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SUPPORTING INFORMATION

Title: Chiral imidate-ferrocenylphosphanes: Synthesis and their application as P,N-ligand in the Iridium(I)-catalyzed hydrogenation of unfunctionalized and poorly functionalized olefins.

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Ref. No.:

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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I. Synthesis of Substrates

Substrates **S3**[1], **S6**[2], **S9**[3], **S10**[4], **S11**[4] were prepared according to literature procedures.

Other substrates were synthesized as follows:

E-2-methyl-cinnamyl acetate (S4):

E-2-Methyl-3-phenyl-2-propen-1-ol (**S5**) (2g, 0.0135 mol) was dissolved in dry CH_2Cl_2 (37 mL) and cooled to 0 °C. Acetic anhydride (1.65 mL, 0.0175 mol), dry Et_3N (2.44 mL, 0.0175 mol) and DMAP (77.6 mg, 0.635 mmol) were added to the reaction mixture. Next, the reaction mixture was stirred and allowed to warm to room temperature. After 5 h the reaction was finished. The solvent was removed *in vacuo*. The product was purified by flash chromatography over silicagel (Hex/EtOAc) resulting in pure **S4** as a colorless oil (2.51 g, yield: 98%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.9 (s, 3H), 2.14 (s, 3H), 4.66 (s, 2H), 6.55 (s, 1H), 7.23-7.38 (m, 5H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 15.5 (CH_3), 21.0 (CH_3), 70.1 (CH_2), 126.8 (CH), 128.1 (CH), 128.3 (CH), 128.9 (CH), 132.7 (C), 137.0 (C), 170.9 (C) ppm. IR (HATR): 3745, 3616, 3592, 3024, 2934, 1736, 1600, 1489, 1443, 1372, 1224, 1048, 1021, 979, 961, 915, 849, 745, 696 cm^{-1}.

1-t.Butyl-6-methoxy-3,4-dihydronaphthalene (S7):

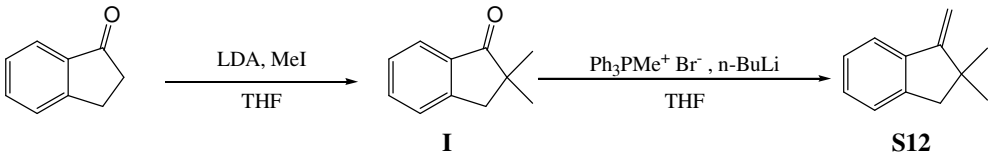
6-Methoxy-1-tetralone (5 g, 0.0284 mol) was dissolved in dry THF (25mL) and cooled to 0 °C. Next, *t*BuMgBr (36.9 mL, 0.0369 mmol) was added dropwise. Afterwards, the reaction mixture was stirred and allowed to warm to room temperature. Stirring was continued overnight. The next day, *t*BuMgBr (1M in THF, 8.5 mL, 8.5 mmol) was added dropwise via syringe at 0°C. After 26 h the reaction was stopped. The reaction mixture was carefully (CAUTION: exothermic and gas evolution) poured into an excess of saturated NH_4Cl-solution and extracted with Et_2O (3 x 200 ml). The combined organic phases were dried on $MgSO_4$, filtered and evaporated *in vacuo*. Next, the crude product was dissolved in $CHCl_3$ (122 mL). An aqueous solution of 10% HCl (122 mL) was added and the reaction mixture was stirred vigorously overnight. Next, the organic phase was separated from the acidic water phase, and washed with water (100 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated *in vacuo*, and purified by flash chromatography over silicagel (pentane/Et_2O: 99/1) resulting in pure **S7**, 1.15 g (19%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H), 2.11-2.18 (m, 2H), 2.60 (t, *J*= 7.4 Hz, 2H), 3.80 (s, 3H), 5.95 (t, *J*= 4.9 Hz, 1H), 6.69-6.73 (m, 2H), 7.55 (d, *J*= 9.0 Hz, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 23.4 (CH_2), 29.9 (CH_2), 31.0 (CH_3), 55.1 (CH_3), 110.1 (CH), 113.7 (CH), 121.7 (CH), 126.9 (CH), 127.8 (C), 140.6 (C), 144.5 (C), 157.3 (C) ppm. IR (HATR): 3058, 2997, 2960, 2937, 2885, 2832, 1608, 1561, 1487, 1464, 1424, 1392, 1352, 1320, 1297, 1279, 1247, 1130, 1048, 992, 936, 882, 828, 793, 721 cm^{-1}.

3-Methyl-2-phenyl-butene (α-isopropylstyrene) (S11):

Methyltriphenylphosphoniumbromide (24.1 g, 0.0675 mol) was dissolved in dry THF (100 mL) and cooled to 0°C. *n*-BuLi (27 mL, 0.0675 mol) was added dropwise at 0°C and the reaction mixture was stirred for 5 min at 0°C. Next, isobutyrophenone (10 g, 0.0675 mol) was dissolved in dry THF (100 mL) and added via a double tipped needle to the reaction mixture at 0°C. The reaction was stirred overnight at room temperature. Afterwards, a solution of 1 M HCl was added until pH=5 and H_2O (100 mL) was added. The reaction mixture was extracted

with Et_2O (3 x 100 mL). The combined organic phases were dried over $MgSO_4$, filtered, evaporated *in vacuo* and purified by flash chromatography over silicagel (pentane) resulting in pure **S11**, 7.93 g (80%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.10 (d, *J*= 6.8 Hz, 6H), 2.84 (h, *J*= 6.8 Hz, 1H, 5.03 (app. t, *J*= 1.3 Hz, 1H), 5.14 (app. s, 1H), 7.22-7.37 (m, 5H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 22.0 (CH_3), 32.3 (CH), 110.0 (C), 126.6 (CH), 127.0 (CH), 128.1 (CH), 142.9 (C) ppm. IR (HATR): 3081, 3056, 3025, 2961, 2929, 2872, 1624, 1602, 1575, 1494, 1463, 1445, 1377, 1362, 1161, 1120, 1093, 1075, 1025, 895, 776, 727, 698 cm^{-1}.

2,2-Dimethyl-1-methylideneindane (S12):



I **S12**

1-Indanone (58.9 mmol, 7.79 g) was dissolved in dry THF and cooled until –78 °C. LDA (88.4 mmol, 44.2 mL) was added dropwise. The reaction mixture was stirred during 1 h and then allowed to warm to room temperature. MeI (58.9 mmol, 3.67 mL) was added. The reaction was stirred at room temperature for 5 h. Next, LDA (29.5 mmol, 14.7 mL) and MeI (58.9 mmol, 3.67 mL) were added. The reaction was stirred overnight at room temperature. Next, the reaction mixture was poured into a solution of saturated NH_4Cl (150 mL) and extracted with EtOAc (3 x 150 mL). The combined organic phases were dried over $MgSO_4$, filtered, evaporated *in vacuo* and purified by flash chromatography over silicagel (hexane/EtOAc: 90/10) resulting in pure **I**, 4.51 g (48%).

Methyltriphenylphosphoniumbromide (10.03 g, 0.0281 mol) was dissolved in dry THF (100 mL) and cooled to 0°C. *n*-BuLi (11.2 mL, 0.0281 mol) was added dropwise and the reaction mixture was stirred for 5 min. at 0°C Next, **I** (4.5 g, 0.0281 mol) was dissolved in dry THF (80 mL) and added via a double tipped needle to the reaction mixture at 0°C. The reaction was stirred during 3h at room temperature. Then, a solution of 1 M HCl was added until pH=5 and H_2O (90 mL) was added. The reaction mixture was extracted with EtOAc (3 x 90 mL). The combined organic phases were dried over $MgSO_4$, evaporated *in vacuo* and purified by flash chromatography over silicagel (pentane) resulting in pure **S12**, 3.75 g (85%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 6H), 2.84 (s, 2H), 4.93 (app. s, 1H), 5.45 (app. s, 1H), 7.17-7.22 (m, 3H), 7.47-7.49 (m, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 29.4 (CH_3), 42.5 (C), 46.9 (CH_2), 101.0 (CH_2), 121.1 (CH), 125.4 (CH), 126.5 (CH), 128.5 (CH), 140.3 (C), 143.5 (C), 159.9 (C) ppm. IR (HATR): 3065, 3024, 2956, 2924, 2863, 1639, 1464, 1416, 1377; 1360, 1294, 1175, 1109, 1023, 938, 872, 776, 728, 687 cm^{-1}.

3,3-Dimethyl-2-phenyl-butene (α-*t.*butylstyrene) (S13):

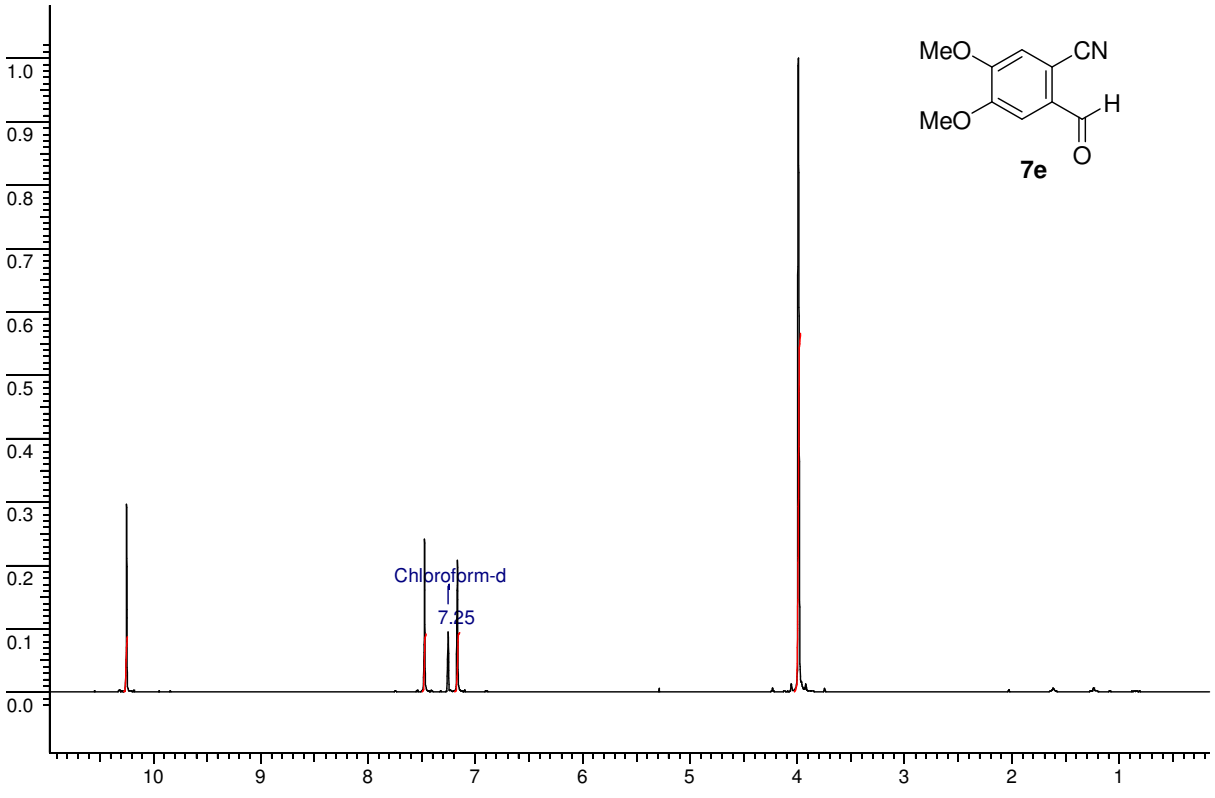
Methyltriphenylphosphoniumbromide (11.03 g, 0.0309 mol) was dissolved in dry THF (110 mL) and cooled to 0°C. *n*-BuLi (12.03 mL, 0.0308 mol) was added dropwise at 0°C and the reaction mixture was stirred for 5 min at 0°C. Next, 2,2-dimethylpropiophenone (5 g, 0.0308 mol) was dissolved in dry THF (90 mL) and added via a double tipped needle to the reaction mixture at 0°C. The reaction was stirred during 23 h at room temperature. Then, a solution of 1 M HCl was added until pH=5 and H_2O (100 mL) was added. The reaction mixture was extracted with EtOAc (3 x 100 mL). The combined organic phases were dried over $MgSO_4$, filtered, evaporated *in vacuo* and purified by flash chromatography over silicagel (pentane)

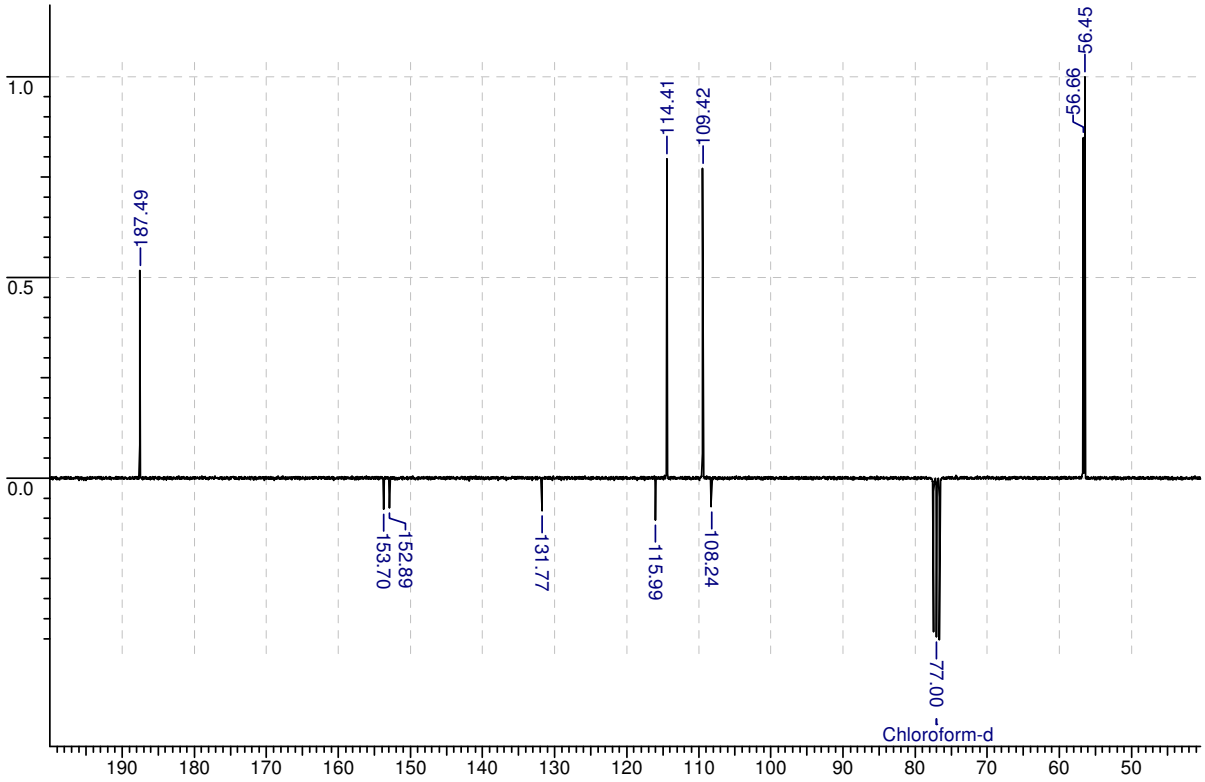
resulting in pure **S13**, 3.86 g (78%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.13 (s, 9H), 4.78 (d, *J*= 1.6 Hz, 1H), 5.19 (d, *J*= 1.6 Hz, 1H), 7.13-7.16 (m, 2H), 7.22-7.32 (m, 3H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 29.7 (CH_3), 36.1 (C), 111.5 (C), 126.2 (CH), 127.3 (CH), 129.0 (CH), 143.5 (C), 159.9 (C) ppm. IR (HATR): 3022, 2955, 2905, 2867, 1624, 1600, 1482, 1460, 1441, 1384, 1360, 1207, 1095, 1072, 1025, 905, 770, 703 cm^{-1}.

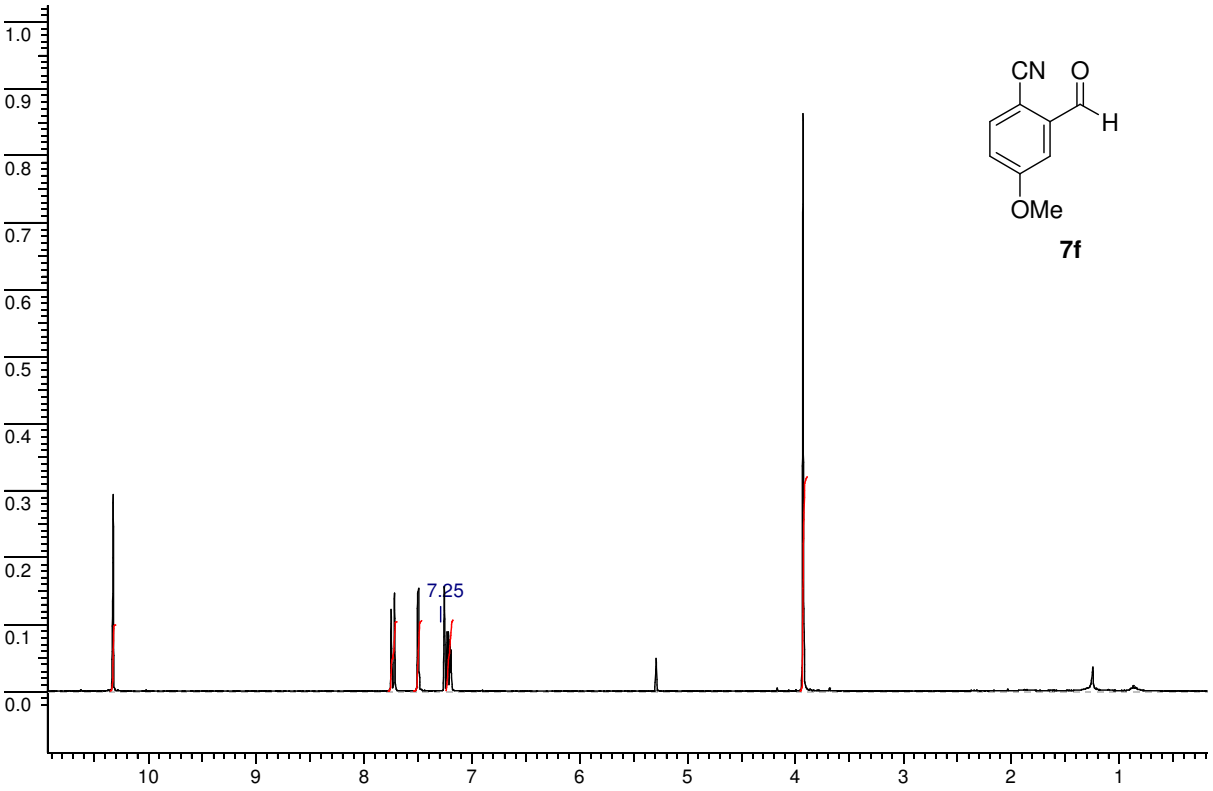
α-Trifluoromethylstyrene (S14):

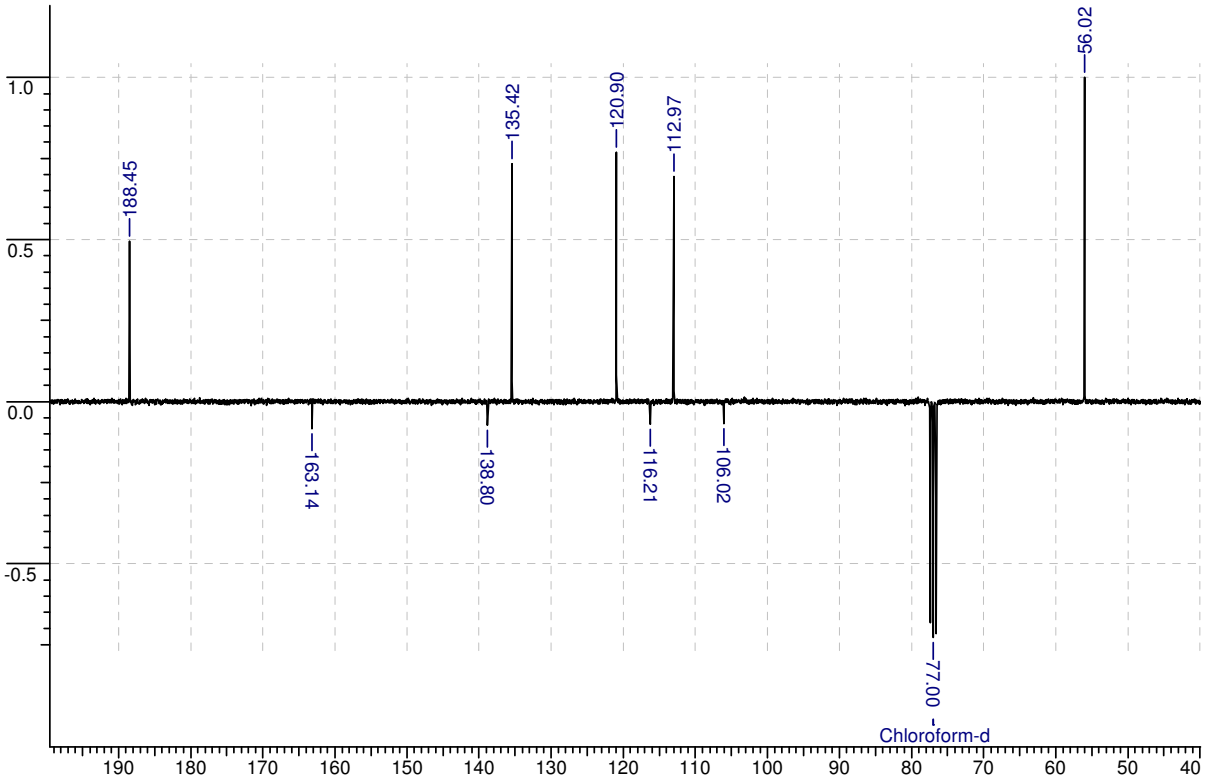
Methyltriphenylphosphoniumbromide (20.52 g, 0.0574 mol) was dissolved in dry THF (100 mL) and cooled to 0°C. *n*-BuLi (23 ml, 0.0574 mol) was added dropwise at 0°C and the reaction mixture was stirred for 5 min at 0°C. Next, 2,2,2-trifluoroacetophenone (8 g, 0.0459 mol) was dissolved in dry THF (100 mL) and added via a double tipped needle to the reaction mixture at 0°C. The reaction mixture was stirred overnight at room temperature. Then, a solution of 1 M HCl was added until pH=5 and H_2O (100 mL) was added. The reaction mixture was extracted with Et_2O (3 x 100 mL). The combined organic phases were dried over $MgSO_4$, evaporated *in vacuo* and purified by flash chromatography over silicagel (pentane) resulting in pure **S14**, 4.26 g (54%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.77 (app. q, *J*= 1.6 Hz, 1H), 5.96 (app. q, *J*= 1.3 Hz, 1H), 7.36-7.41 (m, 3H), 7.43-7.48 (m, 2H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 120.4 (CH_2, q, *J*= 6.2 Hz), 123.4 (CF_3, q, *J*= 273.9 Hz), 127.4 (CH, d, *J*= 1.1 Hz), 128.6 (CH), 129.0 (CH), 133.7 (C), 139.0 (C, q, *J*= 30.0Hz). IR (HATR): 3054, 1497, 1445, 1412, 1354, 1294, 1188, 1162, 1118, 1086, 1073, 1030, 945, 918, 848, 774, 749, 725, 693, 627, 610 cm^{-1}.

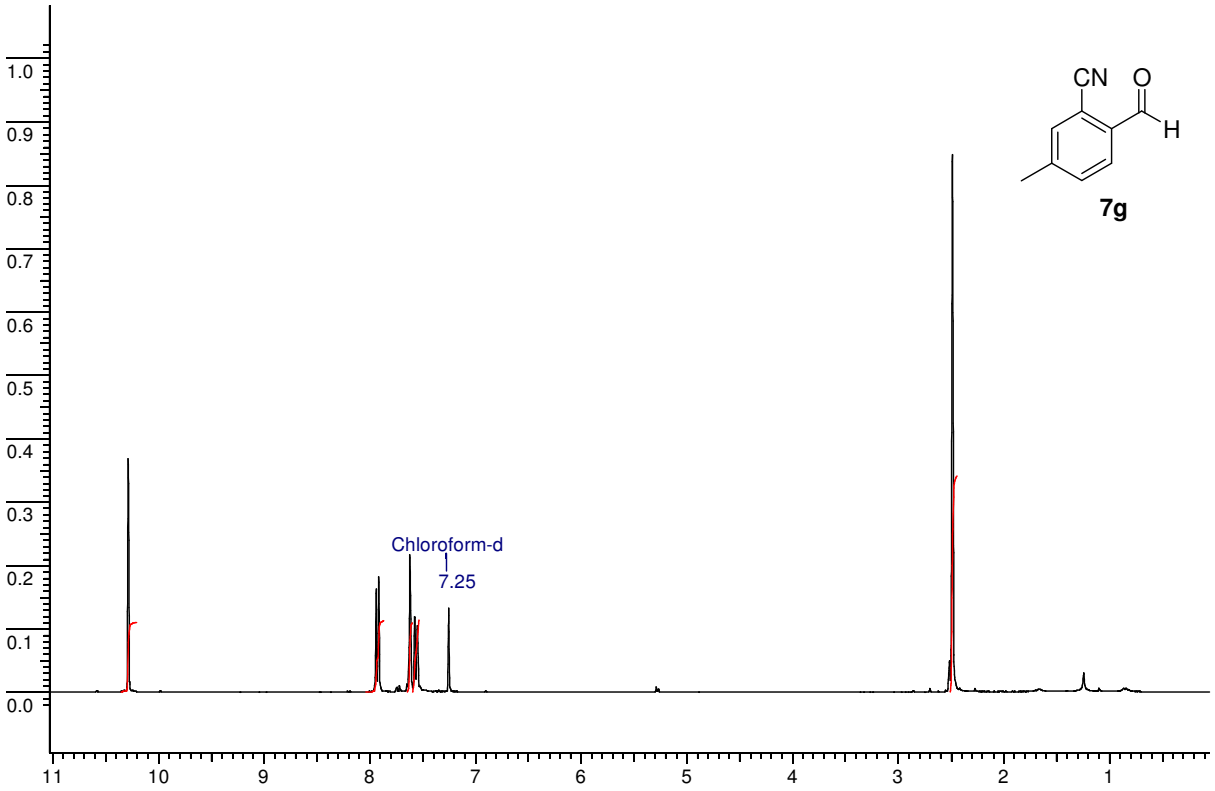
II. ^{1}H NMR and APT Spectra of the Synthesized compounds.

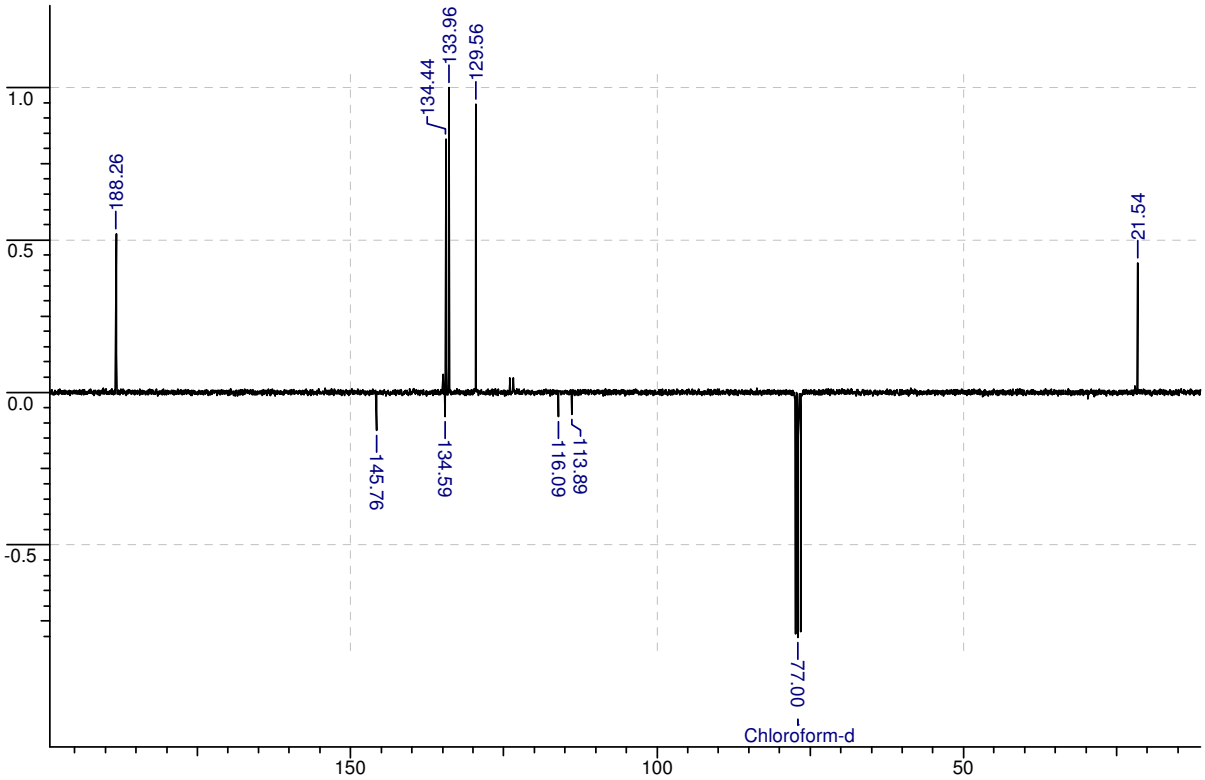


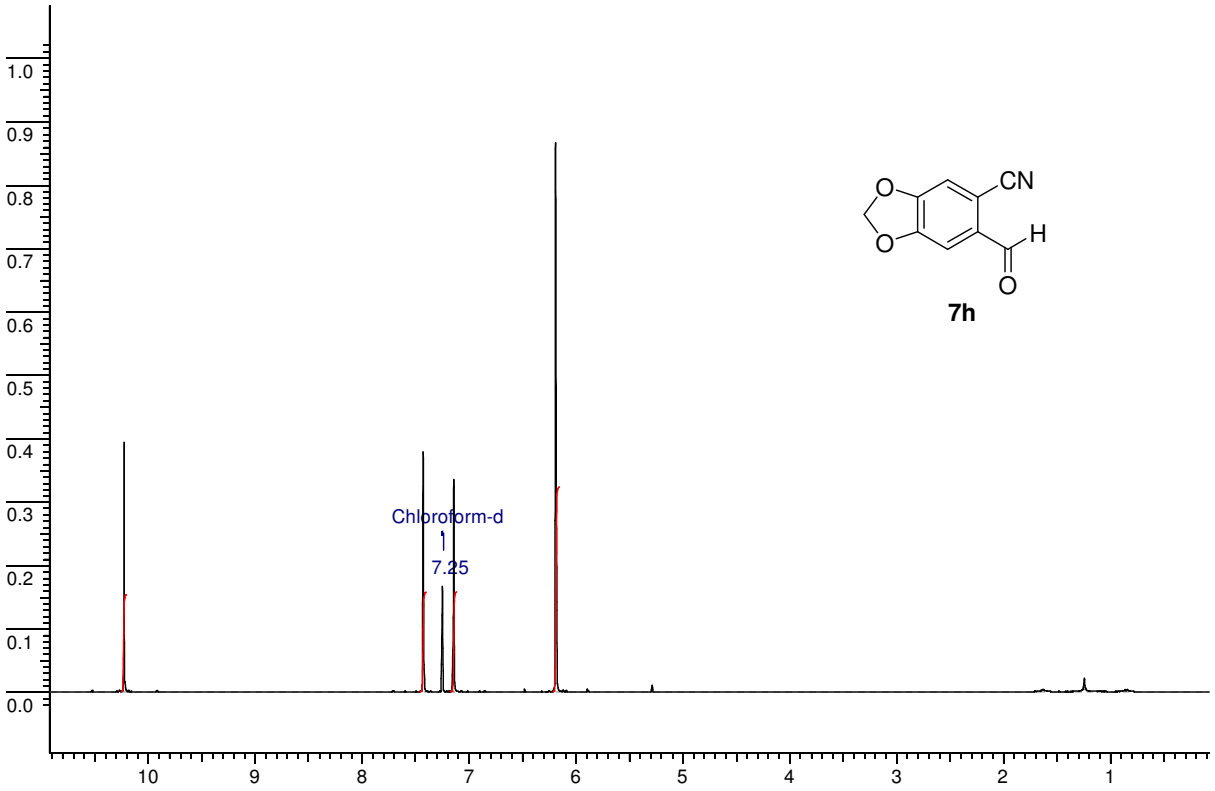


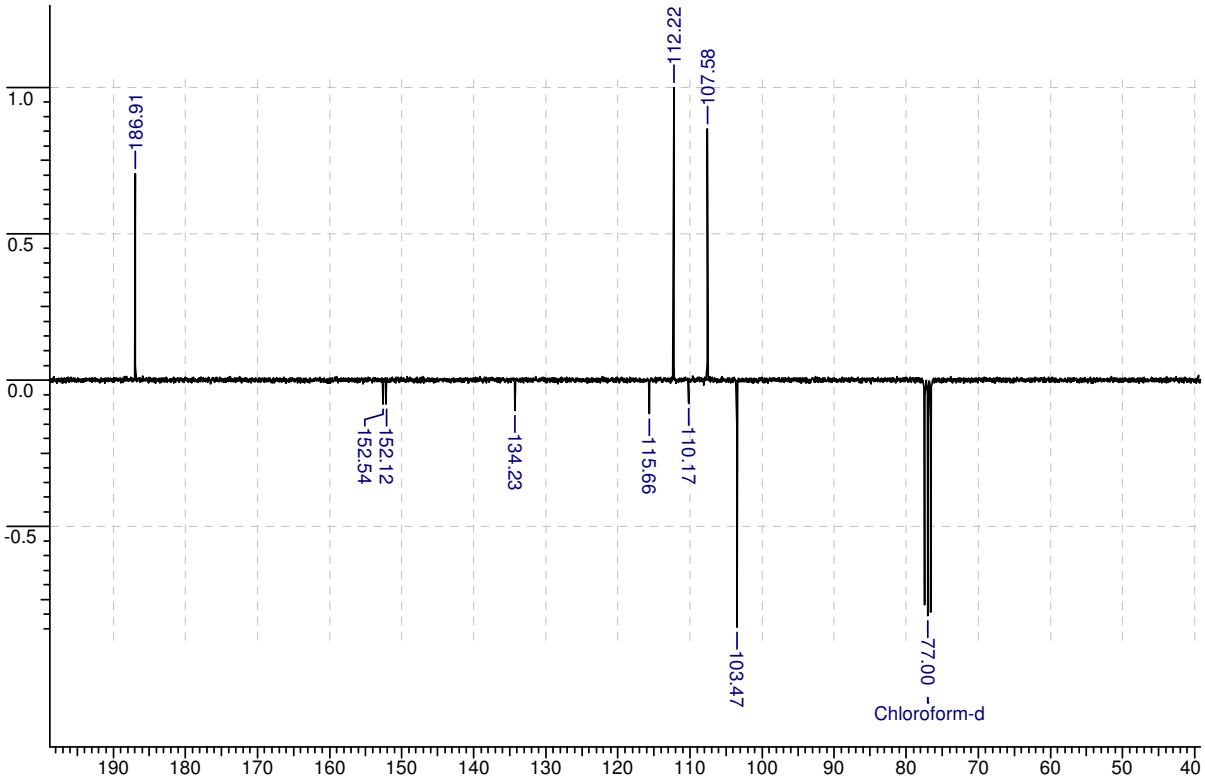




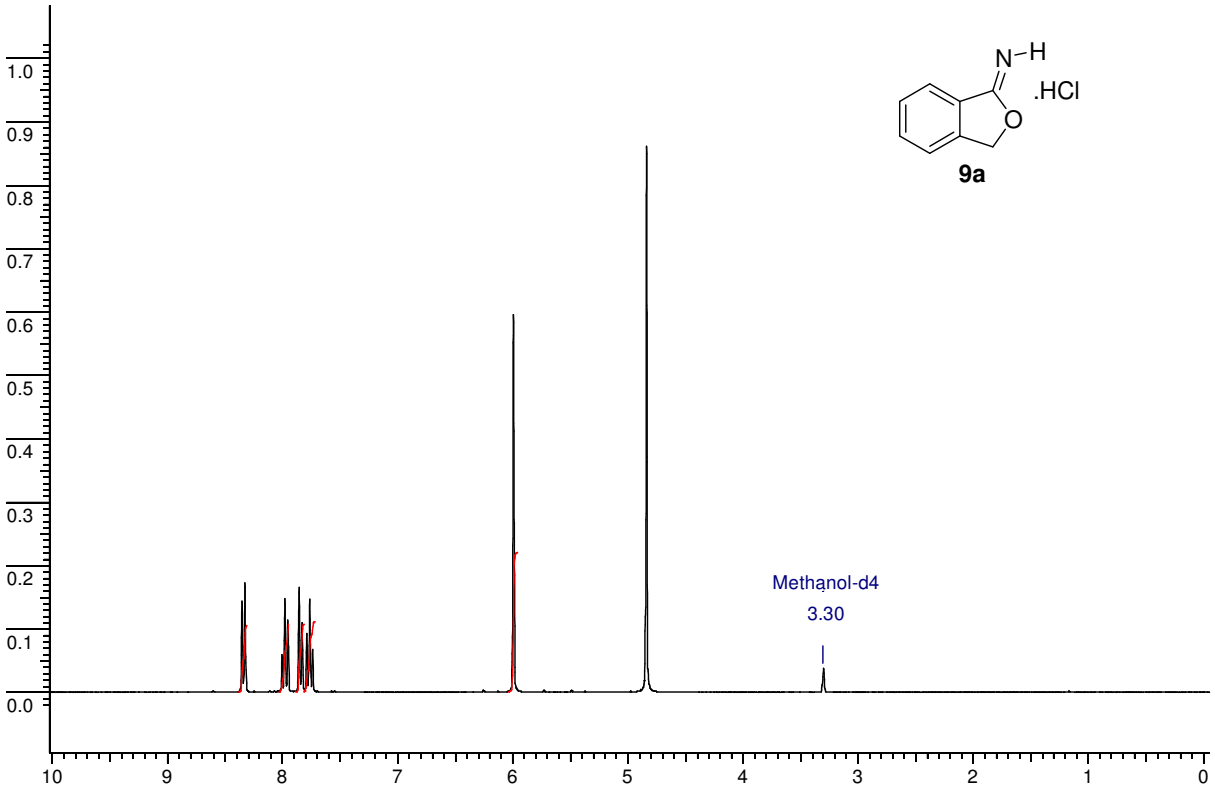


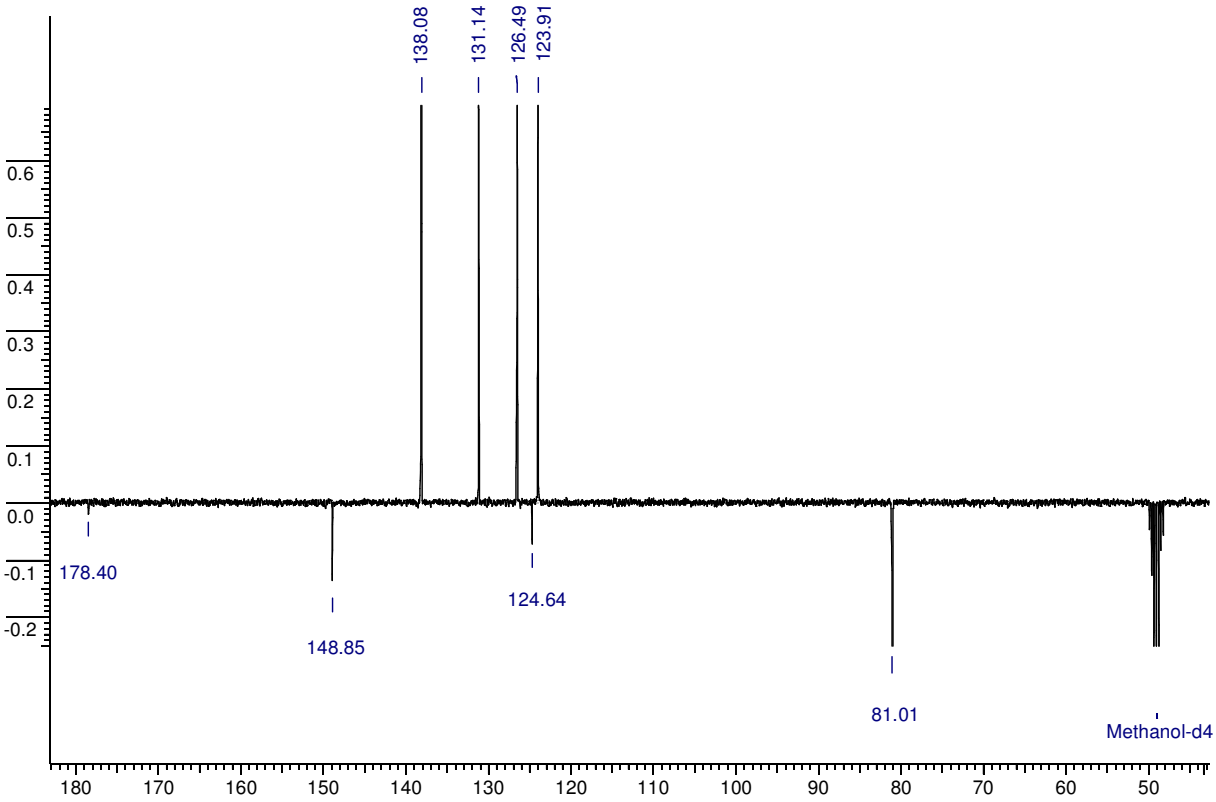


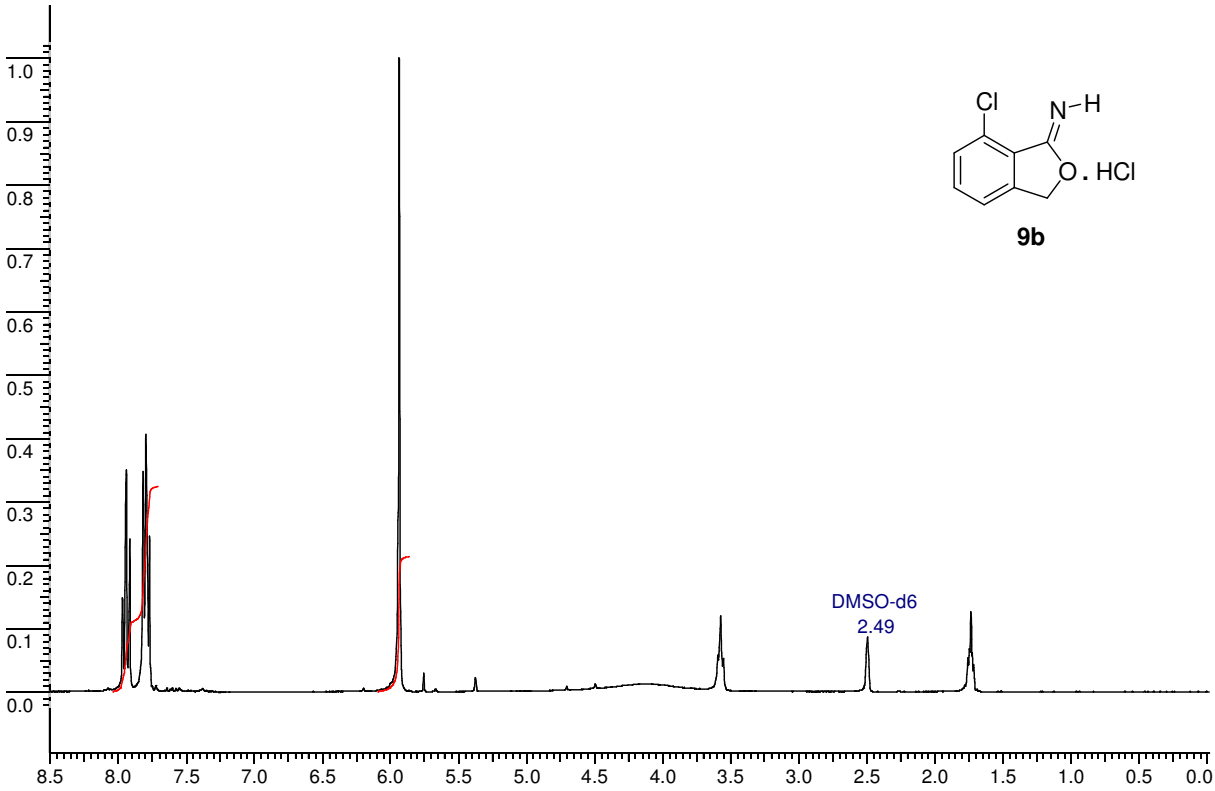




7h







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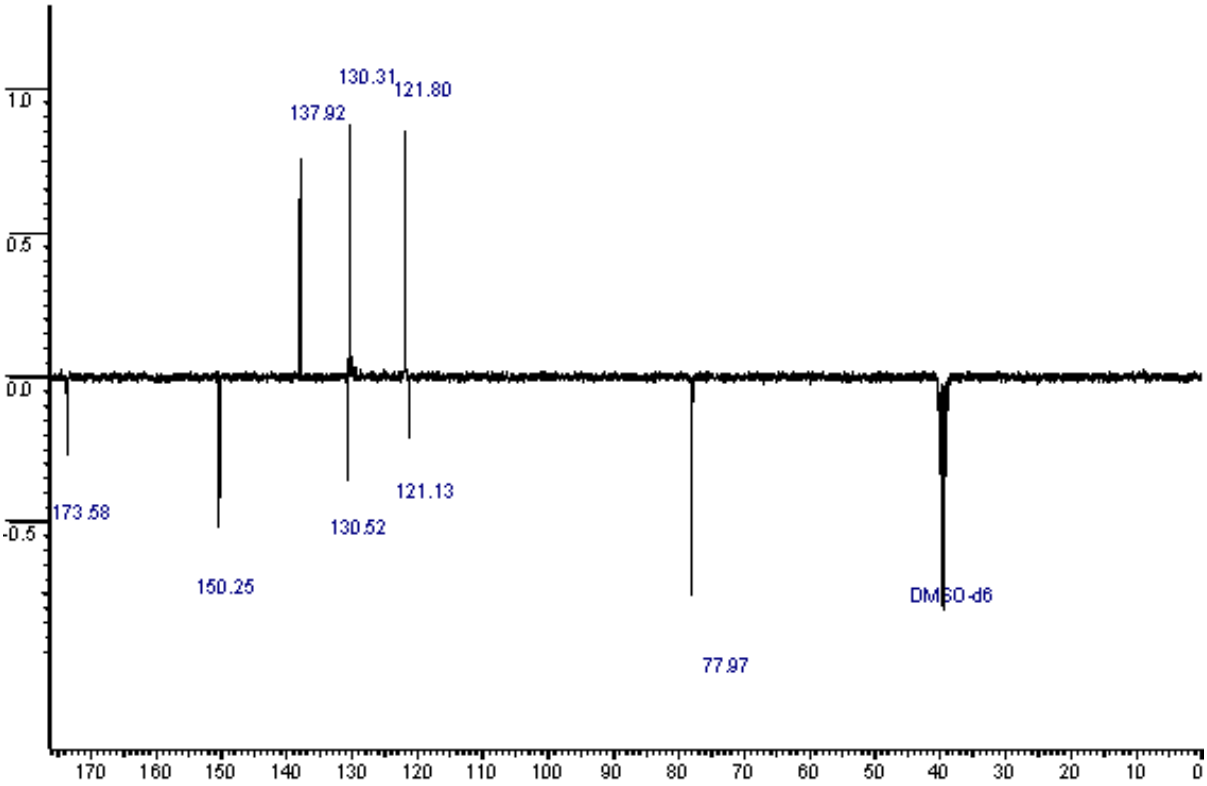
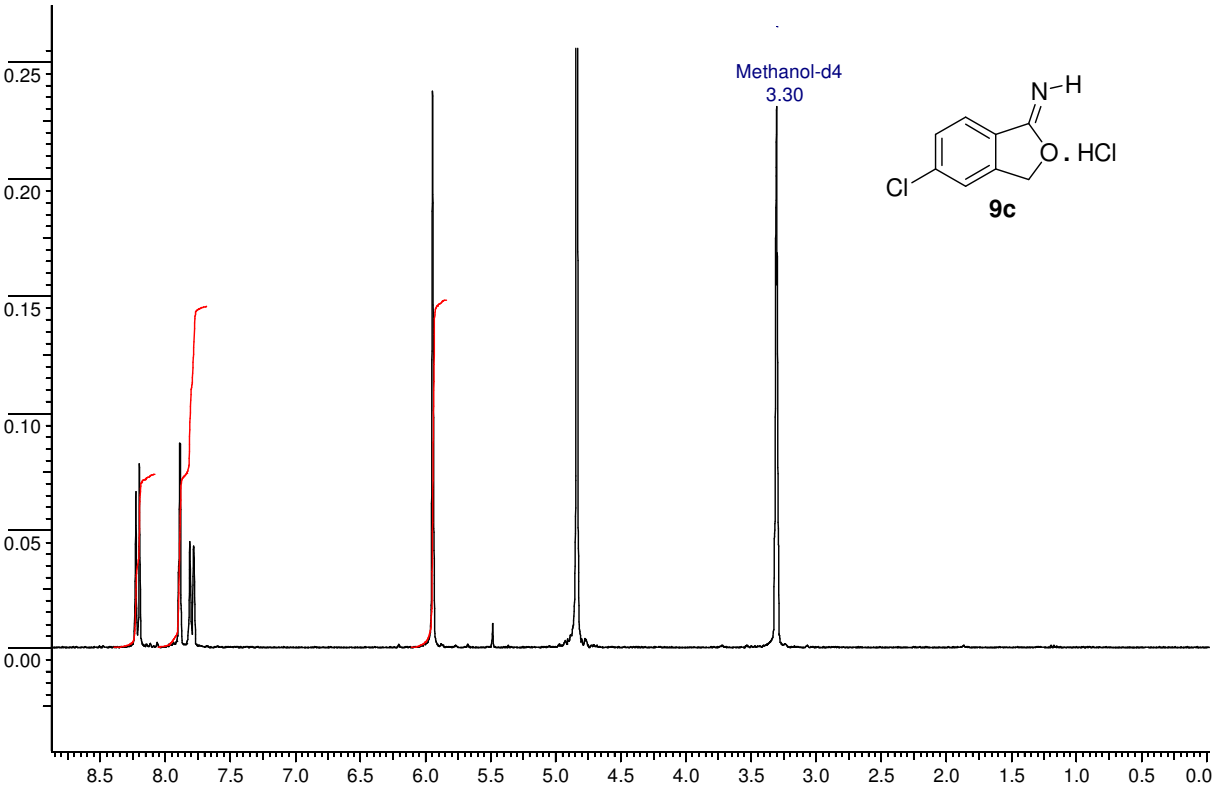
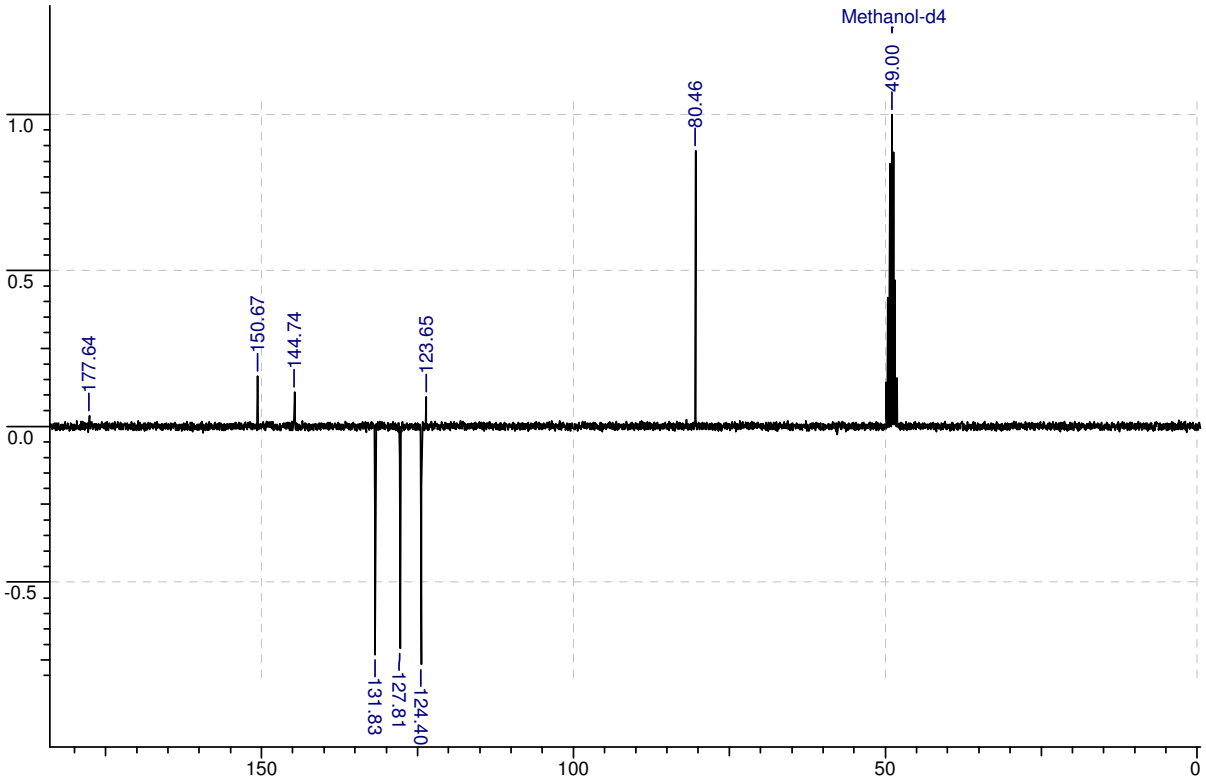
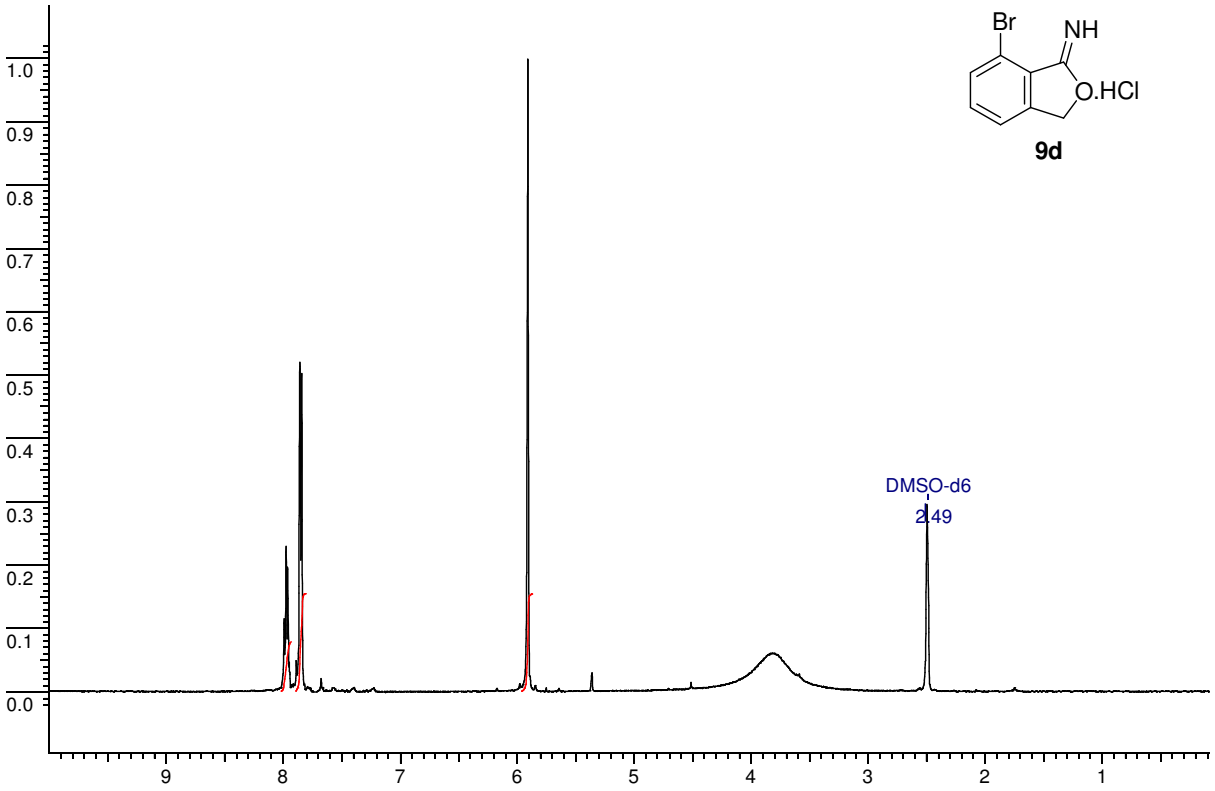
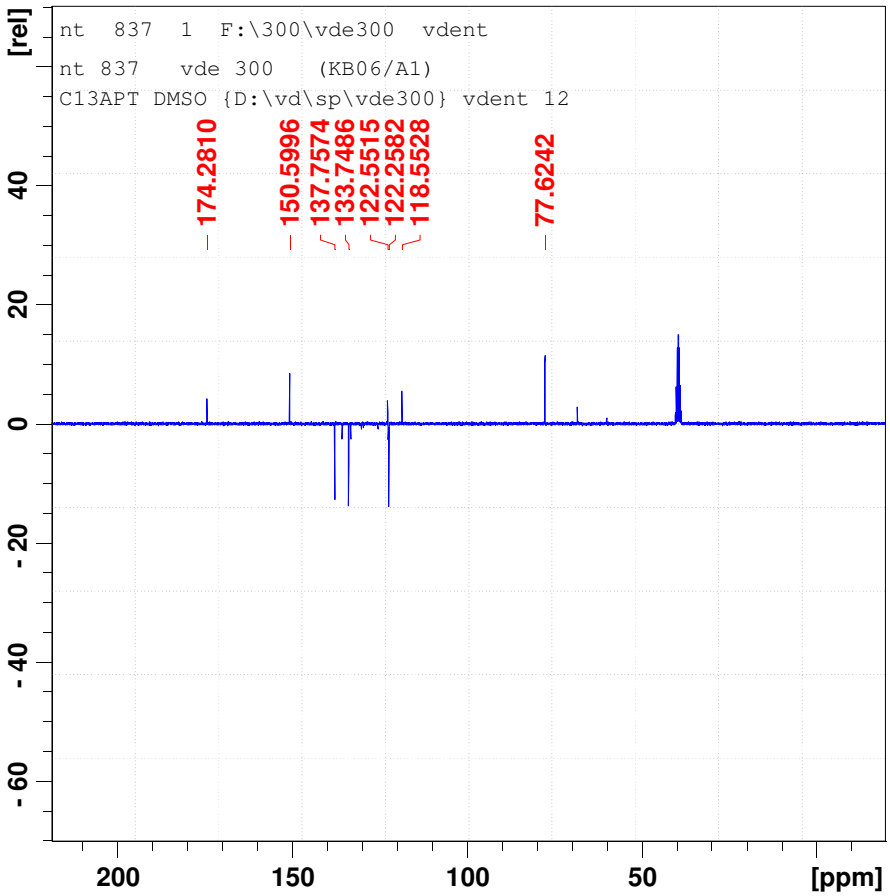
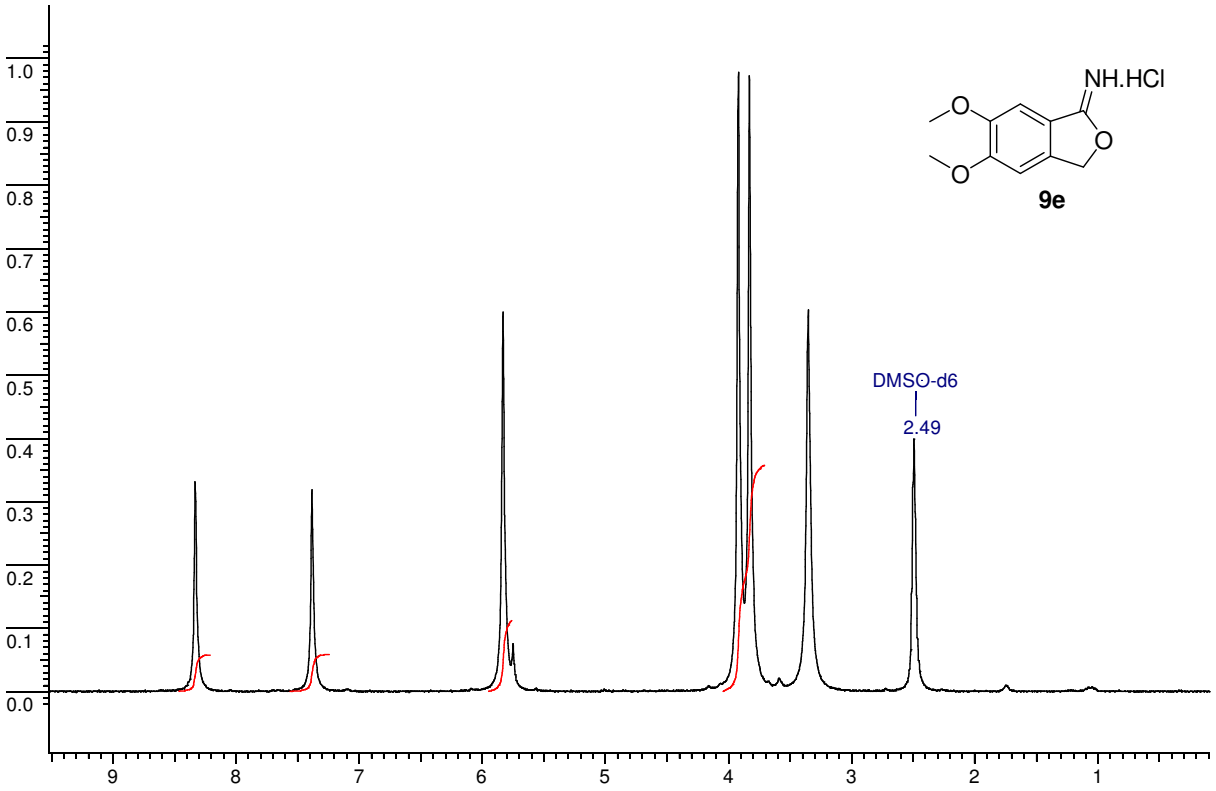


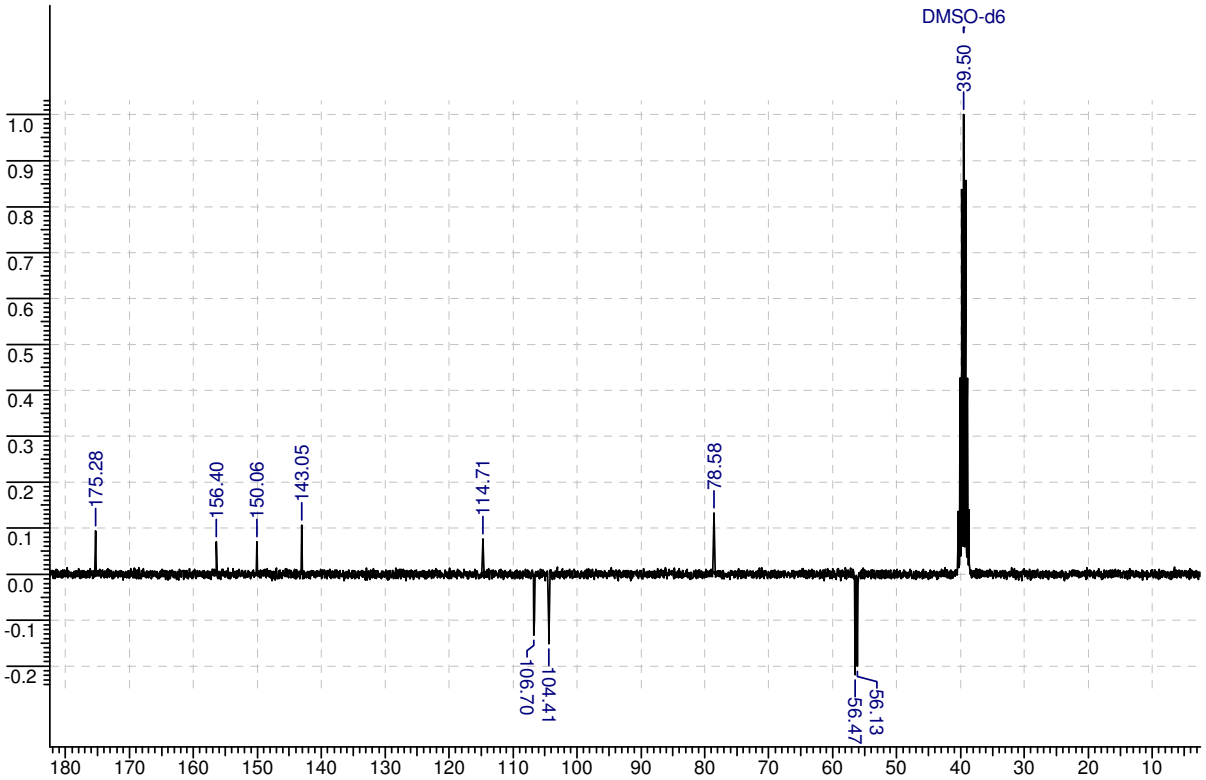


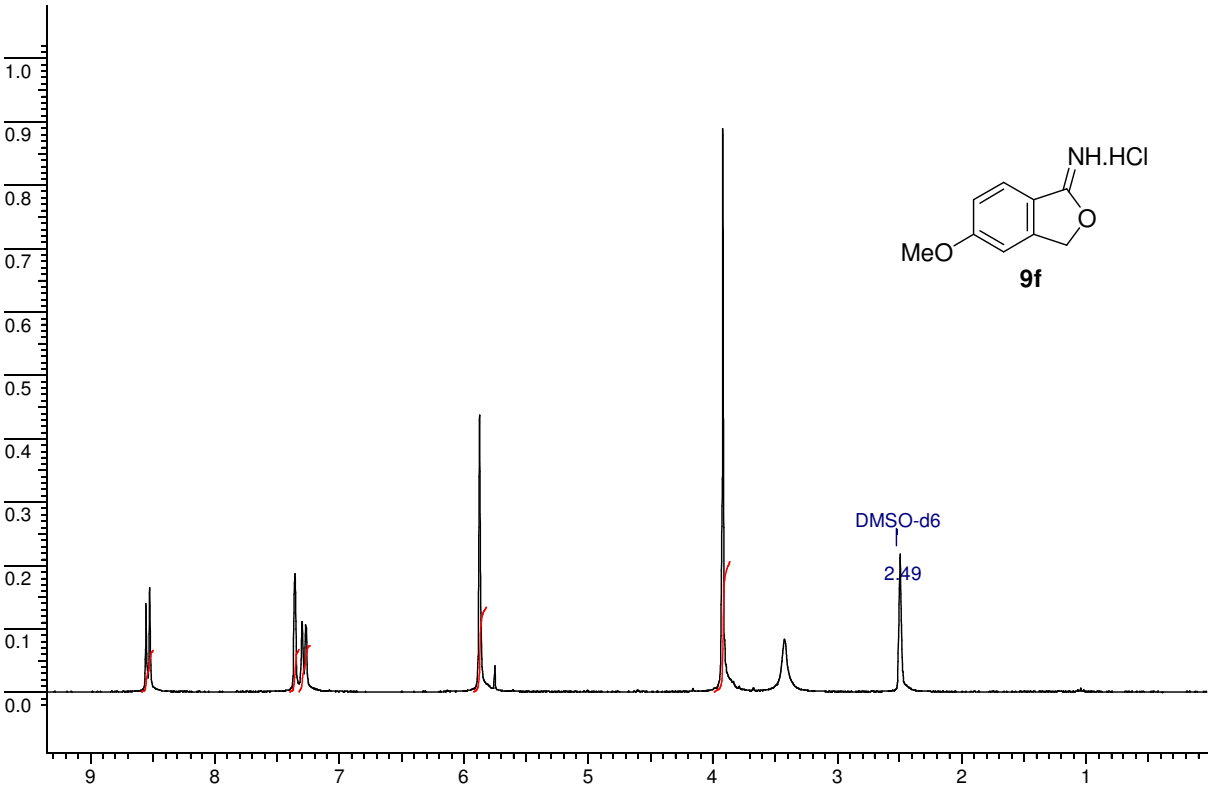


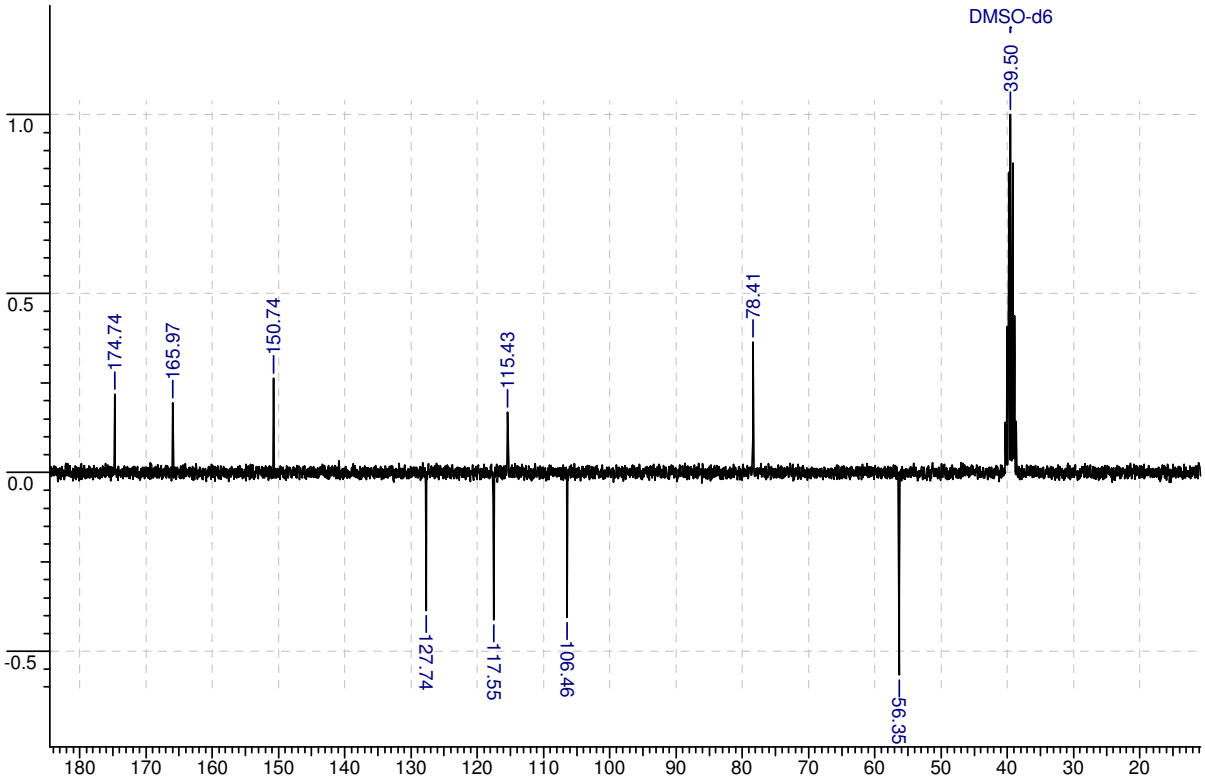


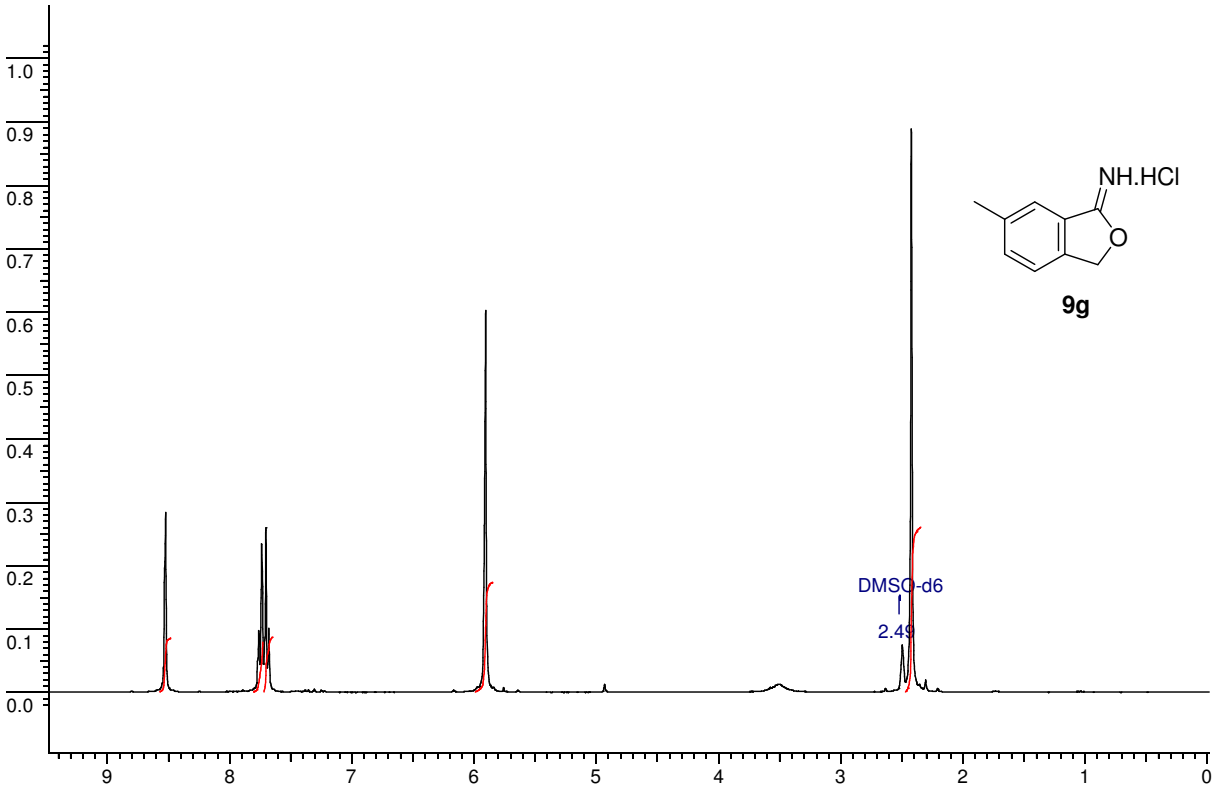


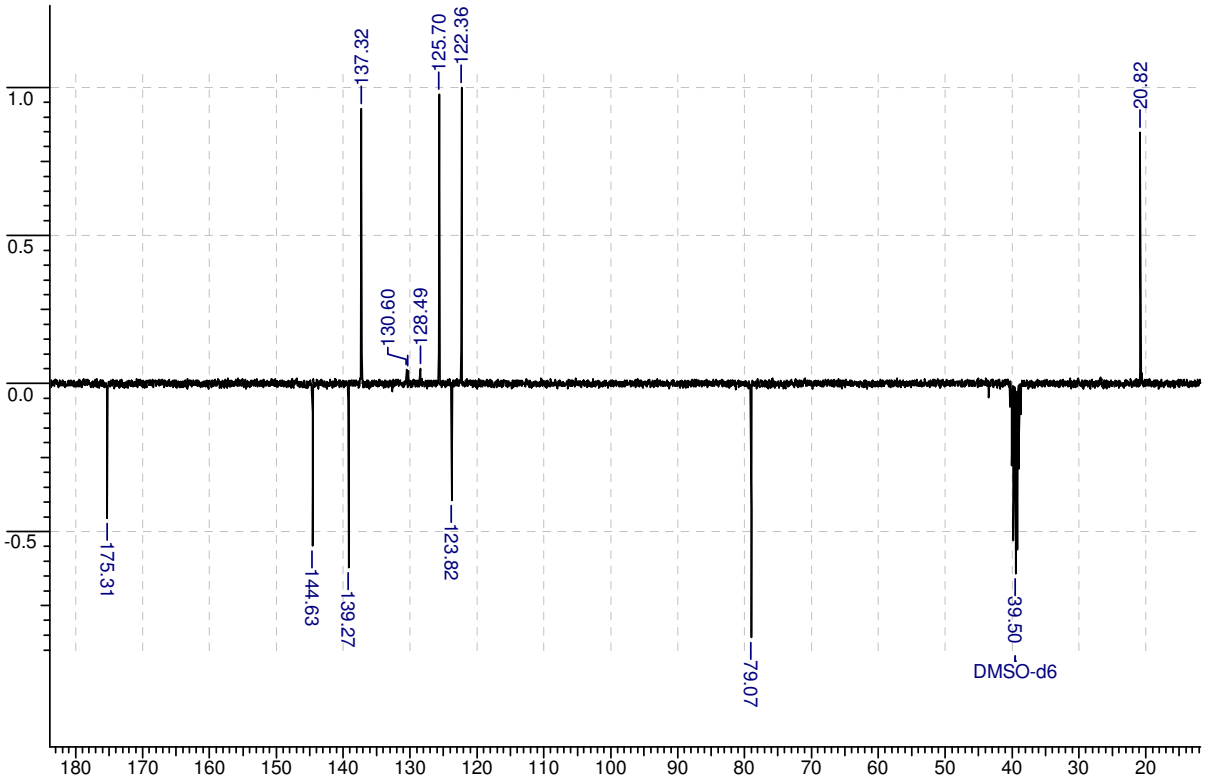


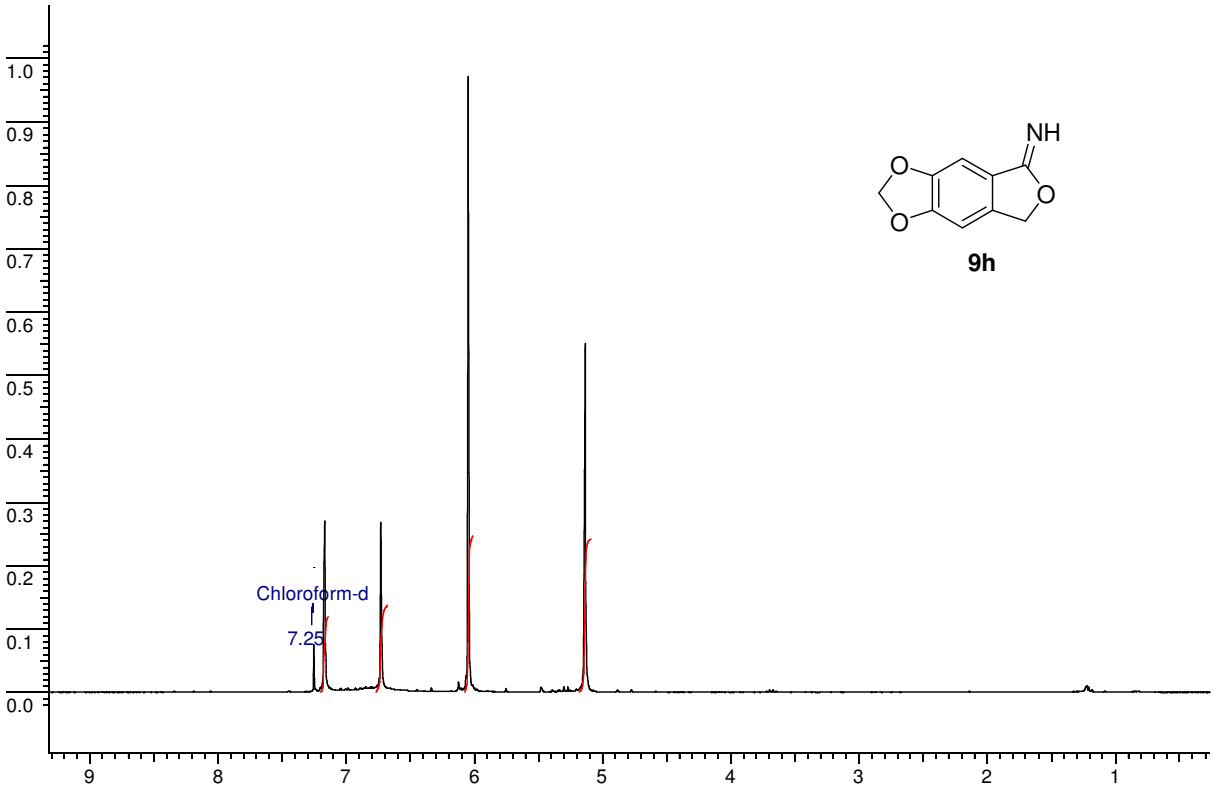


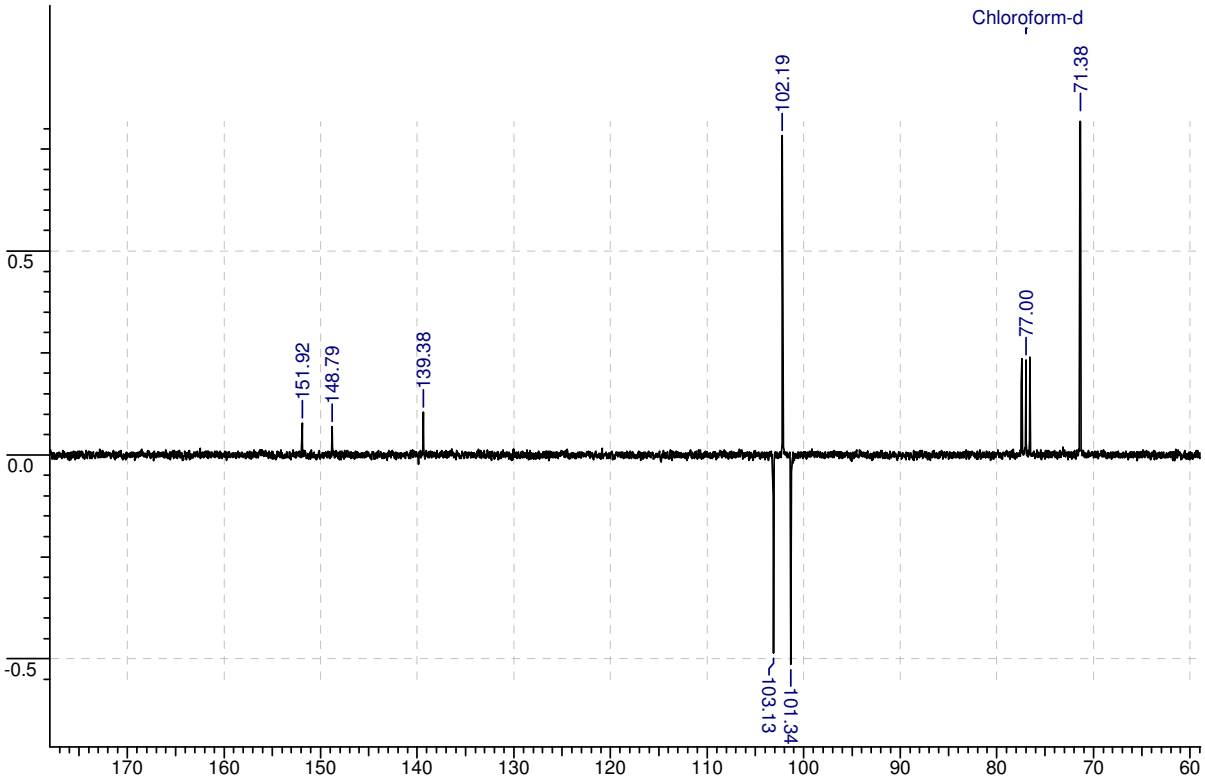


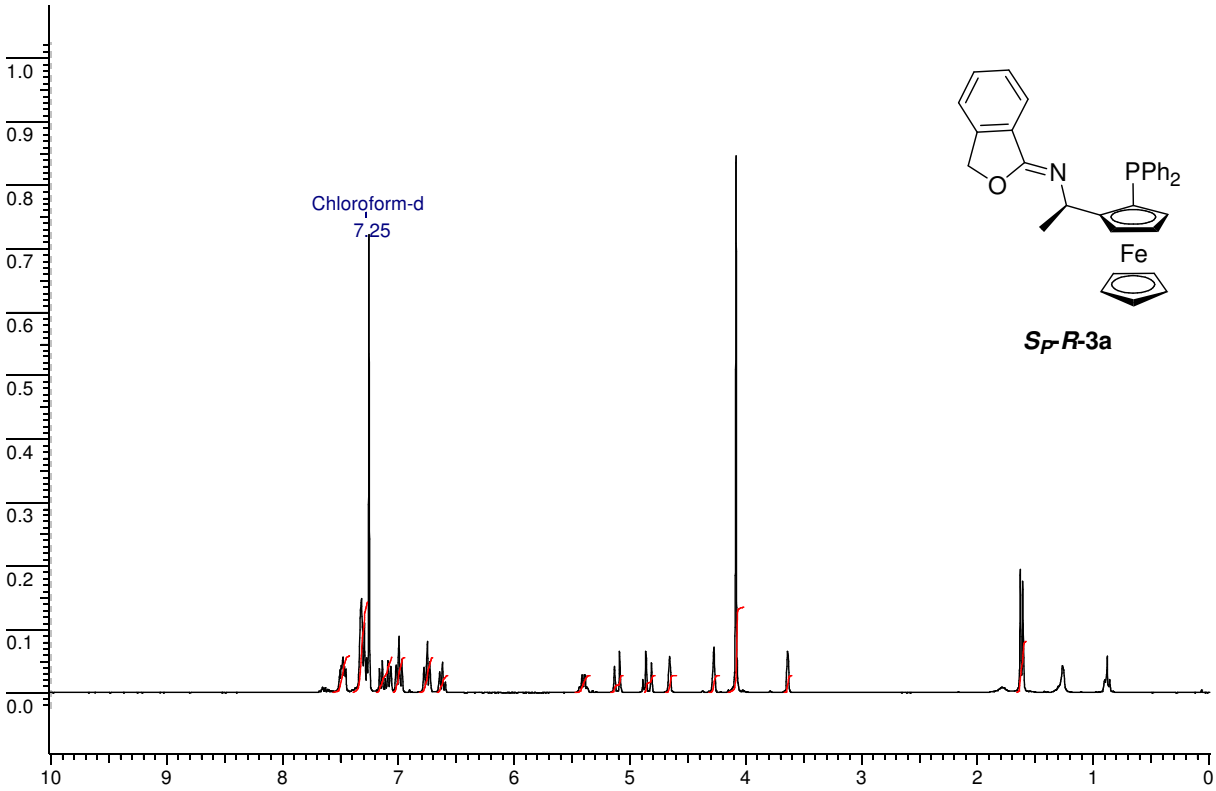




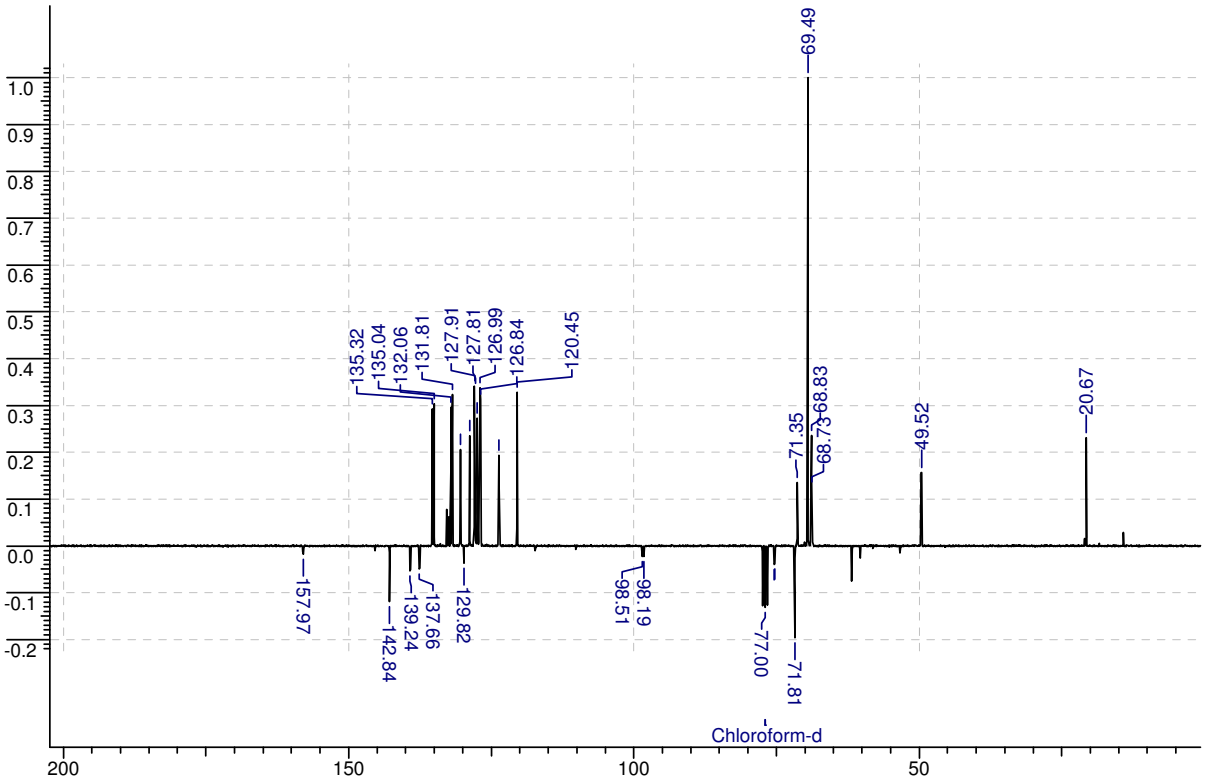


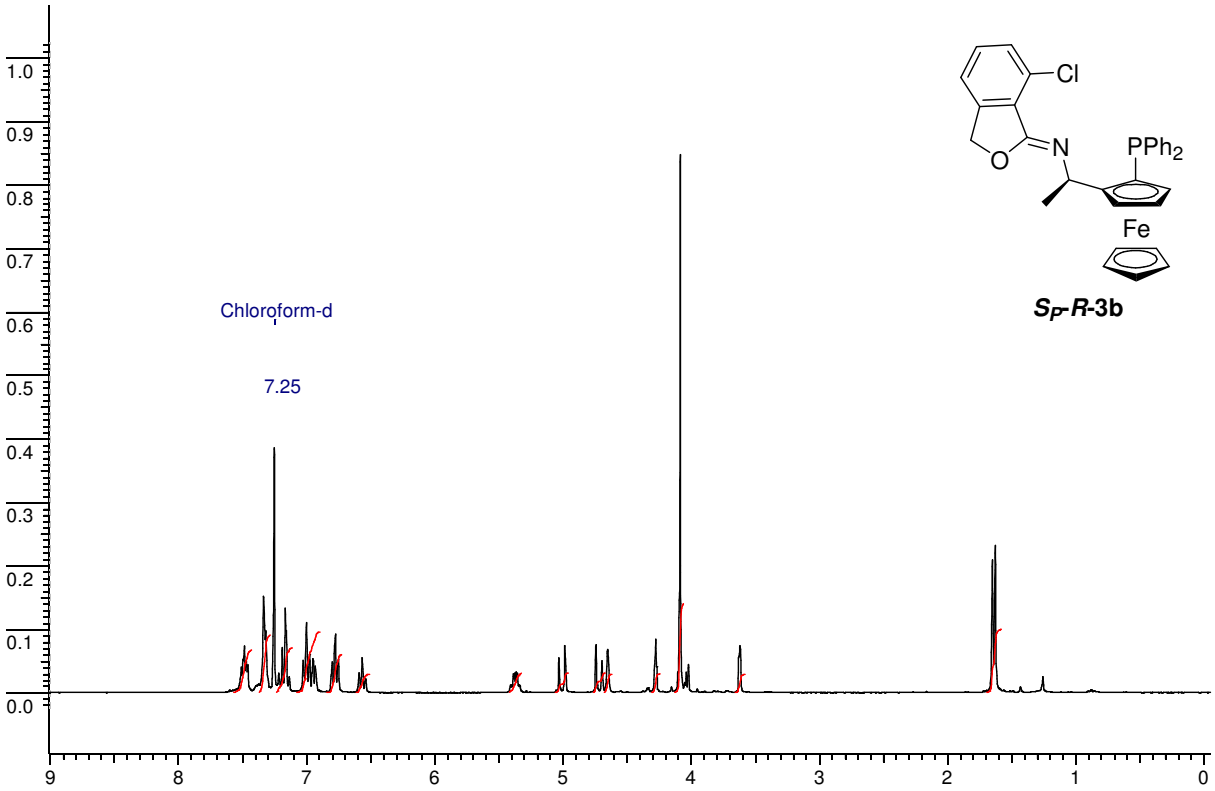






***S*$_P$-*R*-3a**





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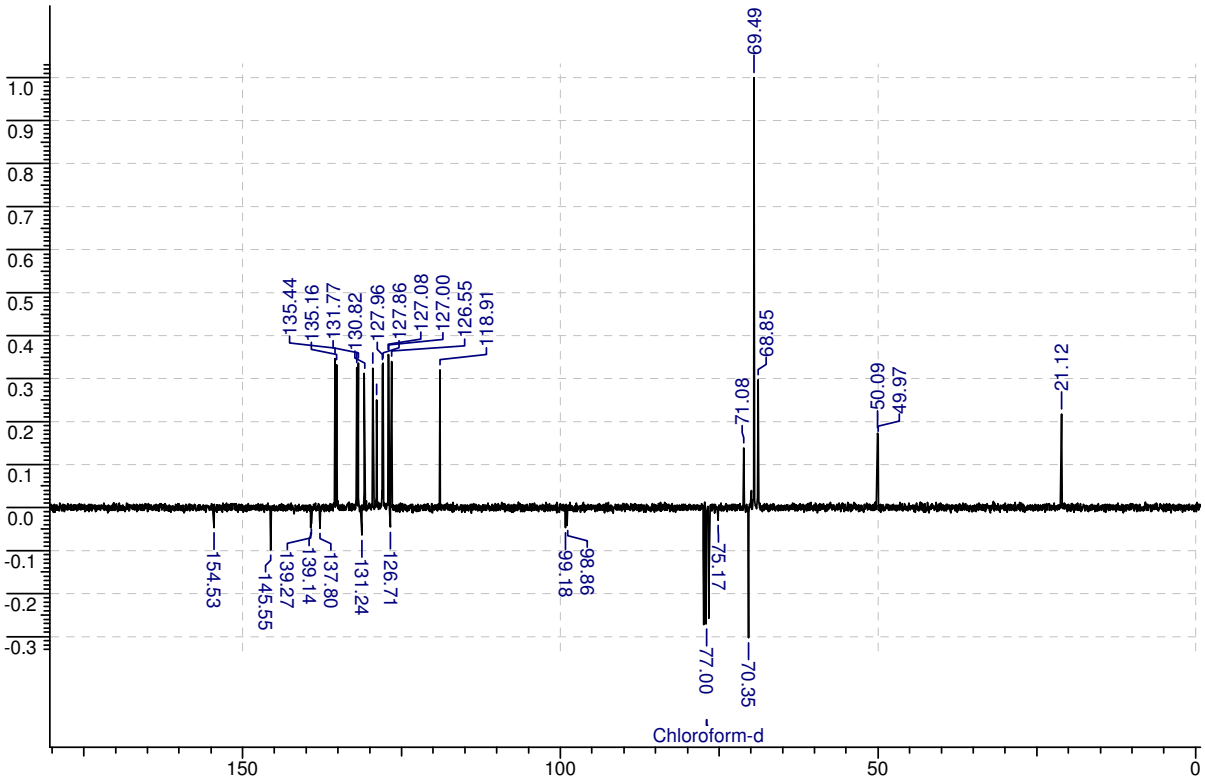

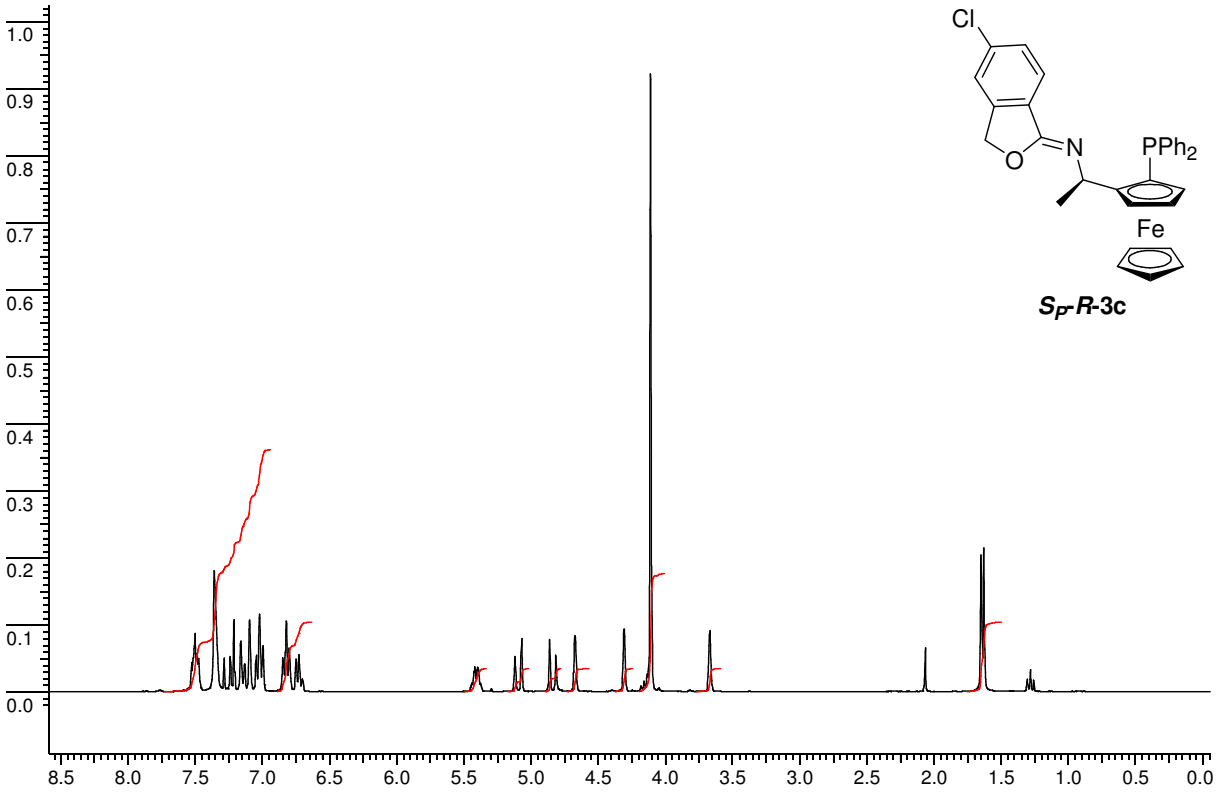

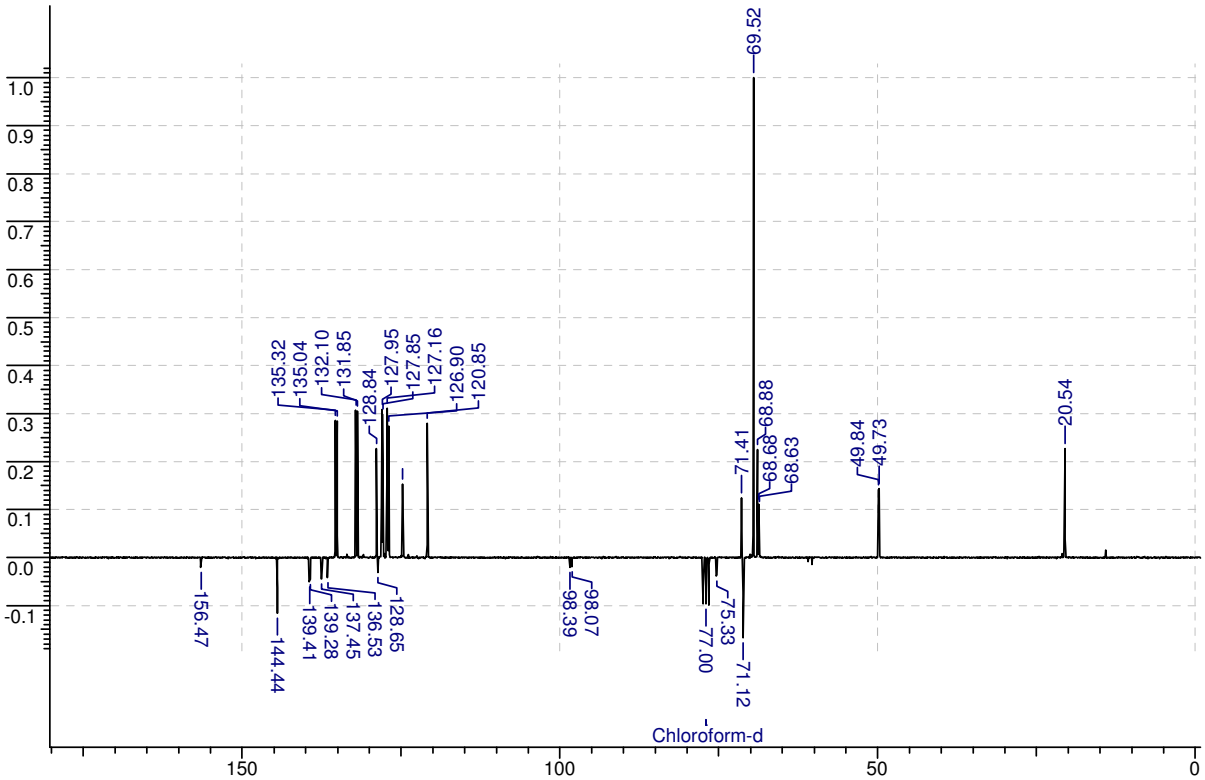

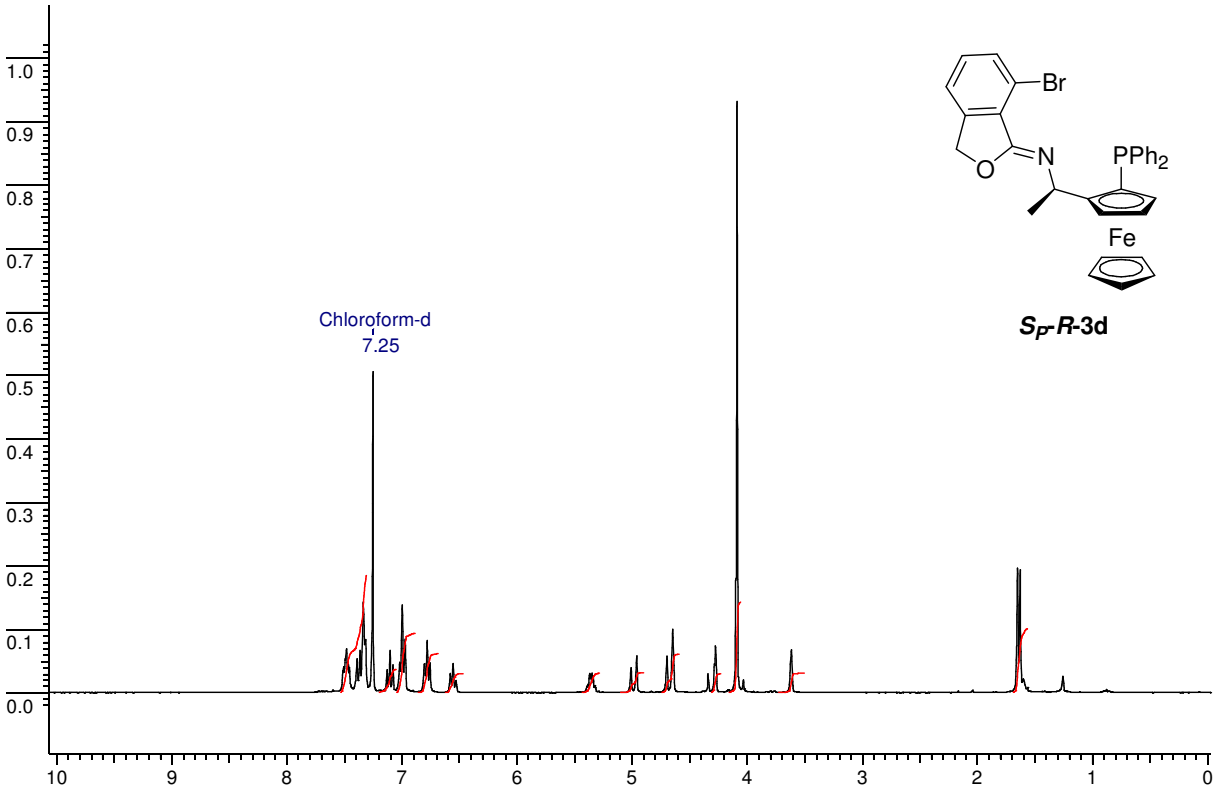

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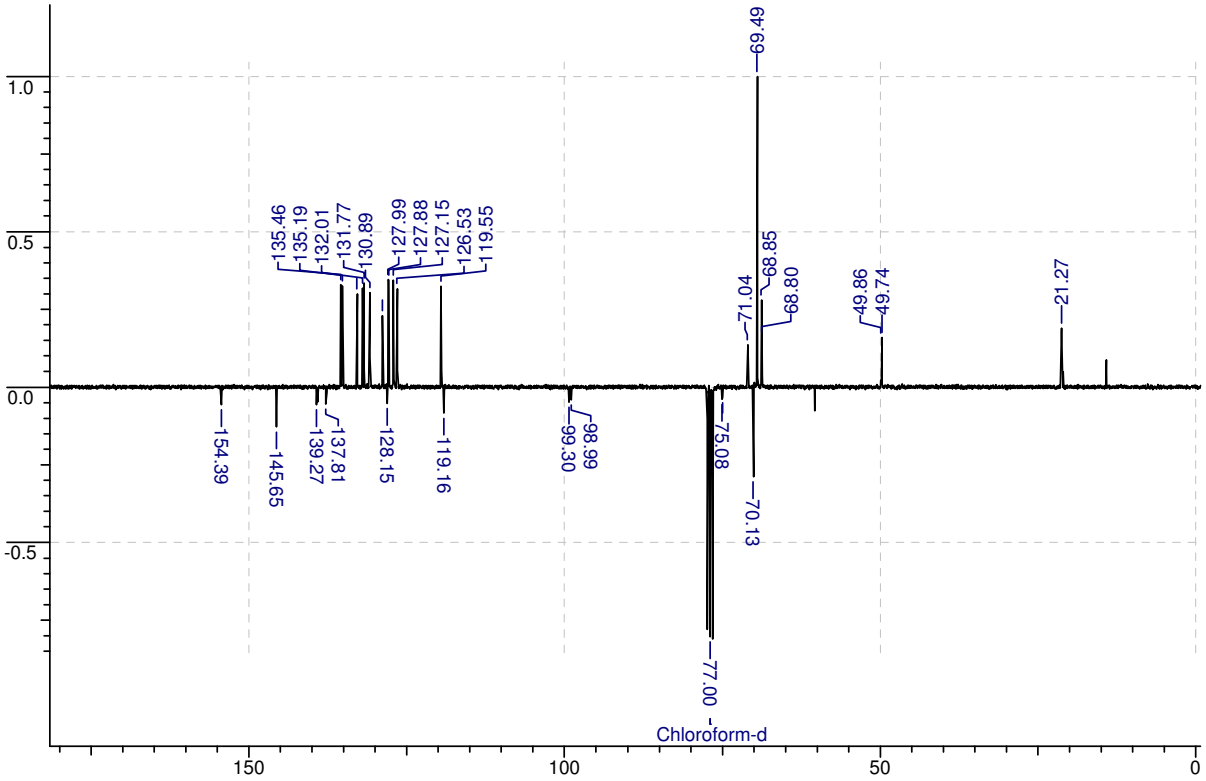
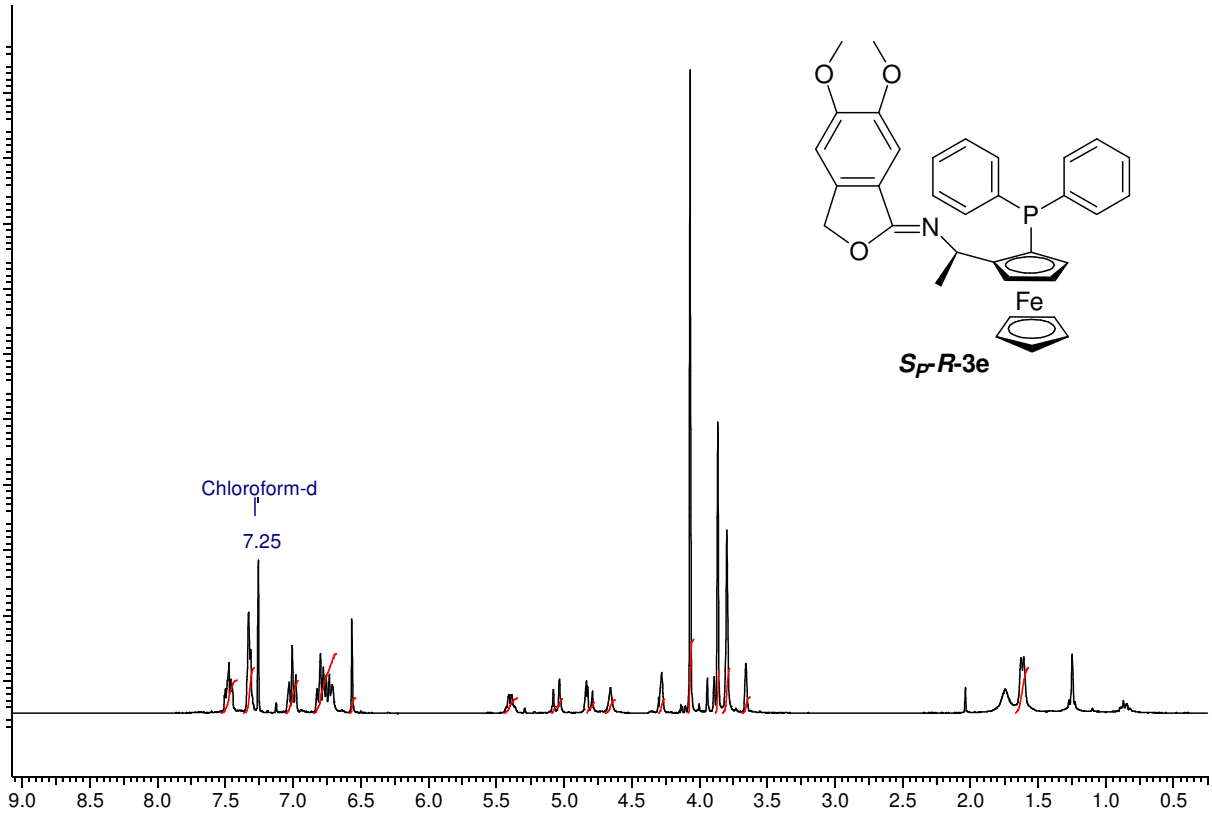
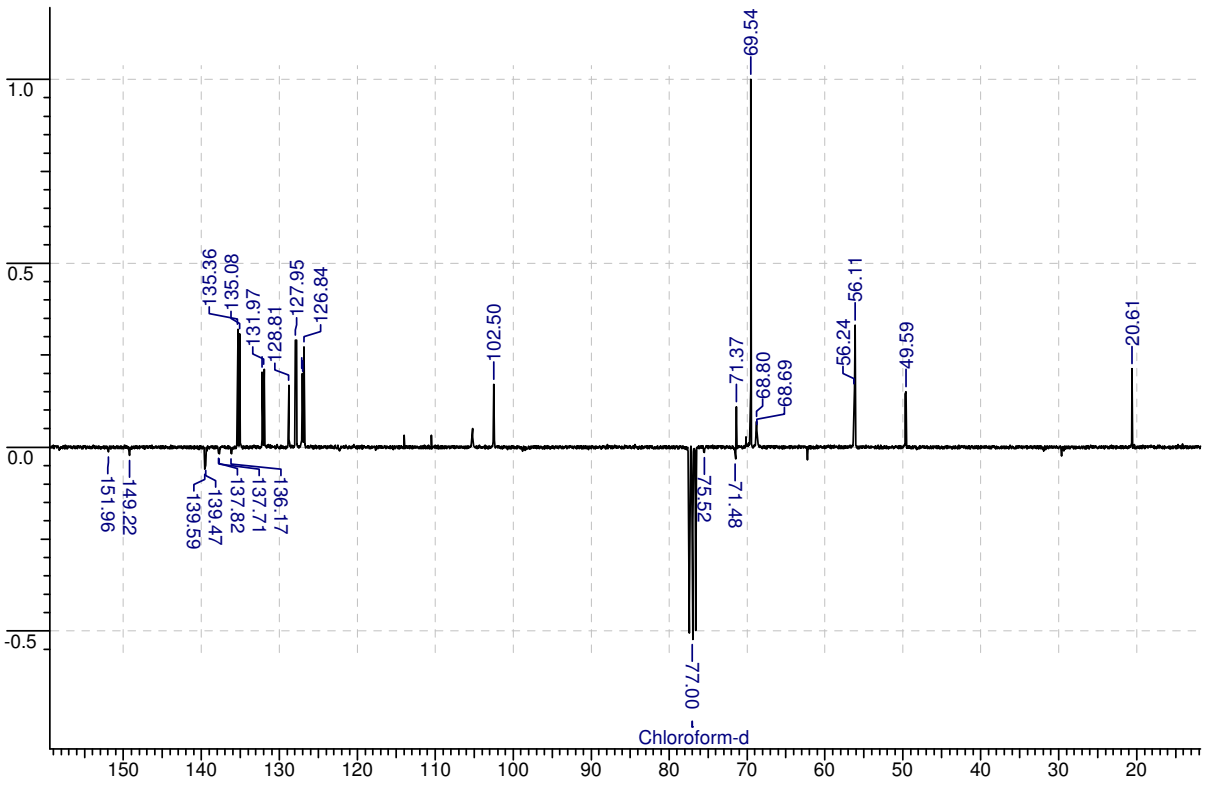
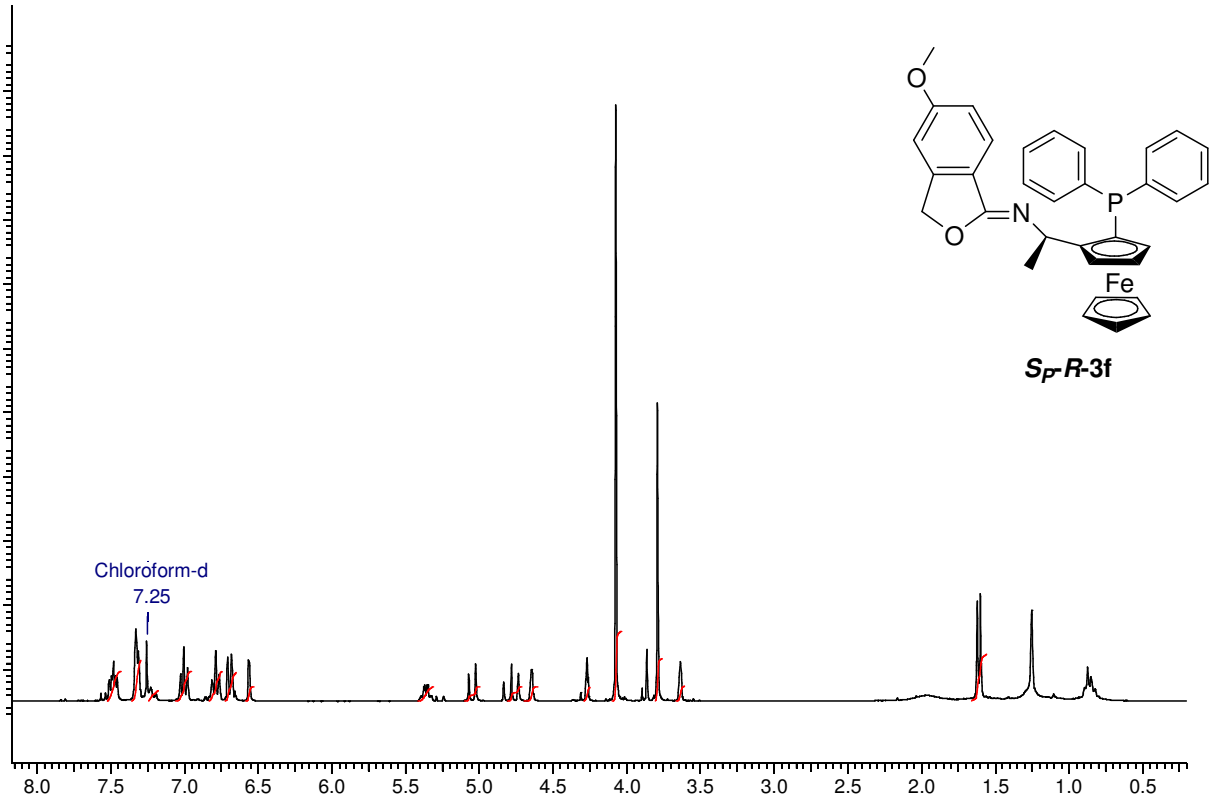


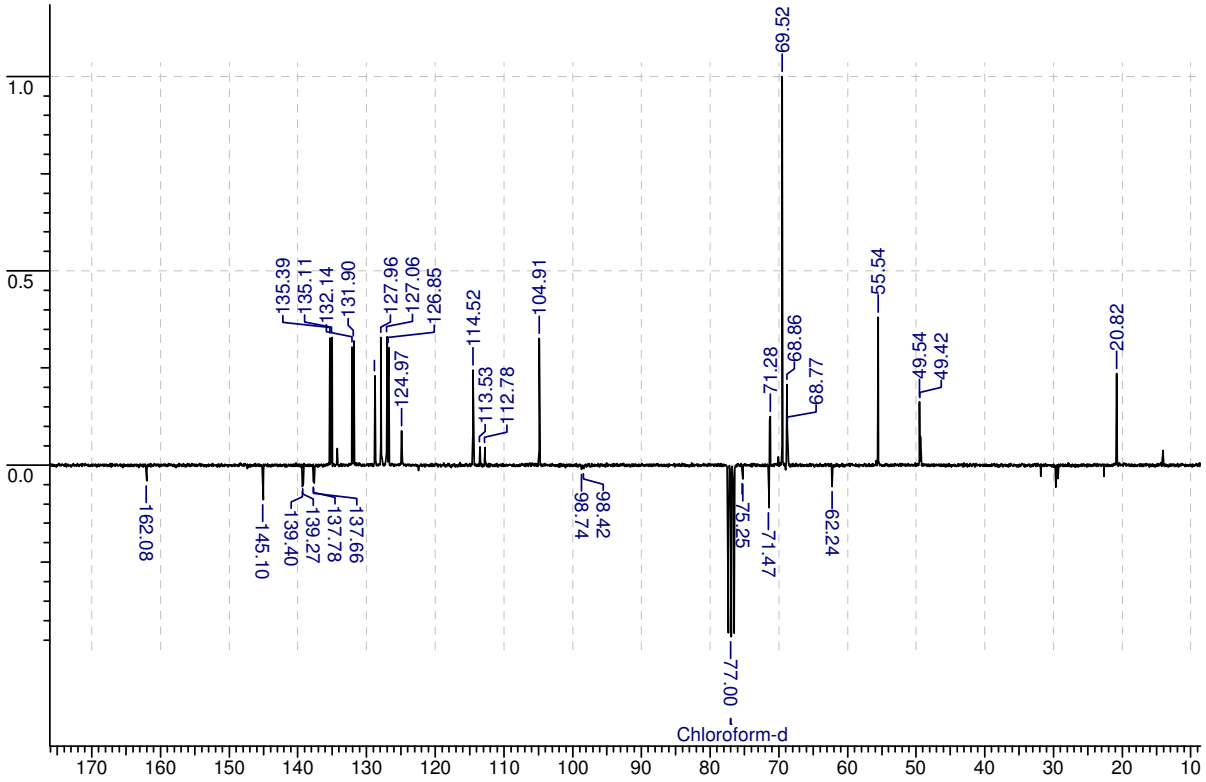


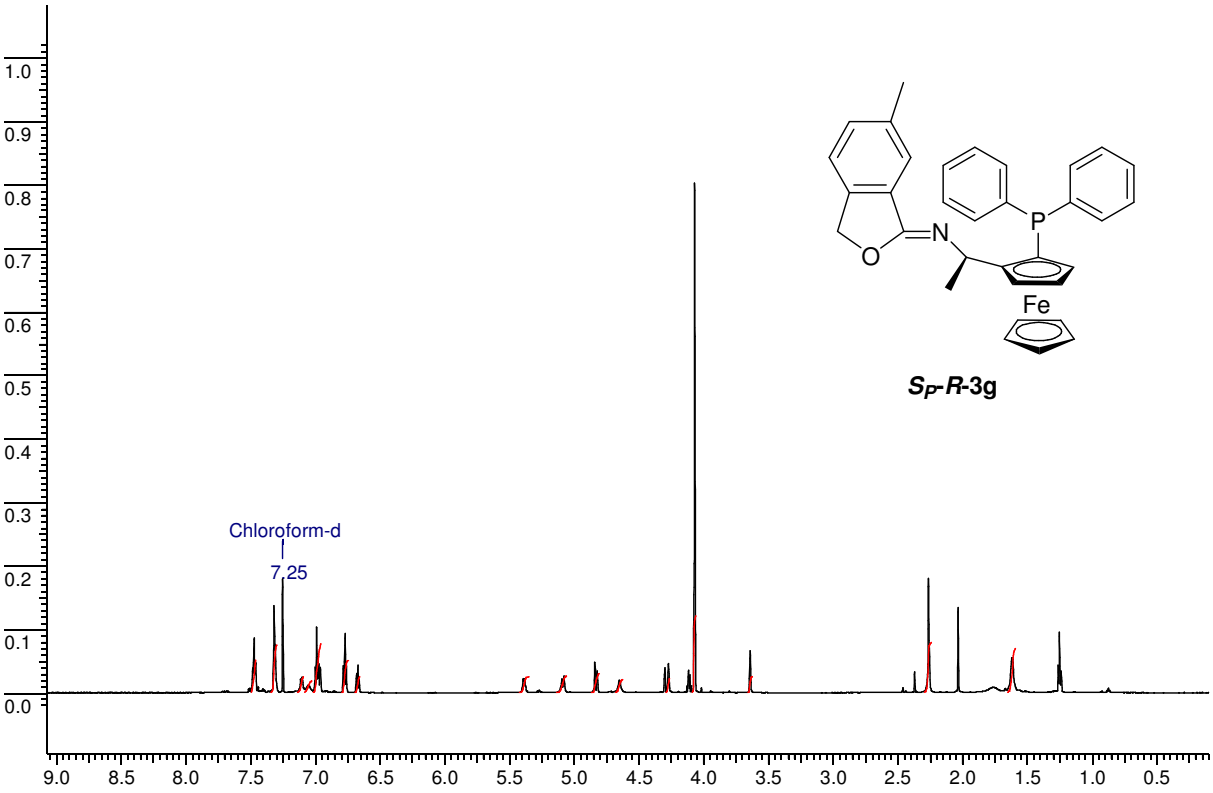


***S*$_P$-*R*-3e**

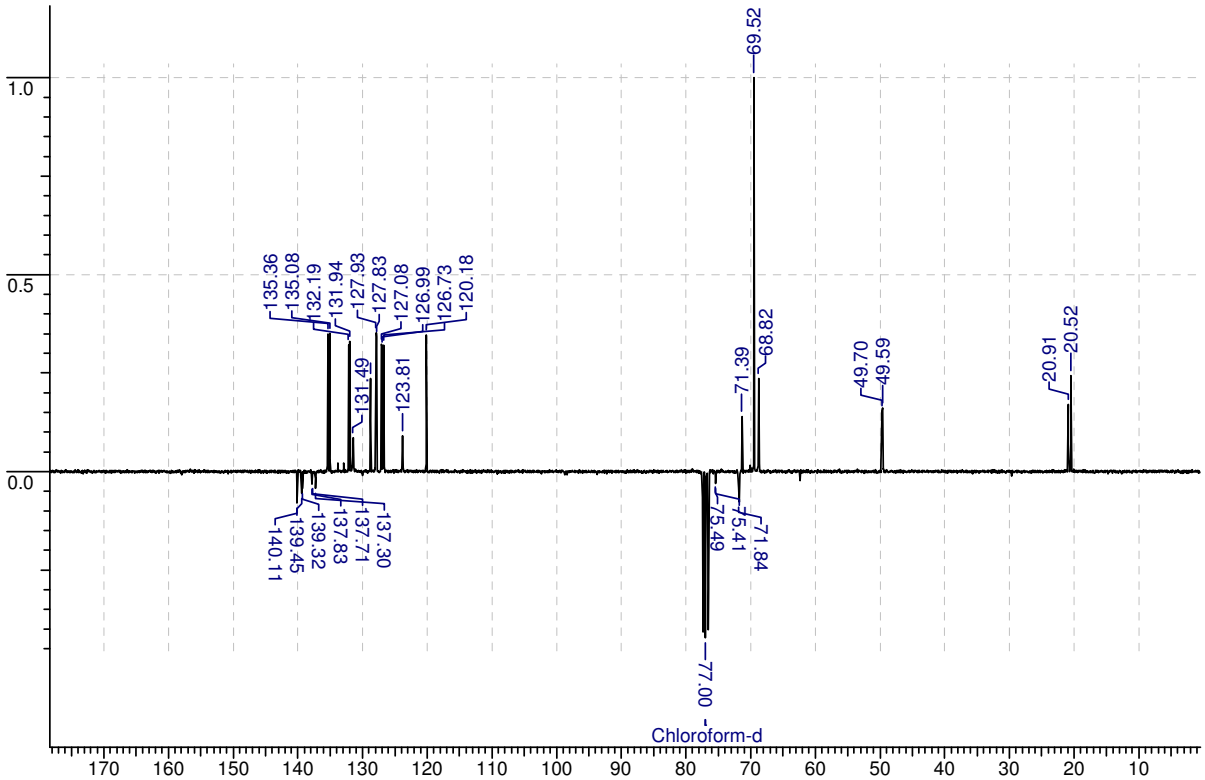


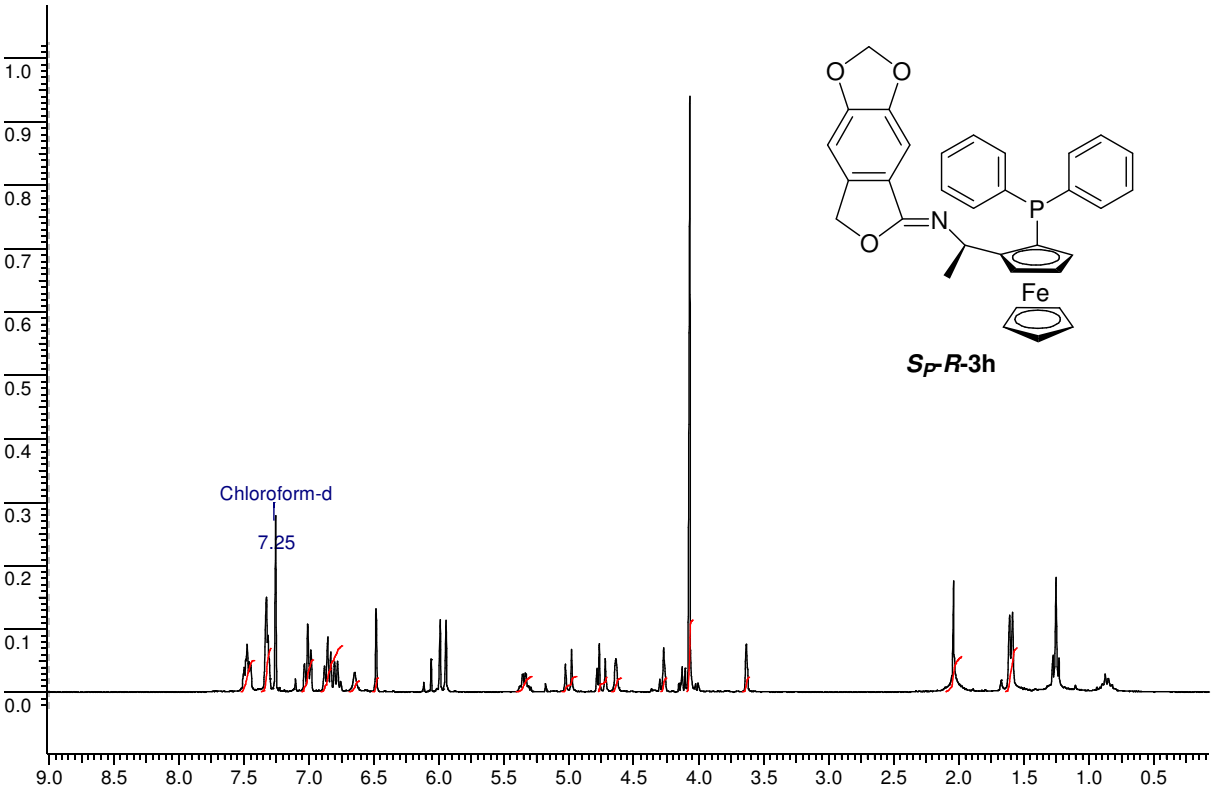
***S*$_P$-*R*-3f**



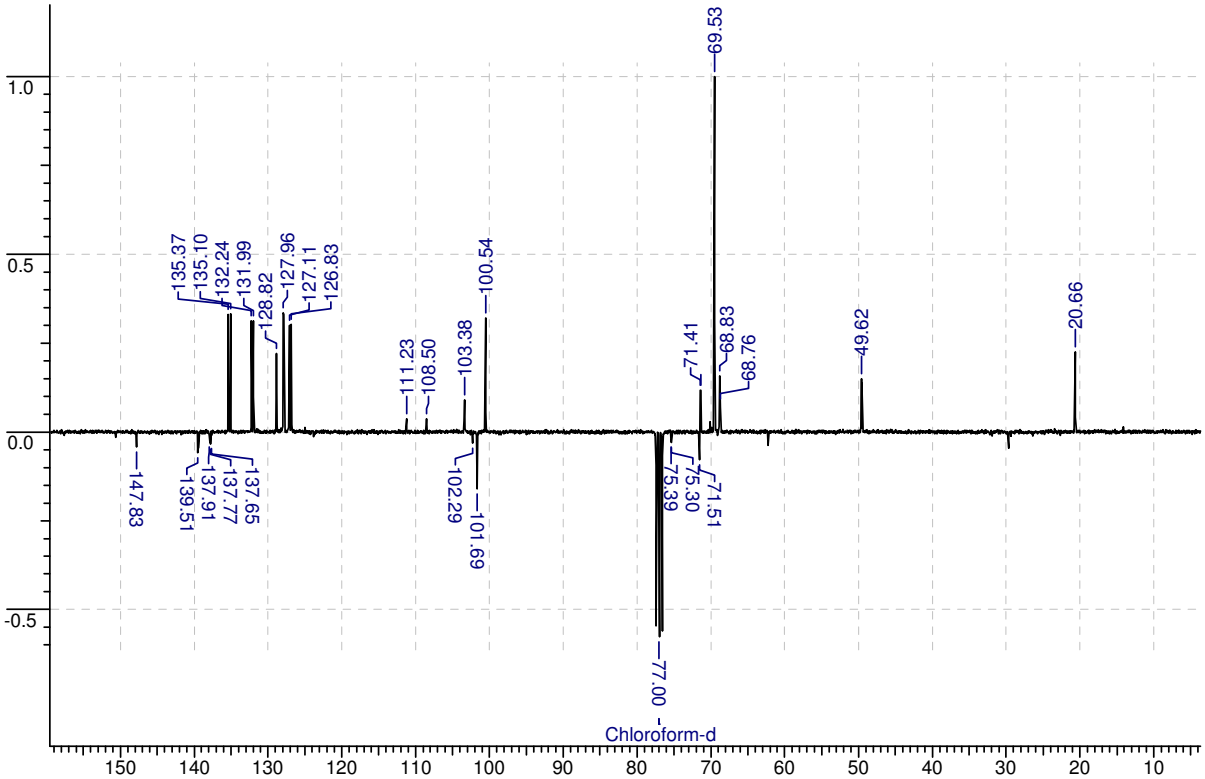


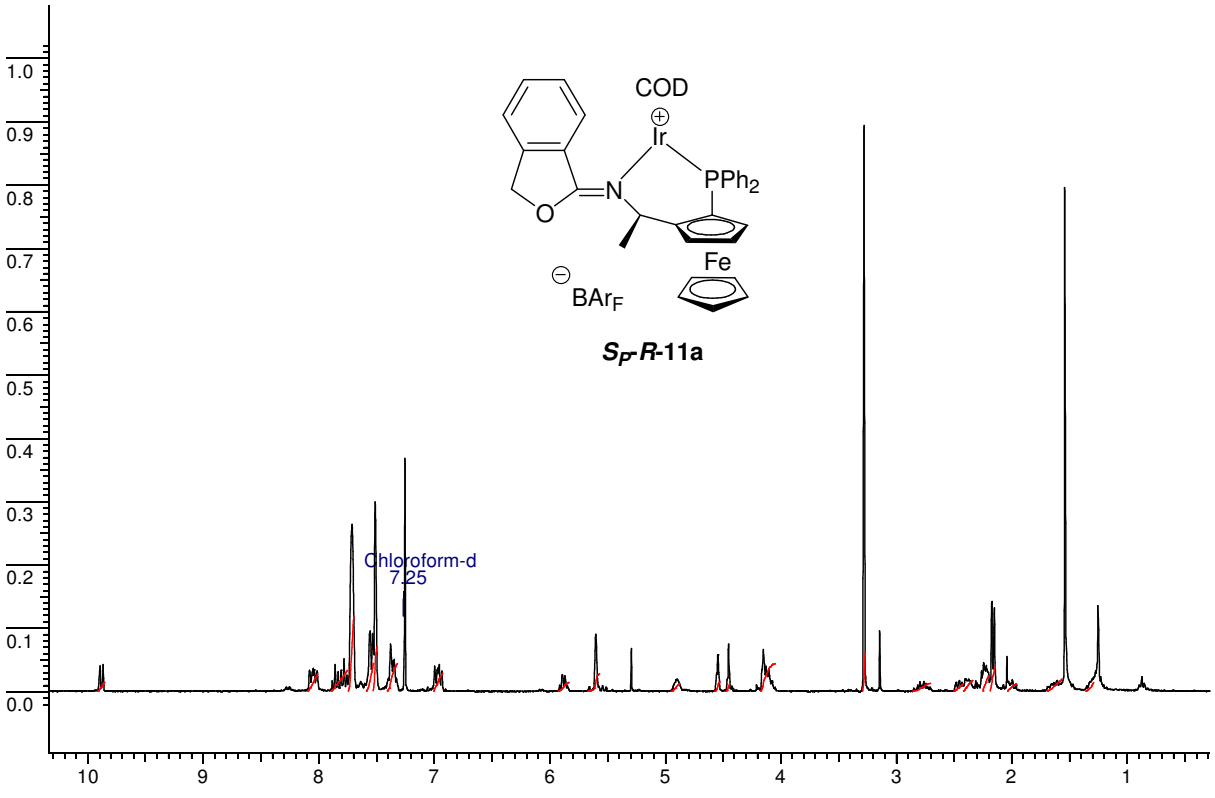
***S*$_P$-*R*-3g**



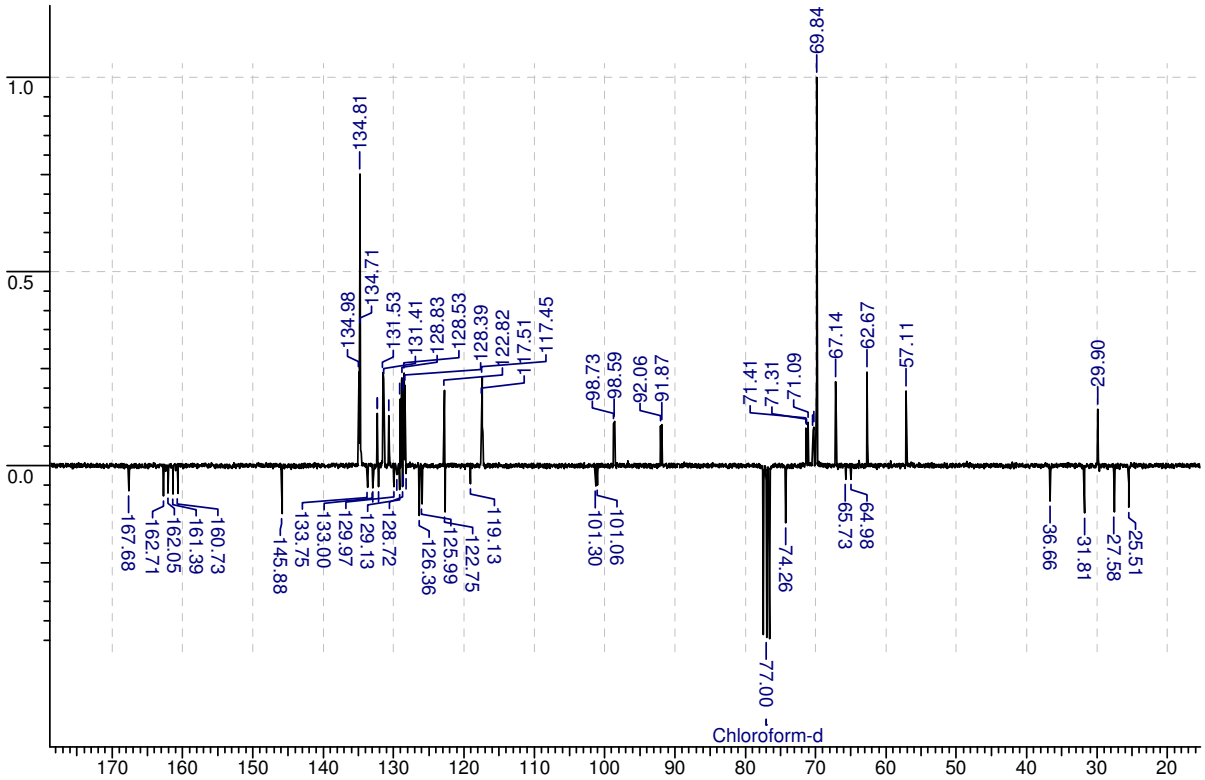


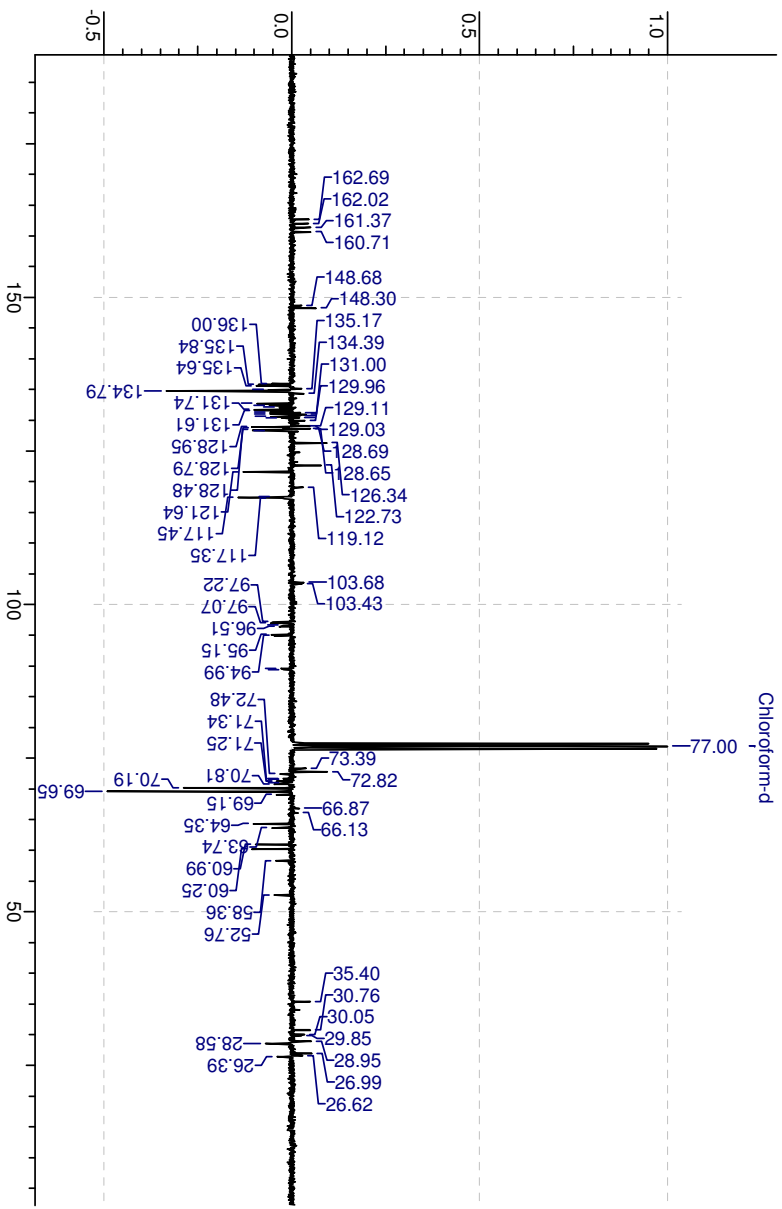
***S*$_P$-*R*-3h**

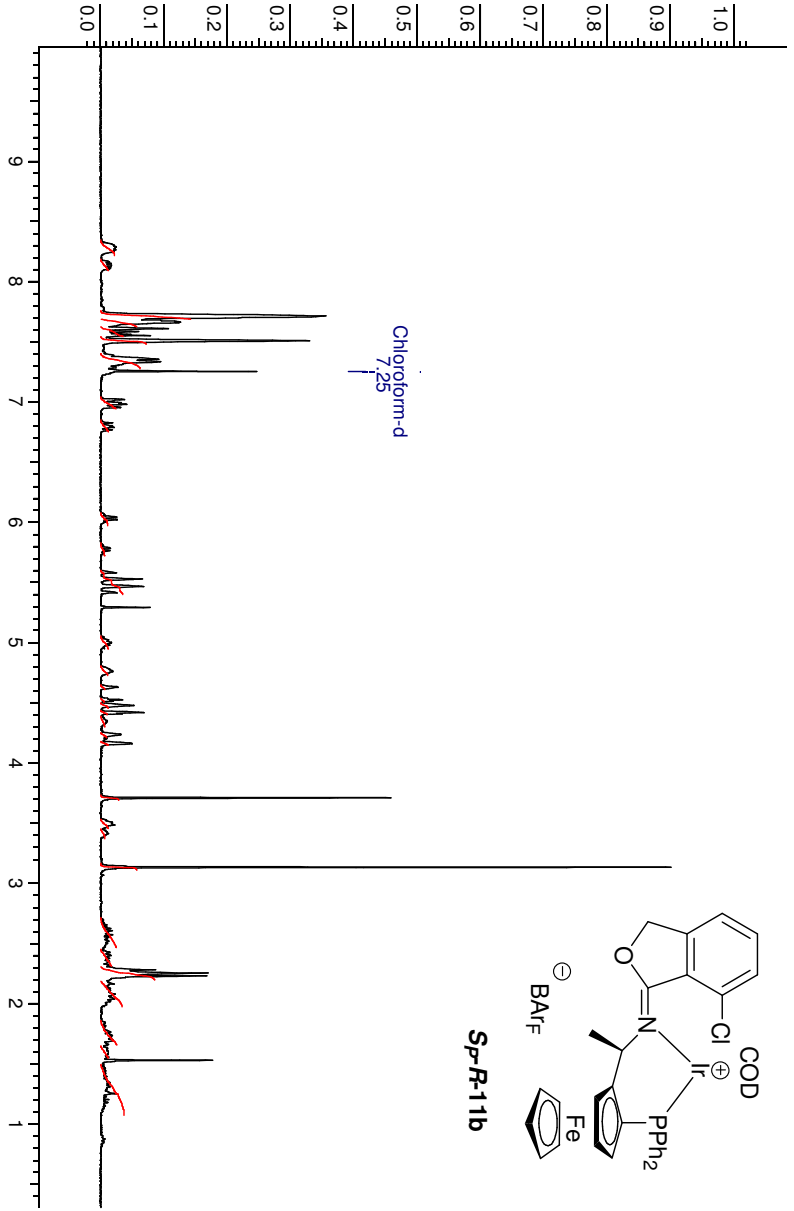




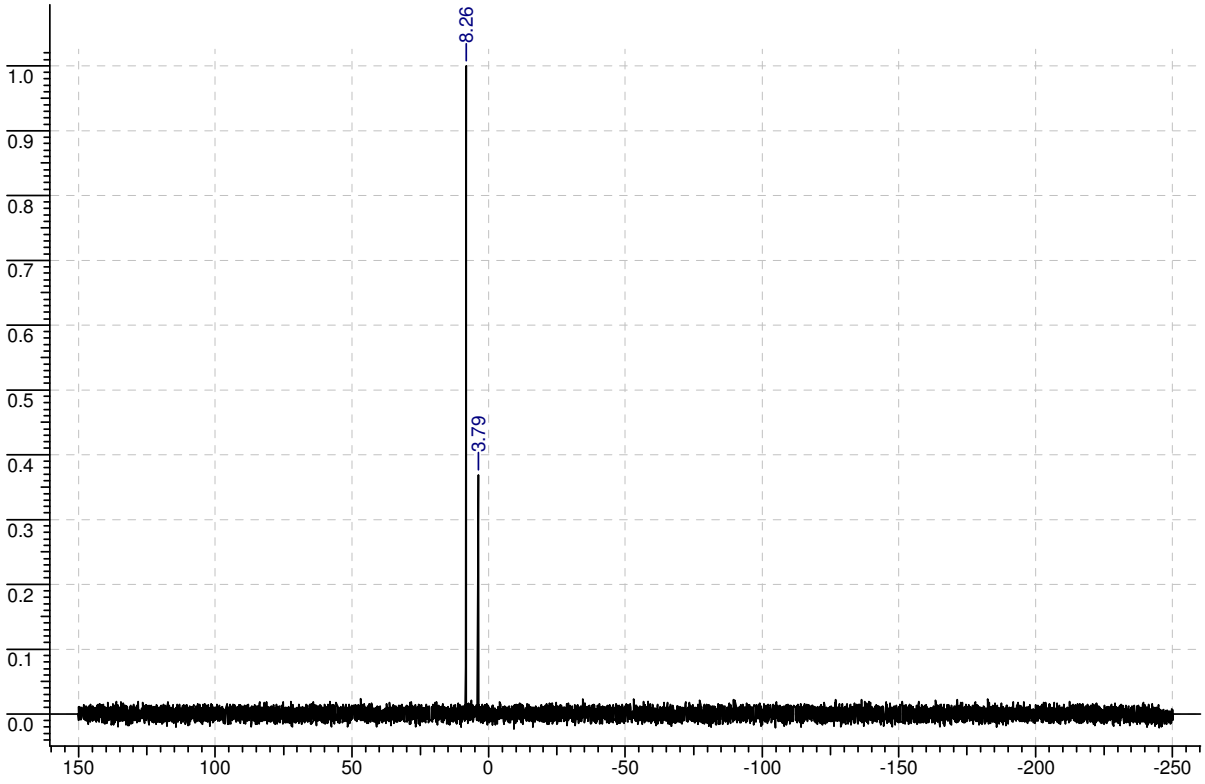
***S*$_P$-*R*-11a**



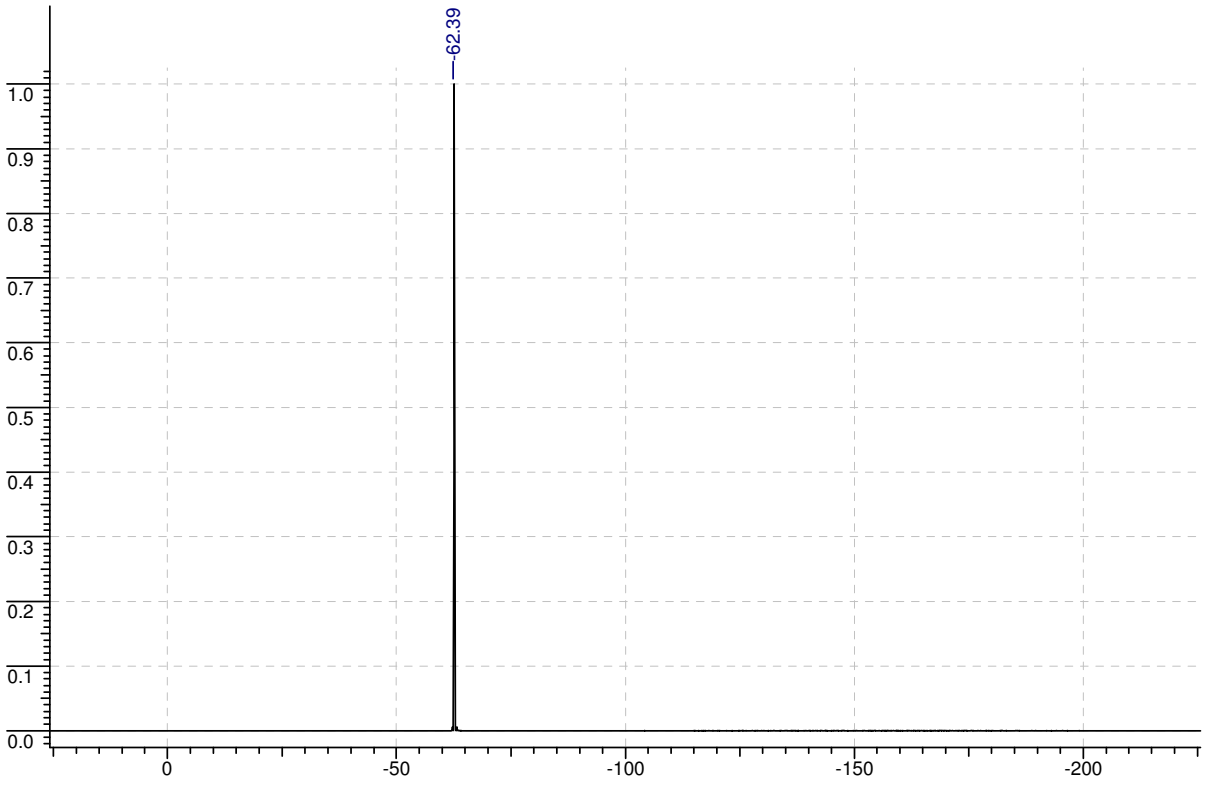


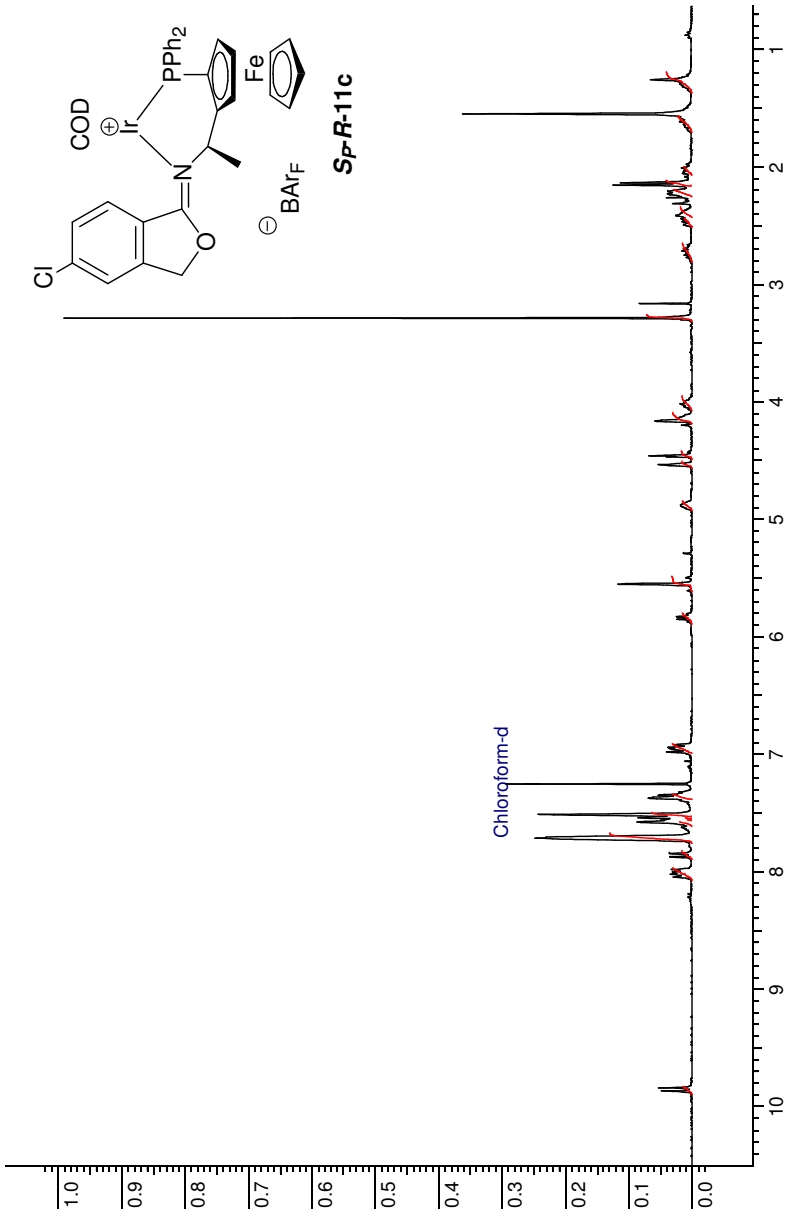


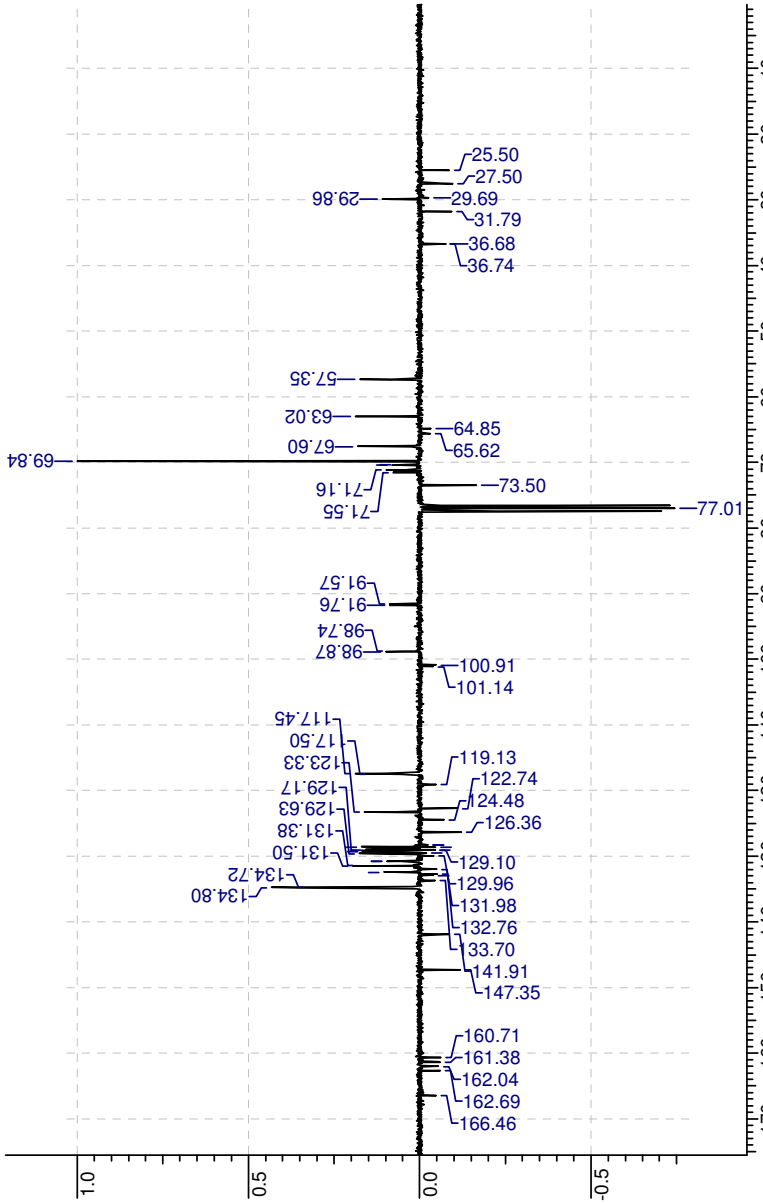
^{31}P-NMR

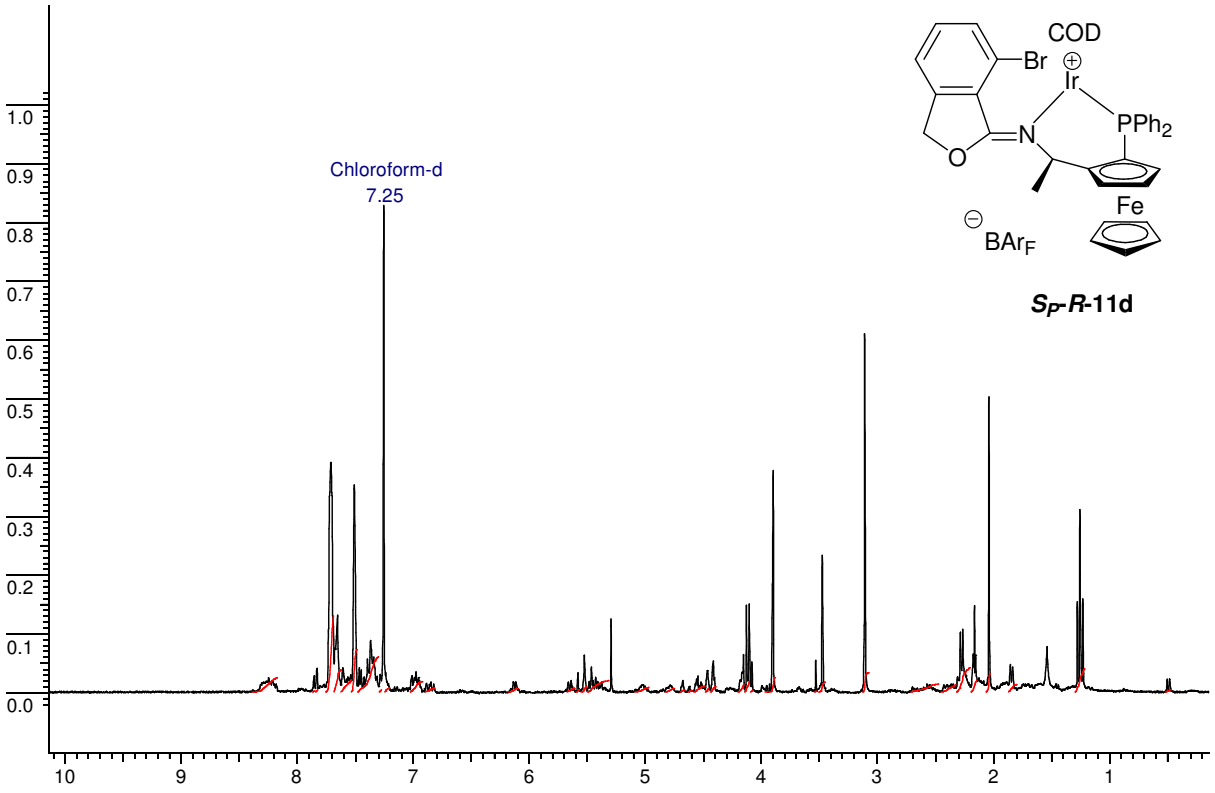


^{9}F-NMR

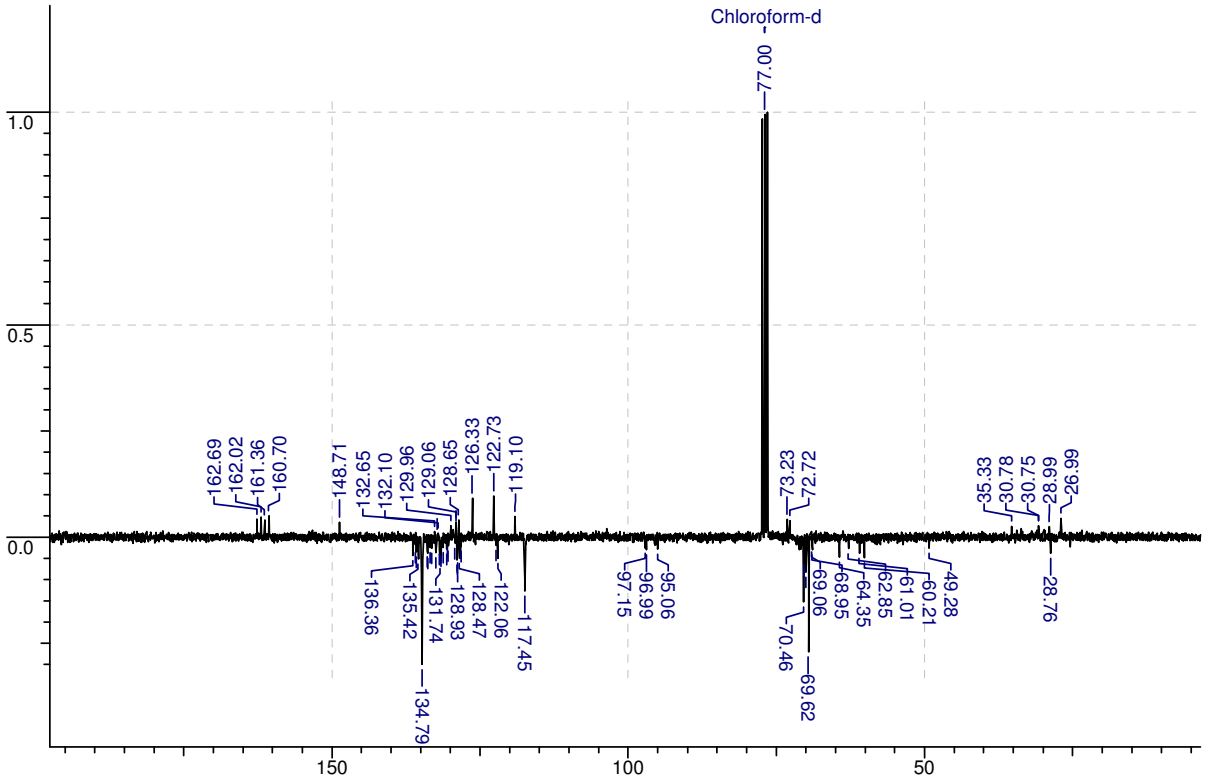




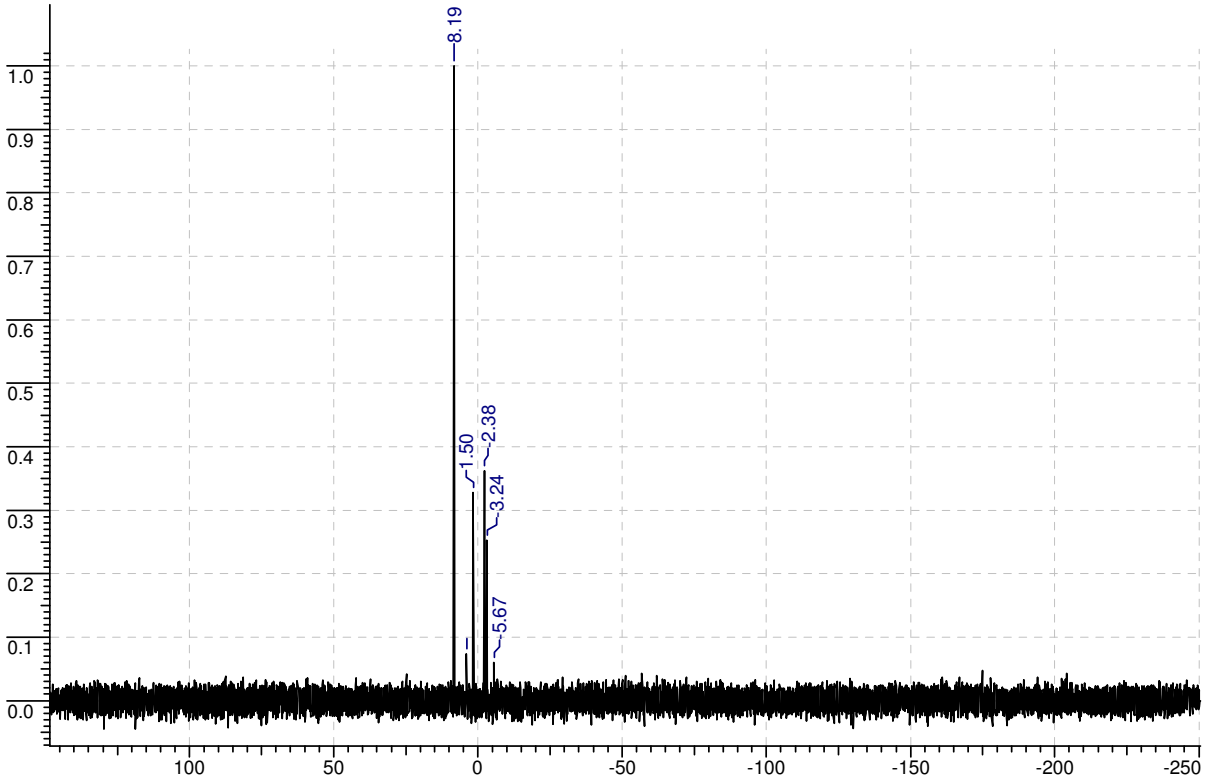


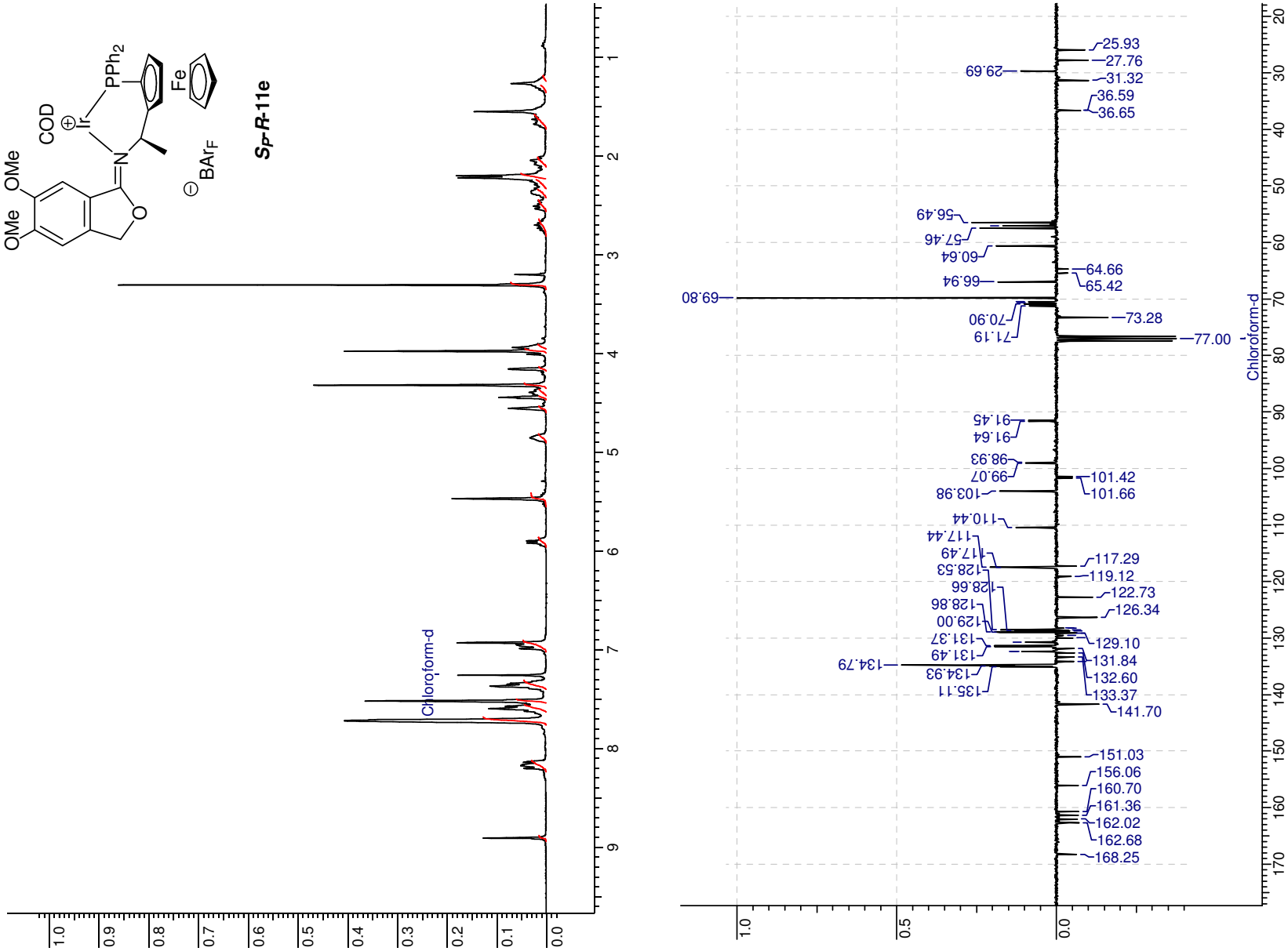


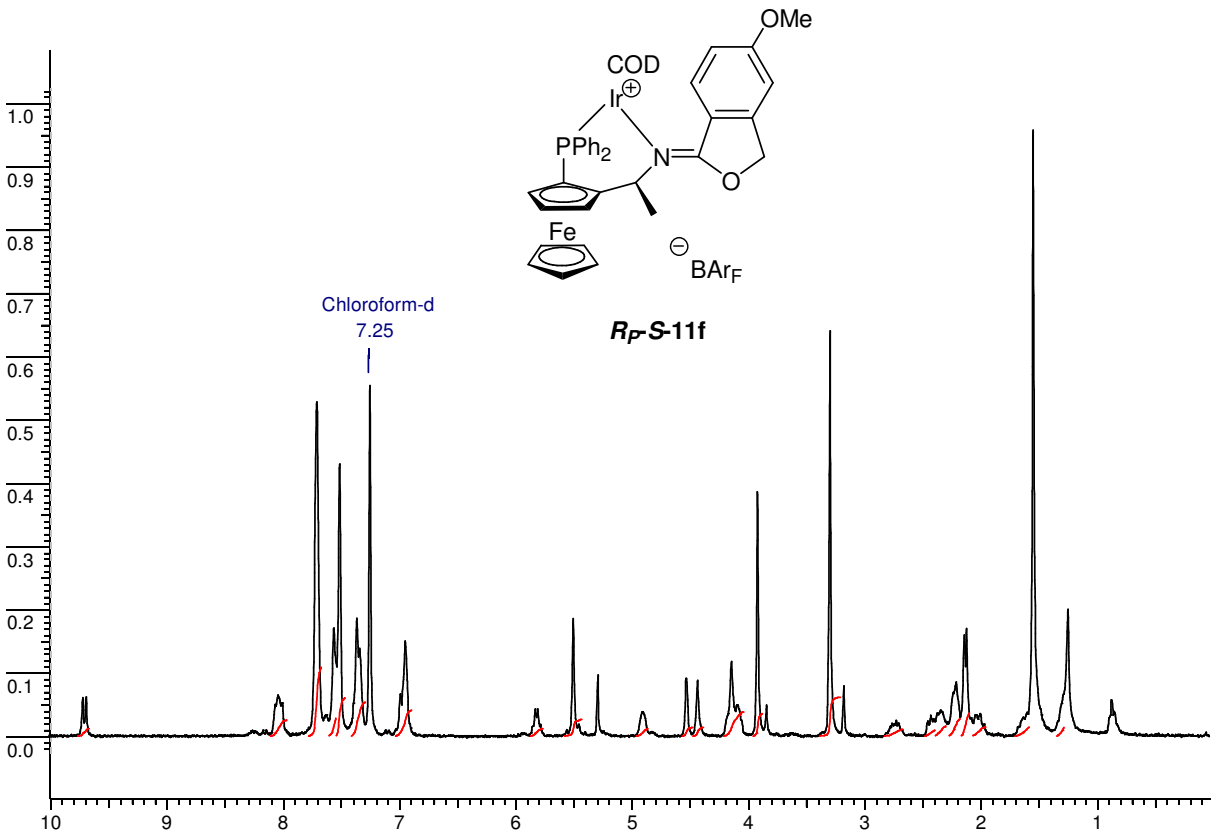
***S*$_P$-*R*-11d**

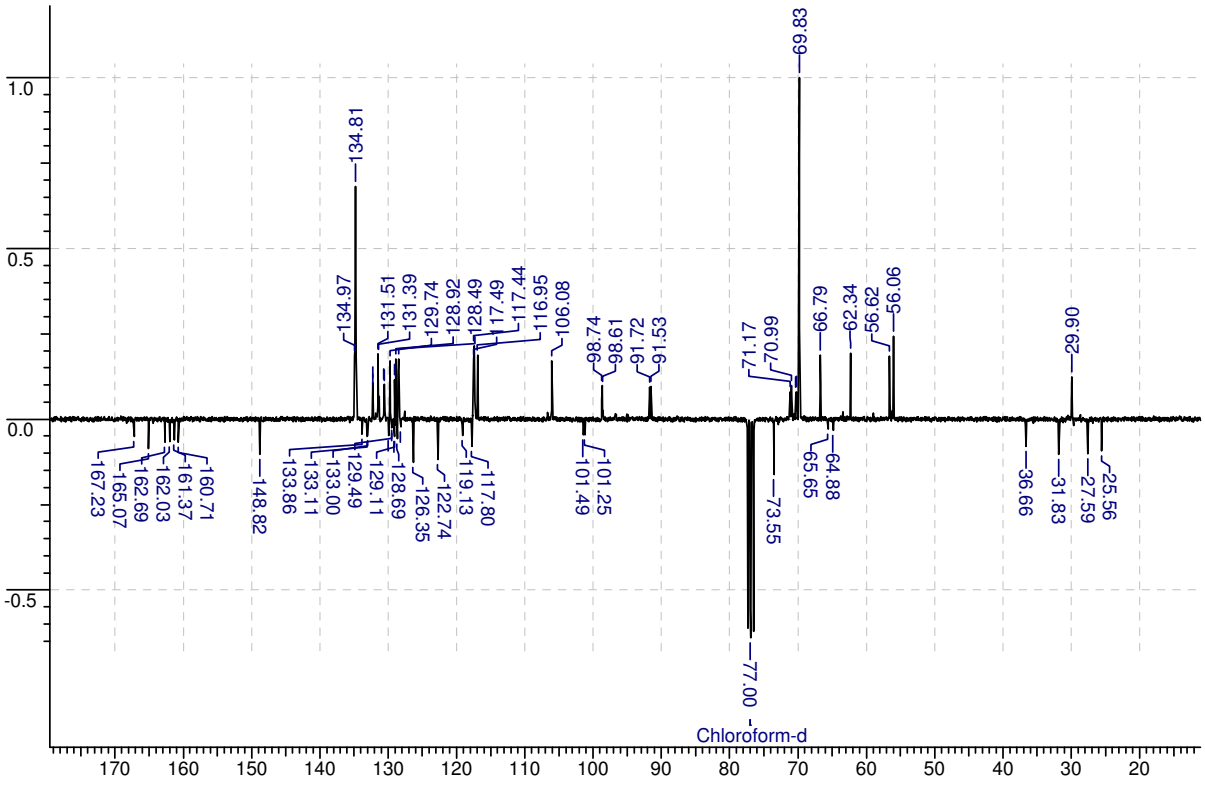


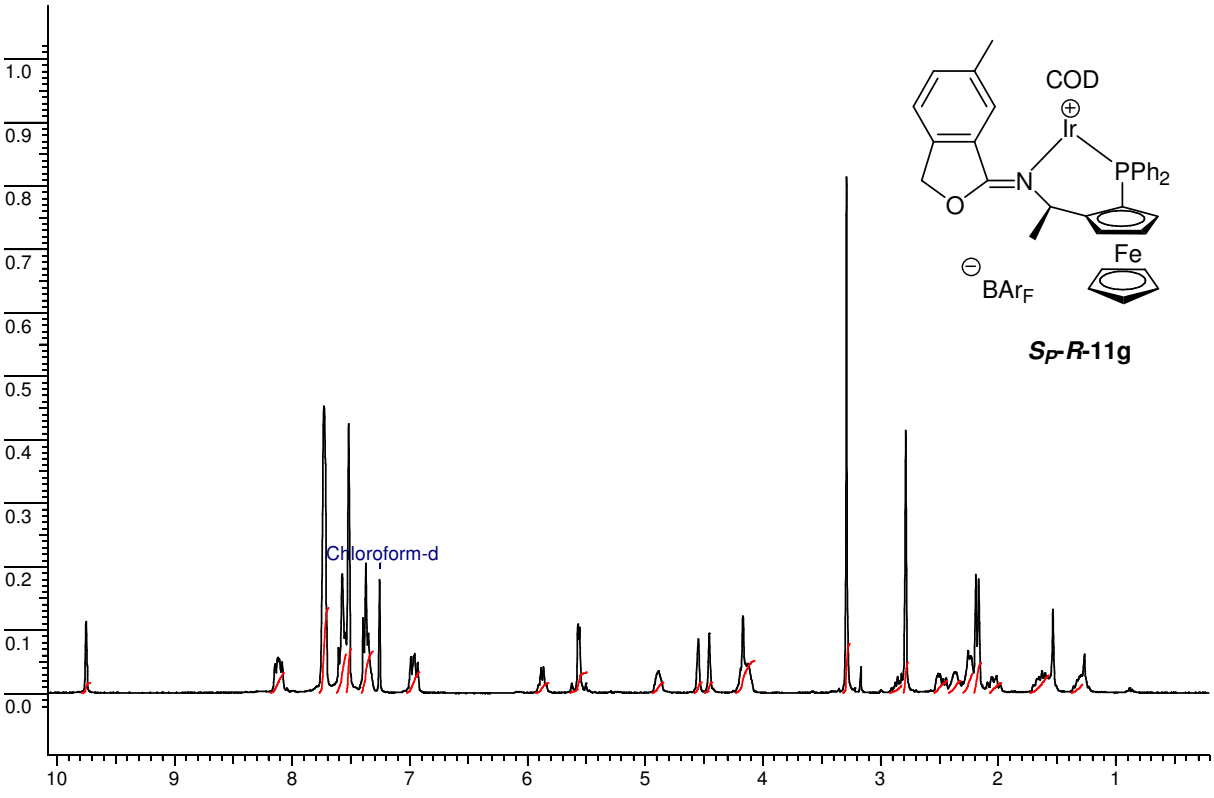
^{31}P-NMR











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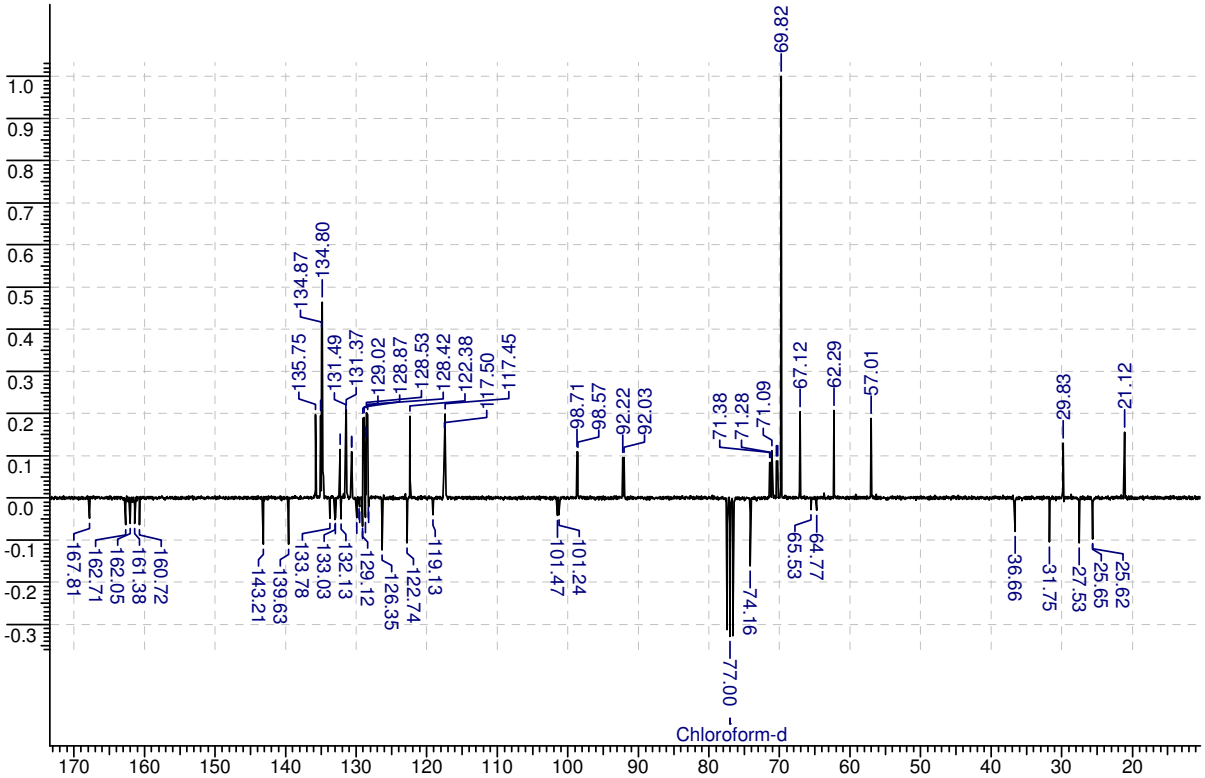
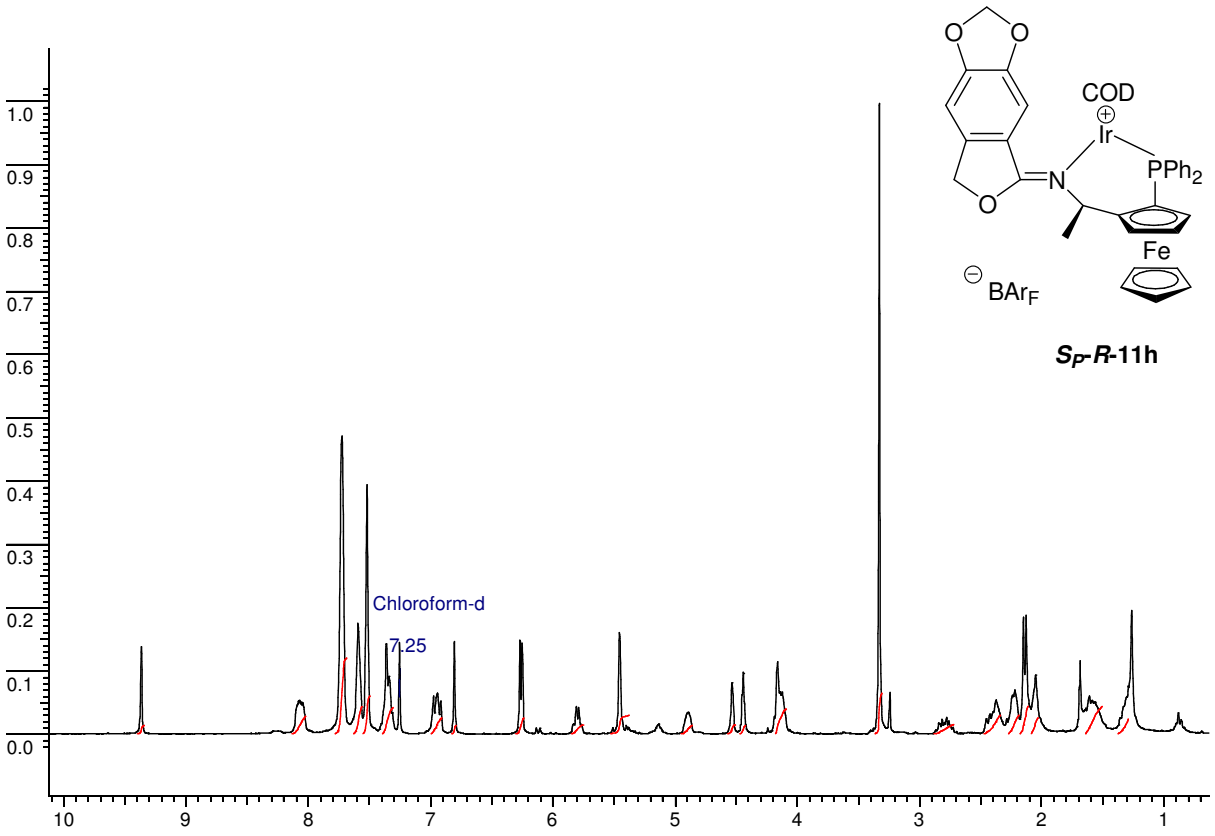
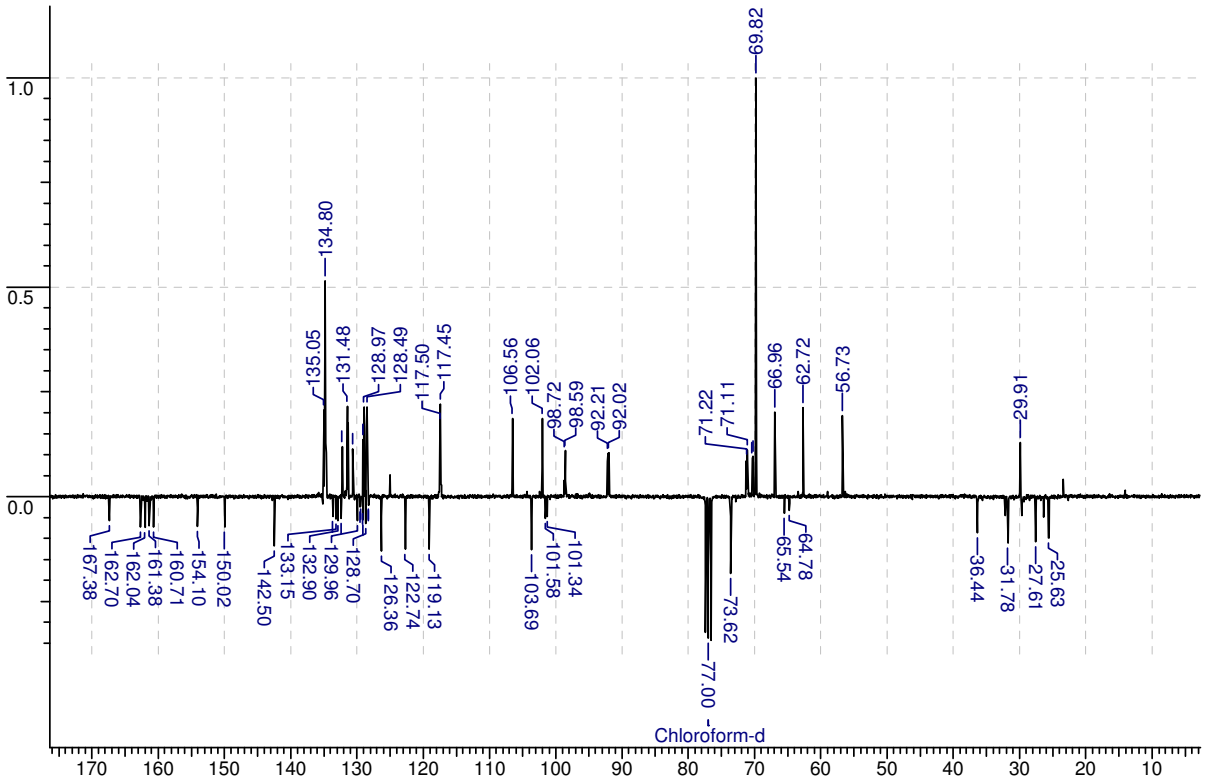




***S*$_P$-*R*-11h**

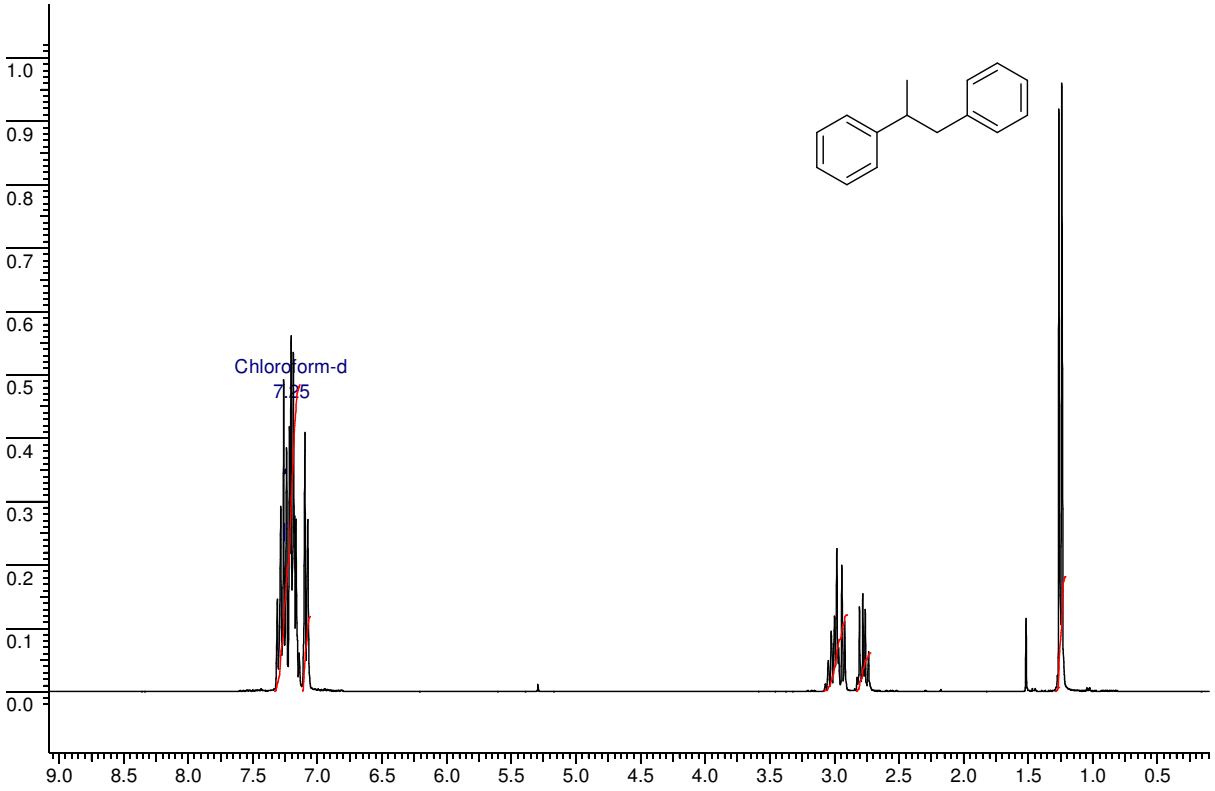


III. ^{1}H NMR and enantiomeric excess determination of the reduction products

The absolute configuration was assigned by comparison of the HPLC retention times and the optical rotation with literature values.[2,5,6]

Separation methods:

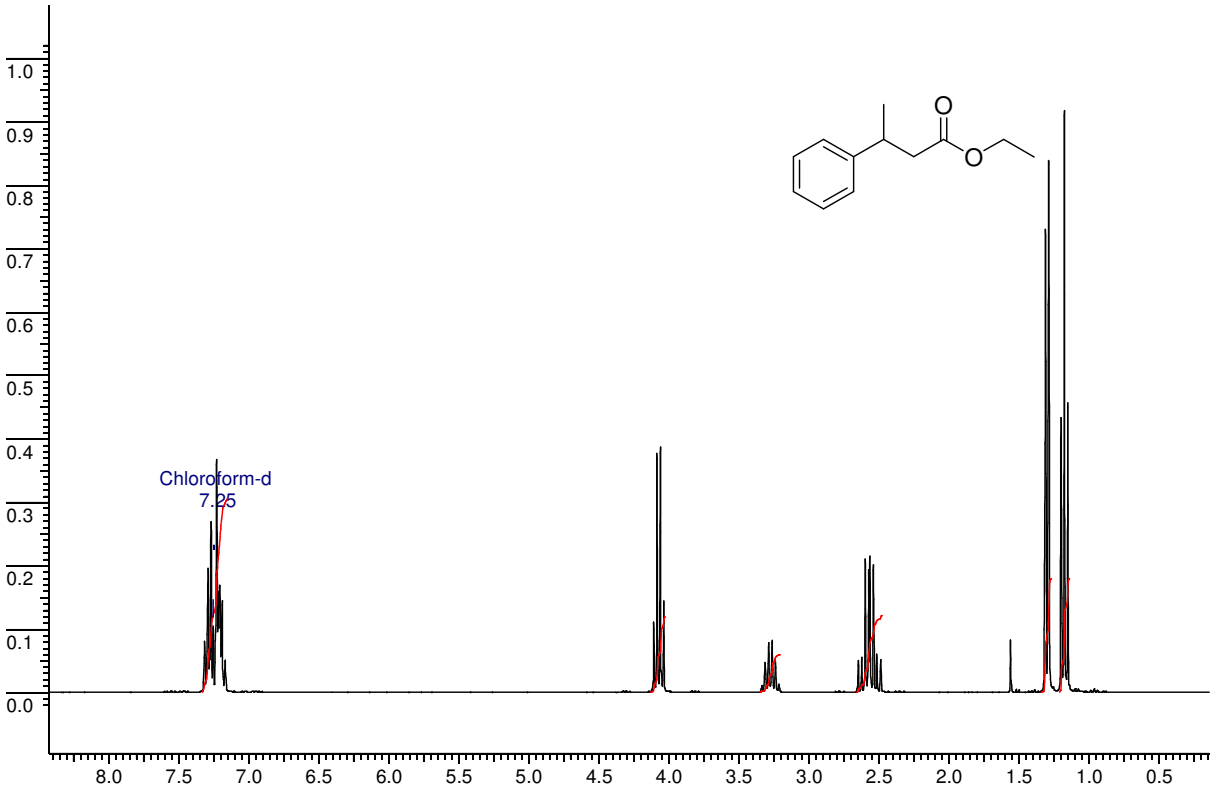
Reduction product from *E*-α-methylstilbene (S1):



Enantiomeric excess was determined by chiral HPLC analysis on a Chiralcel OJ-H column (250 x 4.6 mm, particle size 5 µm), eluent: *n*-hexane/EtOH (98/2), flow rate= 1mL/min, T= 35°C: Retention times: 5.4 min for *R*-(-) and 7.1 min *S*-(+).

Conversion was determined by GC analysis on a Restek XTI-5 column (30 m, 0.25 mm, 0.25 µm), gradient: 50°C, 3min, 20°C/min, 320°C, 5min. Retention times: 11.4 min for the product and 12.4 min for **S1**.

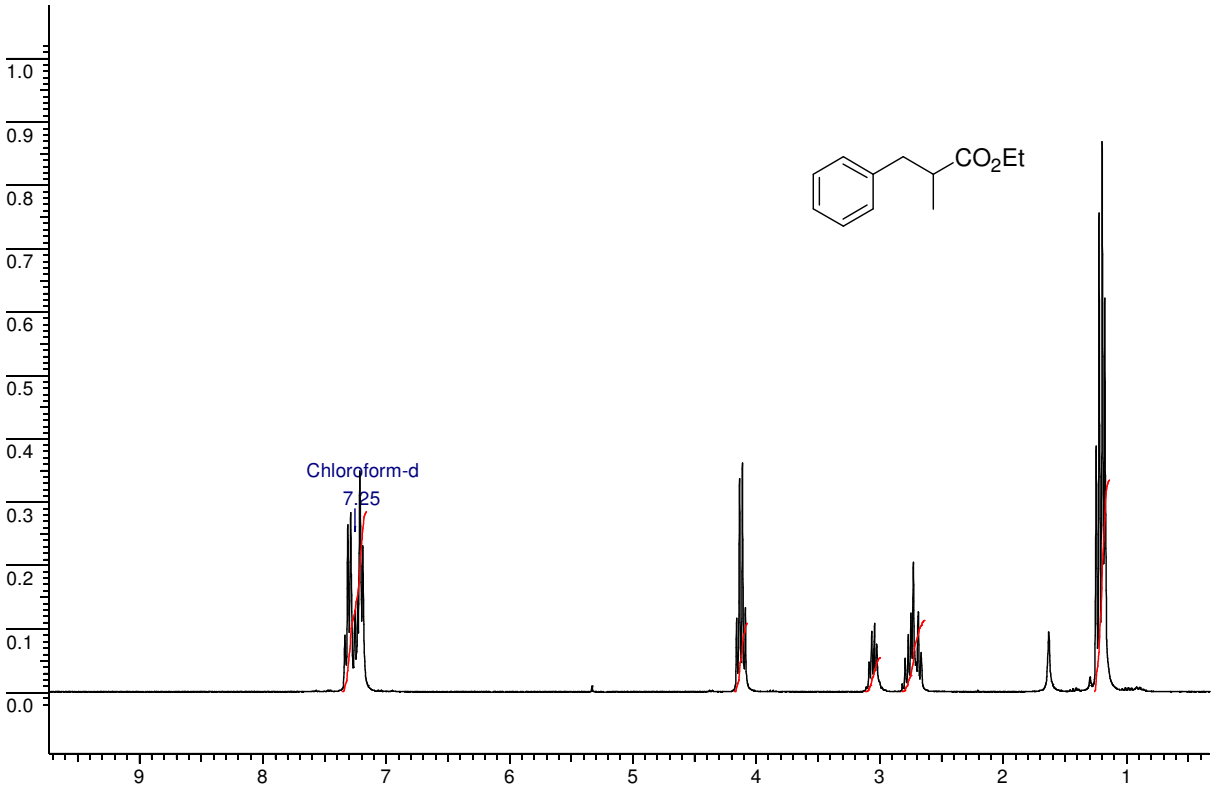
Reduction product from ethyl *E*-β-methyl cinnamate (S2):



Enantiomeric excess was determined by chiral HPLC analysis on a Chiralcel OD-H column (250 x 4.6 mm, particle size 5 µm), eluent: *n*-hexane/*i*PrOH (98/2), flow rate= 1mL/min, T= 35°C. Retention times: 6.1 min for *R*-(-) and 12.2 min for *S*-(+).

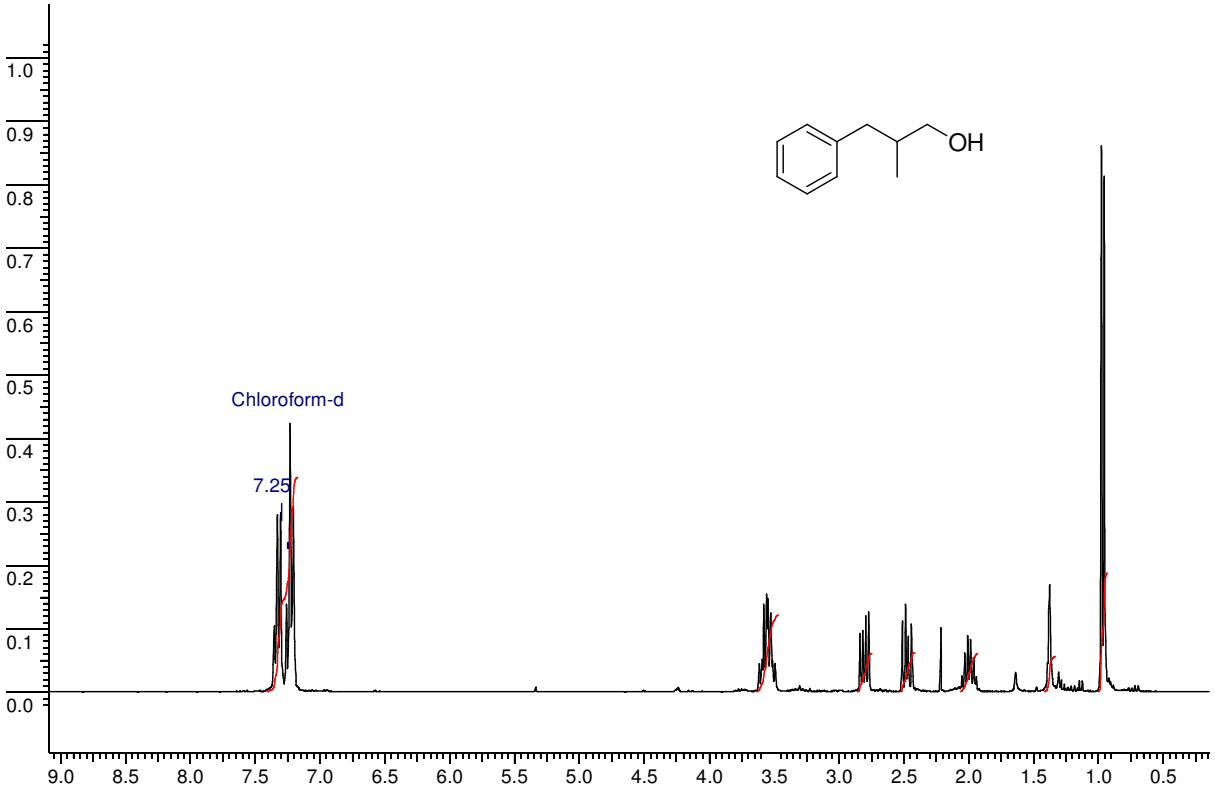
Conversion was determined by GC analysis on a Restek XTI-5 column (30 m, 0.25 mm, 0.25 µm), gradient: 50°C, 3 min, 20°C/min, 320°C, 5 min. Retention times: 10.0 min for the product and 11.0 min for **S2**.

Reduction product from ethyl *E*-α-methyl cinnamate (S3):



Enantiomeric excess and conversion were determined by chiral GC analysis on a Agilent Cyclosyl-B column (30 m, 0.25 mm, 0.25 µm), gradient: 100°C, 3 min, 2°C/min, 200°C, 2 min. Retention times: 21.3 min for *S*-(-), 21.7 min for *R*-(+) and 29.8 min for **S3**.

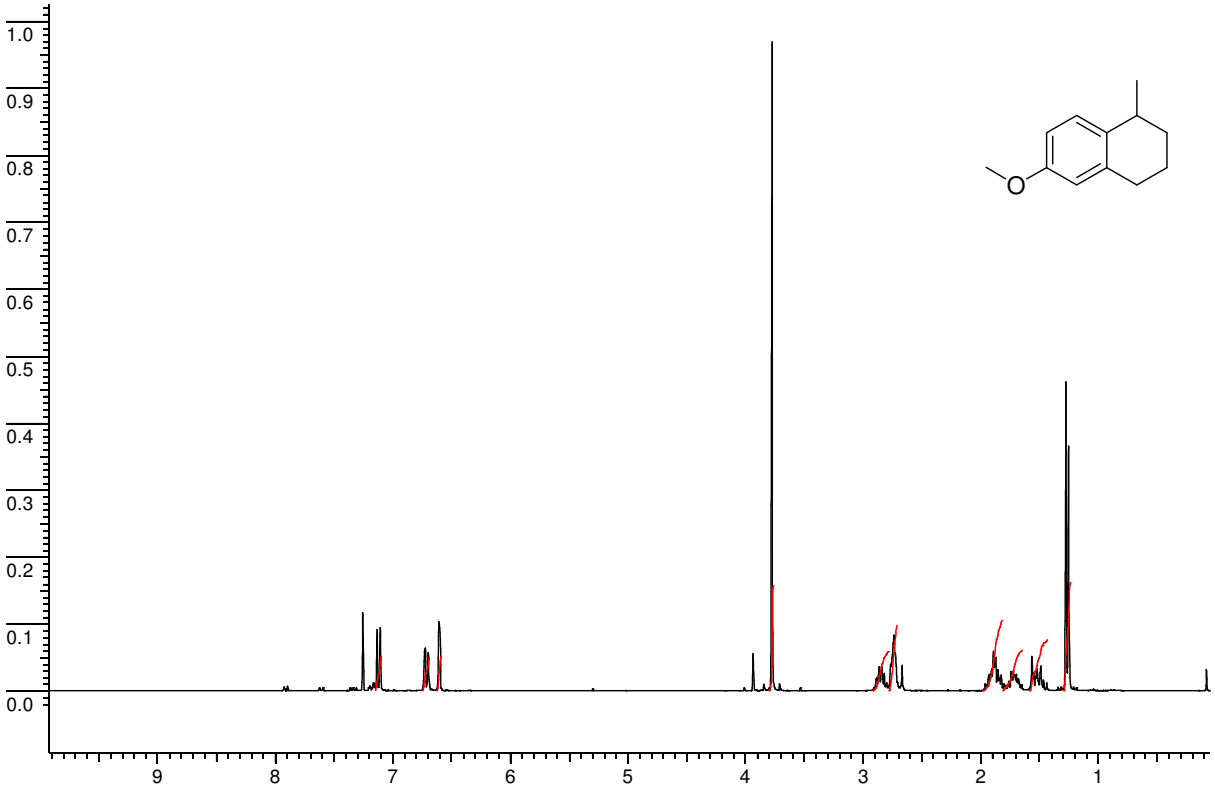
Reduction product from *E*-2-methyl-cinnamyl alcohol (S5):



Enantiomeric excess was determined by chiral HPLC analysis on a Chiralcel OD-H column (250 x 4.6 mm, particle size 5 µm), eluent: *n*-hexane/*i*PrOH (95/5), T= 35°C. Retention times: 9.2 min for *S*-(-), 11.0 min for *R*-(+) and 10.1 min for **S5**.

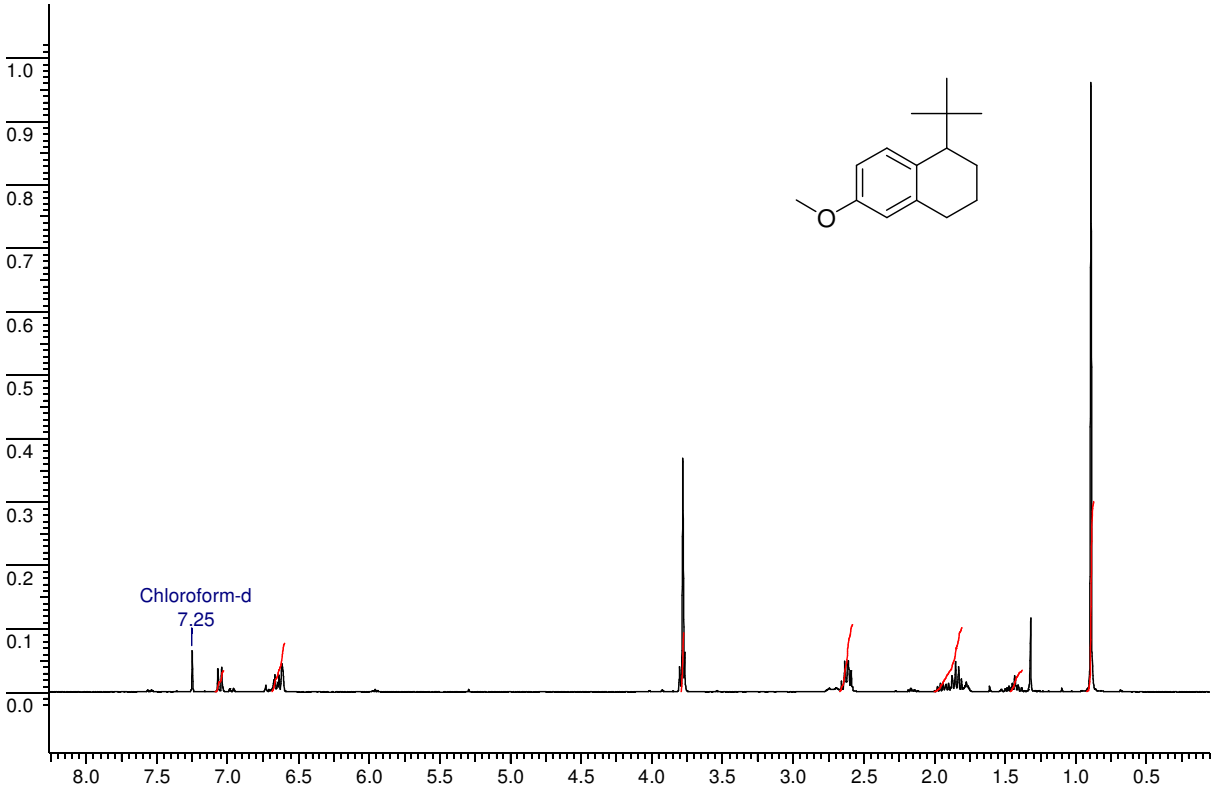
Conversion was determined via GC analysis on a Restek XTI-5 column (30 m, 0.25 mm, 0.25 µm), gradient: 50°C, 3 min, 20°C/min, 320°C, 5 min. Retention times: 9.2 min for the product and 9.9 min for **S5**.

Reduction product from 6-methoxy-1-methyl-3,4-dihydronaphthalene (S6):



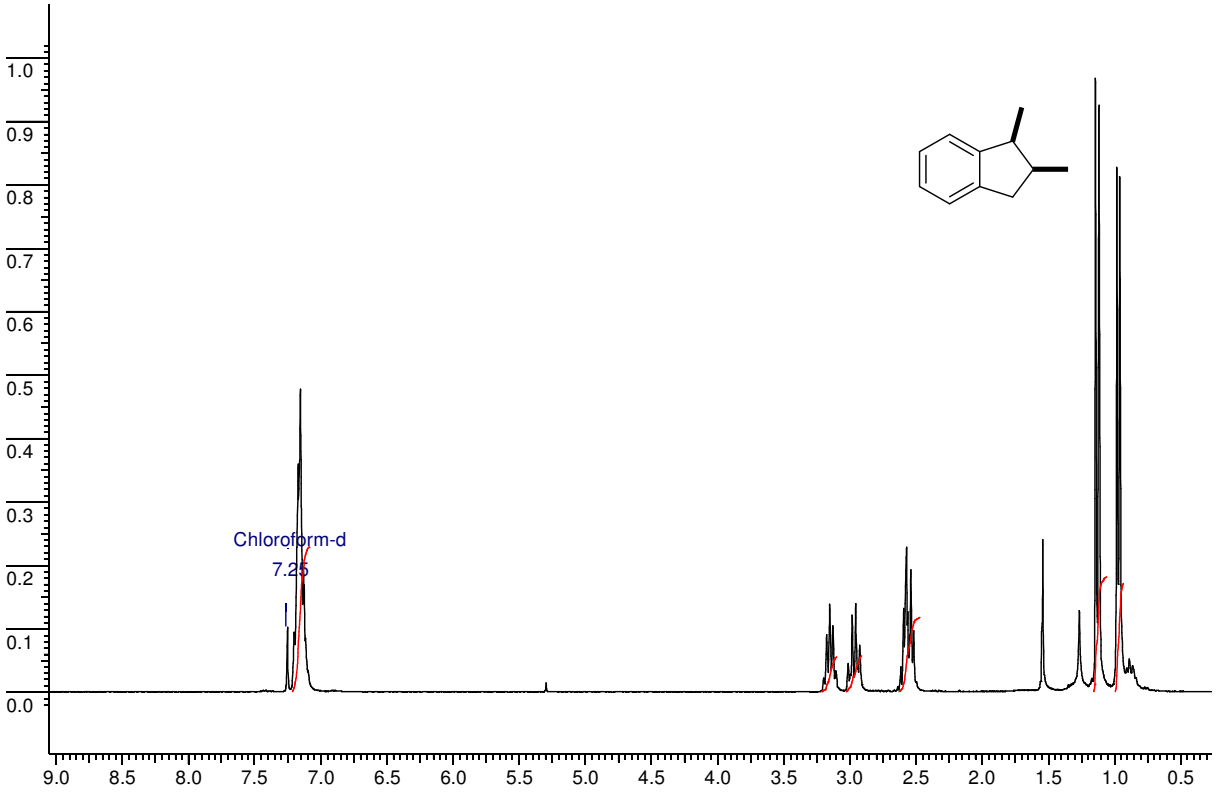
Enantiomeric excess and conversion were determined by chiral GC analysis on a Agilent Cyclosyl-B column (30 m, 0.25 mm, 0.25 µm), gradient: 100°C, 3 min, 5°C/min, 240°C, 5 min. Retention times: 18.2 min for *R*-(-), 18.4 min for *S*-(+) and 19.6 min for **S6**.

Reduction product from 1-t.butyl-6-methoxy-3,4-dihydronaphthalene (S7):



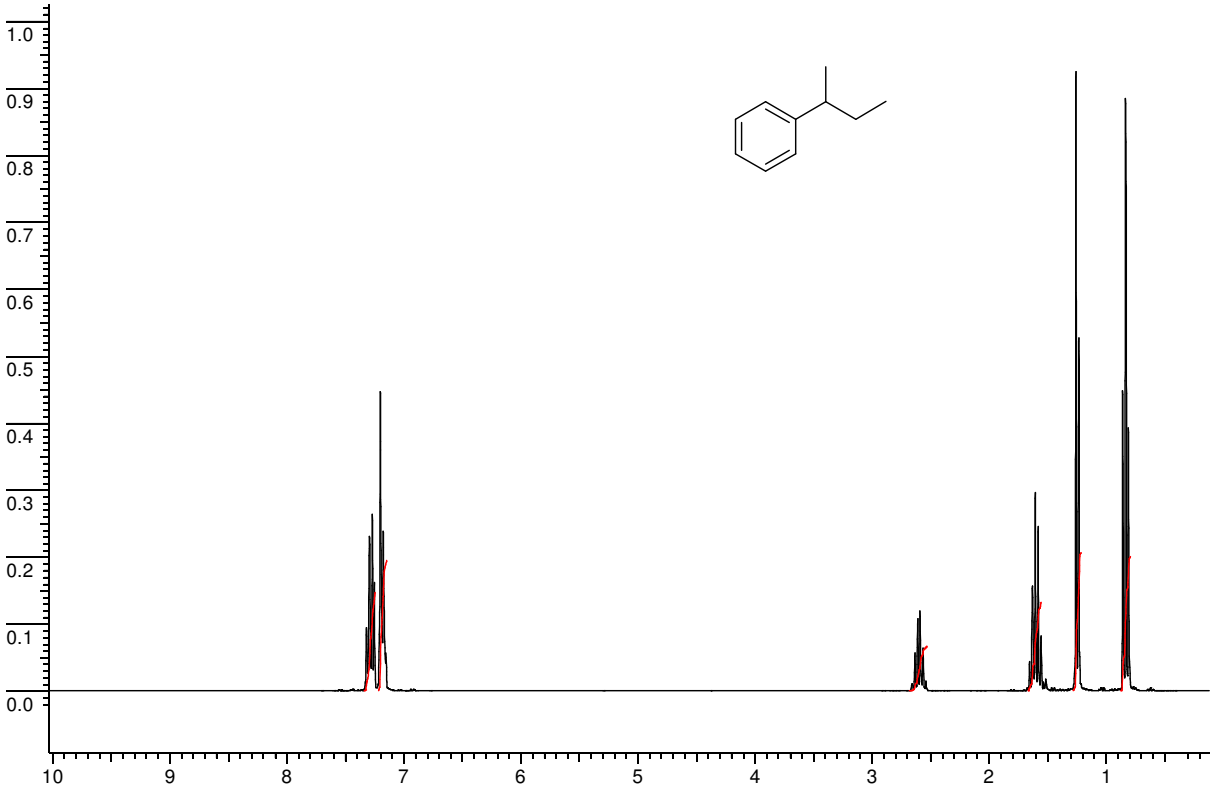
Enantiomeric excess and conversion were determined by chiral GC analysis on a Agilent Cyclosyl-B column (30 m, 0.25 mm, 0.25 µm), gradient: 75°C, 3 min, 5°C/min, 240°C, 10 min. Retention times: 26.6 min for (-), 26.7 min for (+) and 27.8 min for **S7**.

Reduction product from 2,3-dimethyl-1*H*-indene (S8):



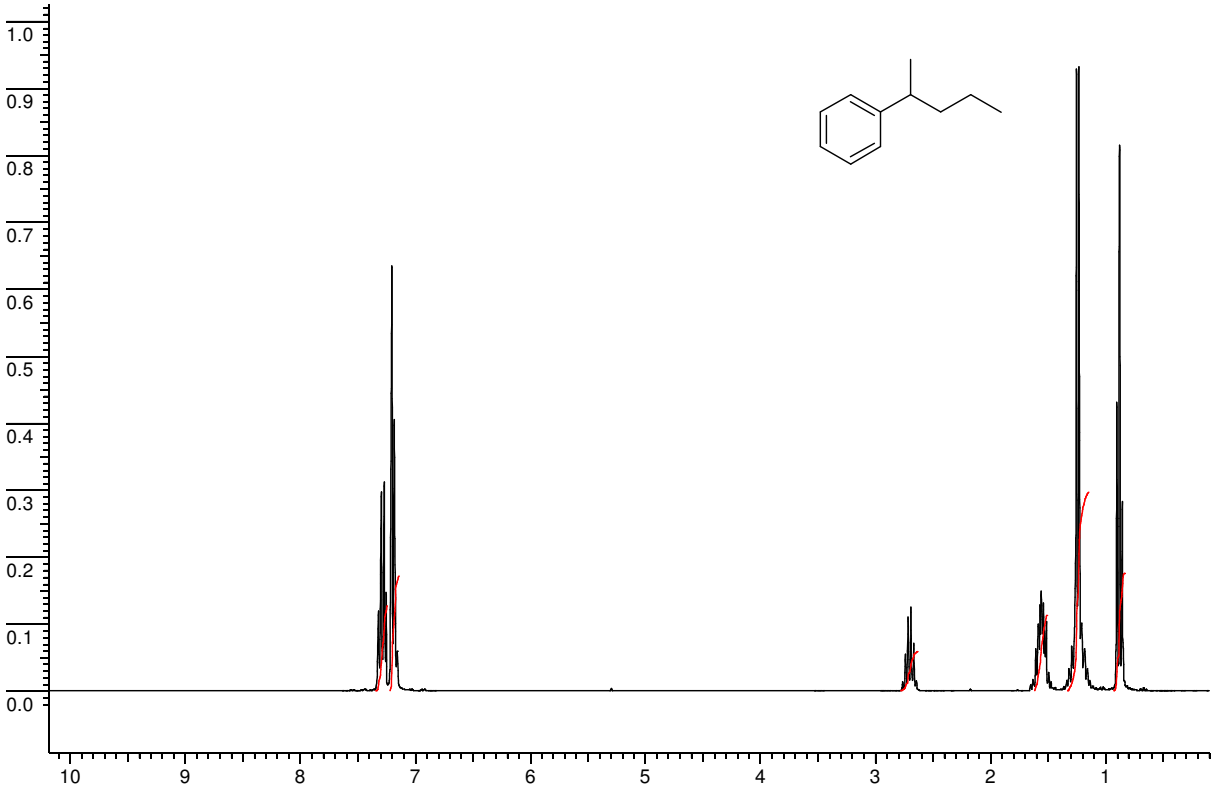
Enantiomeric excess and conversion were determined by chiral GC analysis on a Supelco βDEX-120 column (30 m, 0.25mm, 0.25µm), gradient: 80°C, 3 min, 3°C/min, 170°C, 3 min. Retention times: 15.5 min for (-), 15.8 min for (+) and 20.2 min for **S8**.

Reduction product from 2-ethylstyrene (S9):



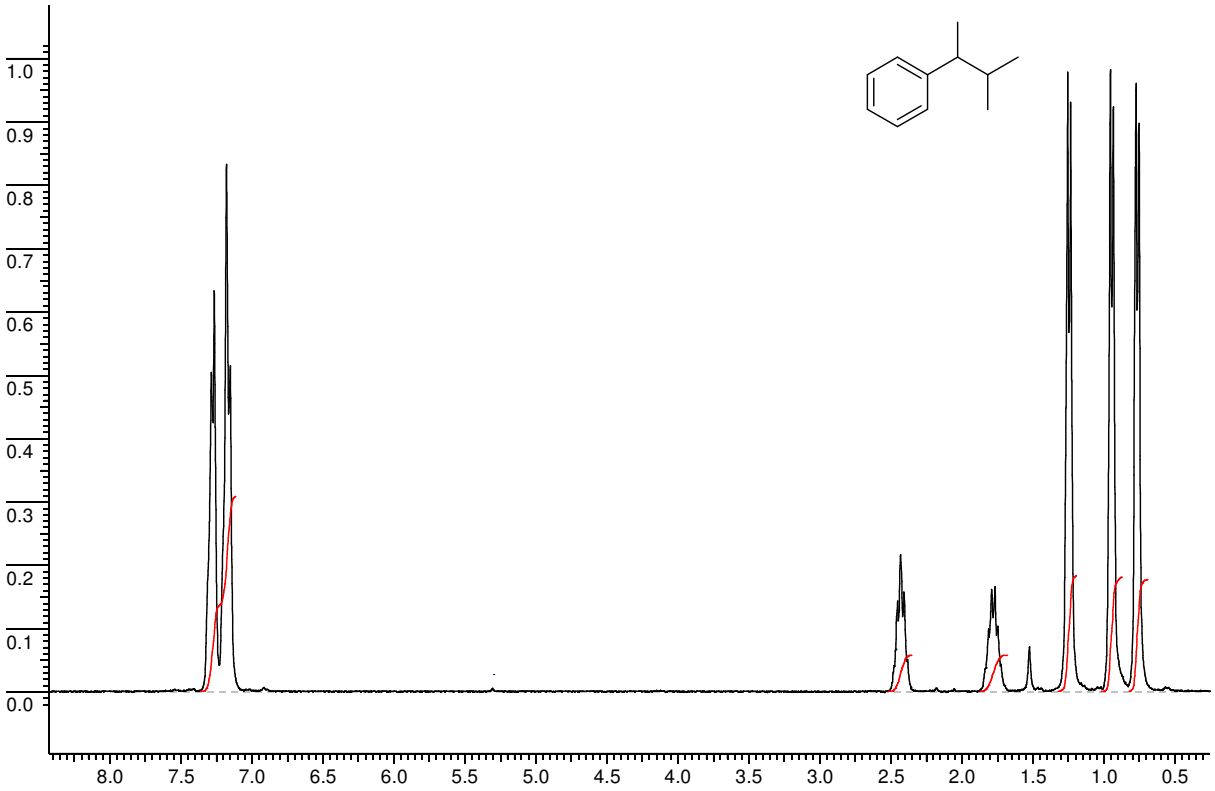
Enantiomeric excess and conversion were determined by chiral GC analysis on a Macherey-Nagel L-Chirasil-Val column (25 m, 0.32mm, 0.20 µm), gradient: 50°C, 3 min, 20°C/min, 170°C, 10 min. Retention times: 4.5 min for *S*-(+), 4.8 min for *R*-(-) and 5.3 min for **S9**.

Reduction product from 2-*n*.propylstyrene (S10):



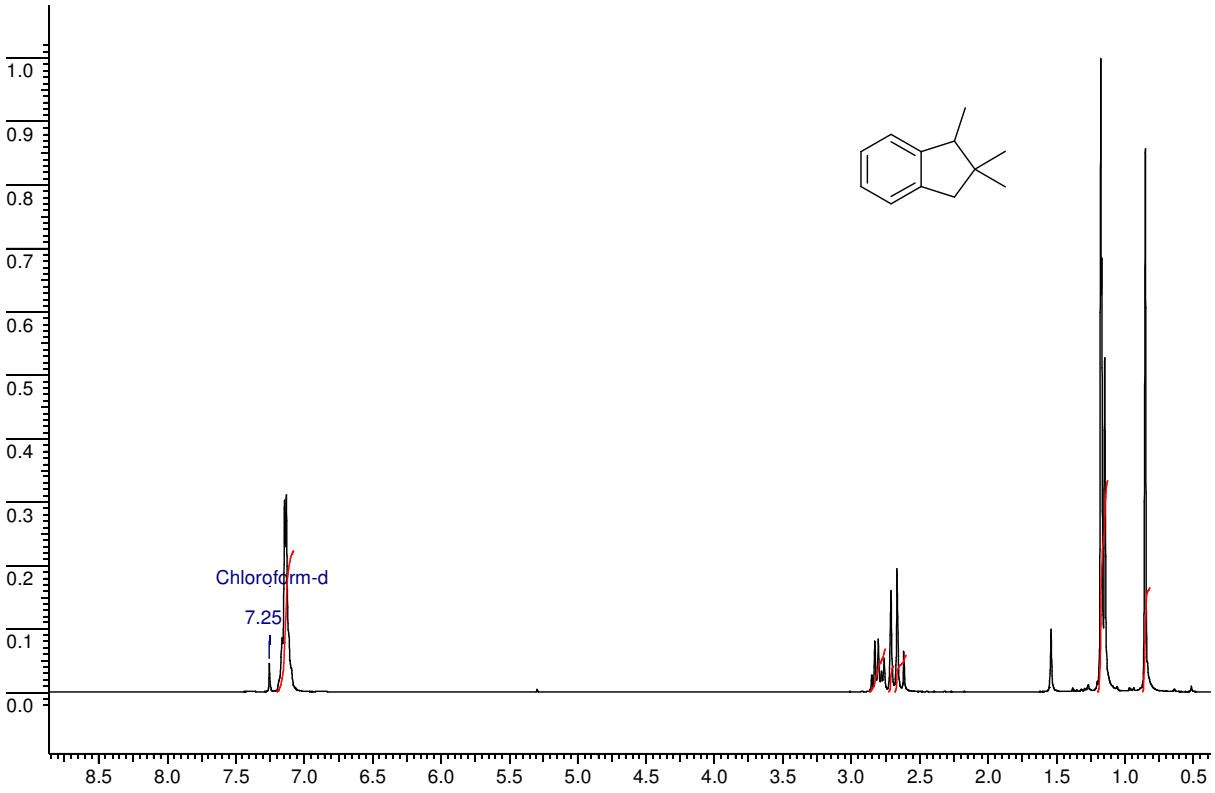
Enantiomeric excess and conversion were determined by chiral GC analysis on a Agilent Cyclosyl-B column (30 m, 0.25 mm, 0.25 µm), gradient: 50°C, 3 min, 5°C/min, 200°C, 5 min. Retention times: 15.3 min for (+), 15.4 min for (-) and 17.2 min for **S10**.

Reduction product from 3-methyl-2-phenyl-butene (α-isopropylstyrene) (S11):



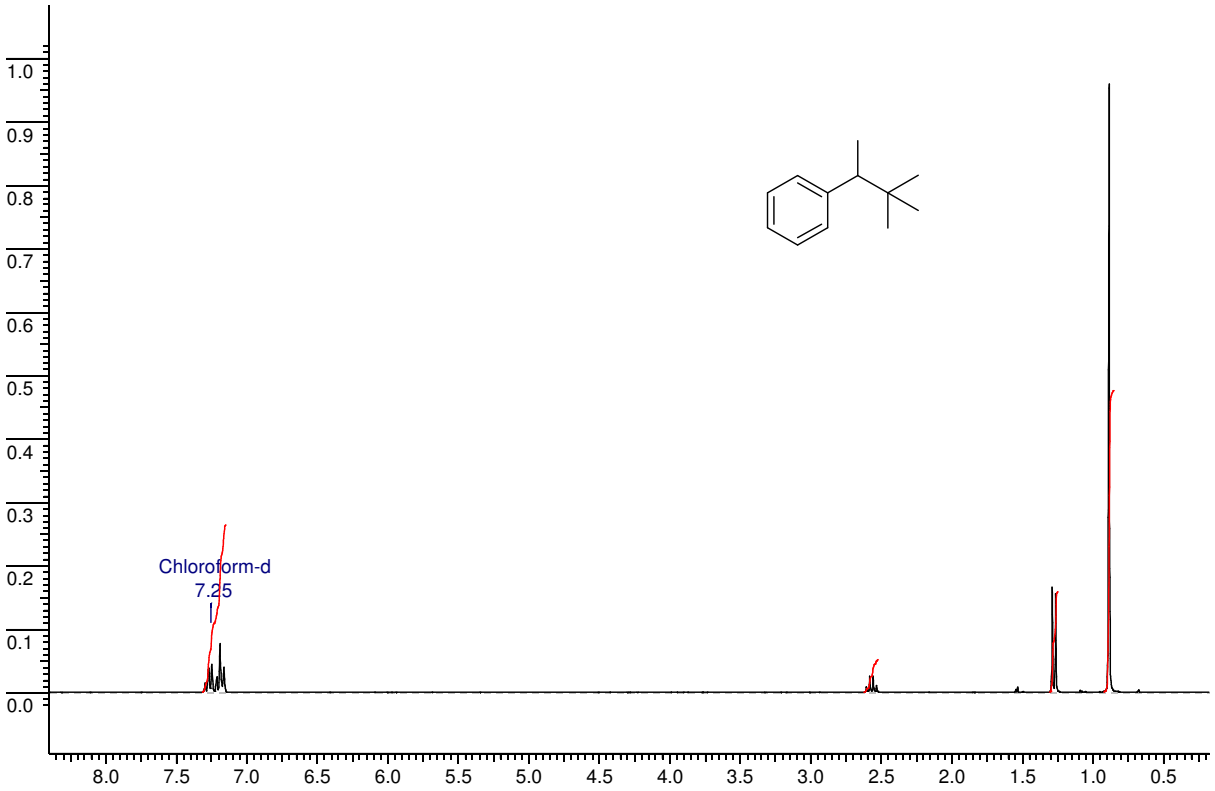
Enantiomeric excess and conversion were determined by chiral GC analysis on a Agilent Cyclosyl-B column (30 m, 0.25 mm, 0.25 µm), gradient: 50°C, 3 min, 20°C/min, 240°C, 5 min. Retention times: 8.3 min for *S*-(+), 8.4 min for *R*-(-) and 8.7 min for **S11**.

Reduction product from 2,2-dimethyl-1-methylidene-indane (S12):



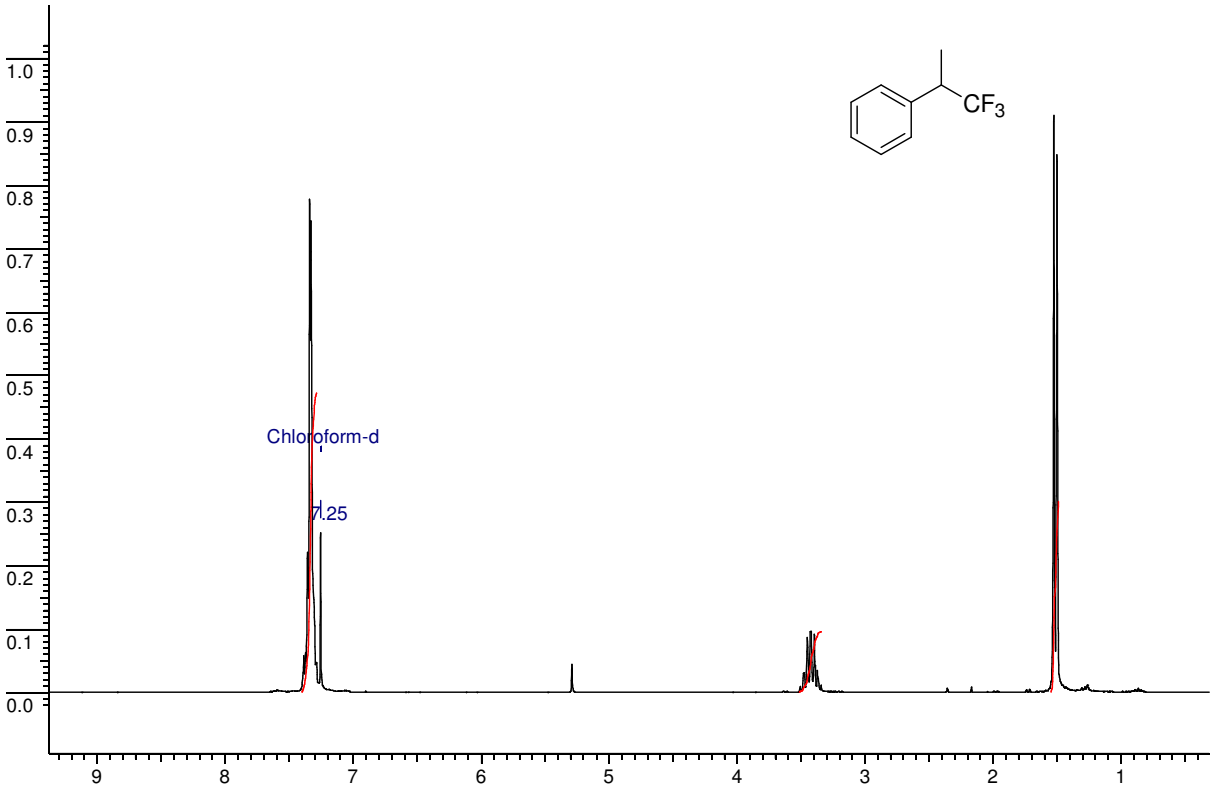
Enantiomeric excess and conversion were determined by chiral GC analysis on a Supelco βDEX-120 column (30 m, 0.25mm, 0.25µm), gradient: 80°C, 3 min, 2°C/min, 150°C, 3 min. Retention times: 17.6 min for (-), 17.9 min for (+) and 20.8 min for **S12**.

Reduction product from 3,3-dimethyl-2-phenyl-butene (α-*t.*butylstyrene) (S13):



Enantiomeric excess and conversion were determined by chiral GC analysis on a Agilent Cyclosyl B column (30 m, 0.25 mm, 0.25 µm), gradient: 50°C, 3 min, 20°C/min, 240°C, 5 min. Retention times: 8.6 min for **S13**, 8.9 min for (+) and 9.0 min for (-).

Reduction product from α-trifluoromethylstyrene (S14):



Enantiomeric excess and conversion were determined by chiral GC analysis: Agilent Cyclosyl-B column (30 m, 0.25 mm, 0.25 µm), gradient: 50°C, 3 min, 6°C/min, 200°C, 2 min. Retention times: 9.1 min for **S14**, 9.75 min for (-) and 9.84 min for (+)

References:

1 J. E. Green, D. M. Bender, S. Jackson, M. J. O'Donnell, J. R. McCarthy, *Org. Lett.* 2009, **11**, 807-810.
2 R. D. Broene, S. L. Buchwald, *J. Am. Chem. Soc.* 1993, **115**, 12569-12570.
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5 (a) J. Blankenstein, A. Pfaltz, *Angew. Chem. Int. Ed.* 2001, **40**, 4445-4447. (b) C. Hedberg, K. Källström, P. Brandt, L. K. Hansen, P. G. Andersson, *J. Am. Chem. Soc.* 2006, **128**, 2995-3001. (c) P. Kaukoranta, M. Engman, C. Hedberg, J. Bergquist, P. G. Andersson, *Adv. Synth. Catal.* 2008, **350**, 1168-1176.
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