Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Iron(0) tricarbonyl η^4-1-azadiene complexes and their catalysis on hydroboration of ketones, aldehydes and aldimines *via* non-iron hydride pathway

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1 Experimental

1.1 Synthesis of 1-azadiene ligands

Generally, the 1-azadiene ligands were prepared by following literature protocol with modifications. Typically, to a flask (100 mL) is charged with cinnamaldehyde (10 mmol) and amine (10 mmol) in dichloromethane (DCM, 20 mL) in which anhydrous $MgSO_4$ (2 g) is added to remove any water to promote the reaction. The mixture is stirred at ambient temperature under open-air atmosphere for 24 h till the cinnamaldehyde is completely consumed as indicated by thin-layer chromatography (TLC). The solvent is removed in vacuum to produce the raw product which is purified with flash chromatography (neutral alumina column) with a mixture of petroleum ether / ethyl acetate (5/1, v/v) as an eluent.

N-(*tert*-butyl)-3-phenylprop-2-en-1-imine (**L_1**)

Cinnamaldehyde (1.32 g, 10 mmol) and tert-butylamine (0.731 g, 10 mmol) were used to result in a yellow oily liquid (**L_1**). Yield: 1.50 g, 80%. UV-vis (DCM, lmax / nm): 279 ($\varepsilon = 5.4 \times 10^4$ L mol^{-1} cm^{-1}), 225 ($\varepsilon = 1.3 \times 10^4$ L mol^{-1} cm^{-1}). ATR-FTIR (ZnSe, cm^{-1}): 3058, 3027, 2966, 1679, 1625, 1447, 978, 746, 687. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (t, J = 4.0 Hz, 1H, N=C*H*, H-2), 7.50 – 7.43 (m, 2H, Ar-*H*), 7.38 – 7.26 (m, 3H, Ar-*H*), 6.97 – 6.90 (m, 2H, C*H*=C*H*, H-3 + H-4), 1.25 (s, 9H, 3 × CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ 157.21, 140.93, 135.91, 129.28, 128.84, 128.73, 127.06, 57.12, 29.66. HR-MS (ES$^+$): m/z = 188.1449 (calcd. for [M + H]$^+$: 188.1434).

N-cyclohexyl-3-phenylprop-2-en-1-imine (**L_2**)

Cinnamaldehyde (1.32 g, 10 mmol) and cyclohexanamine (0.991 g, 10 mmol) were used to produce a brown oily liquid (**L_2**). Yield: 2.02 g, 95%. UV-vis (DCM, λ_{max} / nm): 280 ($\varepsilon = 3.7 \times 10^4$ L mol^{-1} cm^{-1}), 225 ($\varepsilon = 8.4 \times 10^5$ L mol^{-1} cm^{-1}). ATR-FTIR (ZnSe, cm^{-1}): 3057, 2927, 2854, 1633, 1574, 1447, 980, 746, 687. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.08 (dd, J = 4.9, 2.6 Hz, 1H, N=C*H*, H-2), 7.50 (d, J = 7.0 Hz, 2H, Ar-*H*), 7.42 – 7.29 (m, 3H, Ar-*H*), 7.00 – 6.90 (m, 2H, C*H*=C*H*, H-3 + H-4), 3.13 – 3.05 (m, 1H, C*H*), 1.85 (d, J = 12.9 Hz, 2H, CH_2), 1.80 – 1.69 (m, 3H, CH_2 + CH_aCH_b), 1.59 (dd, J = 17.7, 7.4 Hz, 2H, CH_2), 1.38 – 1.20 (m, 3H, CH_2 + CH_aCH_b).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm): δ 160.34, 141.08, 135.82, 128.96, 128.77, 128.53, 127.12, 69.69, 34.43, 25.55, 24.78. HR-MS (ES^+): m/z = 214.1592 (calcd. for $[M + H]^+$: 214.1591).

N-(adamantan-1-yl)-3-phenylprop-2-en-1-imine (**L_3**)

Cinnamaldehyde (1.321 g, 10 mmol) and amantadine (1.511 g, 10 mmol) were used to lead to a pale-yellow solid (**L_3**). Yield: 2.50 g, 94%. UV-vis (DCM, λ_{max} / nm): 280 ($\varepsilon = 3.5 \times 10^4$ L mol^{-1} cm^{-1}), 225 ($\varepsilon = 7.6 \times 10^5$ L mol^{-1} cm^{-1}). ATR-FTIR (ZnSe, cm^{-1}): 3033, 2904, 2844, 1635, 1448, 1342, 970, 752, 690. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.07 – 8.02 (m, 1H, N=C*H*, H-2), 7.46 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.38 – 7.26 (m, 3H, Ar-*H*), 6.96 – 6.92 (m, 2H, C*H*=C*H*, H-3 + H-4), 2.15 (s, 3H, 3 × C*H*), 1.80 – 1.67 (m, 12H, 6 × CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm): δ 157.12, 141.08, 136.17, 129.72, 128.99, 128.91, 127.25, 57.63, 43.28, 36.67, 29.68. HR-MS (ES^+): m/z = 266.1926 (calcd. for $[M + H]^+$: 266.1904).

N,3-diphenylprop-2-en-1-imine (**L_4**)

Cinnamaldehyde (1.32 g, 10 mmol) and aniline (0.930 g, 10 mmol) were used to obtain a brown solid (**L_4**). Yield: 1.93 g, 93%. UV-vis (DCM, λ_{max} / nm): 298 ($\varepsilon = 3.6 \times 10^4$ L mol^{-1} cm^{-1}), 233 ($\varepsilon = 1.4 \times 10^4$ L mol^{-1} cm^{-1}). ATR-FTIR (ZnSe, cm^{-1}): 3047, 3027, 2978, 1674, 1623, 1446, 981, 746, 685. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.27 (dd, *J* = 5.8, 2.1 Hz, 1H, N=C*H*, H-2), 7.55 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.45 – 7.33 (m, 5H, Ar-*H*), 7.27 – 7.12 (m, 5H, Ar-*H* + C*H*=C*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm): δ 161.71, 151.64, 144.11, 135.55, 129.63, 129.20, 128.94, 128.53, 127.52, 126.16, 120.95. HR-MS (ES^+): m/z = 208.1124 (calcd. for $[M + H]^+$: 208.1121).

N-(naphthalen-1-yl)-3-phenylprop-2-en-1-imine (**L_5**)

Cinnamaldehyde (1.32 g, 10 mmol) and naphthylamine (1.43 g, 10 mmol) were used to result in a yellow solid (**L_5**). Yield: 1.49 g, 58%. UV-vis (DCM, λ_{max} / nm): 303 ($\varepsilon = 2.5 \times 10^4$ L mol^{-1} cm^{-1}), 233 ($\varepsilon = 2.7 \times 10^4$ L mol^{-1} cm^{-1}). ATR-FTIR (ZnSe, cm^{-1}): 3042, 3022, 1624, 1505, 1390, 1039, 991, 800, 770, 692. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.34 – 8.26 (m, 2H, N=C*H* + Ar-*H*), 7.83 (dd, *J* = 6.0, 3.0 Hz, 1H, Ar-*H*), 7.69 (d, *J* = 7.2 Hz, 1H, CH_a=CH_b), 7.55 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.50 (dd, *J* = 6.3, 3.2 Hz, 2H, Ar-*H*), 7.46 – 7.34 (m, 4H, Ar-*H*), 7.24 (q, *J* = 7.0 Hz, 1H, Ar-*H*), 7.15 (d, *J* = 16.0 Hz, 1H, Ar-*H*), 6.98 (d, *J* = 7.2 Hz, 1H, CH_a=CH_b). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm): δ 162.18, 149.50, 144.16, 135.70, 134.02, 129.73, 129.05, 128.84, 128.77, 127.76, 127.66, 126.51, 126.11, 125.96, 125.92, 123.95, 112.92. HR-MS (ES^+): m/z = 258.1292 (calcd. for $[M + H]^+$: 258.1278).

1.2 Synthesis of the iron complexes, 1a, 1b, and 1d

Similar proposals were followed as described in Section 4.3 of the experimental with modifications.

$[Fe(\eta^4\text{-}L_1)(CO)_3]$ (1a)

Diironnonacarbonyl (907 mg, 2.5mmol) and $\mathbf{L_1}$ (376 mg, 2 mmol) were employed to synthesise complex **1a** (an orange oil). Yield: 190 mg, 29%. UV-vis (DCM, λ_{max} / nm): 234 ($\varepsilon = 1.4 \times 10^4$ L mol^{-1} cm^{-1}), 280 ($\varepsilon = 3.6 \times 10^4$ L mol^{-1} cm^{-1}). FTIR (DCM, ν_{CO} / cm^{-1}): 2048, 1984, 1963. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 – 7.18 (m, 4H, Ar-*H*), 7.18 – 7.11 (m, 1H, Ar-*H*), 6.83 (s, 1H, H-2), 5.36 (d, *J* = 9.2 Hz, 1H, H-3), 2.99 (d, *J* = 9.0 Hz, 1H, H-4), 1.08 (s, 9H, 3 × C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ 139.80, 128.65, 126.82, 126.46, 110.72, 68.03, 60.87, 56.08, 30.64. HR-MS (ES^+): m/z = 327.0699 (calcd. for $[M]^+$: 327.0558).

$[Fe(\eta^4\text{-}L_2)(CO)_3]$ (1b)

Diironnonacarbonyl (907 mg, 2.5 mmol) and $\mathbf{L_2}$ (426 mg, 2 mmol) were used to prepare complex **1b** (an orange solid). Yield: 310 mg, 44%. UV-vis (DCM, λ_{max} / nm): 236 ($\varepsilon = 2.8 \times 10^4$ L mol^{-1} cm^{-1}), 268 ($\varepsilon = 2.2 \times 10^4$ L mol^{-1} cm^{-1}). FTIR (DCM, ν_{CO} / cm^{-1}): 2051, 1987, 1970. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.51 – 6.98 (m, 5H, Ar-*H*), 6.46 (s, 1H, H-2), 5.39 (d, *J* = 6.5 Hz, 1H, H-3), 2.87 (d, *J* = 7.8 Hz, 1H, H-4), 1.86 – 0.94 (m, 11H, cyclohexyl). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ 139.53, 128.69, 126.61, 126.56, 111.09, 72.02, 67.31, 60.92, 37.93, 36.40, 25.83, 25.04, 24.95. Elemental analysis (%) for $C_{18}H_{19}FeNO_3$ (M.W. = 353.1990), found (calcd.): C, 60.83 (61.21); H, 5.26 (5.42); N, 3.90 (3.97). HR-MS (ES^+): m/z = 354.0802 (calcd. for $[M+H]^+$: 354.0793).

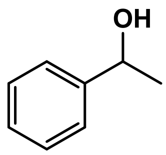
$[Fe(\eta^4\text{-}L_4)(CO)_3]$ (1d)

Diironnonacarbonyl (907 mg, 2.5 mmol) and $\mathbf{L_4}$ (414 mg, 2 mmol) were used to produce complex **1d** (an orange solid). Yield: 380 mg, 55%. UV-vis (DCM, λ_{max} / nm): 278 ($\varepsilon = 1.9 \times 10^4$ L mol^{-1} cm^{-1}). FTIR (DCM, ν_{CO} / cm^{-1}): 2058, 1996, 1983. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 – 7.27 (m, 4H, Ar-*H*), 7.25 – 7.15 (m, 3H, Ar-*H*), 6.99 – 6.90 (m, 4H, Ar-*H* + H-2), 5.72 (dd, *J* = 9.4, 2.7 Hz, 1H, H-3), 3.39 (d,

J = 9.4 Hz, 1H, H-4). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm): δ 153.51, 138.94, 129.13, 128.94, 127.07, 126.74, 122.69, 121.99, 104.00, 74.60, 62.31. Elemental analysis (%) for $C_{18}H_{13}FeNO_3$•(hexane)$_{0.22}$, found (calcd.): C, 63.88 (63.38); H, 3.95 (4.43); N, 4.11 (3.83). HR-MS (ES^+): m/z = 348.0316 (calcd. for $[M+H]^+$: 348.0323).

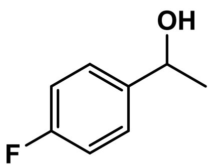
1.3 Synthesis and characterizations of the secondary alcohols, 2a-k

1-phenylethan-1-ol (**2a**)



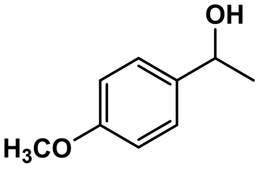
Acetophenone (120 mg, 1 mmol) was used to result a colorless oil. Yield: 108 mg, 88%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30 – 7.17 (m, 4H, Ar-*H*), 7.17 – 7.05 (m, 1H, Ar-*H*), 4.67 (t, 1H, C*H*), 2.88 (s, 1H, O*H*), 1.31 (d, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 145.87, 128.40, 127.32, 125.43, 70.15, 25.12. The data of the known compound are consistent with the reported literature. [1]

1-(4-fluorophenyl)ethan-1-ol (**2b**)



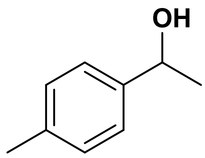
1-(4-fluorophenyl)ethan-1-one (138 mg, 1 mmol) was used to result a colorless oil. Yield: 117 mg, 84%. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.31 (s, 2H, Ar-*H*), 7.02 (s, 2H, Ar-*H*), 4.85 (s, 1H, C*H*), 2.16 (s, 1H, O*H*), 1.45 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.09, 141.67, 127.21, 127.16, 115.48, 115.34, 69.94, 25.44. The data of the known compound are consistent with the reported literature. [1]

1-(4-methoxyphenyl)ethan-1-ol (**2c**)



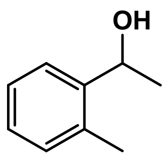
1-(4-methoxyphenyl)ethan-1-one (150 mg, 1 mmol) was used to result color-less oil. Yield: 112 mg, 74%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 – 7.23 (m, 2H, Ar-*H*), 7.06 – 6.78 (m, 2H, Ar-*H*), 4.78 (t, 1H, C*H*), 3.77 (d, J = 6.0 Hz, 3H, OCH_3), 2.75 (s, 1H, O*H*), 1.43 (t, J = 6.2 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 158.77, 138.12, 126.67, 113.72, 69.73, 55.22, 25.04. The data of the known compound are consistent with the reported literature. [1]

1-(p-tolyl)ethan-1-ol (**2d**)



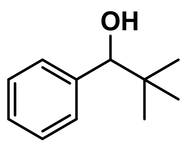
1-(p-tolyl)ethan-1-one (134 mg, 1 mmol) was used to result a colorless oil. Yield: 115 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.18 (dd, J = 38.3, 7.9 Hz, 4H, Ar-*H*), 4.81 (q, J = 6.3 Hz, 1H, C*H*), 2.33 (s, 3H, CH_3), 2.17 (s, 1H, OH), 1.45 (d, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 142.97, 137.15, 129.21, 125.44, 70.25, 25.16, 21.18. The data of the known compound are consistent with the reported literature. [1]

1-(o-tolyl)ethan-1-ol (**2e**)



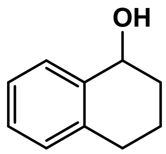
1-(o-tolyl)ethan-1-one (134 mg, 1 mmol) was used to result a colorless oil. Yield: 97 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 7.6 Hz, 1H, Ar-*H*), 7.31 – 7.11 (m, 3H, Ar-*H*), 5.14 – 5.01 (m, C*H*), 2.48 (s, 1H, O*H*), 2.35 (d, J = 7.4 Hz, 3H, CH_3), 1.46 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 143.93, 134.18, 130.33, 127.11, 126.36, 124.55, 66.68, 23.94, 18.94. The data of the known compound are consistent with the reported literature. [1]

2,2-dimethyl-1-phenylpropan-1-ol (**2f**)



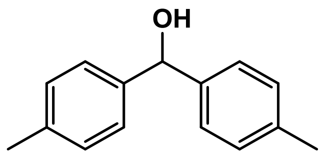
2,2-dimethyl-1-phenylpropan-1-one (162 mg, 1 mmol) was used to result a colorless oil. Yield: 131 mg, 80%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.35 – 7.21 (m, 5H, Ar-*H*), 4.37 (s, 1H, C*H*), 1.95 (s, 1H, O*H*), 0.91 (s, 9H, 3 × CH_3). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 142.31, 127.73, 127.66, 127.38, 82.50, 35.73, 26.04. The data of the known compound are consistent with the reported literature. [1]

1,2,3,4-tetrahydronaphthalen-1-ol (**2g**)



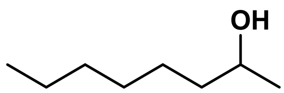
3,4-dihydronaphthalen-1(2H)-one (146 mg, 1 mmol) was used to result a colorless oil. Yield: 133 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 – 7.32 (m, 1H, Ar-*H*), 7.24 – 7.11 (m, 2H, Ar-*H*), 7.06 (d, J = 4.3 Hz, 1H, Ar-*H*), 4.69 (s, 1H, C*H*), 2.73 (tdd, J = 23.1, 17.1, 5.8 Hz, 2H, CH_2), 2.35 (s, 1H, O*H*), 1.98 – 1.66 (m, 4H, 2 × CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 138.82, 137.10, 128.96, 128.72, 127.49, 126.12, 77.48, 77.16, 76.84, 68.02, 32.23, 29.27, 18.87. The data of the known compound are consistent with the reported literature.[2]

Di-p-tolylmethanol (**2h**)



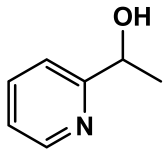
Di-p-tolylmethanone (210 mg, 1 mmol) was used to result a white solid. Yield: 100 mg, 47%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.22 (d, J = 7.8 Hz, 4H, Ar-*H*), 7.10 (d, J = 7.7 Hz, 4H, Ar-*H*), 5.74 (s, 1H, C*H*), 2.29 (s, 6H, 2 × CH_3), 2.14 (d, J = 2.8 Hz, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 141.21, 137.27, 129.26, 126.54, 76.05, 21.25. The data of the known compound are consistent with the reported literature.[3]

Octan-2-ol (**2i**)



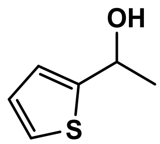
Octan-2-one (128 mg, 1 mmol) was used to result a colorless oil. Yield: 121 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.71 (s, 1H, C*H*), 2.27 (s, 1H, O*H*), 1.48 – 1.05 (m, 13H, CH_3 + 5 × CH_2), 0.82 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 68.02, 39.40, 31.92, 29.42, 25.83, 23.41, 22.68, 14.11. The data of the known compound are consistent with the reported literature.[4]

1-(pyridin-2-yl)ethan-1-ol (**2j**)



1-(pyridin-2-yl)ethan-1-one (121 mg, 1 mmol) was used to result a brown oil. Yield: 116 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.55 (s, 1H, Ar-*H*), 7.70 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.29 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.24 – 7.17 (m, 1H, Ar-*H*), 4.90 (d, *J* = 6.1 Hz, 1H, C*H*), 4.36 (s, 1H, O*H*), 1.51 (d, *J* = 6.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 163.08, 148.23, 136.92, 122.35, 119.93, 68.91, 24.40. The data of the known compound are consistent with the reported literature.[1]

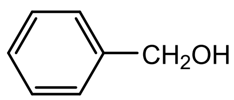
1-(thiophen-2-yl)ethan-1-ol (**2k**)



1-(thiophen-2-yl)ethan-1-one (126 mg, 1 mmol) was used to result a light-yellow oil. Yield: 105 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.29 – 7.15 (m, 1H, Ar-*H*), 6.95 (d, *J* = 4.1 Hz, 2H, Ar-*H*), 5.16 – 4.98 (m, 1H, C*H*), 2.77 – 2.29 (m, 1H, O*H*), 1.58 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 149.95, 126.73, 126.69, 124.50, 124.42, 123.28, 123.24, 66.28, 25.33, 25.29. The data of the known compound are consistent with the reported literature. [1]

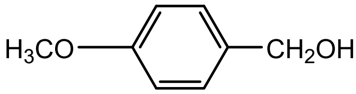
1.4 Synthesis and characterizations of the primary alcohols, 3a-f

Phenylmethanol (**3a**)



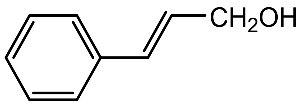
Benzaldehyde (106 mg, 1 mmol) was used to result a colorless oil. Yield: 103 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 – 7.22 (m, 5H, Ar-*H*), 4.66 (d, *J* = 5.2 Hz, 2H, CH_2), 2.24 (t, *J* = 5.9 Hz, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 140.91, 128.64, 127.72, 127.09, 65.31. The data of the known compound are consistent with the reported literature. [1]

(4-methoxyphenyl)methanol (**3b**)



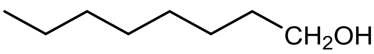
4-methoxybenzaldehyde (136 mg, 1 mmol) was used to result a light-yellow oil. Yield: 97 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.27 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 6.88 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 4.59 (d, *J* = 5.0 Hz, 2H, CH_2), 3.79 (s, 3H, OCH_3), 1.88 – 1.74 (m, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.26, 133.19, 128.78, 114.03, 65.12, 55.41. The data of the known compound are consistent with the reported literature. [1]

3-phenylprop-2-en-1-ol (**3c**)



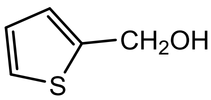
Cinnamaldehyde (132 mg, 1 mmol) was used to result a light-yellow oil. Yield: 113 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52 – 7.21 (m, 5H，Ar-*H*), 6.61 (d, *J* = 15.9 Hz, 1H, CH_a=CH_b), 6.46 – 6.32 (m, 1H, CH_a=CH_b), 4.32 (s, 2H, CH_2), 1.82 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 136.74, 131.19, 128.70, 128.58, 127.80, 126.56, 63.79. The data of the known compound are consistent with the reported literature. [1]

octan-1-ol (**3d**)



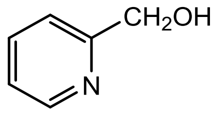
Octanal (128 mg, 1 mmol) was used to result a colorless oil. Yield: 122 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 3.62 (t, *J* = 6.6 Hz, 2H, CH_2), 1.61 – 1.45 (m, 3H, O*H* + CH_2), 1.39 – 1.19 (m, 10H, 5 × CH_2), 0.87 (t, *J* = 6.1 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 63.18, 32.91, 31.95, 29.53, 29.41, 25.87, 22.79, 14.24. The data of the known compound are consistent with the reported literature.[5]

Thiophen-2-ylmethanol (**3e**)



Thiophene-2-carbaldehyde (112 mg, 1 mmol) was used to result a light-yellow oil. Yield: 91 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.34 – 7.21 (m, 1H, Ar-*H*), 7.10 – 6.92 (m, 2H, Ar-*H*), 4.78 (s, 2H, CH_2), 2.47 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 144.03, 126.93, 125.66, 125.56, 59.91. The data of the known compound are consistent with the reported literature. [1]

pyridin-2-ylmethanol (**3f**)

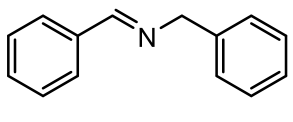


Picolinaldehyde (107 mg, 1 mmol) was used to result a light-yellow oil. Yield: 101 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.44 (s, 1H, Ar-*H*), 7.69 – 7.58 (m, 1H, Ar-*H*), 7.29 (d, *J* = 6.6 Hz, 1H, Ar-*H*), 7.13 (d, *J* = 5.1 Hz, 1H, Ar-*H*), 4.70 (d, *J* = 4.4 Hz, 2H, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.83, 148.44, 136.94, 122.32, 120.85, 64.36. The data of the known compound are consistent with the reported literature. [1]

1.5 Synthesis and characterizations of aldimines

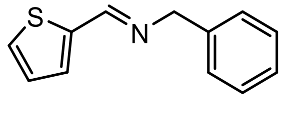
In a typical procedure, 100 mL flask was charged with aldehyde (10 mmol) and amine (10 mmol) in DCM (20 mL). $MgSO_4$ was added in to remove water. The mixture was stirred at ambient temperature under open-air atmosphere for 24 h till the cinnamaldehyde consumed. The solvent was removed by vacuum and the products were purified by neutral alumina-filled flash chromatography with a mixture of petroleum ether / ethyl acetate (5/1 in volumes) as an eluent.

N-benzyl-1-phenylmethanimine



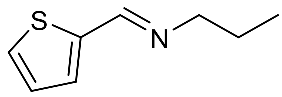
Benzaldehyde (1.06 g, 10 mmol) and phenylmethanamine (1.07 g, 10 mmol) were used to result a yellow oil. Yield: 1.894 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.41 (s, 1H, N=C*H*), 7.80 (t, 2H, Ar-*H*), 7.48 – 7.39 (m, 3H, Ar-*H*), 7.39 – 7.32 (m, 4H, Ar-*H*), 7.31 – 7.24 (m, 1H, Ar-*H*), 4.84 (s, 2H, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 162.16, 139.35, 136.20, 130.90, 128.72, 128.61, 128.39, 128.09, 127.11, 65.15.

N-benzyl-1-(thiophen-2-yl)methanimine



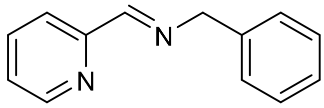
Thiophene-2-carbaldehyde (1.12 g, 10 mmol) and phenylmethanamine (1.18 g, 11 mmol) were used to result a brown oil. Yield: 1.872 g, 93%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.38 (s, 1H, N=C*H*), 7.35 – 7.20 (m, 6H, Ar-*H*), 7.00 (t, 1H, Ar-*H*), 4.74 (s, 2H, CH_2). [13]C NMR (101 MHz, $CDCl_3$, ppm) δ 155.17, 142.36, 139.01, 130.70, 129.02, 128.46, 127.98, 127.35, 126.98, 64.39.

N-propyl-1-(thiophen-2-yl)methanimine



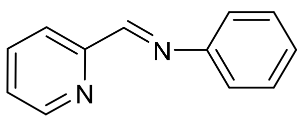
Thiophene-2-carbaldehyde (1.112 g, 10 mmol) and propan-1-amine (0.660 g, 11 mmol) were used to result a brown oil. Yield: 1.4693 g, 96%. [1]H NMR (400 MHz, $CDCl_3$, ppm) δ 8.35 (s, 1H, N=C*H*), 7.38 (d, *J* = 4.8 Hz, 1H, Ar-*H*), 7.28 (d, *J* = 3.0 Hz, 1H, Ar-*H*), 7.06 (t, *J* = 4.2 Hz, 1H, Ar-*H*), 3.54 (t, *J* = 6.9 Hz, 2H, CH_2), 1.71 (dd, *J* = 14.4, 7.2 Hz, 2H, CH_2), 0.94 (t, *J* = 7.4 Hz, 3H, CH_3). [13]C NMR (101 MHz, $CDCl_3$, ppm) δ 154.15, 142.71, 130.19, 128.64, 127.39, 63.28, 24.11, 11.93.

N-benzyl-1-(pyridin-2-yl)methanimine



Benzylamine (1.07 g, 10 mmol) and 2-formalpyridine (1.07 g, 10 mmol) were used to result a yellow oil. Yield: 1.80 g, 92%. [1]H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.4 Hz, 1H), 8.49 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 4.4 Hz, 4H), 4.86 (s, 2H). [13]C NMR (101 MHz, $CDCl_3$) δ 162.64, 154.32, 149.23, 138.52, 136.39, 128.42, 128.02, 127.01, 124.69, 121.18, 64.77.

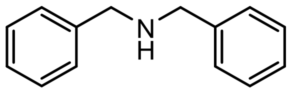
N-phenyl-1-(pyridin-2-yl)methanimine



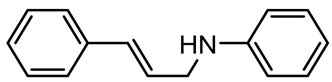
Aniline (1.06 g, 10 mmol) and 2-formalpyridine (1.07 g, 10 mmol) were used to result a yellow oil. Yield: 1.54 g, 85%. [1]H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.0 Hz, 1H), 8.60 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.39 (dt, *J* = 12.2, 7.2 Hz, 3H), 7.29 (d, *J* = 8.0 Hz, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 160.72, 154.61, 151.03, 149.80, 136.80, 129.33, 126.84, 125.26, 122.01, 121.20.

1.6 Synthesis and characterizations of the secondary amines, 4a-g

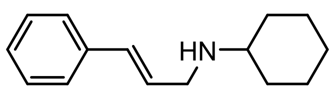
Dibenzylamine (**4a**)

 N-benzyl-1-phenylmethanimine (195 mg, 1 mmol) was used to result a light-yellow oil. Yield: 187 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.53 – 7.20 (m, 10H, Ar-*H*), 3.87 (m, 4H, 2×CH_2), 1.74 (s, 1H, N*H*). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 140.36, 128.45, 128.20, 126.99, 53.20. The data of the known compound are consistent with the reported literature.[6]

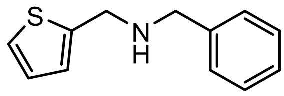
N-cinnamylaniline (**4b**)

 N,3-diphenylprop-2-en-1-imine (207 mg, 1 mmol) was used to result a light-yellow oil. Yield: 196 mg, 94%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.35 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.29 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.23 – 7.15 (m, 3H, Ar-*H*), 6.72 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 6.65 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.60 (d, *J* = 15.9 Hz, 1H, CH_a=CH_b), 6.34 – 6.26 (m, 1H, CH_a=CH_b), 3.91 (d, *J* = 5.6 Hz, 2H, CH_2), 3.81 (s, 1H, N*H*). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 148.14, 136.96, 131.59, 129.38, 128.68, 127.63, 127.15, 126.43, 117.72, 113.15, 46.30. The data of the known compound are consistent with the reported literature. [7]

N-cinnamylcyclohexanamine (**4c**)

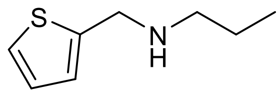
 N-cyclohexyl-3-phenylprop-2-en-1-imine (213 mg, 1 mmol) was used to result a light-yellow oil. Yield: 152 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.39 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.34 – 7.20 (m, 3H, Ar-*H*), 6.56 (d, *J* = 15.9 Hz, 1H, CH=C*H*), 6.35 (dt, *J* = 15.8, 6.5 Hz, 1H, C*H*=CH), 3.49 (d, *J* = 6.4 Hz, 2H, N-CH_2), 2.59 (t, *J* = 10.2 Hz, 1H, N-C*H*), 1.98 (d, *J* = 11.2 Hz, 2H, CH_2), 1.74 (d, *J* = 11.8 Hz, 2H, CH_2), 1.63 (d, *J* = 11.0 Hz, 1H, N*H*), 1.33 – 1.11 (m, 6H, 3 × CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 136.94, 132.20, 128.61, 127.58, 127.27, 126.42, 56.23, 53.54, 48.55, 32.91, 26.00, 25.04. The data of the known compound are consistent with the reported literature. [7]

N-benzyl-1-(thiophen-2-yl)methanamine (**4d**)



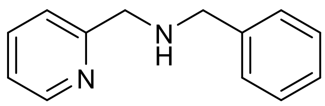
N-benzyl-1-(thiophen-2-yl)methanimine (201 mg, 1 mmol) was used to result a yellow oil. Yield: 83 mg, 41%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 – 7.21 (m, 6H, Ar-*H*), 7.03 – 6.86 (m, 2H, Ar-*H*), 4.00 (s, 2H, CH_2), 3.84 (s, 2H, CH_2), 1.70 (s, 1H, N*H*). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 144.24, 140.06, 128.57, 128.34, 127.17, 126.75, 125.06, 124.55, 52.89, 47.67. The data of the known compound are consistent with the reported literature. [8]

N-(thiophen-2-ylmethyl)propan-1-amine (**4e**)



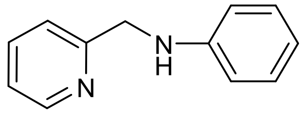
N-propyl-1-(thiophen-2-yl)methanimine (153 mg, 1 mmol) was used to result a brown oil. Yield: 72 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.20 (dd, *J* = 4.9, 1.2 Hz, 1H, Ar-*H*), 7.01 – 6.85 (m, 2H, Ar-*H*), 3.98 (s, 2H, CH_2), 2.62 (t, *J* = 7.2 Hz, 2H, CH_2), 1.53 (dd, *J* = 14.6, 7.3 Hz, 2H, CH_2), 0.92 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 144.40, 126.68, 124.86, 124.33, 51.14, 48.48, 23.18, 11.86. The data of the known compound are consistent with the reported literature.[9]

N-benzyl-1-(pyridin-2-yl)methanamine (**4f**)



N-benzyl-1-(pyridin-2-yl)methanimine (196 mg, 1 mmol) was used to result a yellow oil. Yield: 118 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 3.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.26 (dd, *J* = 18.6, 7.6 Hz, 5H), 7.18 (d, *J* = 5.5 Hz, 1H), 7.12 – 7.03 (m, 1H), 3.85 (s, 2H), 3.77 (s, 2H), 2.13 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.79, 149.39, 140.19, 136.54, 128.49, 128.35, 127.07, 122.46, 122.05, 77.48, 77.16, 76.84, 54.58, 53.59. The data of the known compound are consistent with the reported literature.[10]

N-(pyridin-2-ylmethyl)aniline (**4g**)



N-phenyl-1-(pyridin-2-yl)methanimine (182 mg, 1 mmol) was used to result a colourless oil. Yield: 94 mg, 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 4.0 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.7 Hz, 1H), 7.18 (t, J = 7.3 Hz, 3H), 6.79 – 6.60 (m, 3H), 4.46 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.58, 149.23, 147.93, 136.71, 129.30, 122.15, 121.63, 117.61, 113.08, 77.48, 77.16, 76.84, 49.32. The data of the known compound are consistent with the reported literature.[11]

2 Figures and tables

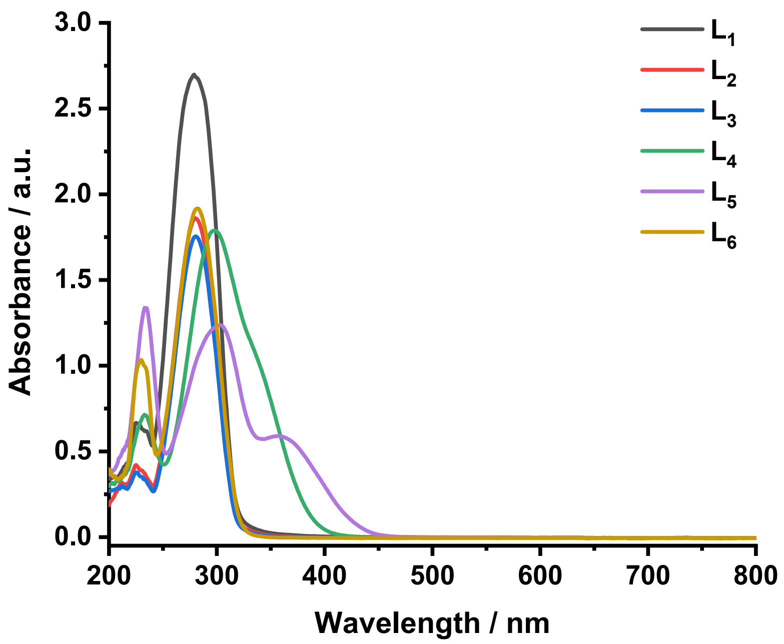


Figure S1 UV-vis spectra of $\mathbf{L_{1-6}}$ in DCM (50 μM).

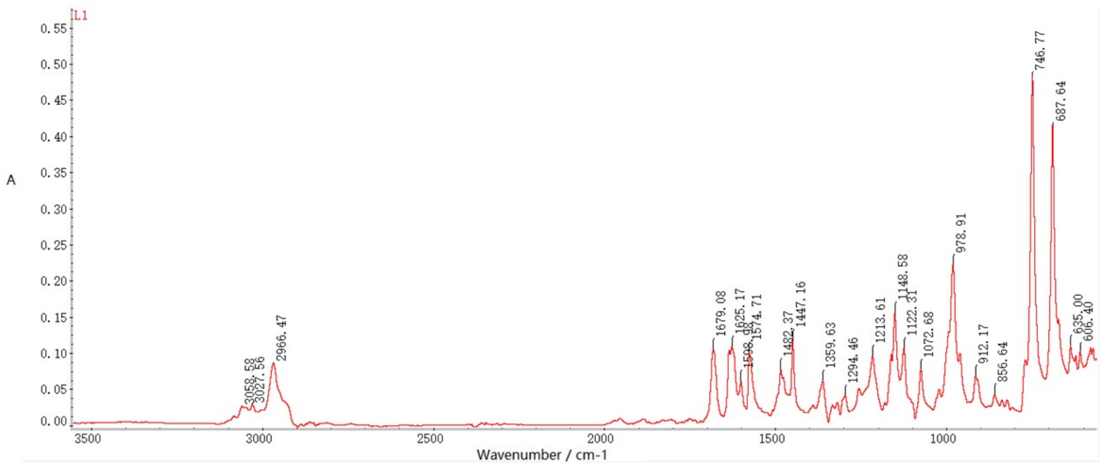


Figure S2 ATR-FTIR spectrum of $\mathbf{L_1}$.

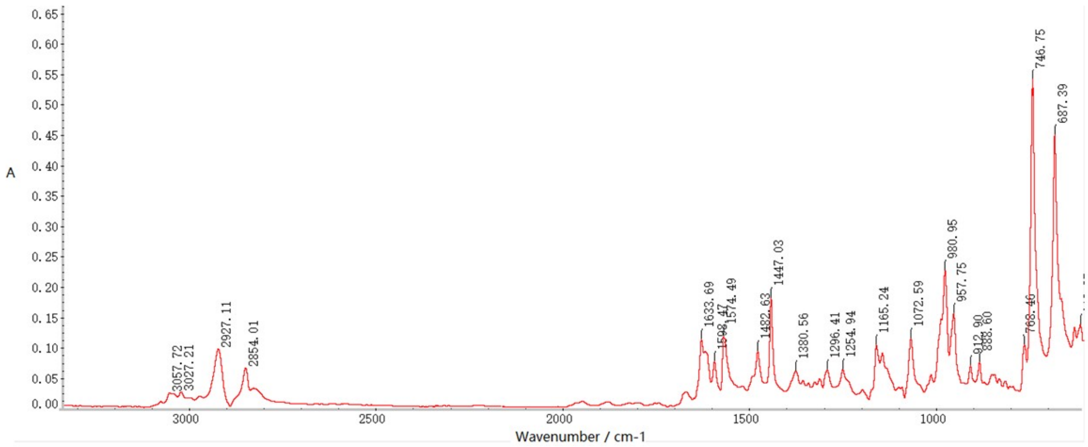


Figure S3 ATR-FTIR spectrum of $\mathbf{L_2}$.

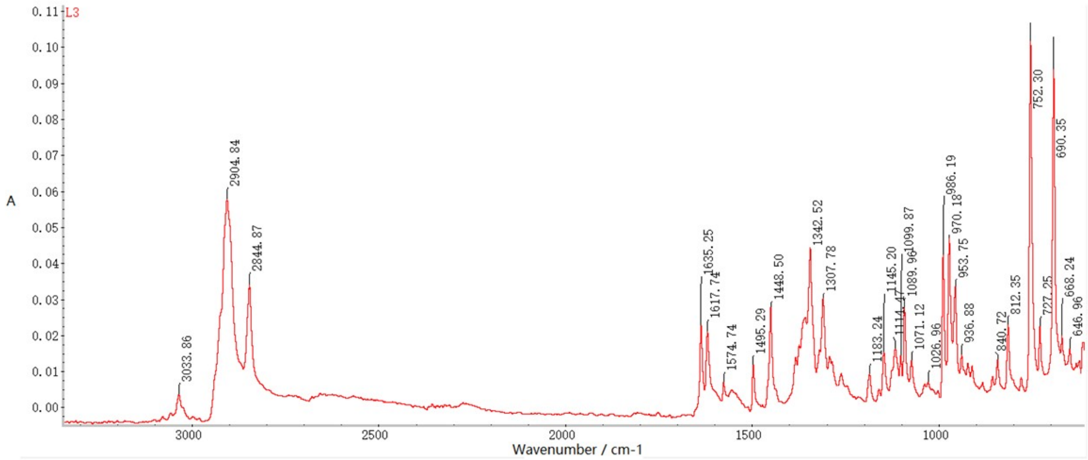


Figure S4 ATR-FTIR spectrum of $\mathbf{L_3}$.

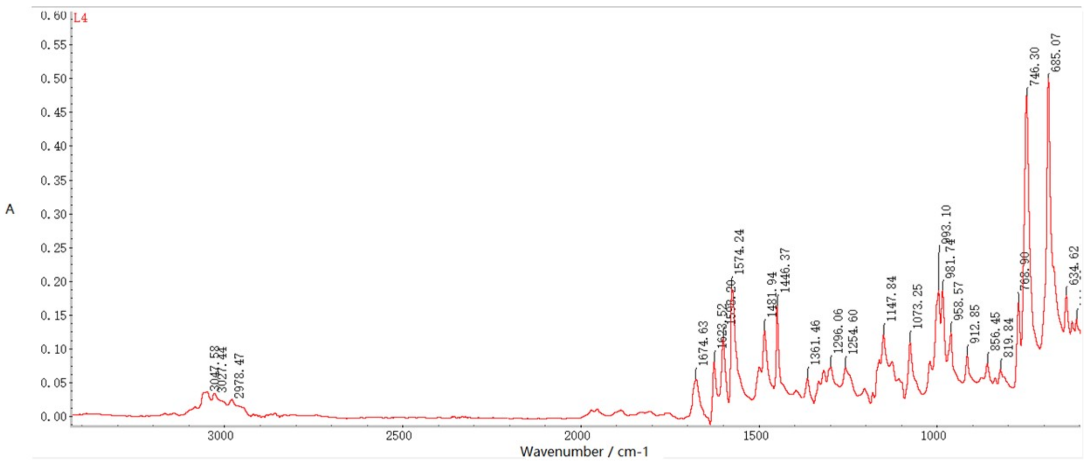


Figure S5 ATR-FTIR spectrum of $\mathbf{L_4}$.

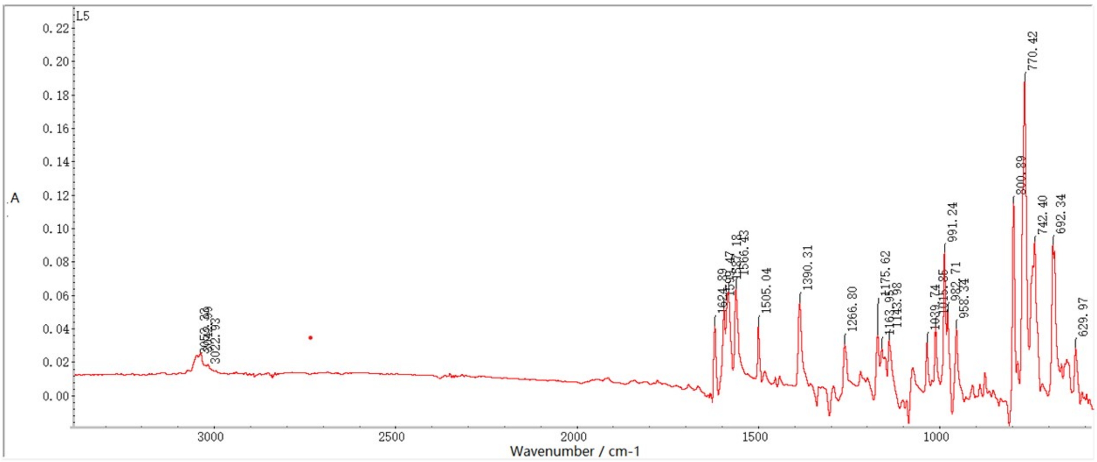


Figure S6 ATR-FTIR spectrum of $\mathbf{L_5}$.

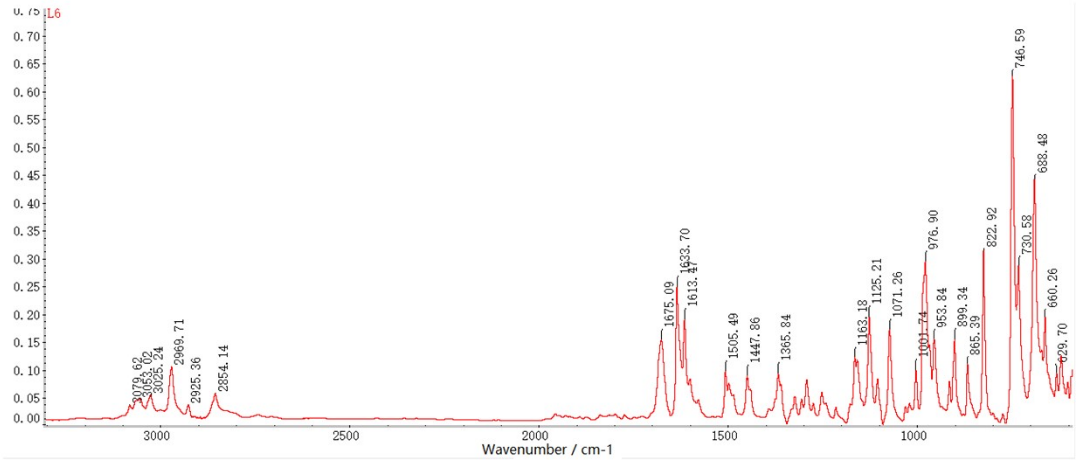


Figure S7 ATR-FTIR spectrum of (*S*)-$\mathbf{L_6}$.

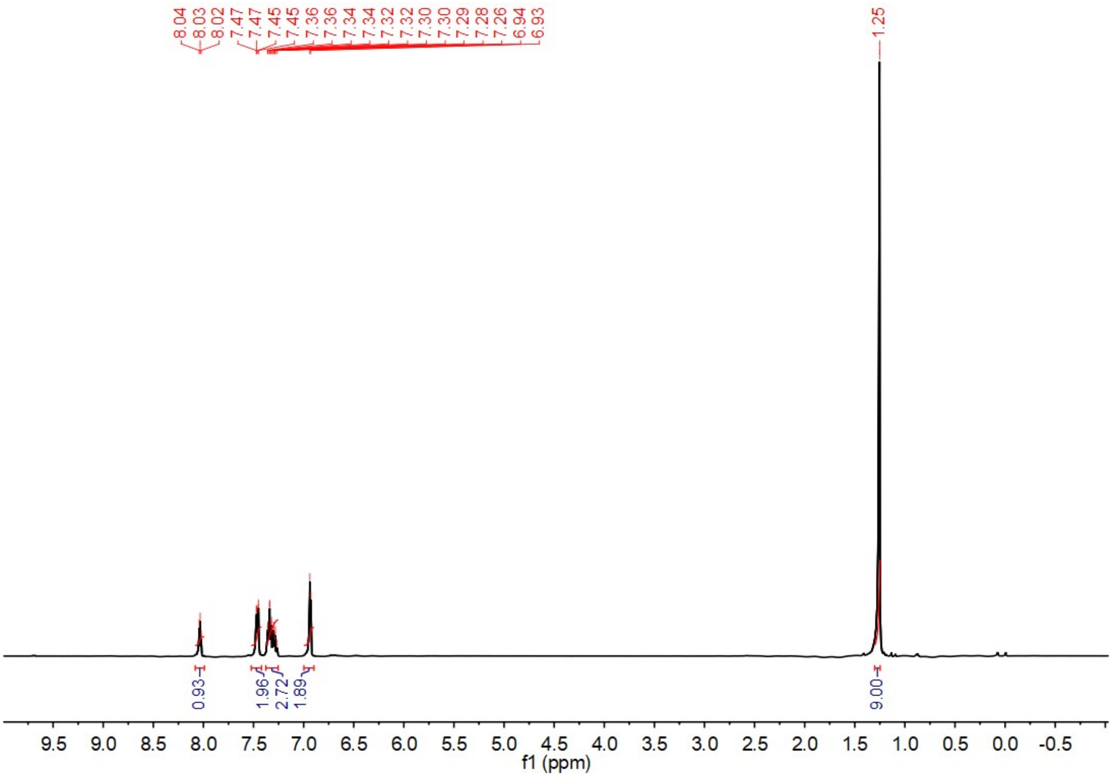


Figure S8 ^{1}H NMR spectrum of $\mathbf{L_1}$ in $CDCl_3$ solvent.

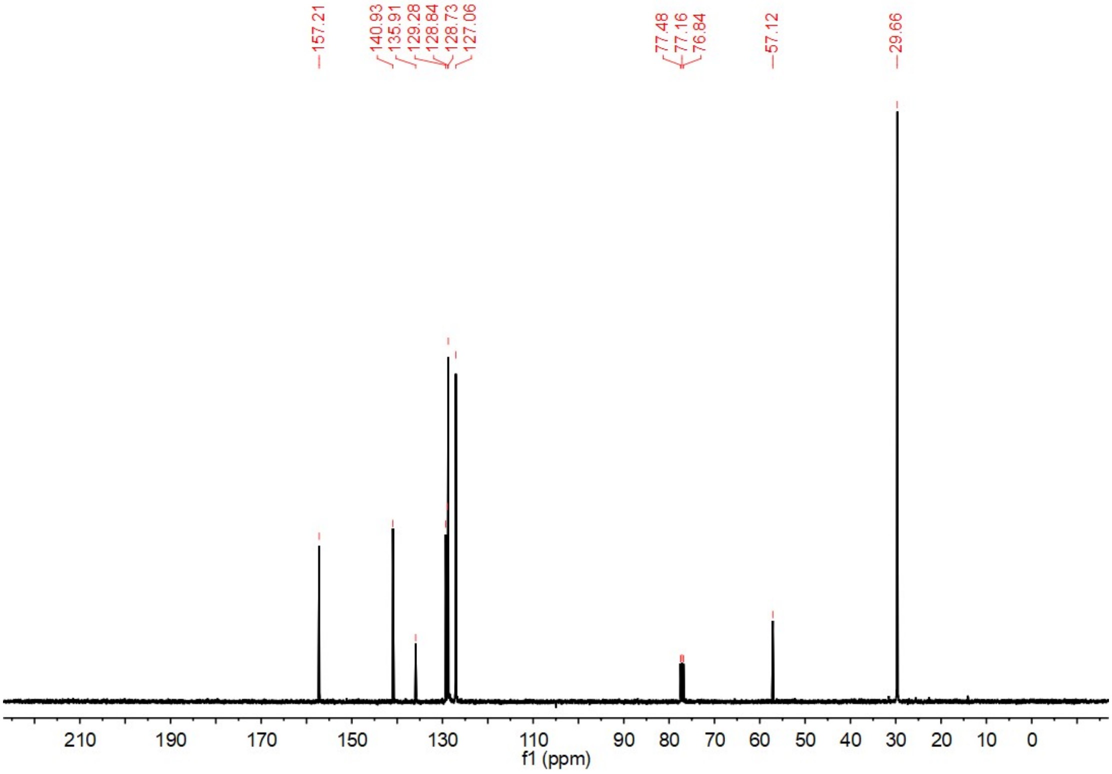


Figure S9 ^{13}C NMR spectrum of $\mathbf{L_1}$ in $CDCl_3$ solvent.

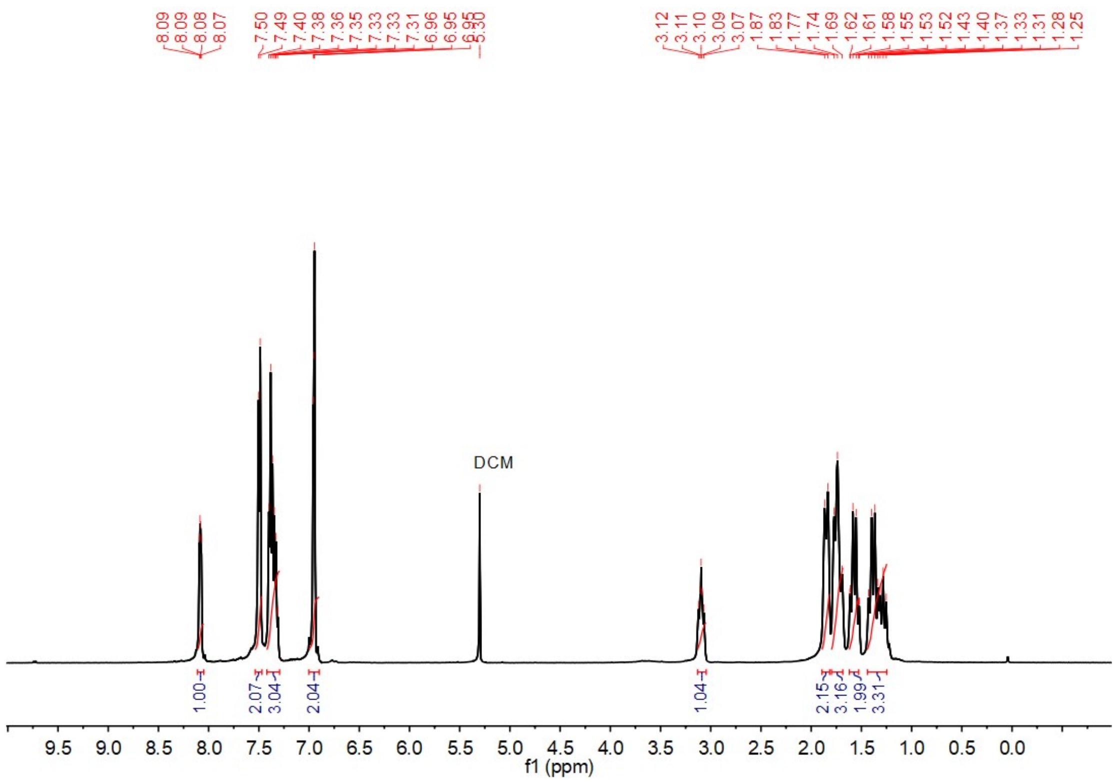


Figure S10 ^{1}H NMR spectrum of $\mathbf{L_2}$ in $CDCl_3$ solvent.

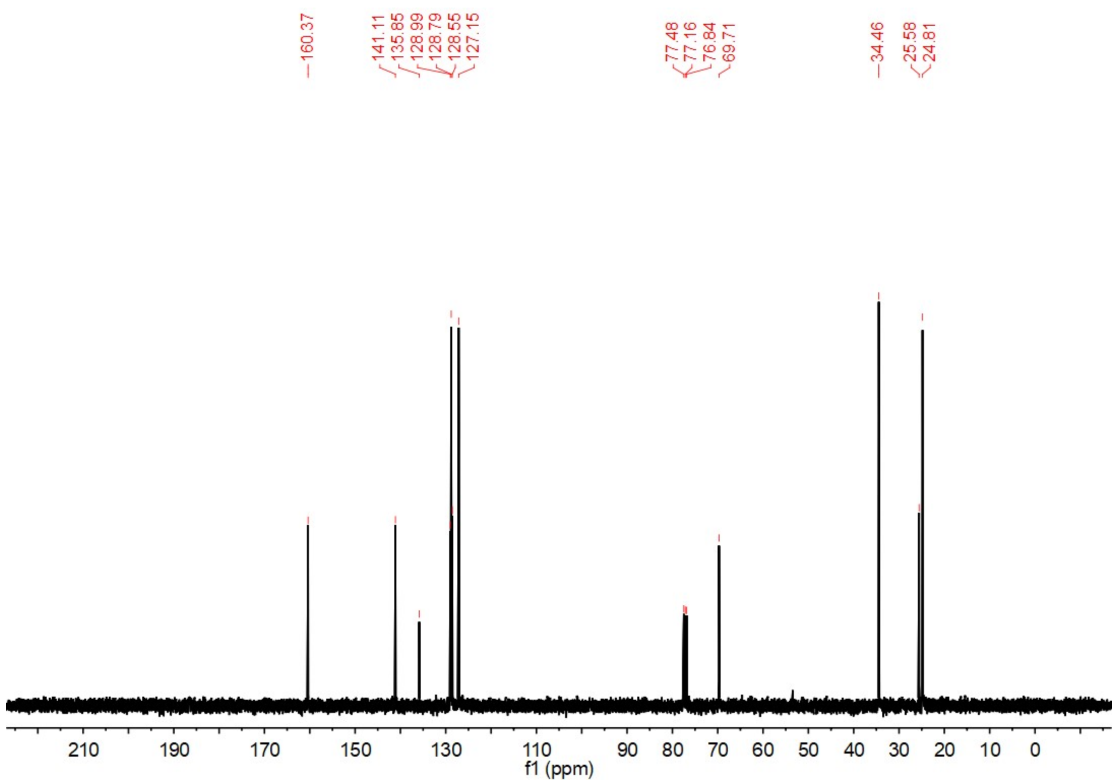


Figure S11 ^{13}C NMR spectrum of $\mathbf{L_2}$ in $CDCl_3$ solvent.

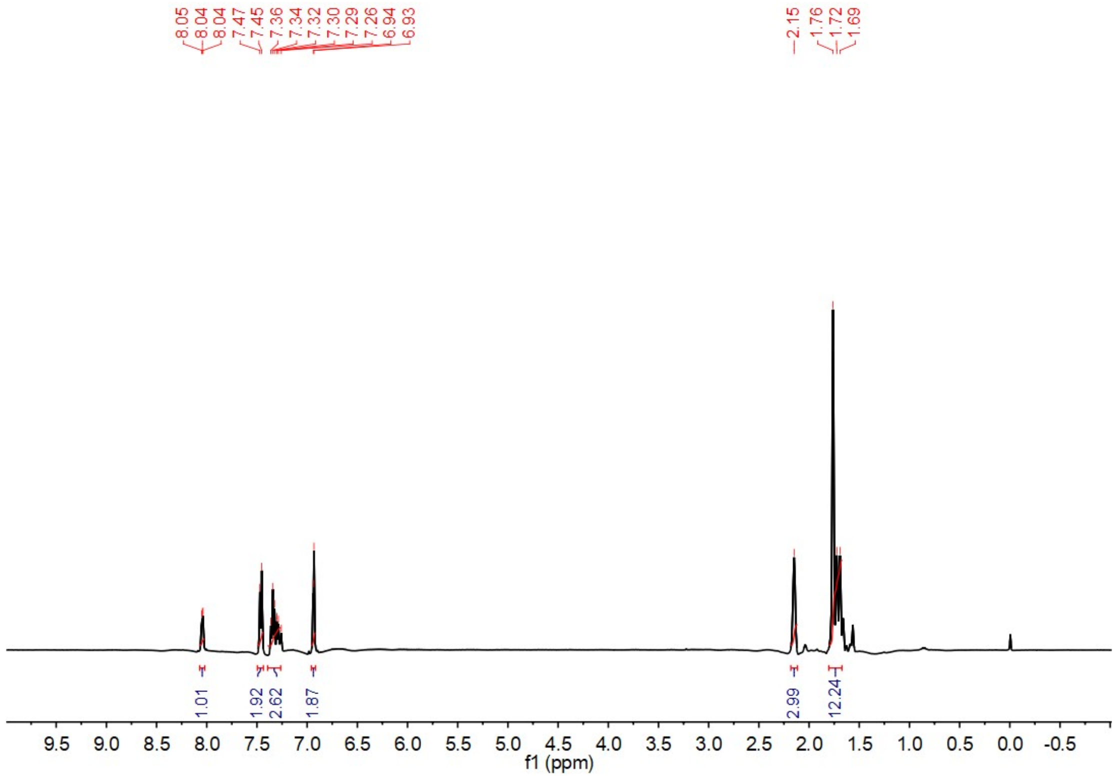


Figure S12 ^{1}H NMR spectrum of $\mathbf{L_3}$ in $CDCl_3$ solvent.

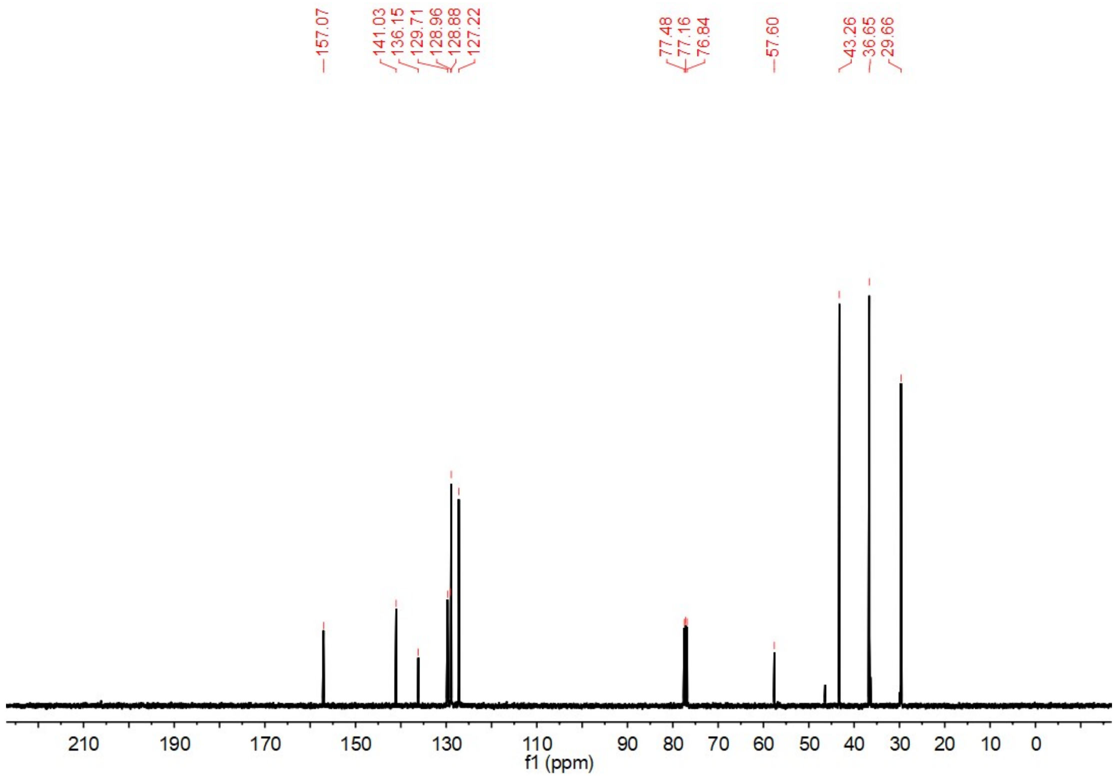


Figure S13 ^{13}C NMR spectrum of $\mathbf{L_3}$ in $CDCl_3$ solvent.

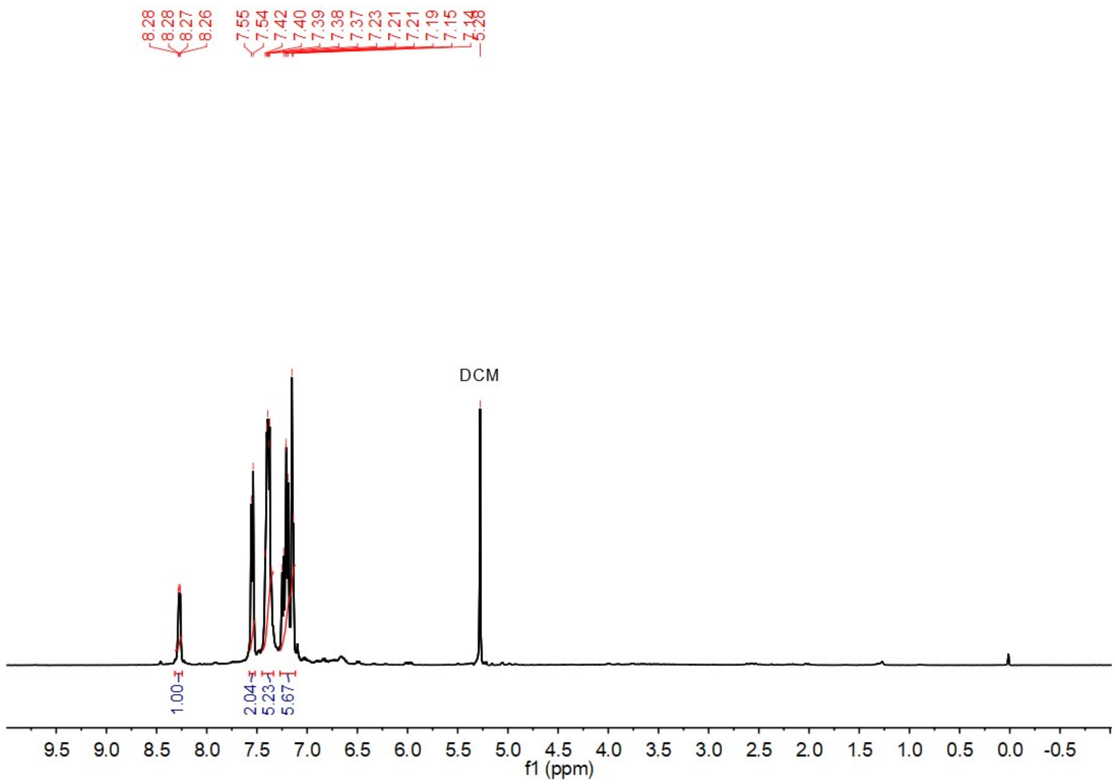


Figure S14 ^{1}H NMR spectrum of $\mathbf{L_4}$ in $CDCl_3$ solvent.

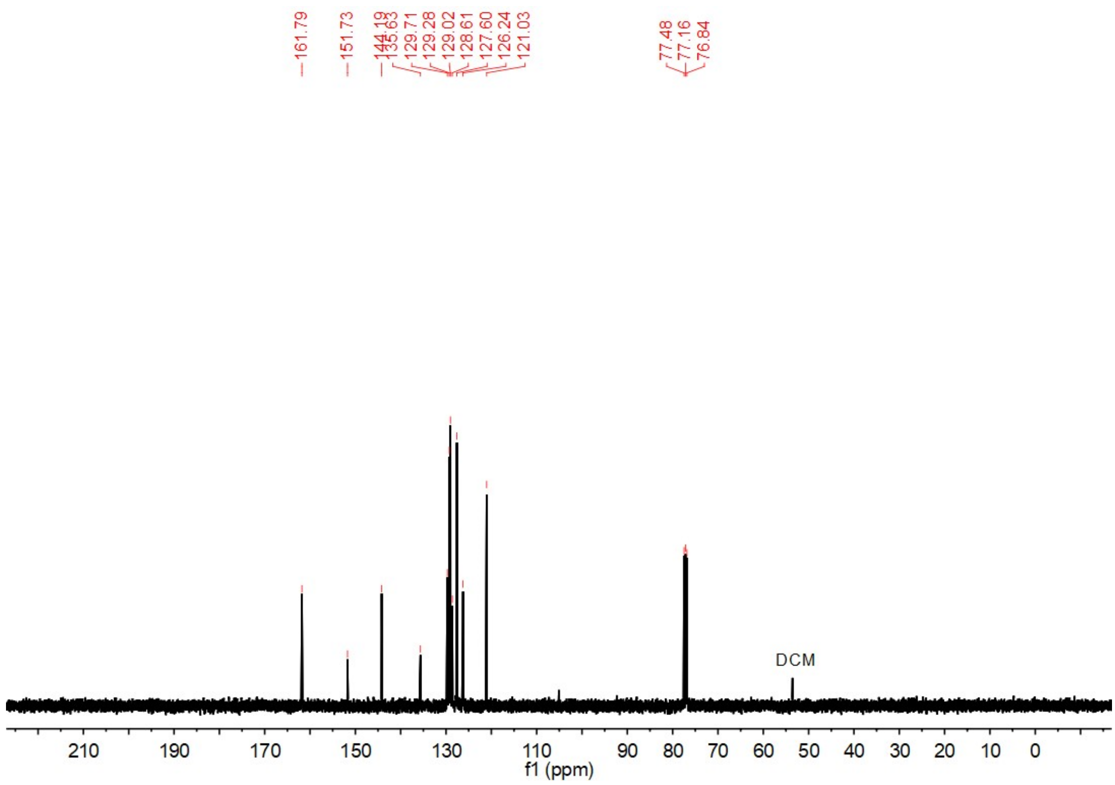


Figure S15 ^{13}C NMR spectrum of $\mathbf{L_4}$ in $CDCl_3$ solvent.

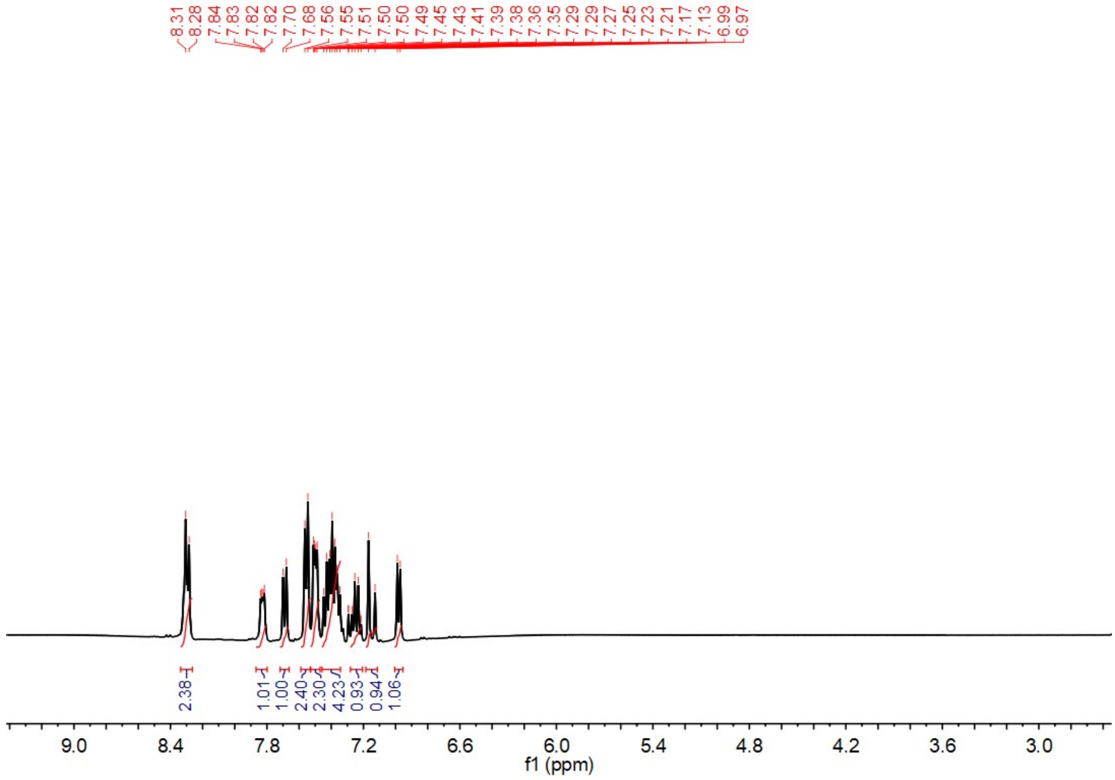


Figure S16 ^{1}H NMR spectrum of $\mathbf{L_5}$ in $CDCl_3$ solvent.

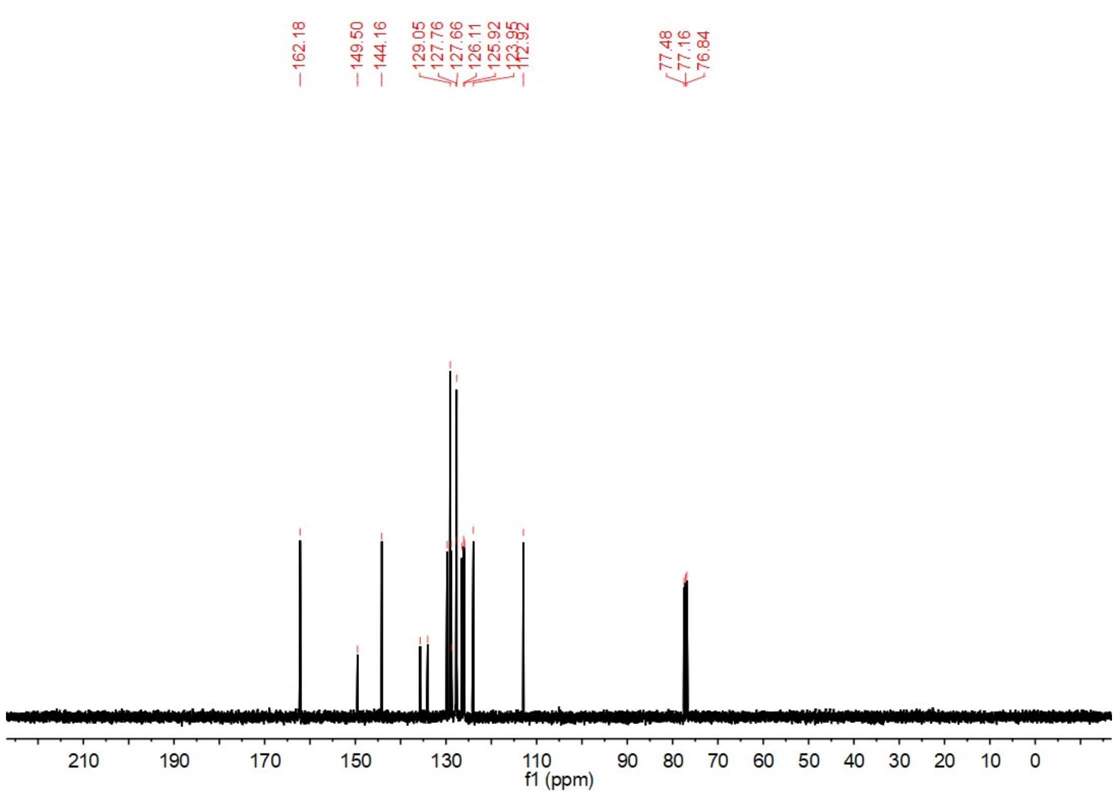


Figure S17 ^{13}C NMR spectrum of $\mathbf{L_5}$ in $CDCl_3$ solvent.

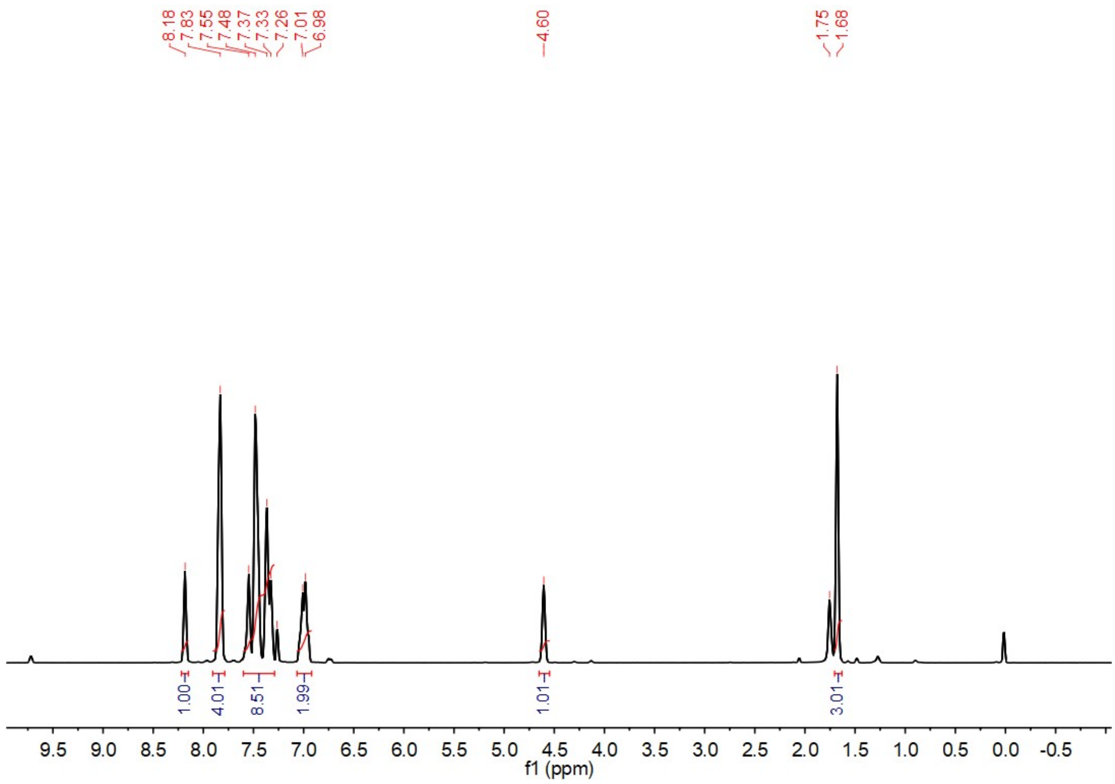


Figure S18 ^{1}H NMR spectrum of $\mathbf{L_6}$ in $CDCl_3$ solvent.

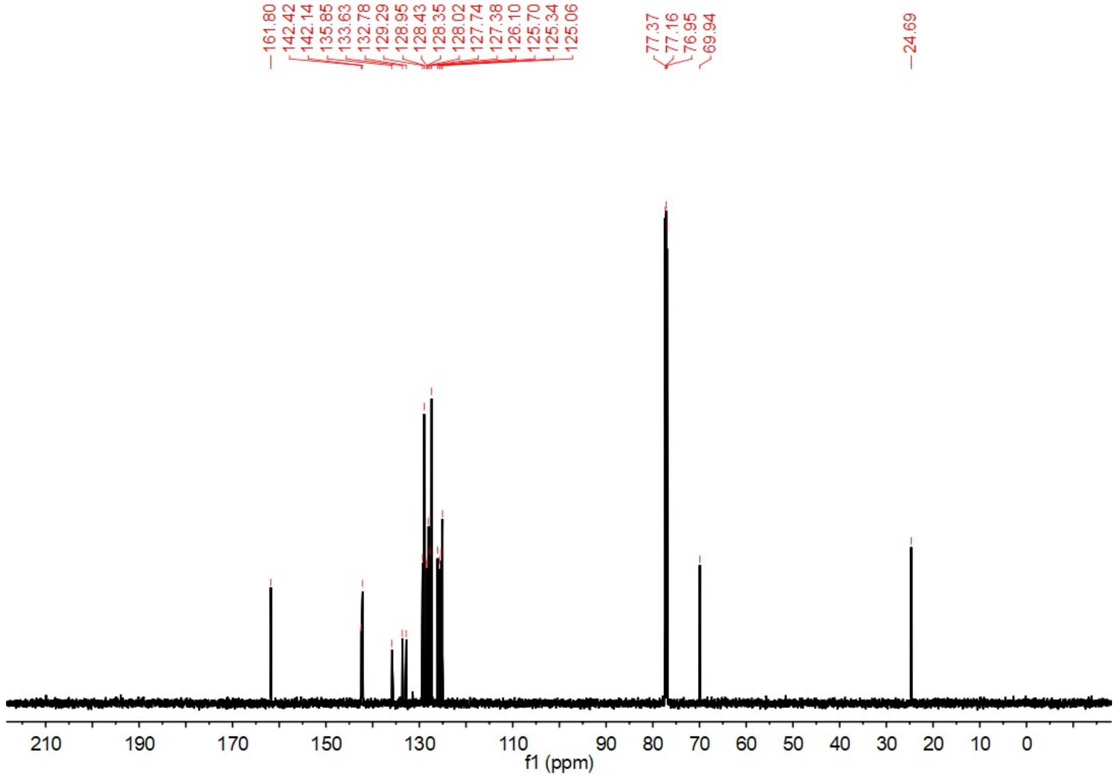


Figure S19 ^{13}C NMR spectrum of $\mathbf{L_6}$ in $CDCl_3$ solvent.

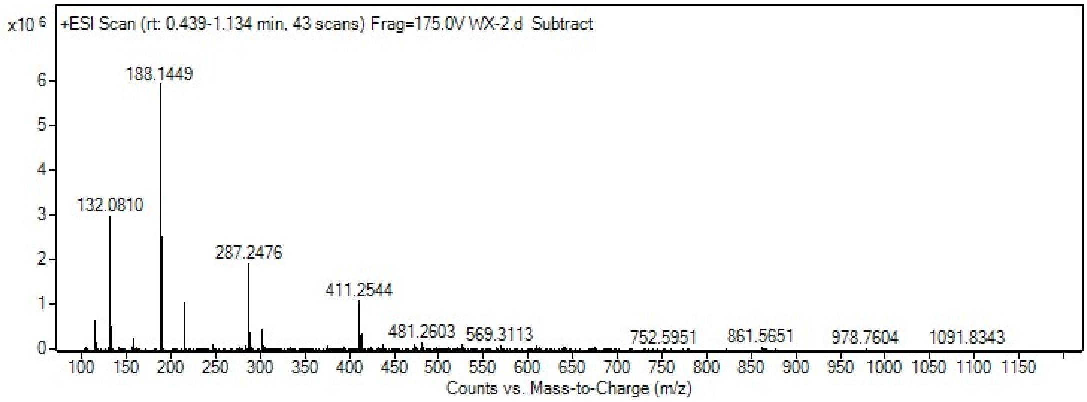


Figure S20 High-resolution mass spectrum of $\mathbf{L_1}$ in methanol.

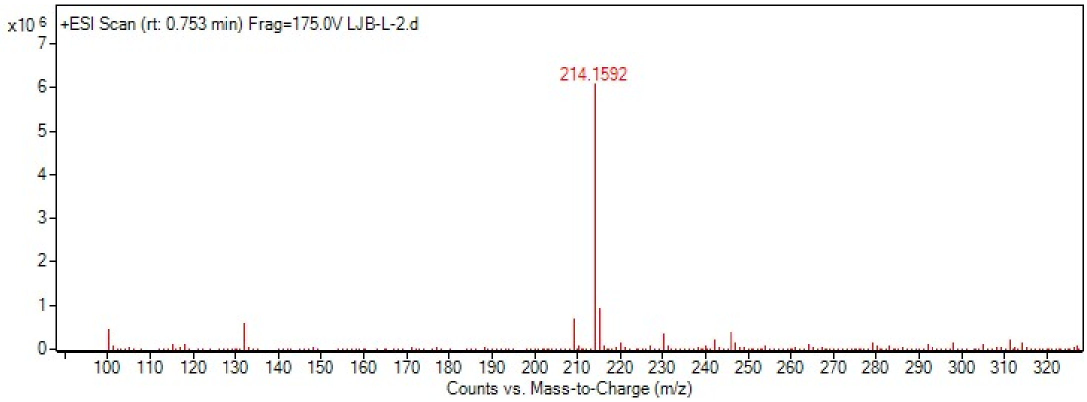


Figure S21 High-resolution mass spectrum of $\mathbf{L_2}$ in methanol.

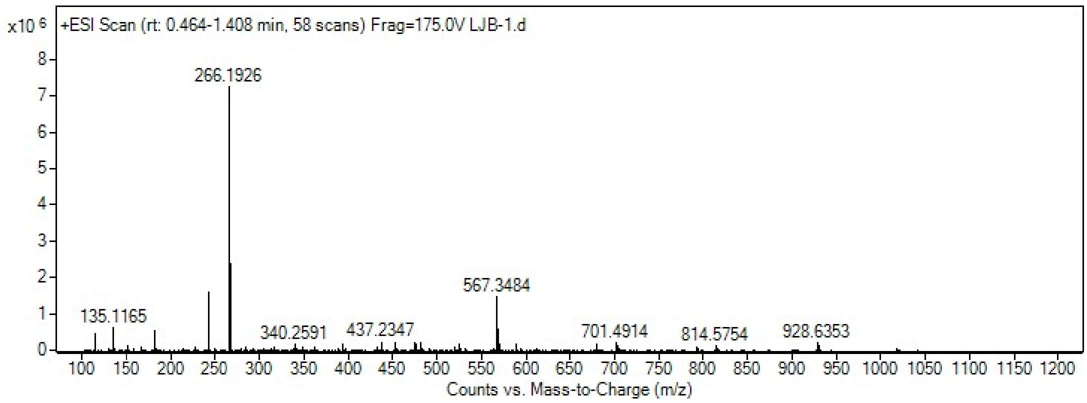


Figure S22 High-resolution mass spectrum of $\mathbf{L_3}$ in methanol.

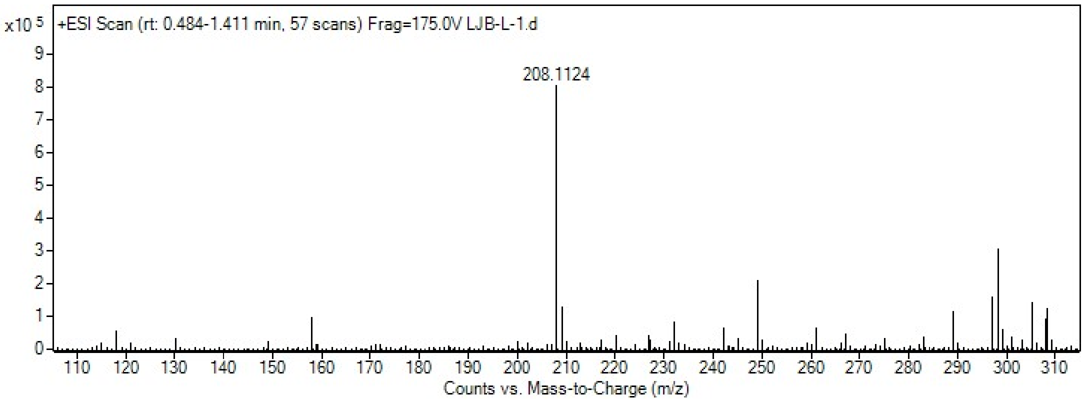


Figure S23 High-resolution mass spectrum of $\mathbf{L_4}$ in methanol.

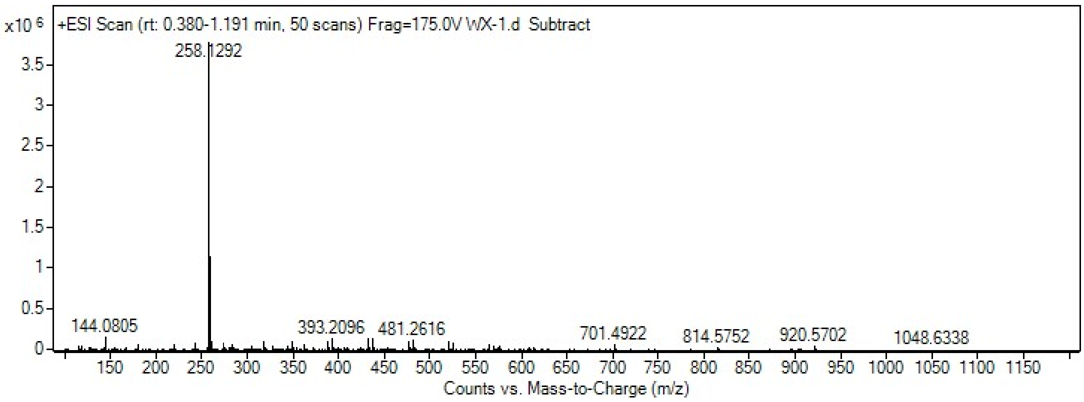


Figure S24 High-resolution mass spectrum of $\mathbf{L_5}$ in methanol.

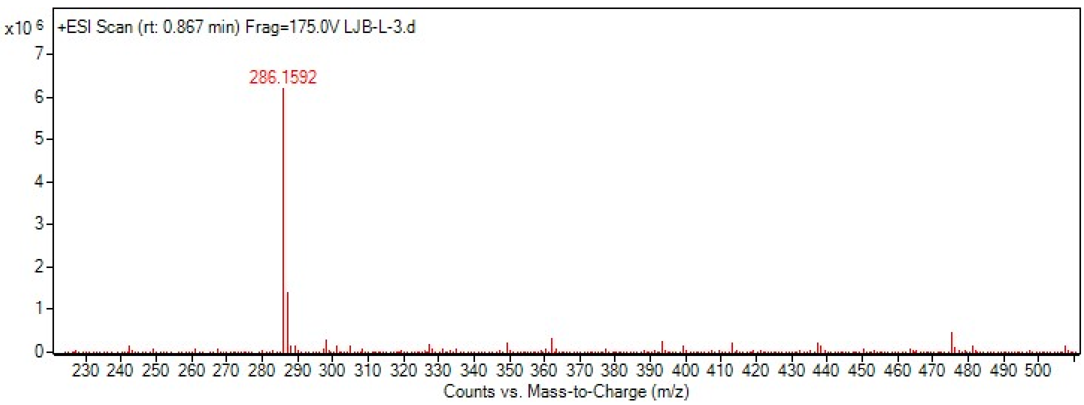


Figure S25 High-resolution mass spectrum of $\mathbf{L_6}$ in methanol.

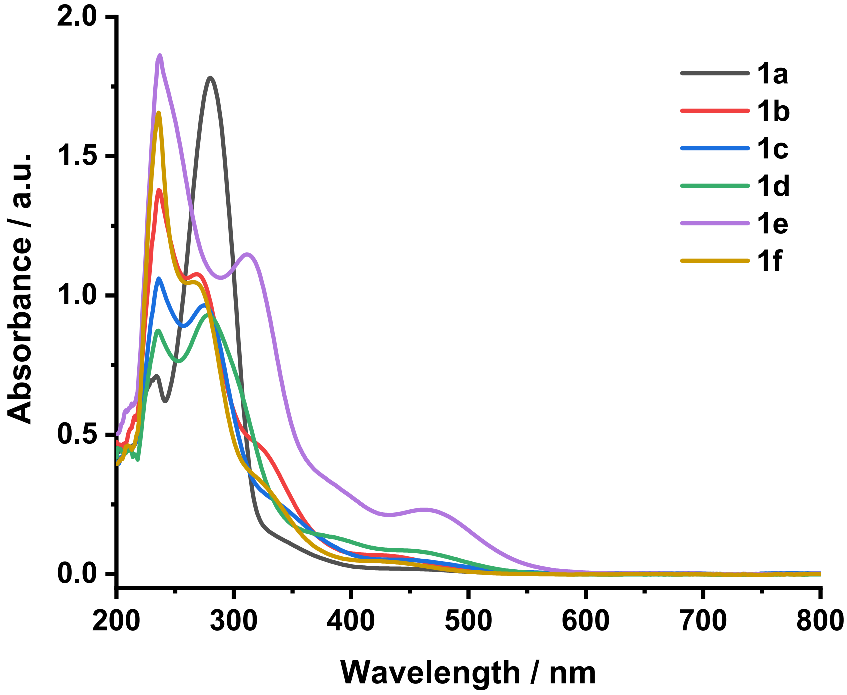


Figure S26 UV-vis spectra of **1a-f** in DCM (50 μM).

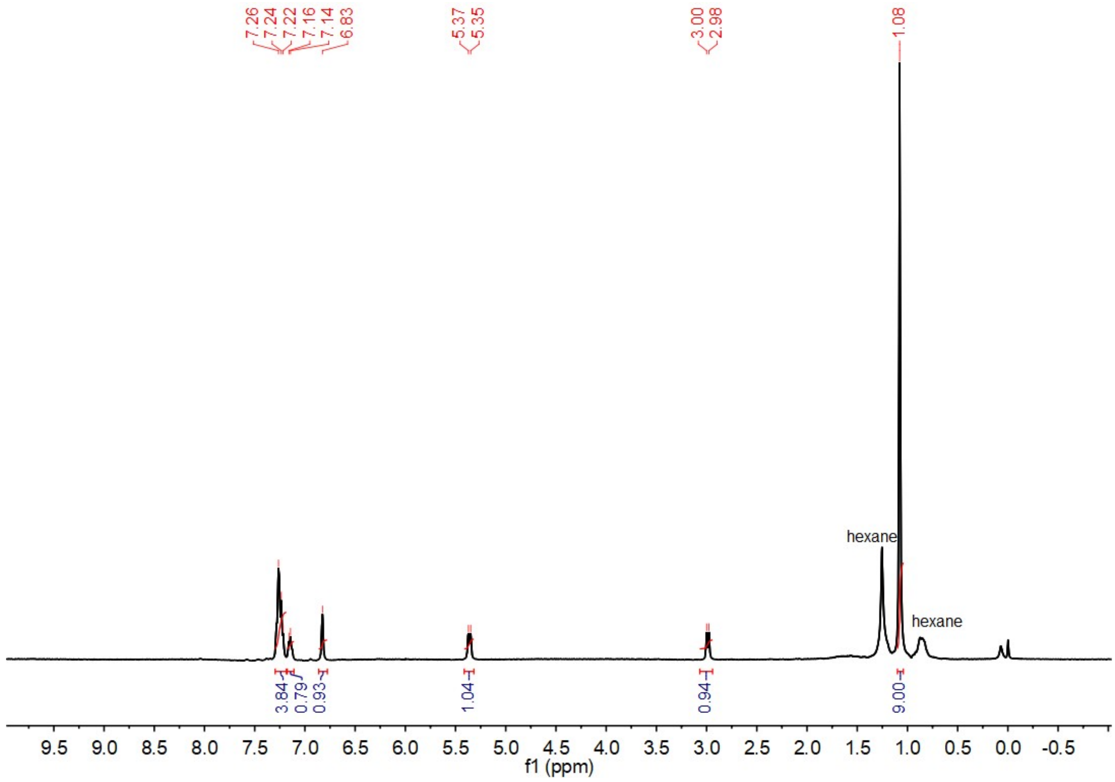


Figure S27 ^{1}H NMR spectrum of **1a** in $CDCl_3$ solvent.

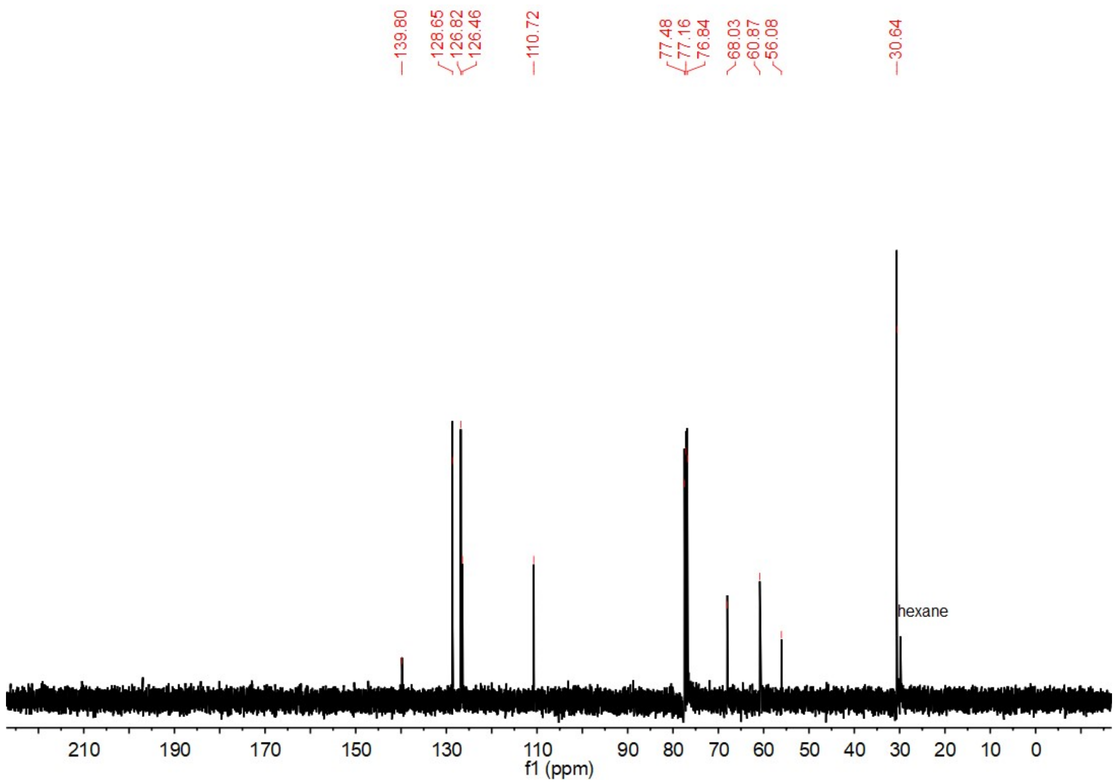


Figure S28 ^{13}C NMR spectrum of **1a** in $CDCl_3$ solvent.

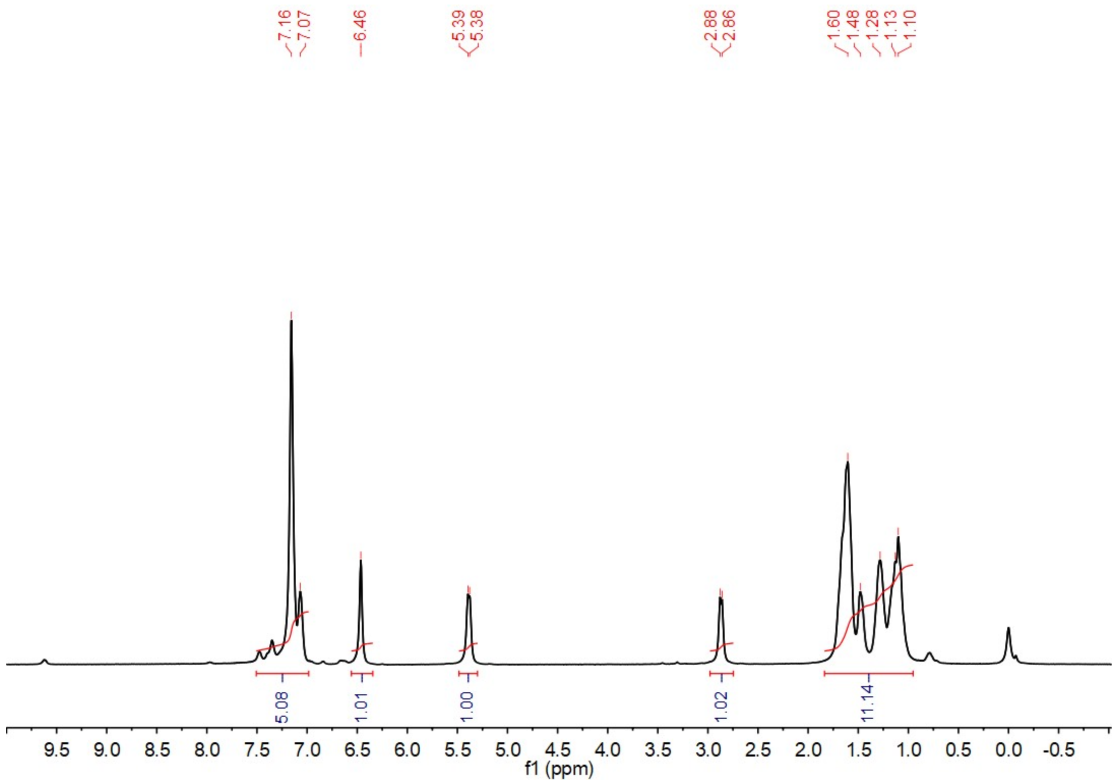


Figure S29 ^{1}H NMR spectrum of **1b** in $CDCl_3$ solvent.

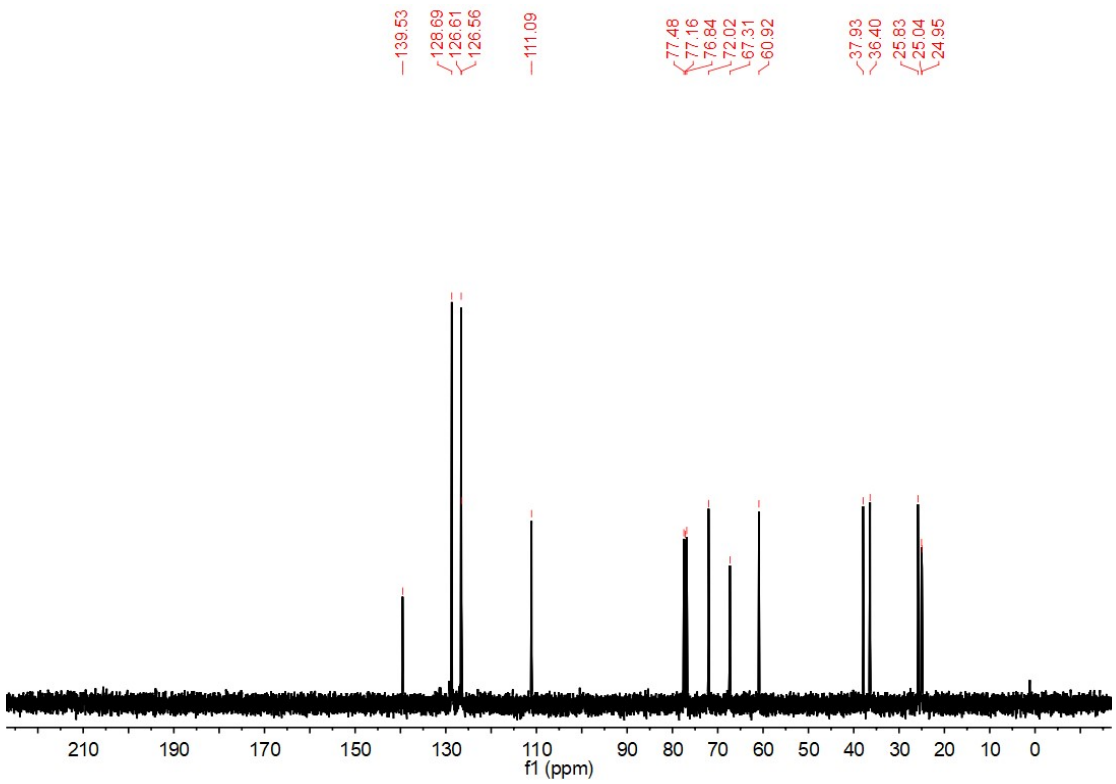


Figure S30 ^{13}C NMR spectrum of **1b** in $CDCl_3$ solvent.

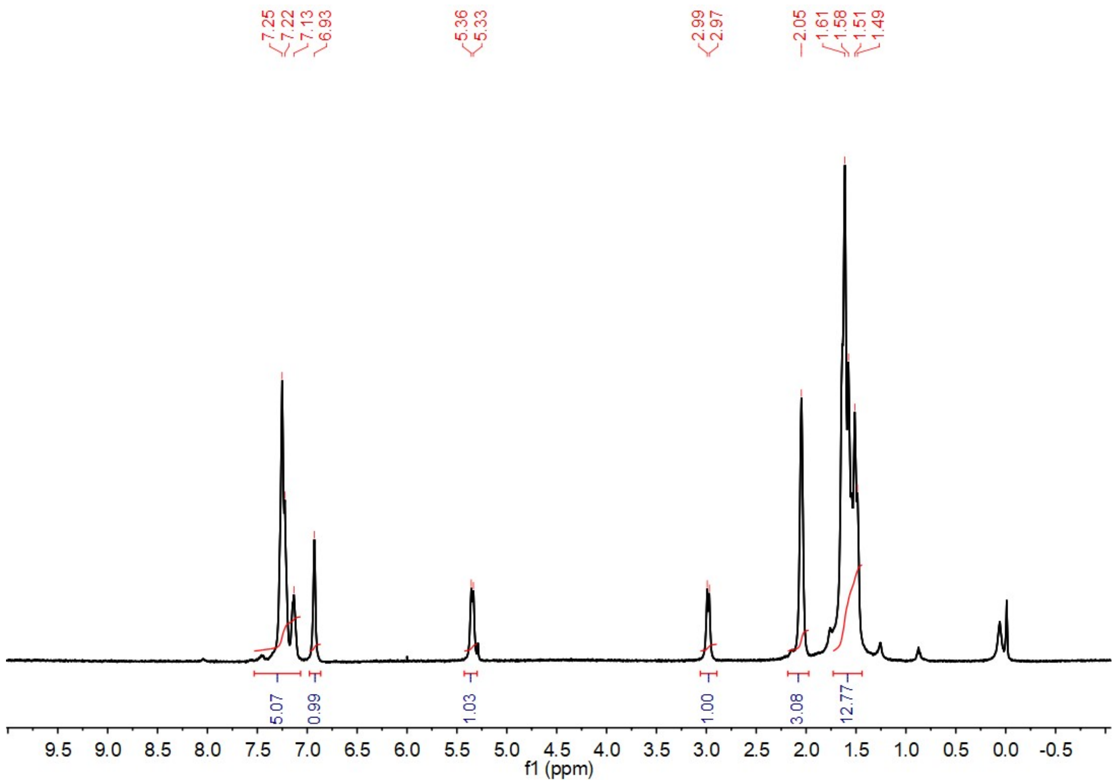


Figure S31 ^{1}H NMR spectrum of **1c** in $CDCl_3$ solvent.

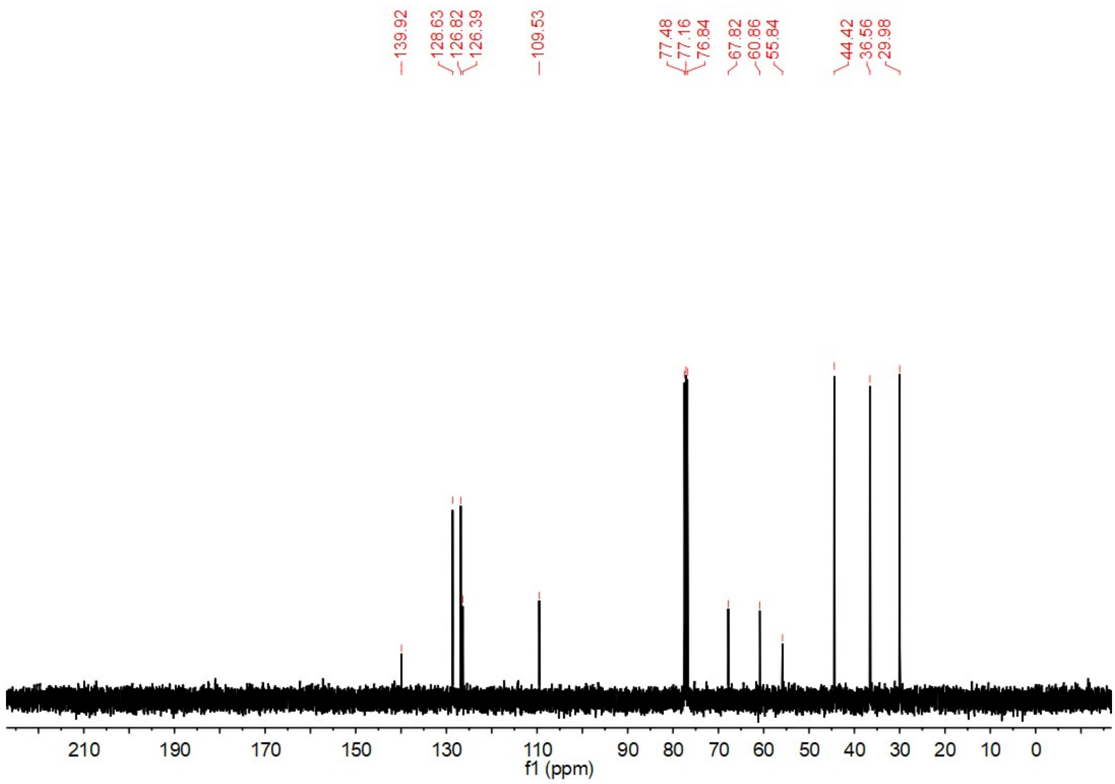


Figure S32 ^{13}C NMR spectrum of **1c** in $CDCl_3$ solvent.

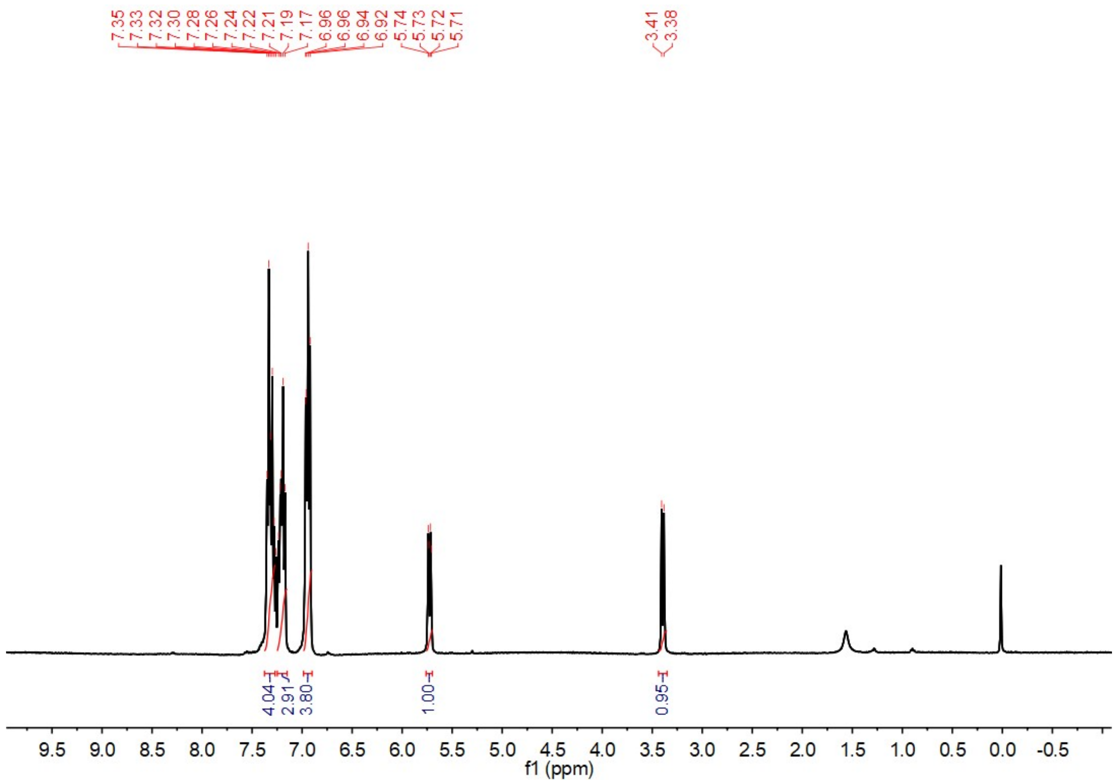


Figure S33 ^{1}H NMR spectrum of **1d** in $CDCl_3$ solvent.

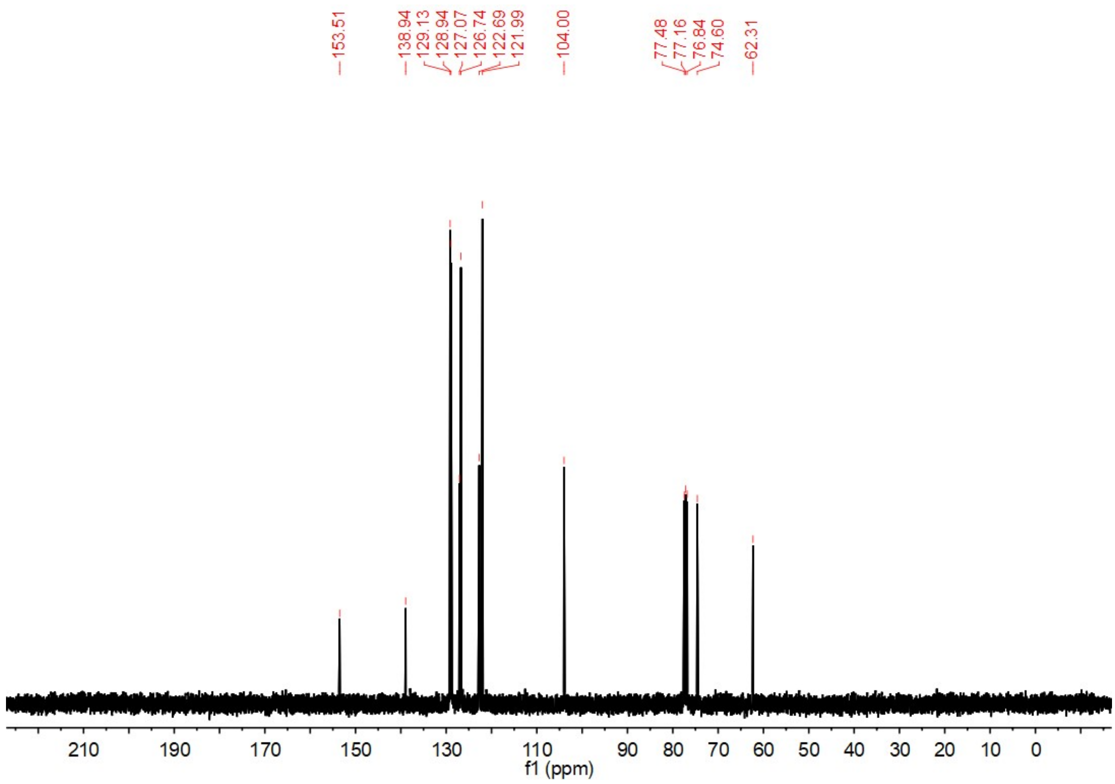


Figure S34 ^{13}C NMR spectrum of **1d** in $CDCl_3$ solvent.

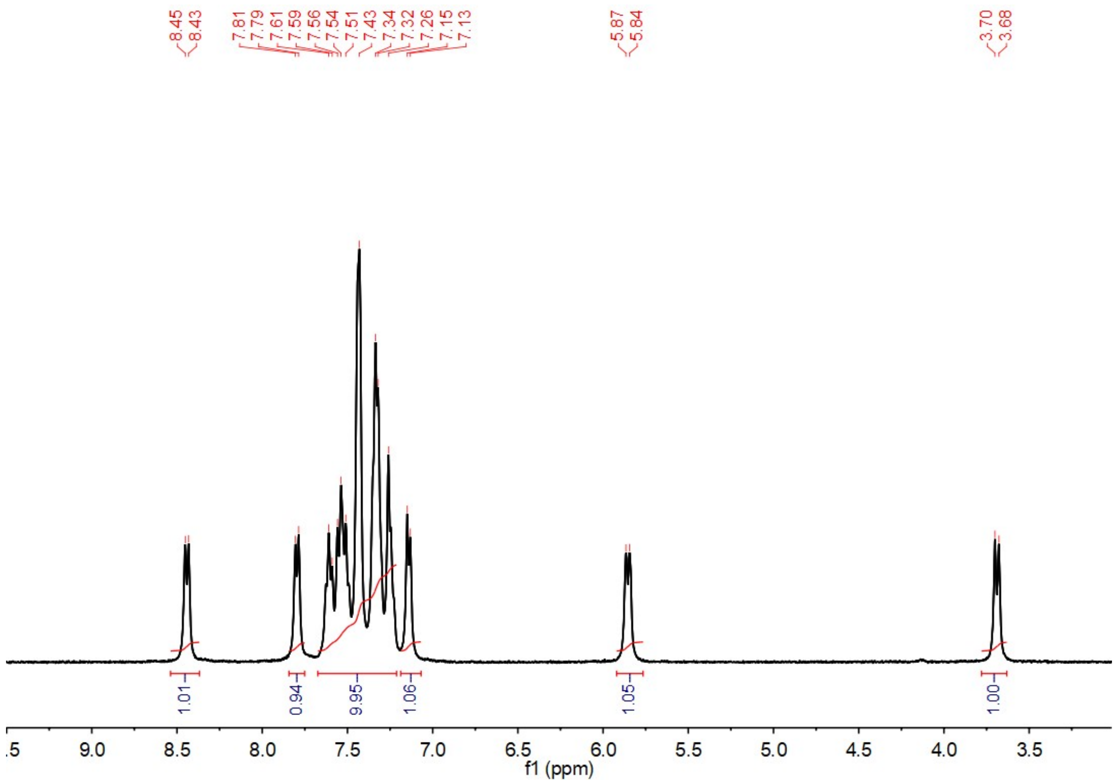


Figure S35 ^{1}H NMR spectrum of **1e** in $CDCl_3$ solvent.

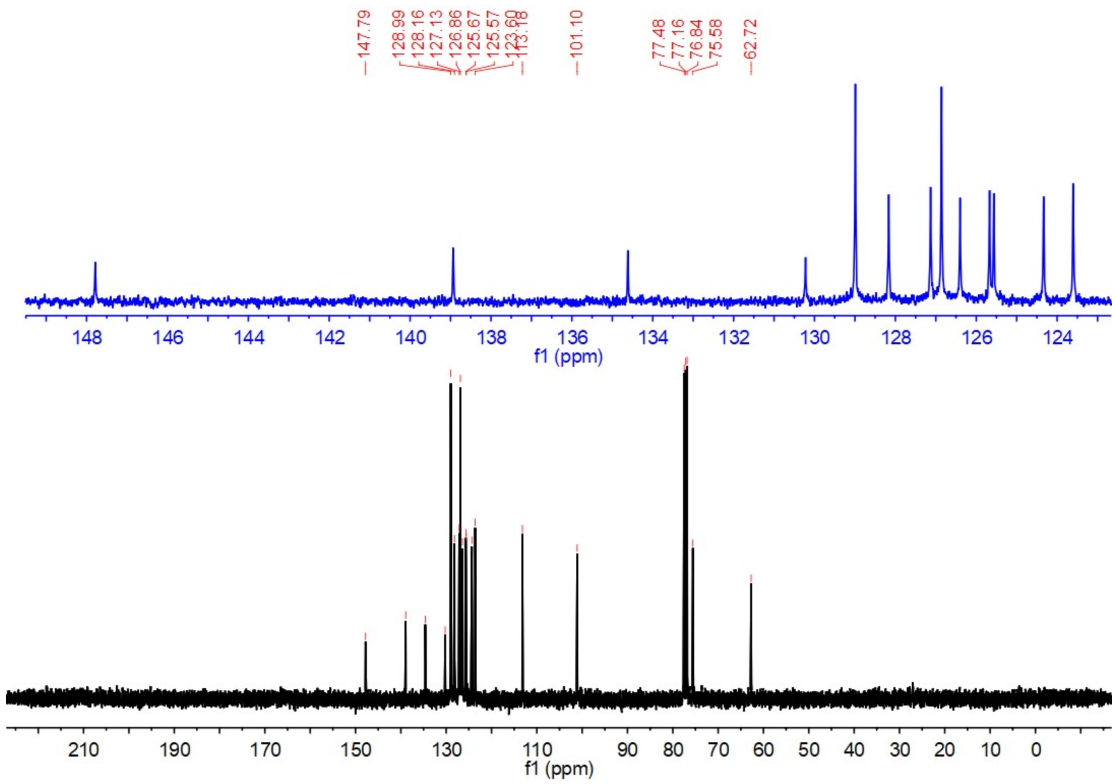


Figure S36 ^{13}C NMR spectrum of **1e** in $CDCl_3$ solvent.

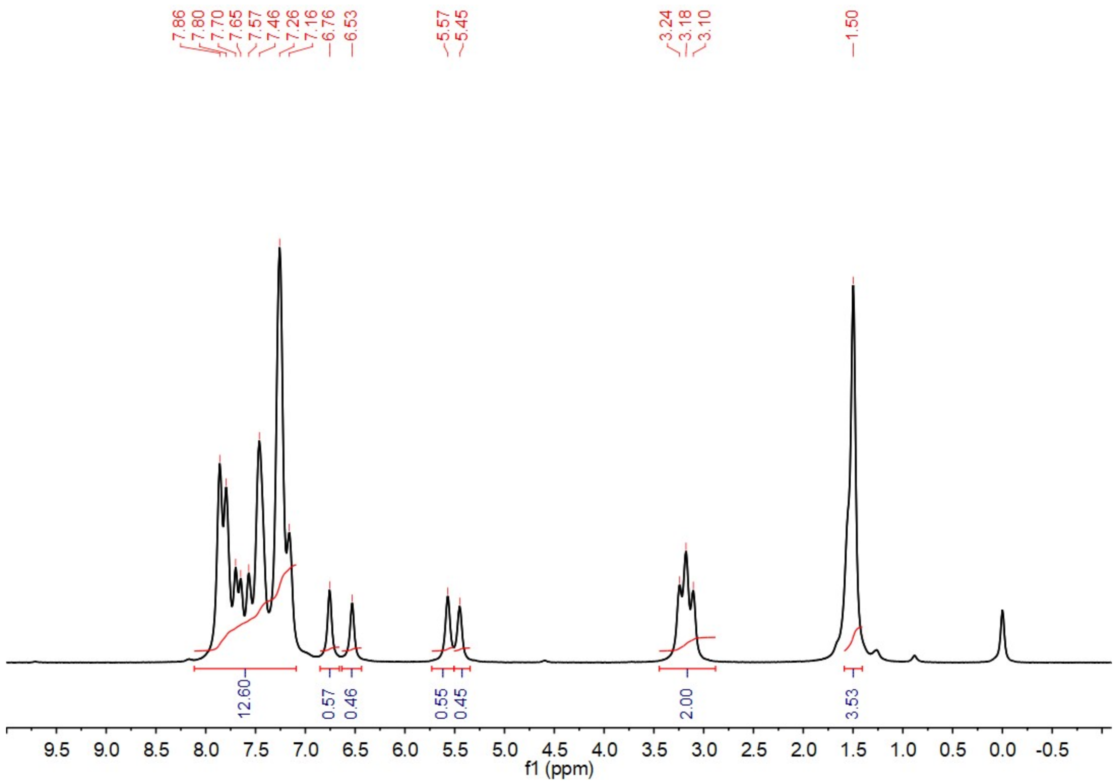


Figure S37 ^{1}H NMR spectrum of **1f** in $CDCl_3$ solvent.

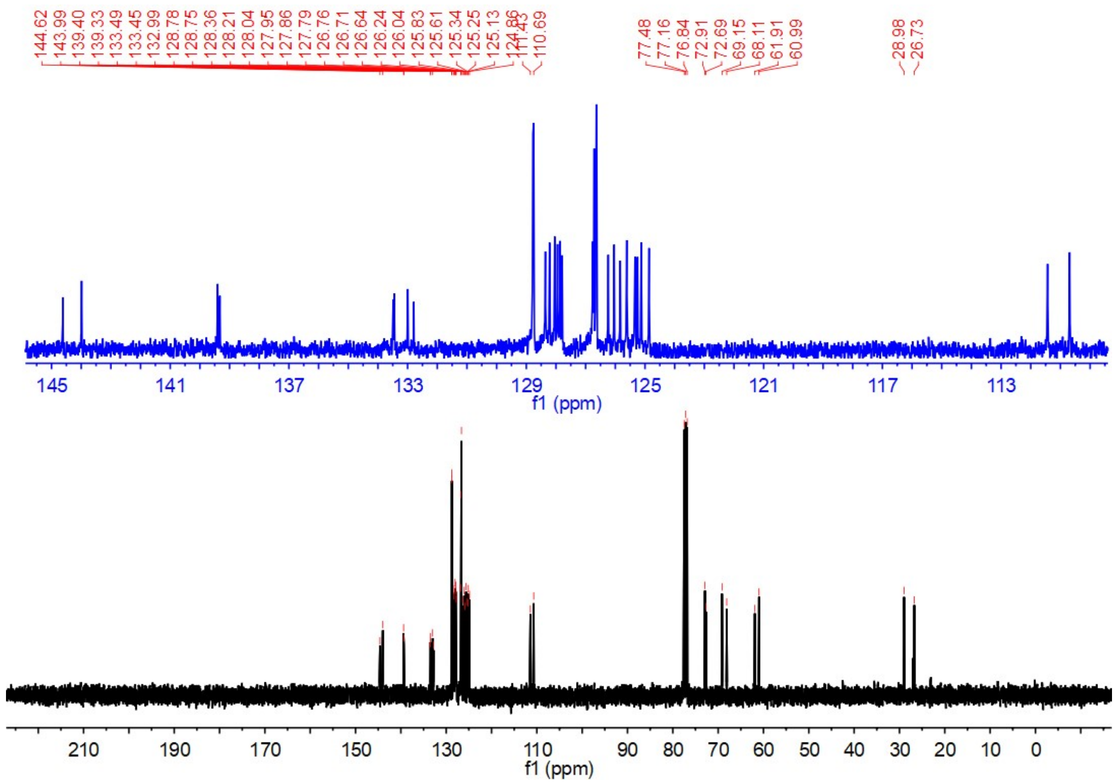


Figure S38 ^{13}C NMR spectrum of **1f** in $CDCl_3$ solvent.

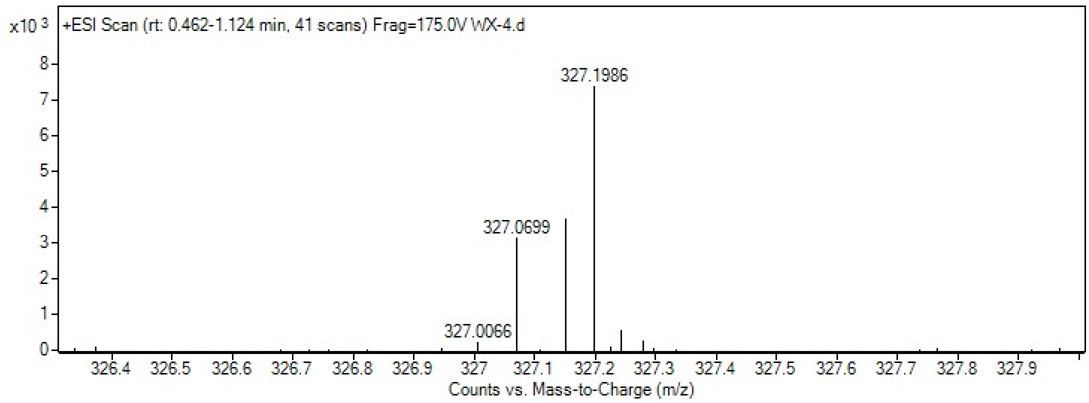


Figure S39 High-resolution mass spectrum of **1a** in methanol.

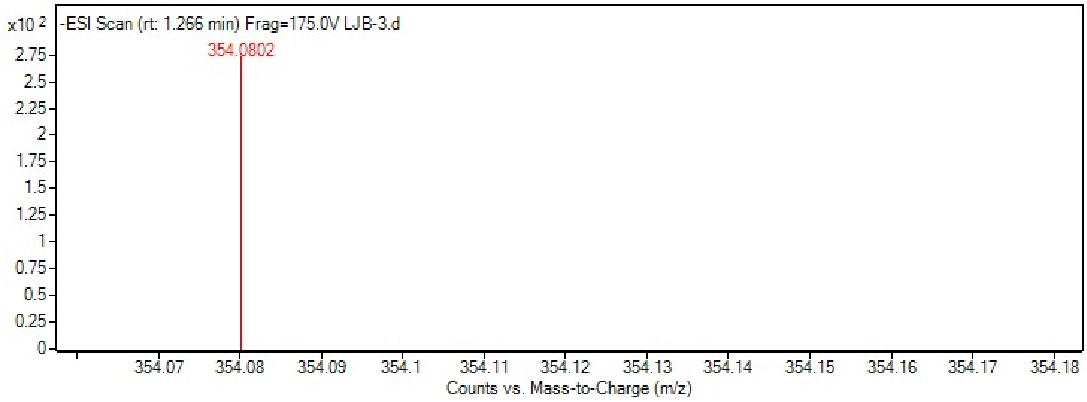


Figure S40 High-resolution mass spectrum of **1b** in methanol.

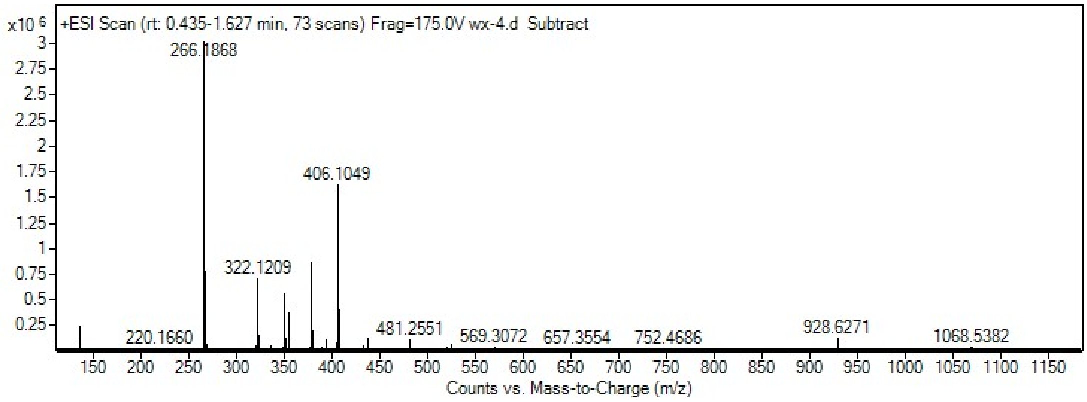


Figure S41 High-resolution mass spectrum of **1c** in methanol.

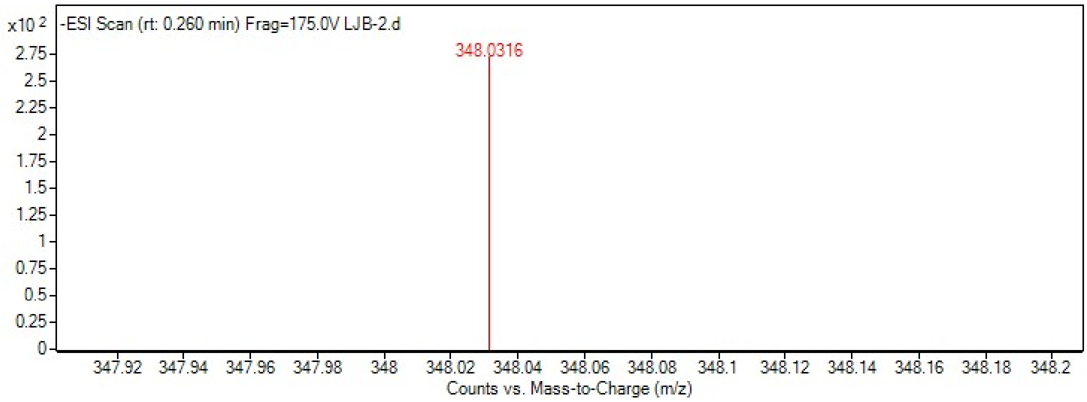


Figure S42 High-resolution mass spectrum of **1d** in methanol.

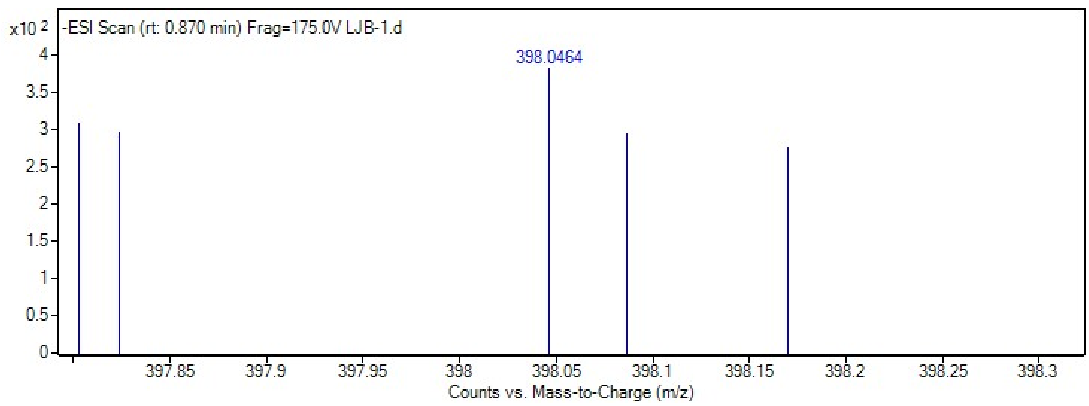


Figure S43 High-resolution mass spectrum of **1e** in methanol.

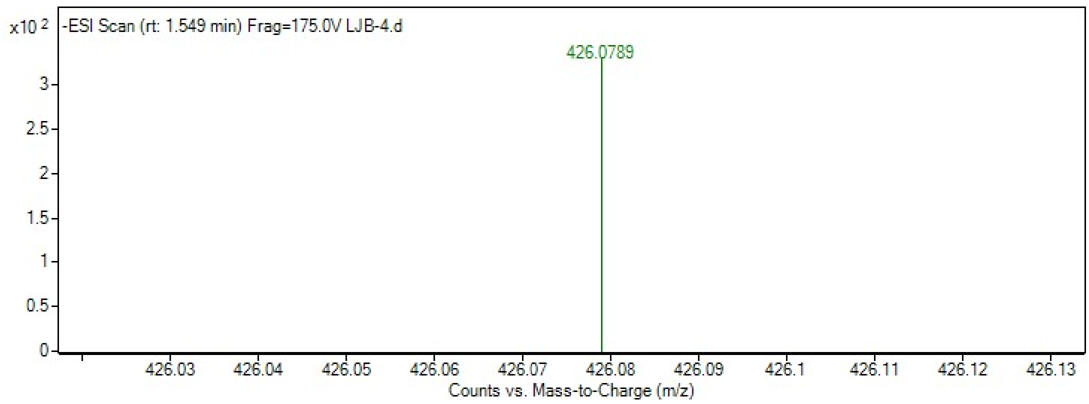
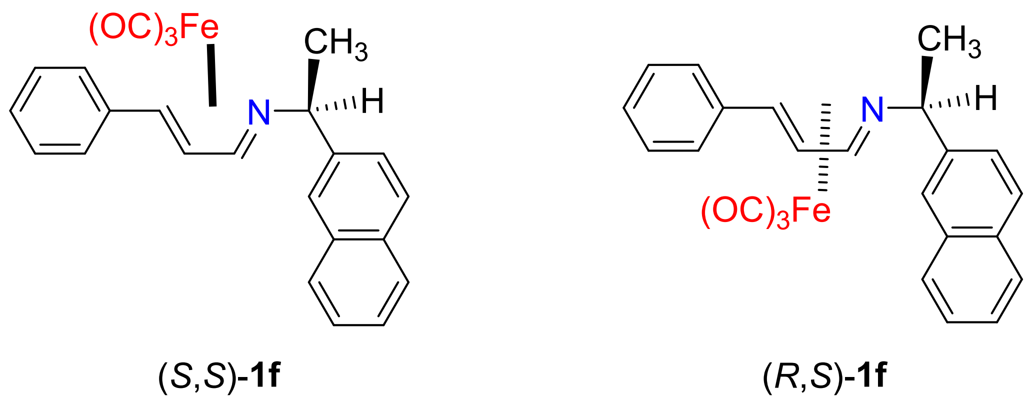


Figure S44 High-resolution mass spectrum of **1f** in methanol.



Scheme S1 The diastereomers of **1f**, (*S*, *S*)-**1f** and (*R*, *S*)-**1f**.

Table S1 Crystallographic data and structure refinements for complex **1e**.

Complex	**1e**
CCDC number	2164134
Formula	$C_{22}H_{15}FeNO_3$
Formula weight	397.20
Crystal system	monoclinic
Space group	C2/c
a/Å	23.427(2)
b/Å	7.6710(5)
c/Å	21.6488(18)
α/°	90
β/°	104.203(9)
γ/°	90
Volume/Å^3	3771.6(5)
Z	8
ρ_{calc}/g cm^{-3}	1.399
μ/mm^{-1}	0.821
F(000)	1632
2θ/°	5.898 to 58.608
Reflections collected	8767
Independent reflections	4393 [R_{int} = 0.0319]
Goodness-of-fit on F^2	1.026
R_1, wR_2 (I≥2σ(I))	0.0470, 0.1165
R_1, wR_2 (all data)	0.0810, 0.1346

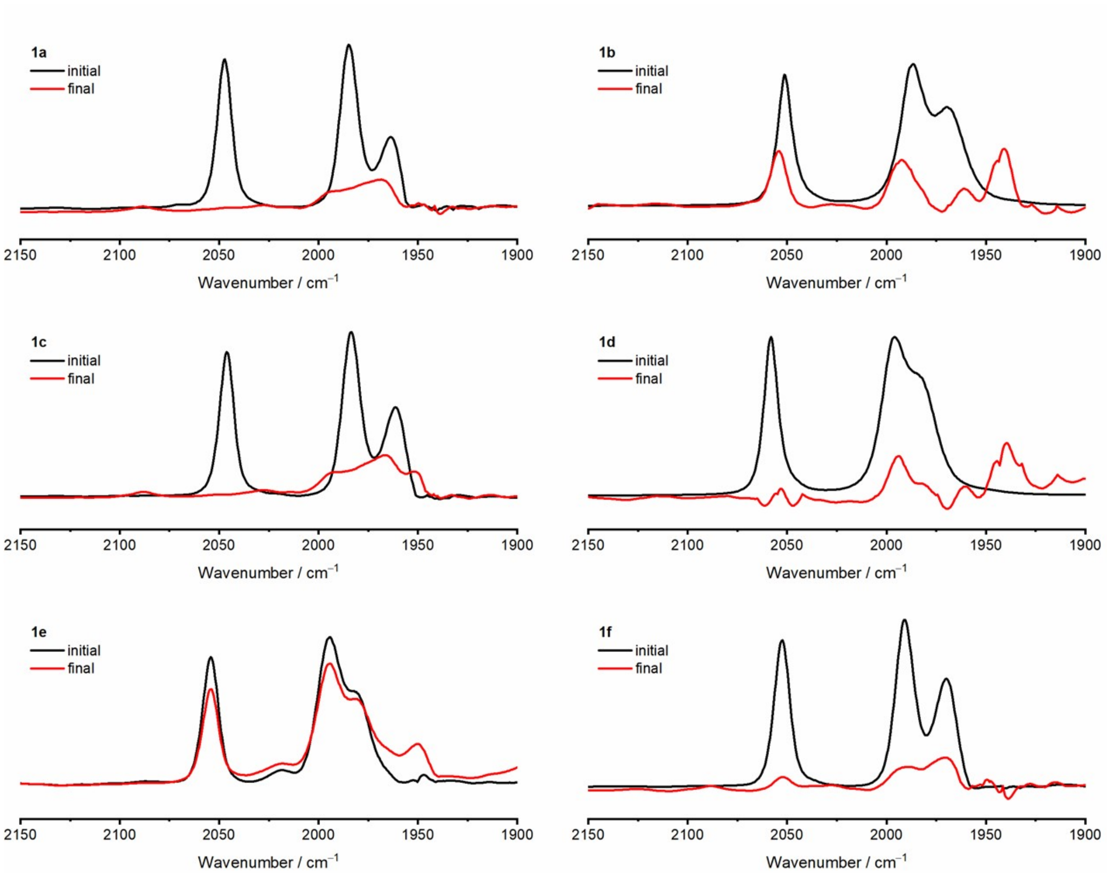


Figure S45 FTIR spectra of the hydroboration of acetophenone with different catalysts at the initial and final stages: (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, (e) **1e**, and (f) **1f**. Conditions: acetophenone (1.0 mmol), HBpin (1.1 mmol), catalyst (0.01 mmol, 1mol%), toluene (2 mL), 50^{o}C, argon atmosphere, 12 h.

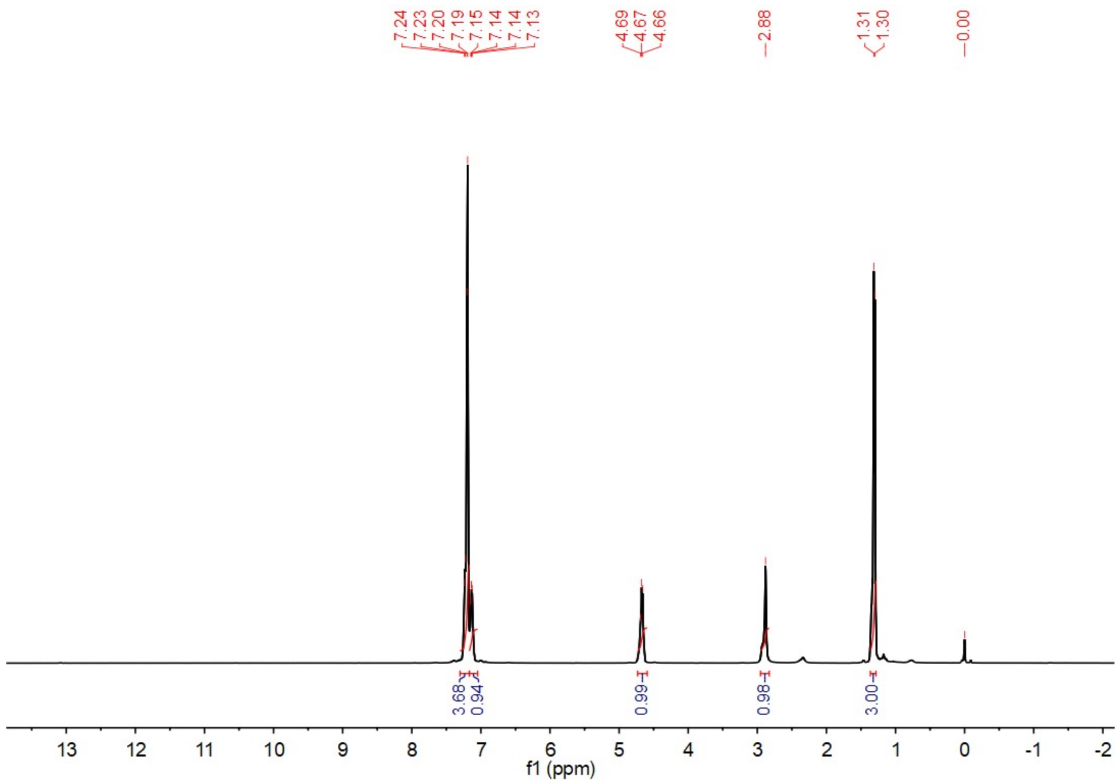


Figure S46 ^{1}H NMR spectrum of **2a** in $CDCl_3$ solvent.

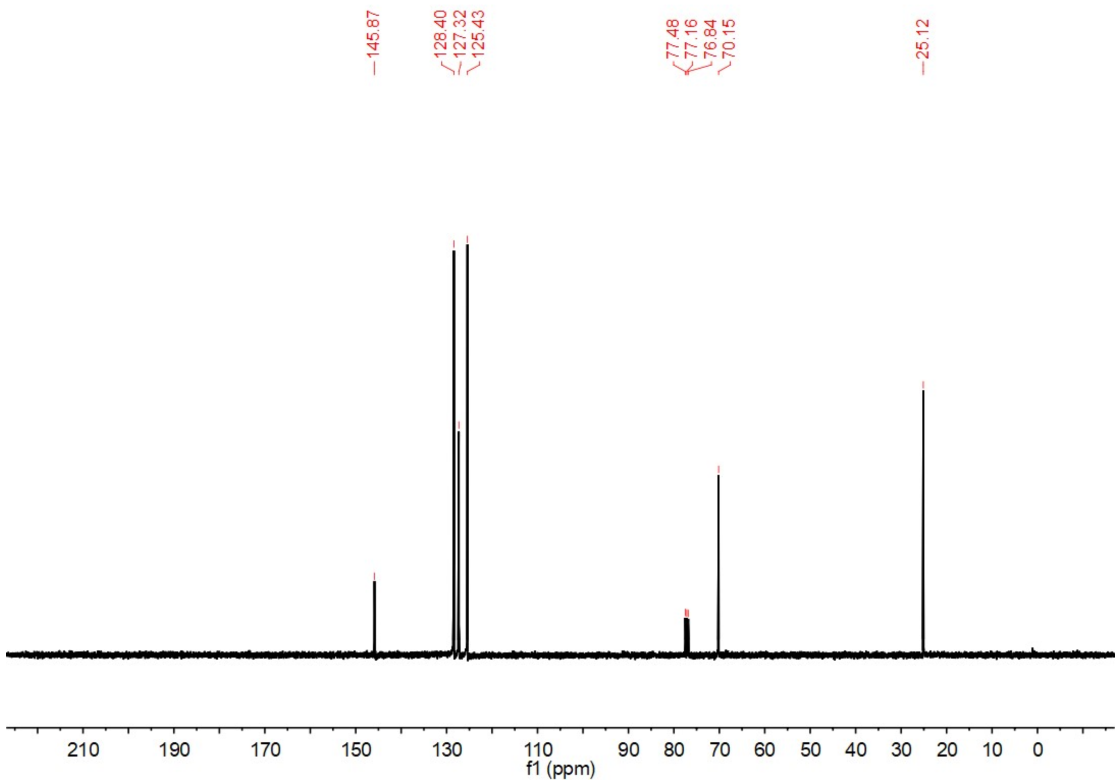


Figure S47 ^{13}C NMR spectrum of **2a** in $CDCl_3$ solvent.

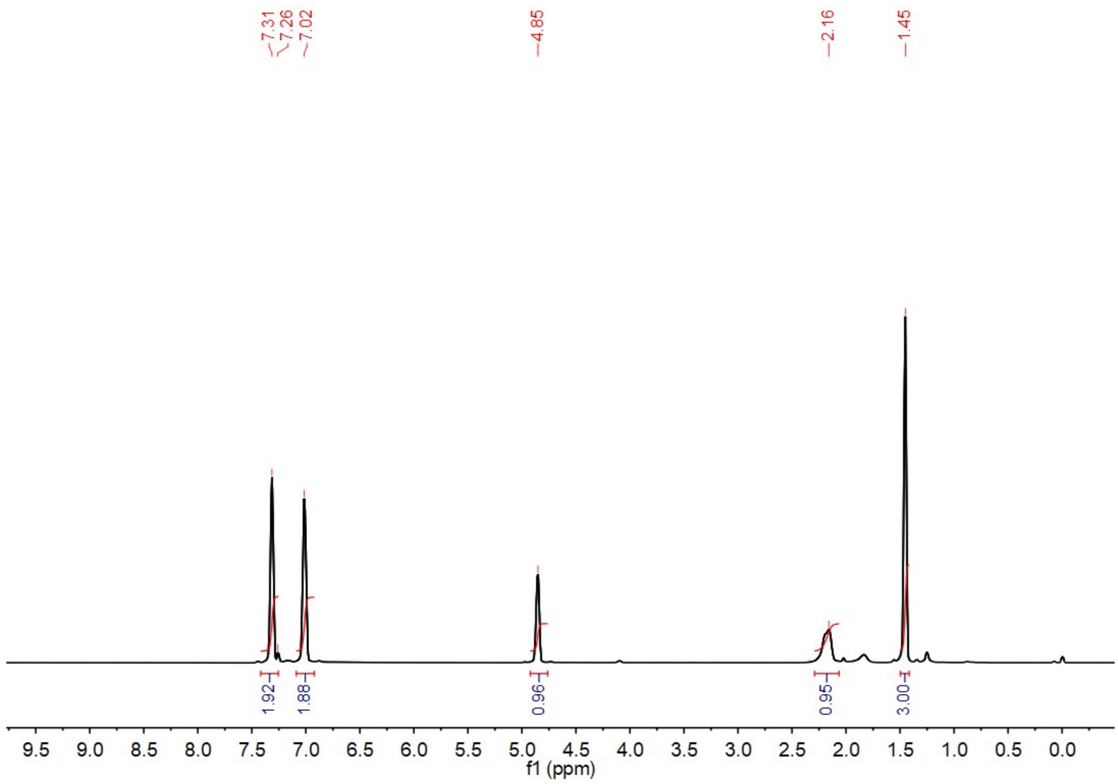


Figure S48 ^{1}H NMR spectrum of **2b** in $CDCl_3$ solvent.

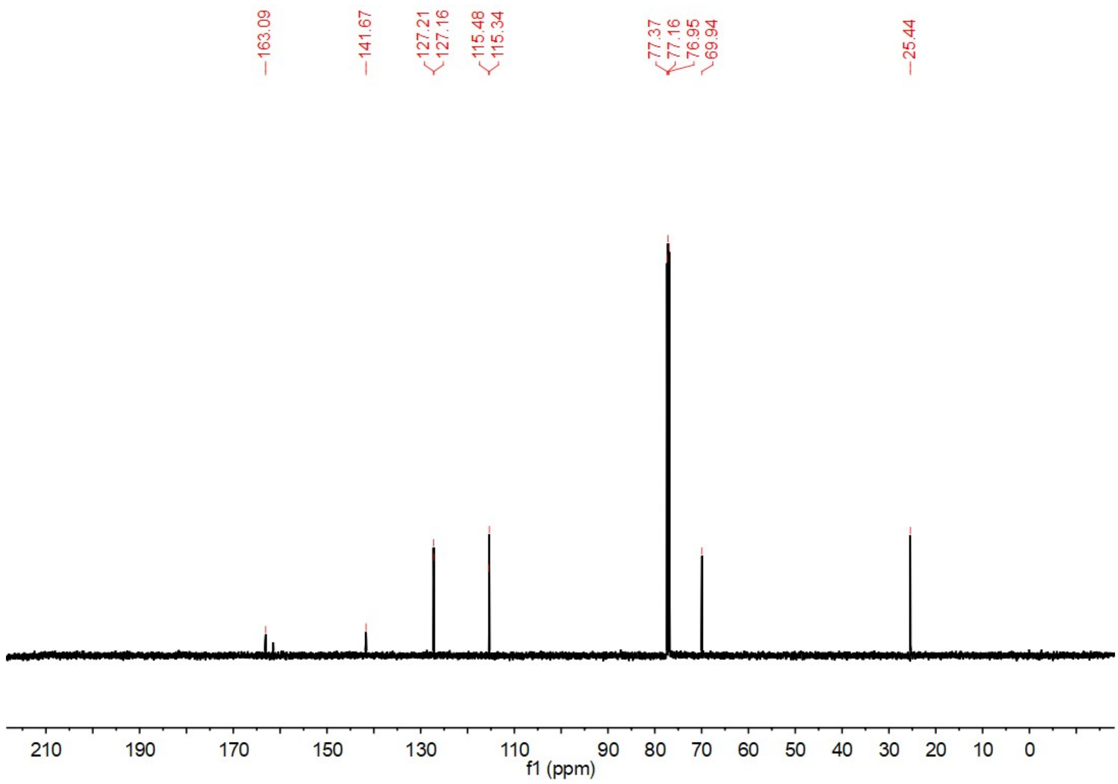


Figure S49 ^{13}C NMR spectrum of **2b** in $CDCl_3$ solvent.

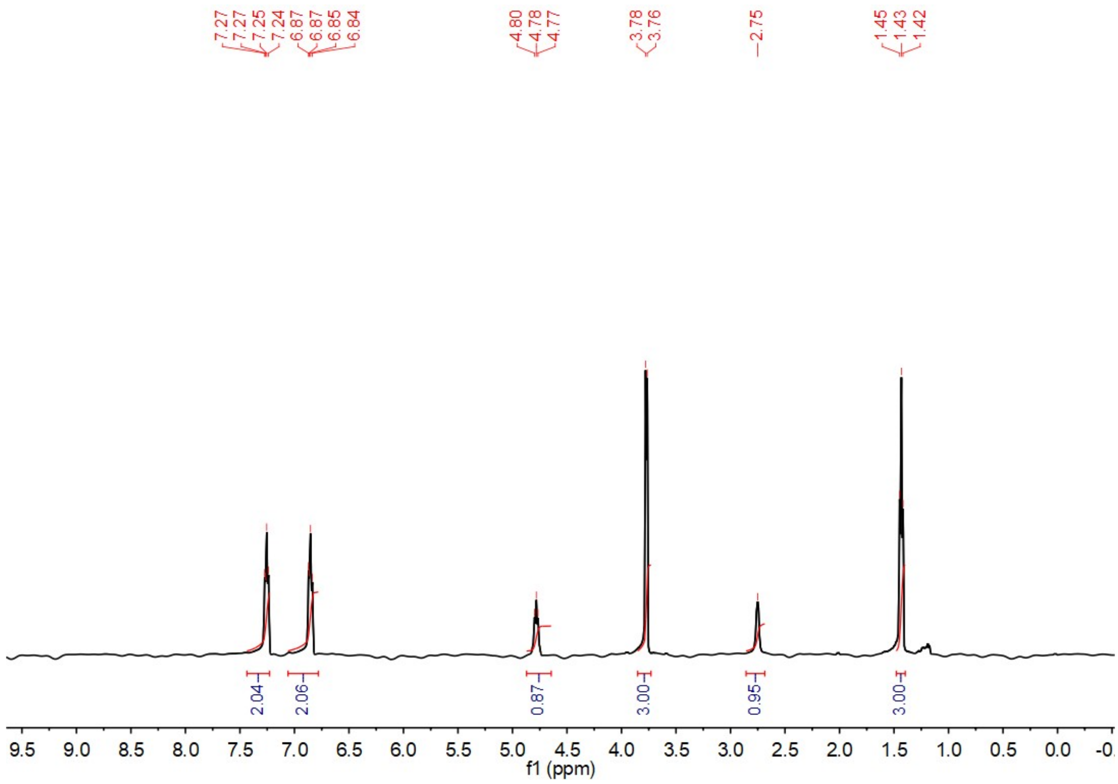


Figure S50 ^{1}H NMR spectrum of **2c** in $CDCl_3$ solvent.

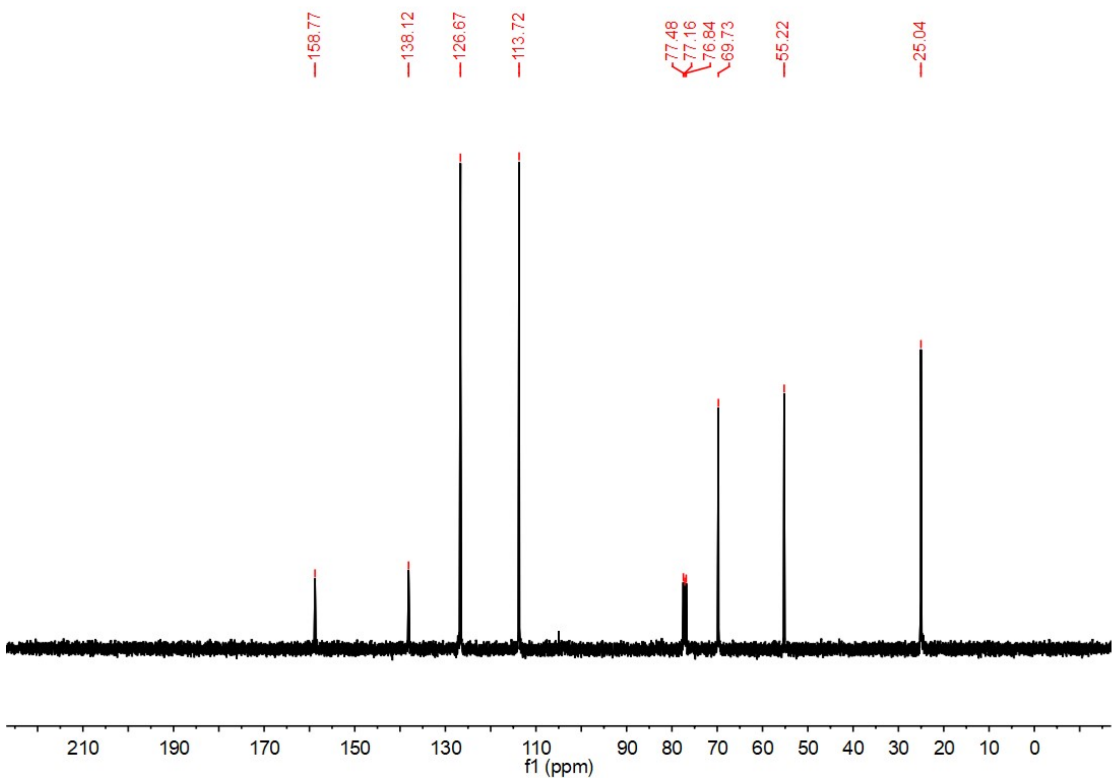


Figure S51 ^{13}C NMR spectrum of **2c** in $CDCl_3$ solvent.

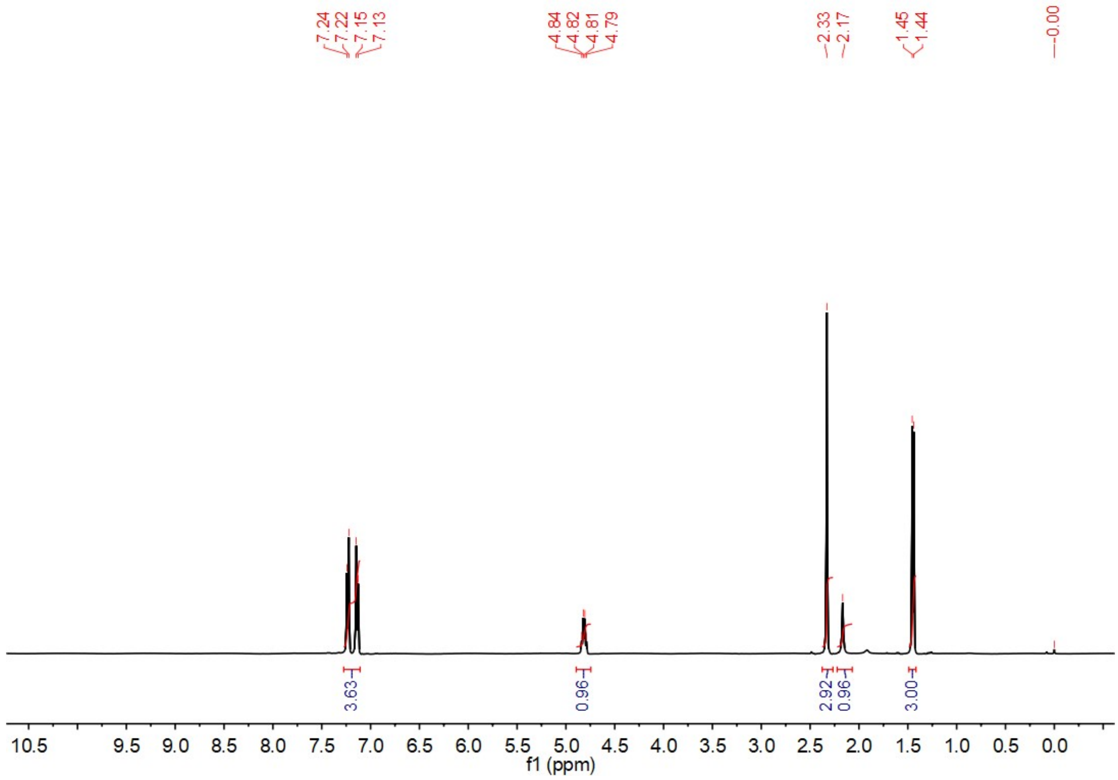


Figure S52 ^{1}H NMR spectrum of **2d** in $CDCl_3$ solvent.

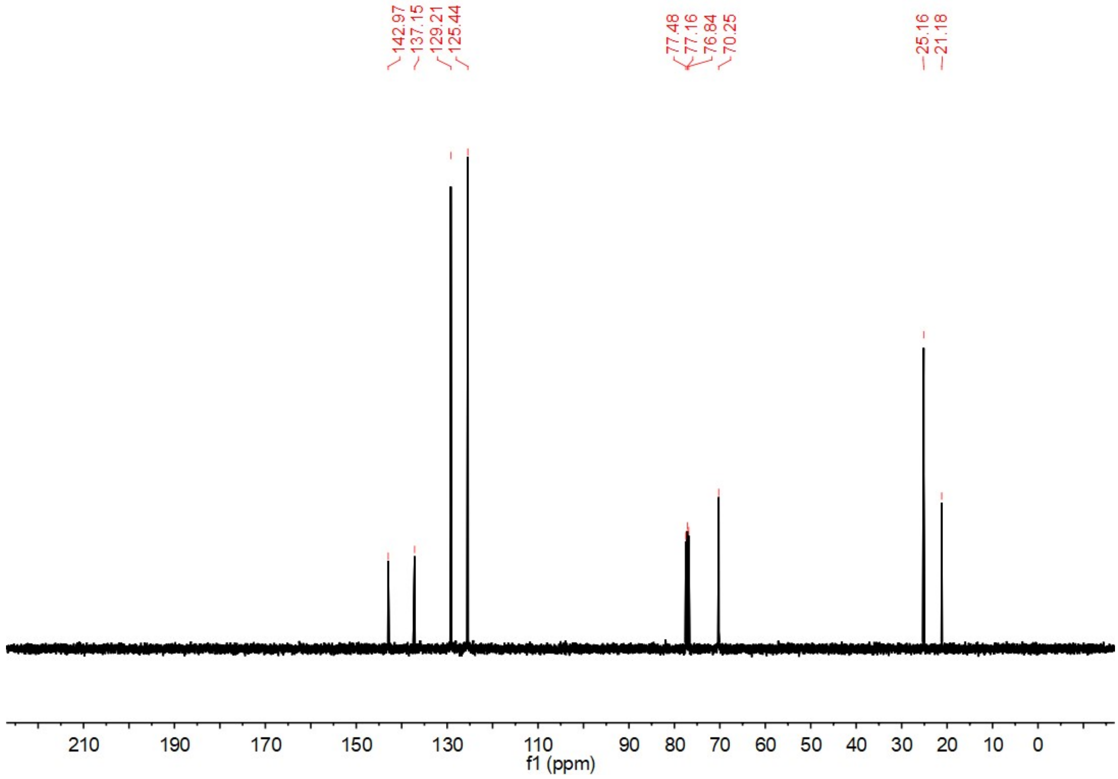


Figure S53 ^{13}C NMR spectrum of **2d** in $CDCl_3$ solvent.

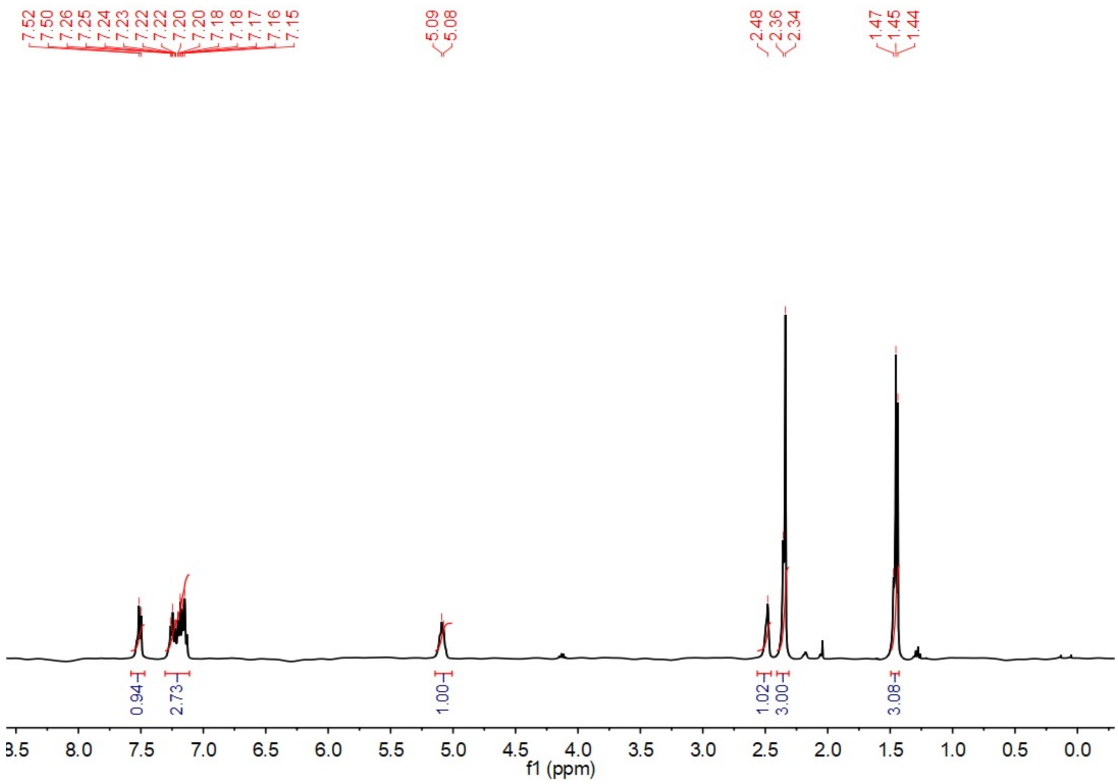


Figure S54 ^{1}H NMR spectrum of **2e** in $CDCl_3$ solvent.

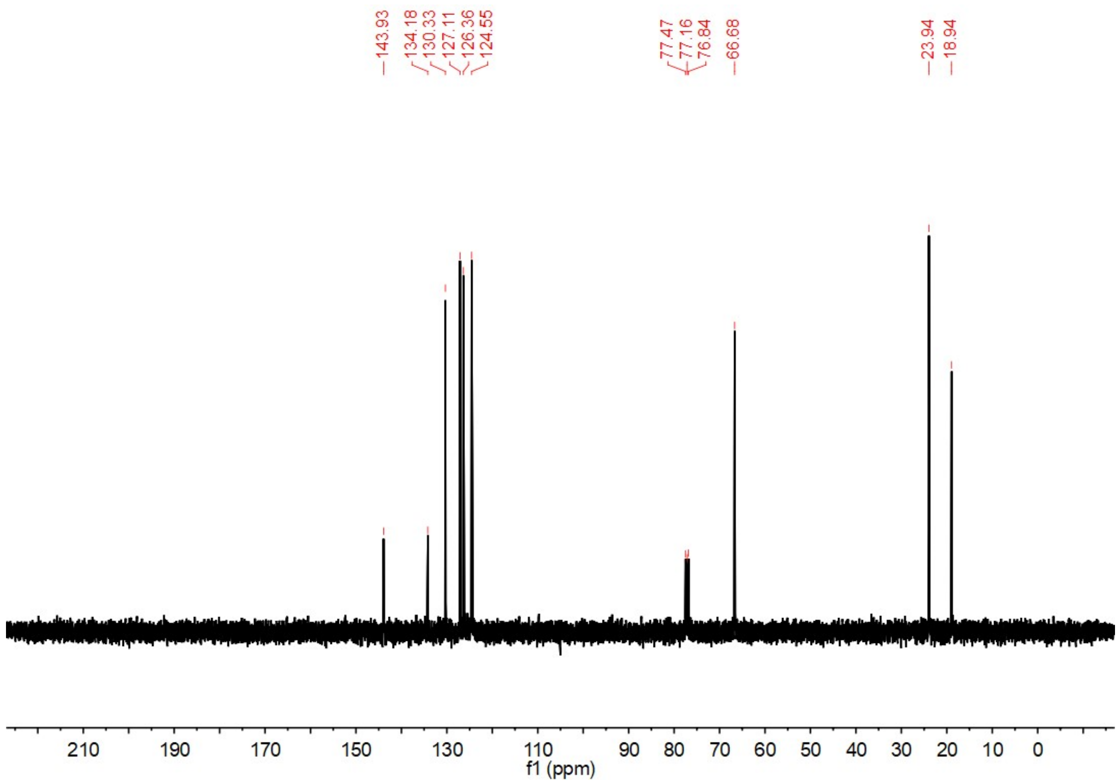


Figure S55 ^{13}C NMR spectrum of **2e** in $CDCl_3$ solvent.

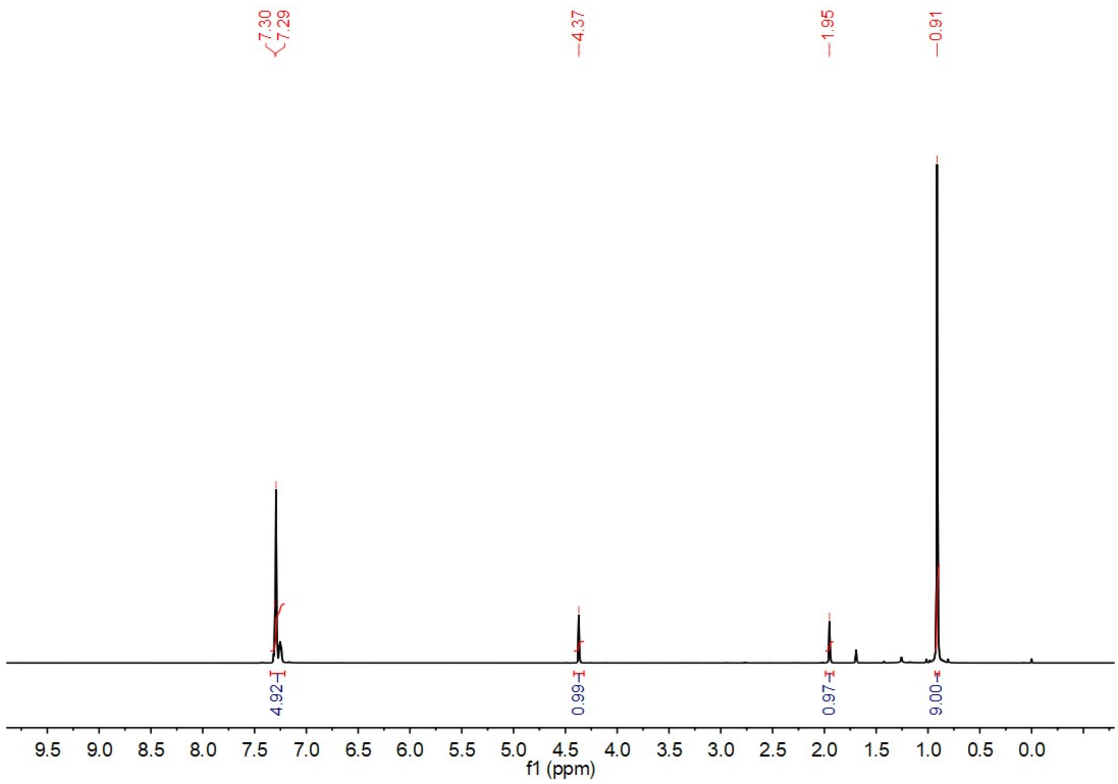


Figure S56 ^{1}H NMR spectrum of **2f** in $CDCl_3$ solvent.

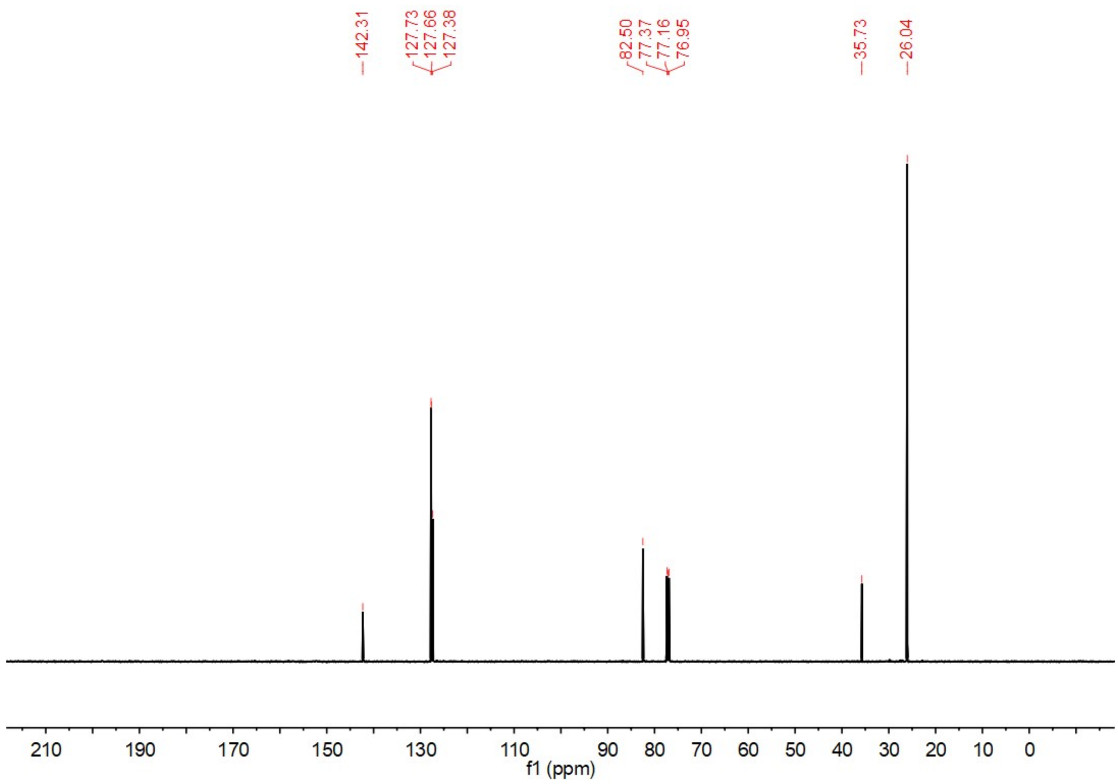


Figure S57 ^{13}C NMR spectrum of **2f** in $CDCl_3$ solvent.

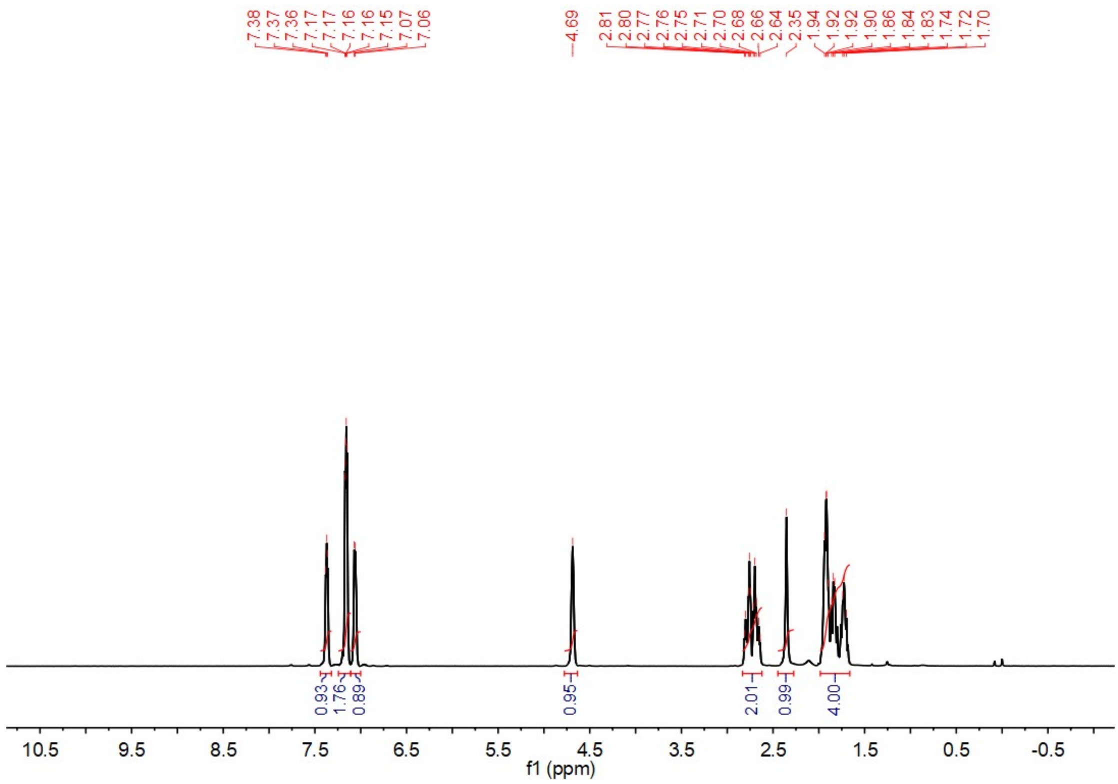


Figure S58 ^{1}H NMR spectrum of **2g** in $CDCl_3$ solvent.

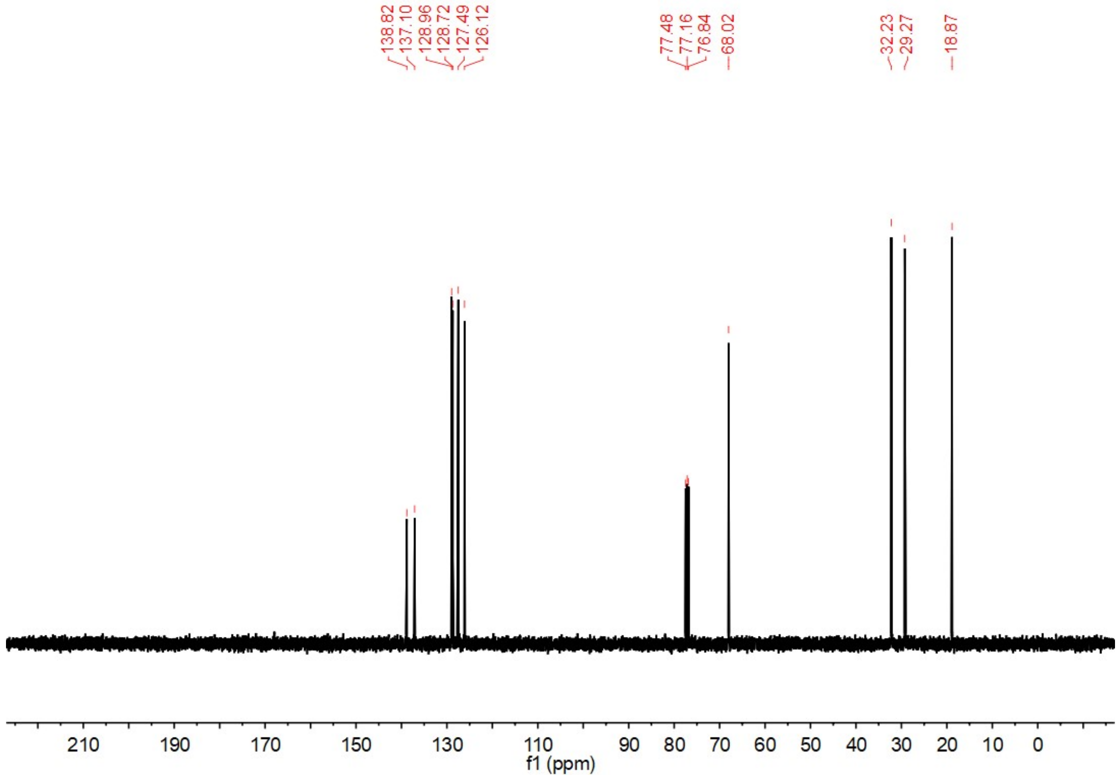


Figure S59 ^{13}C NMR spectrum of **2g** in $CDCl_3$ solvent.

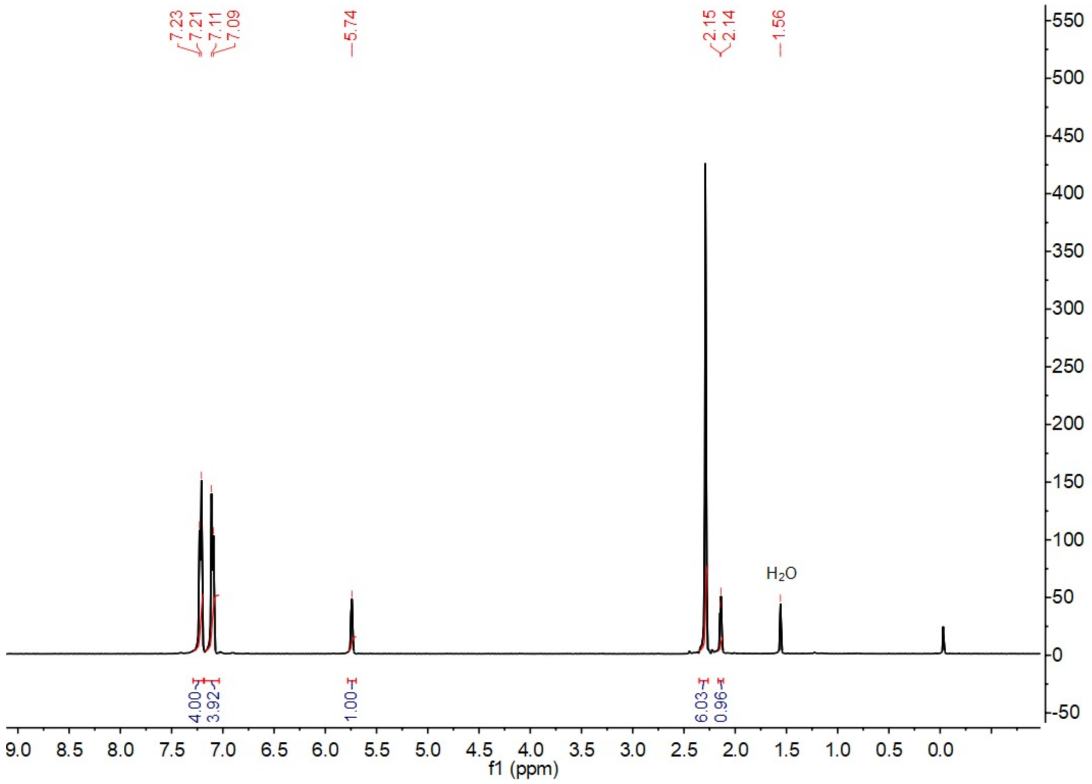


Figure S60 ^{1}H NMR spectrum of **2h** in $CDCl_3$ solvent.

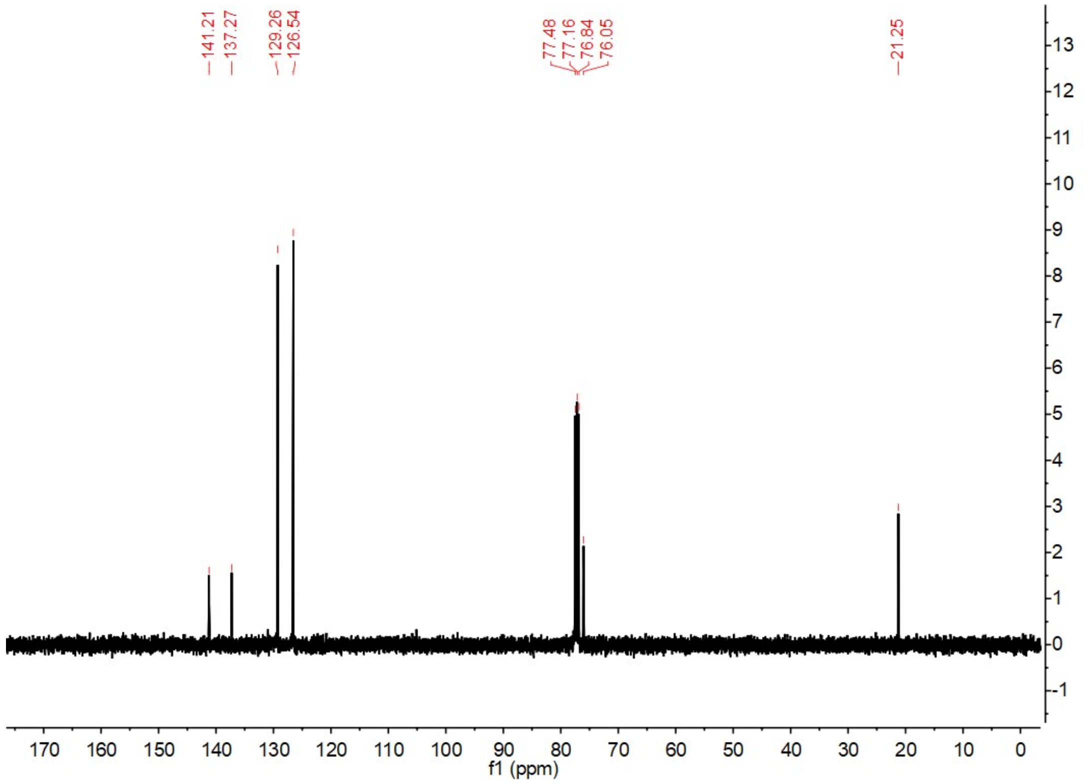


Figure S61 ^{13}C NMR spectrum of **2h** in $CDCl_3$ solvent.

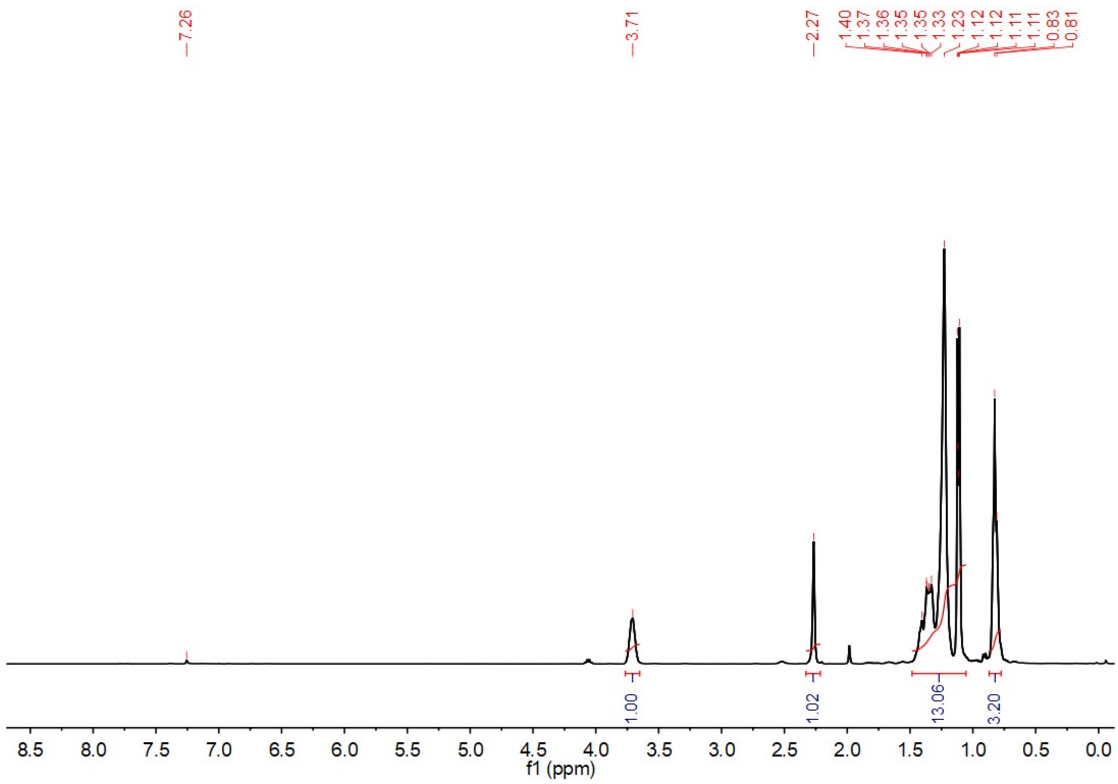


Figure S62 ^{1}H NMR spectrum of **2i** in $CDCl_3$ solvent.

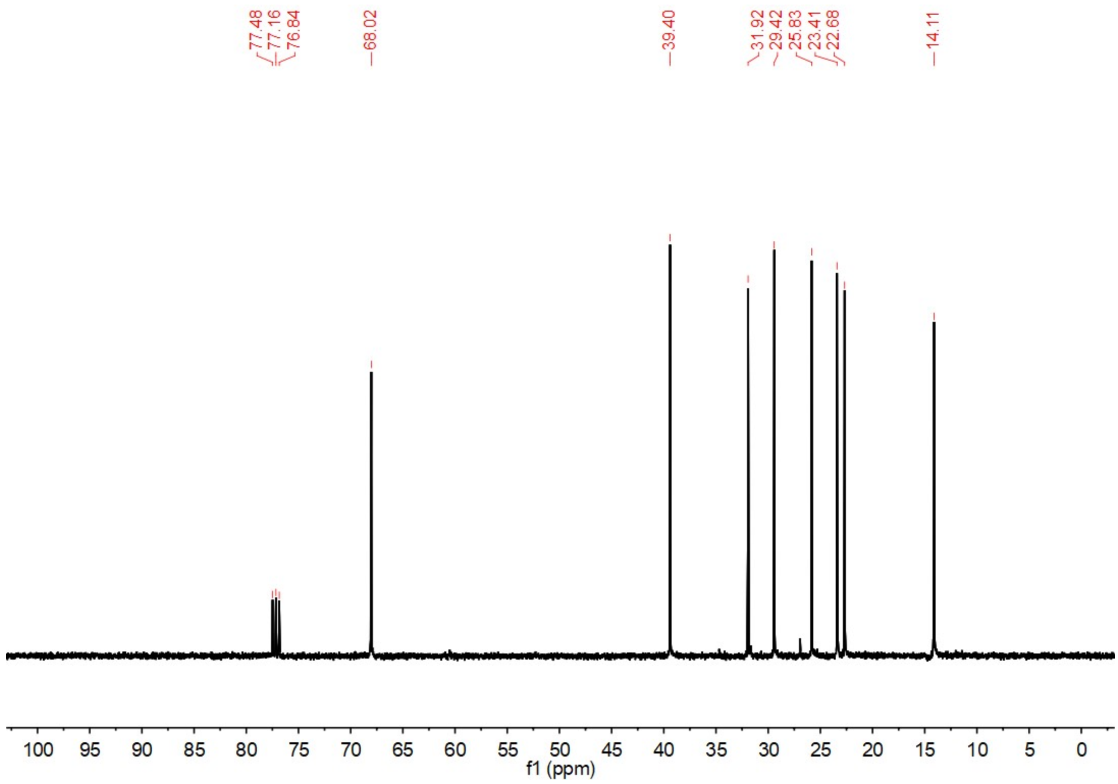


Figure S63 ^{13}C NMR spectrum of **2i** in $CDCl_3$ solvent.

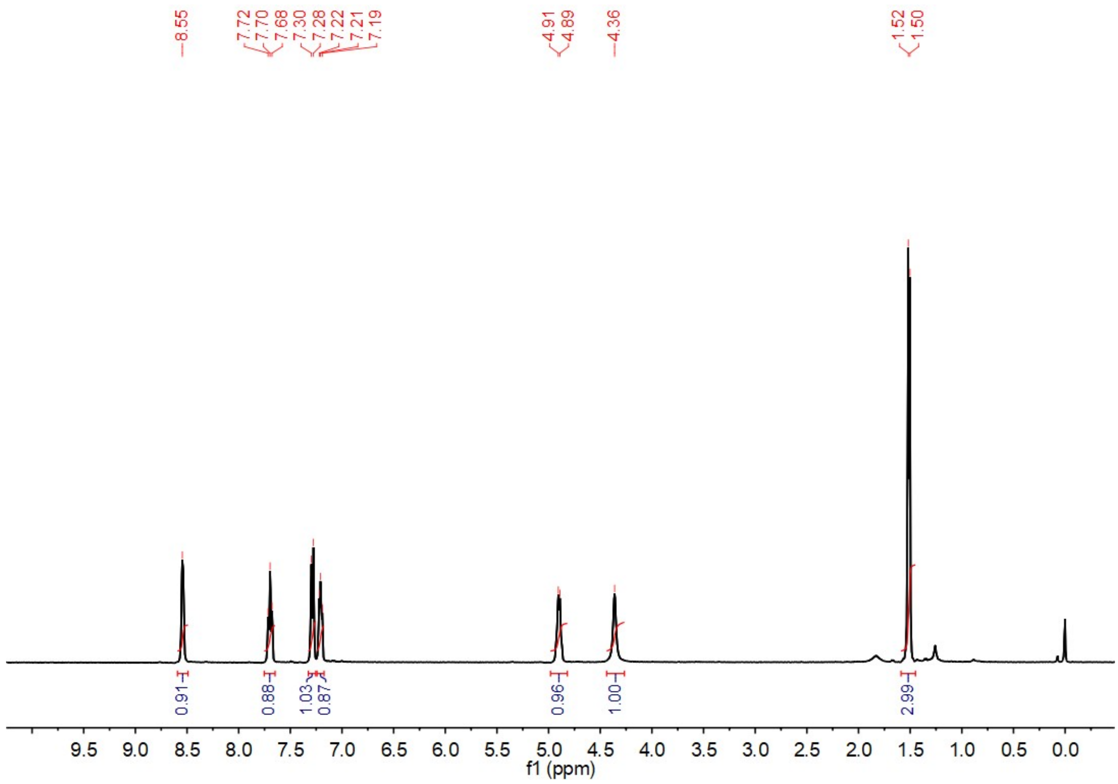


Figure S64 ^{1}H NMR spectrum of **2j** in $CDCl_3$ solvent.

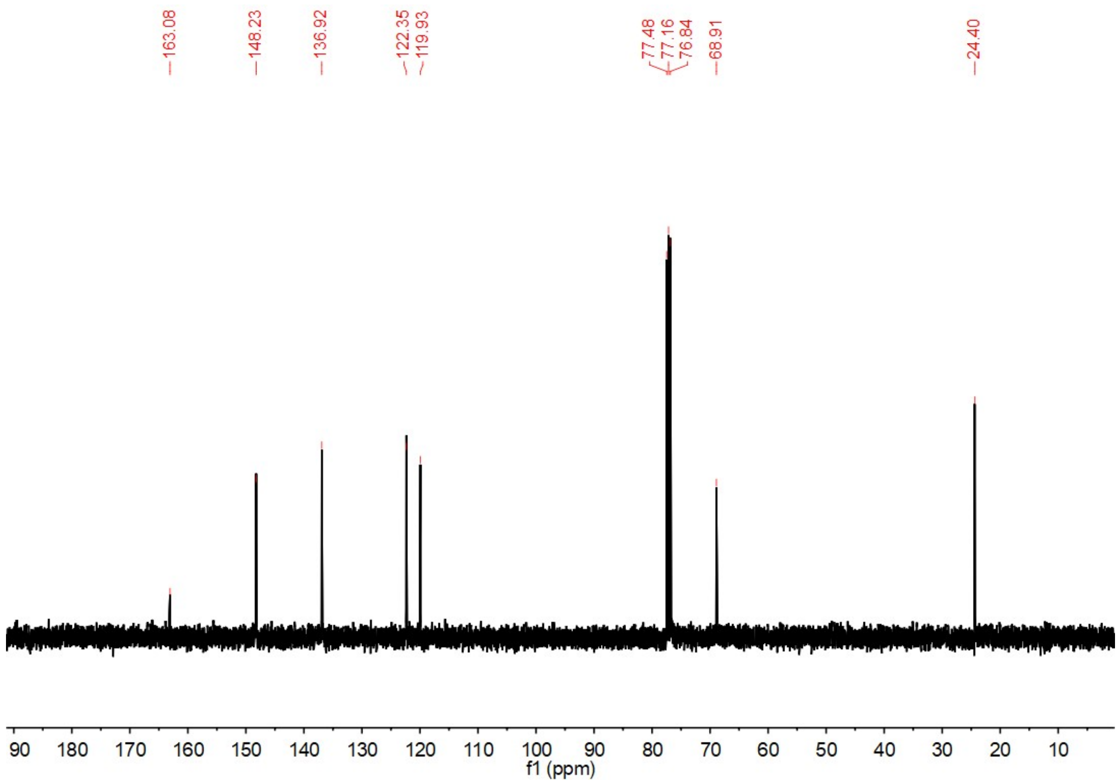


Figure S65 ^{13}C NMR spectrum of **2j** in $CDCl_3$ solvent.

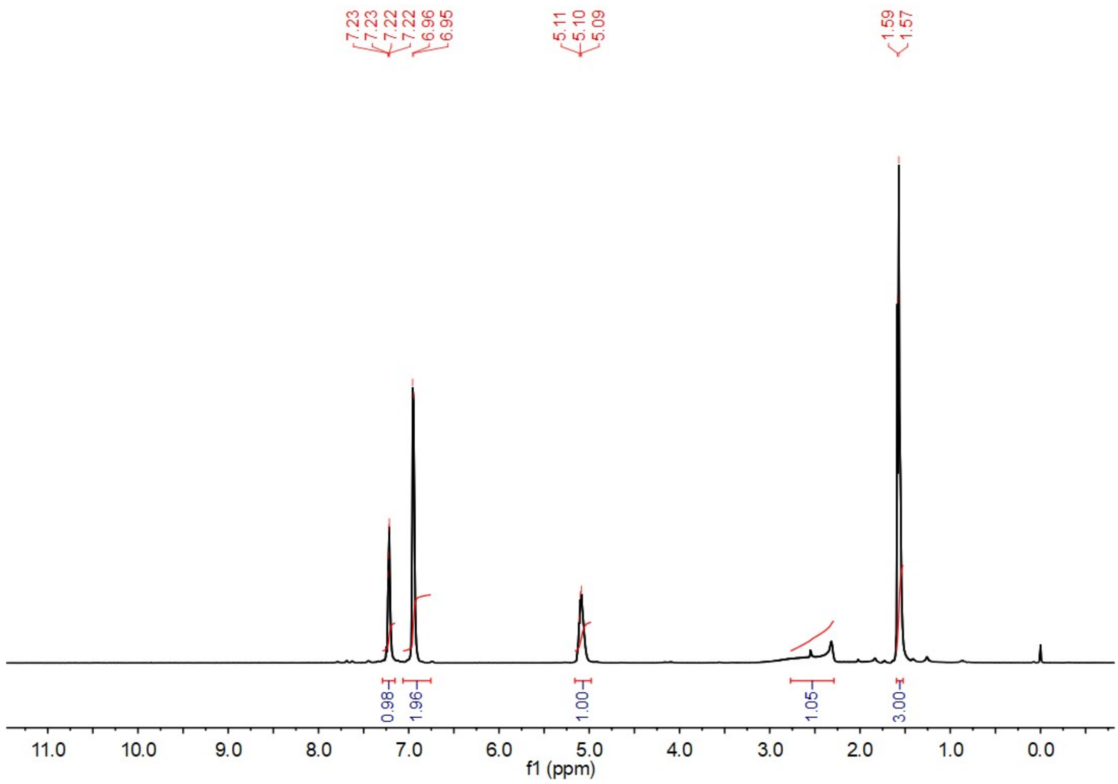


Figure S66 ^{1}H NMR spectrum of **2k** in $CDCl_3$ solvent.

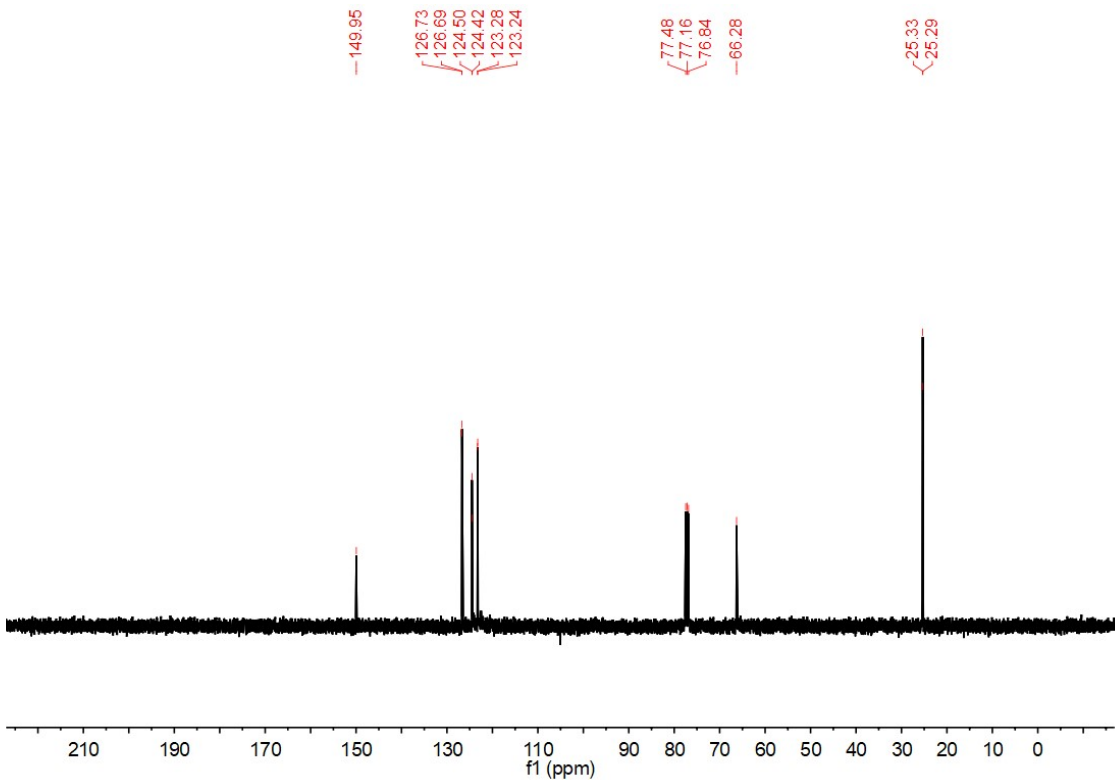


Figure S67 ^{13}C NMR spectrum of **2k** in $CDCl_3$ solvent.

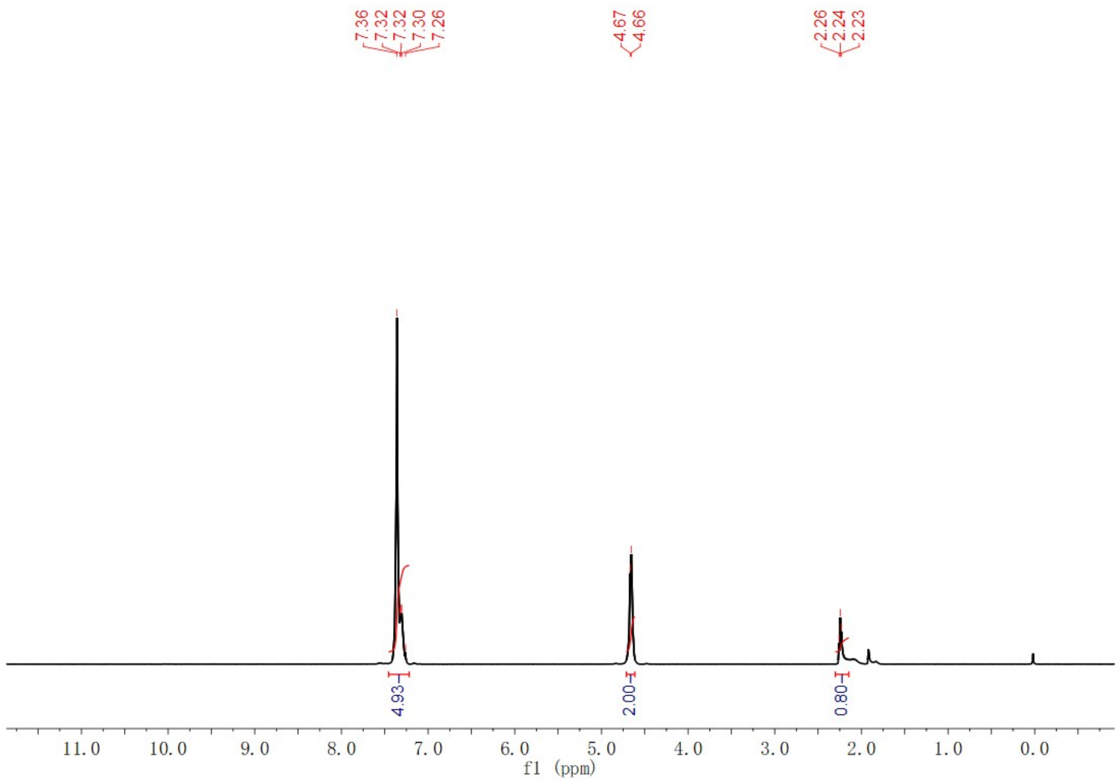


Figure S68 ^{1}H NMR spectrum of **3a** in $CDCl_3$ solvent.

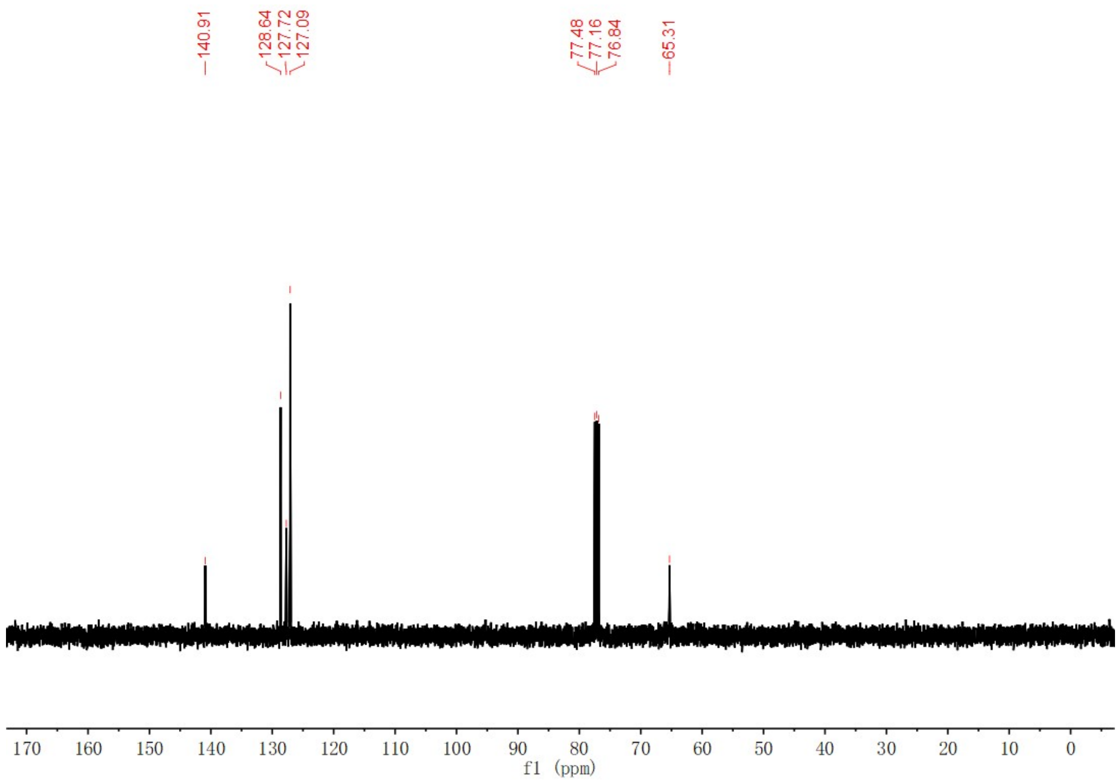


Figure S69 ^{13}C NMR spectrum of **3a** in $CDCl_3$ solvent.

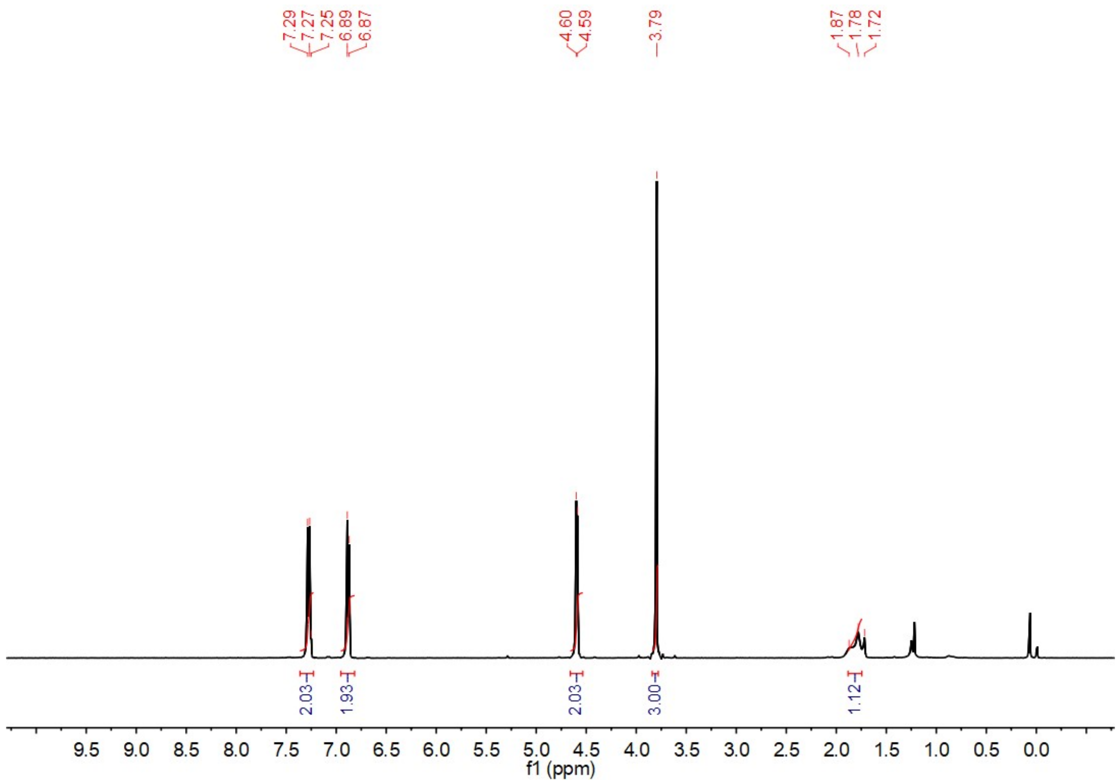


Figure S70 ^{1}H NMR spectrum of **3b** in $CDCl_3$ solvent.

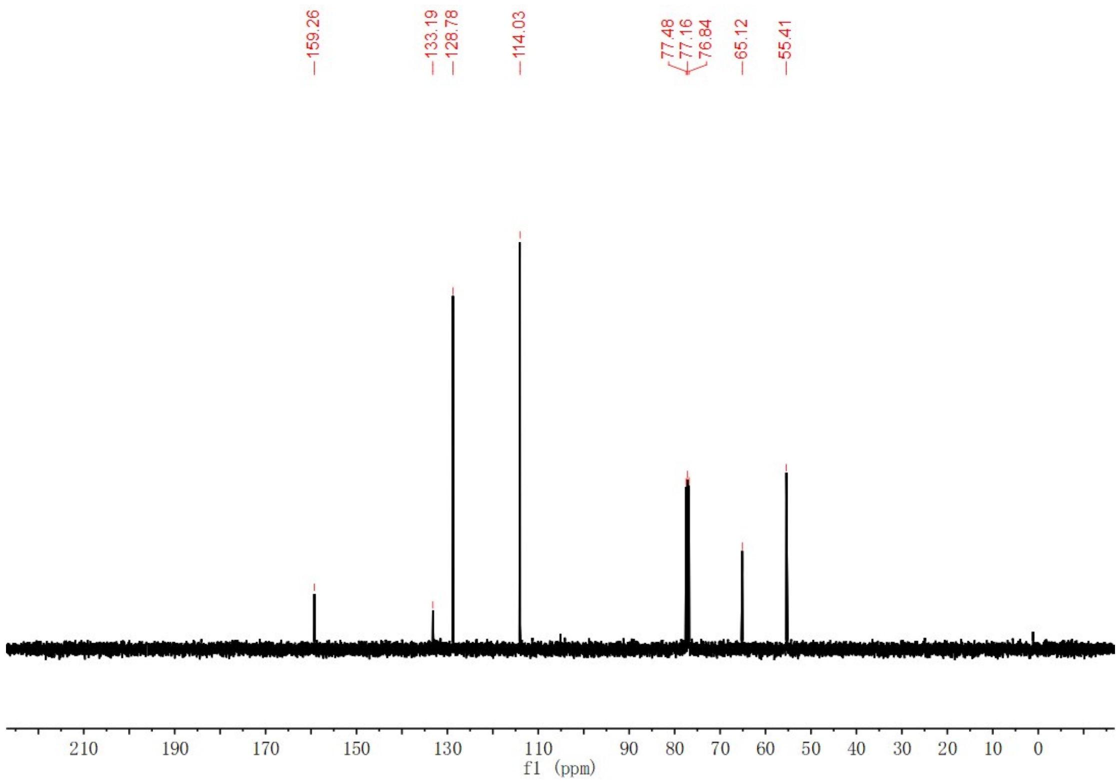


Figure S71 ^{13}C NMR spectrum of **3b** in $CDCl_3$ solvent.

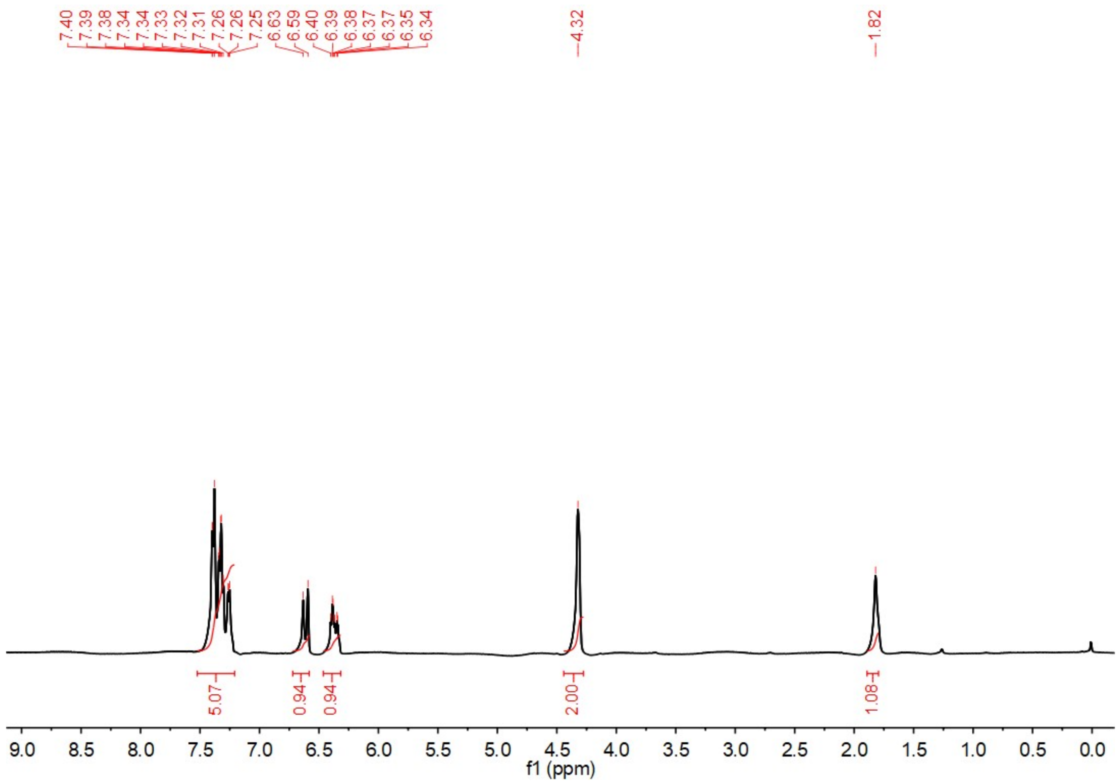


Figure S72 ^{1}H NMR spectrum of **3c** in $CDCl_3$ solvent.

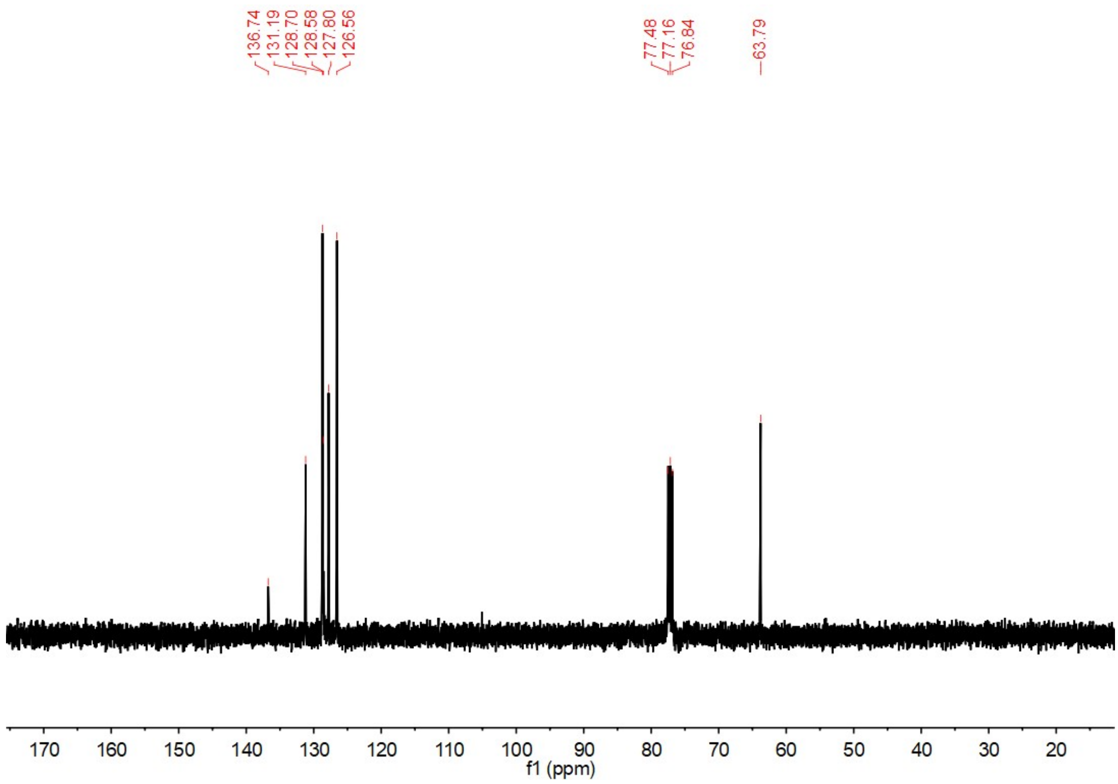


Figure S73 ^{13}C NMR spectrum of **3c** in $CDCl_3$ solvent.

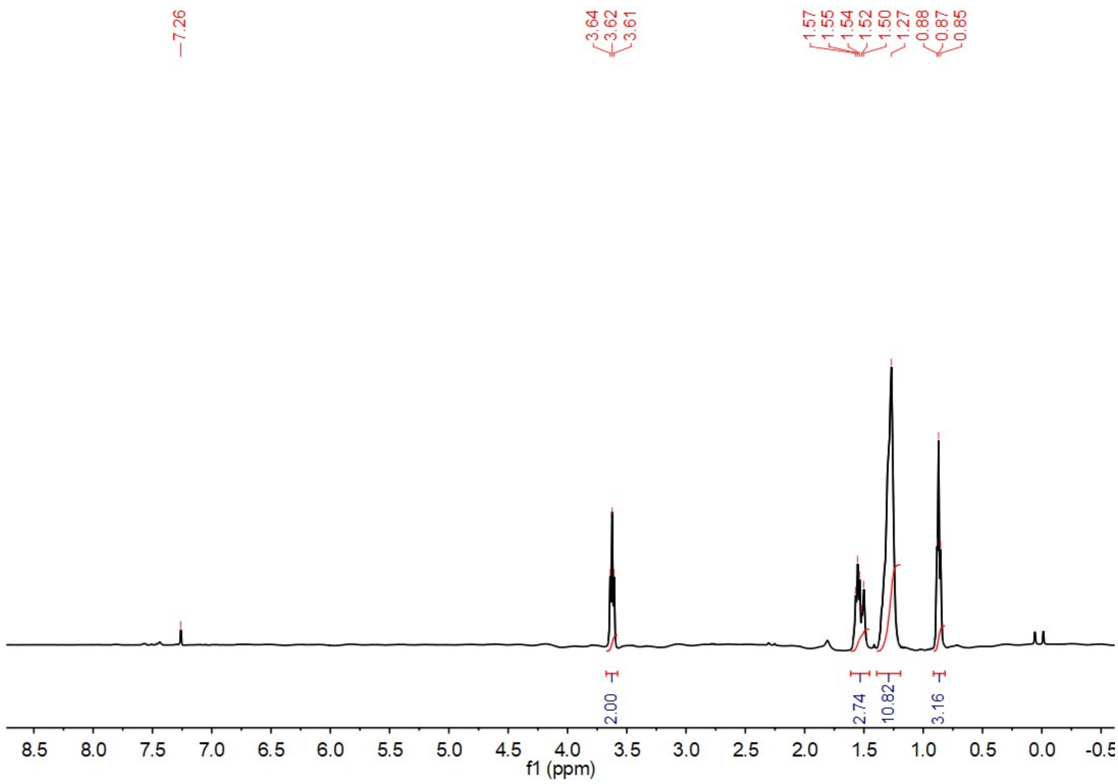


Figure S74 ^{1}H NMR spectrum of **3d** in $CDCl_3$ solvent.

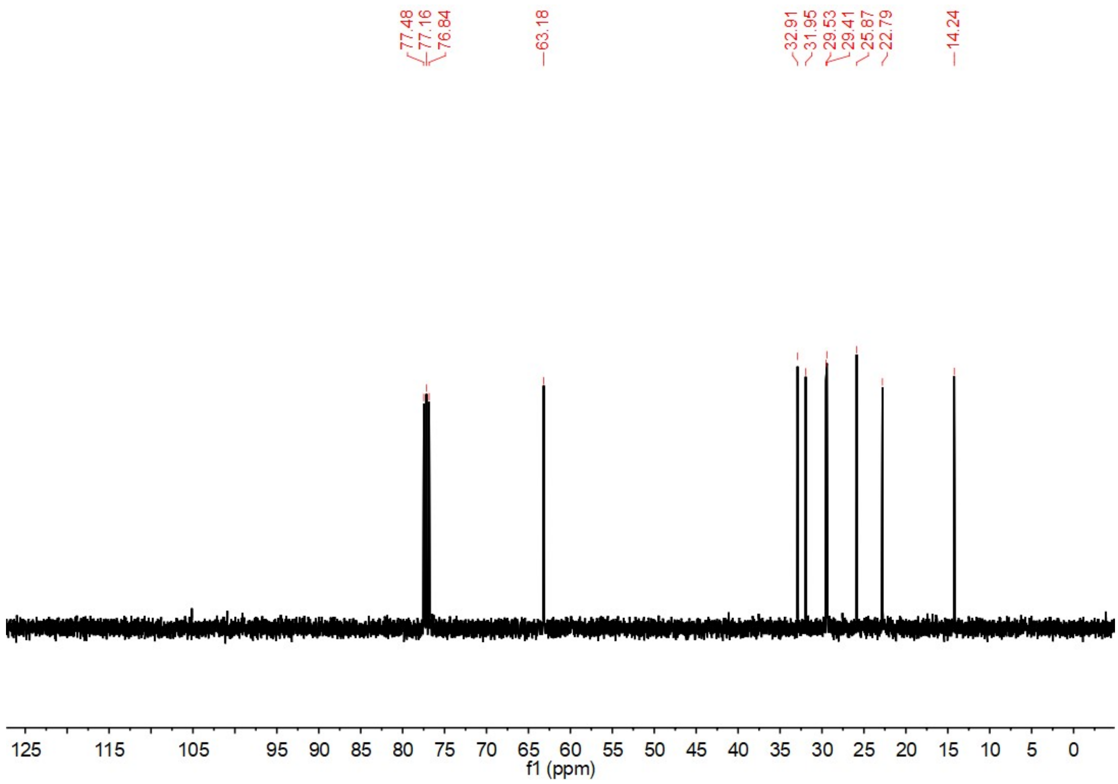


Figure S75 ^{13}C NMR spectrum of **3d** in $CDCl_3$ solvent.

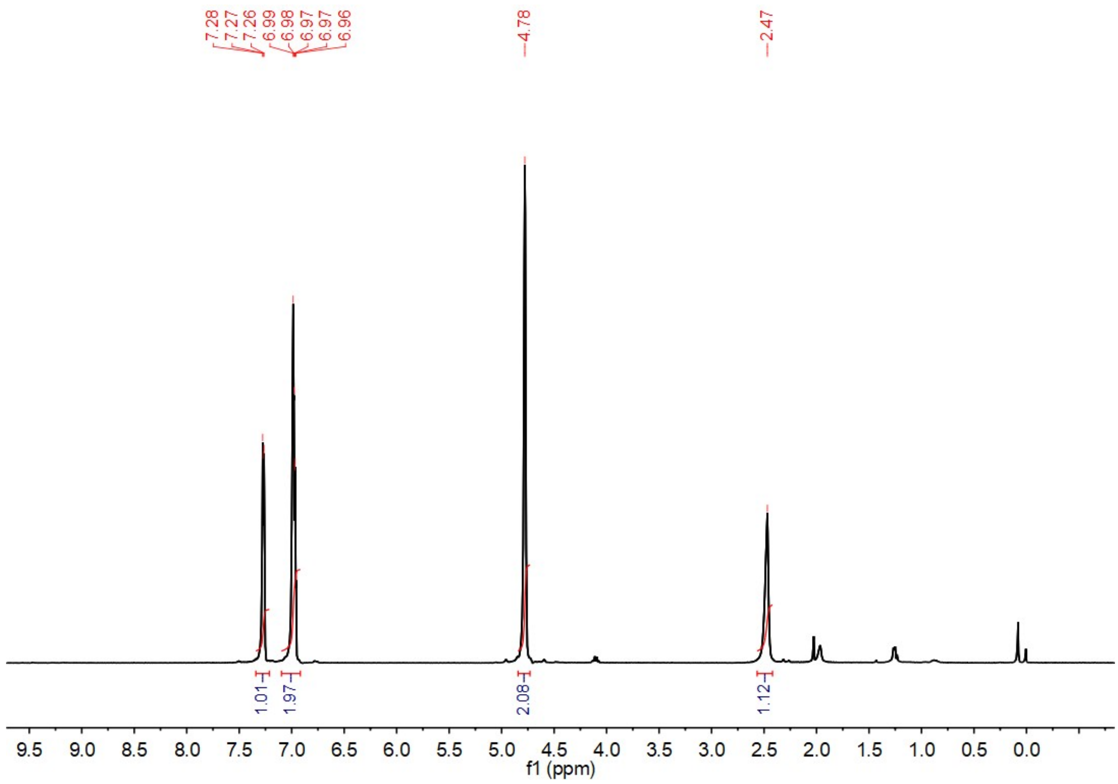


Figure S76 ^{1}H NMR spectrum of **3e** in $CDCl_3$ solvent.

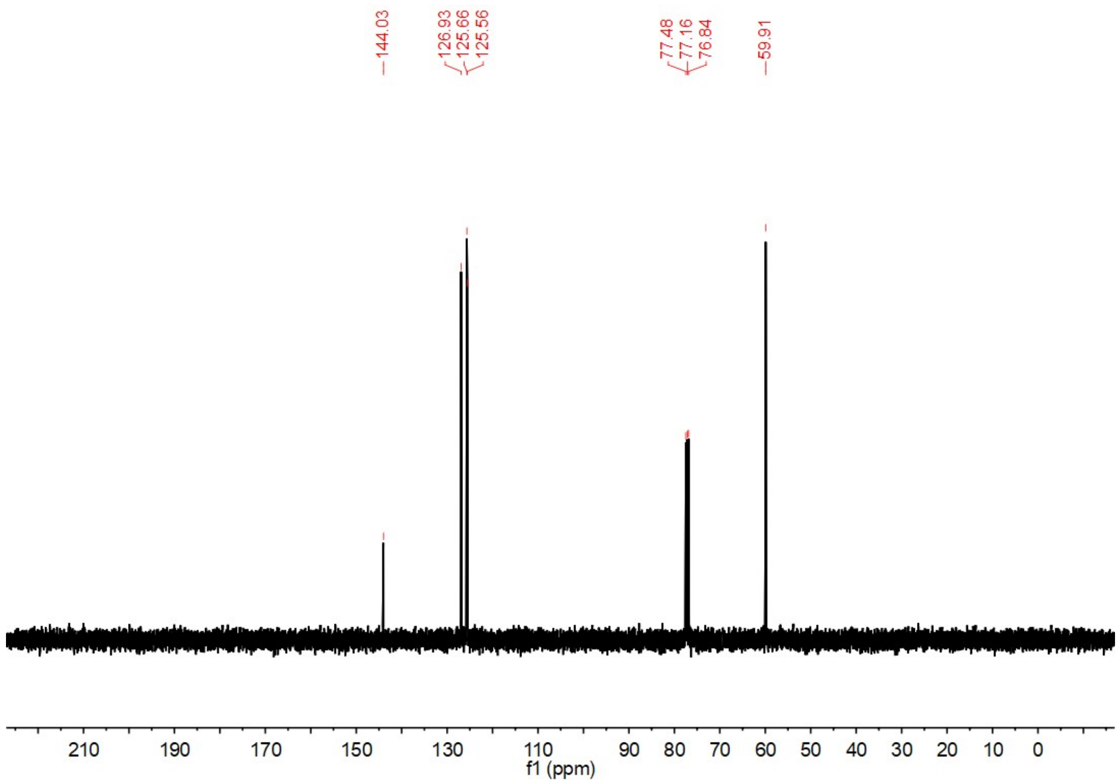


Figure S77 ^{13}C NMR spectrum of **3e** in $CDCl_3$ solvent.

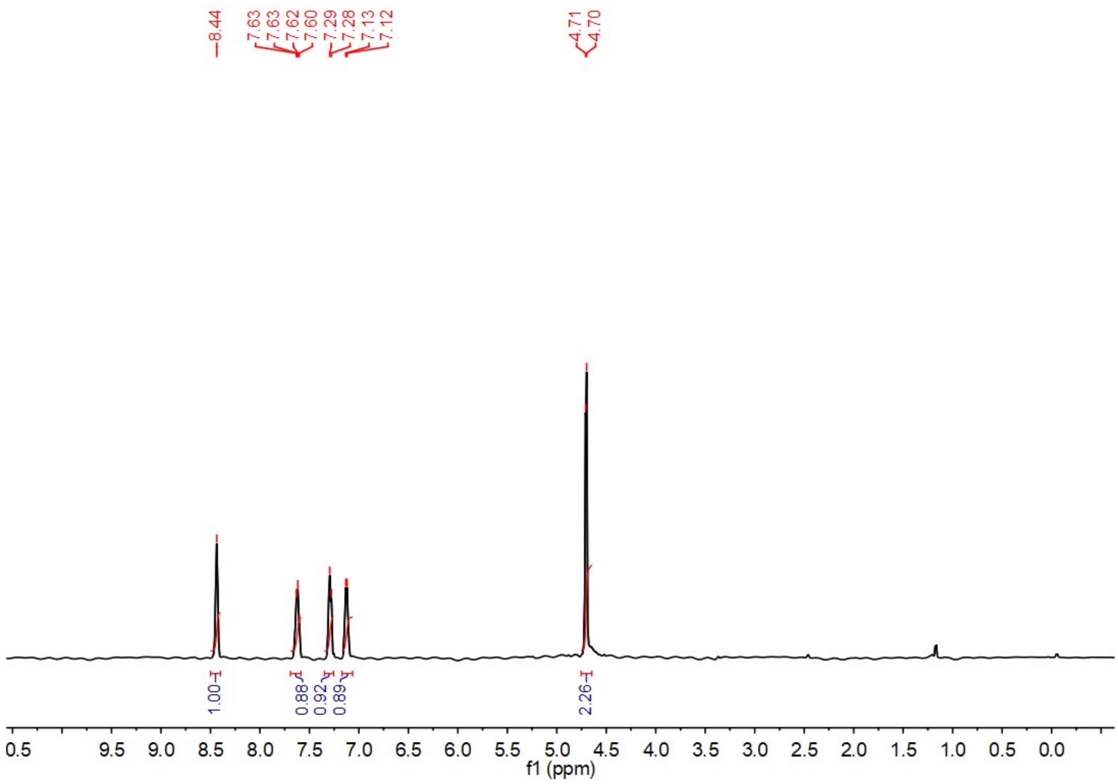


Figure S78 ^{1}H NMR spectrum of **3f** in $CDCl_3$ solvent.

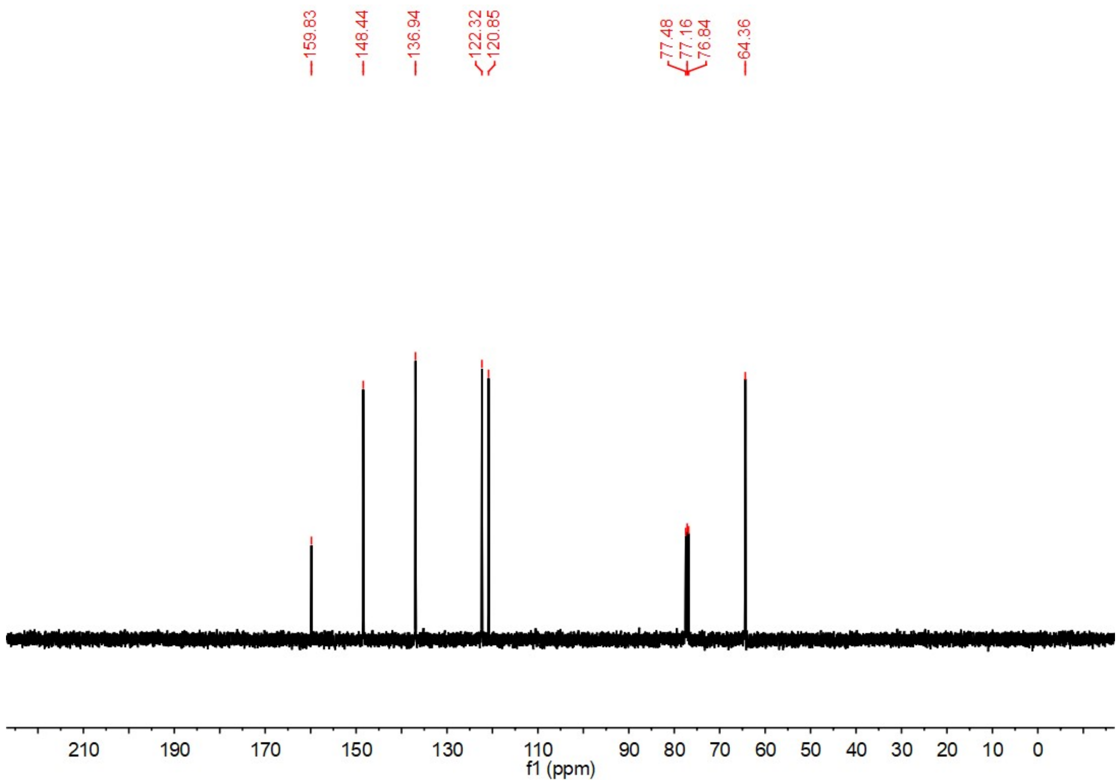


Figure S79 ^{13}C NMR spectrum of **3f** in $CDCl_3$ solvent.

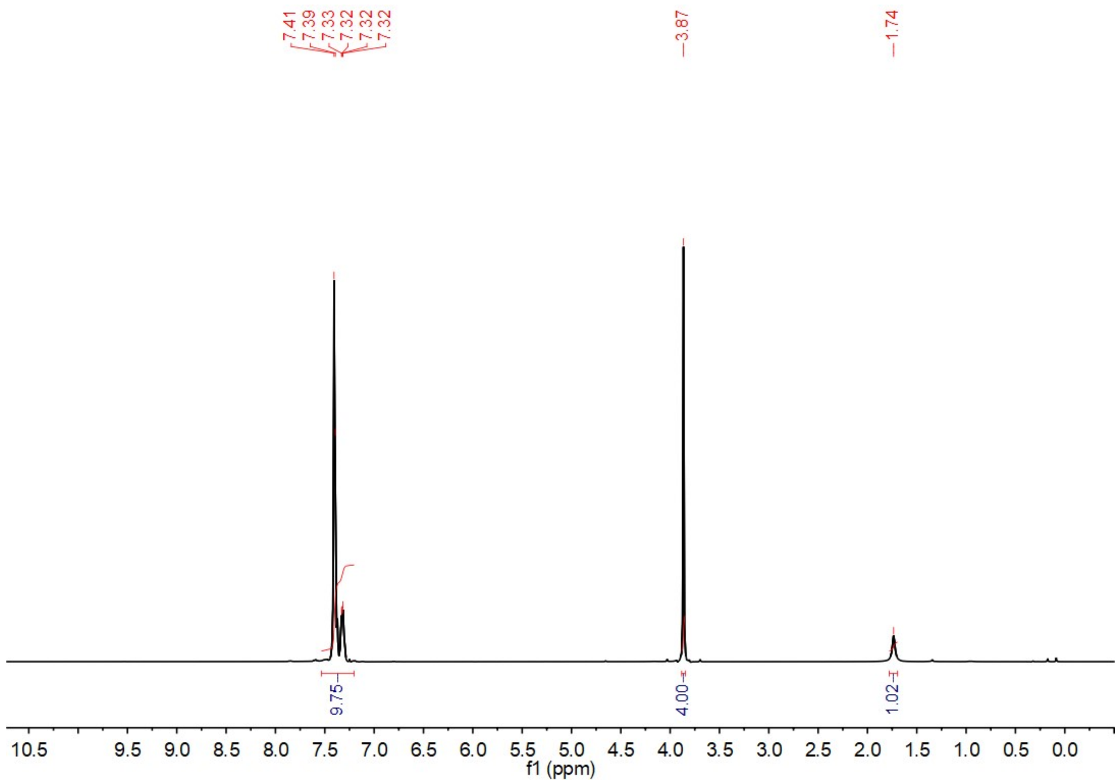


Figure S80 ^{1}H NMR spectrum of **4a** in $CDCl_3$ solvent.

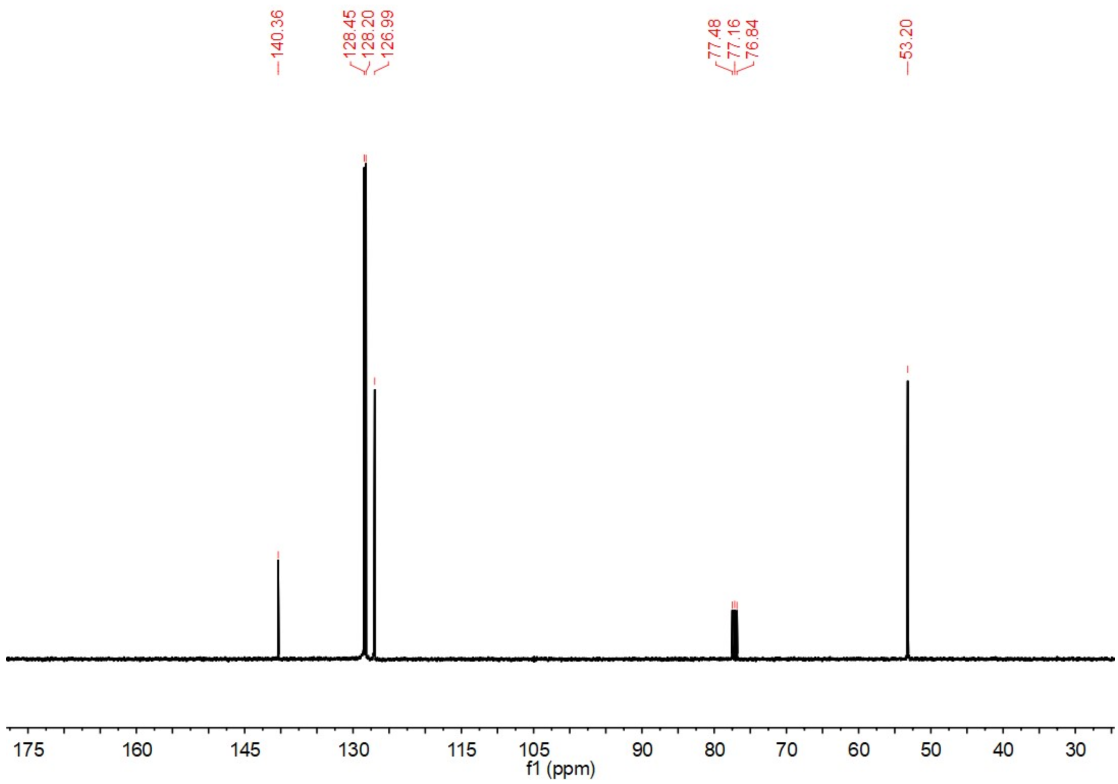


Figure S81 ^{13}C NMR spectrum of **4a** in $CDCl_3$ solvent.

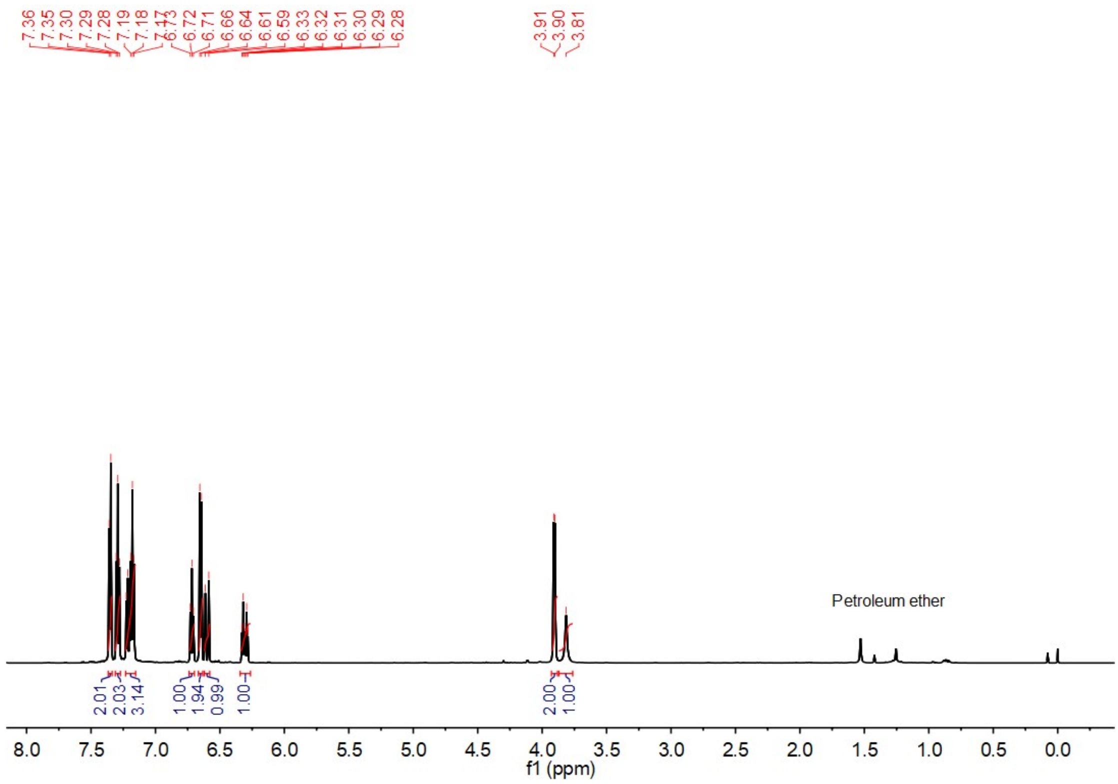


Figure S82 ^{1}H NMR spectrum of **4b** in $CDCl_3$ solvent.

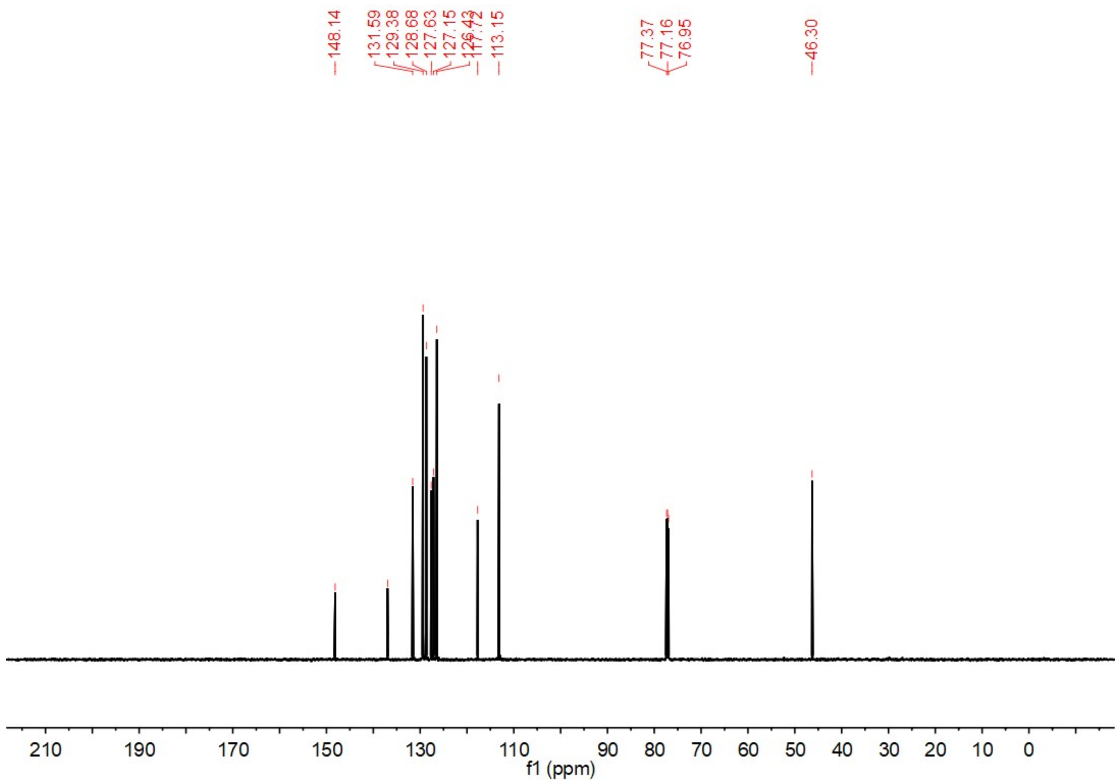


Figure S83 ^{13}C NMR spectrum of **4b** in $CDCl_3$ solvent.

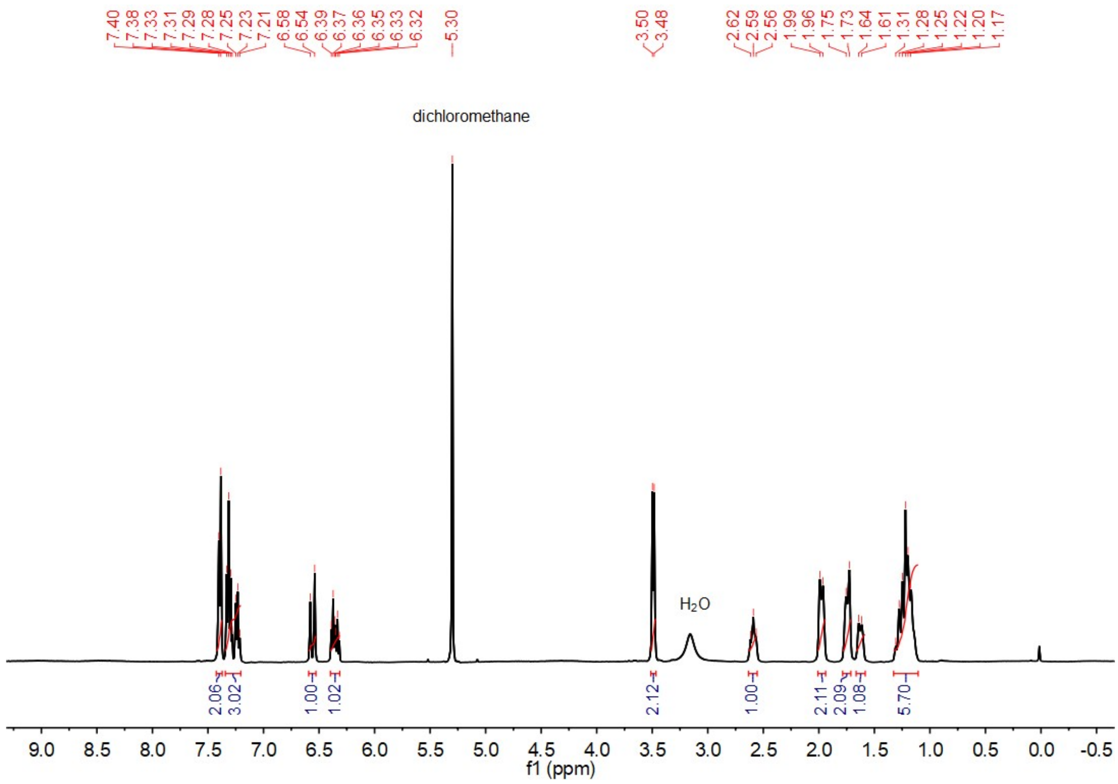


Figure S84 ^{1}H NMR spectrum of **4c** in $CDCl_3$ solvent.

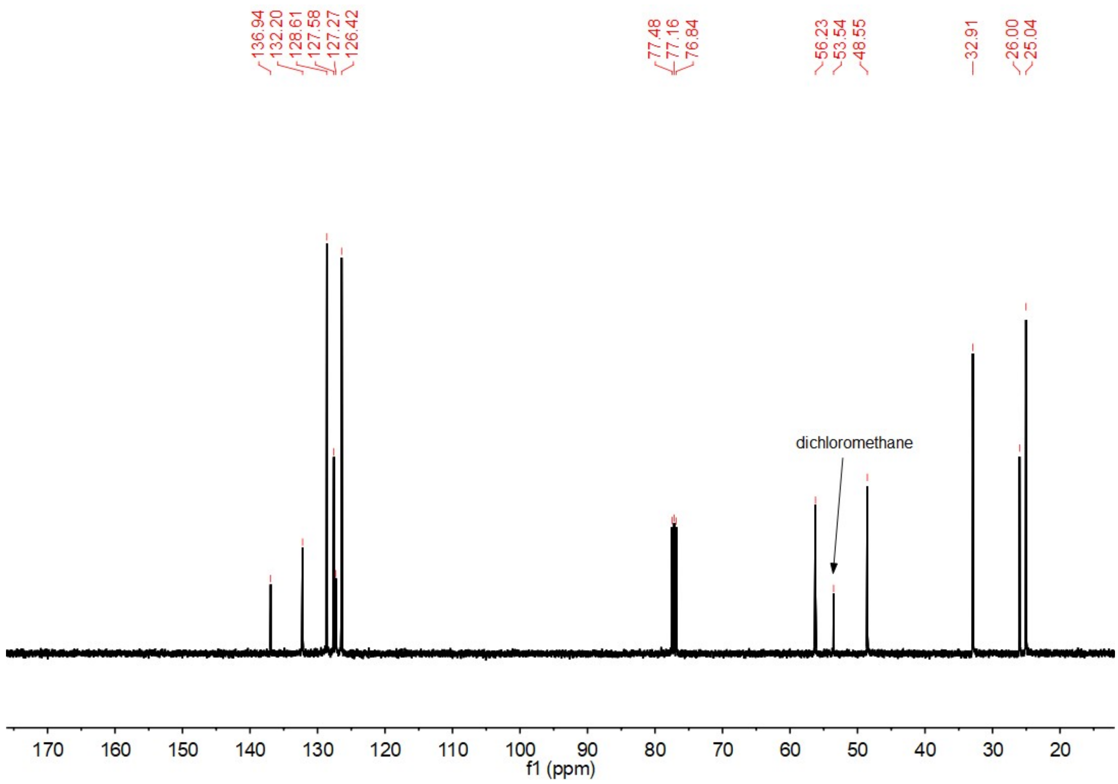


Figure S85 ^{13}C NMR spectrum of **4c** in $CDCl_3$ solvent.

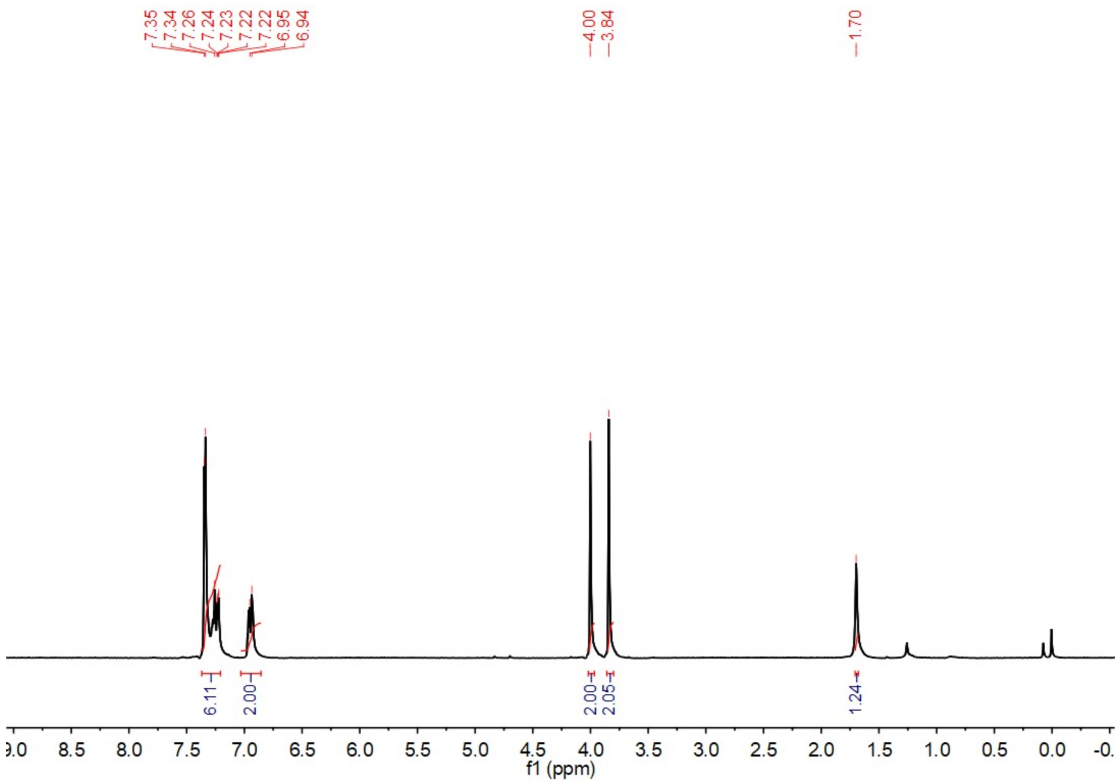


Figure S86 ^{1}H NMR spectrum of **4d** in $CDCl_3$ solvent.

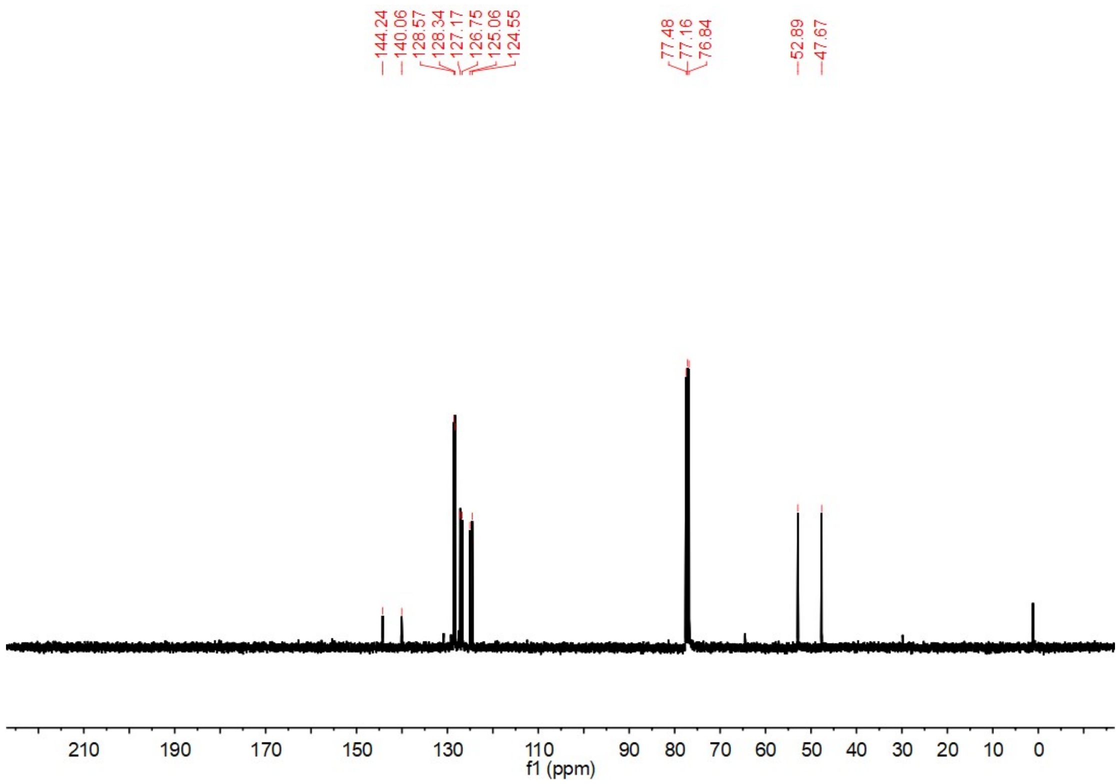


Figure S87 ^{13}C NMR spectrum of **4d** in $CDCl_3$ solvent.

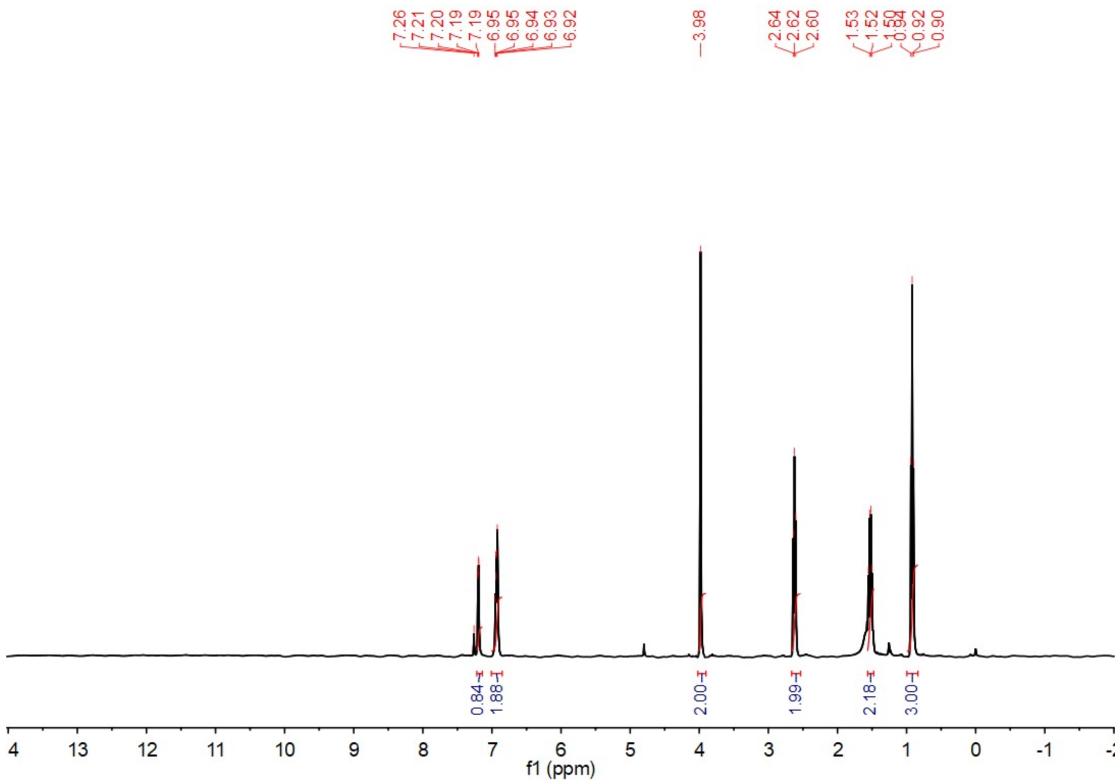


Figure S88 ^{1}H NMR spectrum of **4e** in $CDCl_3$ solvent.

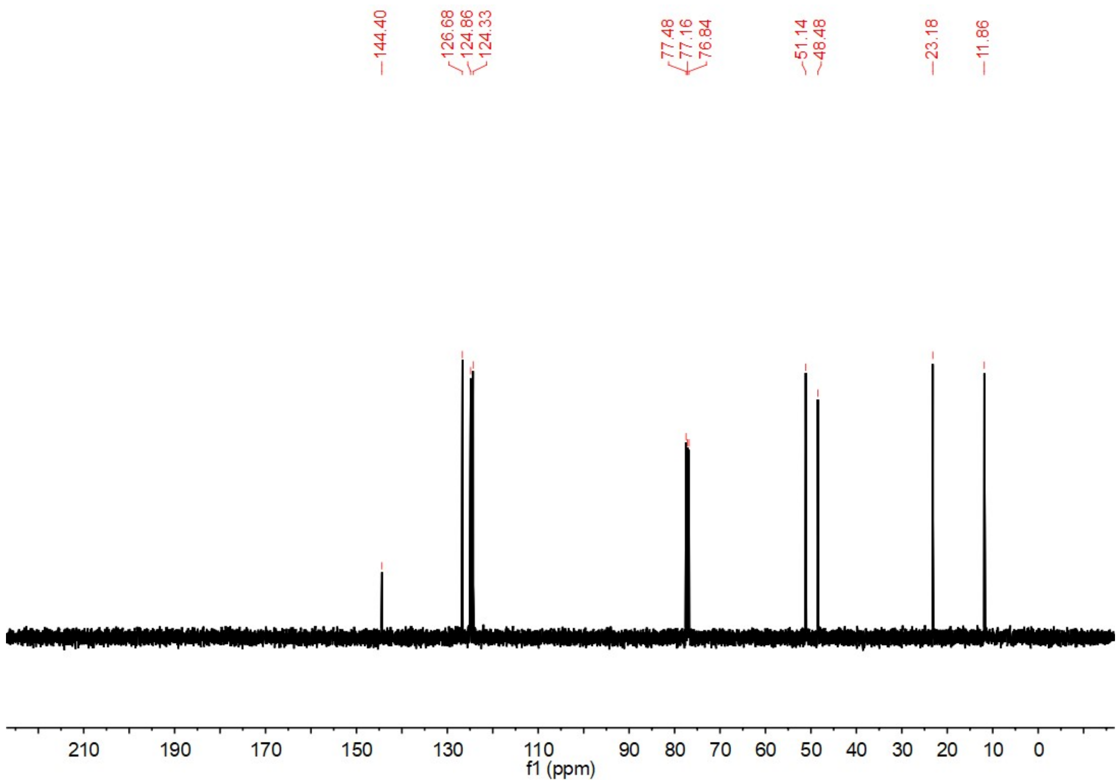


Figure S89 ^{13}C NMR spectrum of **4e** in $CDCl_3$ solvent.

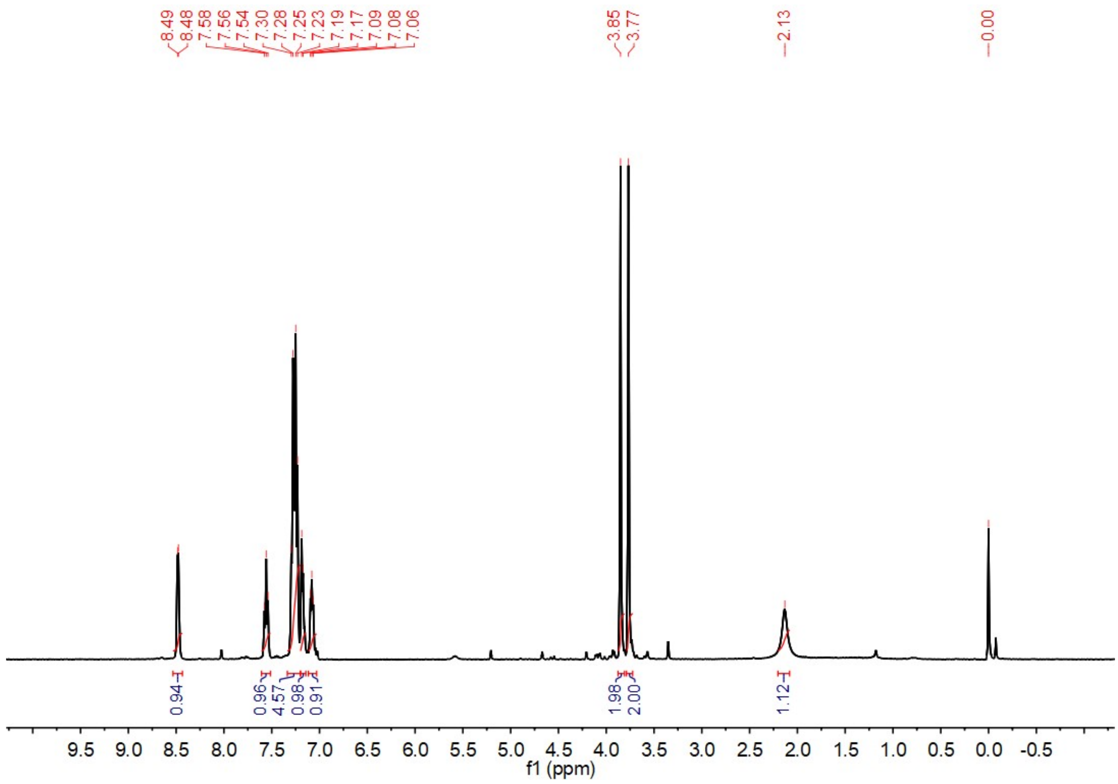


Figure S90 ^{1}H NMR spectrum of **4f** in $CDCl_3$ solvent.

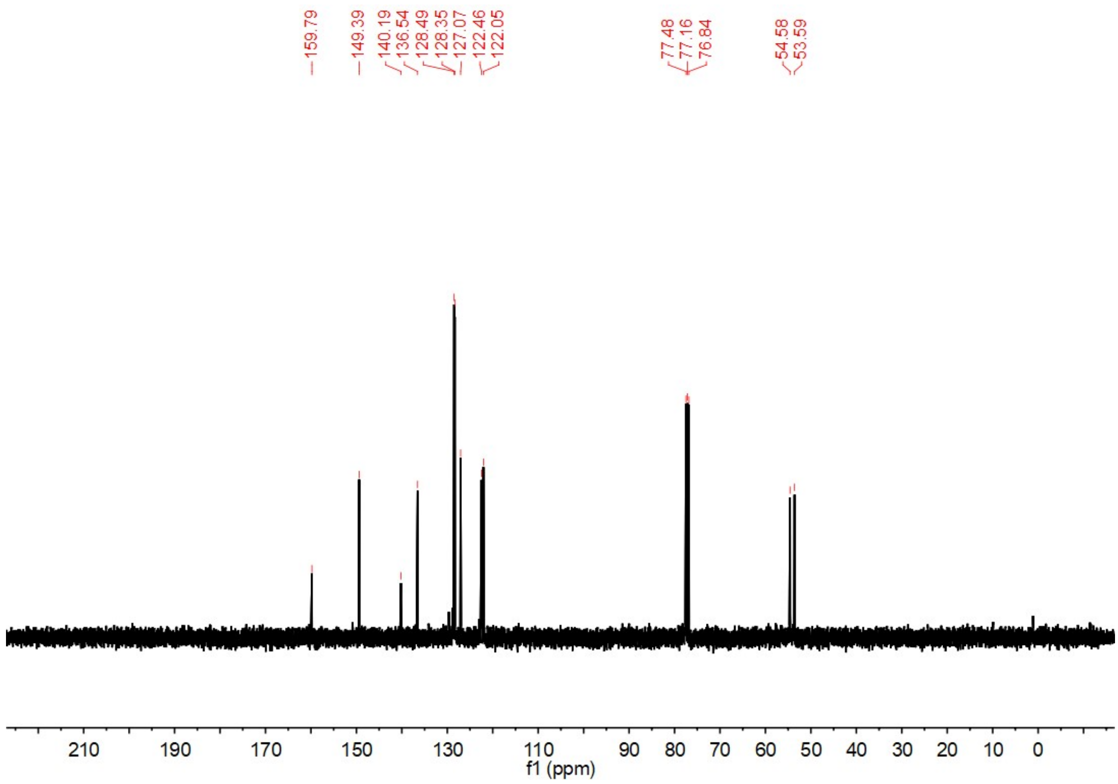


Figure S91 ^{13}C NMR spectrum of **4f** in $CDCl_3$ solvent.

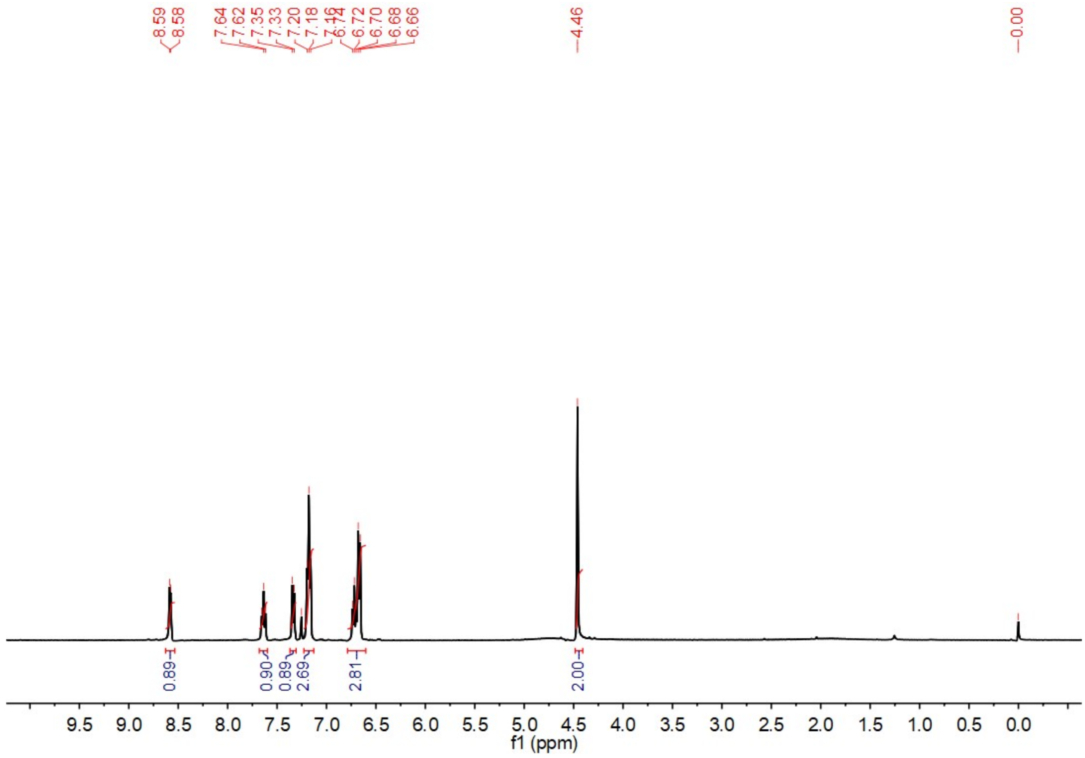


Figure S92 ^{1}H NMR spectrum of **4g** in $CDCl_3$ solvent.

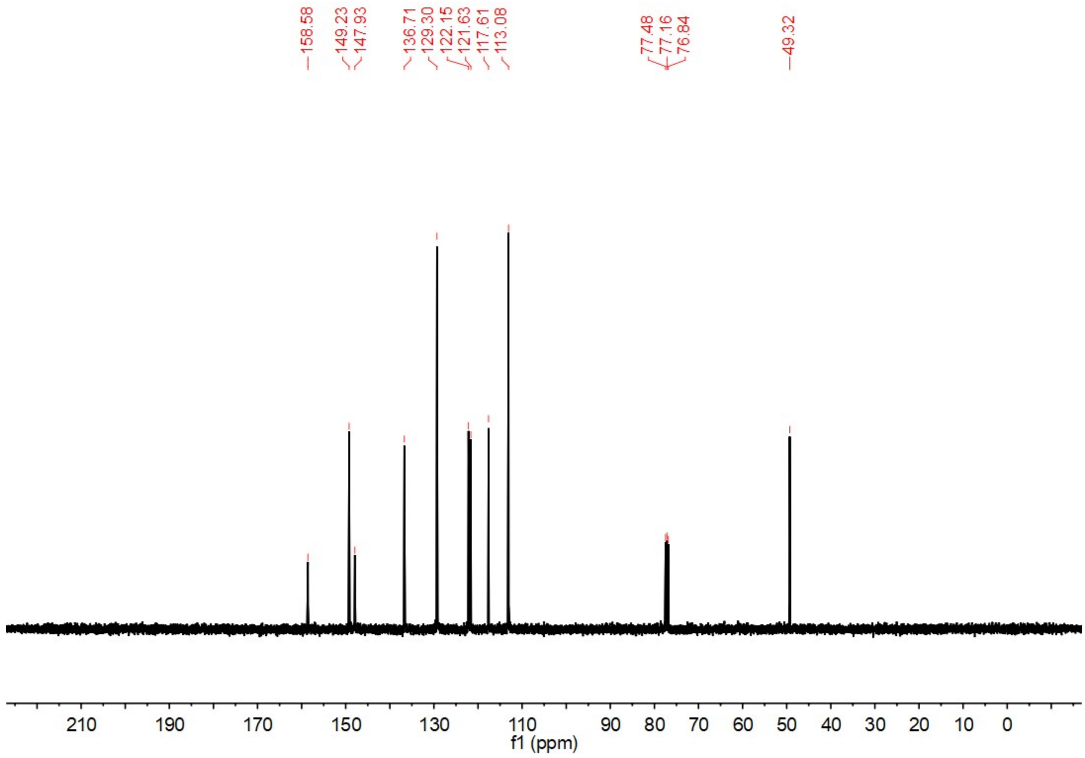


Figure S93 ^{13}C NMR spectrum of **4g** in $CDCl_3$ solvent.

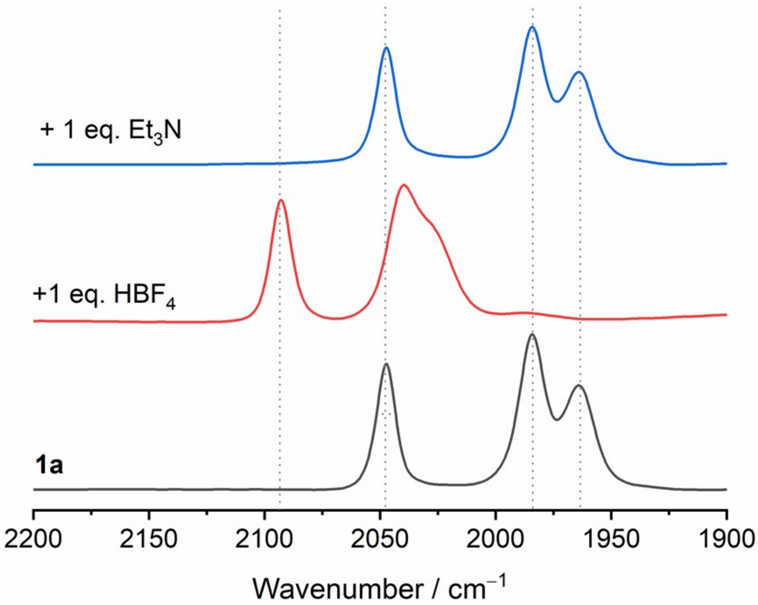


Figure S94 Protonation of complex **1a** in acetonitrile (5 mM, bottom) with 1 eq. of HBF_4•Et_2O (middle) and its full restoration after being neutralized with 1 eq. of Et_3N (top).

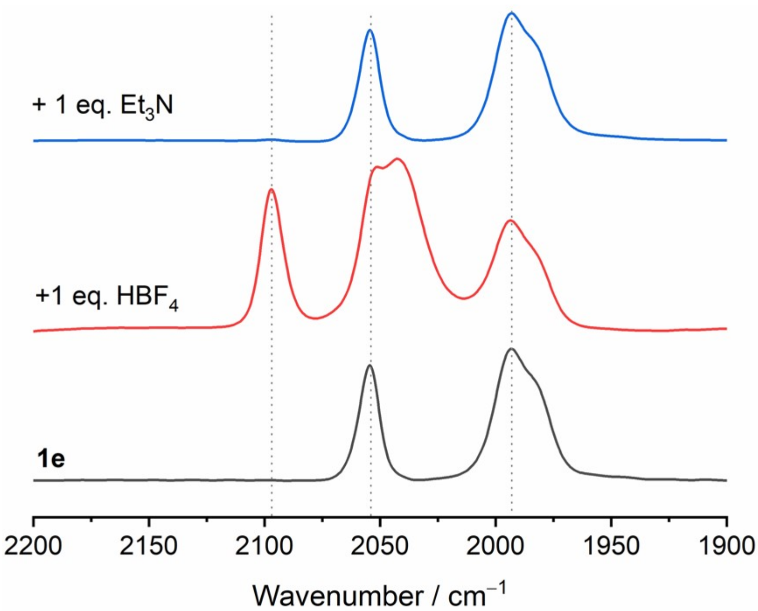


Figure S95 Protonation of complex **1e** in acetonitrile (5 mM, bottom) with 1 eq. of HBF_4•Et_2O (middle) and its full restoration after being neutralized with 1 eq. of Et_3N (top). Please note the complex was not fully protonated with one equivalent of the acid due to the low basicity of the aryl N-atom (please refer to Figure S94 for fully protonated form of **1a**).

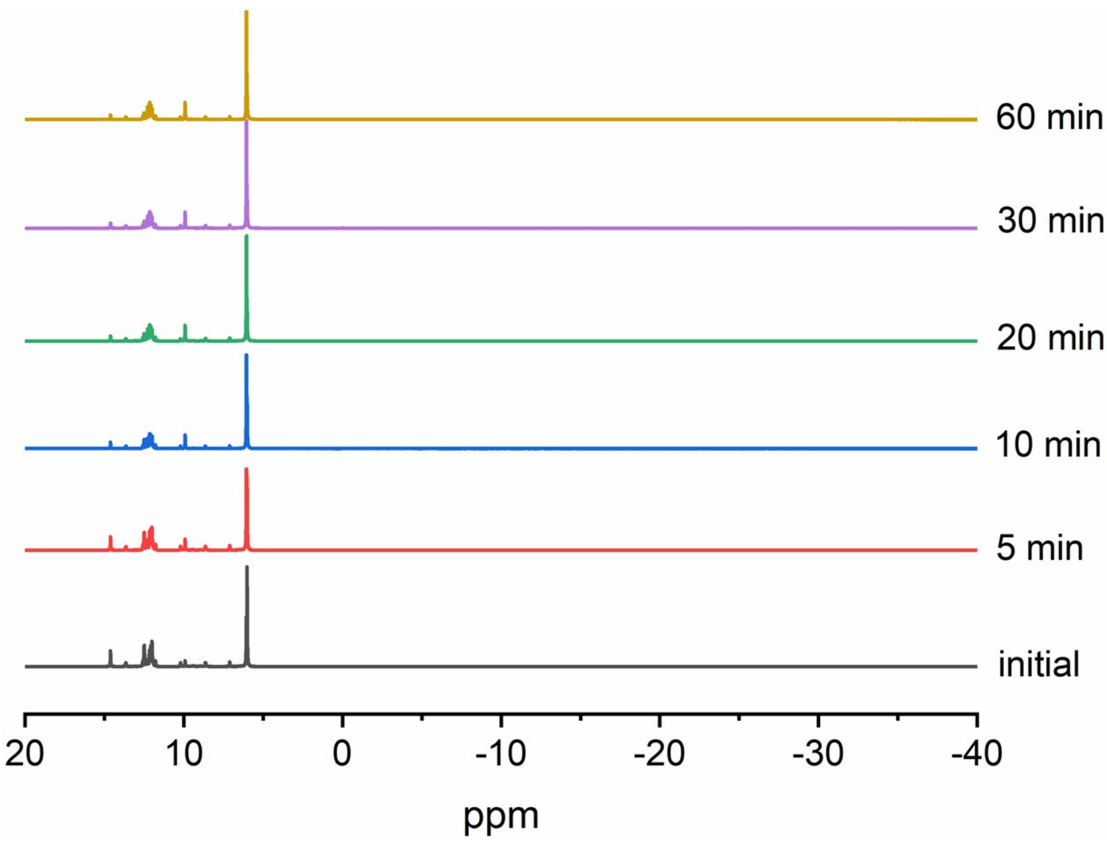


Figure S96 ^{1}H NMR spectral monitoring the hydroboration of benzaldehyde mediated by **1e** with HBpin in deuterated toluene at a low temperature under argon atmosphere. The lack of observation of any resonance in the upfield region of ^{1}H NMR spectrum (0 to –40 ppm), where iron-hydride species are typically detected, supports a non-hydride pathway.

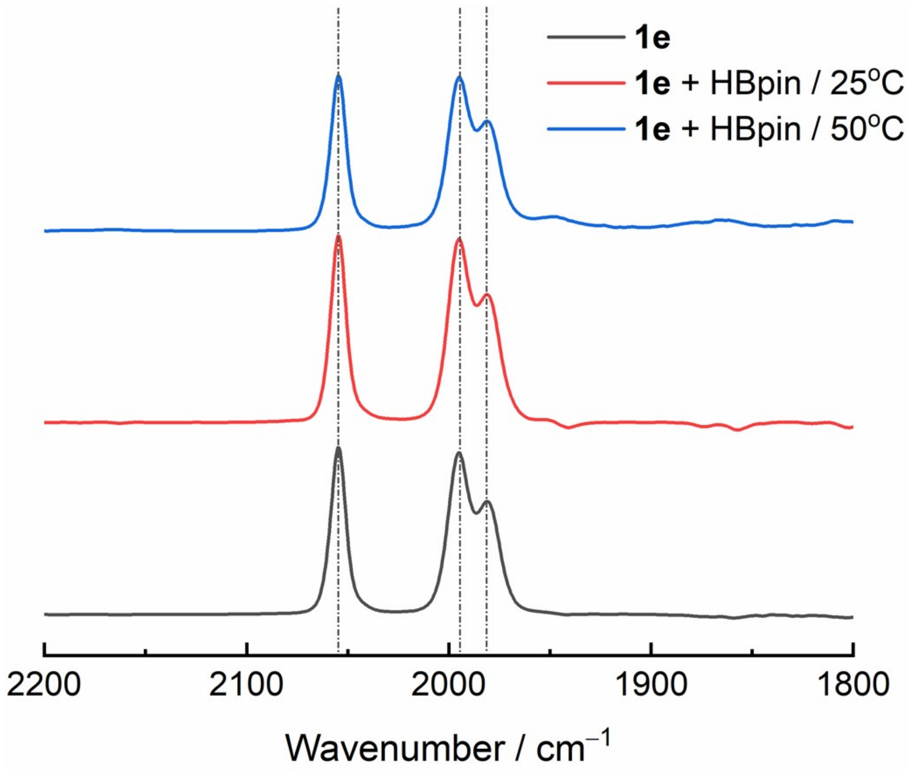


Figure S97 FTIR spectroscopic monitoring the stoichiometric reaction of complex **1e** (5 mM) with HBpin (1 eq.) in toluene at 50^{o}C or room temperature under argon atmosphere for 0.5 h.

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