

## Supporting Information

### From 2- to 3-Substituted Ferrocene Carboxamides or How to Apply Halogen ‘dance’ to the Ferrocene Series

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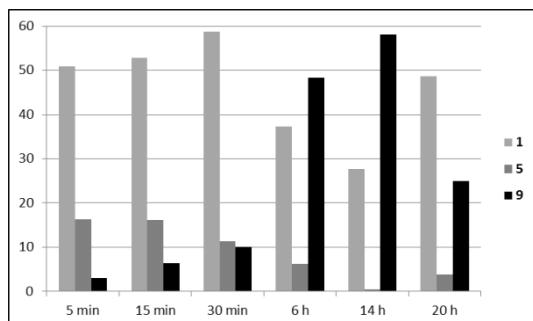
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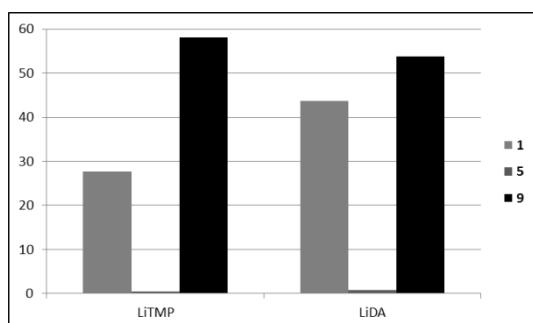
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## Optimization of the halogen ‘dance’ reaction

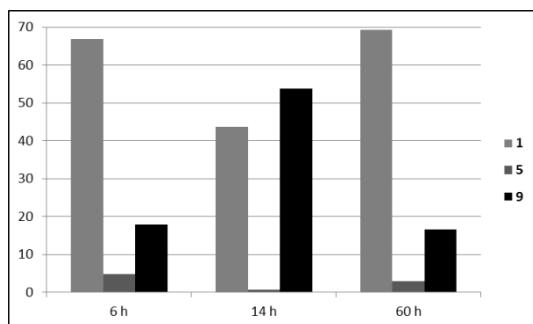
**Table A. Optimization of the halogen ‘dance’ reaction time from 5 using LiTMP (1.1 equiv) in THF at -50 °C.**



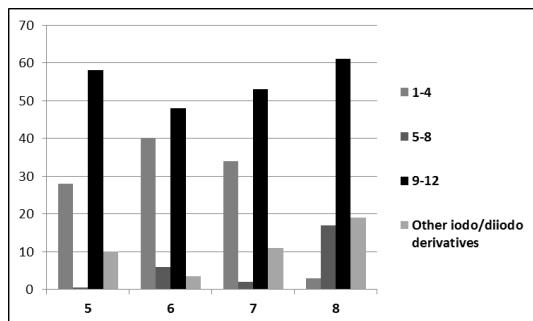
**Table B. Optimization of the halogen ‘dance’ base from 5 using LiTMP or LiDA (1.1 equiv) in THF at -50 °C for 14 h.**



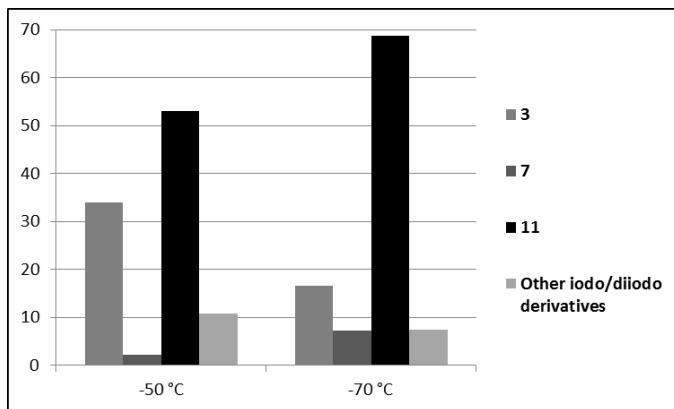
**Table C. Optimization of the halogen ‘dance’ reaction time using LiDA (1.1 equiv) in THF at -50 °C.**



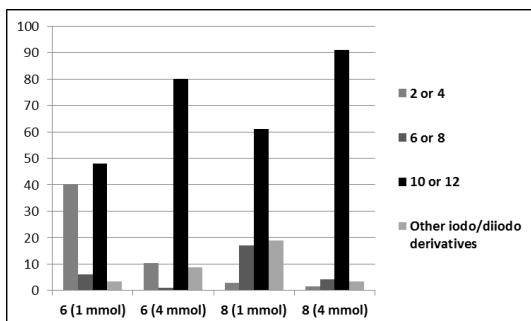
**Table D. Optimized halogen ‘dance’ reaction conditions applied to the different 2-iodoferrocene-carboxamides 5-8.**



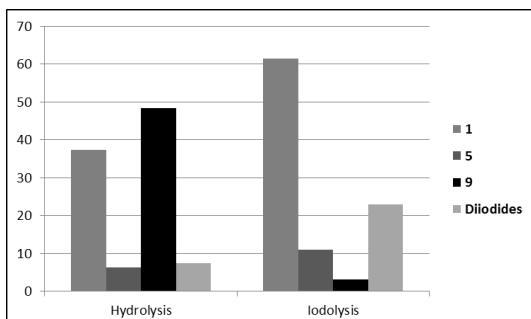
**Table E. Optimization of the halogen ‘dance’ temperature from 7 using LiTMP (1.1 equiv) in THF for 14 h.**



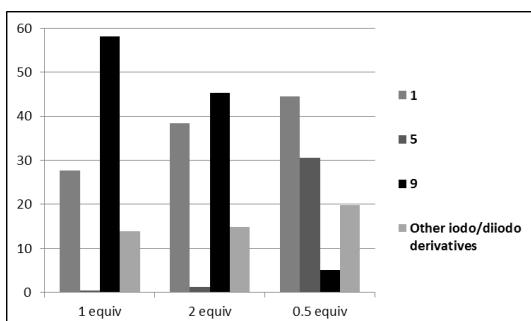
**Table F. Halogen ‘dance’ reaction at 1.0 and 4.0 mmol scale from the 2-iodoferrocenecarboxamides 6 and 8.**



**Table G. Halogen ‘dance’ reaction from 5 using LiTMP in THF at -50 °C for 6 h before hydrolysis or iodolysis.**



**Table H. Optimization of the halogen ‘dance’ amount of base from 5 using LiTMP in THF at -50 °C for 14 h.**



## Experimental data on the compounds 1-4 and 6

**N,N-Diisopropylferrocenecarboxamide (1).** The general procedure 2 using diisopropylamine (8.5 mL) gave **1** (eluent: heptane-AcOEt 80:20;  $R_f = 0.33$ ) in 94% yield as an orange powder: mp 74 °C; IR (ATR): 806, 824, 1026, 1042, 1369, 1463, 1473, 1627, 2972, 3085 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) δ 1.20 (br s, 6H, CH<sub>3</sub>), 1.46 (br s, 6H, CH<sub>3</sub>), 3.41 (br s, 1H, CHMe<sub>2</sub>), 4.21 (s, 5H, Cp-H), 4.25 (t, 2H,  $J = 1.9$  Hz, Cp-H), 4.54 (t, 2H,  $J = 1.9$  Hz, Cp-H), 4.59 (br s, 1H, CHMe<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, 303 K) δ 1.28 (br s, 12H, CH<sub>3</sub>), 3.49 (br s, 1H, CHMe<sub>2</sub>), 4.23 (s, 5H, Cp-H), 4.33 (br s, 2H, Cp-H), 4.48 (br s, 2H, Cp-H), 4.65 (br s, 1H, CHMe<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, 383 K) δ 1.31 (d, 12H,  $J = 6.7$  Hz, CH<sub>3</sub>), 4.04 (sept, 2H,  $J = 6.9$  Hz, CHMe<sub>2</sub>), 4.23 (s, 5H, Cp-H), 4.31 (br s, 2H, Cp-H), 4.51 (br s, 2H, Cp-H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) δ 21.3 (4CH<sub>3</sub>), 46.3 (CHMe<sub>2</sub>), 49.6 (CHMe<sub>2</sub>), 68.9 (2CH), 69.8 (5CH), 70.0 (2CH), 81.3 (C-C=O), 169.4 (C=O). The spectral data were found similar to those already reported.<sup>1</sup>

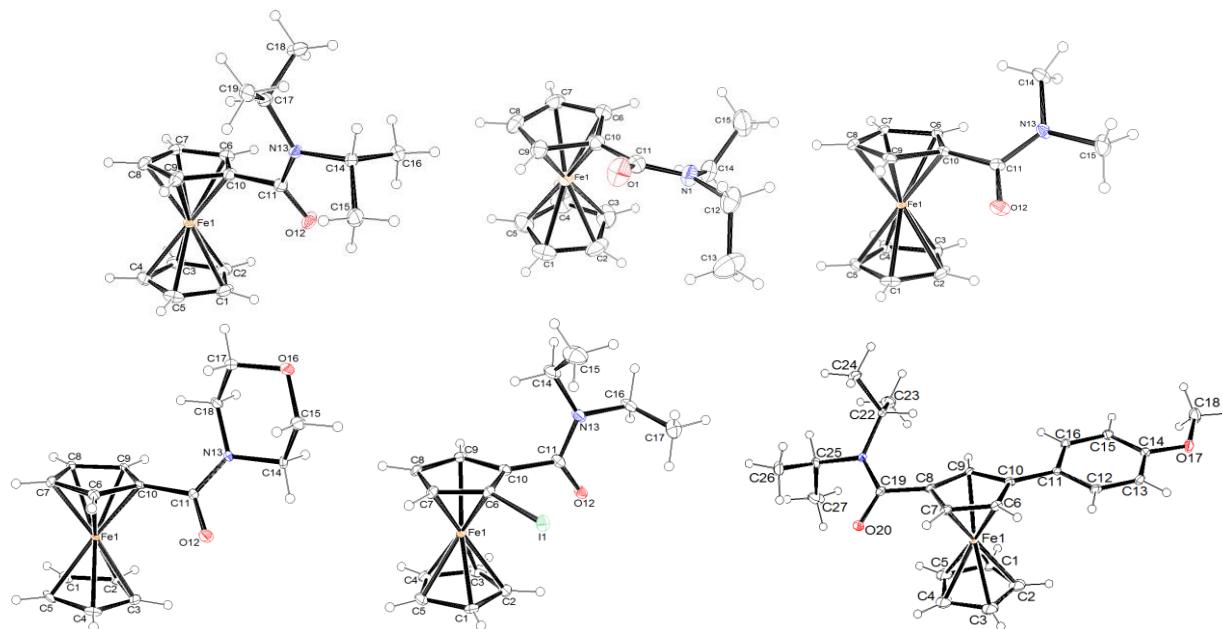
**N,N-Diethylferrocenecarboxamide (2).** The general procedure 1 using ClCONEt<sub>2</sub> (1.6 mL, 7.5 mmol) gave **2** (eluent: heptane-AcOEt 90:10;  $R_f = 0.09$ ) in 86.5% yield as an orange powder: mp 68 °C (lit.<sup>2</sup> 66-67 °C); IR (ATR): 761, 818, 1001, 1106, 1115, 1280, 1378, 1413, 1451, 1462, 1481, 1607, 2932, 2971 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) δ 1.17 (t, 6H,  $J = 6.4$  Hz, CH<sub>3</sub>), 3.46 (br s, 4H, CH<sub>2</sub>), 4.17 (s, 5H, Cp-H), 4.25 (t, 2H,  $J = 2.0$  Hz, Cp-H), 4.57 (t, 2H,  $J = 2.0$  Hz, Cp-H). These data correspond to those already published.<sup>2</sup> <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) δ 12.9 (CH<sub>3</sub>), 14.8 (CH<sub>3</sub>), 40.9 (CH<sub>2</sub>), 42.6 (CH<sub>2</sub>), 69.3 (2CH), 69.7 (5CH), 70.3 (2CH), 78.9 (C-C=O), 169.5 (C=O).

**N,N-Dimethylferrocenecarboxamide (3).** The general procedure 1 using ClCONMe<sub>2</sub> (1.2 mL, 12.5 mmol) gave **3** (eluent: heptane-AcOEt 70:30;  $R_f = 0.12$ ) in 77% yield as an orange powder: mp 112-113 °C (lit.<sup>3</sup> 114-115 °C); IR (ATR): 682, 763, 818, 845, 861, 940, 1000, 1035, 1062, 1103, 1230, 1264, 1390, 1455, 1501, 1611, 2922, 3081 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 291 K) δ 3.09 (br s, 6H, CH<sub>3</sub>), 4.20 (s, 5H, Cp-H), 4.28 (t, 2H,  $J = 1.9$  Hz, Cp-H), 4.60 (t, 2H,  $J = 1.9$  Hz, Cp-H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 291 K) δ 36.8 (CH<sub>3</sub>), 38.8 (CH<sub>3</sub>), 69.4 (2CH), 69.9 (5CH), 70.7 (2CH), 78.6 (C-C=O), 170.9 (C=O). These data correspond to those already published.<sup>4</sup>

**(4-Morpholinocarbonyl)ferrocene (4).** The general procedure 1 using 4-morpholinocarbonyl chloride (1.75 mL, 7.5 mmol) gave **4** (eluent: heptane-AcOEt 70:30;  $R_f = 0.12$ ) in 76% yield as a yellowish powder: mp 126 °C (lit.<sup>2</sup> 127-128 °C); IR (ATR): 674, 757, 825, 911, 941, 1001, 1021, 1047, 1063, 1106, 1175, 1254, 1281, 1301, 1411, 1473, 1615, 2050, 2971 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 291 K) δ 3.66-3.69 (m, 4H, CH<sub>2</sub>), 3.72-3.75 (m, 4H, CH<sub>2</sub>), 4.24 (s, 5H, Cp-H), 4.31 (t, 2H,  $J = 1.9$  Hz, Cp-H), 4.54 (t, 2H,  $J = 1.9$  Hz, Cp-H). These data correspond to those already published.<sup>2</sup> <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 291 K) δ 45.5 (br s, 2CH<sub>2</sub>), 67.0 (2CH<sub>2</sub>), 69.3 (2CH), 69.9 (5CH), 70.3 (2CH), 78.4 (C-C=O), 169.8 (C=O). The <sup>13</sup>C NMR data are similar to those reported previously.<sup>5</sup>

**N,N-Diethyl-2-iodoferrocenecarboxamide (6, racemic mixture).** As already shown,<sup>6</sup> the general procedure 3 using *N,N*-diethylferrocenecarboxamide (**2**, 0.855 g) gave **6** (eluent: heptane-AcOEt 90:10;  $R_f = 0.55$ ) in 88% yield as an orange powder: mp 57 °C; IR (ATR): 688, 808, 1003, 1360, 1442, 1476, 1612, 2966, 3109 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 291 K) δ 0.98 (br t, 3H, CH<sub>3</sub>), 1.21 (br t, 3H, CH<sub>3</sub>), 3.09 (br q, 2H,  $J = 6.4$  Hz, CH<sub>2</sub>), 3.23 (br q, 1H,  $J = 6.4$  Hz, CH<sub>2</sub>), 3.72 (br q, 1H,  $J = 6.3$  Hz, CH<sub>2</sub>), 4.20 (t, 1H,  $J = 2.5$  Hz, Cp-H), 4.34 (s, 5H, Cp), 4.35 (dd, 1H,  $J = 2.6$  and 1.4 Hz, Cp-H), 4.45 (dd, 1H,  $J = 2.4$  and 1.3 Hz, Cp-H); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) δ 0.96 (br s, 3H, CH<sub>3</sub>), 1.19 (br s, 3H, CH<sub>3</sub>), 3.07 (br s, 2H, CH<sub>2</sub>), 3.21 (br s, 1H, CH<sub>2</sub>), 3.69 (br s, 1H, CH<sub>2</sub>), 4.18 (t, 1H,  $J = 2.45$  Hz, Cp-H), 4.32 (s, 5H, Cp-H), 4.33 (br s, 1H, Cp-H), 4.43 (br s, 1H, Cp-H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) δ 13.05 (CH<sub>3</sub>), 14.3 (CH<sub>3</sub>), 39.7 (CH<sub>2</sub>), 41.1 (C-I), 43.1 (CH<sub>2</sub>), 67.8 (CH), 68.1 (CH), 72.9 (5CH, Cp), 74.1 (CH), 89.7 (C-C=O), 167.0 (C=O). These data correspond to those reported previously.<sup>6</sup> It is worth mentioning that the <sup>1</sup>H NMR spectrum recorded in C<sub>6</sub>D<sub>6</sub> at 340 K shows only one signal for the six protons of the methyl groups and one signal for each CH<sub>2</sub>.<sup>6</sup>

## X-ray diffraction data for the compounds 1-4, 6 and 13



**Figure 1.** ORTEP diagrams (30% probability level) of the ferrocenecarboxamides 1 ( $C^6\text{-}C^{10}\text{-}C^{11}\text{-}O^{12}$  torsion angle:  $-66.62^\circ$ ), 2 ( $C^9\text{-}C^{10}\text{-}C^{11}\text{-}O^1$ :  $-22.90^\circ$ ), 3 ( $C^9\text{-}C^{10}\text{-}C^{11}\text{-}O^{12}$ :  $36.07^\circ$ ), 4 ( $C^6\text{-}C^{10}\text{-}C^{11}\text{-}O^{12}$ :  $46.24^\circ$ ), 6 ( $C^9\text{-}C^{10}\text{-}C^{11}\text{-}O^{12}$ :  $-91.57^\circ$ ) and 13.

**Crystal data for *N,N*-diisopropylferrocenecarboxamide (1).** The obtained crystal structure was found to be similar to that described (CCDC 1298115; XUXKUW).<sup>7</sup>

**Crystal data for *N,N*-diethylferrocenecarboxamide (2).**  $C_{15}H_{19}FeNO$ ,  $M = 285.16$ ,  $T = 293(2)$  K, orthorhombic,  $P 2_1 2_1 2_1$ ,  $a = 7.5270(11)$ ,  $b = 9.3585(12)$ ,  $c = 19.310(3)$  Å,  $V = 1360.2(3)$  Å $^3$ ,  $Z = 4$ ,  $d = 1.392$  g cm $^{-3}$ ,  $\mu = 1.096$  mm $^{-1}$ . A final refinement on  $F^2$  with 3106 unique intensities and 167 parameters converged at  $\omega R(F^2) = 0.0888$  ( $R(F) = 0.0357$ ) for 2923 observed reflections with  $I > 2\sigma(I)$ . CCDC 1565036.

**Crystal data for *N,N*-dimethylferrocenecarboxamide (3).**  $C_{13}H_{15}FeNO$ ,  $M = 257.11$ ,  $T = 150(2)$  K, orthorhombic,  $P n a 2_1$ ,  $a = 22.0483(8)$ ,  $b = 17.3768(6)$ ,  $c = 5.8961(2)$  Å,  $V = 2258.97(14)$  Å $^3$ ,  $Z = 8$ ,  $d = 1.512$  g cm $^{-3}$ ,  $\mu = 1.311$  mm $^{-1}$ . A final refinement on  $F^2$  with 4979 unique intensities and 293 parameters converged at  $\omega R(F^2) = 0.0497$  ( $R(F) = 0.0228$ ) for 4638 observed reflections with  $I > 2\sigma(I)$ . CCDC 1565037. These structural data were found close to those already described (CCDC 1298114; XUXKOQ).<sup>7</sup>

**Crystal data for (4-morpholinocarbonyl)ferrocene (4).**  $C_{15}H_{17}FeNO_2$ ,  $M = 299.14$ ,  $T = 150(2)$  K, monoclinic,  $P 2_1$ ,  $a = 5.7178(8)$ ,  $b = 9.4557(13)$ ,  $c = 12.0419(15)$  Å,  $\beta = 92.803(5)$  °,  $V = 650.28(15)$  Å $^3$ ,  $Z = 2$ ,  $d = 1.528$  g cm $^{-3}$ ,  $\mu = 1.156$  mm $^{-1}$ . A final refinement on  $F^2$  with 2919 unique intensities and 173 parameters converged at  $\omega R(F^2) = 0.0653$  ( $R(F) = 0.0246$ ) for 2871 observed reflections with  $I > 2\sigma(I)$ . CCDC 1565038. Note that a similar structure to compound 4 was reported in 2005.<sup>8</sup>

**Crystal data for *N,N*-diethyl-2-iodoferrocenecarboxamide (6, racemic mixture).**  $C_{15}H_{18}FeINO$ ,  $M = 411.05$ ,  $T = 150(2)$  K, monoclinic,  $P 2_1/c$ ,  $a = 11.0250(14)$ ,  $b = 13.6395(16)$ ,  $c = 11.4498(14)$  Å,  $\beta = 117.212(4)$  °,  $V = 1531.2(3)$  Å $^3$ ,  $Z = 4$ ,  $d = 1.783$  g cm $^{-3}$ ,  $\mu = 2.993$  mm $^{-1}$ . A final refinement on  $F^2$  with 3561 unique intensities and 175 parameters converged at  $\omega R(F^2) = 0.0790$  ( $R(F) = 0.0297$ ) for 3105 observed reflections with  $I > 2\sigma(I)$ . CCDC 1565039.

## NMR tables for ferrocene, iodoferrocene and the compounds 1-9

**Table SI-1. Selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR data ( $\delta$ ) of 1-4 in  $\text{CDCl}_3$ .**

Compound	$\text{H}^\alpha$	$\text{H}^\beta$	$\text{H}^{\text{Cp}}$	$\text{C}^{\text{ipso}}$	$\text{C}^\alpha$	$\text{C}^\beta$	$\text{C}^{\text{Cp}}$
<b>1</b>	4.54	4.27	4.21	81.3	70.0	68.9	69.8
<b>2</b>	4.57	4.25	4.17	78.9	70.3	69.3	69.7
<b>3</b>	4.60	4.28	4.20	78.6	70.7	69.4	69.9
<b>4</b>	4.54	4.31	4.24	78.4	70.3	69.3	69.9

<sup>a</sup> Tentative assignment based on chemical shifts ( $^1\text{H}$ )<sup>9</sup> and on HSQC NMR experiment ( $^{13}\text{C}$ ).

**Table SI-2. Selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR data ( $\delta$ ) of 5-8 in  $\text{CDCl}_3$ .**

Compound	$\text{H}^3$		$\text{H}^4$	$\text{H}^5$	Cp	
Compound						
<b>5<sup>a</sup></b>	4.38		4.13	4.24	4.30	
<b>6<sup>b</sup></b>	4.43		4.18	4.33	4.32	
<b>7<sup>b</sup></b>	4.37		4.13	4.26	4.21	
<b>8<sup>b</sup></b>	4.49		4.25	4.36	4.34	
Compound	$\text{C}^1$	$\text{C}^2$	$\text{C}^3$	$\text{C}^4$	$\text{C}^5$	Cp
<b>5<sup>a</sup></b>	92.6	40.5	73.6	67.7	66.8	72.7
<b>6<sup>b</sup></b>	89.7	41.1	74.1	68.1	67.8	72.9
<b>7<sup>b</sup></b>	87.7	40.3	74.4	68.4	68.3	72.7
<b>8<sup>b</sup></b>	87.6	40.2	74.8	68.8	67.0	73.1

<sup>a</sup> Unambiguous assignment based on advanced NMR studies (see Supporting Information).

<sup>b</sup> Tentative assignment based on chemical shifts ( $^1\text{H}$ )<sup>9</sup> and on HSQC NMR experiment ( $^{13}\text{C}$ ).

**Table SI-3. Selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR data ( $\delta$ ) of ferrocene (Fc-H), iodoferrocene (Fc-I), 1, 5 and 9 in  $\text{CDCl}_3$ .**

Compound	$\text{H}^1$	$\text{H}^2$	$\text{H}^3$	$\text{H}^4$	$\text{H}^5$	Cp
Compound	$\text{C}^1$	$\text{C}^2$	$\text{C}^3$	$\text{C}^4$	$\text{C}^5$	Cp
<b>Fc-H</b>	4.18	4.18	4.18	4.18	4.18	4.18
<b>Fc-I<sup>a</sup></b>	-	4.43	4.17	4.17	4.43	4.21
<b>1<sup>a</sup></b>	-	4.54	4.27	4.27	4.54	4.21
<b>5<sup>b</sup></b>	-	-	4.38	4.13	4.24	4.30
<b>9<sup>b</sup></b>	-	4.73	-	4.51	4.58	4.30
<b>Fc-H</b>	68.1	68.1	68.1	68.1	68.1	68.1
<b>Fc-I<sup>a</sup></b>	39.9	74.6	68.9	68.9	74.6	71.2
<b>1<sup>a</sup></b>	81.3	70.0	68.9	68.9	70.0	69.8
<b>5<sup>b</sup></b>	92.6	40.5	73.6	67.7	66.8	72.7
<b>9<sup>b</sup></b>	82.8	75.6	39.6	75.2	71.1	73.0

<sup>a</sup> Tentative assignment based on chemical shifts ( $^1\text{H}$ )<sup>9</sup> and on HSQC NMR experiment ( $^{13}\text{C}$ ).

<sup>b</sup> Unambiguous assignment based on advanced NMR studies (see Supporting Information).

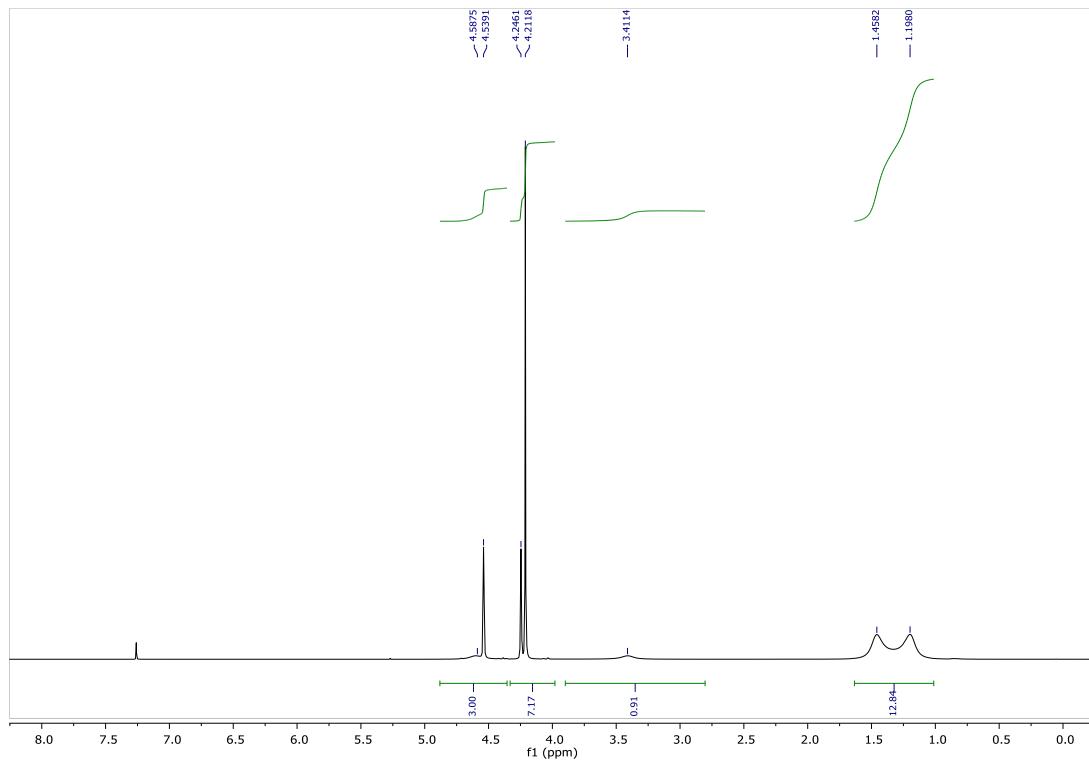
**Table SI-4. Chemical shift increments for  $\alpha$ ,  $\beta$  and Cp positions relative to ferrocene at room temperature in  $\text{CDCl}_3$ .**

Substituent	$\text{H}^\alpha$	$\text{H}^\beta$	$\text{H}^{\text{Cp}}$	
<b>CONiPr<sub>2</sub></b>	+0.36	+0.09	+0.03	
<b>I</b>	+0.25	-0.01	+0.03	
Substituent	$\text{C}^\alpha$	$\text{C}^\beta$	$\text{C}^{\text{Cp}}$	$\text{C}^{\text{ipso}}$
<b>CONiPr<sub>2</sub></b>	+1.9	+0.8	+1.7	+13.2
<b>I</b>	+6.5	+0.8	+3.1	-28.2

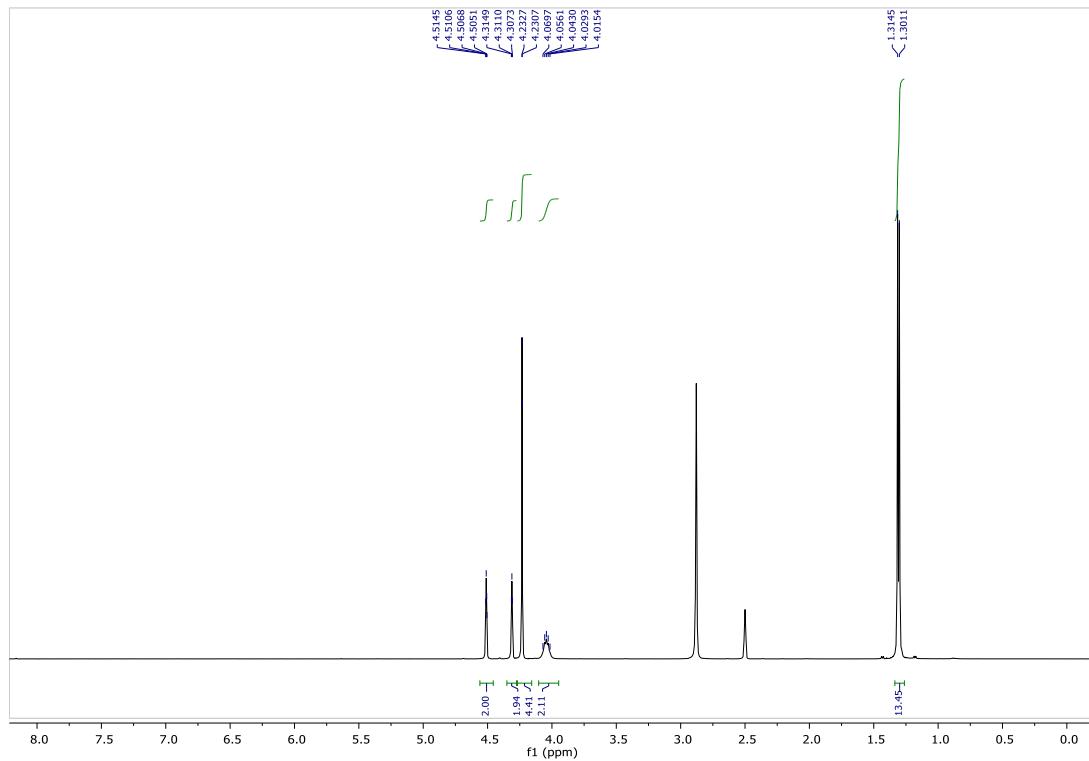
## NMR spectra

### Compound 1

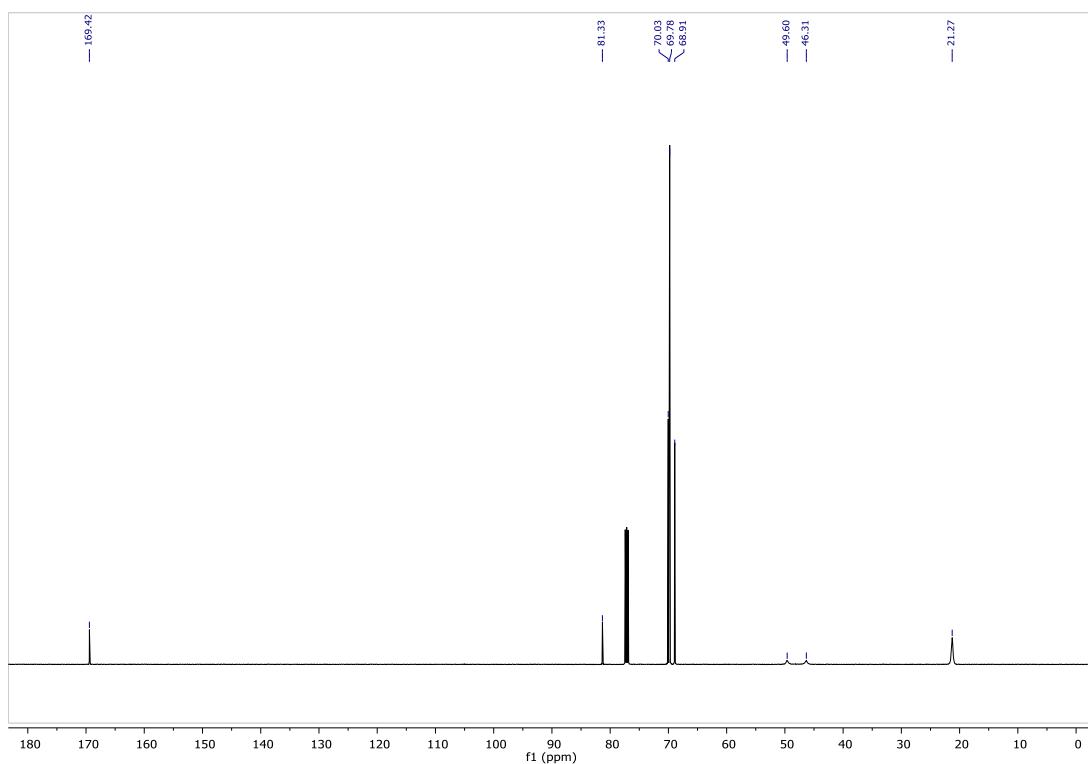
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K)



$^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ , 383 K)

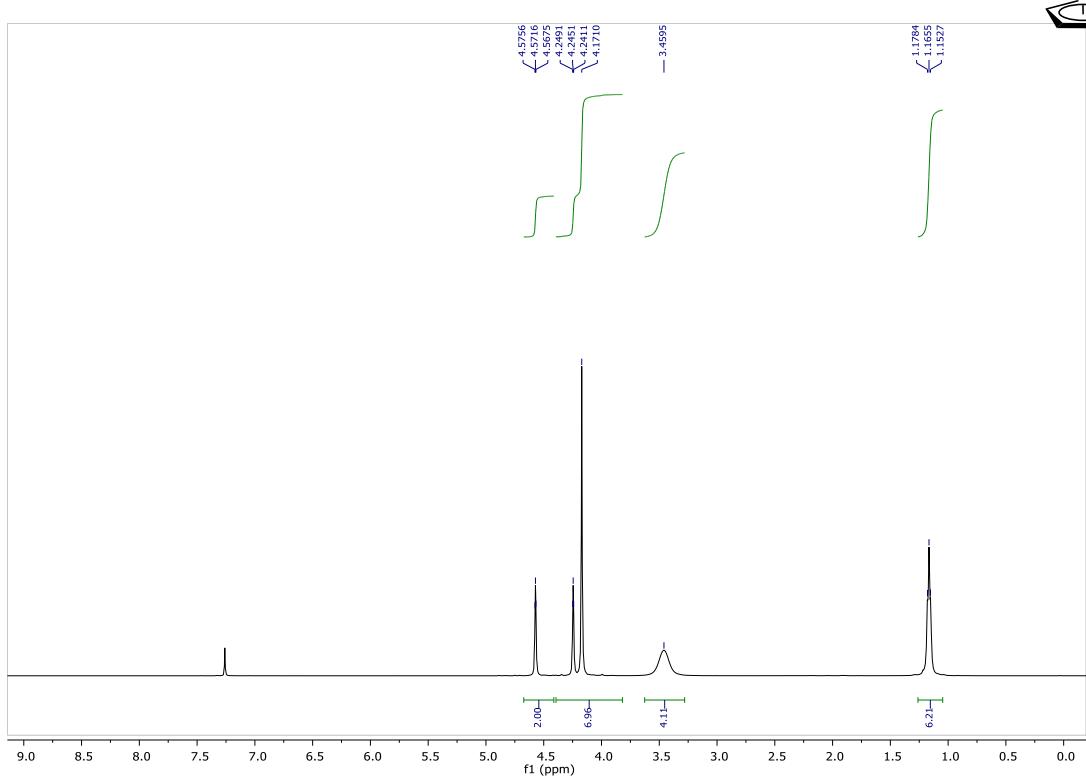


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K)

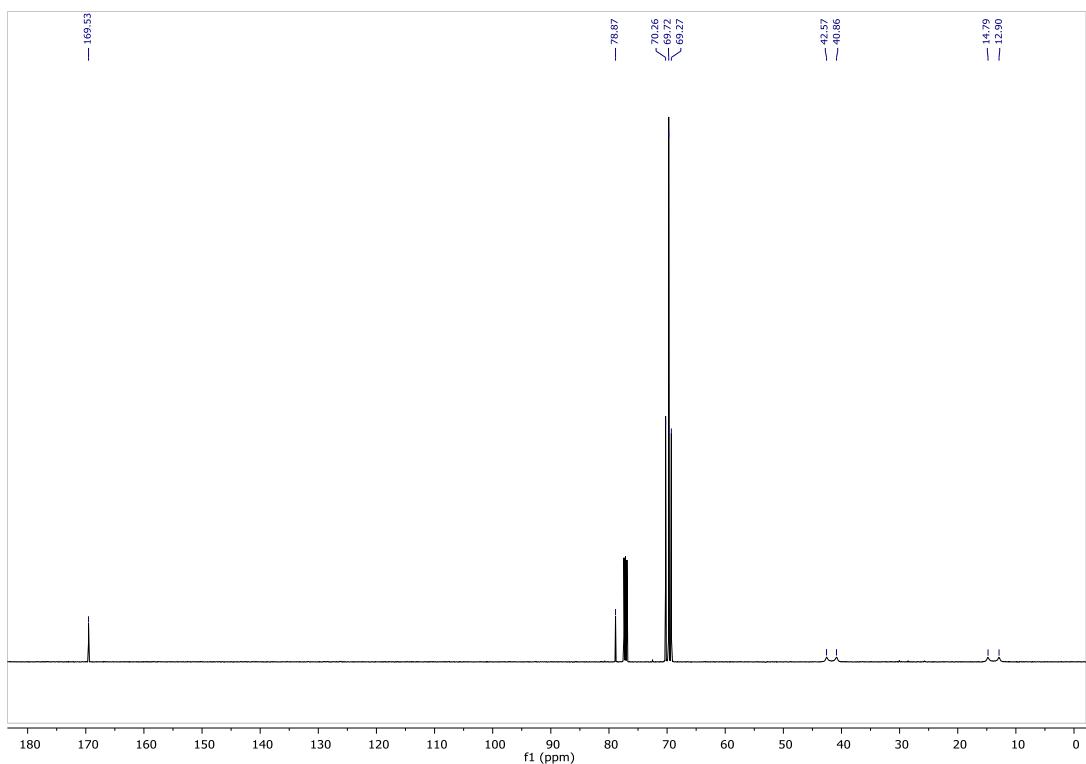


## Compound 2

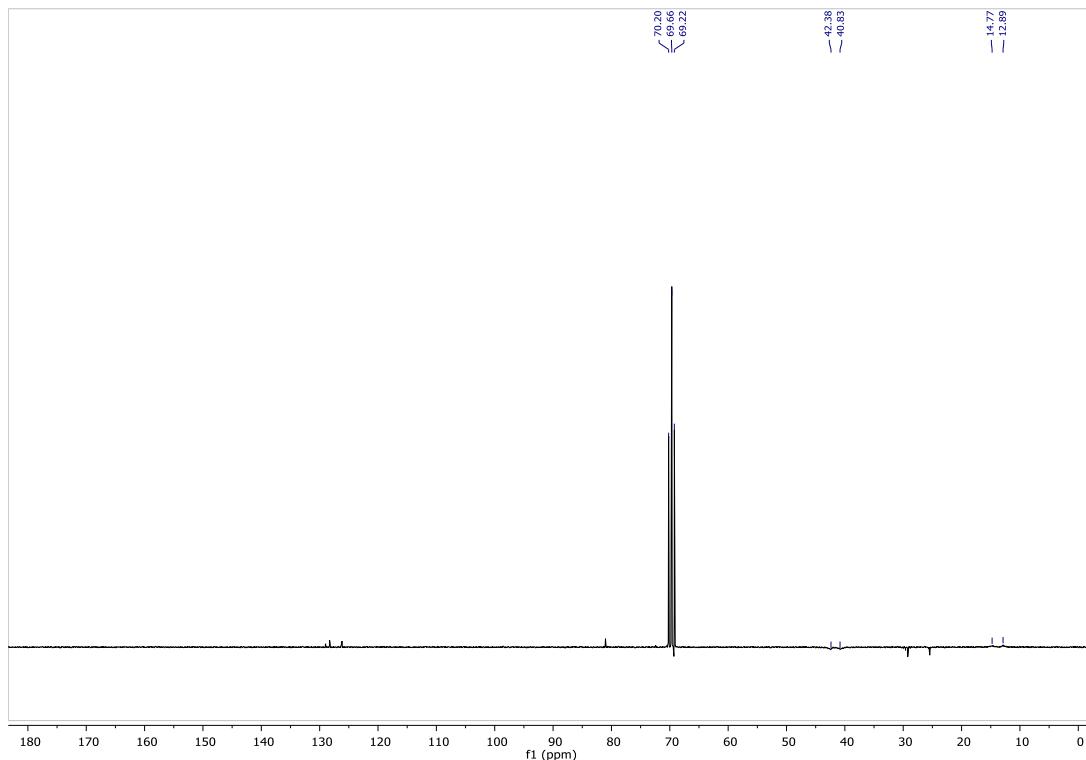
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K)



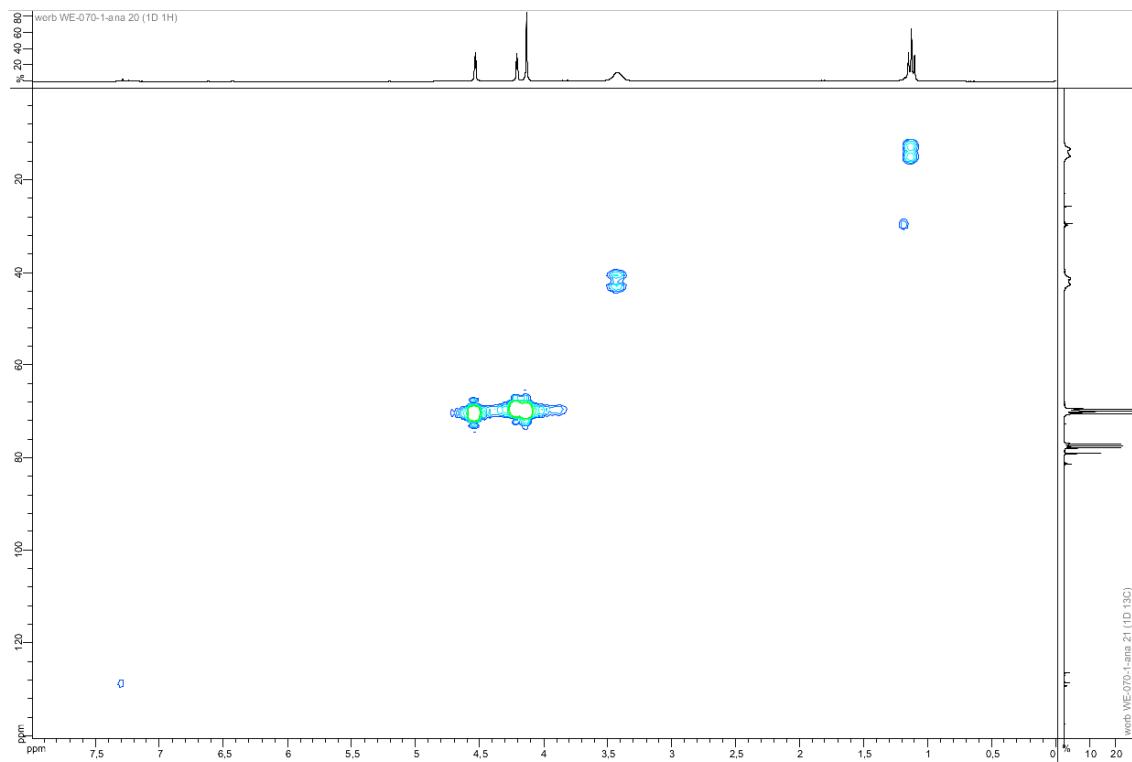
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K)



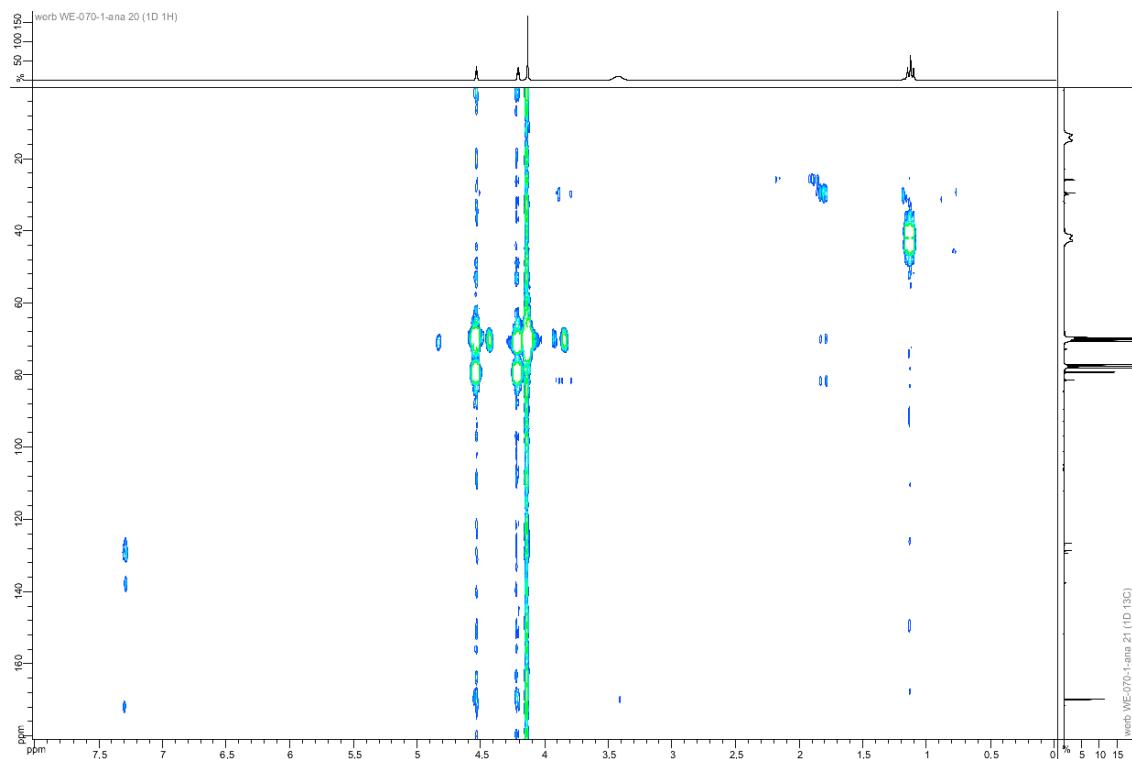
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



HSQC (300 MHz, CDCl<sub>3</sub>, 298 K)

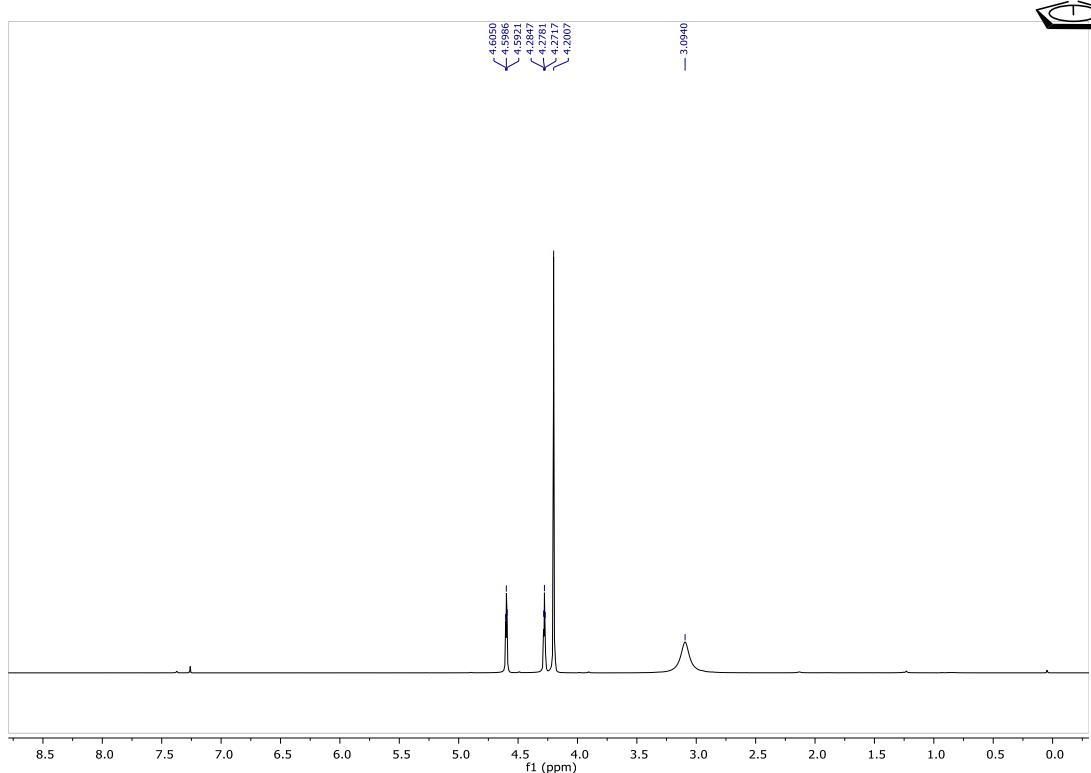


HMBC (300 MHz, CDCl<sub>3</sub>, 298 K)

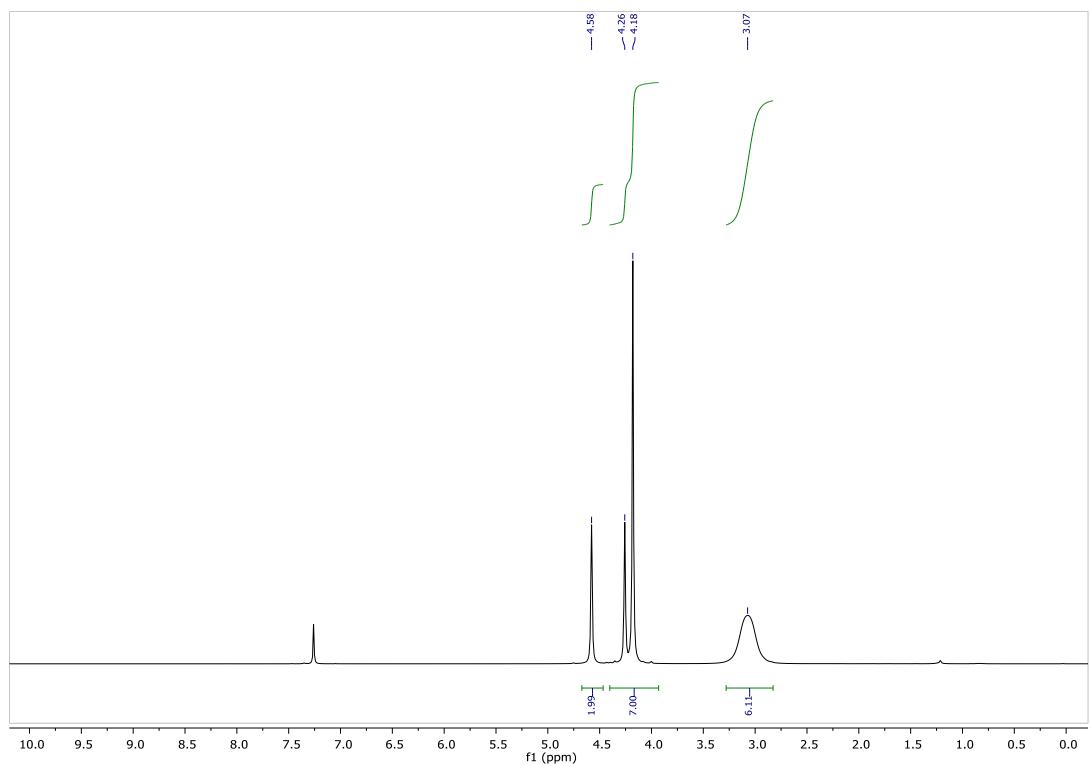


### Compound 3

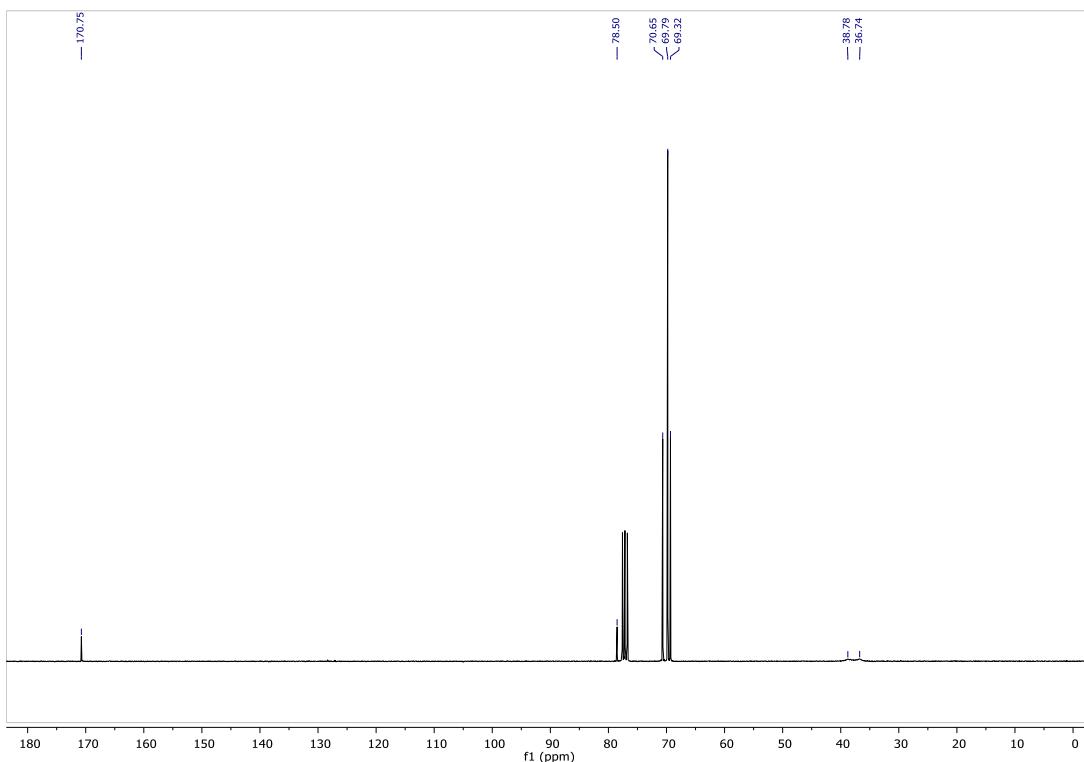
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 291 K)



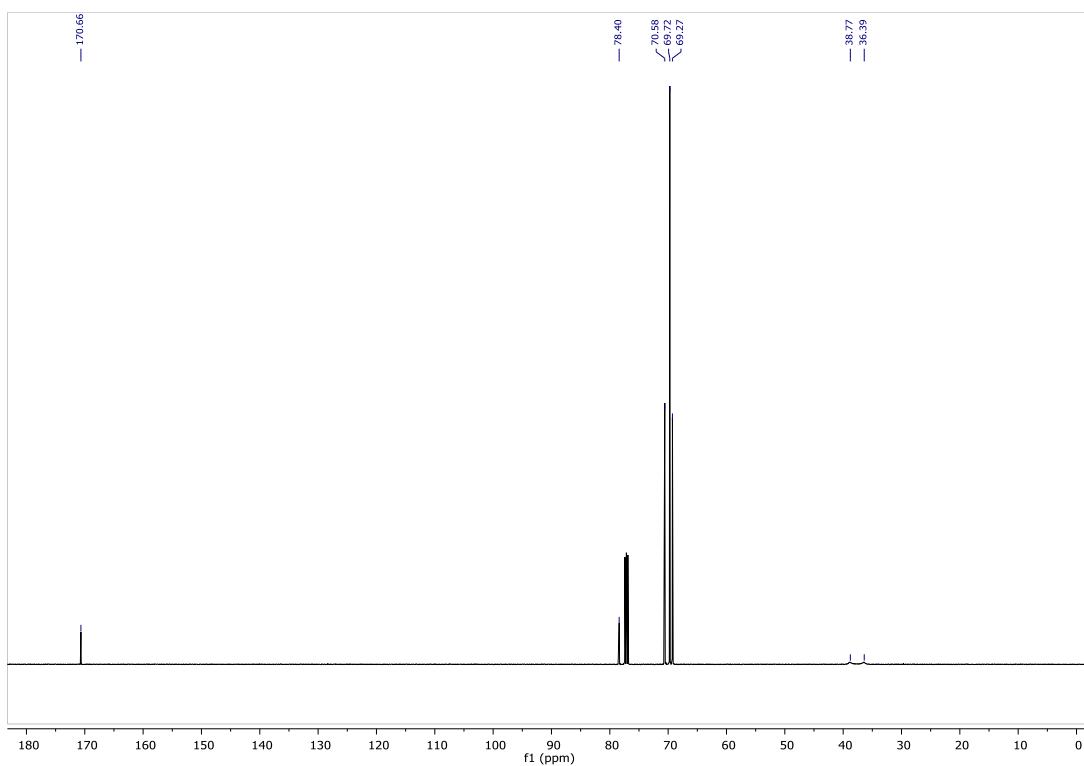
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K)



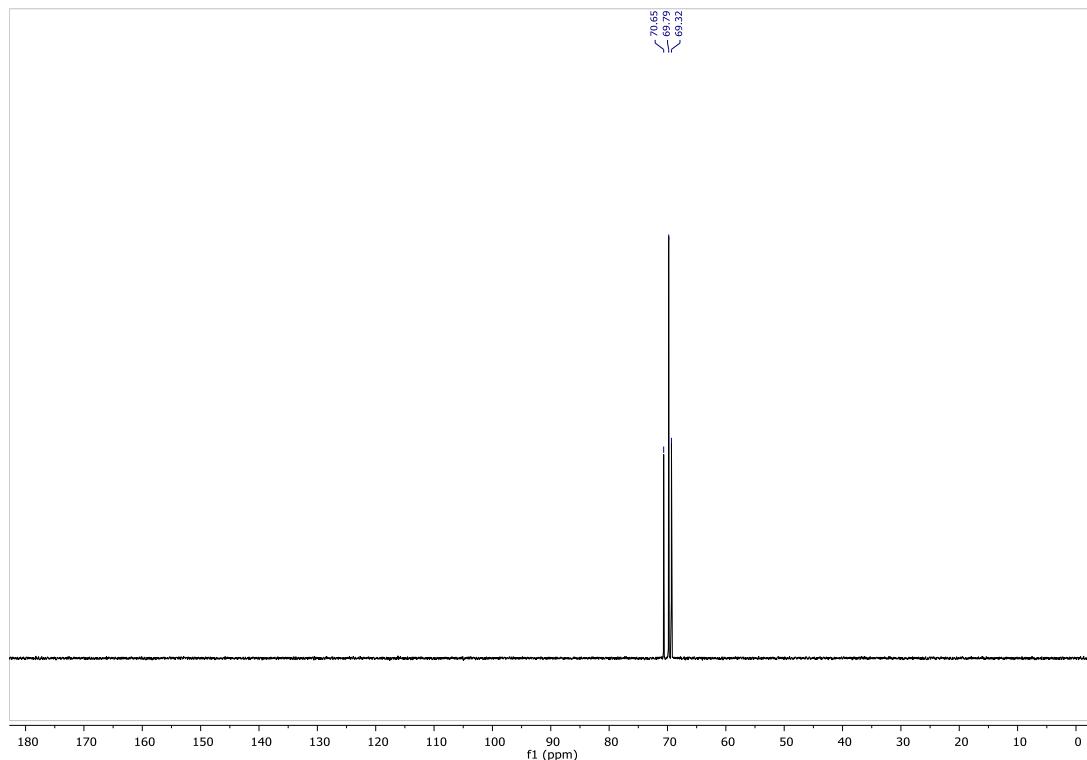
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 291 K)



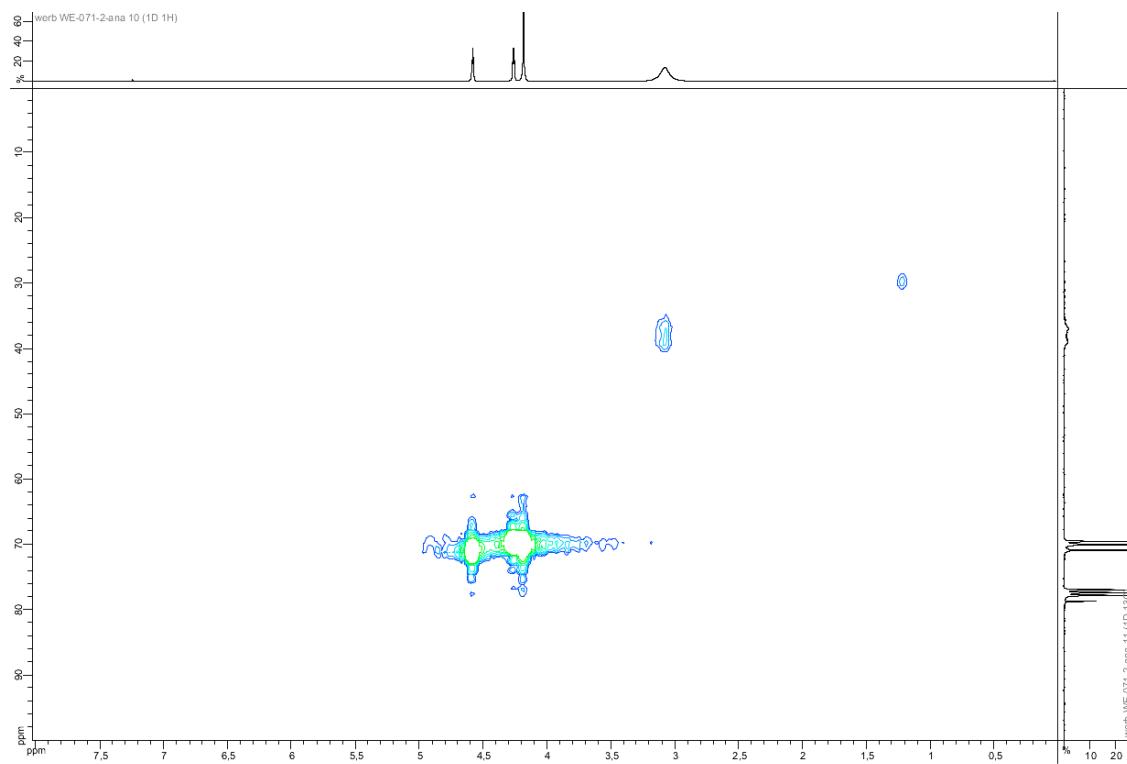
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K)



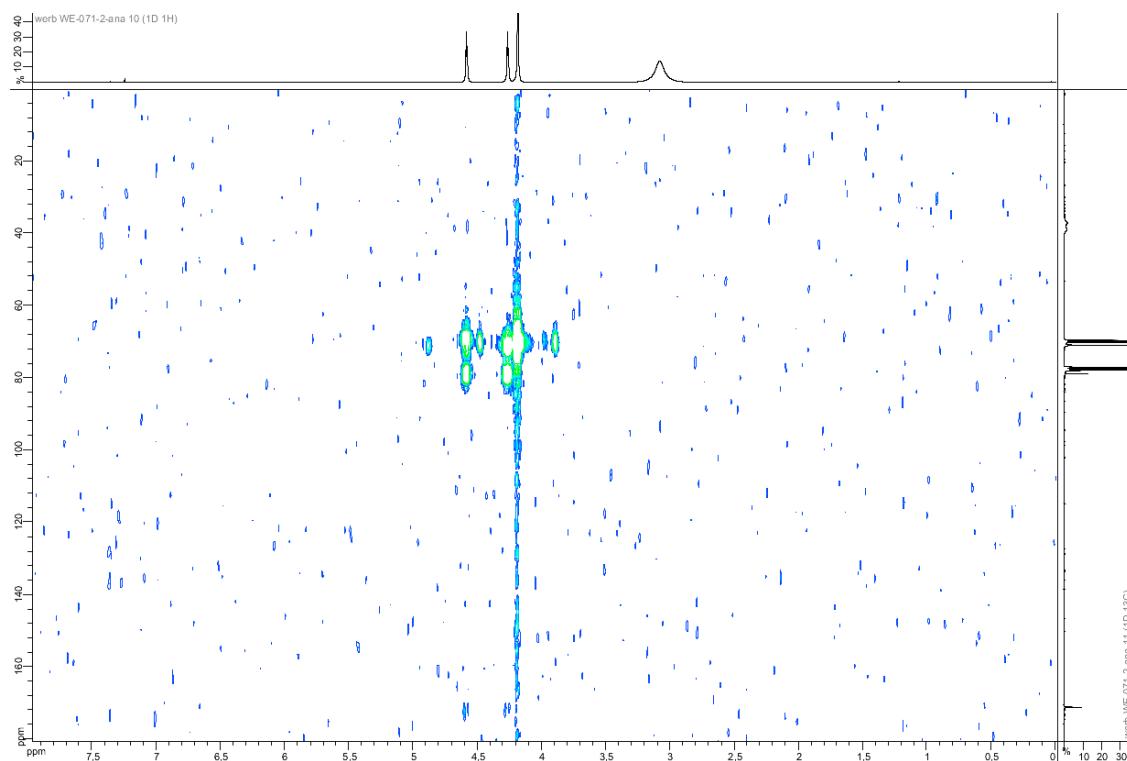
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



HSQC (300 MHz, CDCl<sub>3</sub>, 298 K)

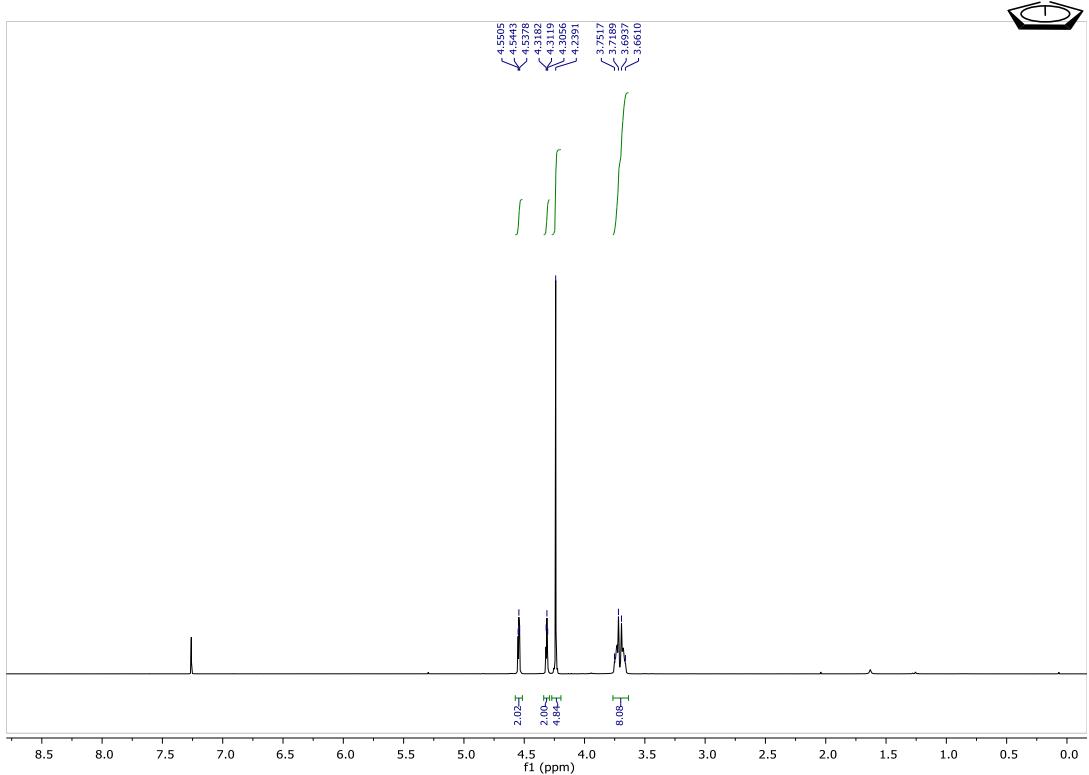


HMBC (300 MHz, CDCl<sub>3</sub>, 298 K)

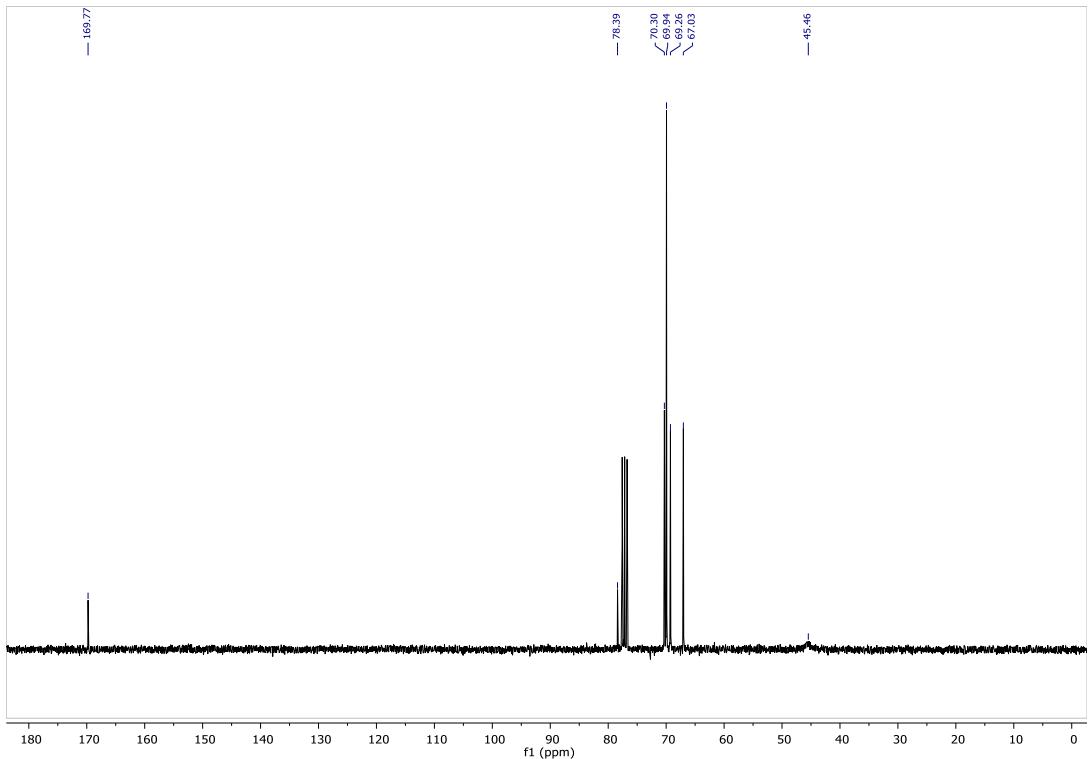


## Compound 4

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 291 K)

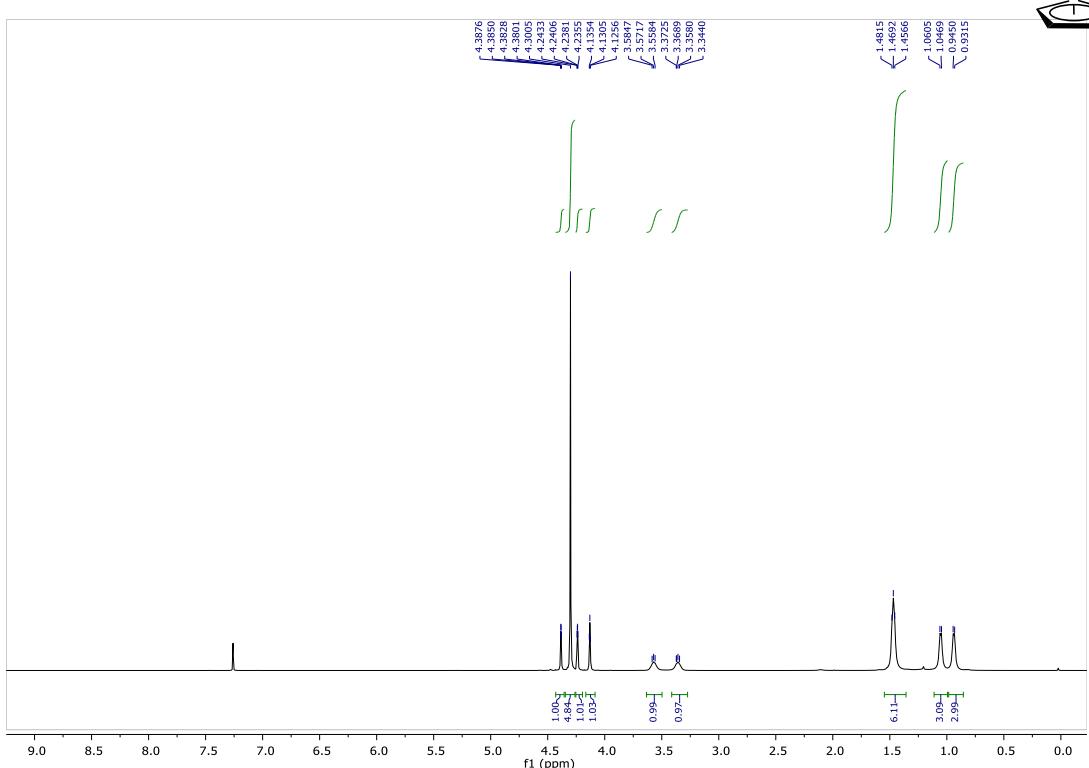


$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 291 K)

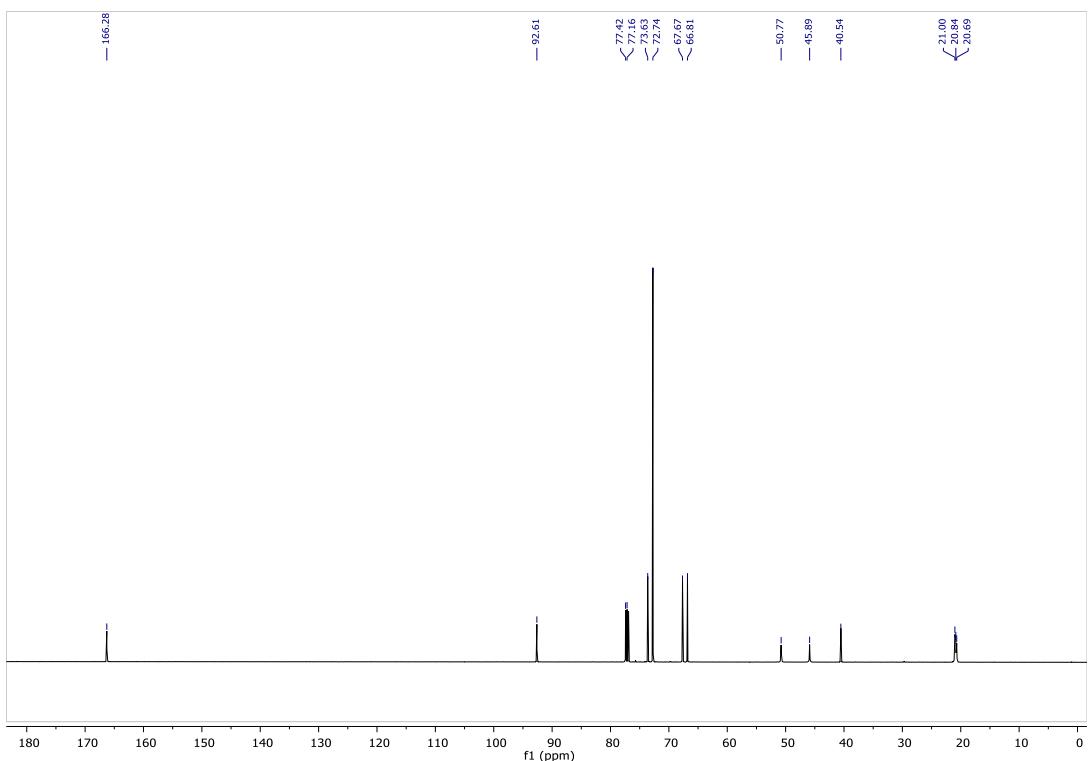


## Compound 5

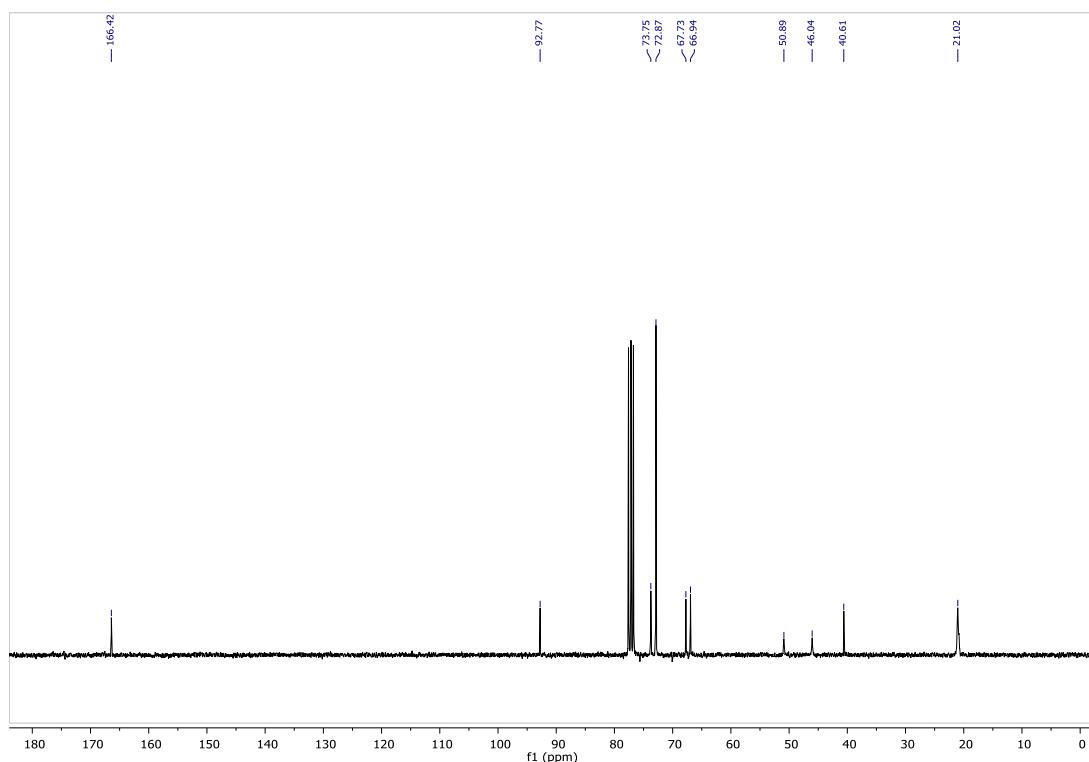
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



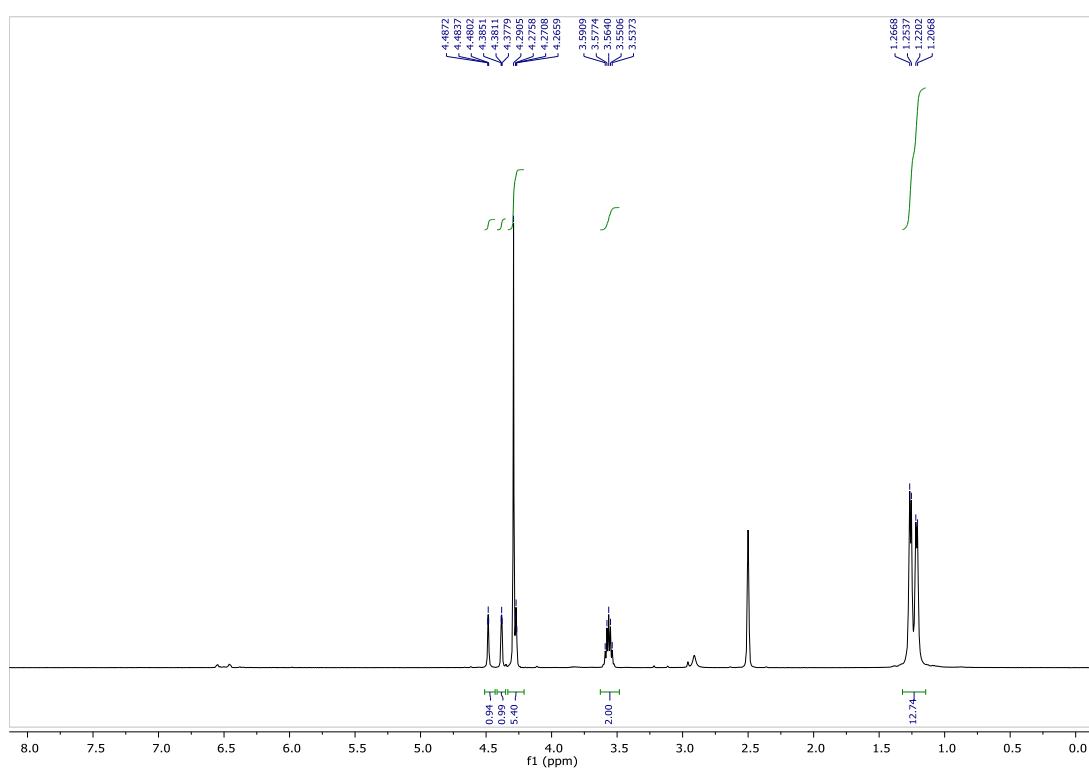
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)



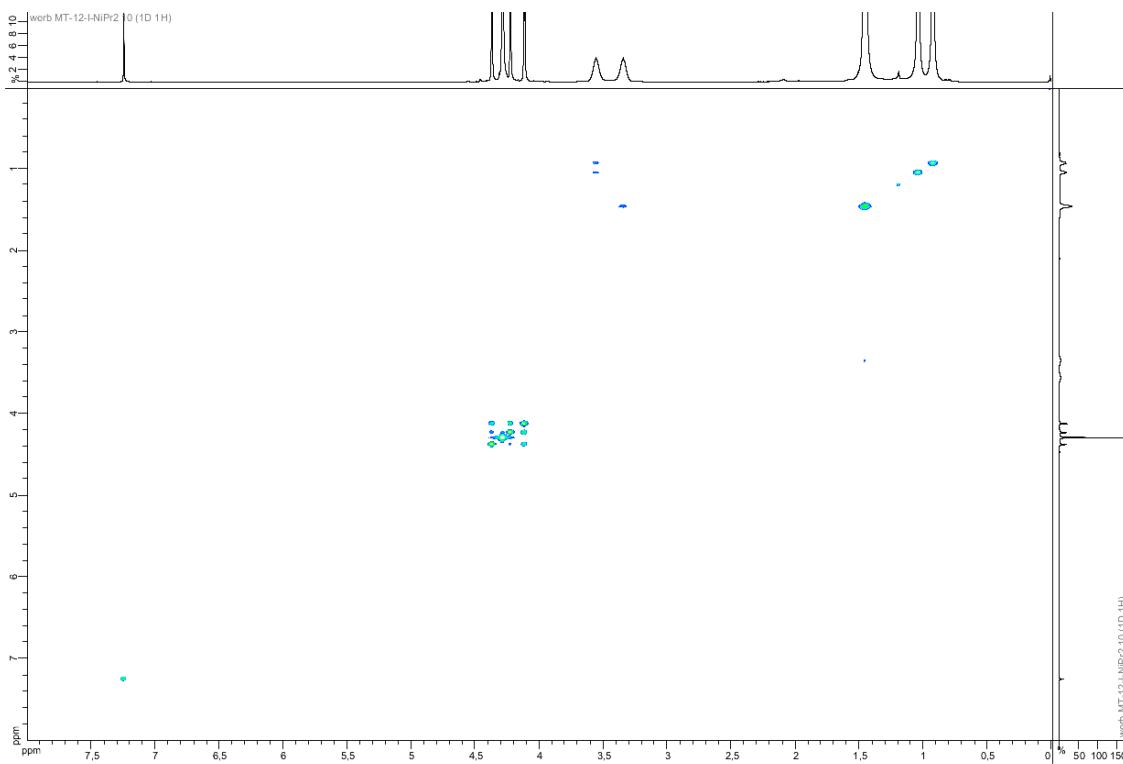
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 291 K)



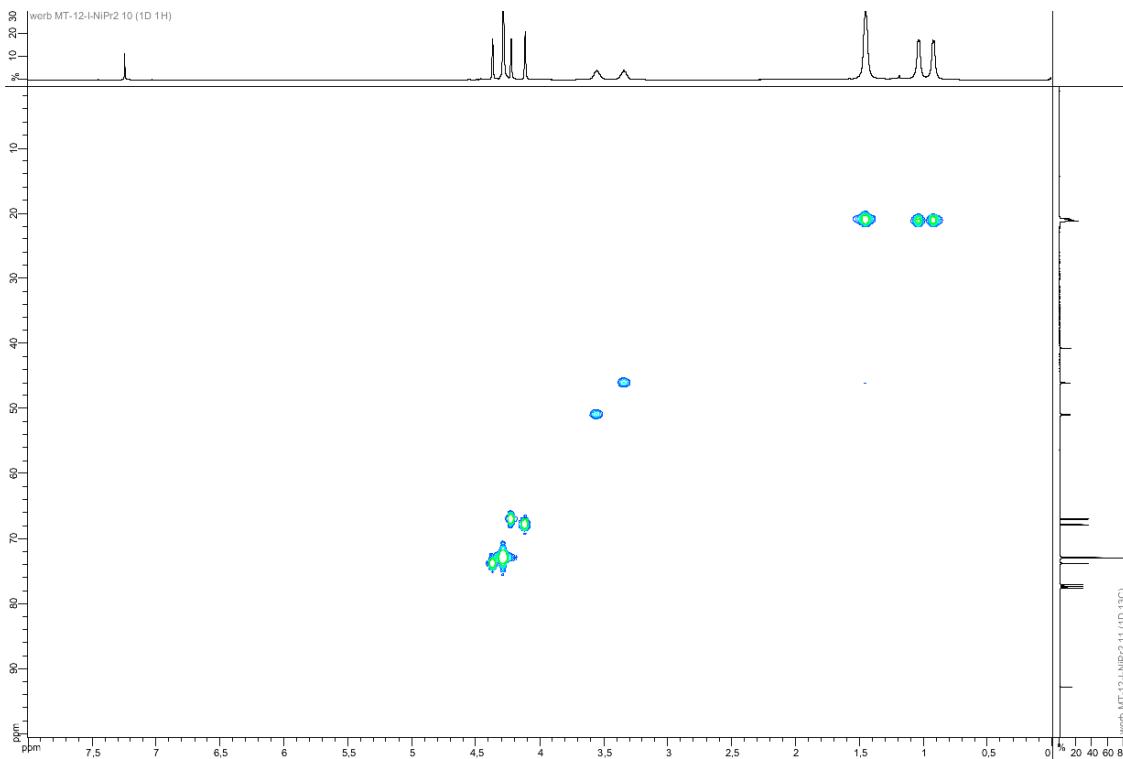
$^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ , 383 K)



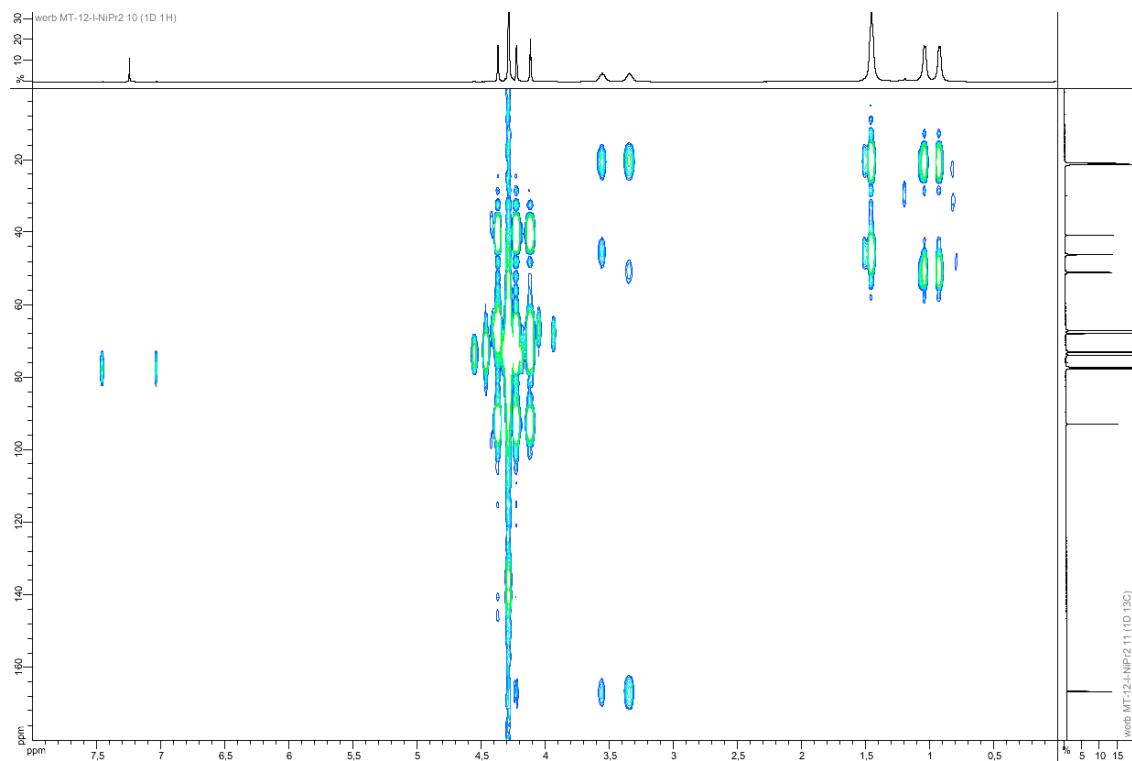
COSY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



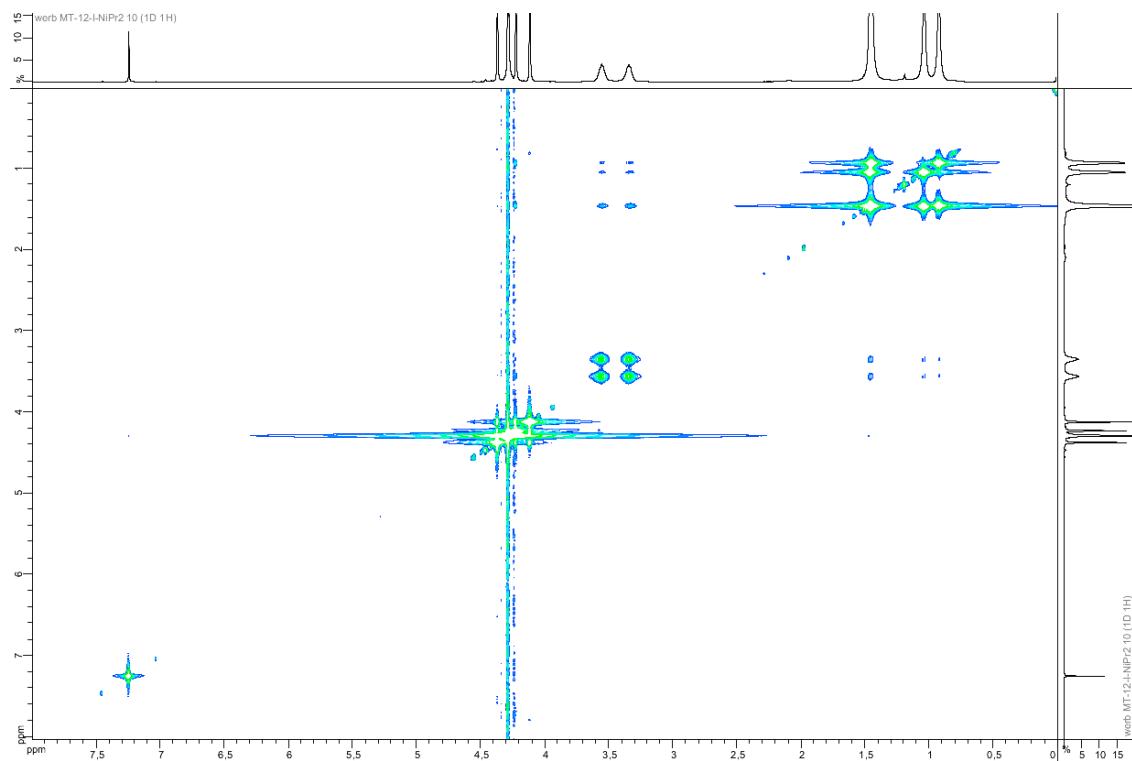
HSQC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



HMBC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

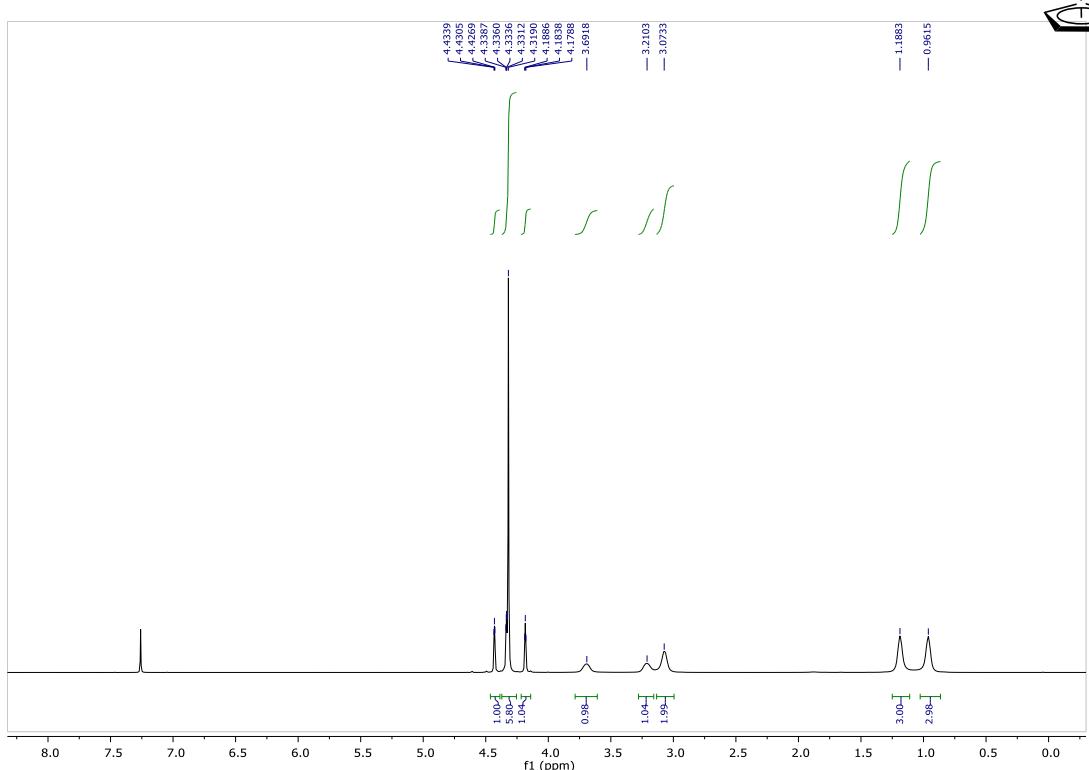


NOESY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

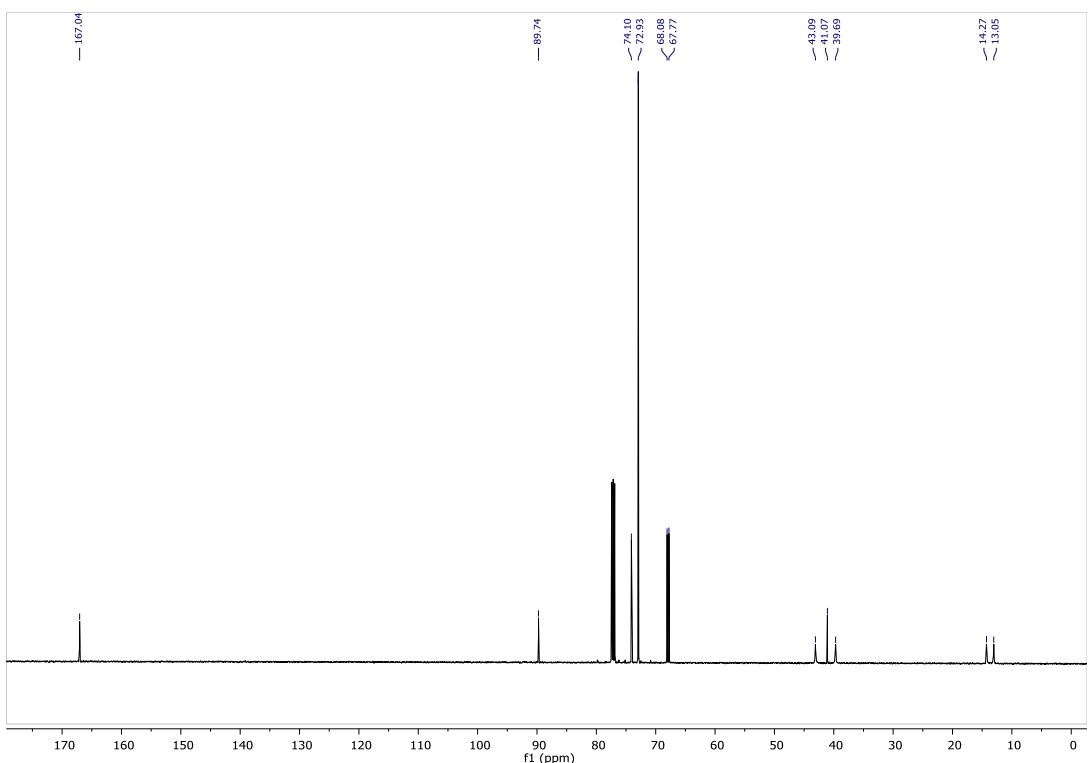


## Compound 6

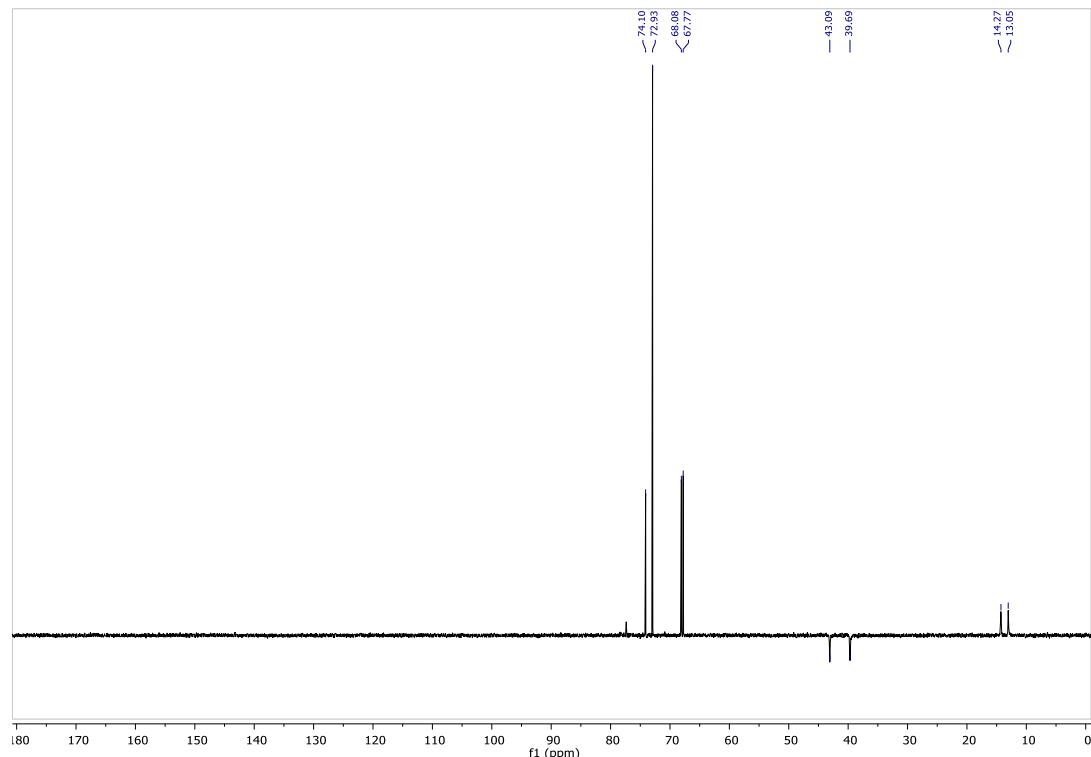
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



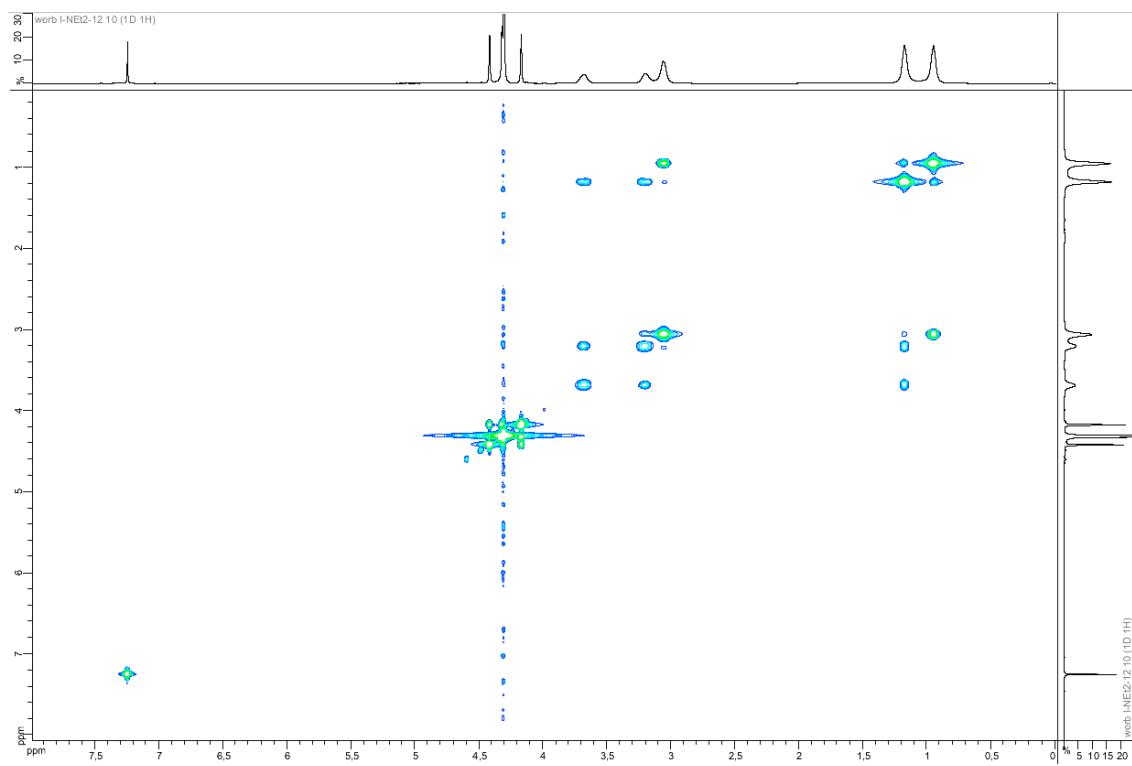
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)



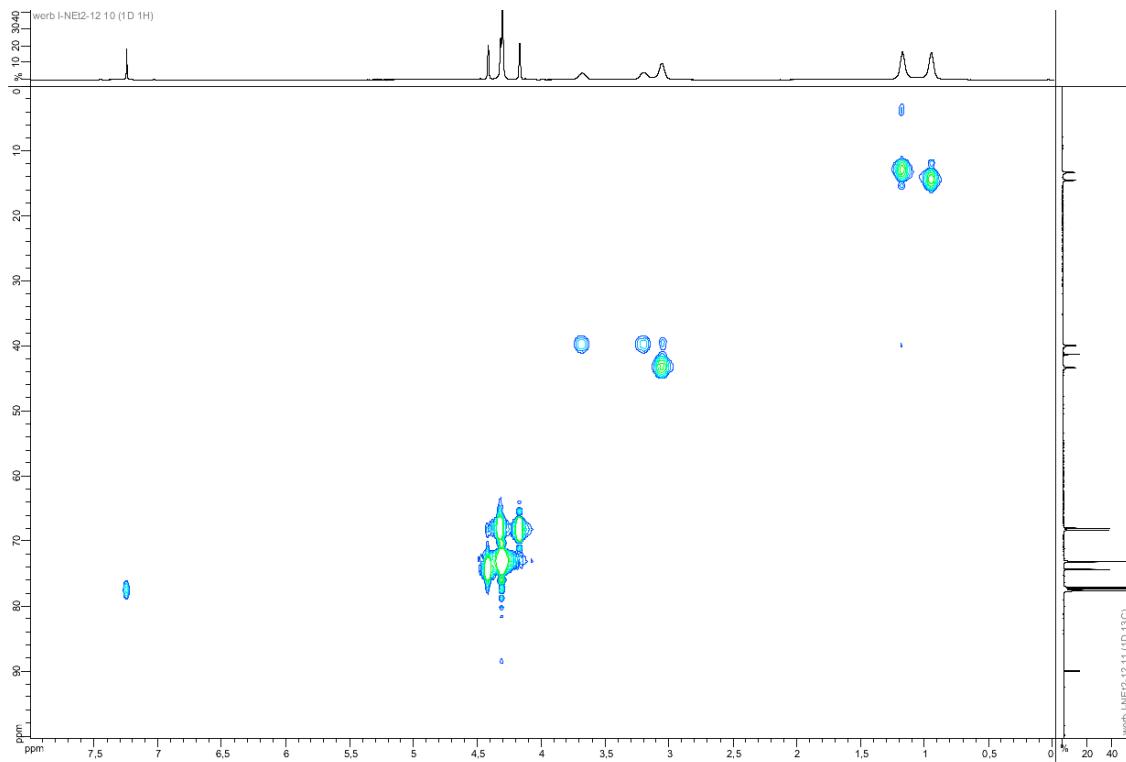
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



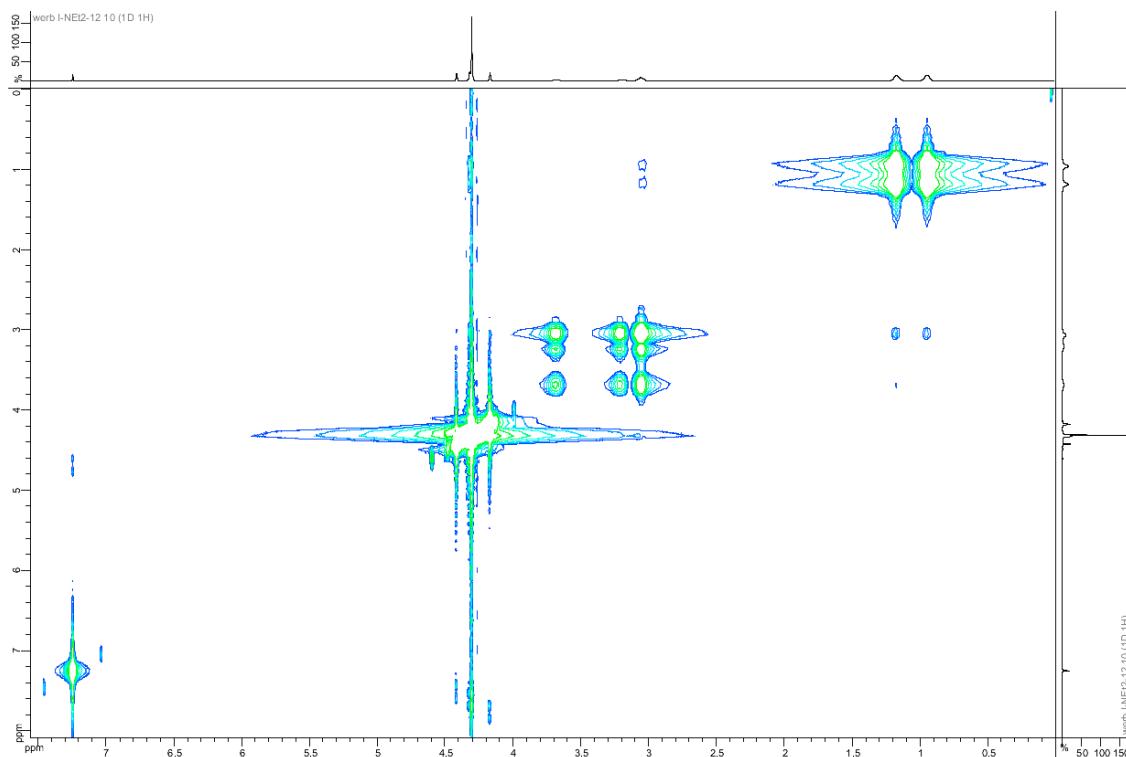
COSY (500 MHz, CDCl<sub>3</sub>, 298 K)



HSQC (500 MHz, CDCl<sub>3</sub>, 298 K)

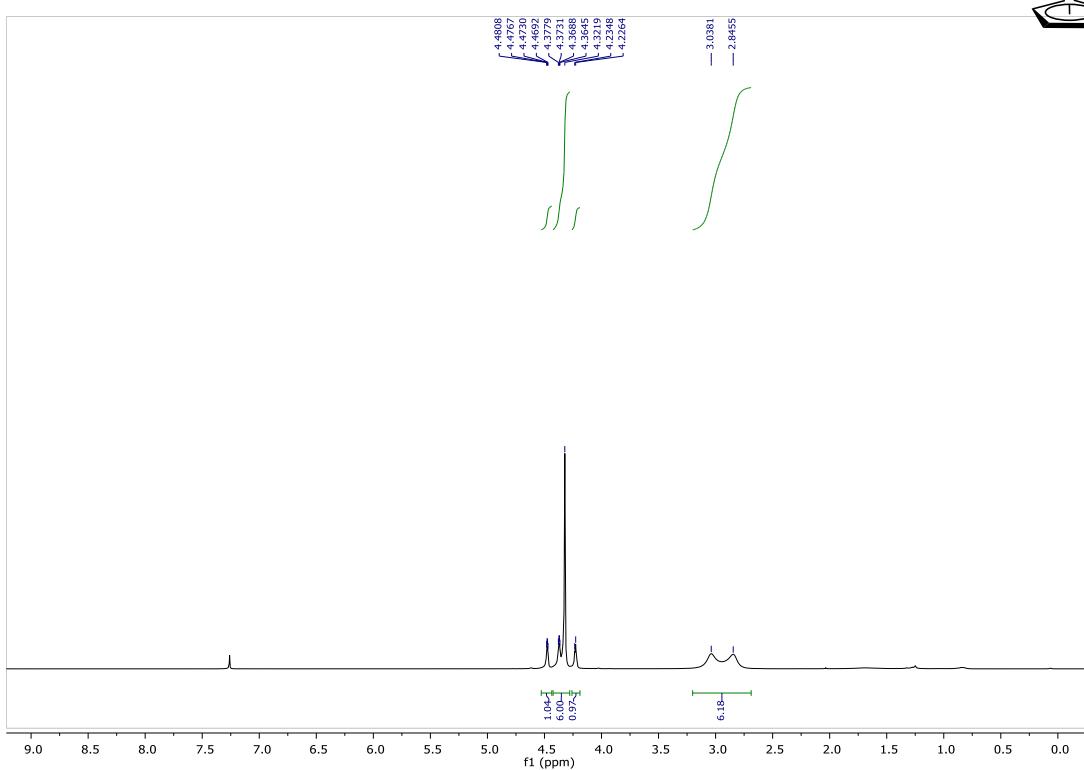


NOESY (500 MHz, CDCl<sub>3</sub>, 298 K)

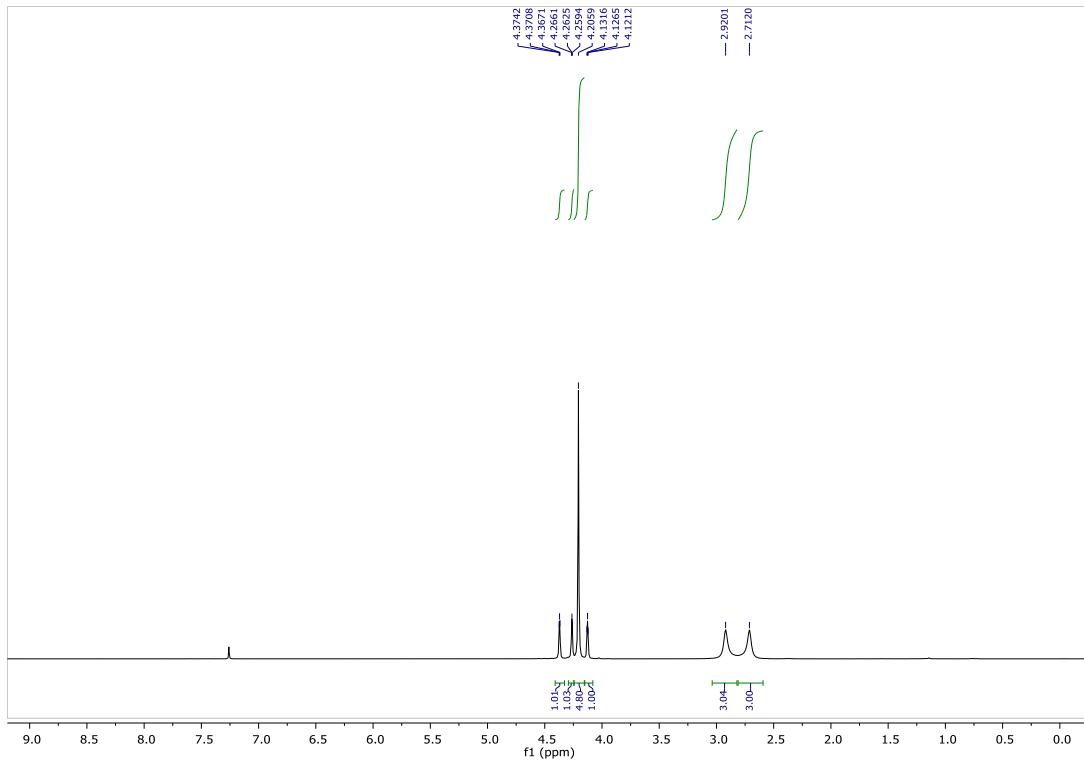


## Compound 7

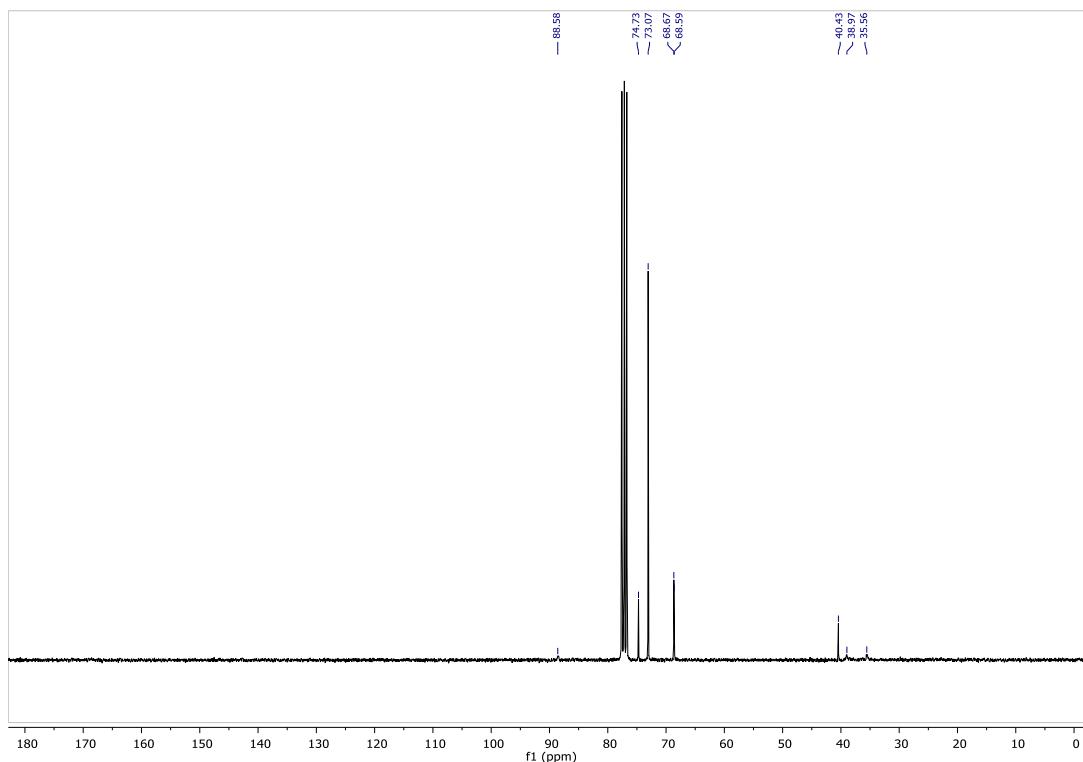
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 291 K)



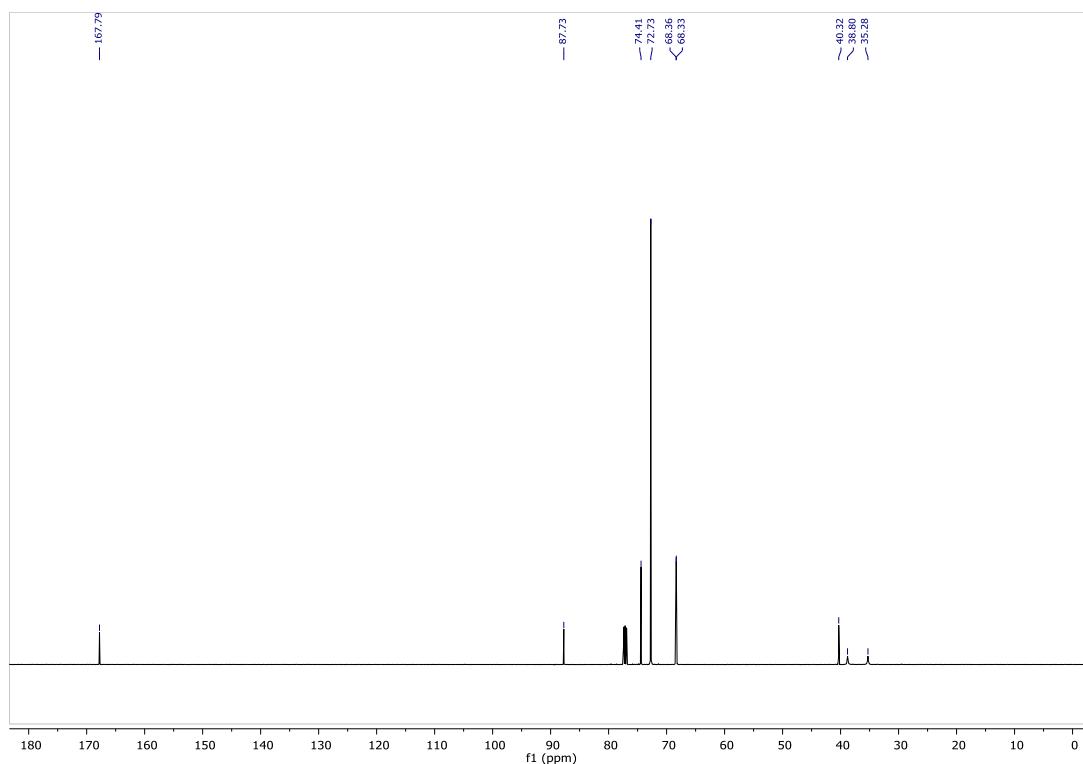
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K)



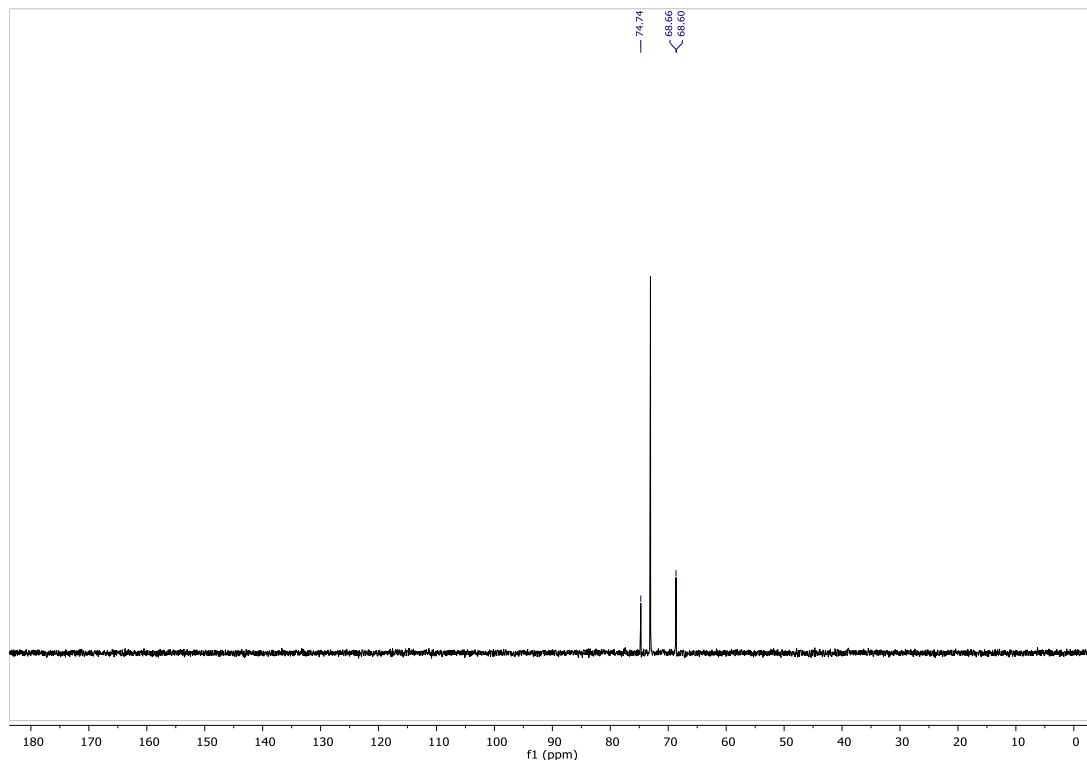
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 291 K)



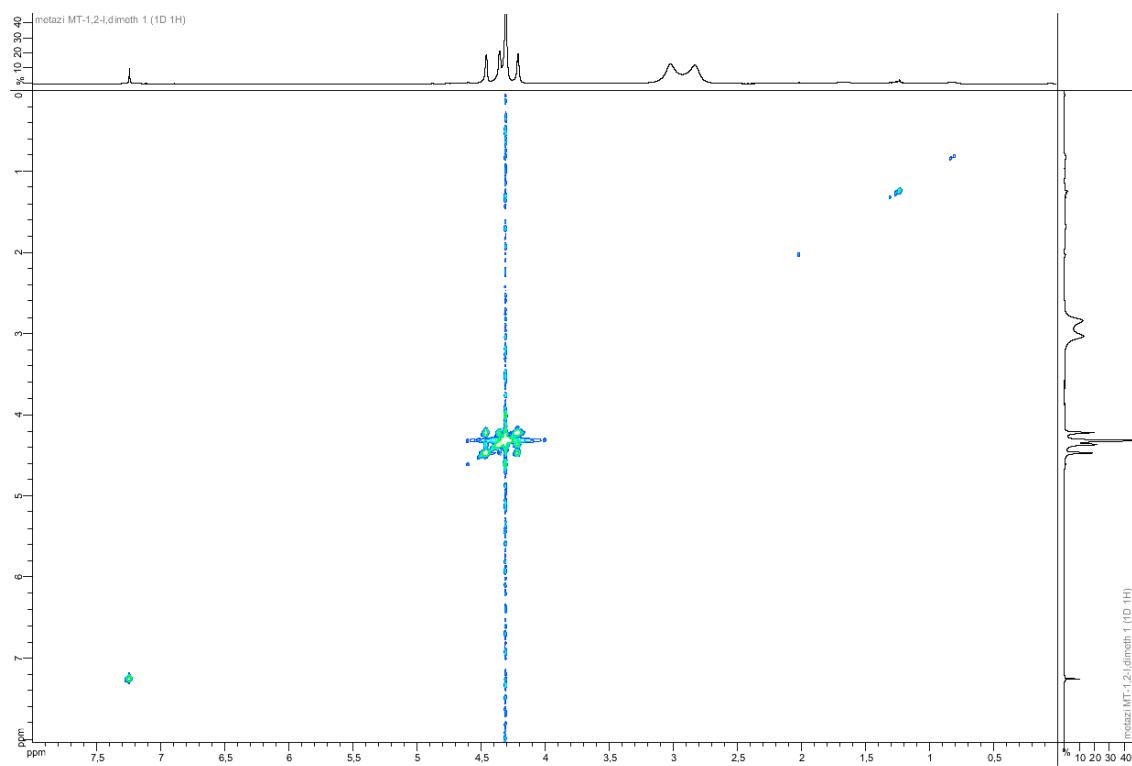
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K)



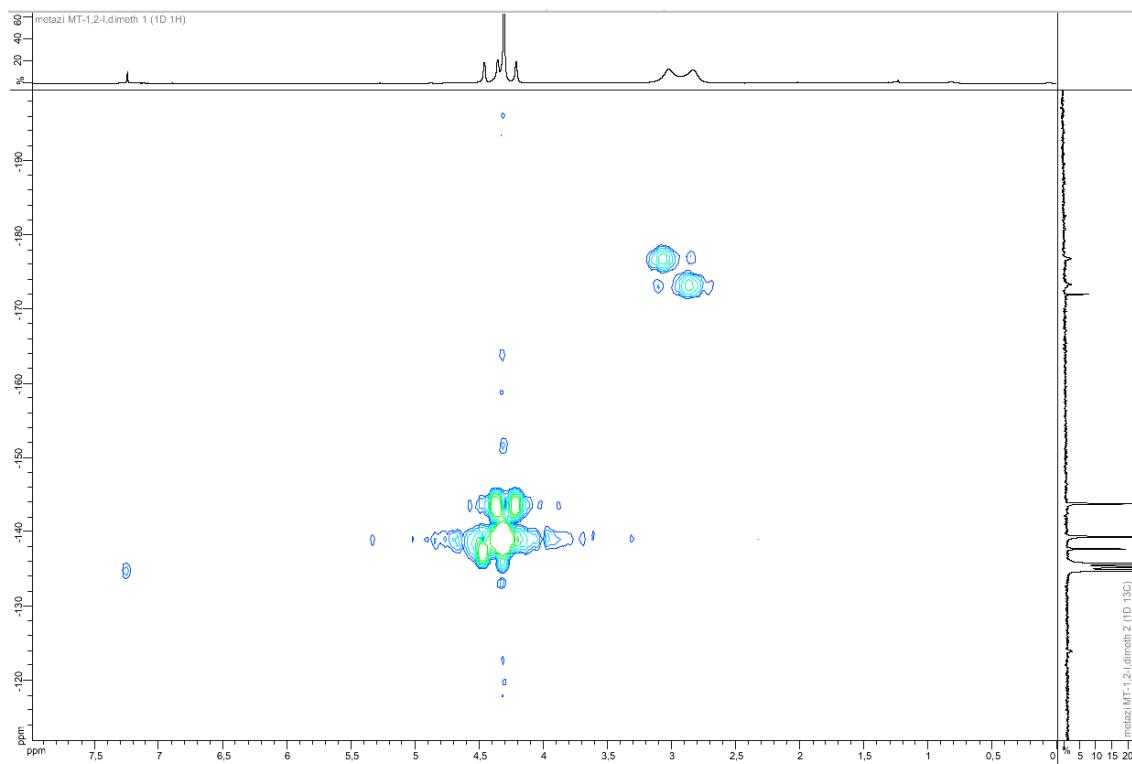
DEPT-135 (75 MHz, CDCl<sub>3</sub>, 291 K)



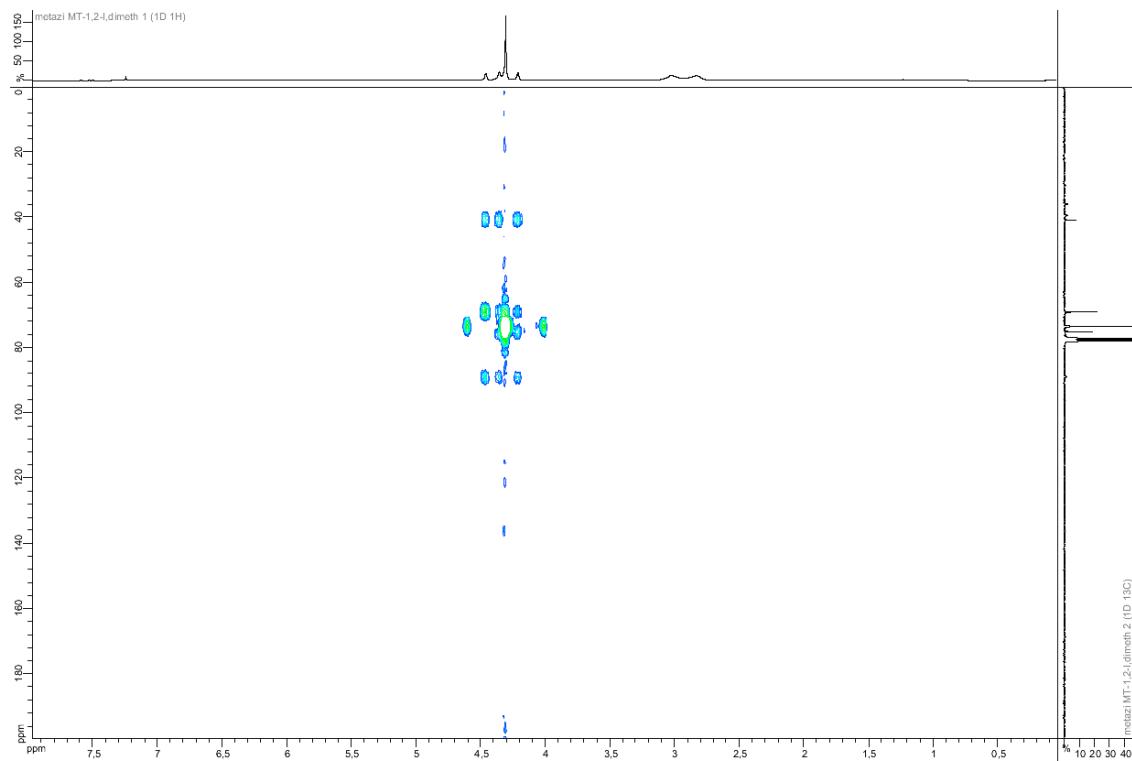
COSY (300 MHz, CDCl<sub>3</sub>, 291 K)



HMBC (300 MHz, CDCl<sub>3</sub>, 291 K)

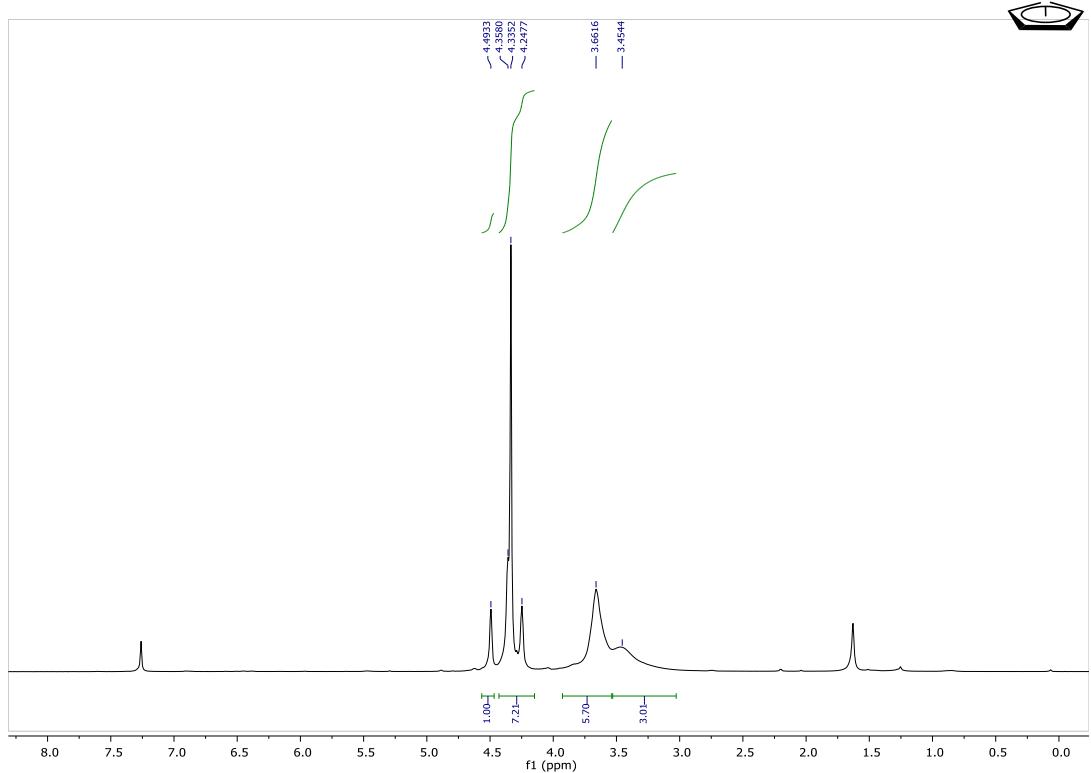


HMBC (300 MHz, CDCl<sub>3</sub>, 291 K)

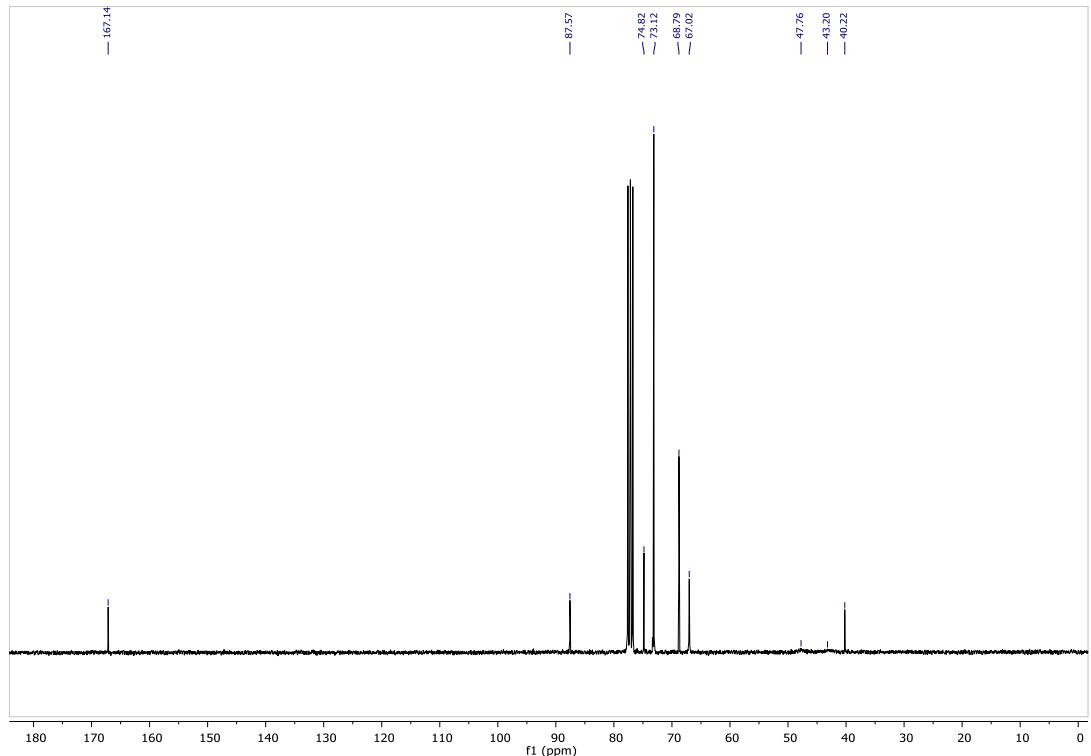


## Compound 8

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 291 K)

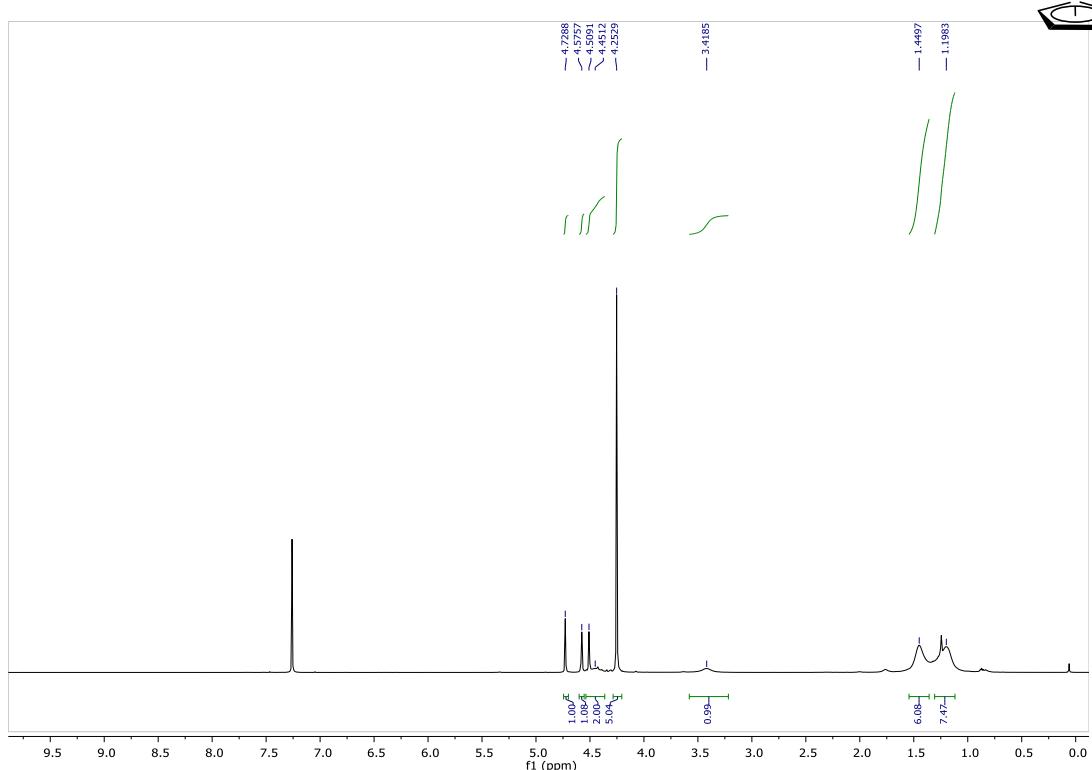


$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 291 K)

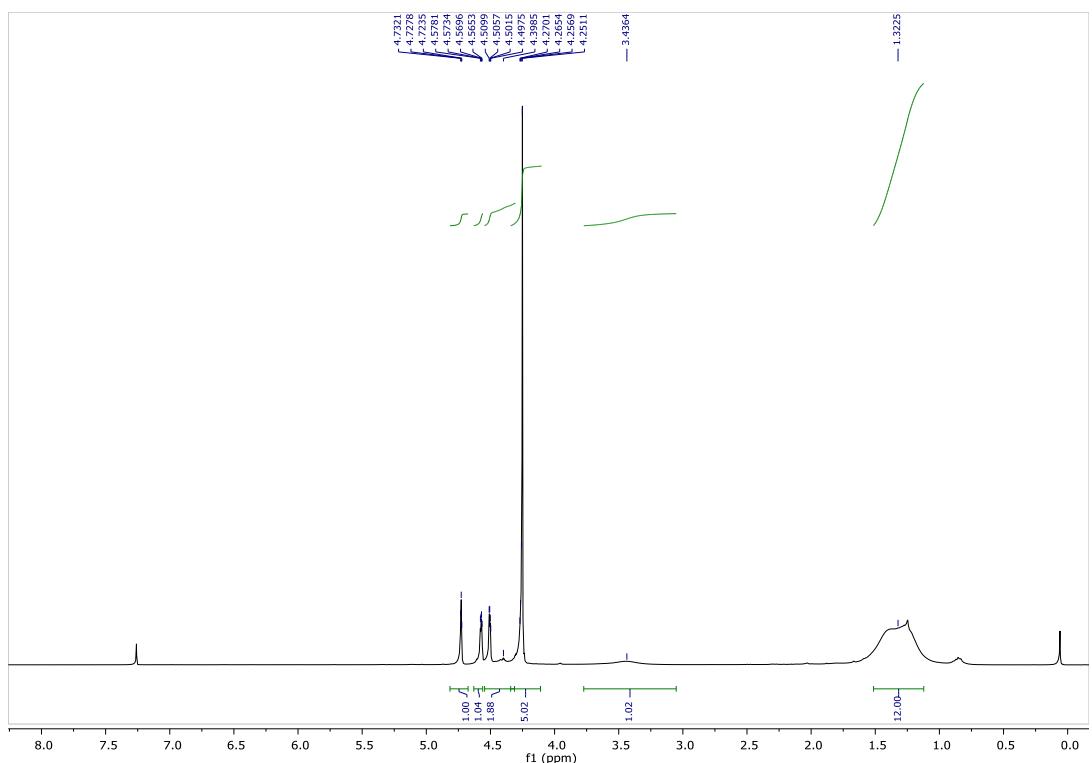


## Compound 9

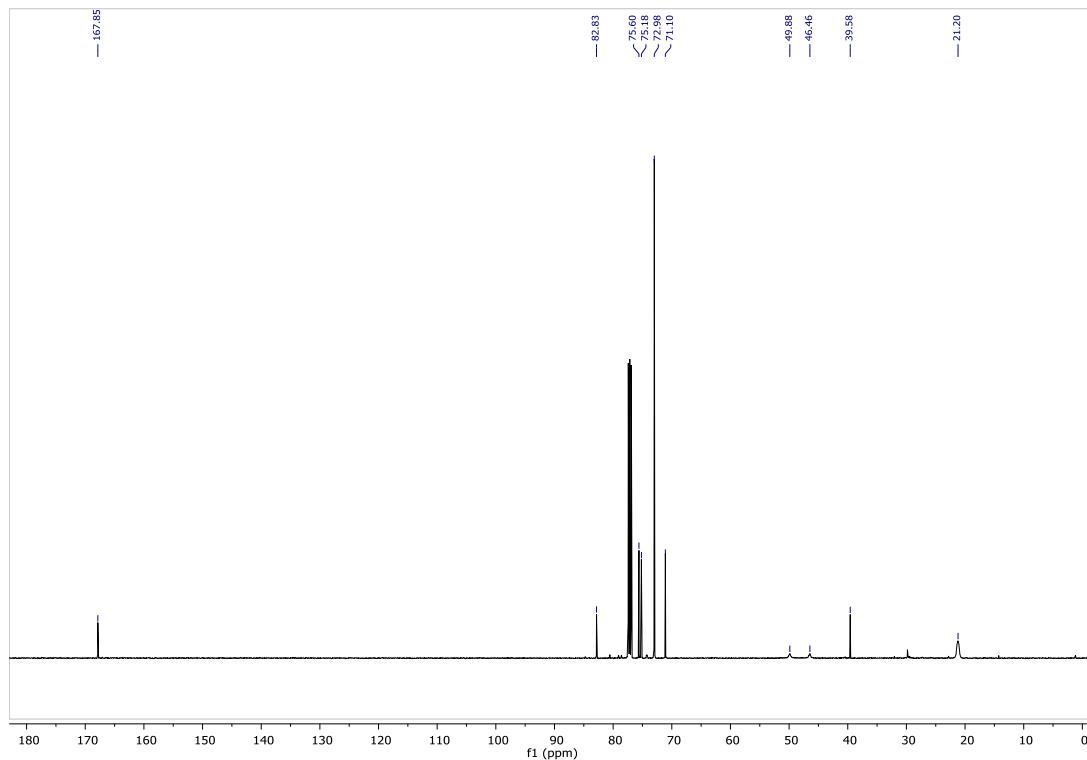
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K)



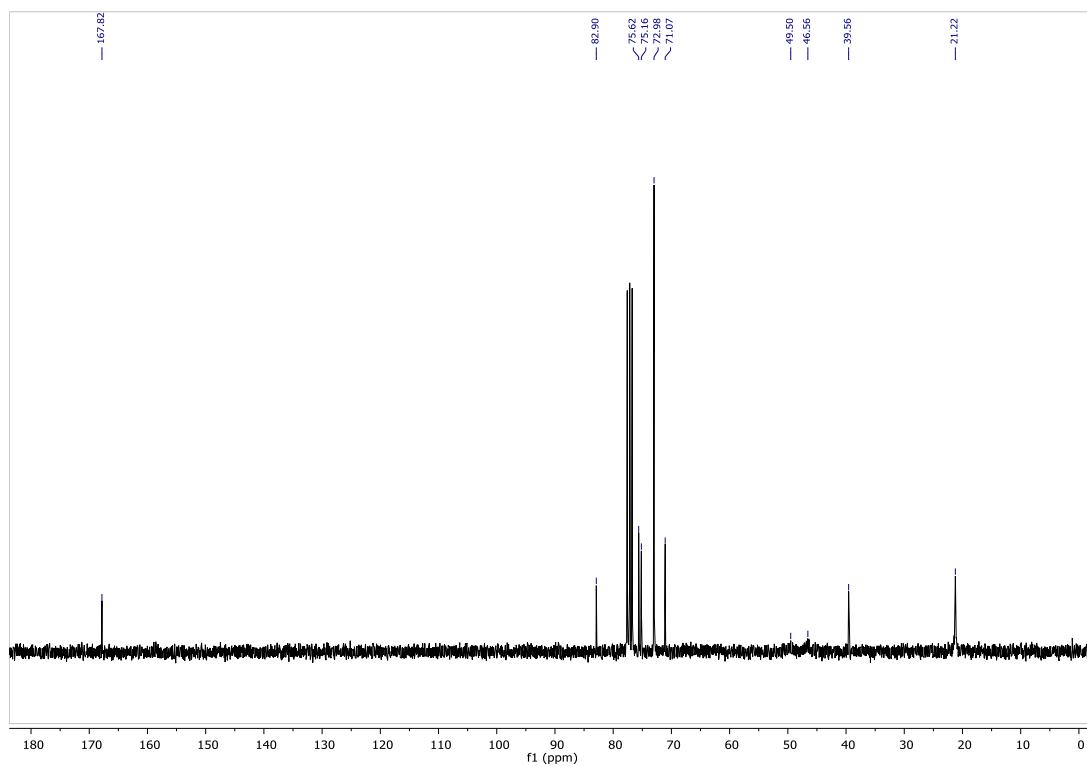
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 291 K)



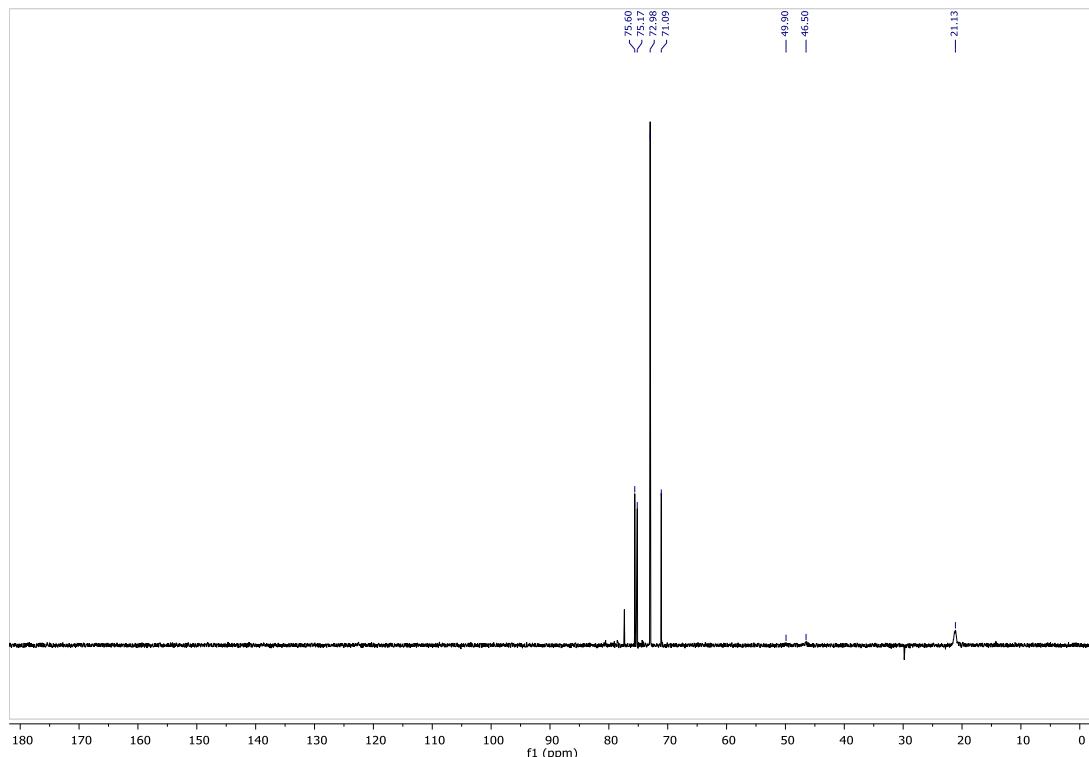
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K)



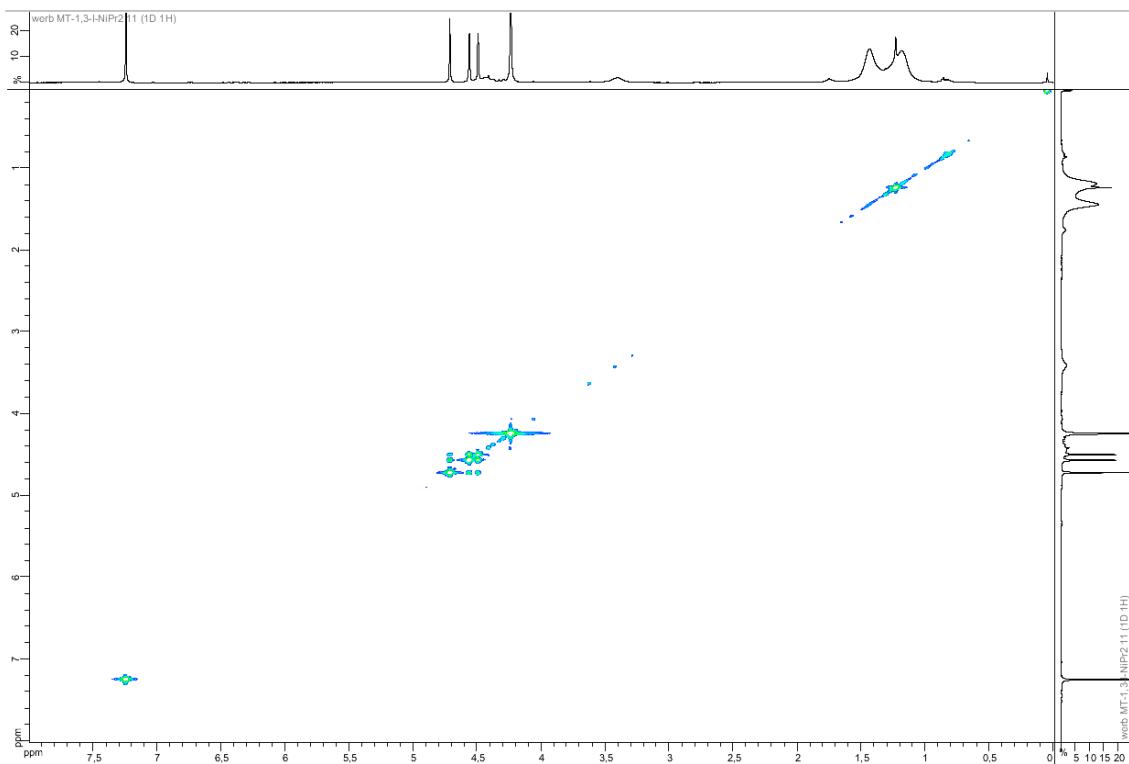
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 291 K)



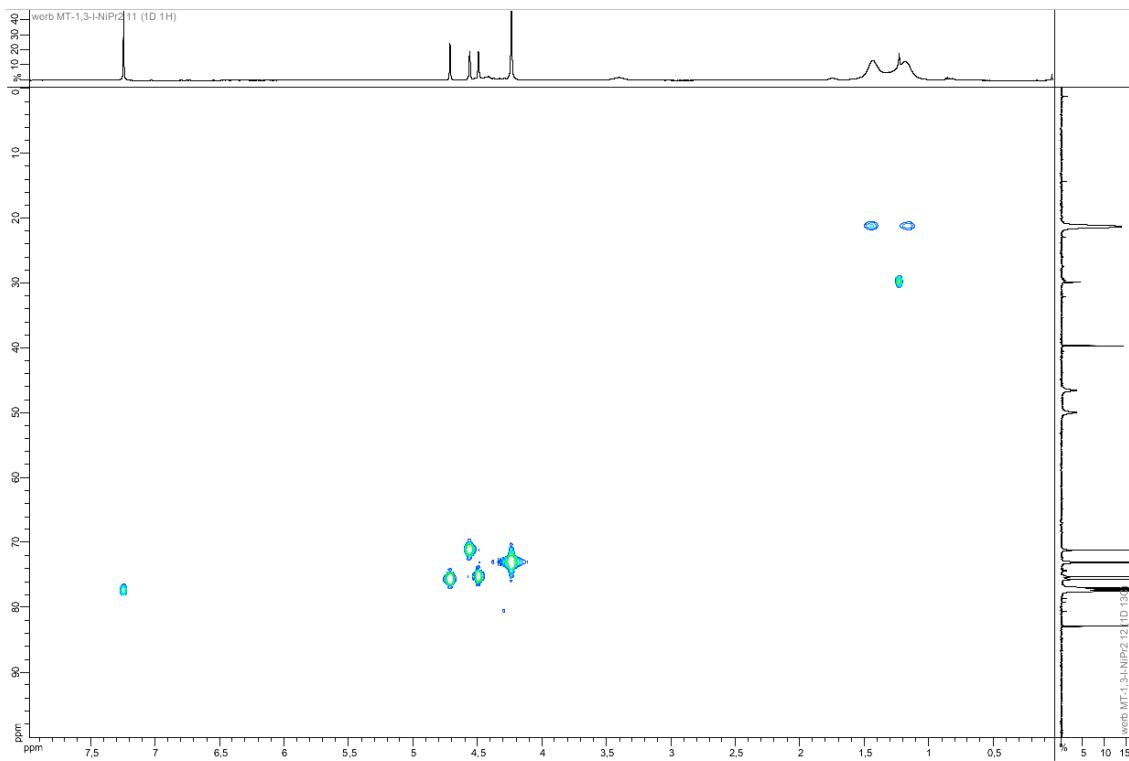
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



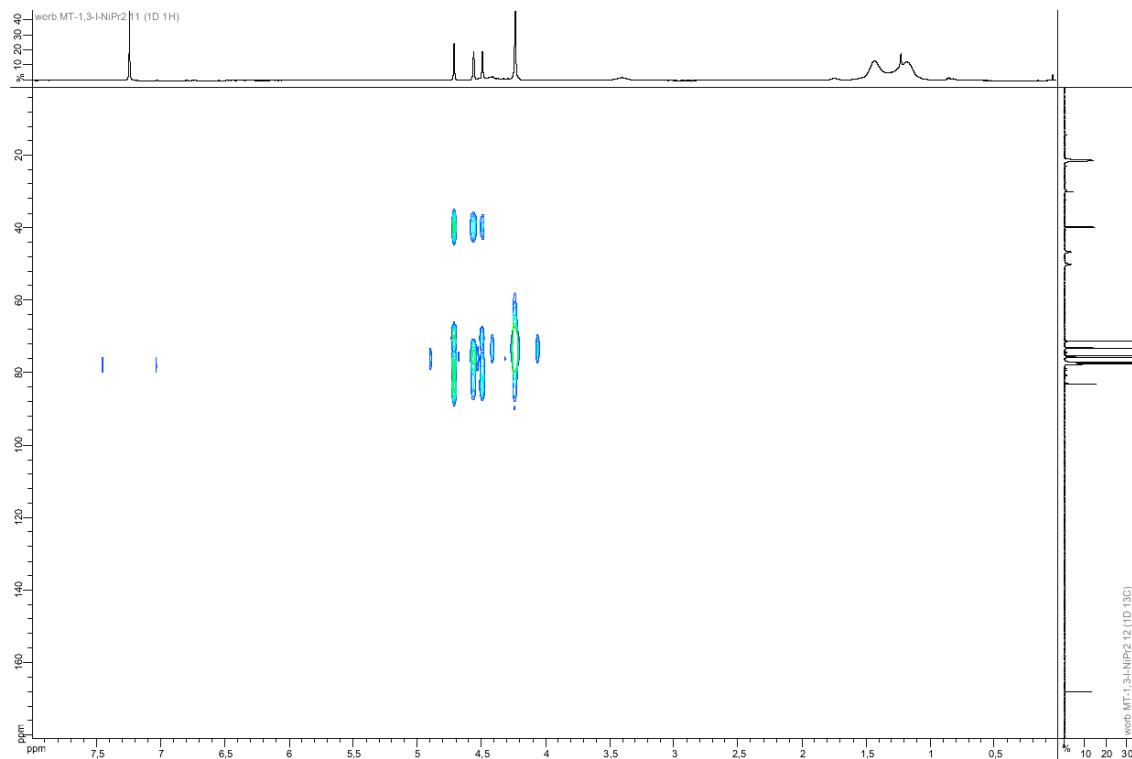
COSY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



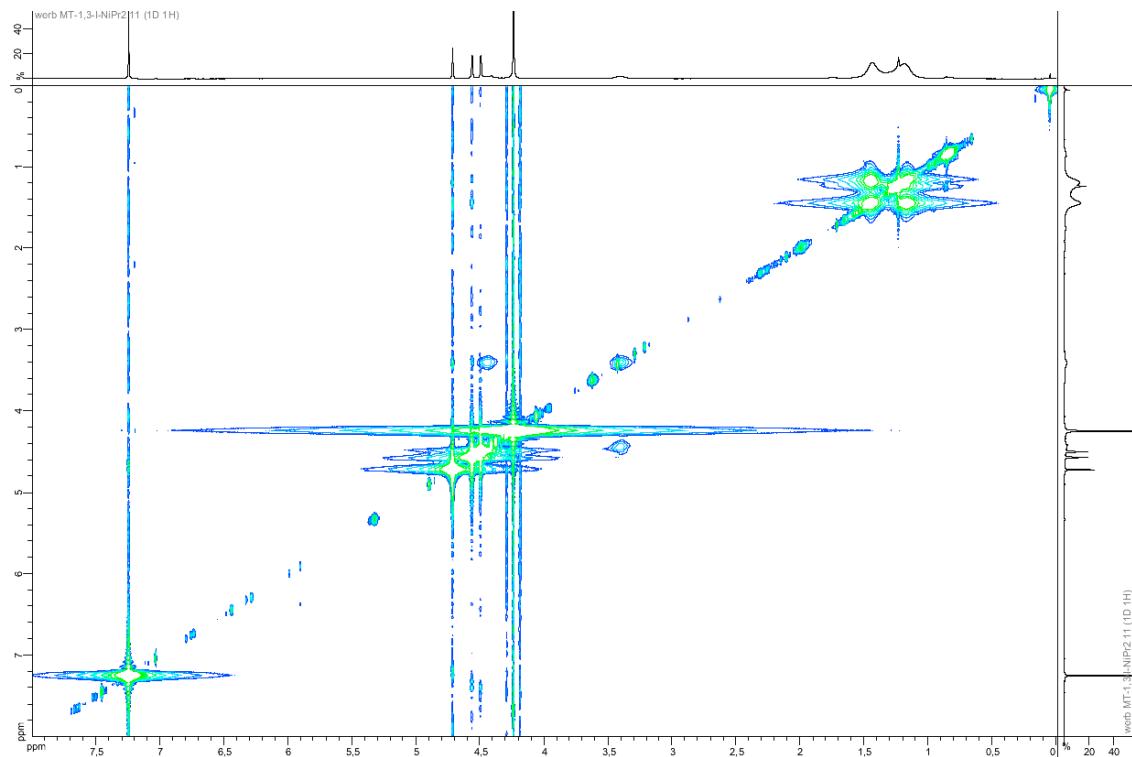
HSQC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



HMBC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

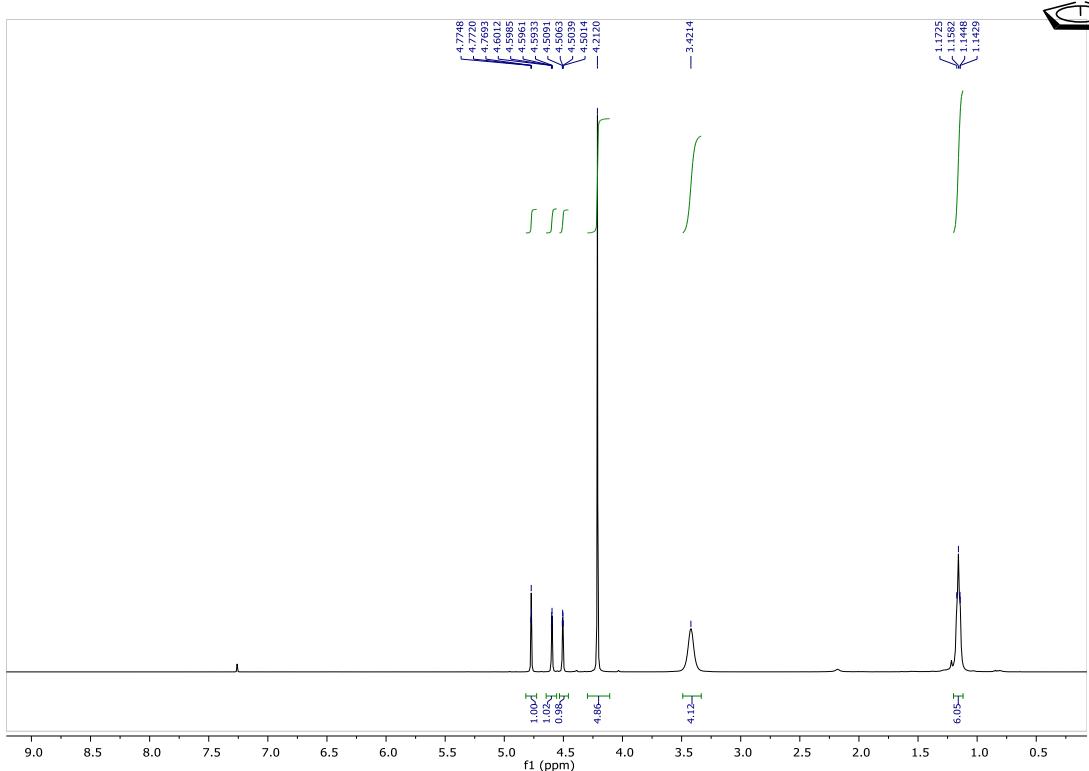


NOESY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

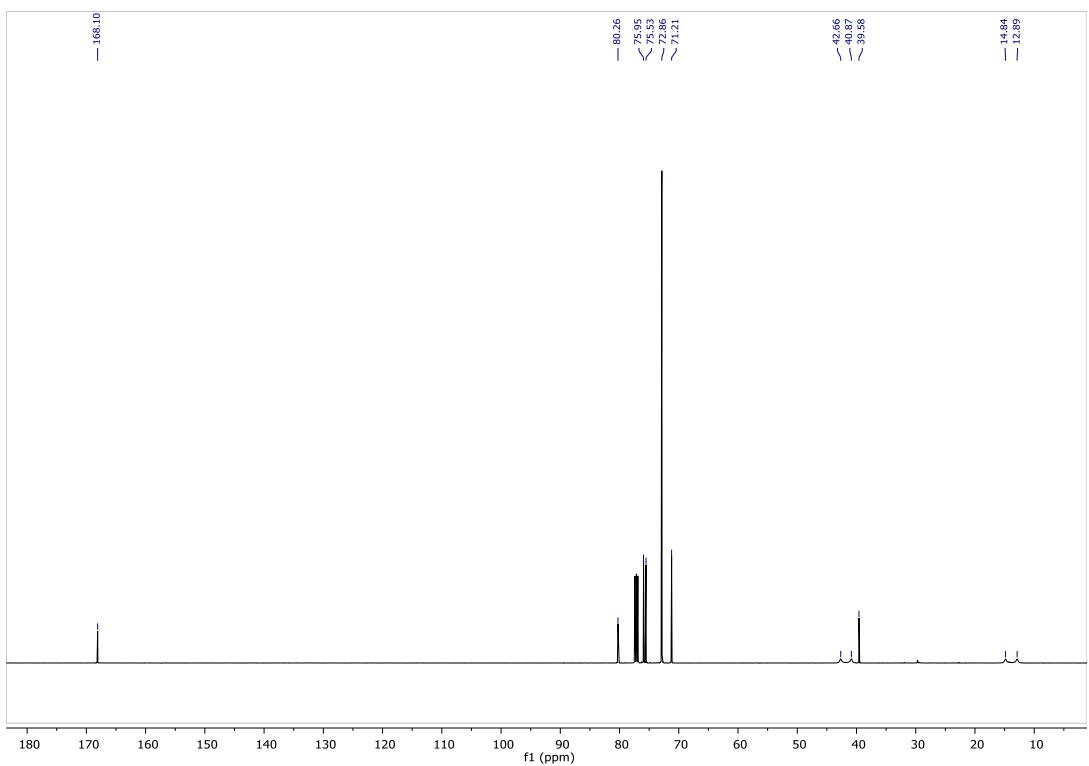


## Compound 10

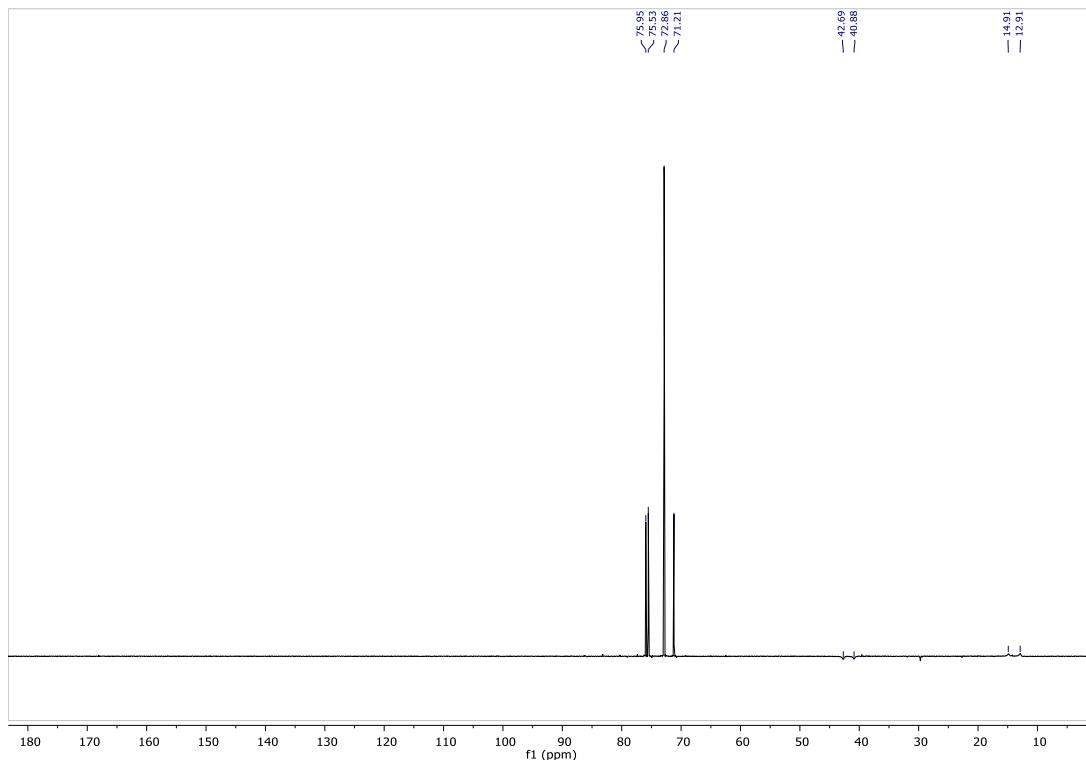
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



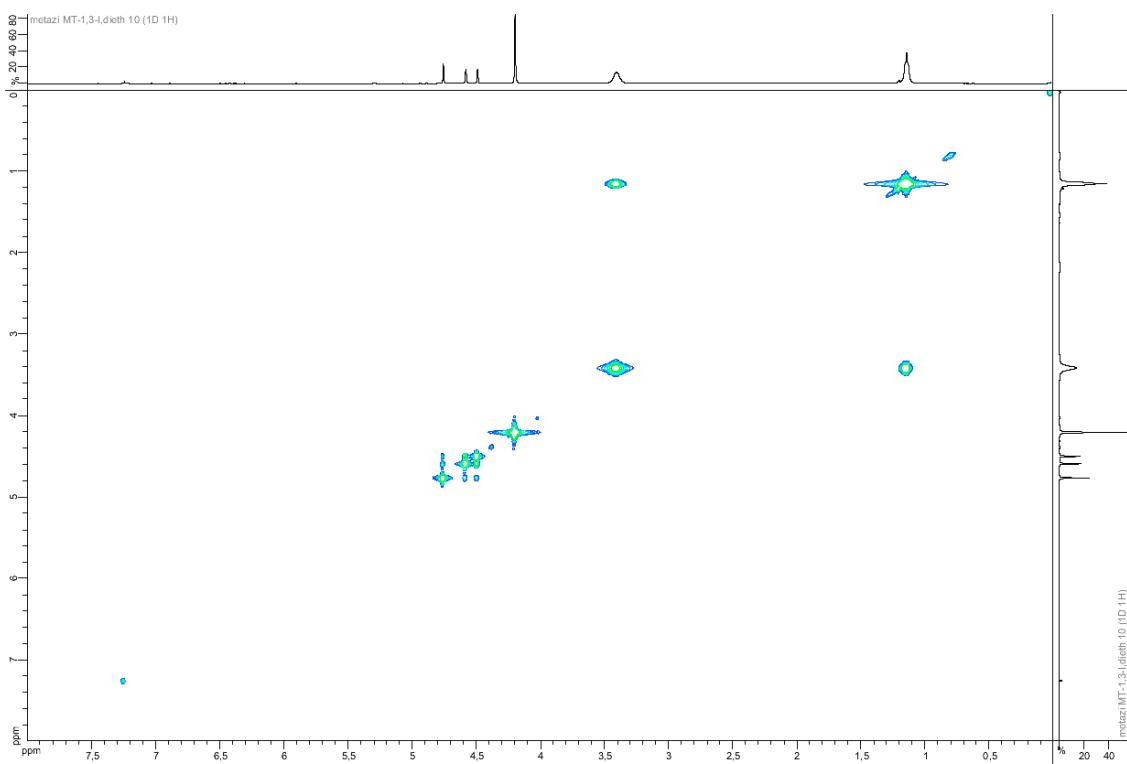
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)



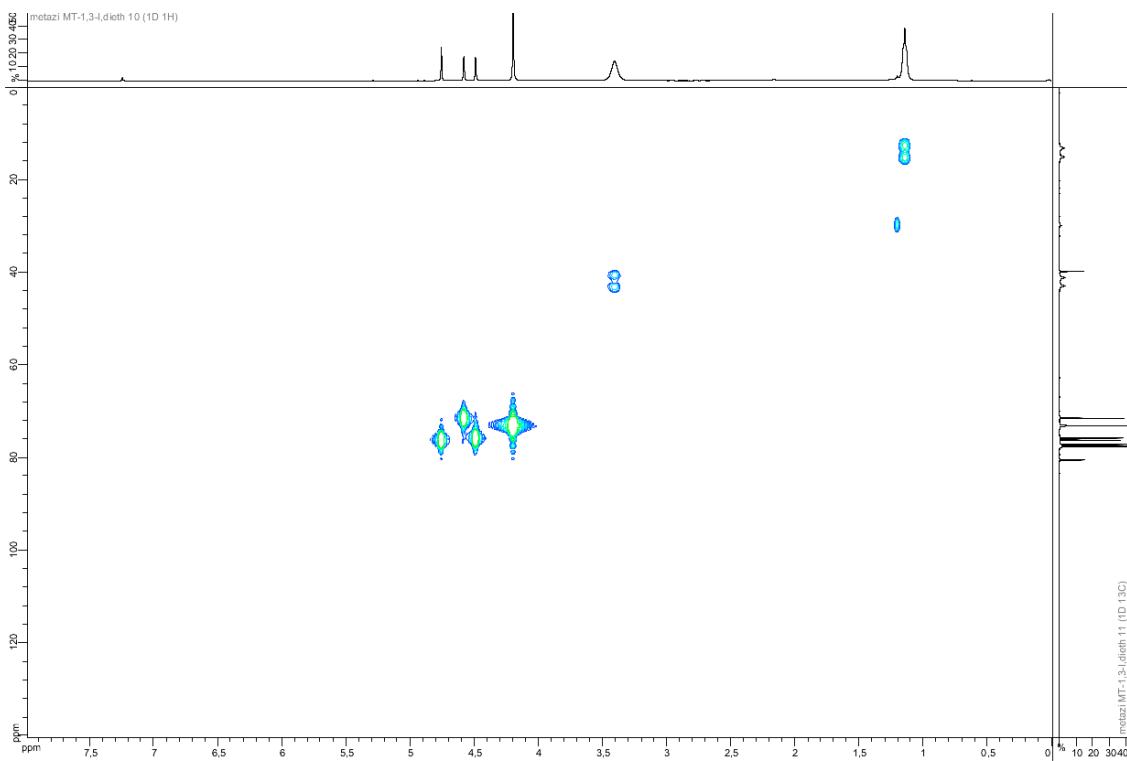
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



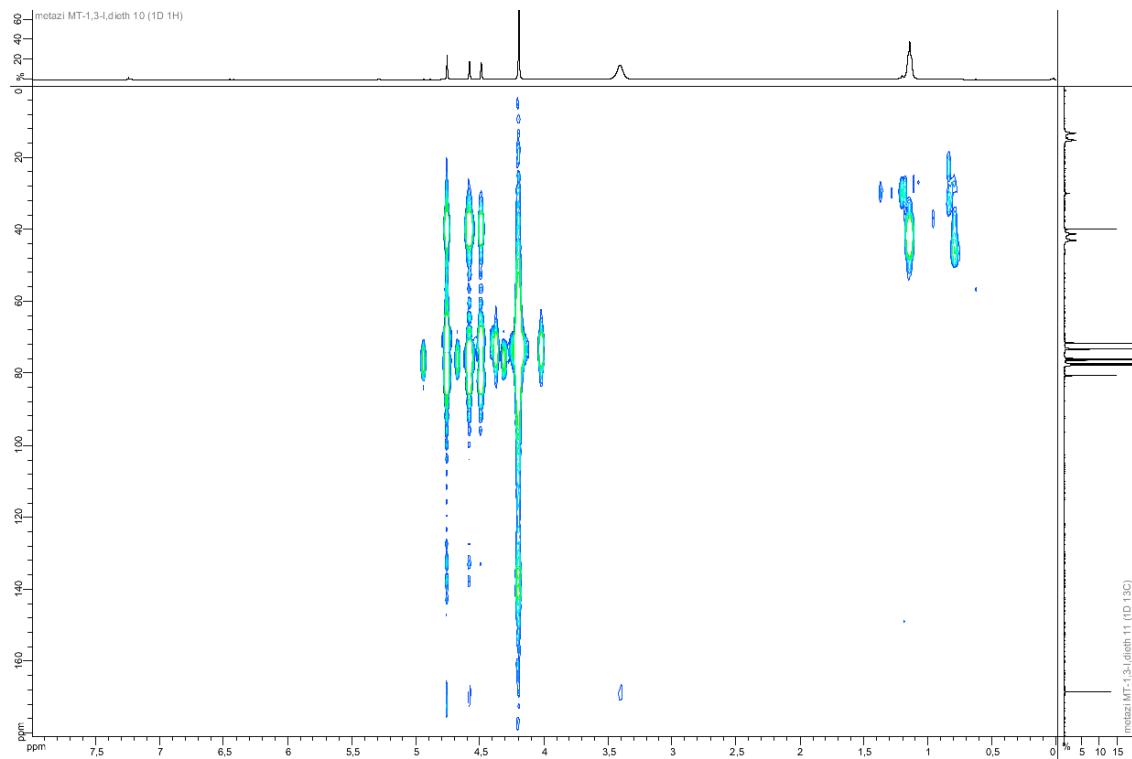
COSY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



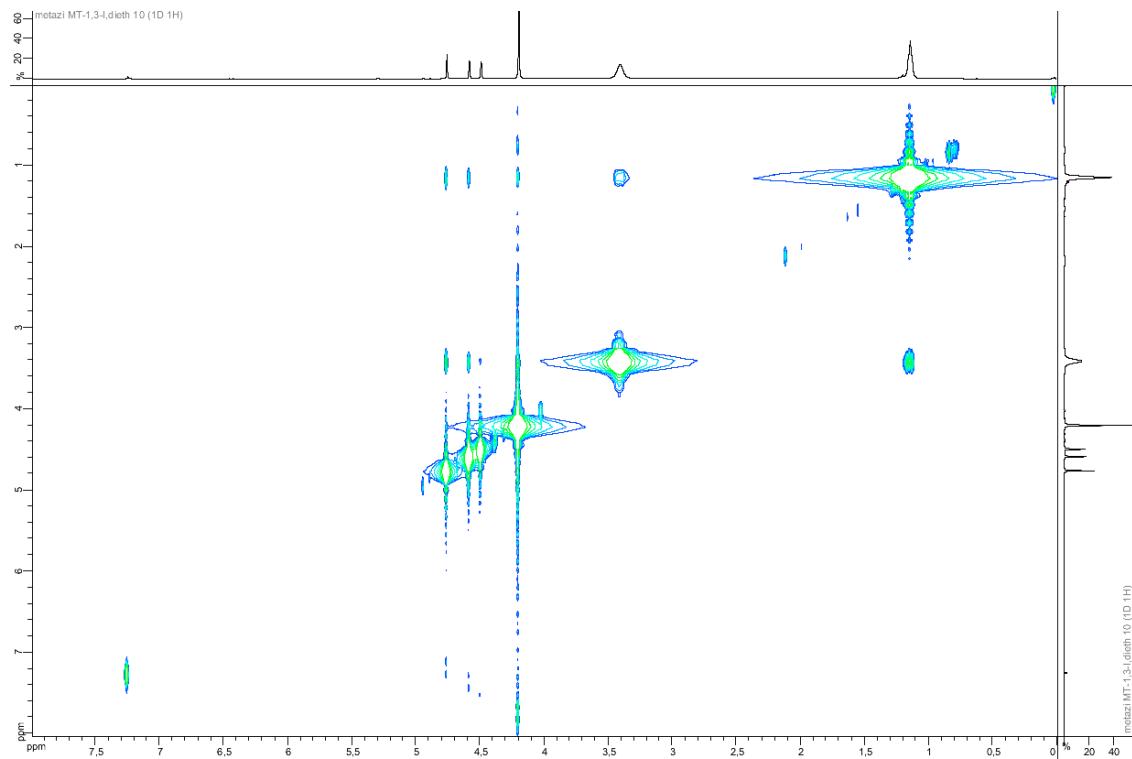
HSQC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



### HMBC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

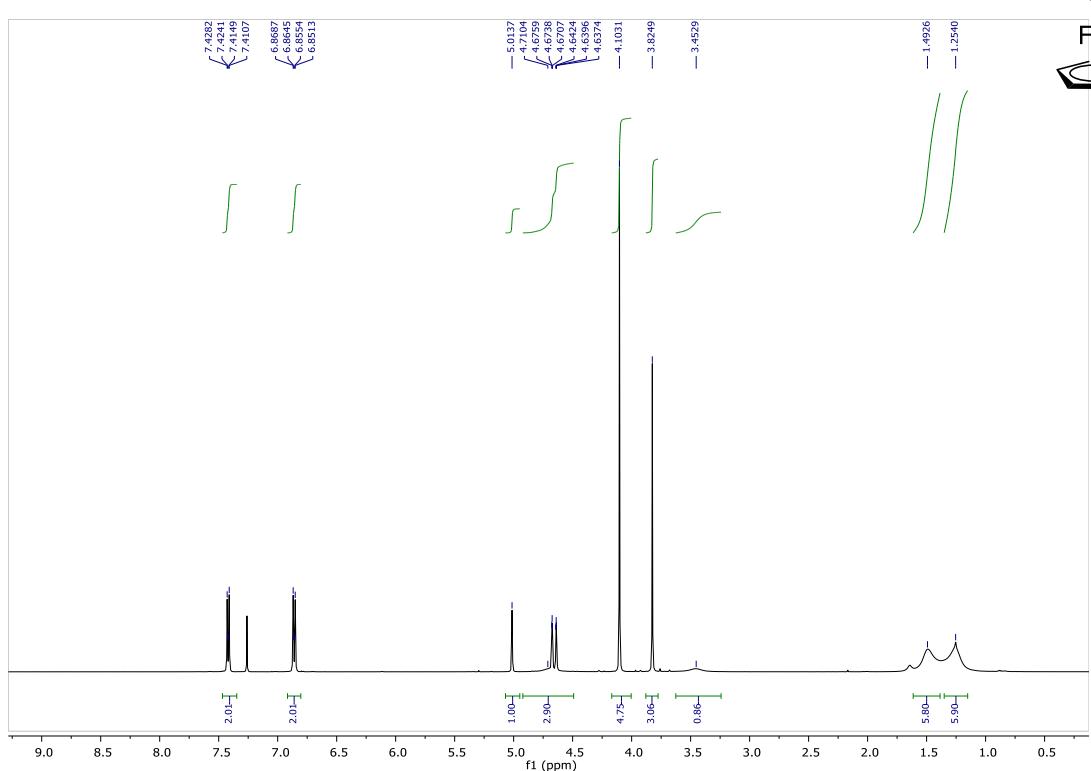


### NOESY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

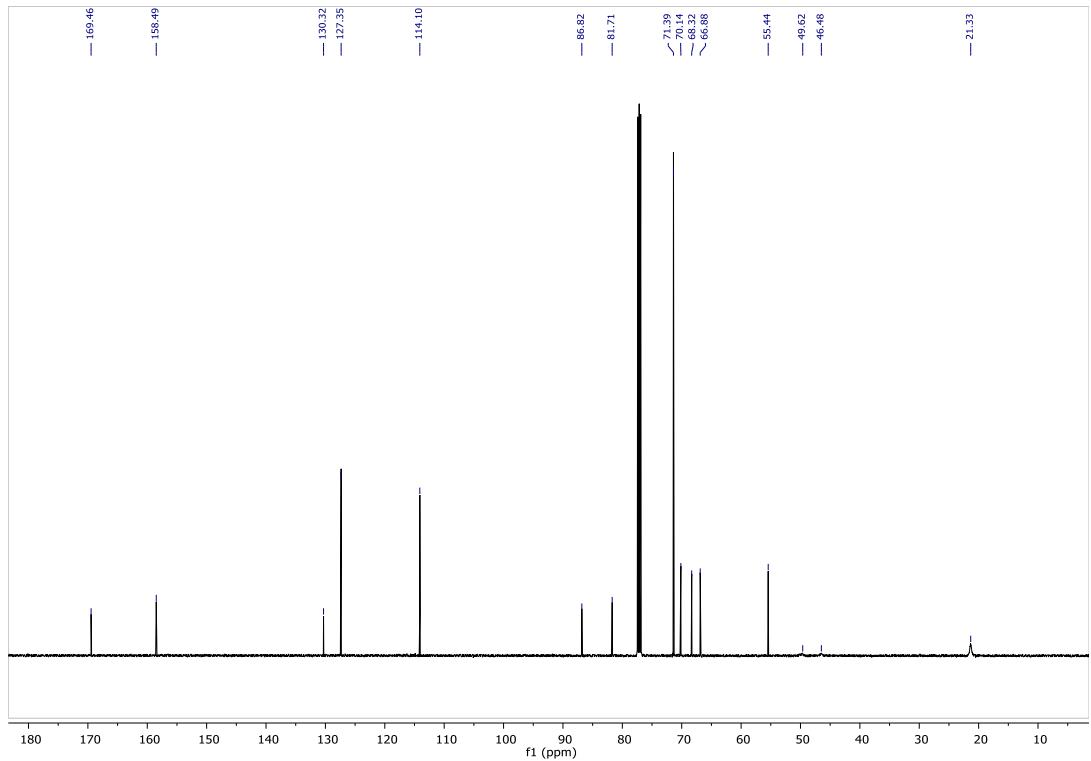


### Compound 13

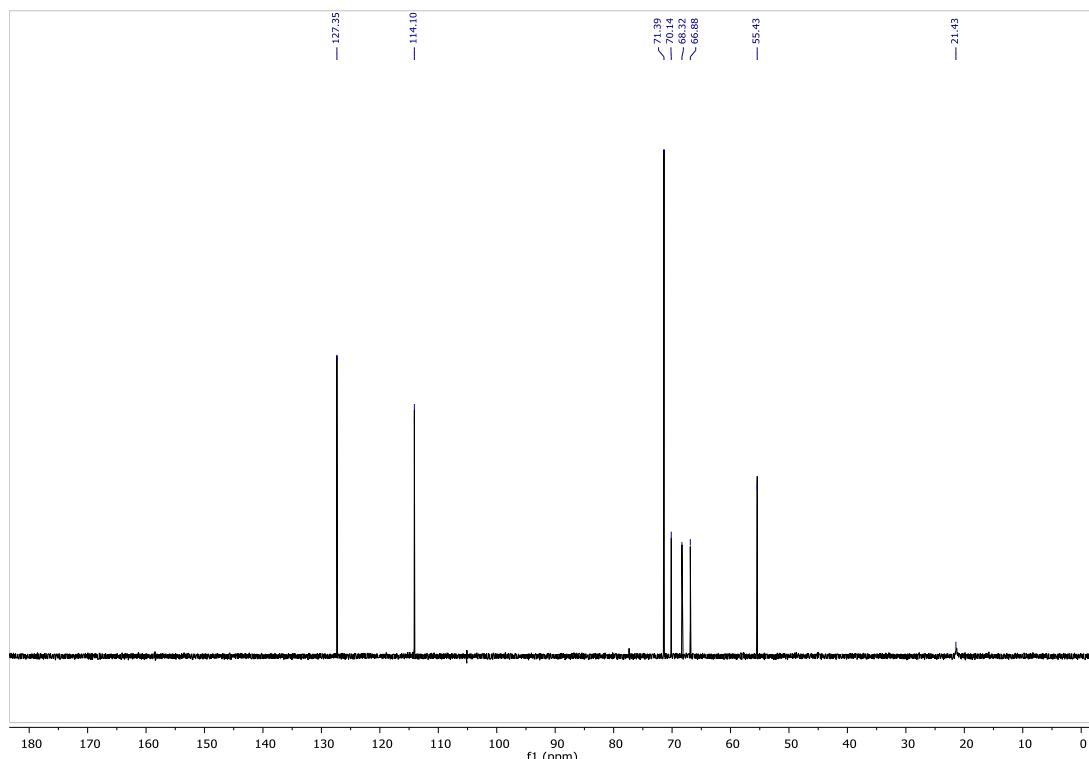
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



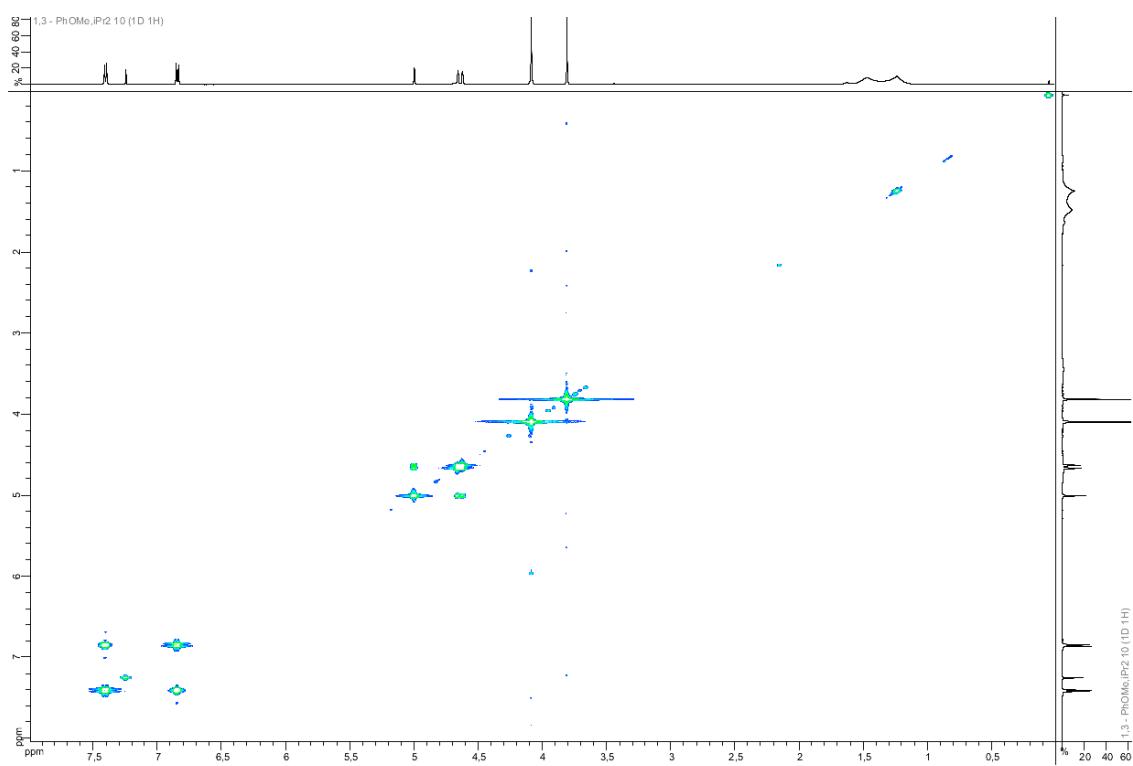
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)



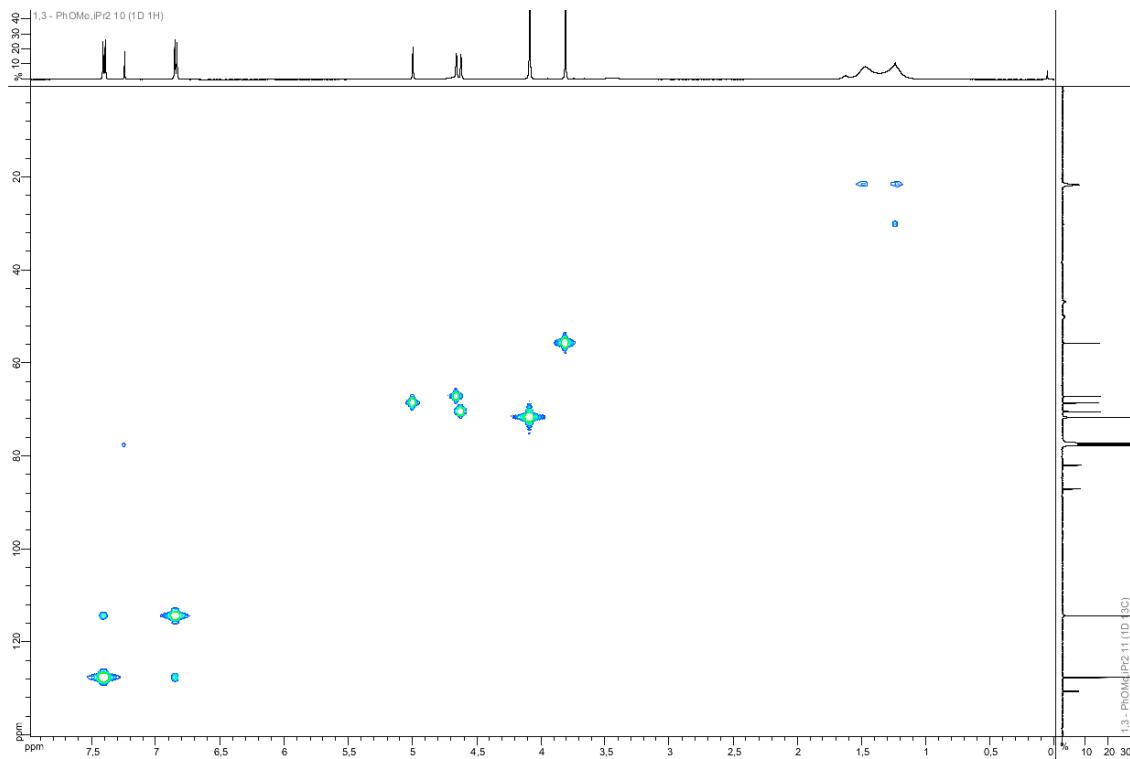
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



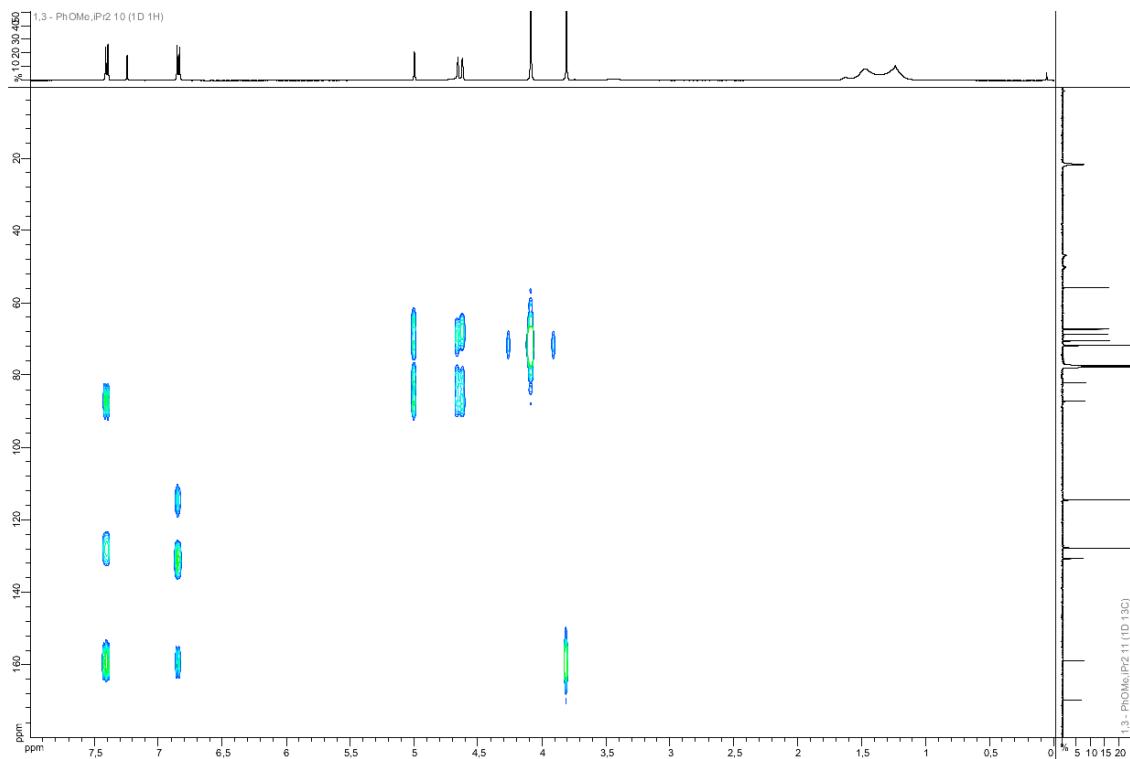
COSY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



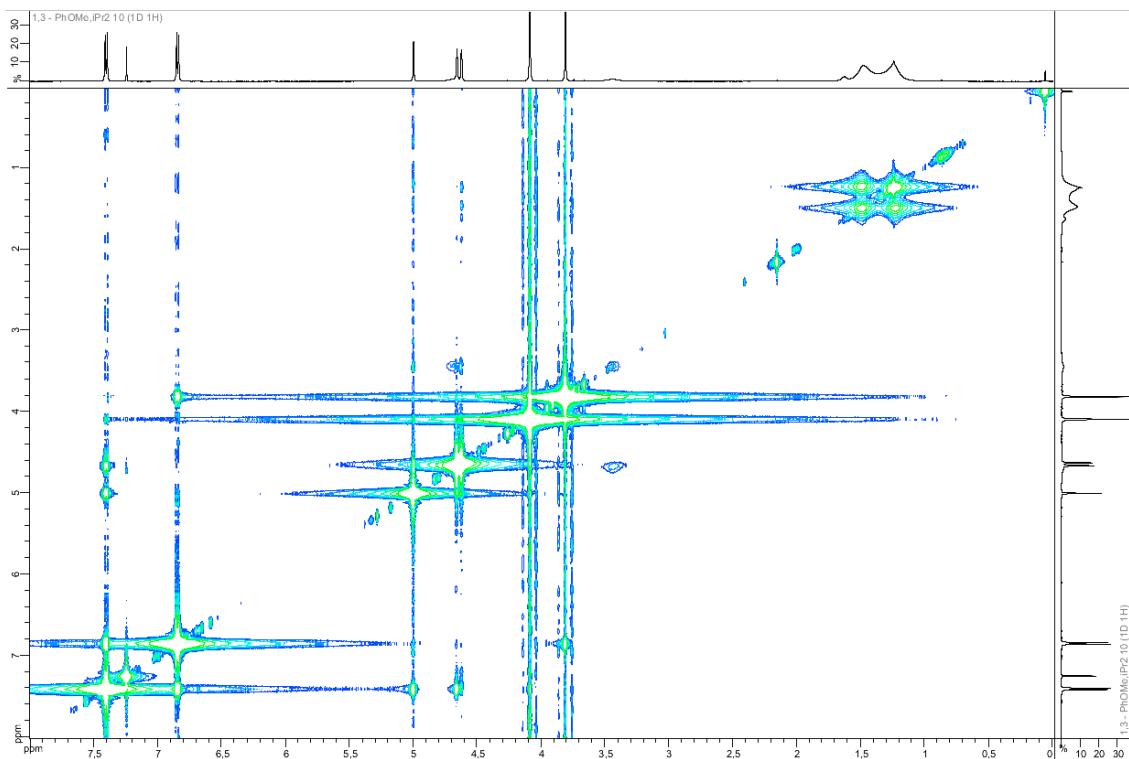
HSQC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



HMBC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

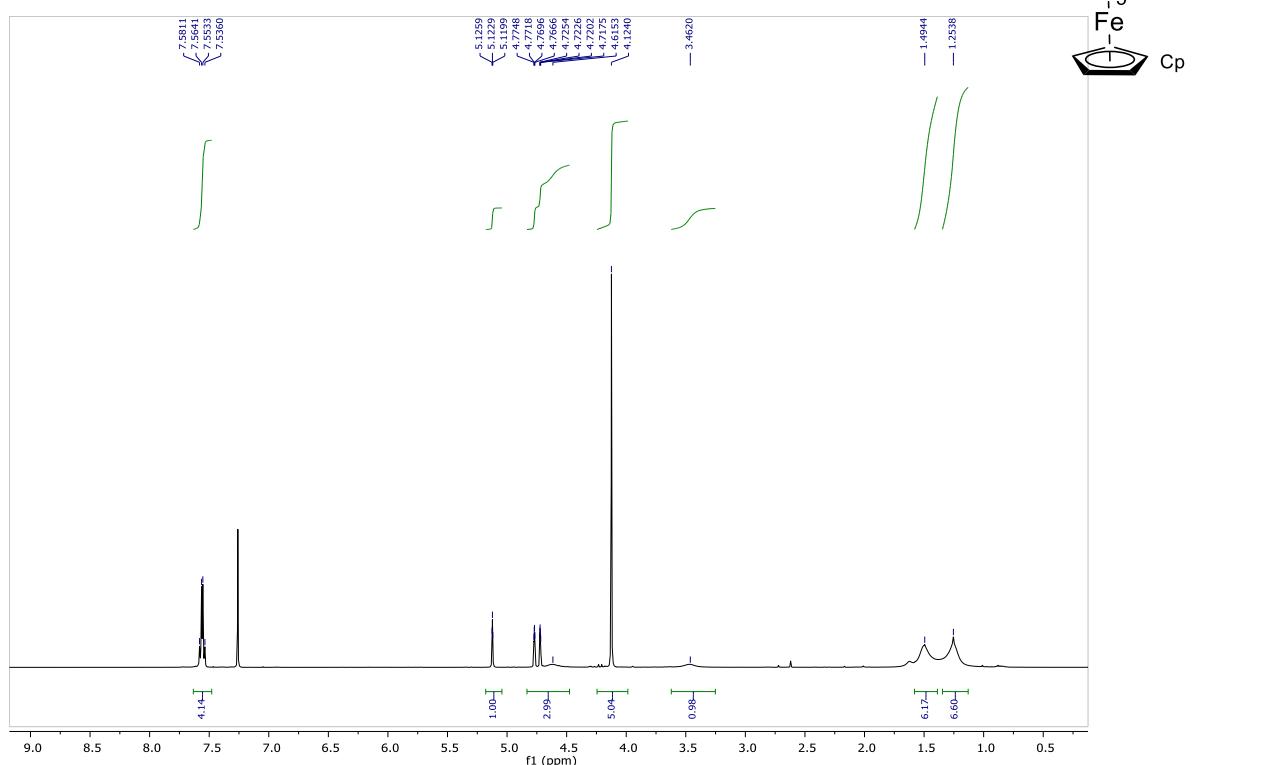


NOESY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

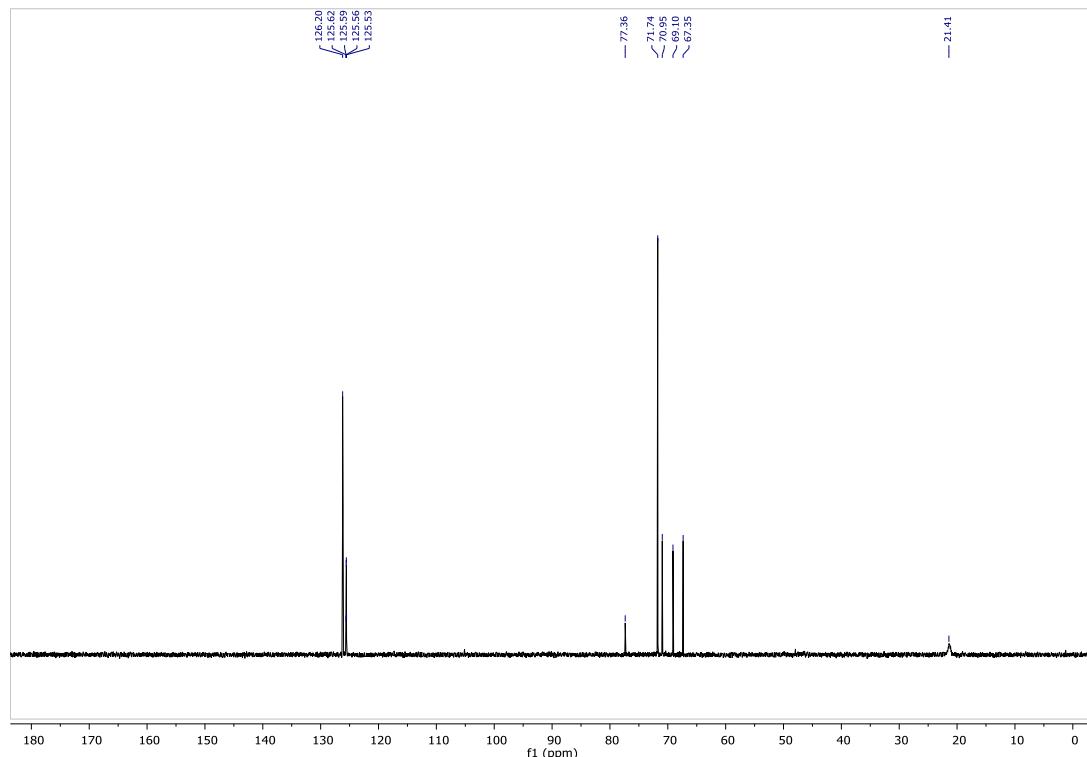


**Compound 14**

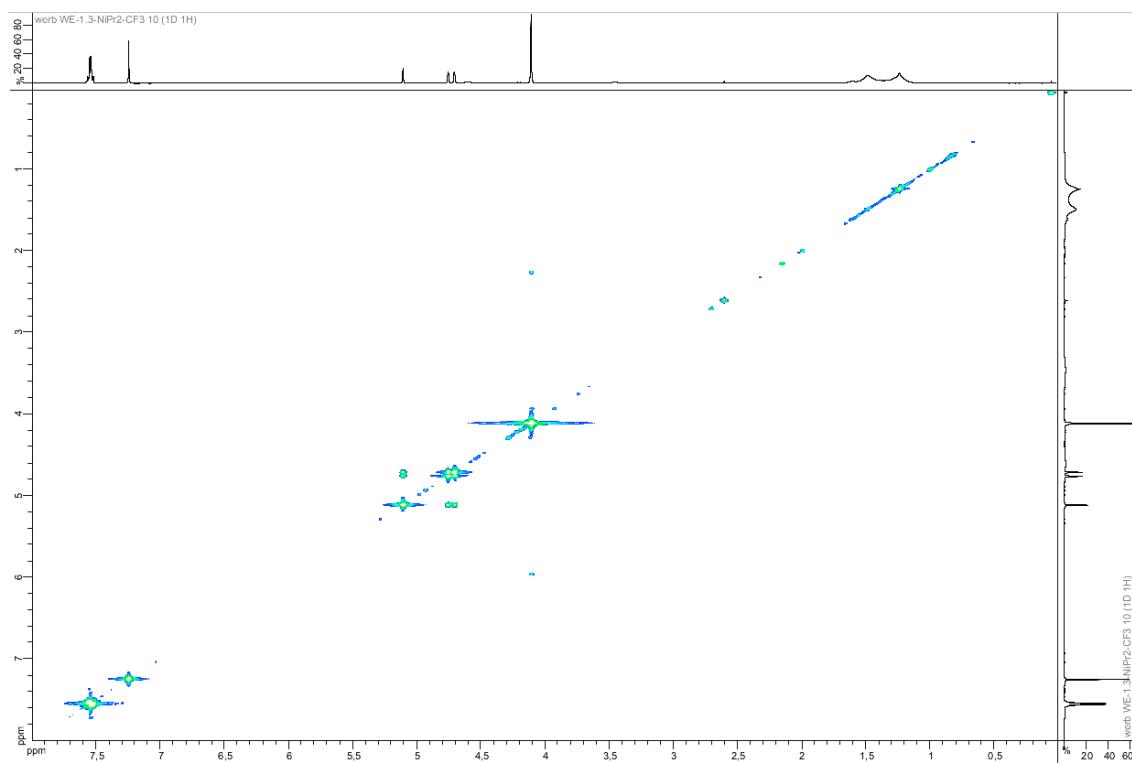
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 291 K)



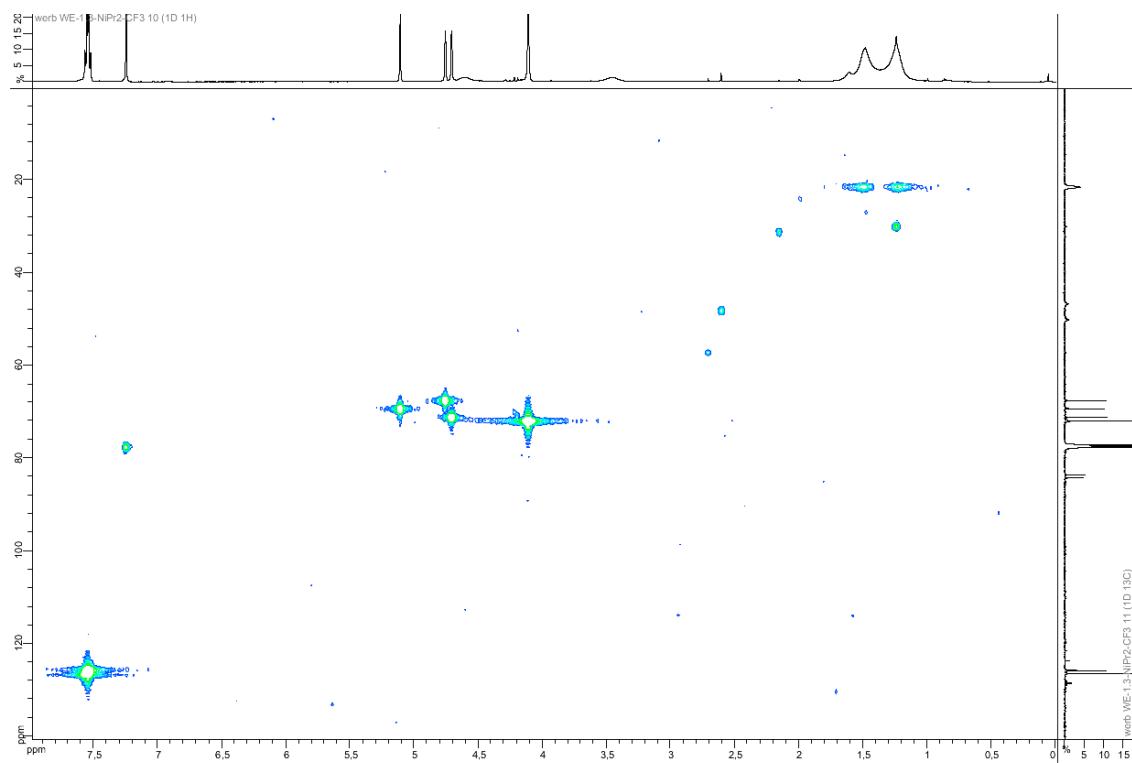
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



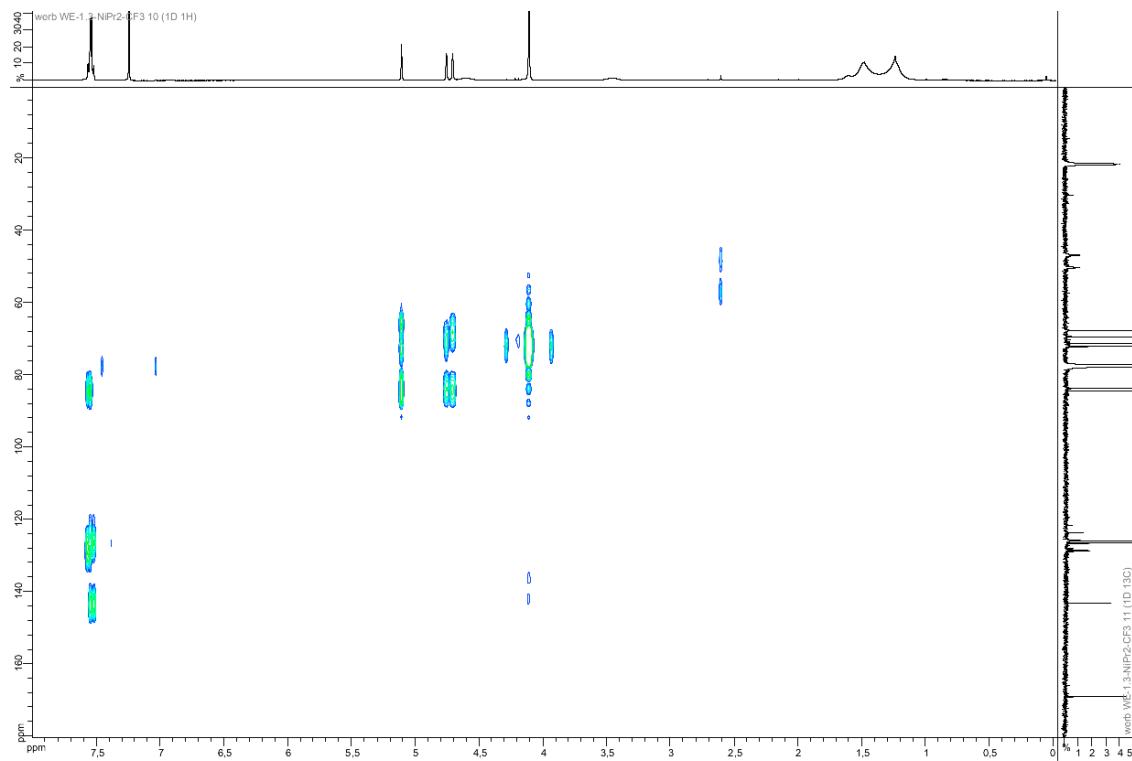
COSY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



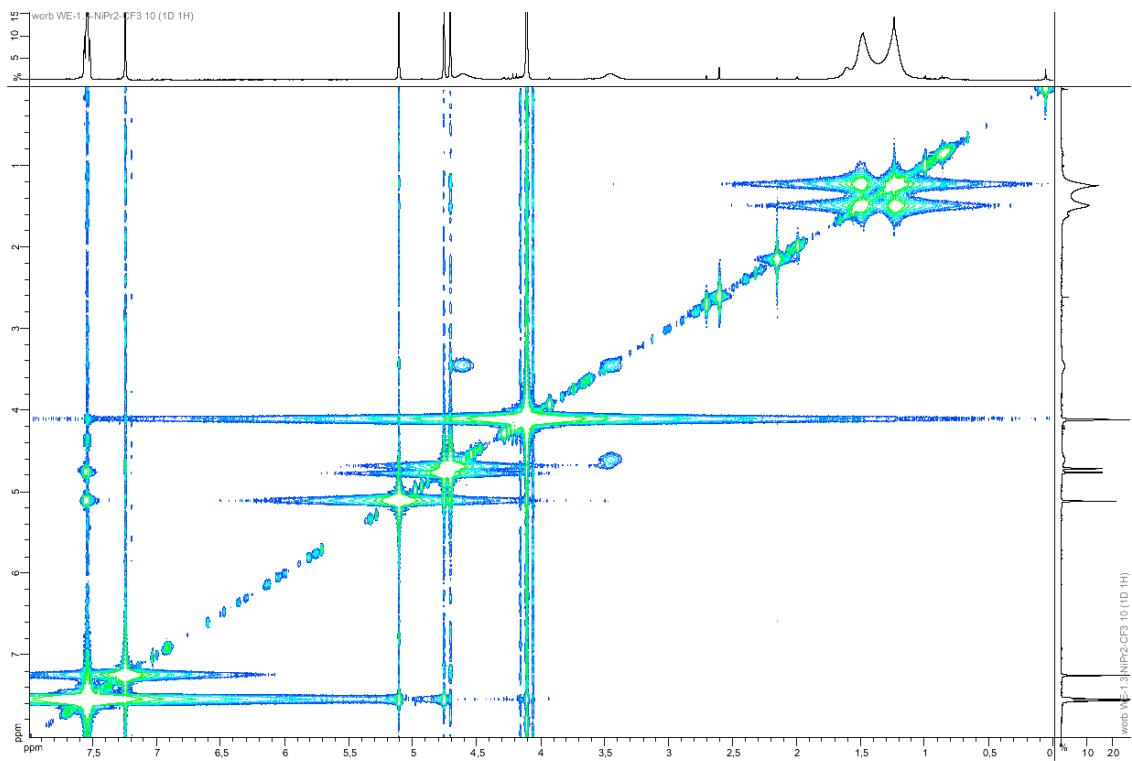
HSQC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



HMBC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

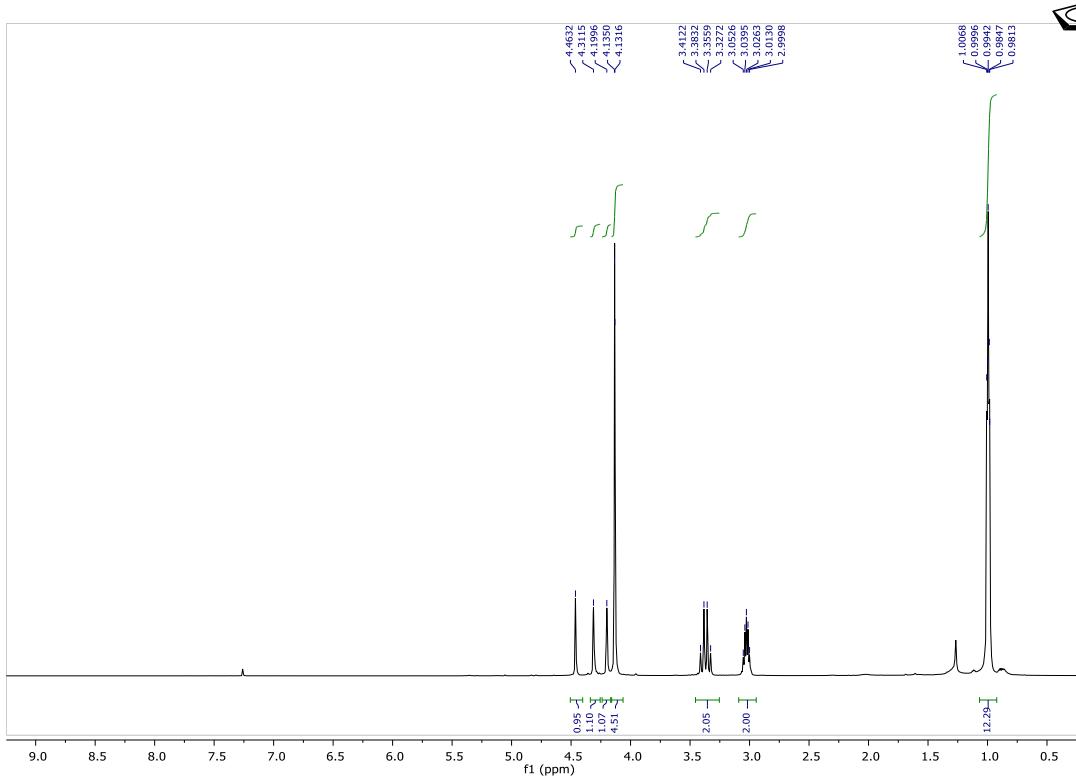


NOESY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

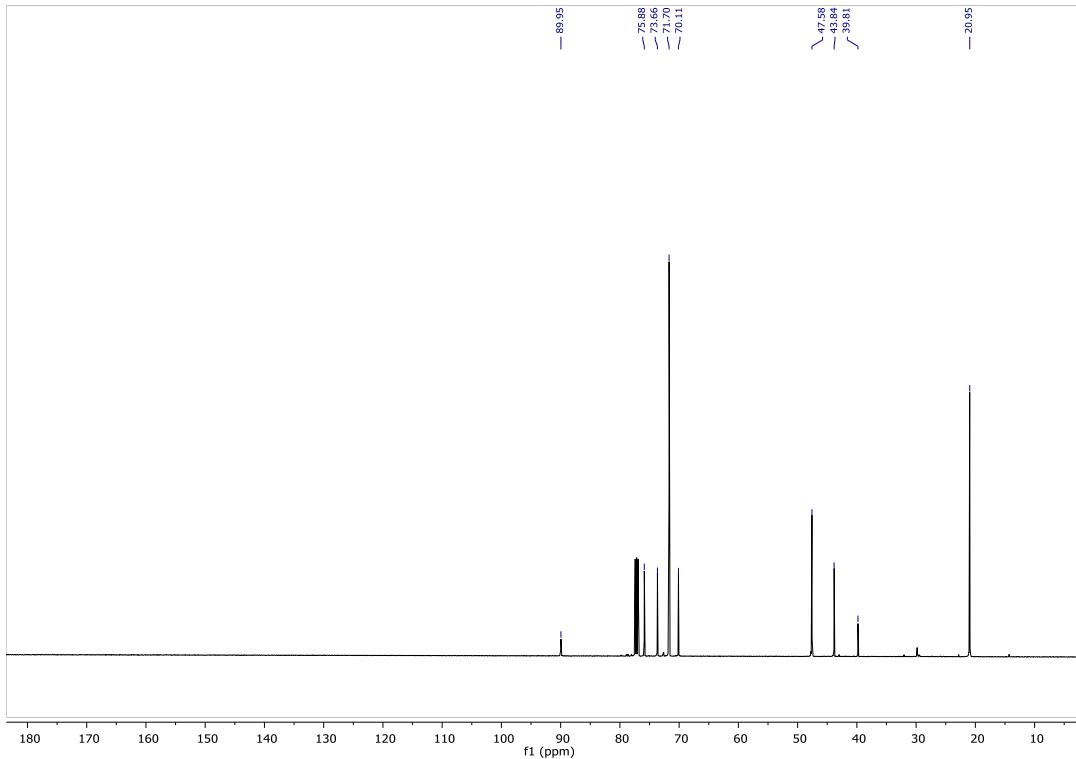


## Compound 15

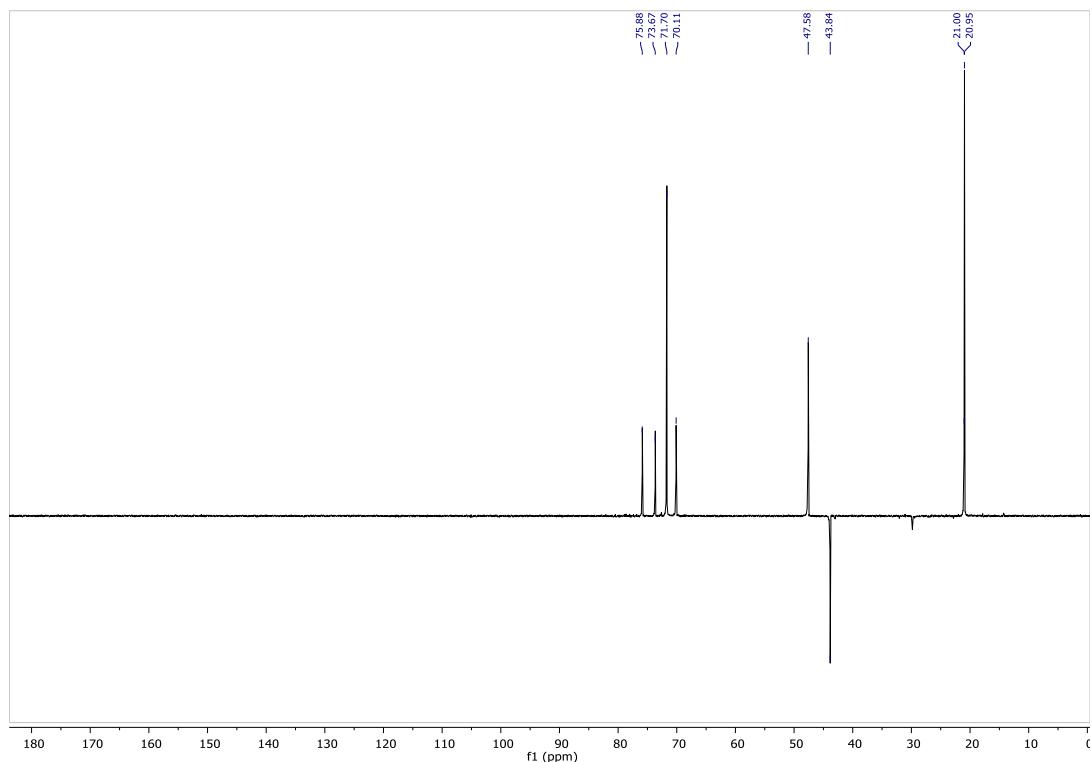
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



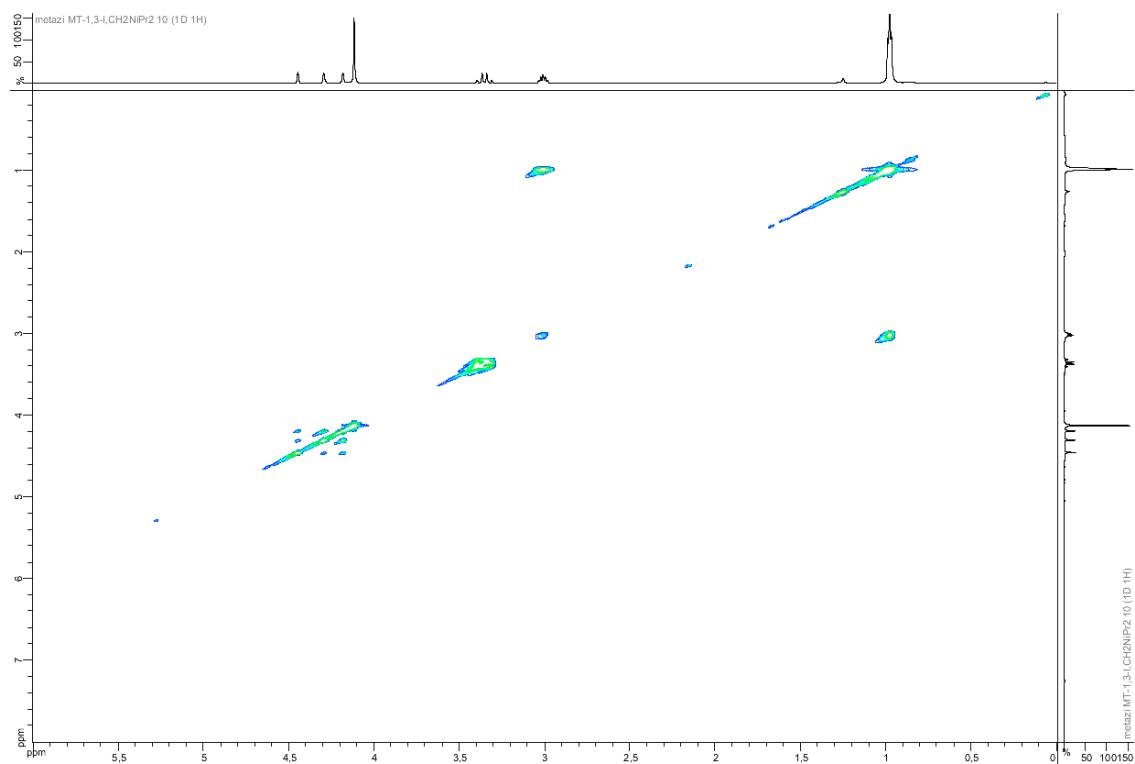
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K)



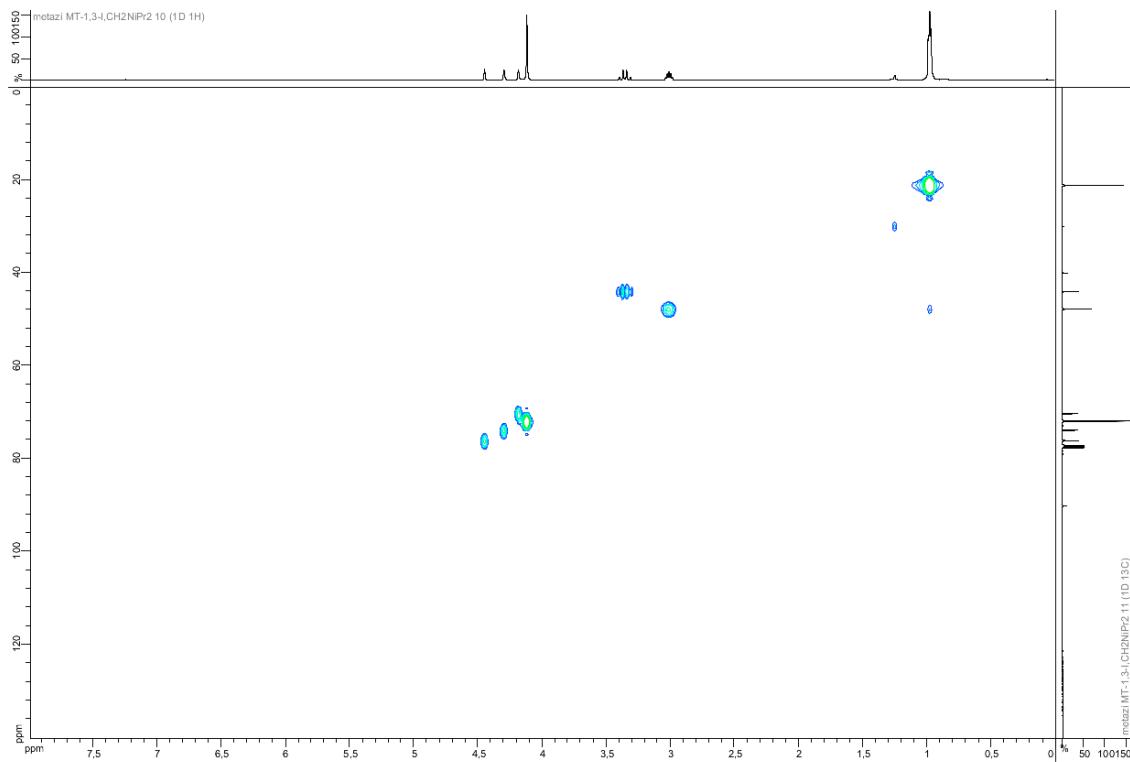
DEPT-135 (126 MHz, CDCl<sub>3</sub>, 298 K)



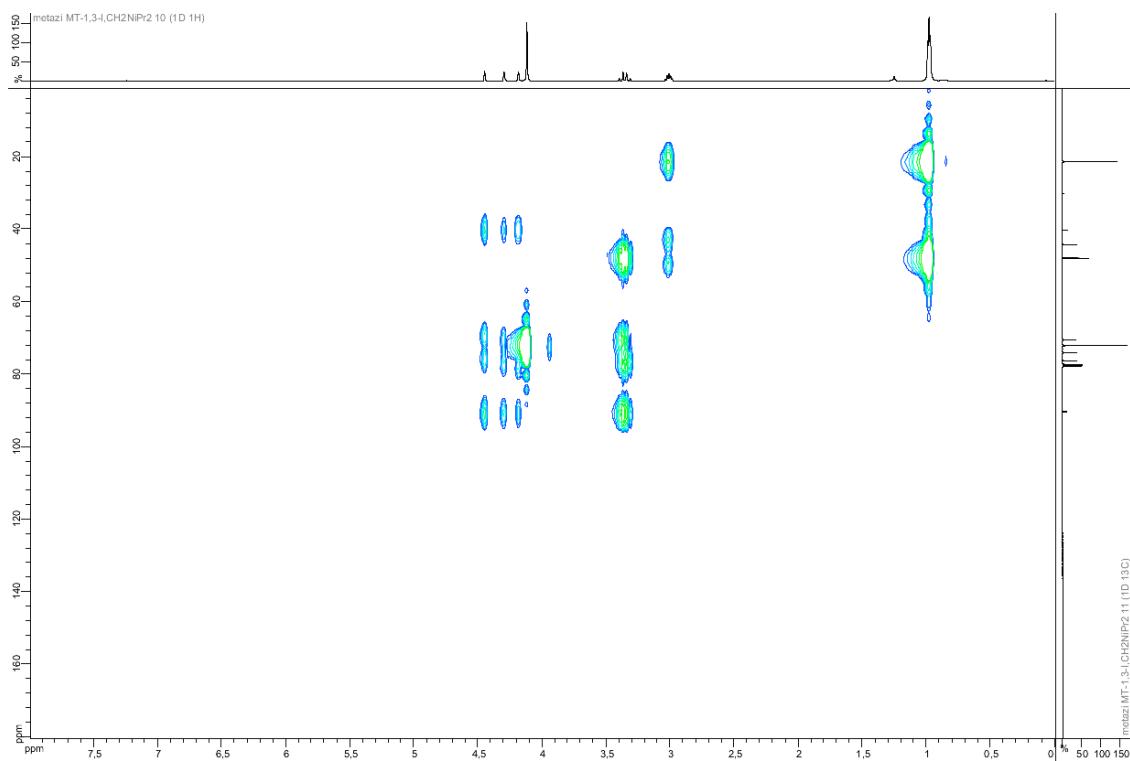
COSY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



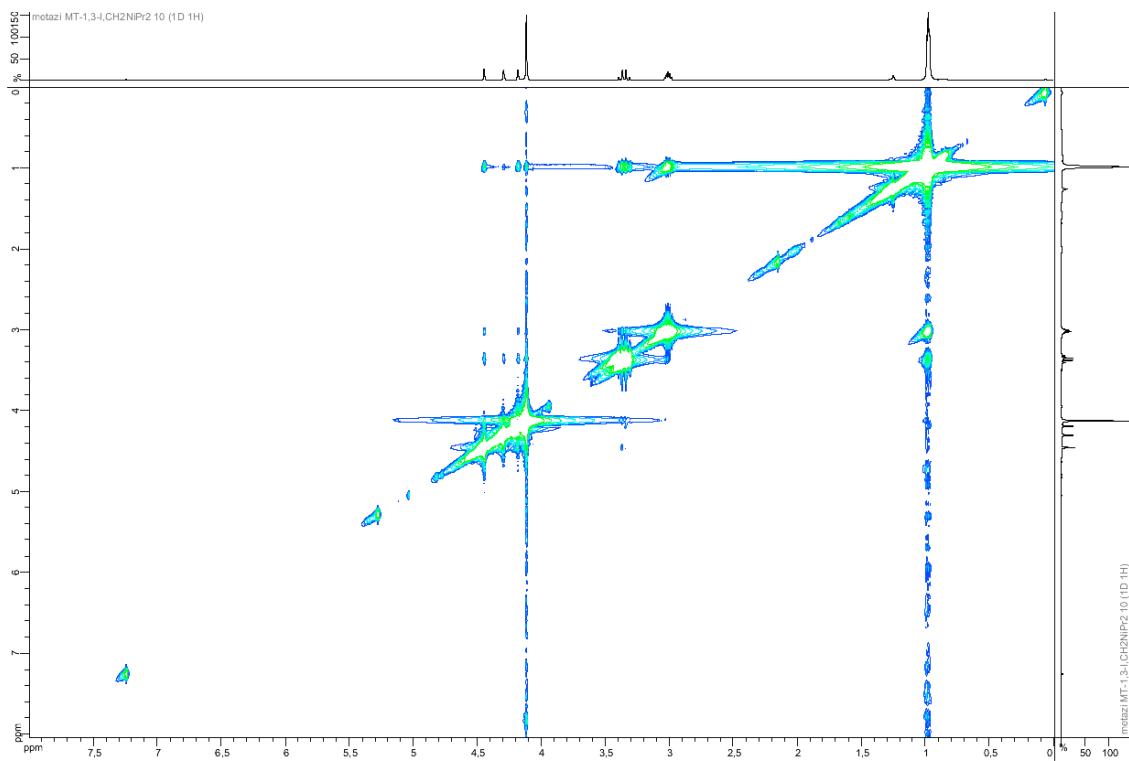
HSQC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)



HMBC NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

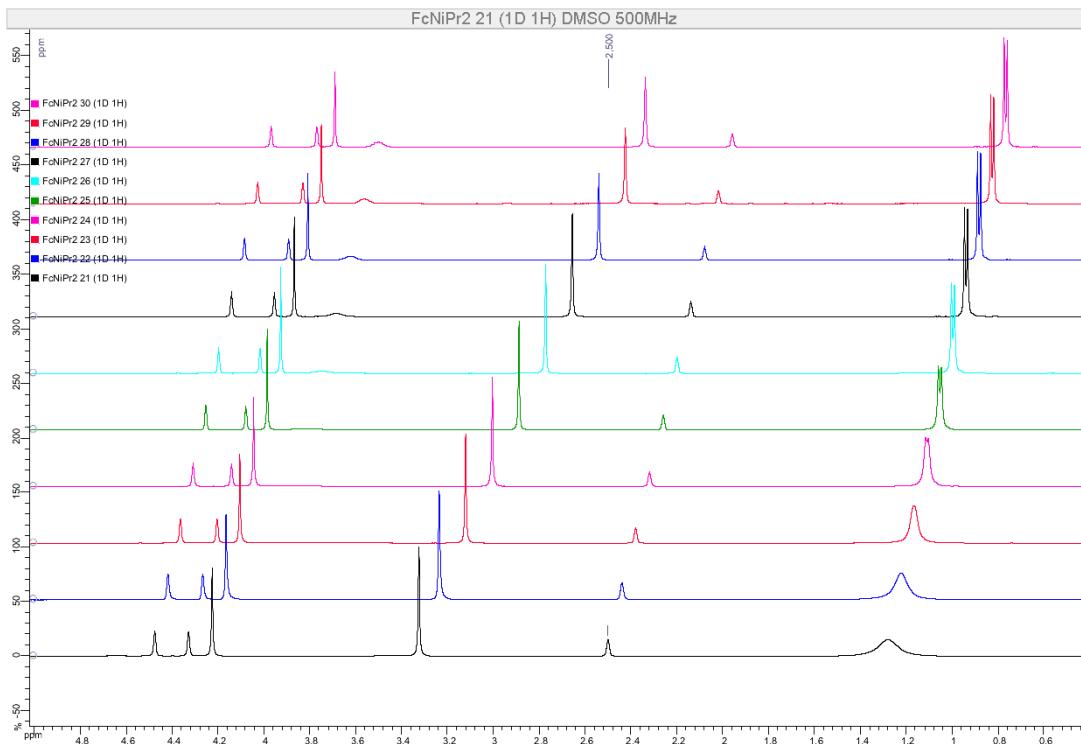
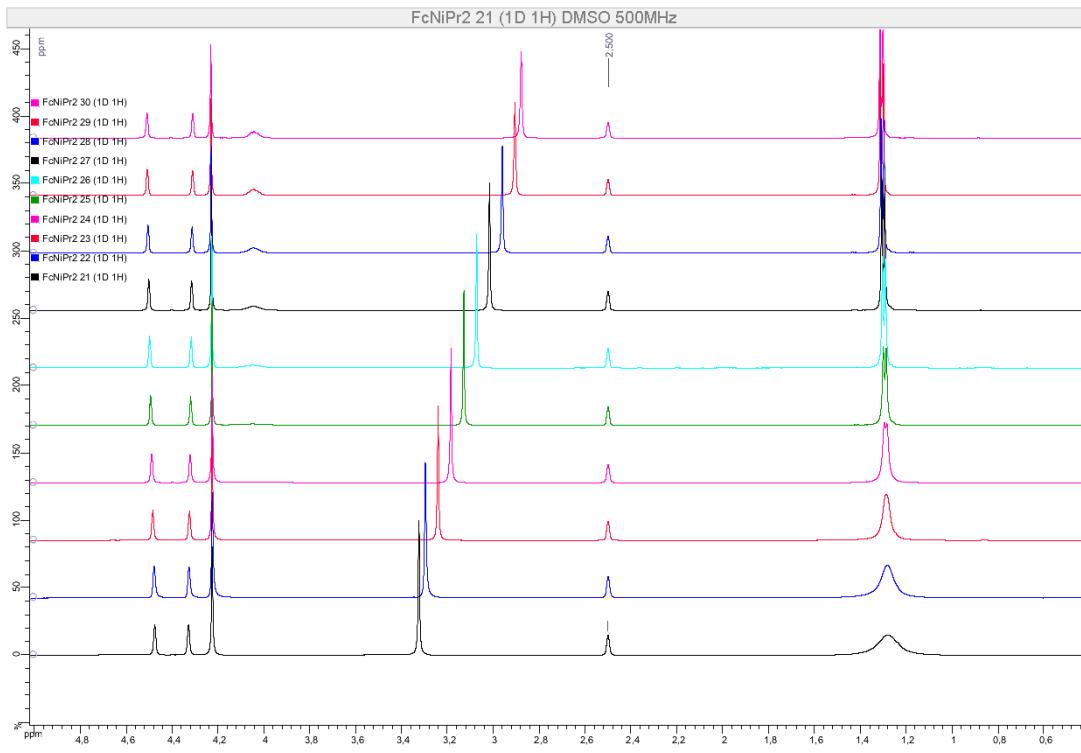
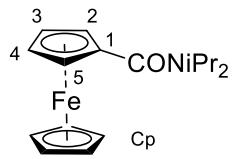


NOESY NMR (500 MHz, CDCl<sub>3</sub>, 298 K)

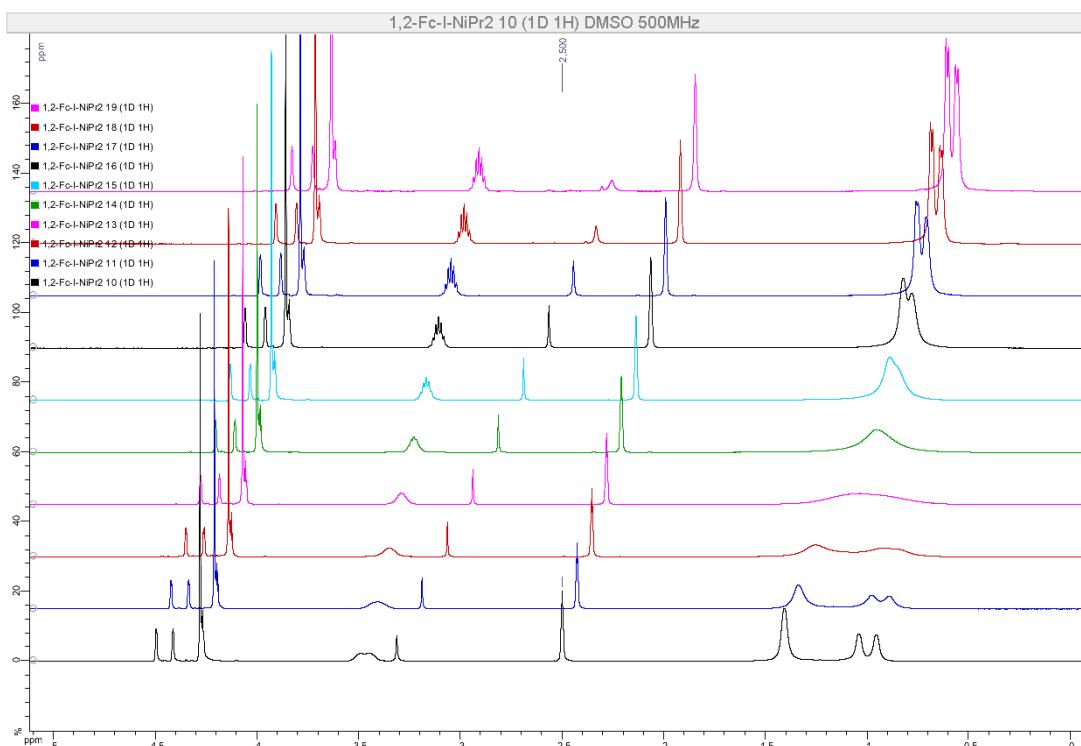
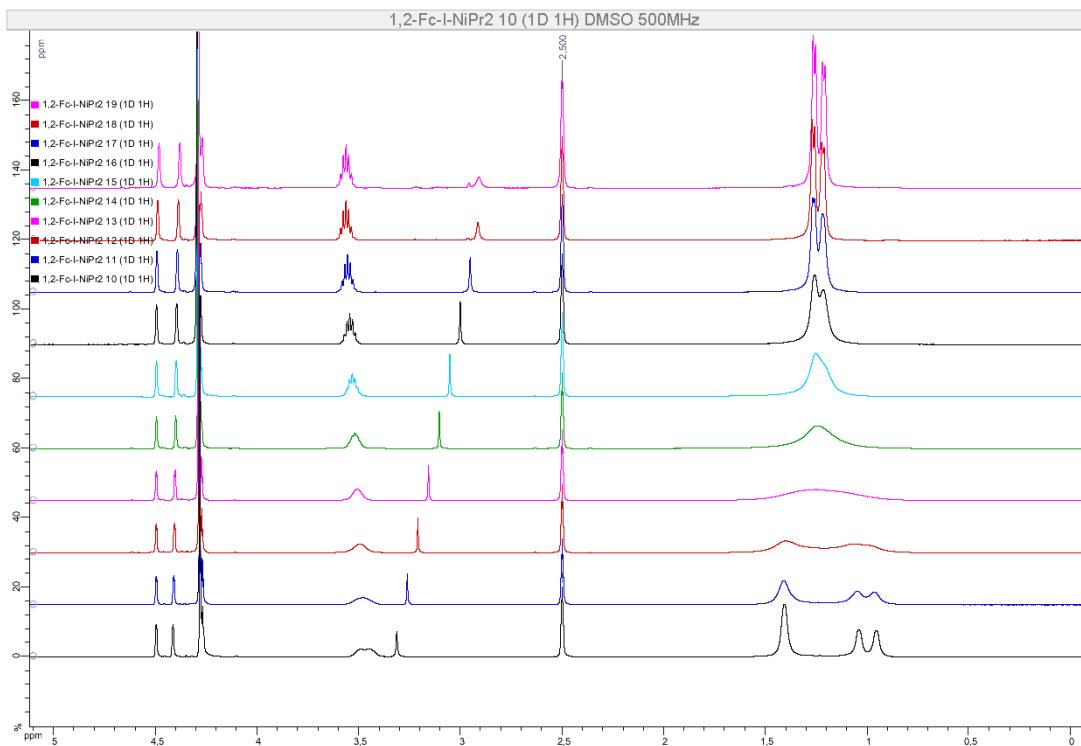
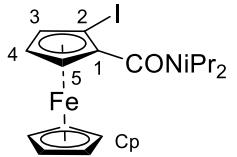


## VT-NMR

**Compound 1.**  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ , 383 K),  
bottom to top: 303 K, 308 K, 318 K, 328 K, 338 K, 348 K, 358 K, 368 K, 378 K, 383 K



**Compound 5.**  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ , 383 K),  
bottom to top: 298 K, 308 K, 318 K, 328 K, 338 K, 348 K, 358 K, 368 K, 378 K, 383 K



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