Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Gold Catalyzed Efficient Preparation of Dihydrobenzofuran from 1, 3-Enyne & Phenol

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Contents:

I. General condition

All reactions were run under an inert atmosphere (Ar) with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. All solvents were dried and purified before use by standard procedures. Commercial reagents were used as supplied or purified by standard techniques where necessary. Column chromatography was performed using 200-300 mesh silica with the proper solvent system according to TLC analysis and UV light to visualize the reaction components. Unless otherwise noted, nuclear magnetic resonance spectra were recorded on 400 MHz spectrometer. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet-doublet, t = triplet, m = multiplet and bs = broad singlet), coupling constant in Hz and integration. Chemical shifts of ^{1}H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 ppm). Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of CDCl3 (77.16 ppm) as the internal standard. HR-MS data were obtained using ESI ionization with 100,000 (FWHM) maximum resolution. The melting point data were measured with micro-melting-point apparatus.

II. X-ray chromatograph for compound 4j

Method for X-ray Crystallographic Studies: Data collections for them were performed on a‘Bruker APEX-II CCD’ diffractometer, using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). Using Olex21, the structures were solved with the ShelXT2 structure solution program using Intrinsic Phasing and refined with the ShelXL3 refinement package using Least Squares minimization. Refinement was performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrix least squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds were summarized.

Accession Codes CCDC 2106929 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

4j's crystal was obtained by slow diffusion of n-pentane into a dilute dichloromethane solution of **4j** at r.t.

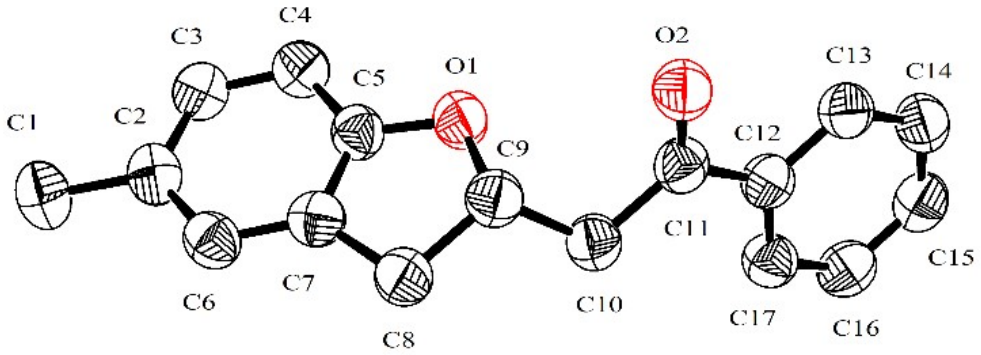


Figure S1. ORTEP picture of compound **4j** with the displacement ellipsoid drawn at 50% probability.

{CCDC: 2106929}

Table S1. Crystal data and structure refinement for cu_0312_3_0m.

Identification code	cu_0312_3_0m
Empirical formula	$C_{17}H_{16}O_2$
Formula weight	252.30
Temperature/K	150.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	13.9976(6)
b/Å	32.7715(15)
c/Å	5.6389(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2586.69(19)
Z	8
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.664
F(000)	1072.0
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.394 to 149.518
Index ranges	$-12 \leq h \leq 17$, $-41 \leq k \leq 23$, $-6 \leq l \leq 7$
Reflections collected	11389
Independent reflections	4345 [R_{int} = 0.0269, R_{sigma} = 0.0265]
Data/restraints/parameters	4345/1/345
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0563, wR_2 = 0.1392
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1428
Largest diff. peak/hole / e Å^{-3}	0.21/-0.23
Flack parameter	0.08(11)

III. General procedures for the synthesis 1, 3 - enynes

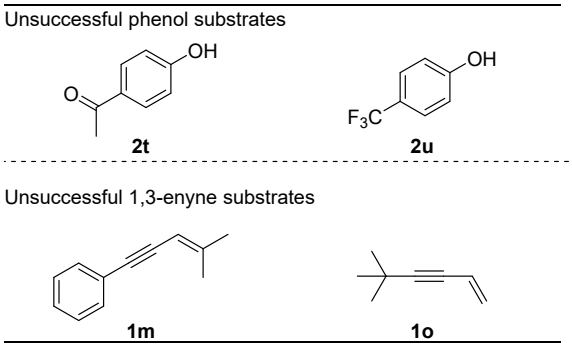
Enyne substrates **1a-1k**[1] were prepared by Sonogashira coupling from their corresponding terminal alkynes with vinyl bromide by a slightly modified method. General Method for the synthesis 1, 3 - enynes is exemplified by the synthesis of **1a**.

General method for the preparation of 4-phenyl-1,3-butenyne (1a): Under Ar atmosphere, to an oven-dried 250 mL round-bottom flask equipped with a magnetic stirring bar was added $Pd(PPh_3)_4$ (462 mg, 0.400 mmol, 2.00 mol%) and CuI (381 mg, 2.00 mmol, 10.0 mol%). Vinyl bromide (1.0 M in THF, 50.0 mL, 2.50 equiv) was added followed by freshly distilled and degassed Et_2NH (10.4 mL, 100 mmol, 5.00 equiv). The mixture was allowed to stir at ambient temperature for ca. 5 min and subsequently phenylacetylene (2.20 mL, 20.0 mmol, 1.00 equiv) was added as a solution in THF (10 mL) dropwise over one hour. The mixture was then allowed to stir at ambient temperature overnight (15-20 h). The reaction contents were then filtered through a pad of celite, eluting with Et_2O (3 × 20 mL). The solution was then concentrated in vacuo. **1a** was obtained by flash silica gel chromatography (99: 1 hexanes: Et_2O) to afford a colorless oil (2.43 g, 18.9 mmol, 94.6%). Spectral data match those previously reported.[1]

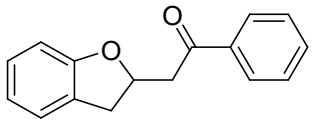
IV. General procedures for the synthesis of dihydrobenzofuran 4a:

To a suspension of 5 mol % of ^{t}BuXPhosAuCl/$AgNTf_2$ in DCE (0.5 mL), was added a mixture solution of 1,3-enyne **1a** (32.1 mg, 0.25 mmol, 1.0 equiv) and phenol **2a** (35.3 mg, 0.375 mmol, 1.5 equiv) in DCE (1mL) at rt. Then, a solution of 2,6-dichloropyridine-*N*-oxide **3a** (61.5 mg, 0.375 mmol, 1.5 equiv) in DCE (1mL) was added via syringe pump in 12 hours. 24 hours later, the reaction mixture was filtered over celite and washed with DCM (2 × 10 mL). Concentration of the filtrate, followed by purification via flash chromatography (petroleum/EtOAc = 50/1 as the eluent) afforded dihydrobenzofuran **4a** as a white solid. (43.1 mg, 73% yield).

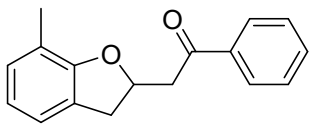
Table S2. Unsuccessful substrates tested in gold catalyzed cyclocoupling of 1,3-enynes with phenols.



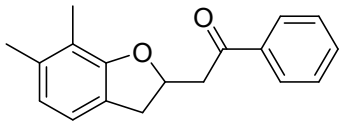
V. Characterization Data for all new compounds



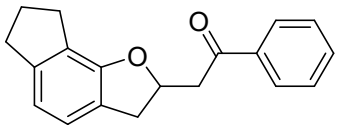
2-(2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4a**)[2]. Obtained as a white solid in 73% yield (43.1 mg); mp 105.8 – 106.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.45 (m, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.42 – 5.36 (m, 1H), 3.67 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.55 (dd, *J* = 15.8, 9.1 Hz, 1H), 3.29 (dd, *J* = 17.1, 7.0 Hz, 1H), 2.95 (dd, *J* = 15.8, 7.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 159.2, 136.8, 133.5, 128.8, 128.3, 128.2, 126.5, 125.2, 120.6, 109.6, 79.1, 44.8, 36.0; HR-MS (ESI) m/z calcd for $C_{16}H_{15}O_2$ $[M + H]^+$: 239.1067, found: 239.1065.



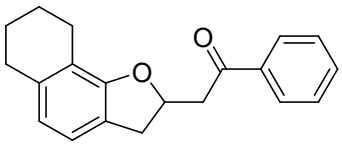
2-(7-methyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4b**). Obtained as a white solid in 55% yield (34.3 mg); mp 75.2 – 76.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.50 – 7.46 (m, 2H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.80 – 6.74 (m, 1H), 5.38 – 5.33 (m, 1H), 3.68 (dd, *J* = 16.8, 5.6 Hz, 1H), 3.55 (dd, *J* = 15.7, 9.0 Hz, 1H), 3.27 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.94 (dd, *J* = 15.7, 6.9 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 157.6, 137.0, 133.5, 129.4, 128.8, 128.3, 125.8, 122.5, 120.5, 119.8, 78.9, 45.0, 36.3, 15.3; HR-MS (ESI) m/z calcd for $C_{17}H_{17}O_2$ $[M + H]^+$: 253.1223, found: 253.1222.



2-(6,7-dimethyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4c**). Obtained as a white solid in 61% yield (40.3 mg); mp 85.5 – 88.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 5.37 – 5.32 (m, 1H), 3.67 (dd, *J* = 16.7, 5.7 Hz, 1H), 3.53 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.26 (dd, *J* = 16.7, 7.5 Hz, 1H), 2.92 (dd, *J* = 15.6, 6.8 Hz, 1H), 2.23 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 157.8, 137.0, 136.8, 133.4, 128.7, 128.3, 123.2, 121.9, 121.7, 118.5, 79.1, 45.0, 36.4, 19.5, 11.8; HR-MS (ESI) m/z calcd for $C_{18}H_{19}O_2$ $[M + H]^+$: 267.1380, found: 267.1380.

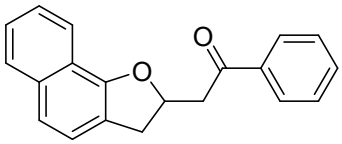


1-phenyl-2-(3,6,7,8-tetrahydro-2H-indeno[4,5-b]-furan-2-yl) ethan-1-one (**4d**). Obtained as a white solid in 53% yield (36.6 mg); mp 72.3 – 74.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.55 (m, 1H), 7.53 –7.43 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.4 Hz, 1H), 5.45 – 5.32 (m, 1H), 3.68 (dd, *J* = 16.9, 5.5 Hz, 1H), 3.53 (dd, *J* = 15.5, 9.0 Hz, 1H), 3.29 (dd, *J* = 16.9, 7.7 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.90 – 2.85 (m, 2H), 2.85 – 2.74 (m, 2H), 2.14 – 2.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 155.3, 146.0, 137.0, 133.4, 128.7, 128.3, 125.0, 124.0, 122.9, 116.4, 79.6, 45.0, 36.0, 33.0, 29.0, 25.7; HR-MS (ESI) m/z calcd for $C_{19}H_{19}O_2$ $[M + H]^+$: 279.1380, found: 279.1379.

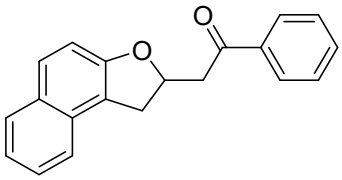


2-(2,3,6,7,8,9-hexahydronaphtho[1,2-b]-furan-2-yl)-1-phenylethan-1-one (**4e**). Obtained as a white solid in 63% yield (46.0 mg); mp 84.5 – 86.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 5.41 – 5.30 (m, 1H), 3.66 (dd, *J* = 16.7, 5.6 Hz, 1H), 3.51 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.26 (dd, *J* = 16.7, 7.6 Hz, 1H), 2.90 (dd, *J* = 15.6, 6.6 Hz, 1H), 2.73 (s, 2H), 2.67 – 2.49 (m, 2H), 1.83 – 1.70 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 157.2, 137.4, 137.1, 133.4, 128.7, 128.3, 122.4, 121.7, 121.2, 119.8, 79.3, 45.1, 36.1, 29.4, 23.2, 23.1, 22.7; HR-MS (ESI) m/z calcd for $C_{20}H_{21}O_2$ $[M + H]^+$: 293.1536,

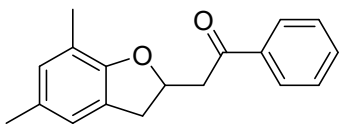
found: 293.1535.



2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-1-phenylethan-1-one (**4f**). Obtained as a white solid in 64% yield (45.9 mg); mp 78.3 – 81.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.93 – 7.86 (m, 1H), 7.83 – 7.77 (m, 1H), 7.60 – 7.54 (m, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.35 (m, 3H), 7.34 – 7.29 (m, 1H), 5.63 – 5.54 (m, 1H), 3.82 – 3.68 (m, 2H), 3.34 (dd, *J* = 16.9, 7.5 Hz, 1H), 3.10 (dd, *J* = 15.6, 6.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 154.5, 137.0, 134.1, 133.5 128.8, 128.3, 127.9, 125.7, 125.4, 123.0, 121.5, 120.7, 120.4, 119.5, 80.0, 45.1, 36.9; HR-MS (ESI) m/z calcd for $C_{20}H_{17}O_2$ $[M + H]^+$: 289.1223, found: 289.1215.

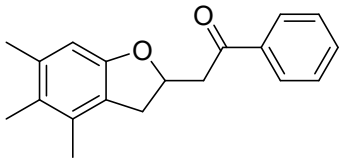


2-(1,2-dihydronaphtho[2,1-b] furan-2-yl)-1-phenylethan-1-one (**4g**). Obtained as a white solid in 77% yield (55.0 mg); mp 107.4 – 109.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.49 – 7.43 (m, 3H), 7.32 – 7.28 (m, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 5.60 – 5.55 (m, 1H), 3.81 (dd, *J* = 15.5, 9.4 Hz, 1H), 3.72 (dd, *J* = 17.2, 6.0 Hz, 1H), 3.35 (dd, *J* = 17.2, 7.3 Hz, 1H), 3.19 (dd, *J* = 15.5, 6.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 156.7, 136.8, 133.5, 130.9, 129.3, 129.2, 128.8, 128.2, 126.8, 123.0, 122.8, 118.1, 112.2, 79.8, 45.1, 34.9; HR-MS (ESI) m/z calcd for $C_{20}H_{17}O_2$ $[M + H]^+$: 289.1223, found: 289.1221.

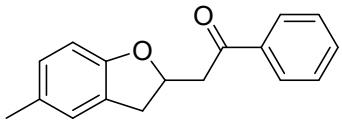


2-(5,7-dimethyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4h**). Obtained as a white solid in 65% yield (43.0 mg); mp 93.2 – 95.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.44 (m, 2H), 6.83 (s, 1H), 6.76 (s, 1H), 5.35 – 5.30 (m, 1H), 3.67 (dd, *J* = 16.7, 5.6 Hz, 1H), 3.51 (dd, *J* = 15.7, 9.0 Hz, 1H), 3.26 (dd, *J* = 16.7, 7.7 Hz, 1H), 2.90 (dd, *J* = 15.7, 6.8 Hz, 1H), 2.25 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 155.4, 137.0,

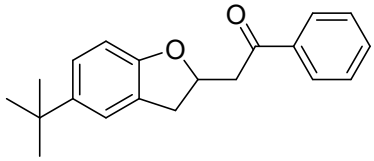
133.5, 129.9, 129.8, 128.7, 128.3, 125.8, 123.0, 119.3, 78.9, 45.0, 36.4, 20.8, 15.3; HR-MS (ESI) m/z calcd for $C_{18}H_{19}O_2$ $[M + H]^+$: 267.1380, found: 267.1377.



1-phenyl-2-(4,5,6-trimethyl-2,3-dihydrobenzofuran-2-yl)-ethan-1-one (**4i**). Obtained as a white solid in 70% yield (49.0 mg); mp 85.5 – 87.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.1 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.55 – 7.44 (m, 2H), 6.51 (s, 1H), 5.42 – 5.30 (m, 1H), 3.67 (dd, *J* = 17.1, 5.7 Hz, 1H), 3.49 (dd, *J* = 15.5, 9.0 Hz, 1H), 3.28 (dd, *J* = 17.1, 7.5 Hz, 1H), 2.86 (dd, *J* = 15.5, 6.7 Hz, 1H), 2.25 (s, 3H), 2.18 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 156.4, 136.9, 136.3, 133.4, 133.1, 128.7, 128.2, 126.7, 123.2, 108.5, 78.9, 45.0, 35.7, 21.2, 16.9, 14.8; HR-MS (ESI) m/z calcd for $C_{19}H_{21}O_2$ $[M + H]^+$: 281.1536, found: 281.1527.

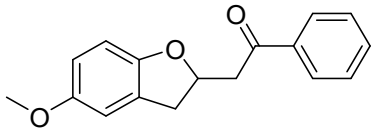


2-(5-methyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4j**)[2]. Obtained as a white solid in 78% yield (49.1 mg); mp 98.4 – 99.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 7.00 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.40 – 5.32 (m, 1H), 3.65 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.51 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.27 (dd, *J* = 17.1, 7.2 Hz, 1H), 2.91 (dd, *J* = 15.8, 6.9 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 157.0, 136.8, 133.4, 129.8, 128.6, 128.3, 128.1, 126.4, 125.6, 109.0, 79.0, 44.7, 35.9, 20.7; HR-MS (ESI) m/z calcd for $C_{17}H_{17}O_2$ $[M + H]^+$: 253.1223, found: 253.1221.

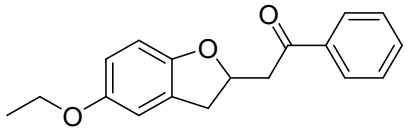


2-(5-(*tert*-butyl)-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4k**)[2]. Obtained as a white solid in 81% yield (59.1 mg); mp 92.1 – 93.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.52 – 7.43 (m, 2H), 7.23 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.42 – 5.35 (m, 1H), 3.67 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.55 (dd, *J* = 15.7, 9.0 Hz, 1H), 3.29 (dd, *J* = 17.1, 7.2 Hz, 1H), 2.94 (dd, *J* = 15.7, 6.9 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 156.8, 143.6, 136.8, 133.4, 128.7, 128.1, 126.0, 124.8, 122.1, 108.7, 79.1, 44.8, 36.1, 34.3,

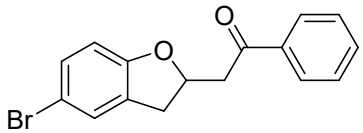
31.7; HR-MS (ESI) m/z calcd for $C_{20}H_{23}O_2$ [M + H] $^+$: 295.1693, found: 295.1685.



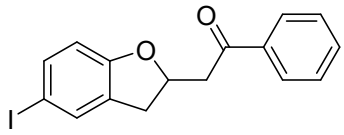
2-(5-methoxy-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4m**)[2]. Obtained as a white solid in 66% yield (43.9 mg); mp 92.5 – 93.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.61 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 6.77 (s, 1H), 6.73 – 6.62 (m, 2H), 5.40 – 5.31 (m, 1H), 3.75 (s, 3H), 3.65 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.52 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.28 (dd, *J* = 17.1, 7.2 Hz, 1H), 2.92 (dd, *J* = 15.9, 7.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 154.2, 153.2, 136.8, 133.4, 128.6, 128.1, 127.4, 113.0, 111.3, 109.4, 79.2, 56.0, 44.6, 36.3; HR-MS (ESI) m/z calcd for $C_{17}H_{17}O_3$ [M + H] $^+$: 269.1172, found: 269.1164.



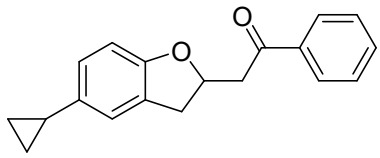
2-(5-ethoxy-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4n**). Obtained as a white solid in 68% yield (47.5 mg); mp 95.1 – 99.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.52 – 7.43 (m, 2H), 6.77 (s, 1H), 6.71 – 6.59 (m, 2H), 5.41 – 5.27 (m, 1H), 3.96 (q, *J* = 7.0 Hz, 2H), 3.65 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.51 (dd, *J* = 15.9, 9.0 Hz, 1H), 3.27 (dd, *J* = 17.1, 7.2 Hz, 1H), 2.92 (dd, *J* = 15.9, 6.9 Hz, 1H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 153.6, 153.3, 136.9, 133.6, 128.8, 128.2, 127.5, 114.0, 112.3, 109.5, 79.3, 64.5, 44.8, 36.5, 15.1; HR-MS (ESI) m/z calcd for $C_{18}H_{19}O_3$ [M + H] $^+$: 283.1329, found: 283.1327.



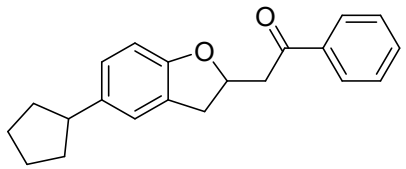
2-(5-bromo-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4o**)[2]. Obtained as a white solid in 55% yield (43.5 mg); mp 121.5 – 122.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.44 (m, 2H), 7.28 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.44 – 5.35 (m, 1H), 3.65 (dd, *J* = 17.2, 5.9 Hz, 1H), 3.54 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.28 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.94 (dd, *J* = 16.1, 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 158.3, 136.6, 133.5, 130.8, 129.0, 128.7, 128.1, 128.0, 112.2, 111.0, 79.7, 44.5, 35.7; HR-MS (ESI) m/z calcd for $C_{16}H_{14}O_2Br$ [M + H] $^+$: 317.0172, found: 317.0168.



2-(5-iodo-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4p**). Obtained as a white solid in 47% yield (42.5 mg); mp 115.9 – 118.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.51 – 7.44 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 5.42 – 5.35 (m, 1H), 3.65 (dd, *J* = 17.2, 5.9 Hz, 1H), 3.53 (dd, *J* = 16.1, 9.1 Hz, 1H), 3.28 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.93 (dd, *J* = 16.1, 7.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 159.2, 137.0, 136.7, 133.9, 133.7, 129.7, 128.8, 128.2, 112.0, 81.9, 79.7, 44.6, 35.6; HR-MS (ESI) m/z calcd for $C_{16}H_{14}O_2I$ $[M + H]^+$: 365.0033, found: 365.0033.

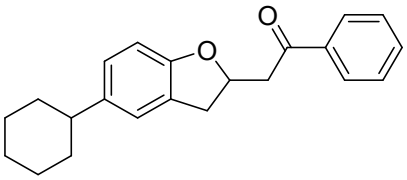


2-(5-cyclopropyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4q**). Obtained as a white solid in 76% yield (52.6 mg); mp 89.2 – 90.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.43 (m, 2H), 6.91 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 5.42 – 5.31 (m, 1H), 3.65 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.50 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.26 (dd, *J* = 17.1, 7.2 Hz, 1H), 2.90 (dd, *J* = 15.8, 6.9 Hz, 1H), 1.90 – 1.79 (m, 1H), 0.92 – 0.84 (m, 2H), 0.64 – 0.56 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 157.1, 136.8, 136.0, 133.4, 128.6, 128.1, 126.5, 125.7, 122.5, 109.1, 79.1, 44.7, 35.9, 14.9, 8.4; HR-MS (ESI) m/z calcd for $C_{19}H_{19}O_2$ $[M + H]^+$: 279.1380, found: 279.1378.

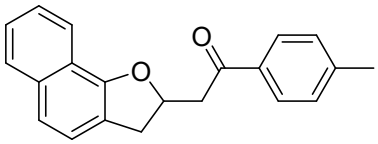


2-(5-cyclopentyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4r**). Obtained as a white solid in 77% yield (58.8 mg); mp 84.0 – 85.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.53 – 7.43 (m, 2H), 7.08 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 5.43 – 5.32 (m, 1H), 3.66 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.53 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.28 (dd, *J* = 17.1, 7.3 Hz, 1H), 3.01 – 2.87 (m, 2H), 2.12 – 1.98 (m, 2H), 1.86 – 1.74 (m, 2H), 1.73 – 1.64 (m, 2H), 1.61 – 1.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 157.3, 138.8, 136.9, 133.4,

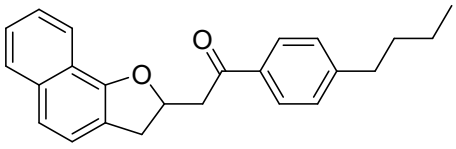
128.7, 128.2, 126.7, 126.4, 123.7, 109.1, 79.2, 45.6, 44.9, 36.1, 35.0, 25.5; HR-MS (ESI) m/z calcd for $C_{21}H_{23}O_2$ [M + H] $^+$: 307.1693, found: 307.1689.



2-(5-cyclohexyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**4s**). Obtained as a white solid in 73% yield (58.0 mg); mp 100.6 – 103.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.43 (m, 2H), 7.04 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 5.42 – 5.31 (m, 1H), 3.66 (dd, *J* = 17.0, 5.9 Hz, 1H), 3.53 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.28 (dd, *J* = 17.0, 7.3 Hz, 1H), 2.93 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.46 – 2.41 (m, 1H), 1.90 – 1.80 (m, 4H), 1.74 (d, *J* = 12.4 Hz, 1H), 1.44 – 1.32 (m, 4H), 1.27 – 1.17 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 157.3, 140.7, 136.9, 133.5, 128.7, 128.2, 126.4, 123.4, 109.1, 79.2, 44.9, 44.2, 36.1, 35.0, 27.1, 26.3; HR-MS (ESI) m/z calcd for $C_{22}H_{25}O_2$ [M + H] $^+$: 321.1849, found: 321.1846.

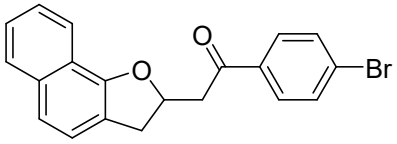


2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-1-(p-tolyl)-ethan-1-one (**7b**). Obtained as a white solid in 65% yield (49.0 mg); mp 88.8 – 90.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 1H), 7.90 – 7.87 (m, 2H), 7.83 – 7.79 (m, 1H), 7.44 – 7.40 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.25 (m, 2H), 5.62 – 5.55 (m, 1H), 3.78 – 3.70 (m, 2H), 3.33 (dd, *J* = 16.8, 7.6 Hz, 1H), 3.11 (dd, *J* = 15.5, 6.7 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 154.5, 144.4, 134.5, 134.0, 129.4, 128.4, 127.9, 125.7, 125.3, 123.0, 121.5, 120.6, 120.3, 119.5, 80.1, 45.0, 36.9, 21.8; HR-MS (ESI) m/z calcd for $C_{21}H_{19}O_2$ [M + H] $^+$: 303.1380, found: 303.1378.

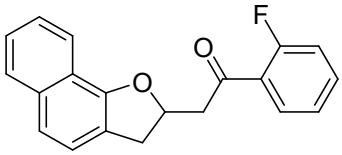


1-(4-butylphenyl)-2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-ethan-1-one (**7c**). Obtained as a white solid in 68% yield (58.5 mg); mp 75.7 – 77.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 3H), 7.81 – 7.77 (m, 1H), 7.42 – 7.39 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.24 (d, *J* = 8.9 Hz, 2H), 5.61 – 5.54 (m, 1H), 3.77 – 3.68 (m, 2H), 3.32 (dd, *J* = 16.8, 7.7 Hz, 1H), 3.10 (dd,

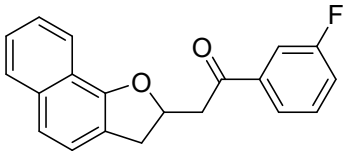
J = 15.5, 6.7 Hz, 1H), 2.69 – 2.63 (m, 2H), 1.63 – 1.59 (m, 2H), 1.39 – 1.31 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 154.5, 149.3, 134.7, 134.1, 128.8, 128.4, 127.9, 125.7, 125.3, 123.0, 121.5, 120.6, 120.3, 119.5, 80.1, 45.0, 36.9, 35.8, 33.3, 22.4, 14.0; HR-MS (ESI) m/z calcd for $C_{24}H_{25}O_2$ [M + H] $^+$: 345.1849, found: 345.1846.



1-(4-bromophenyl)-2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-ethan-1-one (**7d**). Obtained as a white solid in 59% yield (54.0 mg); mp 90.1 – 92.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.82 – 7.78 (m, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 5.59 – 5.53 (m, 1H), 3.75 – 3.68 (m, 2H), 3.29 (dd, *J* = 16.8, 7.1 Hz, 1H), 3.10 (dd, *J* = 15.5, 6.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 154.4, 135.7, 134.1, 132.1, 129.8, 128.7, 127.9, 125.8, 125.4, 123.0, 121.5, 120.6, 120.5, 119.3, 79.9, 45.0, 36.8; HR-MS (ESI) m/z calcd for $C_{20}H_{16}O_2Br$ [M + H] $^+$: 367.0328, found: 367.0328.

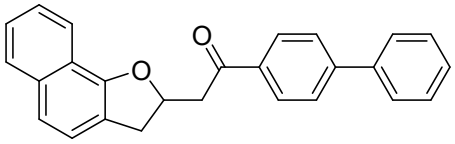


2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-1-(2-fluorophenyl)-ethan-1-one (**7e**). Obtained as a white solid in 63% yield (48.1 mg); mp 72.3 – 73.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (td, *J* = 7.7, 1.8 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.83 – 7.77 (m, 1H), 7.56 – 7.50 (m, 1H), 7.44 – 7.39 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.14 (dd, *J* = 11.2, 8.3 Hz, 1H), 5.63 – 5.55 (m, 1H), 3.79 – 3.68 (m, 2H), 3.42 (ddd, *J* = 17.8, 7.1, 3.1 Hz, 1H), 3.11 (dd, *J* = 15.4, 6.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.8, 162.2 (d, *J* = 254.7 Hz), 154.6, 135.0 (d, *J* = 9.1 Hz), 134.0, 130.7 (d, *J* = 2.3 Hz), 127.9, 125.7, 125.3, 124.6 (d, *J* = 3.4 Hz), 123.0, 121.6, 120.6, 120.3, 119.4, 116.8 (d, *J* = 24.2 Hz), 79.5, 50.1, 36.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -109.1; HR-MS (ESI) m/z calcd for $C_{20}H_{16}O_2F$ [M + H] $^+$: 307.1129, found: 307.1126.

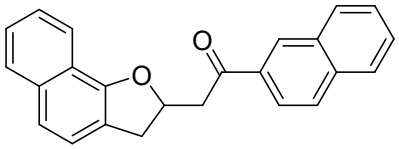


2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-1-(3-fluorophenyl)-ethan-1-one (**7f**). Obtained as a white solid in 65% yield (49.7 mg); mp 79.3 – 82.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 1H),

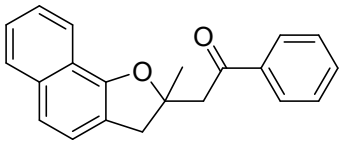
7.83 – 7.78 (m, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.46 – 7.40 (m, 3H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 5.61 – 5.54 (m, 1H), 3.77 – 3.70 (m, 2H), 3.33 (dd, *J* = 16.9, 7.2 Hz, 1H), 3.11 (dd, *J* = 15.5, 6.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.6, 163.8 (d, *J* = 250.2 Hz), 154.4, 139.02 (d, *J* = 6.1 Hz), 134.1, 130.4 (d, *J* = 7.6 Hz), 127.9, 125.8, 125.4, 124.1 (d, *J* = 2.9 Hz), 123.0, 121.5, 120.6, 120.5, 119.3, 115.0 (d, *J* = 23.4 Hz), 79.8, 45.2, 36.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.6; HR-MS (ESI) m/z calcd for $C_{20}H_{16}O_2F$ [M + H] $^+$: 307.1129, found: 307.1129.



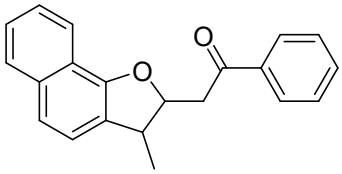
1-([1,1'-biphenyl]-4-yl)-2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-ethan-1-one (**7g**). Obtained as a white solid in 49% yield (44.6 mg); mp 121.1 – 123.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.95 – 7.89 (m, 1H), 7.87 – 7.79 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.41 (m, 3H), 7.41 – 7.38 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 5.65 – 5.58 (m, 1H), 3.80 (dd, *J* = 16.7, 5.8 Hz, 1H), 3.75 (dd, *J* = 15.5, 9.3 Hz, 1H), 3.38 (dd, *J* = 16.7, 7.5 Hz, 1H), 3.14 (dd, *J* = 15.5, 6.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 154.5, 146.2, 139.8, 135.6, 134.1, 129.1, 128.9, 128.4, 127.9, 127.4, 125.7, 125.4, 123.0, 121.5, 120.6, 120.4, 119.5, 80.1, 45.1, 36.9; HR-MS (ESI) m/z calcd for $C_{26}H_{21}O_2$ [M + H] $^+$: 365.1536, found: 365.1536.



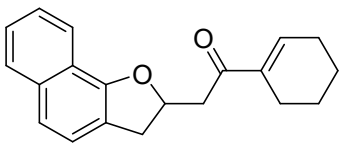
2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-1-(naphthalen-2-yl)-ethan-1-one (**7h**). Obtained as a white solid in 53% yield (44.5 mg); mp 106.2 – 108.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.07 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.97 – 7.89(m, 3H), 7.89 – 7.85 (m, 1H), 7.84 – 7.80 (m, 1H), 7.64 – 7.59 (m, 1H), 7.57 – 7.52 (m, 1H), 7.45 – 7.38 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 1H), 5.70 – 5.61 (m, 1H), 3.91 (dd, *J* = 16.7, 5.8 Hz, 1H), 3.77 (dd, *J* = 15.5, 9.3 Hz, 1H), 3.47 (dd, *J* = 16.7, 7.4 Hz, 1H), 3.17 (dd, *J* = 15.5, 6.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 154.5, 135.8, 134.3, 134.1, 132.5, 130.3, 129.7, 128.7, 128.6, 127.9, 126.9, 125.7, 125.4, 123.8, 123.0, 121.5, 120.6, 120.4, 119.5, 80.2, 45.2, 36.9; HR-MS (ESI) m/z calcd for $C_{24}H_{19}O_2$ [M + H] $^+$: 339.1380, found: 339.1377.



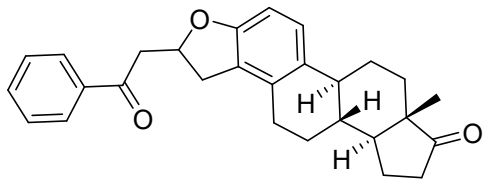
2-(2-methyl-2,3-dihydronaphtho[1,2-b]-furan-2-yl)-1-phenylethan-1-one (**7i**). Obtained as a colorless oil in 30% yield (22.5 mg, solid in refrigerator); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.84 – 7.73 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.37 (m, 4H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 3.64 (d, *J* = 15.9 Hz, 1H), 3.49 (dd, *J* = 15.8, 4.2 Hz, 2H), 3.36 (d, *J* = 15.6 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 153.5, 137.5, 134.1, 133.3, 128.6, 128.4, 127.9, 125.6, 125.2, 123.2, 121.6, 120.7, 120.2, 119.9, 88.2, 48.8, 42.5, 26.9; HR-MS (ESI) m/z calcd for $C_{21}H_{19}O_2$ $[M + H]^+$: 303.1380, found: 303.1370.



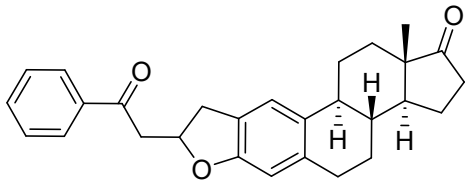
2-(3-methyl-2,3-dihydronaphtho[1,2-b]-furan-2-yl)-1-phenylethan-1-one (**7j**). Obtained as a colorless oil in 33% yield (24.9 mg, solid in refrigerator); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.92 – 7.86 (m, 1H), 7.83 – 7.78 (m, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 1H), 5.18 – 5.12 (m, 1H), 3.70 (dd, *J* = 16.7, 6.4 Hz, 1H), 3.45 – 3.38 (m, 1H), 3.31 (dd, *J* = 16.7, 6.6 Hz, 1H), 1.48 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 153.9, 137.1, 134.2, 133.5, 130.1, 129.0, 128.8, 128.4, 127.9, 125.8, 125.4, 122.1, 121.7, 120.5, 87.3, 44.4, 43.9, 20.48; HR-MS (ESI) m/z calcd for $C_{21}H_{19}O_2$ $[M + H]^+$: 303.1380, found: 303.1380.



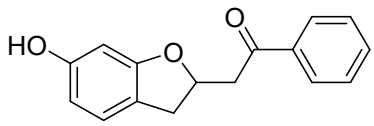
1-(cyclohex-1-en-1-yl)-2-(2,3-dihydronaphtho[1,2-b]-furan-2-yl)-ethan-1-one (**7k**). Obtained as a colorless oil in 25% yield (18.0 mg, solid in refrigerator); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.88(m, 1H), 7.81 – 7.78 (m, 1H), 7.42 – 7.39 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 6.95 – 6.91 (m, 1H), 5.47 – 5.41 (m, 1H), 3.64 (dd, *J* = 15.5, 9.2 Hz, 1H), 3.41 (dd, *J* = 16.3, 5.8 Hz, 1H), 3.06 – 2.99 (m, 2H), 2.28 – 2.19 (m, 4H), 1.68 – 1.60 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 154.5, 141.5, 139.7, 134.0, 127.9, 125.7, 125.3, 123.1, 121.5, 120.6, 120.2, 119.6, 80.4, 43.6, 36.7, 26.3, 23.0, 21.9, 21.6; HR-MS (ESI) m/z calcd for $C_{20}H_{21}O_2$ $[M + H]^+$: 293.1536, found: 293.1533.



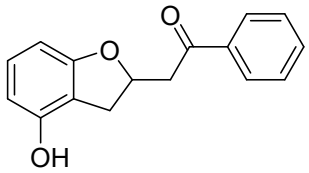
(5b***S***,7a***S***,10a***S***,10b***R***)-7a-methyl-2-(2-oxo-2-phenylethyl)-1,2,5b,6,7,7a,9,10,10a,10b,11,12-dodecahydro-8H-cyclopenta[7,8]-phenanthro[2,1-b]-furan-8-one (**9a**). Obtained as a white solid in 32% yield (33.0 mg); mp 151.0 – 153.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.64 – 7.56 (m, 1H), 7.53 – 7.44 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.44 – 5.32(m, 1H), 3.74 – 3.64 (m, 1H), 3.49 – 3.35 (m, 1H), 3.34 – 3.22 (m, 1H), 2.87 – 2.76 (m, 1H), 2.76 – 2.60 (m, 2H), 2.57 – 2.46 (m, 1H), 2.44 – 2.34 (m, 1H), 2.32 – 2.21 (m, 1H), 2.20 – 2.11 (m, 1H), 2.11 – 2.01 (m, 2H), 2.01 – 1.91 (m, 1H), 1.65 – 1.42 (m, 6H), 0.91 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 156.9, 136.8, 133.7, 133.6, 132.1, 128.8, 128.2, 125.2, 125.0, 106.8, 79.4, 50.5, 48.0, 45.1, 44.2, 38.2, 36.0, 35.1, 31.7, 27.2, 26.3, 21.7, 13.9; HR-MS (ESI) m/z calcd for $C_{28}H_{31}O_3$ [M + H] $^{+}$: 415.2268, found: 415.2269.



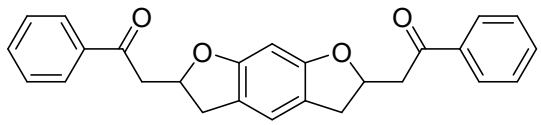
(3a***S***,3b***R***,10b***S***,12a***S***)-12a-methyl-8-(2-oxo-2-phenylethyl)-2,3,3a,3b,4,5,8,9,10b,11,12,12a-dodecahydro-1H-cyclopenta[7,8]-phenanthro[2,3-b]-furan-1-one (**9b**). Obtained as a white solid in 32% yield (32.8 mg); mp 133.7 – 135.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.52 – 7.43 (m, 2H), 7.13 (s, 1H), 6.53 (s, 1H), 5.42 – 5.31 (m, 1H), 3.68 – 3.61 (m, 1H), 3.54 – 3.47 (m, 1H), 3.31 – 3.22 (m, 1H), 2.95 – 2.89 (m, 1H), 2.90 – 2.82 (m, 2H), 2.56 – 2.45 (m, 1H), 2.43 – 2.34 (m, 1H), 2.29 – 2.20 (m, 1H), 2.19 – 2.10 (m, 1H), 2.09 – 2.04 (m, 1H), 2.03 – 1.98 (m, 1H), 1.97 – 1.91 (m, 1H), 1.71 – 1.59 (m, 2H), 1.58 – 1.52 (m, 1H), 1.51 – 1.44 (m, 2H), 1.44 – 1.35 (m, 1H), 0.91 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 157.4, 136.8, 136.6, 133.5, 132.1, 128.8, 128.2, 124.2, 122.0, 109.5, 79.3, 50.5, 48.1, 44.9, 44.3, 38.6, 36.0, 31.7, 29.9, 26.7, 26.3, 21.7, 14.0; HR-MS (ESI) m/z calcd for $C_{28}H_{31}O_3$ [M + H] $^{+}$: 415.2268, found: 415.2273.



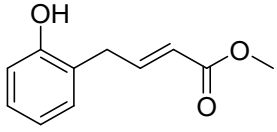
2-(6-hydroxy-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**13a**). Obtained as a white solid in 54% yield (34.0 mg); mp 130.5 – 134.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.38 – 6.28 (m, 2H), 5.44 – 5.36 (m, 1H), 5.22 (s, 1H), 3.65 (dd, *J* = 17.1, 6.2 Hz, 1H), 3.45 (dd, *J* = 15.3, 9.0 Hz, 1H), 3.27 (dd, *J* = 17.1, 6.9 Hz, 1H), 2.85 (dd, *J* = 15.3, 6.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 160.4, 156.3, 136.7, 133.6, 128.8, 128.3, 125.3, 118.4, 107.4, 97.9, 80.1, 44.8, 35.2; HR-MS (ESI) m/z calcd for $C_{16}H_{15}O_3$ $[M + H]^+$: 255.1016, found: 255.1014.



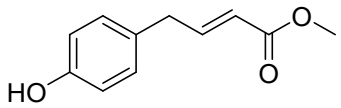
2-(4-hydroxy-2,3-dihydrobenzofuran-2-yl)-1-phenylethan-1-one (**13b**). Obtained as a white solid in 13% yield (8.0 mg); mp 158.3 – 161.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 7.03 – 6.96 (m, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 6.33 (d, *J* = 8.1 Hz, 1H), 5.45 – 5.40 (m, 1H), 4.80 (s, 1H), 3.67 (dd, *J* = 17.1, 5.9 Hz, 1H), 3.51 (dd, *J* = 15.5, 9.1 Hz, 1H), 3.31 (dd, *J* = 17.1, 7.3 Hz, 1H), 2.89 (dd, *J* = 15.5, 6.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 161.0, 152.7, 136.8, 133.6, 129.4, 128.8, 128.3, 112.1, 107.9, 102.7, 79.6, 44.9, 33.0; HR-MS (ESI) m/z calcd for $C_{16}H_{15}O_3$ $[M + H]^+$: 255.1016, found: 255.1017.



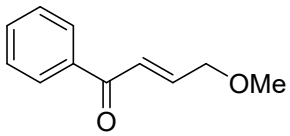
2,2'-(2,3,5,6-tetrahydrobenzo[1,2-b:5,4-b']-difuran-2,6-diyl)-bis(1-phenylethan-1-one) (**14**). Obtained as a white solid in 57% yield (56.4 mg); mp 134.0 – 136.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 4H), 7.61 – 7.56 (m, 2H), 7.49 – 7.45 (m, 4H), 6.93 (s, 1H), 6.26 (s, 1H), 5.44 – 5.33 (m, 2H), 3.64 (dd, *J* = 17.0, 5.9 Hz, 2H), 3.44 (dd, *J* = 15.3, 9.0 Hz, 2H), 3.27 (dd, *J* = 17.0, 7.2 Hz, 2H), 2.84 (dd, *J* = 15.3, 6.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 159.5, 136.8, 133.5, 128.8, 128.2, 120.8, 118.0, 93.0, 80.2, 44.8, 35.5; HR-MS (ESI) m/z calcd for $C_{26}H_{23}O_4$ $[M + H]^+$: 399.1591, found: 399.1591.



methyl (***E***)-4-(2-hydroxyphenyl)-but-2-enoate (**16a**)[3]. Obtained as a colorless oil in 48% yield (22.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dt, *J* = 15.6, 6.5 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.91 – 6.85 (m, 1H), 6.80 – 6.75 (m, 1H), 5.83 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.38 (s, 1H), 3.72 (s, 3H), 3.53 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 153.7, 147.5, 130.7, 128.3, 124.2, 121.6, 121.1, 115.5, 51.7, 33.1; HR-MS (ESI) m/z calcd for $C_{11}H_{13}O_3$ $[M + H]^+$: 193.0859, found: 193.0859.



methyl (***E***)-4-(4-hydroxyphenyl)-but-2-enoate (**16b**)[4]. Obtained as a colorless oil in 33% yield (15.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dt, *J* = 15.6, 6.8 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 5.80 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.24 (s, 1H), 3.73 (s, 3H), 3.45 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 154.6, 148.4, 130.0, 129.7, 121.6, 115.6, 51.7, 37.7; HR-MS (ESI) m/z calcd for $C_{11}H_{13}O_3$ $[M + H]^+$: 193.0859, found: 193.0857.



(***E***)-4-methoxy-1-phenylbut-2-en-1-one (**17**)[5]. Obtained as a colorless oil in 45% yield (19.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 7.17 (dt, *J* = 15.5, 1.9 Hz, 1H), 7.05 (dt, *J* = 15.5, 4.0 Hz, 1H), 4.21 (dd, *J* = 4.0, 2.0 Hz, 2H), 3.45 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.4, 144.4, 137.7, 133.0, 128.8, 128.7, 124.8, 71.7, 58.9; HR-MS (ESI) m/z calcd for $C_{11}H_{13}O_2$ $[M + H]^+$: 177.0910, found: 177.0910.

VI. Copies of NMR spectra for all new compounds

Figure S2. ^{1}H NMR spectra for **4a** (600MHz, $CDCl_3$)

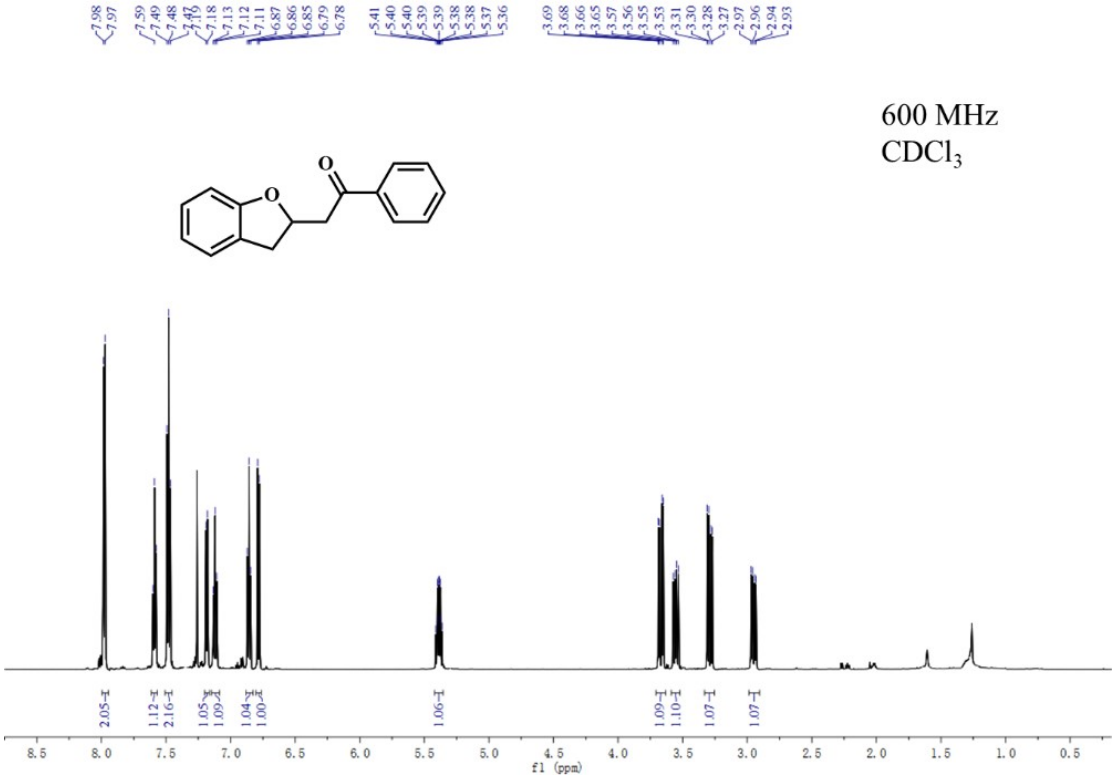


Figure S3. ^{13}C NMR spectra for **4a** (151MHz, $CDCl_3$)

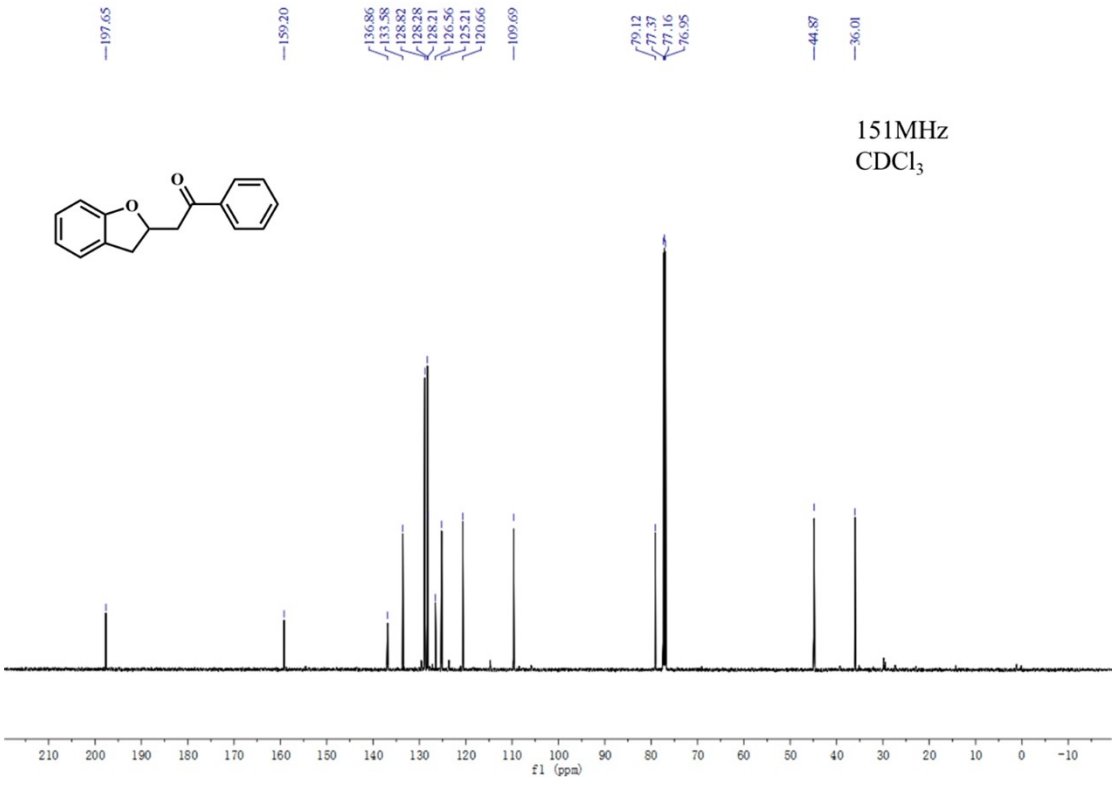


Figure S4. ^{1}H NMR spectra for **4b** (600MHz, $CDCl_3$)

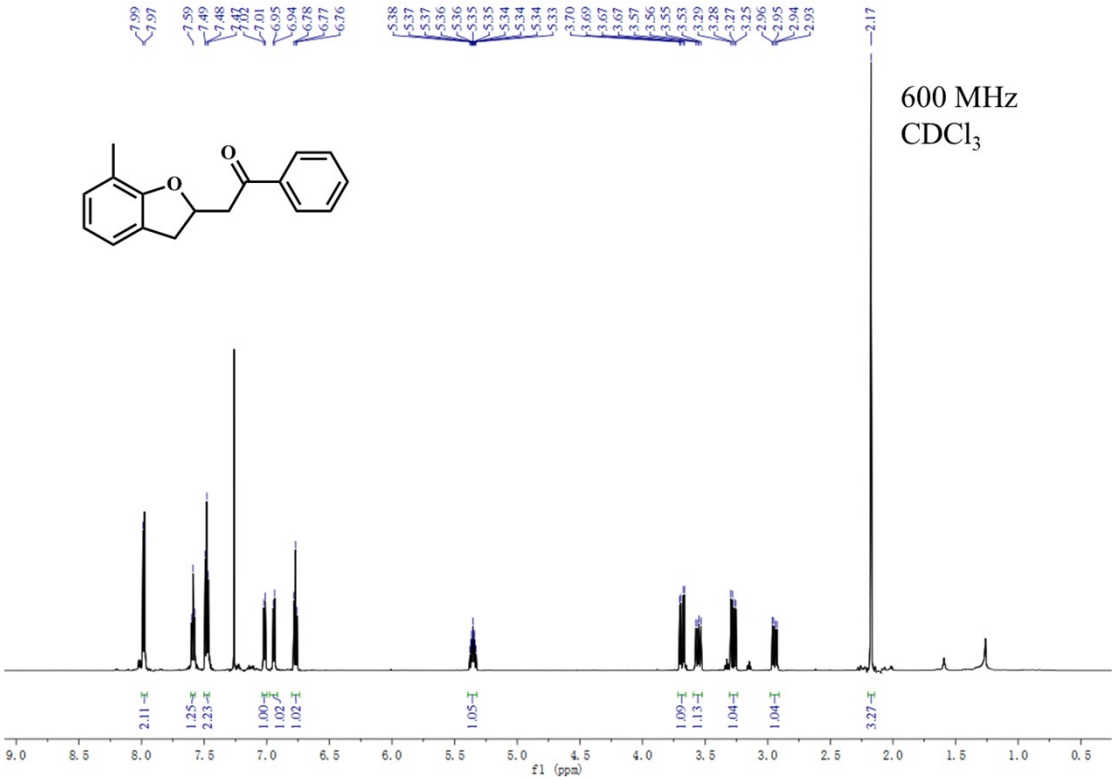


Figure S5. ^{13}C NMR spectra for **4b** (151MHz, $CDCl_3$)

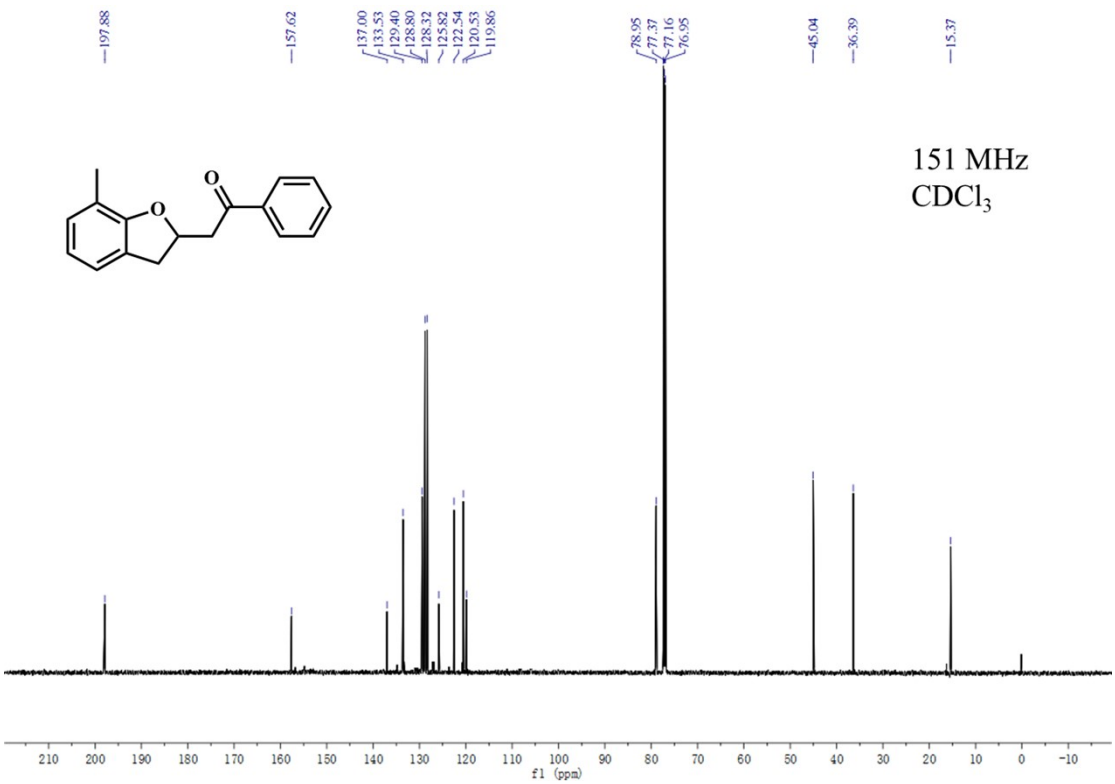


Figure S6. ^{1}H NMR spectra for **4c** (600MHz, $CDCl_3$)

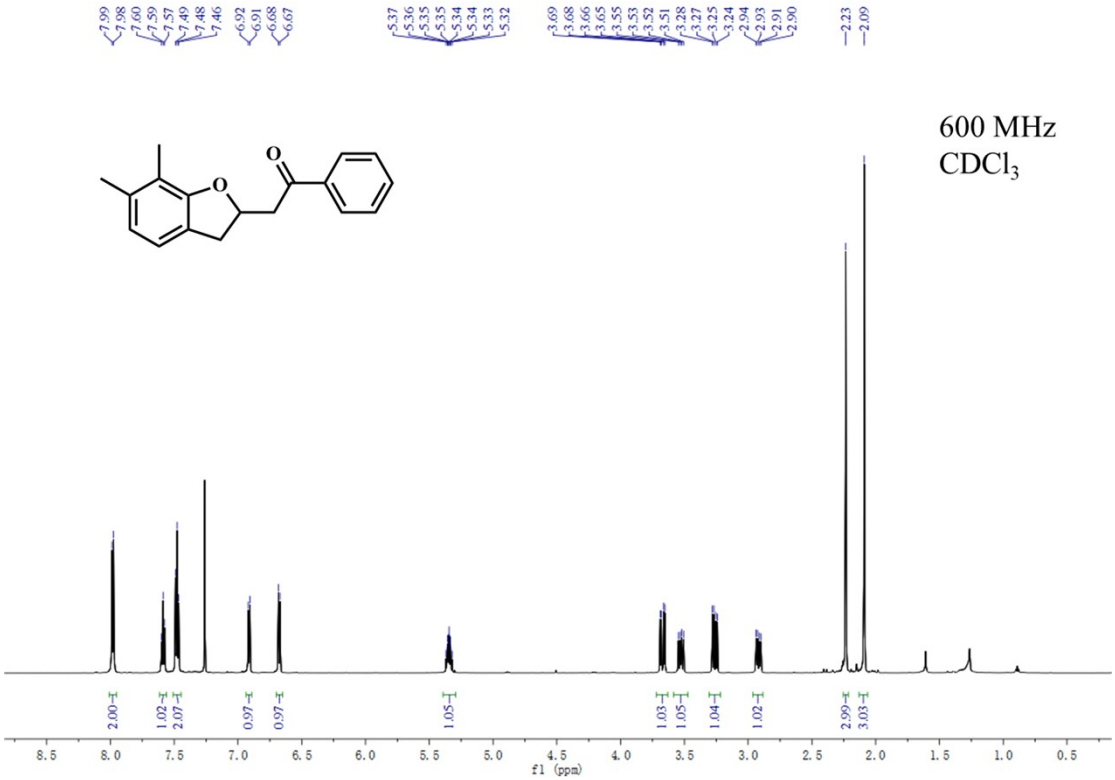


Figure S7. ^{13}C NMR spectra for **4c** (151MHz, $CDCl_3$)

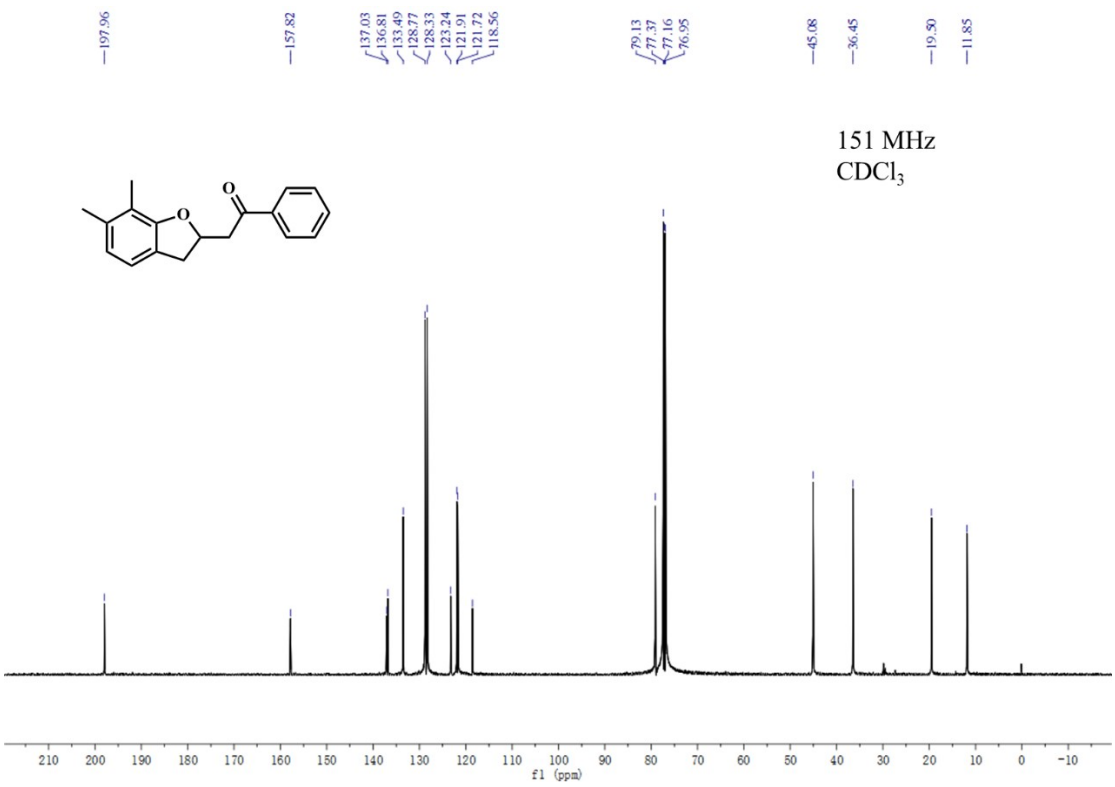


Figure S8. ^{1}H NMR spectra for **4d** (400MHz, $CDCl_3$)

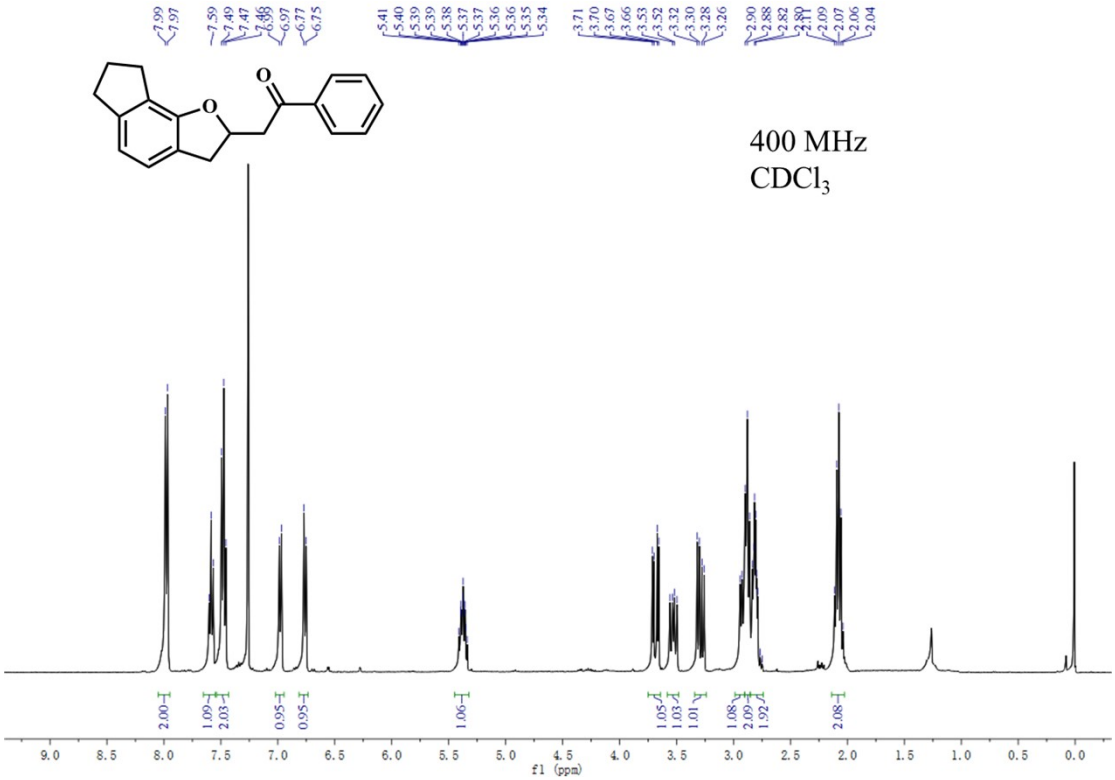


Figure S9. ^{13}C NMR spectra for **4d** (101MHz, $CDCl_3$)

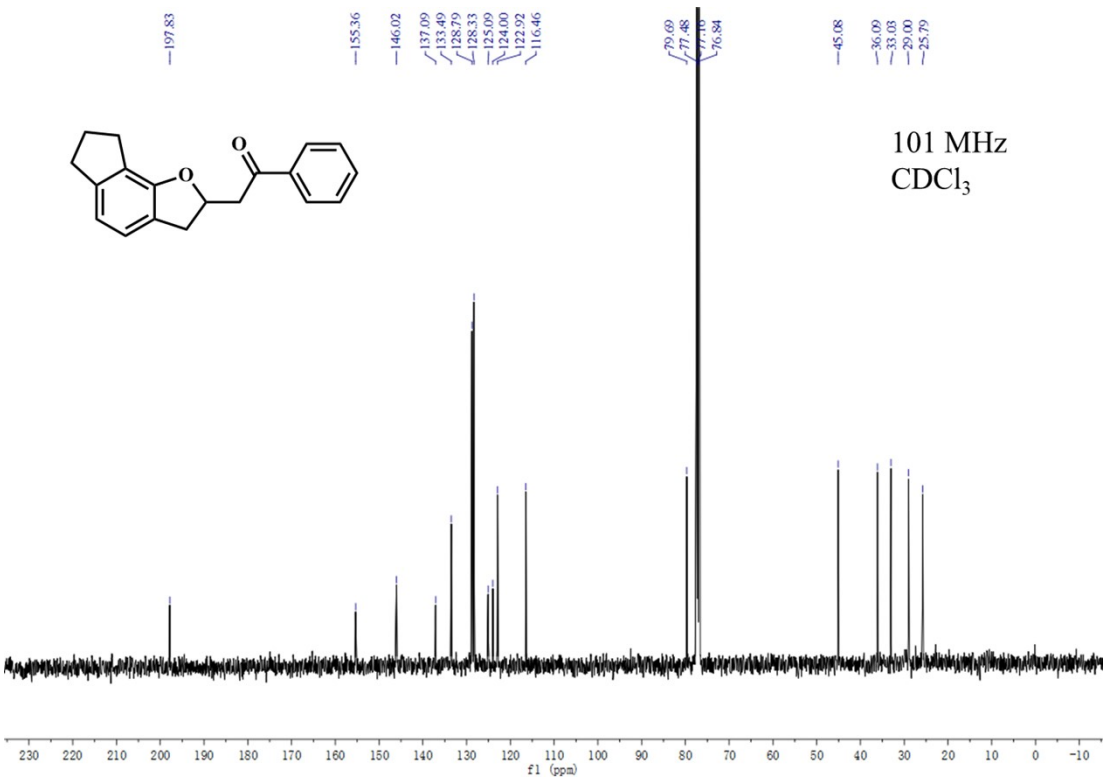


Figure S10. ^{1}H NMR spectra for **4e** (400MHz, $CDCl_3$)

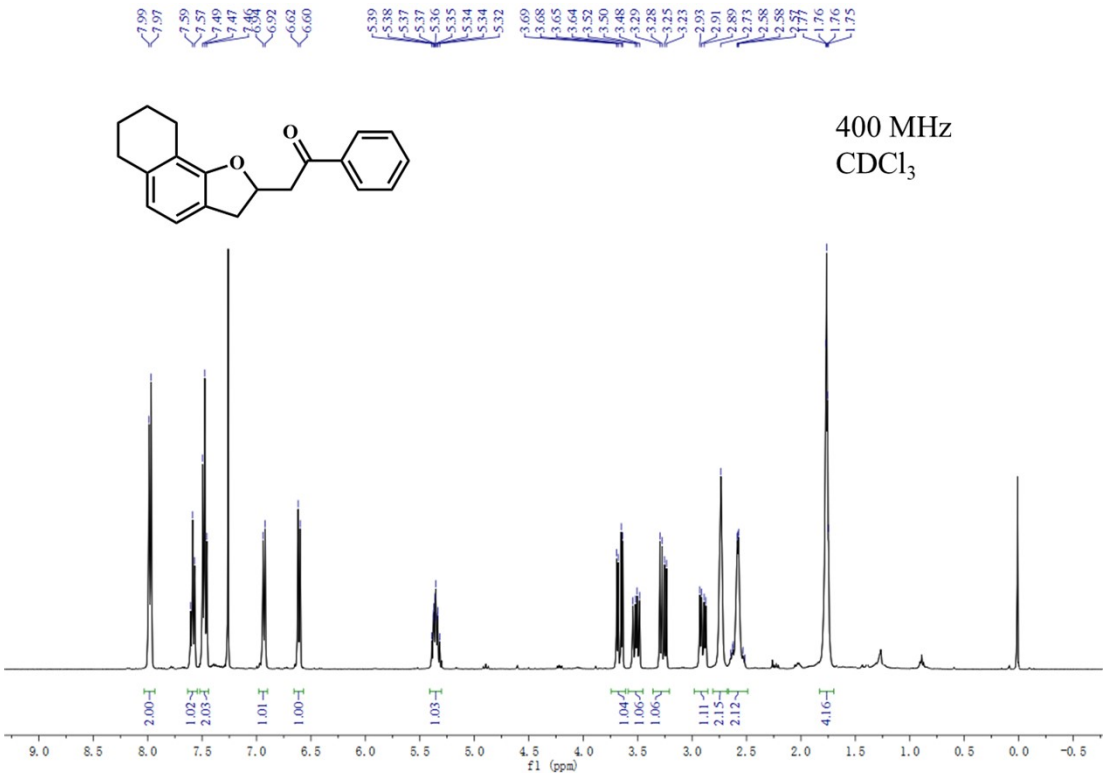


Figure S11. ^{13}C NMR spectra for **4e** (101MHz, $CDCl_3$)

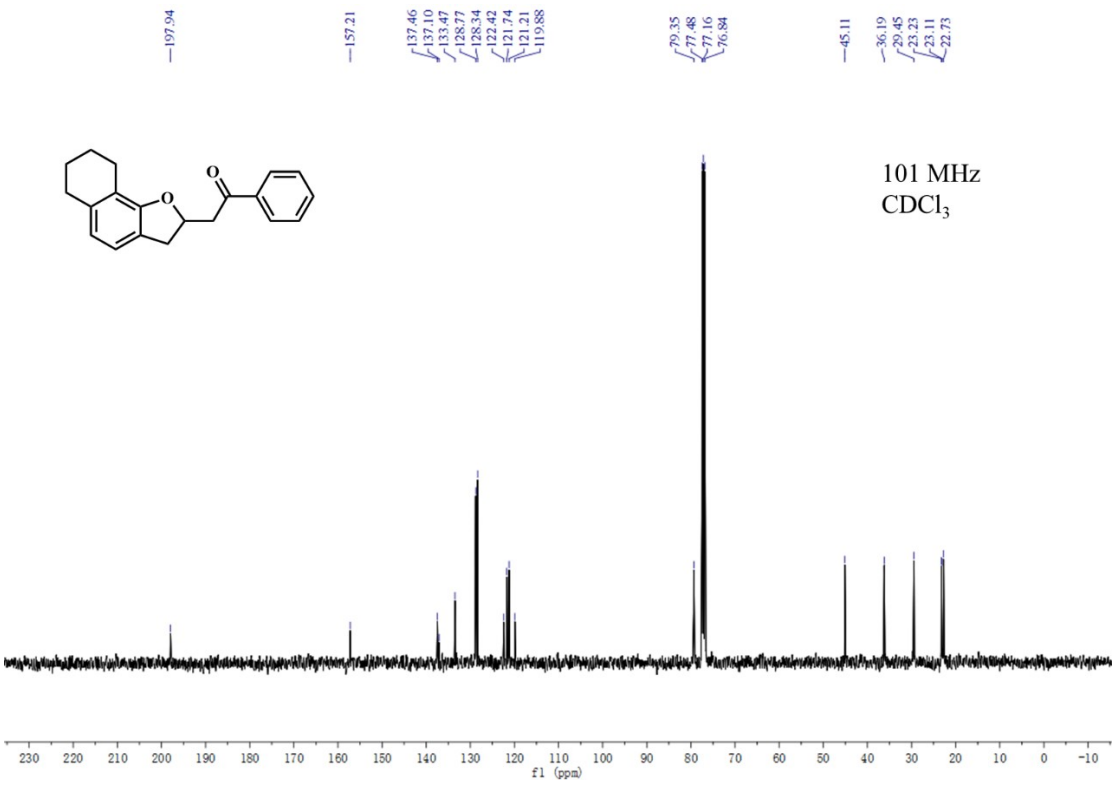


Figure S12. ^{1}H NMR spectra for **4f** (400MHz, $CDCl_3$)

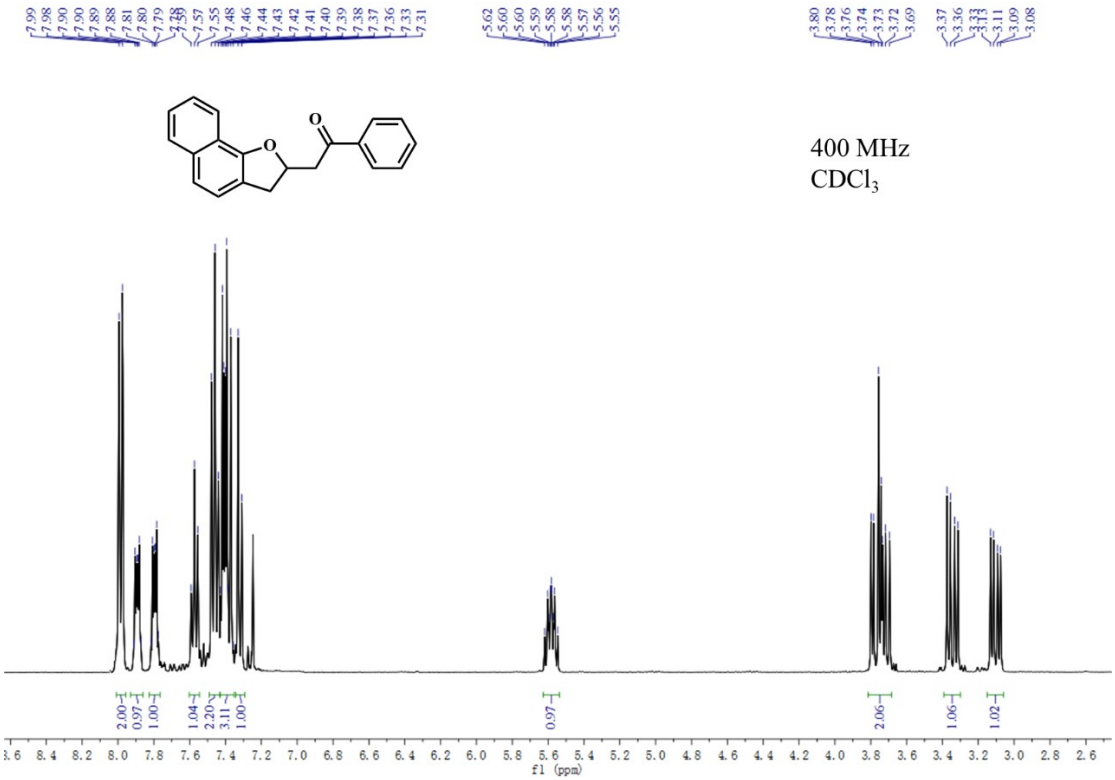


Figure S13. ^{13}C NMR spectra for **4f** (101MHz, $CDCl_3$)

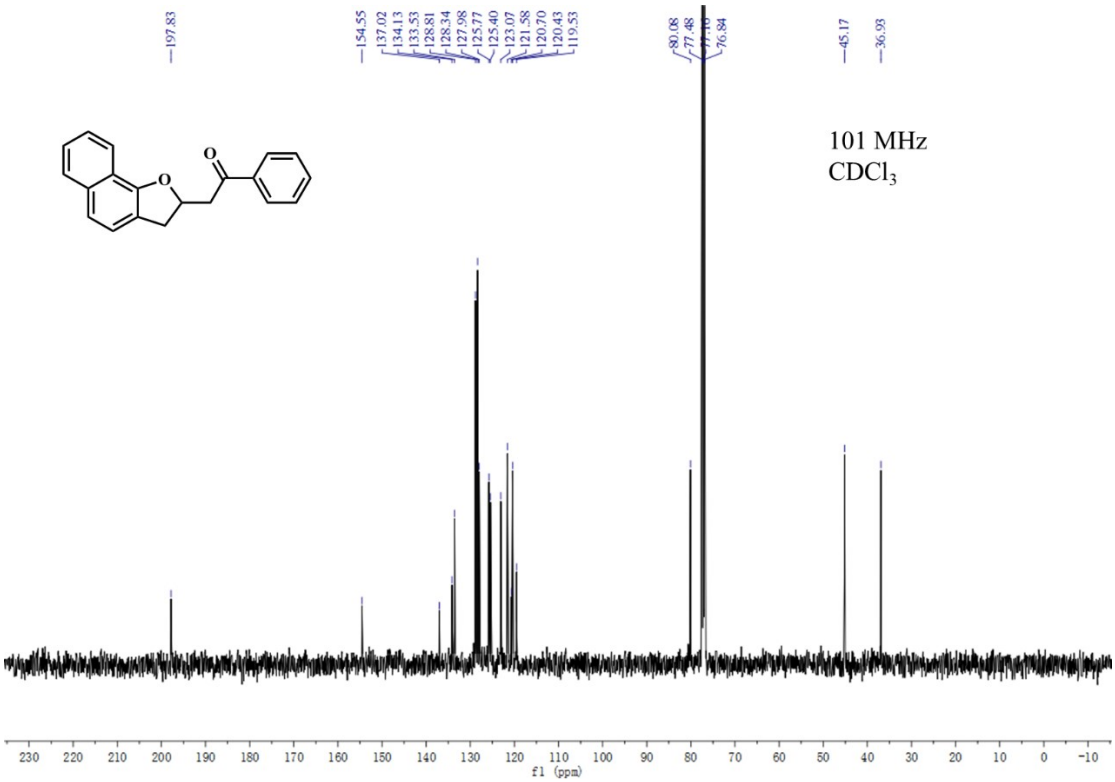


Figure S14. ^{1}H NMR spectra for **4g** (600MHz, $CDCl_3$)

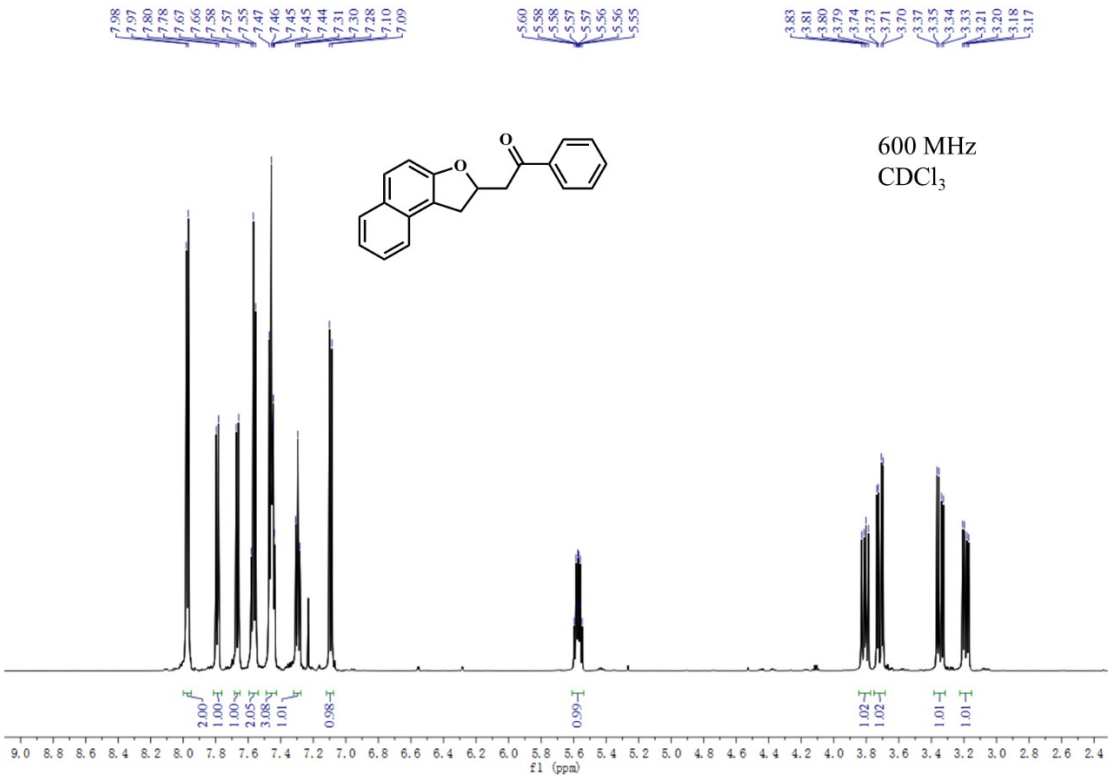


Figure S15. ^{13}C NMR spectra for **4g** (151MHz, $CDCl_3$)

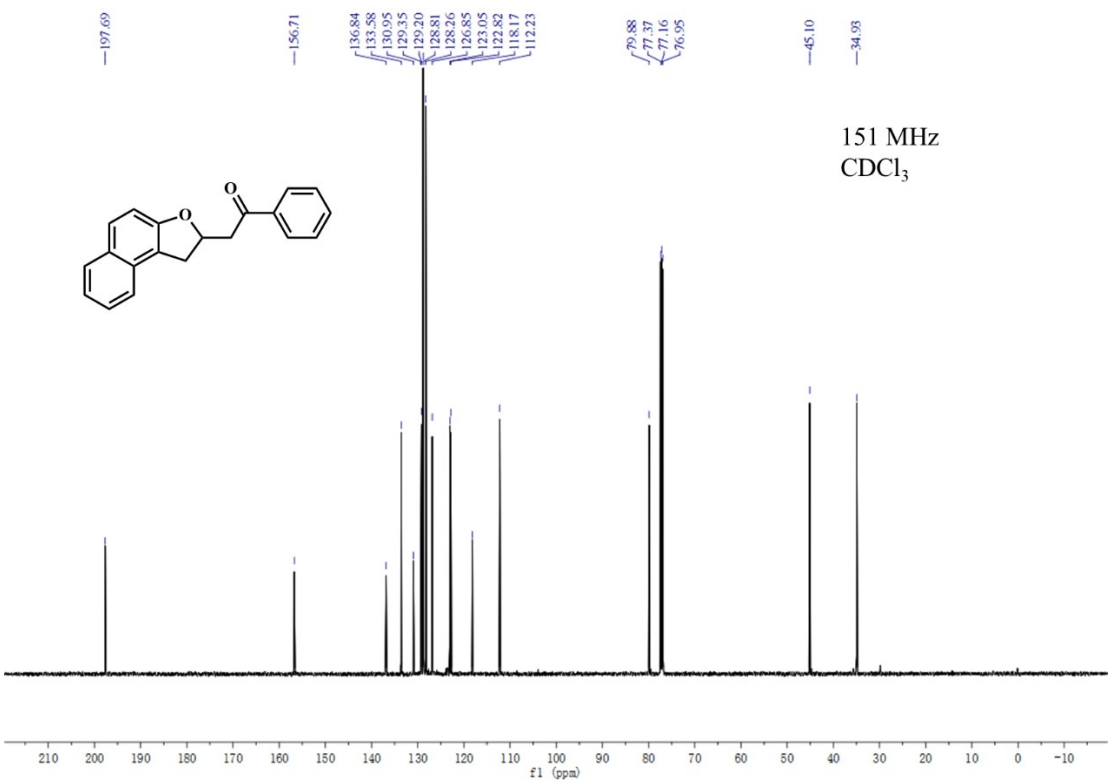


Figure S16. ^{1}H NMR spectra for **4h** (600MHz, $CDCl_3$)

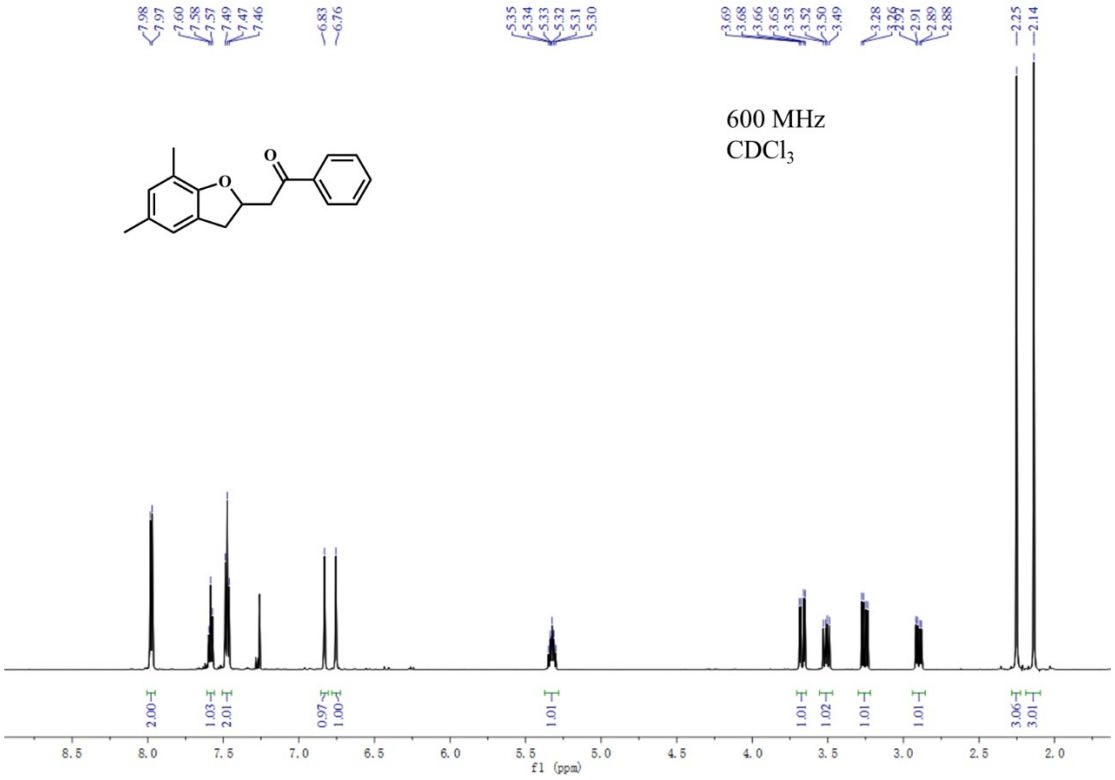


Figure S17. ^{13}C NMR spectra for **4h** (151MHz, $CDCl_3$)

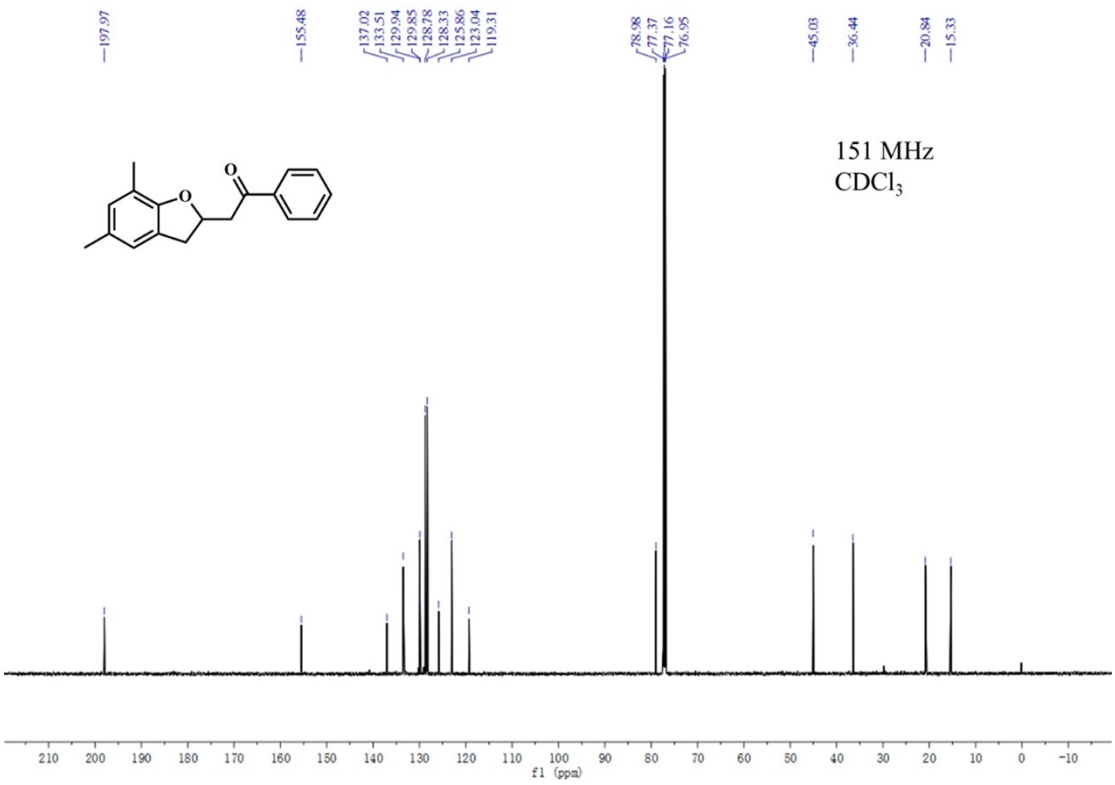


Figure S18. ^{1}H NMR spectra for **4i** (400MHz, $CDCl_3$)

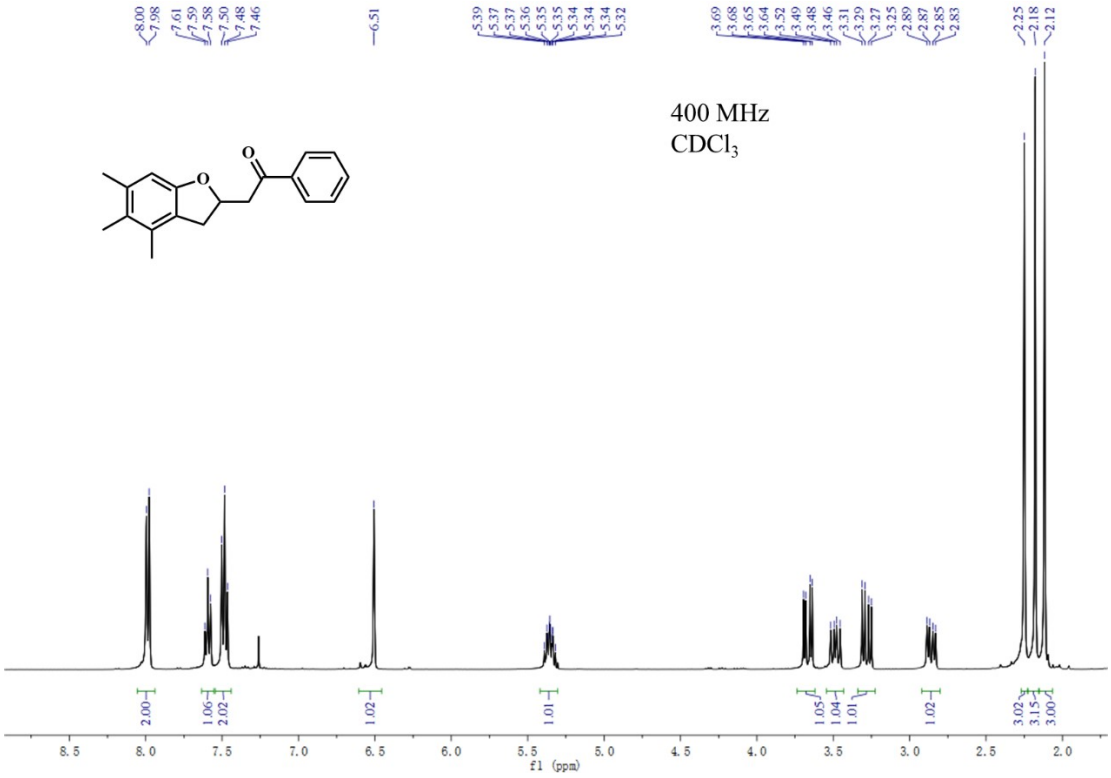


Figure S19. ^{13}C NMR spectra for **4i** (101MHz, $CDCl_3$)

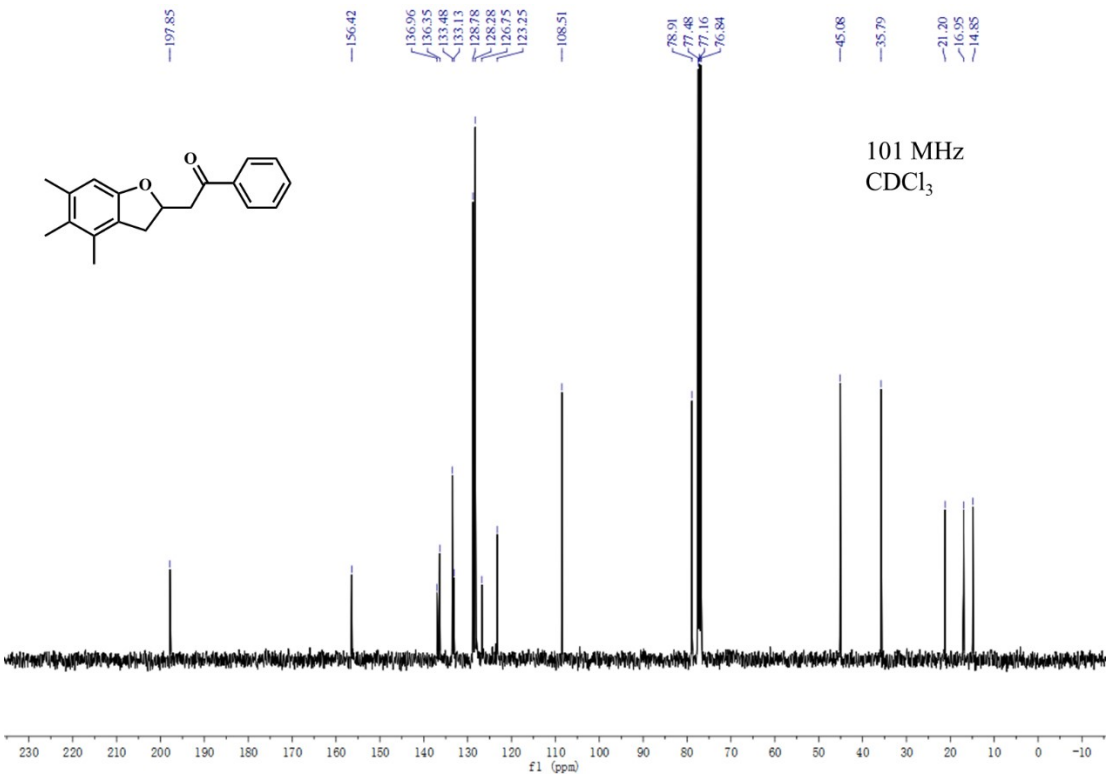


Figure S20. ^{1}H NMR spectra for **4j** (400MHz, $CDCl_3$)

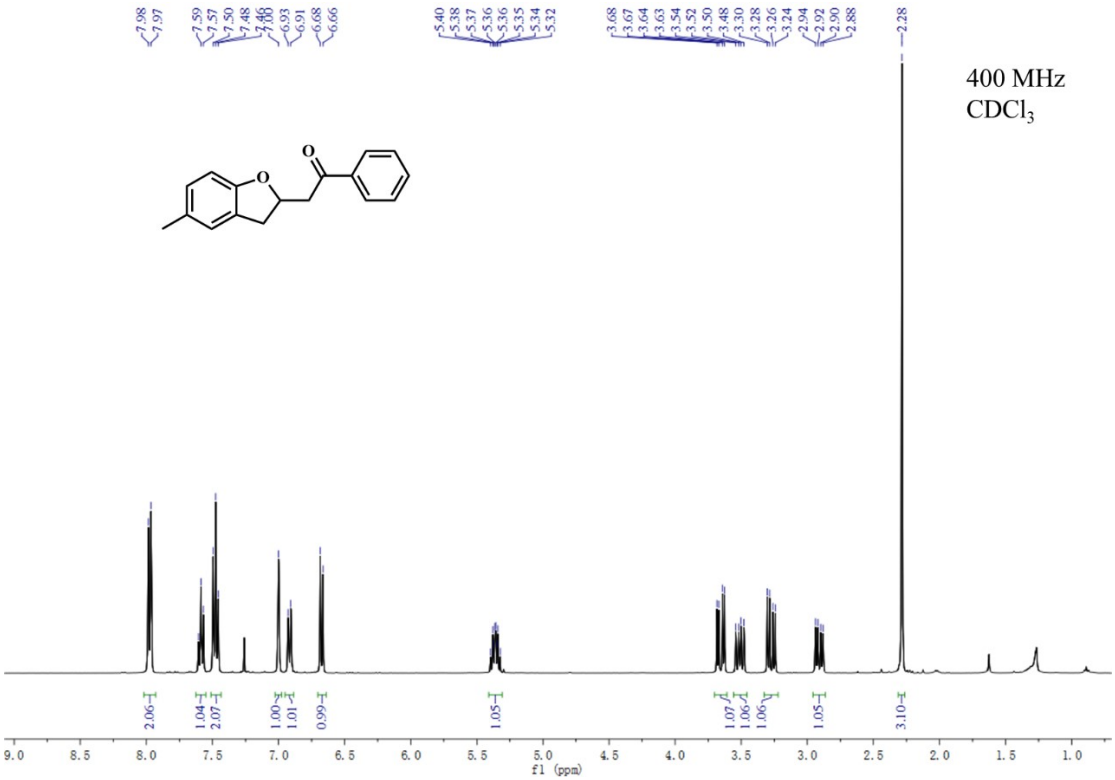


Figure S21. ^{13}C NMR spectra for **4j** (101MHz, $CDCl_3$)

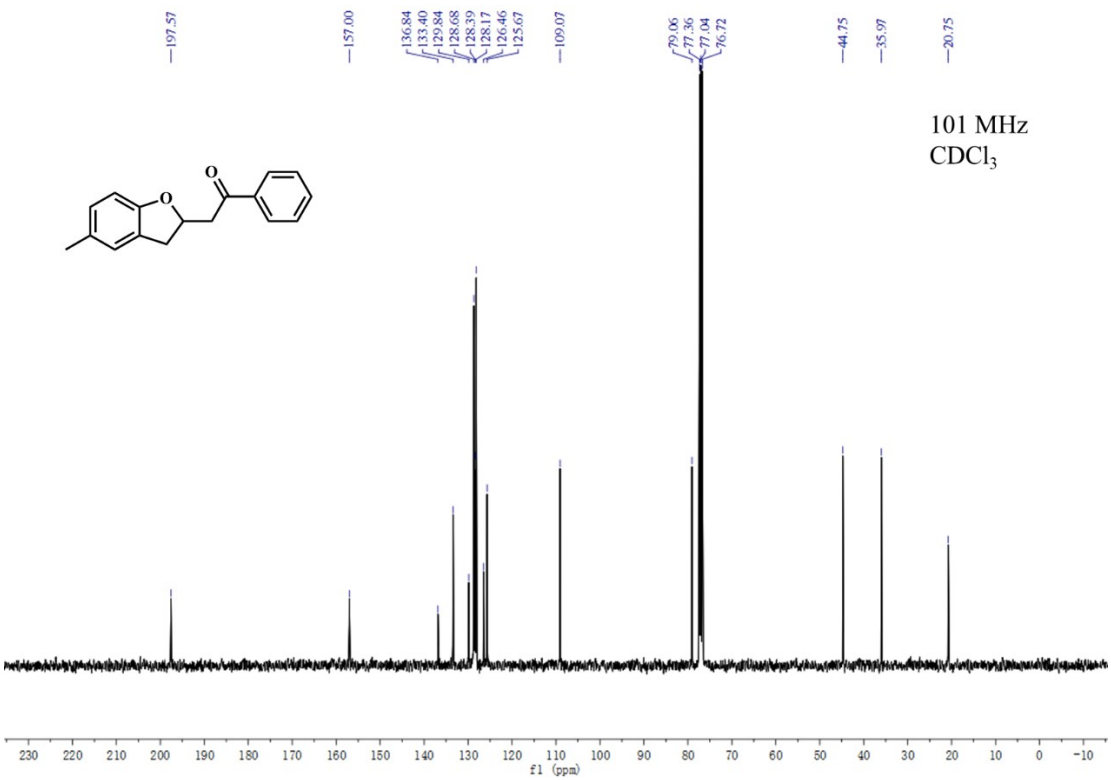


Figure S22. ^{1}H NMR spectra for **4k** (400MHz, $CDCl_3$)

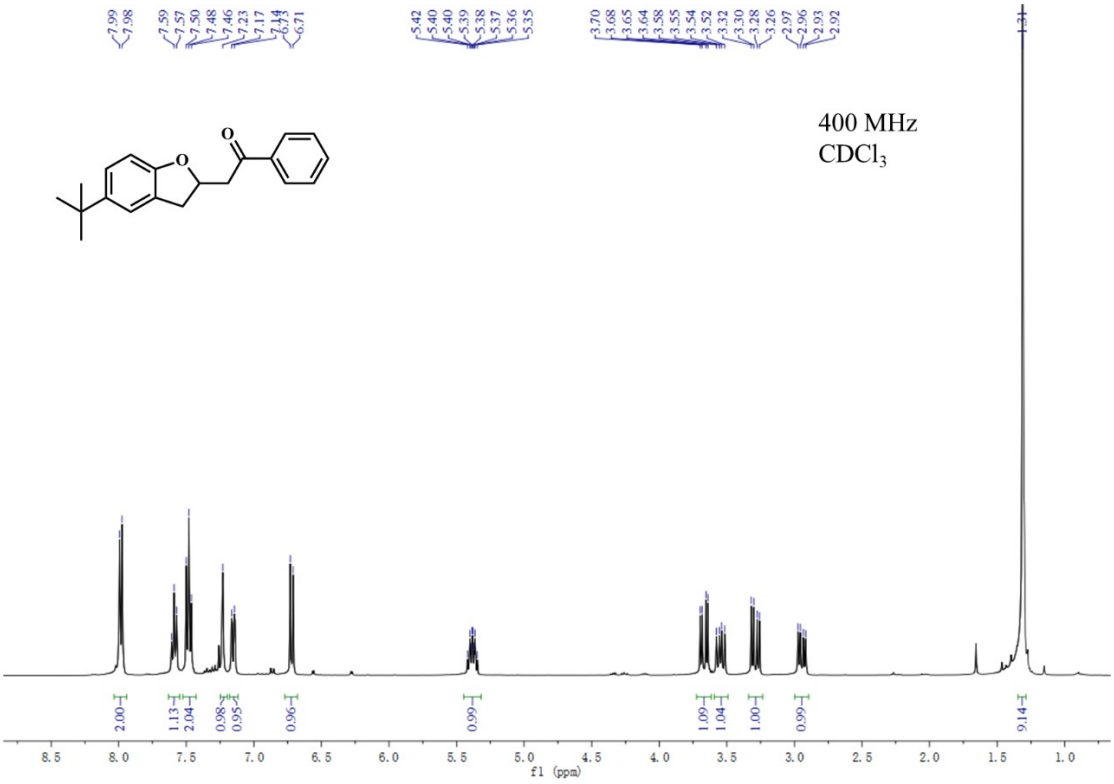


Figure S23. ^{13}C NMR spectra for **4k** (101MHz, $CDCl_3$)

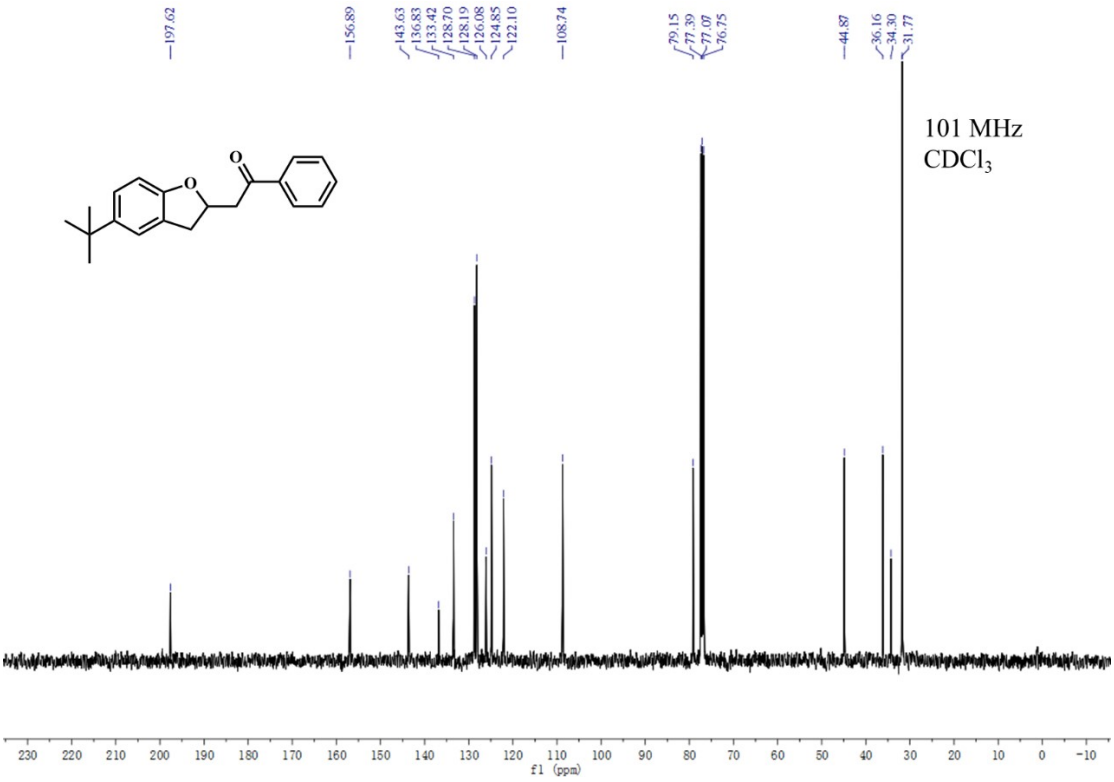


Figure S24. ^{1}H NMR spectra for **4m** (400MHz, $CDCl_3$)

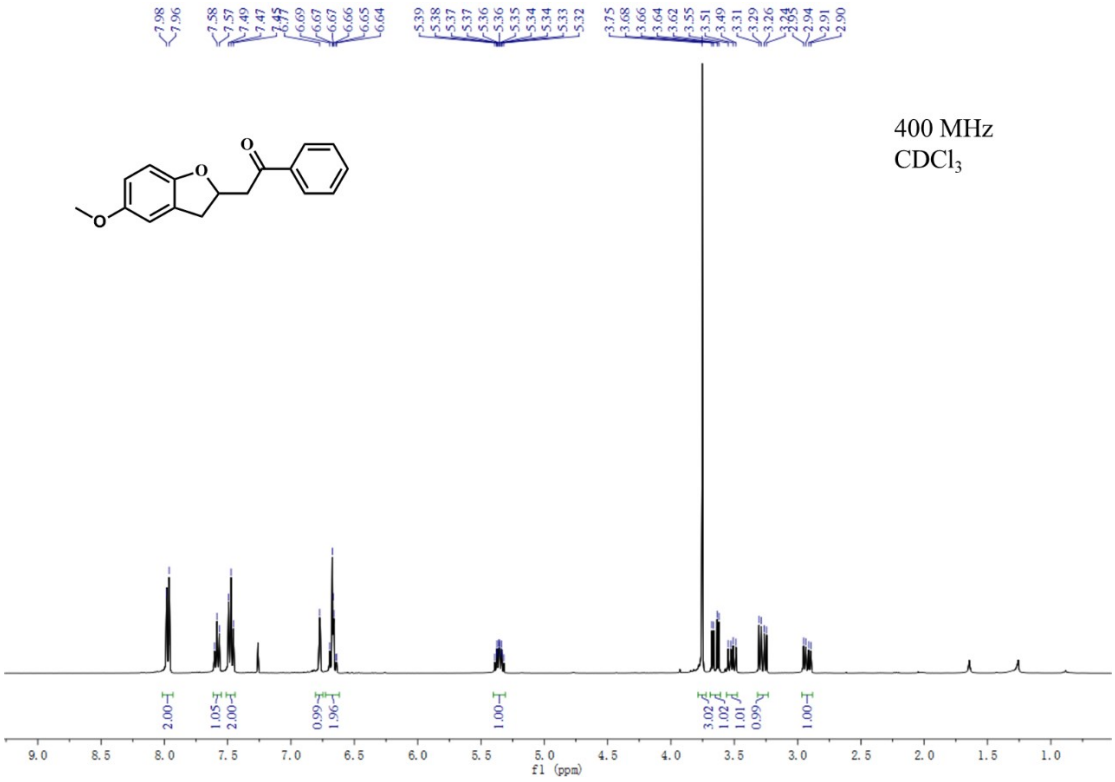


Figure S25. ^{13}C NMR spectra for **4m** (101MHz, $CDCl_3$)

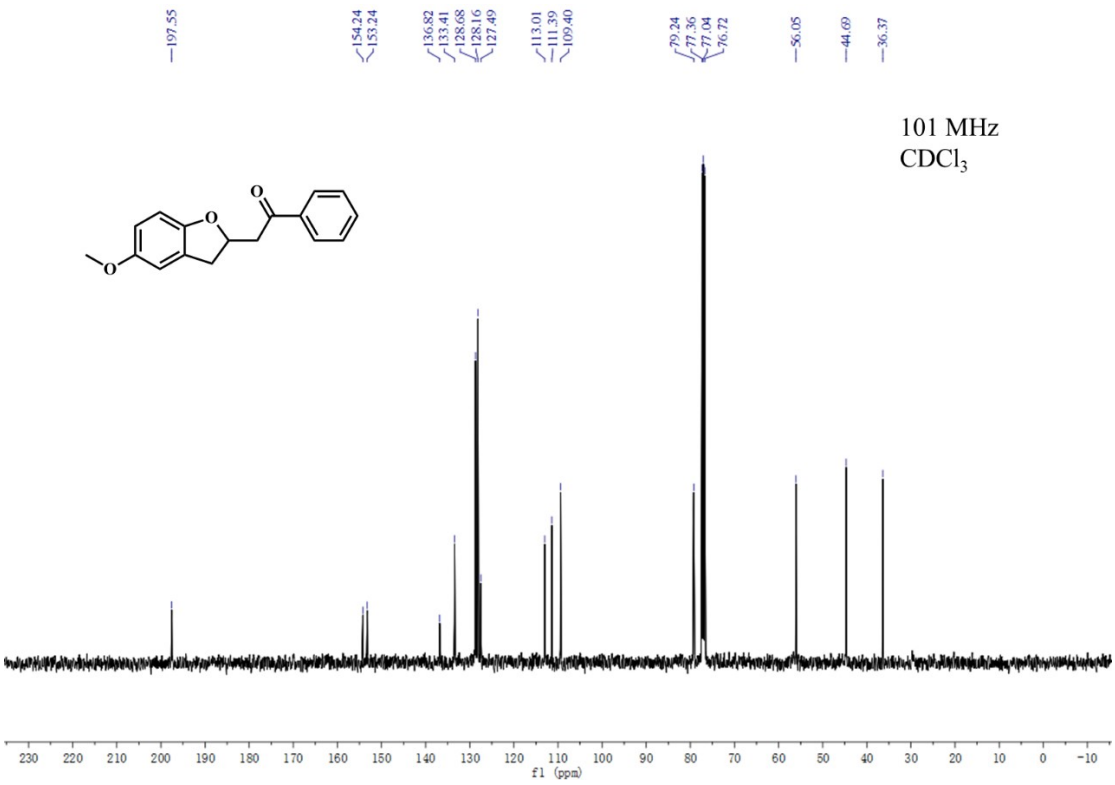


Figure S26. ^{1}H NMR spectra for **4n** (400MHz, $CDCl_3$)

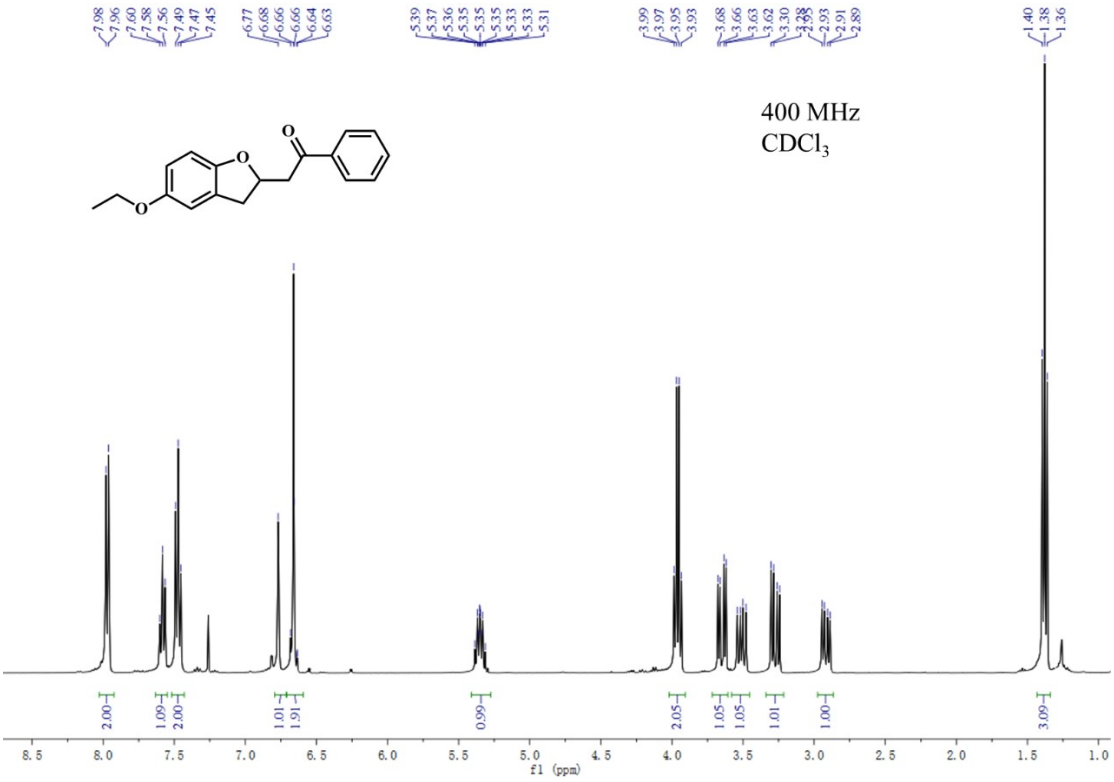


Figure S27. ^{13}C NMR spectra for **4n** (101MHz, $CDCl_3$)

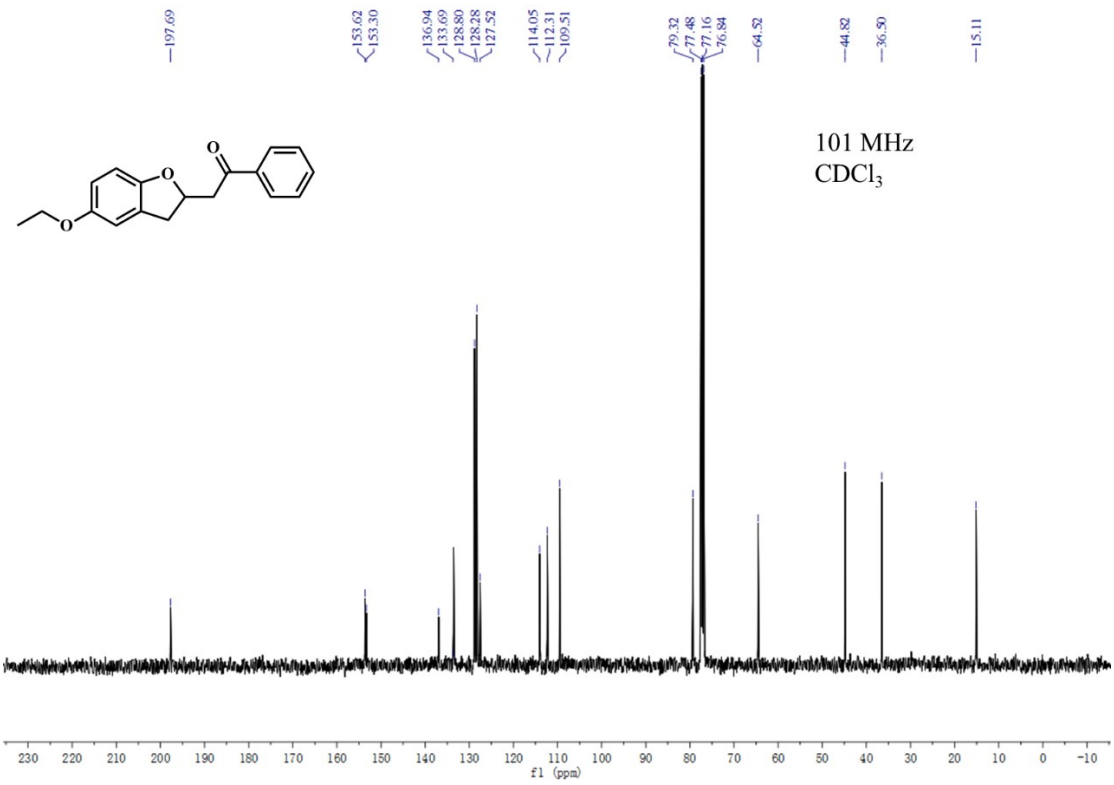


Figure S28. ^{1}H NMR spectra for **4o** (400MHz, $CDCl_3$)

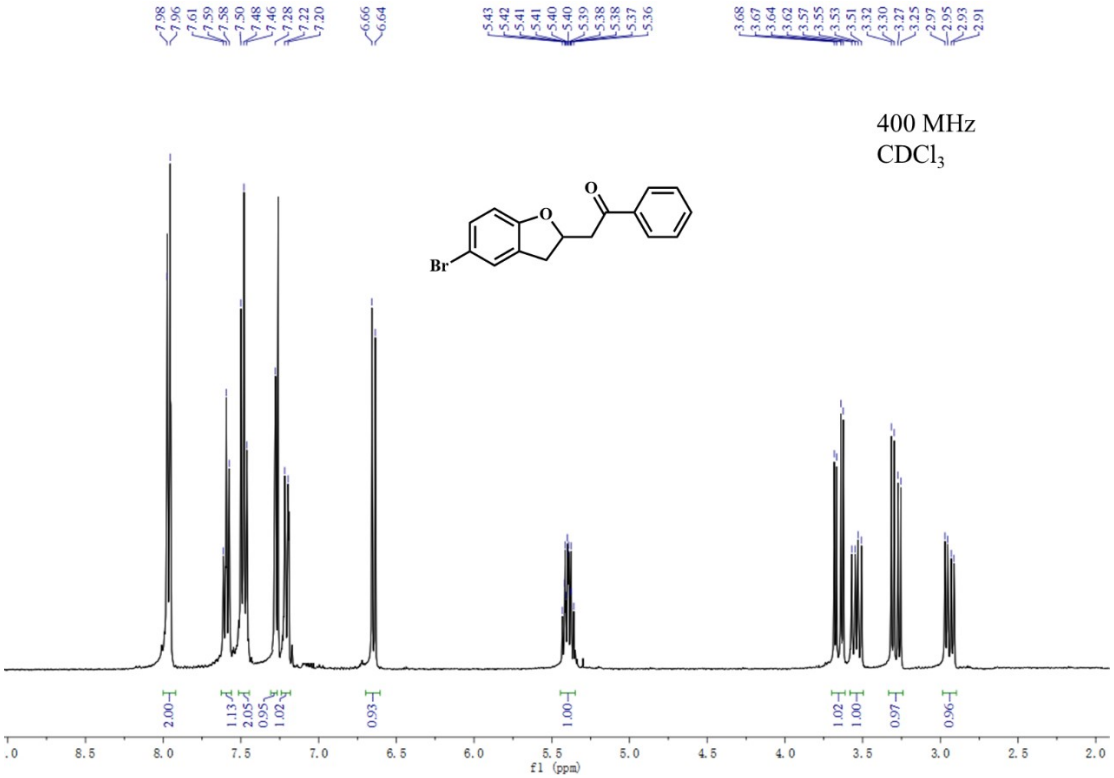


Figure S29. ^{13}C NMR spectra for **4o** (101MHz, $CDCl_3$)

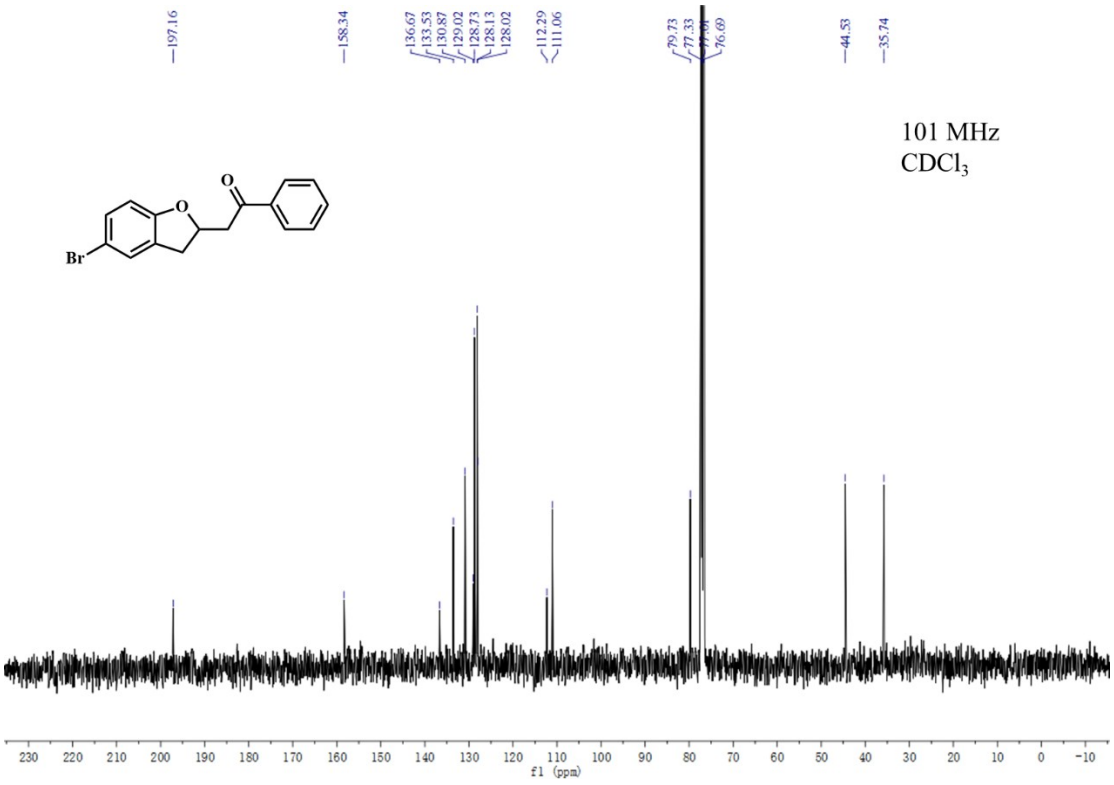


Figure S30. ^{1}H NMR spectra for **4p** (400MHz, $CDCl_3$)

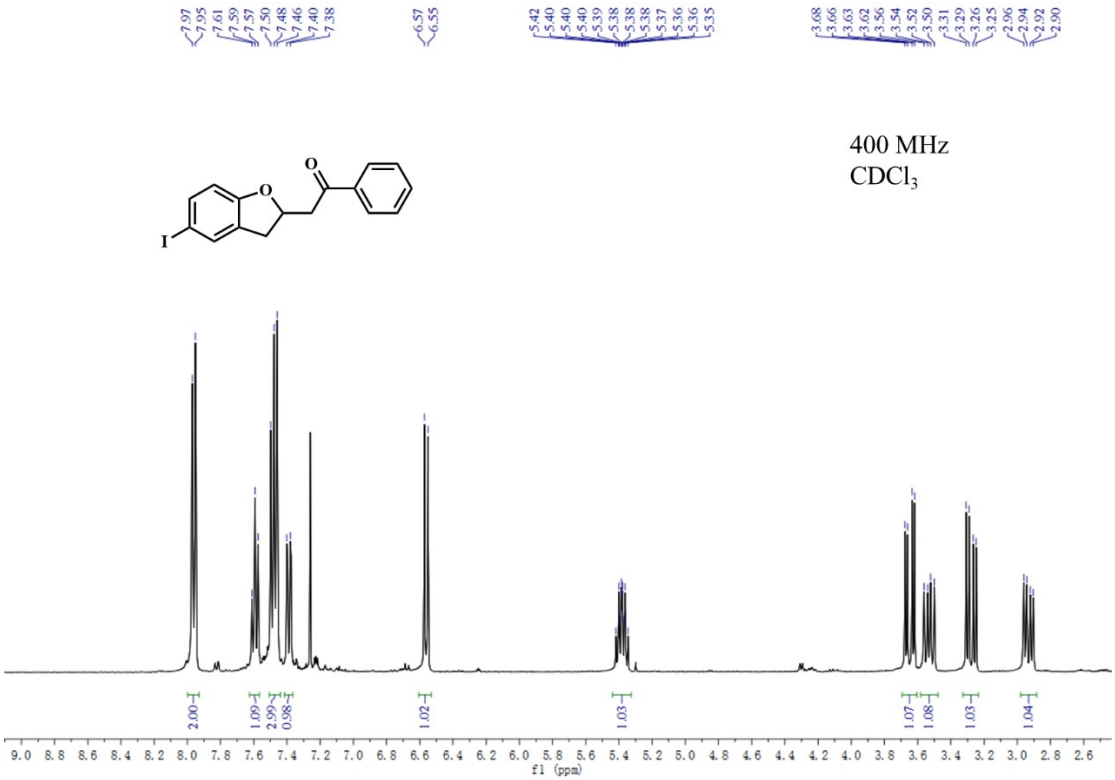


Figure S31. ^{13}C NMR spectra for **4p** (151MHz, $CDCl_3$)

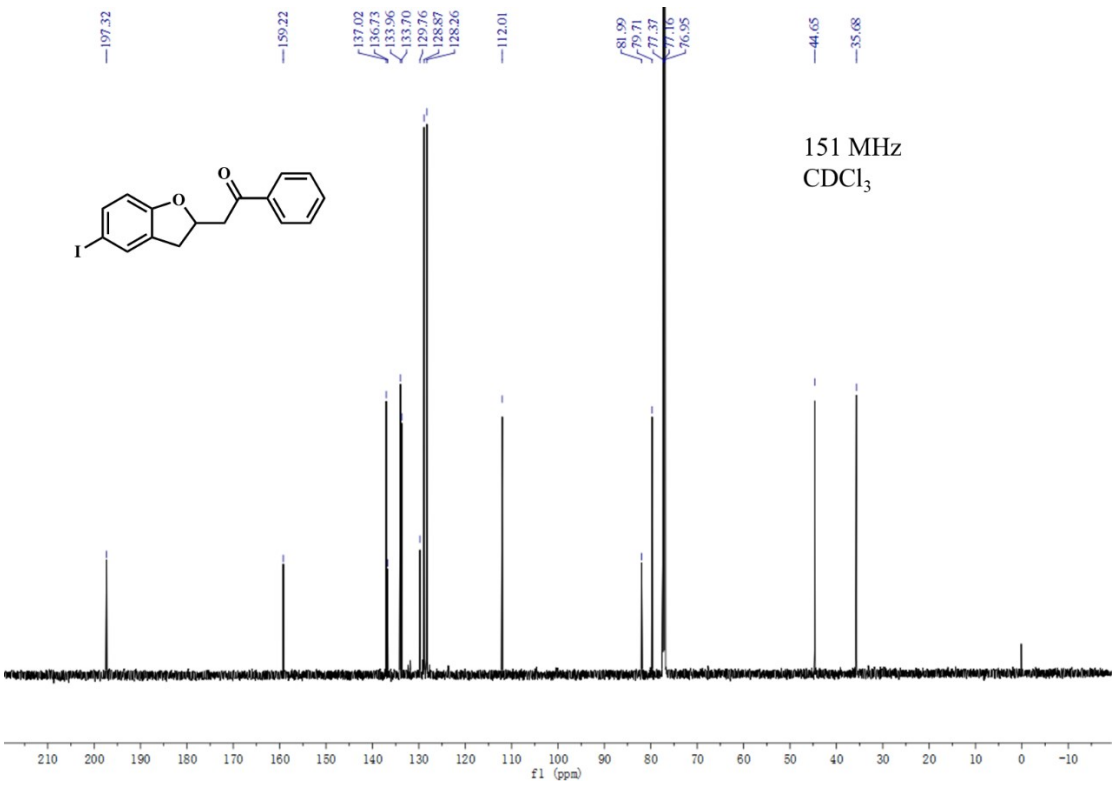


Figure S32. ^{1}H NMR spectra for **4q** (400MHz, $CDCl_3$)

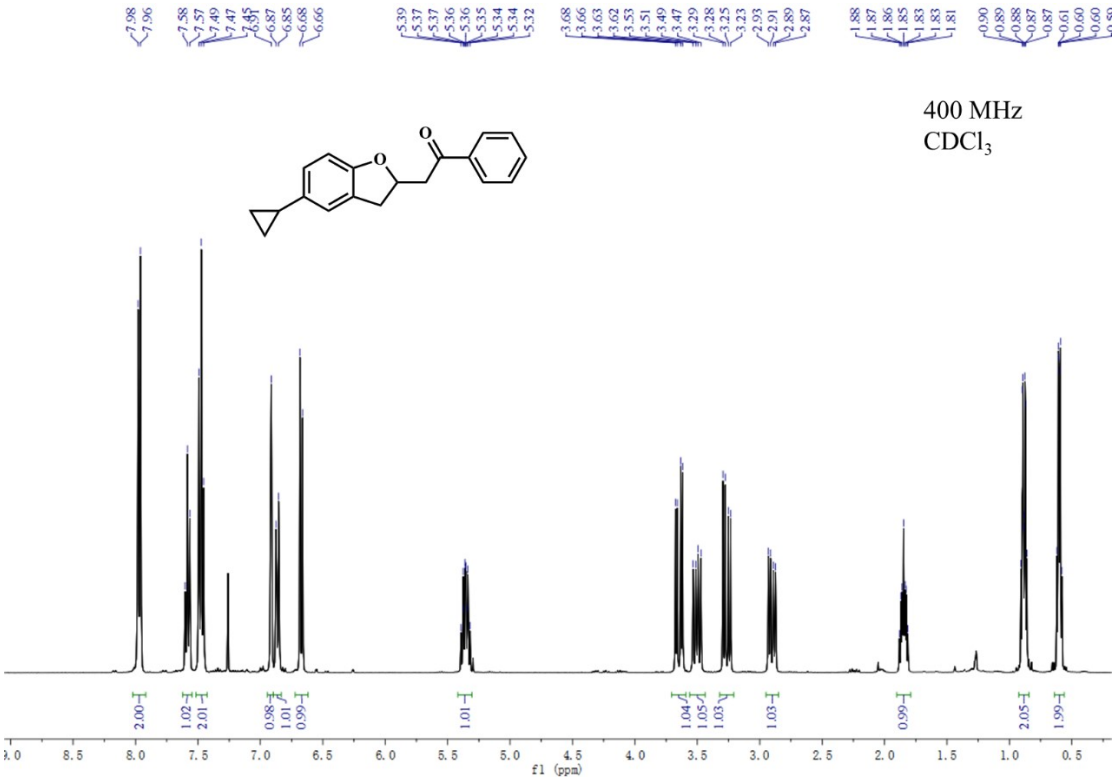


Figure S33. ^{13}C NMR spectra for **4q** (101MHz, $CDCl_3$)

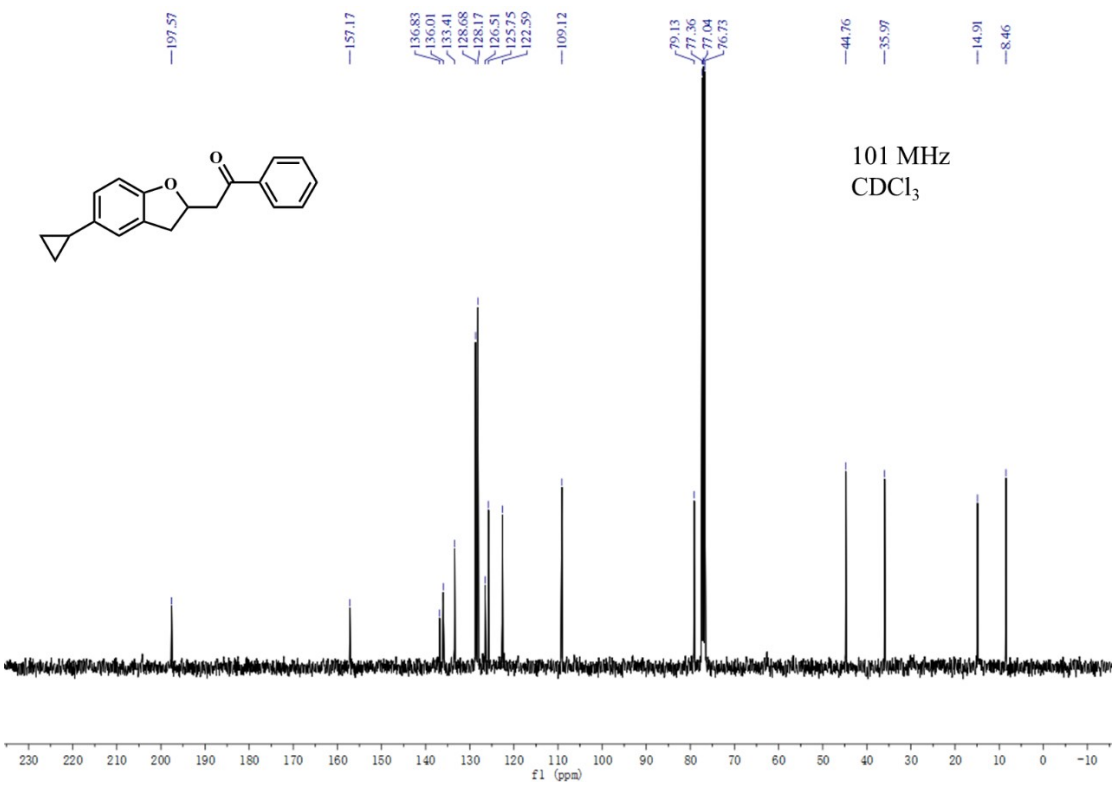


Figure S34. ^{1}H NMR spectra for **4r** (400MHz, $CDCl_3$)

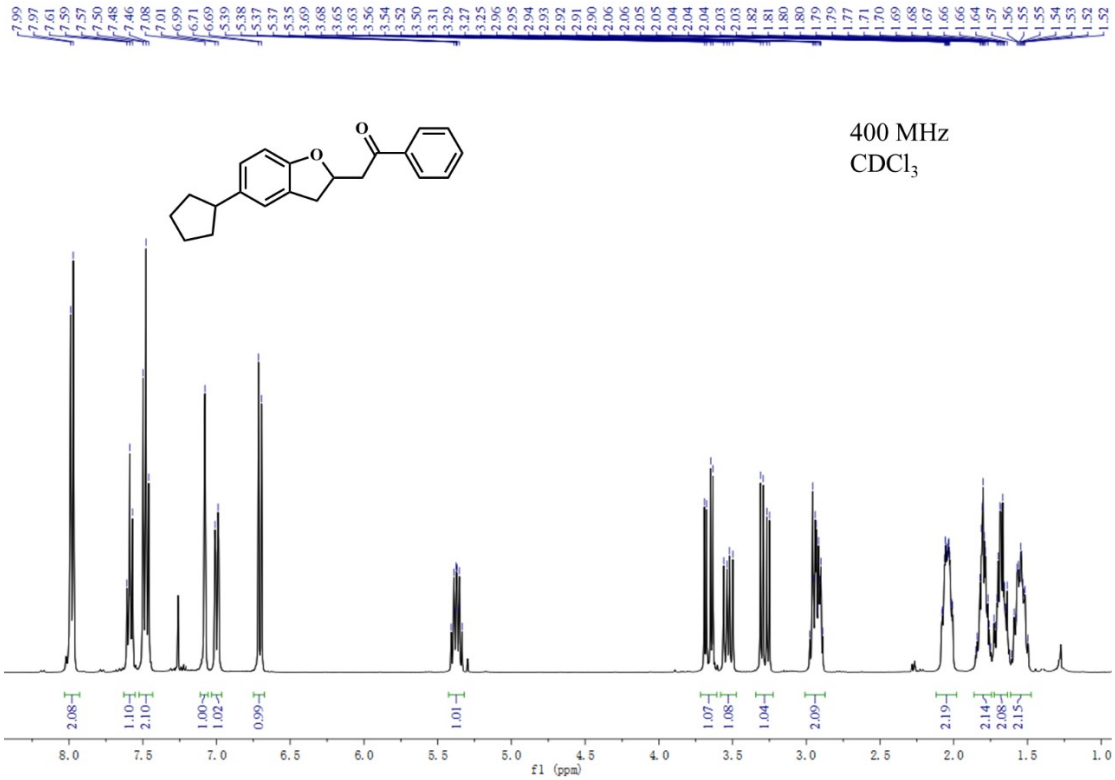


Figure S35. ^{13}C NMR spectra for **4r** (101MHz, $CDCl_3$)

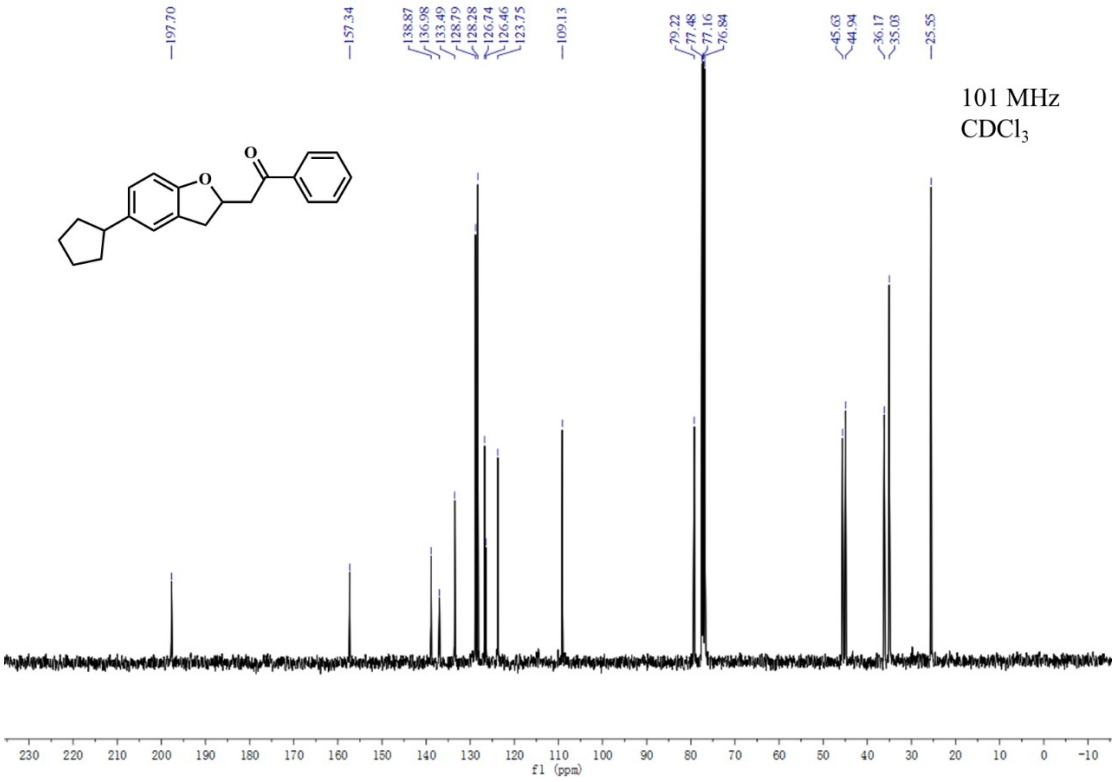


Figure S36. ^{1}H NMR spectra for **4s** (400MHz, $CDCl_3$)

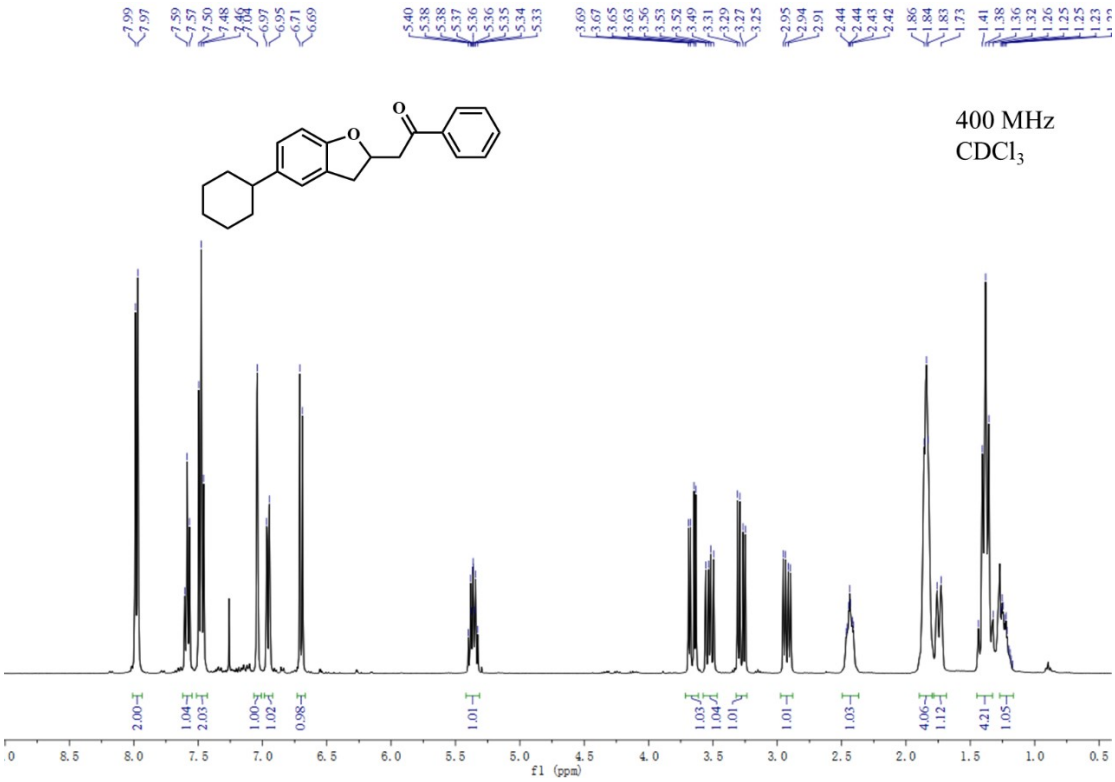


Figure S37. ^{13}C NMR spectra for **4s** (101MHz, $CDCl_3$)

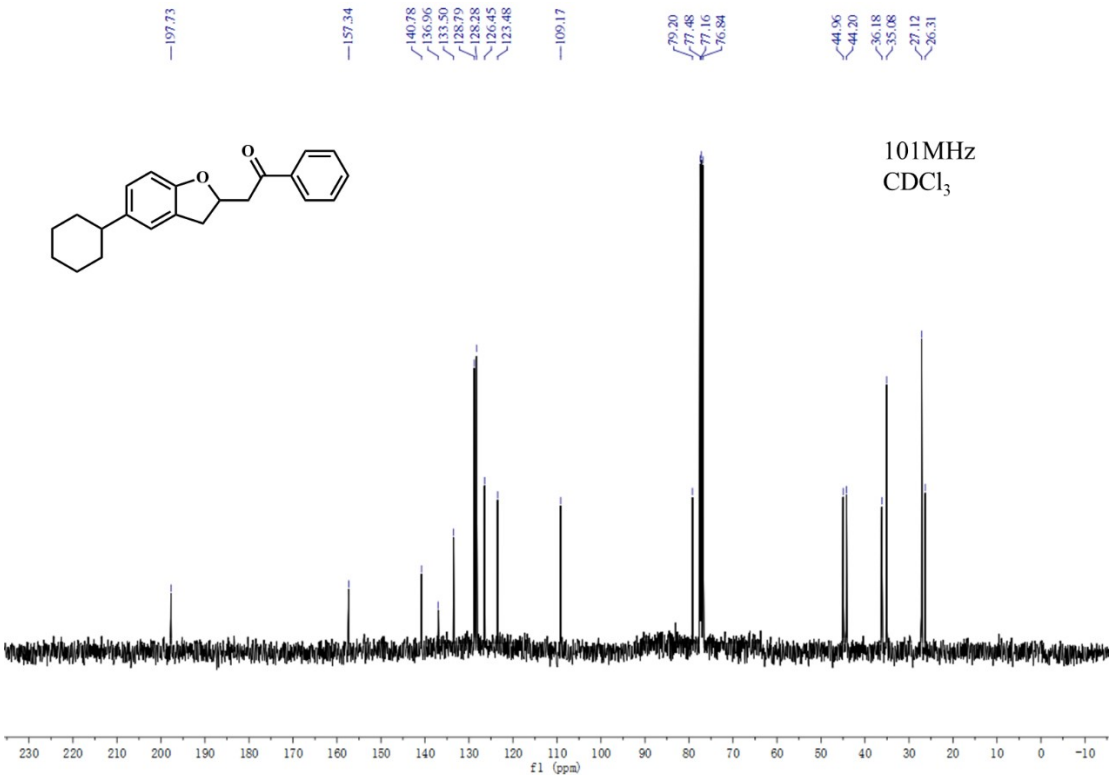


Figure S38. ^{1}H NMR spectra for **7b** (600MHz, $CDCl_3$)

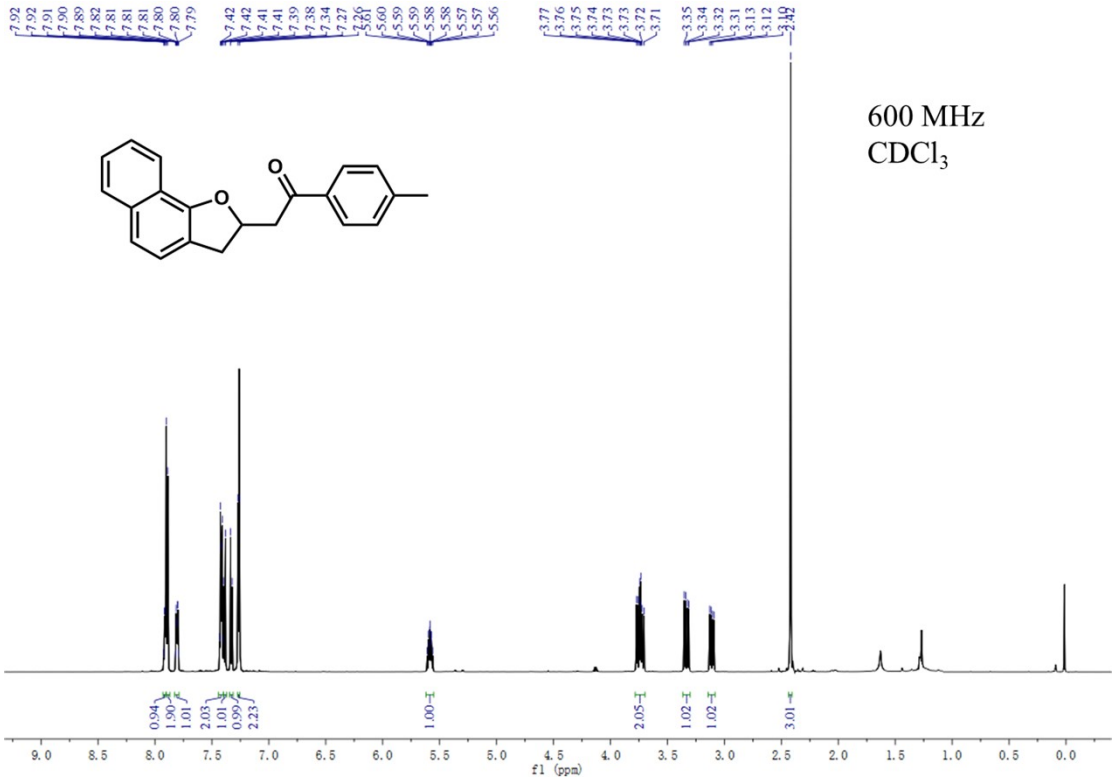


Figure S39. ^{13}C NMR spectra for **7b** (151MHz, $CDCl_3$)

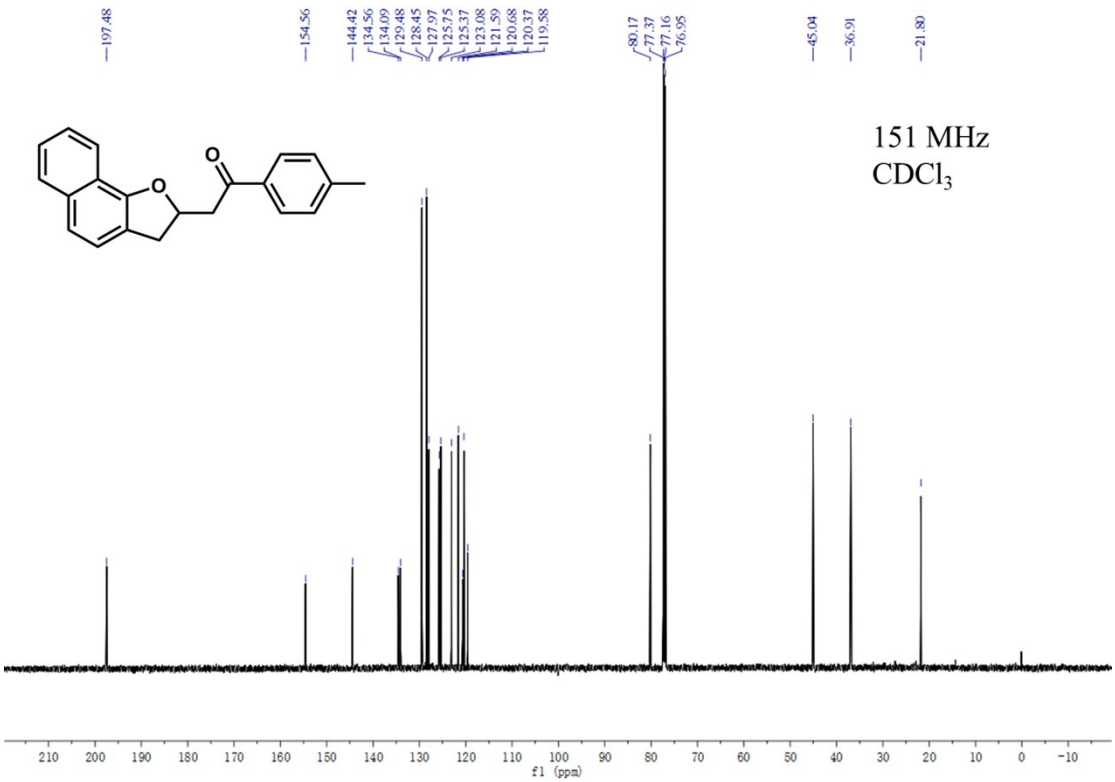


Figure S40. ^{1}H NMR spectra for **7c** (600MHz, $CDCl_3$)

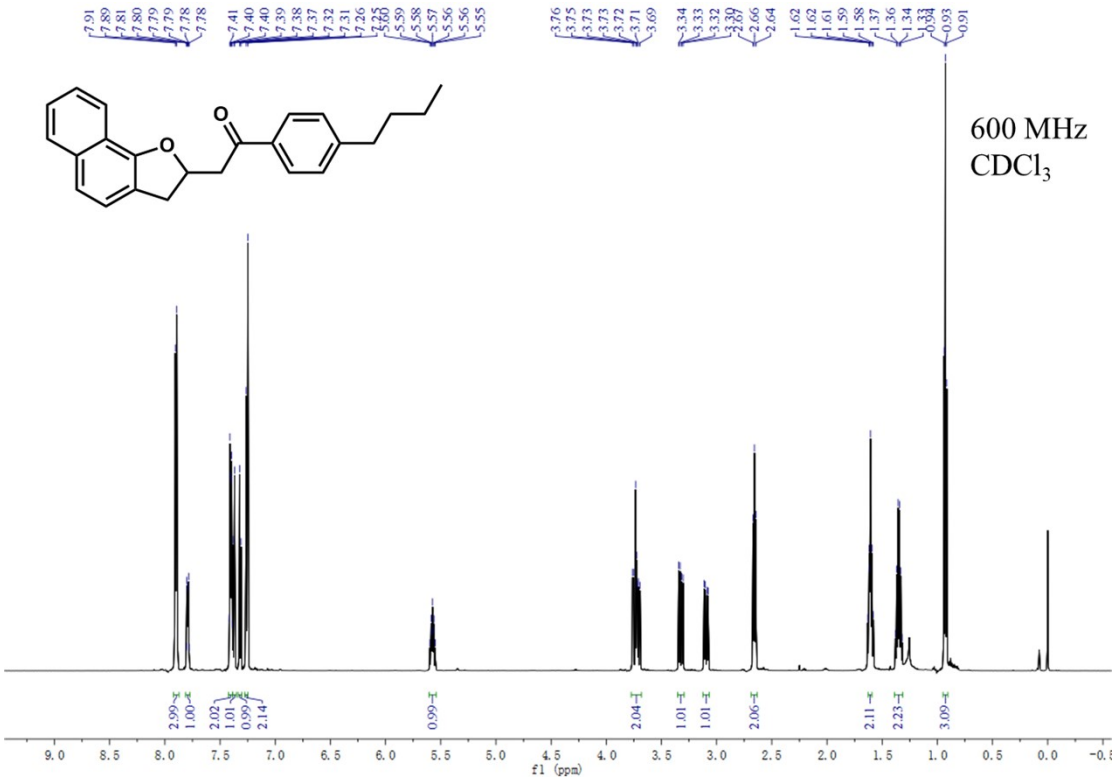


Figure S41. ^{13}C NMR spectra for **7c** (151MHz, $CDCl_3$)

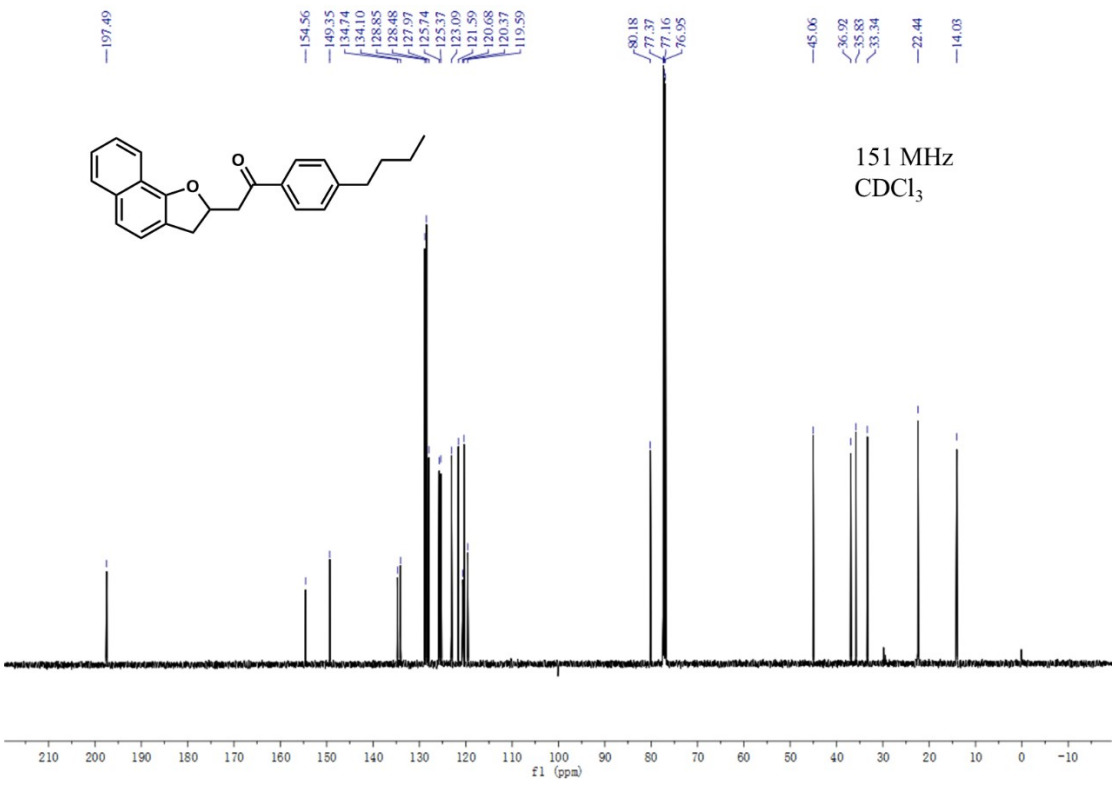


Figure S42. ^{1}H NMR spectra for **7d** (600MHz, $CDCl_3$)

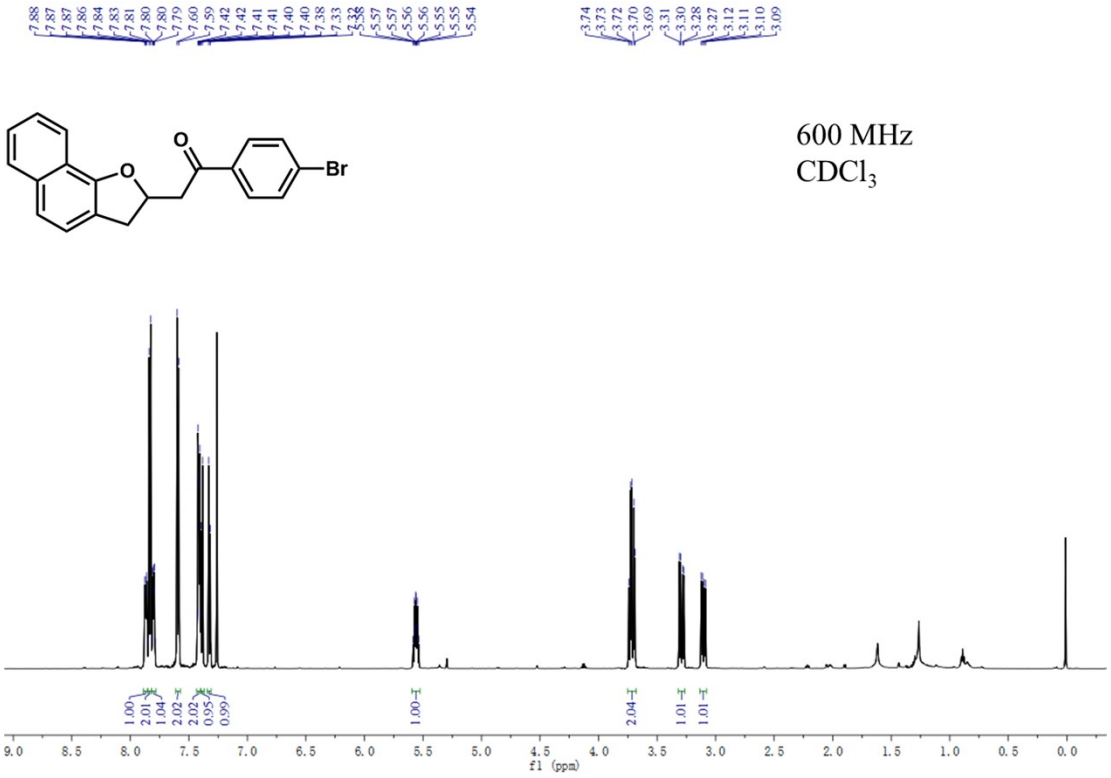


Figure S43. ^{13}C NMR spectra for **7d** (151MHz, $CDCl_3$)

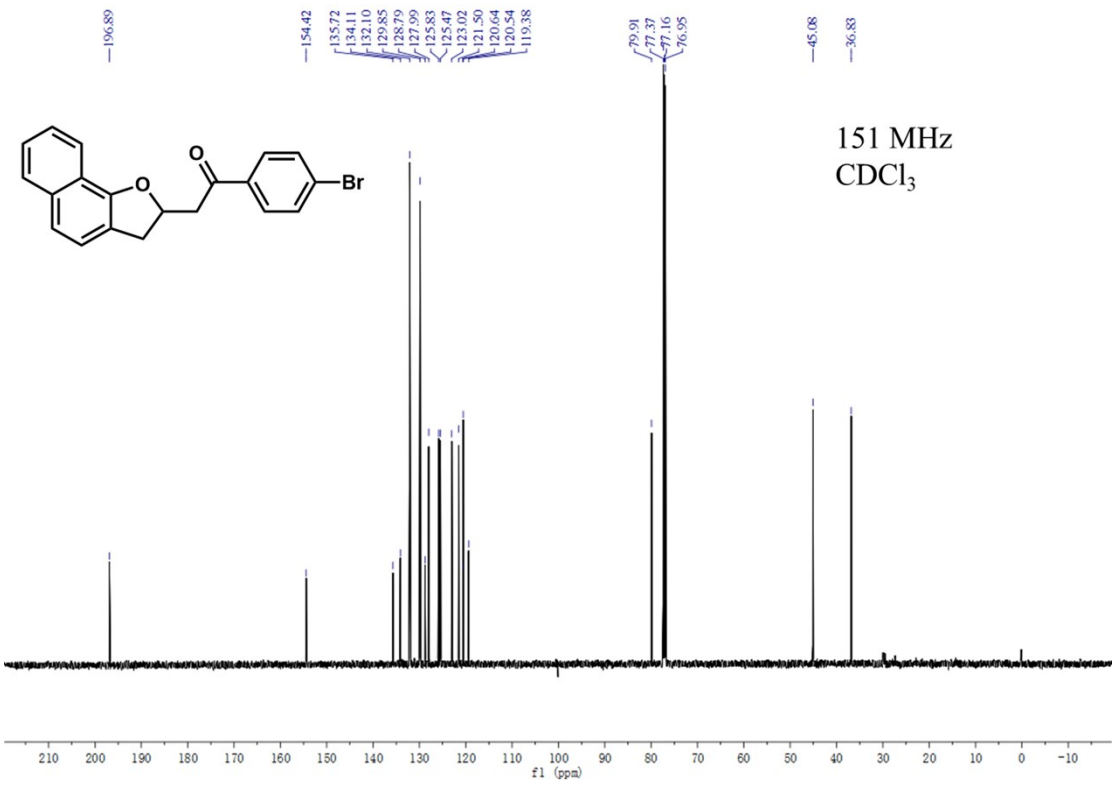


Figure S44. ^{1}H NMR spectra for **7e** (600MHz, $CDCl_3$)

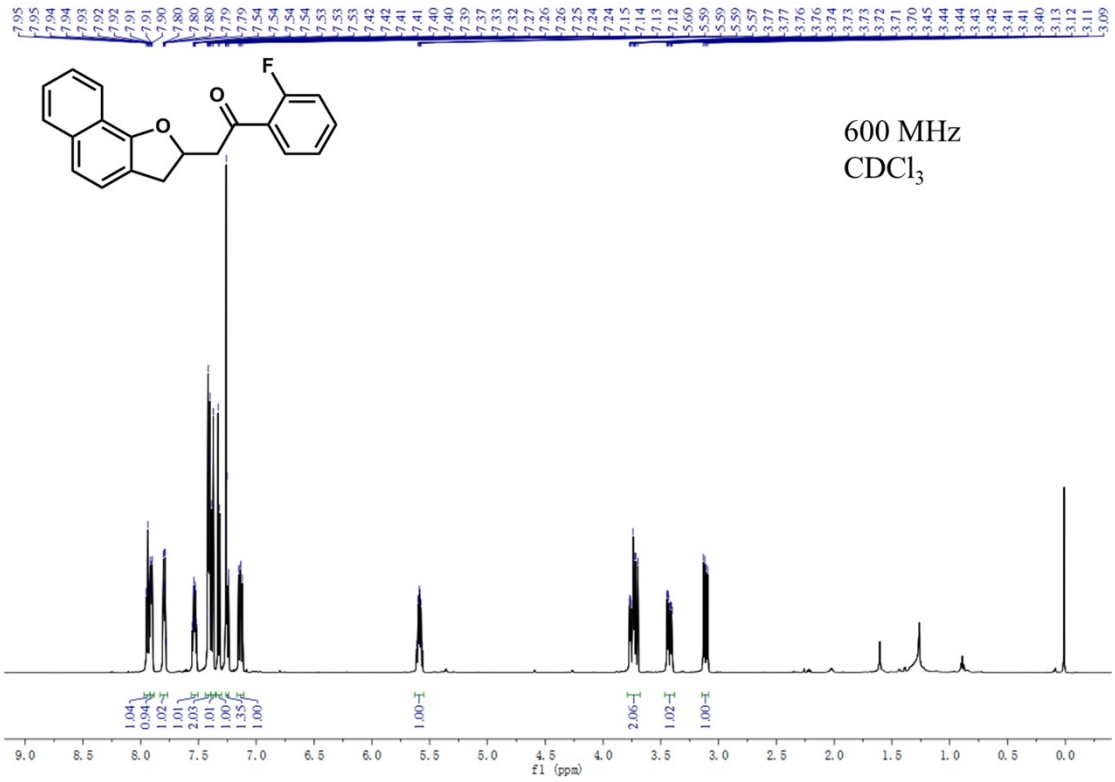


Figure S45. ^{13}C NMR spectra for **7e** (151MHz, $CDCl_3$)

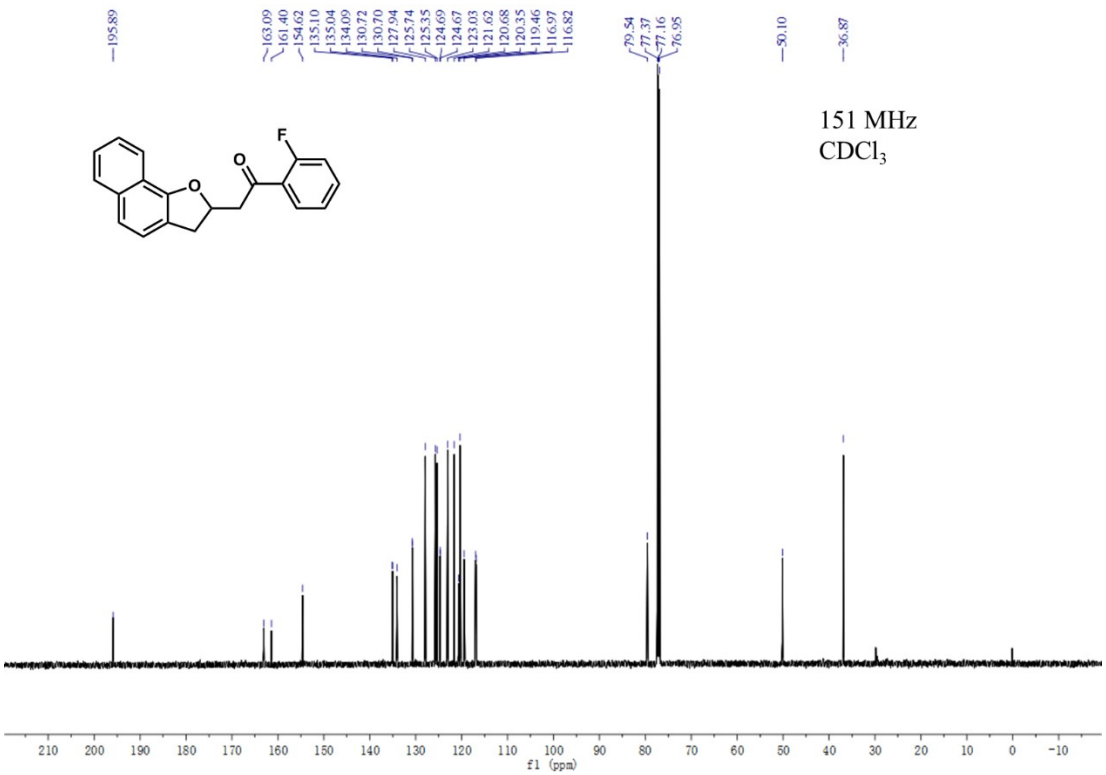


Figure S46. ^{19}F NMR spectra for **7e** (565MHz, $CDCl_3$)

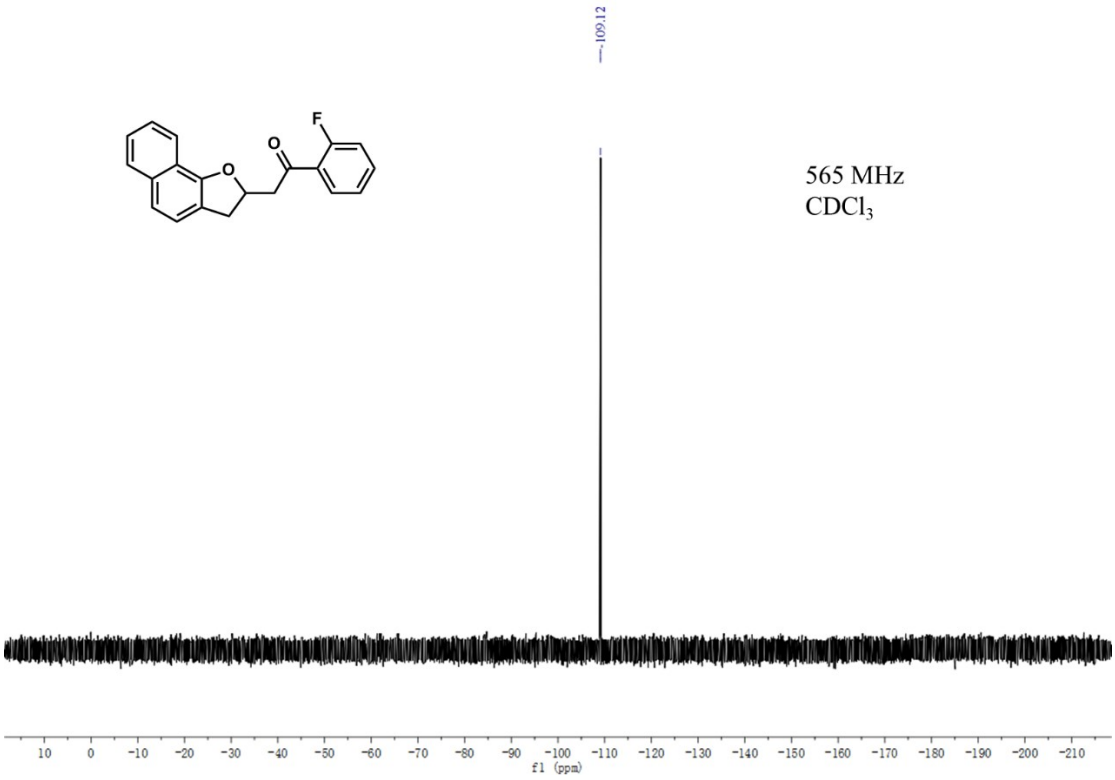


Figure S47. ^{1}H NMR spectra for **7f** (600MHz, $CDCl_3$)

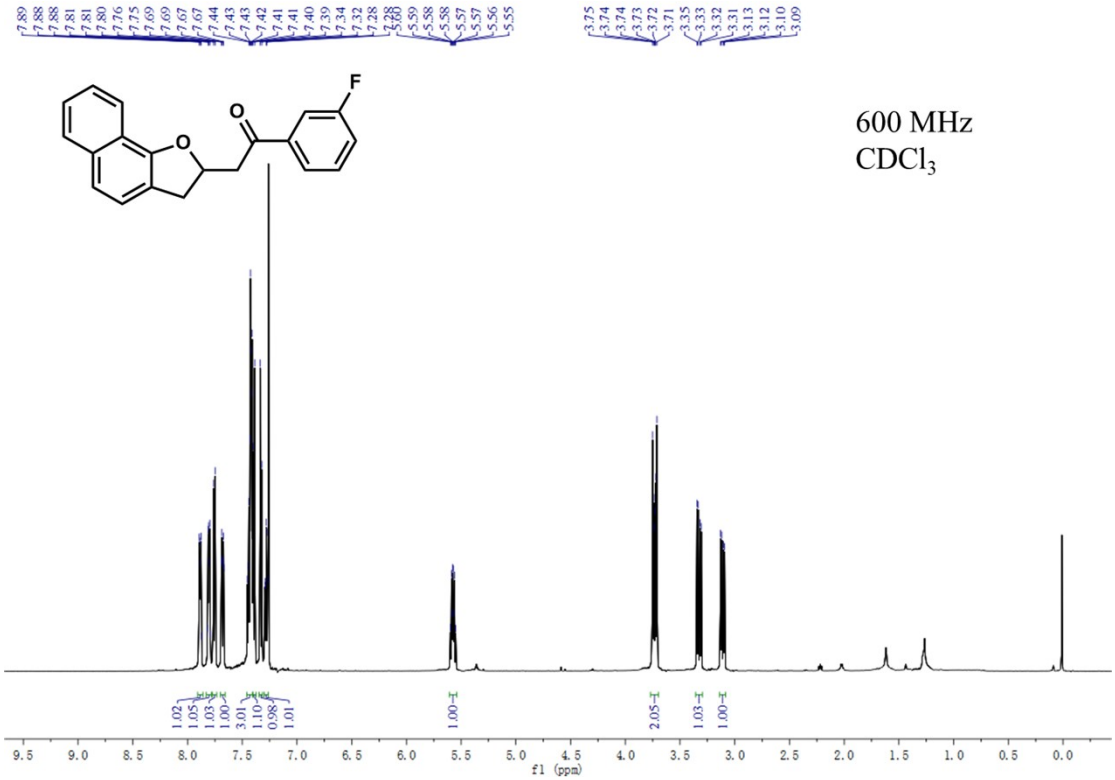


Figure S48. ^{13}C NMR spectra for **7f** (151MHz, $CDCl_3$)

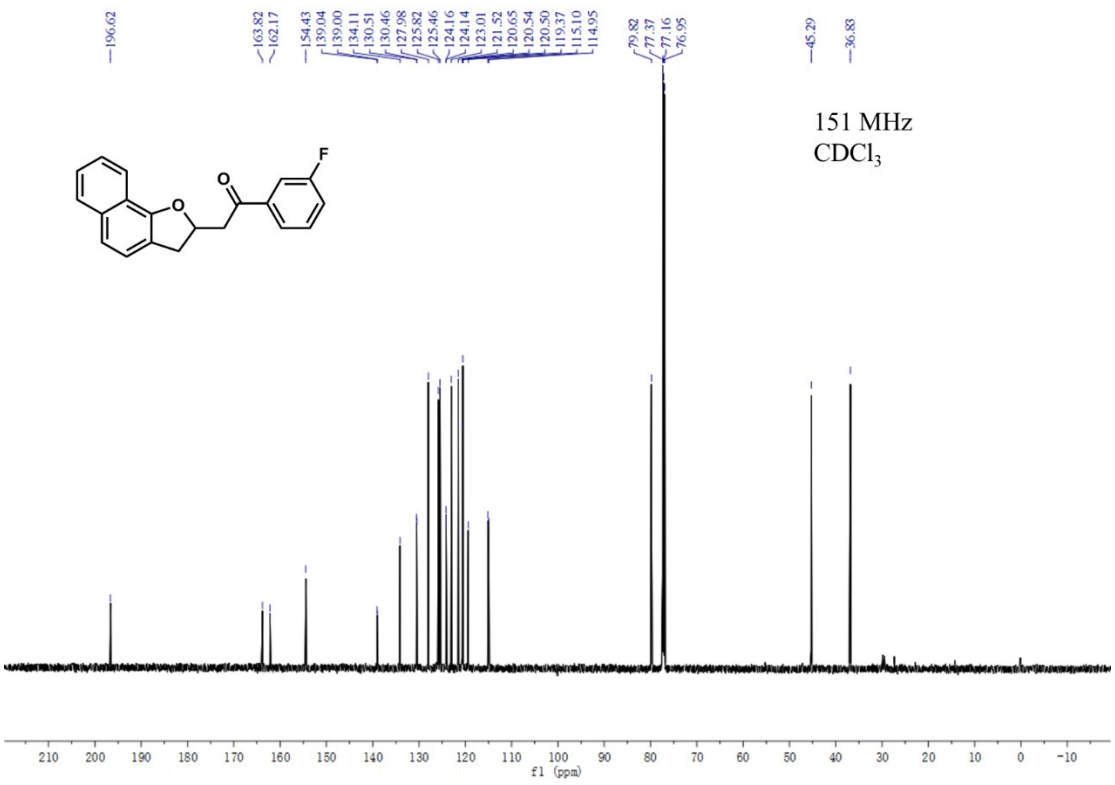


Figure S49. ^{19}F NMR spectra for **7f** (565MHz, $CDCl_3$)

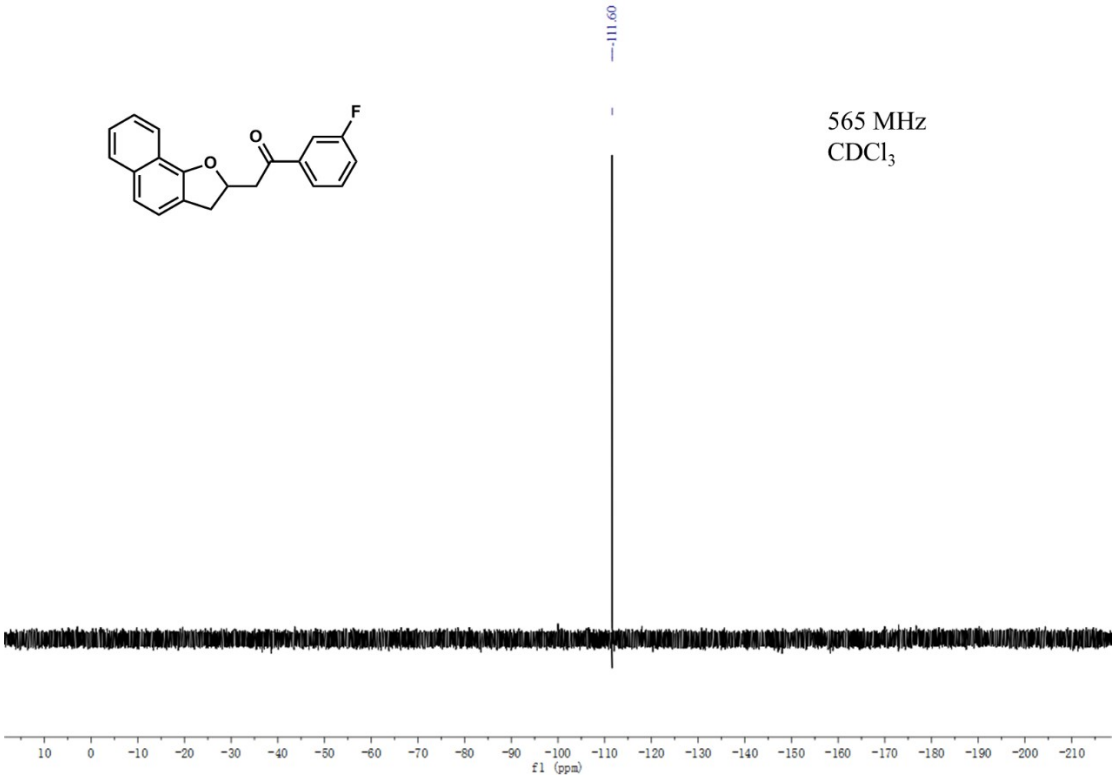


Figure S50. ^{1}H NMR spectra for **7g** (600MHz, $CDCl_3$)

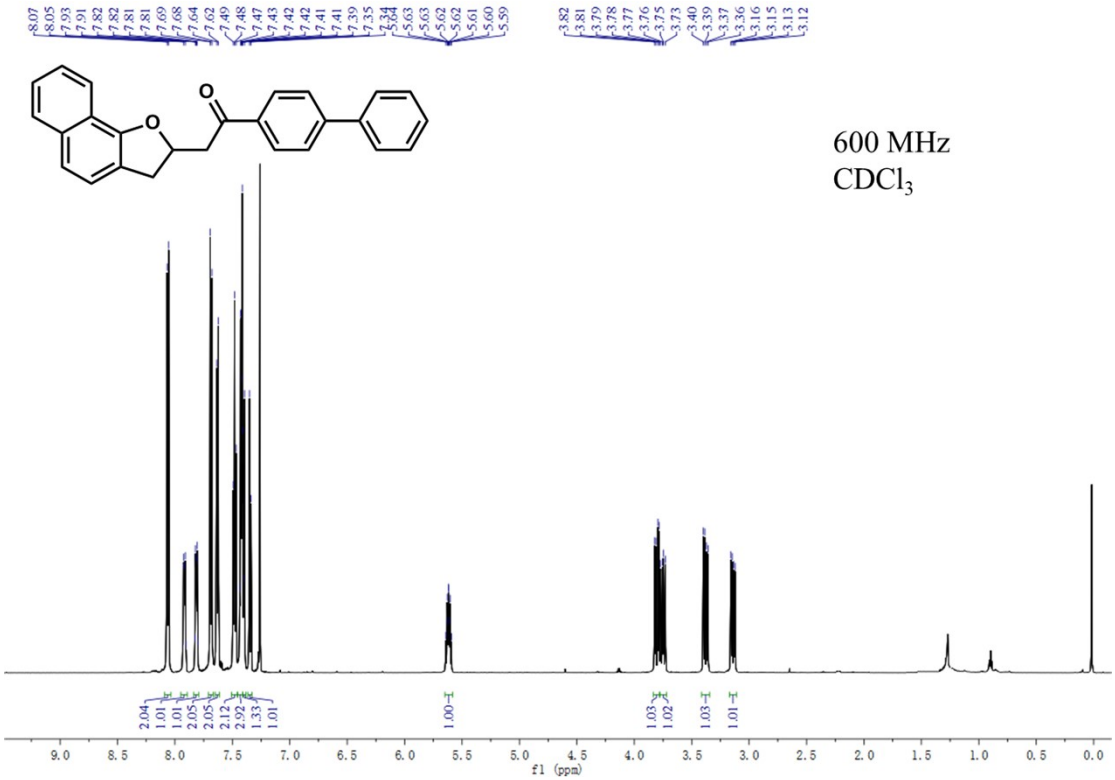


Figure S51. ^{13}C NMR spectra for **7g** (151MHz, $CDCl_3$)

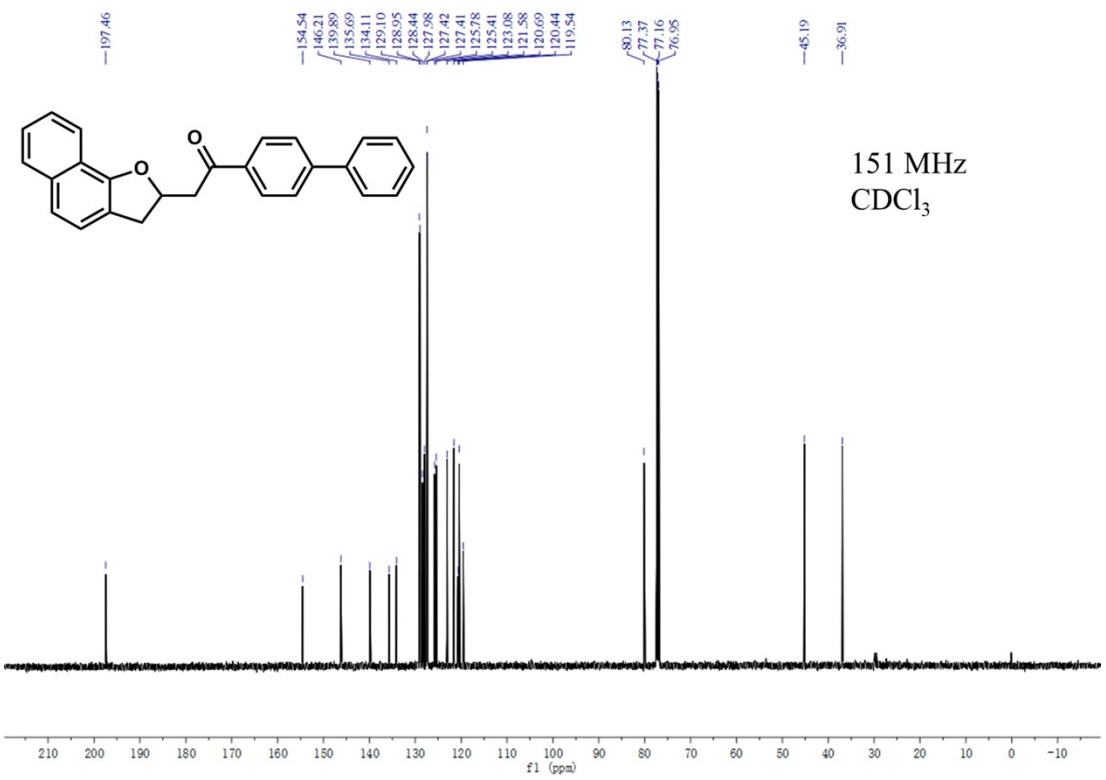


Figure S52. ^{1}H NMR spectra for **7h** (600MHz, $CDCl_3$)

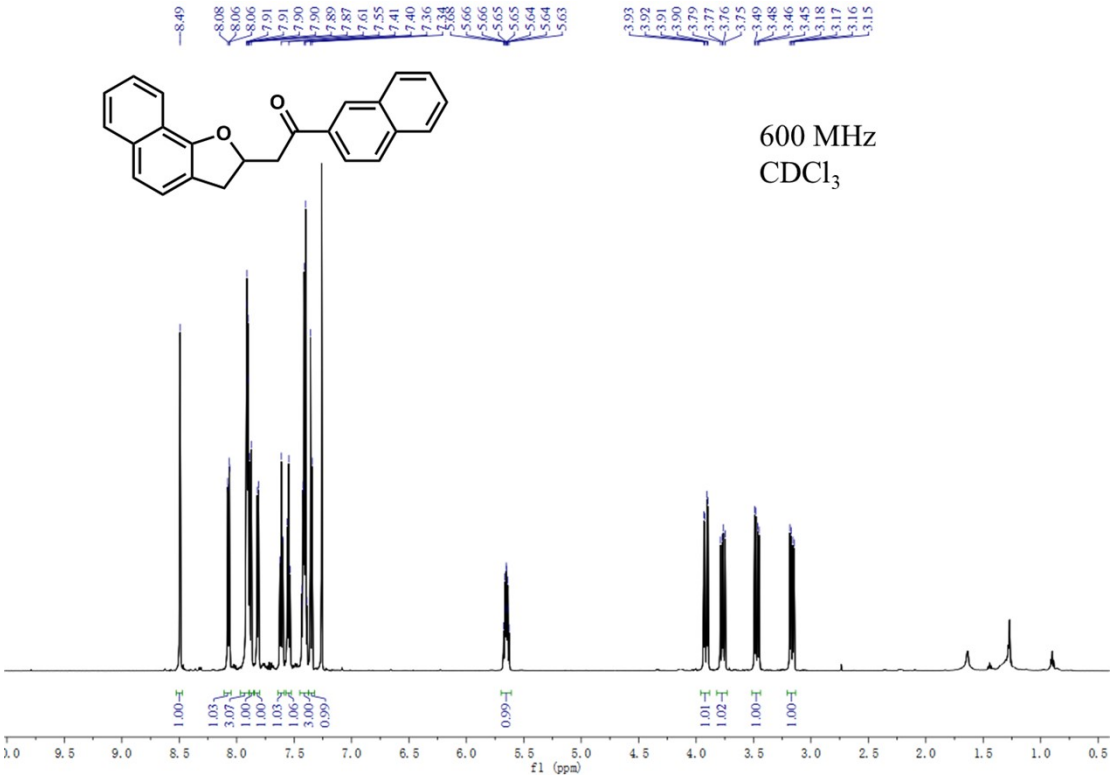


Figure S53. ^{13}C NMR spectra for **7h** (151MHz, $CDCl_3$)

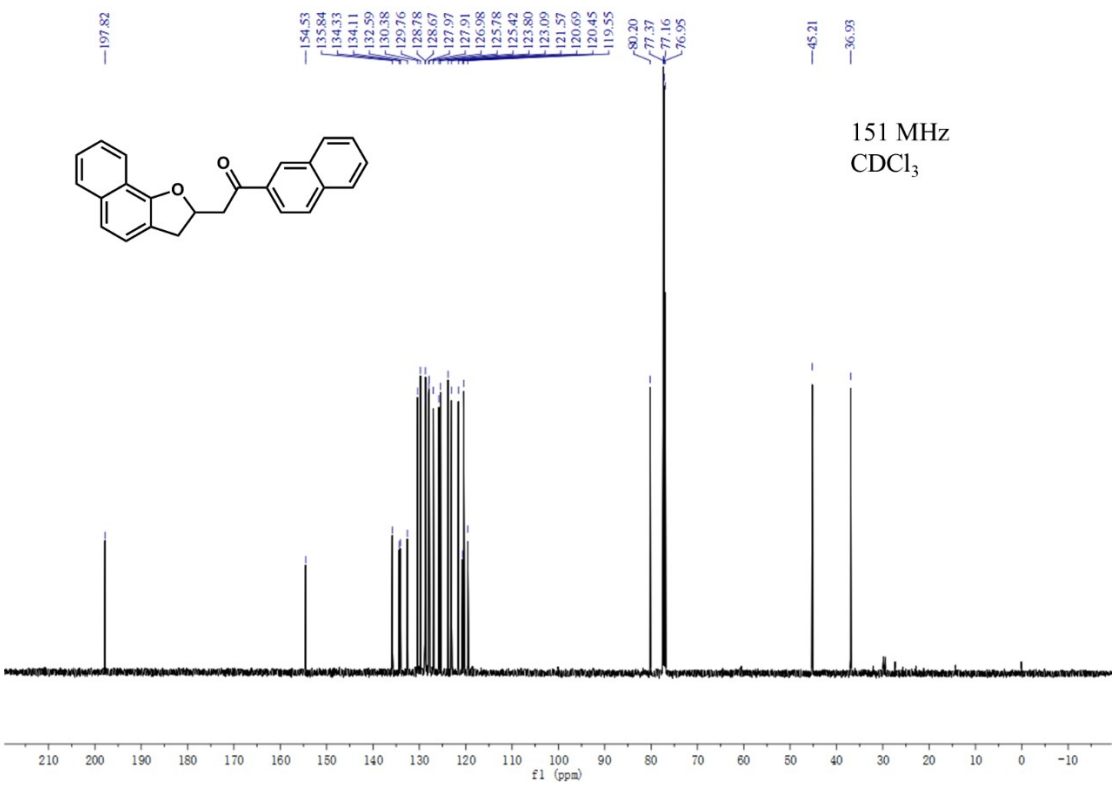


Figure S54. ^{1}H NMR spectra for **7i** (600MHz, $CDCl_3$)

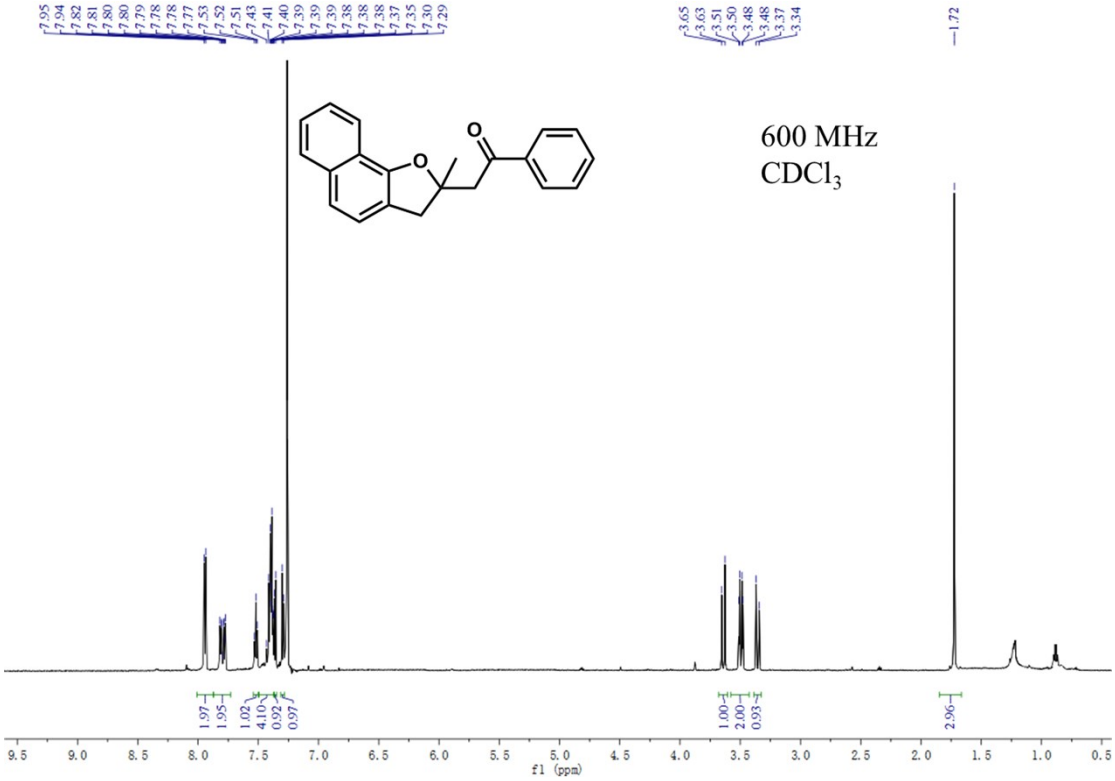


Figure S55. ^{13}C NMR spectra for **7i** (151MHz, $CDCl_3$)

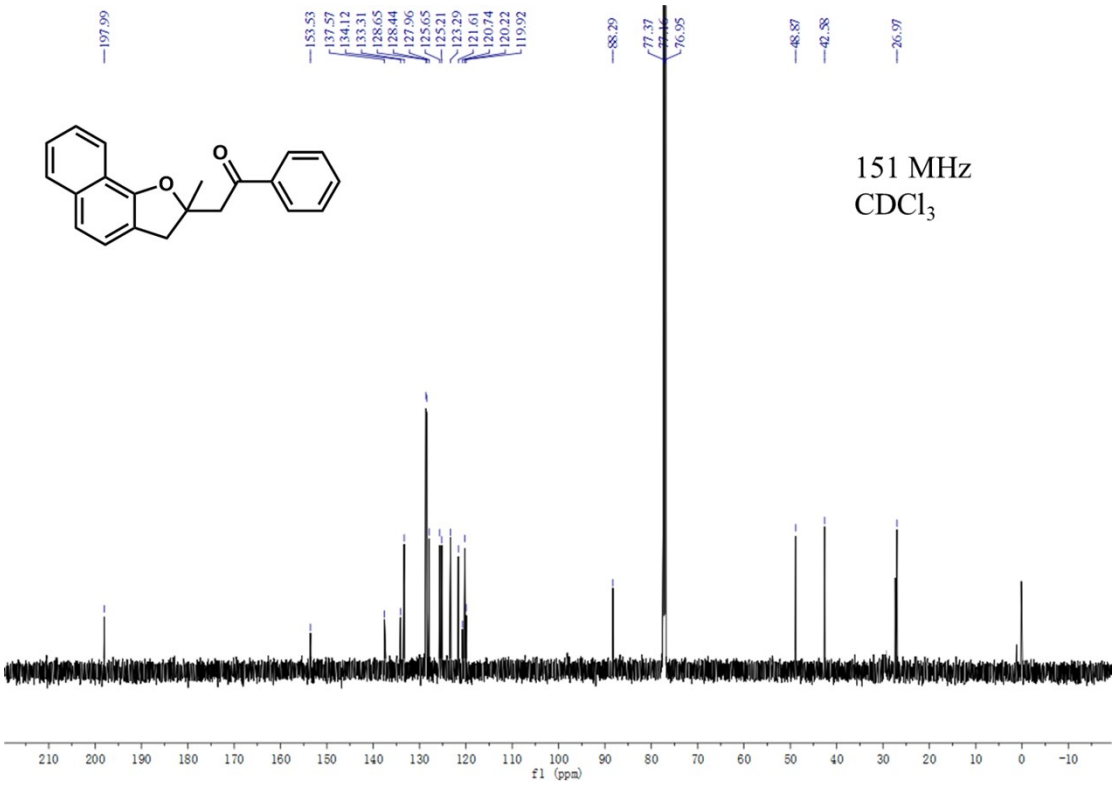


Figure S56. ^{1}H NMR spectra for **7j** (600MHz, $CDCl_3$)

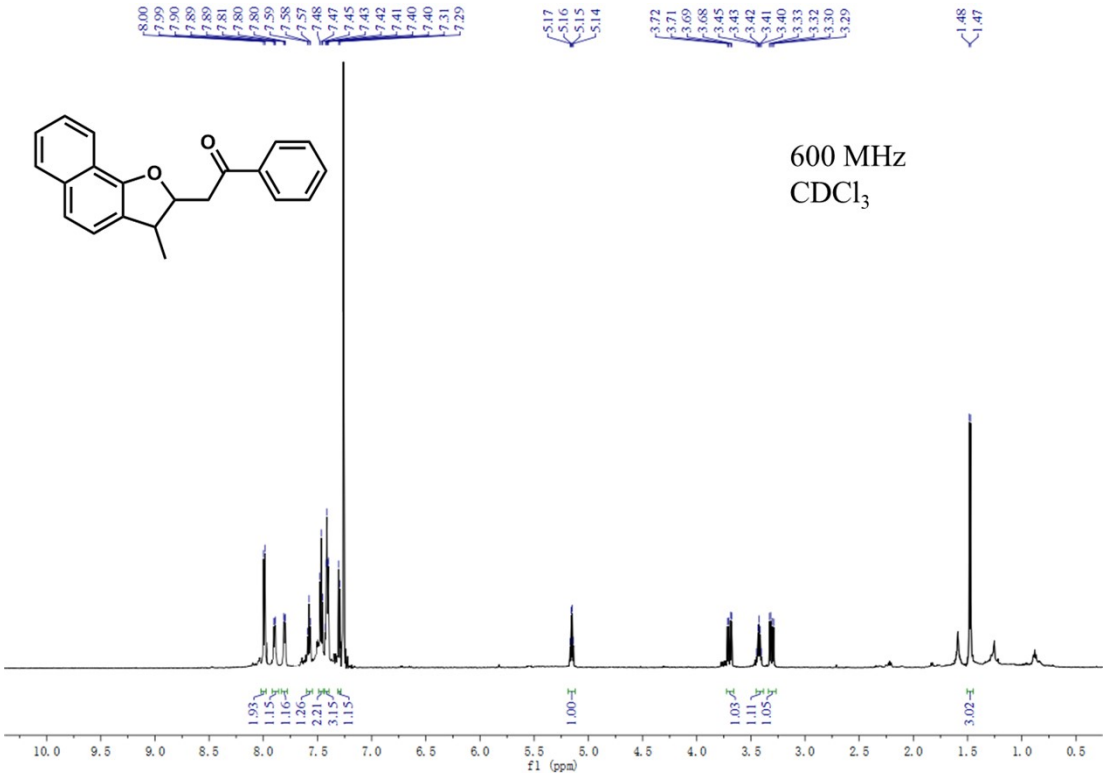


Figure S57. ^{13}C NMR spectra for **7j** (151MHz, $CDCl_3$)

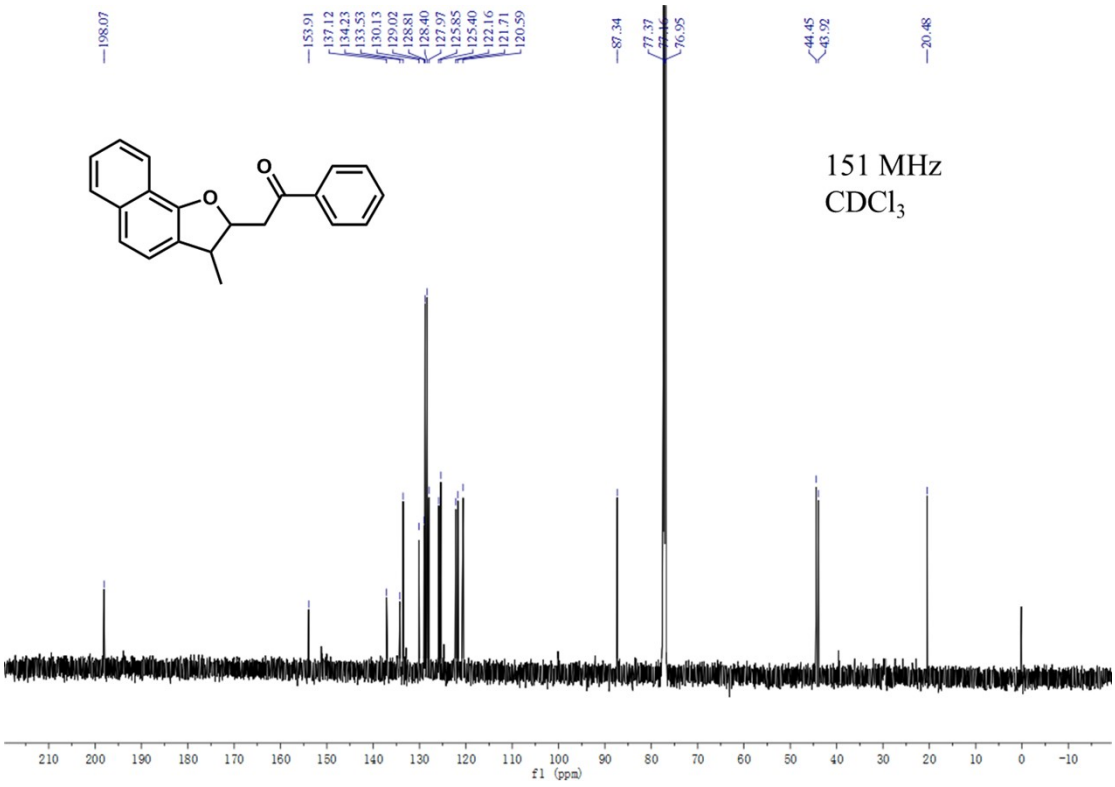


Figure S58. ^{1}H NMR spectra for **7k** (600MHz, $CDCl_3$)

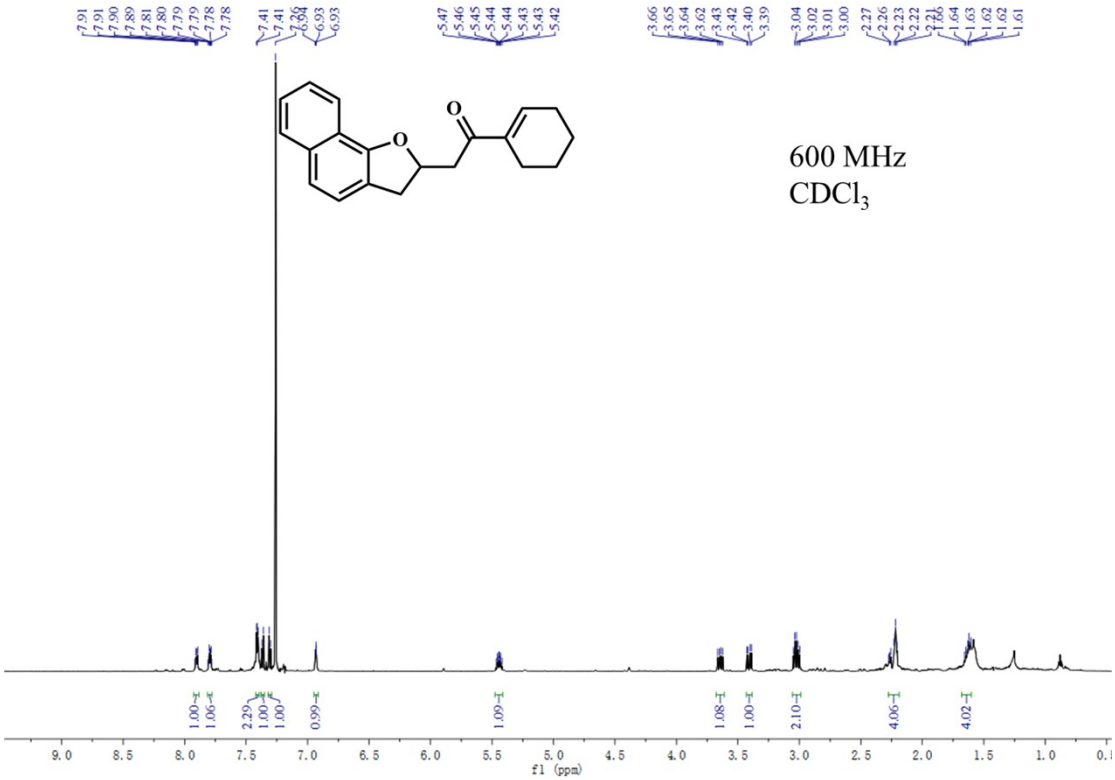


Figure S59. ^{13}C NMR spectra for **7k** (151MHz, $CDCl_3$)

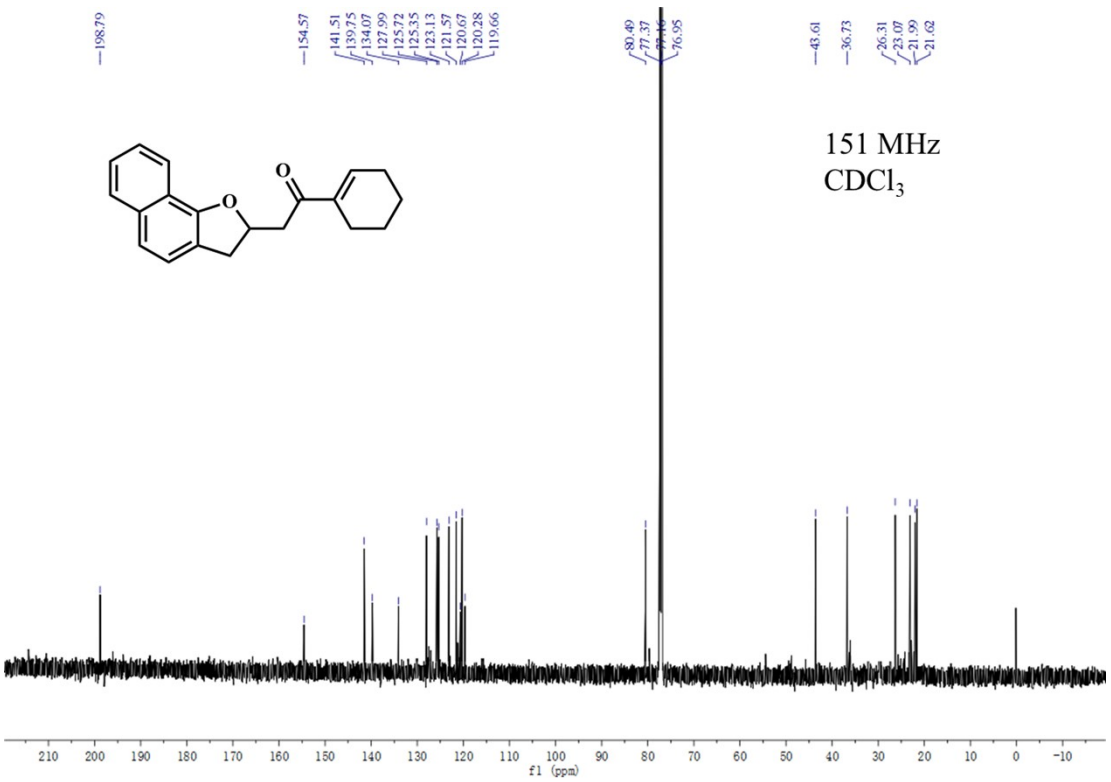


Figure S60. ^{1}H NMR spectra for **9a** (400MHz, $CDCl_3$)

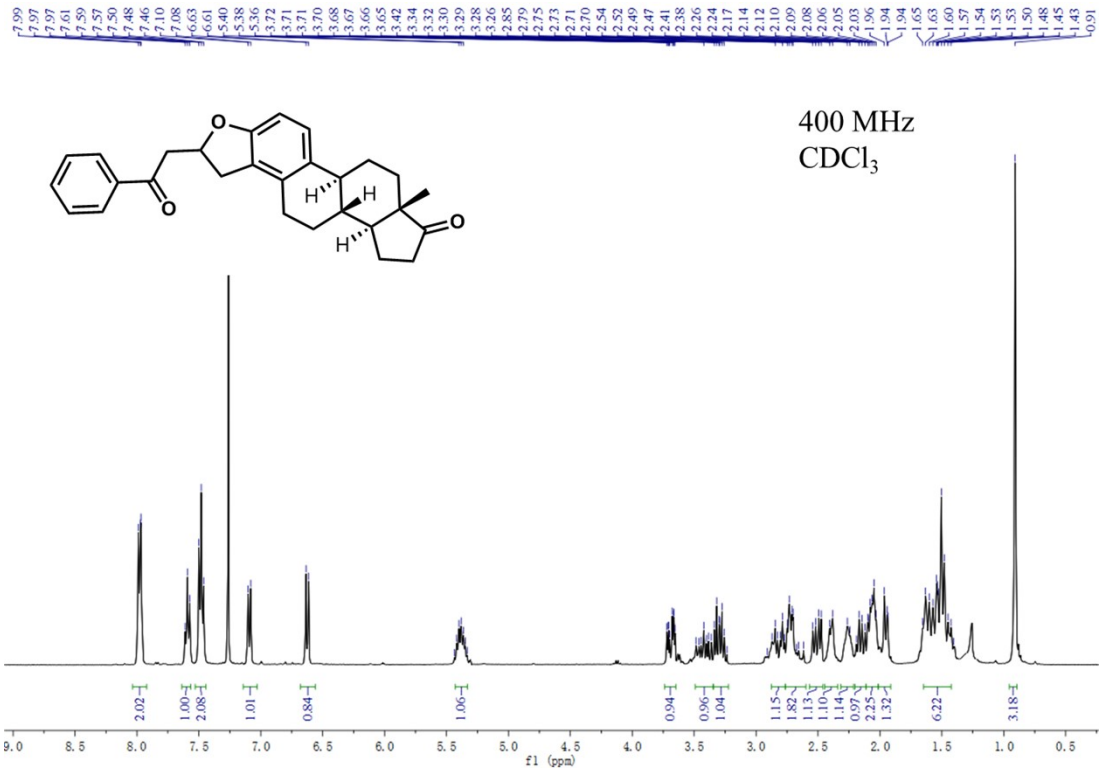


Figure S61. ^{13}C NMR spectra for **9a** (151MHz, $CDCl_3$)

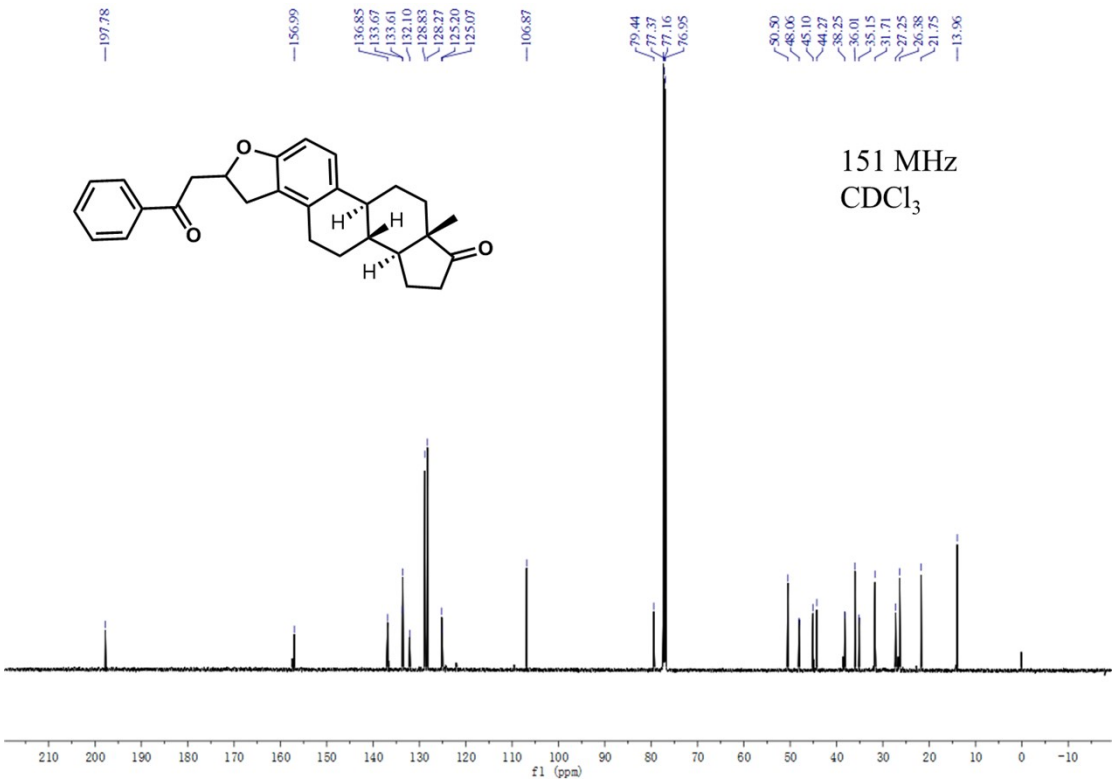


Figure S62. ^{1}H NMR spectra for **9b** (400MHz, $CDCl_3$)

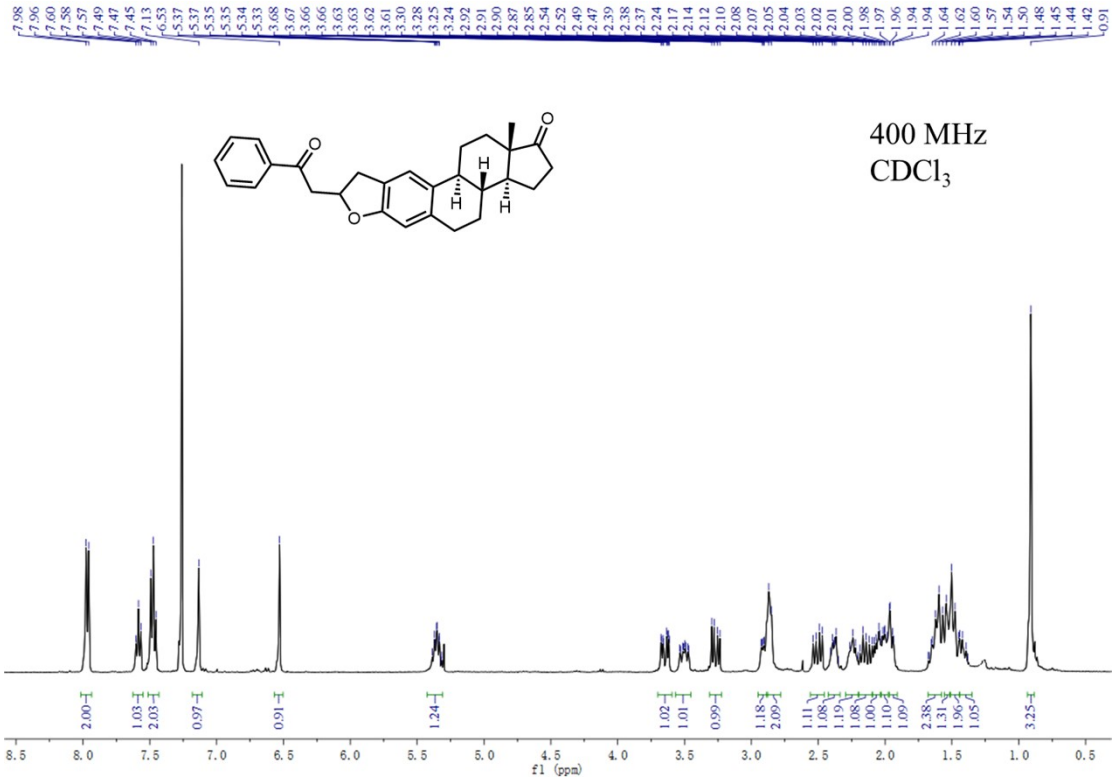


Figure S63. ^{13}C NMR spectra for **9b** (151MHz, $CDCl_3$)

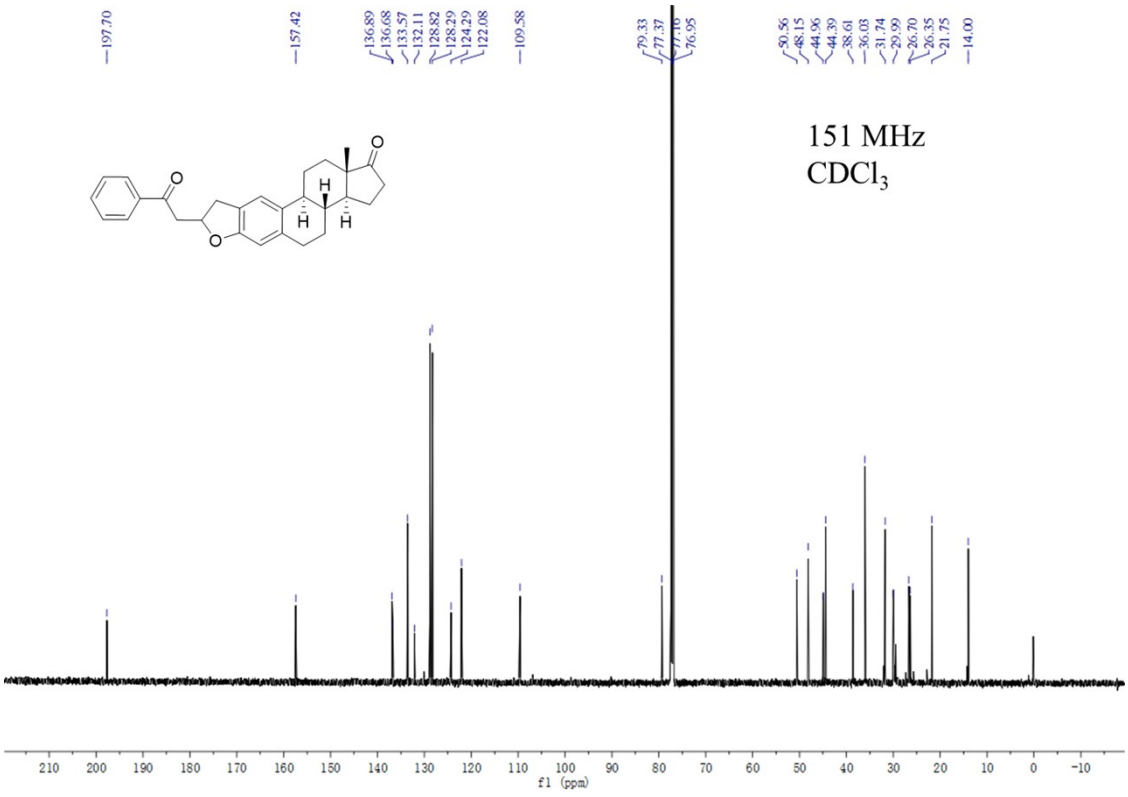


Figure S64. ^{1}H NMR spectra for **13a** (600MHz, $CDCl_3$)

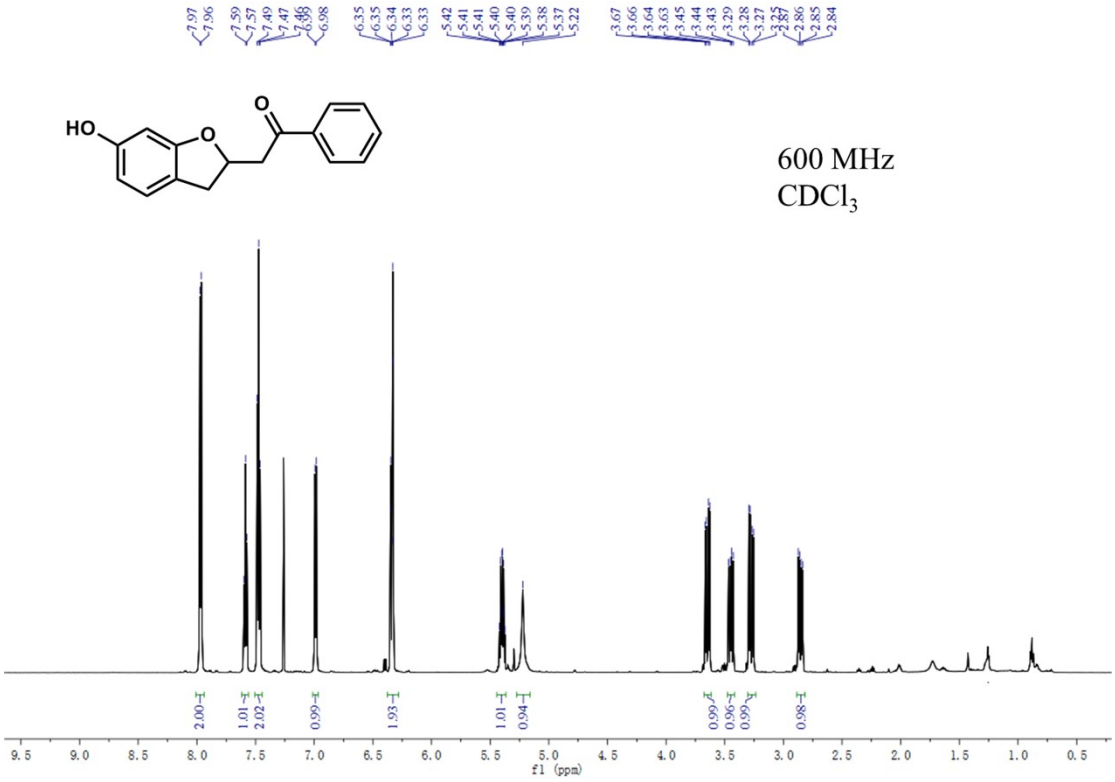


Figure S65. ^{13}C NMR spectra for **13a** (151MHz, $CDCl_3$)

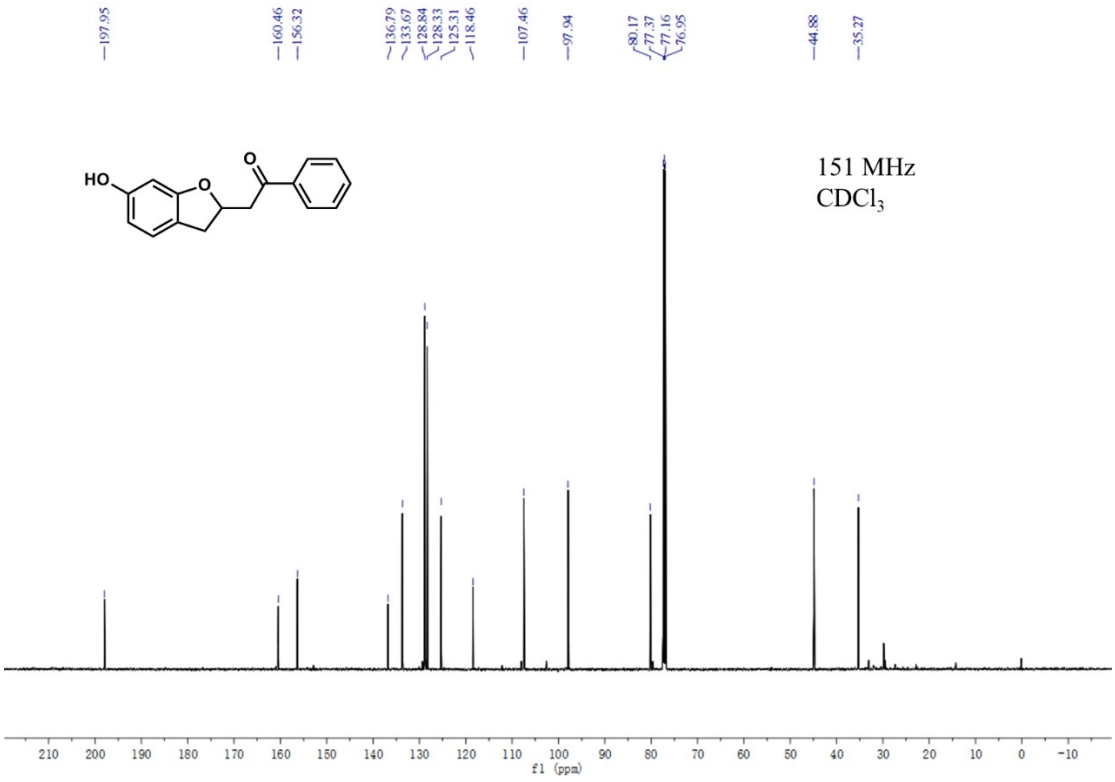


Figure S66. ^{1}H NMR spectra for **13b** (600MHz, $CDCl_3$)

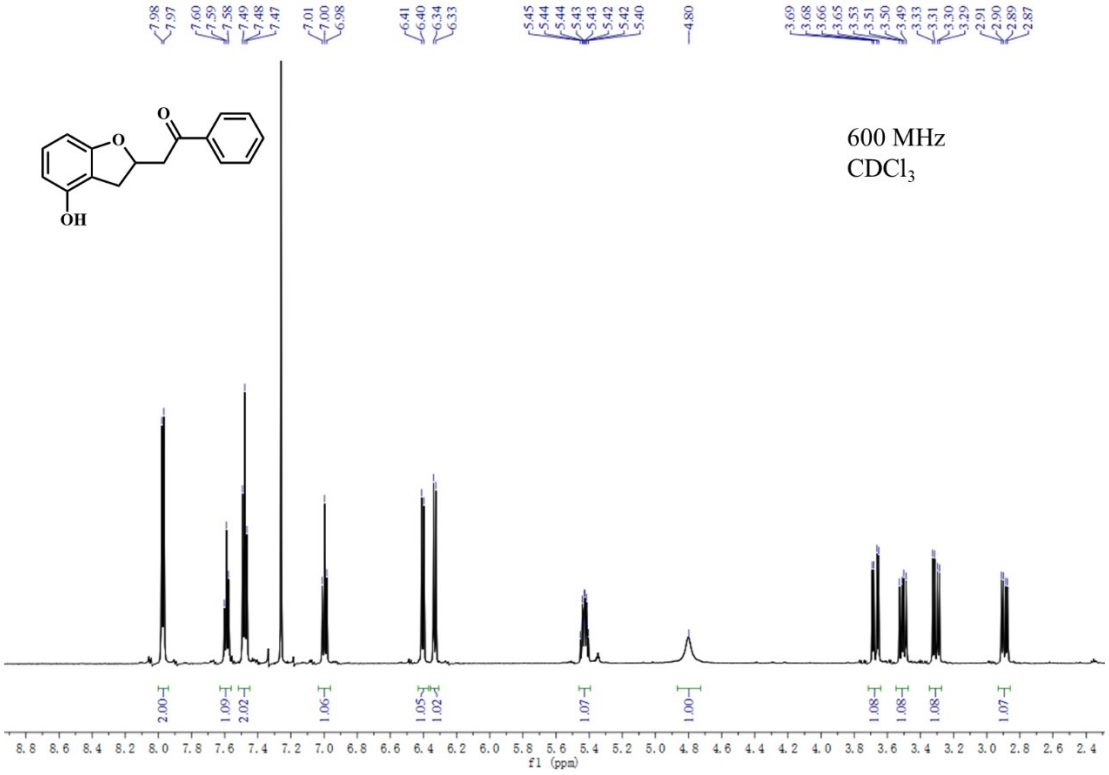


Figure S67. ^{13}C NMR spectra for **13b** (151MHz, $CDCl_3$)

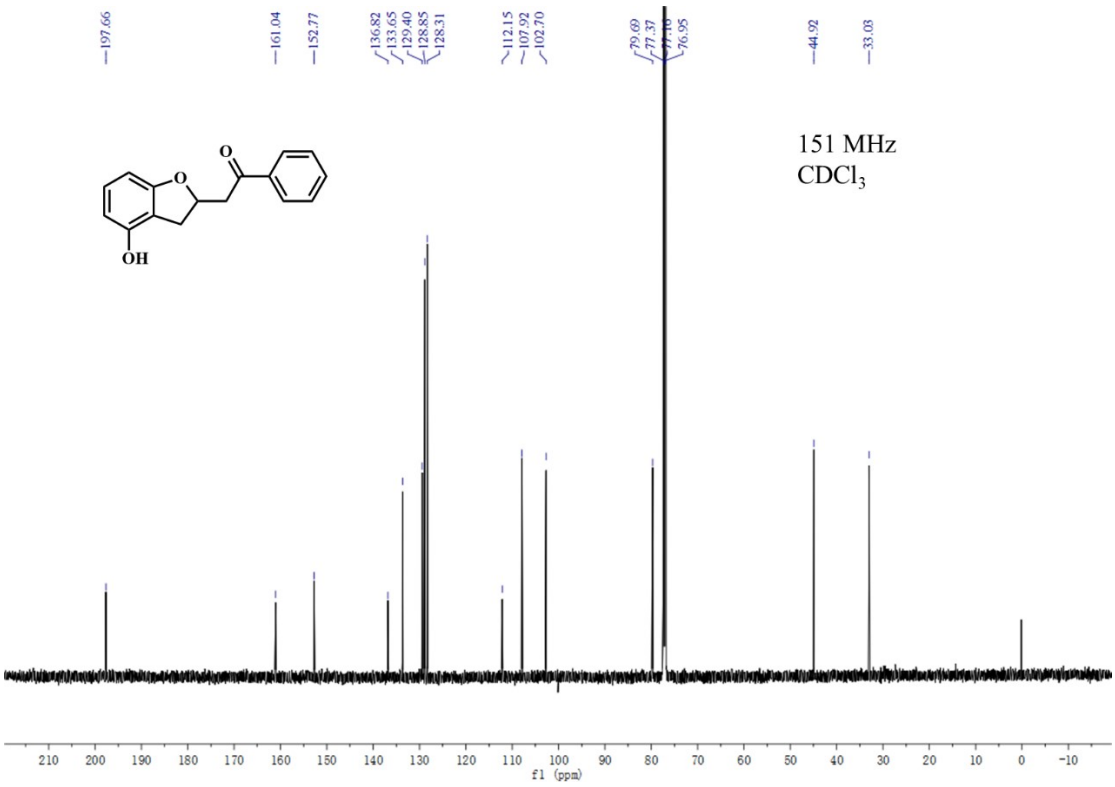


Figure S68. ^{1}H NMR spectra for **14** (600MHz, $CDCl_3$)

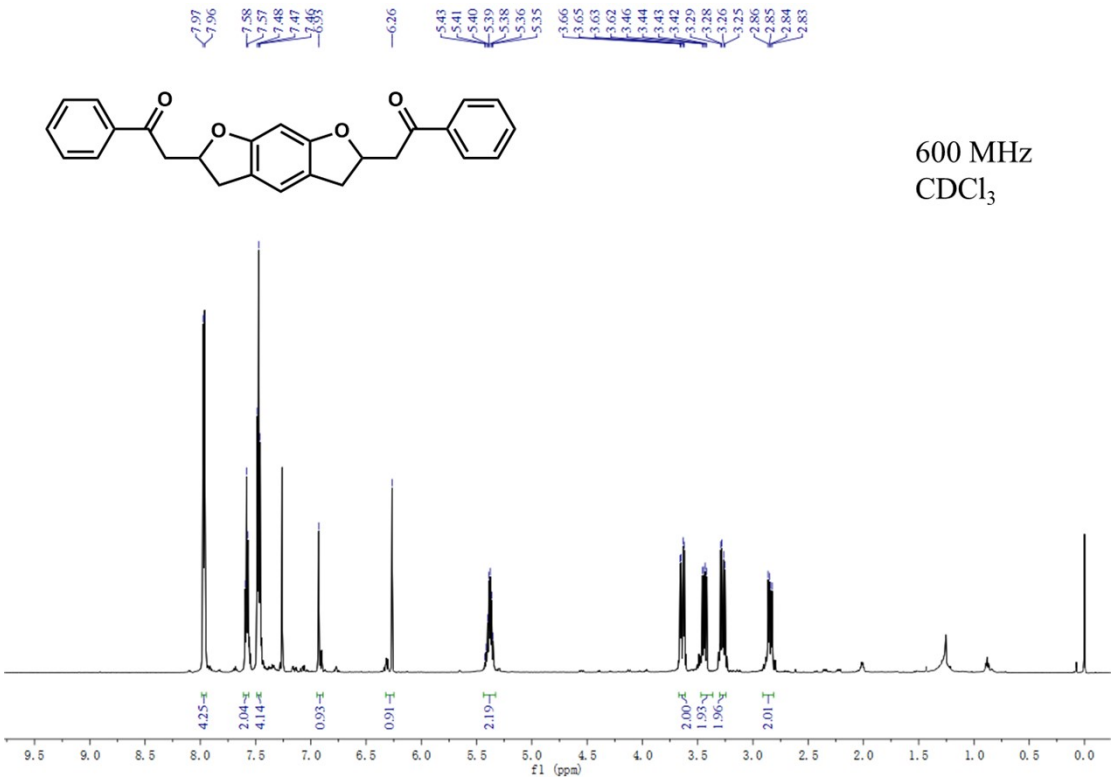


Figure S69. ^{13}C NMR spectra for **14** (151MHz, $CDCl_3$)

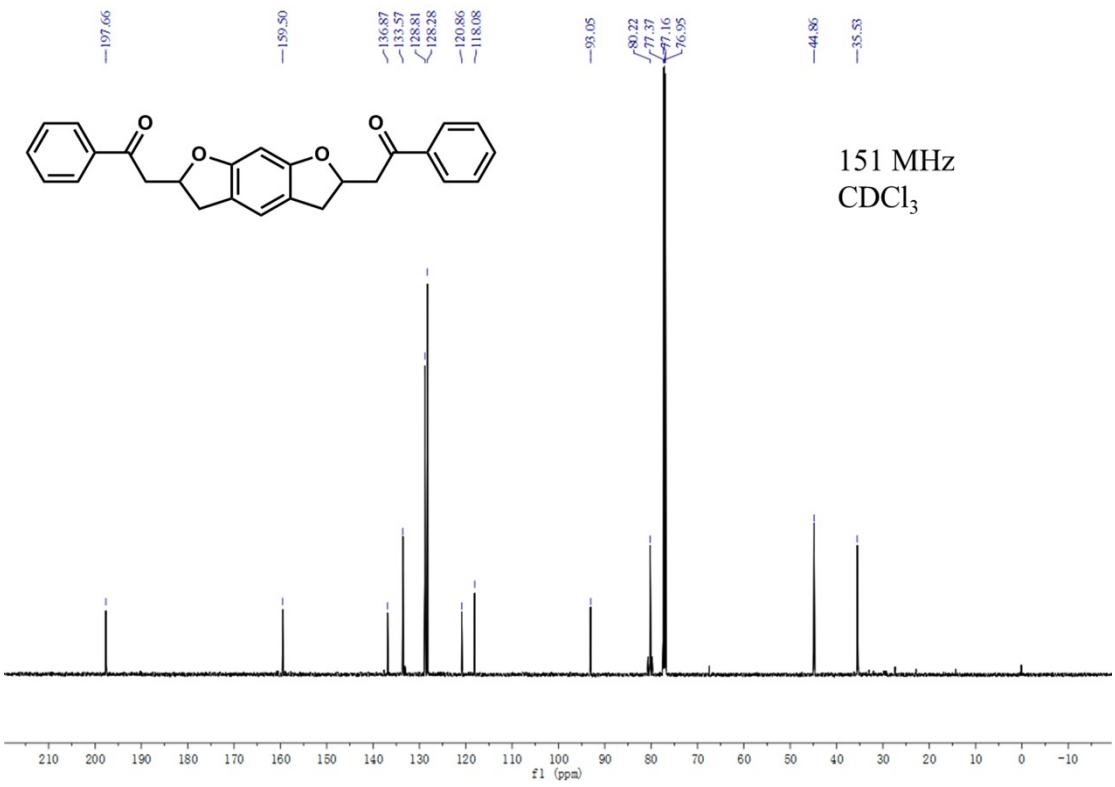


Figure S70. ^{1}H NMR spectra for **16a** (400MHz, $CDCl_3$)

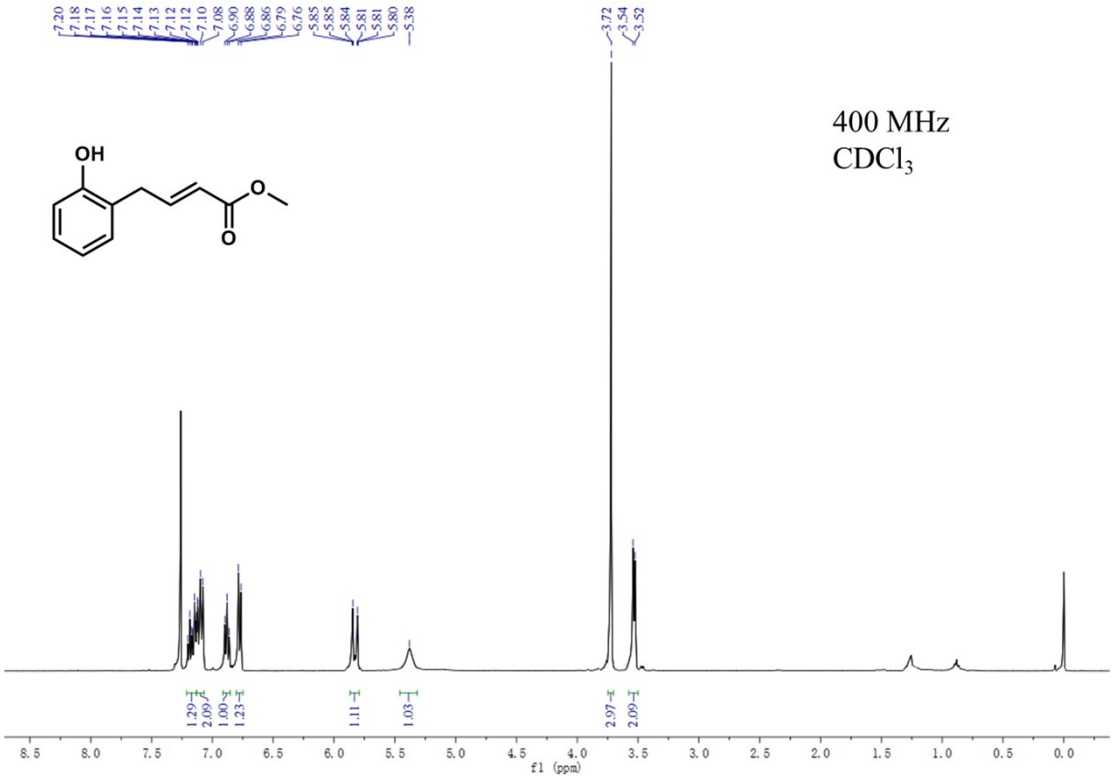


Figure S71. ^{13}C NMR spectra for **16a** (151MHz, $CDCl_3$)

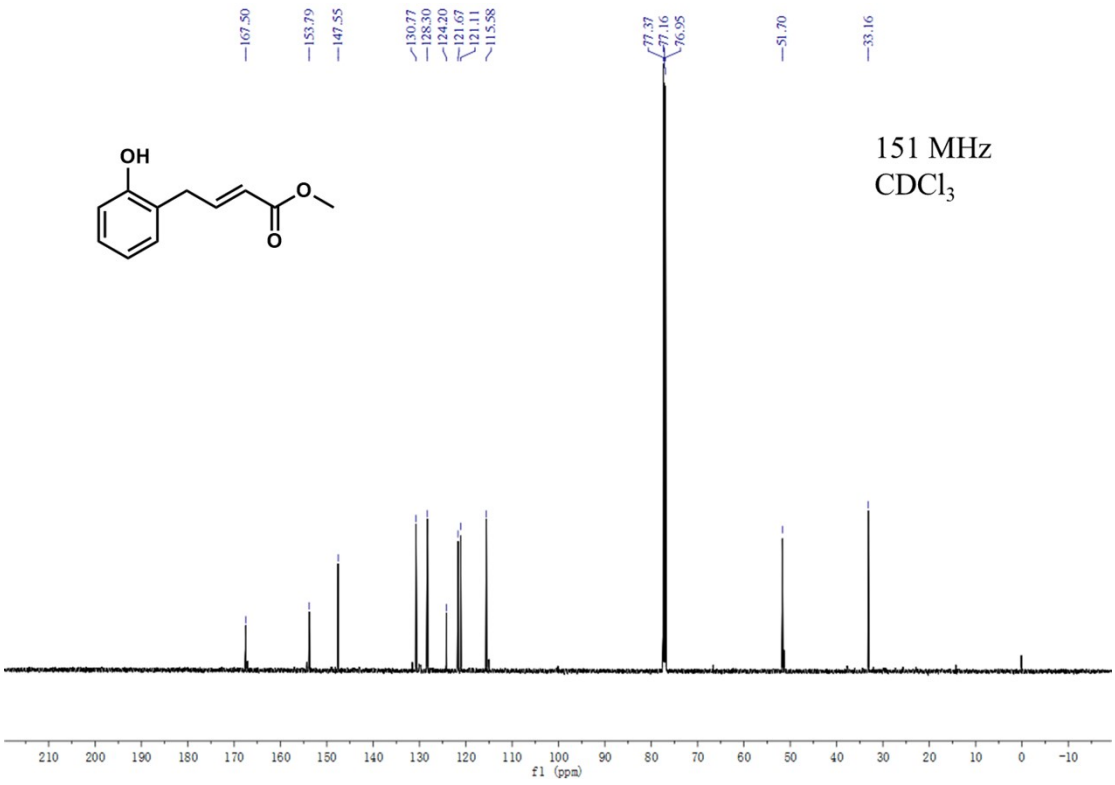


Figure S72. ^{1}H NMR spectra for **16b** (400MHz, $CDCl_3$)

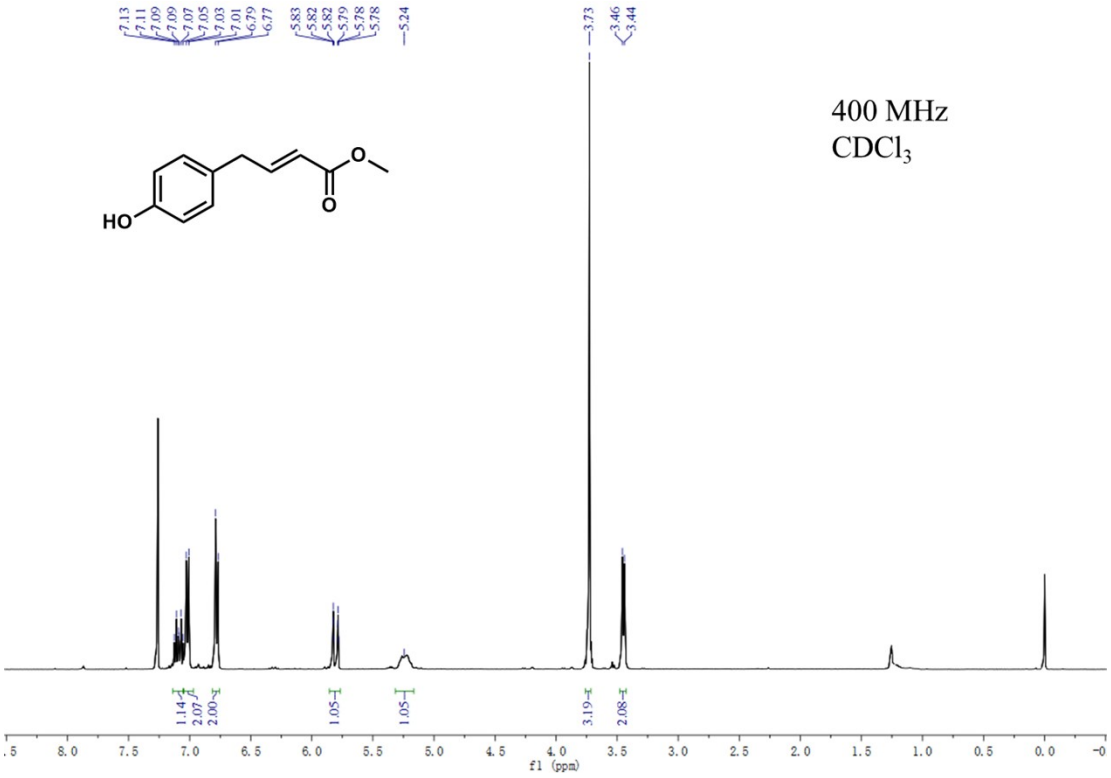


Figure S73. ^{13}C NMR spectra for **16b** (151MHz, $CDCl_3$)

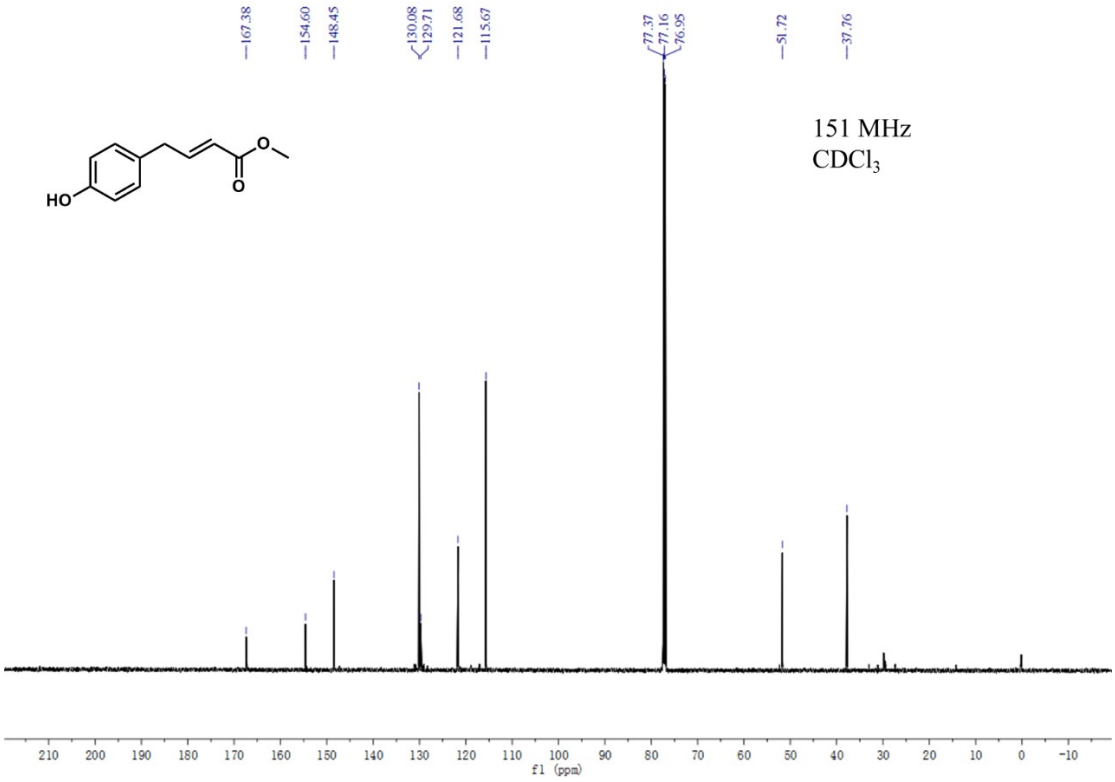


Figure S74. ^{1}H NMR spectra for **17** (600MHz, $CDCl_3$)

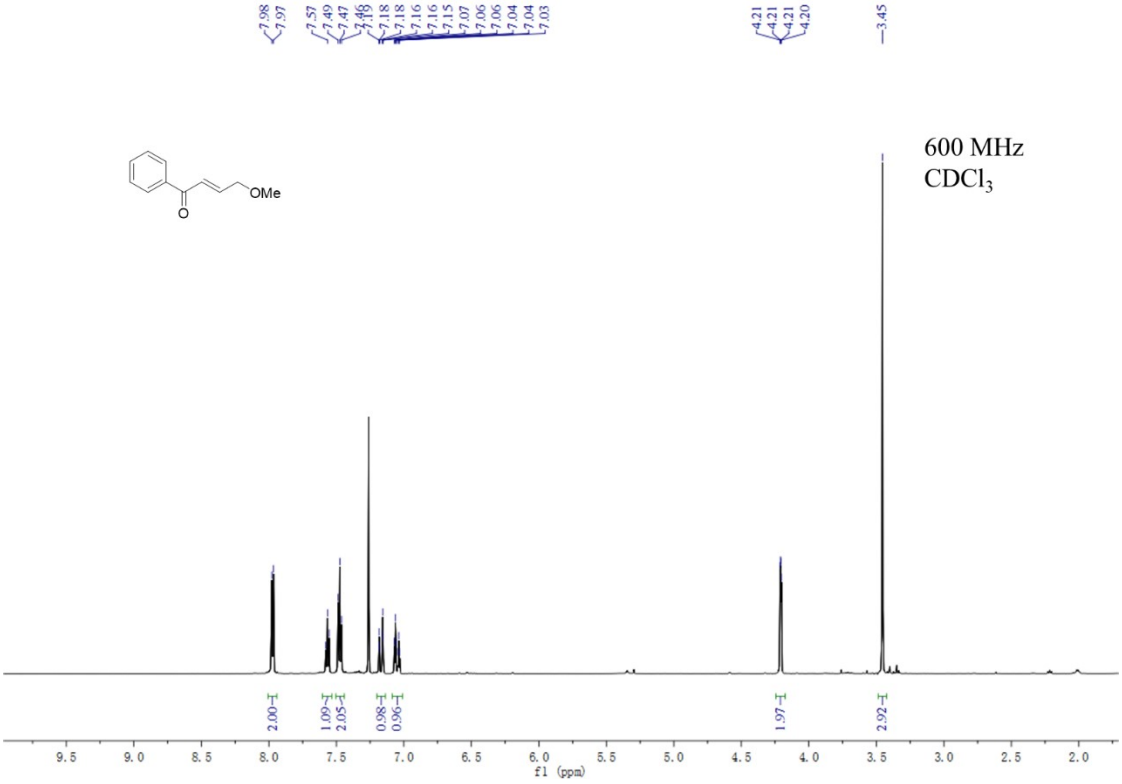
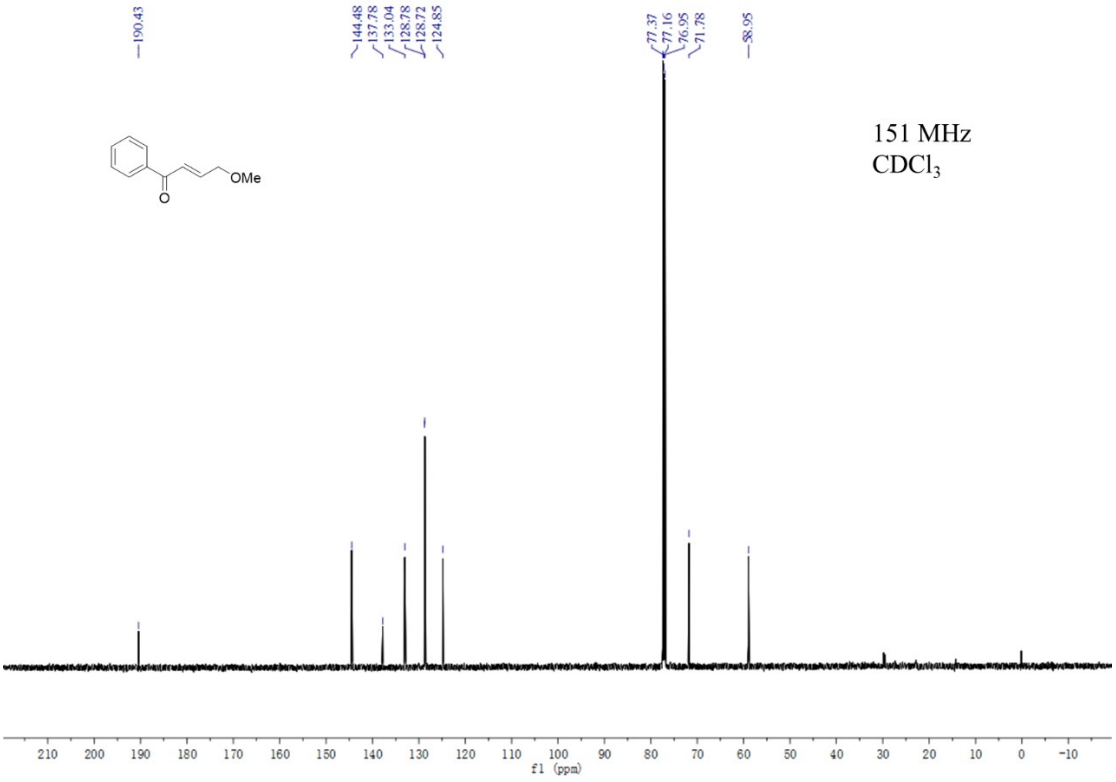


Figure S75. ^{13}C NMR spectra for **17** (151MHz, $CDCl_3$)



VII. References

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