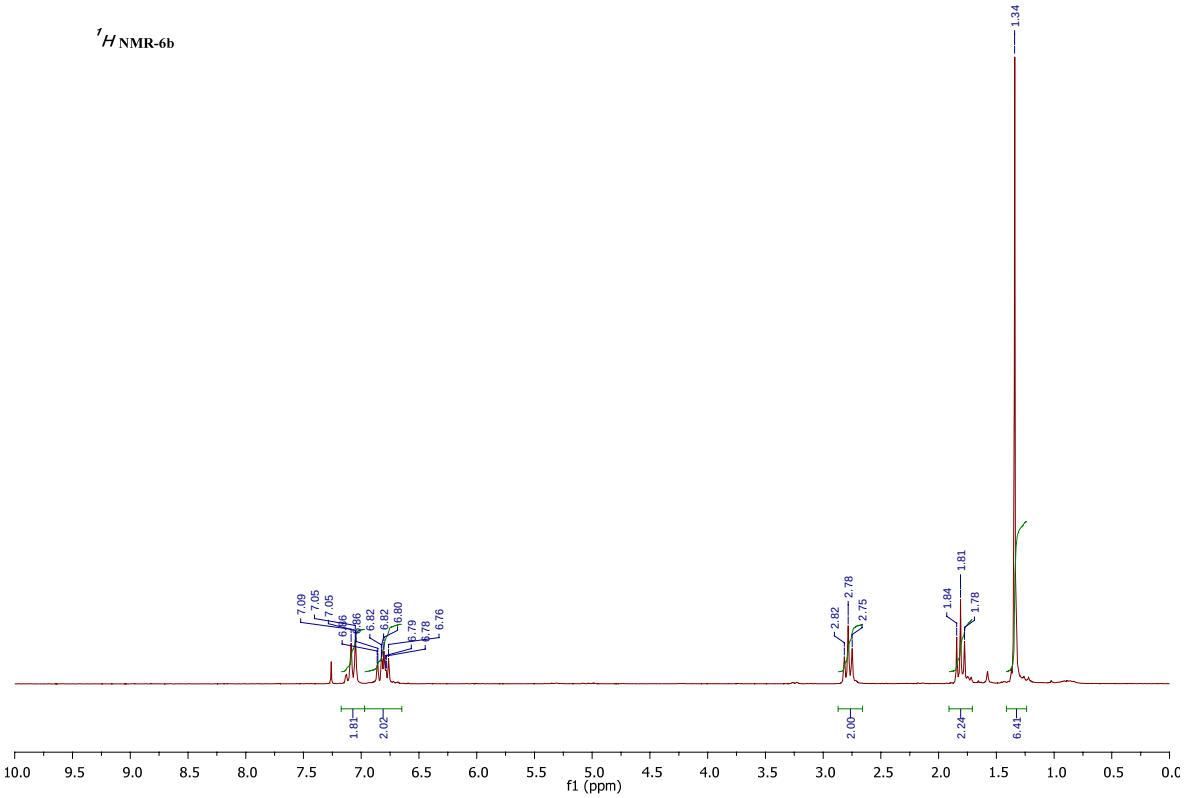
^{1}H NMR-5b



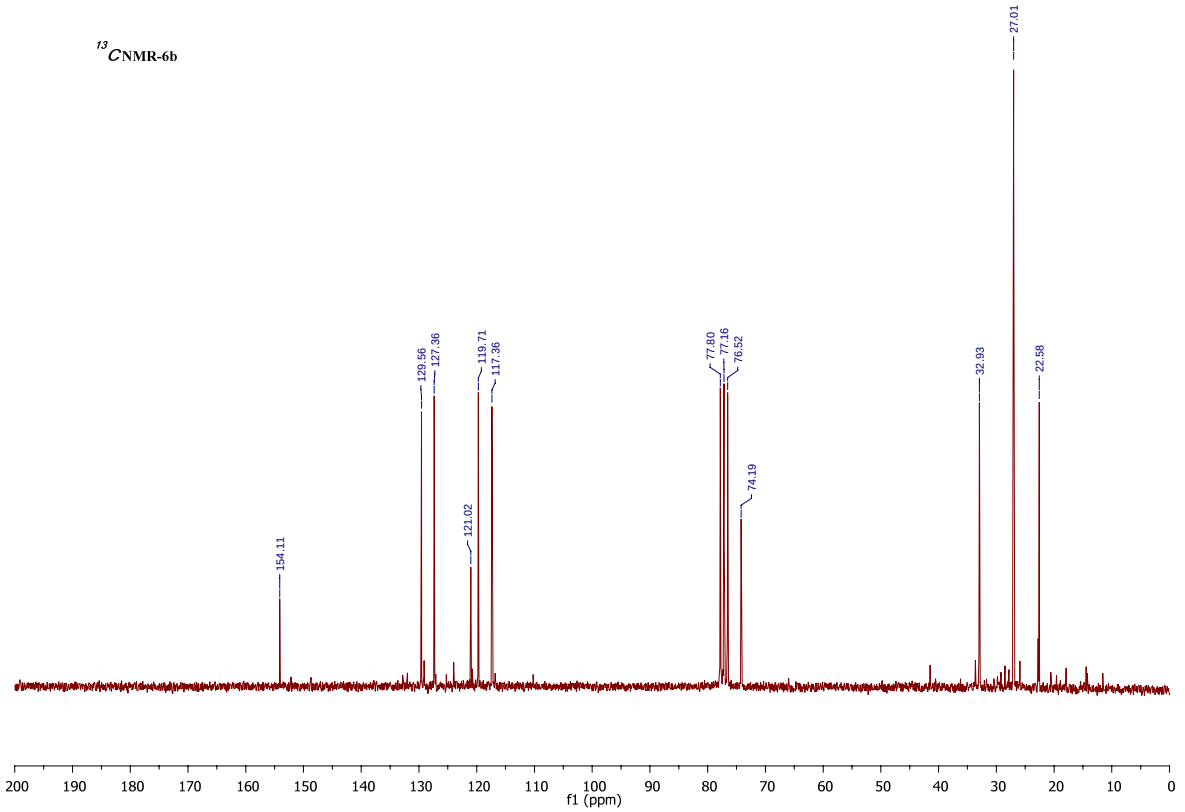
^{13}C NMR-5b



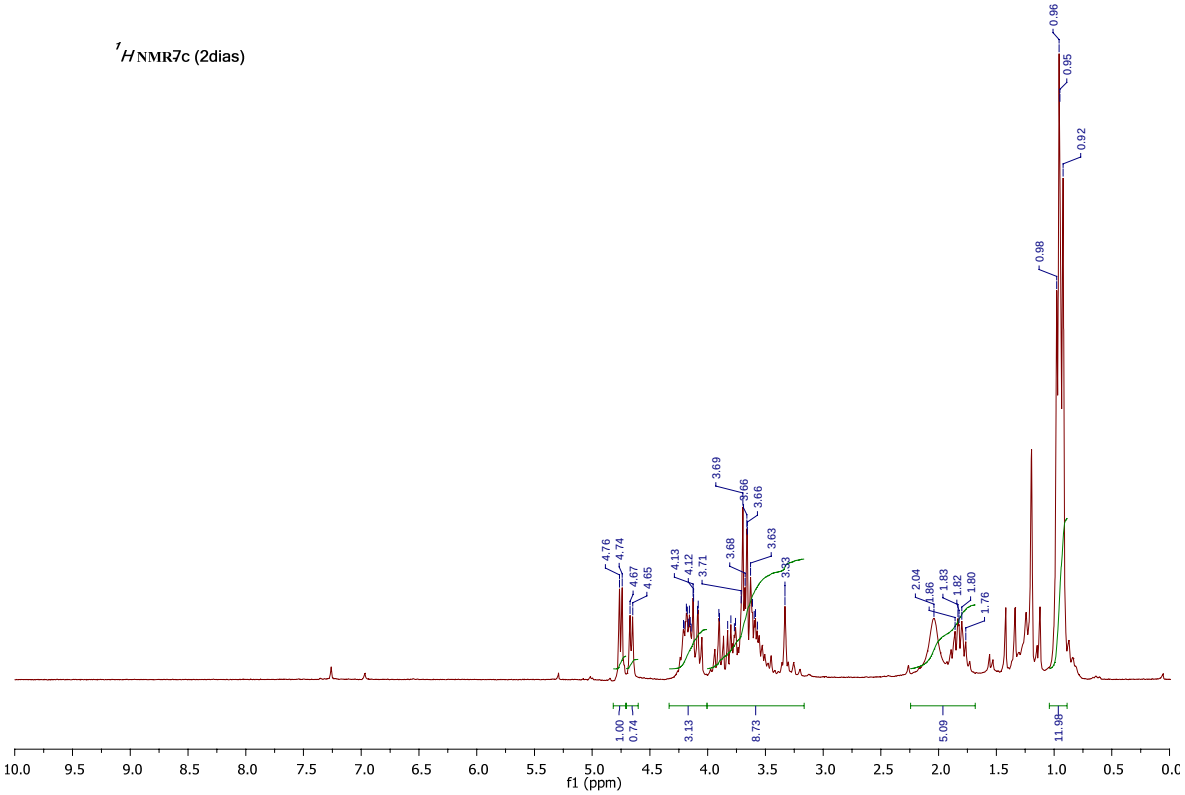
^{1}H NMR-6b



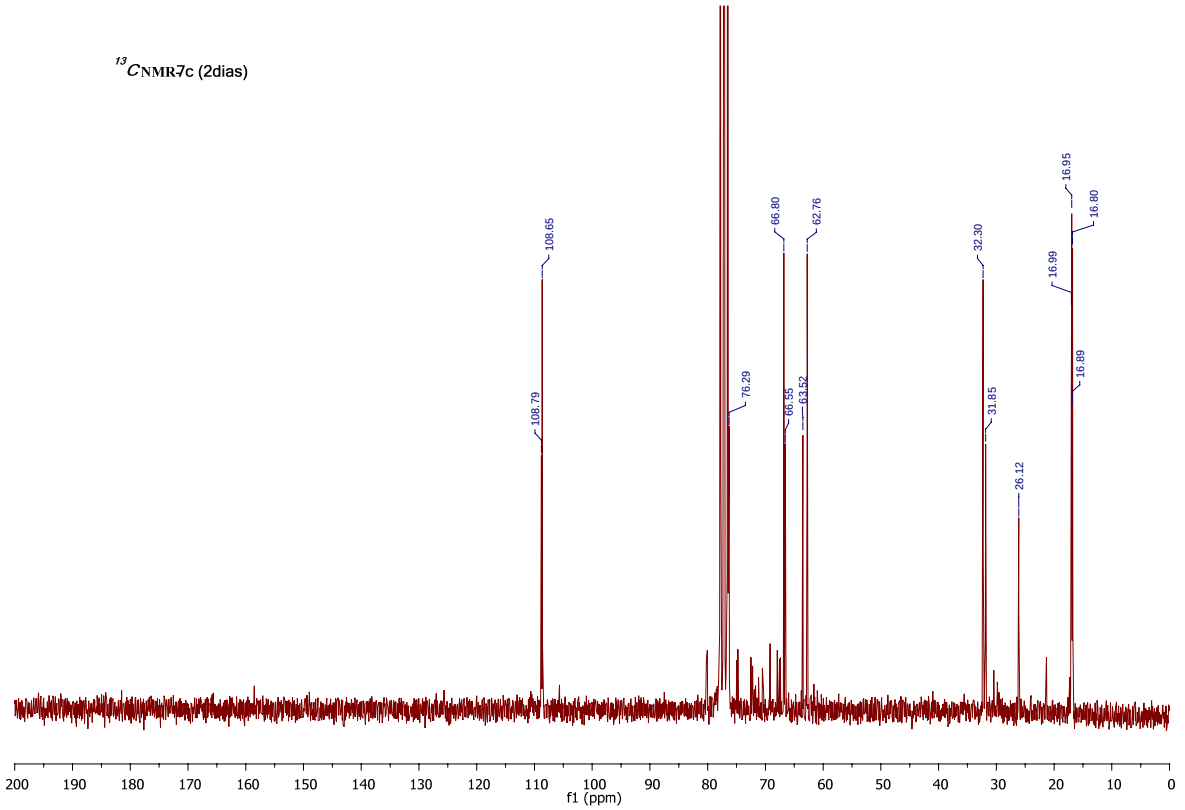
^{13}C NMR-6b



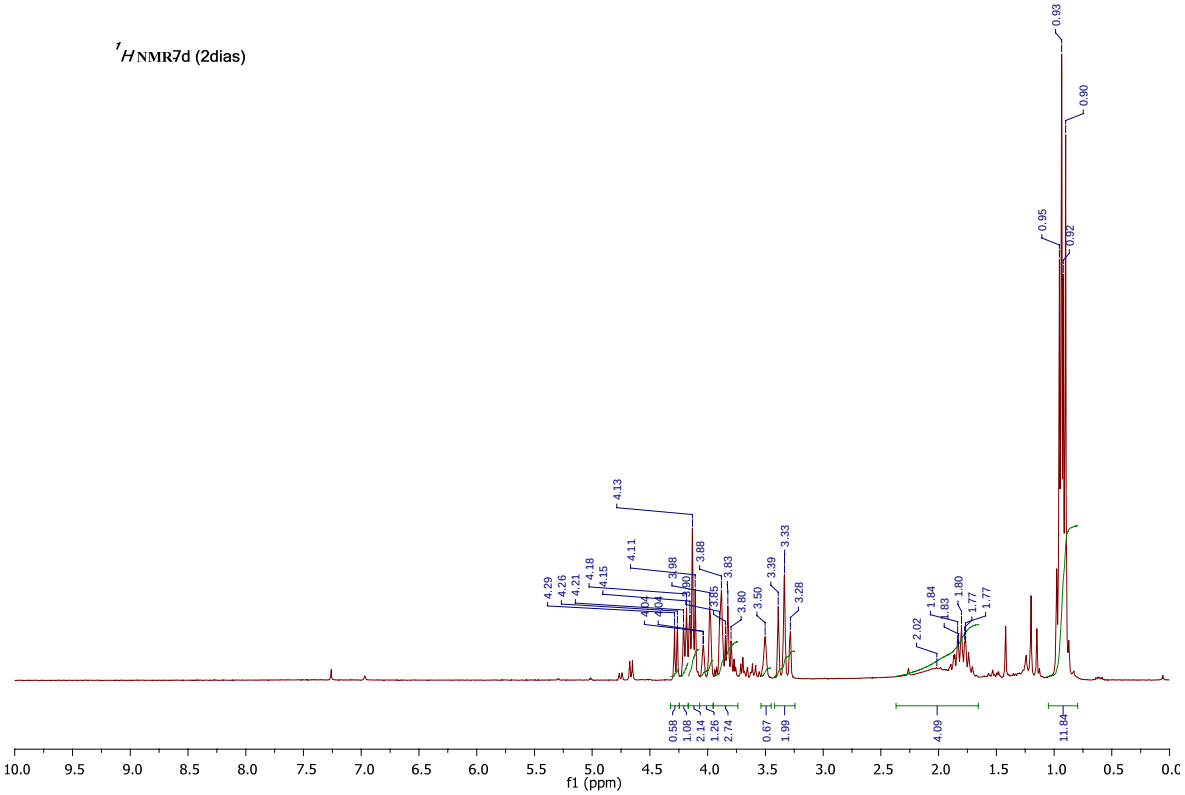
^{1}H NMR7c (2dias)



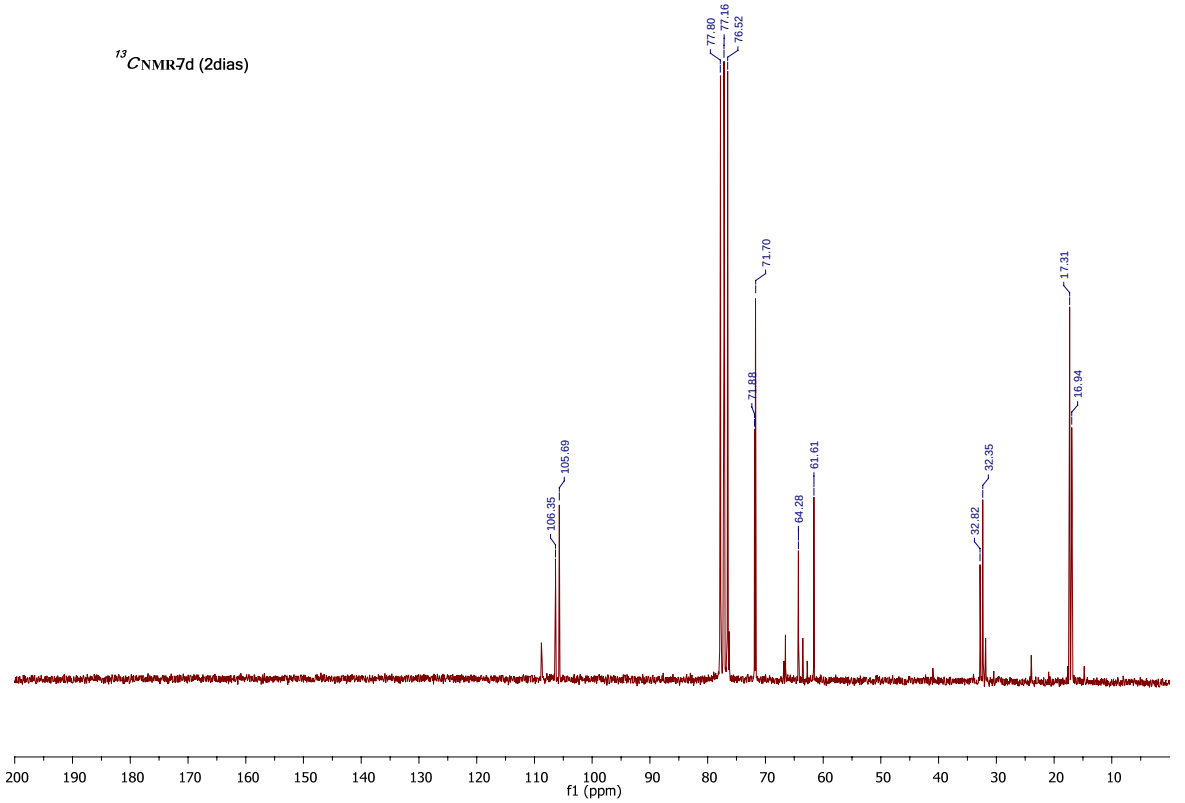
^{13}C NMR7c (2dias)



^{1}H NMR7d (2dias)



^{13}C NMR7d (2dias)



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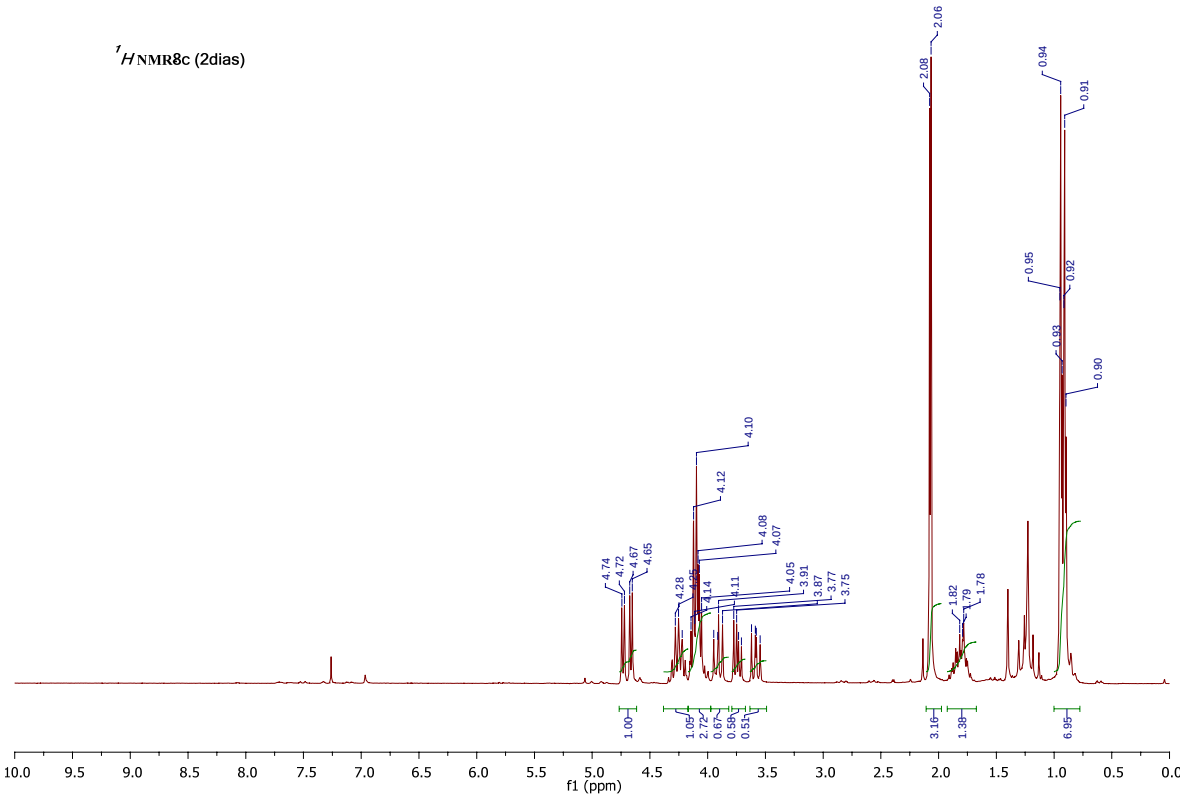
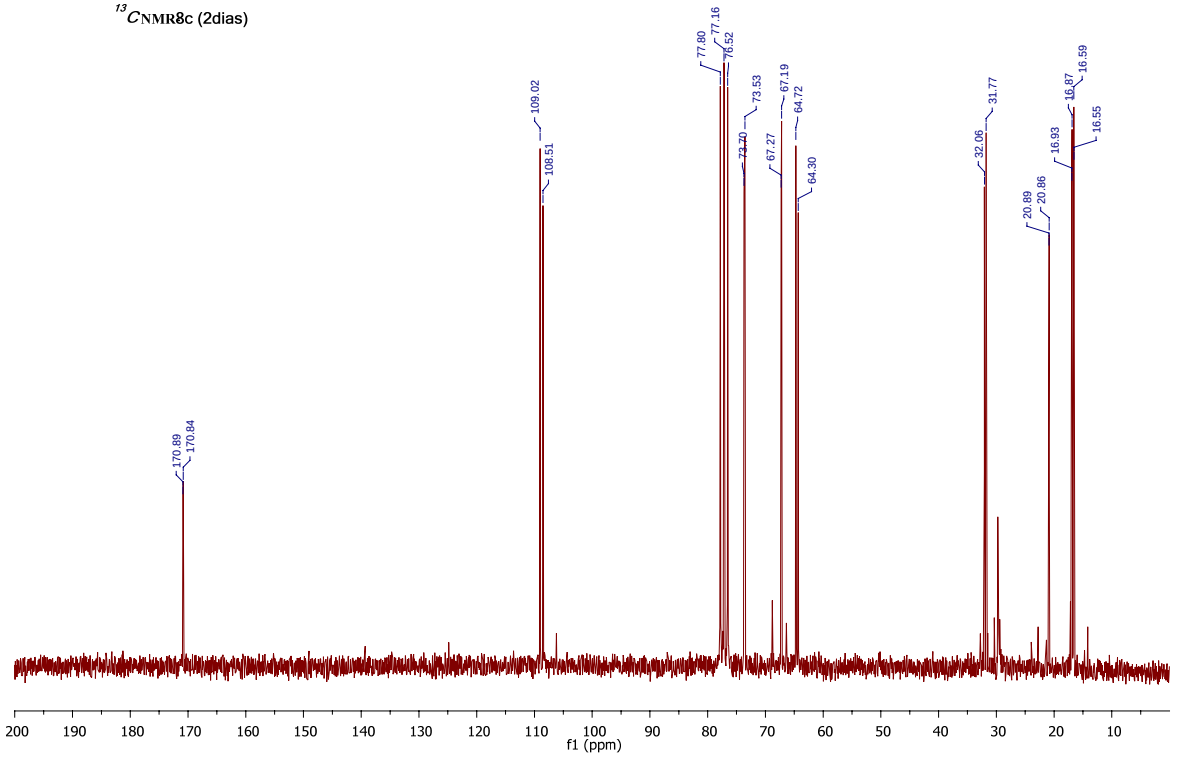
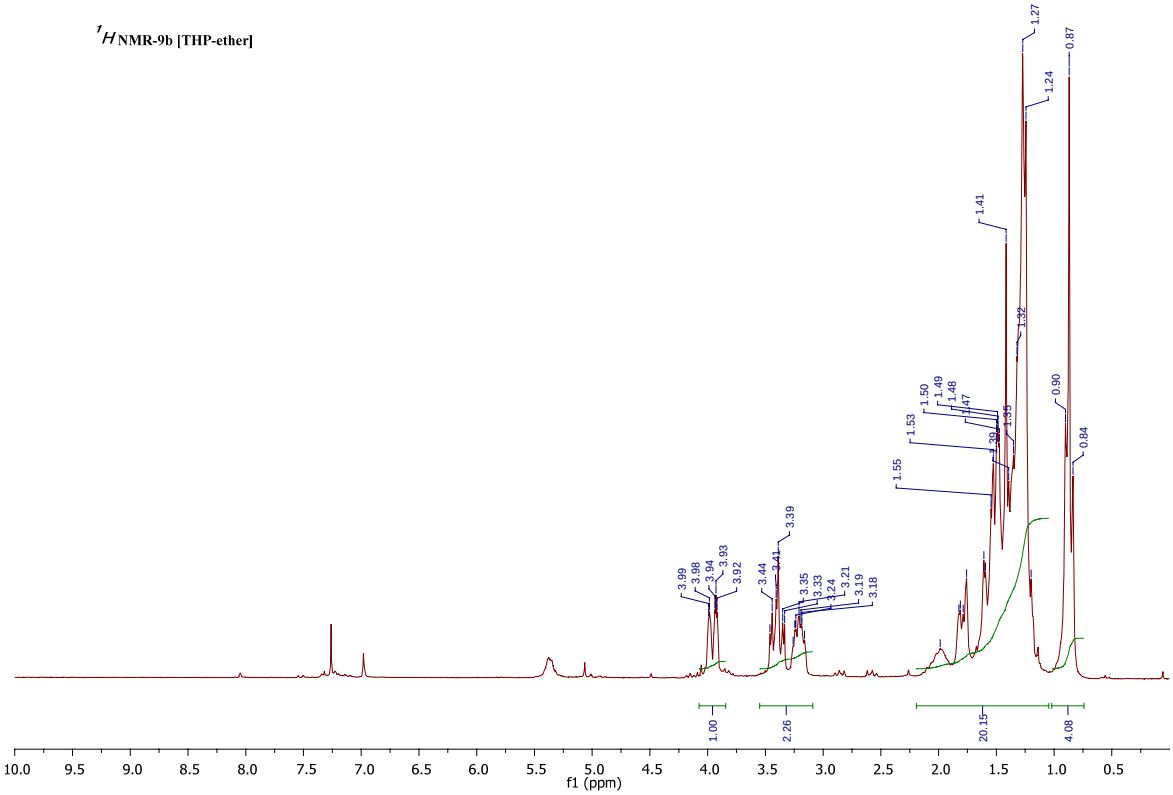


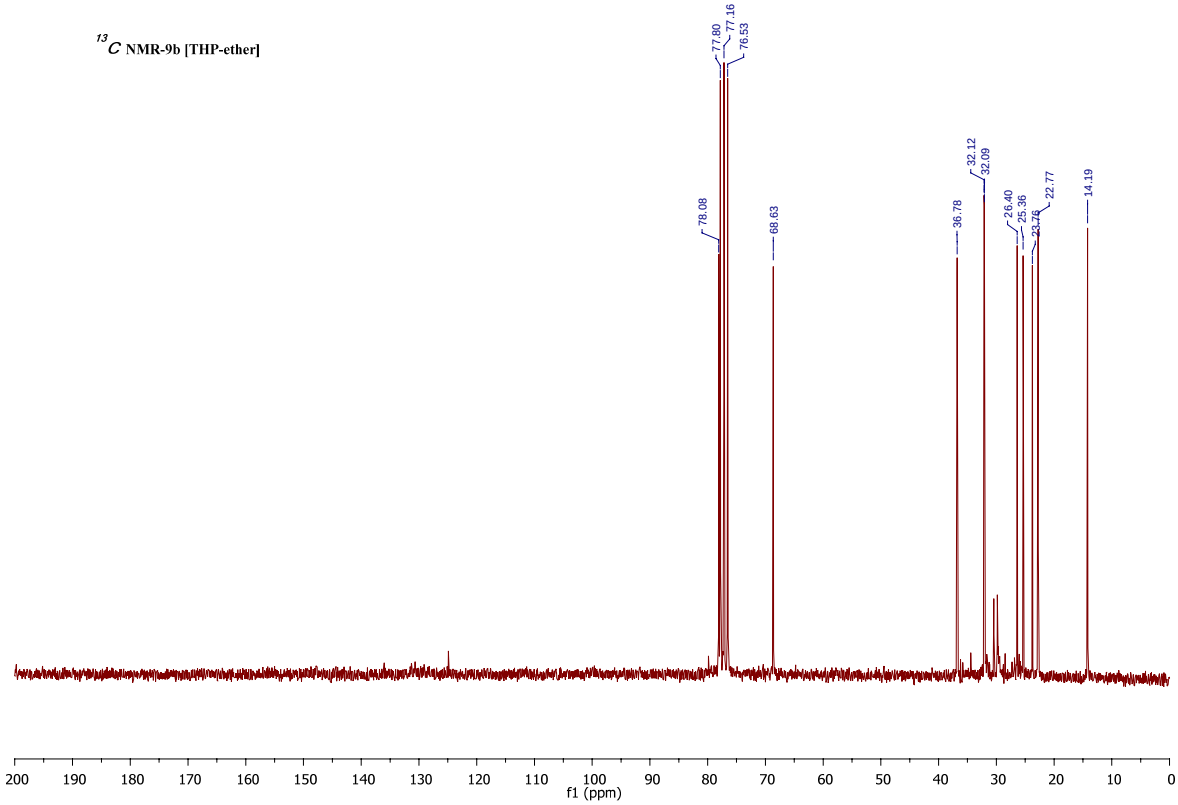
^{13}C NMR8c (2dias)



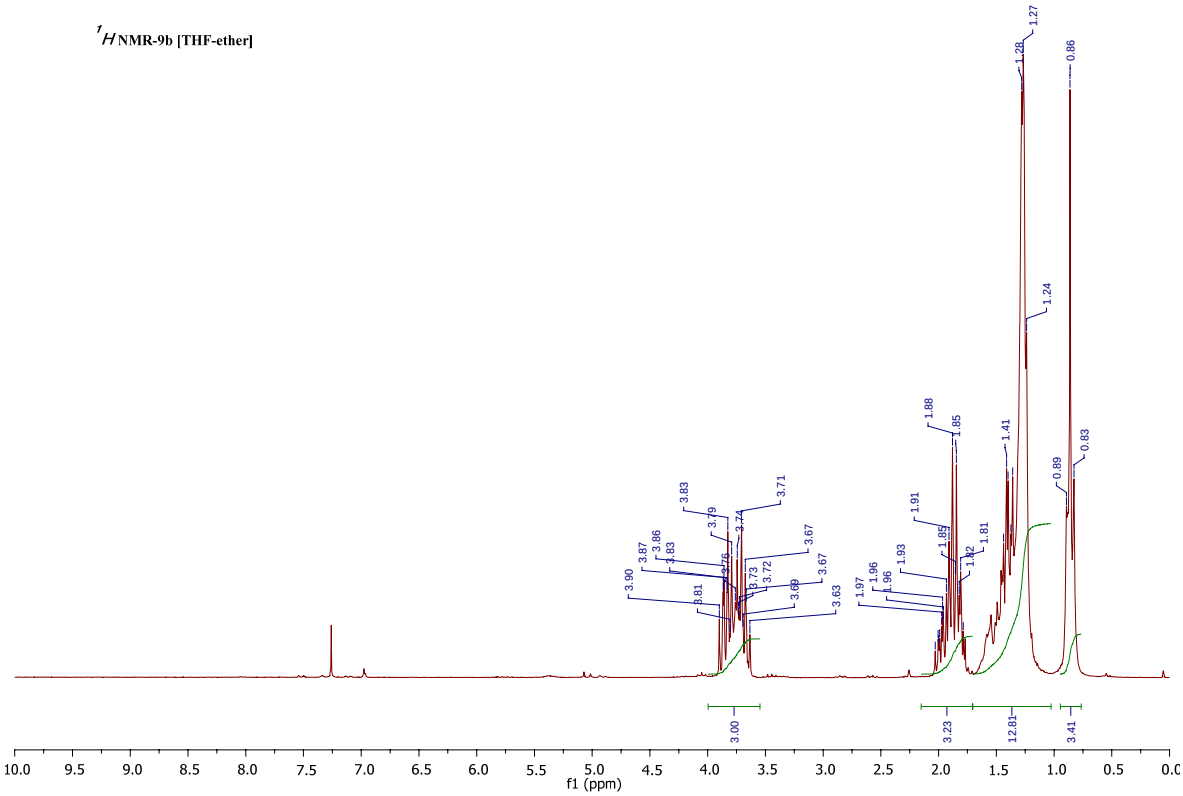
^{1}H NMR-9b [THP-ether]



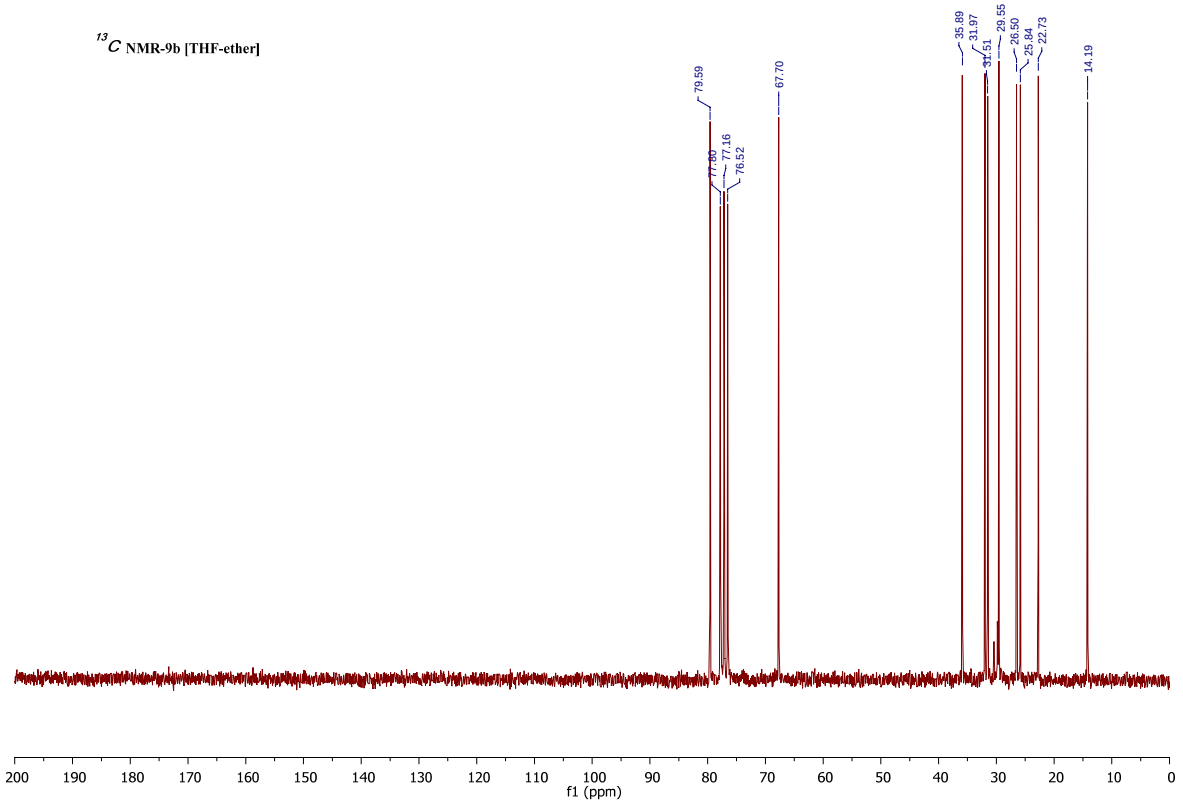
^{13}C NMR-9b [THP-ether]



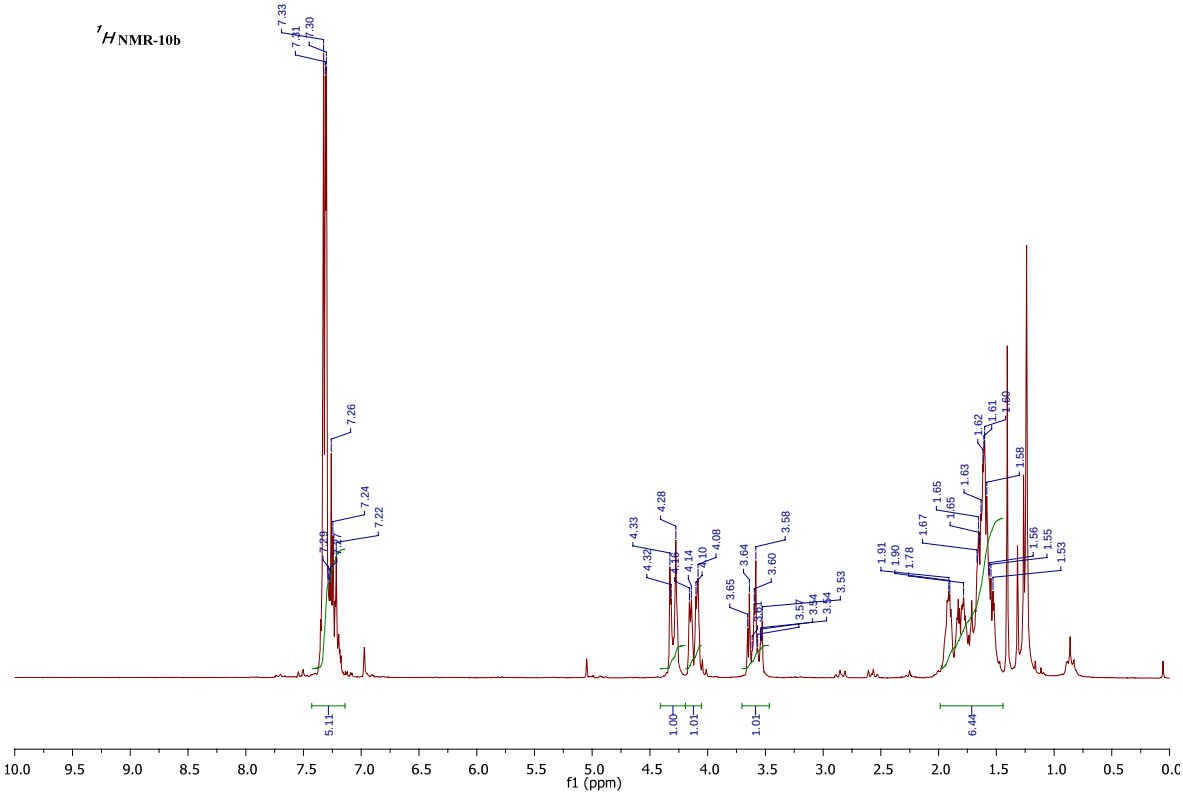
^{1}H NMR-9b [THF-ether]



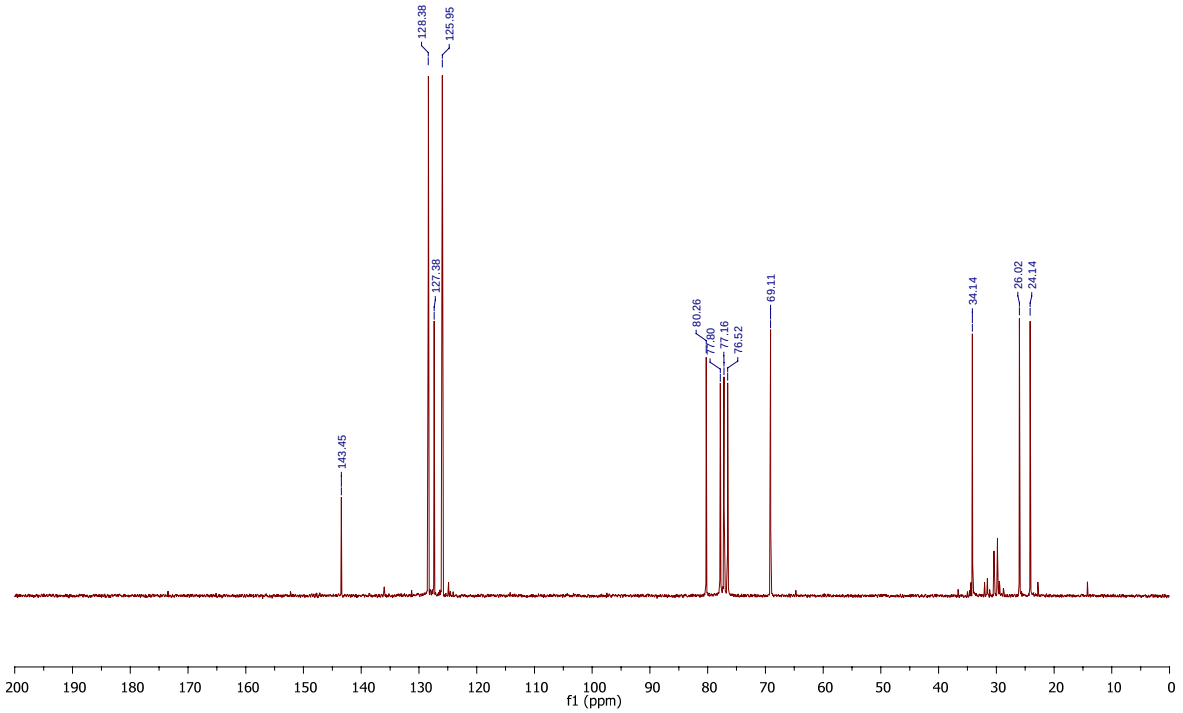
^{13}C NMR-9b [THF-ether]



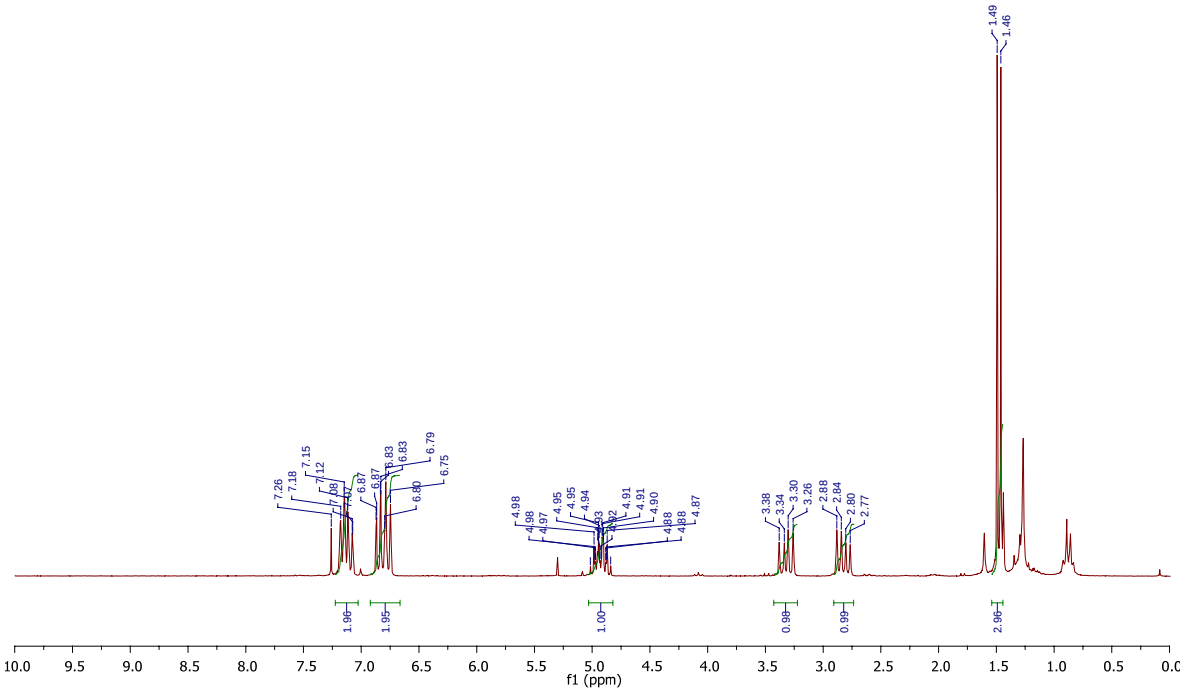
^{1}H NMR-10b



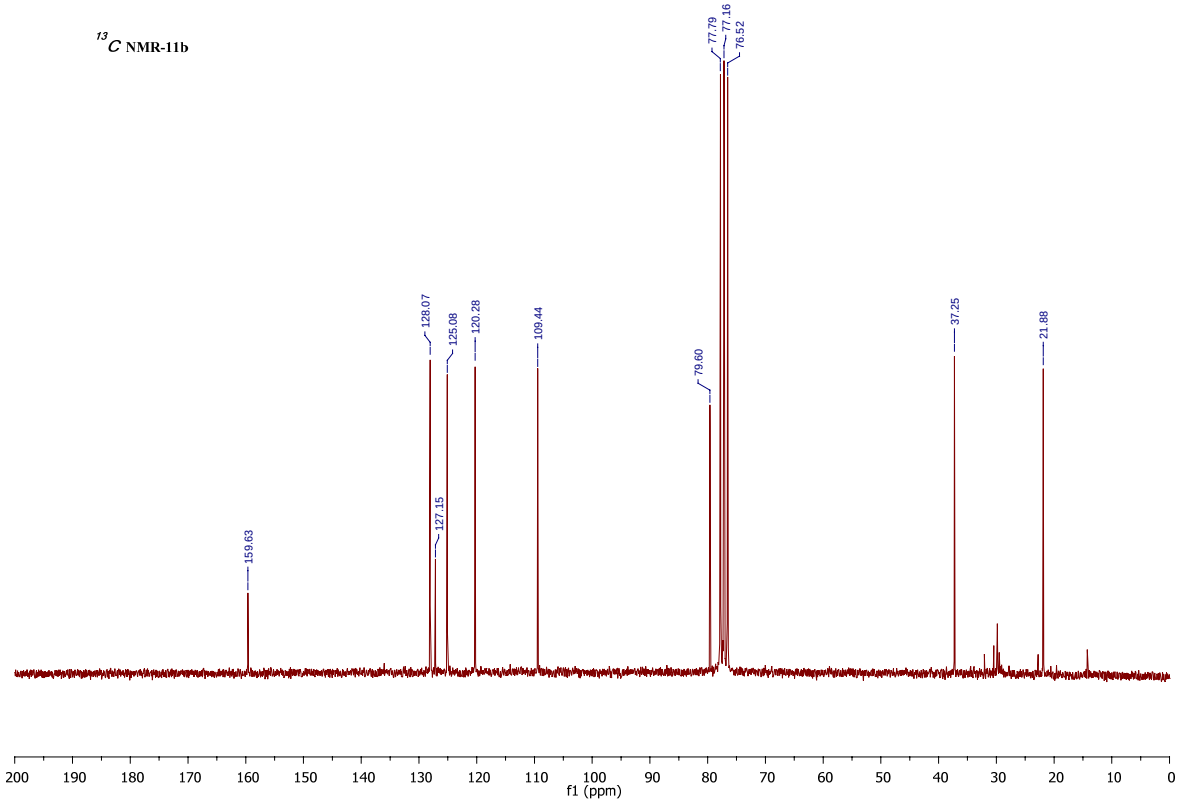
^{13}C NMR-10b



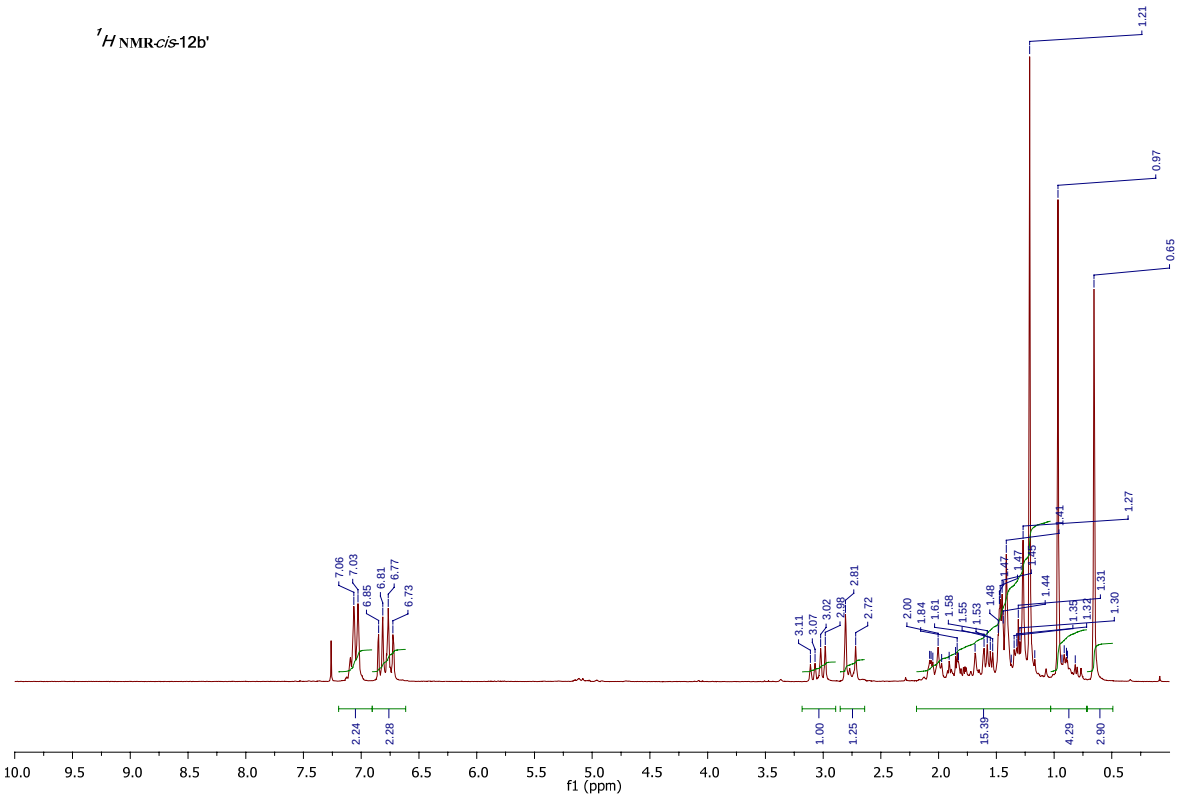
^{1}H NMR-11b



^{13}C NMR-11b



^{1}H NMR-*cis*-12b'



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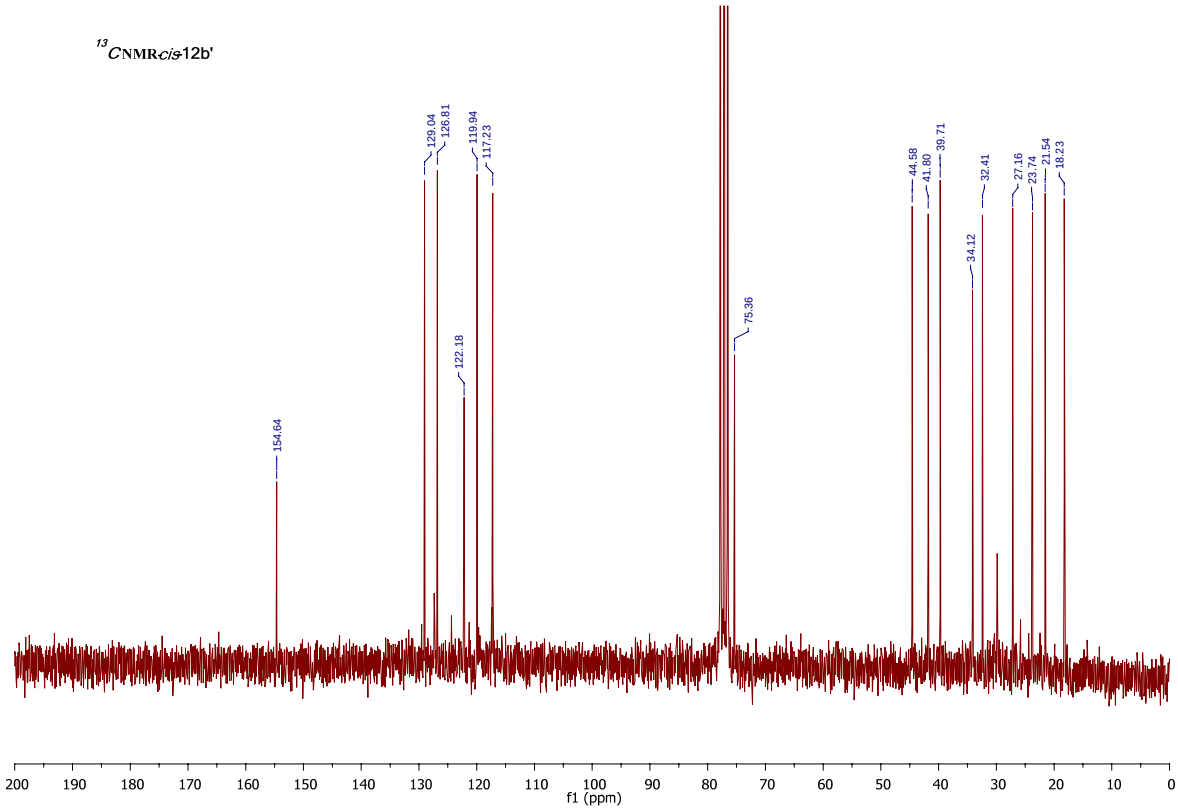
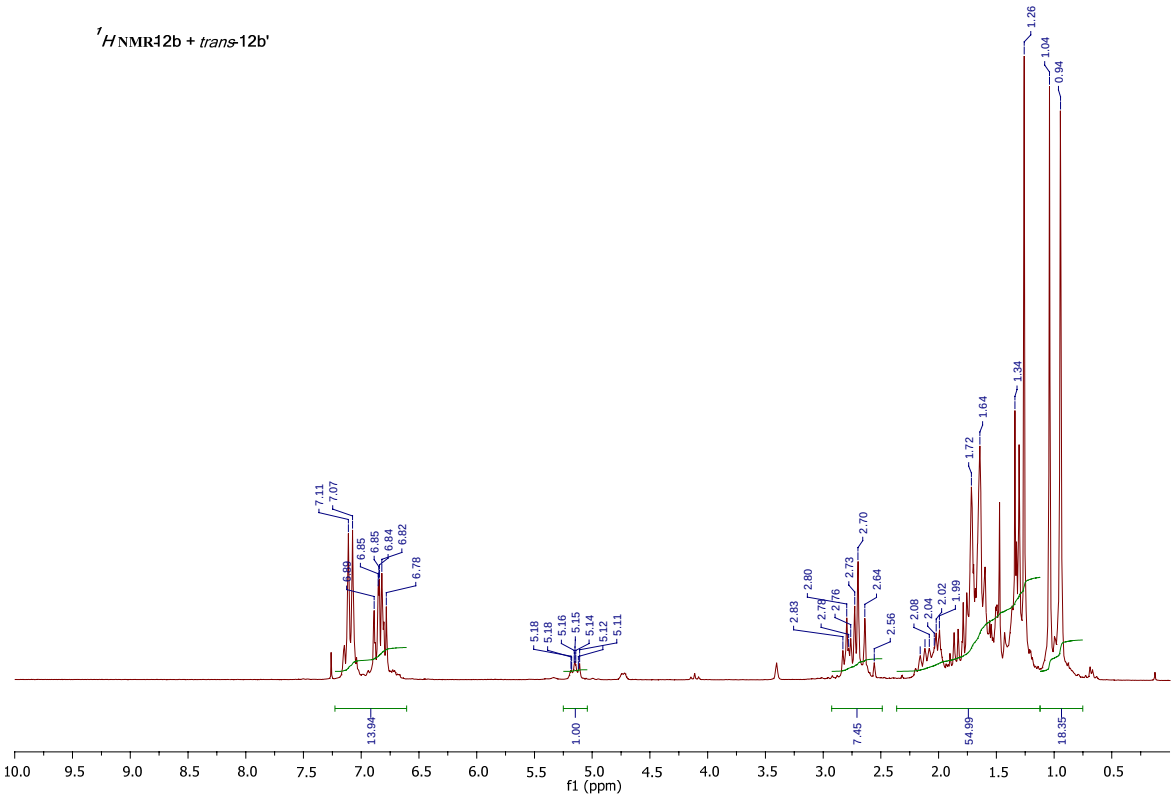
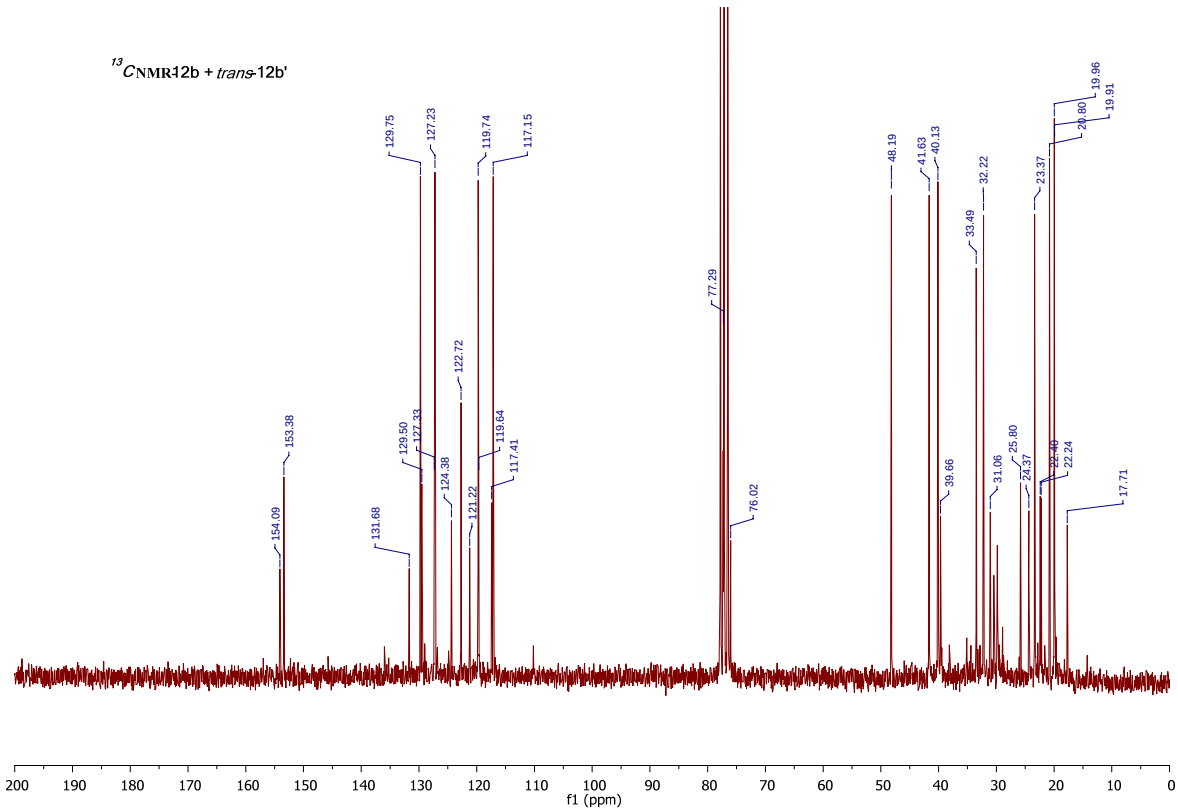
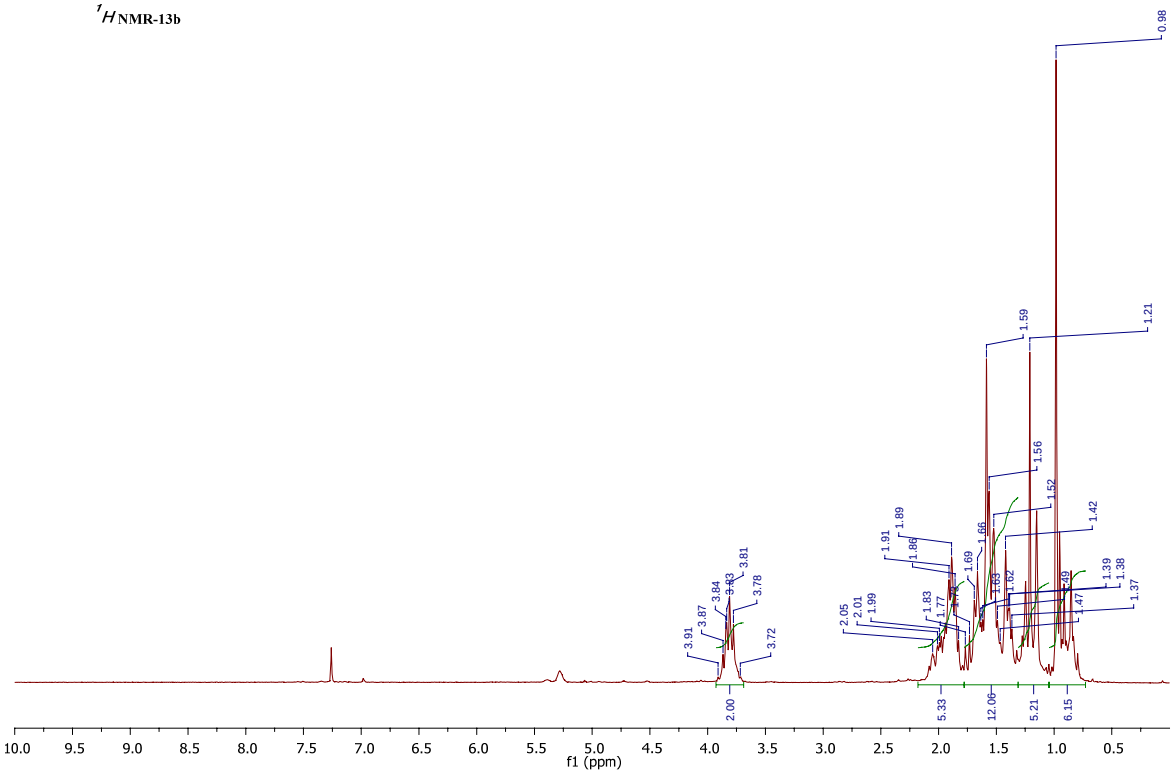


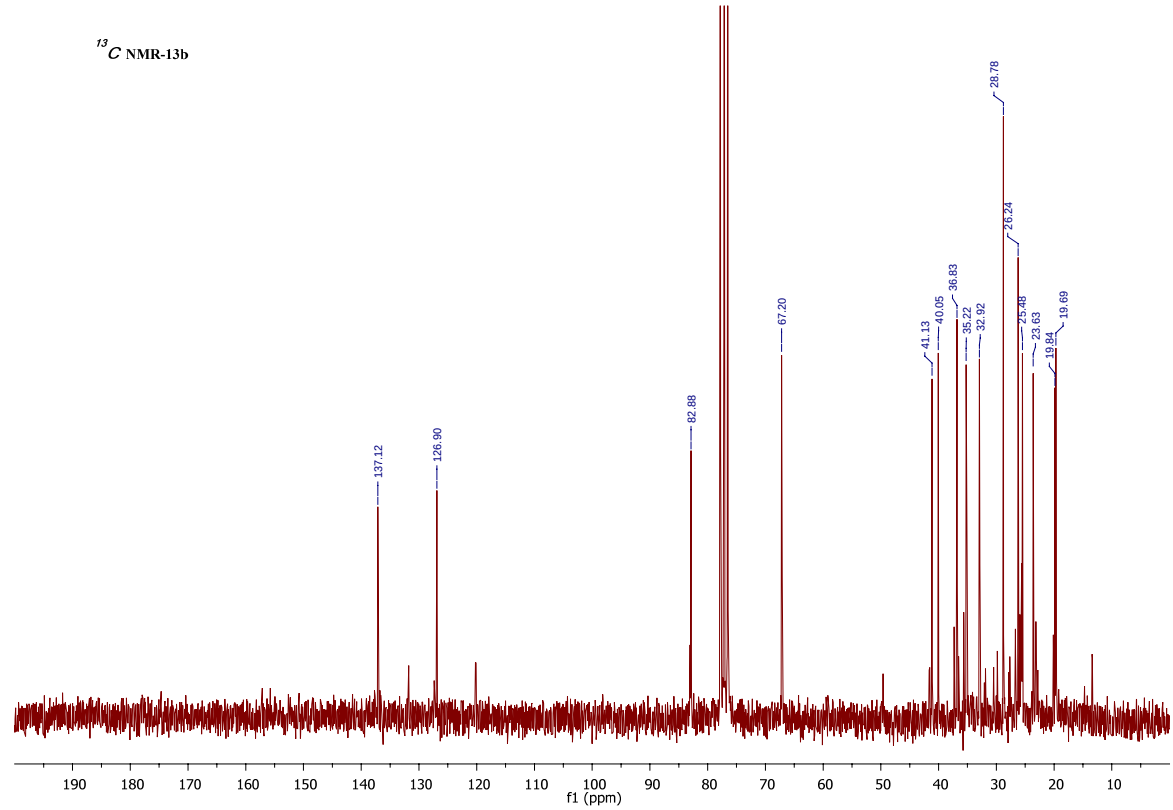

1H NMR 12b + trans-12b'
7.11
7.07
6.86
6.85
6.84
6.82
6.80
6.78
5.18
5.18
5.16
5.15
5.14
5.12
5.11
2.83
2.80
2.79
2.76
2.73
2.70
2.64
2.56
2.08
2.04
2.02
1.99
1.72
1.64
1.34
1.26
1.04
0.94
13.94
1.00
7.45
54.99
18.35
f1 (ppm)


13C NMR 12b + trans-12b'
153.38
154.09
131.68
129.75
129.50
127.33
127.23
124.38
122.72
121.22
119.74
119.64
117.41
117.15
77.29
76.02
48.19
41.63
40.13
39.66
33.49
32.22
31.06
25.80
24.37
23.37
22.48
22.24
20.80
19.96
19.91
17.71
f1 (ppm)

^{1}H NMR-13b



^{13}C NMR-13b



1. **X. Mao, C. Fan, X. Zhang, Y. Wang, Y. Wang and G. Ding, *Crystal Research and Technology*, 2013, 48, 496.**