Supporting Information for:

Synthesis of directly fused porphyrin dimers through $Fe(OTf)_3$-mediated oxidative coupling

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1. Instrumentations and Materials

All NMR solvents were used as received. Chemical shifts of NMR spectra were reported in ppm down field from internal Me_4Si. UV-Vis-NIR spectra were recorded on spectrophotometer (Shimadzu, Japan). High-resolution mass spectra (HRMS) were recorded on a VG ZAB-HS mass spectrometer under electron spray ionization (ESI) and a Bruker ultra fleXtreme MALDI-TOF/TOF spectrometer. EPR spectra were collected with a Bruker A300 spectrometer equipped with a liquid helium cryostat. The electrochemical experiments were carried out by cyclic voltammetry (CV) using a BAS-100B electrochemical apparatus in deaerated CH_2Cl_2 under argon atmosphere at 298 K. And *n*-Bu_4NPF_6 (0.1 M) in CH_2Cl_2 was employed as the supporting electrolyte. A standard three-electrode cell consists of a glassy carbon disk as work electrode, a platinum wire as a counter electrode, and 0.1 M $AgNO_3$/Ag (in 0.1 M n-Bu_4NPF_6 in acetonitrile) as reference electrode. The ferrocenium/ferrocene redox couple (Fc^+/Fc) was taken as the internal standard. All of the solvents were purified and distilled according to the standard procedure. The commercially obtained materials were used directly without further purification unless otherwise noted. $Fe(OTf)_3$ (98%) was purchased from Aldrich.

2. The Procedure for the Synthesis of Singly Linked Dimers 4d, 4e, 4g, and 5.

General method for the *meso-meso* linked dimers **4**

Under the nitrogen atmosphere, to a stirred solution of porphyrin monomer (0.06 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise a solution of PIFA (13 mg, 0.03 mmol, 0.5 equiv) in dry CH_2Cl_2 (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 50 min at the same temperature. Et_3N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with $CHCl_3$, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). Compound **4** was obtained after recrystallization from $CHCl_3/CH_3OH$.

4d: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 8.83 – 8.79 (m, 8 H), 8.60 (d, J = 5.0 Hz, 4H), 8.12 – 8.08 (m, 8H), 7.88 (d, J = 1.6 Hz, 8H), 7.73 – 7.68 (m, 6H), 7.65 (s, 4H), 1.40 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 148.87, 146.71, 143.44, 142.55, 142.51, 141.17, 139.88, 133.88, 133.67, 132.54, 132.34, 132.04, 128.78, 127.72, 126.86, 121.10, 121.07, 119.45, 115.66, 34.94, 31.61.
HRMS (MALDI) m/z $[M]^+$ calcd. for $C_{108}H_{110}N_8Ni_2$: 1636.7519, found 1636.7565; Ultraviolet-visible absorption : (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 419 (1.89×10^5), 449 (2.16×10^5), 539 (5.22×10^4).

4e: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 9.58 (d, J = 5.0 Hz, 4 H), 8.85 (d, J = 5.0 Hz, 4 H), 8.53(d, J = 5.0 Hz, 4 H), 8.02 (d, J = 5.0 Hz, 4 H), 7.83 (d, J = 1.6 Hz, 8 H), 7.66 (s, 4 H), 1.41 (s, 72 H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 149.00, 146.84, 143.95, 142.72, 142.26, 139.41, 134.08, 133.54, 133.10, 133.00, 128.71, 121.62, 121.30, 115.83, 102.97, 34.94, 31.60.
HRMS (MALDI) m/z $[M]^+$ calcd. for $C_{96}H_{100}Br_2N_8Ni_2$: 1643.5158, found 1643.5175; Ultraviolet-visible absorption : (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 421 (1.64×10^5), 449 (1.84×10^5), 539 (4.20×10^4).

4g: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 8.90 – 8.86 (m, 8 H), 8.61 (d, J = 5.0 Hz, 4H), 8.25 (d, J = 5.5 Hz, 4H), 8.10 – 8.00 (m, 12H), 7.82 – 7.76 (m, 6H), 7.69 (s, 4H), 1.43 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 148.71, 145.80, 142.30, 142.00, 141.42, 141.41, 140.66, 134.06, 132.57, 131.49, 131.21, 130.92, 129.30, 127.78, 126.74, 123.92, 122.23, 121.05, 118.94, 34.99, 31.66.
HRMS (MALDI) m/z $[M]^+$ calcd. for $C_{108}H_{110}N_8Pd_2$: 1732.6929, found 1732.6968; Ultraviolet-visible absorption : (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 423 (3.22×10^5), 447 (4.81×10^5), 539 (1.31×10^5).

For the *meso-β* singly linked **5**

Under the nitrogen atmosphere, to a stirred solution of **1e** (49 mg, 0.06 mmol) and $BF_3{\cdot}Et_2O$ (4 mg, 0.03 mmol, 0.5 equiv) in dry CH_2Cl_2 (50 mL) was added dropwise a solution of PIFA (13 mg, 0.03 mmol, 0.5 equiv) in dry CH_2Cl_2 (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 10 min at the same temperature. Et_3N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with $CHCl_3$, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). **5** (39 mg, 80%) was obtained after recrystallization from $CHCl_3/CH_3OH$.

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 9.66 (d, J = 5.0 Hz, 1H), 9.63 (s, 1H), 9.60 – 956 (m, 3H), 9.07 – 9.04 (m, 2H), 8.91 – 8.86 (m, 3H), 8.76 (d, J = 5.0 Hz, 2H), 8.66 (bs, 3H), 8.46 (d, J = 4.8 Hz, 1H), 8.10 (d, J = 1.7 Hz, 2H), 7.80 (d, J = 1.7 Hz, 2H), 7.71 – 7.68 (m, 4H), 1.48 – 1.40 (m, 72H). ^{1}H NMR (400 MHz, $CDCl_3$, -40°C): δ = 9.66 (s, 1H), 9.68 (d, J = 5.0 Hz, 1H), 9.62 – 9.58 (m, 3H), 9.14 (d, J = 5.0 Hz, 1H), 9.01 (s, 1H), 8.96 (d, J = 5.0 Hz, 2H), 8.92 (d, J = 5.0 Hz, 1H), 8.80 (d, J = 5.0 = Hz, 2H), 8.73– 8.67 (m, 3H), 8.47 (d, J = 4.8 Hz, 1H), 8.17 – 8.12 (m, 4H), 7.80 (d, J = 1.8 Hz, 2H), 7.71 (bs, 1H), 7.69 (s, 3H), 7.59 (s, 2H), 1.51 – 1.46 (m, 32H), 1.44 (s, 18H), 1.40 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 149.24, 149.09, 149.04, 145.90, 144.42, 143.90, 143.85, 143.78, 143.62, 143.56, 143.34, 143.05, 142.43, 142.38, 142.24, 141.38, 139.55, 139.35, 137.88, 133.72, 133.68, 133.64, 133.20, 133.16, 133.12, 133.07, 132.52, 129.27, 128.90,

128.74, 121.46, 121.32, 121.21, 121.12, 120.54, 112.16, 106.74, 102.76, 102.66, 35.00, 34.96, 31.67, 31.62.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{96}H_{100}Br_2N_8Ni_2$: 1642.5080, found 1642.5073; Ultraviolet-visible absorption : (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 417 (2.14×10^5), 431 (1.80×10^5), 534 (3.57×10^4).

3. The General Procedure for the Synthesis of Fused Dimers 2 and 3.

Under the nitrogen atmosphere, to a stirred solution of **1** (0.03 mmol) in dry 25 mL CH_2Cl_2/CH_3NO_2 (4:1) was added 75 mg $Fe(OTf)_3$ (0.15 mmol, 5 equiv) at RT. The reaction mixture was stirred for additional 2 h. Saturated aqueous sodium bicarbonate (10 mL) was added, and the mixture was extracted with $CHCl_3$. The combined organic layer was washed with saturated sodium bicarbonate aqueous solution and dried over anhydrous Na_2SO_4, then evaporated to dryness. The crude residue was purified by silica-gel column chromatography. Compounds **2** and **3** were obtained after recrystallization from $CHCl_3/CH_3OH$.
2a: HRMS (ESI) m/z $[M]^+$ calcd. for $C_{108}H_{106}N_8Cu_2$: 1642.7117, found 1642.7131; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 410 (5.11×10^5), 558 (3.83×10^4), 574 (4.04×10^4), 780 (0.58×10^4), 995 (1.00×10^4).

2b: HRMS (MALDI) m/z $[M]^+$ calcd. for $C_{96}H_{96}Br_2N_8Cu_2$: 1650.4835, found 1650.4868; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 416 (1.06×10^5), 563 (9.34×10^4), 885 (1.74×10^4), 997 (2.79×10^4).

2d: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 7.75 – 7.70 (m, 12H), 7.61 (s, 4H), 7.59 (s, 8H), 7.56 – 7.52 (m, 10H), 1.43 (s, 72H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 149.16, 146.97, 146.49, 145.86, 145.38, 140.14, 138.77, 134.74, 132.44, 131.03, 130.76, 127.77, 127.74, 127.20, 127.07, 124.55, 123.76, 121.19, 113.26, 34.93, 31.63.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{108}H_{106}N_8Ni_2$: 1632.7206, found 1632.7218; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 406 (7.81×10^4), 573 (8.70×10^4), 647 (1.09×10^4), 873 (1.34×10^4), 932 (1.37×10^4).

2e: ^{1}H NMR (400 MHz, V($CDCl_3$)/V(CS_2) = 4:1, RT): δ = 8.52 (d, J = 4.9 Hz, 4H), 7.77 (d, J = 4.9 Hz, 4H), 7.60 (s, 4H), 7.54 (s, 8H), 7.47 (s, 4H), 1.43 (s, 72H). ^{13}C NMR (100 MHz, V($CDCl_3$)/V(CS_2) = 4:1, RT): δ = 149.15, 147.45, 146.53, 145.52, 145.47, 138.37, 134.76, 132.04, 131.70, 127.65, 127.49, 125.01, 121.40, 113.31, 107.89, 34.81, 31.59.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{96}H_{96}Br_2N_8Ni_2$: 1638.4767, found 1638.4787; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 411 (1.58×10^5), 572 (1.23×10^5), 651 (1.37×10^4), 864 (1.72×10^4), 937 (2.10×10^4).

2f: ^{1}H NMR (400 MHz, V($CDCl_3$)/V(CS_2) = 4:1, RT): δ = 7.83 – 7.79 (m, 4H), 7.79 – 7.76 (m, 4H), 7.74 – 7.72 (m, 4H), 7.71 – 7.69 (m, 8H), 7.65 – 7.61 (m, 8H), 7.59 – 7.55 (m, 6H), 1.46 (s, 72H). ^{13}C NMR (100 MHz, V($CDCl_3$)/V(CS_2) = 4:1, RT): δ = 148.91, 144.77, 144.51, 143.86, 143.45, 140.49, 139.30, 134.01, 132.70, 130.21, 130.13, 128.19, 127.71, 127.11, 126.36, 125.55, 121.15, 116.02, 110.88, 34.82, 31.63.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{108}H_{106}N_8Pd_2$: 1728.6616, found 1728.6632; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 407 (6.51×10^4), 567 (8.70×10^4), 604 (3.06×10^4), 638 (9.20×10^3), 931(6.62×10^3).

3a: HRMS (ESI) m/z $[M]^+$ calcd. for $C_{108}H_{108}N_8Cu_2$: 1644.7273, found 1644.7291; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 418 (5.72×10^4), 543 (8.12×10^4), 717 (1.68×10^4), 777 (5.56×10^4).

3b: HRMS (MALDI) m/z $[M]^+$ calcd. for $C_{96}H_{98}Br_2N_8Cu_2$: 1648.4678, found 1648.4708; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 419 (7.62×10^4), 541 (5.43×10^4), 779 (3.48×10^4).

3c: HRMS (MALDI) m/z $[M]^+$ calcd. for $C_{96}H_{98}N_{10}Cu_2O_4$: 1582.6348, found 1582.6375; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 420 (5.54×10^4), 538 (3.92×10^4), 780 (2.53×10^4).

3d: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 9.50 (d, J = 5.0 Hz, 2H), 9.06 (s, 2 H), 8.80 (d, J = 4.9 Hz, 2 H), 8.41 – 8.39 (m, 4 H), 8.36 – 8.33 (m, 4H), 7.96 – 7.94 (m, 8H), 7.84 (d, J = 1.8 Hz, 4 H), 7.76 (bs, 2 H), 7.72 (bs, 2 H), 7.76 – 7.62 (m, 6 H), 1.54 (s, 36H), 1.51 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 149.32, 149.28, 144.30, 144.15, 143.67, 143.48, 143.22, 142.87, 142.23, 141.83, 140.29, 139.95, 139.24, 139.03, 134.56, 133.67, 133.24, 132.62, 132.13, 132.03, 131.95, 131.54, 129.00, 128.65, 127.77, 127.08, 122.57, 122.09, 121.43, 121.21, 120.86, 109.82, 35.08, 35.03, 31.74, 31.68.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{108}H_{108}N_8Ni_2$: 1634.7363, found 1634.7359; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 413 (6.45×10^4), 502 (4.82×10^4), 544 (4.87×10^4), 754 (3.52×10^4)

3e: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 9.41 (s, 2H), 9.12 – 9.11 (m, 4H), 8.96 (s, 2H), 8.74 (d, J = 3.8 Hz, 2H), 8.44 (d, J = 5.0 Hz, 2H), 8.39 (d, J = 4.8 Hz, 2H), 7.91 (s, 4H), 7.84 – 7.65 (m, 8H), 1.54 (s, 36H), 1.51 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 149.44, 149.41, 144.68, 144.61, 143.45, 143.37, 143.31, 142.84, 142.39, 142.11, 140.22, 138.83, 138.61, 134.96, 134.00, 133.70, 133.21, 132.91, 132.41, 132.27, 128.90, 128.55, 123.15, 122.55, 121.66, 121.43, 110.10, 104.24, 35.09, 35.04, 31.73, 31.68.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{96}H_{98}Br_2N_8Ni_2$: 1640.4924, found 1640.4943; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 419 (8.56×10^4), 498 (5.85×10^4), 533 (5.62×10^4), 684 (1.16×10^4), 756 (4.66×10^4).

3f: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 9.38 (d, J = 4.9 Hz, 2H), 8.94 (s, 2H), 8.88 (bs, 4H), 8.73 (d, J = 4.9 Hz, 2H), 8.50 (d, J = 5.1 Hz, 2H), 8.45 (d, J = 5.1 Hz, 2H), 7.88 (d, J = 1.4 Hz, 4H), 7.77 (bs, 8H), 1.54 (s, 36H), 1.52 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 149.70, 149.69, 144.56, 144.46, 144.19, 144.16, 143.15, 141.55, 139.75, 139.14, 139.10, 138.26, 137.98, 135.27, 135.06, 134.99, 134.96, 133.01, 129.61, 129.07, 128.84, 128.79, 128.40, 125.05, 124.18, 122.08, 121.85, 112.81, 35.11, 35.07, 31.71, 31.65.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{96}H_{98}N_{10}Ni_2O_4$: 1572.6438, found 1572.6453; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 442 (6.14×10^4), 533 (5.56×10^4), 765 (4.10×10^4)

3g: ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ = 9.74 (d, J = 5.0 Hz, 2H), 9.33 (s, 2H), 8.78 (d, J = 5.0 Hz, 2H), 8.57 (d, J = 4.9 Hz, 2H), 8.51 (d, J = 4.9 Hz, 2H), 8.48 – 8.35 (m, 4H), 8.15 (s, 4H), 8.11 – 8.05 (m, 4H), 8.01 (d, J = 1.4 Hz, 4H), 7.84 (s, 2H), 7.79 (s, 2H), 7.70 (d, J = 6.1 Hz, 6H), 1.60 (s, 36H), 1.56 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, RT): δ = 149.18, 149.09, 143.11, 143.00, 142.66, 142.60, 142.41, 141.37, 141.27, 141.21, 140.35, 140.30, 140.27, 140.07, 133.90, 133.61, 133.53, 133.38, 131.11, 131.09, 130.82, 130.79, 129.68, 129.52, 127.79, 126.95, 125.47, 124.98, 123.47, 121.40, 121.12, 111.80, 35.17, 35.11, 31.83, 31.74.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{108}H_{108}N_8Pd_2$: 1730.6773, found 1730.6790; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 417 (7.51×10^4), 543 (6.53×10^4), 606 (1.07×10^4), 684 (1.44×10^4), 747 (4.06×10^4).

3h: ^{1}H NMR (400 MHz, V($CDCl_3$)/V(CS_2) = 4:1, RT): δ = 9.61 (d, J = 4.9 Hz, 2 H), 9.21 (s, 2 H), 8.84 (d, J = 5.1 Hz, 4 H), 8.72 (d, J = 5.0 Hz, 2 H), 8.67 (d, J = 5.1 Hz, 2 H), 8.61 (d, J = 5.1 Hz, 2 H), 8.10 (d, J = 1.3 Hz, 4 H), 7.95 (d, J = 1.4 Hz, 4 H), 7.86 (s, 2 H), 7.82 (s, 2 H), 1.63 (s, 36 H), 1.59 (s, 36 H). ^{13}C NMR (100 MHz, V$CDCl_3$/VCS_2 = 4:1, RT): δ = 149.34, 149.24, 143.62, 143.42, 143.39, 142.87, 141.08, 141.00, 140.35, 139.32, 139.13, 137.51, 137.38, 135.26, 133.75, 133.44, 133.32, 132.59, 130.32, 129.55, 129.27, 127.52, 127.43, 127.29, 126.57, 121.89, 121.66, 114.37, 34.96, 34.89, 31.69, 31.63.
HRMS (ESI) m/z $[M]^+$ calcd. for $C_{96}H_{98}N_{10}Pd_2O_4$: 1668.5878, found 1668.5880; Ultraviolet-visible-infrared absorption: (in $CHCl_3$, λ_{max}/nm, ε/mol^{-1}dm^{3}cm^{-1}): 426 (1.16×10^5), 528 (1.07×10^5), 749 (1.37×10^4).

4. NMR Spectra

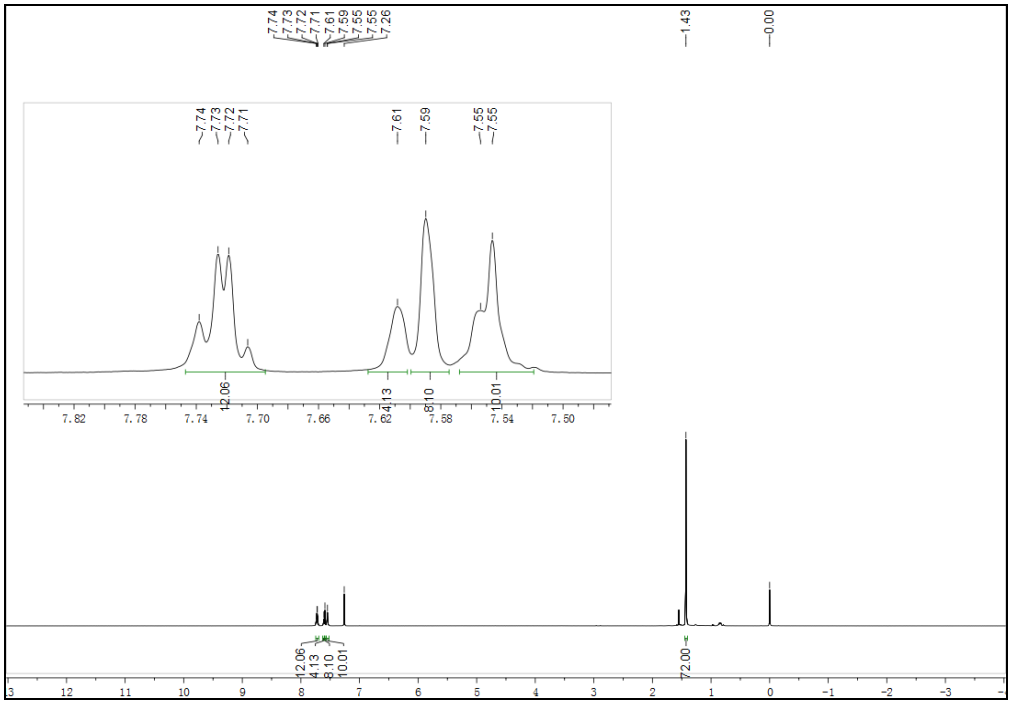

Figure S1. ^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$ at 25°C).

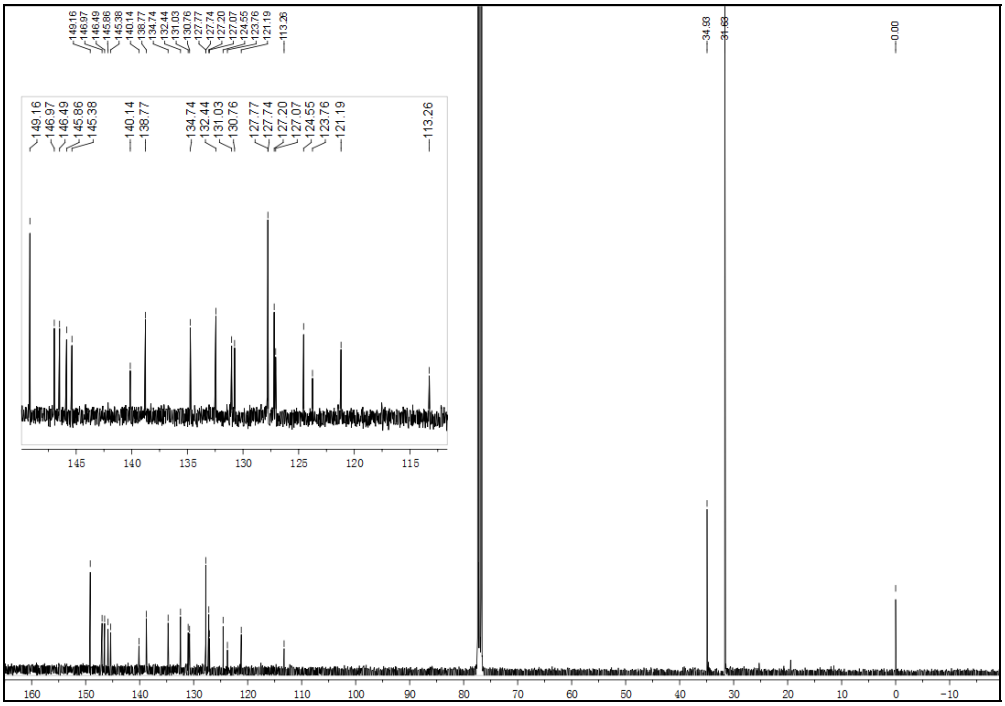

Figure S2. ^{13}C NMR spectrum of **2d** (100 MHz, $CDCl_3$ at 25°C).

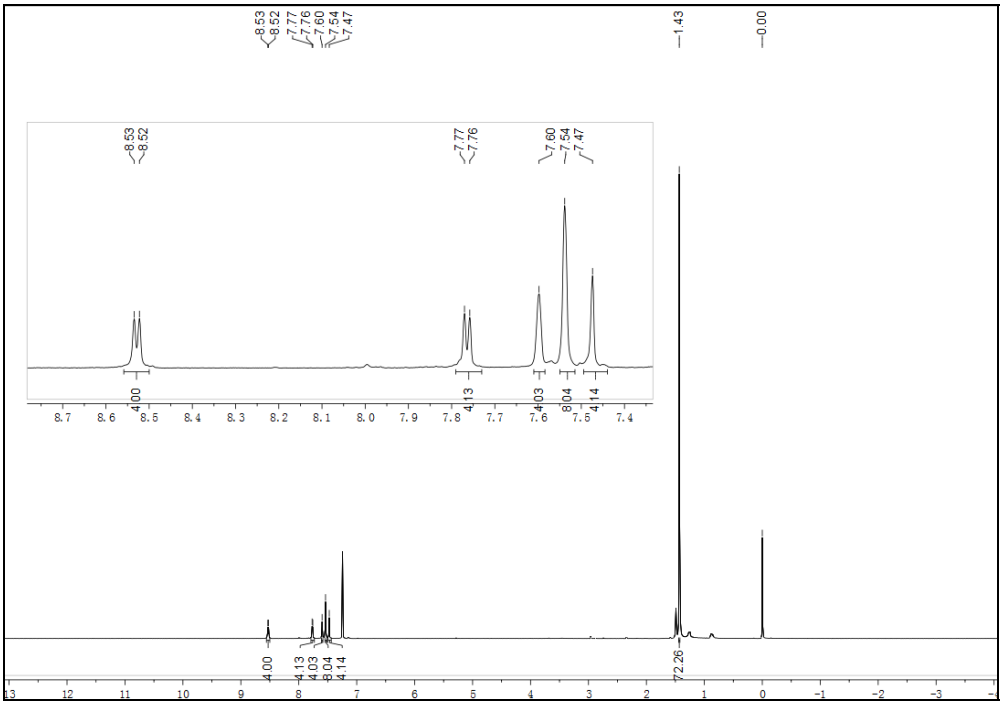

Figure S3. ^{1}H NMR spectrum of **2e** (400 MHz, V_{CDCl_3}/V_{CS_2} = 4:1 at 25°C).

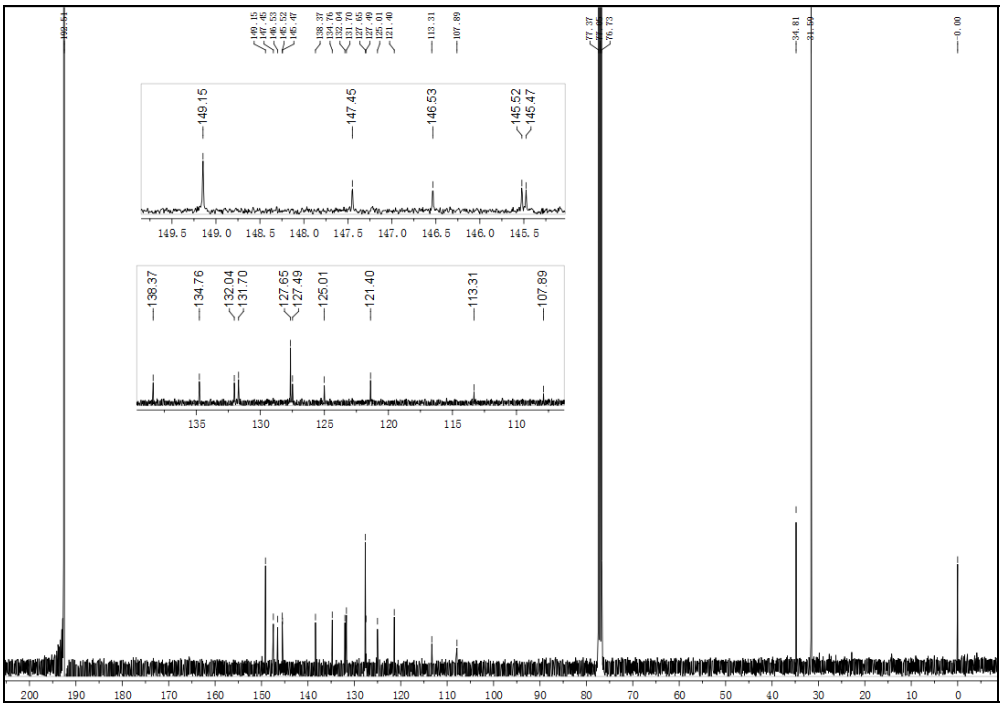

Figure S4. ^{13}C NMR spectrum of **2e** (100 MHz, V_{CDCl_3}/V_{CS_2} = 4:1 at 25°C, δ ($^{13}C_{CS_2}$) = 192.51).

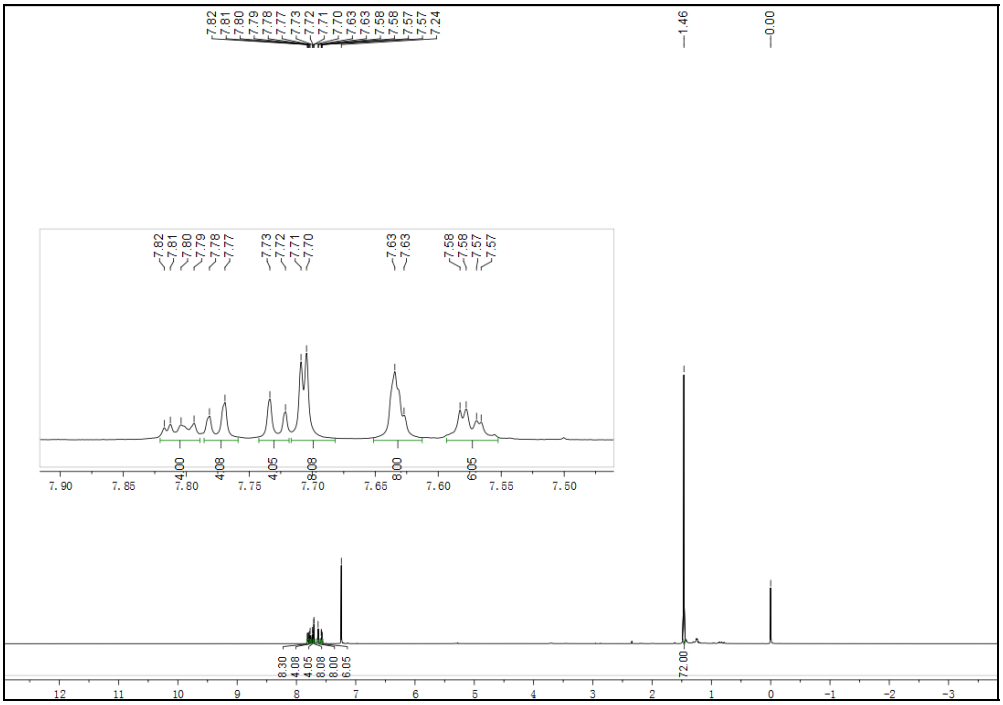

Figure S5. ^{1}H NMR spectrum of **2g** (400 MHz, V_{CDCl_3}/V_{CS_2} = 4:1 at 25°C).

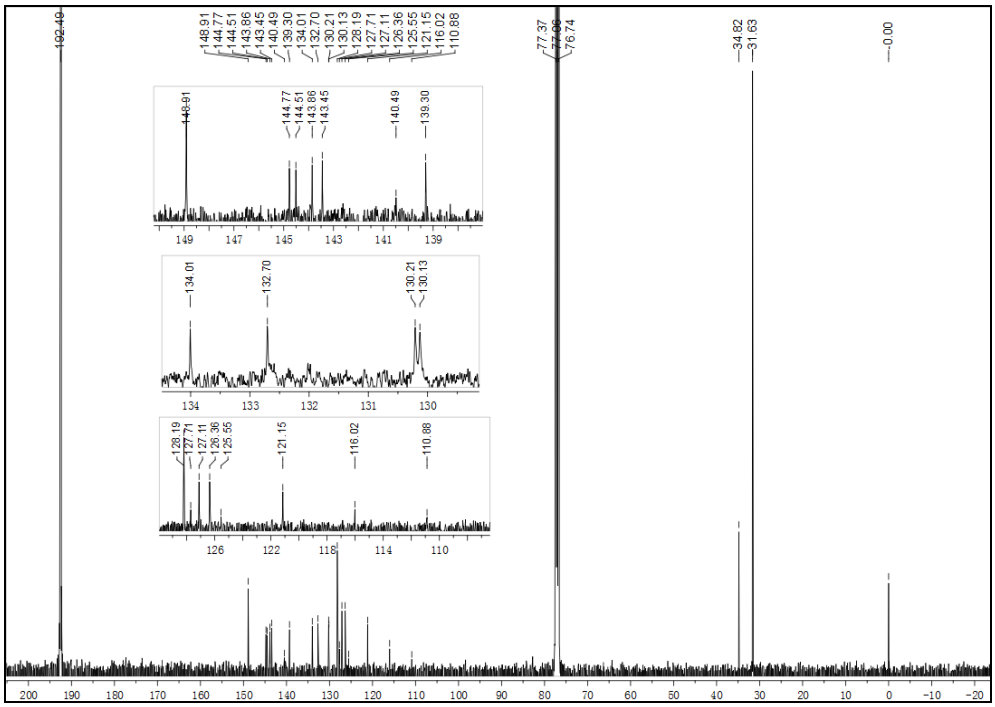

Figure S6. ^{13}C NMR spectrum of **2g** (100 MHz, V_{CDCl_3}/V_{CS_2} = 4:1 at 25°C, δ ($^{13}C_{CS_2}$) = 192.49).

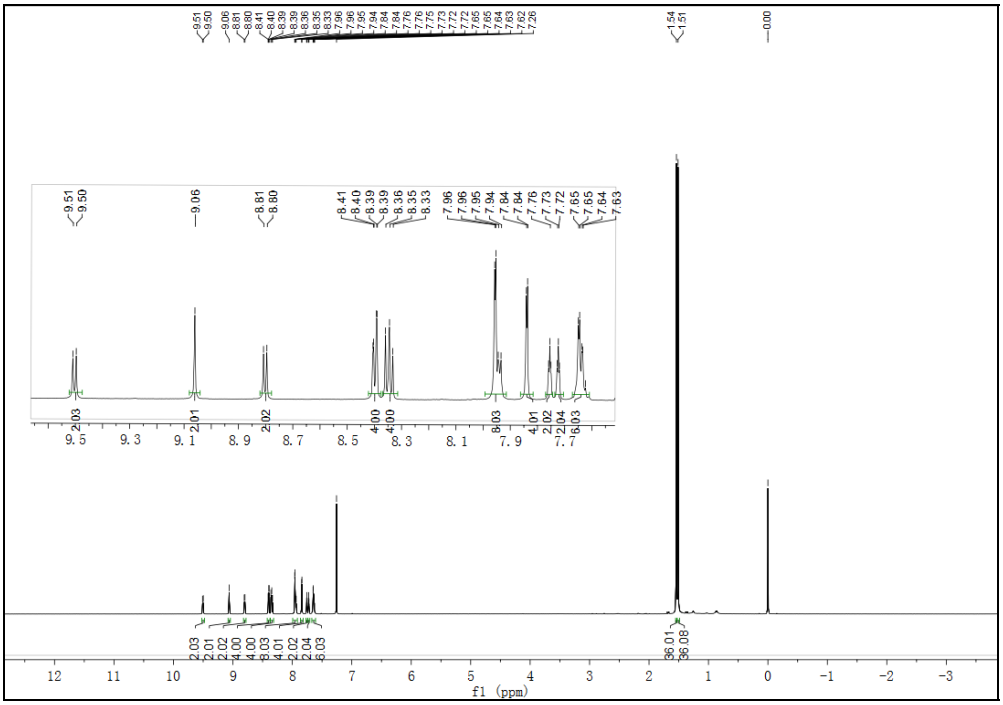

Figure S7. ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$ at 25°C).

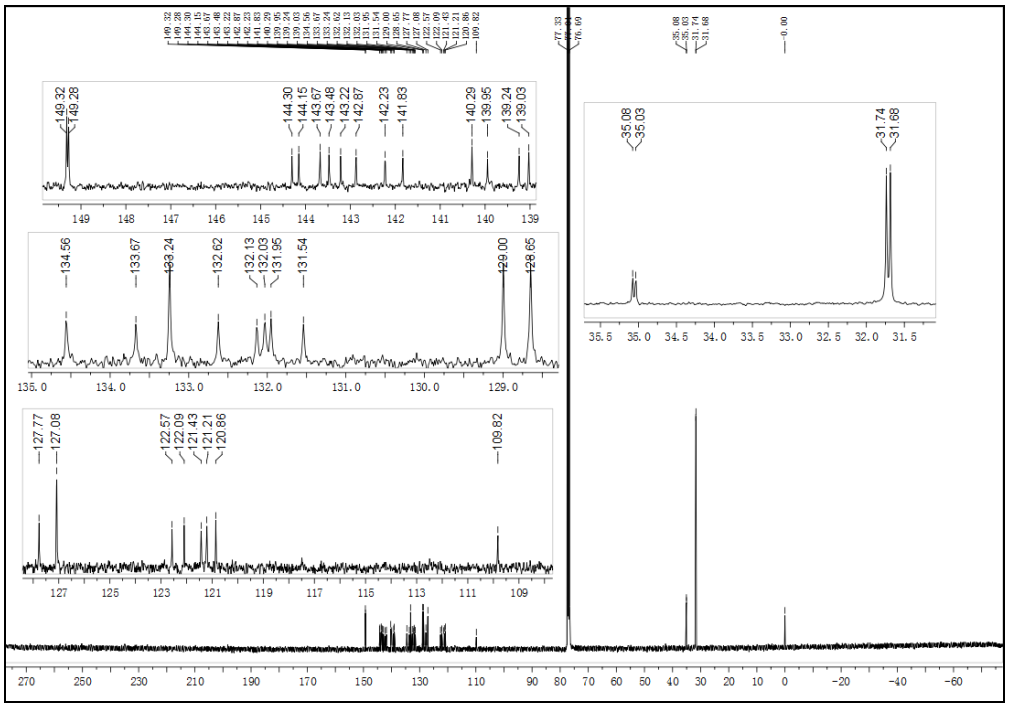

Figure S8. ^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$ at 25°C).

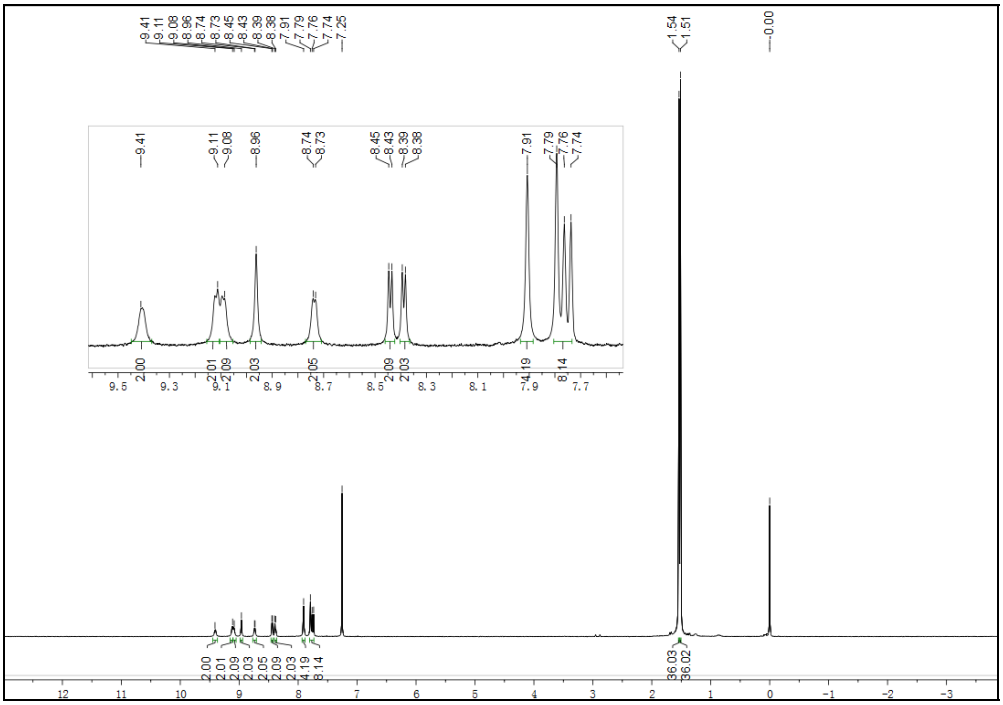

Figure S9. ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$ at 25°C).

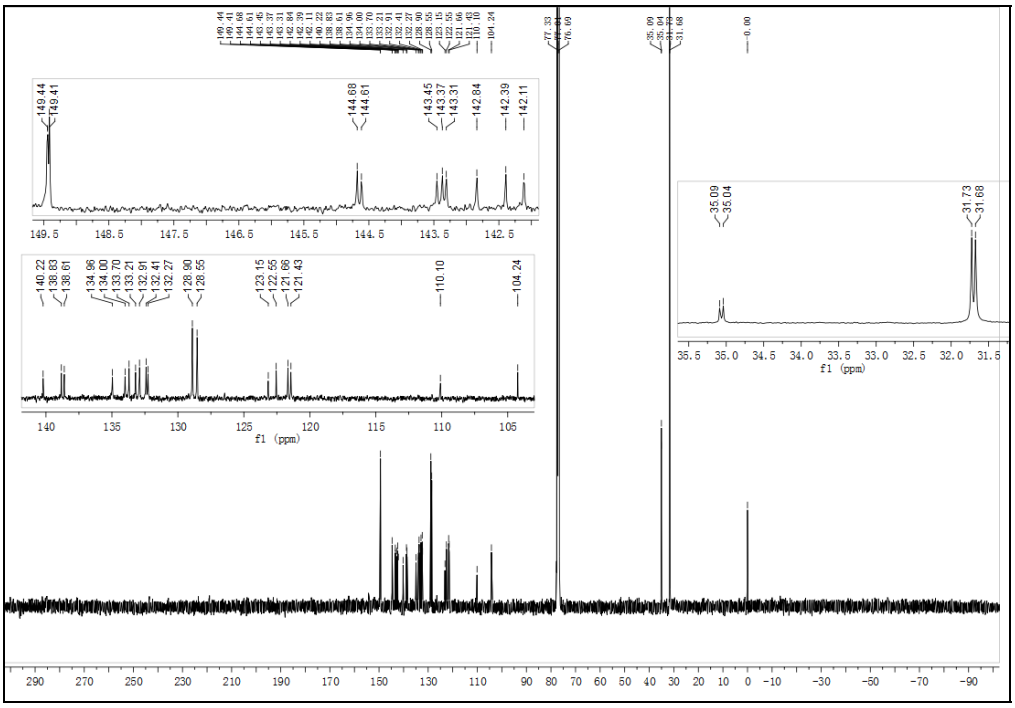

Figure S10. ^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$ at 25°C).

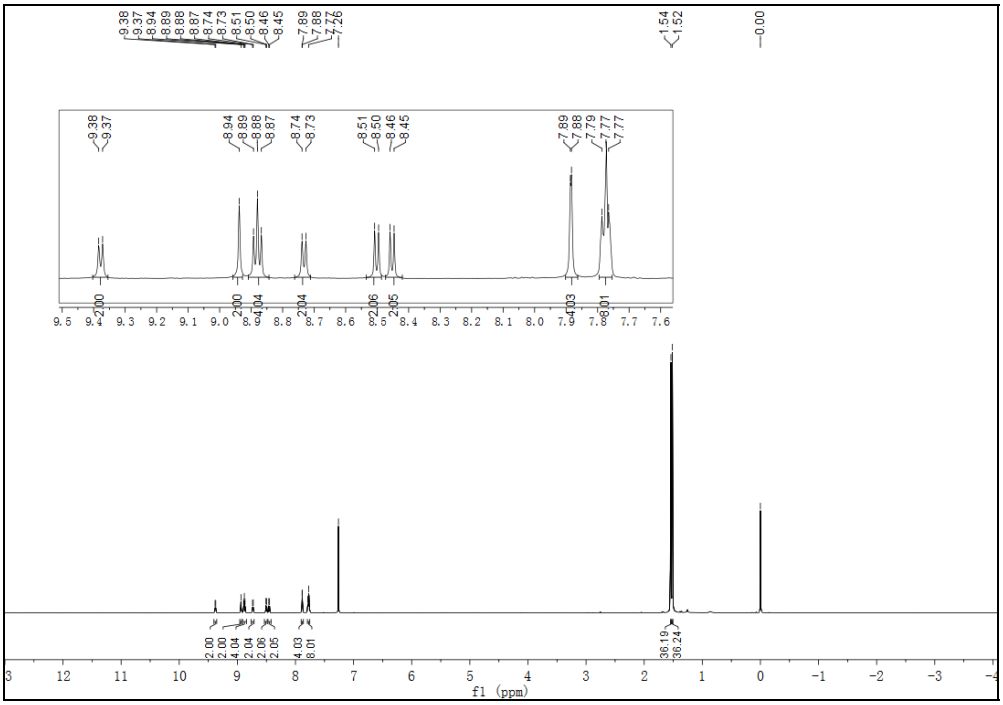

Figure S11. ^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$ at 25°C).

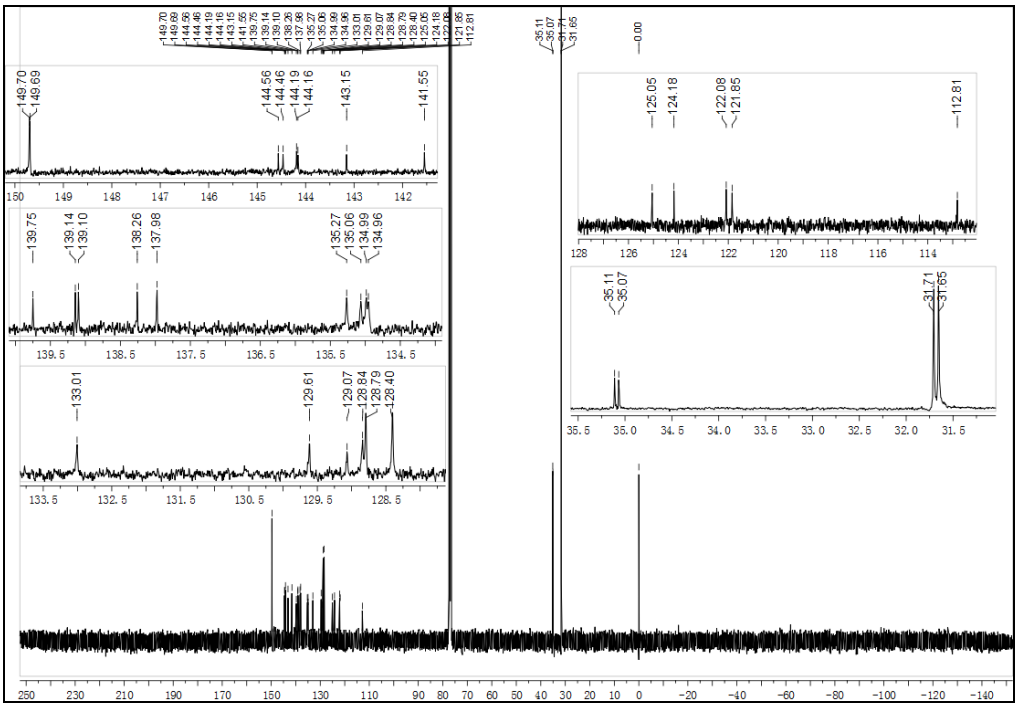

Figure S12. ^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$ at 25°C).

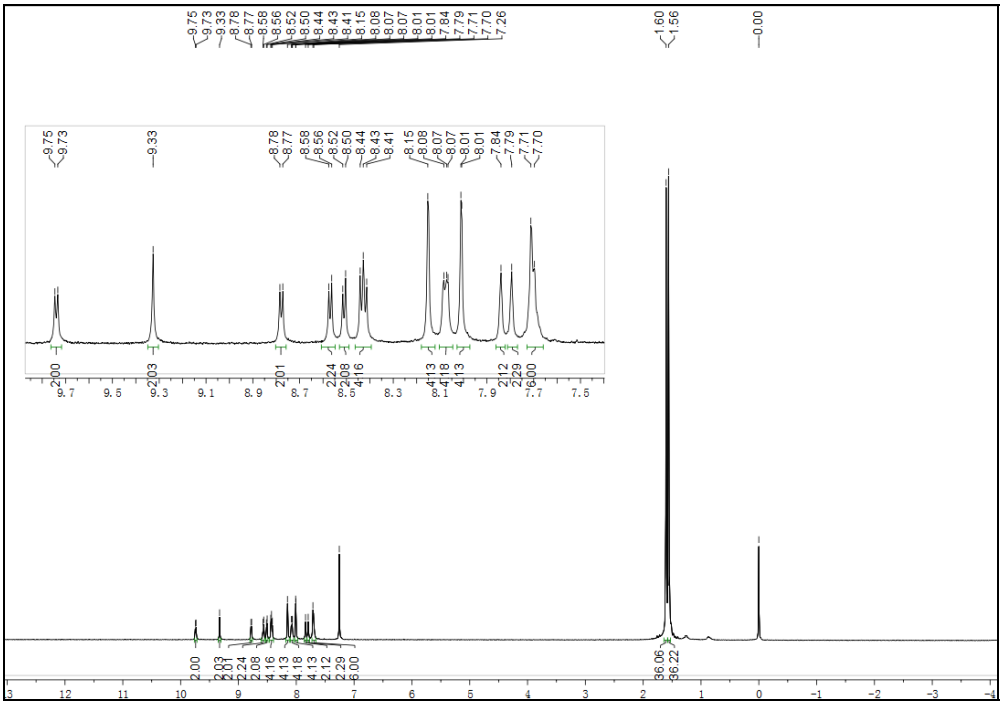

Figure S13. [1]H NMR spectrum of **3g** (400 MHz, $CDCl_3$ at 25°C).

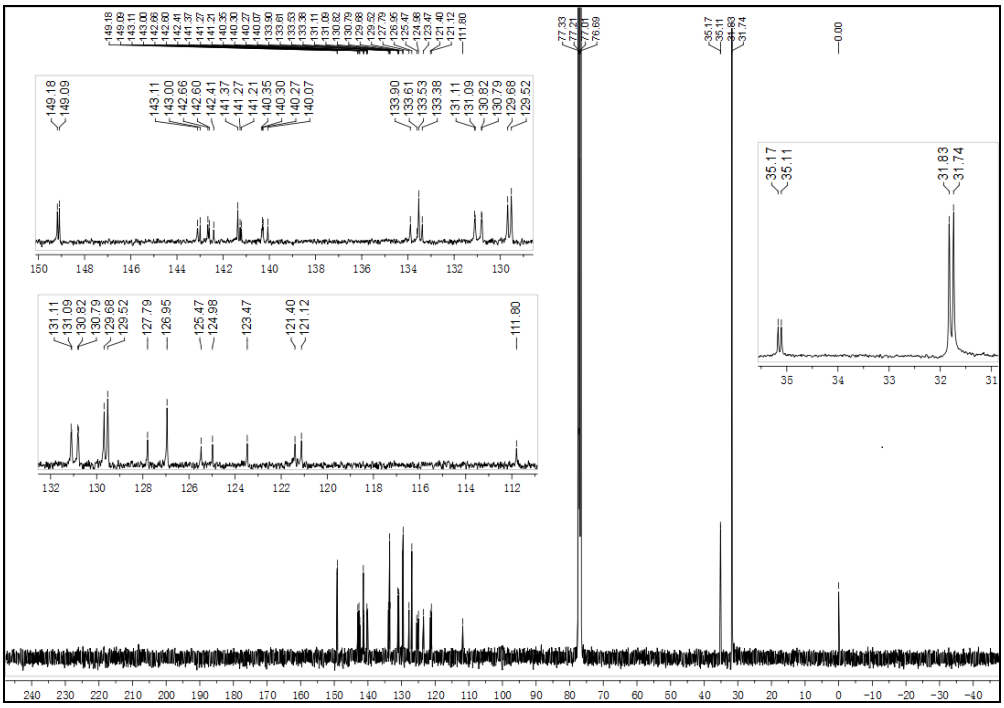

Figure S14. [13]C NMR spectrum of **3g** (100 MHz, $CDCl_3$ at 25°C).

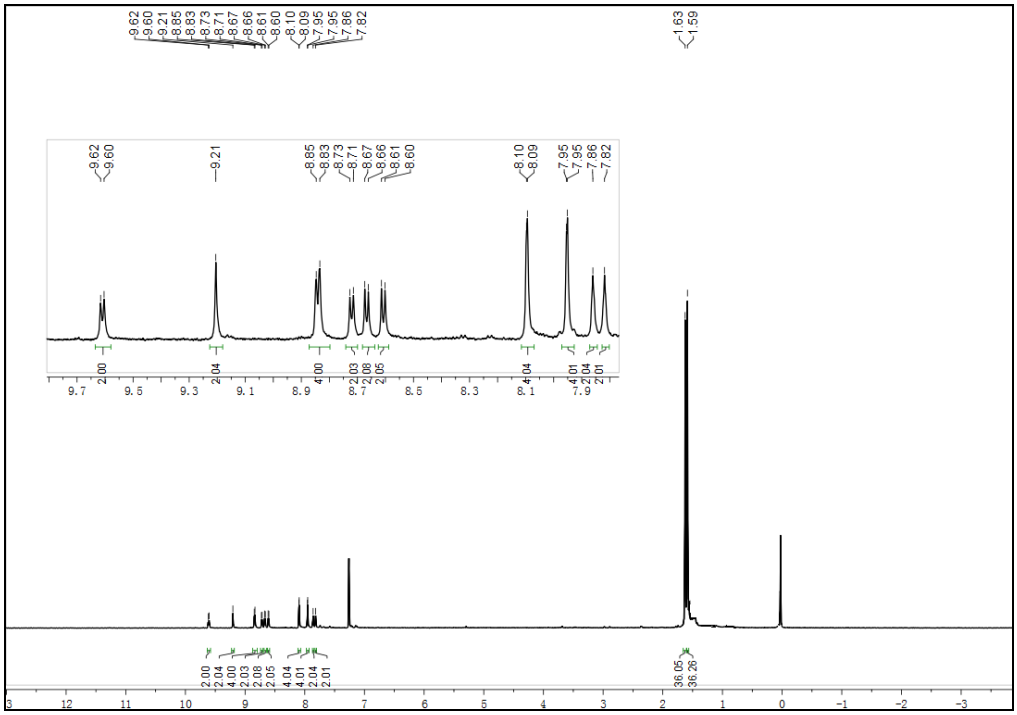

Figure S15. ^{1}H NMR spectrum of **3h** (400 MHz, V_{CDCl_3}/V_{CS_2} = 4:1 at 25°C).

.

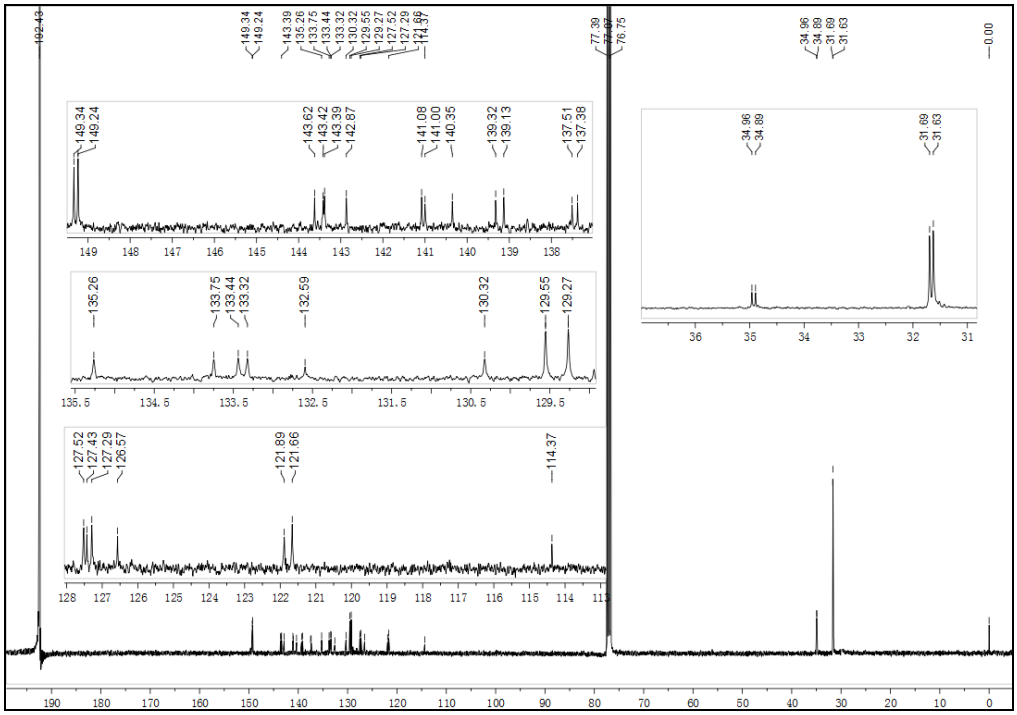

Figure S16. ^{13}C NMR spectrum of **3h** (100 MHz, V_{CDCl_3}/V_{CS_2} = 4:1 at 25°C, δ ($^{13}C_{CS_2}$) = 192.43).

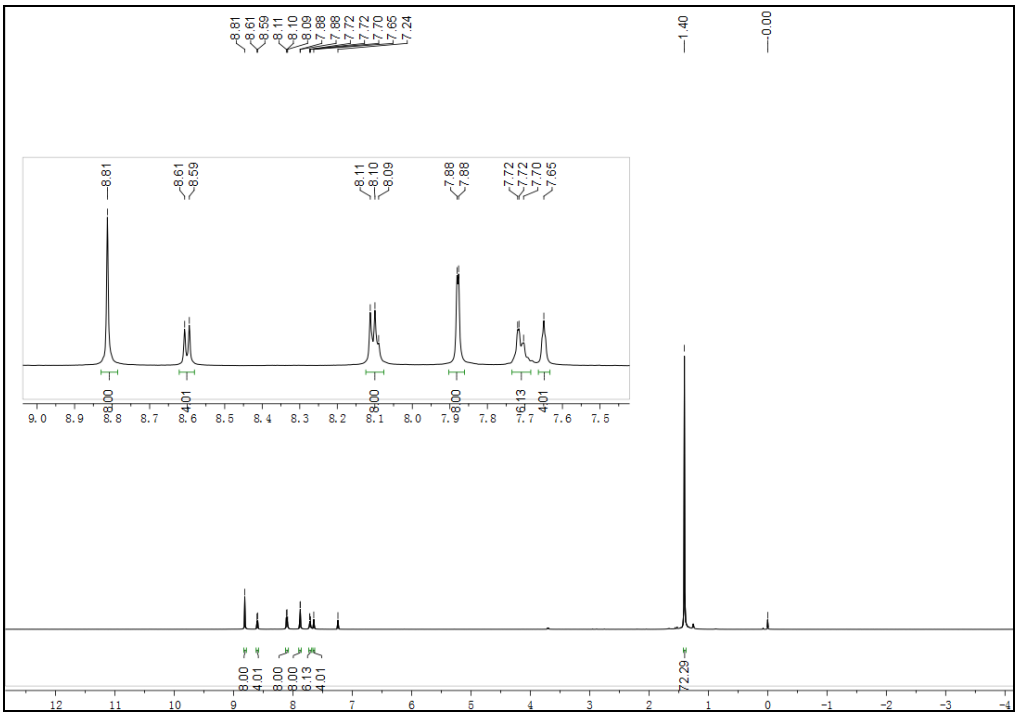

Figure S17. ^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$ at 25°C).

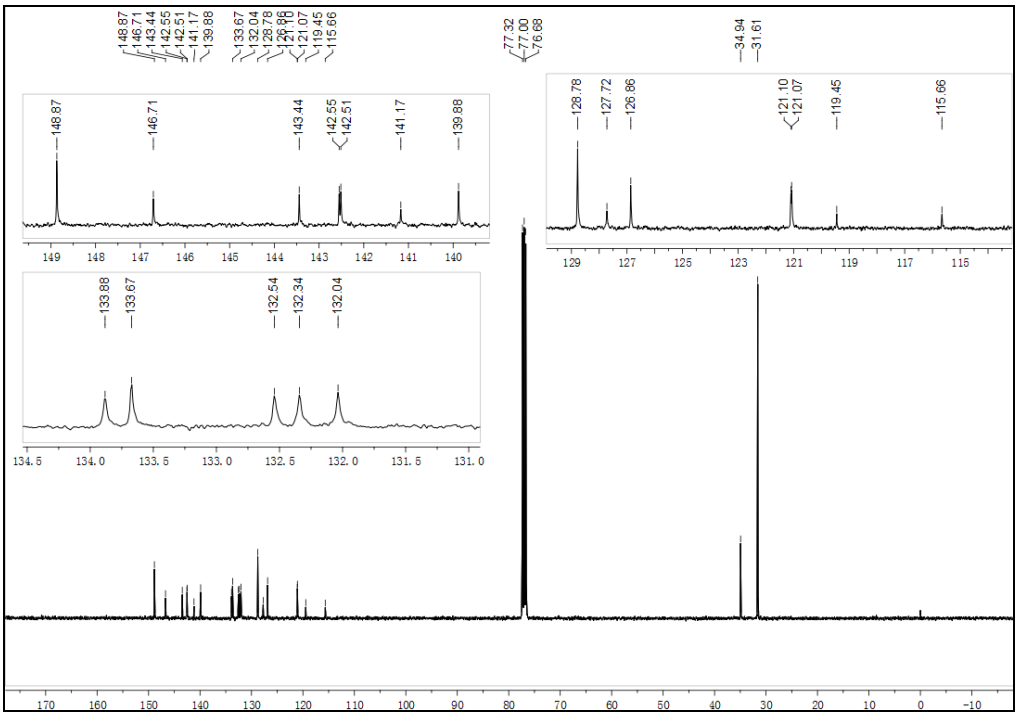

Figure S18. ^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$ at 25°C).

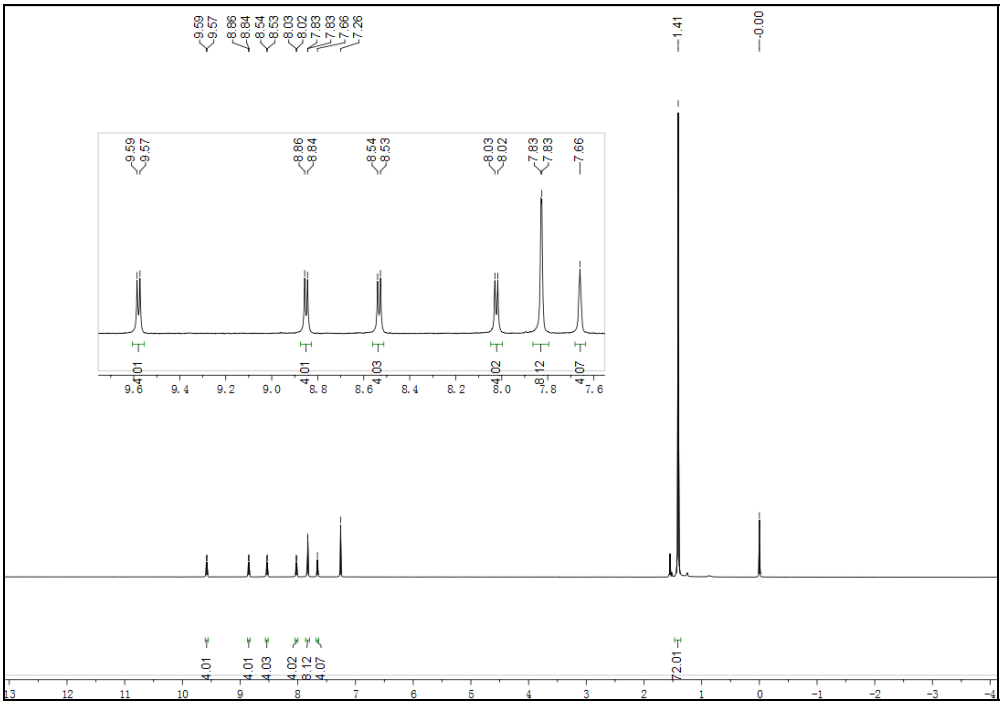

Figure S19. ^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$ at 25°C).

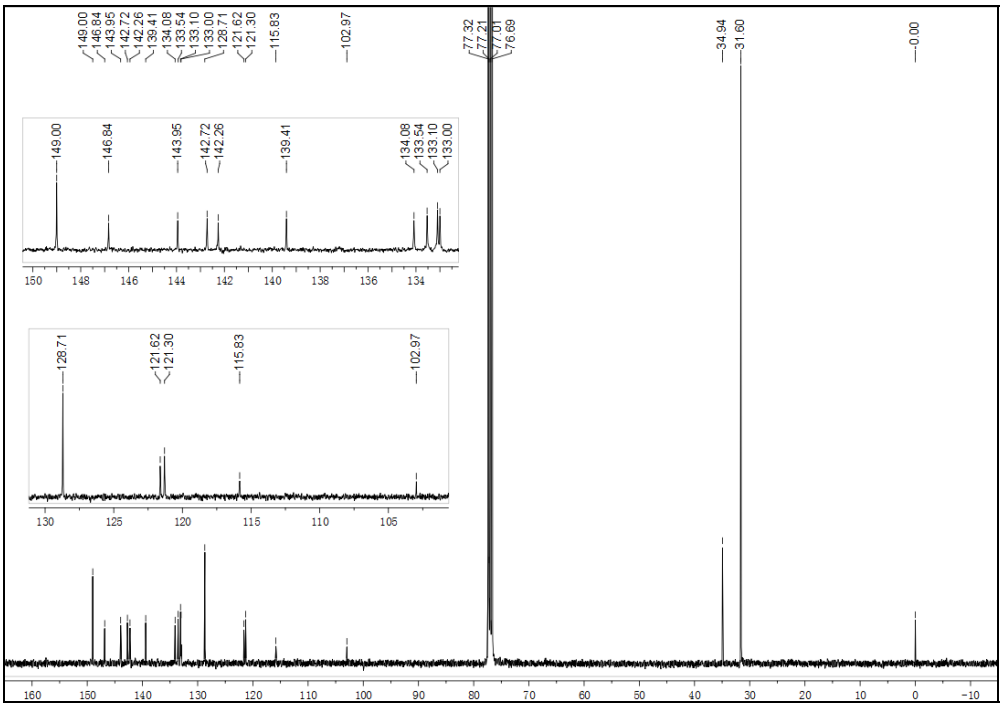

Figure S20. ^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$ at 25°C).

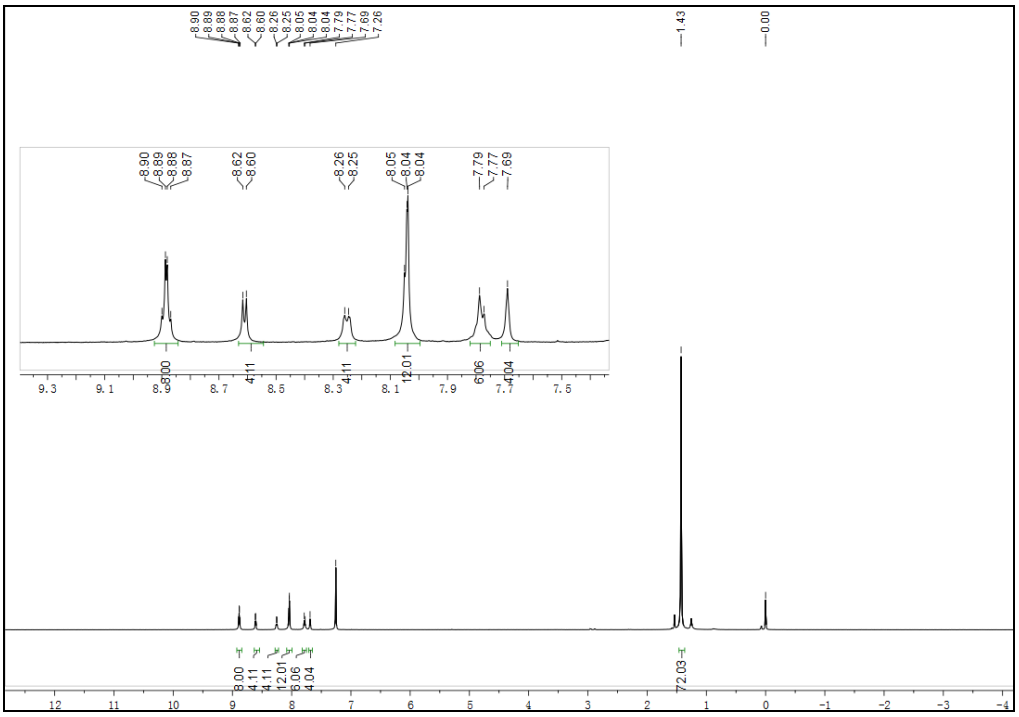

Figure S21. ^{1}H NMR spectrum of **4g** (100 MHz, $CDCl_3$ at 25°C).

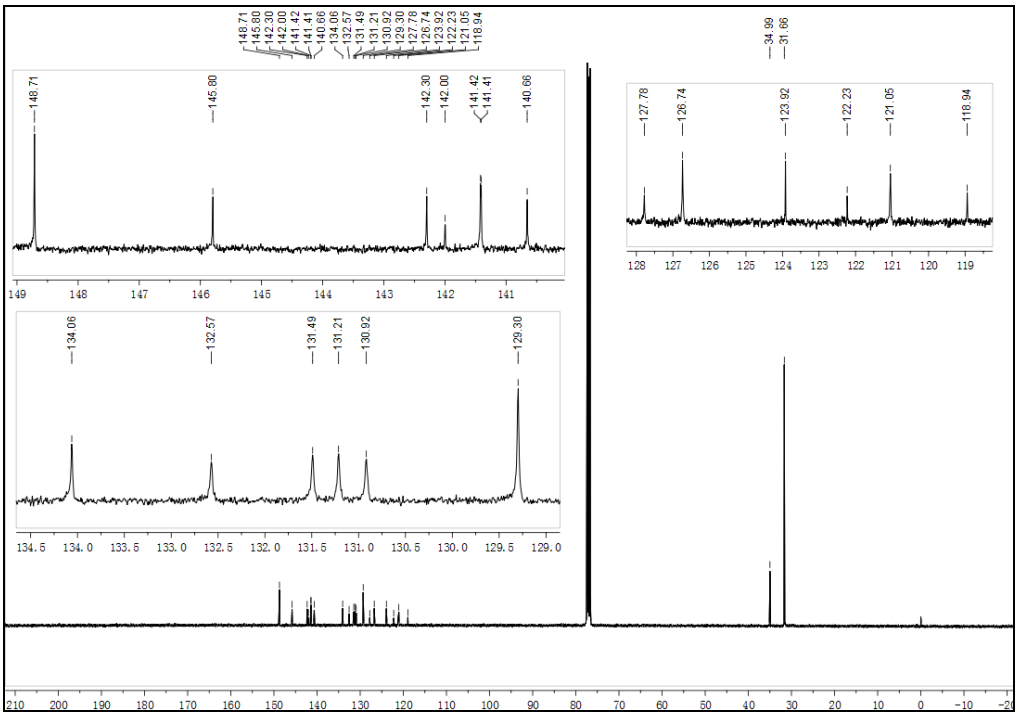

Figure S22. ^{13}C NMR spectrum of **4g** (400 MHz, $CDCl_3$ at 25°C).

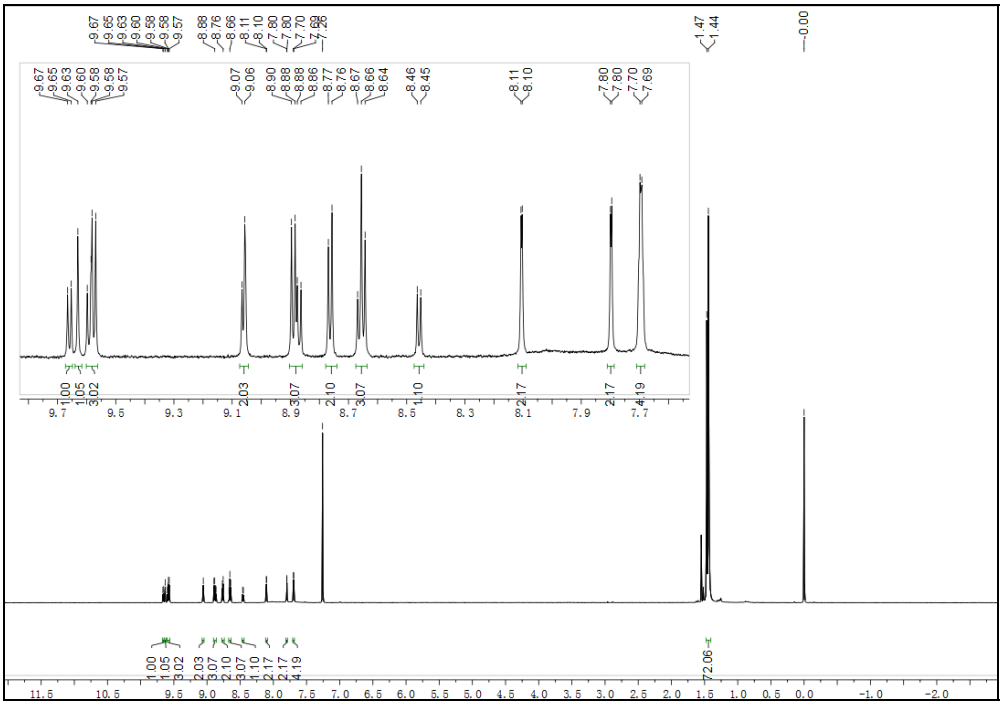

Figure S23. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$ at 25°C).

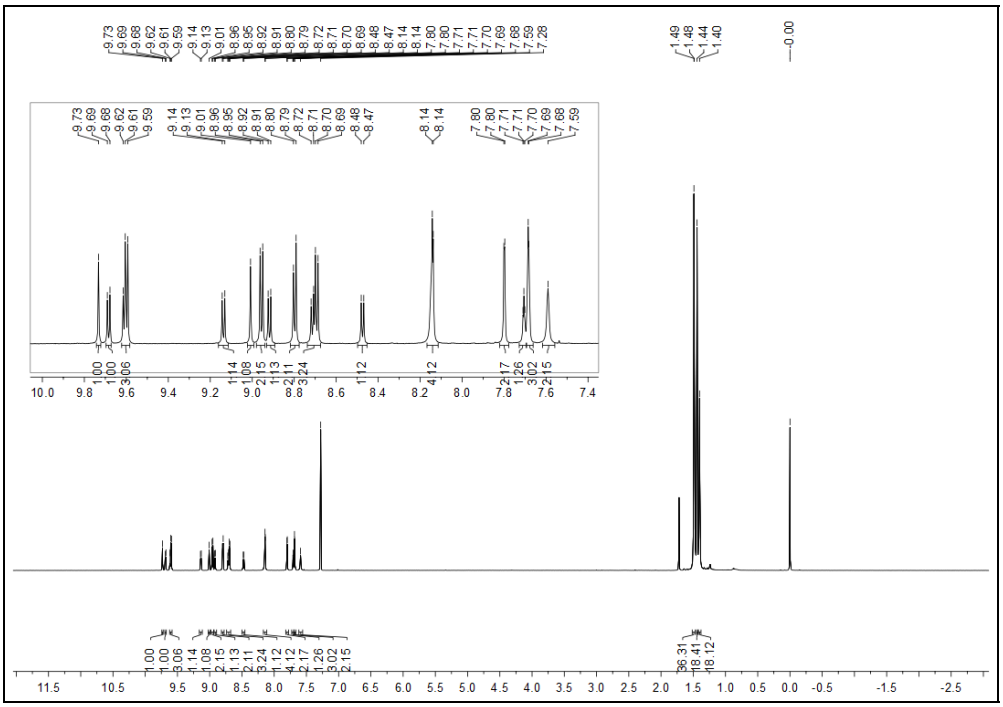

Figure S24. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$ at -40°C).

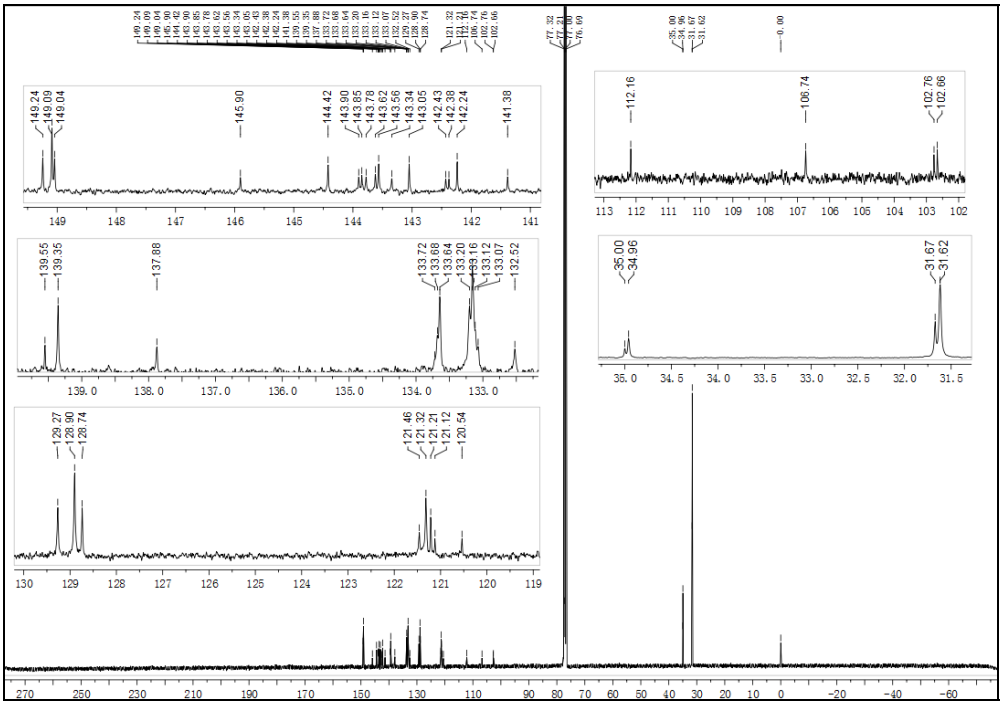

Figure S25. ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$ at 25°C).

5. ESR Spectrum

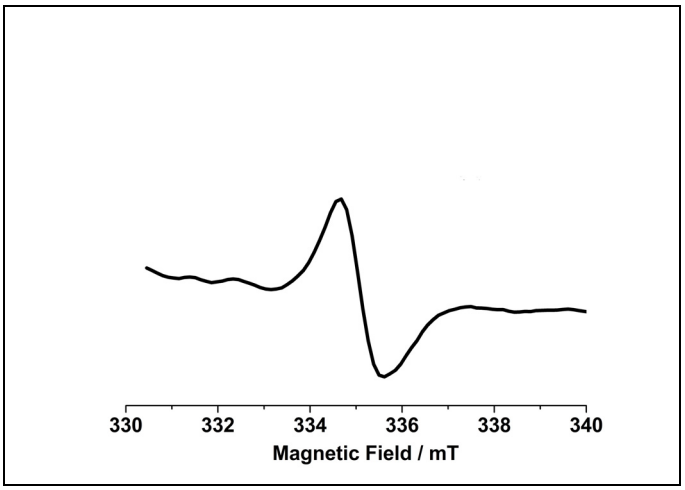

Figure S26. ESR spectrum of $Fe(OTf)_3$-mediated oxidative coupling of **1f**. (g = 2.0082)

6. The CV Spectra of 1a-1h