Electronic Supplementary Information (ESI) for Chemical Communications

Syntheses and crystal structures of neutral tetrairon complexes with the unique $SCPPh_2S$ ligand.

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Experimental details.

General Procedures.

All reactions were carried out under a prepurified N_2 atmosphere with standard Schlenk techniques. All solvents employed were dried by refluxing over appropriate drying agents and stored under an N_2 atmosphere. THF was distilled from sodium-benzophenone, petroleum ether (60-90 °C) and CH_2Cl_2 from P_2O_5. $Fe_3(CO)_{12}$ was prepared according to the literature procedure.[1] The progress of all reactions was monitored by TLC (silica gel H). NMR spectra were recorded on a Bruker Avance 600 spectrometer. ESI-HR-MS data were obtained on a Bruker Maxis spectrometer. IR spectra were carried out on a Bruker Tensor 27 spectrometer as KBr disks in the range 400-4000 cm^{-1}. Analyses for C and H were performed on a PE 2400 Series III instrument. Melting points were measured on a Yanagimoto apparatus and uncorrected.

Under a nitrogen atmosphere, a mixture of 0.551 g (5 mmol) of PhSH, 0.506 g (5 mmol) of Et_3N and 2.518 g (5 mmol) of $Fe_3(CO)_{12}$ in 50 mL of THF was stirred for 0.5 h at room temperature to give a brown-red $[(\mu\text{-PhS})Fe_2(CO)_6(\mu\text{-CO})]^-$ solution. After addition of 0.381 g (5 mmol) of CS_2, the mixture was stirred for 1 h at room temperature to form a red $[(\mu\text{-PhS})Fe_2(CO)_6(\mu\text{-}CS_2)]^-$ solution.[2-8] To this solution was added 2.518 g (5 mmol) of $Fe_3(CO)_{12}$, the mixture was stirred for 0.5 h until $Fe_3(CO)_{12}$ disappeared. The solution was cooled to 0 °C. After 1.103 g (5 mmol) of Ph_2PCl was added, the new mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo and the residue was subjected to TLC separation. Elution with acetone/petroleum ether (1:20, v/v) yielded an orange-red, air-stable complex **1** which was recrystallized from CH_2Cl_2/petroleum ether to give red block crystals (R_f = 0.40). The same procedure as for **2** was followed, but $CH_3O_2CCH_2SH$ (0.531g, 5.00 mmol) was used instead of PhSH. Elution with acetone/petroleum ether (1:10, v/v) supplied an orange-red, air-stable complex

2 which was recrystallized from CH_2Cl_2/petroleum ether to afford red needle crystals (R_f = 0.35).[9]

Treatment of the preparepared [(μ-$CH_3O_2CCH_2S$)$Fe_2(CO)_6$(μ-CS_2)]$^-$ solution generated from 0.531g (5.00 mmol) of $CH_3O_2CCH_2SH$, 0.506 g (5 mmol) of Et_3N, 2.518 g (5 mmol) of $Fe_3(CO)_{12}$ and 0.381 g (5 mmol) of CS_2 in 50 mL of THF with 0.710 g (5 mmol) of CH_3I and elution with CH_2Cl_2/petroleum ether (1:4, v/v) provided an orange-red, air-stable complex **3** which was recrystallized from CH_2Cl_2/petroleum ether to give red block crystals (R_f = 0.30).

Data for **1**: yield 12%, 0.558 g; mp, 168-170 °C; anal. calcd for $C_{31}H_{15}Fe_4O_{12}PS_3$: C, 40.04; H, 1.63%; found: C, 40.37; H, 1.72%. IR (KBr disk): ν(C≡O) 2077 (s), 2043 (vs), 2006 (vs), 1970 (s) cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): 7.18 (s, 5H, C_6H_5), 7.43-7.49, 7.52-7.58, 8.10-8.19 (3m, 4H, 2H, 4H, 2C_6H_5) ppm. ^{31}P-NMR (242.9 MHz, $CDCl_3$, 85% H_3PO_4): 102.4 (s) ppm. ^{13}C-NMR (150.9 MHz, $CDCl_3$, TMS): 127.36, 128.02-128.09 (d, $^1J_{C\text{-}P}$ = 11.62 Hz), 128.38, 130.66, 131.10, 131.70, 132.57-132.59 (d, $^2J_{C\text{-}P}$ = 2.87 Hz), 133.73-133.79 (d, $^1J_{C\text{-}P}$ = 9.20 Hz), 138.52, 206.68, 209.89 ppm.

Data for **2**: yield 11%, 0.509 g; mp, 174-176 °C; anal. calcd for $C_{28}H_{15}Fe_4O_{14}PS_3$: C, 36.32; H, 1.63%; found: C, 36.67; H, 1.77%. IR (KBr disk): ν(C≡O) 2079 (s), 2042 (vs), 2008 (s), 1967 (s); ν(C=O) 1739 (m) cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): 3.04 (s, 2H, CH_2), 3.64 (s, 3H, CH_3), 7.43-7.51, 7.52-7.58, 8.10-8.13 (3m, 4H, 2H, 4H, 2C_6H_5) ppm. ^{31}P-NMR (242.9 MHz, $CDCl_3$, 85% H_3PO_4): 102.9 (s) ppm. ^{13}C-NMR (150.9 MHz, $CDCl_3$, TMS): 39.15 (SCH_2), 52.55 (OCH_3), 128.25-128.32 (d, $^1J_{C\text{-}P}$ = 11.62 Hz), 130.29, 130.74, 132.70-132.71 (d, $^2J_{C\text{-}P}$ = 2.72 Hz), 134.12-134.18 (d, $^1J_{C\text{-}P}$ = 9.05 Hz), 169.13, 210.24 ppm.

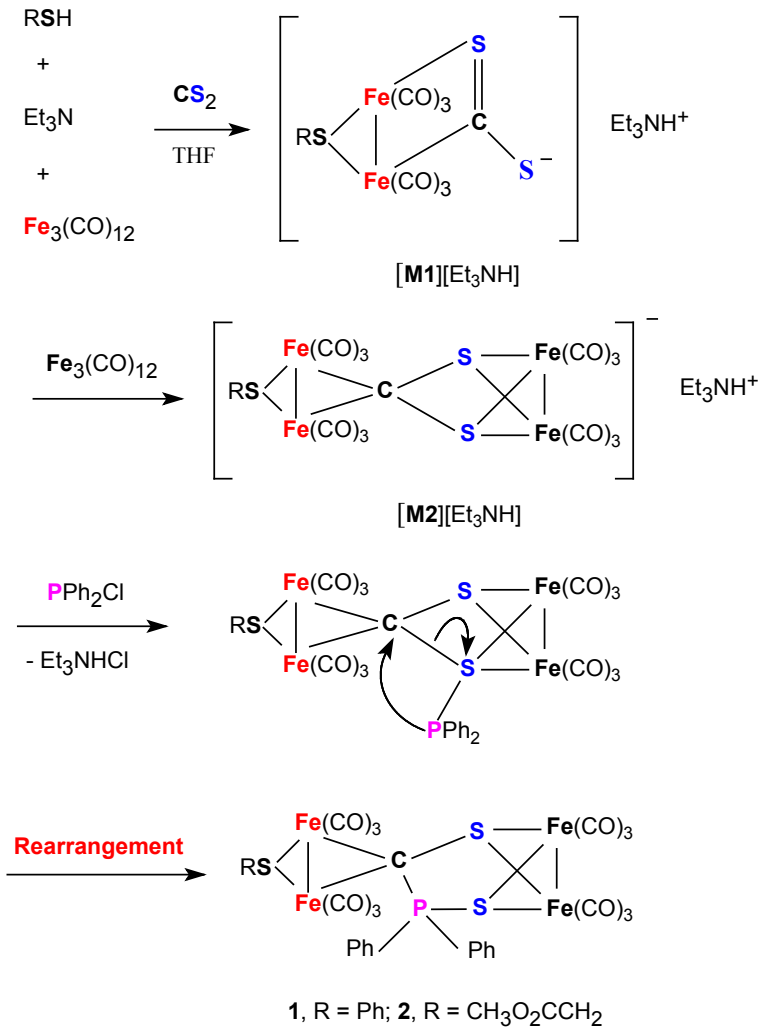
Data for **3**: yield 85%, 2.023 g; mp, 86-88 °C; anal. calcd for $C_{11}H_8Fe_2O_8S_3$: C, 27.75; H, 1.69%; found: C, 27.91; H, 1.74%. IR (KBr disk): ν(C≡O) 2067 (s), 2033 (s), 1995 (vs); ν(C=O) 1732 (m) cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): 2.57 (s, 3H, SCH_3), 3.26, 3.28, 3.35, 3.37 (q, AB, 2H, CH_2), 3.82 (s, 3H, OCH_3) ppm. ^{13}C-NMR (150.9 MHz, $CDCl_3$, TMS): 24.36 (SCH_3), 41.39 (SCH_2), 52.73 (OCH_3), 169.34 (CO_2), 206.32, 209.89, 210.67 ppm.

Crystal data for **1**: $C_{31}H_{15}Fe_4O_{12}PS_3$, M = 930.01, monoclinic, space group $P2_1/c$, a = 13.1351(12) Å, b = 18.8283(16) Å, c = 17.9612(13) Å, α = 90.00°, β = 126.2481(13)°, γ = 90.00°, Z = 4, V = 3582.3(5) Å^3; ρ_{cal} = 1.724 g cm^{-3}; μ(Mo-K$_\alpha$) = 1.867 mm^{-1}; λ = 0.71073 Å; T = 296 K. 52525 reflections measured, 8223 unique (R_{int} = 0.0522). S = 1.02. R_1 = 0.0325 ($I > 2\sigma(I)$). wR_2 =

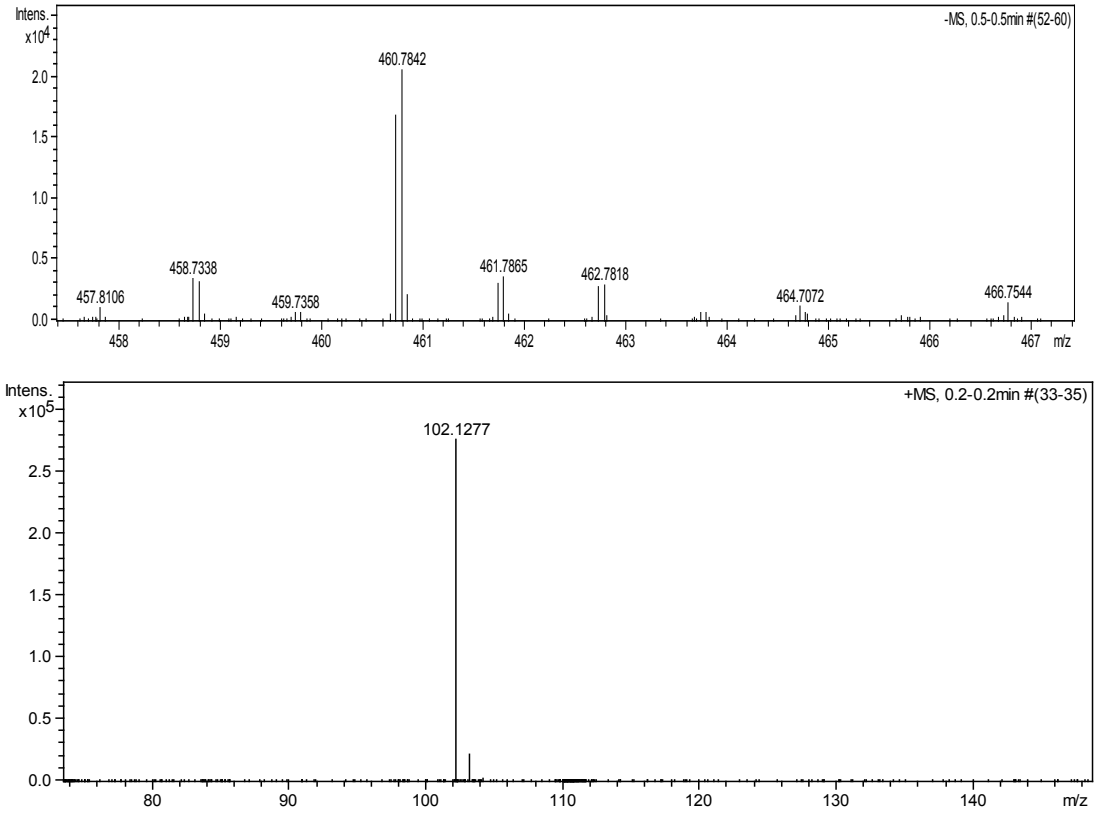
0.0727 (all data). CCDC 912951.

Crystal data for **2**: $C_{28}H_{15}Fe_4O_{14}PS_3$, M = 925.98, monoclinic, space group $P2_1/c$, a = 10.0883(9) Å, b = 13.9167(13) Å, c = 25.9381(14) Å, α = 90.00°, β = 102.271(3)°, γ = 90.00°, Z = 4, V = 3558.4(5) Å^3; ρ_{cal} = 1.729 g cm^{-3}; μ(Mo-K$_\alpha$) = 1.883 mm^{-1}; λ = 0.71073 Å; T = 296 K. 30961 reflections measured, 8149 unique (R_{int} = 0.0461). S = 1.03. R_1 = 0.0357 ($I > 2\sigma(I)$). wR_2 = 0.0889 (all data). CCDC 912952.

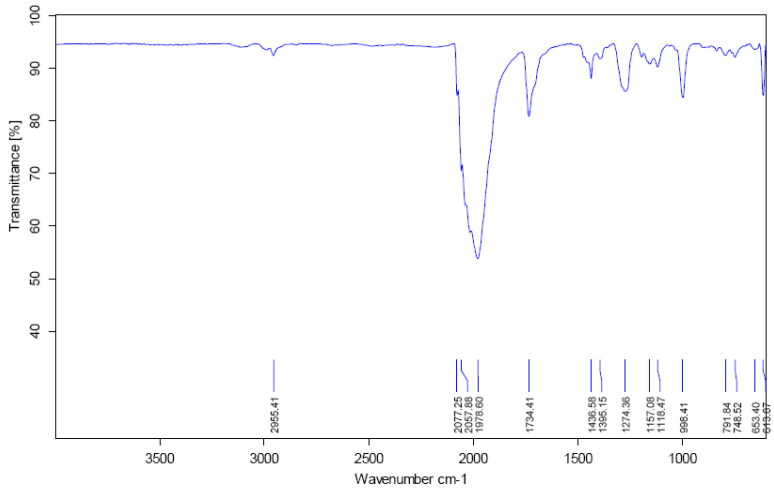
Crystal data for **3**: $C_{11}H_8Fe_2O_8S_3$, M = 476.08, triclinic, space group $P\bar{1}$, a = 7.9461(11) Å, b = 8.1411(12) Å, c = 14.798(2) Å, α = 98.041(2)°, β = 101.942(2)°, γ = 104.491(3)°, Z = 2, V = 888.0(2) Å^3; ρ_{cal} = 1.781 g cm^{-3}; μ(Mo-K$_\alpha$) = 2.020 mm^{-1}; λ = 0.71073 Å; T = 296 K. 7707 reflections measured, 3932 unique (R_{int} = 0.0282). S = 1.02. R_1 = 0.0287 ($I > 2\sigma(I)$). wR_2 = 0.0823 (all data). CCDC 917815.



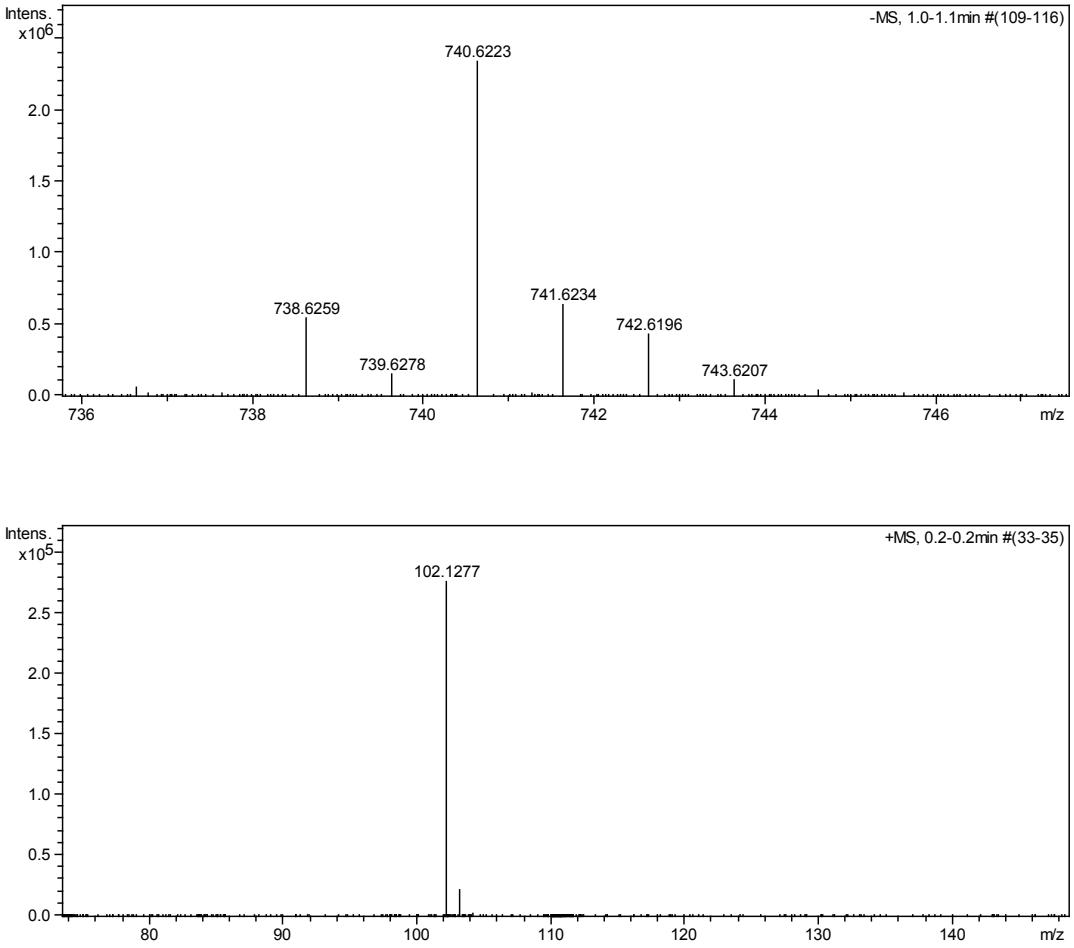
S-1. Proposed mechanism for the formation of **1** and **2**



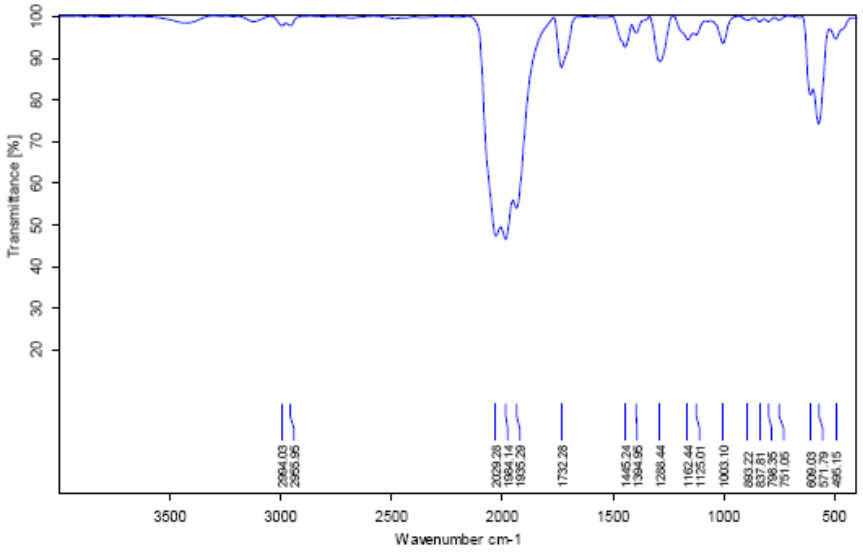
S-2. HR-MS of $[(\mu\text{-}CH_3O_2CCH_2S)Fe_2(CO)_6(\mu\text{-}SCS^-)][HNEt_3^+]$



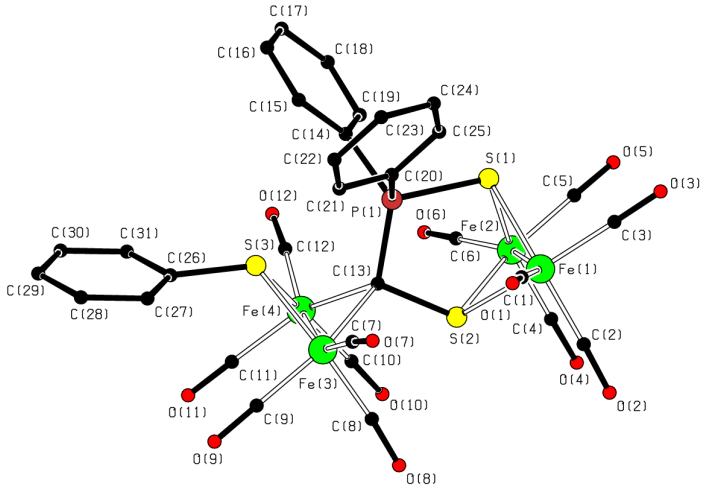
S-3. IR of $[(\mu\text{-}CH_3O_2CCH_2S)Fe_2(CO)_6(\mu\text{-}SCS^-)][HNEt_3^+]$



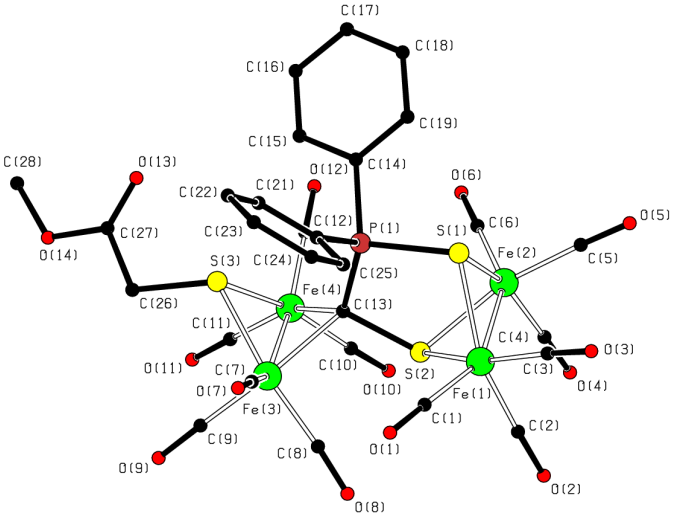
S-4. HR-MS of $[(\mu\text{-}CH_3O_2CCH_2S)Fe_2(CO)_6(\mu\text{-}SCS)Fe_2(CO)_6^-]$ $[HNEt_3^+]$



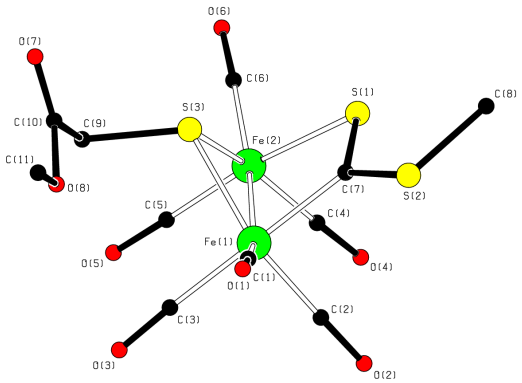
S-5. IR of $[(\mu\text{-}CH_3O_2CCH_2S)Fe_2(CO)_6(\mu\text{-}SCS)Fe_2(CO)_6^-][HNEt_3^+]$



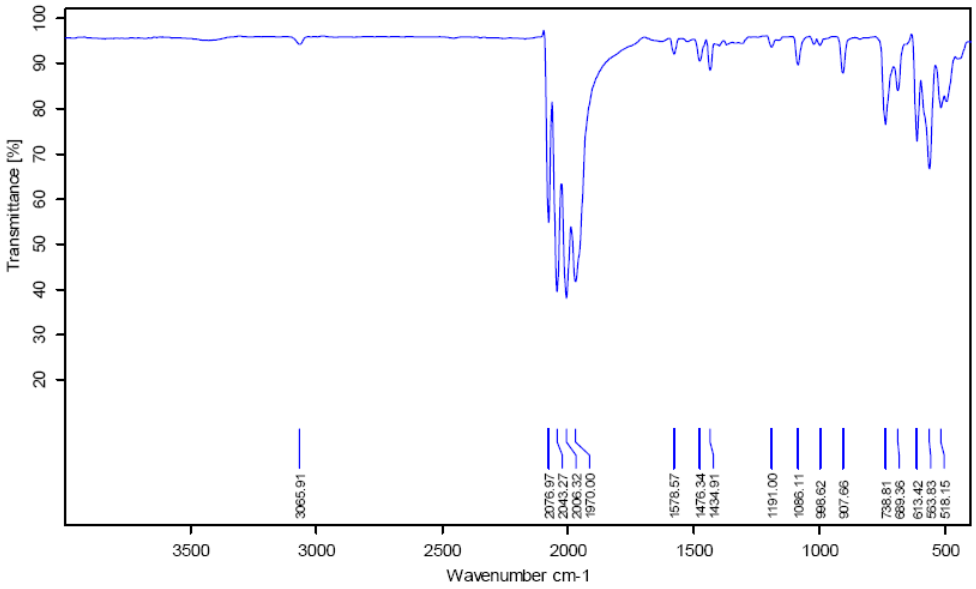
S-6. Platon view of **1**



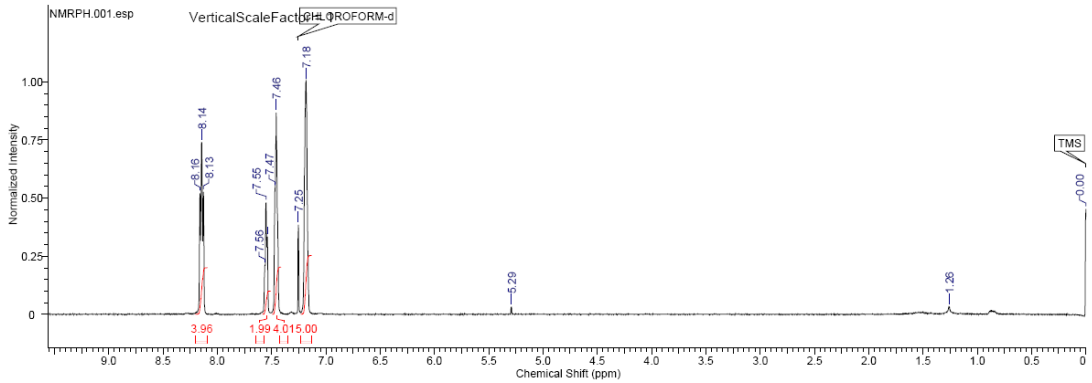
S-7. Platon view of **2**



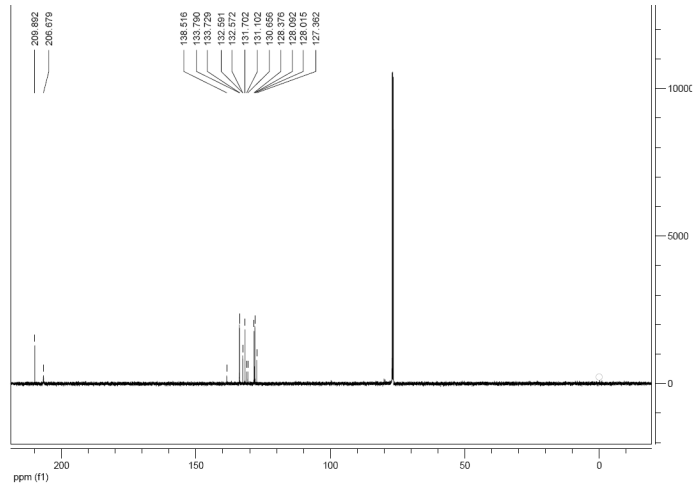
S-8. Platon view of **3**



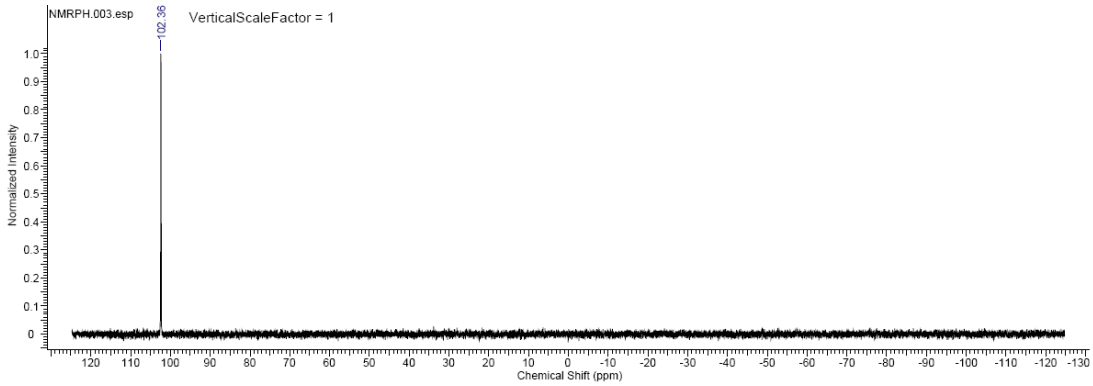
S-9. IR of **1**



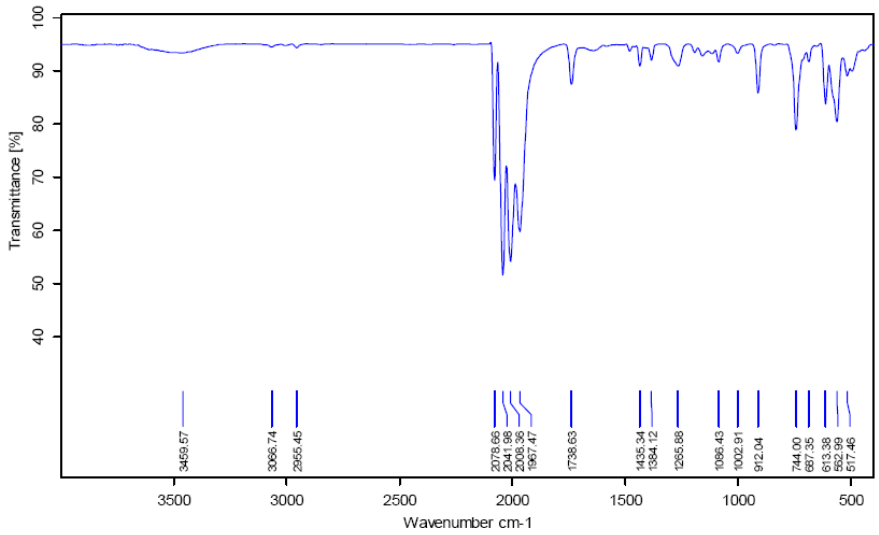
S-10. ^{1}H-NMR of **1**



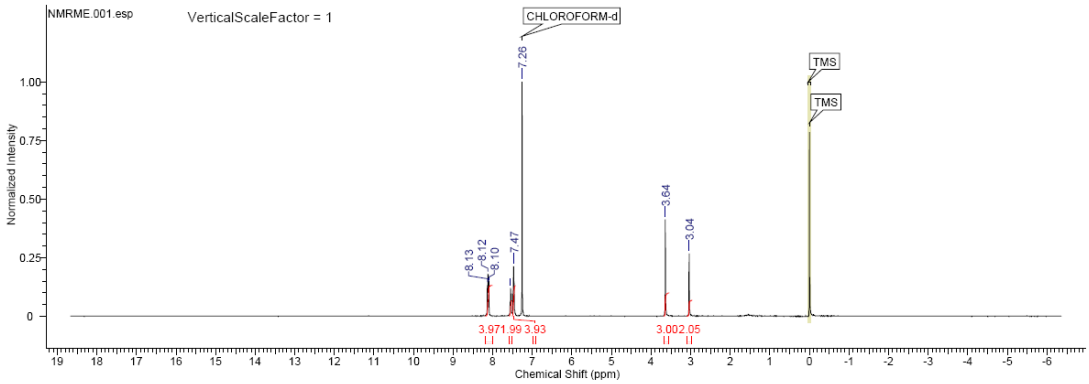
S-11. ^{13}C-NMR of **1**



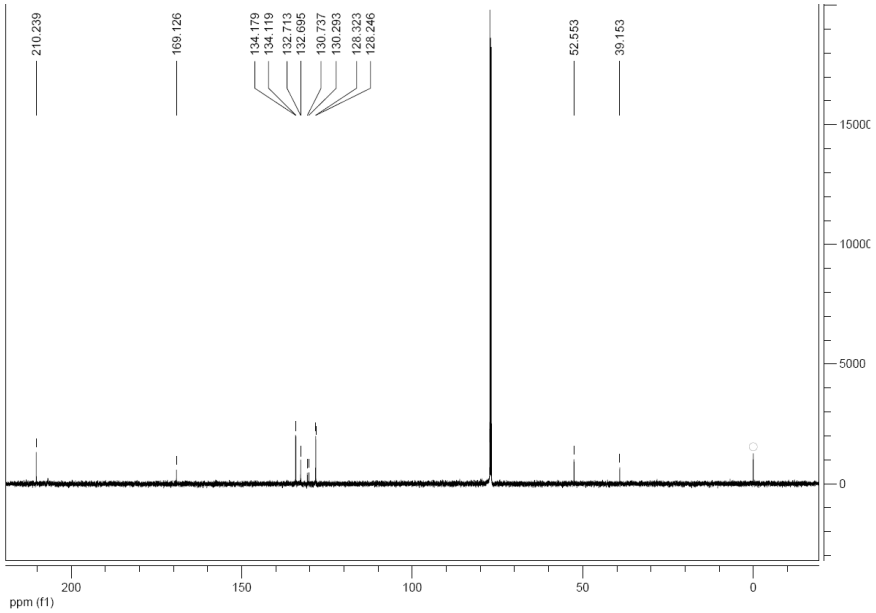
S-12. ^{31}P-NMR of **1**



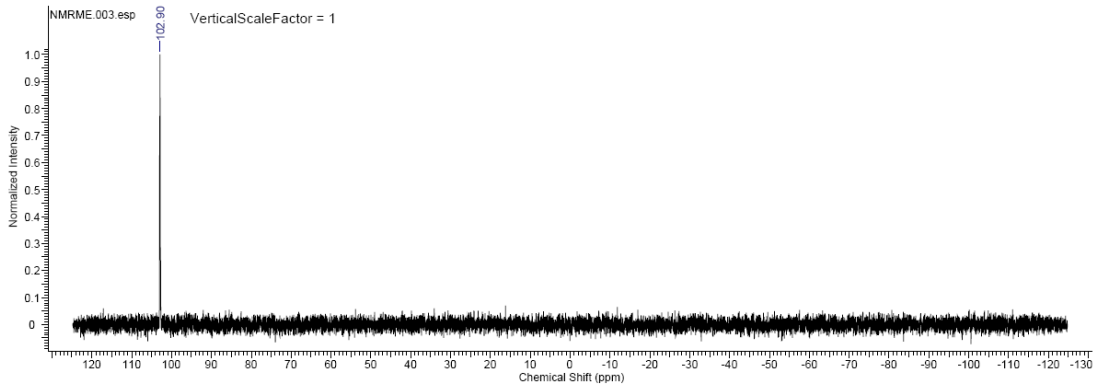
S-13. IR of **2**



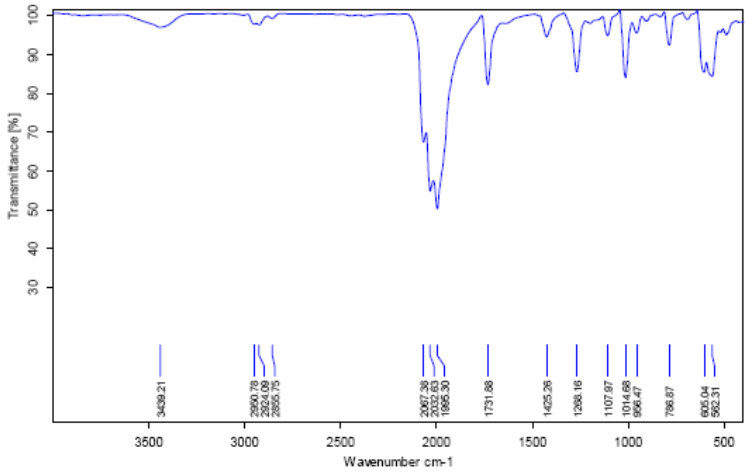
S-14. ^{1}H-NMR of **2**



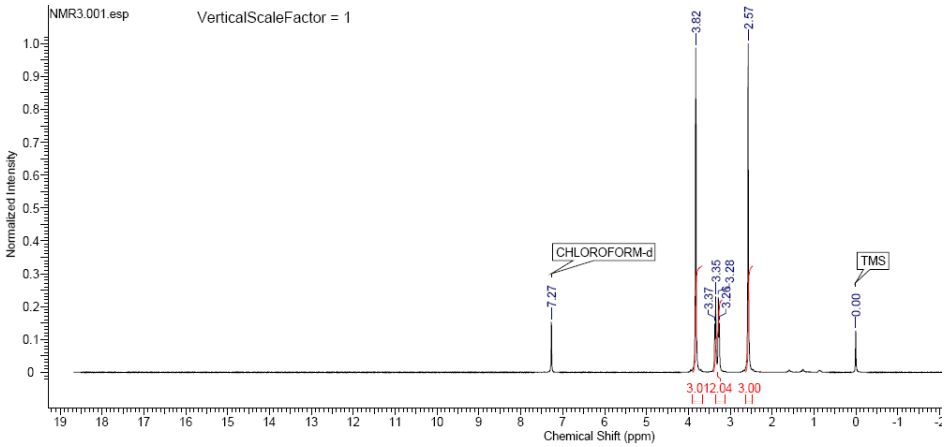
S-15. ^{13}C-NMR of **2**



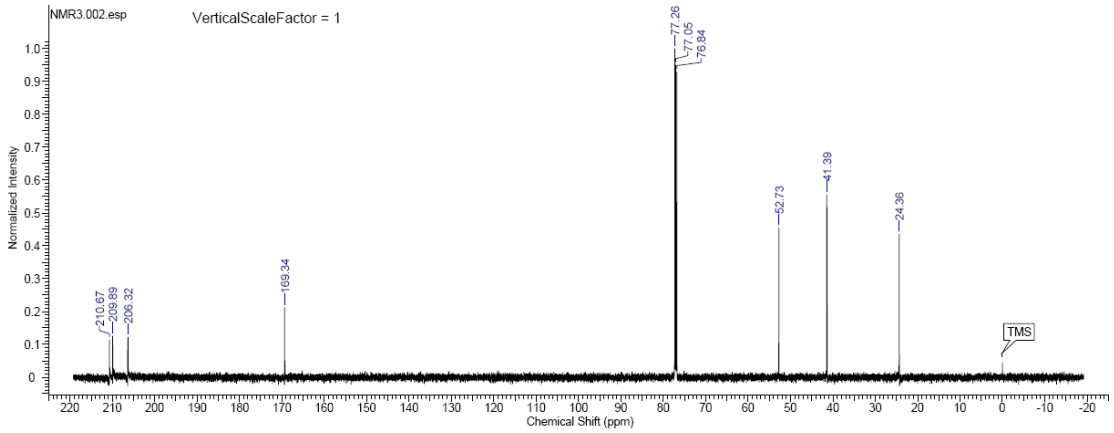
S-16. ^{31}P-NMR of **2**



S-17. IR of **3**



S-18. ^{1}H-NMR of **3**



S-19. ^{13}C-NMR of **3**

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