Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Efficient synthesis of ferrocifens and other ferrocenyl-substituted ethylenes via a 'sulfur approach'

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Products obtained in the study - supplementation

S-1. Alkyl ferrocenyl ketones

S-1.1. Ethyl ferrocenyl ketone. Orange solid; yield: 213 mg (88%); m.p. 66.5–68.7 °C (ref.[S1] 67–68 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 2.73 (q, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 4.18 (bs, 5H, 5 Fc-CH), 4.48 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.78 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): 8.5 (CH_3), 32.7 (CH_2), 69.2, 72.0 (4 CH-Fc), 69.6 (5 CH-Fc), 78.9 (C-Fc), 204.8 (C=O) ppm.

S-1.2. Ferrocenyl propyl ketone. Red solid; yield: 192 mg (75%); m.p. 36.1–38.3 °C (ref.[S2] 36.0–38.0 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.02 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.72–1.79 (m, 2H, CH_2), 2.69 (t, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 4.20 (bs, 5H, 5 Fc-CH), 4.49 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.79 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 4.10 (CH_3), 18.0 (CH_2), 41.7 (CH_2), 69.3, 72.0 (4 CH-Fc), 69.7 (5 CH-Fc), 79.3 (C-Fc), 204.4 (C=O) ppm.

S-1.3.Ferrocenyl (*sec*-butyl) ketone.Thick orange oil; yield: 221 mg (82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.00 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.20 (d, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 1.42–1.52, 1.77–1.87 (2m, CH_2), 2.88–2.94 (m, 1H, CH), 4.21 (bs, 5H, 5 Fc-CH), 4.50 (bs, 2H, 2 Fc-CH), 4.78 (bs, 1H, Fc-CH), 4.80 (bs, 1H, Fc-CH) ppm. ^{13}C{^{1}H }NMR (150 MHz, $CDCl_3$): δ 12.0, 17.2 (2 CH_3), 26.9 (CH_2), 44.3 (CH), 69.3, 72.0, 72.1 (4 CH-Fc), 69.5 (5 CH-Fc), 78.9 (C-Fc), 208.3 (C=O) ppm. IR (KBr): υ 3098*w*, 2965*m*, 2933*m*, 2873*w*, 1666*vs* (C=O), 1451*m*, 1378*m*, 1268*m*, 1239*m*, 1106*m*, 1062*m*, 1030*m*, 1002*m*, 888*m*, 827*m* cm^{-1}. Anal. calcd. for $C_{15}H_{18}FeO$ (270.15): C 66.69, H 6.73; found: C 66.48, H 6.72.

S-2. Alkyl ferrocenyl thioketones 7b−d

S-2.1. Ethyl ferrocenyl thioketone (7b). Violet solid; yield: 206 mg (80%); m.p. 37.0–39.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.39 (t, 3H, $J_{H,H}$= 6.6 Hz, CH_3), 3.09 (q, 2H, $J_{H,H}$ = 6.6 Hz, CH_2), 4.18 (bs, 5H, 5 Fc-CH), 4.73 (bs, 2H, 2 Fc-CH), 5.05 (bs, 2H, 2 Fc-CH) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 14.6 (CH_3), 42.1 (CH_2), 69.9, 74.0 (4 CH-Fc), 71.2 (5 CH-Fc), 89.0 (C-Fc), 247.9 (C=S) ppm. IR (KBr): υ 3110*w,* 2969*w,* 1440*s,* 1373*m,* 1262*s,* 1223*m,* 1154*m,* 1105*m,* 1043*m,* 967*m,* 836*m,* 819*s,* 776*m,* 513*s,* 480*m* cm^{-1}. Anal. calcd. for $C_{13}H_{14}FeS$ (258.16): C 60.48, H 5.47, S 12.42; found: C 60.58, H 5.50, S 12.49.

S-2.2. Ferrocenyl propyl thioketone (7c). Violet solid; yield: 199 mg (73%); m.p. 30.0–32.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.04 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.84–1.92 (m, 2H, CH_2), 3.03–3.09 (m, 2H, CH_2), 4.19 (bs, 5H, 5 Fc-CH), 4.73 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 5.03 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 13.9 (CH_3), 24.0 (CH_2), 51.5 (CH_2), 70.0, 74.2 (4 CH-Fc), 71.3 (5 CH-Fc), 89.3 (C-Fc), 246.7 (C=S) ppm. IR (KBr): υ 3091*w,* 2960*s,* 2930*m,* 2871*m,* 1669*s,* 1443*vs,* 1380*s,* 1285*m,* 1107*m,* 1052*m,* 1002*m,* *822vs,* 500*m* cm^{-1}. Anal. calcd. for $C_{14}H_{16}FeS$ (272.19): C 61.78, H 5.92, S 11.78; found: C 61.81, H 5.90, S 11.73.

S-2.3. Ferrocenyl (sec-butyl) thioketone (7d). Violet solid; yield: 215 mg (75%); m.p. 35.0–37.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.96 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.34 (d, 3H, $J_{H,H}$ = 6.6 Hz, CH_3), 1.57–1.67, 1.83–1.95 (2m, 2H, CH_2), 3.34–3.45 (m, 1H, CH), 4.19 (bs, 5H, 5 Fc-CH), 4.68–4.78 (m, 2H, 2 Fc-CH), 5.01 (bs, 1H, Fc-CH), 5.08 (bs, 1H, Fc-CH) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 12.2 (CH_3), 22.1 (CH_3), 31.5 (CH_2), 51.6 (CH), 69.7, 70.0, 73.9, 74.2 (4 CH-Fc), 71.0 (5 CH-Fc), 90.0 (C-Fc), 253.7 (C=S) ppm. IR (KBr): υ 3104*m,* 2961*s,* 2923*m,* 1451*m,* 1439*vs,* 1378*m,* 1283*m,* 1252*m,* 1223*m,* 1163*m,* 1036*m,* 827*m,* 685*m,* 511*m* cm^{-1}. Anal. calcd. for $C_{15}H_{18}FeS$ (286.21): C 62.95, H 6.34, S 11.20; found: C 62.89, H 6.34, S 11.19.

S-3. *Ferrocenyl substituted thiiranes 8d,f*

S-3.1. 3-Ferrocenyl-3-methyl-2,2-diphenylthiirane (8d). Yellow solid; yield: 271 mg (66%); m.p. 156.1–158.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.87 (s, CH_3), 3.57 (bs, 1H, Fc-CH), 3.87 (bs, 1H, Fc-CH), 4.14 (bs, 1H, Fc-CH), 4.19 (bs, 5H, 5 Fc-CH), 4.42 (bs, 1H, Fc-CH), 7.02–7.06 (m, 3H, 3 $CH_{arom.}$), 7.13–7.20 (m, 3H, 3 $CH_{arom.}$), 7.24–7.28 (m, 2H, 2 $CH_{arom.}$), 7.48–7.51 (m, 2H, 2 $CH_{arom.}$) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 26.3 (CH_3), 55.0 (C_q), 67.5, 67.9, 70.0 (4 CH-Fc), 69.0 (5 CH-Fc), 70.3 (C_q), 91.1 (C-Fc), 126.3, 126.8, 127.2, 128.0, 128.9, 130.2 (10 $CH_{arom.}$), 142.6, 142.7 (2 $C_{arom.}$) ppm. IR (KBr): υ 3079*w*, 3050*w*, 2923*m*, 2851*w*, 1594*w*, 1486*m*, 1442*m*, 1366*w*, 1103*m*, 1021*m*, 815*m*, 780*s*, 745*m*, 704*vs*, 691*s*, 675*m* cm^{-1}. Anal. calcd. for $C_{25}H_{22}FeS$ (410.35): C 73.17, H 5.40, S 7.81; found: C 73.37, H 5.48, S 7.78

S-3.2. 3'-Ferrocenyl-3'-methyl-10,11-dihydro-5*H*-spiro[dibenzo[a,d][7]annulene-5,2'-thiirane] (8f). Yellow solid; yield: 306 mg (66%); m.p. 154.0–156.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.84 (bs, 3H, CH_3), 2.45–2.55, 2.88–2.98, 3.09–3.19, 3.35–3.43 (4m, 4H, 2 CH_2), 3.60 (bs, 1H, Fc-CH), 3.82 (bs, 1H, Fc-CH), 4.00 (bs, 1H, Fc-CH), 4.19 (bs, 5H, 5 Fc-CH), 4.39 (bs, 1H, Fc-CH), 6.83–6.87 (m, 1H, $CH_{arom.}$), 7.03–7.20 (m, 5H, 5 $CH_{arom.}$), 7.59–7.62 (m, 1H, $CH_{arom.}$), 7.67–7.71 (m, 1H, $CH_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 25.3 (CH_3), 30.9 (CH_2), 32.5 (CH_2), 57.3 (C_q), 67.3, 67.6, 69.2, 69.4 (4 CH-Fc), 69.1 (5 CH-Fc), 71.6 (C_q), 89.9 (C-Fc), 125.6, 125.7, 127.4, 127.5, 127.7, 130.2, 130.3, 130.5 (8 $CH_{arom.}$), 137.4, 138.3, 138.5, 141.0 (6 $C_{arom.}$) ppm. IR (KBr): υ 2958*w*, 2889*w*, 2917*w*, 2857*w*, 2828*w*, 1479*s*, 1454*m*, 1440*m*, 1369*m*, 1271*m*, 1258*m*, 1160*m*, 1107*m*, 1025*m*, 999*m*, 941*m*, 816*vs*, 772*s*, 750*vs*, 737*m*, 713*m*, 682*m*, 648*m*, 513*s*, 492*vs* cm^{-1}. Anal. calcd. for $C_{27}H_{24}FeS$ (436.39): C 74.31, H 5.54, S 7.35; found: C 74.42, H 5.67, S 7.36.

S-4. *Ferrocenyl substituted ethylenes 9d,f−g,j−k,m*

S-4.1. 2-Ferrocenyl-1,1-diphenylprop-1-ene (9d). Orange solid; yield: 367 mg (97%); m.p. 157.5–159.8 °C; desulfurization of thiirane. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.20 (s, CH_3), 3.93 (t, 2H, $J_{H,H}$= 1.8 Hz, 2 Fc-CH), 4.11 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.17 (bs, 5H, 5 Fc-CH), 7.05–7.09 (m, 2H, 2 $CH_{arom.}$), 7.16–7.28 (m, 6H, 6 $CH_{arom.}$), 7.33–7.37 (m, 2H, 2 $CH_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 21.8 (CH_3), 68.0, 69.2 (4 CH-Fc), 69.0 (5 CH-Fc), 87.4 (C-Fc), 126.1, 126.2, 127.9, 128.0, 129.8, 130.3 (10 $CH_{arom.}$), 130.9, 138.2, 144.3, 144.4 (C=C, 2 $C_{arom.}$) ppm. IR KBr): υ 3072w, 3012*w*, 2917*m*, 2857*w*, 1609*m*, 1594*m*, 1489*m*, 1435*m*, 1271*m*, 1103*m*, 1002*m*, 913*m*, 812*m*, 764*m*, 694*vs*, 656*m*, 514*m* cm^{-1}. Anal. calcd. for $C_{25}H_{22}Fe$ (378.29): C 79.38, H 5.86; found: C 79.34, H 5.97.

S-4.2. 2-Ferrocenyl-1,1-diphenylpent-1-ene (9f). Orange solid; yield: 312 mg (77%); m.p. 137.0–139.7 °C; spontaneous desulfurization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.83 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.46–1.56 (m, 2H, CH_2), 2.55–2.59 (m, 2H, CH_2), 3.89 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.08 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.13 (bs, 5H, 5 Fc-CH), 7.07–7.11 (m, 2H, 2 $CH_{arom.}$), 7.15–7.19 (m, 1H, $CH_{arom.}$), 7.21–7.24 (m, 5H, 5 $CH_{arom.}$), 7.31–7.35 (m, 2H, 2 $CH_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 14.4 (CH_3), 24.0 (CH_2), 37.0 (CH_2), 68.1, 69.4 (4 CH-Fc), 69.2 (5 CH-Fc), 87.0 (C-Fc), 126.1, 126.2, 128.1, 128.2, 129.4, 129.9 (10 $CH_{arom.}$), 135.9, 138.5, 144.7, 144.8 (C=C, 2 $C_{arom.}$) ppm. IR (KBr): υ 3091*m*, 3015*w*, 2952*s*, 2876*m*, 2866*m*, 1609*m*, 1591*m*, 1489*m*, 1464*m*, 1435*m*, 1454*m*, 1103*m*, 1052*m*, 1040*m*, 1002*m*, 1017*m*, 919*m*, 812*m*, 755*m*, 704*vs*, 694*s,* 520*m*, 495*m* cm^{-1}. Anal. calcd. for $C_{27}H_{26}Fe$ (406.34): C 79.81, H 6.45; found: C 79.82, H 6.51.

S-4.3. 2-Ferrocenyl-3-methyl-1,1-diphenylpent-1-ene (9g). Orange solid; yield: 302 mg (72%); m.p. 102.9–105.8 °C; spontaneous desulfurization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.90 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.33 (d, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 1.40–1.47, 1.72–1.79 (2m, 2H, CH_2), 2.77–2.84 (m, 1H, CH), 3.79 (bs, 1H, Fc-CH), 3.91 (bs, 1H, Fc-CH), 4.06 (bs, 2H, 2 Fc-CH), 4.12 (bs, 5H, 5 Fc-CH), 7.04–7.07 (m, 2H, 2 $CH_{arom.}$), 7.10–7.15 (m, 1H, $CH_{arom.}$), 7.17–7.22 (m, 5H, 5 $CH_{arom.}$), 7.28–7.31 (m, 2H, 2 $CH_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 13.2 (CH_3), 21.2 (CH_3), 29.6 (CH_2), 41.7 (CH), 67.5, 67.6, 70.0, 70.1 (4 CH-Fc), 69.1 (5 CH-Fc), 86.6 (C-Fc), 125.9, 126.1, 127.9, 128.0, 129.2, 129.5 (10 $CH_{arom.}$), 139.5, 140.1, 145.0, 145.5 (C=C, 2 $C_{arom.}$) ppm. Anal. calcd. for $C_{28}H_{28}Fe$ (420.37): C 80.0, H 6.71; found: C 80.04, H 6.67.

S-4.4. 9-(1-Ferrocenylbutylidene)-9*H*-fluorene (9j). Orange solid; yield: 384 mg (95%); m.p. >207 ºC (decomposition); spontaneous desulfurization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.16 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.83–1.92 (m, 2H, CH_2), 3.33–3.40 (m, 2H, CH_2), 4.24 (bs, 5H, 5 Fc-CH), 4.45 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.51 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 6.94–7.00 (m, 1H, $CH_{arom.}$), 7.17–7.21 (m, 2H, 2 $CH_{arom.}$), 7.34–7.38 (m, 2H, 2 $CH_{arom.}$), 7.66–7.71 (m, 1H, $CH_{arom.}$), 7.77–7.80 (m, 1H, $CH_{arom.}$), 7.84–7.88 (m, 1H, $CH_{arom.}$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 14.7 (CH_3), 23.8 (CH_2), 41.3 (CH_2), 68.7, 71.0 (4 CH-Fc), 69.5 (5 CH-Fc), 91.8 (C-Fc), 118.8, 119.4, 124.6, 125.5, 125.7, 126.3, 126.6, 126.8 (8 $CH_{arom.}$), 134.0, 138.8, 139.0, 139.4, 139.9, 146.0 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 3104*w*, 3050*w*, 2949*m*, 2923*m*, 2863*m*, 1609*m*, 1591*m*, 1461*m*, 1445*s*, 1429*m*, 1106*m*, 1021*m*, 995*m*, 815*m*, 786*m*, 729*vs*, 476*s* cm^{-1}. Anal. calcd. for $C_{27}H_{24}Fe$ (404.32): C 80.21, H 5.98; found: C 80.34, H 6.03.

S-4.5. 9-(1-Ferrocenyl-2-methylbutylidene)-9*H*-fluorene (9k).Orange solid; yield: 343 mg (82%); m.p. 177.0–179.0 ºC; spontaneous desulfurization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.10 (t, 3H, $J_{H,H}$= 7.2 Hz, CH_3), 1.75 (d, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 2.12–2.22, 2.40–2.49 (2m, 2H, CH_2), 3.82–3.91 (m, 1H, CH), 4.18 (bs, 1H, Fc-CH), 4.24 (bs, 1H, Fc-CH), 4.29 (bs, 5H, 5 Fc-CH), 4.51 (bs, 1H, Fc-CH), 4.55 (bs, 1H, Fc-CH), 5.86–5.93 (m, 1H, $CH_{arom.}$), 6.85–6.90 (m, 1H, $CH_{arom.}$), 7.12–7.16 (m, 1H, $CH_{arom.}$), 7.31–7.37 (m, 2H, 2 $CH_{arom.}$), 7.61–7.65 (m, 1H, $CH_{arom.}$), 7.71–7.75 (m, 1H, $CH_{arom.}$), 7.92–7.98 (m, 1H, $CH_{arom.}$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 13.1 (CH_3), 17.2 (CH_3), 26.0 (CH_2), 40.9 (CH), 68.1, 68.2, 72.1, 72.8 (4 CH-Fc), 69.7 (5 CH-Fc), 89.5 (C-Fc), 118.5, 119.3, 125.6, 126.0, 126.3, 126.5, 126.7, 126.8 (8 $CH_{arom.}$), 137.8, 138.1, 139.0, 139.4, 140.4, 148.6 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 3104*w*, 3085*w*, 2955*m*, 1572*m*, 1442*s*, 1105*m*, 1021*m*, 995*m*, 834*s*, 780*m*, 729*vs*, 489*m* cm^{-1}. Anal. calcd. for $C_{28}H_{26}Fe$ (418.35): C 80.39, H 6.26; found: C 80.36, H 6.33.

S-4.6. 5-(1-Ferrocenylpropylidene)-10,11-dihydro-5*H*-dibenzo[a,d][7]annulene (9m). Orange solid; yield: 410 mg (98%); m.p. 190.5–193.0 ºC; desulfurization of thiirane. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.33 (bs, 3H, CH_3), 1.45–1.52, 2.28–2.36 (2m, 2H, CH_2), 2.38–2.48, 2.82–2.93, 2.97–3.09, 3.27–3.36 (4m, 4H, 2 CH_2), 3.45 (bs, 1H, Fc-CH), 3.79 (bs, 1H, Fc-CH), 4.07 (bs, 1H, Fc-CH), 4.18 (bs, 5H, 5 Fc-CH), 4.46 (bs, 1H, Fc-CH), 6.83–6.90 (m, 1H, $CH_{arom.}$), 6.95–7.00 (m, 1H, $CH_{arom.}$), 7.04–7.15 (m, 4H, 4 $CH_{arom.}$), 7.54–7.65 (m, 2H, 2 $CH_{arom.}$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 16.6 (CH_3), 27.1 (CH_2), 31.8, 32.7 (2 CH_2), 68.0, 68.1, 69.1, 69.5 (4 CH-Fc), 69.0 (5 CH-Fc), 85.8 (C-Fc), 126.7, 126.8, 128.7, 129.4, 129.9 (8 $CH_{arom.}$), 135.7, 136.5, 136.6, 137.4, 142.4, 143.8 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 2990*w*, 2961*w*, 2936*w*, 2895*w*, 1480*m*, 1458*m*, 1293*m*, 1287*m*, 1201*w*, 1103*m*, 1030*m*, 986*m*, 935*m*, 817*s*, 772*s*, 749*vs*, 647*m*, 512*m*, 493*s*, 481*s*, cm^{-1}. Anal. calcd. for $C_{28}H_{26}Fe$ (418.35): C 80.39, H 6.26; found: C 80.27, H 6.40.

References

S1 X. Sun, J. Zhang and L. Jin, *Asian J. Chem*., 2013, **25**, 170.

S2 J. B. Heilmann, E. A. Hillard, M.-A. Plamont, P. Pigeon, M. Bolte, G. Jaouen and A. Vessières, *J. Organometal. Chem.* 2008, **693**, 1716.

Collection of the ^{1}H and ^{13}C NMR spectra

1. The ^{1}H- and ^{13}C-NMR for ferrocifens 1a−c.

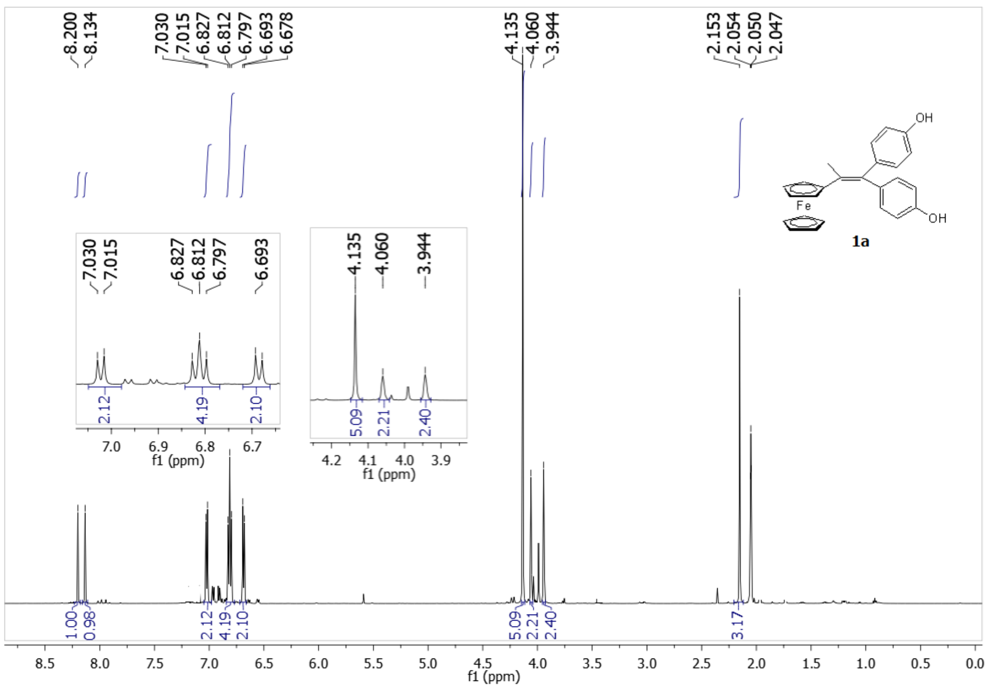


Figure S1. The ^{1}H NMR spectrum of**1a**.

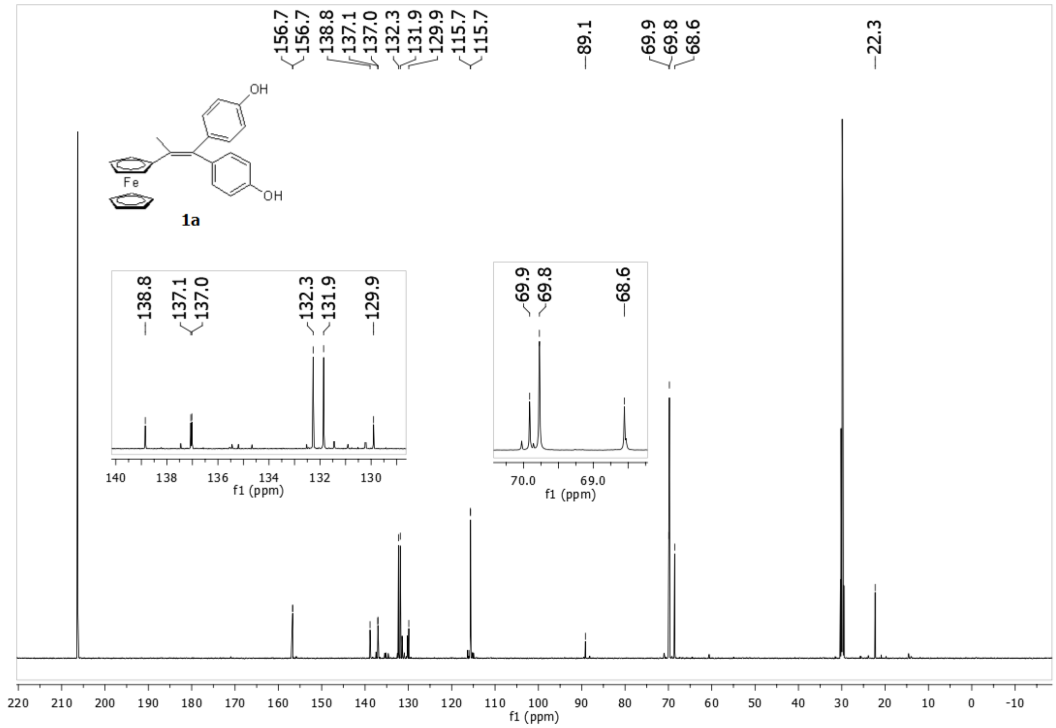


Figure S2. The ^{13}C NMR spectrum of **1a**.

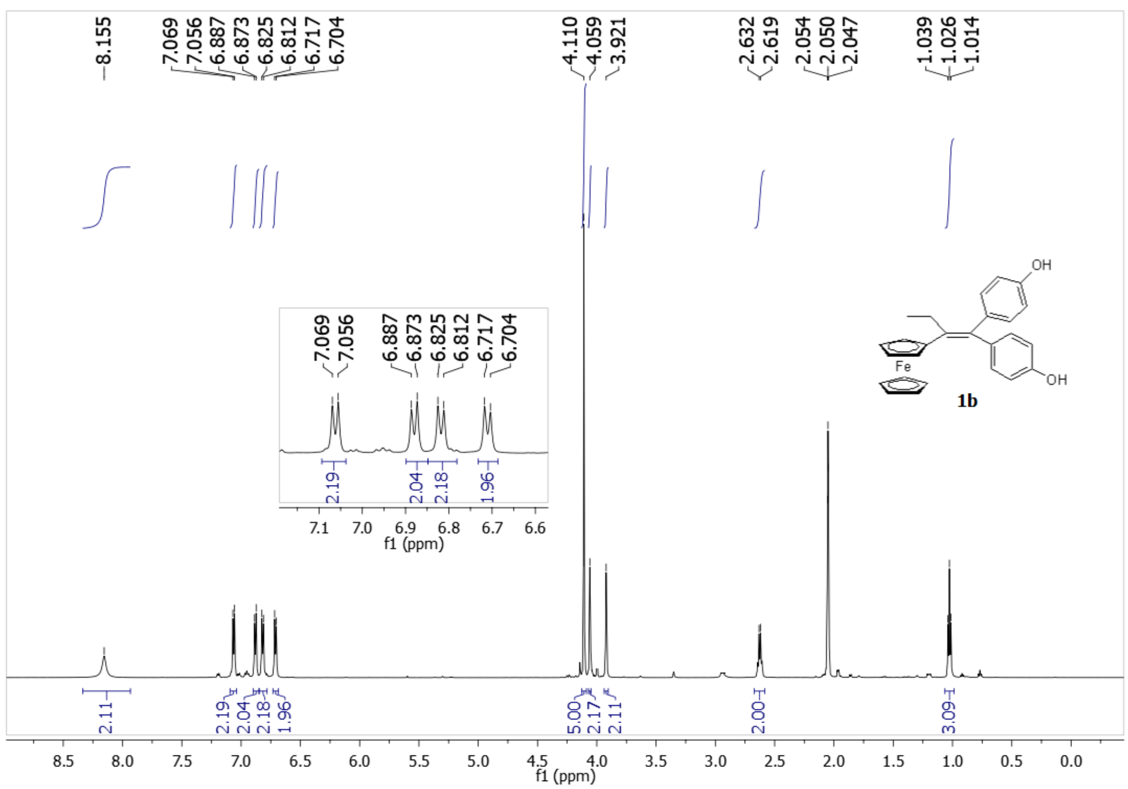


Figure S3. The ^{1}H NMR spectrum of **1b**.

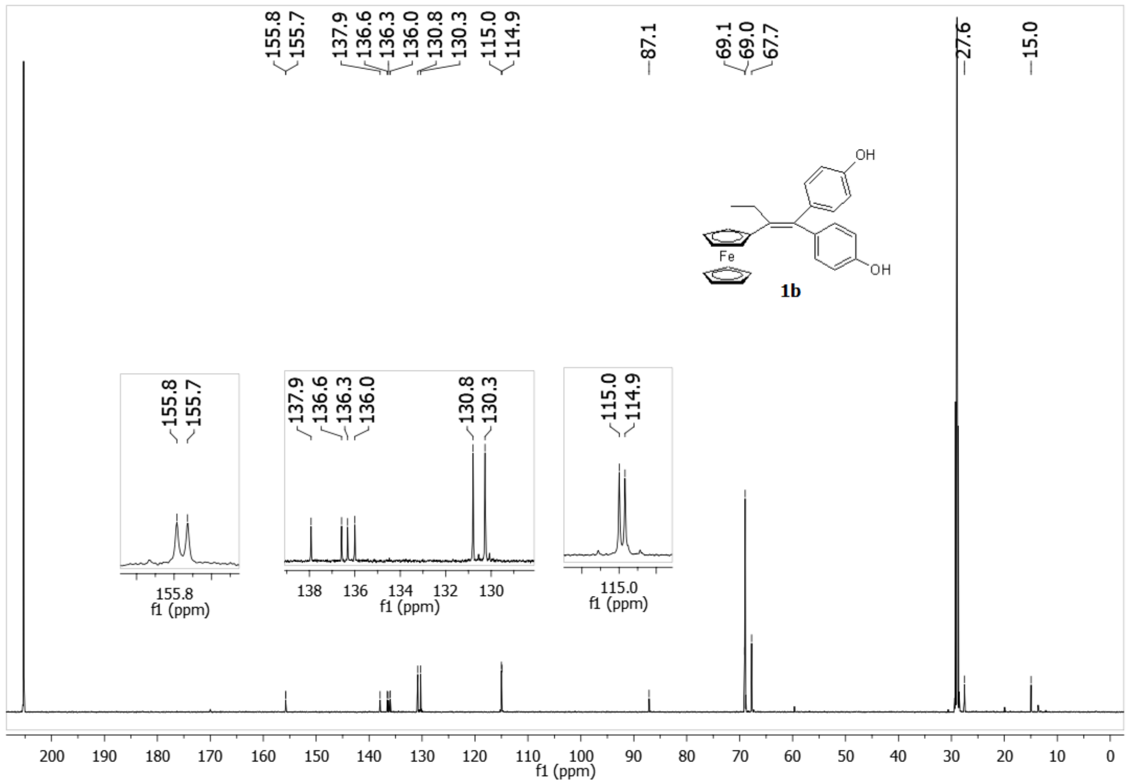


Figure S4. The ^{13}C NMR spectrum of **1b**.

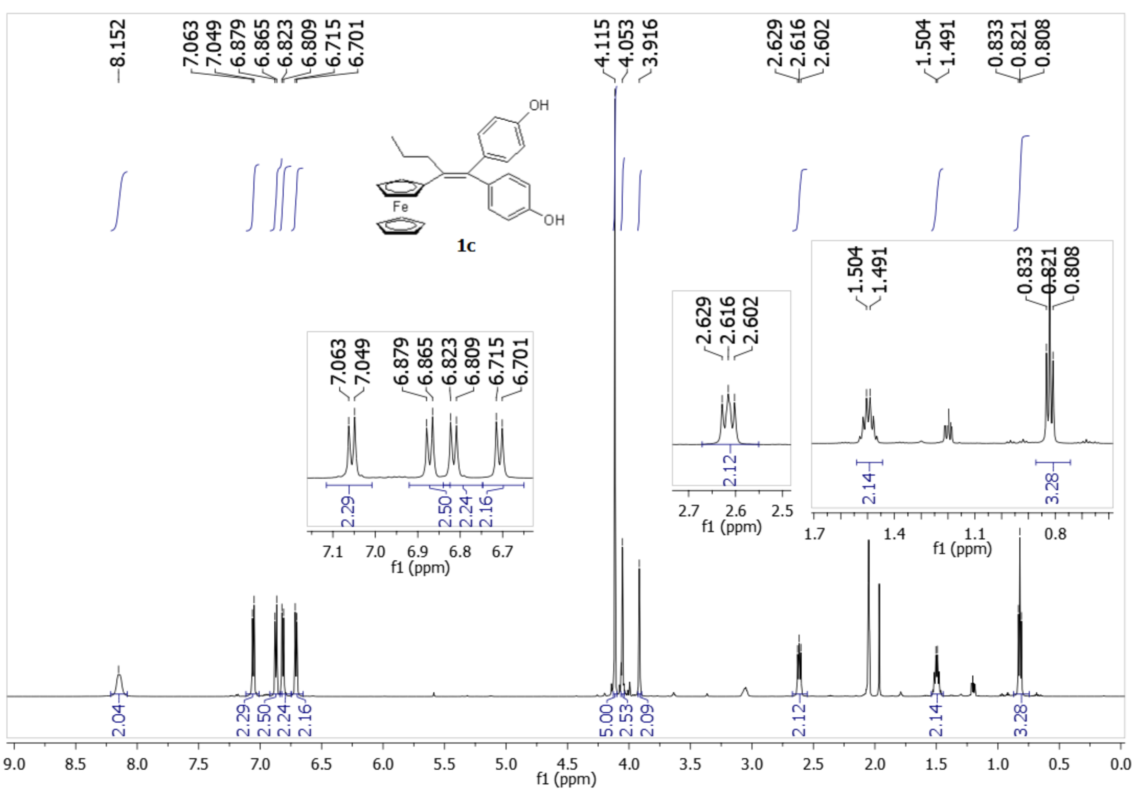


Figure S5. The ^{1}H NMR spectrum of **1c**.

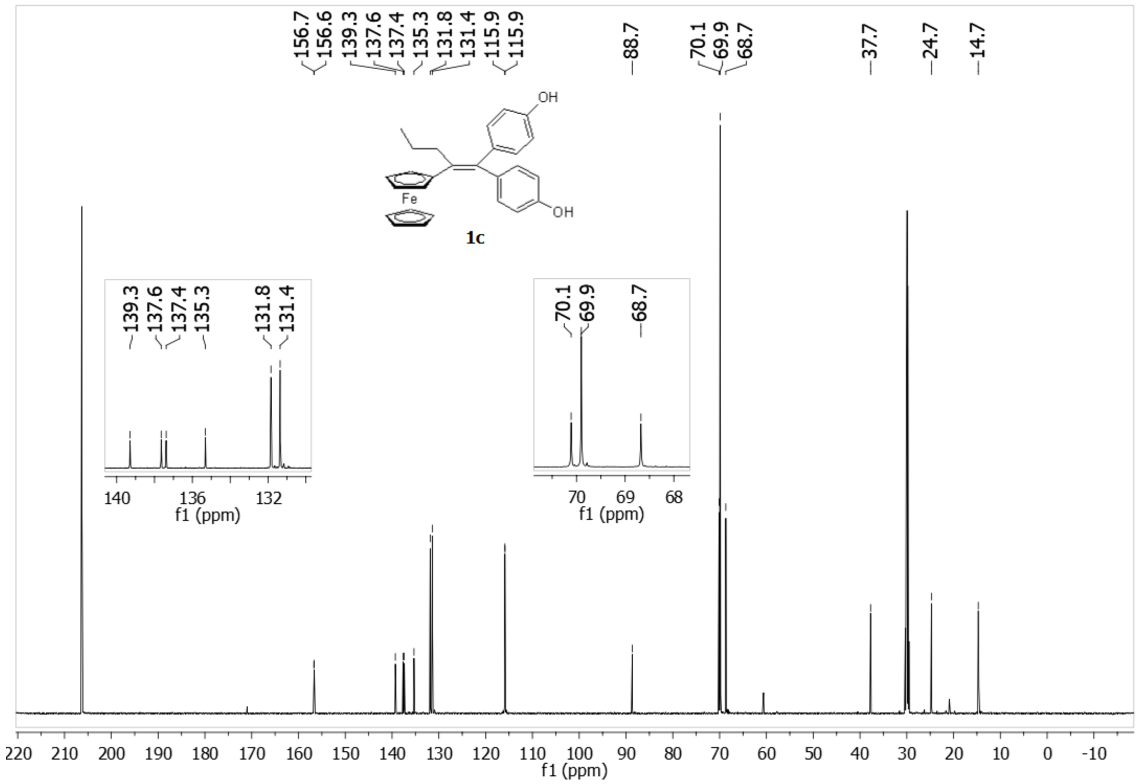


Figure S6. The ^{13}C NMR spectrum of **1c**

2. The ^{1}H- and ^{13}C-NMR for the ferrocenyl ketones (not numbered in the manuscript).

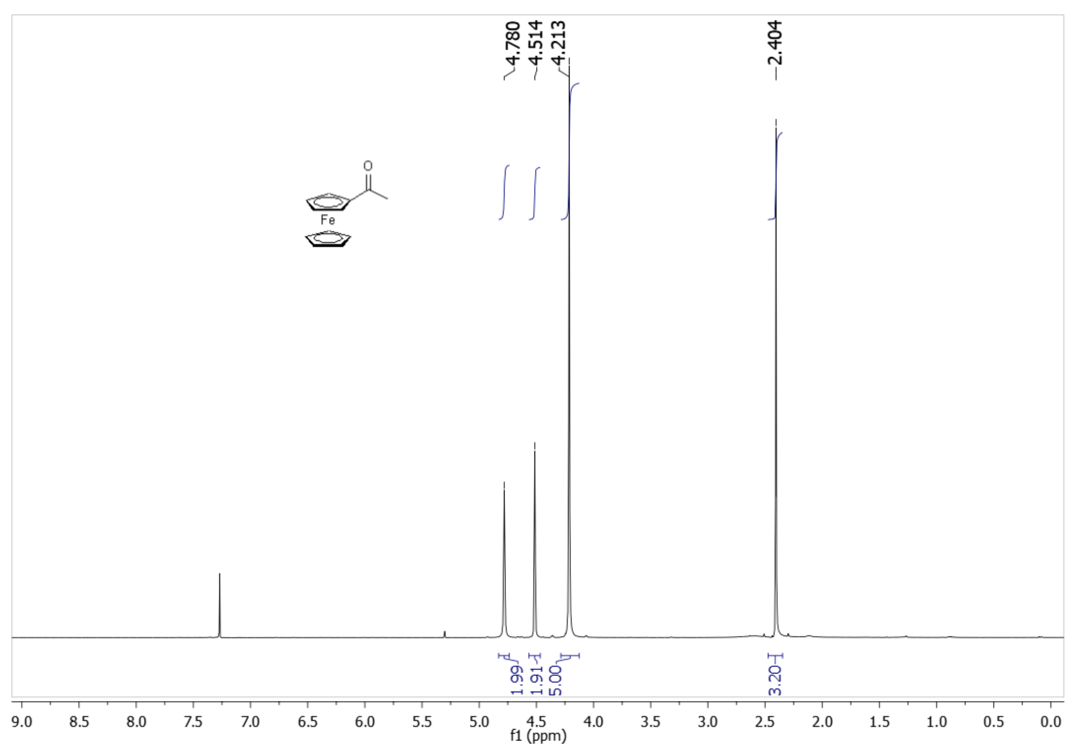


Figure S9. The ^{1}H NMR spectrum of ferrocenyl methyl ketone.

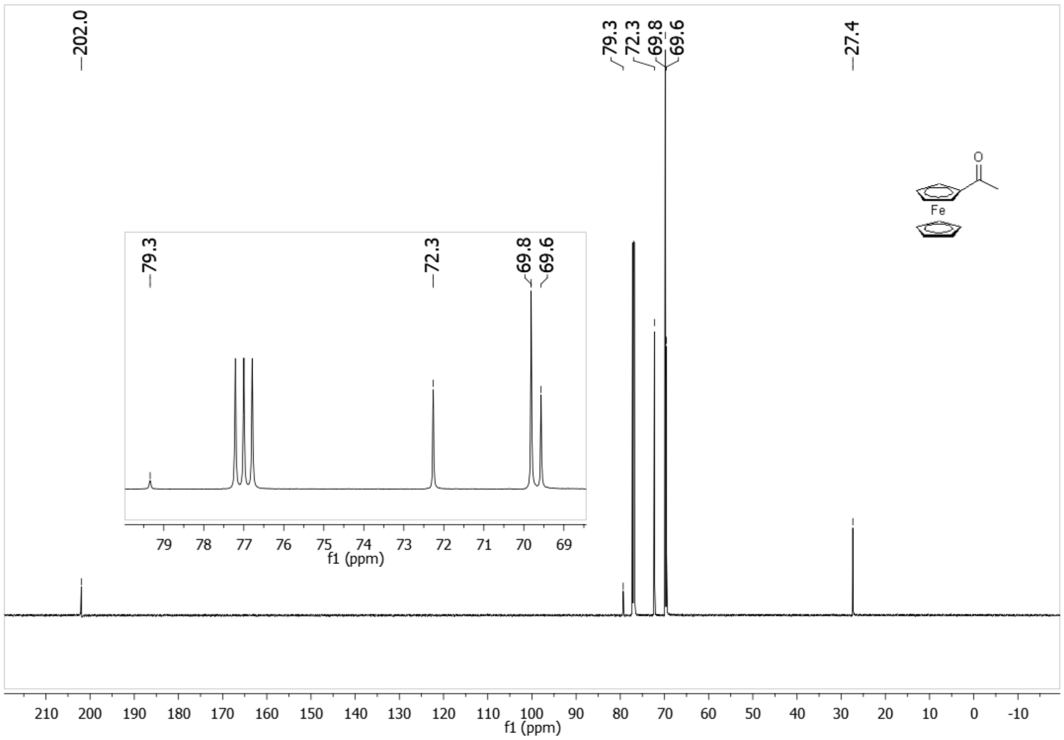


Figure S10. The ^{13}C NMR spectrum of ferrocenyl methyl ketone.

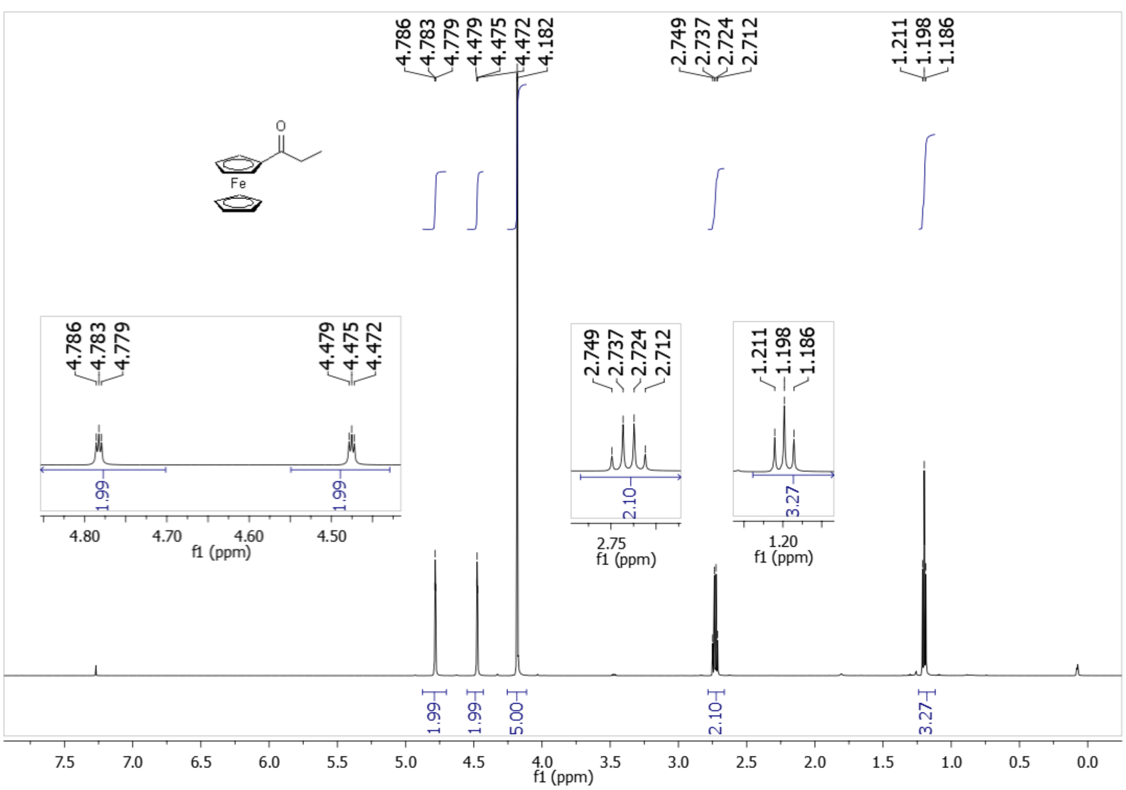


Figure S11. The ^1H NMR spectrum of ferrocenyl ethyl ketone.

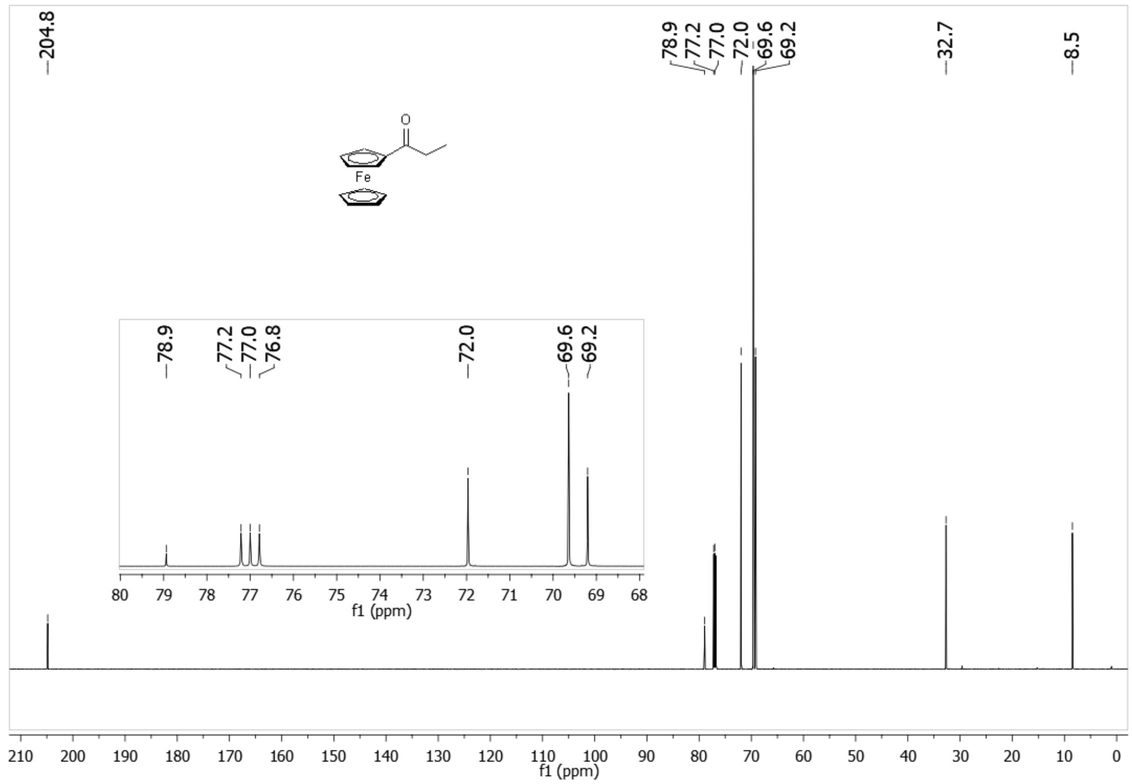


Figure S12. The ^{13}C NMR spectrum of ferrocenyl ethyl ketone.

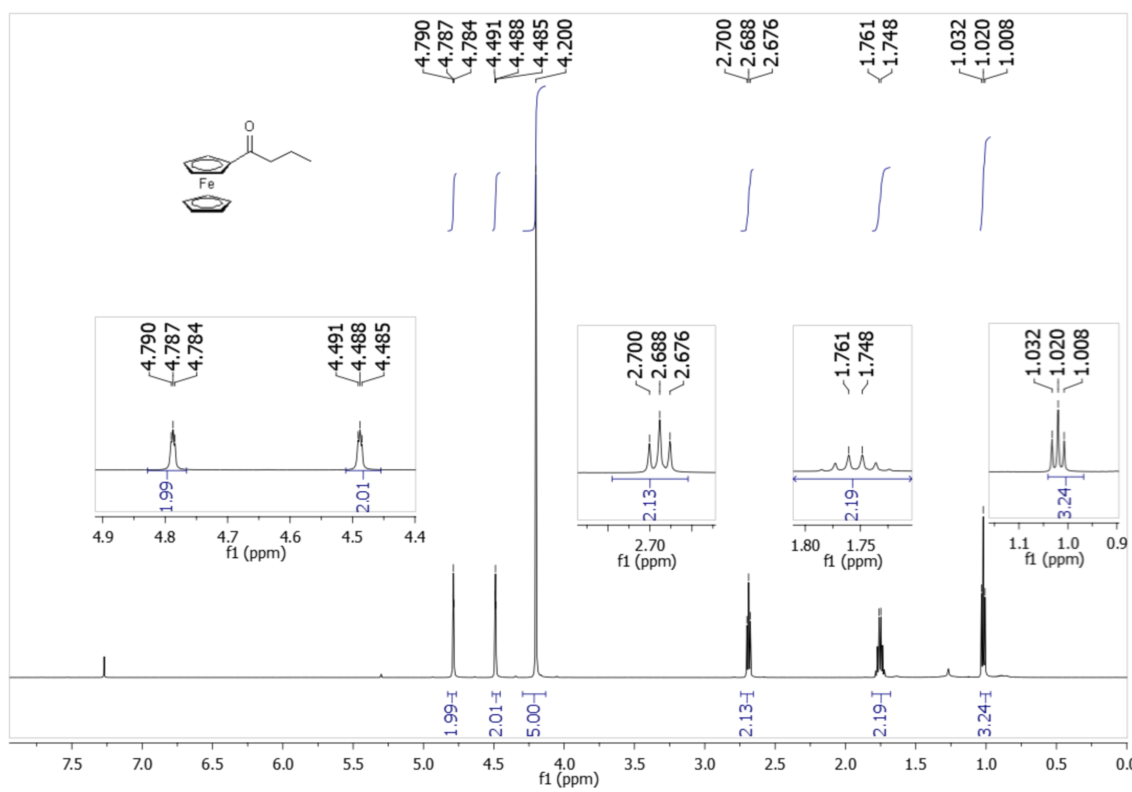


Figure S13. The ^{1}H NMR spectrum of ferrocenyl *n*-propyl ketone.

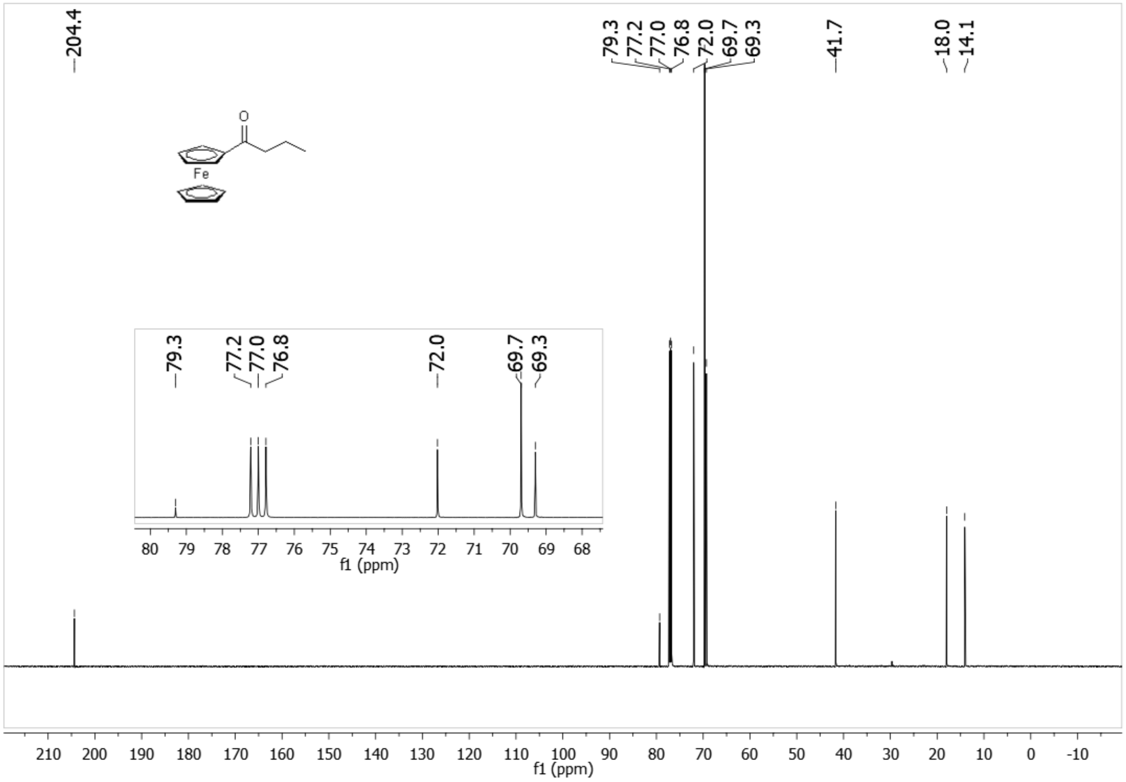
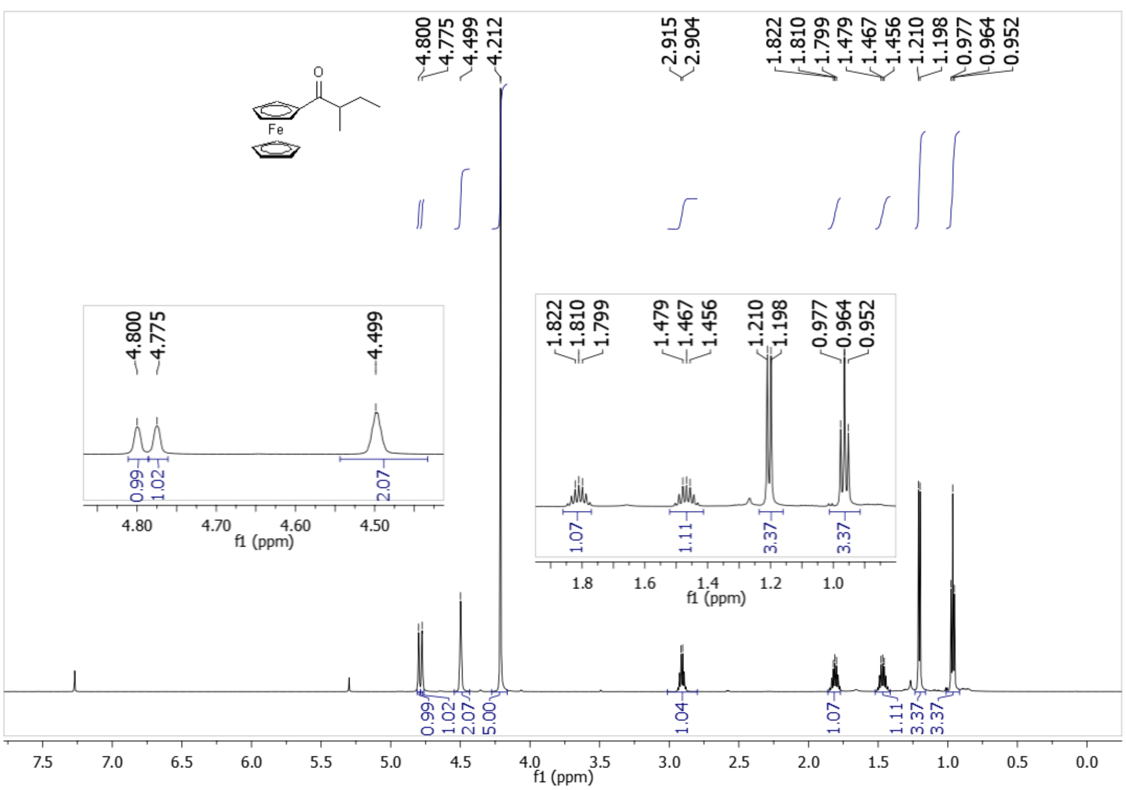


Figure S14. The ^{13}C NMR spectrum of ferrocenyl *n*-propyl ketone.



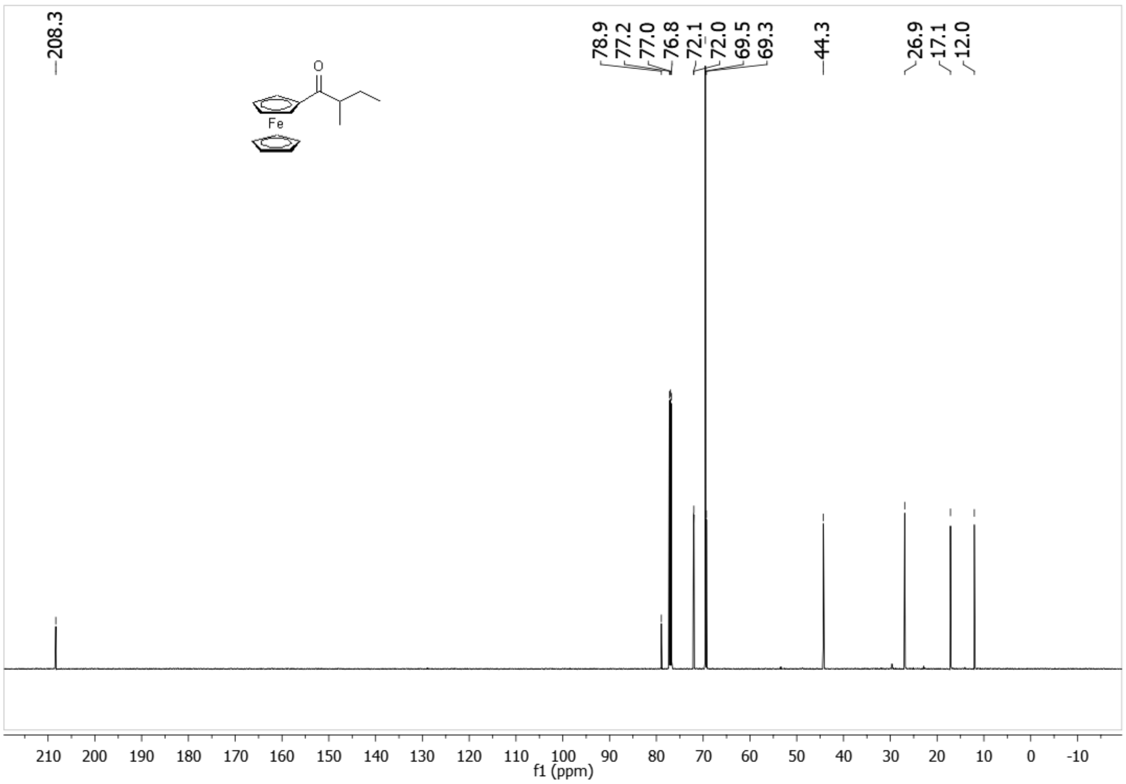


Figure S16. The ^{13}C NMR spectrum of ferrocenyl *sec*-butyl ketone.

3. **The ^{1}H- and ^{13}C-NMR for the described ferrocenyl thioketones 7a–d.**

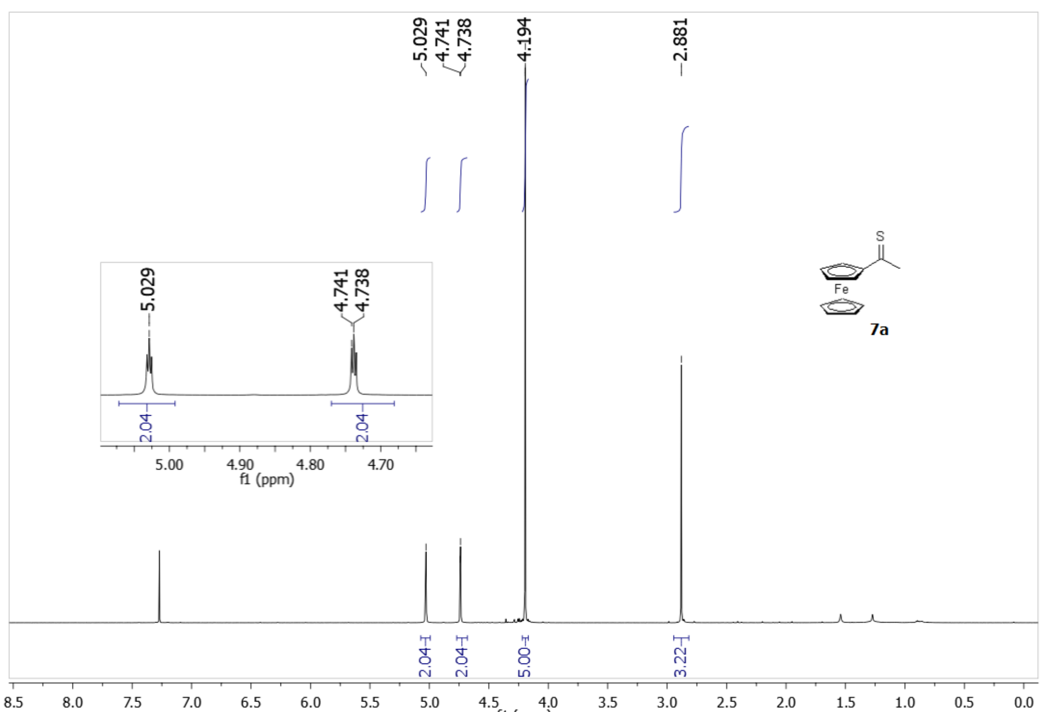


Figure S17. The ^{1}H NMR spectrum of ferrocenyl methyl thioketone (**7a**).

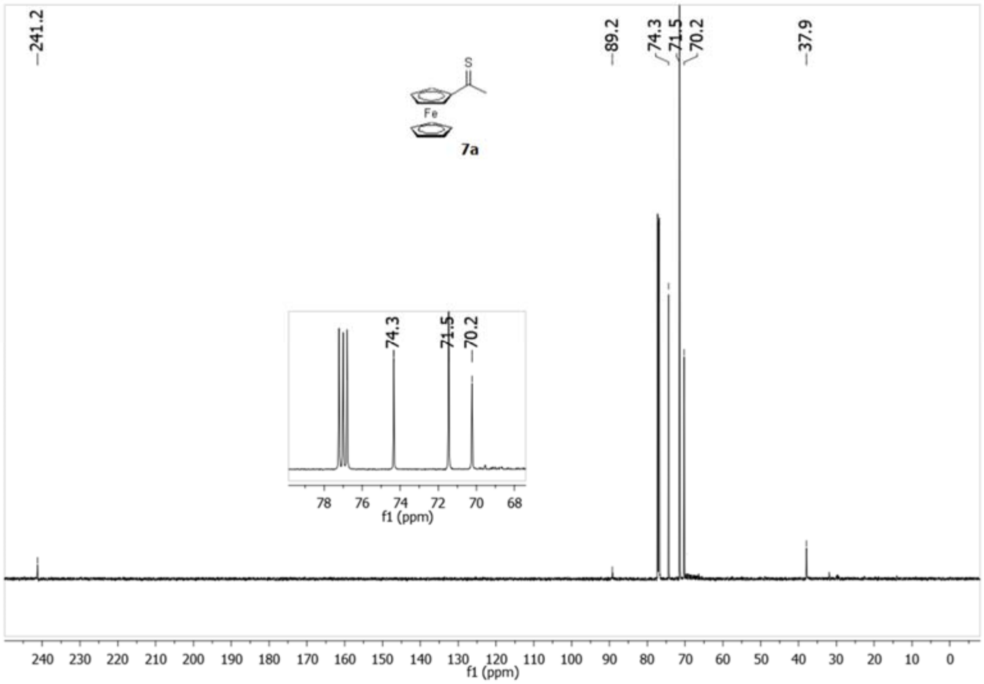


Figure S18. The ^{13}C NMR spectrum of ferrocenyl methyl thioketone (**7a**).

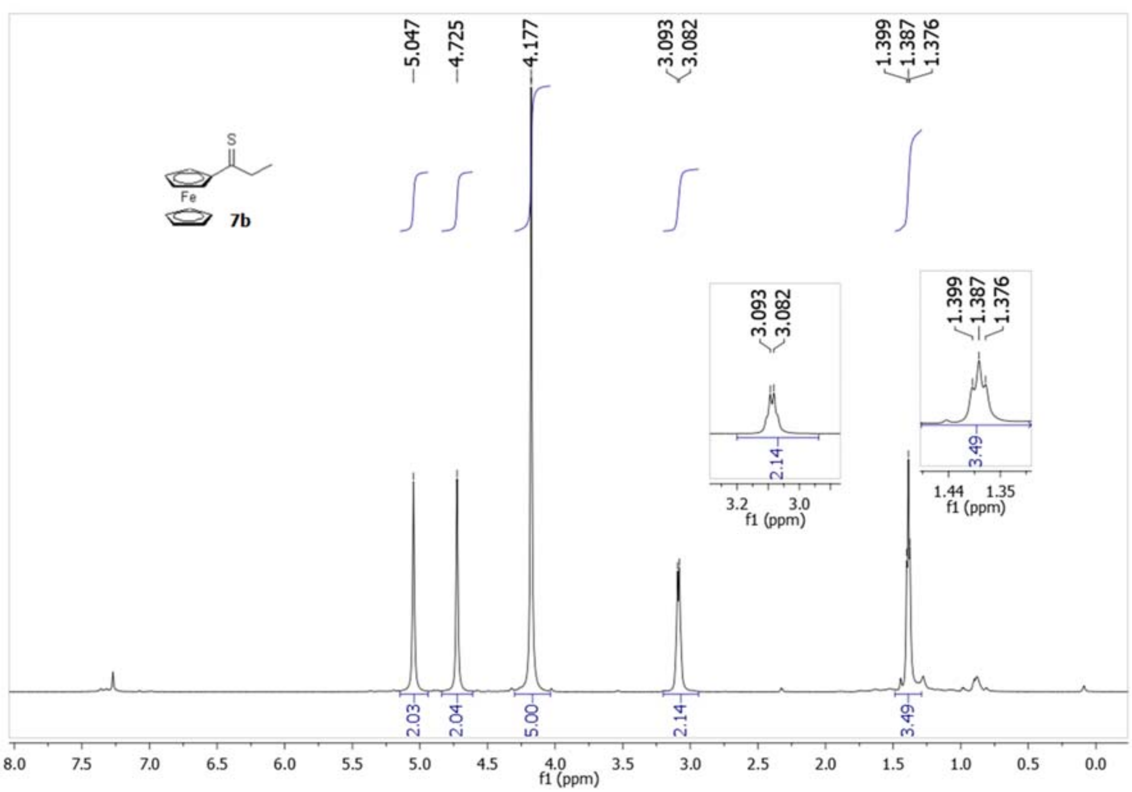


Figure S19. The ^{1}H NMR spectrum of ferrocenyl ethyl thioketone (**7b**).

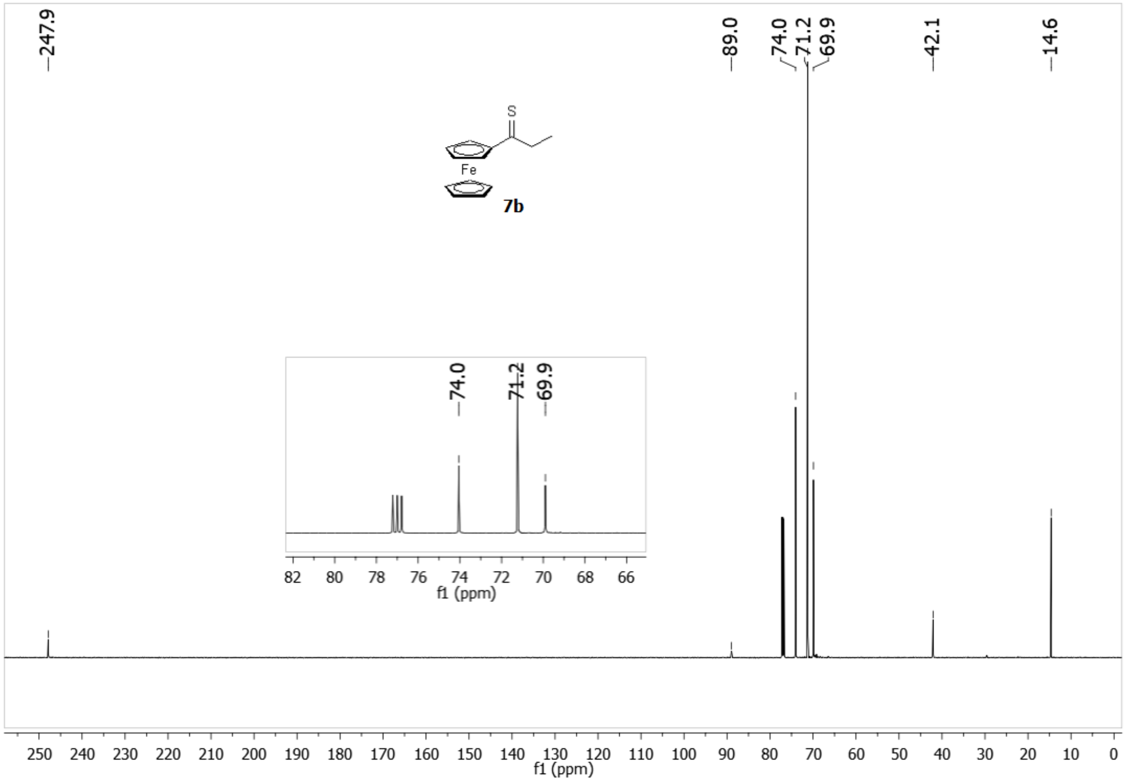


Figure S20. The ^{13}C NMR spectrum of ferrocenyl ethyl thioketone (**7b**).

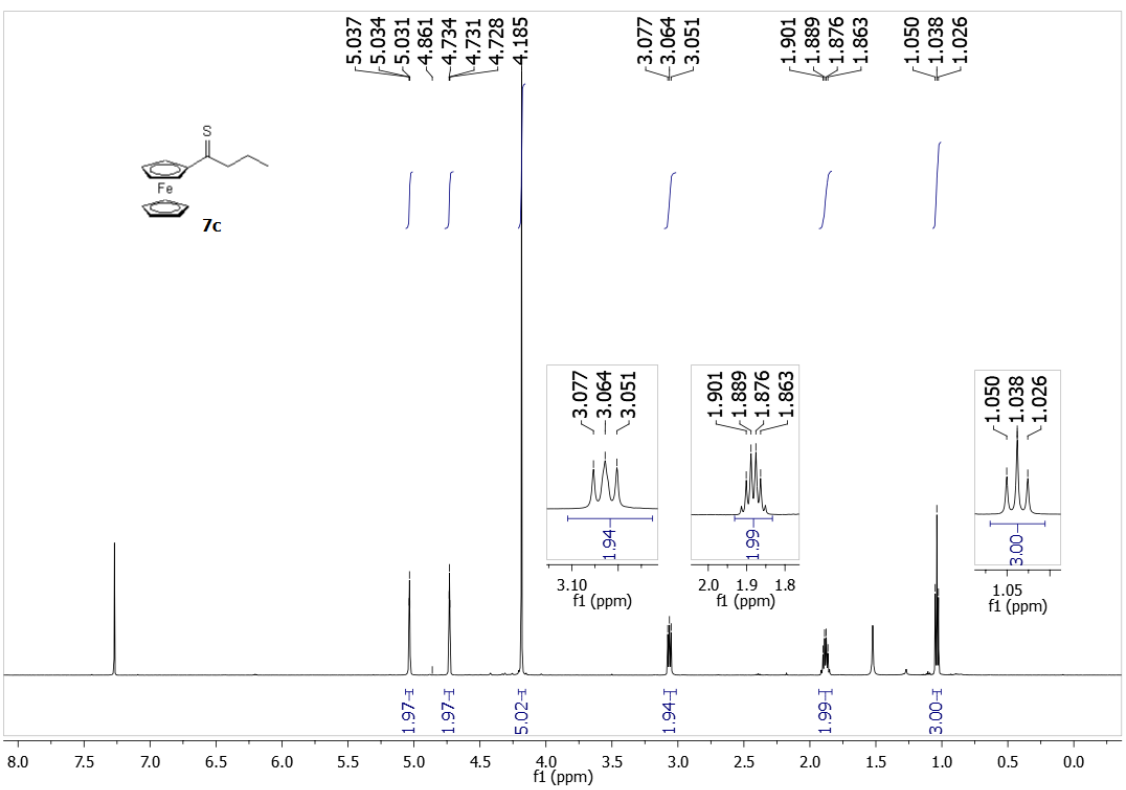


Figure S21. The [1]H NMR spectrum of ferrocenyl *n*-propyl thioketone (**7c**).

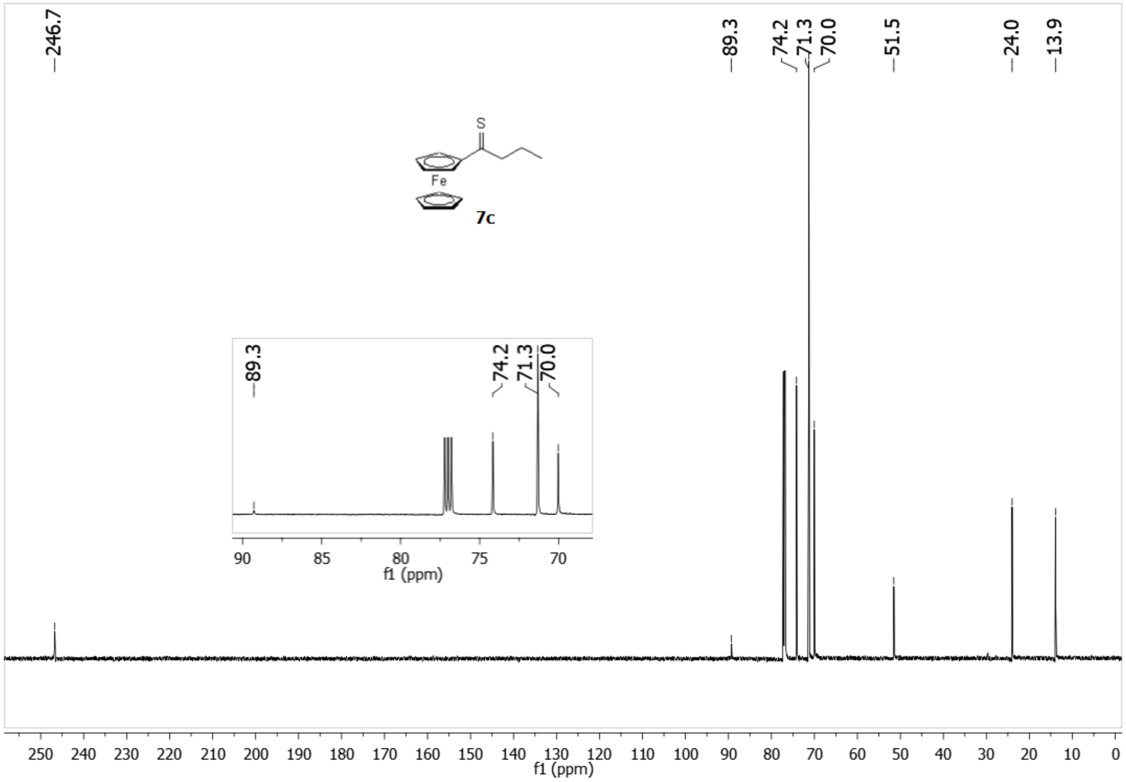


Figure S22. The [13]C NMR spectrum of ferrocenyl *n*-propyl thioketone (**7c**).

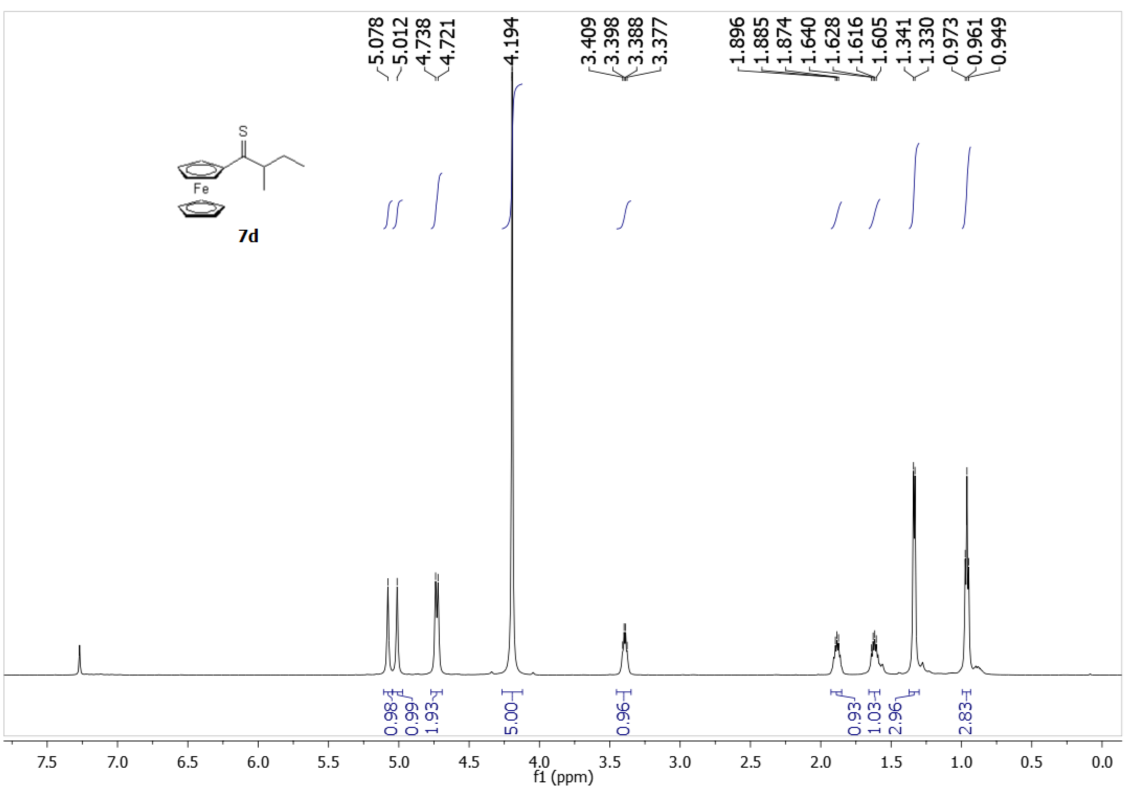


Figure S23. The ^1H NMR spectrum of ferrocenyl *sec*-butyl thioketone (**7d**).

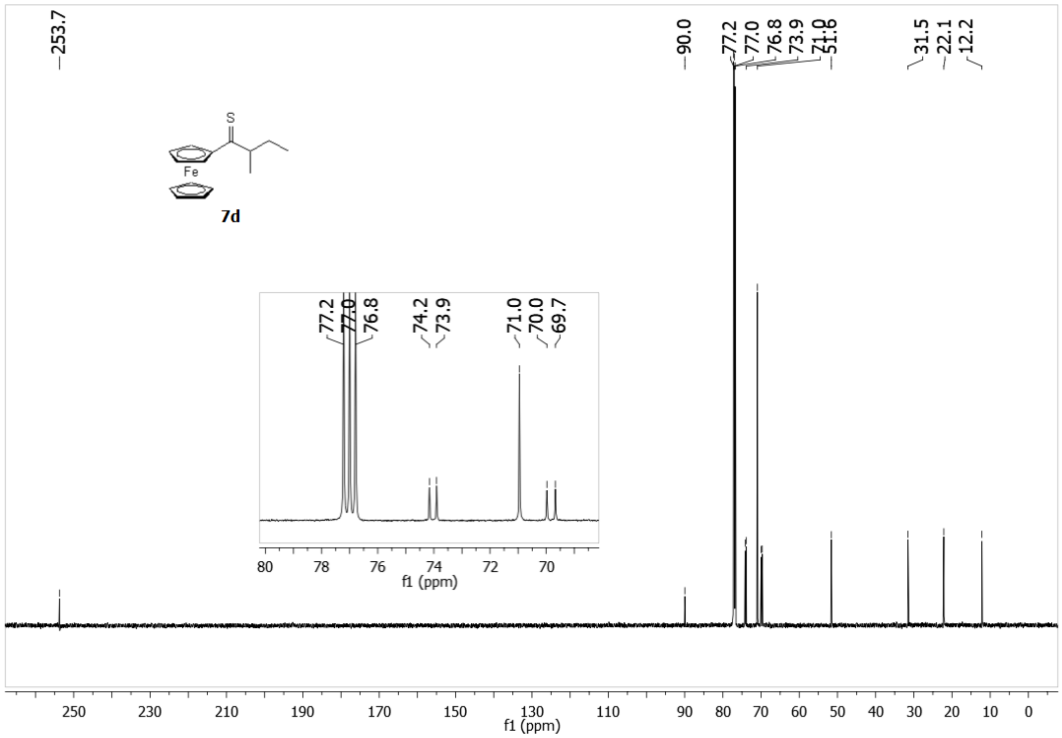


Figure S24. The ^{13}C NMR spectrum of ferrocenyl *sec*-butyl thioketone (**7d**)

4. The ^1H- and ^{13}C-NMR spectra for thiirane derivatives8a−g.

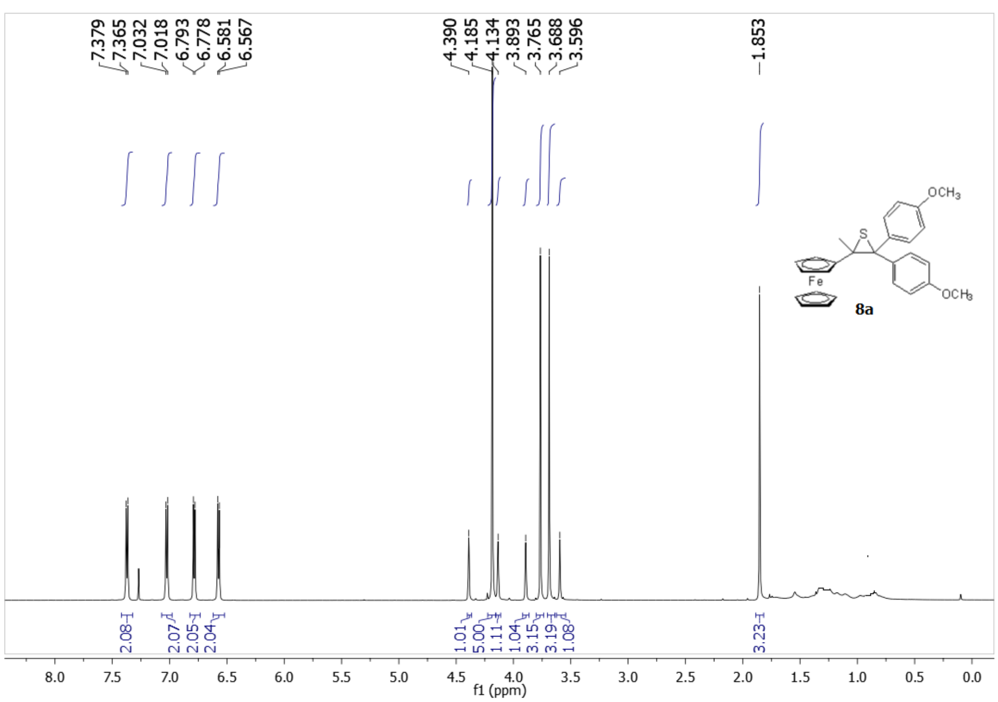


Figure S25. The ^{1}H NMR spectrum of **8a**.

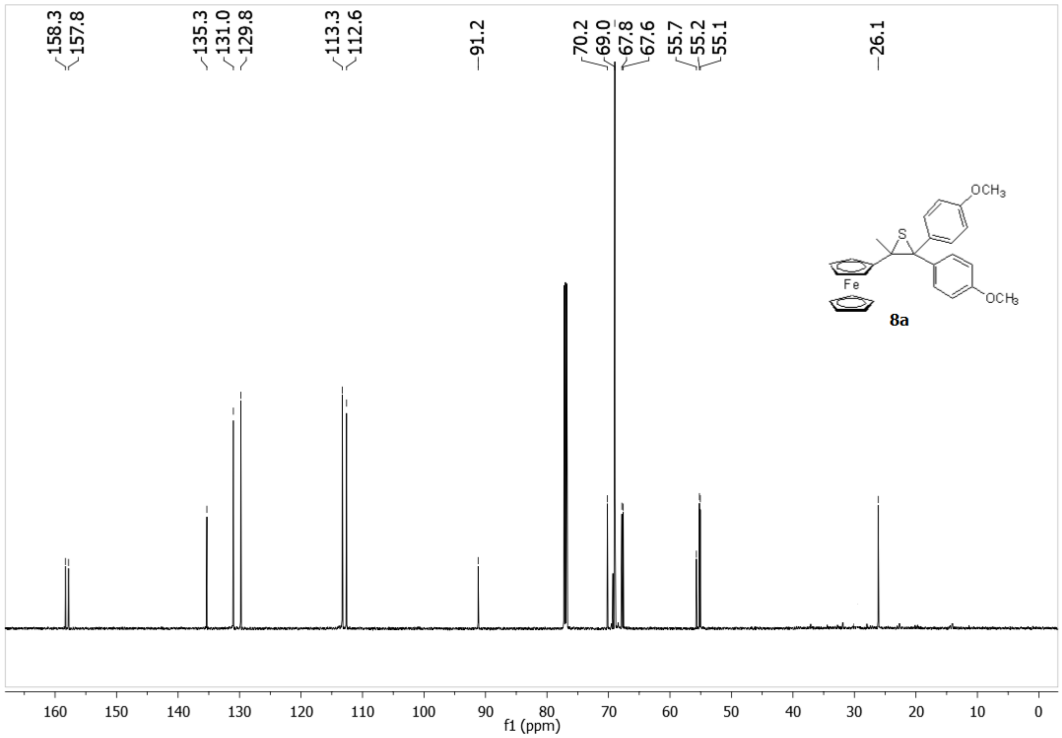


Figure S26. The ^{13}C NMR spectrum of **8a**.

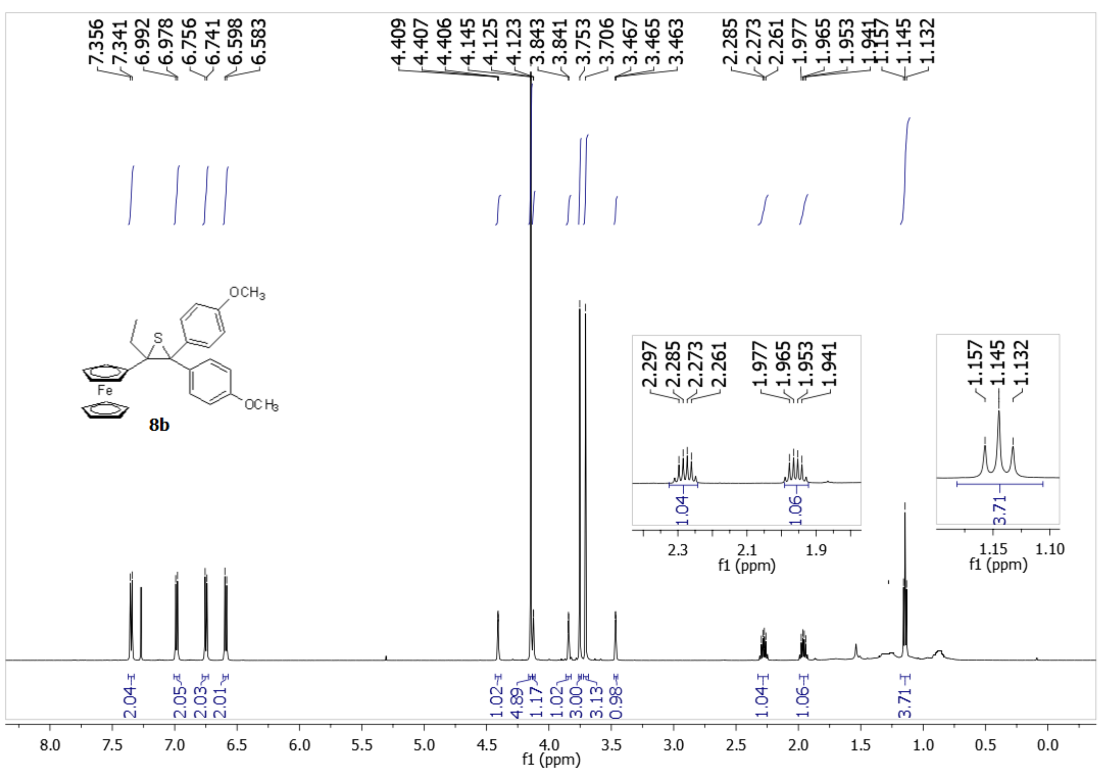


Figure S27. The ^{1}H NMR spectrum of **8b**.

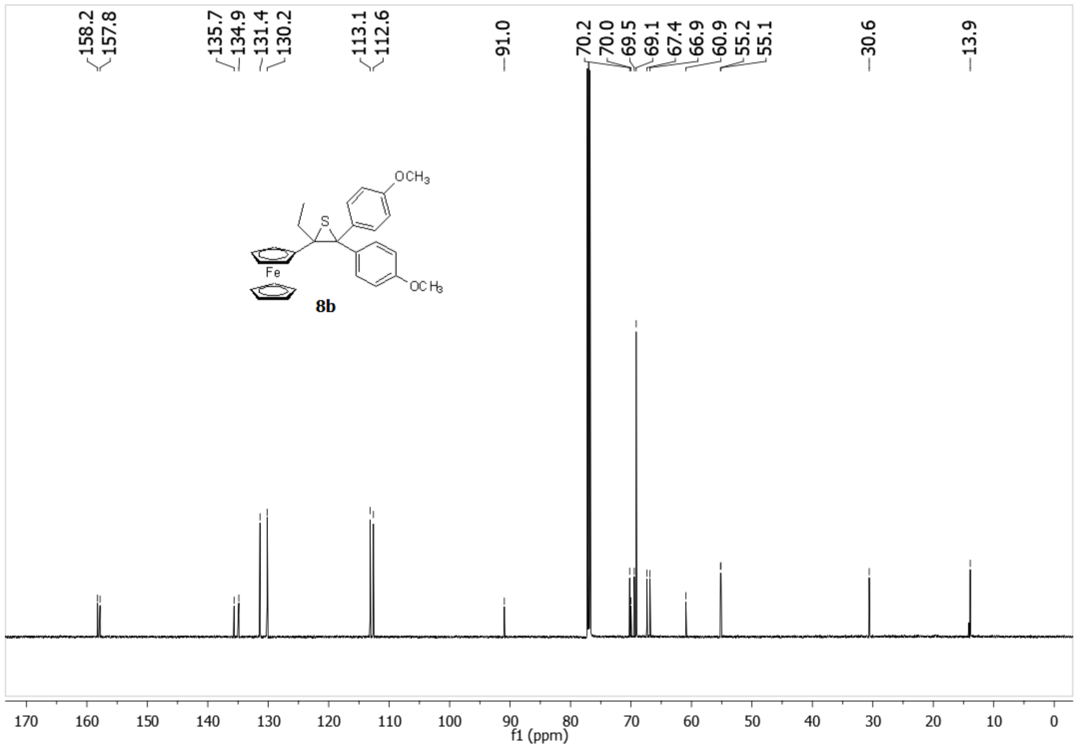


Figure S28. The ^{13}C NMR spectrum of **8b.**

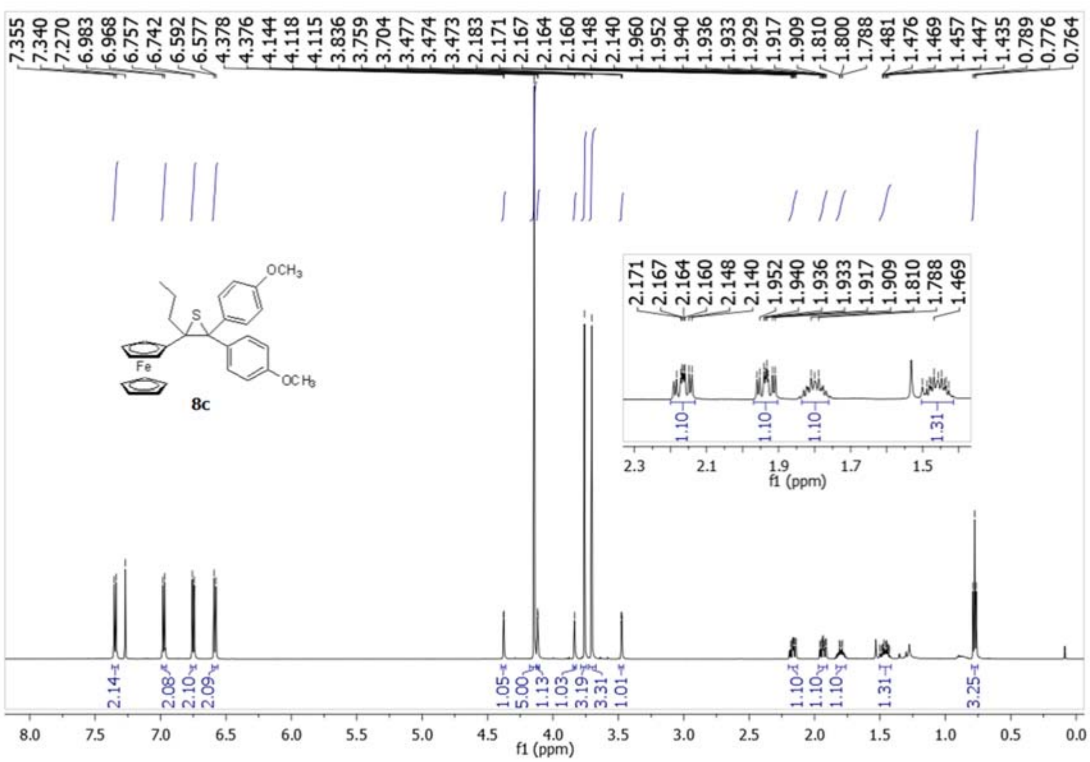


Figure S29. The ^{1}H NMR spectrum of **8c**.

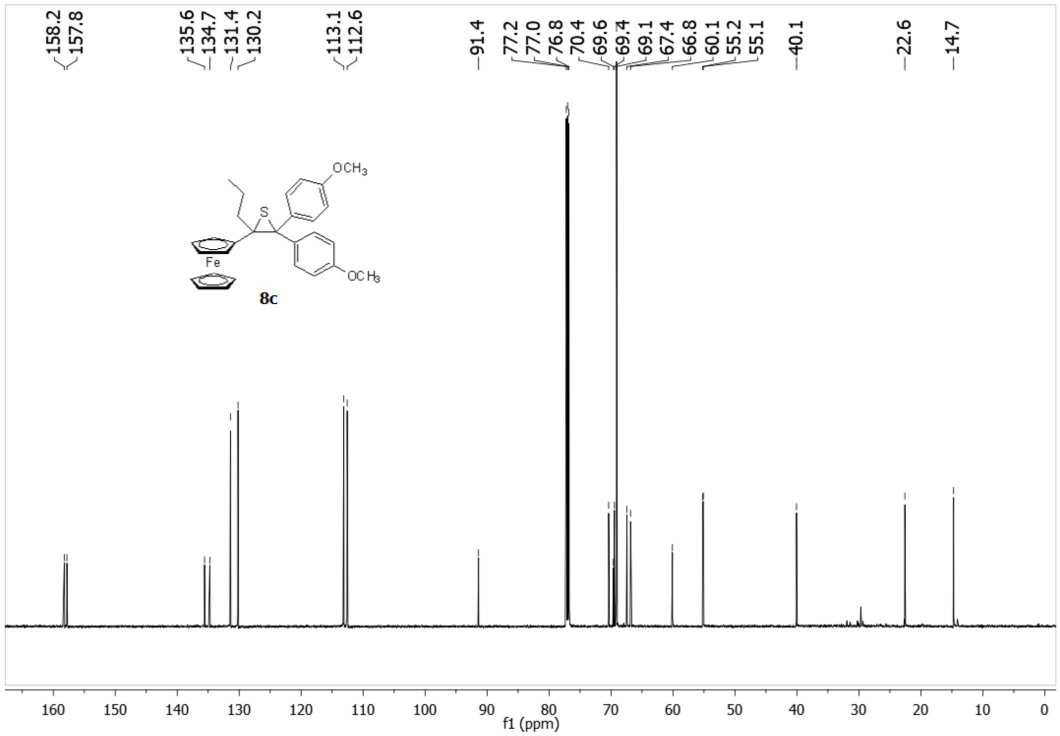


Figure S30. The ^{13}C NMR spectrum of **8c**.

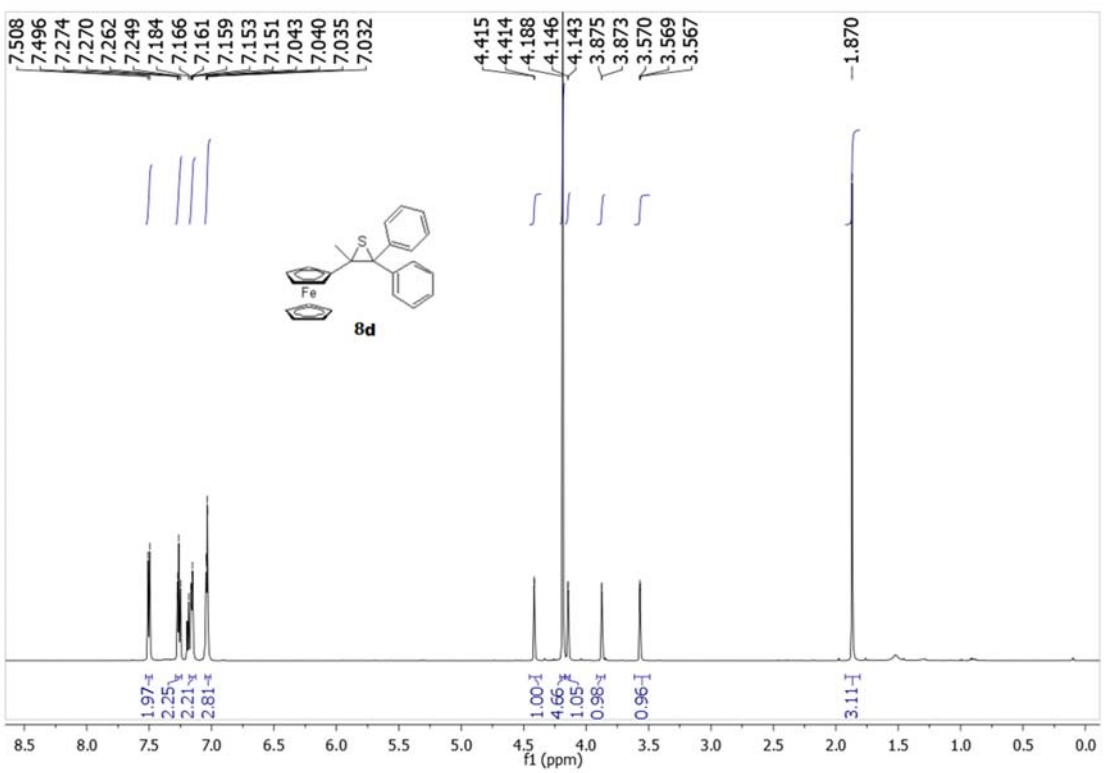


Figure S33. The ^{1}H NMR spectrum of **8d**.

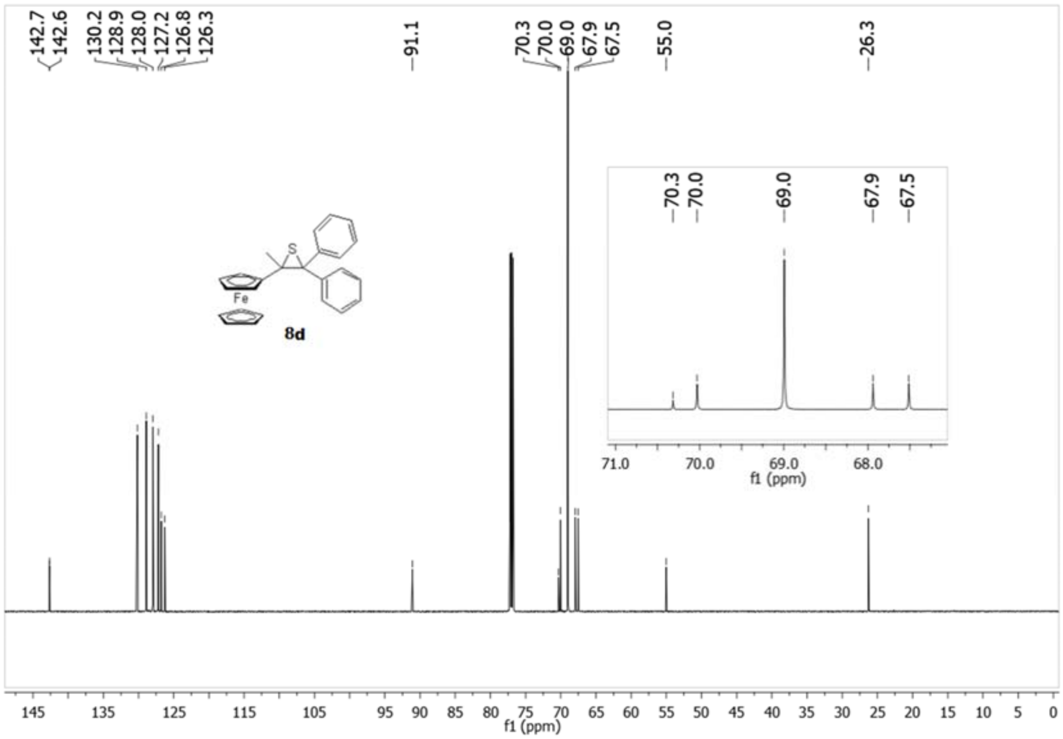


Figure S34. The ^{13}C NMR spectrum of **8d.**

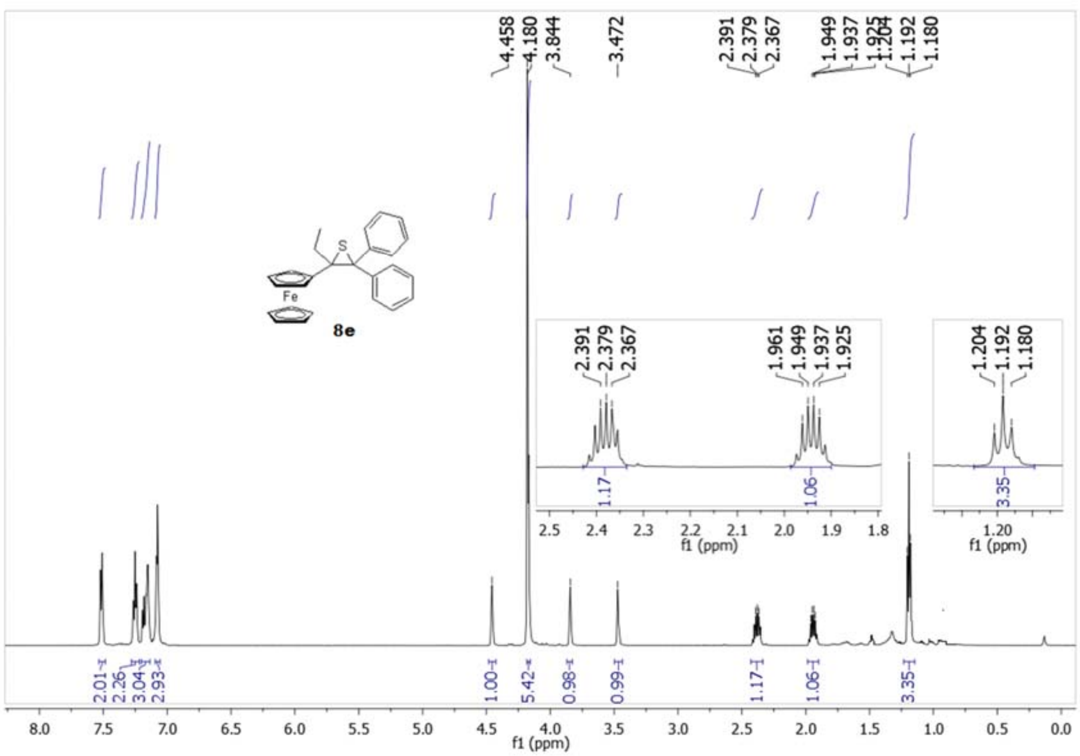


Figure S35. The ^1H NMR spectrum of **8e**.

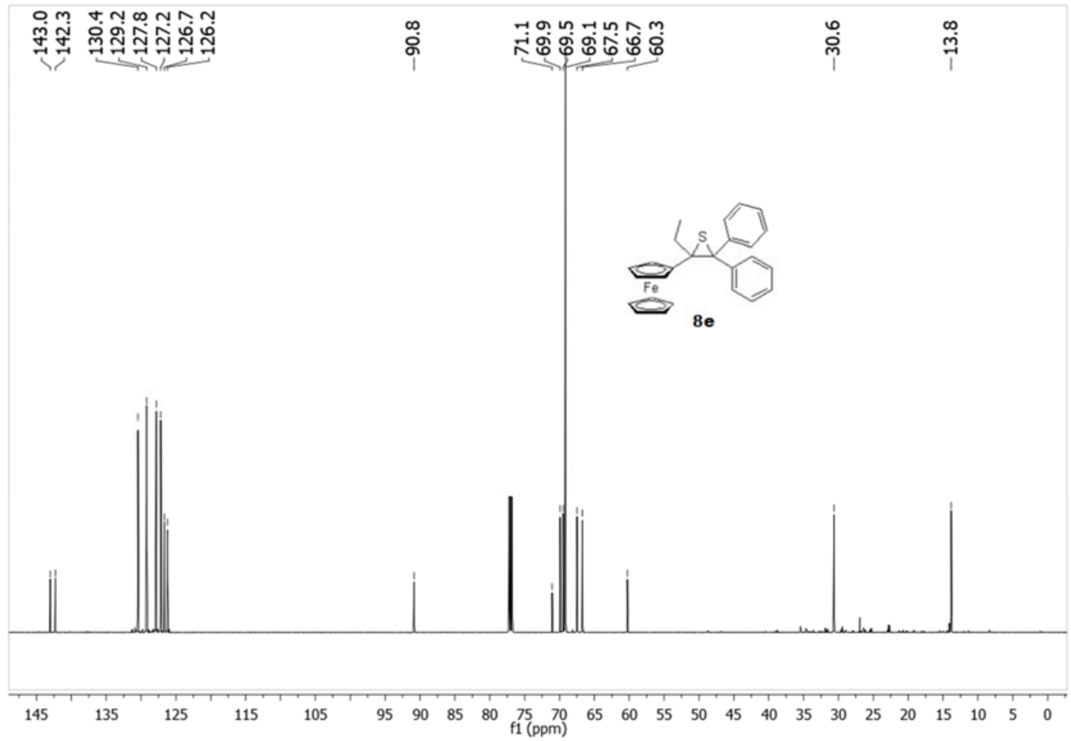


Figure S36. The ^{13}C NMR spectrum of **8e.**

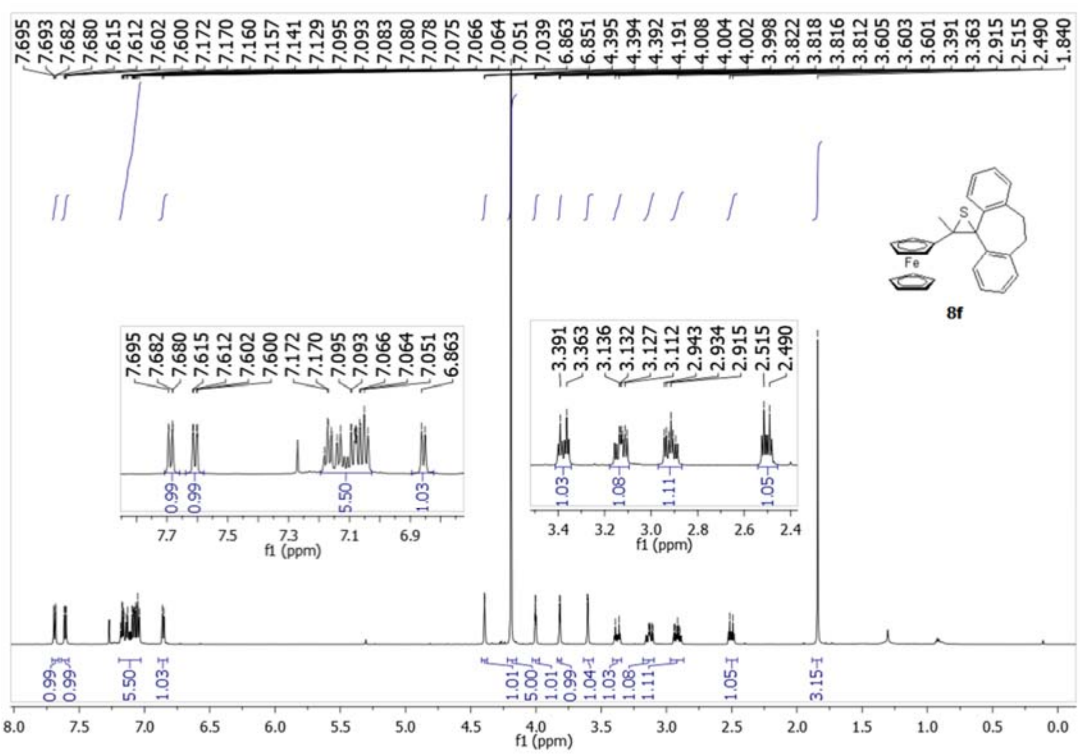


Figure S37. The ^{1}H NMR spectrum of **8f**.

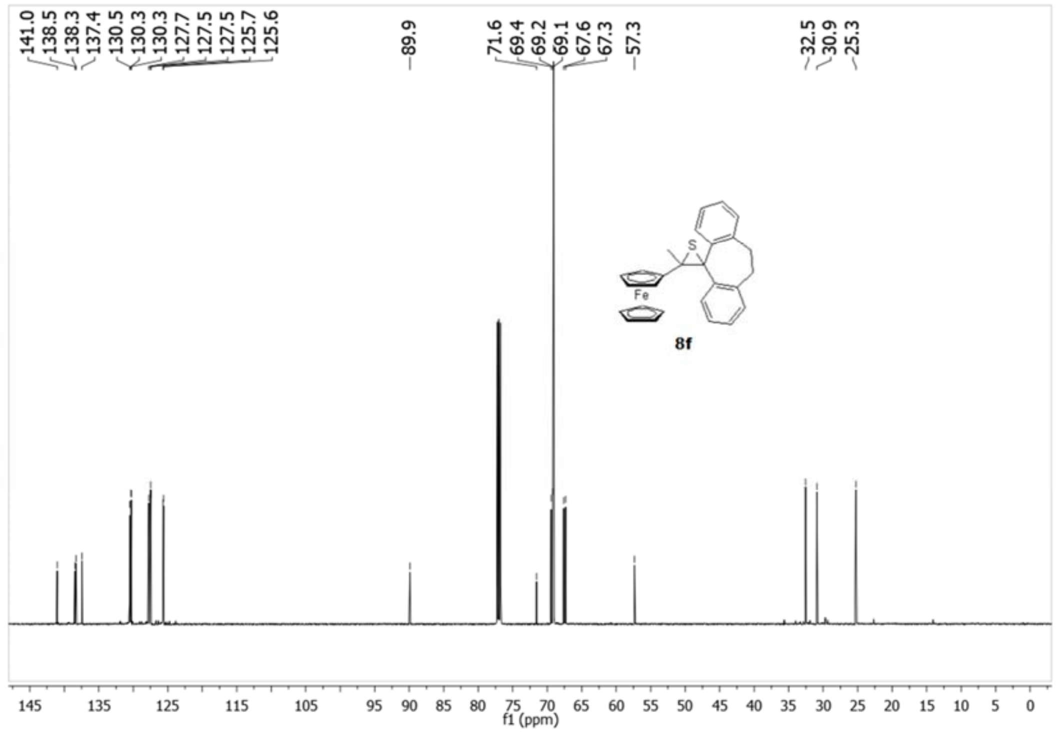


Figure S38. The ^{13}C NMR spectrum of **8f**.

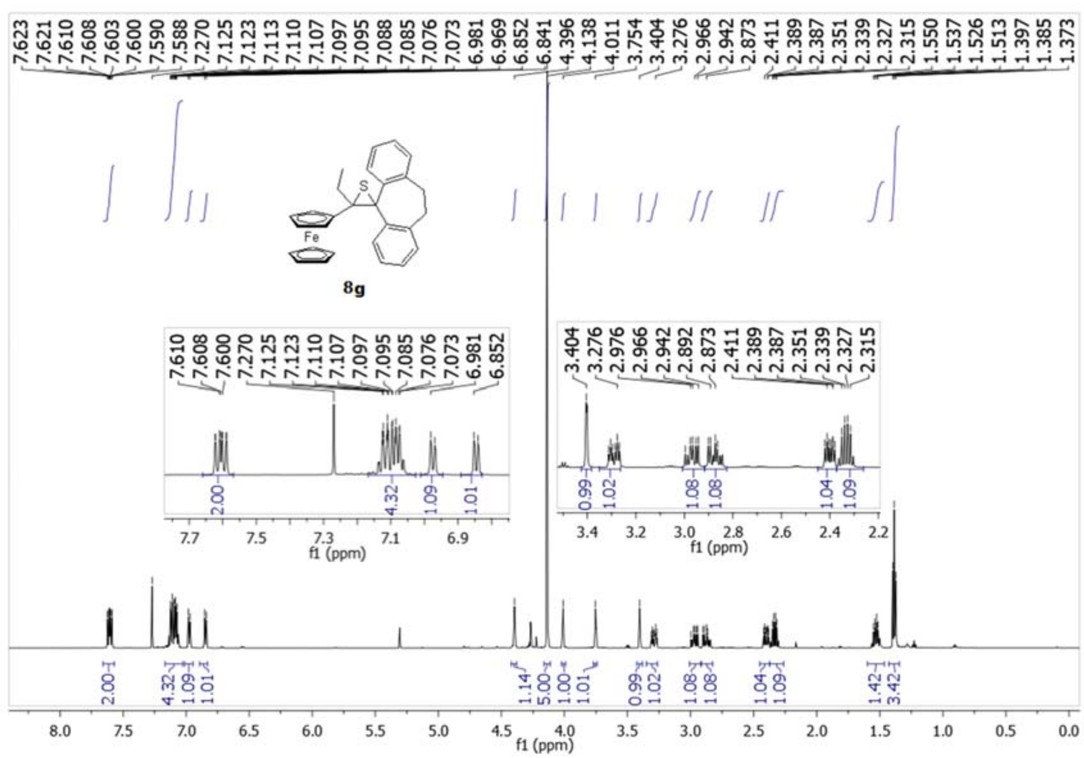


Figure S35. The ^{1}H NMR spectrum of **8g**.

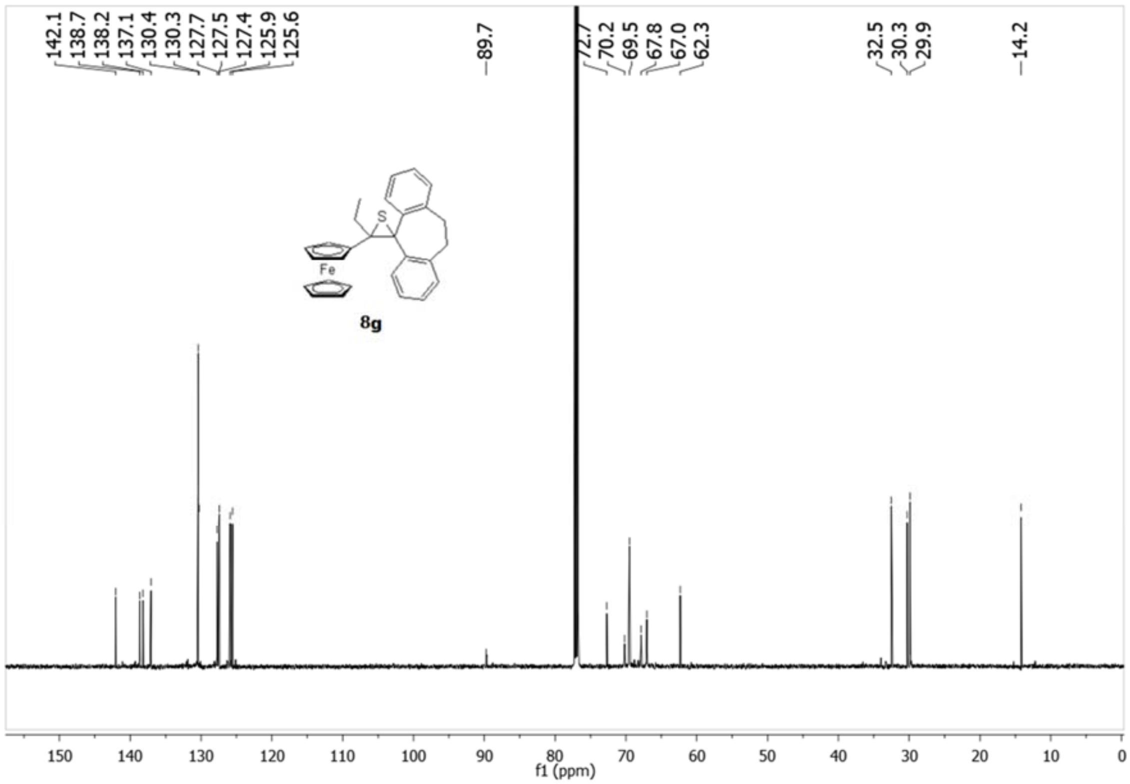


Figure S36. The [13]C NMR spectrum of compound **8g.**

5. **The [1]H- and [13]C-NMR spectra of ethylene derivatives 9a-m**.

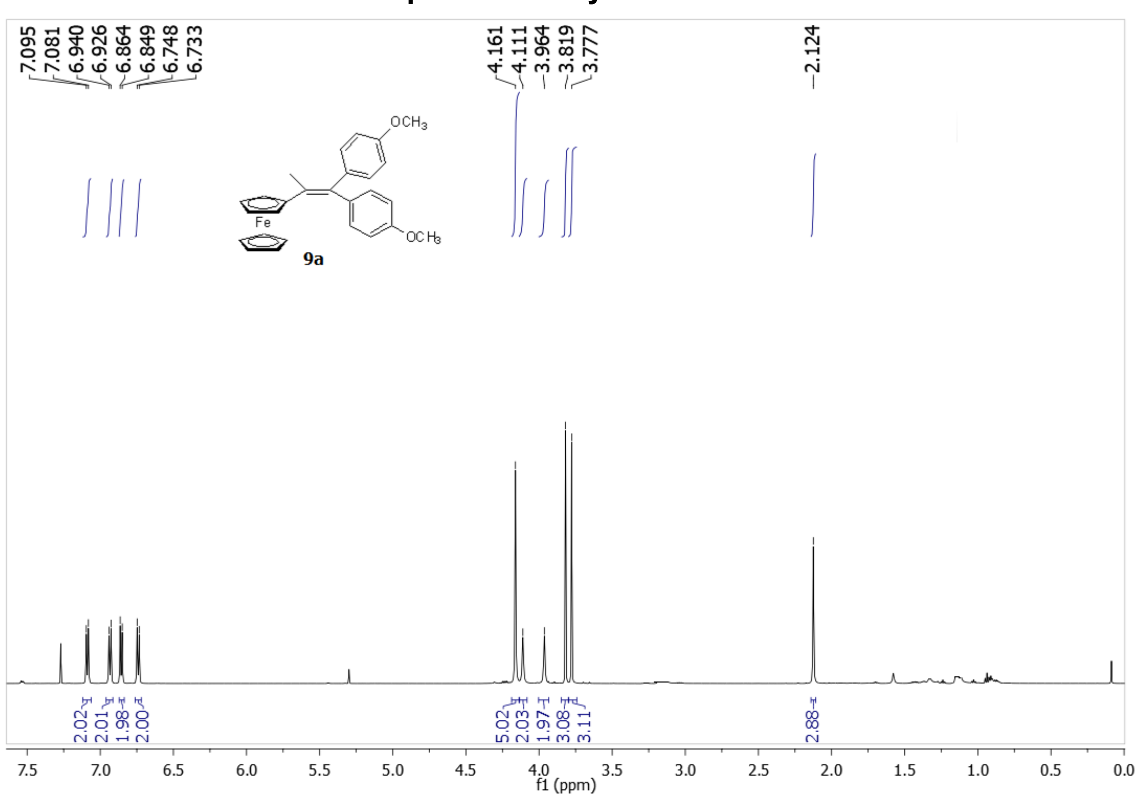


Figure S37. The [1]H NMR spectrum of **9a**.

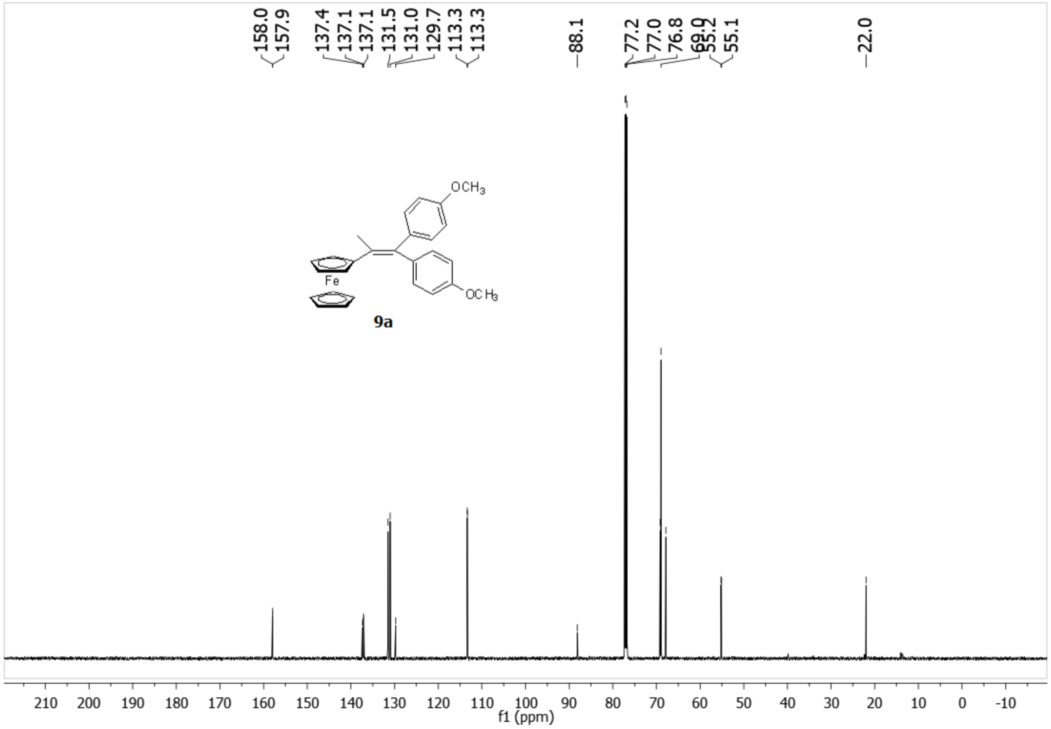


Figure S38. The [13]C NMR spectrum of **9a**.

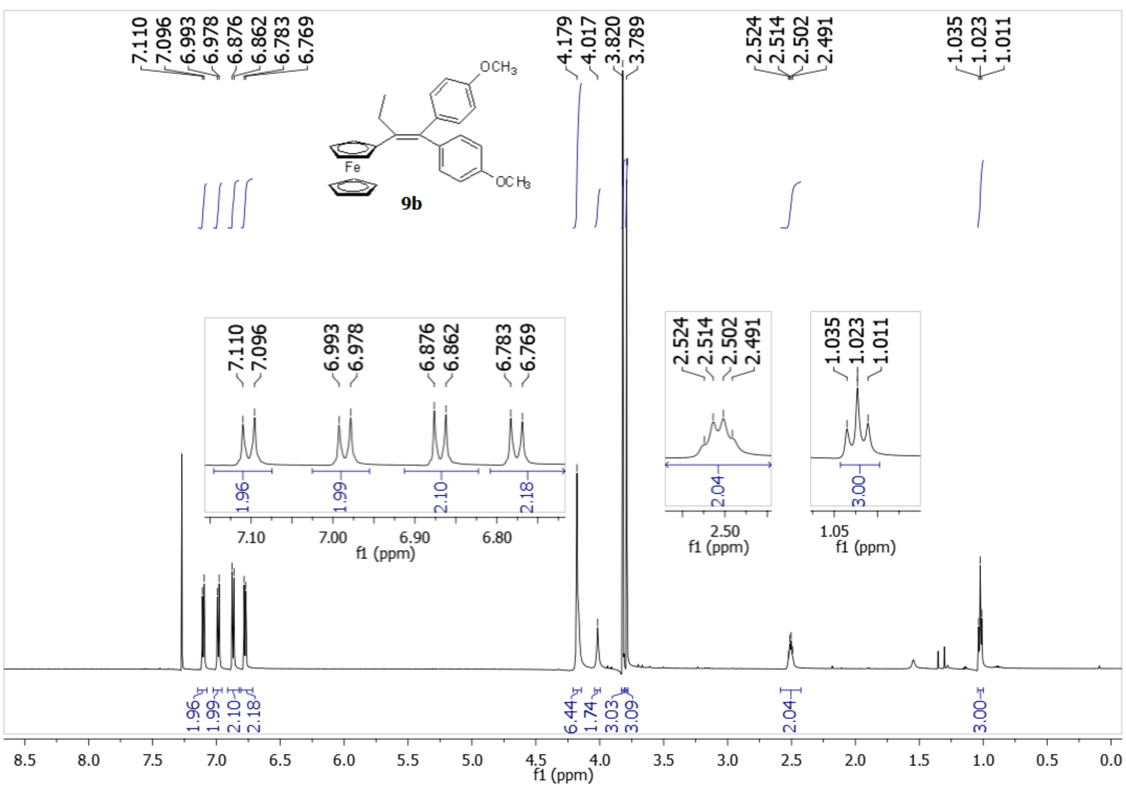


Figure S39. The ^{1}H NMR spectrum of **9b**.

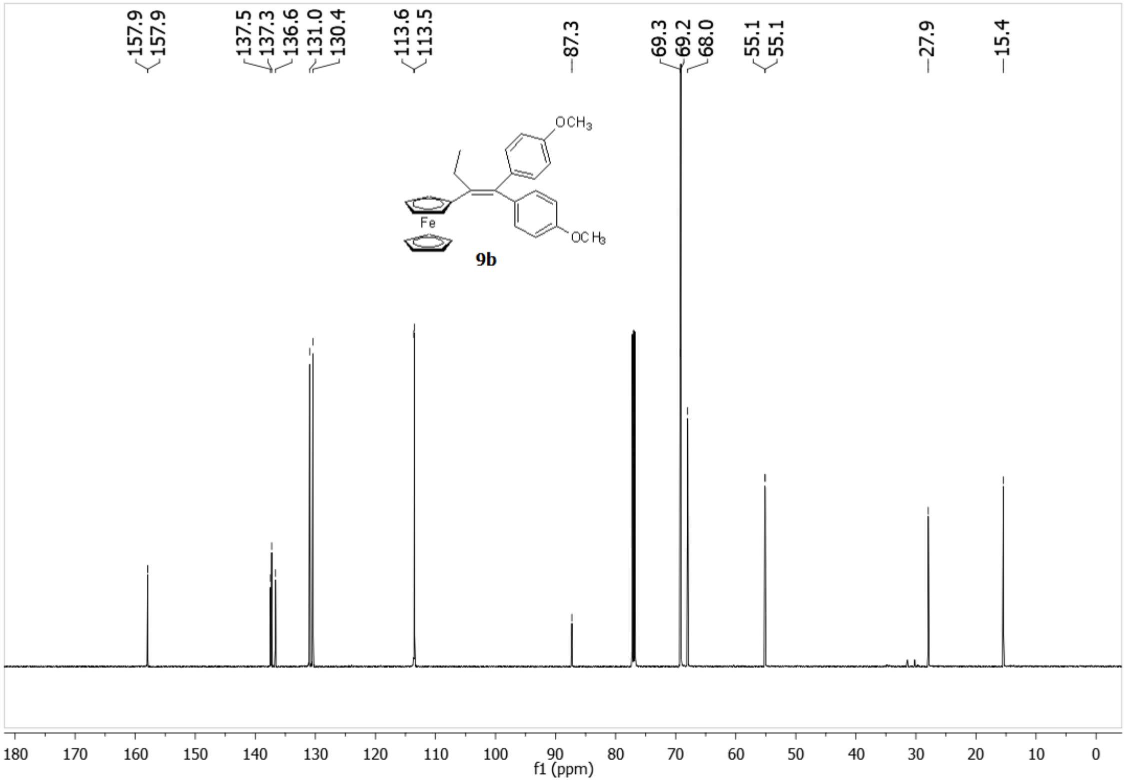


Figure S40. The ^{13}C NMR spectrum of **9b.**

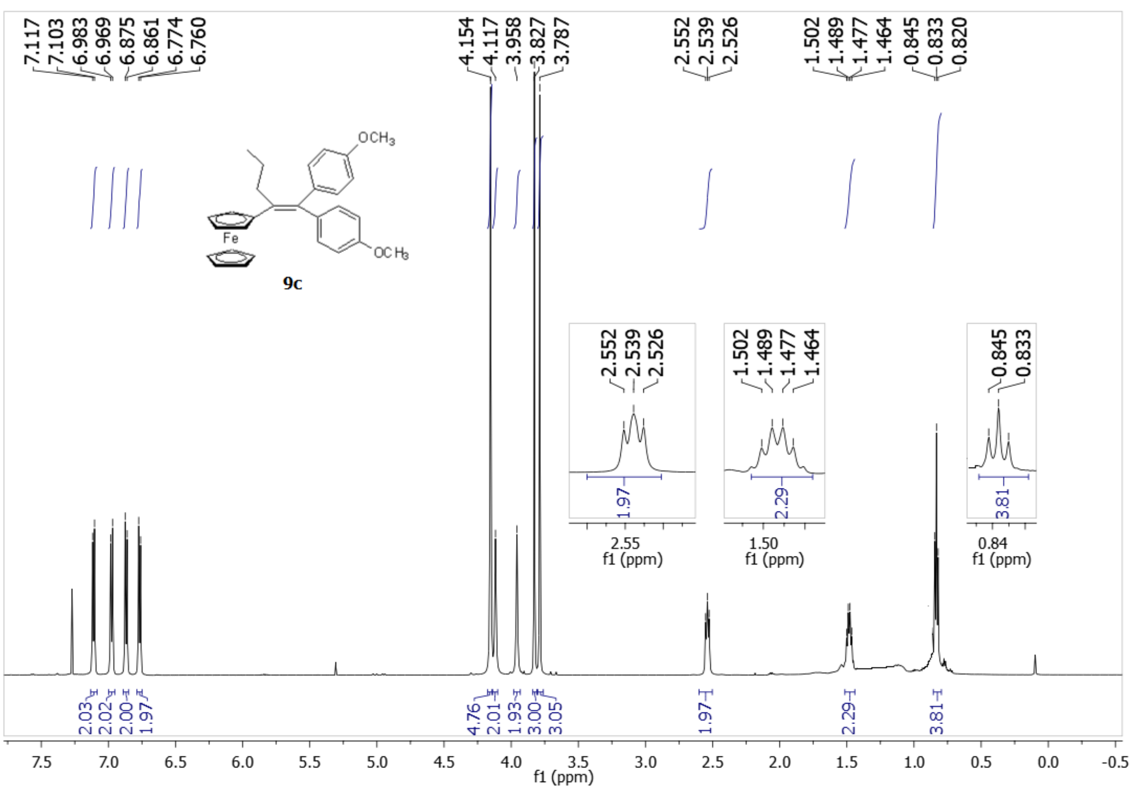


Figure S41. The ^{1}H NMR spectrum of **9c**.

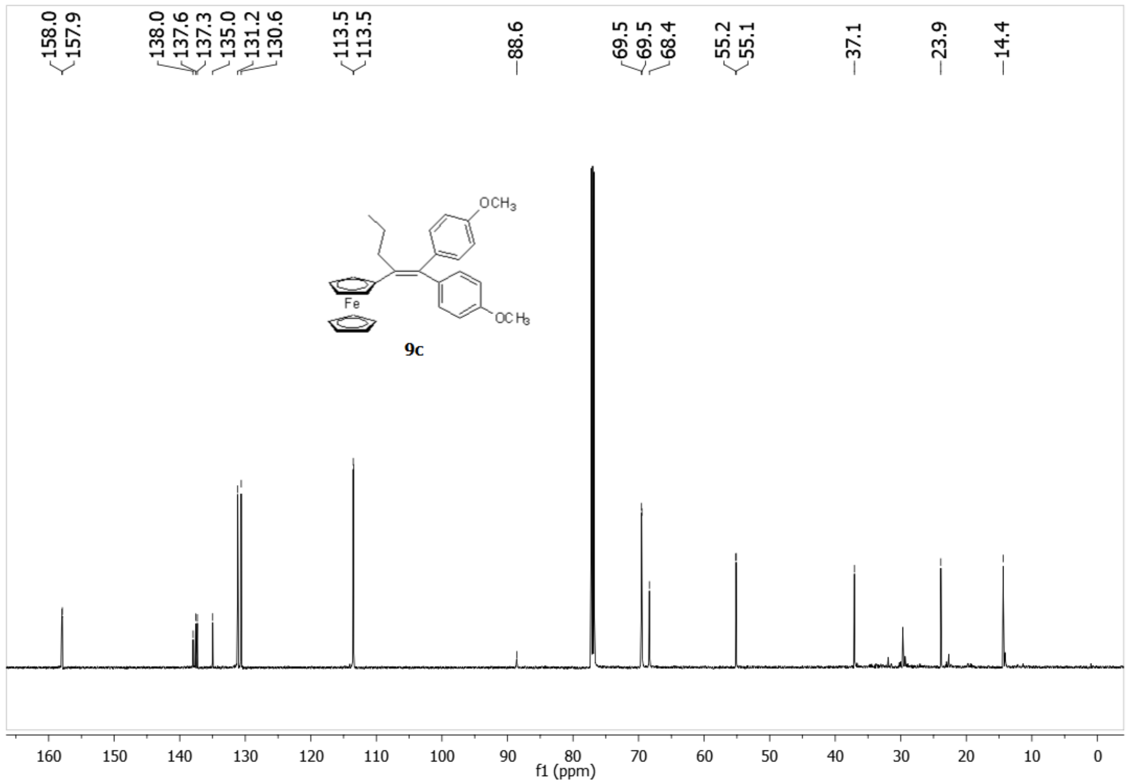


Figure S42. The ^{13}C NMR spectrum of **9c**.

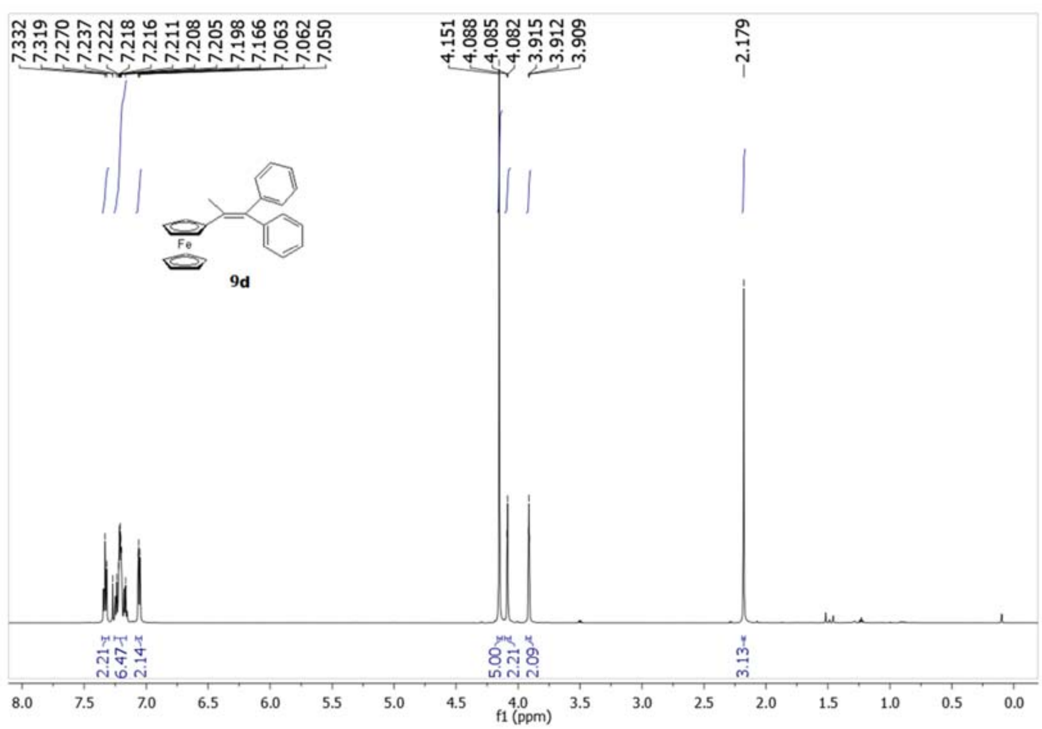


Figure S43. The ^{1}H NMR spectrum of **9d**.

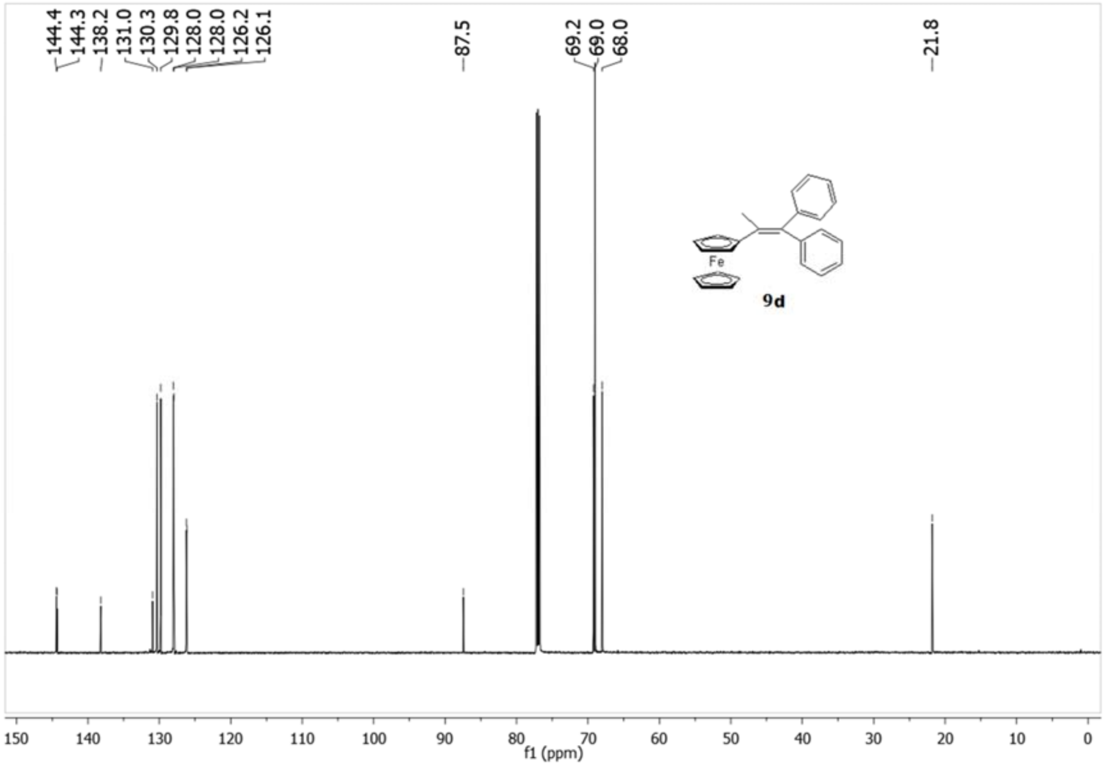


Figure S44. The ^{13}C NMR spectrum of **9d.**

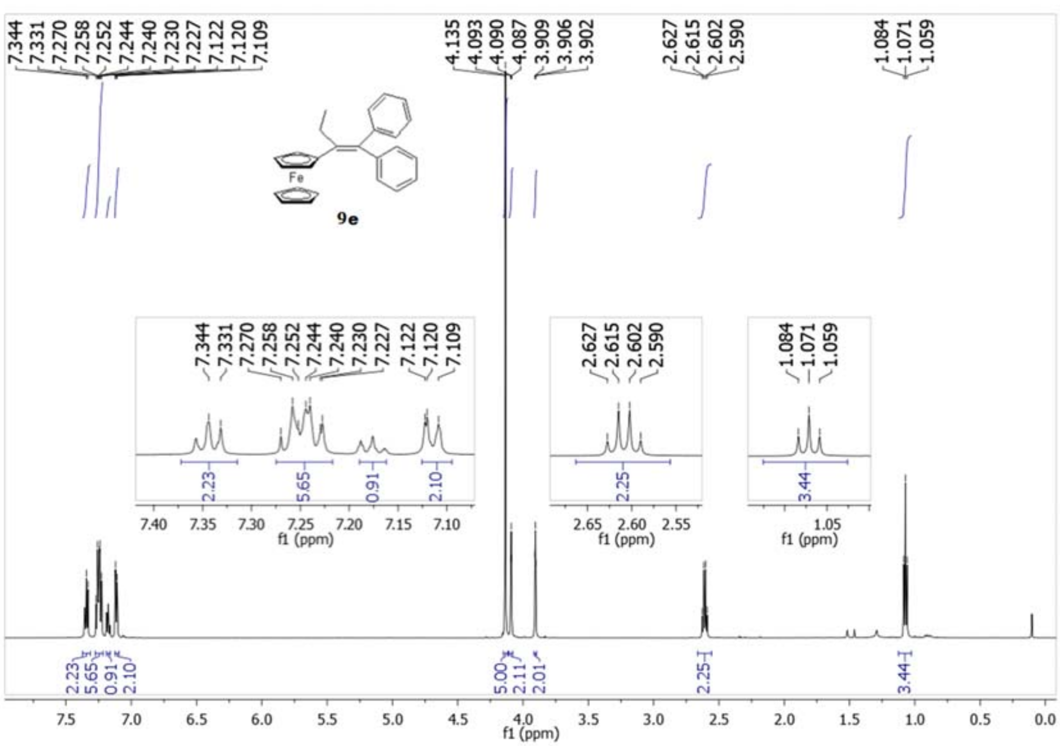


Figure S45. The ^{1}H NMR spectrum of **9e**.

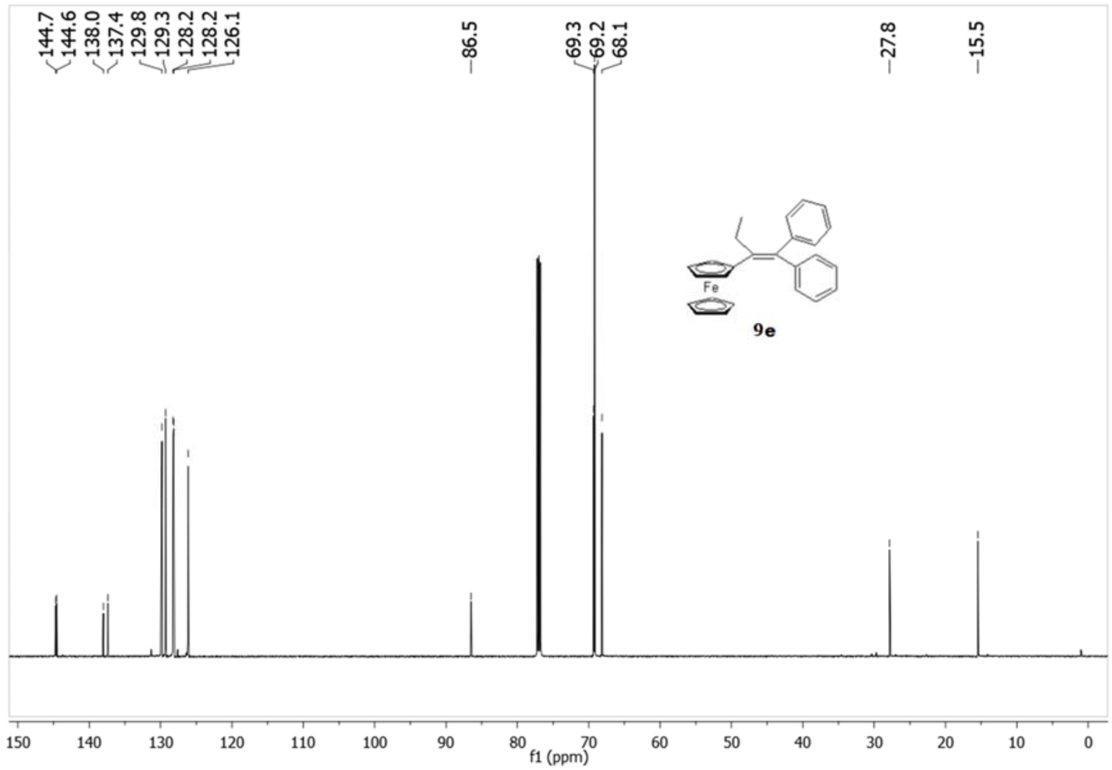


Figure S46. The ^{13}C NMR spectrum of **9e**.

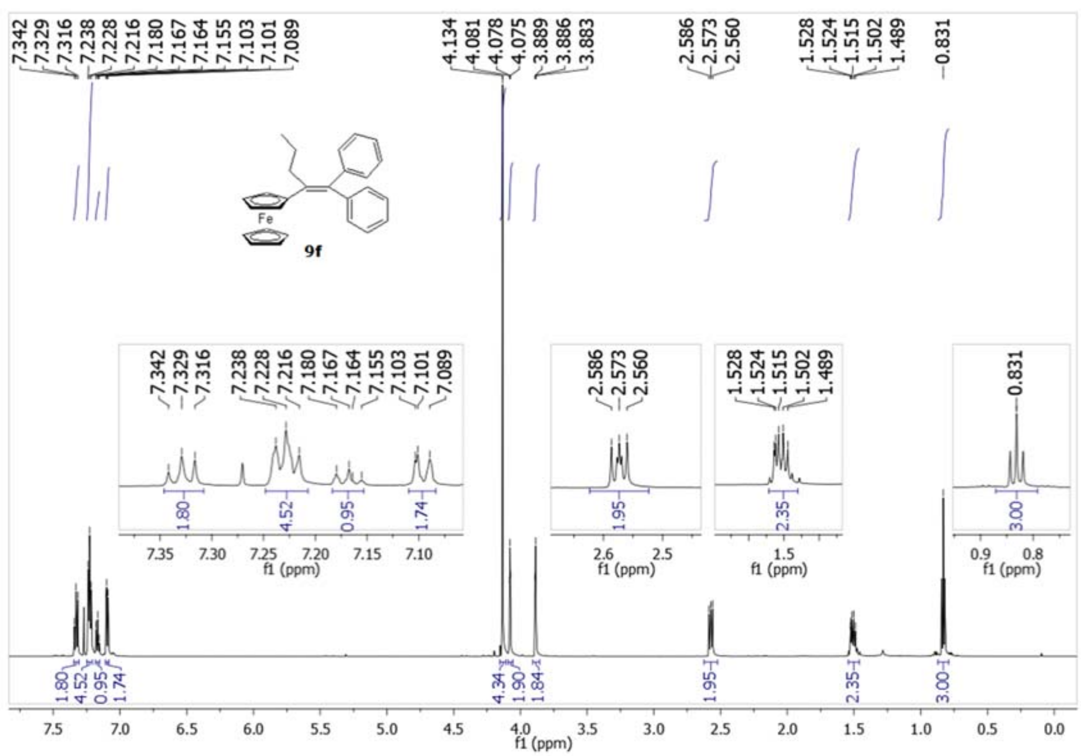


Figure S47. The ^{1}H NMR spectrum of **9f**.

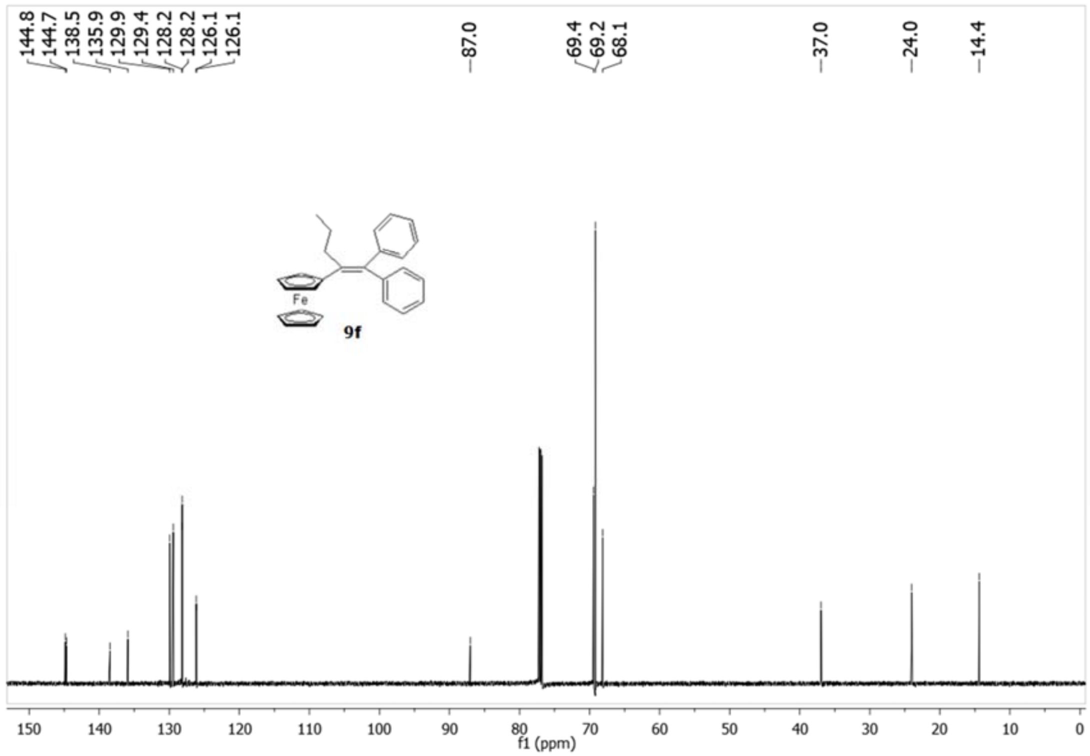


Figure S48. The ^{13}C NMR spectrum of **9f**.

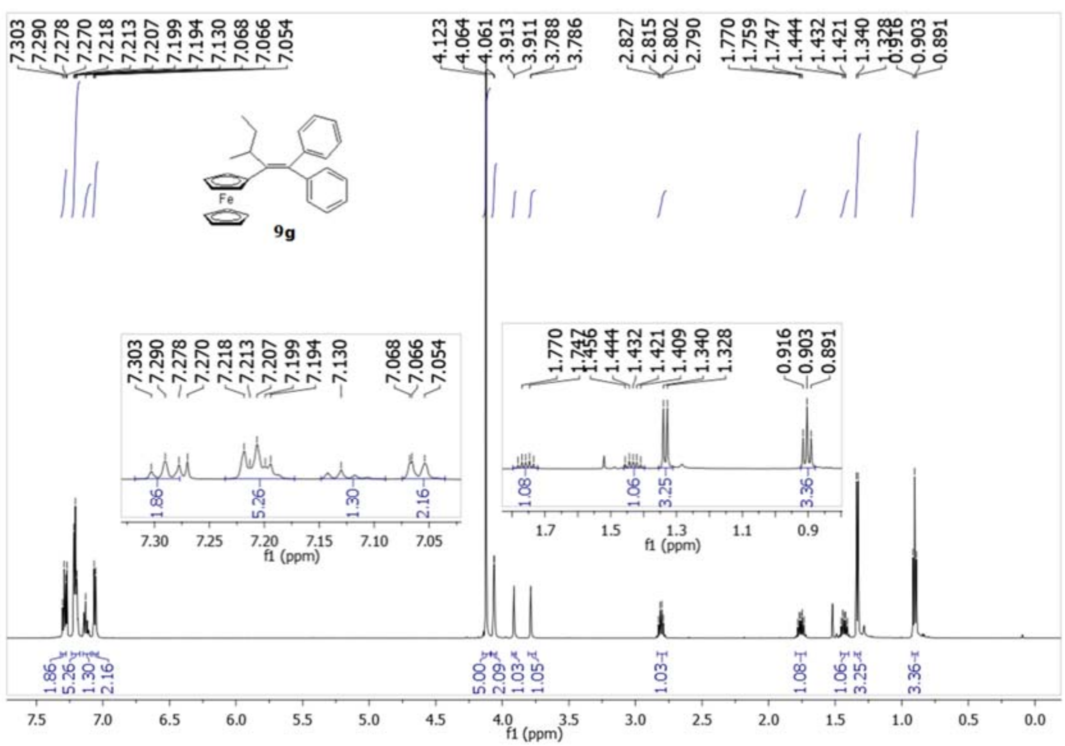


Figure S49. The ^{1}H NMR spectrum of **9g**.

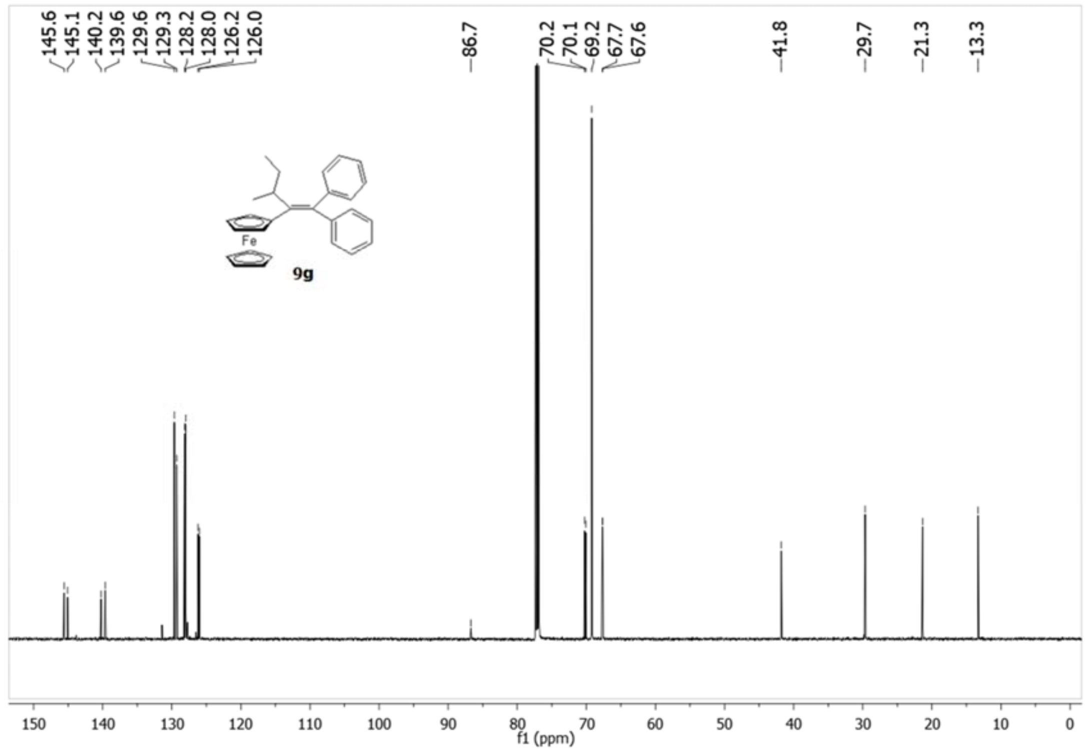


Figure S50. The ^{13}C NMR spectrum of **9g.**

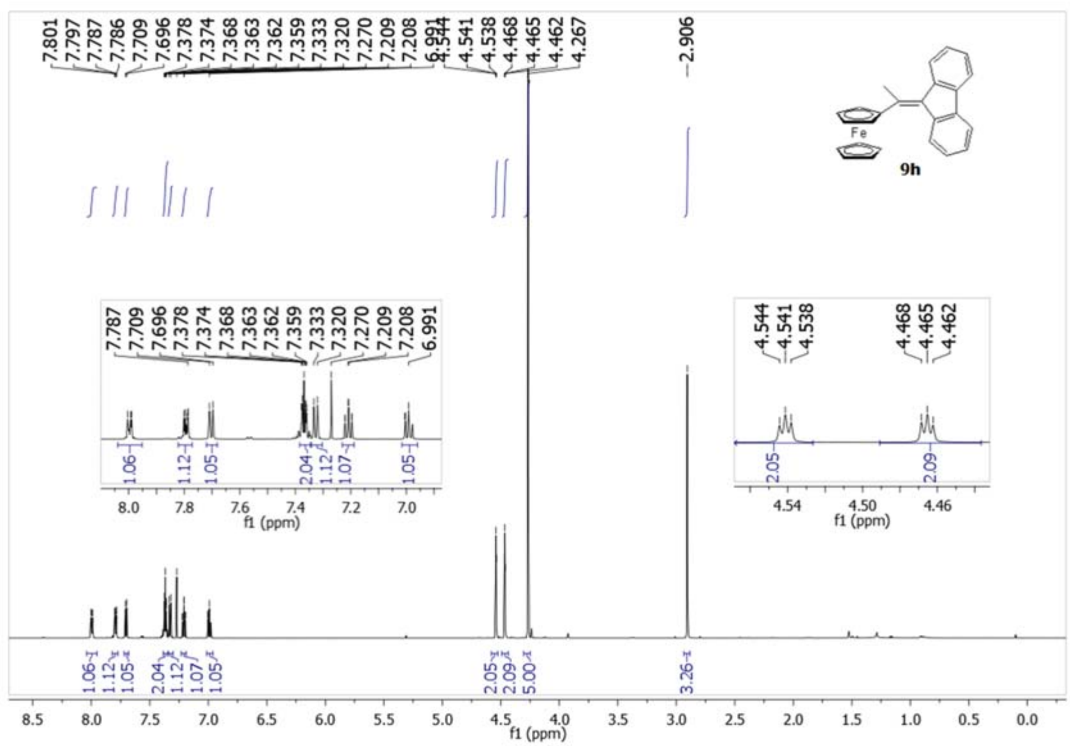


Figure S51. The ^{1}H NMR spectrum of **9h**.

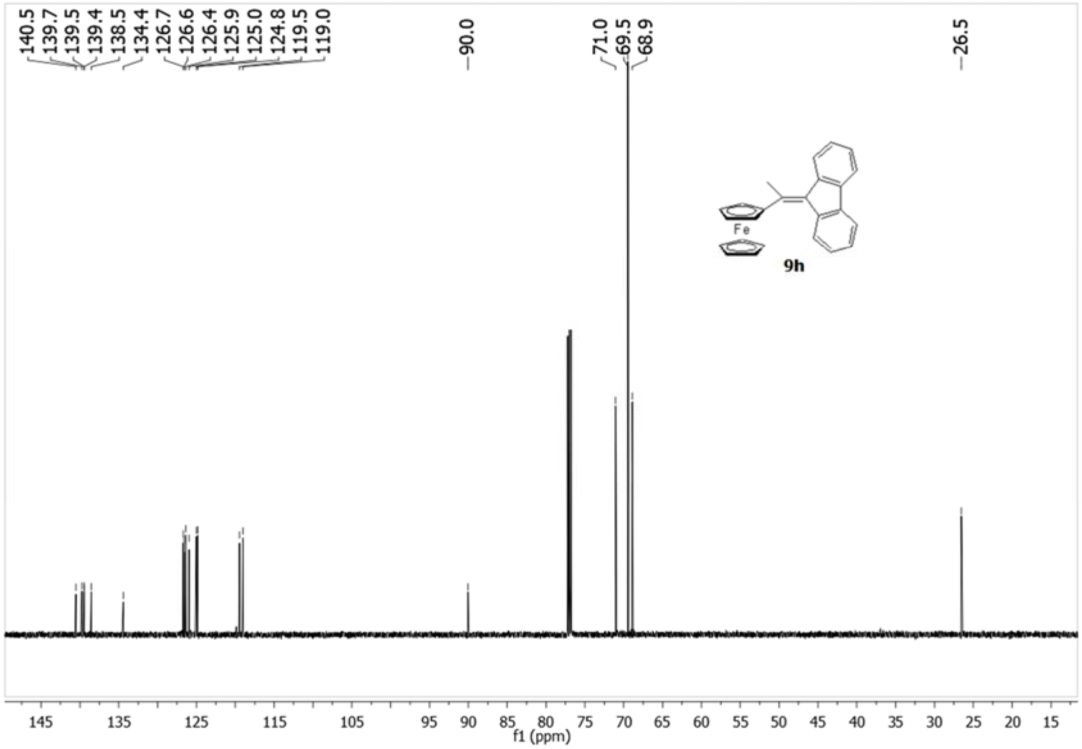


Figure S52. The ^{13}C NMR spectrum of **9h.**

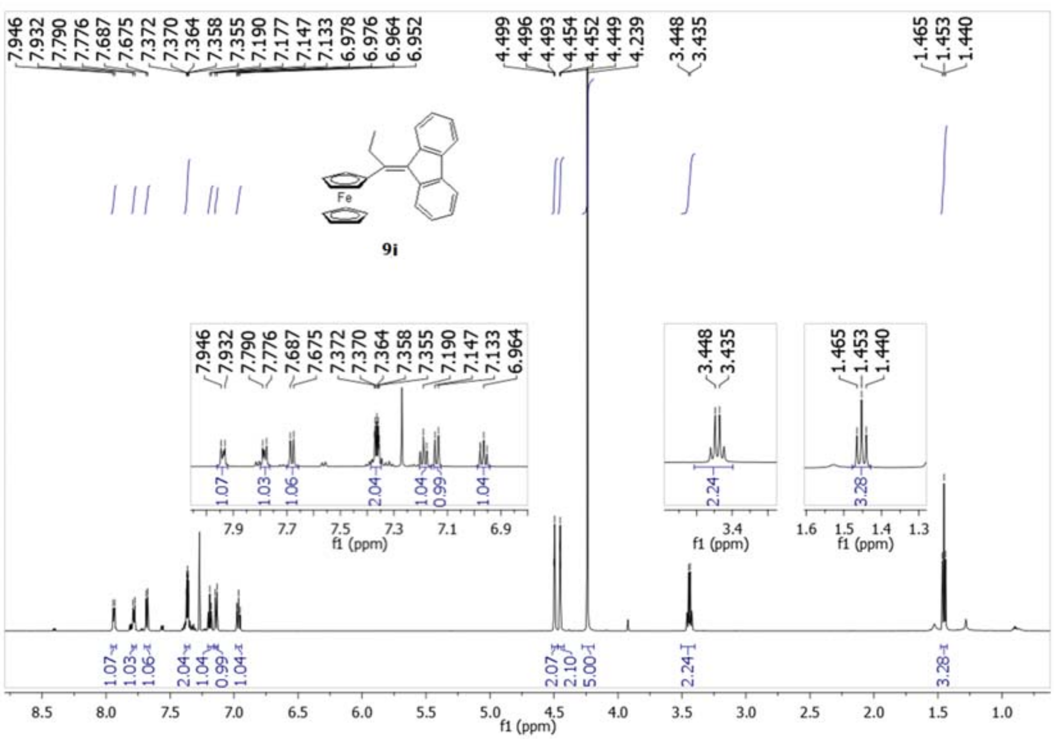


Figure S53. The ^{1}H NMR spectrum of **9i.**

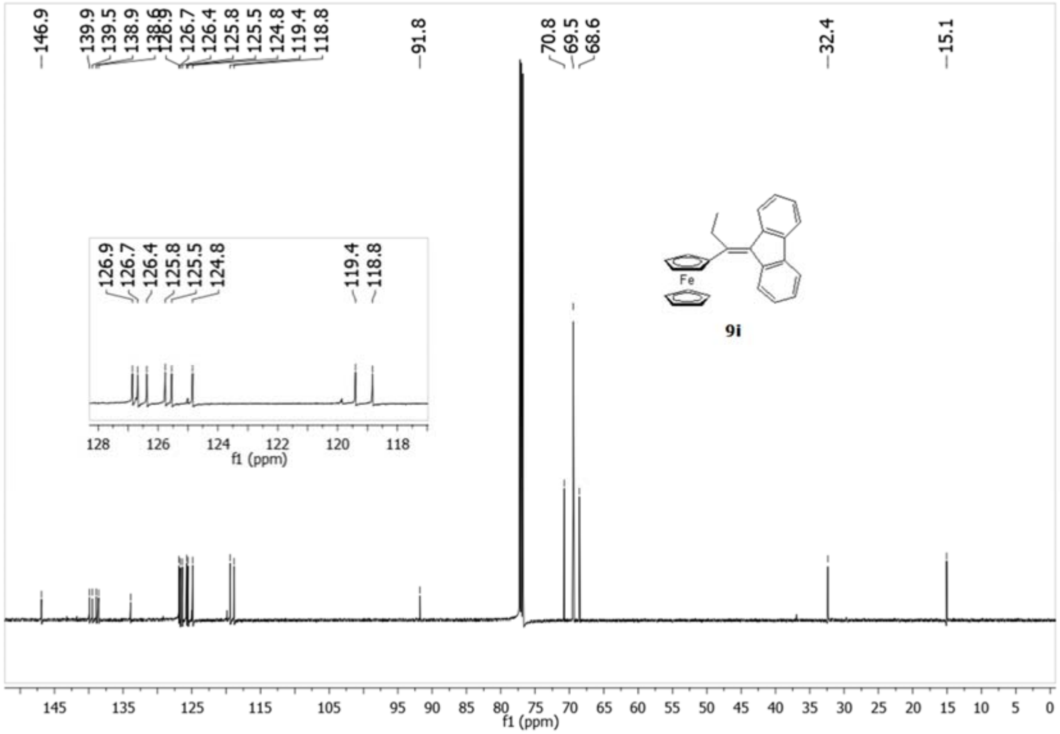


Figure S54. The ^{13}C NMR spectrum of **9i**.

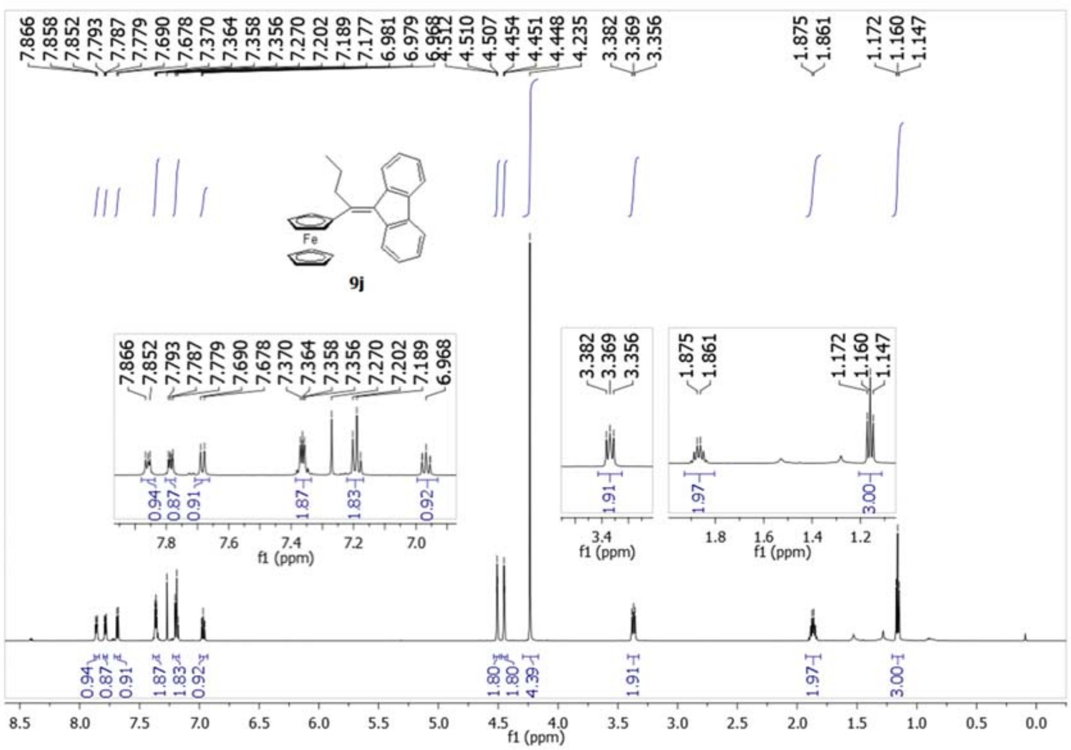


Figure S55. The ^{1}H NMR spectrum of **9j**.

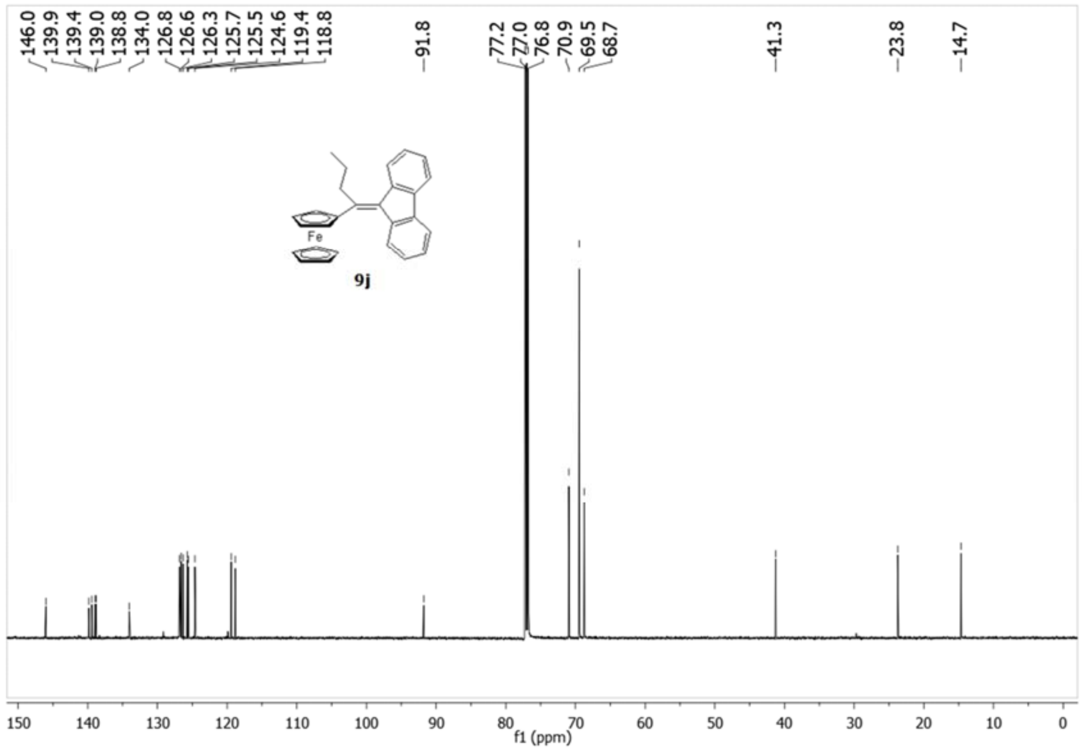


Figure S56. The ^{13}C NMR spectrum of **9j**.

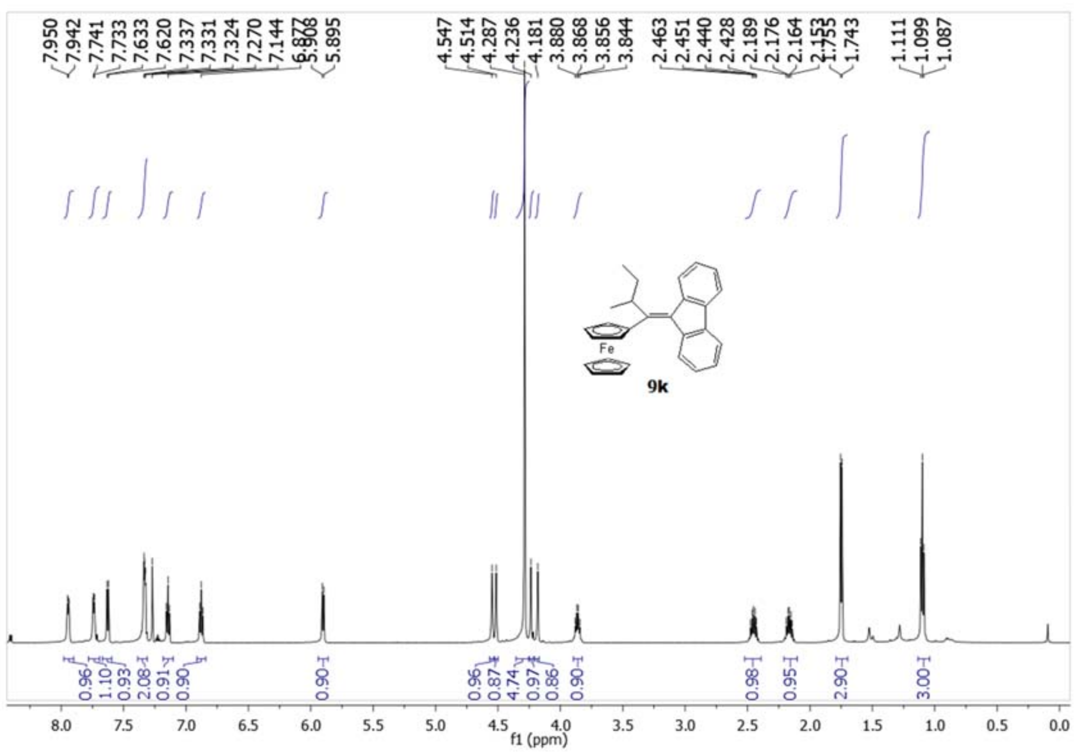


Figure S57. The ^{1}H NMR spectrum of **9k**.

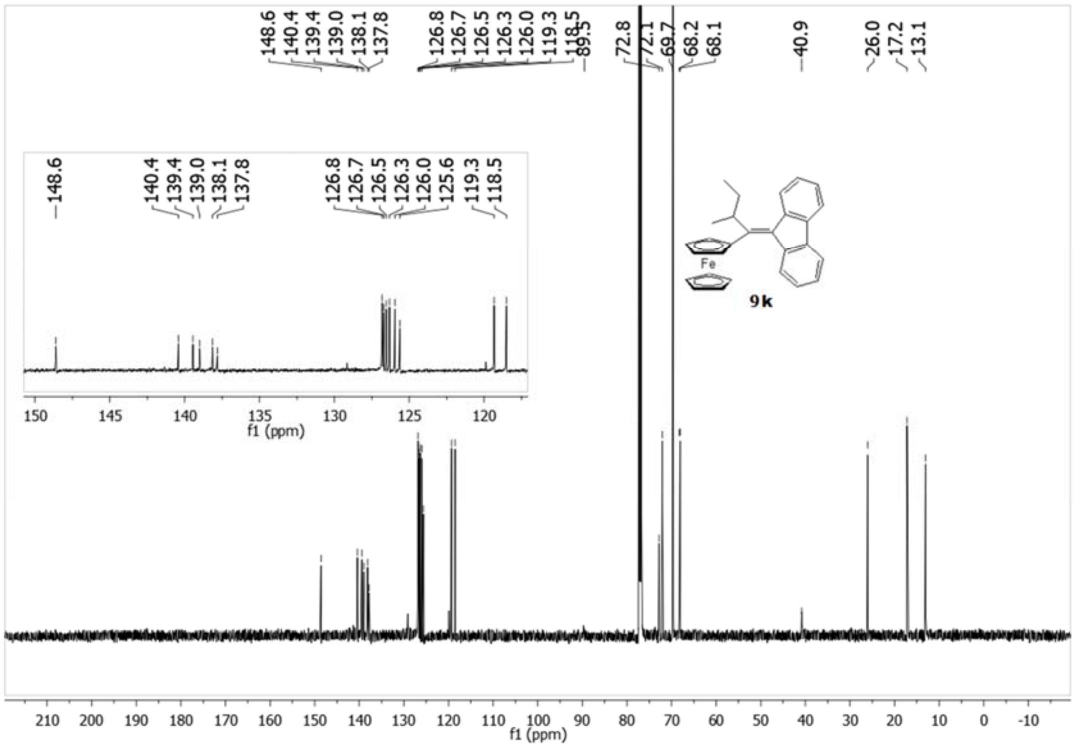


Figure S58. The ^{13}C NMR spectrum of **9k**.

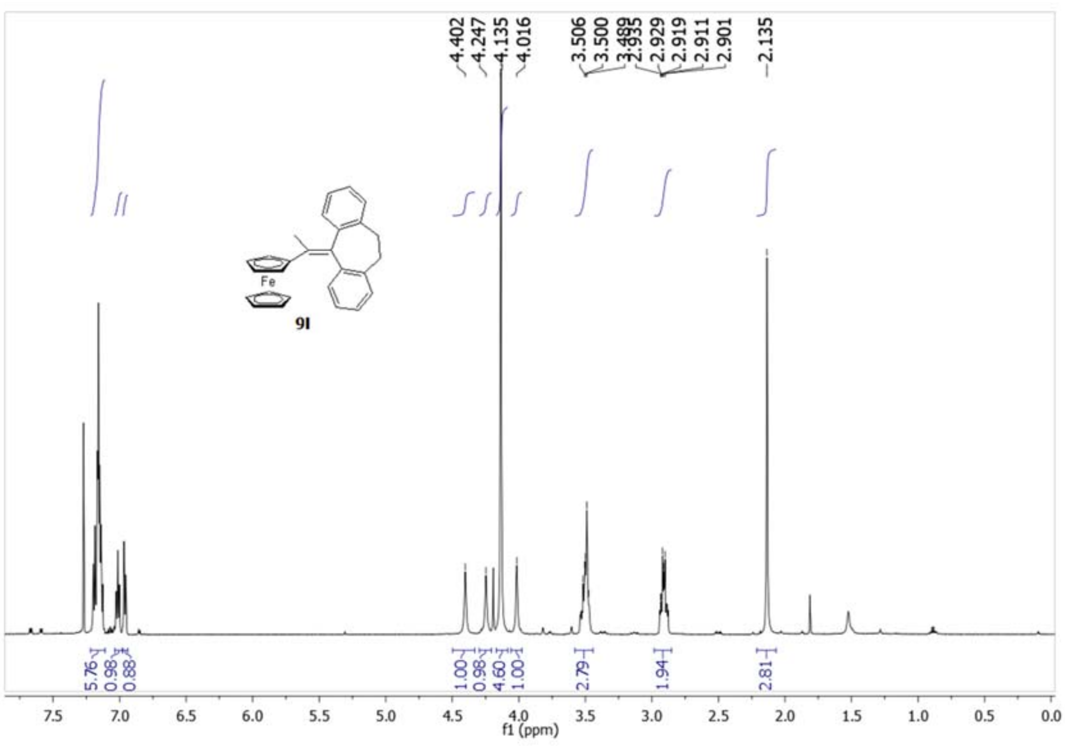


Figure S59. The ^{1}H NMR spectrum of **9l**.

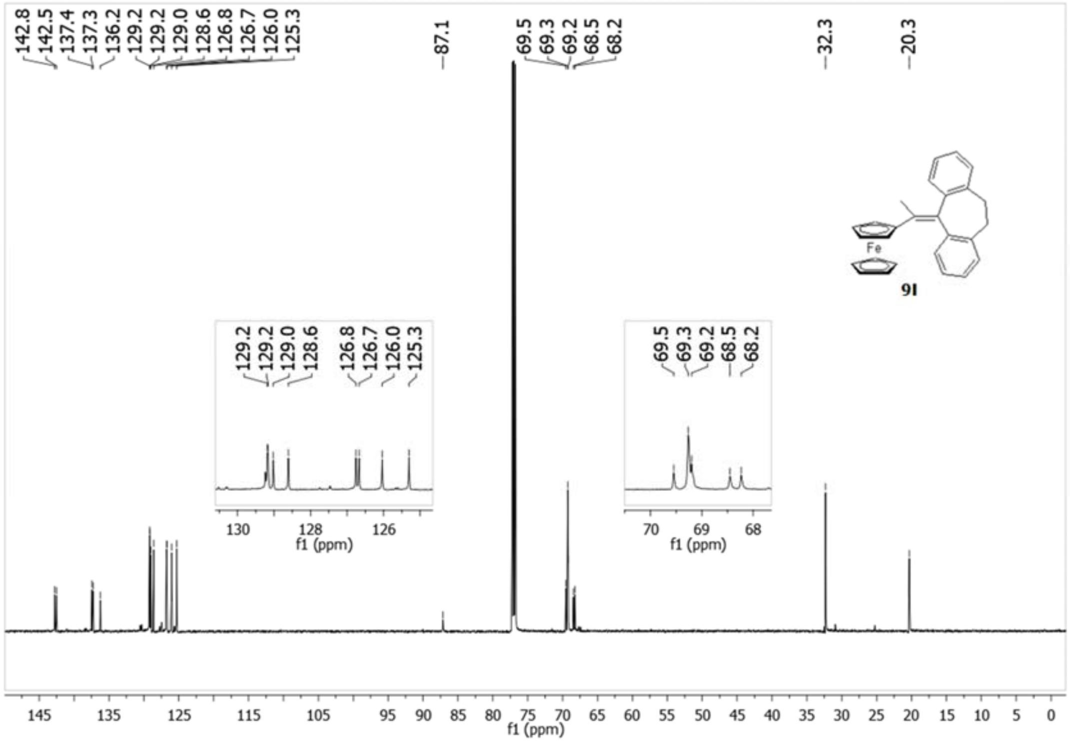


Figure S60. The ^{13}C NMR spectrum of **9l**.

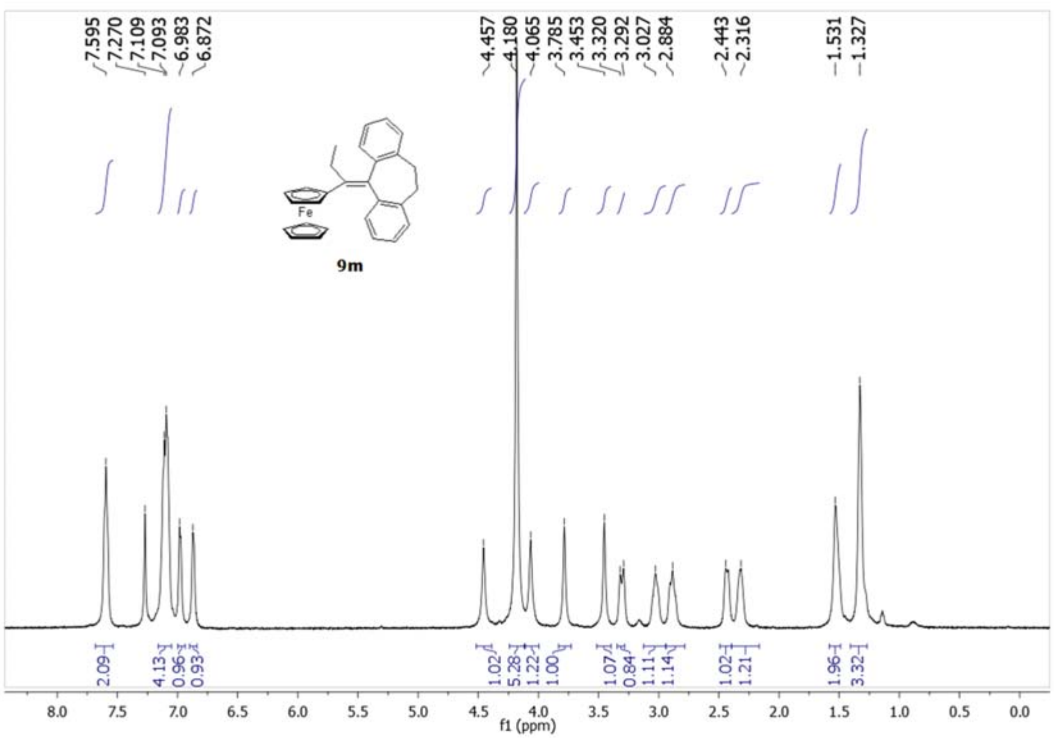


Figure S61. The ^{1}H NMR spectrum of **9m**.

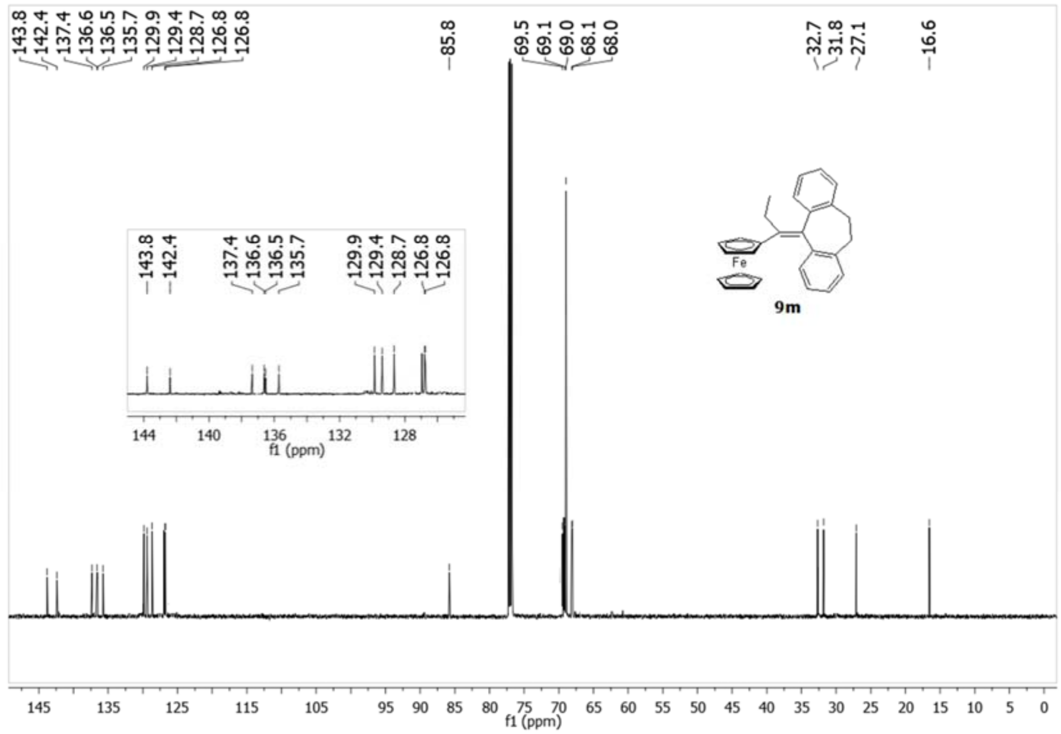


Figure S64. The ^{13}C NMR spectrum of **9m**.