Electronic Supplementary Information (ESI)

Chemoselective synthesis of multifunctional ferrocene-containing derivatives by the cross Rauhut-Currier reaction

Dragana Stevanović,[a]* Jovana Bugarinović,[a] Marko Pešić,[a] Anka Todosijević,[b] Goran A. Bogdanović,[c] and Ivan Damljanović[a]

[a] *Faculty of Science, University of Kragujevac, 34000 Kragujevac, Serbia*

[b] *Faculty of Agriculture, University of Niš, 37000 Kruševac, Serbia*

[c] *VINČA Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, 11001 Belgrade, Serbia*

dragana.stevanovic@pmf.kg.ac.rs

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General information

All commercially available reagents were used directly without purification. All solvents were purified following standard procedures. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM), whereas silica gel 60 on Al plates, layer thickness 0.2 mm (Merck) was used for TLC. Melting points (uncorrected) were determined on a Mel-Temp capillary melting points apparatus, model 1001. The ^{1}H and ^{13}C NMR spectra of the samples in $CDCl_3$ were recorded on a Varian Gemini (^{1}H at 200 MHz, ^{13}C at 50 MHz) NMR spectrometer. Chemical shifts are expressed in ppm (δ) using tetramethylsilane as the internal standard. Coupling constants are reported in Hz. IR measurements were carried out with a Perkin–Elmer FTIR 31725-X spectrophotometer. Microanalyses of carbon, hydrogen, and nitrogen were carried out with a Carlo Erba 1106 model microanalyzer.

Synthetic procedures

Nitroalkenes are prepared according to reported procedures.[1-5]

General procedure for the synthesis of 2-nitro-1-ferrocenylethylene (**1**)

Nitroalkene **1** is prepared according to the literature.[1] To a solution of ferrocenecarbaldehyde (1.07 g, 5 mmol) in nitromethane (3.20 ml, 60 mmol), acetic acid (0.289 ml, 5 mmol) and ammonium acetate (0.925 g, 12 mmol) were added. The reaction mixture was placed in an ultrasonic cleaner and irradiated for 3.5 hours. After evaporation of nitromethane, the crude product was dissolved in dichloromethane and the organic layer was washed with water, then with brine solution, and dried over anhydrous Na_2SO_4. The solution was filtrated and the solvent was evaporated under reduced pressure. The product was obtained in >99% yields (1.280 g) as a purple solid and used without additional purification. Spectral data of **1** were consistent with the literature.[1] The same procedure was applied for the synthesis of **4a-g** and their spectra were consistent with the literature.[2-5]

General procedure for the synthesis of aromatic vinyl ketones

Aromatic vinyl ketones are prepared in two steps according to reported procedures.[6-9] The synthetic strategy included Friedel-Crafts acylation of the corresponding aromatic compound by 3-chloropropionyl chloride and then dehydrohalogenation of the obtained acylated product.

Friedel-Crafts acylation. [6,7] To a solution of aluminum chloride (6.15 g, 46.1 mmol) in 35 ml of dry dichloromethane, 3-chloropropionyl chloride (4.04 ml, 42.2 mmol) was added dropwise at 0°C, followed by the corresponding aromatic compound (38.4 mmol). The reaction mixture was warmed to room temperature and stirred overnight. After quenched by adding ice water, the organic layer was separated and dried over anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate = 95:5 as eluent. The corresponding acylated products were obtained in high yields (90-95%).

Dehydrohalogenation.[8] To a stirred solution of the corresponding acylated product (1 mmol) in 2 ml chloroform, triethyl amine (180 µl, 2.4 mmol) was added. The reaction mixture was stirred overnight and then washed with 0.1 M HCl, distilled water, saturated aqueous $NaHCO_3$, and brine solution. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The corresponding vinyl ketone **2c-i** was obtained in quantitative yield and further used without purification.

General procedure for the synthesis of acryloylferrocene (2j)

Acryloylferrocene is prepared according to reported procedure.[9]

General procedure for the cross Rauhut-Currier reaction

To a solution of nitroalkene **1** (51.4 mg, 0.2 mmol, 1 equiv.) and the corresponding vinyl ketone **2a-j** (0.24 mmol, 1.2 equiv.) in chloroform (1 ml) at room temperature, triphenylphosphine (10.5 mg, 20 mol%) was added. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel with *n*-hexane/ethyl acetate as eluent.

*4-Ferrocenyl-3-methylene-5-nitropentan-2-one (**3a**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow solid in 92% yield (60.2 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); mp 82 – 83 °C; IR (KBr, cm^{-1}) 1674 (C=O), 1549 (NO_2), 1381 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.12 (s, 1H, CH_2=C), 5.81 (s, 1H, CH_2=C), 5.06 – 4.74 (m, 2H, CH_2), 4.64 – 4.42 (m, 1H, CH), 4.17 – 4.13 (overlapped m, 2H, C_5H_4), 4.15 (overlapped s, 5H, C_5H_5), 4.11 – 4.06 (m, 1H, C_5H_4), 4.06 – 4.01 (m, 1H, C_5H_4), 2.34 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.0, 147.8, 127.6, 87.2 78.7, 69.3, 68.3, 68.2, 66.8, 39.5, 26.2. Anal. Calcd for $C_{16}H_{17}FeNO_3$: C, 58.74; H, 5.24; Fe, 17.07; N, 4.28; O, 14.67. Found: C, 58.81; H, 5.25; N, 4.28.

*5-Ferrocenyl-4-methylene-6-nitrohexan-3-one (**3b**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow solid in 83% yield (53.0 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 95:5); mp 62 – 64 °C; IR (KBr, cm^{-1}) 1677 (C=O), 1547 (NO_2), 1381 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.10 (s, 1H, CH_2=C), 5.76 (s, 1H, CH_2=C), 5.02 – 4.81 (m, 2H, CH_2), 4.61 – 4.49 (m, 1H, CH), 4.18 – 4.12 (overlapped m, 2H, C_5H_4), 4.15 (overlapped s, 5H, C_5H_5), 4.12 – 4.07 (m, 1H, C_5H_4), 4.06 – 4.00 (m, 1H, C_5H_4), 2.69 (qd, *J* = 7.3, 2.0 Hz, 2H, **CH_2**CH_3), 1.08 (t, *J* = 7.3 Hz, 3H, CH_2**CH_3**); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.9, 147.6, 126.0, 86.9, 78.9, 68.9, 68.0, 67.9, 66.5, 40.1, 31.3, 8.3. Anal. Calcd for $C_{17}H_{19}FeNO_3$: C, 59.85; H, 5.61; Fe, 16.37; N, 4.11; O, 14.07. Found: C, 59.94; H, 5.63; N, 4.10.

*3-Ferrocenyl-2-methylene-4-nitro-1-phenylbutan-1-one (**3c**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow solid in 64% yield (49.9 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); mp 119 – 120 °C; IR (KBr, cm^{-1}) 1655 (C=O), 1544 (NO_2), 1379 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H, C_6H_5), 7.56 – 7.49 (m, 1H, C_6H_5), 7.47 – 7.37 (m, 2H, C_6H_5), 5.88 (d, *J* = 0.7 Hz, 1H, CH_2=C), 5.72 (br s, 1H, CH_2=C), 5.18 – 4.98 (m, 2H, CH_2), 4.64 (dd, *J* = 8.6, 5.7 Hz, 1H, CH), 4.20 – 4.13 (overlapped m, 3H, C_5H_4), 4.17 (overlapped s, 5H, C_5H_5), 4.13 – 4.08 (m, 1H, C_5H_4); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.6, 146.7, 137.4, 132.4, 129.5, 128.2, 128.0, 86.5, 78.8, 69.0, 68.1, 66.3, 41.5. Anal. Calcd for $C_{21}H_{19}FeNO_3$: C, 64.80; H, 4.92; Fe, 14.35; N, 3.60; O, 12.33. Found: C, 64.76; H, 4.94; N, 3.61.

*3-Ferrocenyl-2-methylene-4-nitro-1-(p-tolyl)butan-1-one (**3d**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow solid in 83% yield (66.9 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 95:5); mp 89 – 91 °C; IR (KBr, cm^{-1}) 1651 (C=O), 1542 (NO_2), 1382 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 2H, C_6H_4), 7.25 – 7.17 (m, 2H, C_6H_4), 5.83 (d, *J* = 0.7 Hz, 1H, CH_2=C), 5.68 (s, 1H, CH_2=C), 5.18 – 4.95 (m, 2H, CH_2), 4.62 (dd, *J* = 8.8, 5.7 Hz, 1H, CH), 4.19 – 4.12 (overlapped m, 3H, C_5H_4), 4.16 (overlapped s, 5H, C_5H_5), 4.11 – 406 (m, 1H, C_5H_4), 2.40 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.3, 146.7, 143.4, 134.6, 129.8, 128.9, 127.1, 86.5, 78.9, 69.0, 68.1, 66.3, 41.7, 21.6. Anal. Calcd for $C_{22}H_{21}FeNO_3$: C, 65.53; H, 5.25; Fe, 13.85; N, 3.47; O, 11.90. Found: C, 65.64; H, 5.27; N, 3.46.

*3-Ferrocenyl-1-(4-methoxyphenyl)-2-methylene-4-nitrobutan-1-one (**3e**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow oil in 80% yield (67.1 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); IR (KBr, cm^{-1})

1601 (C=O), 1579 (NO_2), 1312 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 2H, C_6H_4), 6.95 – 6.86 (m, 2H, C_6H_4), 5.79 (d, *J* = 0.8 Hz, 1H, CH_2=C), 5.64 (s, 1H, CH_2=C), 5.19 – 4.93 (m, 2H, CH_2), 4.60 (dd, *J* = 9.0, 5.6 Hz, 1H, CH), 4.19 – 4.10 (overlapped m, 3H, C_5H_4), 4.15 (overlapped s, 5H, C_5H_5), 4.10 – 4.06 (m, 1H, C_5H_4), 3.86 (s, 3H, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.3, 163.3, 146.6, 132.0, 129.8, 126.0, 113.5, 86.5, 78.9, 69.0, 68.1, 66.3, 55.5, 42.0. Anal. Calcd for $C_{22}H_{21}FeNO_4$: C, 63.03; H, 5.05; Fe, 13.32; N, 3.34; O, 15.26. Found: C, 63.18; H, 5.07; N, 3.33.

3-Ferrocenyl-2-methylene-4-nitro-1-(5,6,7,8-tetrahydronaphthalen-2-yl)butan-1-one ***(3f)***. Following the general procedure for the RC reaction, the title compound was obtained as a yellow oil in 91% yield (80.7 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); IR (KBr, cm^{-1}) 1650 (C=O), 1551 (NO_2), 1376 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 2H, C_6H_3), 7.16 -7.01 (m, 1H, C_6H_3), 5.82 (d, *J* = 0.5 Hz, 1H, CH_2=C), 5.70 (s, 1H, CH_2=C), 5.20 – 4.91 (m, 2H, CH_2), 4.62 (dd, *J* = 8.7, 5.8 Hz, 1H, CH), 4.17 – 4.11 (overlapped m, 3H, C_5H_4), 4.15 (overlapped s, 5H, C_5H_5), 4.11 – 4.05 (m, 1H, C_5H_4), 2.86 – 8.69 (m, 4H, 2 × CH_2), 1.85 – 1.71 (m, 4H, 2 × CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.5, 146.7, 142.7, 137.3, 134.6, 130.4, 128.8, 127.1, 126.8, 86.6, 79.0, 69.0, 68.0, 66.4, 41.7, 29.6, 29.4, 23.0, 22.9. Anal. Calcd for $C_{25}H_{25}FeNO_3$: C, 67.73; H, 5.68; Fe, 12.60; N, 3.16; O, 10.83. Found: C, 67.80; H, 5.70; N, 3.17.

Following the general procedure for the RC reaction between **1** and **2g** (see page S13), the product mixture was obtained in a total yield of 56% (44.3 mg) after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1). ^{1}H NMR analysis of the mixture showed the presence of both cross-coupling products **3g** and **3g'** (the ratio was 70:30 for **3g** and **3g'**, respectively). Product separation was not possible. Pure product **3g** (26.9 mg, 34%) was isolated by column chromatography on silica gel (toluene), while **3g'** could not be separated.

3-Ferrocenyl-2-methylene-4-nitro-1-(thiophen-2-yl)butan-1-one ***(3g)***. Yellow solid: mp 102 – 104 °C; IR (KBr, cm^{-1}) 1639 (C=O), 1543 (NO_2), 1379 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 4.9, 1.2 Hz, 1H, C_4H_3S), 7.61 (dd, *J* = 3.8, 1.2 Hz, 1H, C_4H_3S), 7.11 (dd, *J* = 4.9, 3.8 Hz, 1H, C_4H_3S), 5.92 (s, 1H, CH_2=C), 5.79 (d, *J* = 0.8 Hz, 1H, CH_2=C), 5.17 – 4.90 (m, 2H, CH_2), 4.58 (dd, *J* = 8.8, 5.6 Hz, 1H, CH), 4.19 – 4.10 (overlapped m, 3H, C_5H_4), 4.13 (overlapped s, 5H, C_5H_5), 4.09 – 4.05 (m, 1H, C_5H_4); ^{13}C NMR (50 MHz, $CDCl_3$) δ 188.0, 146.8, 143.1, 134.4, 134.1, 127.9, 125.5, 86.1, 78.9, 69.0, 68.1, 68.0, 66.4, 42.2. Anal. Calcd for $C_{19}H_{17}FeNO_3S$: C, 57.74; H, 4.34; Fe, 14.13; N, 3.54; O, 12.14; S, 8.11. Found: C, 57.83; H, 4.35; N, 3.53.

*5-(4-Ferrocenyl)-4-nitro-1-(thiophen-2-yl)pent-4-en-1-one (**3g'**)* Dark purple solid; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.01 (s, 1H, CH=C), 7.80 (dd, *J* = 3.8, 1.1 Hz, 1H, C_4H_3S), 7.69 (dd, *J* = 5.0, 1.1 Hz, 1H, C_4H_3S), 7.17 (dd, *J* = 5.0, 3.8 Hz, 1H, C_4H_3S), 4.69 – 4.62 (m, 2H, C_5H_4), 4.63 – 4.57 (m, 2H, C_5H_4), 4.22 (s, 5H, C_5H_5), 3.31 – 3.15 (m, 4H, CH_2CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.2, 145.0, 143.6, 137.1, 134.0, 132.3, 128.2, 74.4, 72.6, 71.3, 69.9, 36.8, 23.2.

*3-Ferrocenyl-2-methylene-1-(naphthalen-2-yl)-4-nitrobutan-1-one (**3h**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow oil in 72% yield (63.2 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 95:5); IR (KBr, cm^{-1}) 1651 (C=O), 1550 (NO_2), 1377 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.18 (br s, 1H, $C_{10}H_7$), 7.96 – 7.76 (m, 4H, $C_{10}H_7$), 7.64 – 7.49 (m, 2H, $C_{10}H_7$), 5.92 (d, *J* = 0.6 Hz, 1H, CH_2=C), 5.78 (s, 1H, CH_2=C), 5.23 – 5.00 (m, 2H, CH_2), 4.69 (dd, *J* = 8.8, 5.6 Hz, 1H, CH), 4.22 – 4.14 (overlapped m, 3H, C_5H_4), 4.18 (overlapped s, 5H, C_5H_5), 4.14 – 4.10 (m, 1H, C_5H_4); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.5, 146.8, 135.3, 134.5, 132.1, 131.3, 129.4, 128.3, 128.2, 127.8, 127.7, 126.7, 125.3, 86.5, 78.9, 69.0, 68.1, 66.3, 41.7. Anal. Calcd for $C_{25}H_{21}FeNO_3$: C, 68.35; H, 4.82; Fe, 12.71; N, 3.19; O, 10.93. Found: C, 68.49; H, 4.84 N, 3.18.

*3-Ferrocenyl-1-(6-methoxynaphthalen-2-yl)-2-methylene-4-nitrobutan-1-one (**3i**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow oil in 81% yield (76.0 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); IR (KBr, cm^{-1}) 1622 (C=O), 1551 (NO_2), 1378 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.13 (br s, 1H, $C_{10}H_6$), 7.88 – 7.68 (m, 3H, $C_{10}H_6$), 7.23 – 7.09 (m, 2H, $C_{10}H_6$), 5.88 (s, 1H, CH_2=C), 5.75 (s, 1H, CH_2=C), 5.23 – 4.99 (m, 2H, CH_2), 4.67 (dd, *J* = 8.8, 5.6 Hz, 1H, CH), 4.20 – 4.14 (overlapped m, 3H, C_5H_4), 4.17 (overlapped s, 5H, C_5H_5), 4.14 – 4.08 (m, 1H, C_5H_4), 3.94 (s, 3H, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.3, 159.7, 146.8, 137.1, 132.4, 131.4, 131.0, 127.5, 126.9, 126.0, 119.7, 105.8, 86.6, 79.0, 69.0, 68.1, 66.3, 55.5, 41.9. Anal. Calcd for $C_{26}H_{23}FeNO_4$: C, 66.54; H, 4.94; Fe, 11.90; N, 2.98; O, 13.64. Found: C, 66.47; H, 4.96; N, 2.99.

*1,3-Diferrocenyl-2-methylene-4-nitrobutan-1-one (**3j**)*. Following the general procedure for the RC reaction, the title compound was obtained as an orange solid in 51% yield (50.7 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 95:5); mp 157 – 160 °C; IR (KBr, cm^{-1}) 1630 (C=O), 1544 (NO_2), 1380 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.03 (s, 1H, CH_2=C), 5.72 (s, 1H, CH_2=C), 5.25 – 4.99 (m, 2H, CH_2), 4.83 (dt, *J* = 2.6, 1.3 Hz, 1H, C_5H_4), 4.65 (dt, *J* = 2.6, 1.3 Hz, 1H, C_5H_4), 4.53 – 4.44 (overlapped m, 3H, CH and C_5H_4), 4.20 – 4.11 (overlapped m, 4H, C_5H_4), 4.16 (overlapped s, 5H, C_5H_5), 4.08 (s, 5H, C_5H_5); ^{13}C NMR (50 MHz, $CDCl_3$) δ

199.0, 147.6, 124.6, 86.7, 79.3, 78.4, 72.2, 71.8, 70.3, 70.1, 69.0, 68.4, 68.1, 67.9, 66.7, 42.8. Anal. Calcd for $C_{25}H_{23}Fe_2NO_3$: C, 60.40; H, 4.66; Fe, 22.47; N, 2.82; O, 9.65. Found: C, 60.29; H, 4.68; N, 2.82.

*4-(4-Methoxyphenyl)-3-methylene-5-nitropentan-2-one (**5b**)*. Following the general procedure for the RC reaction, the title compound was obtained as a white solid in 18% yield (9.0 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); mp 100 – 102 °C; IR (KBr, cm^{-1}) 1675 (C=O), 1548 (NO_2), 1382 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 2H, C_6H_4), 6.91 – 6.80 (m, 2H, C_6H_4), 6.24 (d, *J* = 0.7 Hz, 1H, CH_2=C), 5.89 (s, 1H, CH_2=C), 4.94 – 4.65 (m, 3H, $CHCH_2$), 3.78 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.9, 159.0, 147.3, 129.1, 128.9, 126.3, 114.3, 77.8, 55.3, 43.2, 26.2. Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62; O, 25.67. Found: C, 62.59; H, 6.09; N, 5.60.

*4-(4-(Dimethylamino)phenyl)-3-methylene-5-nitropentan-2-one (**5c**).* Following the general procedure for the RC reaction, the title compound was obtained as a yellow solid in 25% yield (13.1 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); mp 91 – 93 °C; IR (KBr, cm^{-1}) 1671 (C=O), 1546 (NO_2), 1375 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 2H, C_6H_4), 6.75 – 6.55 (m, 2H, C_6H_4), 6.21 (s, 1H, CH_2=C), 5.88 (s, 1H, CH_2=C), 4.95 – 4.60 (m, 3H, $CHCH_2$), 2.92 (s, 6H, $N(CH_3)_2$), 2.32 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.1, 150.0, 147.6, 128.5, 125.9, 124.5, 112.7, 78.0, 43.2, 40.4, 26.3. Anal. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.11; H, 6.92; N, 10.68; O, 18.30. Found: C, 64.21; H, 6.94 N, 10.70.

*3-Methylene-4-(naphthalen-1-yl)-5-nitropentan-2-one (**5d**).* Following the general procedure for the RC reaction, the title compound was obtained as a white solid in 53% yield (28.5 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); mp 100 – 102 °C; IR (KBr, cm^{-1}) 1672 (C=O), 1551 (NO_2), 1378 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 1H, 1-Naph), 7.91 – 7.83 (m, 1H, 1-Naph), 7.79 (br d, *J* = 8.1 Hz, 1H, 1-Naph), 7.63 – 7.30 (m, 4H, 1-Naph), 6.31 (s, 1H CH_2=C), 5.85 (overlapped s, 1H, CH_2=C), 5.84 (overlapped t, *J* = 7.7 Hz, 1H, $CHCH_2$), 4.88 (dd, *J* = 7.9, 1.1 Hz, 2H, $CHCH_2$), 2.38 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.8, 147.1, 134.3, 133.4, 131.0, 129.0, 128.6, 127.9, 126.9, 126.1, 125.0, 124.0, 122.8, 76.9, 38.5, 26.1. Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20; O, 17.82. Found: C, 71.45; H, 5.63; N, 5.19.

*4-(Anthracen-9-yl)-3-methylene-5-nitropentan-2-one (**5e**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow solid in 32% yield (20.4 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); mp 103 – 105 °C; IR (KBr,

cm^{-1}) 1664 (C=O), 1554 (NO_2), 1377 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 8.46 (s, 1H, 9-Ant), 8.36 – 7.76 (m, 4H, 9-Ant), 7.60 – 7.41 (m, 4H, 9-Ant), 6.43 (ddt, *J* = 7.5, 5.4, 2.1 Hz, 1H, $CHCH_2$), 6.29 (dd, *J* = 2.1, 0.8 Hz, 1H, CH_2=C), 5.75 (dd, *J* = 2.2, 0.8 Hz, 1H, CH_2=C), 5.46 (dd, *J* = 14.0, 6.8 Hz, 1H, CH_2NO_2), 4.94 (dd, *J* = 14.0, 5.4 Hz, 1H, CH_2NO_2), 2.36 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.0, 147.8, 131.8, 130.2, 129.7, 129.5, 128.8, 127.0, 126.5, 124.9, 124.1, 78.1, 38.7, 26.6. Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39; O, 15.03. Found: C, 75.34; H, 5.39; N, 4.38.

*3-Methylene-5-nitro-4-(o-tolyl)pentan-2-one (**5f**)*. Following the general procedure for the RC reaction, the title compound was obtained as a white solid in 30% yield (14.0 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8:2); IR (KBr, cm^{-1}) 1680 (C=O), 1554 (NO_2), 1376 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 7.21 – 7.06 (m, 4H, *o*-Tol), 6.29 (s, 1H, CH_2=C), 5.84 (s, 1H, CH_2=C), 5.15 (t, *J* = 8.0 Hz, 1H, $CHCH_2$), 4.82 (dd, *J* = 13.2, 7.9 Hz, 1H, CH_2NO_2), 4.65 (dd, *J* = 13.2, 8.0 Hz, 1H, CH_2NO_2), 2.39 (s, 3H, CH_3), 2.35 (s, 3H CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.8, 147.0, 136.7, 135.4, 131.2, 127.6, 127.0, 126.3, 126.0, 77.2, 39.3, 26.1, 19.4. Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00; O, 20.58. Found: C, 67.03 H, 6.50; N, 5.99.

*4-(4-Methoxyphenyl)-3-methylene-5-nitrononane-2,8-dione (**6b**).* Following the general procedure for the RC reaction, the title compound was obtained as a colorless oil in 26% yield (16.6 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); IR (KBr, cm^{-1}) 1718 (C=O), 1679 (C=O), 1551 (NO_2), 1366 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H, C_6H_4), 6.90 – 6.79 (m, 2H, C_6H_4), 6.13 (d, *J* = 1.0 Hz, 1H, CH_2=C), 6.08 (t, *J* = 0.8 Hz, 1H, CH_2=C), 5.20 (ddd, *J* = 11.8, 9.9, 4.0 Hz, 1H, $CHNO_2$), 4.53 (d, *J* = 11.8 Hz, 1H, CH), 3.77 (s, 3H, OCH_3), 2.49 – 2.37 (m, 2H, CH_2CH_2), 2.24 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.07 – 1.81 (m, 2H, CH_2CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.9, 197.5, 159.1, 147.8, 129.7, 128.8, 124.5, 114.4, 89.3, 55.3, 48.0, 38.8, 29.9, 26.6, 25.9. Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39; O, 25.05. Found: C, 64.01; H, 63.96; N, 4.39.

*4-(4-(Dimethylamino)phenyl)-3-methylene-5-nitrononane-2,8-dione (**6c**).* Following the general procedure for the RC reaction, the title compound was obtained as a colorless oil in 22% yield (14.6 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); IR (KBr, cm^{-1}) 1717 (C=O), 1680 (C=O), 1549 (NO_2), 1356 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 7.18 – 7.07 (m, 2H, C_6H_4), 6.71 – 6.58 (m, 2H, C_6H_4), 6.11 (d, *J* = 0.9 Hz, 1H, CH_2=C), 6.05 (br s, 1H, CH_2=C), 5.18 (ddd, *J* = 11.8, 10.1, 3.8 Hz, 1H, $CHNO_2$), 4.49 (d, *J* = 11.8 Hz, 1H, CH), 2.92 (s, 6H,

$N(CH_3)_2$), 2.40 (dd, *J* = 14.3, 7.7 Hz, 2H, CH_2CH_2), 2.23 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.06 – 1.76 (m, 2H, CH_2CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.0, 197.6, 149.9, 148.0, 129.2, 124.0, 123.9, 112.7, 89.5, 47.9, 40.4, 38.9, 30.0, 26.7, 26.0. Anal. Calcd for $C_{18}H_{24}N_2O_4$: C, 65.04; H, 7.28; N, 8.43; O, 19.25. Found: C, 65.21; H, 7.30; N, 8.46.

*3-Methylene-4-(naphthalen-1-yl)-5-nitrononane-2,8-dione (**6d**).* Following the general procedure for the RC reaction, the title compound was obtained as a colorless oil in 15% yield (10.2 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); IR (KBr, cm^{-1}) 1717 (C=O), 1681 (C=O), 1550 (NO_2), 1363 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.5 Hz, 1H, 1-Naph), 7.85 (dd, *J* = 8.0, 1.5 Hz, 1H, 1-Naph), 7.81 – 7.75 (m, 1H, 1-Naph), 7.62 (ddd, *J* = 8.5, 6.8, 1.6 Hz, 1H, 1-Naph), 7.53 (dd, *J* = 6.8, 1.3 Hz, 1H, 1-Naph), 7.48 (d, *J* = 1.7 Hz, 1H, 1-Naph), 7.45 (br s, 1H, 1-Naph), 6.25 (d, *J* = 1.1 Hz, 1H, CH_2=C), 6.21 (br s, 1H, CH_2=C), 5.61 (d, *J* = 11.4 Hz, 1H, CH), 5.43 – 5.28 (m, 1H, $CHNO_2$), 2.42 – 2.32 (m, 2H, CH_2CH_2), 2.23 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.98 – 1.80 (m, 2H, CH_2CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.9, 197.7, 148.0, 134.2, 133.5, 132.1, 128.9, 128.5, 126.8, 126.0, 125.8, 125.4, 125.2, 123.6, 90.8, 42.2, 38.8, 29.9, 26.4, 26.0. Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13; O, 18.86. Found: C, 70.88; H, 6.27; N, 4.12.

*4-(Anthracen-9-yl)-3-methylene-5-nitrononane-2,8-dione (**6e**)*. Following the general procedure for the RC reaction, the title compound was obtained as a yellow solid in 19% yield (14.8 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1); IR (KBr, cm^{-1}) 1717 (C=O), 1677 (C=O), 1548 (NO_2), 1362 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 8.80 (d, *J* = 9.0 Hz, 1H, 9-Ant), 8.44 (s, 1H, 9-Ant), 8.28 (d, *J* = 8.6 Hz, 1H, 9-Ant), 8.06 – 7.96 (m, 2H, 9-Ant), 7.70 (ddd, *J* = 9.1, 6.5, 1.4 Hz, 1H, 9-Ant), 7.56 – 7.40 (m, 3H, 9-Ant), 6.41 – 6.29 (m, 3H, overlapped signals of CH_2=C and CH-Fc), 6.02 (td, *J* = 11.3, 3.5 Hz, 1H, $CHNO_2$), 2.29 – 2.14 (m, 2H, CH_2CH_2), 2.05 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.88 – 1.69 (m, 1H, CH_2CH_2), 1.52 – 1.34 (m, 1H, CH_2CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.5, 198.7, 148.6, 132.2, 131.8, 131.7, 130.2, 129.9, 129.4, 129.3, 127.1, 127.0, 125.9, 125.1, 124.9, 124.7, 124.2, 123.5, 88.6, 42.7, 38.6, 29.7, 26.4. Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60; O, 16.43. Found: C, 73.98; H, 5.97; N, 3.59.

*3-Methylene-5-nitro-4-(o-tolyl)nonane-2,8-dione (**6f**)*. Following the general procedure for the RC reaction, the title compound was obtained as a colorless oil in 20% yield (12.1 mg), after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8:2); IR (KBr, cm^{-1}) 1717 (C=O), 1681 (C=O), 1551 (NO_2), 1366 (NO_2);^1H NMR (200 MHz, $CDCl_3$) δ 7.24 – 7.05 (m, 4H, *o*-Tol),

6.21 (d, *J* = 1.1 Hz, 1H, CH_2=C), 6.14 (t, *J* = 0.9 Hz, 1H, CH_2=C), 5.16 (ddd, *J* = 11.6, 9.8, 4.1 Hz, 1H, $CHNO_2$), 4.90 (d, *J* = 11.6 Hz, 1H, CH), 2.57 (s, 3H, CH_3), 2.46 – 2.34 (m, 2H, CH_2CH_2), 2.24 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.01 – 1.82 (m, 2H CH_2CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.7, 197.7, 147.9, 137.7, 135.0, 131.2, 127.5, 127.1, 126.4, 125.2, 90.4, 43.6, 39.0, 29.9, 26.0, 25.8, 20.2. Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62; O, 21.10. Found: C, 67.42; H, 6.70; N, 4.61.

Following the general procedure for the RC reaction between **4g** and **2a**, the product mixture (17.1 mg) was obtained as a colorless oil after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1). The reaction efficiency (32%) was determined based on recovered **4g**. ^{1}H NMR analysis of the mixture showed the presence of both products **5g** and **6g** (the ratio was 82:18 for **5g** and **6g**, respectively). Product separation was not possible. *4-Mesityl-3-methylene-5-nitropentan-2-one (**5g**)*. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.83 (s, 2H, Mes), 6.24 (d, *J* = 1.7 Hz, 1H, CH_2=C,), 5.70 (d, *J* = 2.0 Hz, 1H, CH_2=C), 5.27 (tt, *J* = 7.6, 1.9 Hz, 1H, $CHCH_2$), 5.07 (dd, *J* = 13.1, 7.7 Hz, 1H, CH_2NO_2), 4.65 (dd, *J* = 13.1, 7.0 Hz, 1H, CH_2NO_2), 2.35 (s, 3H, CH_3), 2.32 (s, 6H, 2 × CH_3), 2.23 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.8, 146.6, 137.1, 130.8, 130.5, 126.4, 123.9, 87.5, 39.7, 26.6, 21.2, 20.7. *4-Mesityl-3-methylene-5-nitrononane-2,8-dione (**6g**)*. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.88 (s, 1H, Mes), 6.73 (s, 1H, Mes), 6.25 (overlapped signal of CH_2=C), 6.02 (t, *J* = 1.5 Hz, 1H, CH_2=C), 5.62 – 5.44 (m, 1H, $CHCHNO_2$), 5.18 – 5.07 (overlapped m, 1H, $CHCHNO_2$), 2.64 (s, 3H, CH_3), 2.45 – 2.17 (overlapped signals of one methylene group and three methyl groups), 2.10 (s, 3H, CH_3), 1.80 (dt, *J* = 8.4, 6.4 Hz, 2H, CH_2CH_2).

6-Ferrocenyl-5-nitrohex-5-en-2-one (***3a'**). Following the general procedure for the RC reaction using DBU or TMG as the catalyst during the optimization of reaction conditions, product **3a'** was isolated in low yield (<5%) as a dark purple solid; mp 82 – 83 °C; IR (KBr, cm^{-1}) 1711 (C=O), 1640 (C=C), 1503 (NO_2), 1294 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.96 (s, 1H, CH=C), 4.58 (s, 4H, C_5H_4), 4.22 (s, 5H, C_5H_5), 3.10 – 2.65 (m, 4H, CH_2CH_2), 2.24 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.6, 145.3, 136.6, 74.5, 72.5, 71.2, 69.9, 40.9, 30.0, 22.1.

X-ray analysis of compound 3j

Single-crystal X-ray diffraction data for compound **3j** were collected on a Gemini S (Oxford Diffraction) diffractometer with monochromatized Mo*Kα* radiation (*λ* = 0.71073 Å). Data reduction and empirical absorption correction were preformed with CrysAlisPro program package.[10] The crystal structure was solved by direct methods using SHELXS and refined on F2

by full-matrix least-squares using SHELXL.[11] All H atoms were placed in geometrically calculated positions and refined using the riding model. A structural analysis was carried out in PLATON[12] and Mercury[13] which was also used for molecular graphics. Crystallographic details are summarized in Table S2.

Control experiments

To a solution of RC adduct **5b** or **5b'** (12.5 mg, 0.05 mmol) and **2a** (4.2 mg, 5 µl, 0.06 mmol, 1.2 equiv.) in chloroform (0.25 ml), triphenylphosphine (2.6 mg, 20 mol%) was added. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and ^{1}H NMR analysis of the reaction mixtures showed that **5b** and **5b'** did not react with **2a** under the applied conditions.

Gram-scale synthesis of 3a

To a solution of nitroalkene **1** (1.285 g, 5 mmol, 1 equiv.) and methyl vinyl ketone **2a** (420.5 mg, 500 µl, 6 mmol, 1.2 equiv.) in chloroform (25 ml), triphenylphosphine (262.3 mg, 20 mol%) was added. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel with *n*-hexane/ethyl acetate = 9:1 as eluent. Product **3a** was isolated in 83% yield (1.357 g).

Synthetic transformations of product 3a

Thia-Michael addition. To a solution of **3a** (65.4 mg, 0.2 mmol, 1 equiv.) in DCM (2 ml) were added 1.5 equivalents of 4-chlorothiophenol (43.4 mg, 0.3 mmol) and 20 mol% of DABCO (4.5 mg). The reaction mixture was stirred at room temperature for 2 hours. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel with *n*-hexane/ethyl acetate = 9:1 as eluent. Product **8** was obtained as orange oil in 86% yield (81.1 mg). ^{1}H NMR analysis confirmed the presence of two diastereoisomers (d.r. >10:1).

*3-(((4-Chlorophenyl)thio)methyl)-4-ferrocenyl-5-nitropentan-2-one (major diastereoisomer **8**).* IR (KBr, cm^{-1}) 1713 (C=O), 1553 (NO_2), 1378 (NO_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H, C_6H_4), 7.08 – 6.98 (m, 2H, C_6H_4), 4.89 (dd, *J* = 13.5, 5.6 Hz, 1H, C**Ha**HbNO$_2$), 4.73 (dd, *J* = 13.5, 7.1 Hz, 1H CHa**Hb**NO$_2$), 4.25 (td, *J* = 2.5, 1.2 Hz, 1H, C_5H_4), 4.21 (td, *J* = 2.5, 1.3 Hz, 1H, C_5H_4), 4.14 (s, 5H, C_5H_5) 4.08 (dt, *J* = 2.5, 1.3 Hz, 1H, C_5H_4), 3.92 (dt, *J* = 2.5, 1.3 Hz, 1H,

C_5H_4), 3.79 (ddd, *J* = 7.1, 5.6, 3.9 Hz, 1H, $CHCH_2NO_2$), 3.04 (dd, *J* = 13.5, 10.8 Hz, 1H CHC**Ha**HbS), 2.88 (m, 2H, C**H**CHa**Hb**S), 2.03 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.2, 133.2, 132.7, 131.0, 129.2, 86.0, 76.4, 69.2, 68.4, 68.3, 66.0, 55.7, 39.2, 31.6, 31.1. Anal. Calcd for $C_{22}H_{23}FeNO_3S$: C, 60.42; H, 5.30; Fe, 12.77; N, 3.20; O, 10.97; S, 7.33. Found: C, 60.59; H, 5.32; N, 3.19.

Henry reaction. To a solution of **3a** (65.4 mg, 0.2 mmol, 1 equiv.) in DCM (0.5 ml), ethyl glyoxylate (0.12 ml, 0.6 mmol, 3 equiv., ~50% in toluene) was added followed by DBU (15.2 mg, 15 µl, 0.5 equiv.). The reaction mixture was stirred at room temperature for 30 minutes. After completion of the reaction, DCM (20 ml) was added and the organic layer was washed with 2% aqueous HCl, then with water and brine solution. The organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product **9** was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1 as eluent) and the corresponding *Z*/*E* isomers were separated. The total yield of **9** was 77% (*Z*/*E* = 2:1).

*Ethyl (Z)-4-ferrocenyl-5-methylene-3-nitro-6-oxohept-2-enoate ((Z)-**9**).* Following the procedure for the Henry reaction, (*Z*)-**9** was isolated as a yellow solid in 51% (42.2 mg). mp 86 – 87 °C; IR (KBr, cm^{-1}) 1729 (C=O), 1678 (C=O), 1536 (NO_2), 1351 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 6.35 (s, 1H, =C**H**$COOCH_2CH_3$), 5.87 (br s, 1H, CH_2=C), 5.66 (d, *J* = 1.3 Hz, 1H, CH_2=C), 5.40 (br s, 1H, CH_2=C-C**H**), 4.27 (td, *J* = 2.5, 1.3 Hz, 1H, C_5H_4), 4.24 – 4.12 (overlapped m, 2H, C_5H_4), 4.19 (overlapped q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 4.09 (s, 5H, C_5H_5), 3.89 (td, *J* = 2.4, 1.1 Hz, 1H, C_5H_4), 2.47 (s, 3H, CH_3), 1.26 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.5, 162.7, 160.7, 146.3, 128.5, 118.2, 84.1, 69.2, 68.9, 68.4, 67.35, 61.8, 41.4, 25.7, 13.8. Anal. Calcd for $C_{20}H_{23}FeNO_5$: C, 58.13; H, 5.61; Fe, 13.51; N, 3.39; O, 19.36. Found: C, 57.99; H, 5.59; N, 3.38.

*Ethyl (E)-4-ferrocenyl-5-methylene-3-nitro-6-oxohept-2-enoate ((E)-**9**).* Following the procedure for the Henry reaction, (*E*)-**9** was isolated as orange oil in 26% (21.2 mg). IR (KBr, cm^{-1}) 1729 (C=O), 1679 (C=O), 1534 (NO_2), 1337 (NO_2); ^1H NMR (200 MHz, $CDCl_3$) δ 7.01 (s, 1H, =C**H**$COOCH_2CH_3$), 6.18 (d, *J* = 1.4 Hz, 1H, CH_2=C), 5.94 (pseudo t, *J* = 1.3 Hz, 1H, CH_2=C), 5.75 (d, *J* = 1.8 Hz, 1H, CH_2=C-C**H**), 4.33 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 4.20 (pseudo t, *J* = 1.9 Hz, 2H, C_5H_4), 4.10 (s, 5H, C_5H_5), 4.07 – 4.03 (m, 1H, C_5H_4), 4.03 – 3.99 (m, 1H, C_5H_4), 2.35 (s, 3H, CH_3), 1.38 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.0, 163.9, 161.0, 148.2, 128.7, 121.7, 83.6, 69.9, 69.4, 68.5, 67.7, 67.3, 61.9, 38.4, 26.0, 14.1.

Crystallographic data of compound 3j

Table S1. Selected bond lengths (Å) and angles (°) for **3j**.

N(1)-O(2)	1.187(5)
N(1)-O(3)	1.213(5)
N(1)-C(4)	1.491(4)
O(1)-C(1)	1.213(4)
C(1)-C(6)	1.478(4)
C(1)-C(2)	1.496(4)
C(2)-C(5)	1.319(5)
C(2)-C(3)	1.525(4)
C(3)-C(4)	1.502(5)
C(3)-C(16)	1.518(4)
O(2)-N(1)-O(3)	123.5(4)
O(2)-N(1)-C(4)	120.1(4)
O(3)-N(1)-C(4)	116.4(4)
O(1)-C(1)-C(6)	121.4(3)
O(1)-C(1)-C(2)	119.8(3)
C(6)-C(1)-C(2)	118.8(3)
C(5)-C(2)-C(1)	121.7(3)
C(5)-C(2)-C(3)	119.1(3)
C(1)-C(2)-C(3)	118.9(3)
C(4)-C(3)-C(16)	110.1(3)
C(4)-C(3)-C(2)	112.4(3)
C(16)-C(3)-C(2)	112.8(2)
N(1)-C(4)-C(3)	113.3(3)
C(7)-C(6)-C(10)	107.3(3)
C(7)-C(6)-C(1)	129.3(3)
C(10)-C(6)-C(1)	123.3(3)

Table S2. Crystallographic data and structure refinement for **3j**.

Empirical formula	C_{25} H_{23} Fe_2 N O_3
Formula weight	497.14
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P1*−
Unit cell dimensions	
a (Å)	5.89550(10)
b (Å)	12.6957(3)
c (Å)	15.6399(4)
α (°)	66.206(2)
β (°)	86.515(2)
γ (°)	80.988(2)
V (Å^3)	1057.88(4)
Z	2
D_{calc} (Mg/m^3)	1.561
μ (mm^{-1})	1.399
F(000)	512
Crystal size (mm^3)	0.15 x 0.32 x 0.52
Color, shape	Orange, prism
θ range for data collection (°)	2.68 to 26.39
Index ranges	−7<=h<=5, −15<=k<=15, −19<=l<=19
Reflections collected	16769
Independent reflections, R_{int}	4350 [R(int) = 0.0172]
Completeness to θ = 26.37°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4350 / 0 / 280
Goodness-of-fit on F^2	1.272
Final R_1/wR_2 indices [I >2σ(I)]	0.0364, 0.0937
Final R_1/wR_2 indices (all data)	0.0386, 0.0946
Largest diff. peak and hole (e Å^{-3})	0.573 and −0.303

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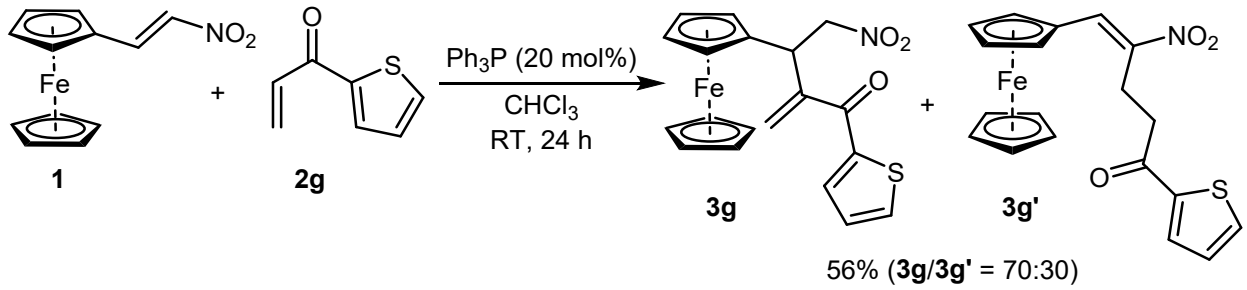
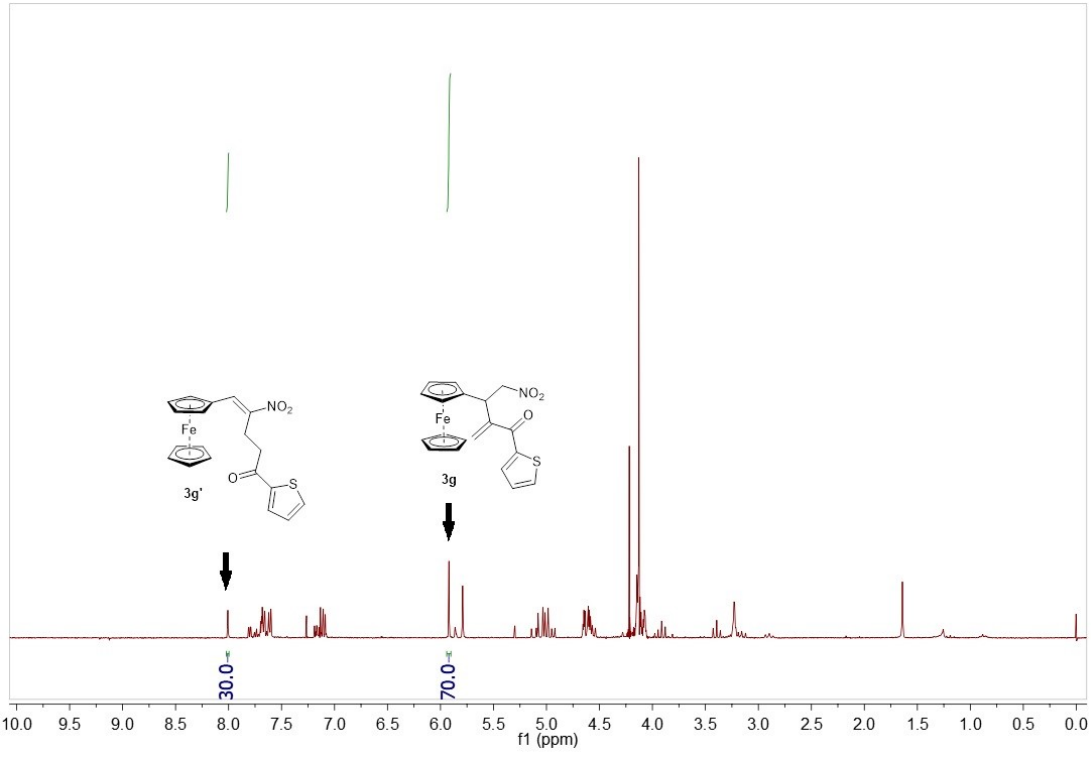
^{1}H NMR analysis of cross RC reaction between 1 and 2g



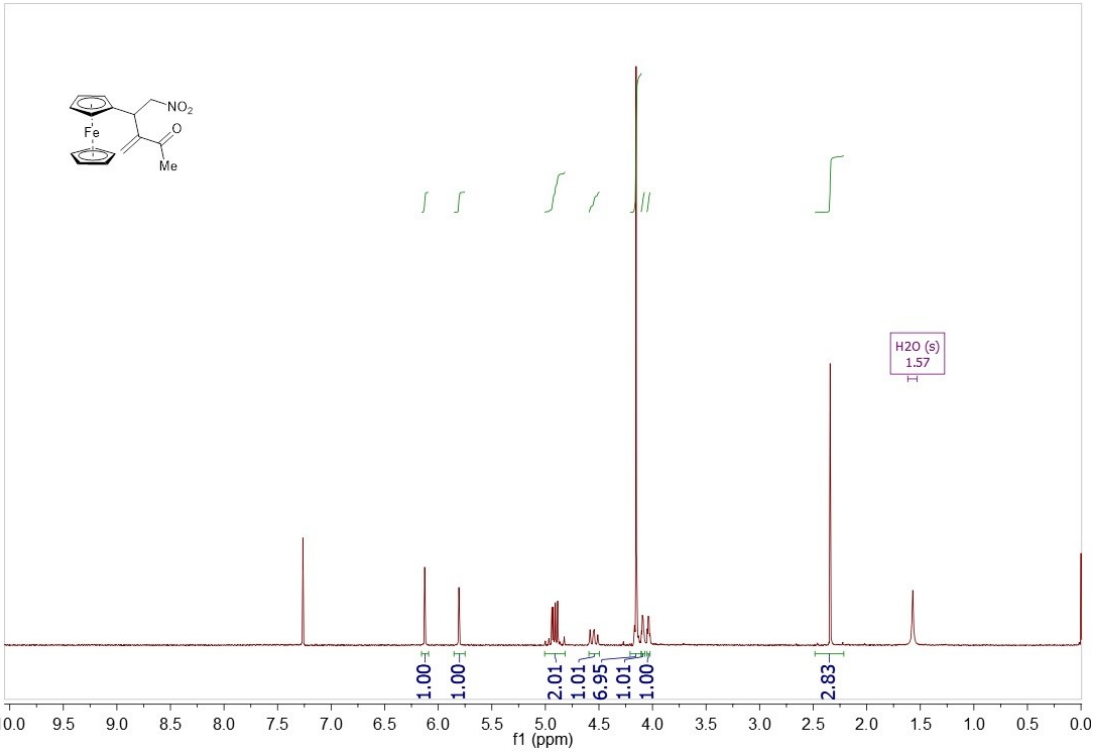
Scheme S1. Cross RC reaction between nitroalkene 1 and 2-thienyl vinyl ketone (2g)

The RC reaction between **1** and **2g** gave the product mixture in a total yield of 56% after flash chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1). ^{1}H NMR analysis of the product mixture showed the presence of both cross-coupling products **3g** and **3g'** (the ratio was 70:30 for **3g** and **3g'**, respectively). The ratio was determined based on the chemical shifts of hydrogen atoms bound to the carbon of the double bond. These signals appeared at different chemical shifts (8.01 and 5.92 ppm for **3g** and **3g'**, respectively) as singlets. Product separation was not possible. Pure product **3g** was isolated by column chromatography on silica gel (toluene), while **3g'** could not be separated.

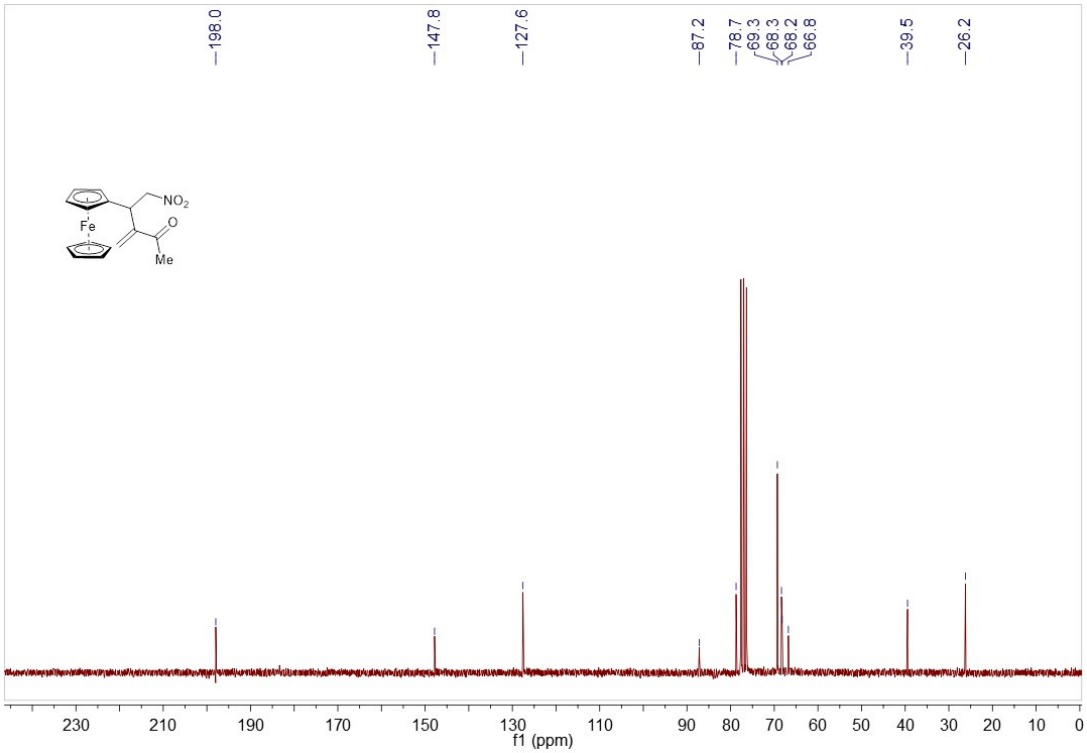


^{1}H NMR (200 MHz, $CDCl_3$) spectrum of product mixture

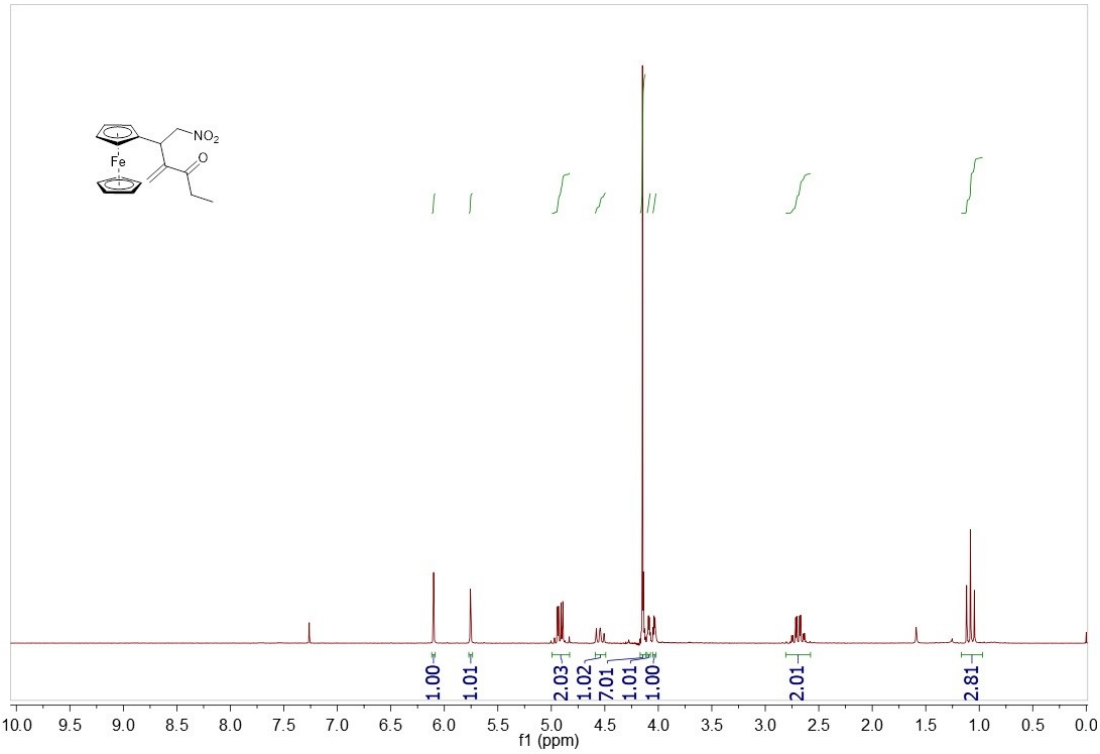
^{1}H and ^{13}C NMR spectra



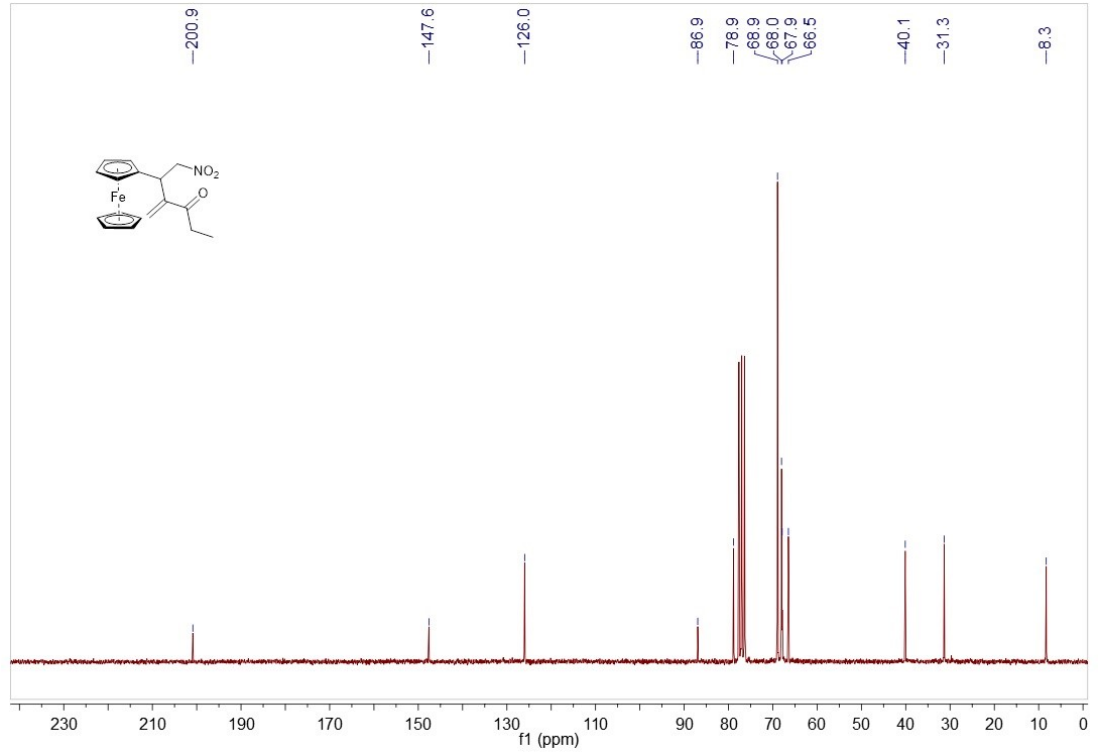
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3a**



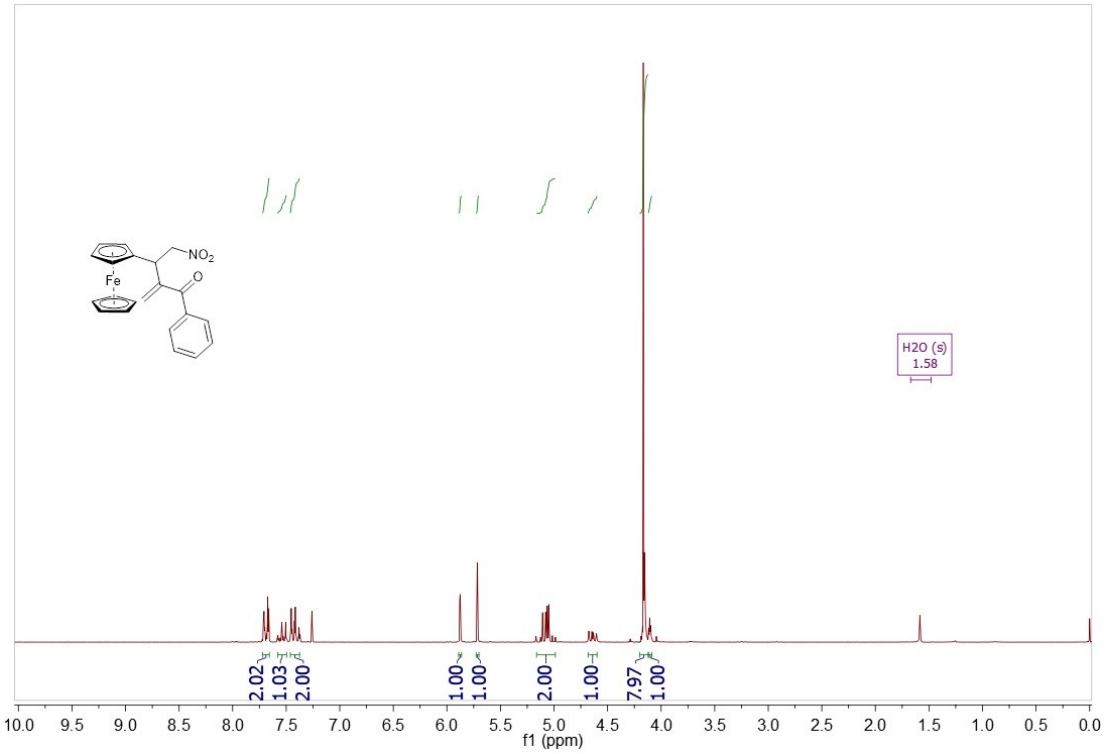
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3a**



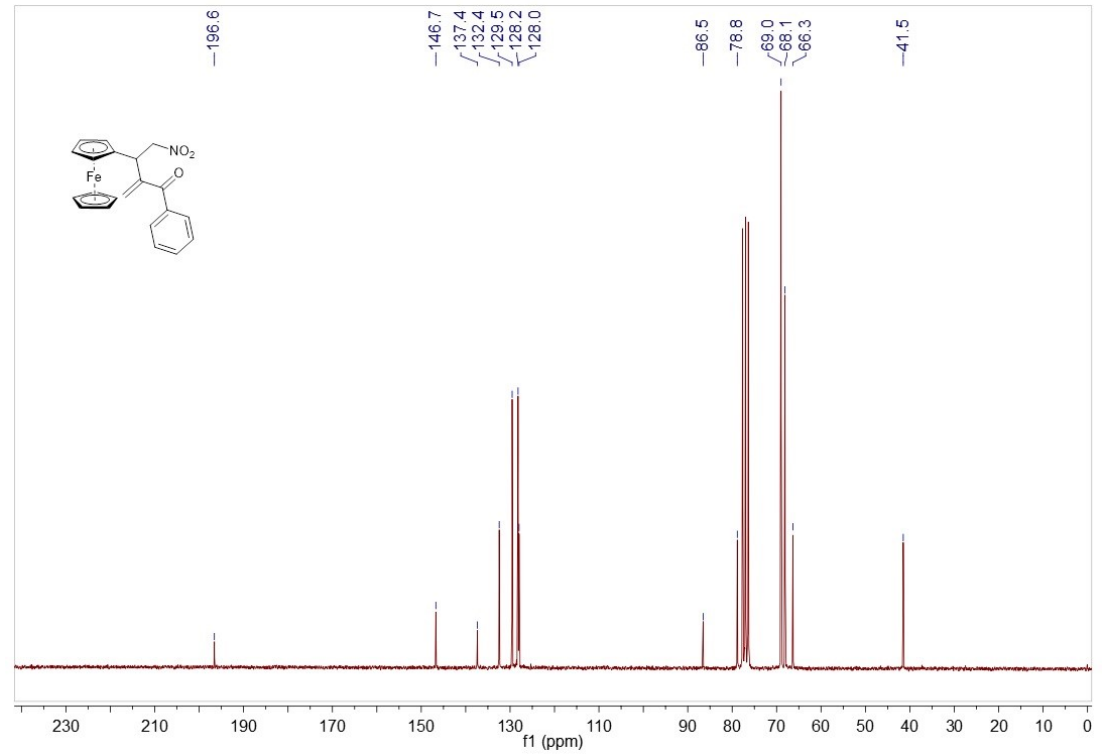
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3b**



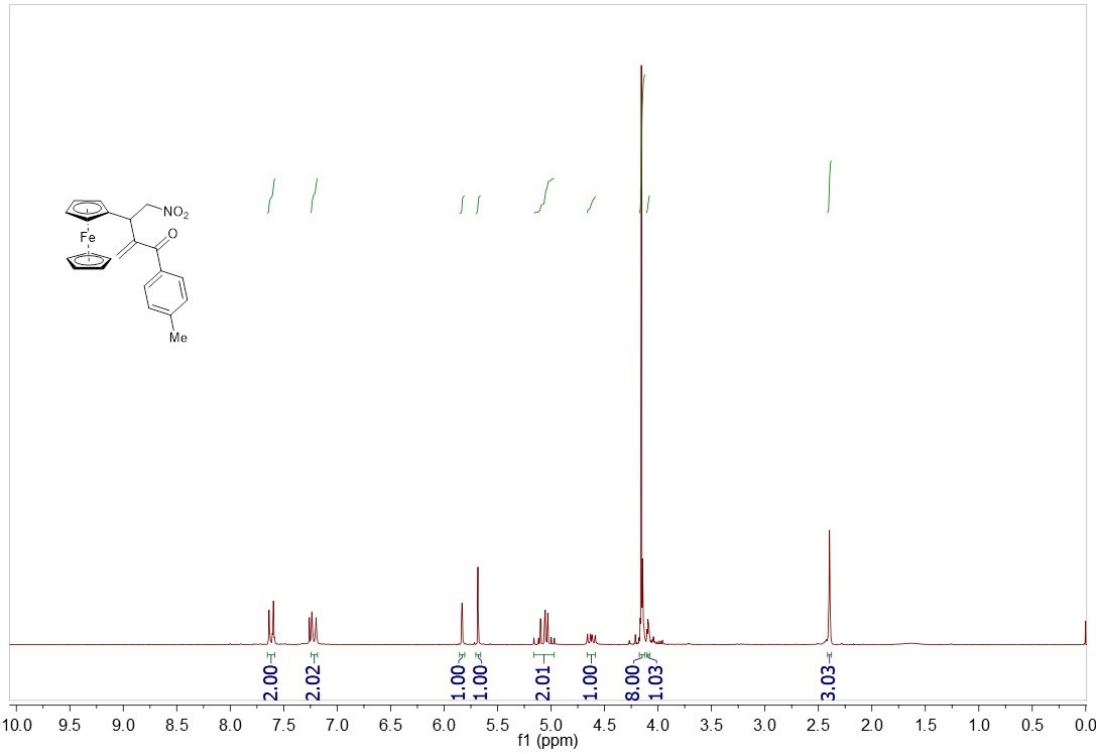
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3b**



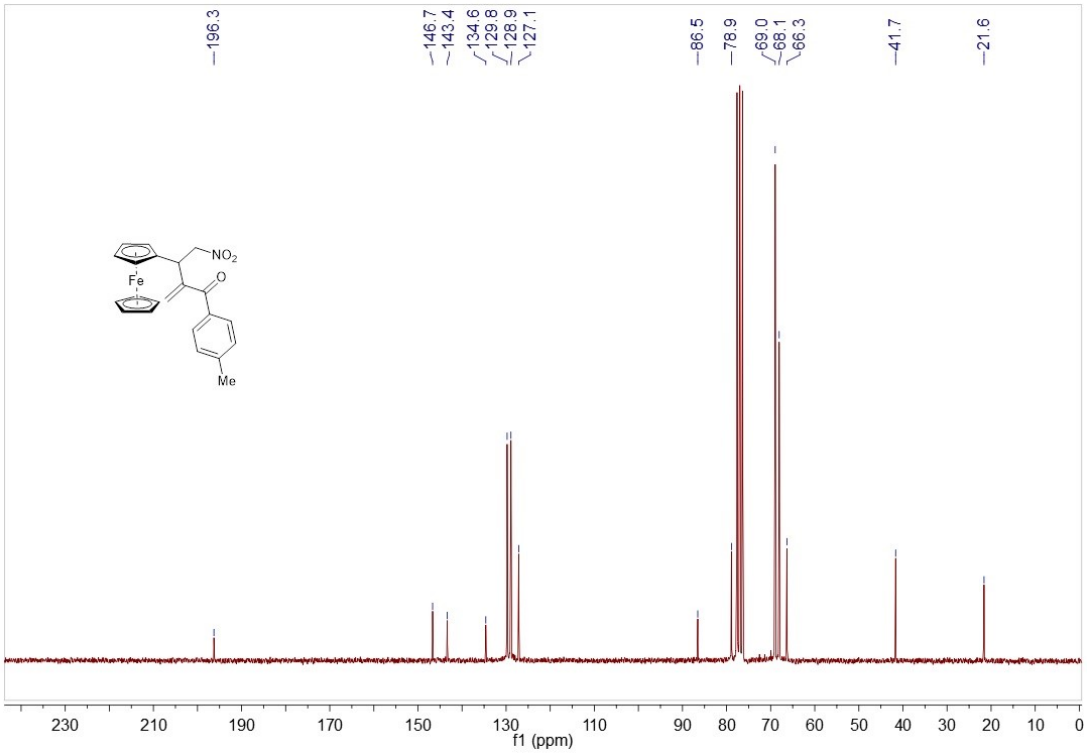
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3c**



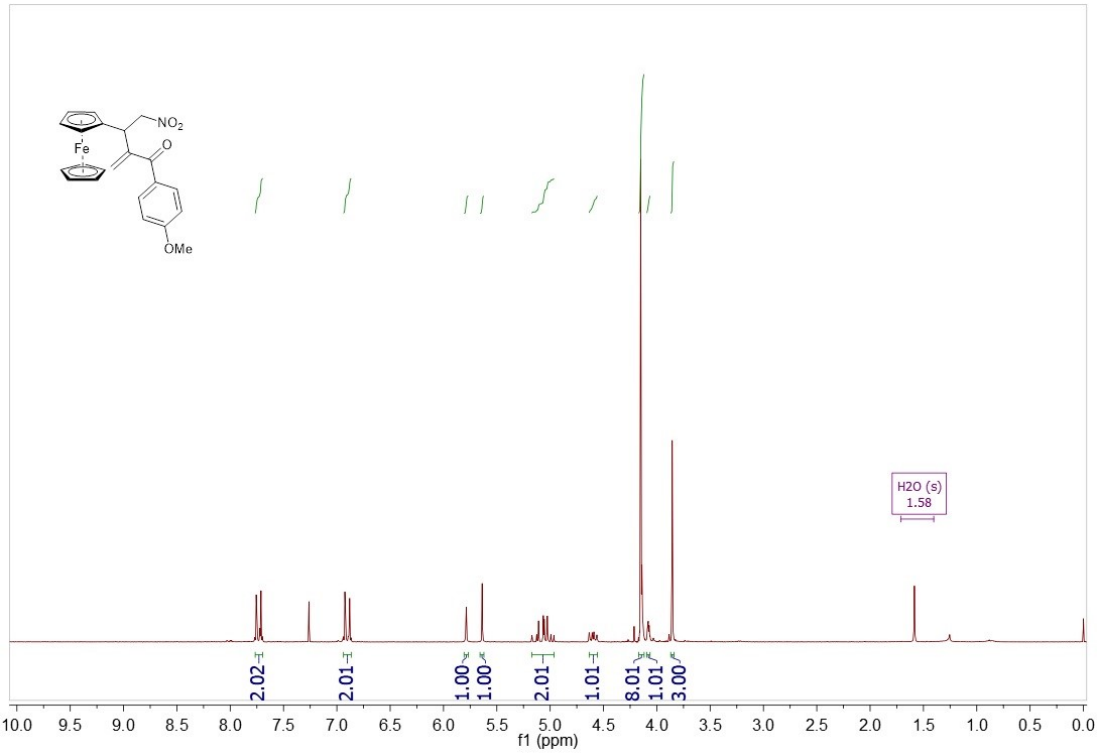
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3c**



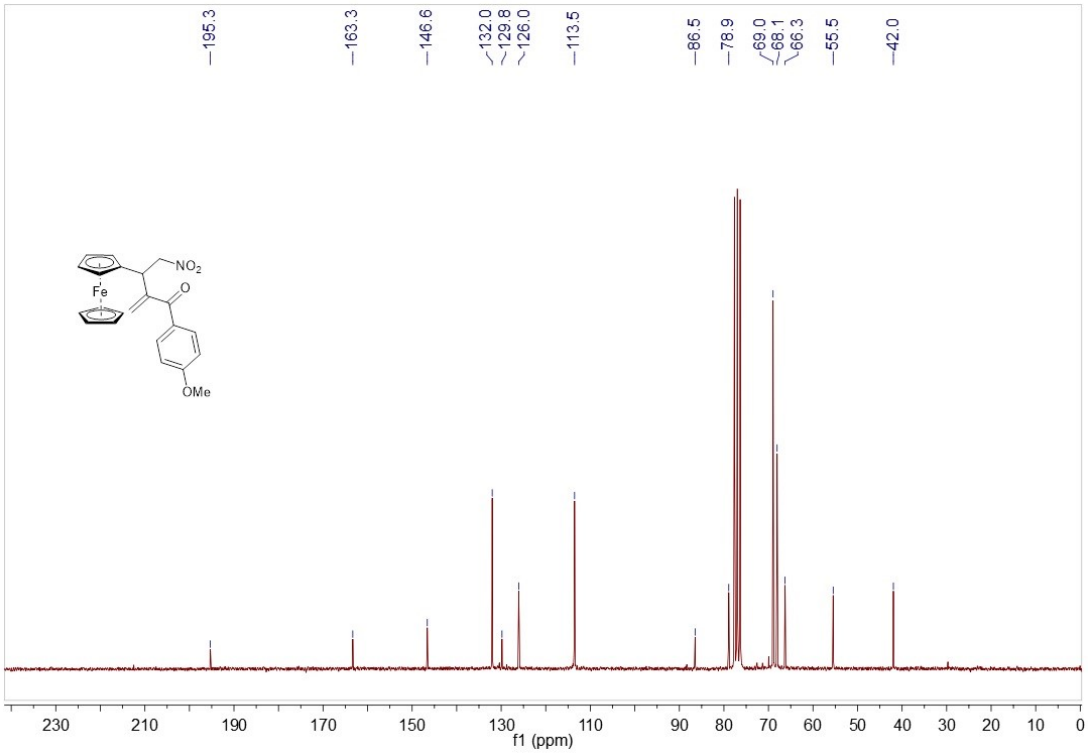
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3d**



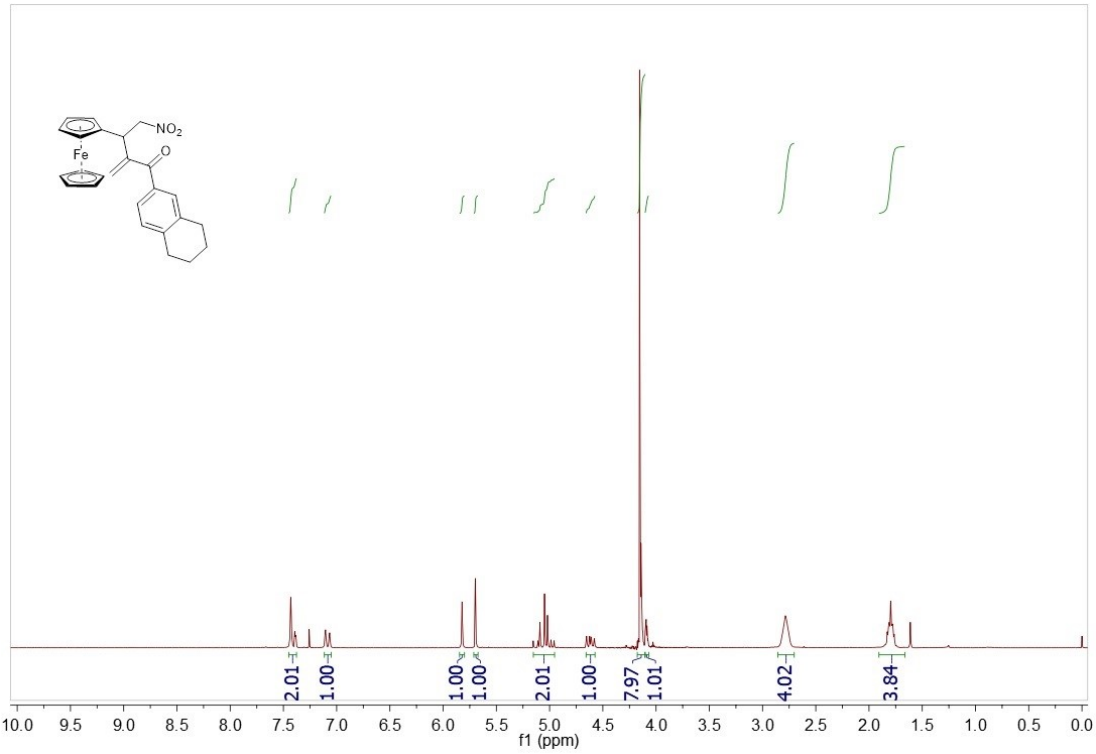
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3d**



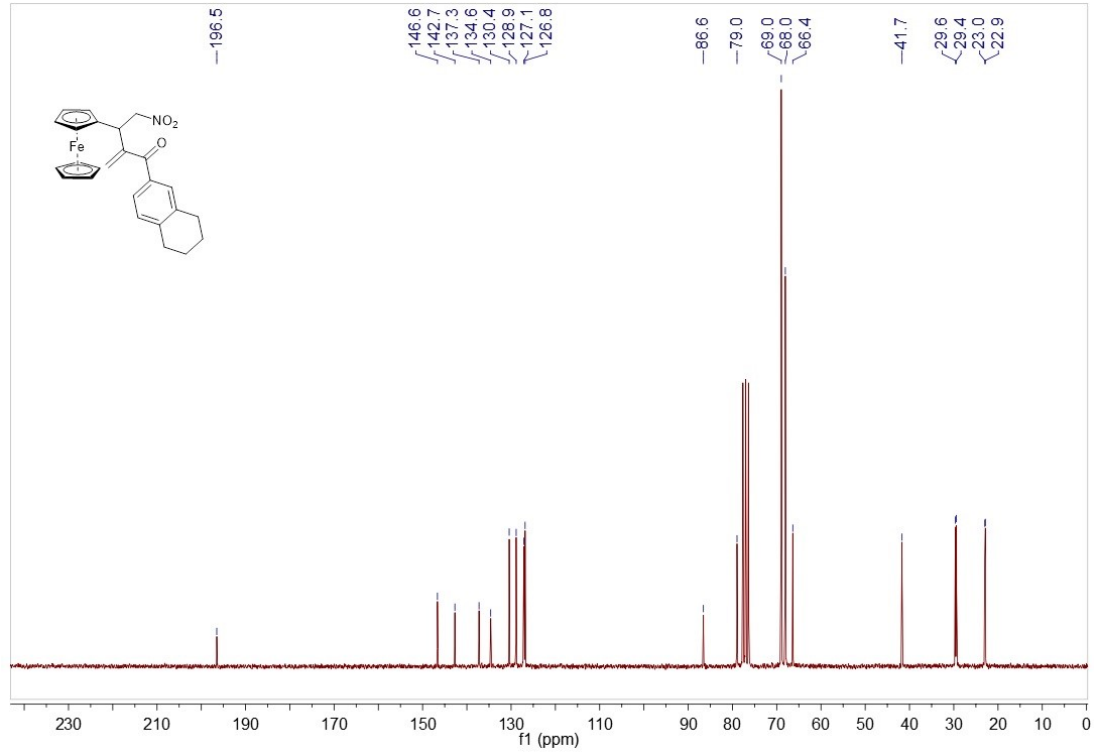
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3e**



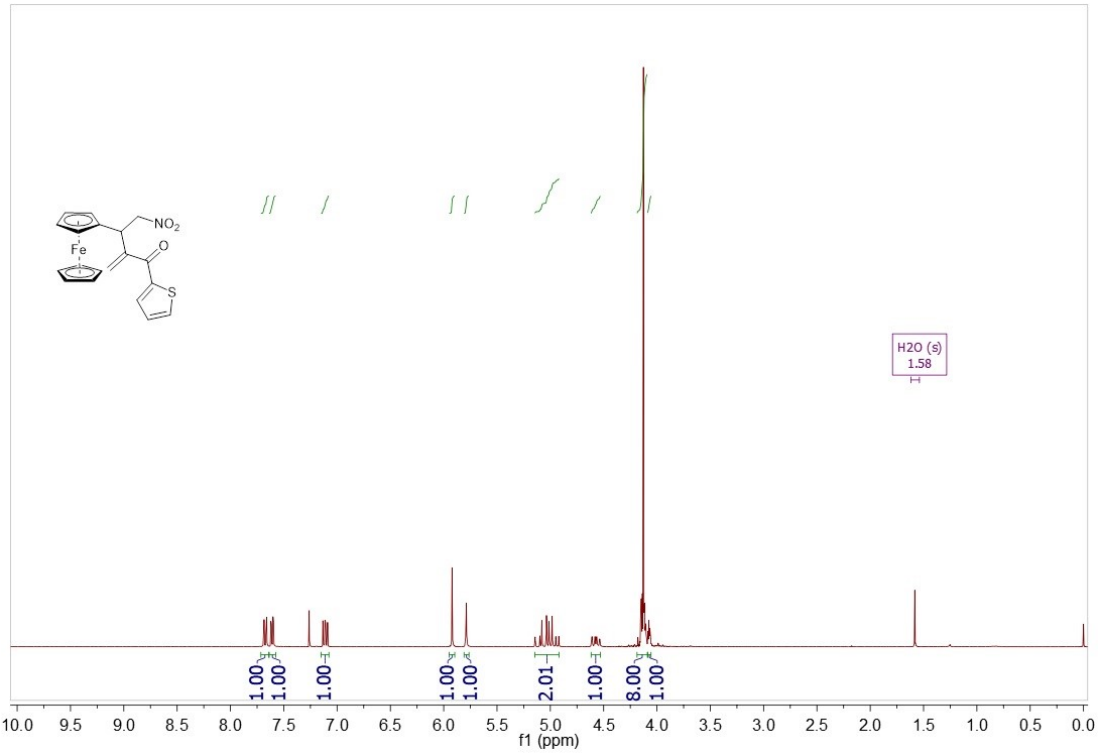
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3e**



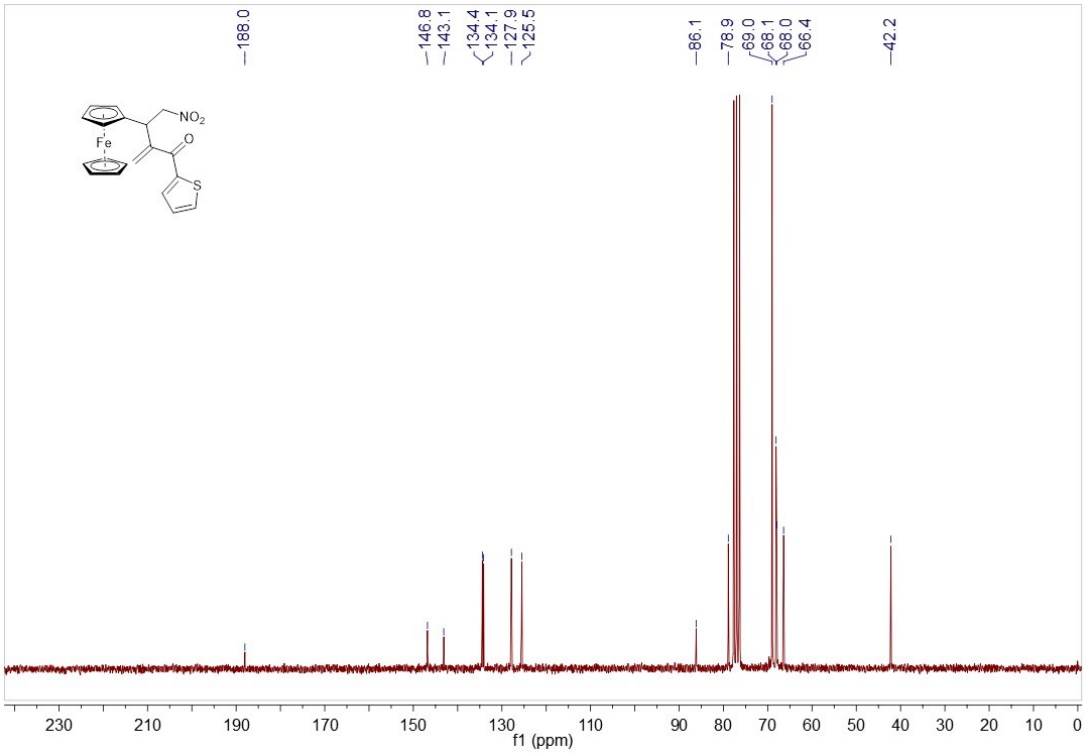
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3f**



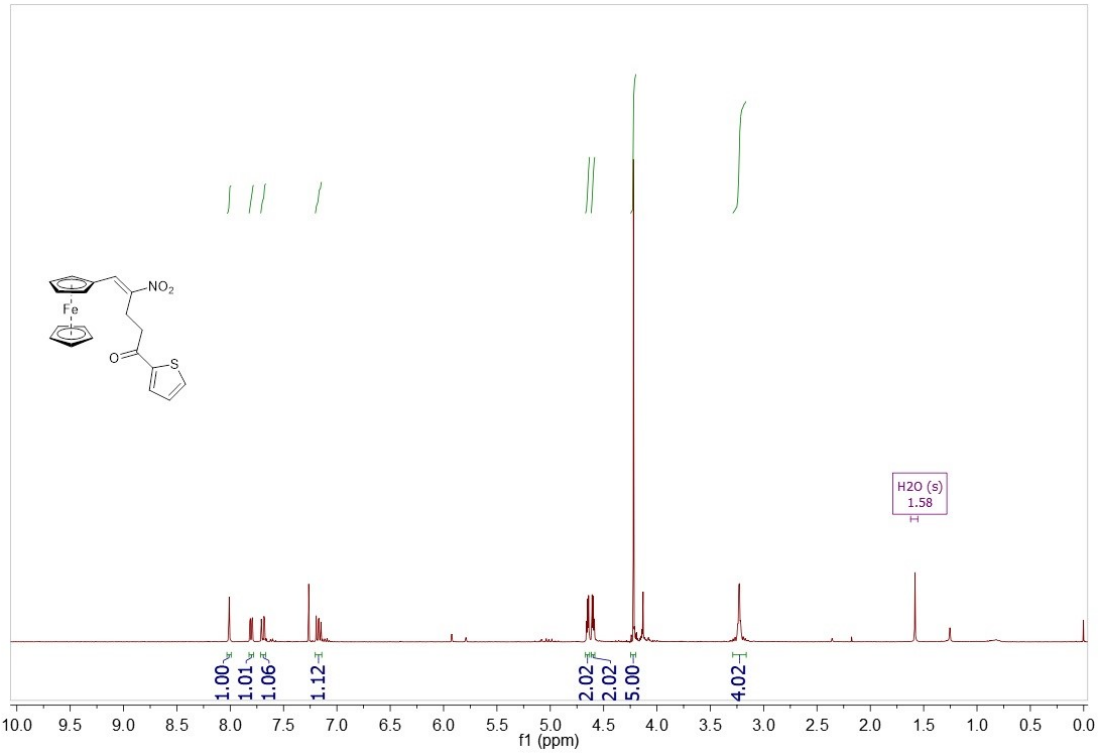
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3f**



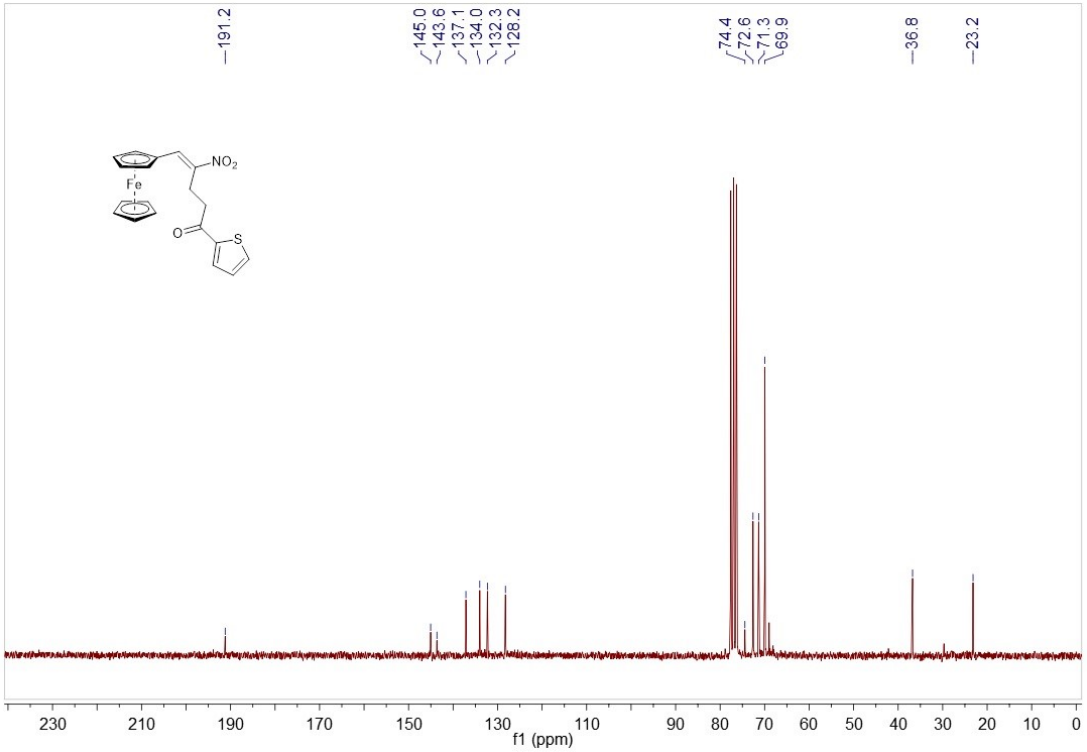
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3g**



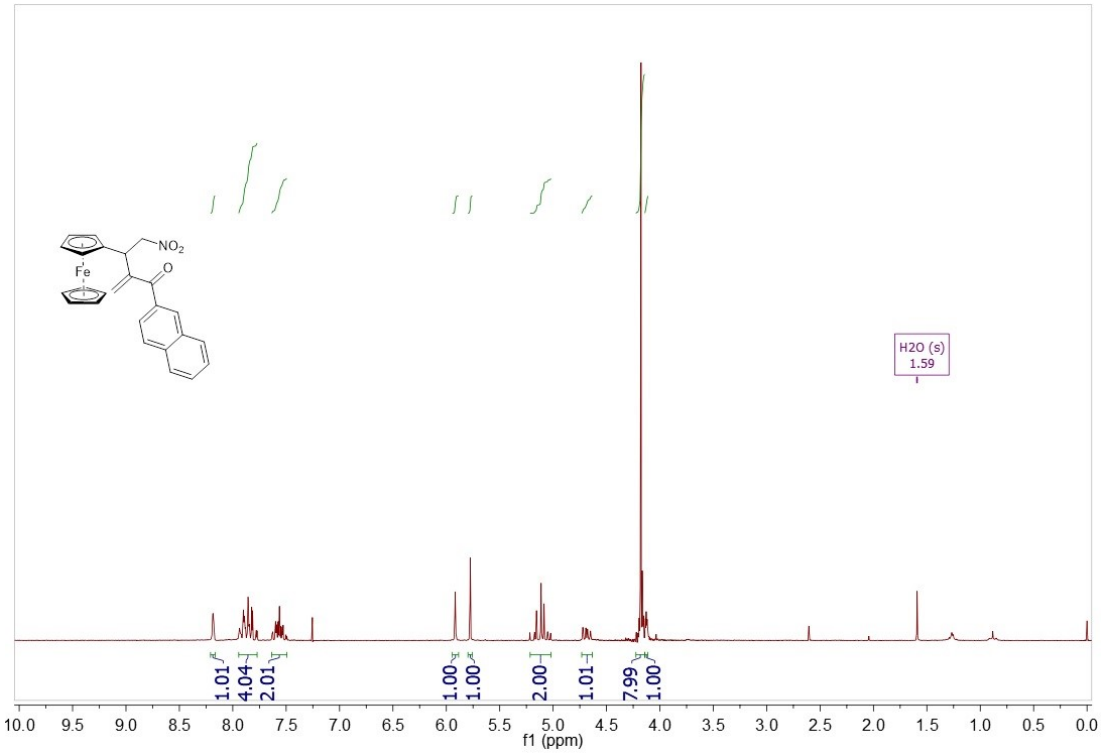
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3g**



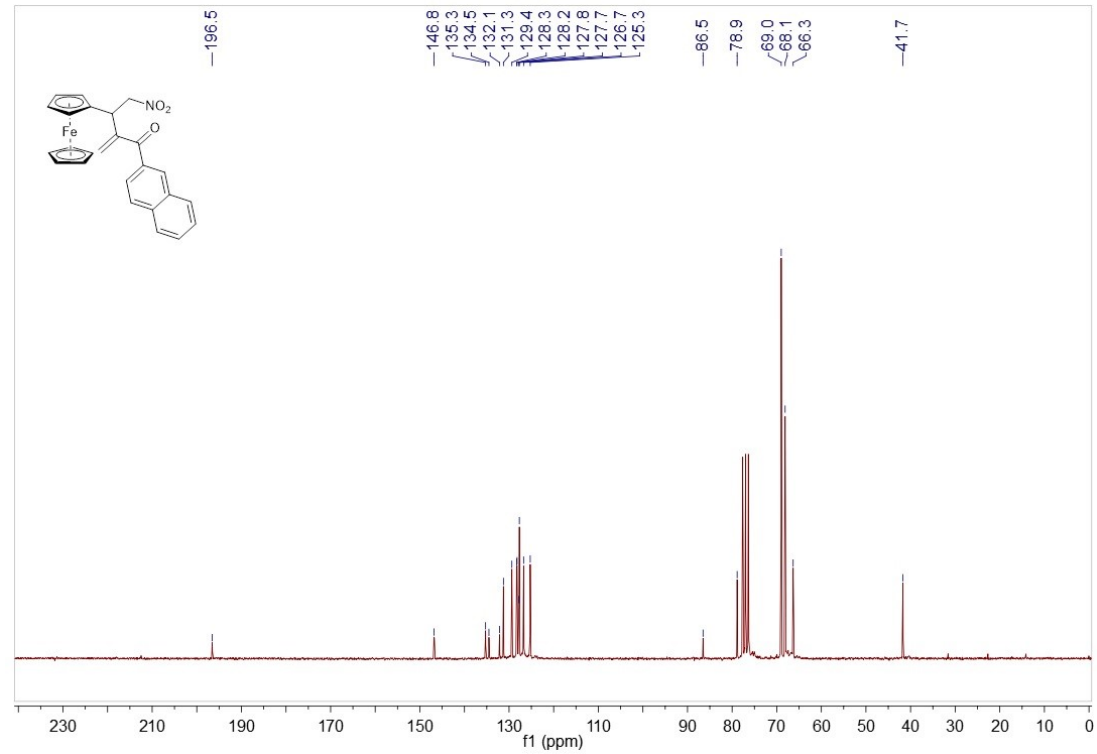
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3g'**



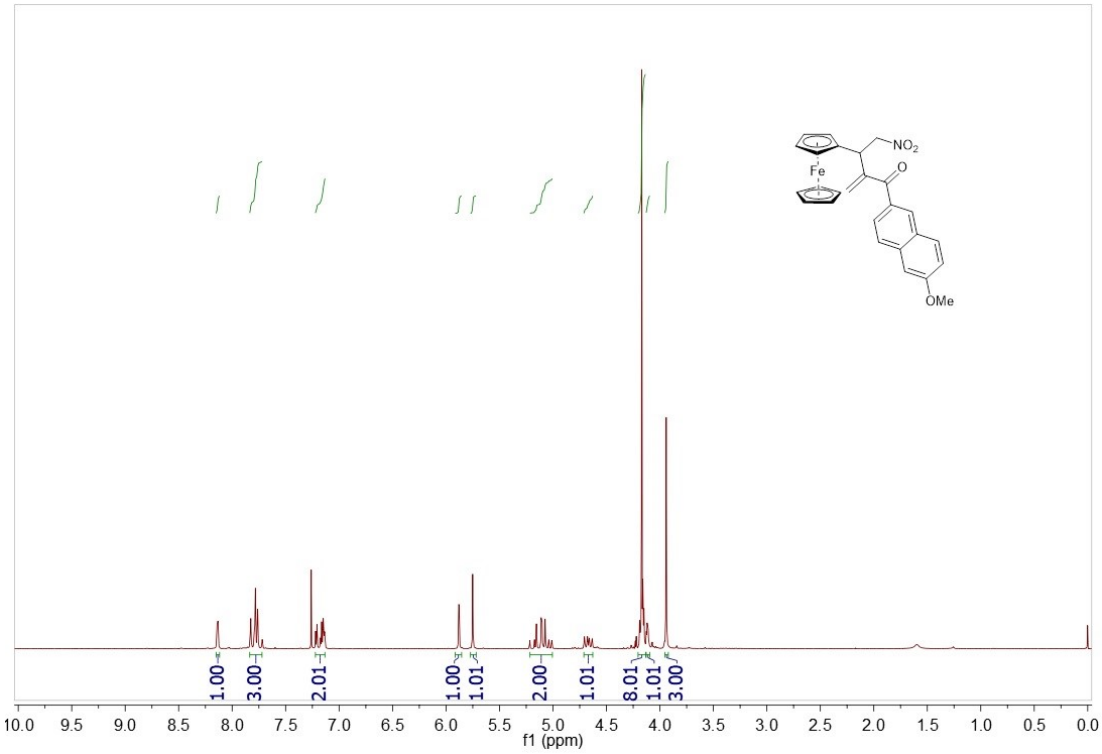
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3g'**



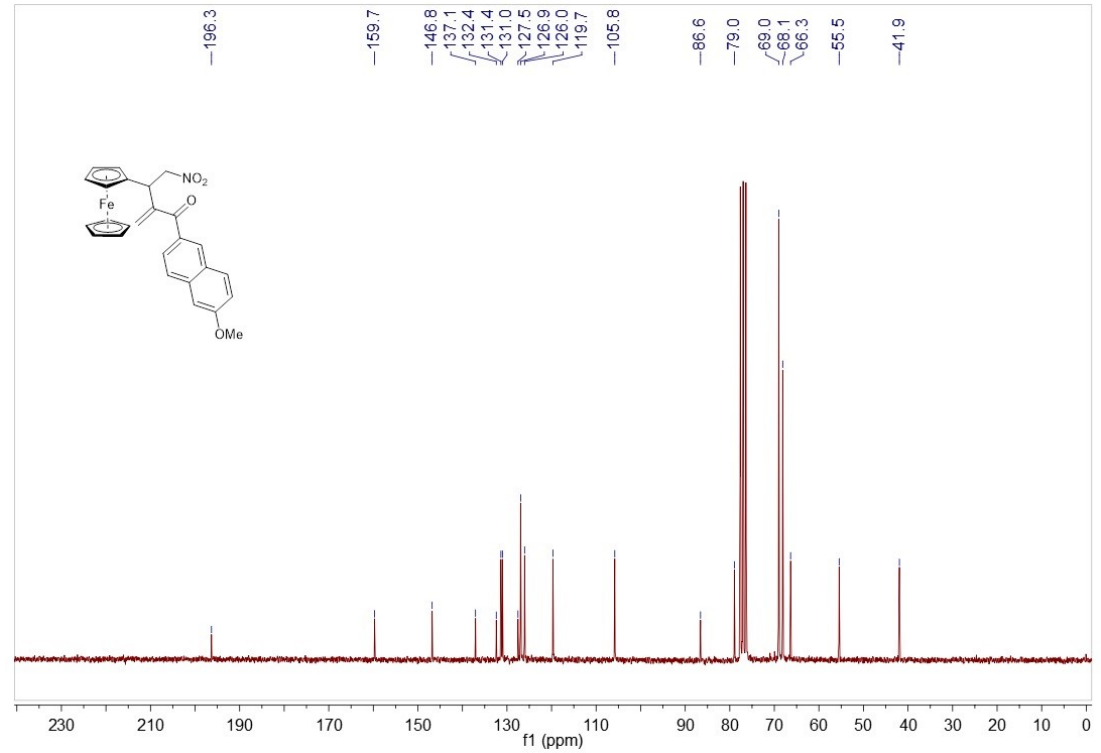
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3h**



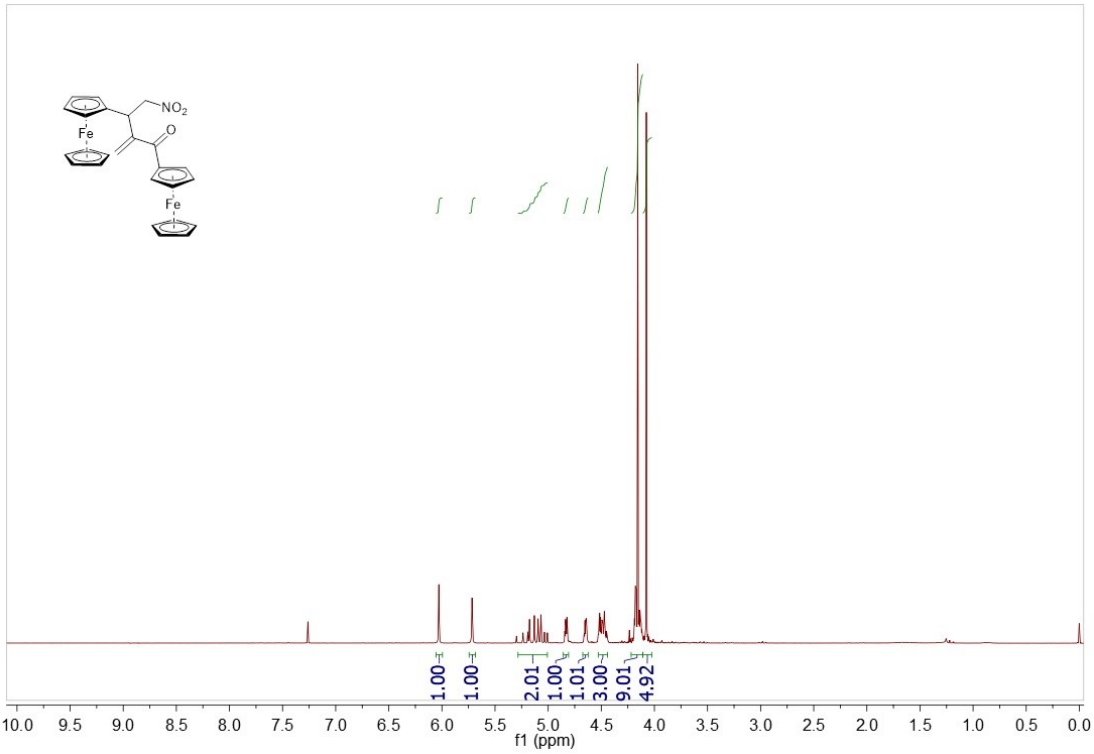
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3h**



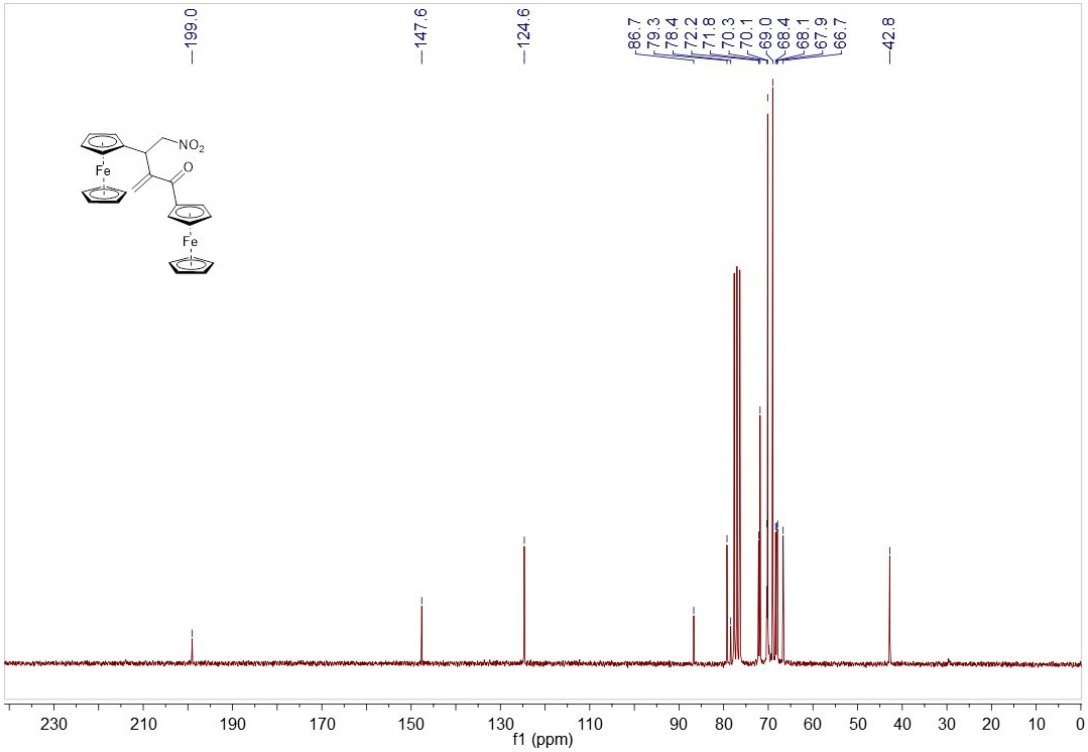
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3i**



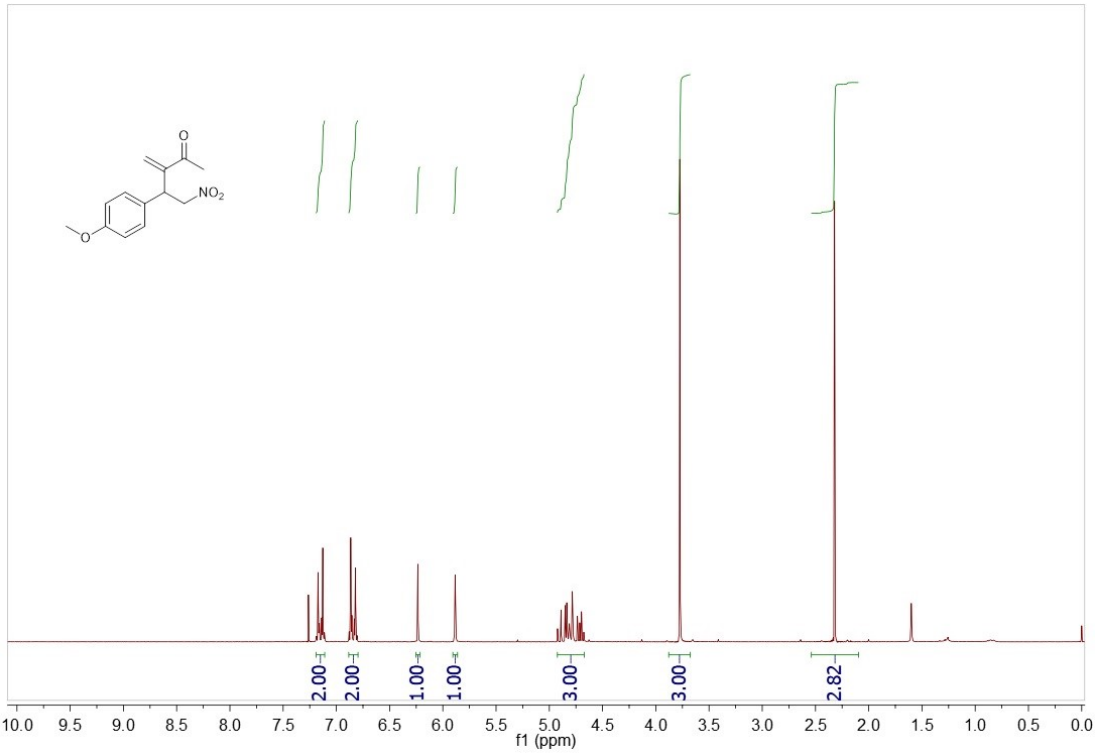
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3i**



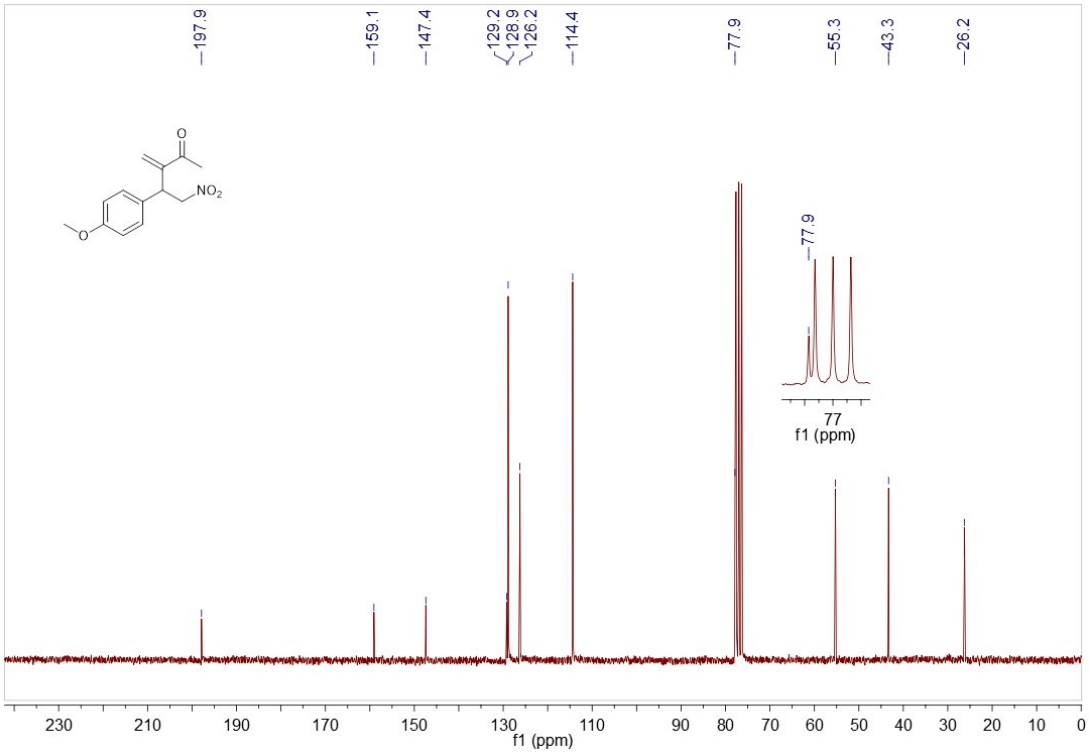
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3j**



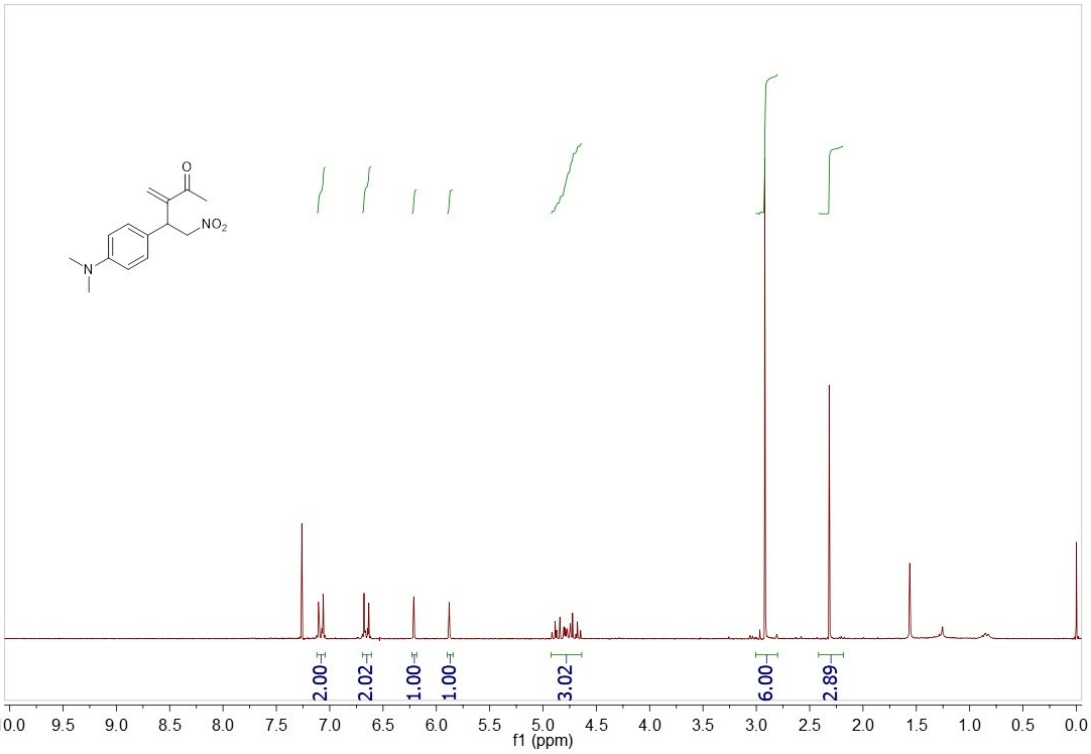
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3j**



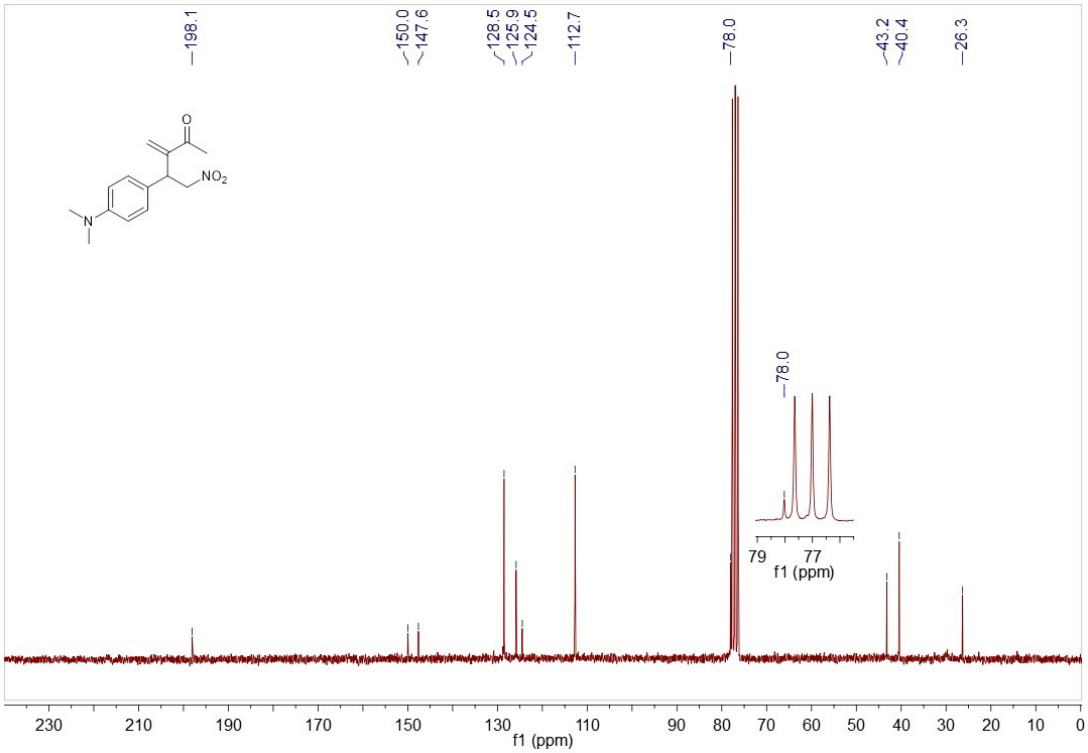
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **5b**



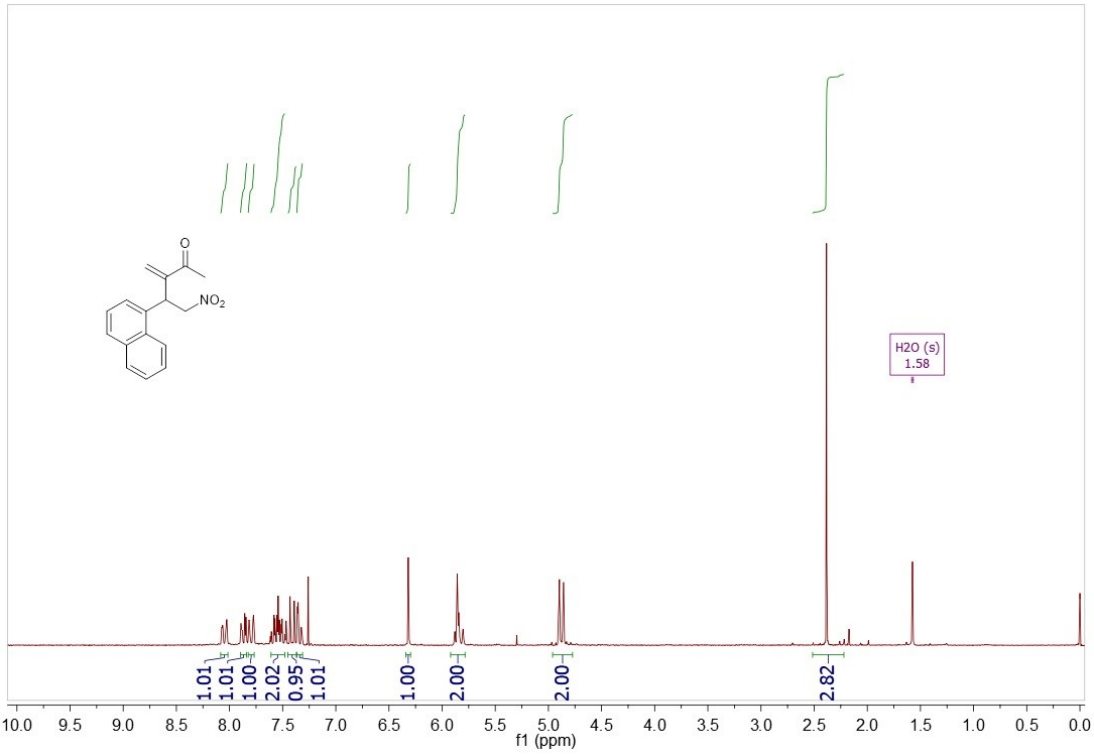
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **5b**



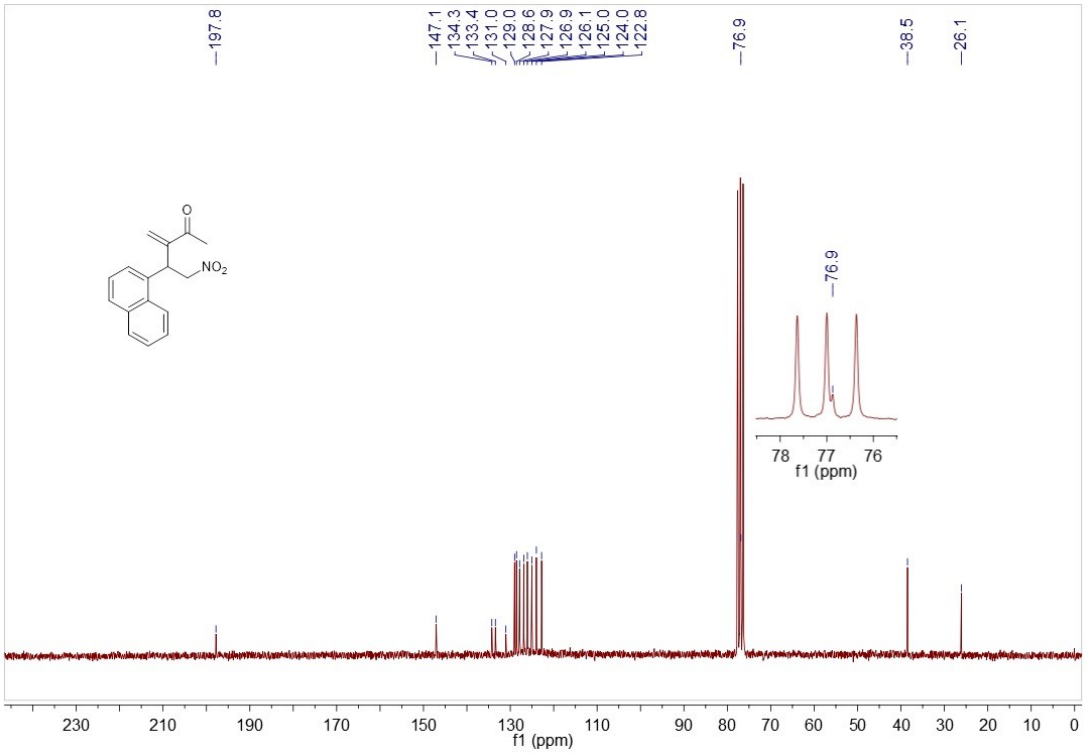
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **5c**



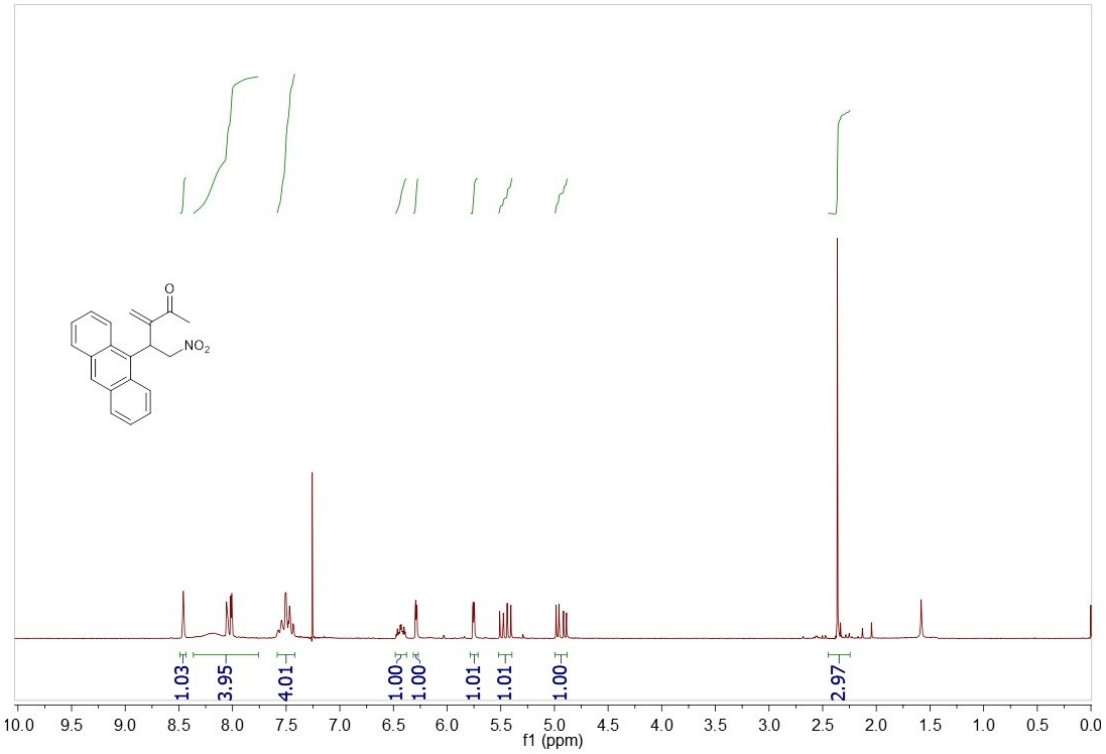
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **5c**



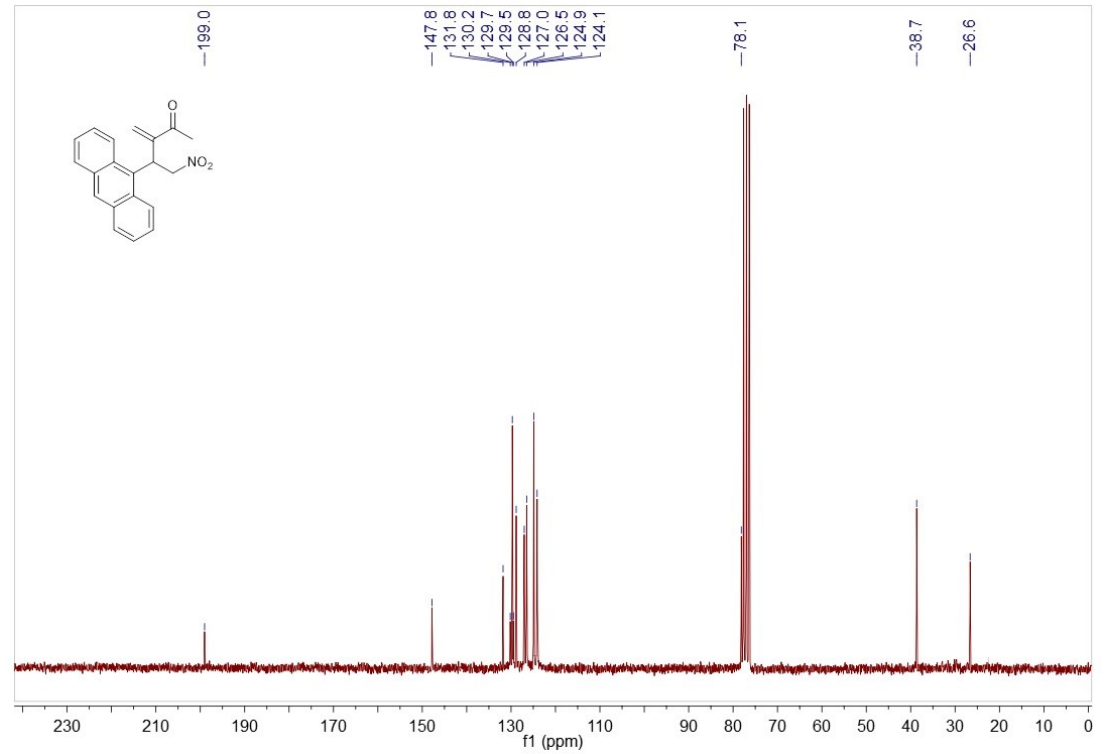
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **5d**



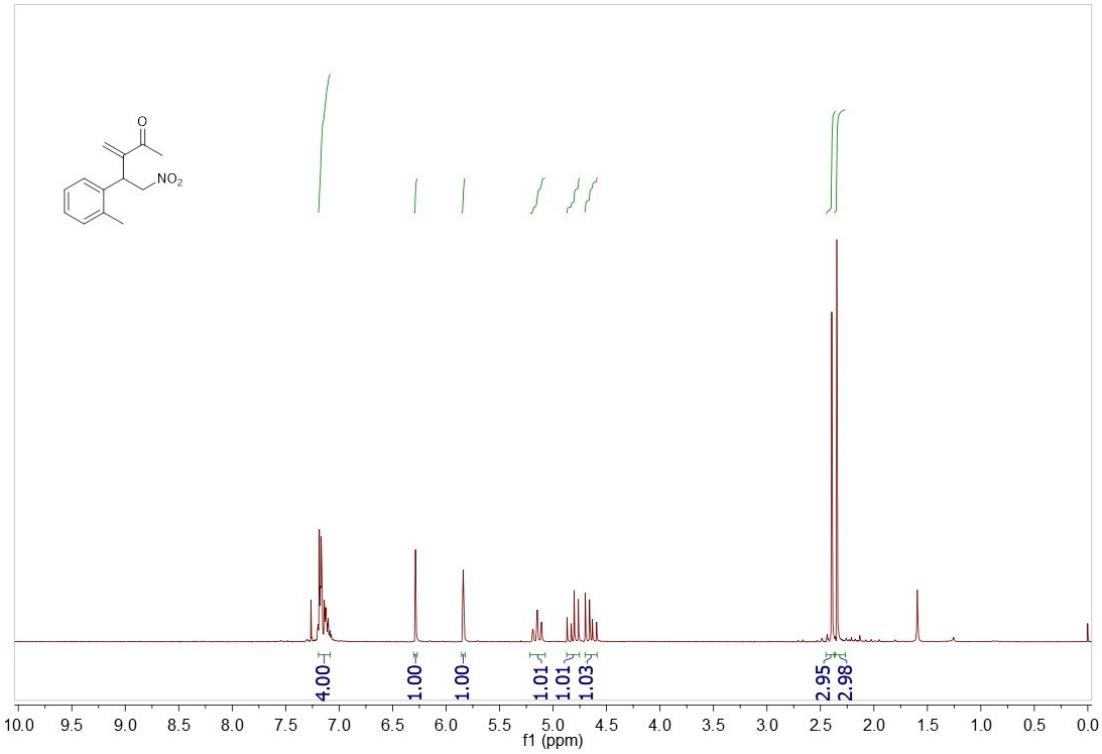
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **5d**



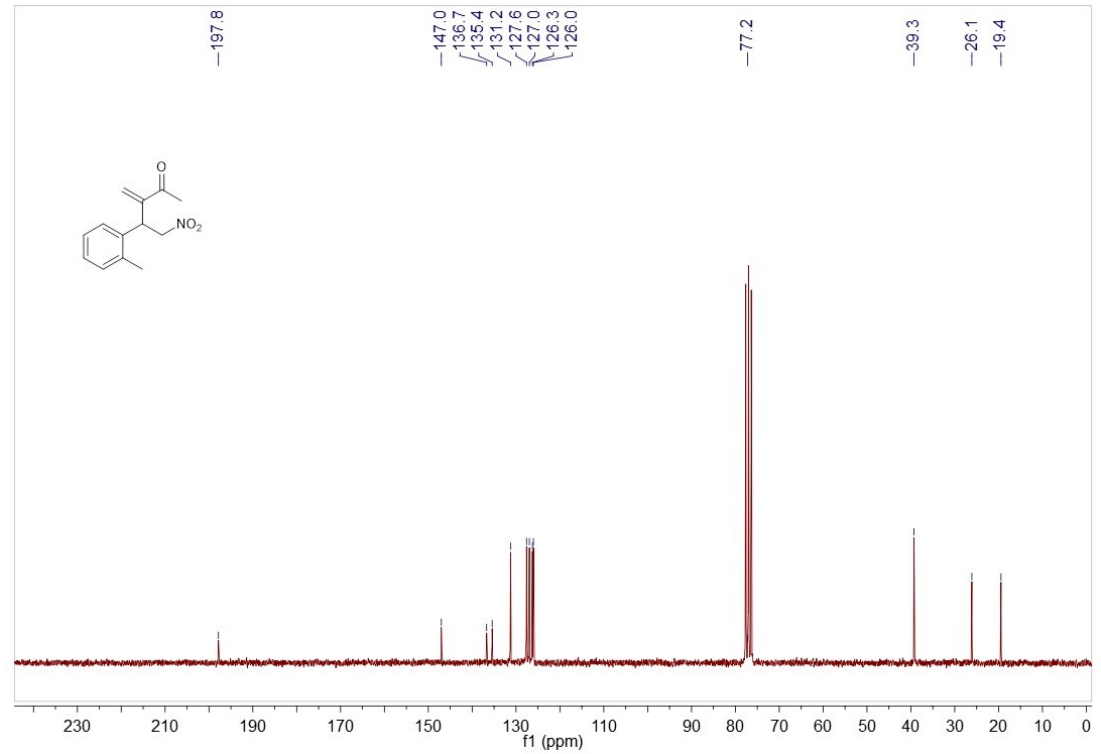
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **5e**



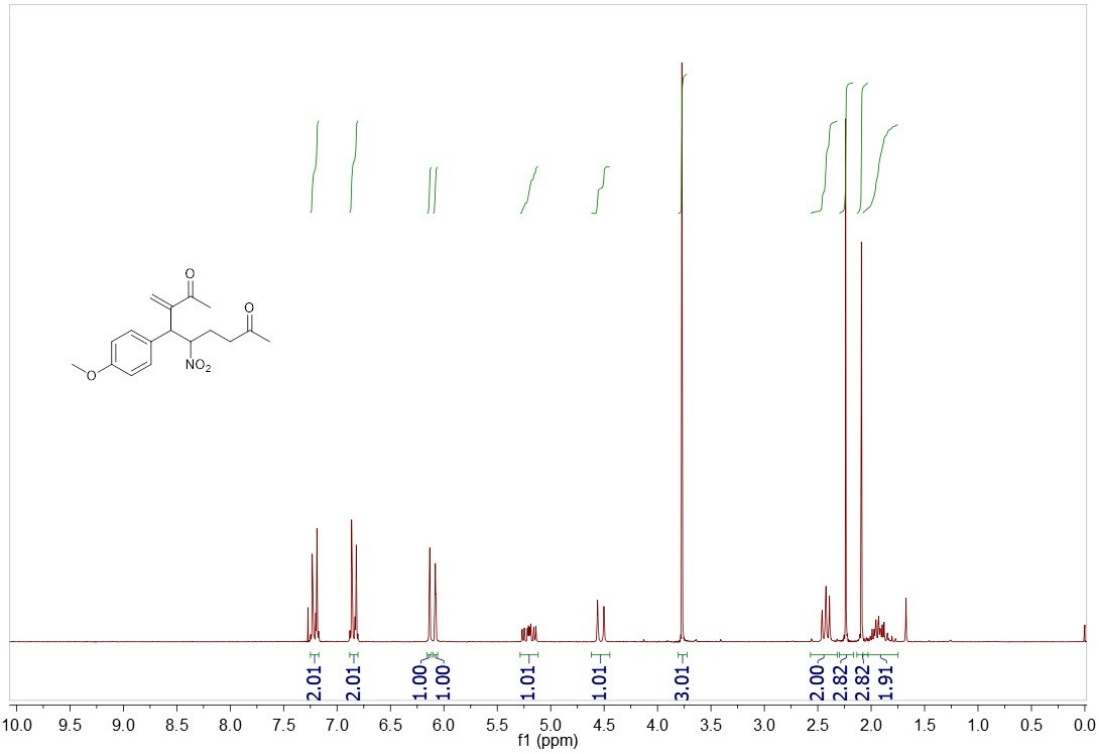
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **5e**



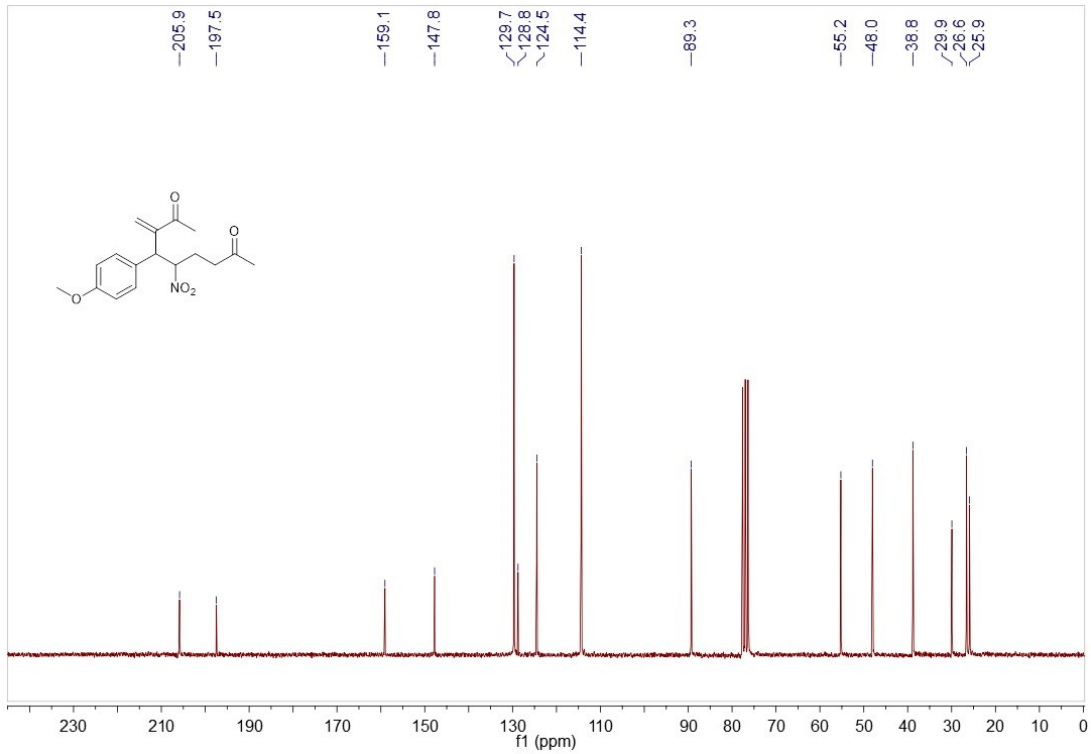
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **5f**



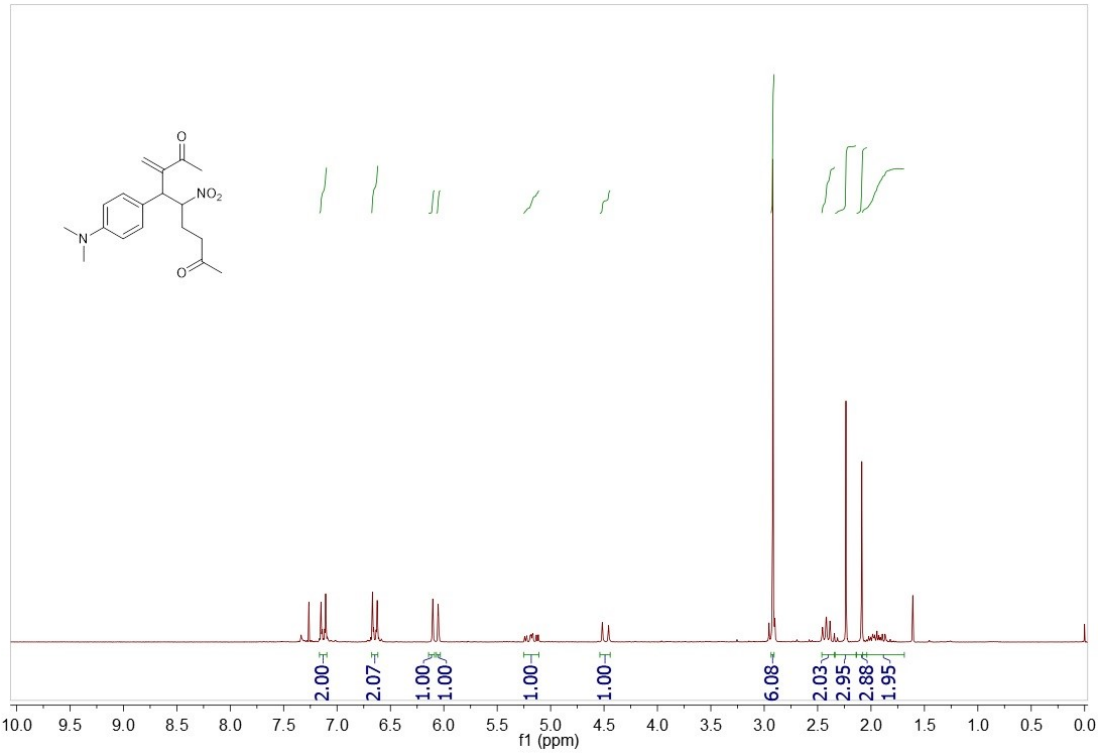
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **5f**



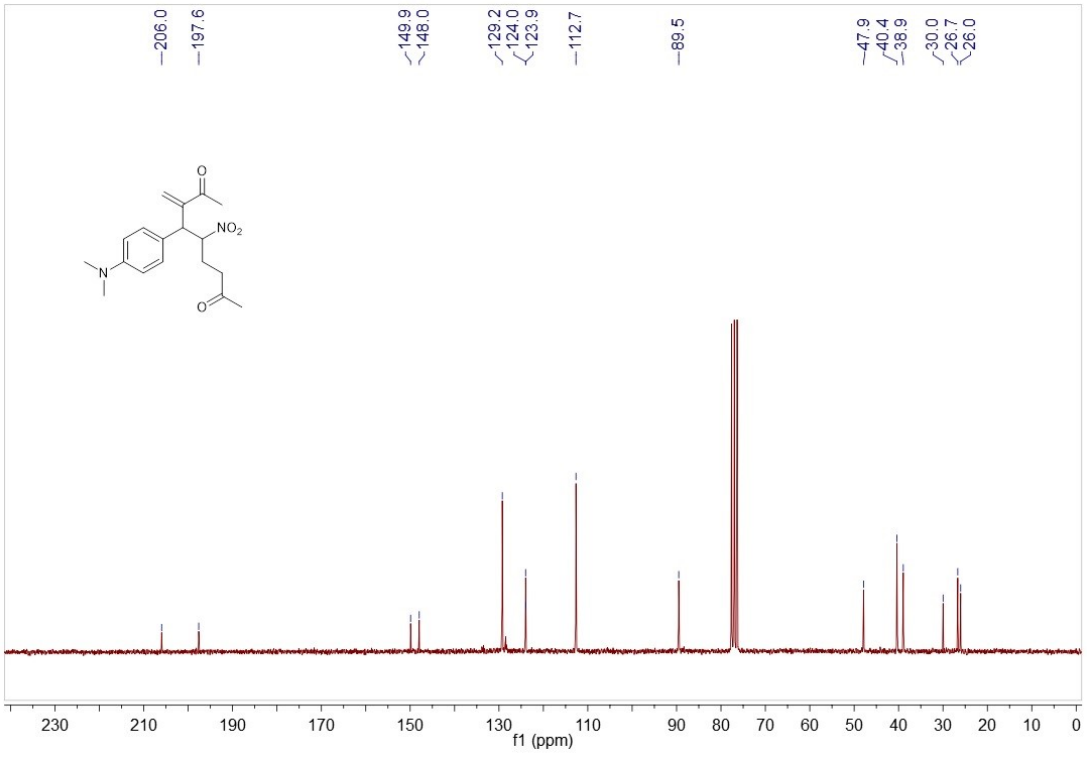
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6b**



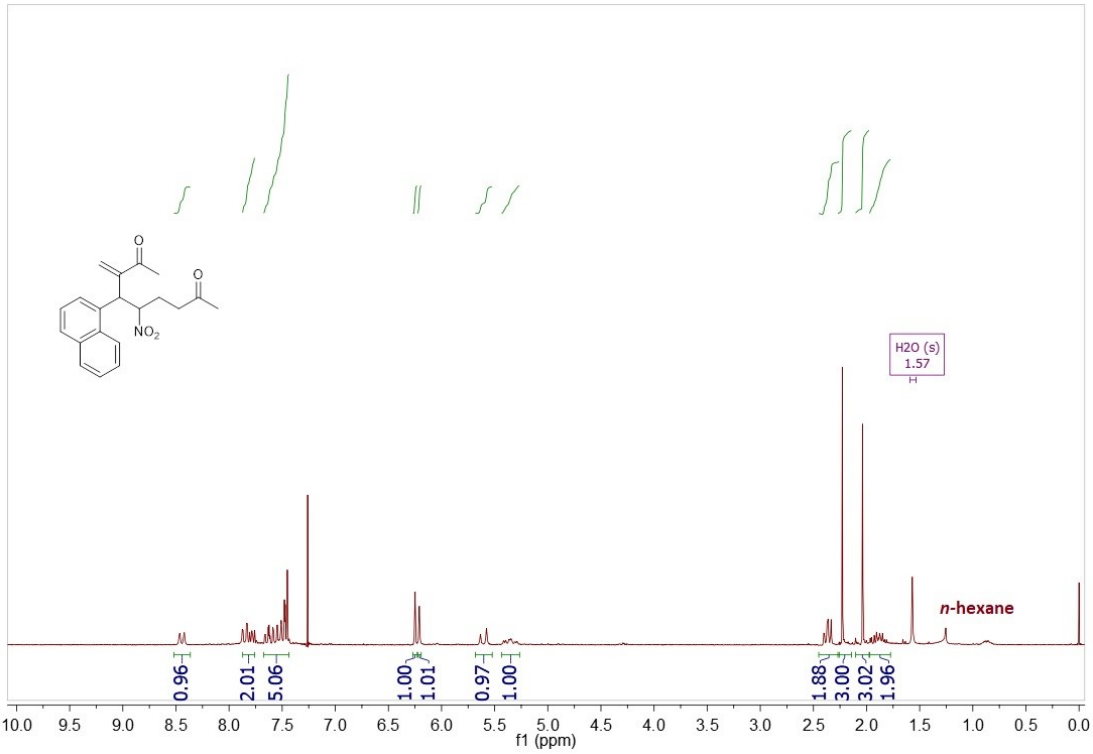
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6b**



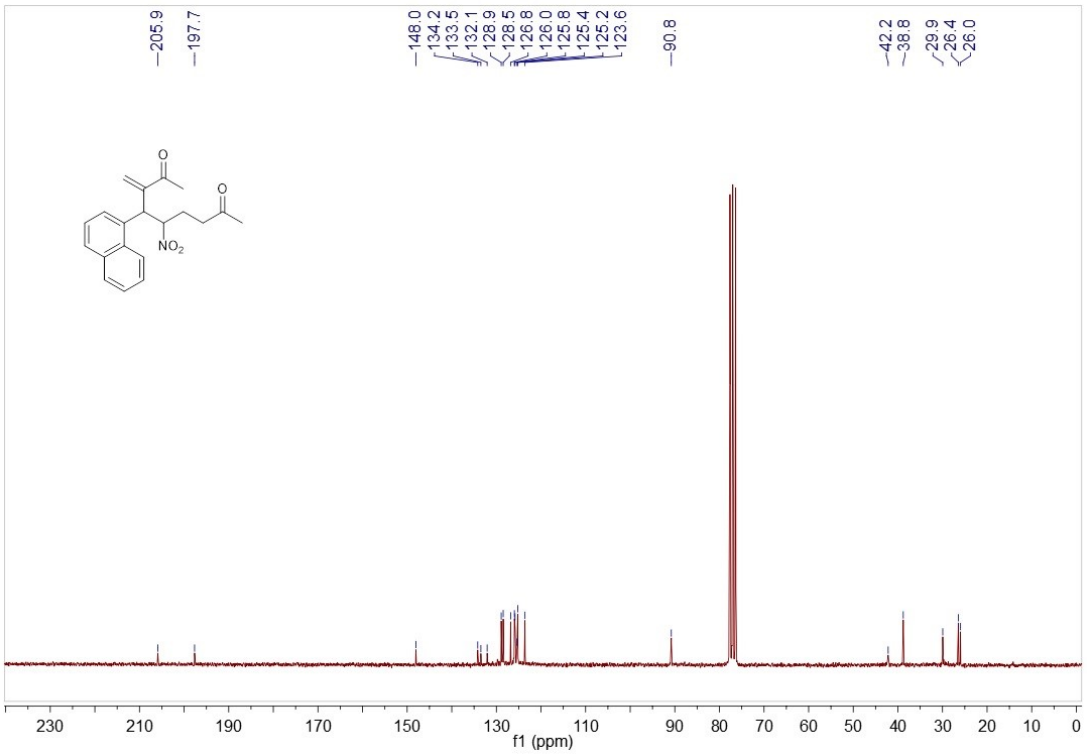
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6c**



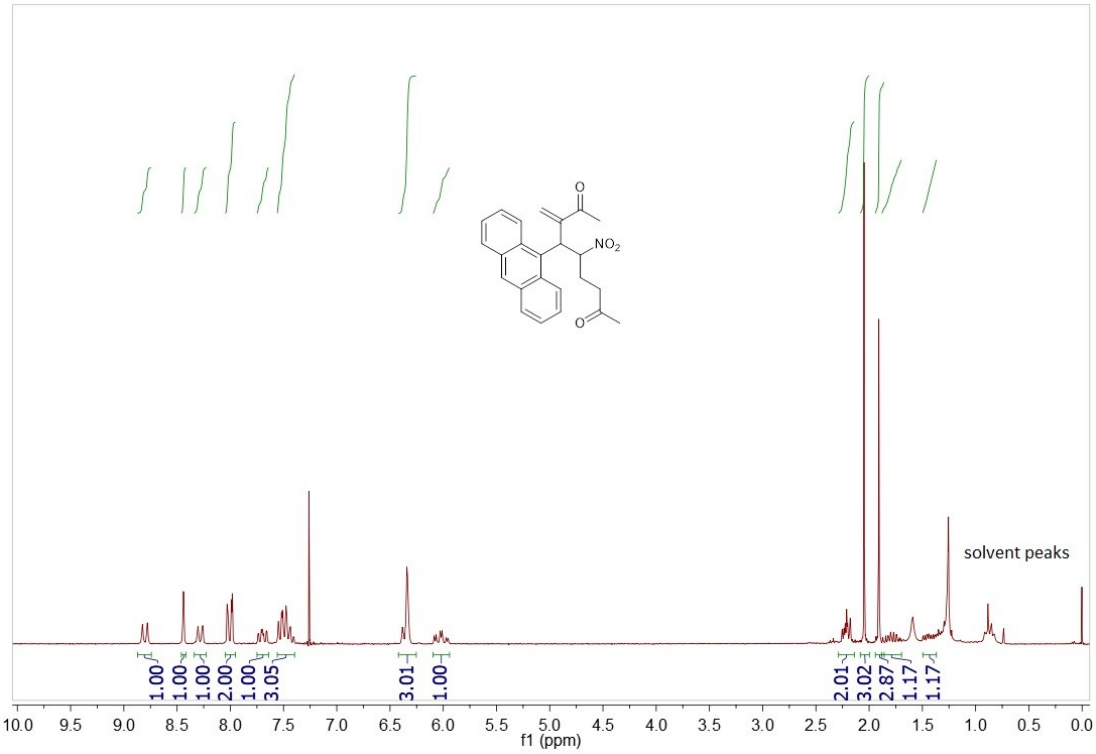
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6c**



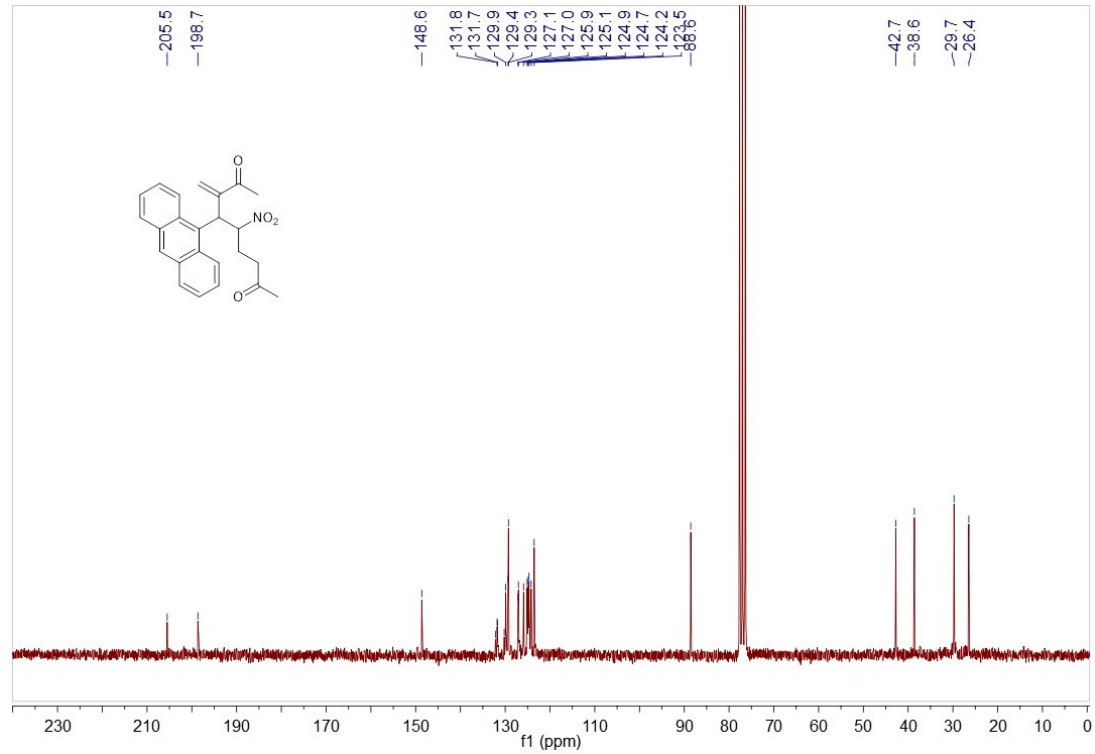
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6d**



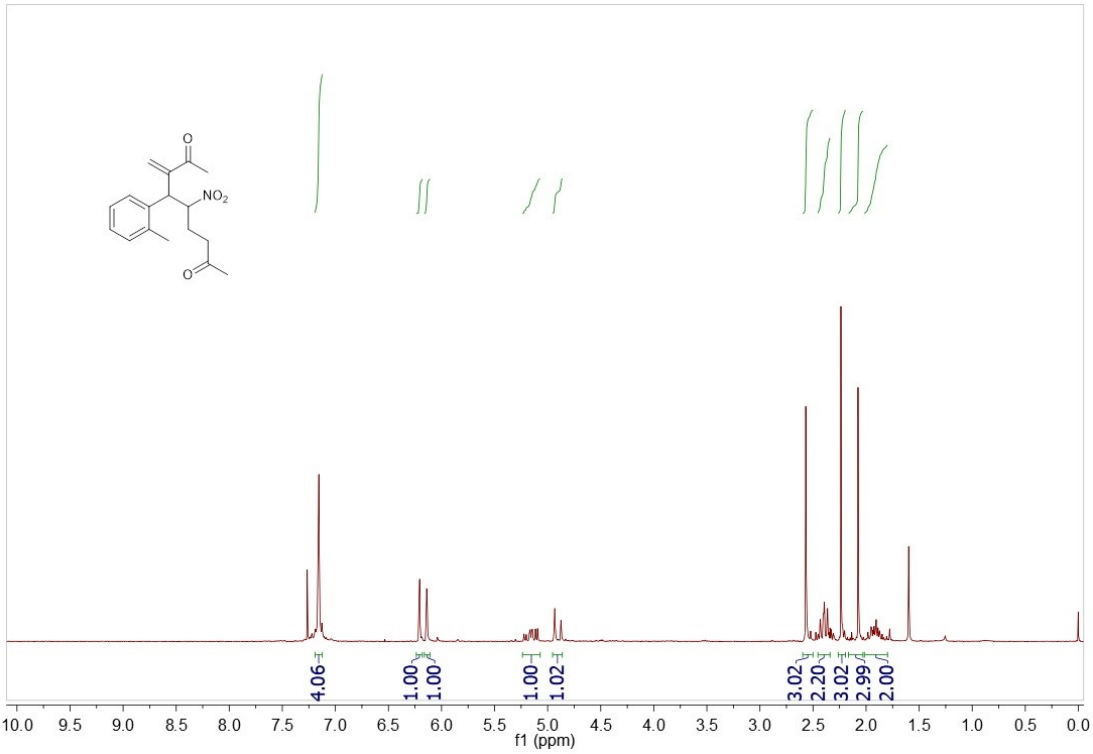
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6d**



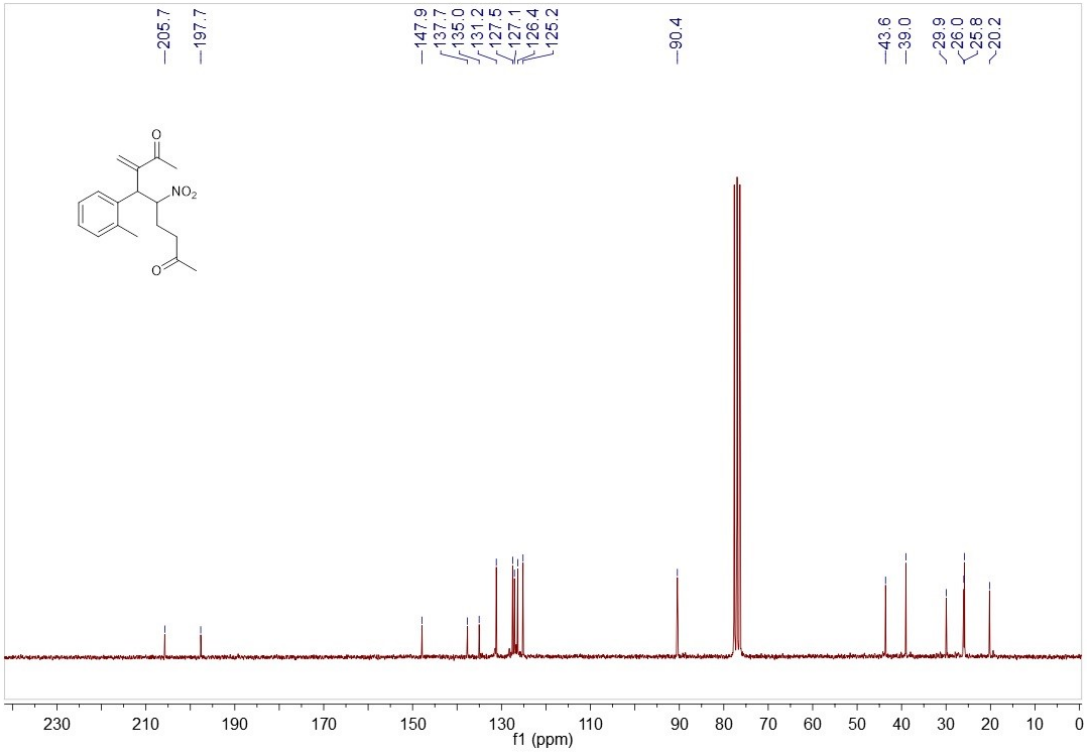
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6e**



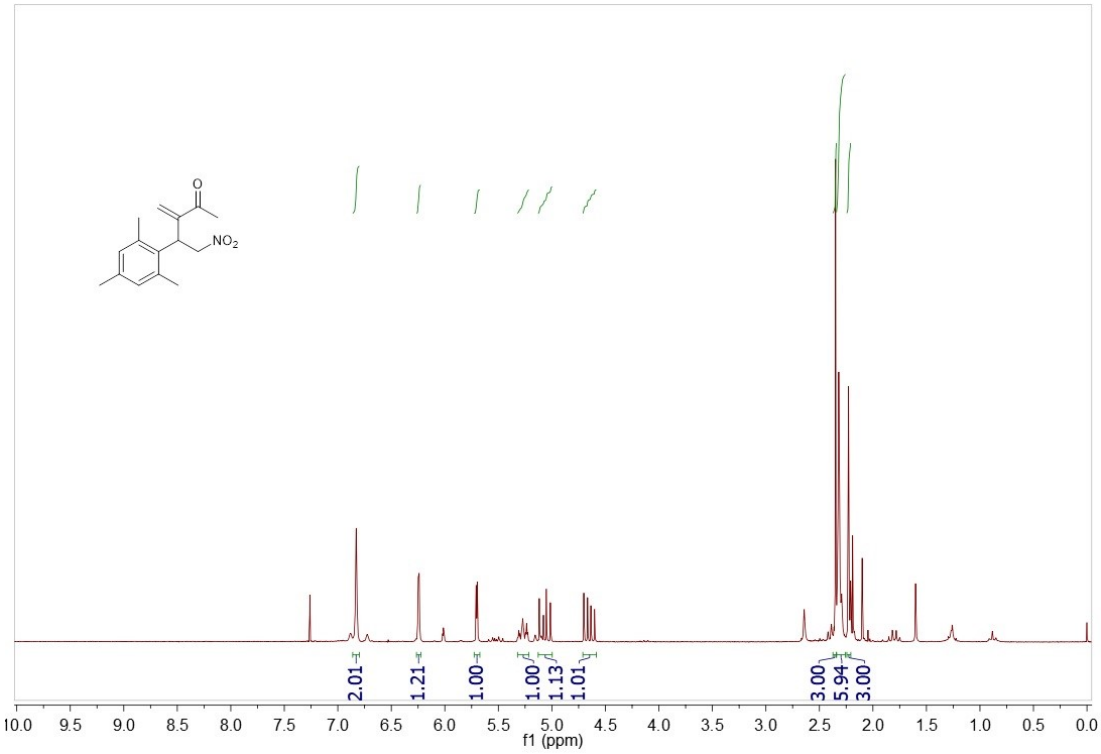
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6e**



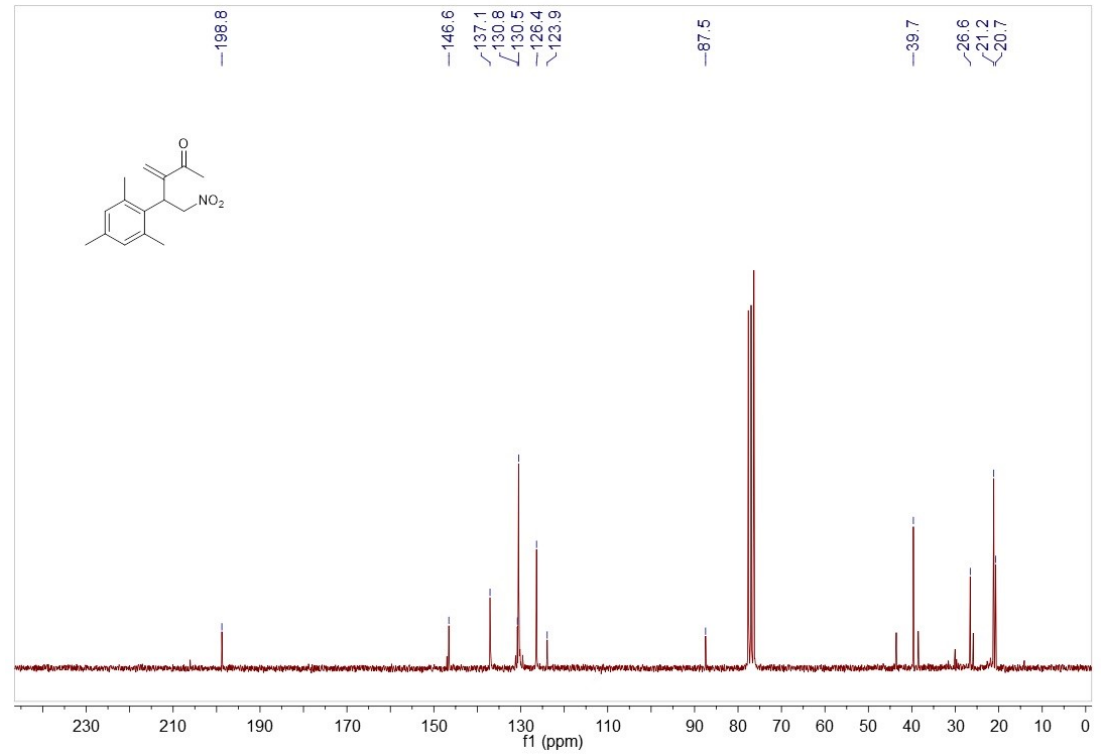
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **6f**



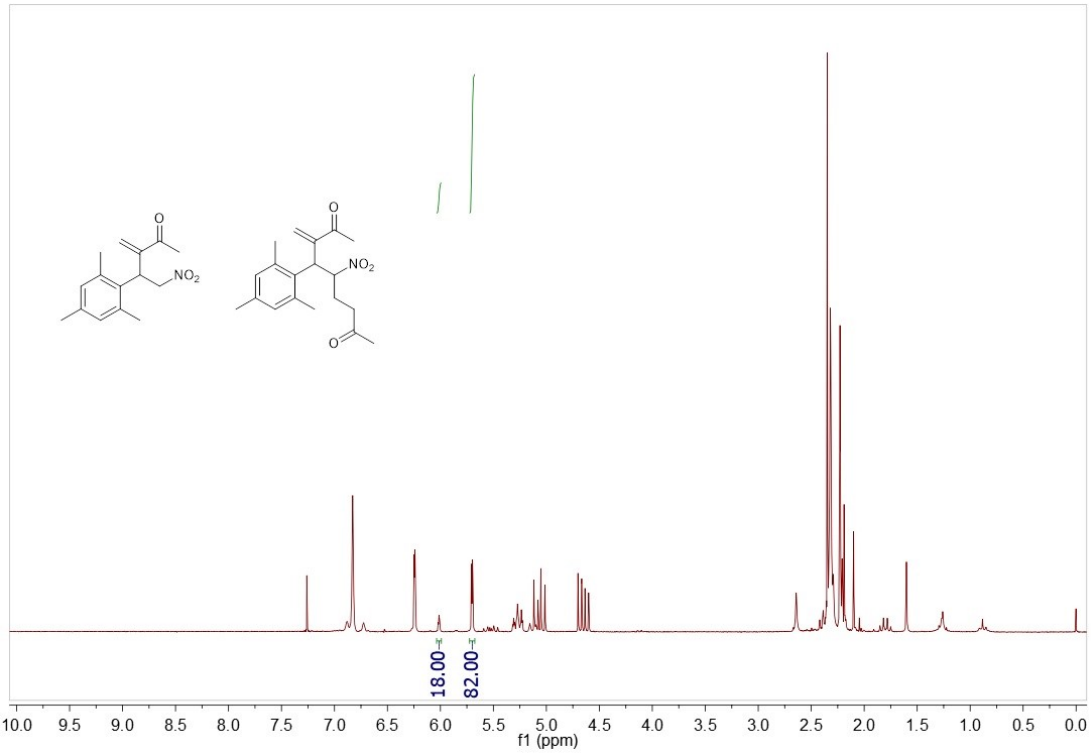
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **6f**



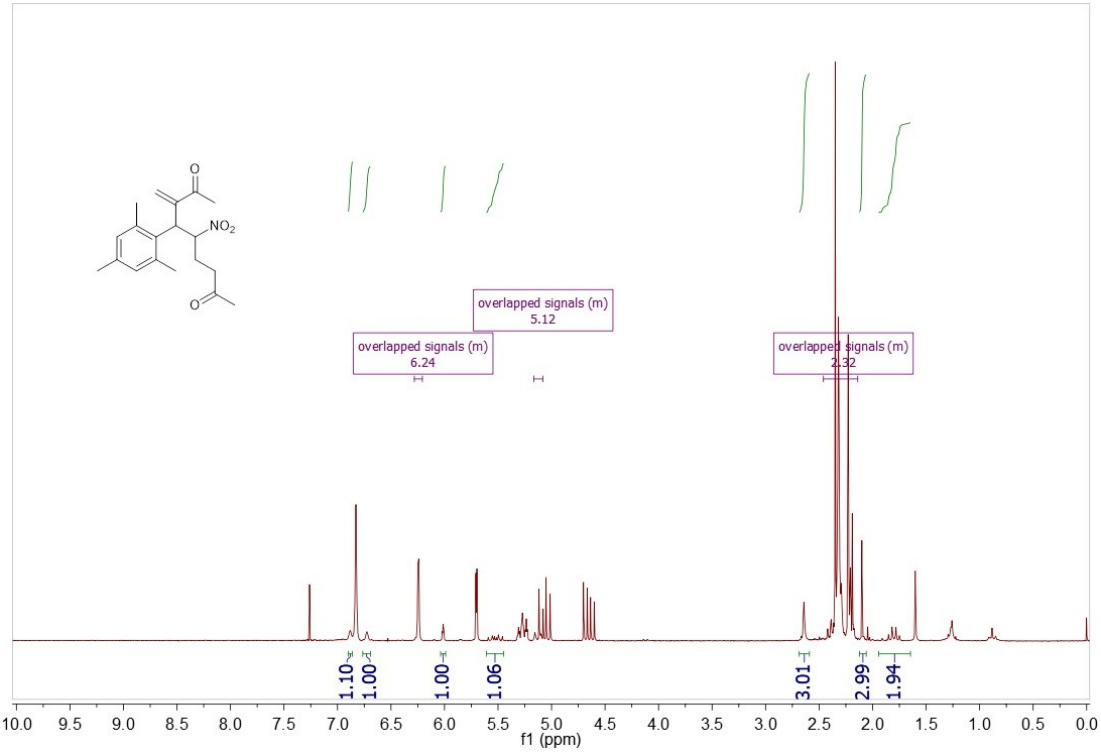
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of product mixture with integrals for **5g**



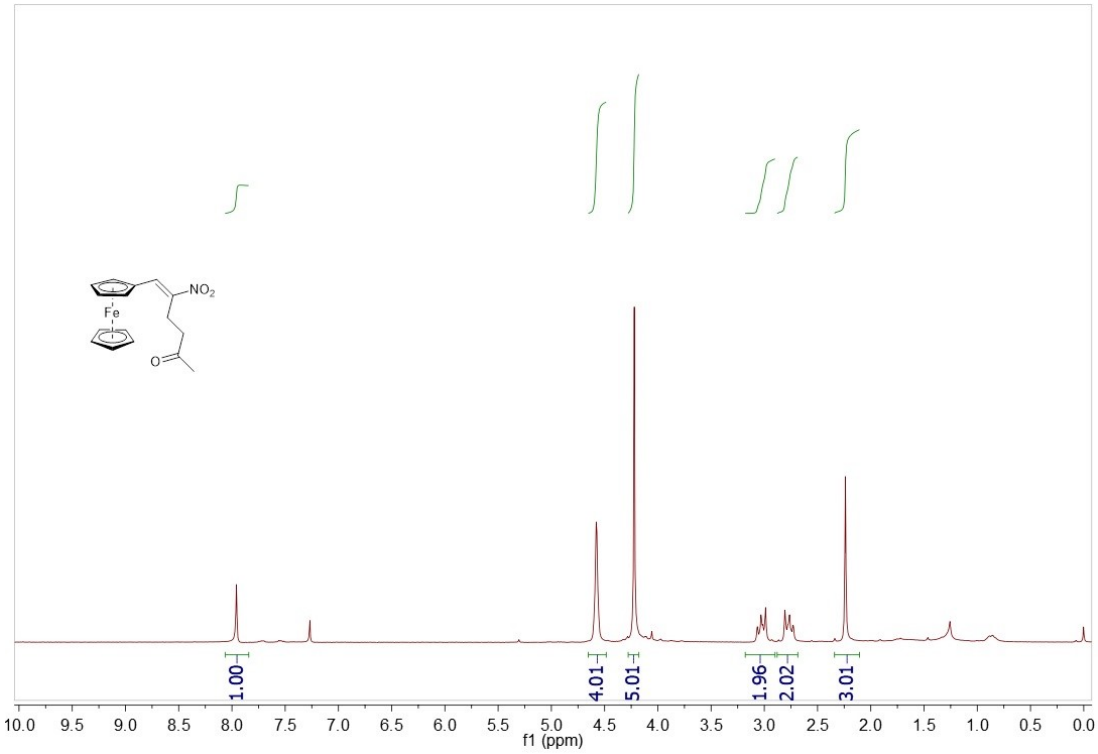
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of product mixture with marked peaks for **5g**



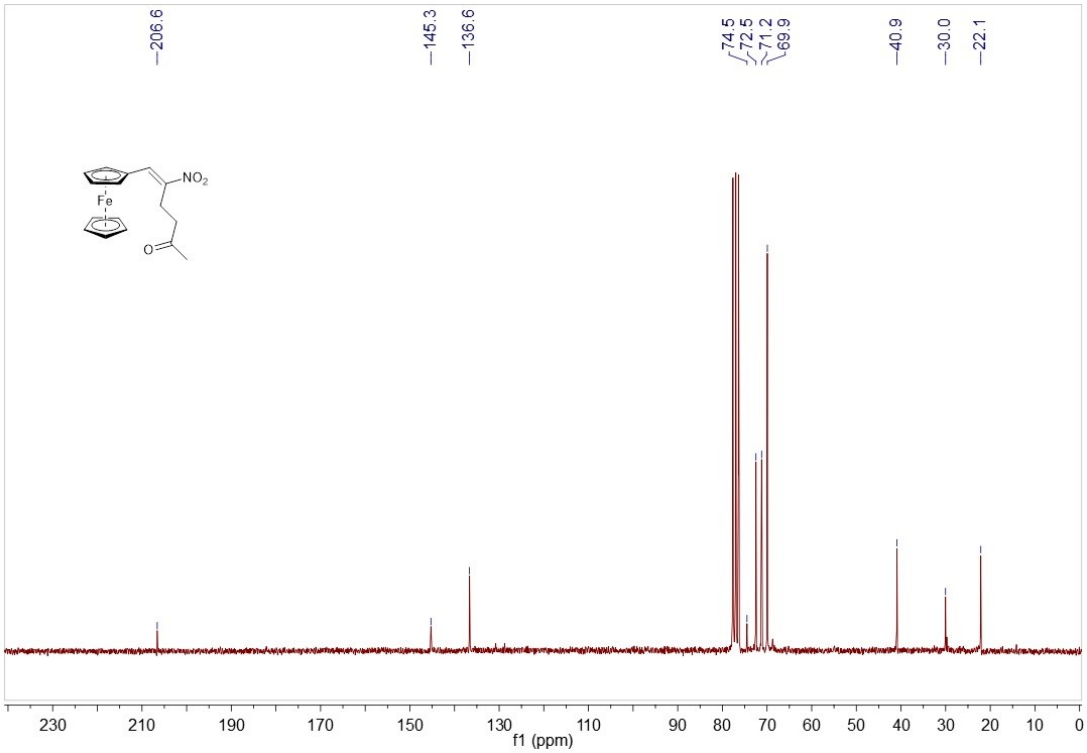
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of product mixture (**5g** and **6g**) with determined ratio



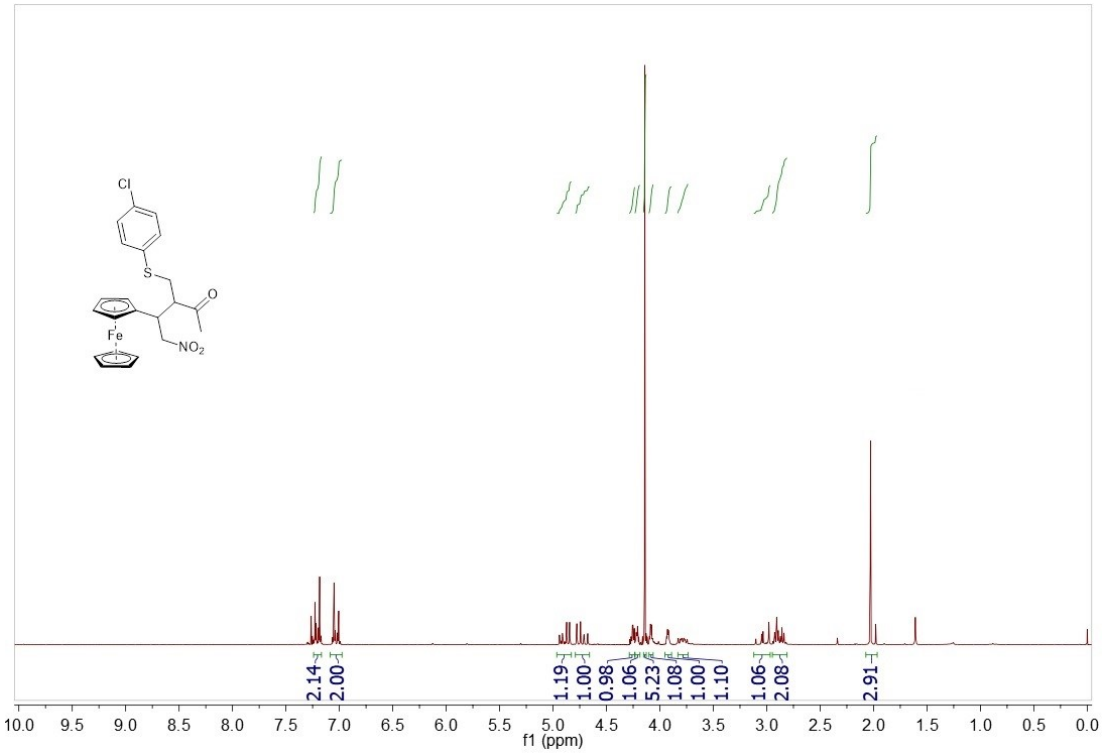
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of product mixture with integrals for **6g**



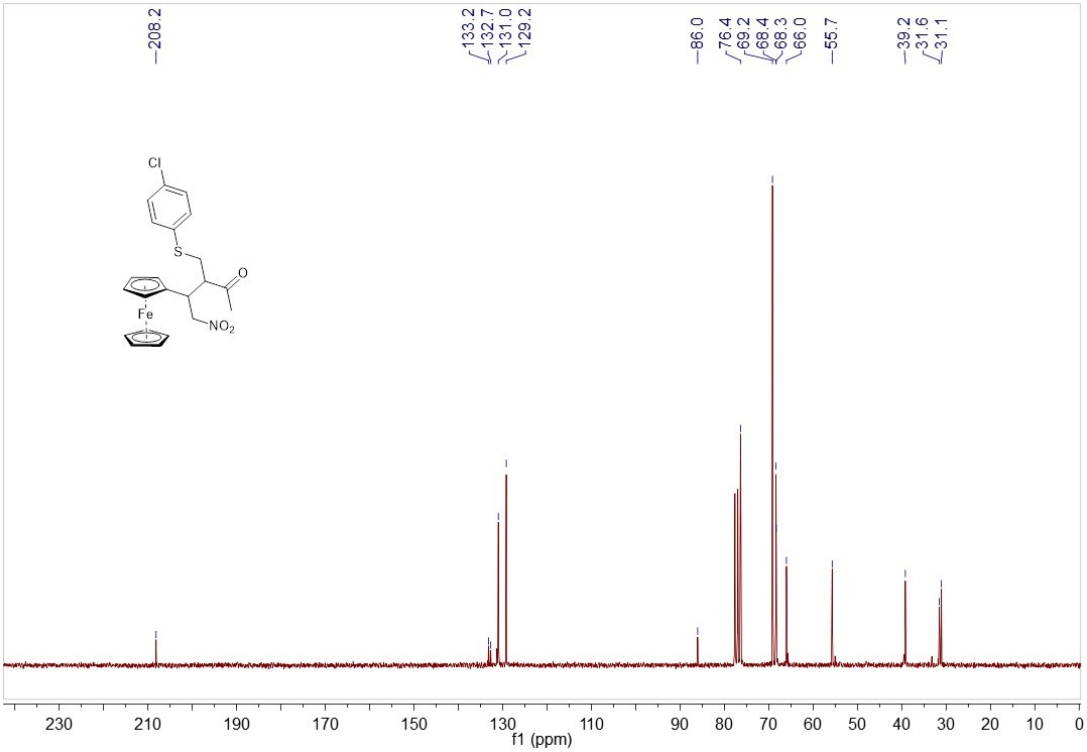
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **3a'**



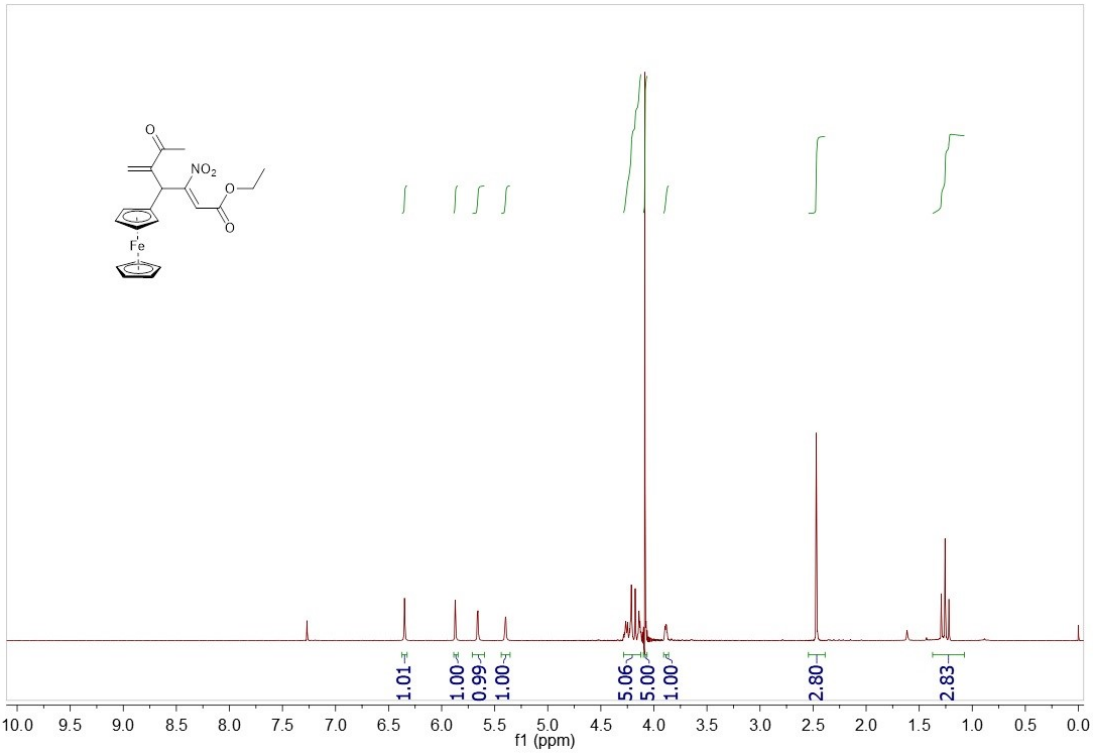
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **3a'**



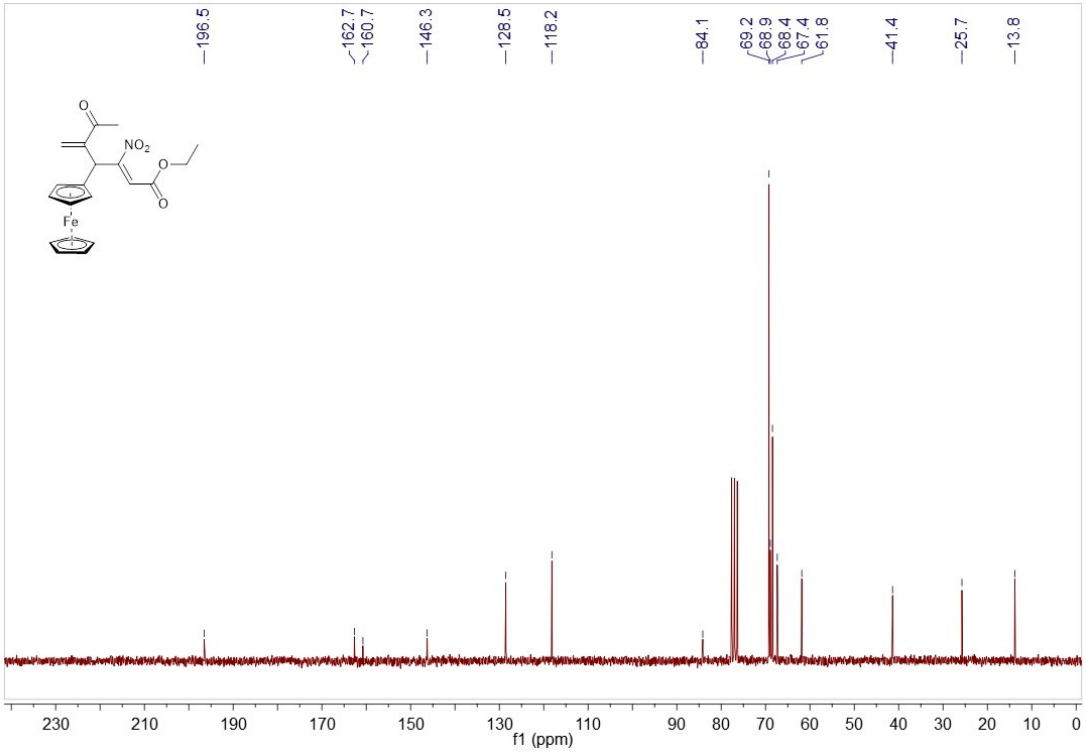
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **8**



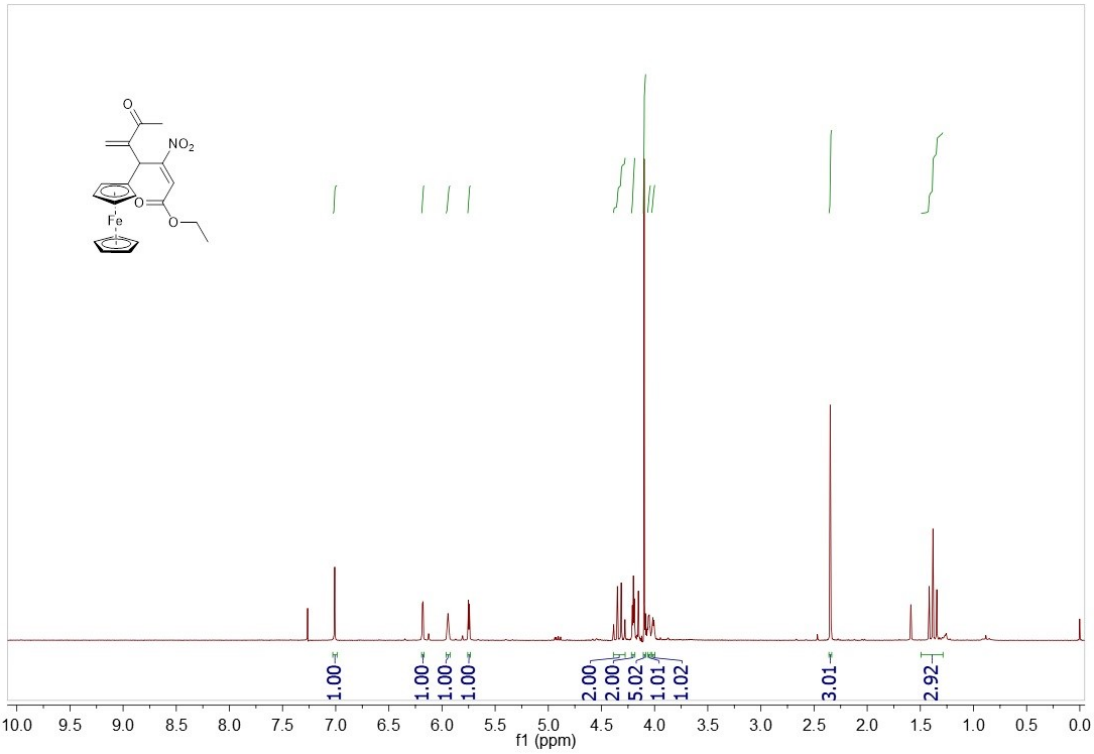
^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **8**



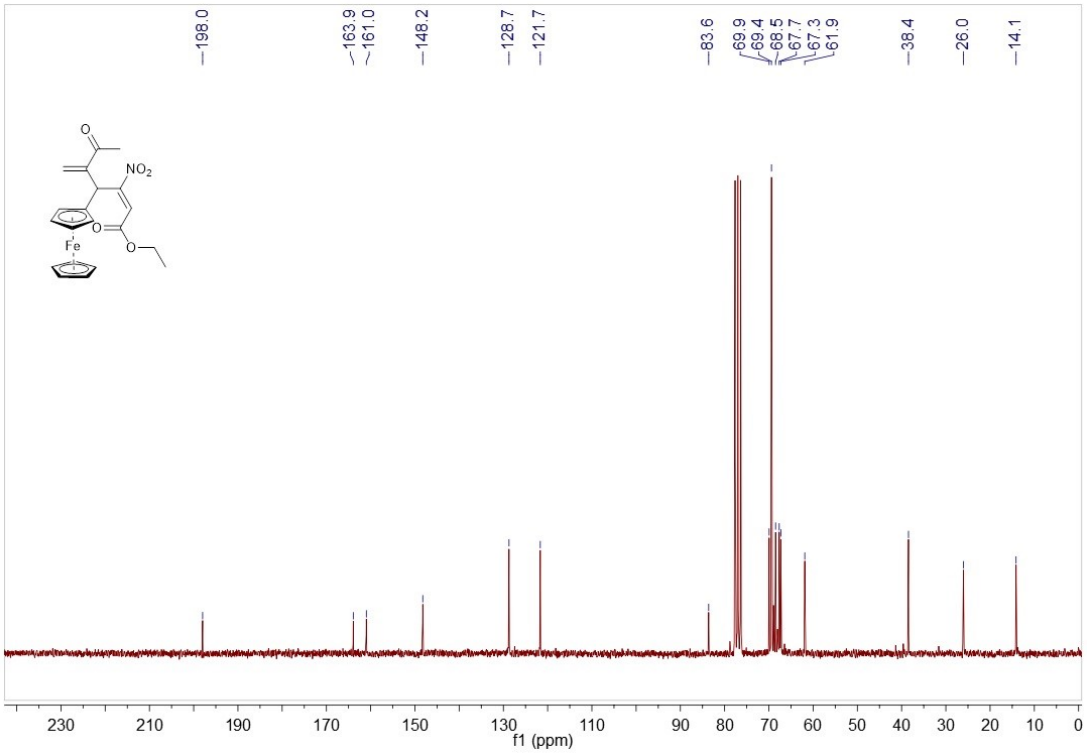
^{1}H NMR (200 MHz, $CDCl_3$) spectrum of *(Z)*-***9***



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of *(Z)*-***9***



^{1}H NMR (200 MHz, $CDCl_3$) spectrum of *(E)*-***9***



^{13}C NMR (50 MHz, $CDCl_3$) spectrum of *(E)*-***9***