Supporting Information

Switching Mesoionic Carbene-Organocatalysis from Radical to Ionic Pathway through Base-Controlled Formation of Breslow Intermediates versus Breslow Enolates

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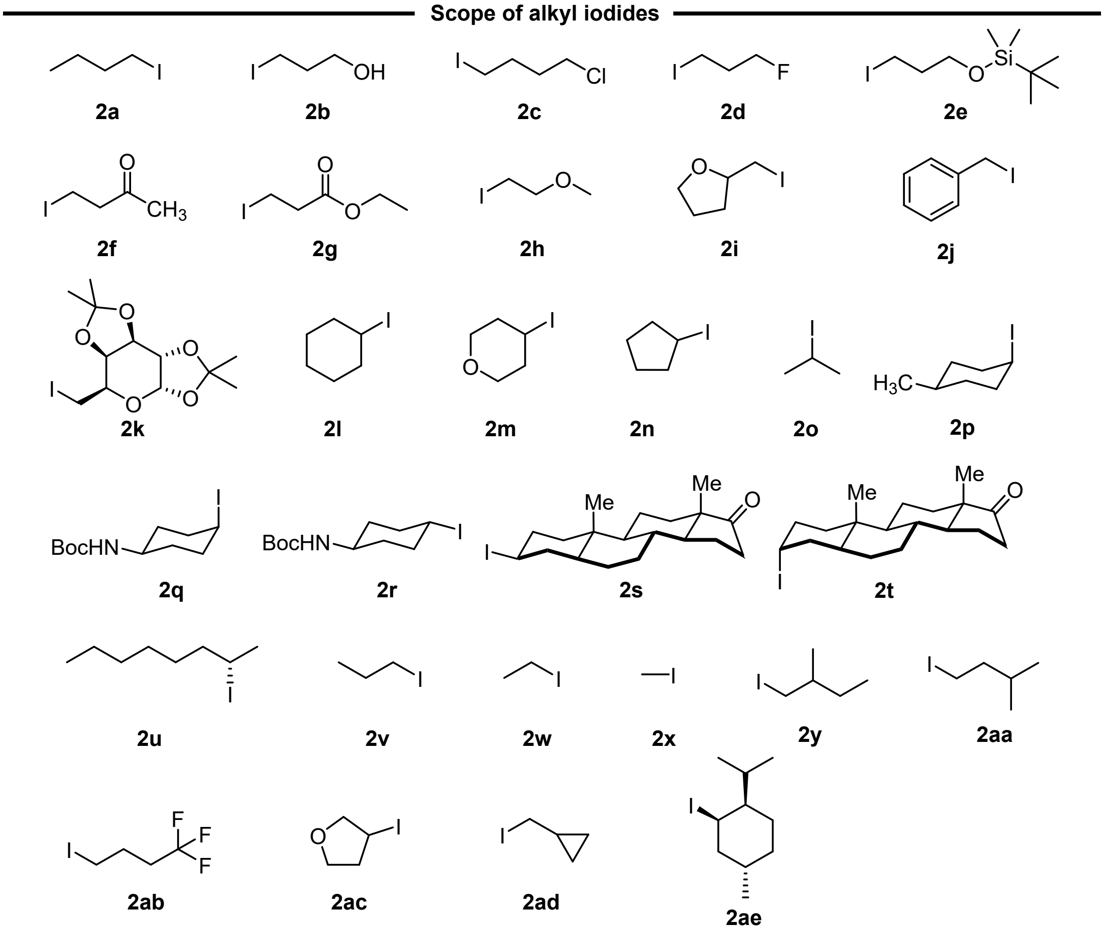
1. General

Unless otherwise noted, all the reagents were obtained from commercial suppliers and used directly without further purification. Solvents were obtained directly from a solvent purification system to get rid of moisture and oxygen. All air sensitive synthetic manipulations were performed in glovebox or carried out in flame-dried glassware equipped with magnetic agitators under nitrogen atmosphere using Schlenk techniques. All reactions that required heating were carried out under oil bath conditions. Analytical thin layer chromatography was carried out with silica gel pre-coated glass plates (TLC-Silica gel HSGF254) purchased from Xinnuo Chemical (Yantai, China). Chromatographic purification of the products was performed on silica gel 200-300 mesh purchased from Qingdao Haiyang Chemical Co., Ltd.

NMR spectra were recorded on Bruker 400 MHz spectrometers. The chemical shift data for each signal were given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0, or referenced to the residual solvent resonances ($CDCl_3$: δ 7.26 ($CHCl_3$)). NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad signal. Coupling constants *J* were given in Hz. High-resolution mass spectra were acquired on Thermo Q Exactive Focus Hybrid Quadrupole-Orbitrap mass spectrometer using electrospray ionization mode (ESI).

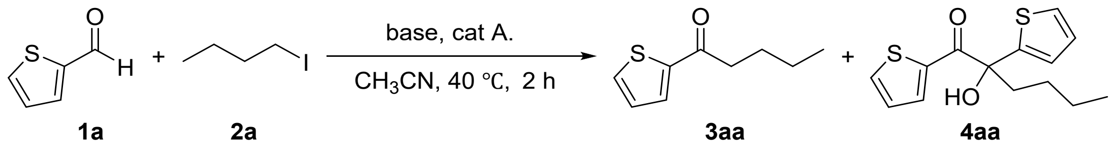
2. Scope for alkyl iodides

Scope of alkyl iodides



Most alkyl iodides were purchased from commercial source or were synthesized by simple and general methods according to literature procedures[1-7].

3. Base screening

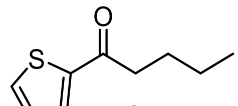


Entry	1 (mmol)	2 (mmol)	Base	T (°C)	**3aa** (%)	**4aa** (%)
1	0.2	0.2	DBU	40	4	10
2	0.2	0.2	DIPEA	40	trace	trace
3	0.2	0.2	DABCO	40	trace	trace
4	0.2	0.2	TEA	40	trace	trace
5	0.2	0.2	DMAP	40	trace	trace
6	0.2	0.2	K_3PO_4	40	2	10
7	0.2	0.2	K_2SO_3	40	trace	trace
8	0.2	0.2	Na_2HPO_4	40	trace	trace
9	0.2	0.2	Na_2CO_3	40	trace	trace
10	0.2	0.2	K_2CO_3	40	trace	trace
11	0.2	0.2	$NaHCO_3$	40	trace	trace
12	0.2	0.2	Cs_2CO_3	40	88	trace
13	0.2	0.2	NaOAc	40	trace	trace
14	0.2	0.2	KOAc	40	trace	trace
15	0.2	0.2	CsOAc	40	trace	trace

Reactions were performed with 0.20 mmol of **1a**, 0.20 mmol of **2a** and 20 mol% of **A** in 1.0 mL CH_3CN for 2 h.

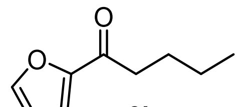
4. General procedure for alkylation of aldehydes

In a glovebox, a 25 mL seal bottle was charged with aldehyde (0.2 mmol), catalyst **A** (21.4 mg, 0.04 mmol), Cs_2CO_3 (260.6 mg, 0.8 mmol), alkyl iodide (0.2 mmol) and CH_3CN (1 mL). The solution was heated to 40 °C in oil bath and stirred for 2 h. The reaction was then quenched with water (2 mL) and extracted with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel chromatography: PE/AcOEt →100/1 to 5/1, unless otherwise stated.



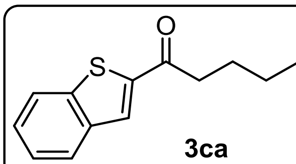
3aa

3aa was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as colorless oil (29 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 3.8 Hz, 1H), 7.61 (d, J = 4.9 Hz, 1H), 7.12 (t, J = 4.4 Hz, 1H), 2.89 (t, J = 7.5 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.46 – 1.39 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.5, 144.5, 133.2, 131.6, 127.9, 39.1, 26.8, 22.4, 13.8. All the characterization data are consistent with previous report.[8]



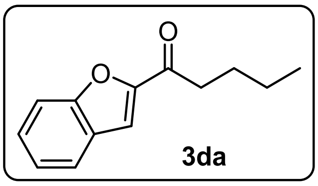
3ba

3ba was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as colorless oil (17 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 3.6 Hz, 1H), 7.21 (d, J = 3.6 Hz, 1H), 6.53 (dd, J = 3.6, 1.7 Hz, 1H), 2.81 (t, J = 7.5 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.45 – 1.39 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.7, 152.7, 146.1, 116.7, 112.0, 38.2, 26.4, 22.4, 13.9. All the characterization data are consistent with previous report.[9]

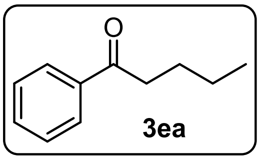


3ca

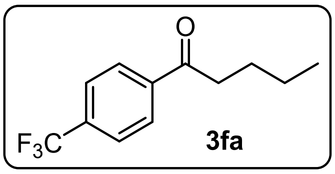
3ca was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as white solid (37 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.90 – 7.84 (m, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 3.00 (t, J = 7.5 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.49 – 1.40 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.2, 144.0, 142.5, 139.3, 128.9, 127.4, 126.0, 125.0, 123.1, 39.1, 27.0, 22.6, 14.1. All the characterization data are consistent with previous report.[10]



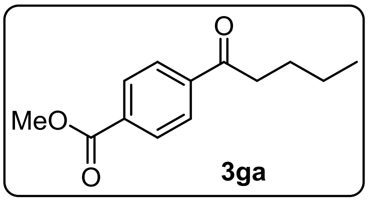
3da was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as yellow oil (26 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 1H), 7.59 – 7.55 (m, 1H), 7.49 (s, 1H), 7.48 – 7.44 (m, 1H), 7.33 – 7.29 (m, 1H), 2.97 (t, J = 7.5 Hz, 2H), 1.78 – 1.73 (m, 2H), 1.41 – 1.38 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 191.7, 155.5, 152.6, 128.1, 127.0, 123.8, 123.2, 122.5, 122.4, 38.7, 26.4, 22.4, 13.9. All the characterization data are consistent with previous report.[8]



3ea was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as colorless oil (10 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 1.76 – 1.69 (m, 2H), 1.46 – 1.37 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.2, 136.8, 132.6, 128.3, 127.9, 38.1, 26.2, 22.3, 13.7. All the characterization data are consistent with previous report.[8]

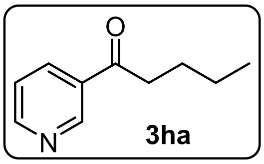


3fa was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as colorless oil (21 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 2.99 (t, J = 7.4 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.45 – 1.38 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 139.7, 134.2 (q, $J_{C\text{-}F}$ = 32.6 Hz), 128.4, 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.7 (q, $J_{C\text{-}F}$ = 271.2 Hz), 38.6, 26.2, 22.4, 13.9. All the characterization data are consistent with previous report.[8]



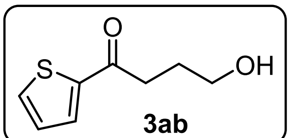
3ga

3ga was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as white solid (23 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H), 2.98 (t, J = 7.4 Hz, 2H), 1.66 – 1.48 (m, 2H), 1.45 – 1.37 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.9, 166.3, 140.6, 134.0, 129.6, 127.6, 52.6, 38.7, 26.4, 22.4, 13.9. All the characterization data are consistent with previous report.[11]



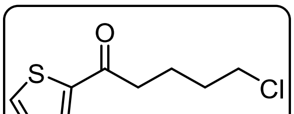
3ha

3ha was purified by column chromatography on silica gel (PE/AcOEt = 5/1) as white solid (23 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (br, 1H), 8.77 (dd, J = 4.9, 1.7 Hz, 1H), 8.22 (dt, J = 8.0, 2.0 Hz, 1H), 7.41 (dd, J = 8.0, 4.8 Hz, 1H), 2.98 (t, J = 7.4 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.46 – 1.37 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.2, 153.3, 149.6, 135.3, 132.2, 123.6, 38.6, 26.1, 22.4, 13.9. All the characterization data are consistent with previous report.[12]



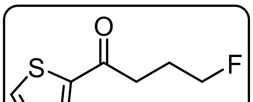
3ab

3ab was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as colorless oil (29 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 3.8, 1.2 Hz, 1H), 7.61 (dd, J = 4.9, 1.2 Hz, 1H), 7.10 (dd, J = 5.0, 3.8 Hz, 1H), 3.69 (t, J = 6.1 Hz, 2H), 2.87 (t, J = 7.1 Hz, 2H), 2.25 – 2.18 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.5, 144.2, 133.9, 131.9, 128.4, 62.6, 36.3, 27.4. All the characterization data are consistent with previous report.[13]



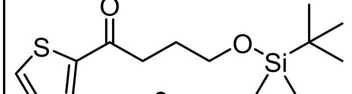
3ac

3ac was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as white solid (30 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.8, 1.2 Hz, 1H), 7.63 (dd, J = 5.0, 1.2 Hz, 1H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 3.58 (t, J = 6.1 Hz, 2H), 2.95 (t, J = 6.7 Hz, 2H), 1.96 – 1.84 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.5, 144.2, 133.5, 131.7, 128.1, 44.6, 38.3, 32.0, 21.9. All the characterization data are consistent with previous report.[14]



3ad

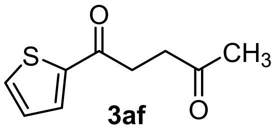
3ad was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as light-yellow oil (22 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 3.8 Hz, 1H), 7.64 (d, J = 5.0 Hz, 1H), 7.13 (t, J = 4.4 Hz, 1H), 4.54 (dt, J = 47.2, 5.8 Hz, 2H), 3.08 (t, J = 7.2 Hz, 2H), 2.21 – 2.08 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.0, 144.0, 133.6, 131.9, 128.1, 83.1 (d, J_{C-F} = 164.8 Hz), 34.6 (d, J_{C-F} = 4.3 Hz), 25.1 (d, J_{C-F} = 20.1 Hz). ^{19}F NMR (376 MHz, CDCl3) δ -220.2. All the characterization data are consistent with previous report.[15]



3ae

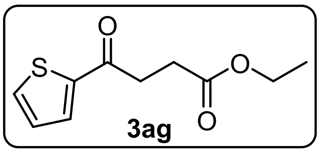
3ae was purified by column chromatography on silica gel (PE/AcOEt = 50/1) as light-yellow oil (44 mg, 78%). IR (KBr): ν_{max} 2955, 2921, 2858, 1672, 1469, 1419, 1257, 1098, 843, 753, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 3.8, 1.1

Hz, 1H), 7.61 (dd, J = 4.9, 1.2 Hz, 1H), 7.12 (dd, J = 5.0, 3.8 Hz, 1H), 3.69 (t, J = 6.0 Hz, 2H), 3.00 (t, J = 7.3 Hz, 2H), 1.96 (tt, J = 7.3, 6.0 Hz, 2H), 0.89 (s, 9H), 0.04 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.2, 144.4, 133.3, 131.7, 128.0, 62.1, 35.6, 27.6, 25.9, 18.3, -5.4. HRMS (ESI+): m/z calcd for $C_{14}H_{24}O_2SSi+H^+$: 285.1340, $[M+H]^+$, found: 285.1333.



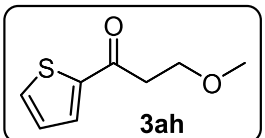
3af

3af was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as colorless oil (15 mg, 41%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 3.8, 1.2 Hz, 1H), 7.63 (dd, J = 5.0, 1.2 Hz, 1H), 7.13 (dd, J = 4.9, 3.8 Hz, 1H), 3.22 (t, J = 6.4 Hz, 2H), 2.88 (t, J = 6.4 Hz, 2H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 207.1, 191.4, 143.7, 133.5, 132.0, 128.1, 37.0, 32.9, 30.0. All the characterization data are consistent with previous report.[16]



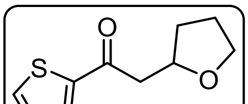
3ag

3ag was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as light-yellow oil (35 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 3.8, 1.1 Hz, 1H), 7.63 (dd, J = 5.0, 1.1 Hz, 1H), 7.13 (dd, J = 4.9, 3.8 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.25 (t, J = 6.8 Hz, 2H), 2.75 (t, J = 6.8 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.0, 172.7, 143.7, 133.6, 131.9, 128.1, 60.7, 33.9, 28.3, 14.2. All the characterization data are consistent with previous report.[17]



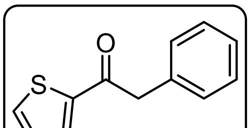
3ah

3ah was purified by column chromatography on silica gel (PE/AcOEt = 5/1) as light-yellow oil (22 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 3.8, 1.2 Hz, 1H), 7.64 (dd, J = 5.0, 1.2 Hz, 1H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 3.80 (t, J = 6.4 Hz, 2H), 3.36 (s, 3H), 3.17 (t, J = 6.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.1, 144.4, 133.8, 132.2, 128.1, 67.8, 58.9, 39.5. All the characterization data are consistent with previous report.[18]



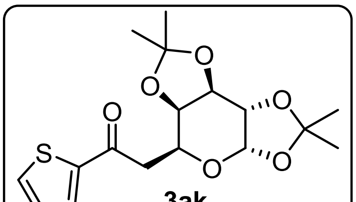
3ai

3ai was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as yellow oil (30 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 3.8 Hz, 1H), 7.63 (d, J = 4.9 Hz, 1H), 7.13 (t, J = 4.4 Hz, 1H), 4.42 – 4.35 (m, 1H), 3.92 – 3.86 (m, 1H), 3.77 – 3.72 (m, 1H), 3.30 (dd, J = 15.4, 6.3 Hz, 1H), 2.98 (dd, J = 15.4, 6.5 Hz, 1H), 2.22 – 2.11 (m, 1H), 1.98 – 1.87 (m, 2H), 1.65 – 1.56 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 191.1, 144.6, 133.8, 132.3, 128.1, 75.5, 67.9, 45.4, 31.5, 25.6. All the characterization data are consistent with previous report.[19]



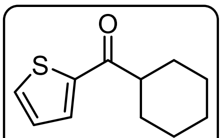
3aj

3aj was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as colorless oil (14 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 3.6 Hz, 1H), 7.60 (d, J = 4.8 Hz, 1H), 7.34 – 7.26 (m, 5H), 7.12 (dd, J = 4.9, 3.8 Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 144.0, 134.5, 134.1, 132.5, 129.6, 128.8, 128.3, 127.4, 45.4. All the characterization data are consistent with previous report.[20]



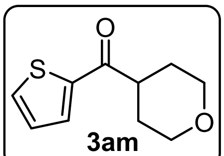
3ak

3ak was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as white solid (31 mg, 44%). IR (KBr): v_{max} 2955, 2923, 2850, 1668, 1379, 1273, 770, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 3.8 Hz, 1H), 7.63 (d, J = 4.9 Hz, 1H), 7.12 (t, J = 4.4 Hz, 1H), 5.49 (d, J = 5.0 Hz, 1H), 4.64 (dd, J = 7.9, 2.4 Hz, 1H), 4.50 (t, J = 6.6 Hz, 1H), 4.36 – 4.29 (m, 2H), 3.38 – 3.16 (m, 2H), 1.61 (s, 3H), 1.49 (s, 3H), 1.34 (d, J = 3.9 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.2, 144.3, 133.7, 132.3, 128.0, 109.2, 108.9, 96.4, 72.5, 70.9, 70.5, 64.2, 40.0, 26.1, 26.0, 25.0, 24.4. HRMS (ESI+): *m/z* calcd for $C_{17}H_{22}O_6S+H^+$: 355.1210, $[M+H]^+$, found: 355.1201.



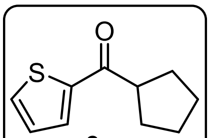
3al

3al was purified by column chromatography on silica gel (PE/AcOEt = 40/1) as colorless oil (29 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 3.8, 1.1 Hz, 1H), 7.61 (dd, J = 4.9, 1.1 Hz, 1H), 7.13 (dd, J = 4.9, 3.7 Hz, 1H), 3.10 (tt, J = 11.6, 3.3 Hz, 1H), 1.93 – 1.89 (m, 2H), 1.85 – 1.82 (m, 2H), 1.75 – 1.72 (m, 1H), 1.58 – 1.52 (m, 2H), 1.41 – 1.32 (m, 2H), 1.32 – 1.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 143.9, 133.5, 131.4, 128.0, 47.6, 29.9, 25.8, 25.7. All the characterization data are consistent with previous report.[12]



3am

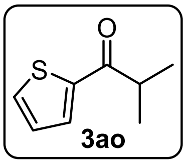
3am was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as yellow solid (29 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 3.8, 1.1 Hz, 1H), 7.63 (dd, J = 4.9, 1.2 Hz, 1H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 4.06 – 4.03 (m, 2H), 3.55 – 3.49 (m, 2H), 3.33 (tt, J = 14.8, 4.1 Hz, 1H), 1.96 – 1.89 (m, 2H), 1.81 – 1.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 143.5, 133.5, 131.2, 128.0, 67.5, 44.3, 29.1. All the characterization data are consistent with previous report.[21]



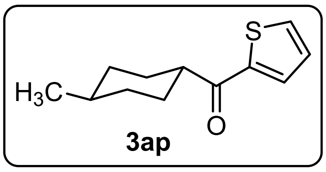
3an

3an was purified by column chromatography on silica gel (PE/AcOEt = 80/1) as yellow solid (22 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.8, 1.1 Hz, 1H), 7.59 (dd, J = 5.0, 1.1 Hz, 1H), 7.11 (dd, J = 5.0, 3.8 Hz, 1H), 3.60 – 3.52 (m, 1H), 1.94 – 1.89 (m, 4H), 1.75 – 1.66 (m, 2H), 1.67 – 1.58 (m, 2H). ^{13}C NMR (101 MHz,

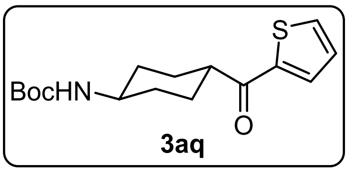
$CDCl_3$) δ 195.8, 144.5, 133.1, 131.0, 128.0, 47.5, 30.3, 26.1. All the characterization data are consistent with previous report.[22]



3ao was purified by column chromatography on silica gel (PE/AcOEt = 50/1) as light-yellow oil (13 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 (dd, J = 5.0, 1.1 Hz, 1H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 3.44 – 3.34 (m, 1H), 1.23 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 143.0, 133.5, 131.0, 127.5, 37.4, 19.4. All the characterization data are consistent with previous report.[21]

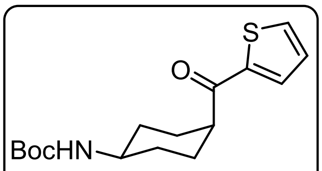


3ap was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as colorless oil (20 mg, 48%, trans: cis = 11: 1). IR (KBr): v_{max} 2923, 2862, 1664, 1517, 1452, 1412, 1257, 1200, 932, 786, 721 cm^{-1}; The following data is for trans isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 3.8, 1.1 Hz, 1H), 7.61 (dd, J = 4.9, 1.1 Hz, 1H), 7.12 (dd, J = 5.0, 3.8 Hz, 1H), 3.03 (tt, J = 12.0, 3.4 Hz, 1H), 1.95 – 1.89 (m, 2H), 1.85 – 1.78 (m, 2H), 1.64 – 1.55 (m, 2H), 1.47 – 1.36 (m, 1H), 1.10 – 0.99 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.9, 143.9, 133.3, 131.4, 128.0, 47.3, 34.5, 32.0, 29.6, 22.6. HRMS (ESI+): m/z calcd for $C_{12}H_{16}OS+H^+$: 209.0995, $[M+H]^+$, found: 209.0990.



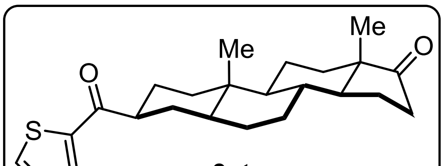
3aq was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as white solid (43 mg, 70%, trans: cis = 6: 1). IR (KBr): v_{max} 3362, 2980, 2923, 2858, 1704, 1664, 1533, 1412, 753 cm^{-1}; The following data is for trans isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.9, 1.1 Hz, 1H), 7.63 (dd, J = 5.0, 1.1 Hz, 1H), 7.12 (dd,

J = 5.0, 3.8 Hz, 1H), 4.42 (br, 1H), 3.45 (br, 1H), 3.03 (tt, J = 12.0, 3.4 Hz, 1H), 2.17 – 2.11 (m, 2H), 2.00 – 1.94 (m, 2H), 1.74 – 1.62 (m, 2H), 1.44 (s, 9H), 1.28 – 1.17 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.8, 155.1, 143.6, 133.6, 131.5, 128.0, 79.2, 49.1, 46.4, 32.7, 28.4, 28.4. HRMS (ESI+): *m/z* calcd for $C_{16}H_{23}NO_3S+H^+$: 310.1472, $[M+H]^+$, found: 310.1469.



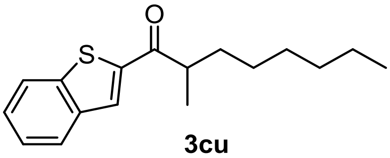
3ar

3ar was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as white solid (32 mg, 51%, trans : cis = 7 : 10). The following data is for cis isomer. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.8, 1.1 Hz, 1H), 7.63 (dd, J = 5.0, 1.1 Hz, 1H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 4.73 (br, 1H), 3.80 (br, 1H), 3.23 – 3.17 (m, 1H), 1.87 – 1.77 (m, 6H), 1.74 – 1.66 (m, 2H), 1.44 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.2, 155.2, 143.5, 133.6, 131.6, 128.1, 79.2, 45.8, 44.9, 29.5, 28.4, 24.9. HRMS (ESI+): *m/z* calcd for $C_{16}H_{23}NO_3S+H^+$: 310.1472, $[M+H]^+$, found: 310.1473.



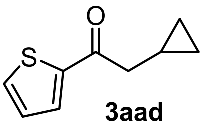
3at

3at was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as white solid (42 mg, 55%, dr = 4: 1). IR (KBr): ν_{max} 2923, 2850, 1736, 1655, 1452, 1412, 1266, 1054, 746 cm^{-1}; The following data is for major isomer. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 (dd, J = 5.0, 1.1 Hz, 1H), 7.12 (dd, J = 5.0, 3.8 Hz, 1H), 3.15 (tt, J = 12.0, 4.1 Hz, 1H), 2.48 – 2.40 (m, 1H), 2.11 – 2.02 (m, 1H), 1.98 – 1.89 (m, 1H), 1.86 – 1.73 (m, 5H), 1.71 – 1.55 (m, 4H), 1.54 – 1.47 (m, 2H), 1.38 – 1.26 (m, 5H), 1.12 – 0.97 (m, 2H), 0.87 (s, 3H), 0.86 (s, 3H), 0.80 – 0.74 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 210.3, 196.4, 143.8, 133.4, 131.4, 128.0, 54.6, 51.5, 47.9, 47.8, 46.2, 37.8, 36.1, 35.8, 35.0, 31.7, 31.5, 30.9, 28.4, 25.1, 21.7, 20.2, 13.8, 12.3. HRMS (ESI+): *m/z* calcd for $C_{24}H_{32}O_2S+H^+$: 385.2196, $[M+H]^+$, found: 385.2193.



3cu

3cu was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as light-yellow oil (30 mg, 54%, er = 62 : 38). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 0.8 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.48 – 7.38 (m, 2H), 3.46 – 3.37 (m, 1H), 1.91 – 1.81 (m, 1H), 1.55 – 1.47 (m, 1H), 1.37 – 1.28 (m, 8H), 1.26 (d, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 199.0, 143.8, 142.6, 139.2, 128.5, 127.3, 125.9, 124.9, 123.0, 42.5, 34.1, 31.7, 29.4, 27.5, 22.6, 17.6, 14.0. HRMS (ESI+): *m*/*z* calcd for $C_{17}H_{22}OS+H^+$: 275.1465, $[M+H]^+$, found: 275.1458.

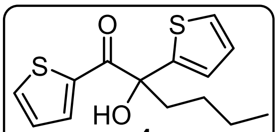


3aad

3aad was purified by column chromatography on silica gel (PE/AcOEt = 100/1) as colorless oil (12 mg, 35%). IR (KBr): ν_{max} 2955, 2923, 2858, 1665, 1469, 1419, 1379, 1266, 753 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.63 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.8 Hz, 1H), 2.80 (d, *J* = 6.9 Hz, 2H), 1.22 – 1.13 (m, 1H), 0.63 – 0.57 (m, 2H), 0.24 – 0.20 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 192.9, 144.4, 133.5, 131.8, 128.0, 44.5, 7.1, 4.6. HRMS (ESI+): *m*/*z* calcd for $C_9H_{10}OS+H^+$: 167.0526, $[M+H]^+$, found: 167.0521.

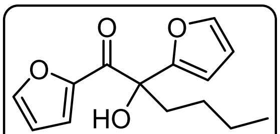
5. General procedure for the synthesis of α-alkylated benzoin derivatives

In a glovebox, a 25 mL seal bottle was charged with aldehyde (0.2 mmol), catalyst **A** (10.7 mg, 0.02 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), alkyl iodide (0.1 mmol) and CH_3OH (1 mL). The solution was heated to 60 °C in oil bath and stirred for 2 h. The reaction was then quenched with water (2 mL) and extracted with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and filtered. The volatiles were removed in vacuo and the crude product was purified by silica gel chromatography: PE/AcOEt → 100/1 to 10/1, unless otherwise stated.



4aa

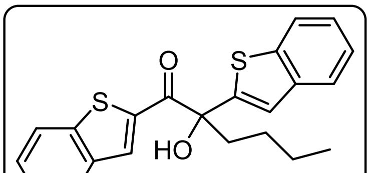
4aa was purified by column chromatography on silica gel (PE/AcOEt = 40/1) as light-yellow solid (25 mg, 88%). IR (KBr): ν_{max} 2964, 2918, 2858, 1704, 1387, 1273, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.62 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.12 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.81 (s, 1H), 2.55 – 2.34 (m, 2H), 1.61 – 1.48 (m, 1H), 1.39 – 1.26 (m, 2H), 1.14 – 1.03 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.9, 147.1, 138.5, 135.0, 134.9, 128.1, 126.9, 126.1, 125.7, 79.5, 40.0, 25.3, 22.8, 13.8. HRMS (ESI+): *m/z* calcd for $C_{14}H_{16}O_2S_2+H^+$: 281.0665, $[M+H]^+$, found: 281.0675.



4ba

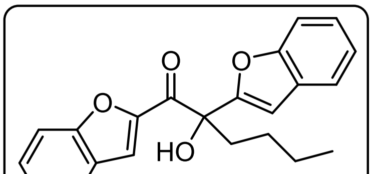
4ba was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as colorless oil (12 mg, 48%). IR (KBr): ν_{max} 2964, 2923, 2858, 1664, 1469, 1371, 1257, 1064, 835, 798, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.7 Hz, 1H), 7.34

(d, J = 1.8 Hz, 1H), 7.11 (d, J = 3.7 Hz, 1H), 6.48 (dd, J = 3.7, 1.7 Hz, 1H), 6.46 (d, J = 3.3 Hz, 1H), 6.36 (dd, J = 3.3, 1.8 Hz, 1H), 4.78 (s, 1H), 2.41 – 2.29 (m, 2H), 1.54 – 1.47 (m, 1H), 1.35 – 1.27 (m, 2H), 1.09 – 1.01 (m, 1H), 0.86 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 187.3, 154.5, 149.2, 147.4, 142.5, 120.9, 112.3, 110.6, 107.7, 77.1, 36.9, 24.9, 22.8, 13.8. HRMS (ESI+): m/z calcd for $C_{14}H_{16}O_4$+K^+: 287.0681, $[M+K]^+$, found: 287.0674.



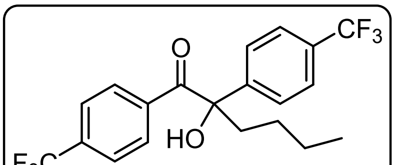
4ca

4ca was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as yellow solid (22 mg, 57%). IR (KBr): ν_{max} 2964, 2923, 2866, 1655, 1509, 1273, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 0.8 Hz, 1H), 7.83 – 7.78 (m, 3H), 7.75 (dd, J = 5.0, 1.1 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.37 – 7.29 (m, 3H), 4.76 (s, 1H), 2.70 – 2.62 (m, 1H), 2.55 – 2.48 (m, 1H), 1.64 – 1.54 (m, 1H), 1.41 – 1.31 (m, 2H), 1.22 – 1.13 (m, 1H), 0.88 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.0, 147.5, 142.8, 139.8, 139.4, 138.7, 138.0, 132.4, 127.9, 126.4, 125.0, 124.7, 124.4, 123.9, 122.6, 122.4, 122.3, 80.5, 39.9, 25.4, 22.8, 13.9. HRMS (ESI+): m/z calcd for $C_{22}H_{20}O_2S_2$+H^+: 381.0978, $[M+H]^+$, found: 381.0971.



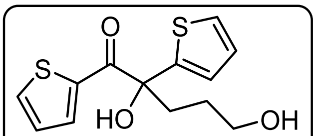
4da

4da was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as colorless oil (16 mg, 45%). IR (KBr): ν_{max} 2964, 2914, 2850, 1672, 1542, 1460, 1397, 1038, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 1H), 7.60 (d, J = 1.0 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.55 – 7.52 (m, 1H), 7.49 – 7.44 (m, 1H), 7.43 – 7.40 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 6.94 (d, J = 1.0 Hz, 1H), 4.88 (s, 1H), 2.67 – 2.59 (m, 1H), 2.55 – 2.48 (m, 1H), 1.40 – 1.29 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 188.9, 157.0, 155.7, 154.9, 149.1, 129.1, 127.9, 126.6, 124.7, 124.1, 123.6, 123.0, 121.3, 116.9, 112.5, 111.5, 104.6, 78.1, 37.0, 25.0, 22.8, 13.8. HRMS (ESI+): *m*/*z* calcd for $C_{22}H_{20}O_4$+Na $^+$: 371.1254, [M+Na]$^+$, found: 371.1262.



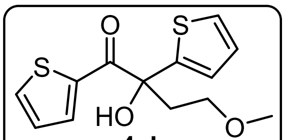
4fa

4fa was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as light-yellow solid (32 mg, 78%). IR (KBr): ν_{max} 2964, 2940, 2866, 1679, 1419, 1323, 1176, 1135, 1063, 1013, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.78 (m, 2H), 7.66 – 7.64 (m, 2H), 7.61 – 7.58 (m, 4H), 4.08 (s, 1H), 2.36 – 2.26 (m, 2H), 1.37 – 1.28 (m, 3H), 1.12 – 1.03 (m, 1H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.3, 145.4, 137.0, 134.2 (q, *J* = 33.0 Hz), 130.4 (q, *J* = 32.8 Hz), 130.1, 126.2, 125.9 (q, *J* = 3.8 Hz), 125.4 (q, *J* = 3.6 Hz), 125.0 (q, *J* = 270.9 Hz), 122.2 (q, *J* = 270.4 Hz), 82.2, 38.5, 25.1, 22.8, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7, -63.4. HRMS (ESI+): *m*/*z* calcd for $C_{20}H_{18}F_6O_2$+Na$^+$: 427.1104, [M+Na]$^+$, found: 427.1096.



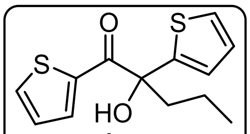
4ab

4ab was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as light-yellow solid (20 mg, 72%). IR (KBr): ν_{max} 2964, 2923, 2858, 1639, 1509, 1412, 1355, 1240, 1046, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.59 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.25 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.08 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.02 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.57 (s, 1H), 3.67 (t, *J* = 6.0 Hz, 2H), 2.66 – 2.58 (m, 1H), 2.49 – 2.42 (m, 1H), 1.82 – 1.72 (m, 1H), 1.65 – 1.52 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.0, 147.2, 138.7, 135.4, 134.9, 127.9, 127.0, 125.8, 125.2, 80.4, 62.7, 37.9, 26.6. HRMS (ESI+): *m*/*z* calcd for $C_{13}H_{14}O_3S_2$+H$^+$: 283.0458, [M+H]$^+$, found: 283.0454.



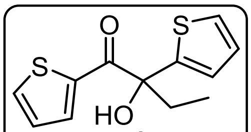
4ah

4ah was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as white solid (17 mg, 60%). IR (KBr): ν_{max} 2964, 2931, 2858, 1655, 1412, 1347, 1282, 1103, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 3.8, 1.4 Hz, 1H), 7.59 (dd, J = 4.9, 1.2 Hz, 1H), 7.24 (dd, J = 5.1, 1.2 Hz, 1H), 7.05 (dd, J = 5.0, 3.9 Hz, 1H), 7.01 (dd, J = 5.1, 3.9 Hz, 1H), 6.95 (dd, J = 5.1, 3.5 Hz, 1H), 5.76 (s, 1H), 3.73 – 3.68 (m, 1H), 3.59 – 3.54 (m, 1H), 3.29 (s, 3H), 2.73 – 2.67 (m, 1H), 2.50 – 2.43 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.6, 147.3, 139.2, 135.7, 134.6, 127.6, 127.2, 125.3, 124.3, 82.6, 70.1, 59.0, 39.5. HRMS (ESI+): m/z calcd for $C_{13}H_{14}O_3S_2+H^+$: 283.0458, $[M+H]^+$, found: 283.0450.



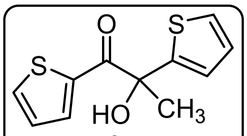
4av

4av was purified by column chromatography on silica gel (PE/AcOEt = 40/1) as colorless oil (21 mg, 78%). IR (KBr): ν_{max} 2964, 2923, 2858, 1639, 1460, 1412, 1351, 1249, 1063, 859, 729, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 3.9, 1.2 Hz, 1H), 7.62 (dd, J = 5.0, 1.1 Hz, 1H), 7.30 (dd, J = 5.1, 1.2 Hz, 1H), 7.12 (dd, J = 3.6, 1.2 Hz, 1H), 7.03 (dd, J = 5.0, 3.9 Hz, 1H), 6.98 (dd, J = 5.1, 3.6 Hz, 1H), 4.83 (s, 1H), 2.52 – 2.33 (m, 2H), 1.64 – 1.53 (m, 1H), 1.20 – 1.07 (m, 1H), 0.92 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.8, 147.1, 138.5, 135.0, 134.9, 128.1, 126.9, 126.1, 125.7, 79.5, 42.5, 16.6, 14.2. HRMS (ESI+): m/z calcd for $C_{13}H_{14}O_2S_2+K^+$: 305.0067, $[M+K]^+$, found: 305.0062.



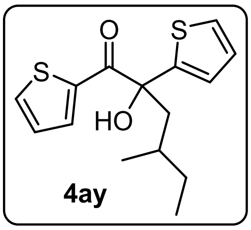
4aw

4aw was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as light-yellow oil (19 mg, 75%). IR (KBr): ν_{max} 2971, 2923, 2850, 1721, 1452, 1273, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.62 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.13 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.82 (s, 1H), 2.60 – 2.40 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.8, 146.9, 138.5, 135.0, 134.9, 128.1, 126.9, 126.1, 125.7, 79.7, 33.2, 7.6. HRMS (ESI+): *m*/*z* calcd for $C_{12}H_{12}O_2S_2$+H$^+$: 253.0352, [M+H]$^+$, found: 253.0350.



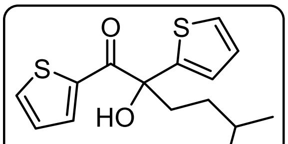
4ax

4ax was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as light-yellow oil (13 mg, 56%). IR (KBr): v_{max} 2964, 2923, 2850, 1704, 1460, 1257, 770 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.32 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.13 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 4.9, 3.9 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.80 (s, 1H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.1, 147.0, 138.2, 135.4, 135.1, 128.1, 127.0, 126.4, 125.9, 76.8, 28.1. HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{10}O_2S_2$+H$^+$: 239.0195, [M+H]$^+$, found: 239.0185.



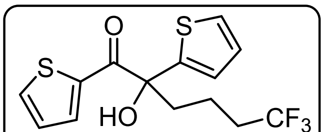
4ay

4ay was purified by column chromatography on silica gel (PE/AcOEt = 50/1) as light-yellow solid (16 mg, 55%, dr = 1: 1.5). IR (KBr): v_{max} 2964, 2923, 2874, 1655, 1419, 1347, 1240, 1063, 851, 746, 696 cm^{-1}; The following data is for mixed isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 3.9 Hz, 0.4H), 7.67 (d, *J* = 3.9 Hz, 0.6H), 7.61 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.29 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.10 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.03 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.97 (dd, *J* = 5.2, 3.5 Hz, 1H), 4.78 (s, 1H), 2.61 – 2.48 (m, 1H), 2.41 – 2.25 (m, 1H), 1.54 – 1.42 (m, 1H), 1.29 – 1.05 (m, 2H), 1.00 (d, *J* = 6.7 Hz, 1.8H), 0.87 (t, *J* = 7.4 Hz, 1.2H), 0.74 (d, *J* = 6.7 Hz, 1.2H), 0.68 (t, *J* = 7.4 Hz, 1.8H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.3, 193.1, 147.9, 147.8, 138.9, 138.7, 135.1, 134.8, 128.0, 126.9, 126.9, 126.0, 125.5, 80.2, 79.9, 46.8, 46.2, 30.9, 30.8, 30.6, 30.1, 21.1, 20.2, 11.1, 10.9. HRMS (ESI+): *m/z* calcd for $C_{15}H_{18}O_2S_2$+K^+: 333.0380, $[M+H]^+$, found: 333.0375.



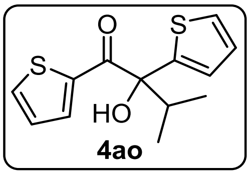
4aaa

4aaa was purified by column chromatography on silica gel (PE/AcOEt = 50/1) as light-yellow solid (15 mg, 50%). IR (KBr): ν_{max} 2955, 2923, 2858, 1647, 1469, 1412, 1355, 1244, 1046, 756, 721, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.62 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.30 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.12 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.73 (s, 1H), 2.54 – 2.36 (m, 2H), 1.59 – 1.42 (m, 2H), 1.04 – 0.95 (m, 1H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.9, 147.2, 138.5, 135.0, 134.8, 128.0, 126.9, 126.0, 125.6, 79.7, 38.2, 32.0, 28.1, 22.4, 22.3. HRMS (ESI+): *m/z* calcd for $C_{15}H_{18}O_2S_2$+K^+: 333.0380, $[M+K]^+$, found: 333.0376.



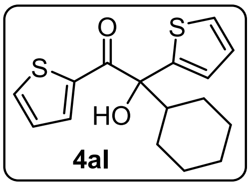
4aab

4aab was purified by column chromatography on silica gel (PE/AcOEt = 20/1) as yellow solid (28 mg, 83%). IR (KBr): ν_{max} 2947, 2914, 2858, 1672, 1266, 1046, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.65 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.32 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.11 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.06 (dd, *J* = 5.0, 3.9 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.83 (s, 1H), 2.61 – 2.42 (m, 2H), 2.17 – 2.06 (m, 2H), 1.89 – 1.79 (m, 1H), 1.50 – 1.41 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.2, 146.3, 138.0, 135.4, 135.3, 128.2, 127.0, 126.8 (q, $J_{C\text{-}F}$ = 274.0 Hz), 126.4, 125.8, 79.3, 39.0, 33.6 (q, $J_{C\text{-}F}$ = 28.7 Hz), 16.2 (q, $J_{C\text{-}F}$ = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2. HRMS (ESI+): *m/z* calcd for $C_{14}H_{13}F_3O_2S_2$+K^+: 372.9941, $[M+K]^+$, found: 372.9950.



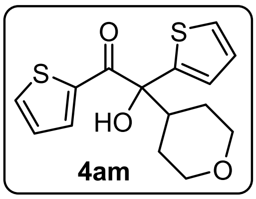
4ao

4ao was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as colorless oil (23 mg, 87%). IR (KBr): ν_{max} 2971, 2914, 2858, 1664, 1476, 1371, 1273, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 3.9, 1.1 Hz, 1H), 7.63 (dd, J = 4.9, 1.1 Hz, 1H), 7.27 (dd, J = 5.0, 1.1 Hz, 1H), 7.19 (dd, J = 3.6, 1.1 Hz, 1H), 7.07 (dd, J = 5.0, 3.9 Hz, 1H), 6.99 (dd, J = 5.0, 3.6 Hz, 1H), 4.59 (s, 1H), 3.04 – 2.95 (m, 1H), 1.13 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 193.1, 146.4, 138.7, 134.8, 134.7, 127.9, 126.9, 125.9, 125.8, 83.7, 36.0, 17.0, 16.9. HRMS (ESI+): m/z calcd for $C_{13}H_{14}O_2S_2+H^+$: 267.0508, $[M+H]^+$, found: 267.0502.



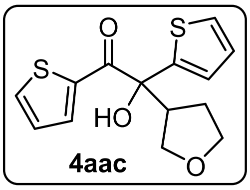
4al

4al was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as light-yellow oil (24 mg, 77%). IR (KBr): ν_{max} 2931, 2850, 1647, 1412, 1338, 1240, 1054, 761, 713, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 3.9, 1.1 Hz, 1H), 7.63 (dd, J = 5.0, 1.1 Hz, 1H), 7.25 (dd, J = 5.1, 1.2 Hz, 1H), 7.15 (dd, J = 3.6, 1.2 Hz, 1H), 7.08 (dd, J = 5.0, 3.9 Hz, 1H), 6.97 (dd, J = 5.1, 3.6 Hz, 1H), 4.58 (s, 1H), 2.61 (tt, J = 11.2, 3.0 Hz, 1H), 1.91 – 1.78 (m, 2H), 1.75 – 1.65 (m, 2H), 1.37 – 1.30 (m, 2H), 1.25 – 1.15 (m, 2H), 0.88 – 0.81 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 193.2, 146.1, 138.8, 134.8, 134.7, 127.9, 126.9, 125.8, 125.6, 84.0, 46.4, 27.1, 26.7, 26.4, 26.2, 26.2. HRMS (ESI+): m/z calcd for $C_{16}H_{18}O_2S_2+K^+$: 345.0380, $[M+K]^+$, found: 345.0377.



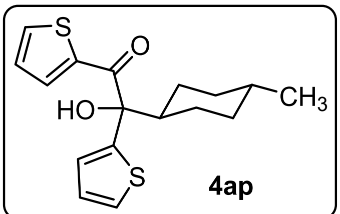
4am

4am was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as colorless oil (27 mg, 87%). IR (KBr): ν_{max} 2964, 2931, 2850, 1651, 1428, 1355, 1240, 1078, 859, 729, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 3.9, 1.2 Hz, 1H), 7.64 (dd, J = 5.0, 1.1 Hz, 1H), 7.27 (dd, J = 5.1, 1.2 Hz, 1H), 7.16 (dd, J = 3.7, 1.2 Hz, 1H), 7.09 (dd, J = 5.0, 3.9 Hz, 1H), 6.98 (dd, J = 5.1, 3.6 Hz, 1H), 4.51 (s, 1H), 4.06 – 3.93 (m, 2H), 3.49 – 3.35 (m, 2H), 2.83 (tt, J = 11.8, 3.6 Hz, 1H), 1.82 – 1.64 (m, 2H), 1.34 – 1.26 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.4, 145.0, 138.7, 135.1, 135.1, 128.0, 127.0, 126.1, 125.6, 83.2, 68.0, 67.5, 43.7, 26.9, 26.5. HRMS (ESI+): *m/z* calcd for $C_{15}H_{16}O_3S_2$+K^+: 347.0173, $[M+K]^+$, found: 347.0168.



4aac

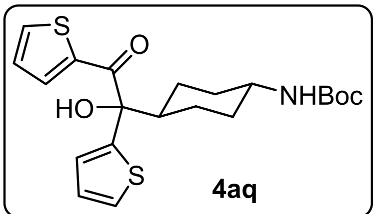
4aac was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as colorless oil (26 mg, 89%, dr = 1: 1). IR (KBr): v_{max} 2931, 2866, 1655, 1509, 1412, 1355, 1249, 1135, 1063, 916, 737 cm^{-1}; The following data is for mixed isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 1H), 7.64 – 7.62 (m, 1H), 7.29 – 7.27 (m, 1H), 7.14 – 7.11 (m, 1H), 7.07 – 7.04 (m, 1H), 6.99 – 6.97 (m, 1H), 4.79 (s, 0.5H), 4.69 (s, 0.5H), 4.01 – 3.90 (m, 2H), 3.79 – 3.66 (m, 2H), 3.57 – 3.48 (m, 1H), 2.13 – 2.06 (m, 1H), 1.96 – 1.87 (m, 0.5H), 1.83 – 1.75 (m, 0.5H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.6, 191.9, 146.4, 145.8, 138.6, 138.6, 135.6, 135.5, 135.2, 135.2, 128.0, 127.9, 127.2, 127.1, 126.4, 126.0, 125.8, 125.5, 82.7, 82.2, 69.6, 69.3, 68.5, 68.4, 47.1, 46.9, 27.4, 27.0. HRMS (ESI+): *m/z* calcd for $C_{14}H_{14}O_3S_2$+H^+: 295.0458, $[M+H]^+$, found: 295.0452.



4ap

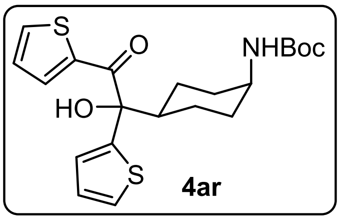
4ap was purified by column chromatography on silica gel (PE/AcOEt = 50/1) as light-yellow oil (18 mg, 57%). IR (KBr): v_{max} 2955, 2923, 2858, 1639, 1452, 1419, 1355, 1237, 1059, 753, 721, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 3.9, 1.1 Hz, 1H), 7.62 (dd, J = 5.0, 1.2 Hz, 1H), 7.24 (dd, J = 5.1, 1.2 Hz, 1H), 7.15 (dd, J

= 3.6, 1.2 Hz, 1H), 7.07 (dd, J = 5.0, 3.9 Hz, 1H), 6.97 (dd, J = 5.1, 3.6 Hz, 1H), 4.61 (s, 1H), 2.56 (tt, J = 11.8, 3.2 Hz, 1H), 1.91 – 1.84 (m, 1H), 1.81 – 1.73 (m, 1H), 1.72 – 1.66 (m, 1H), 1.46 – 1.28 (m, 4H), 1.07 – 0.91 (m, 2H), 0.87 (d, J = 6.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.2, 146.2, 138.8, 134.8, 134.7, 127.9, 126.9, 125.8, 125.6, 83.7, 46.0, 34.9, 34.8, 32.4, 26.9, 26.5, 22.4. HRMS (ESI+): *m/z* calcd for $C_{17}H_{20}O_2S_2+K^+$: 359.0537, $[M+K]^+$, found: 359.0533.



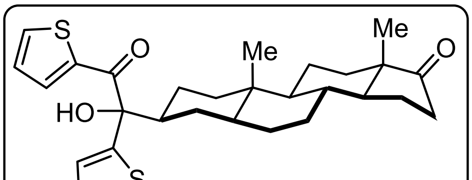
4aq

4aq was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as colorless oil (31 mg, 74%). IR (KBr): ν_{max} 3346, 2964, 2914, 2842, 1655, 1517, 1412, 1347, 1266, 1055, 746, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 3.8 Hz, 1H), 7.64 (dd, J = 5.0, 1.1 Hz, 1H), 7.25 (d, J = 1.2 Hz, 1H), 7.14 (dd, J = 3.6, 1.2 Hz, 1H), 7.08 (dd, J = 5.0, 3.9 Hz, 1H), 6.97 (dd, J = 5.1, 3.6 Hz, 1H), 5.29 (s, 1H), 4.82 (br, 1H), 3.86 (br, 1H), 2.63 (t, J = 10.8 Hz, 1H), 1.92 – 1.73 (m, 4H), 1.63 – 1.46 (m, 4H), 1.43 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.7, 155.2, 145.7, 138.5, 135.0, 134.9, 128.0, 127.0, 126.0, 125.6, 83.6, 79.1, 45.5, 44.7, 30.1, 30.0, 28.4, 21.5, 20.9. HRMS (ESI+): *m/z* calcd for $C_{21}H_{27}NO_4S_2+K^+$: 460.1014, $[M+K]^+$, found: 460.1006.



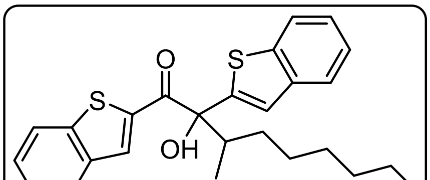
4ar

4ar was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as colorless oil (27 mg, 63%). IR (KBr): ν_{max} 3362, 2940, 2858, 1696, 1647, 1509, 1395, 1266, 1159, 1064, 753, 737, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 3.9, 1.1 Hz, 1H), 7.63 (dd, J = 5.0, 1.2 Hz, 1H), 7.25 (dd, J = 5.0, 1.1 Hz, 1H), 7.13 (dd, J = 3.6, 1.2 Hz, 1H), 7.08 (dd, J = 5.0, 3.9 Hz, 1H), 6.96 (dd, J = 5.1, 3.6 Hz, 1H), 4.48 (br, 1H), 4.36 (br, 1H), 3.38 (br, 1H), 2.55 (tt, J = 11.7, 3.4 Hz, 1H), 2.09 – 1.98 (m, 2H), 1.90 – 1.86 (m, 1H), 1.58 – 1.49 (m, 1H), 1.42 (s, 9H), 0.94 – 0.82 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.7, 155.1, 145.9, 138.6, 135.0, 134.9, 128.0, 126.9, 126.0, 125.5, 83.4, 79.1, 49.4, 45.4, 33.2, 33.0, 28.4, 25.7, 25.3. HRMS (ESI+): *m*/*z* calcd for $C_{21}H_{27}NO_4S_2+K^+$: 460.1014, $[M+K]^+$, found: 460.1012.



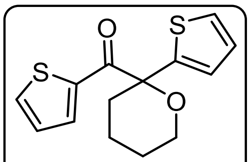
4at

4at was purified by column chromatography on silica gel (PE/AcOEt = 10/1) as white solid (27 mg, 55%, dr = 1 : 1). The following data is for mixed isomers. IR (KBr): ν_{max} 2923, 2842, 1736, 1655, 1271, 1054, 892, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 1H), 7.64 – 7.62 (m, 1H), 7.26 – 7.23 (m, 1H), 7.18 – 7.13 (m, 1H), 7.10 – 7.06 (m, 1H), 6.99 – 6.96 (m, 1H), 4.79 (s, 0.5H), 4.66 (s, 0.5H), 2.73 – 2.63 (m, 1H), 2.46 – 2.39 (m, 0.5H), 2.28 – 2.19 (m, 0.5H), 2.11 – 1.99 (m, 0.5H), 1.92 – 1.86 (m, 1.5H), 1.82 – 1.75 (m, 1H), 1.74 – 1.57 (m, 5H), 1.55 – 1.45 (m, 2H), 1.40 – 1.29 (m, 3H), 1.25 – 1.15 (m, 5.5H), 1.09 – 0.94 (m, 2.5H), 0.91 (s, 2H), 0.84 (s, 3H), 0.81 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 209.6, 193.0, 193.0, 146.1, 146.0, 138.7, 138.7, 134.9, 134.8, 134.8, 134.7, 127.9, 127.8, 126.9, 125.9, 125.7, 125.6, 125.5, 83.6, 83.5, 54.7, 54.5, 51.5, 51.4, 49.3, 49.3, 48.0, 47.8, 46.6, 46.5, 46.3, 46.3, 38.1, 38.0, 36.2, 36.2, 36.0, 35.8, 35.0, 34.6, 31.6, 31.5, 31.1, 31.0, 29.1, 29.0, 28.6, 28.5, 22.3, 21.7, 20.3, 20.3, 14.6, 13.8, 12.3, 12.3. HRMS (ESI+): *m*/*z* calcd for $C_{29}H_{36}O_3S_2+K^+$: 535.1738, $[M+K]^+$, found:535.1731.

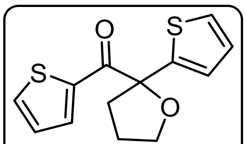


4cu

4cu was purified by column chromatography on silica gel (PE/AcOEt = 100/1) as yellow oil (38 mg, 87%, dr = 1 : 1). IR (KBr): ν_{max} 2964, 2923, 2874, 1647, 1509, 1282, 761 cm^{-1}; The following data is for mixed isomers. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 0.5H), 8.23 (s, 0.5H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.38 – 7.16 (m, 5H), 4.46 (s, 0.5H), 4.30 (s, 0.5H), 2.93 – 2.84 (m, 0.5H), 2.84 – 2.75 (m, 0.5H), 1.71 – 1.65 (m, 0.5H), 1.46 – 1.32 (m, 1H), 1.29 – 1.14 (m, 6.5H), 1.12 – 1.04 (m, 2H), 1.05 (d, *J* = 6.7 Hz, 1.5H), 0.91 (d, *J* = 6.6 Hz, 1.5H), 0.77 (t, *J* = 6.5 Hz, 1.5H), 0.70 (t, *J* = 6.9 Hz, 1.5H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.4, 194.1, 147.0, 146.9, 142.7, 139.9, 139.9, 139.6, 139.6, 138.7, 138.6, 138.6, 138.4, 132.4, 132.3, 127.8, 127.7, 126.3, 125.0, 124.9, 124.4, 124.3, 124.2, 124.2, 123.7, 123.6, 122.5, 122.5, 122.4, 122.2, 122.2, 85.8, 85.4, 41.4, 41.2, 31.8, 31.6, 31.4, 30.8, 29.4, 29.1, 27.7, 27.3, 22.6, 22.5, 14.1, 14.0, 14.0, 13.6. HRMS (ESI+): *m/z* calcd for $C_{26}H_{28}O_2S_2$+K^+: 475.1163, $[M+K]^+$, found:475.1158.


5ac

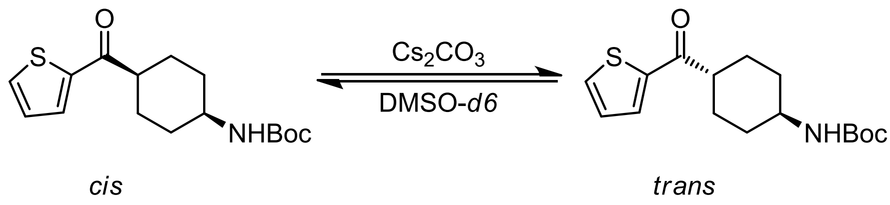
5ac was purified by column chromatography on silica gel (PE/AcOEt = 30/1) as light-yellow oil (23 mg, 82%). IR (KBr): ν_{max} 2923, 2874, 1664, 1412, 1351, 1249, 1054, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.22 (dd, *J* = 4.1, 2.4 Hz, 1H), 7.05 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.92 – 6.88 (m, 2H), 4.05 – 4.00 (m, 1H), 3.73 – 3.65 (m, 1H), 2.72 – 2.66 (m, 1H), 1.93 – 1.86 (m, 1H), 1.80 – 1.67 (m, 3H), 1.62 – 1.53 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.2, 146.1, 139.2, 135.2, 134.3, 127.6, 126.9, 125.1, 124.0, 84.5, 65.9, 34.8, 24.9, 20.4. HRMS (ESI+): *m/z* calcd for $C_{14}H_{14}O_2S_2$+H^+: 279.0508, $[M+H]^+$, found: 279.0503.

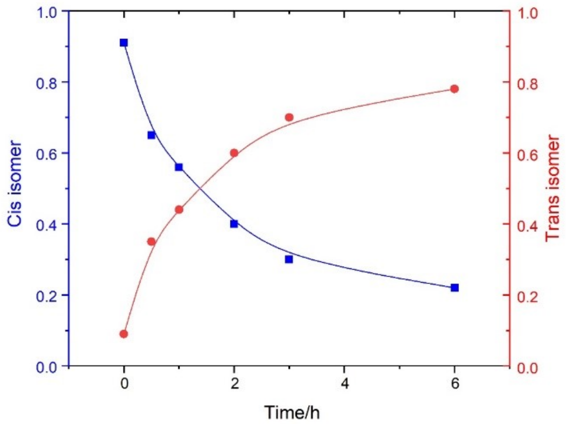

5ad

5ad was purified by column chromatography on silica gel (PE/AcOEt = 50/1) as colorless oil (22 mg, 85%). IR (KBr): ν_{max} 2964, 2931, 2874, 1647, 1492, 1419, 1347, 1038, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 4.0, 1.1 Hz, 1H), 7.61 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.20 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.07 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.98 (dd, *J* = 3.7, 1.1 Hz, 1H), 6.92 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.11 –

4.06 (m, 1H), 3.05 – 2.98 (m, 1H), 2.28 – 2.20 (m, 1H), 2.11 – 1.91 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 192.2, 146.1, 139.1, 135.8, 134.8, 127.6, 127.2, 124.8, 124.1, 91.0, 69.6, 38.4, 25.6. HRMS (ESI+): *m*/*z* calcd for $C_{13}H_{12}O_2S_2+H^+$: 265.0352, $[M+H]^+$, found: 265.0347.

6. Kinetic experiments for cis-trans isomerization





The ratio were determined by ^{1}H NMR.

7. Computational details

Geometry optimizations were performed using M06-2X functional[23] theory combining with the basis set of 6-31+G(d,p)[24]. Frequencies calculations were carried out at the same level of theory to verify that we have obtained the minimum in the potential energy surface and to obtain the thermo correction data. The solvent free energy was treated at M05-2X/6-31G* level[25] based on the optimized structures. This method is shown to be accurate for the calculations of solvent free energy as demonstrated by Truhlar and workers. All these calculations were done with GAUSSIAN 16[26]. Single point energy calculations were further conducted at DLPNO-CCSD(T)/cc-pVTZ level[27, 28] utilizing ORCA 6.0.0[29].

Table S1. The summary of electronic energy in solvent model and gas phase based on the optimized geometries. ΔG_{solv} refers to the solvent free energy as calculated at M05-2X/6-31G* level. All units are given by Hartree.

Filename	Energy_solv	Energy_gas	ΔG_{solv}
TZ_BI	-1053.448067	-1053.415971	-0.0321
TZ_BI_Anion	-1052.929825	-1052.828048	-0.10178
DBU	-462.0453161	-462.0284954	-0.01682
DBU_H^+	-462.5329725	-462.4443285	-0.08864
MIC_BI	-1521.480317	-1521.443839	-0.03648
MIC_BI_Anion	-1520.958619	-1520.858983	-0.09964
MIC_BI_K^+	-2120.806048	-2120.760194	-0.04585
NHC_BI	-1269.65781	-1269.625684	-0.03213
NHC_BI_Anion	-1269.137833	-1269.038819	-0.09901
NMe_3	-174.4374401	-174.4322716	-0.00517
NMe_3_H^+	-174.9122086	-174.8086009	-0.10361
NS_BI	-1616.091511	-1616.063721	-0.02779
NS_BI_Anion	-1615.584976	-1615.49222	-0.09276
^{t}BuOH	-233.6340169	-233.626428	-0.00759
^{t}BuOK	-832.9341539	-832.9134657	-0.02069

Table S2. The summary of single point energy (SP) and the correction of Gibbs free energy (G_{corr}), given by Hartree.

Filename	SP(a.u.)	G_{corr}(a.u.)
124_BI	-1051.639101	0.349023
124_BI_Anion	-1051.054654	0.336181
DBU	-461.2580299	0.213072
DBU_H$^+$	-461.6730627	0.227786
MIC_BI	-1518.856753	0.606583
MIC_BI_Anion	-1518.274888	0.591816
MIC_BI_K$^+$	-2117.676128	0.592019
NHC_BI	-1267.445211	0.451483
NHC_BI_Anion	-1266.860143	0.439182
NMe_3	-174.1596041	0.094287
NMe_3_H$^+$	-174.5381663	0.109624
NS_BI	-1613.545906	0.508875
NS_BI_Anion	-1612.975527	0.495658
^{t}BuOH	-233.2845547	0.107784
^{t}BuOK	-832.0482765	0.091092

Cartesian coordinates

TZ_BI_Anion

C	-0.56461800	0.41395000	-0.06367100
C	1.97044700	0.26099300	0.07210300
C	3.06191400	0.62743200	-0.74501300
C	2.11465700	-0.77664800	1.01756900
C	4.27874300	-0.03223700	-0.58639500
C	3.34719900	-1.42349600	1.11457100
C	4.44523900	-1.07018500	0.33174300
H	5.11262500	0.25254600	-1.22798600

H	3.45332800	-2.22243300	1.84813100
N	0.75940800	0.94337100	-0.07000100
C	-0.90491600	-0.84375500	-0.51770000
C	-2.28767400	-1.34986000	-0.25868900
C	-3.06858200	-0.98193500	0.85023700
C	-2.78902600	-2.35110100	-1.10872300
C	-4.32821400	-1.54050800	1.06224300
H	-2.66296400	-0.27137200	1.56830700
C	-4.05022000	-2.90016900	-0.90542100
H	-2.14012300	-2.68010300	-1.91502100
C	-4.83670200	-2.49310500	0.17747900
H	-4.90787500	-1.24538200	1.93427600
H	-4.42380700	-3.66110400	-1.58710000
H	-5.81804200	-2.92977100	0.34249700
O	-0.06237200	-1.64329500	-1.07389800
C	-0.49323700	2.62955500	0.20036200
N	-1.35107200	1.54186600	0.34912900
C	5.75315500	-1.81512200	0.43991700
H	5.78566500	-2.66766400	-0.24953500
H	6.60148400	-1.16574000	0.20009700
H	5.90260600	-2.20667600	1.45143900
C	0.99920100	-1.16272600	1.94990200
H	0.48943900	-0.27663000	2.34397100
H	0.25482000	-1.76595500	1.42055900
H	1.39995100	-1.74006400	2.78915700
C	2.89789200	1.66134400	-1.82760100
H	1.95645800	1.49002300	-2.36019600
H	2.84970100	2.67607200	-1.42250900
H	3.72736300	1.59782300	-2.53858700
N	0.73465400	2.34436200	-0.02251500

C	-2.63875100	1.93559200	-0.20823200
C	-2.72141800	3.42485100	0.18193800
C	-1.25548200	3.92056700	0.14889900
H	-3.46209800	1.34859500	0.20009800
H	-2.62911800	1.78963100	-1.30260300
H	-3.12364900	3.51022900	1.19572100
H	-3.37541100	3.98755800	-0.48883500
H	-1.01756800	4.44366500	-0.78163600
H	-1.01262600	4.58675700	0.98096800

TZ_BI

C	-1.62414900	0.05201000	0.84225100
C	-0.11055400	1.19892500	2.47667500
C	1.07695700	0.75483400	3.07592700
C	-0.96234100	2.10852000	3.11330300
C	1.39936900	1.24207000	4.33912700
C	-0.60861600	2.55440000	4.39168900
C	0.56531800	2.13801700	5.01627000
H	2.31612600	0.90187000	4.81688300
H	-1.26211300	3.26093500	4.89936700
N	-0.44511200	0.70131800	1.18796100
C	-2.43879000	-0.66245200	1.67327400
C	-3.81305500	-1.05381900	1.38362200
C	-4.64656800	-0.29039500	0.54339100
C	-4.36981700	-2.18301800	2.01340200
C	-5.96239400	-0.67287700	0.29946800
H	-4.26421800	0.63245000	0.11207300
C	-5.68774000	-2.55491700	1.77336100
H	-3.74477700	-2.76261000	2.68517300
C	-6.49140800	-1.81155000	0.90663400

H	-6.58571400	-0.06349800	-0.34888200
H	-6.09183400	-3.43585000	2.26368300
H	-7.51935500	-2.10563000	0.72126600
O	-1.89630700	-1.04956200	2.89607300
H	-2.21689100	-0.47270000	3.60437000
C	-0.52403500	0.85907300	-0.91690100
N	-1.71053200	0.25897400	-0.53015500
C	0.94582300	2.64887000	6.38317300
H	1.18024300	1.82206300	7.06031400
H	1.83212200	3.28909800	6.32718800
H	0.13624500	3.23297100	6.82702100
C	-2.22100600	2.60719800	2.44986200
H	-2.05546200	2.78935500	1.38327500
H	-3.03691000	1.87836300	2.52677100
H	-2.55139800	3.53899400	2.91405300
C	1.94325600	-0.25053800	2.36867300
H	1.35528100	-1.14120900	2.12357500
H	2.32690200	0.15547600	1.42828100
H	2.78585600	-0.54588900	2.99742900
N	0.24756200	1.16534500	0.06290500
C	-2.26994500	-0.53902100	-1.61428800
C	-1.73135900	0.21452200	-2.84966400
C	-0.37827200	0.82553800	-2.40718800
H	-3.35922700	-0.56977400	-1.57647400
H	-1.89341000	-1.56879200	-1.54755000
H	-2.43001300	1.01460700	-3.10877000
H	-1.63358200	-0.44169300	-3.71563200
H	0.46511200	0.17942600	-2.66796500
H	-0.19217000	1.81167200	-2.83599600

DBU

C	0.01275400	0.75216500	0.39680500
C	0.99207900	1.34129500	-0.65876000
C	1.87156700	2.46654600	-0.15661900
C	-0.13990200	1.57393600	1.68303700
C	-0.82027900	2.93048200	1.47483200
C	-0.23250300	3.67831600	0.26866600
H	-0.97539600	0.61018500	-0.05831200
H	1.68206100	0.57286500	-1.00777200
H	0.85405200	1.72968700	2.12075700
H	-0.71423300	3.53496500	2.38385900
H	0.36778900	-0.24428500	0.67560500
H	0.44026200	1.69304400	-1.53747800
H	-0.70974200	0.99303700	2.41608000
H	-1.89667200	2.79689700	1.30870900
H	-0.52993600	4.73230900	0.28274100
H	-0.63439300	3.26083600	-0.65833200
C	3.94923700	3.39613800	0.33419300
C	3.26853000	4.13611400	1.48345300
C	1.92059400	4.65246100	1.00093800
H	4.92446800	3.00954300	0.64306000
H	3.12380400	3.43611800	2.31468600
H	3.87740700	4.96901900	1.84708700
H	1.29187100	4.93095700	1.85647100
H	2.05338000	5.55326500	0.38577100
H	4.13100500	4.09691000	-0.49560600
N	1.22126500	3.62985200	0.22131800
N	3.14272700	2.28234400	-0.13798800

DBU_H$^+$

C	-0.03898000	0.73838700	0.37567100
C	0.97168200	1.33659800	-0.65135300
C	1.79814000	2.47982900	-0.12518500
C	-0.18650900	1.51331400	1.69081400
C	-0.83775300	2.89166900	1.53068800
C	-0.26378200	3.66284600	0.33884300
H	-1.01608000	0.65163600	-0.10932500
H	1.65586000	0.56094100	-1.00202400
H	0.79844800	1.61961600	2.16405700
H	-0.70961500	3.46953300	2.45198000
H	0.28113600	-0.27936700	0.60879100
H	0.45240200	1.70255900	-1.54317100
H	-0.78325200	0.91485700	2.38387800
H	-1.91598000	2.78896900	1.36982600
H	-0.52343900	4.72266000	0.37495600
H	-0.65372600	3.27436600	-0.60451900
C	4.02587000	3.40784600	0.37195300
C	3.30196700	4.19585500	1.45389400
C	1.96430000	4.68630300	0.91975900
H	4.92187600	2.92297000	0.76152000
H	3.14292400	3.55726600	2.32882100
H	3.90667700	5.04938100	1.76576400
H	1.34968800	5.08639500	1.72986100
H	2.09442300	5.47479400	0.17045700
H	4.31635700	4.05403000	-0.46308100
N	1.20710800	3.57944900	0.30632200
N	3.12131800	2.36228900	-0.11363200
H	3.51339000	1.50136900	-0.46887700

MIC_BI_Anion

C	0.49379500	1.12993400	-0.41558700
H	0.86080100	2.09525800	-0.72772800
C	-0.81187700	0.59066000	-0.41067500
C	2.75755100	0.26299100	-0.02546400
C	3.41542700	1.00364700	0.97056300
C	3.43158400	-0.43978200	-1.03385800
C	4.81198900	1.04124900	0.91885300
C	4.82795800	-0.38375600	-1.03201800
C	5.51138200	0.35146700	-0.06836300
H	5.36330500	1.60758500	1.66213600
H	5.38492300	-0.91558000	-1.79851400
H	6.59695500	0.38921800	-0.08530000
C	-1.49213900	-1.63793100	0.60997200
C	-1.73829000	-2.90591900	0.04684200
C	-2.07036700	-1.26502000	1.83331400
C	-2.61526400	-3.77274200	0.69670100
C	-2.97251900	-2.14904200	2.43783700
C	-3.24525400	-3.39130500	1.88061500
H	-2.82539600	-4.74966100	0.27019200
H	-3.46069300	-1.86071000	3.36615300
H	-3.94388500	-4.06612600	2.36842300
C	2.62915500	1.67039300	2.09160000
H	1.75039600	2.15128300	1.64893500
C	2.68040600	-1.23733600	-2.08673600
H	1.62387200	-0.95573600	-2.03486800
C	3.18170100	-0.93154500	-3.50278800
H	4.20861000	-1.28243500	-3.65582500
H	2.54714700	-1.44035200	-4.23521700
H	3.15216800	0.14214400	-3.71157300
C	2.77098000	-2.73818800	-1.78108100

H	2.35602800	-2.94085900	-0.79028200
H	2.19851300	-3.30898300	-2.52106900
H	3.81323500	-3.07978600	-1.81596300
C	3.41969200	2.75110700	2.83044900
H	2.76024300	3.26680400	3.53472500
H	4.24277300	2.31913800	3.41126000
H	3.83619200	3.49499100	2.14349500
C	2.12056000	0.60639700	3.07843500
H	1.51450100	-0.14996700	2.56941900
H	2.97098500	0.10439700	3.55578000
H	1.51269300	1.07541000	3.86004200
C	-1.76273000	0.06299400	2.50287200
H	-0.90597500	0.50818500	1.98868400
C	-2.95317300	1.02305700	2.36534400
H	-3.27526100	1.09319700	1.32274900
H	-3.79955800	0.65671700	2.96085100
H	-2.68807900	2.02303900	2.72907800
C	-1.36741900	-0.11663100	3.97380700
H	-0.52682900	-0.81078300	4.07447100
H	-1.07462600	0.84856600	4.40388600
H	-2.20110400	-0.50276500	4.57085800
C	-1.11219500	-3.25659800	-1.29165300
H	-0.14794200	-2.74034500	-1.33514400
C	-0.85082200	-4.75284200	-1.47425000
H	-0.29621200	-4.92042900	-2.40453700
H	-0.26281200	-5.16193100	-0.64545200
H	-1.78365600	-5.32430400	-1.54768900
C	-1.99574200	-2.70609800	-2.42098500
H	-2.94963400	-3.24875700	-2.44627300
H	-2.21740000	-1.64687200	-2.25232200

H	-1.50218900	-2.83438300	-3.39292000
N	1.33140900	0.18404100	-0.01019400
N	0.78496500	-1.00450900	0.30264300
N	-0.58605400	-0.80105200	-0.10180000
C	-2.04153200	1.05883200	-0.88595300
C	-2.18534700	2.49444900	-1.23795800
C	-1.44368300	3.54858600	-0.66891300
C	-3.19038400	2.83563300	-2.16449000
C	-1.64680800	4.86876200	-1.06290000
H	-0.73962000	3.33794700	0.13140600
C	-3.39175600	4.15345700	-2.55674500
H	-3.79824700	2.02346900	-2.55124800
C	-2.61389500	5.18433700	-2.01978900
H	-1.06325000	5.66107000	-0.59968100
H	-4.16630600	4.38514600	-3.28435400
H	-2.77622700	6.21537500	-2.32101200
O	-3.03832500	0.27164700	-1.04151300

MIC_BI

C	0.48587200	1.21179300	0.22022800
H	0.85026000	2.21524300	0.35015500
C	-0.83454100	0.66993800	0.17369400
C	2.75710400	0.29398400	-0.14704100
C	3.50540600	-0.00343300	0.99846100
C	3.30870900	0.67856000	-1.37221500
C	4.89193700	0.11770700	0.88993200
C	4.70126100	0.78996500	-1.42556600
C	5.48176500	0.51644000	-0.30743100
H	5.51840500	-0.10452300	1.74810200
H	5.17763900	1.08862700	-2.35498200

H	6.56168900	0.60775000	-0.36971400
C	-1.46597800	-1.79032200	-0.24710100
C	-2.16841800	-1.94679500	-1.44939000
C	-1.57654800	-2.67669500	0.83263900
C	-3.01957000	-3.04691500	-1.55473600
C	-2.43523300	-3.76911600	0.67794600
C	-3.14918400	-3.95003200	-0.50233100
H	-3.59135400	-3.20032900	-2.46391100
H	-2.54979800	-4.48423600	1.48561100
H	-3.81426600	-4.80241500	-0.60319100
C	2.84482200	-0.50621600	2.27034800
H	1.78536200	-0.22449400	2.23751800
C	2.45625800	0.94524000	-2.60078400
H	1.40712500	0.76562300	-2.34133600
C	2.58084200	2.40524300	-3.05227800
H	3.60938200	2.63943600	-3.34691900
H	1.93266400	2.59036400	-3.91390900
H	2.29167800	3.09293300	-2.25218300
C	2.82070600	-0.02207900	-3.73363700
H	2.72293800	-1.06182700	-3.40821200
H	2.15703500	0.13460100	-4.58944700
H	3.85011200	0.13544000	-4.07259200
C	3.44475400	0.11747100	3.53374900
H	2.86438400	-0.18969400	4.40859400
H	4.47627700	-0.21153200	3.69499600
H	3.43737600	1.20990000	3.48268100
C	2.92477800	-2.03953100	2.32218300
H	2.46525300	-2.48711900	1.43575100
H	3.96981600	-2.36505800	2.37067600
H	2.40777100	-2.41713400	3.21084200

C	-0.83674800	-2.40827000	2.13347200
H	0.14301500	-1.99150600	1.87328600
C	-1.59198600	-1.35824600	2.96350400
H	-1.71693600	-0.41967200	2.41304500
H	-2.58503200	-1.73518300	3.23415800
H	-1.04760100	-1.13902500	3.88854400
C	-0.58863400	-3.66855600	2.96345100
H	-0.09220500	-4.44690900	2.37595300
H	0.04872200	-3.42642300	3.81934300
H	-1.52180900	-4.07929900	3.36324400
C	-1.97154700	-0.95721900	-2.58318300
H	-1.80923200	0.02718100	-2.13109900
C	-0.72066100	-1.32974000	-3.39429400
H	-0.53327100	-0.58042900	-4.17159600
H	0.16486100	-1.39759300	-2.75411300
H	-0.85830800	-2.30133800	-3.88222000
C	-3.19411700	-0.83284700	-3.49256400
H	-3.36273100	-1.74496100	-4.07543300
H	-4.09373400	-0.61544200	-2.91004700
H	-3.04083800	-0.01615400	-4.20401500
N	1.32385400	0.19719600	-0.05688000
N	0.75266800	-0.94822500	-0.27034000
N	-0.56686500	-0.67970200	-0.11992500
C	-2.07998700	1.24180000	0.31855100
C	-2.32829800	2.61820600	0.70157600
C	-1.40988200	3.39555600	1.44063900
C	-3.56159200	3.22080800	0.36939500
C	-1.69312100	4.71325400	1.78432400
H	-0.48978500	2.94842300	1.80237100
C	-3.83817000	4.53619400	0.72200100

H	-4.28967400	2.63966000	-0.18647300
C	-2.90476100	5.30190800	1.42287400
H	-0.96559300	5.27931500	2.35966300
H	-4.79313800	4.97149300	0.44077100
H	-3.12269600	6.32966600	1.69380300
O	-3.18288500	0.47099300	-0.06352900
H	-3.67970400	0.20548900	0.72200400

MIC_BI_K$^+$

C	0.93591000	1.05301700	-0.31913500
H	1.46137500	1.98959900	-0.40883900
C	-0.45124100	0.72372200	-0.45057800
C	3.02737000	-0.19613100	-0.06942200
C	3.67058600	-0.11589900	1.17142600
C	3.69501700	-0.39243900	-1.28243600
C	5.06569300	-0.18321100	1.16668900
C	5.09056800	-0.45964500	-1.23407000
C	5.76831300	-0.34573700	-0.02488300
H	5.60927700	-0.11701900	2.10392000
H	5.65027300	-0.60517000	-2.15386900
H	6.85276900	-0.39582700	-0.00749500
C	-1.44253900	-1.47162000	0.28318400
C	-2.16355800	-2.41840500	-0.47681900
C	-1.68027400	-1.30476100	1.65911200
C	-3.11605900	-3.21097800	0.17225000
C	-2.66316300	-2.10112200	2.26747200
C	-3.36672600	-3.05599500	1.53829200
H	-3.66805500	-3.95893400	-0.38887900
H	-2.86202300	-1.98620100	3.33021700
H	-4.09915000	-3.68809600	2.03261600

C	2.87789000	0.04706600	2.45626400
H	1.87649500	-0.34804200	2.26036200
C	2.95145900	-0.54257300	-2.59823400
H	1.87777400	-0.47136100	-2.39833400
C	3.32625500	0.57739400	-3.57589000
H	4.39000500	0.53770000	-3.83497400
H	2.75049200	0.47895100	-4.50113300
H	3.11698000	1.56149100	-3.14616900
C	3.21163100	-1.92560800	-3.20769900
H	2.92809500	-2.71608800	-2.50714100
H	2.62578400	-2.04881300	-4.12401800
H	4.26910000	-2.05403300	-3.46391700
C	2.74749200	1.52699000	2.84216300
H	2.14079800	1.63285400	3.74841000
H	3.73423800	1.96096900	3.03969900
H	2.27282100	2.10610300	2.04471800
C	3.46658500	-0.76188700	3.61550100
H	3.61053600	-1.80929500	3.33560200
H	4.42932900	-0.35731600	3.94505400
H	2.78804000	-0.72539400	4.47357600
C	-0.93745600	-0.26999500	2.48605100
H	-0.11118300	0.11344700	1.88417900
C	-1.85573300	0.91844400	2.80404400
H	-2.21906400	1.38331700	1.88036300
H	-2.71032500	0.59668600	3.41364800
H	-1.31196900	1.68214800	3.36992300
C	-0.34023200	-0.87472000	3.76107900
H	0.29443500	-1.73539400	3.52673600
H	0.27114800	-0.12525400	4.27588900
H	-1.11640700	-1.20064300	4.46170900

C	-1.89112100	-2.53884600	-1.96534700
H	-1.71181400	-1.51773800	-2.31795300
C	-0.61559800	-3.35997200	-2.20758800
H	-0.39316500	-3.40200100	-3.27938400
H	0.23869600	-2.91727300	-1.68858600
H	-0.74909500	-4.38684300	-1.84651100
C	-3.06391500	-3.12391900	-2.75343600
H	-3.23156100	-4.18142300	-2.51931300
H	-3.99658900	-2.57863800	-2.56612100
H	-2.85316100	-3.05886200	-3.82454600
N	1.59386300	-0.07934100	-0.11907800
N	0.88209400	-1.19458300	-0.09521100
N	-0.43322700	-0.72375400	-0.39829800
C	-1.58733700	1.45302900	-0.71386800
C	-1.54313200	2.93139600	-0.74055300
C	-0.65853200	3.70918200	0.02912200
C	-2.48835500	3.60889200	-1.53182200
C	-0.67919400	5.10013800	-0.03728800
H	0.01920900	3.22339600	0.72623200
C	-2.50654500	4.99764400	-1.59874900
H	-3.19583300	3.00781700	-2.09401200
C	-1.59589100	5.75591500	-0.85927900
H	0.01090800	5.67581200	0.57359800
H	-3.23562800	5.49611100	-2.23204400
H	-1.61226400	6.84020400	-0.90901500
O	-2.73732000	0.86150400	-0.94651300
K	-4.40372800	-0.38449600	0.21119400

NHC_BI_Anion

C	-0.35871300	-0.27185100	0.15428200

C	-2.83161900	-0.60615300	-0.06639700
C	-3.51815100	-0.38607500	-1.27192400
C	-3.44912600	-0.36270600	1.16585100
C	-4.84344500	0.03805900	-1.21723500
C	-4.78230000	0.06551300	1.17706100
C	-5.49464600	0.26650300	-0.00123100
H	-5.37828600	0.21300400	-2.14996600
H	-5.26397600	0.25797600	2.13503800
N	-1.49531400	-1.11678900	-0.12072500
C	-0.29199700	1.04972600	-0.22381700
C	0.87877200	1.88343000	0.18651100
C	1.66443000	1.66887100	1.33189800
C	1.17473400	3.00322100	-0.60791100
C	2.72552100	2.51143400	1.64572800
H	1.42418200	0.83653500	1.98633500
C	2.24199800	3.84358100	-0.29892800
H	0.52654500	3.18521300	-1.45979800
C	3.03135600	3.60230200	0.82640500
H	3.31713300	2.31780900	2.53784800
H	2.45813400	4.69702300	-0.93803400
H	3.86441000	4.25669300	1.06909700
O	-1.17026700	1.58466900	-1.00984500
C	1.98018400	-1.14177500	0.11554900
C	2.22531300	-0.93630300	-1.26016400
C	3.05209900	-1.35378700	0.99949400
C	3.54824200	-0.88883800	-1.69433100
C	4.36169900	-1.30778000	0.51219300
C	4.63337700	-1.05414100	-0.82768500
H	3.73766700	-0.73294900	-2.75611500
H	5.18616500	-1.45312000	1.20932500

C	-1.21794000	-2.36095200	0.45953200
H	-1.97918500	-3.12809800	0.49362300
C	0.04694400	-2.40078600	0.90233300
H	0.60608400	-3.22412700	1.32158700
N	0.66483800	-1.14349200	0.66514200
C	2.80137200	-1.62718500	2.46017400
H	1.93123800	-1.06801700	2.81508900
H	2.58984000	-2.68858900	2.64408600
H	3.67635600	-1.35706500	3.05865100
C	6.04887100	-0.94025700	-1.33641600
H	6.16957400	-1.45821100	-2.29373900
H	6.32669700	0.10819100	-1.49333100
H	6.76013600	-1.37048500	-0.62507900
C	1.11341800	-0.81492200	-2.27282900
H	0.27587000	-1.47621500	-2.02926700
H	0.70409300	0.20078700	-2.30994000
H	1.49601000	-1.08139100	-3.26364100
C	-6.92345200	0.75302400	0.02117100
H	-6.99565600	1.77540400	-0.36610100
H	-7.56827500	0.12128200	-0.59909900
H	-7.32474300	0.75142900	1.03869300
C	-2.69422800	-0.53639900	2.46018200
H	-2.56528900	-1.59486100	2.71477800
H	-1.69388900	-0.10026400	2.38012600
H	-3.23038900	-0.04957900	3.27986200
C	-2.79913300	-0.54271500	-2.58069000
H	-2.01000600	0.22025500	-2.60550800
H	-2.32000900	-1.52366400	-2.65786900
H	-3.48643600	-0.40855400	-3.42165700

NHC_BI

C	0.40619300	-0.43280200	0.22413400
C	2.88412700	-0.57519300	0.12441200
C	3.77361500	-0.32067900	1.17453900
C	3.21533800	-0.30857800	-1.20868600
C	5.02732000	0.20192000	0.86154900
C	4.48071600	0.22205700	-1.47678600
C	5.39867700	0.47748500	-0.45802600
H	5.72797200	0.41021900	1.66763100
H	4.75372500	0.43444100	-2.50843300
N	1.59882500	-1.13093000	0.42474800
C	0.27739700	0.92997300	0.29718200
C	-0.87491100	1.72424300	-0.11166100
C	-1.63627200	1.40970700	-1.25251400
C	-1.23797400	2.86822200	0.62407100
C	-2.75409800	2.15863200	-1.59949000
H	-1.33556800	0.57092200	-1.87427100
C	-2.34661700	3.62791600	0.26215900
H	-0.64347100	3.14002200	1.49125800
C	-3.12207300	3.27166400	-0.84163300
H	-3.33186300	1.88103700	-2.47674800
H	-2.61245200	4.50015300	0.85256400
H	-3.99051500	3.86138300	-1.11739000
O	1.27955700	1.58752800	1.02032600
H	1.79778800	2.14415700	0.42418300
C	-1.97408500	-1.22466500	0.13934400
C	-2.51398100	-0.69939700	1.32289000
C	-2.78551500	-1.56535300	-0.95111500
C	-3.88821300	-0.46316300	1.36248500
C	-4.15692100	-1.32985000	-0.85586200

C	-4.72288700	-0.75680400	0.28315200
H	-4.31845200	-0.04158000	2.26887600
H	-4.79367600	-1.57772800	-1.70267000
C	1.34985200	-2.50605900	0.31054800
H	2.14982600	-3.22220200	0.41451700
C	0.03982000	-2.67797000	0.07549200
H	-0.55131600	-3.57493500	-0.01843200
N	-0.56588400	-1.41312900	0.02016300
C	-2.18940800	-2.13901300	-2.21129000
H	-1.25027800	-1.63857200	-2.46857300
H	-1.96031200	-3.20503100	-2.10214100
H	-2.88515700	-2.03351600	-3.04666600
C	-6.19461500	-0.43657800	0.34255400
H	-6.60161000	-0.62712700	1.33929400
H	-6.36424800	0.62078300	0.11255200
H	-6.76024400	-1.03130200	-0.37891700
C	-1.65828000	-0.39712300	2.52486400
H	-0.81345700	-1.08835200	2.59916400
H	-1.24683600	0.61642200	2.46663200
H	-2.25455300	-0.47483700	3.43719000
C	6.77246200	1.01618000	-0.76948800
H	7.08175900	1.75946500	-0.02958700
H	7.51578700	0.21197500	-0.75977300
H	6.79981400	1.48379600	-1.75663400
C	2.22709800	-0.56415300	-2.31855300
H	1.73860800	-1.53721900	-2.19978600
H	1.43833900	0.19706500	-2.31536800
H	2.72518400	-0.54142500	-3.29026400
C	3.34402300	-0.55810100	2.59631900
H	2.46982900	0.06260400	2.81856000

H	3.05597700	-1.60092200	2.76088100
H	4.14762500	-0.30661700	3.29182600

NMe_3

N	1.40099200	1.14012800	0.00008100
C	1.85062900	-0.23969900	-0.00006500
H	1.46677600	-0.75406600	0.88535700
H	1.46980300	-0.75300000	-0.88738000
H	2.95517200	-0.32209900	0.00182300
C	1.84857600	1.82915100	1.19630900
H	1.46663400	2.85383700	1.19792900
H	1.46427500	1.31809500	2.08344900
H	2.95298800	1.86990100	1.26988400
C	1.85279300	1.83085200	-1.19358500
H	1.47253300	1.32038300	-2.08277800
H	1.46997000	2.85520800	-1.19567700
H	2.95745700	1.87260900	-1.26264500

NMe_3_H^+

C	1.85151200	-0.28964800	-0.00016000
H	1.46764400	-0.78145400	0.89330300
H	1.47108500	-0.78014900	-0.89580300
H	2.94208100	-0.30154000	0.00192900
C	1.84955200	1.85407800	1.23964400
H	1.46750600	2.87440900	1.21789500
H	1.46593000	1.32425100	2.11119200
H	2.94009800	1.85989600	1.25171200
C	1.85395600	1.85593700	-1.23681000
H	1.47338900	1.32743100	-2.11051100
H	1.47187500	2.87624400	-1.21486800

H	2.94454200	1.86174600	-1.24502400
H	0.37735600	1.14027900	-0.00173700
N	1.40207300	1.14018100	0.00007600

NS_BI_Anion

C	-1.01558700	0.38926600	-0.02449500
C	1.16057100	-0.78890500	0.13002200
C	1.79024300	-1.49239300	-0.91299600
C	1.26790300	-1.23307400	1.46028000
C	2.55984800	-2.61270200	-0.59197800
C	2.02983000	-2.37388500	1.72810300
C	2.68868900	-3.07176000	0.71771600
H	3.05912000	-3.15821700	-1.39179300
H	2.11635100	-2.72829600	2.75429600
N	0.41661100	0.40041500	-0.17948800
C	-1.77081300	-0.56943200	-0.67057800
C	-3.26160400	-0.58137200	-0.50485100
C	-3.95748400	-0.06169100	0.59653000
C	-4.00865100	-1.19783300	-1.52227600
C	-5.35107400	-0.11370300	0.65457400
H	-3.41330900	0.35138200	1.44145500
C	-5.39695800	-1.24566500	-1.46834500
H	-3.44972500	-1.64019200	-2.34114200
C	-6.08100700	-0.69590700	-0.37992800
H	-5.86577400	0.29152800	1.52239600
H	-5.95333500	-1.71846700	-2.27439700
H	-7.16611700	-0.73564300	-0.33316400
O	-1.24895900	-1.47610400	-1.41355400
C	0.96877000	1.65079500	0.11370600
C	0.10255600	2.57982400	0.55288100

C	3.48243400	-4.31815800	1.02600400
H	2.86031100	-5.21446800	0.92140200
H	4.33161300	-4.42536500	0.34417100
H	3.86696600	-4.29968500	2.05025500
C	0.54540300	-0.52718400	2.59557300
H	0.19973700	0.44352600	2.23398000
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C	1.45787500	-0.26238600	3.79870000
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H	-1.26026700	-0.78398300	3.77894400
C	1.09070300	-2.21954300	-3.21610500
H	0.91185600	-1.86943500	-4.23992800
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C	2.42737600	1.91601300	-0.13416900

H	1.15736100	4.13442400	1.59770800
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H	2.92338500	0.97215500	-0.37596000
H	2.89791200	2.28788200	0.78811600

NS_BI

C	-0.90039800	0.63623700	-0.16694300
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H	4.00470600	4.45437400	-0.91808000
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^{t}BuOH

C	0.13220300	1.49950500	0.05053400
C	0.70707900	0.09428800	-0.07700900
H	0.35097200	-0.37339900	-0.99909100
H	1.79913100	0.13855000	-0.11224700
H	0.40512800	-0.52421700	0.77310300
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H	-1.80820500	2.47708800	0.11183200
H	-1.76041200	0.99760800	-0.86966400
C	0.65892400	2.18930300	1.30962600

H	1.75101100	2.23895900	1.28070800
H	0.26816300	3.21112100	1.38338700
H	0.35444700	1.64828200	2.21100700
O	0.59615500	2.19510100	-1.10861900
H	0.26151200	3.09948000	-1.08423400

^{t}BuOK

C	0.05597500	1.59510900	0.11983000
C	0.72099700	0.23698800	-0.18206600
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H	1.80568200	0.37476600	-0.25889000
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C	0.57726800	2.10771200	1.47757000
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H	0.36771900	1.41555100	2.30322000
O	0.34489000	2.49844300	-0.87335700
K	0.82355600	3.99396800	-2.51768500

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9. NMR Spectra

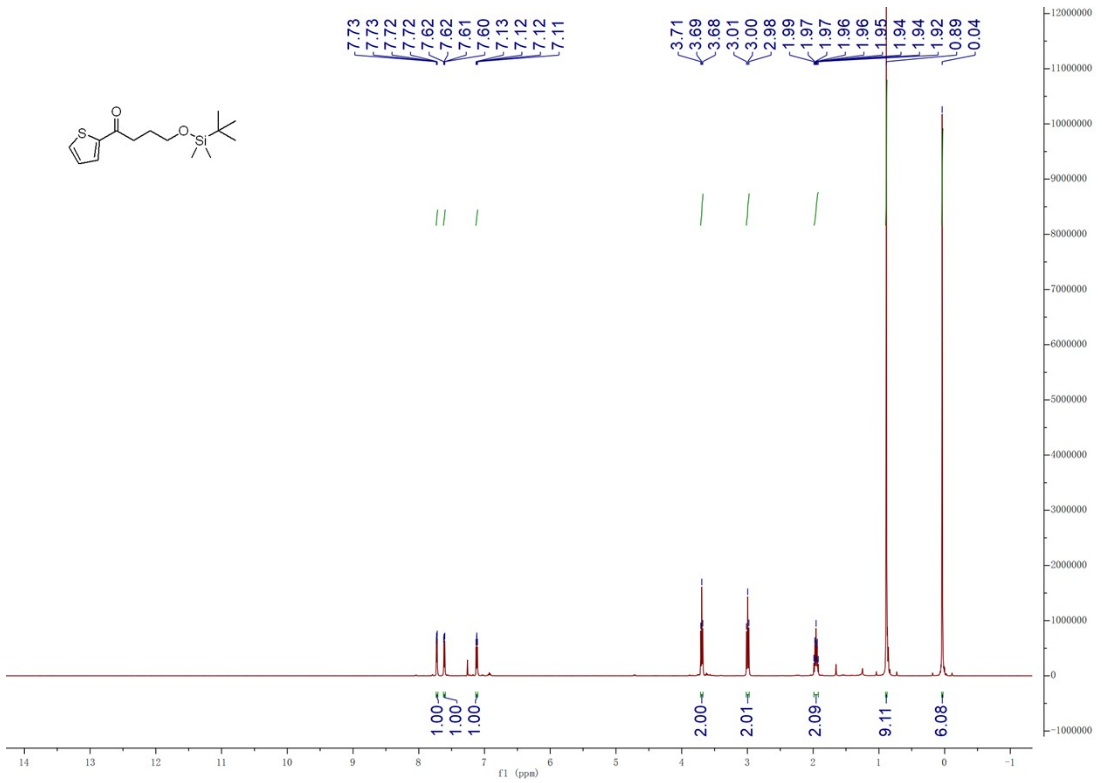

Figure S1 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **3ae**

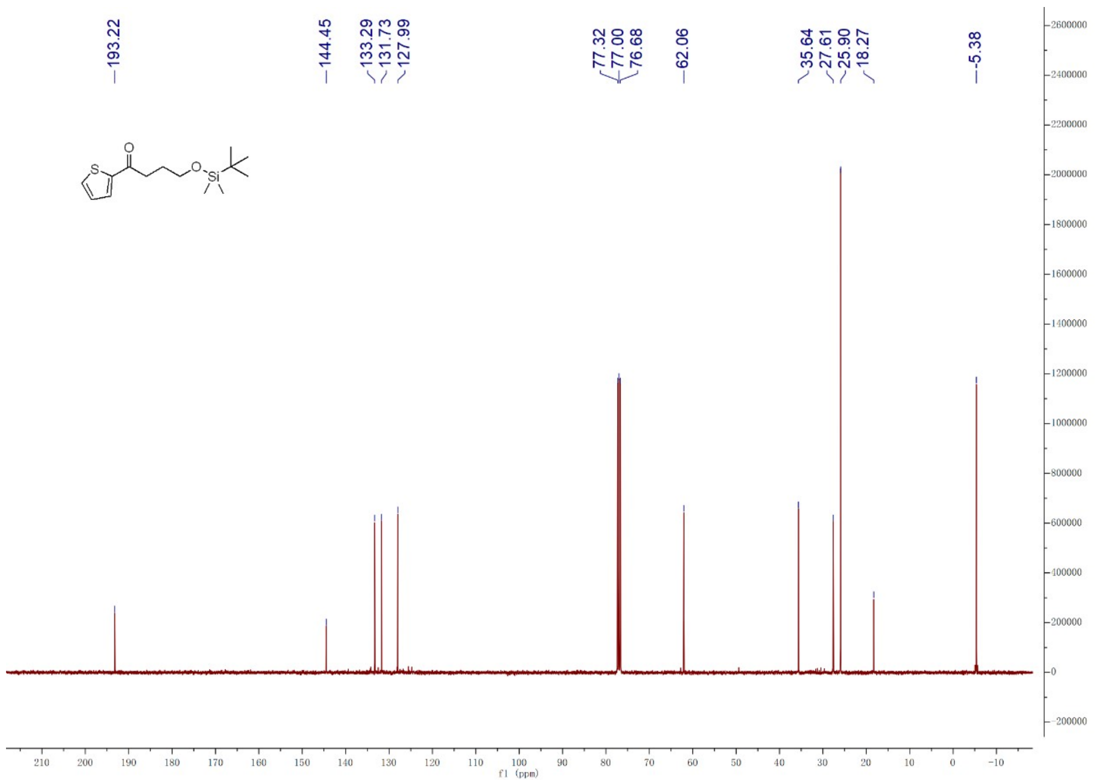

Figure S2 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **3ae**

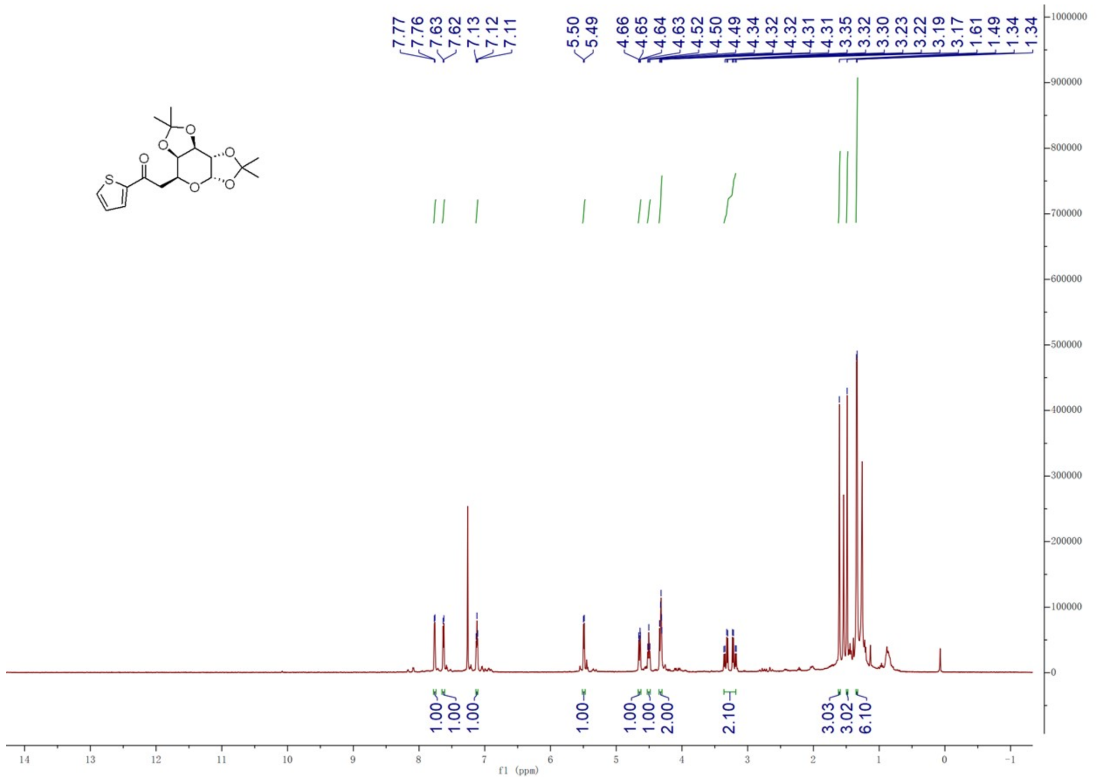

Figure S3 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **3ak**

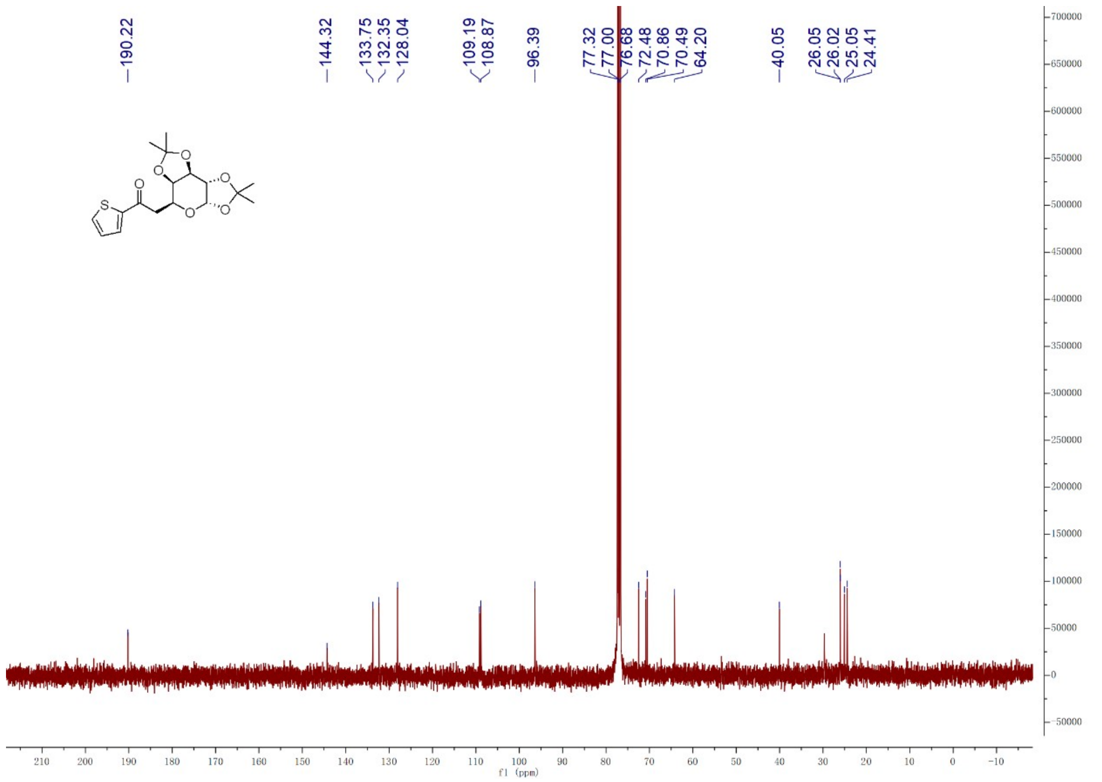

Figure S4 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **3ak**

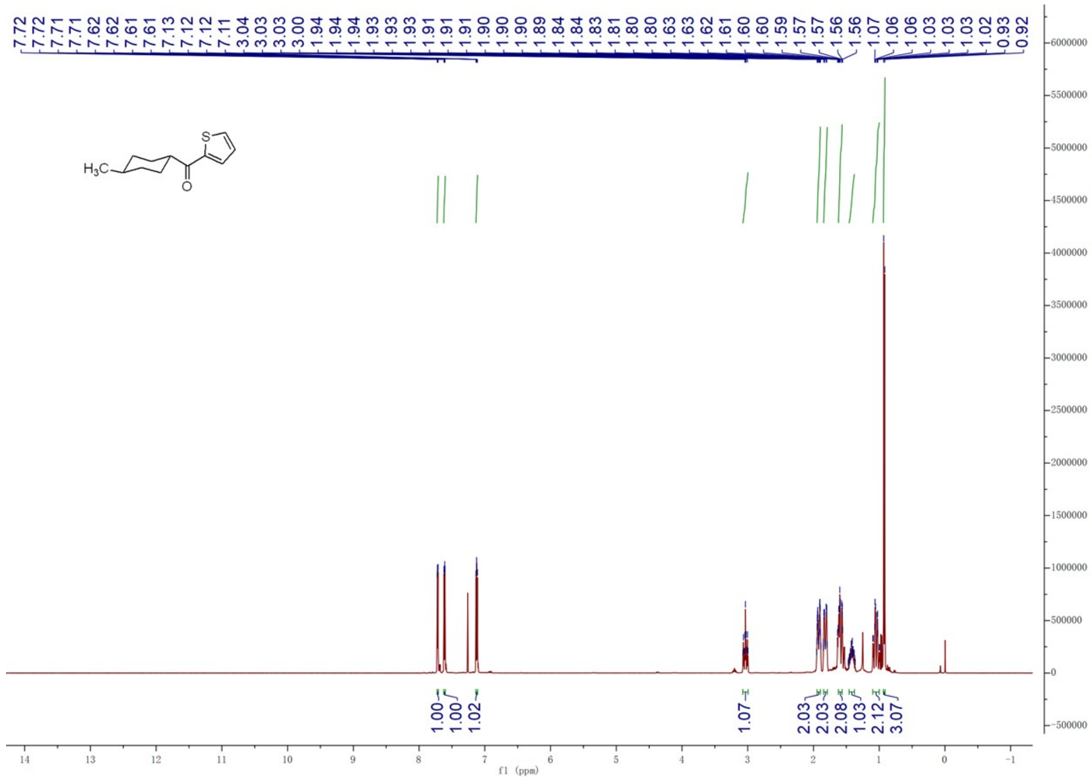

Figure S5 ^{1}H NMR (25 °C, 400 MHz, $CDCl_3$) of **3ap**

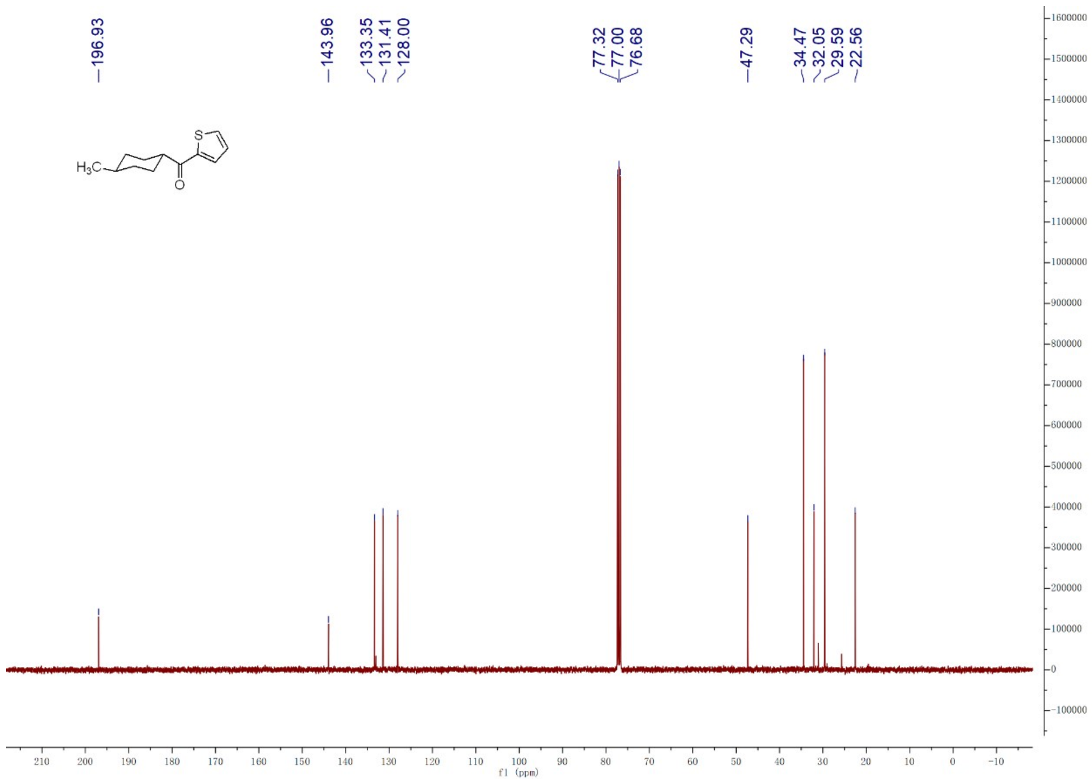

Figure S6 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **3ap**

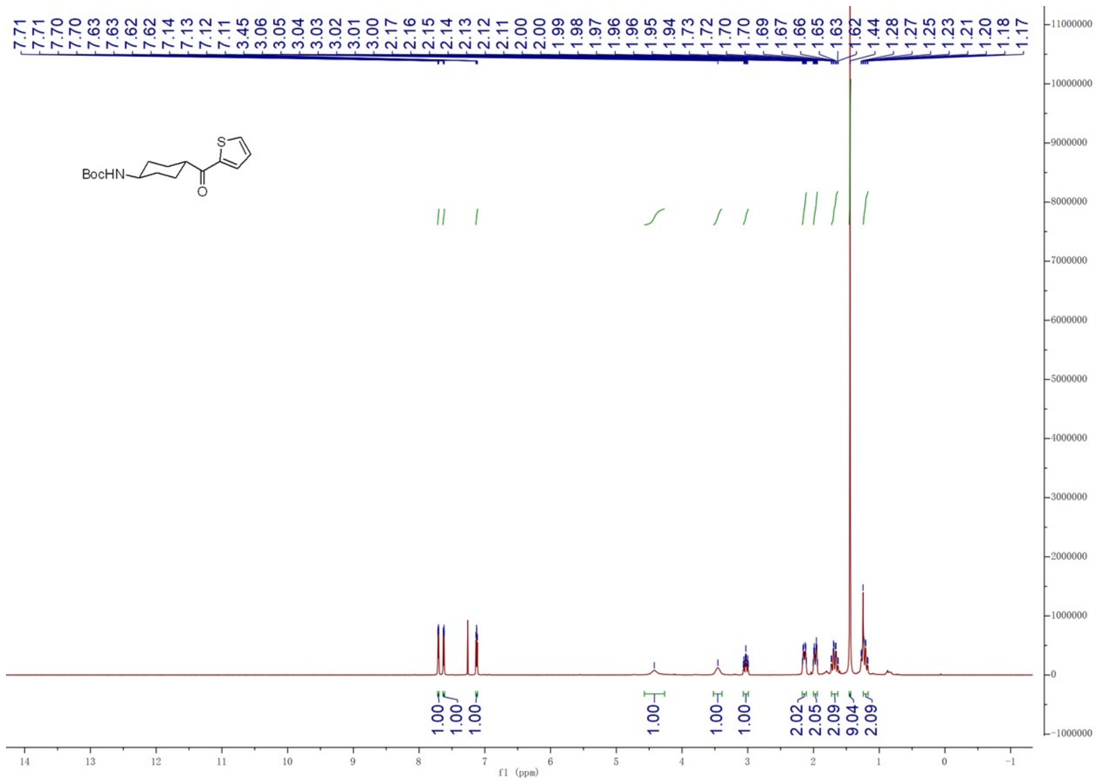

Figure S7 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **3aq**

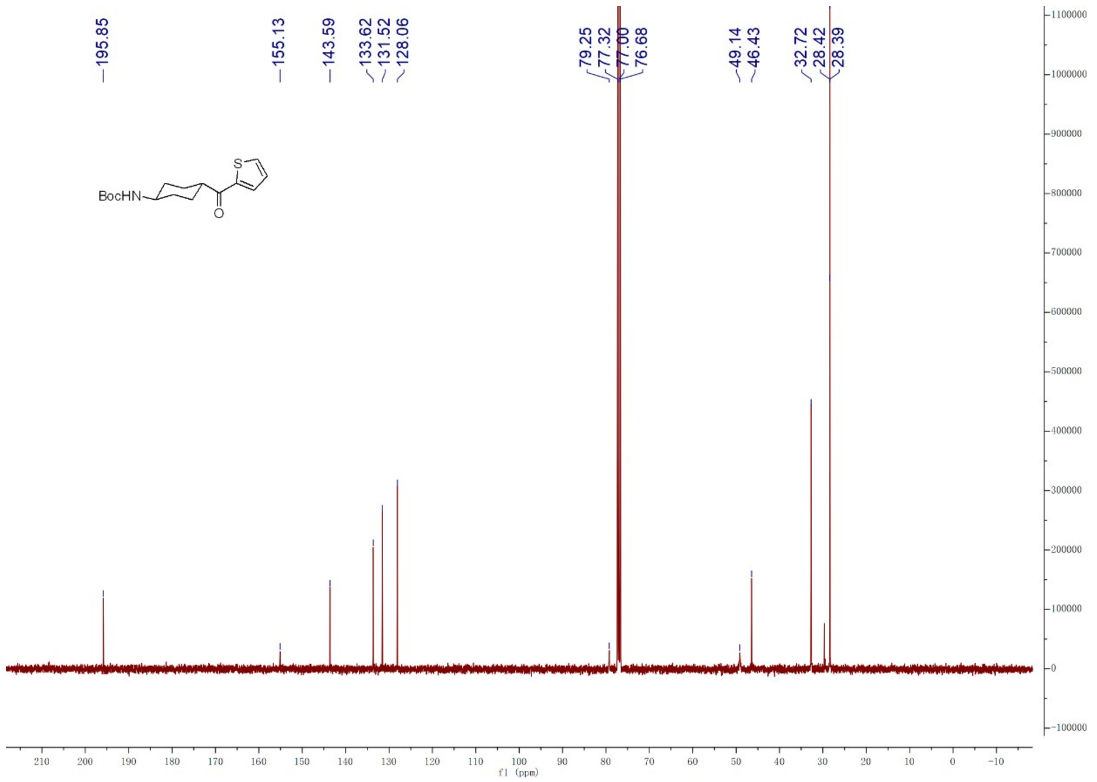

Figure S8 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **3aq**

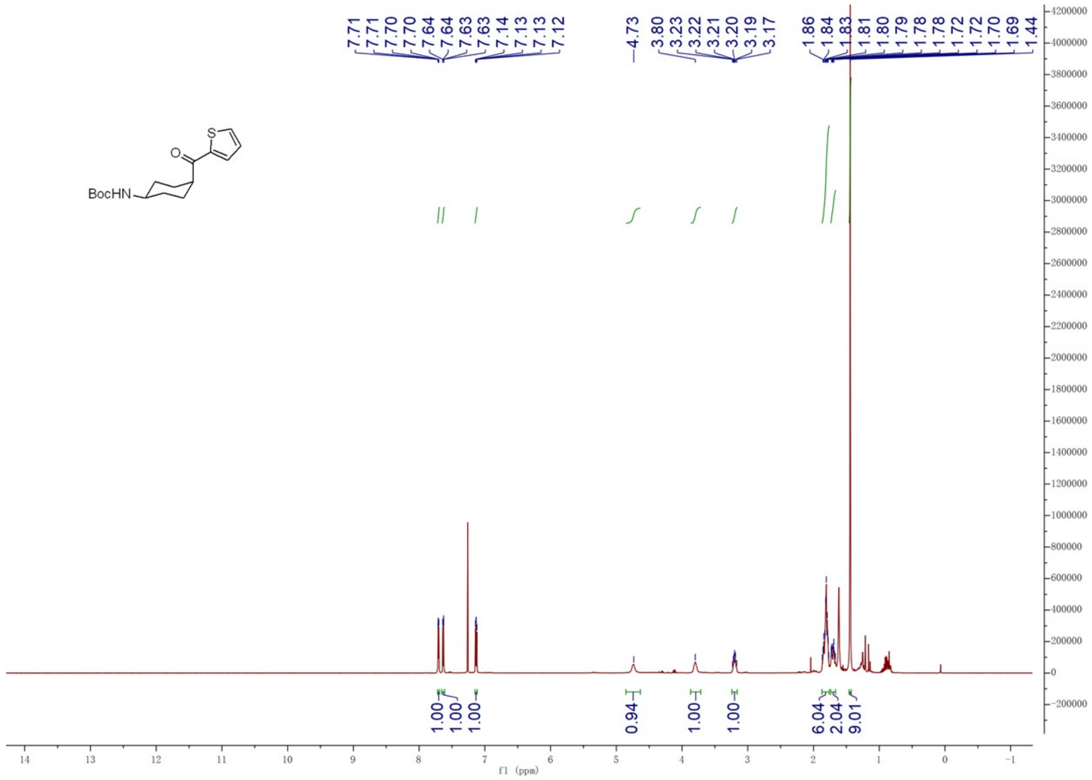

Figure S9 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **3ar**

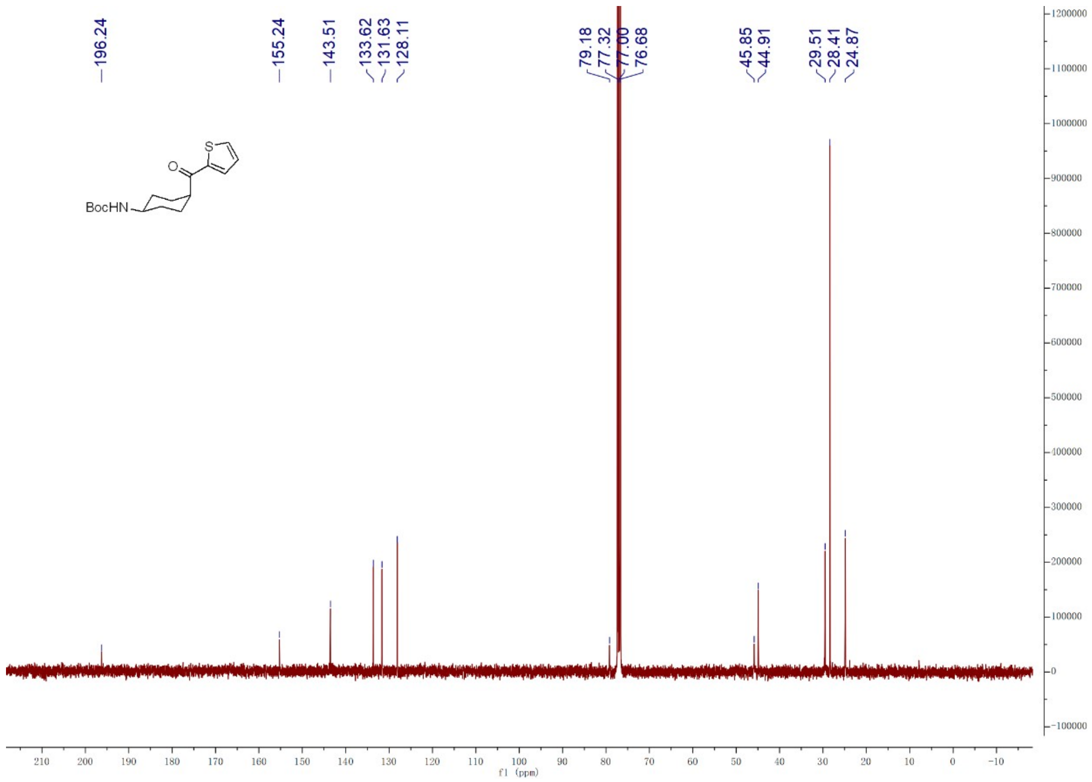

Figure S10 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **3ar**

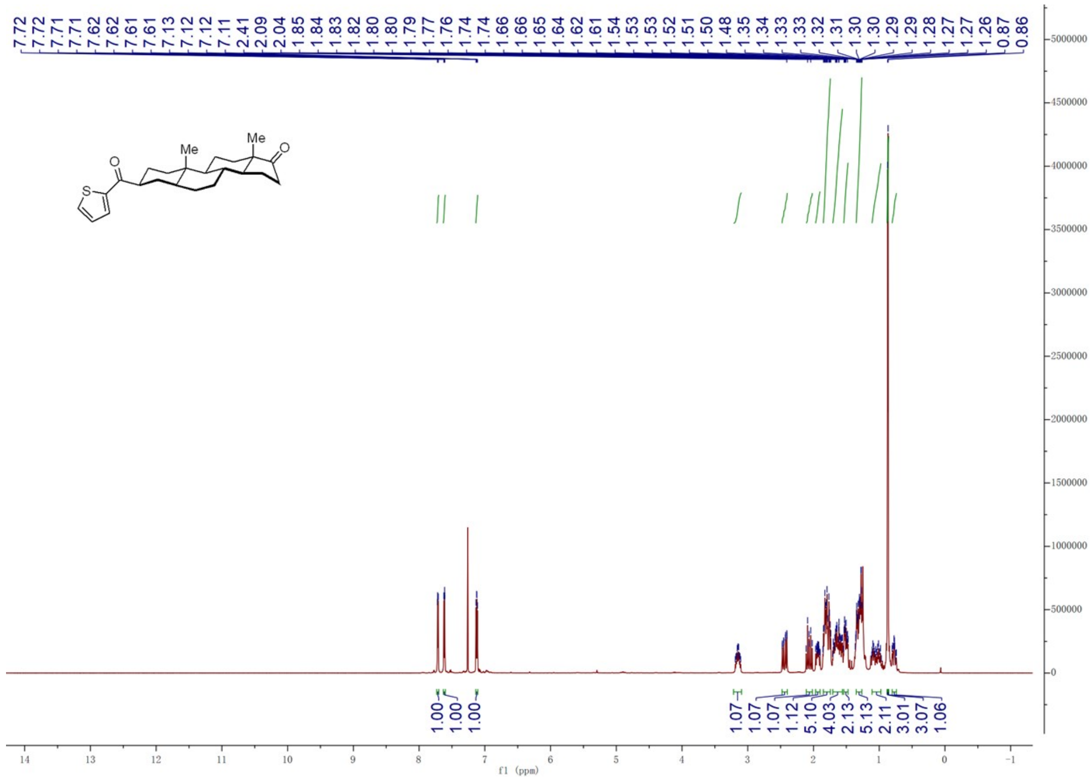

Figure S11 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **3at**

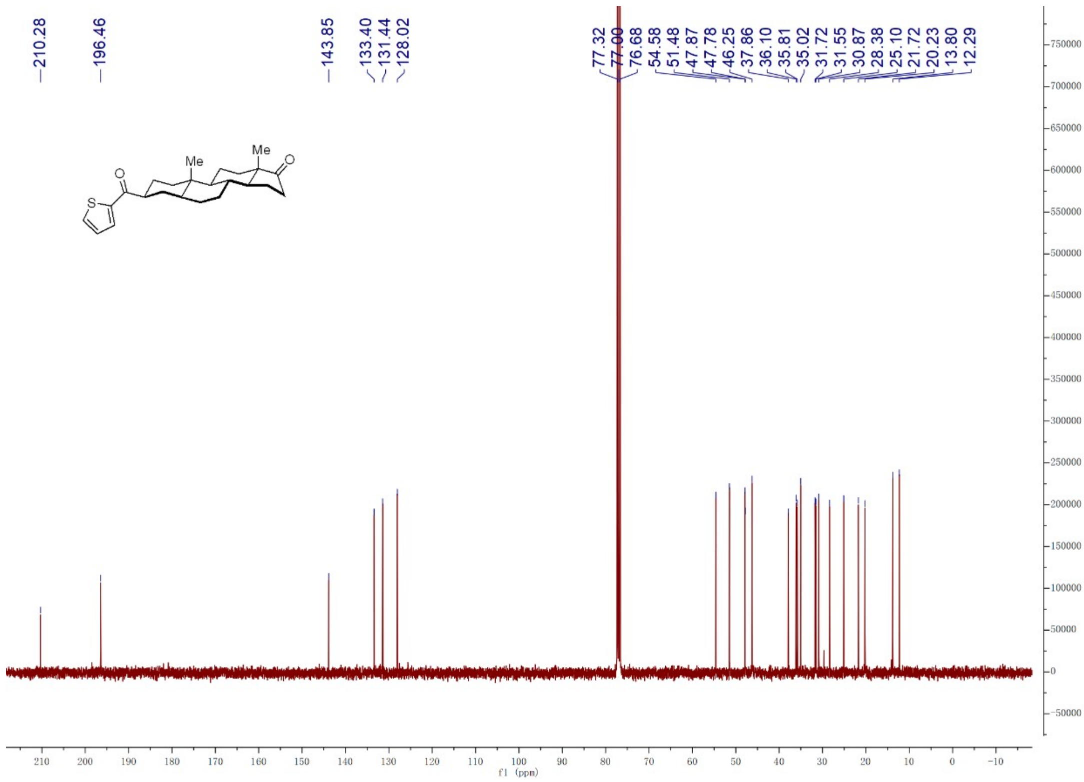

Figure S12 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **3at**

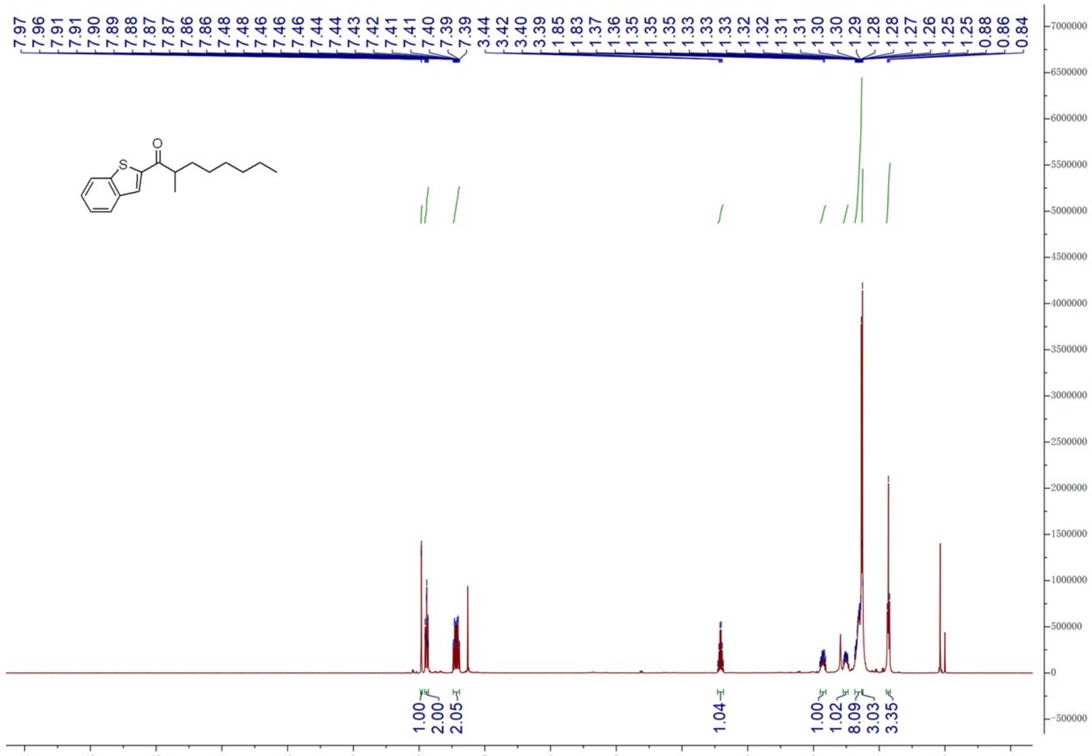

Figure S13 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **3cu**

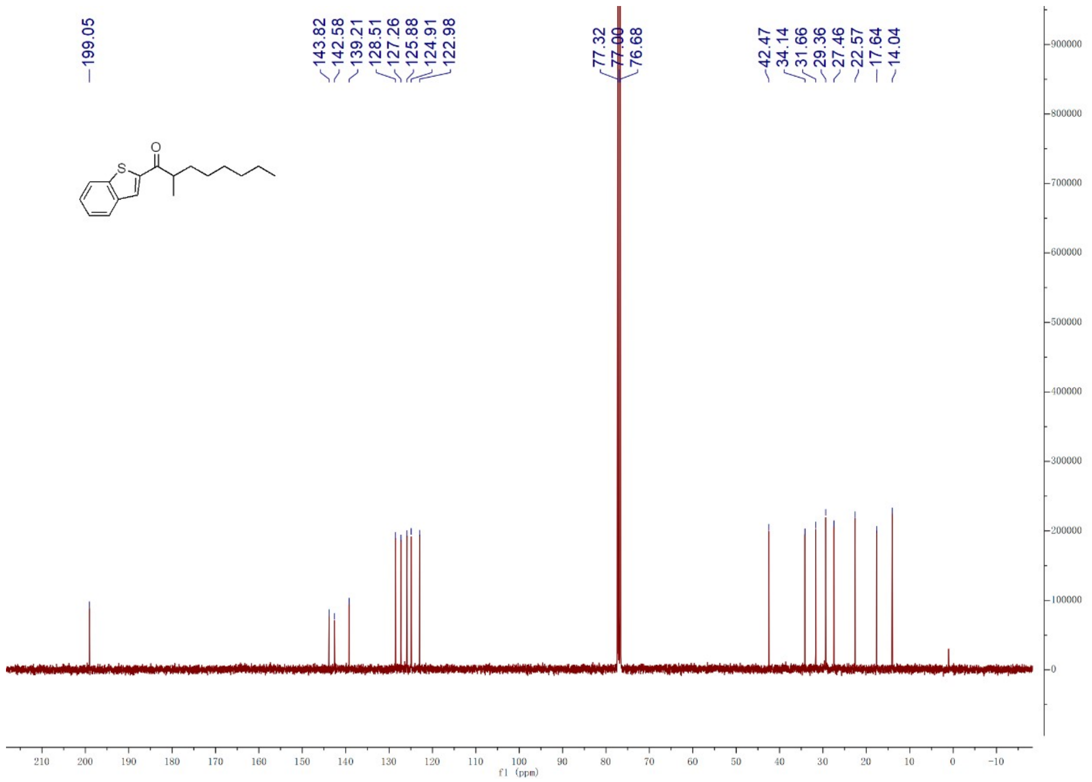

Figure S14 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **3cu**

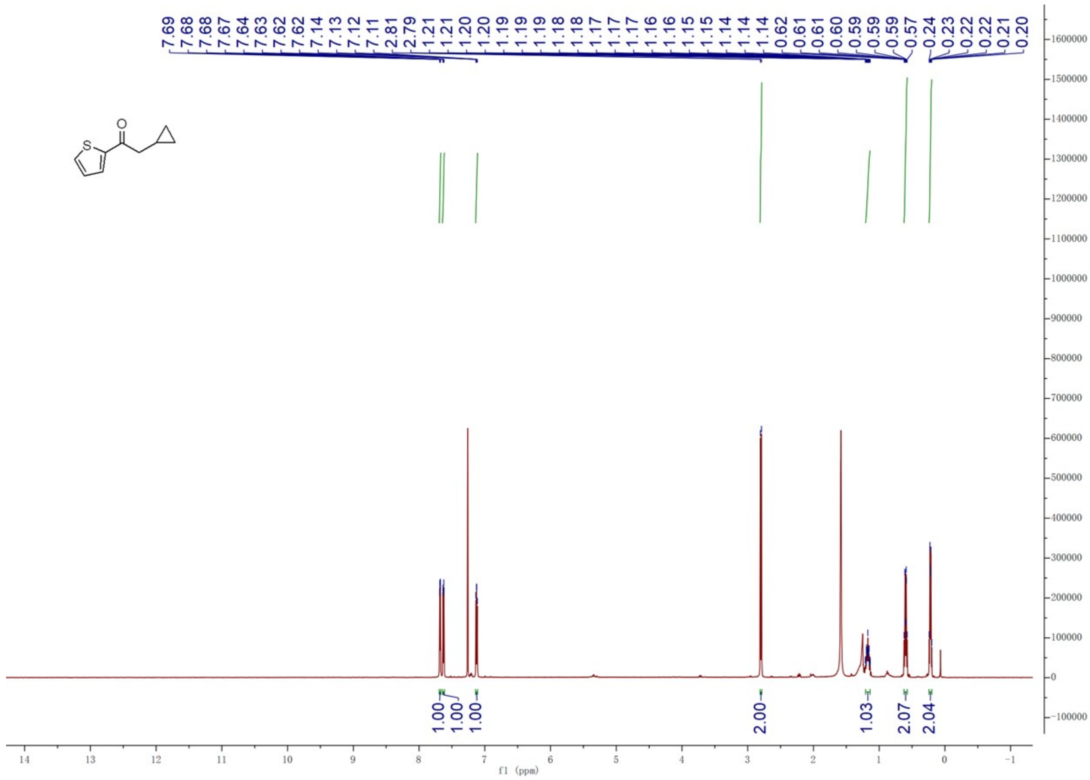

Figure S15 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **3aad**

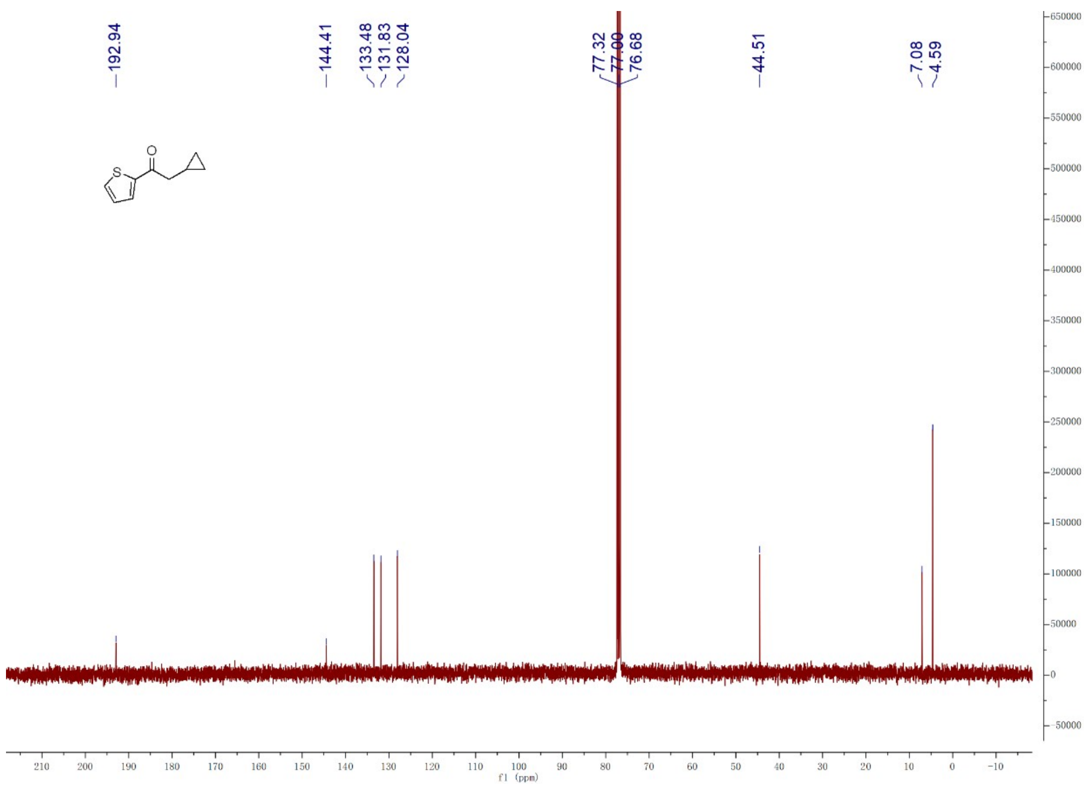

Figure S16 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **3aad**

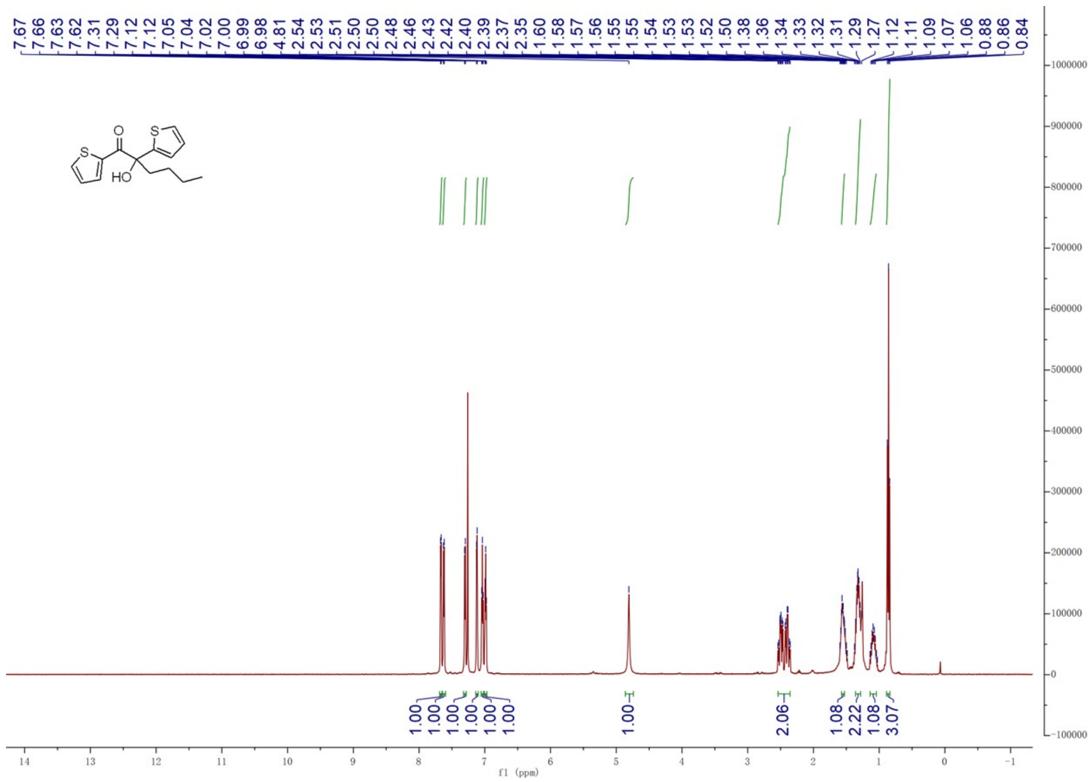

Figure S17 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4aa**

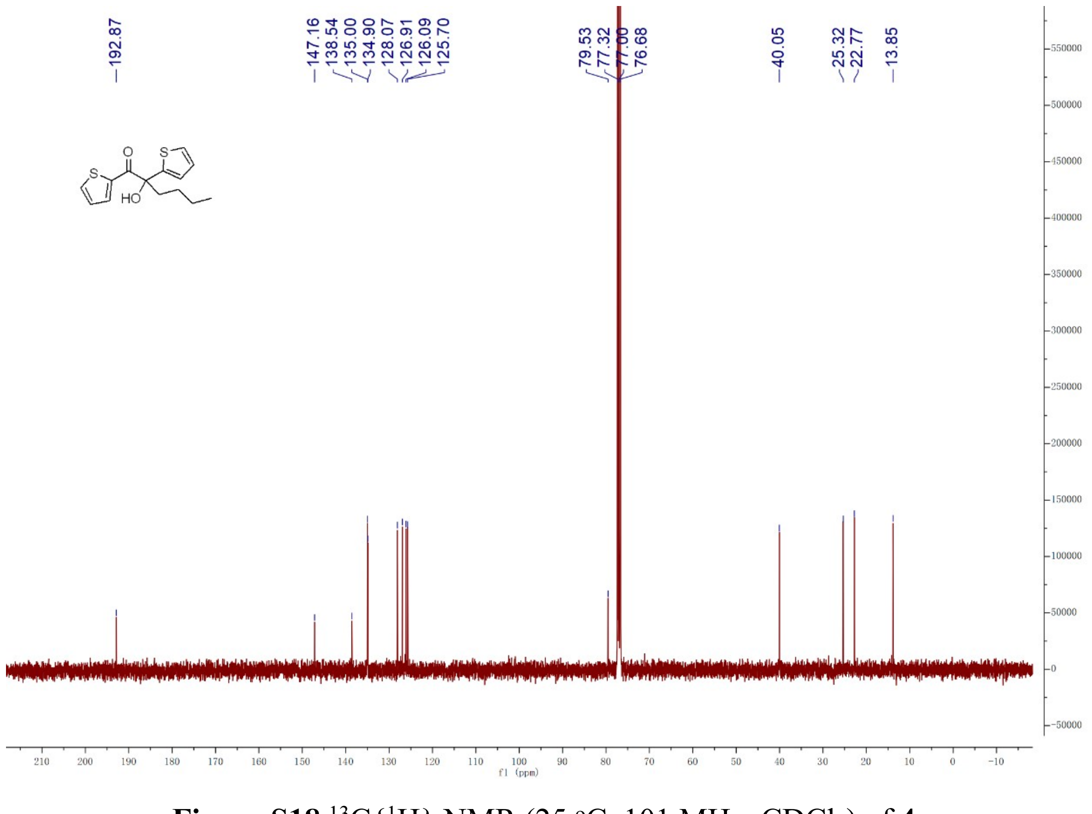

Figure S18 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4aa**

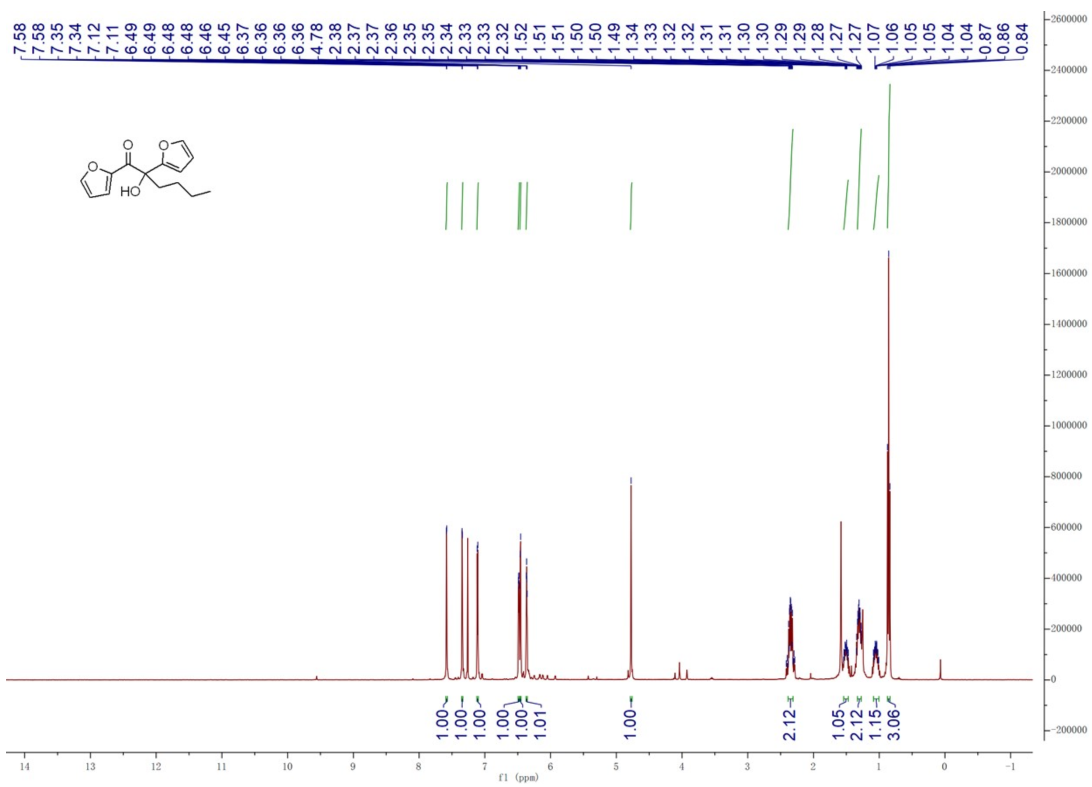

Figure S19 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4ba**

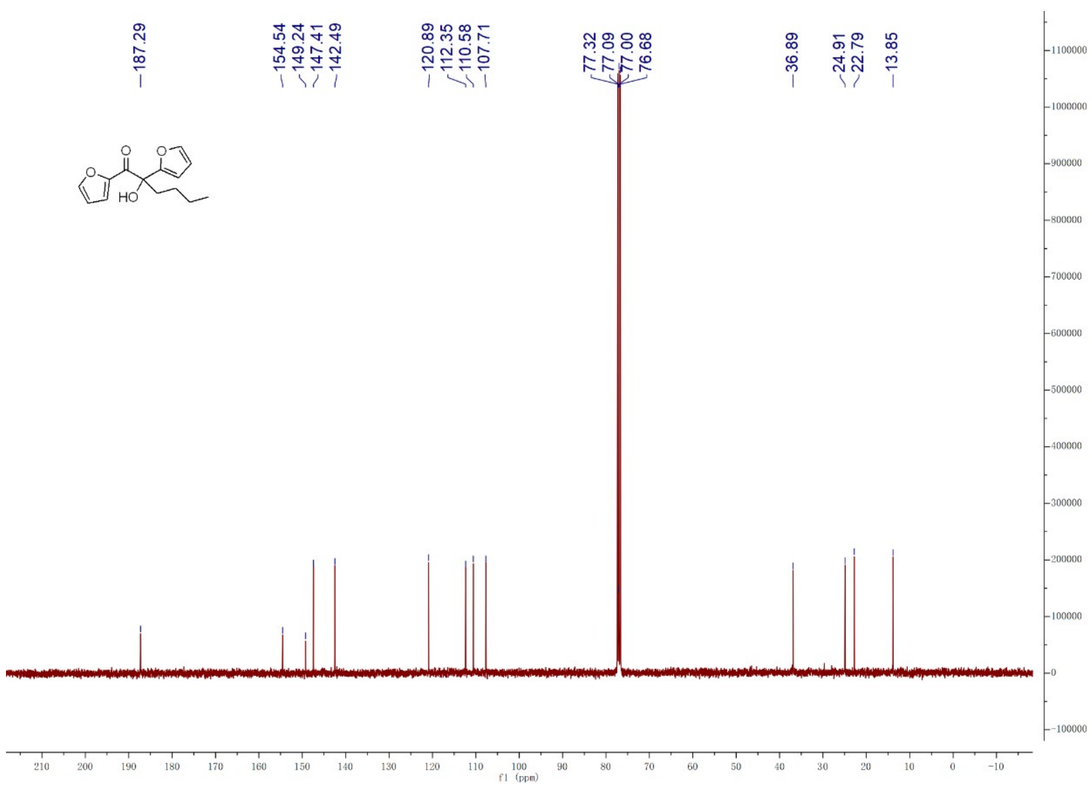

Figure S20 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4ba**

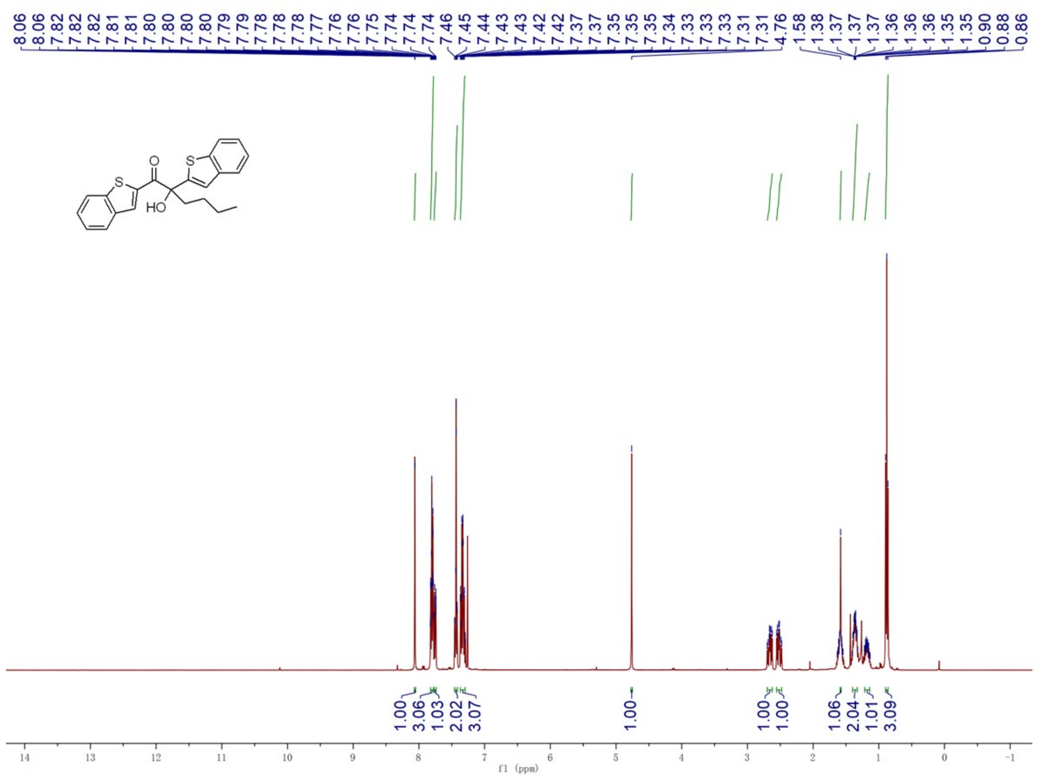

Figure S21 ^{1}H NMR (25 °C, 400 MHz, $CDCl_3$) of **4ca**

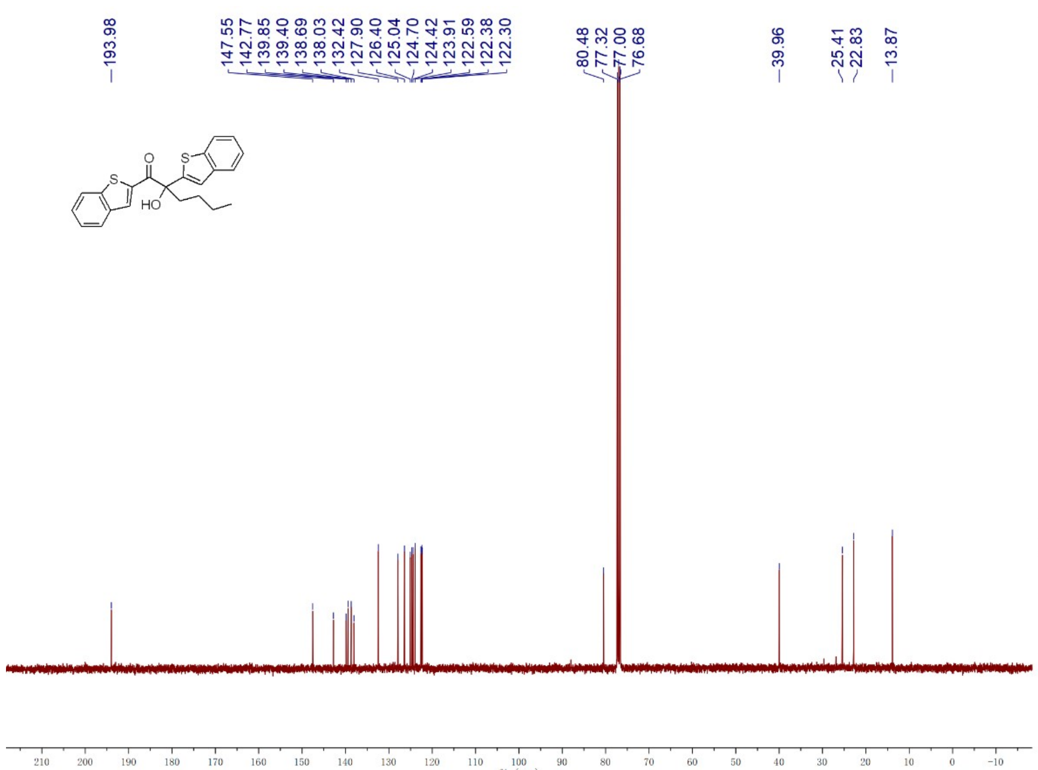

Figure S22 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **4ca**

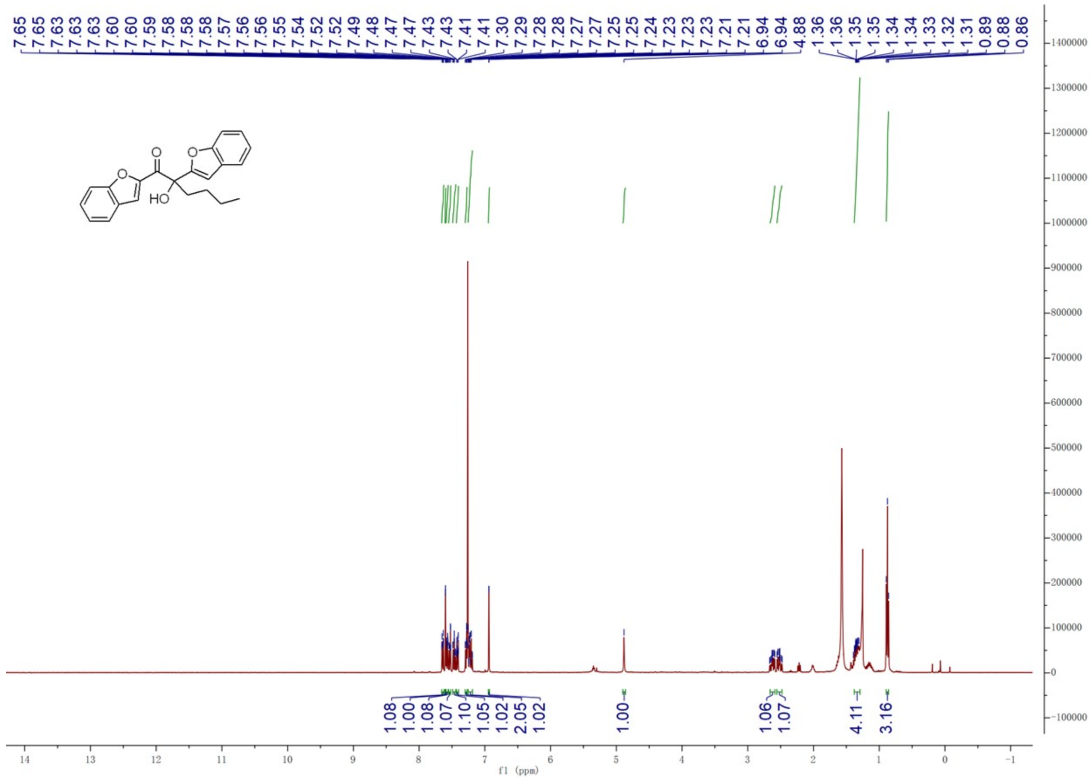

Figure S23 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4da**

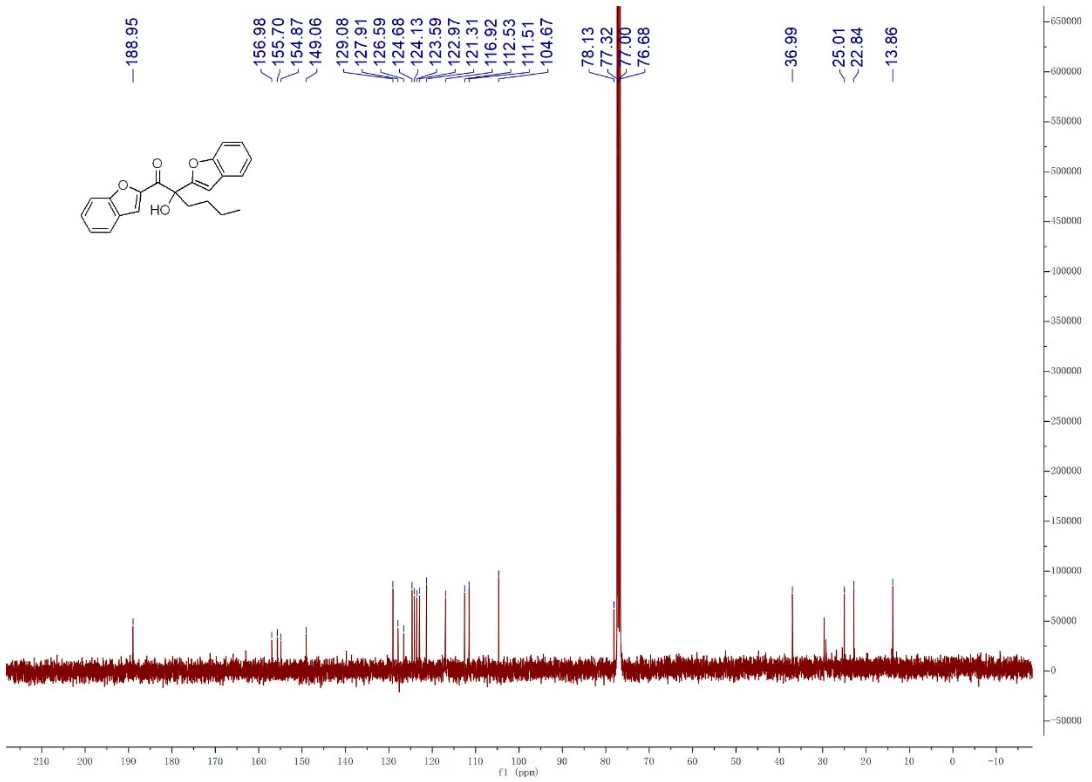

Figure S24 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4da**

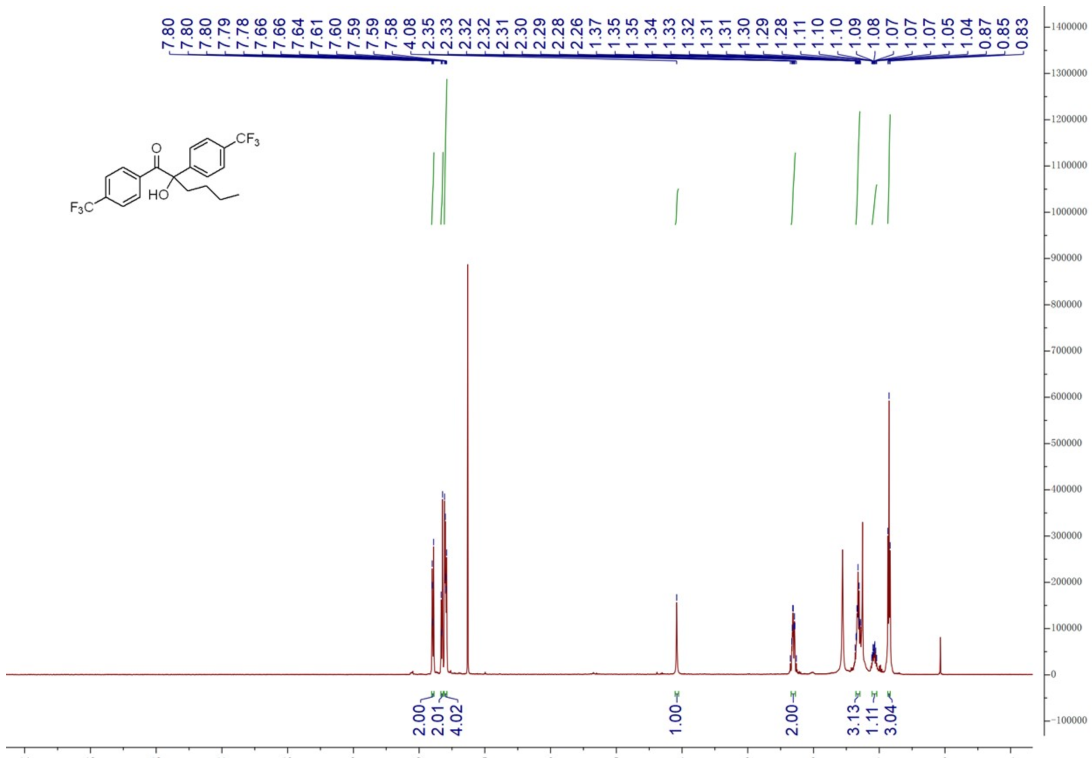

Figure S25 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4fa**

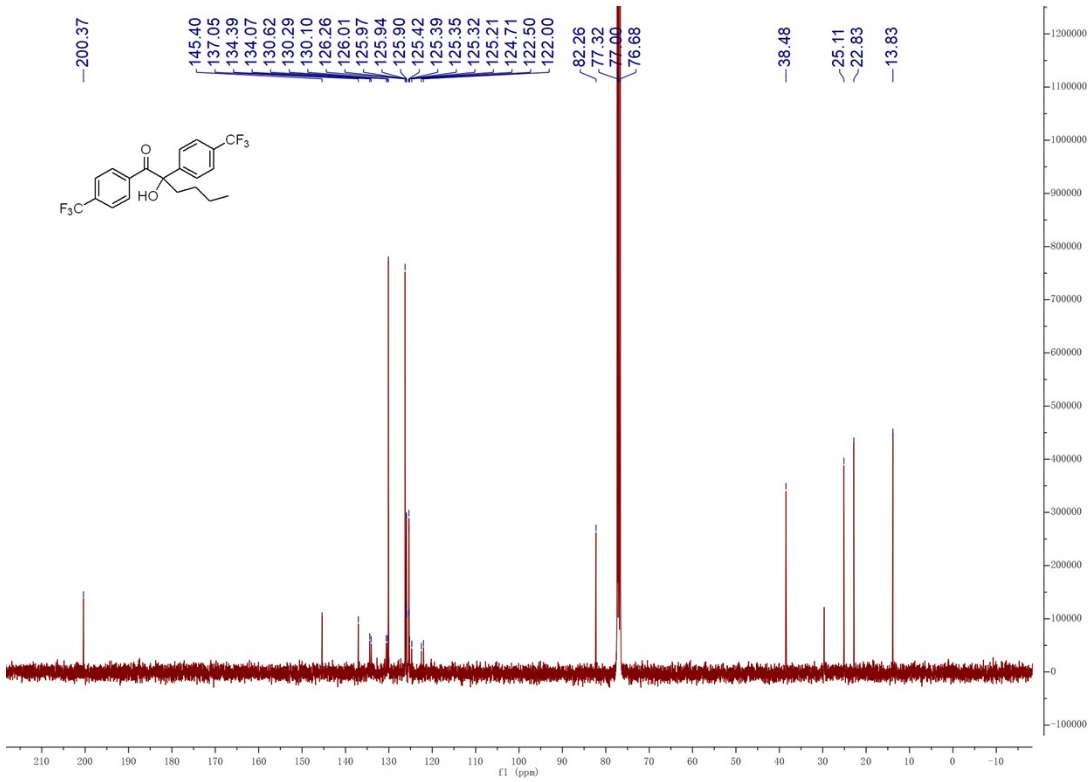

Figure S26 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4fa**

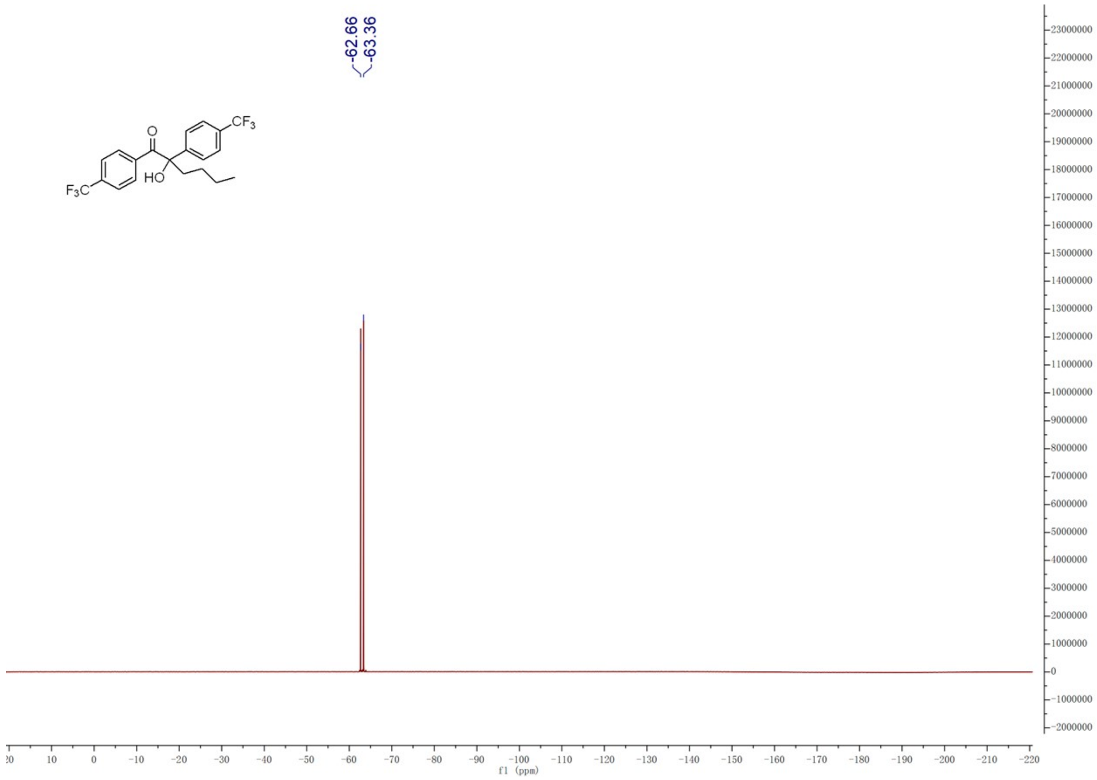

Figure S27 ^{19}F NMR (25 ^{o}C, 376 MHz, $CDCl_3$) of **4fa**

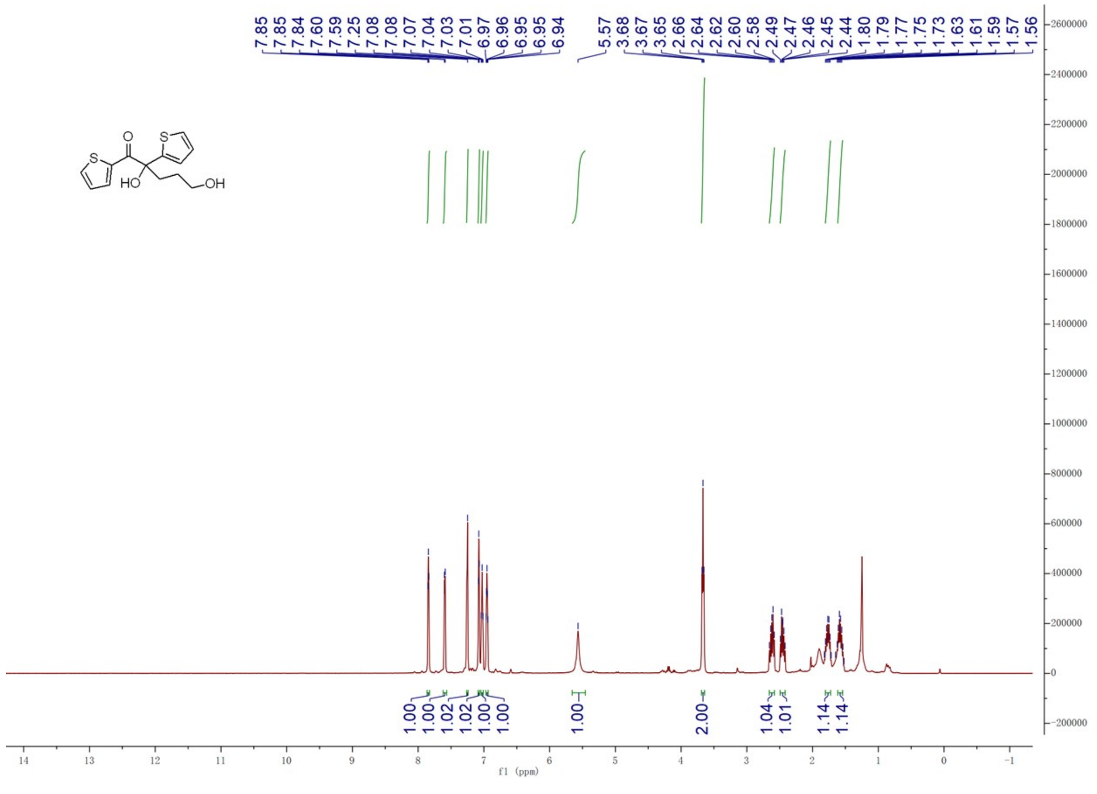

Figure S28 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4ab**

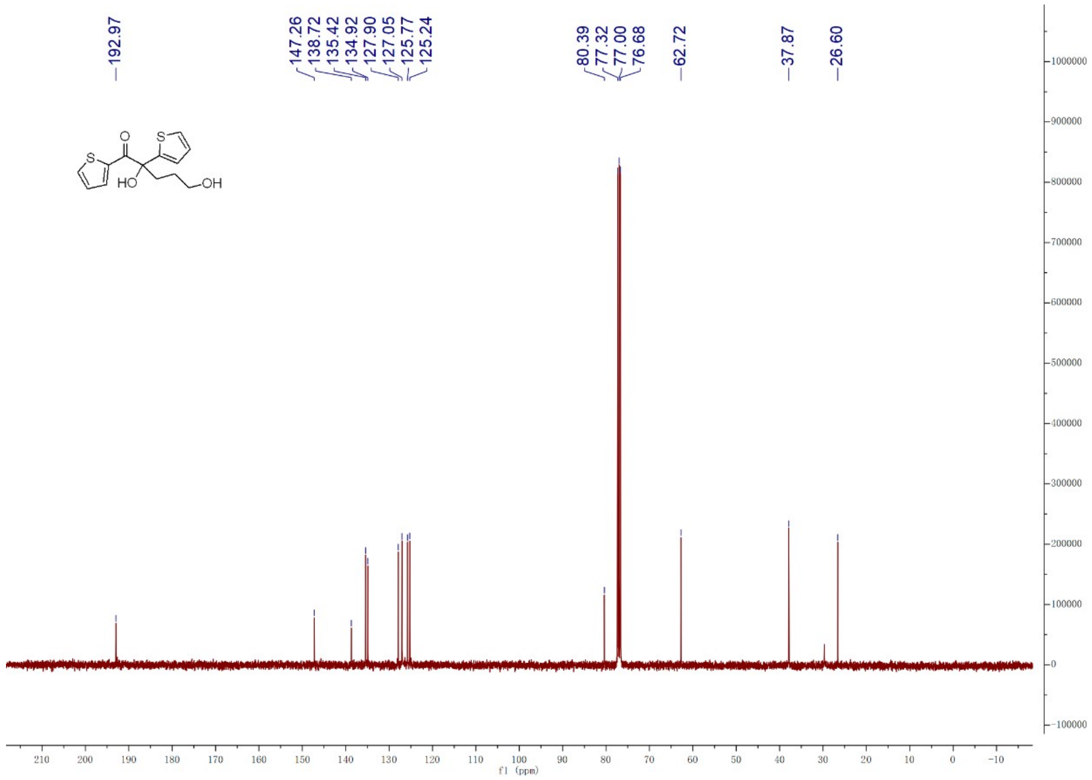

Figure S29 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **4ab**

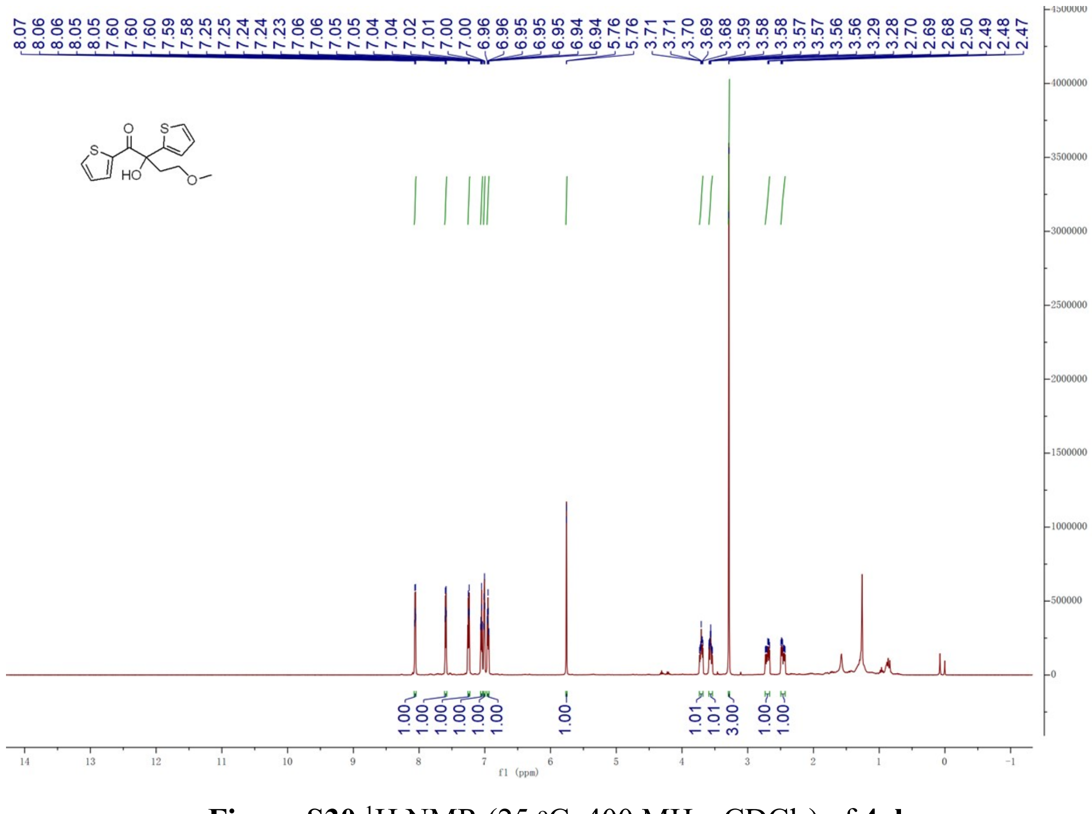

Figure S30 ^{1}H NMR (25 °C, 400 MHz, $CDCl_3$) of **4ah**

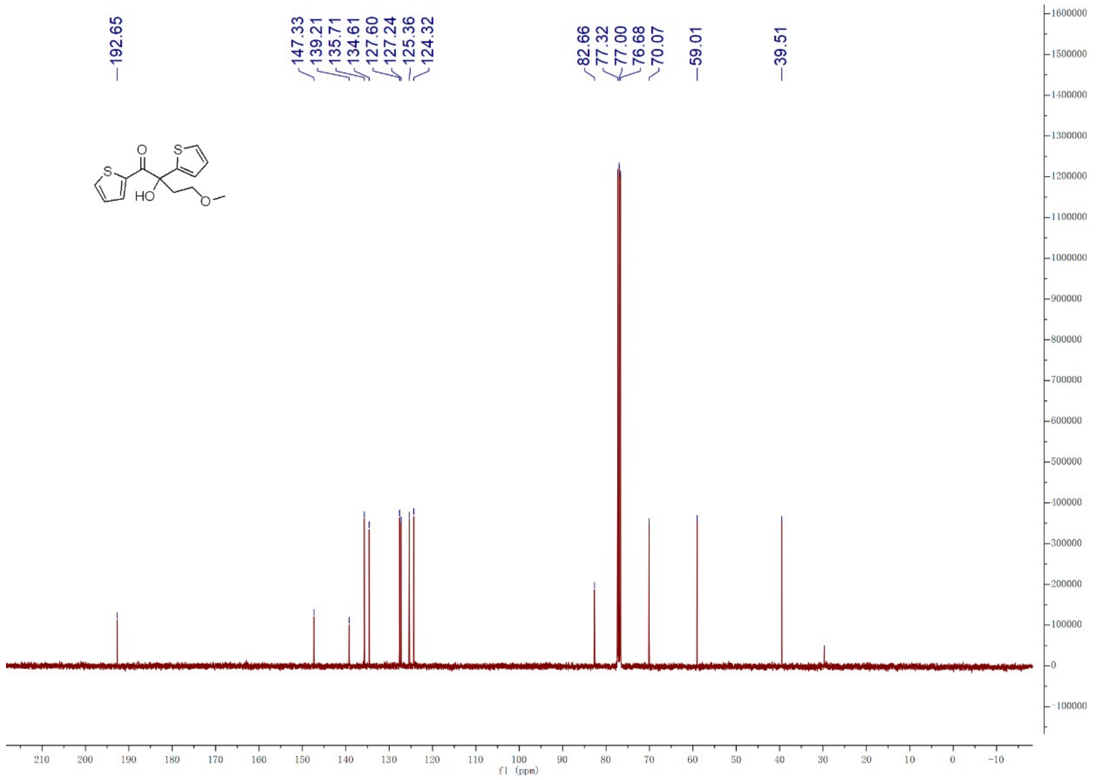

Figure S31 $^{13}C\{^1H\}$ NMR (25 ^oC, 101 MHz, $CDCl_3$) of **4ah**

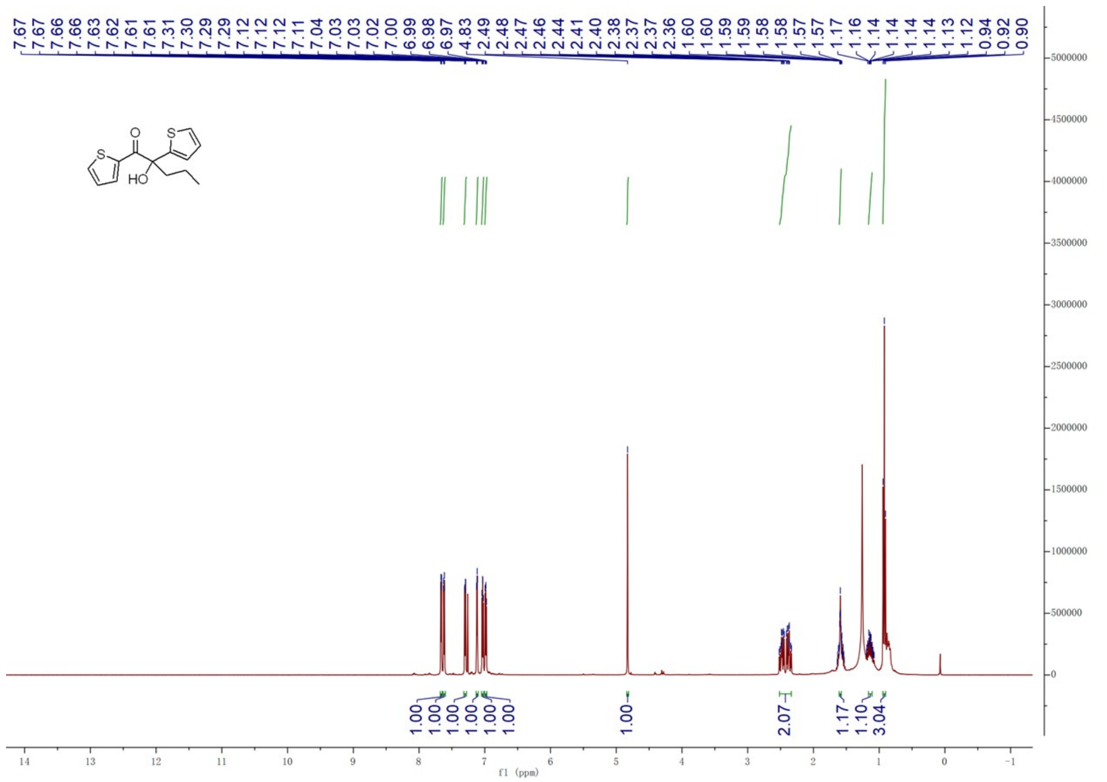

Figure S32 ^1H NMR (25 ^oC, 400 MHz, $CDCl_3$) of **4av**

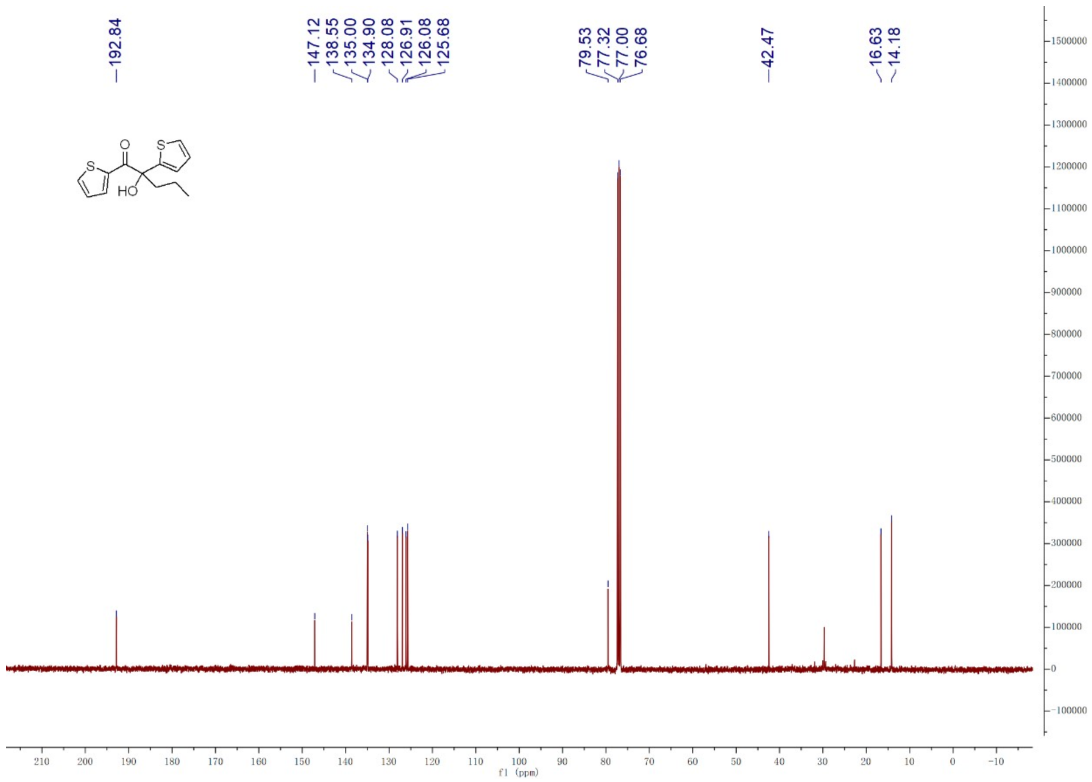

Figure S33 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **4av**

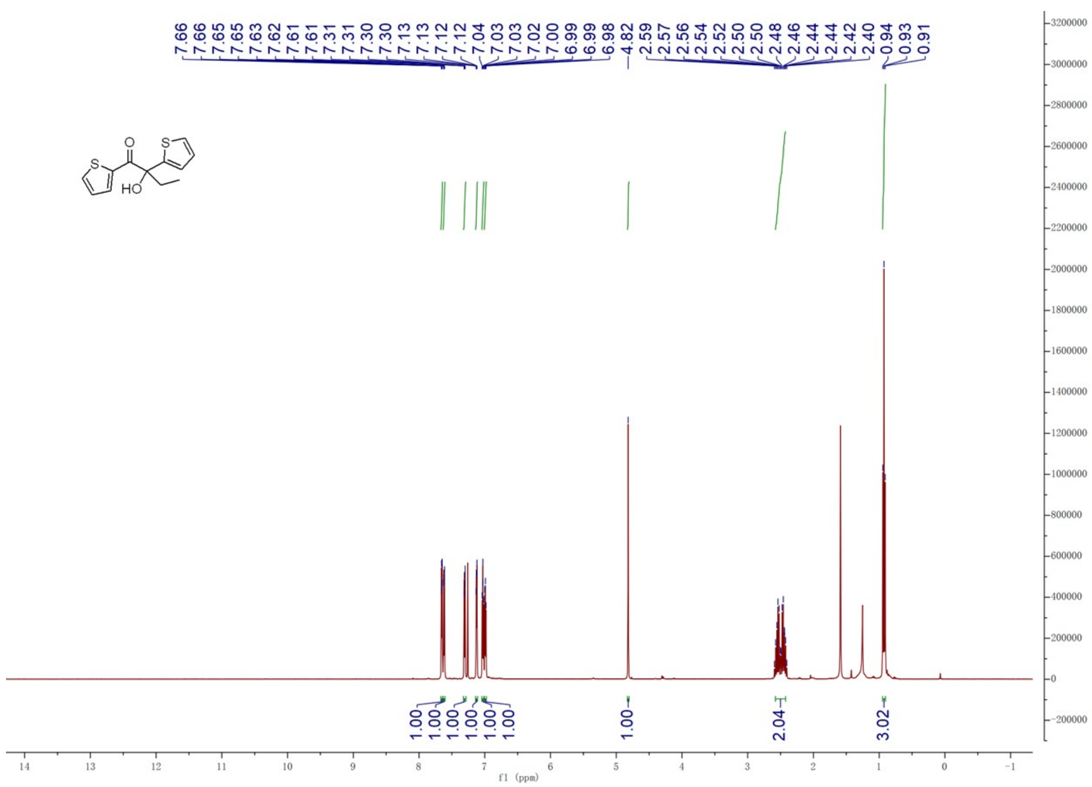

Figure S34 ^{1}H NMR (25 °C, 400 MHz, $CDCl_3$) of **4aw**

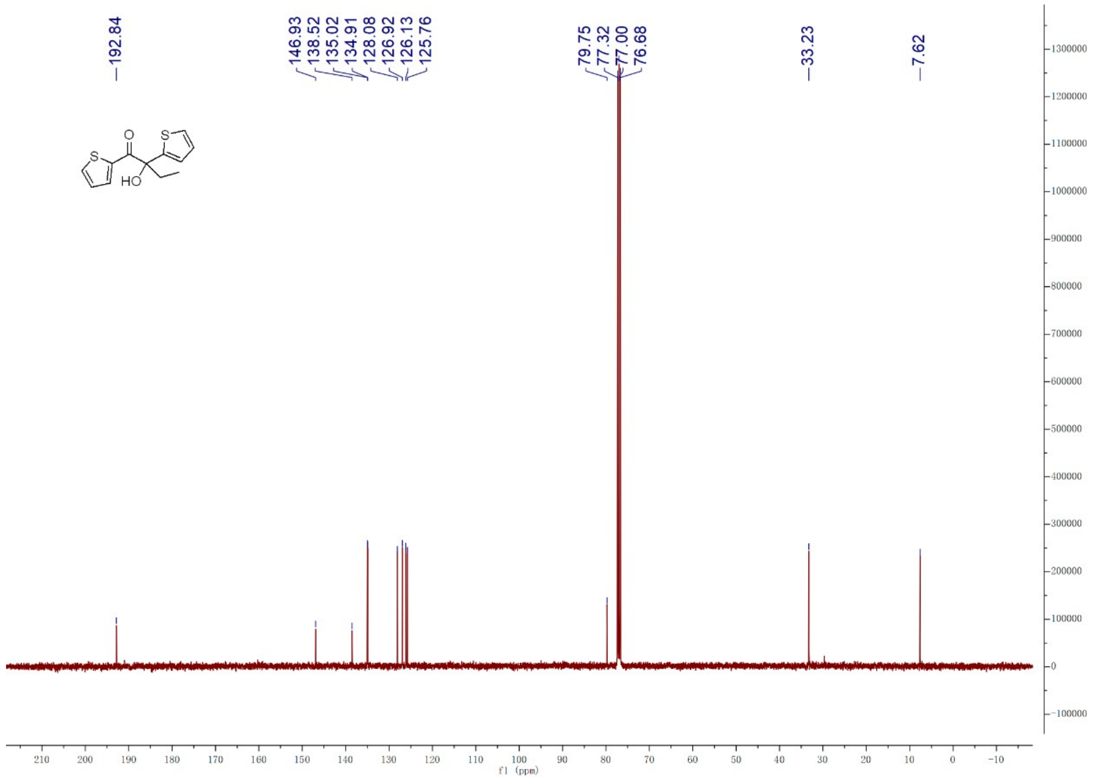

Figure S35 $^{13}C\{^1H\}$ NMR (25 ^oC, 101 MHz, $CDCl_3$) of **4aw**

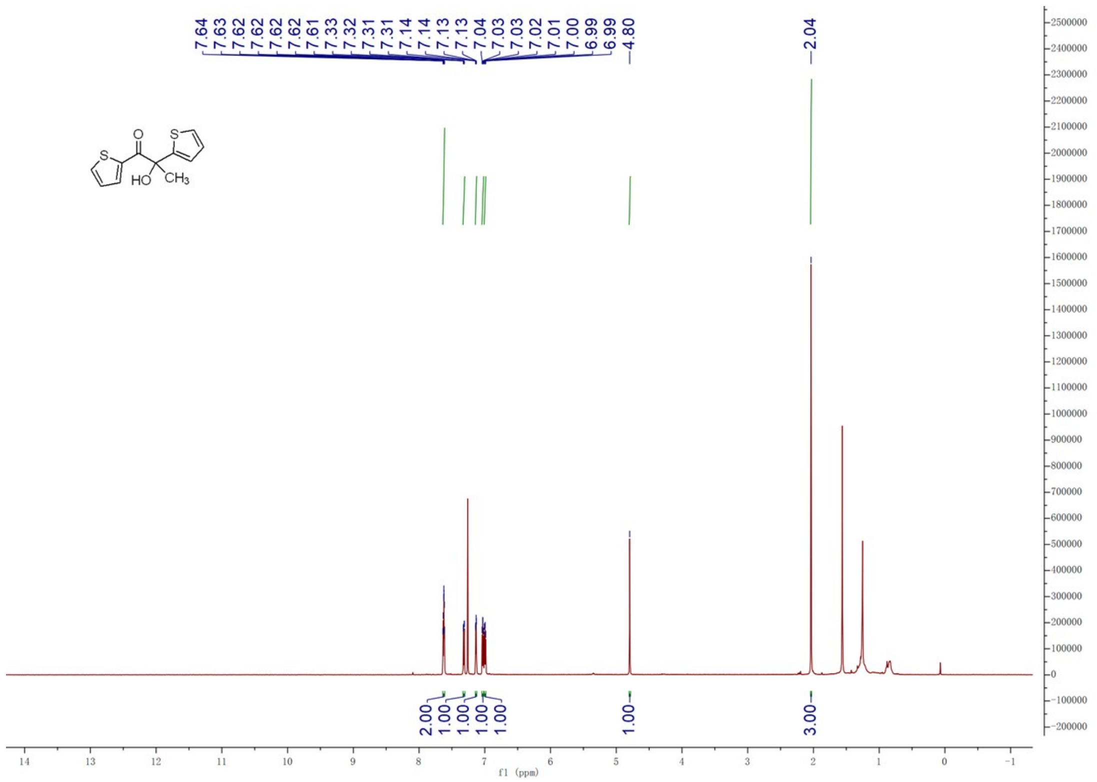

Figure S36 ^1H NMR (25 ^oC, 400 MHz, $CDCl_3$) of **4ax**

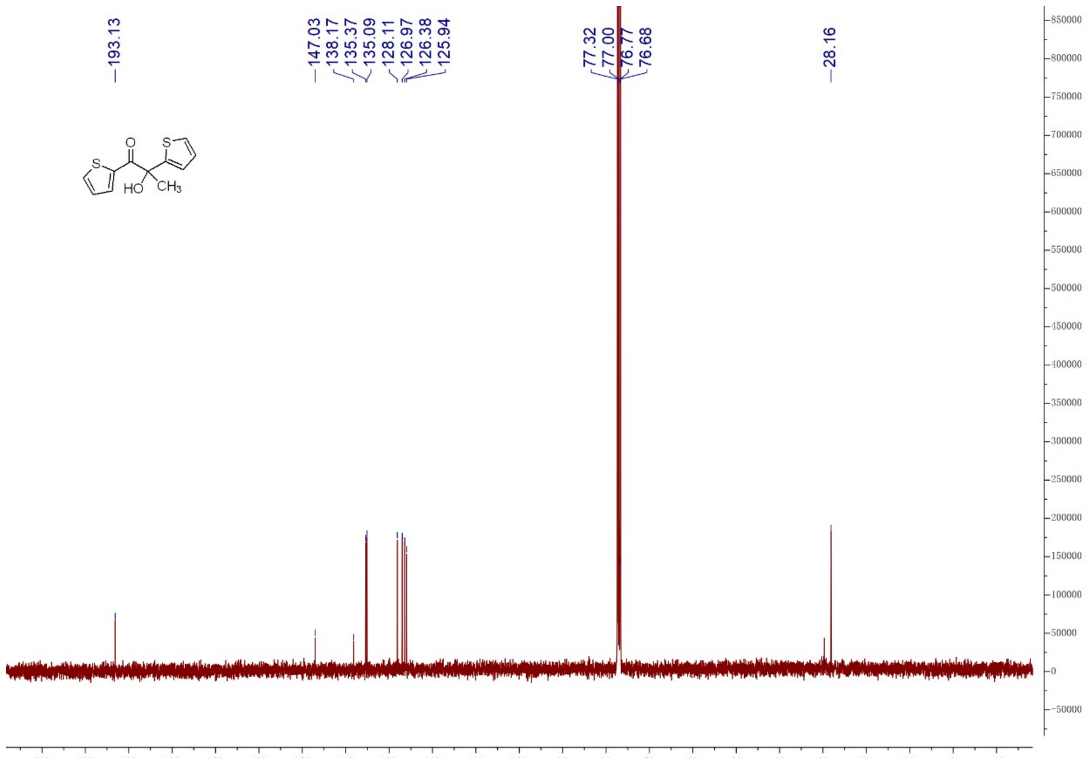

Figure S37 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **4ax**

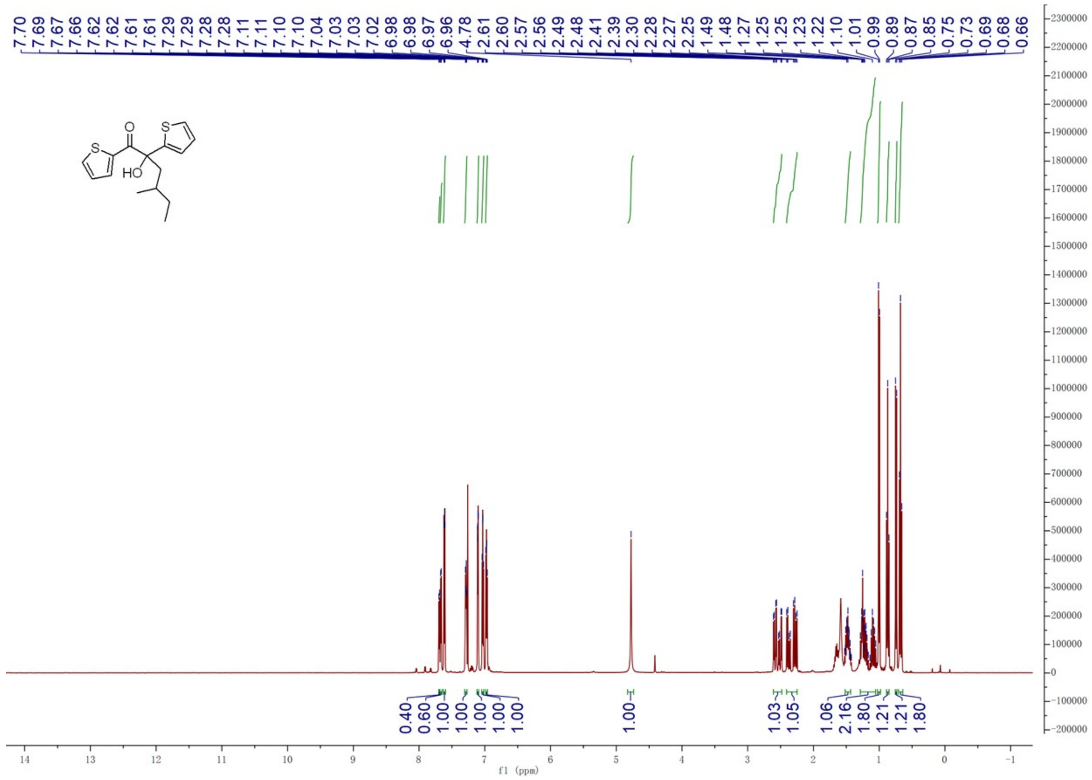

Figure S38 ^{1}H NMR (25 °C, 400 MHz, $CDCl_3$) of **4ay**

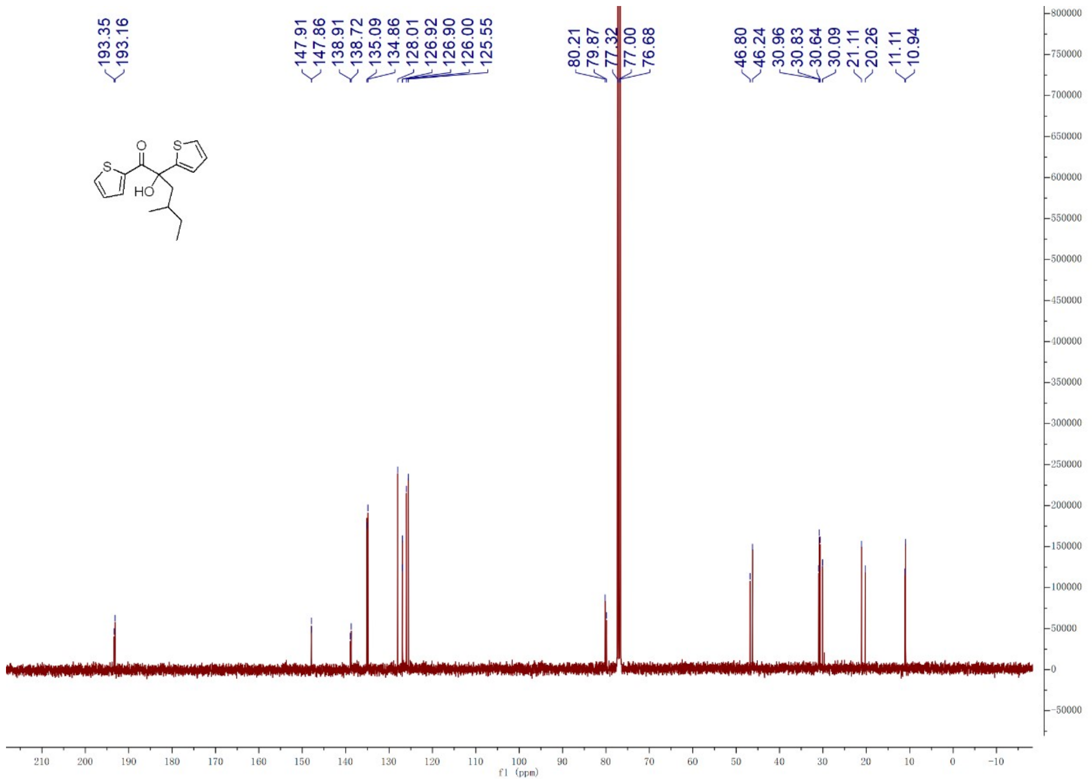

Figure S39 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **4ay**

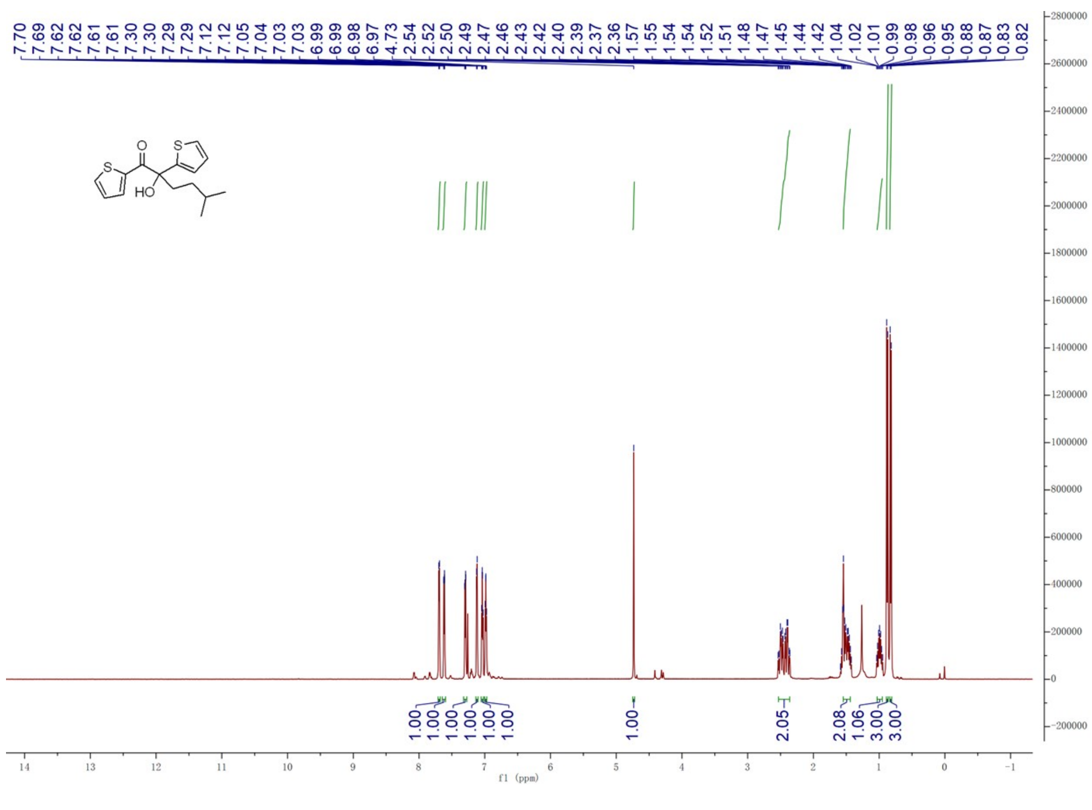

Figure S40 ^{1}H NMR (25 °C, 400 MHz, $CDCl_3$) of **4aaa**

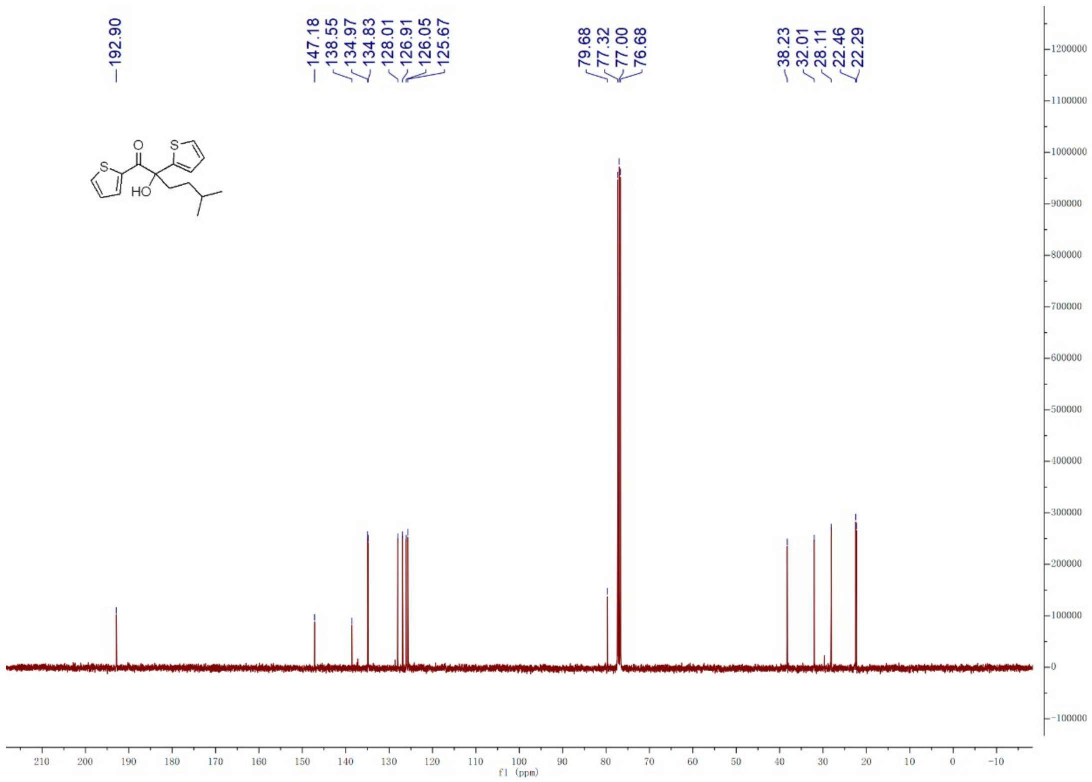

Figure S41 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **4aaa**

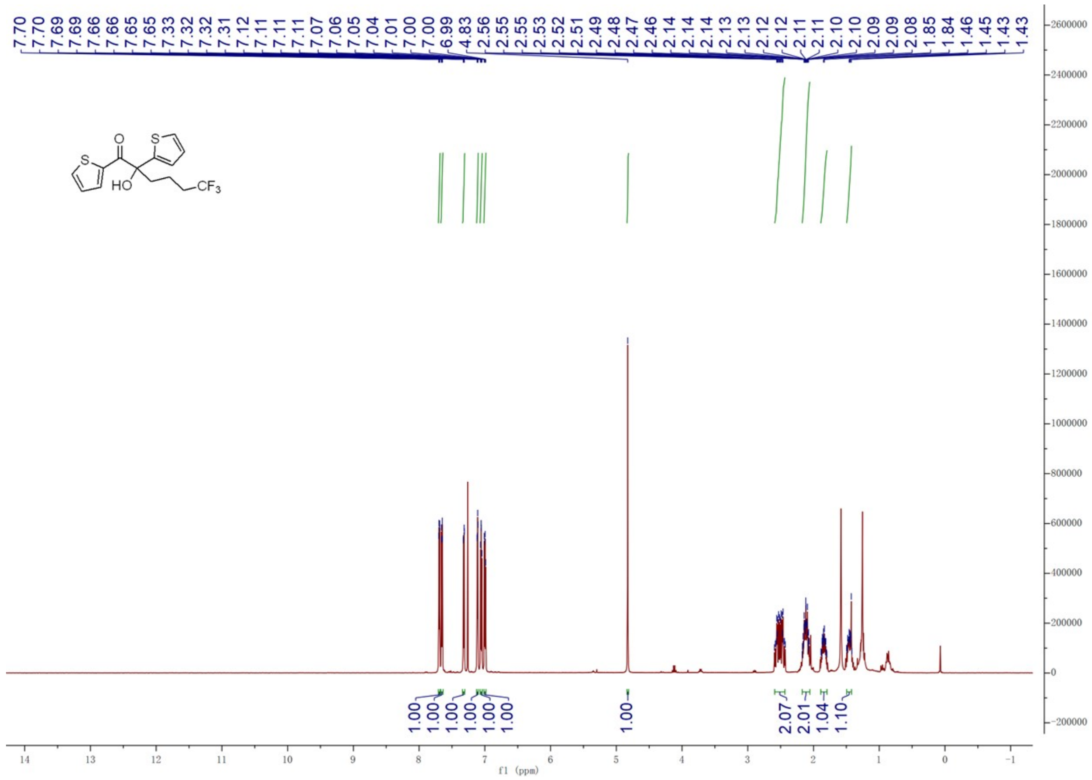

Figure S42 ^{1}H NMR (25 °C, 400 MHz, $CDCl_3$) of **4aab**

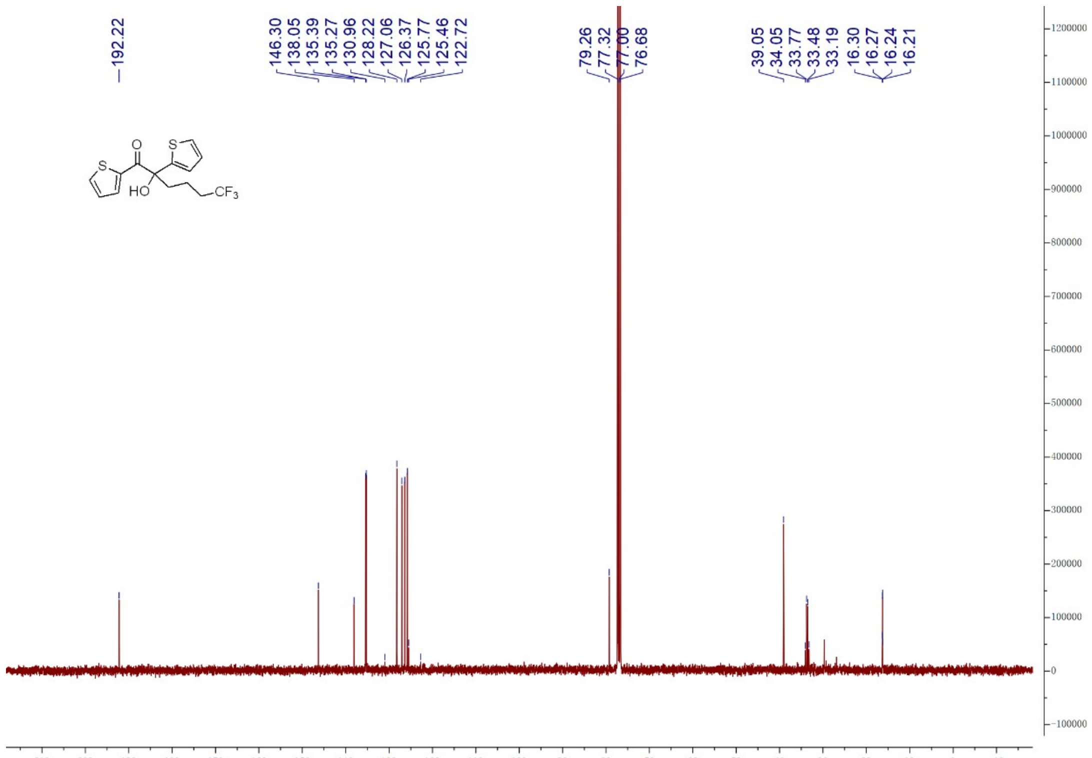

Figure S43 $^{13}C\{^{1}H\}$ NMR (25 °C, 101 MHz, $CDCl_3$) of **4aab**

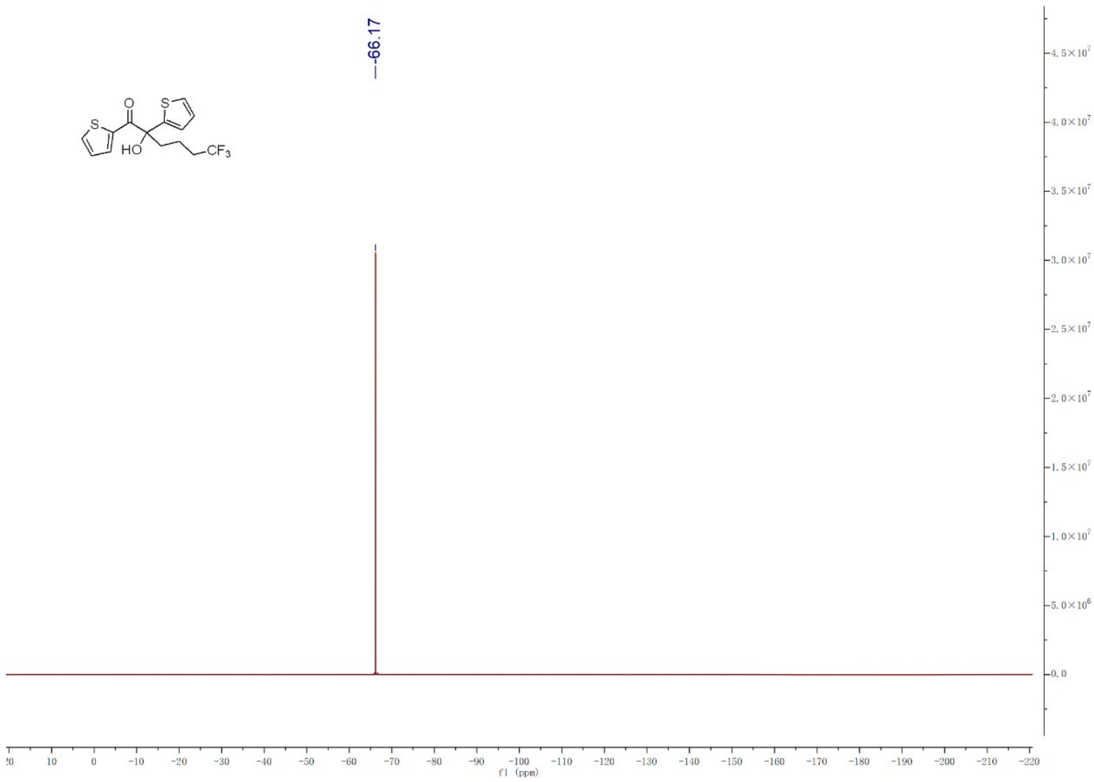

Figure S44 ^{19}F NMR (25 °C, 376 MHz, $CDCl_3$) of **4aab**

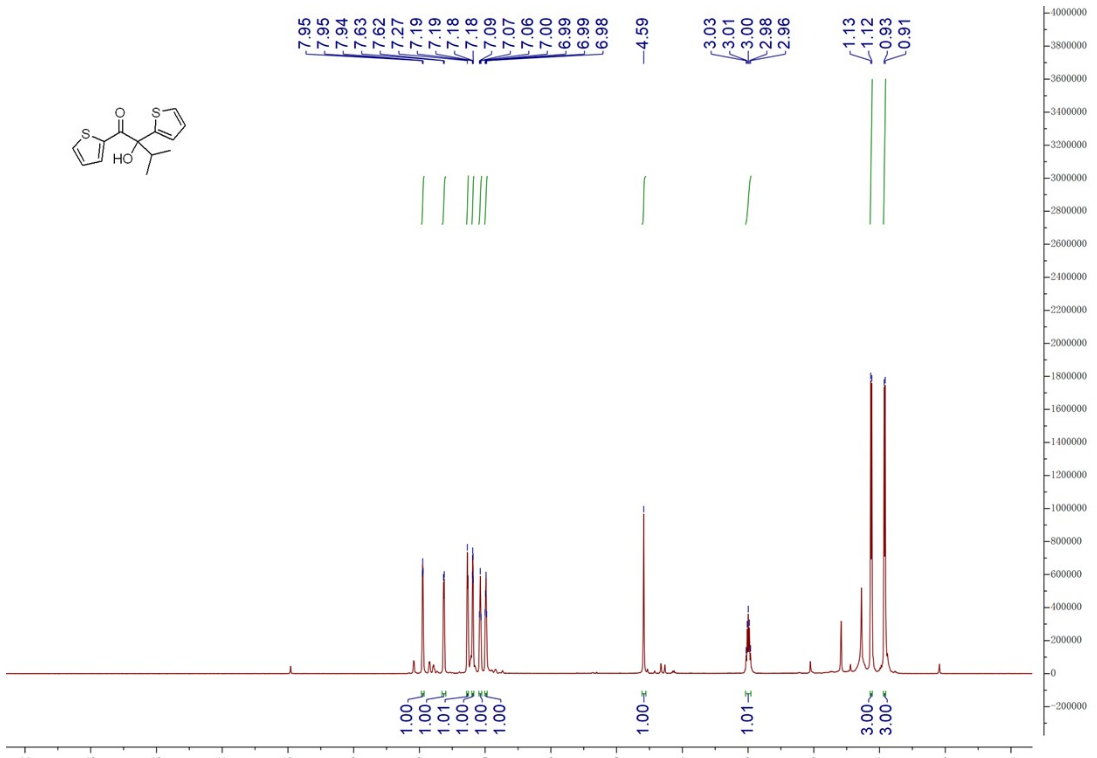

Figure S45 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4ao**

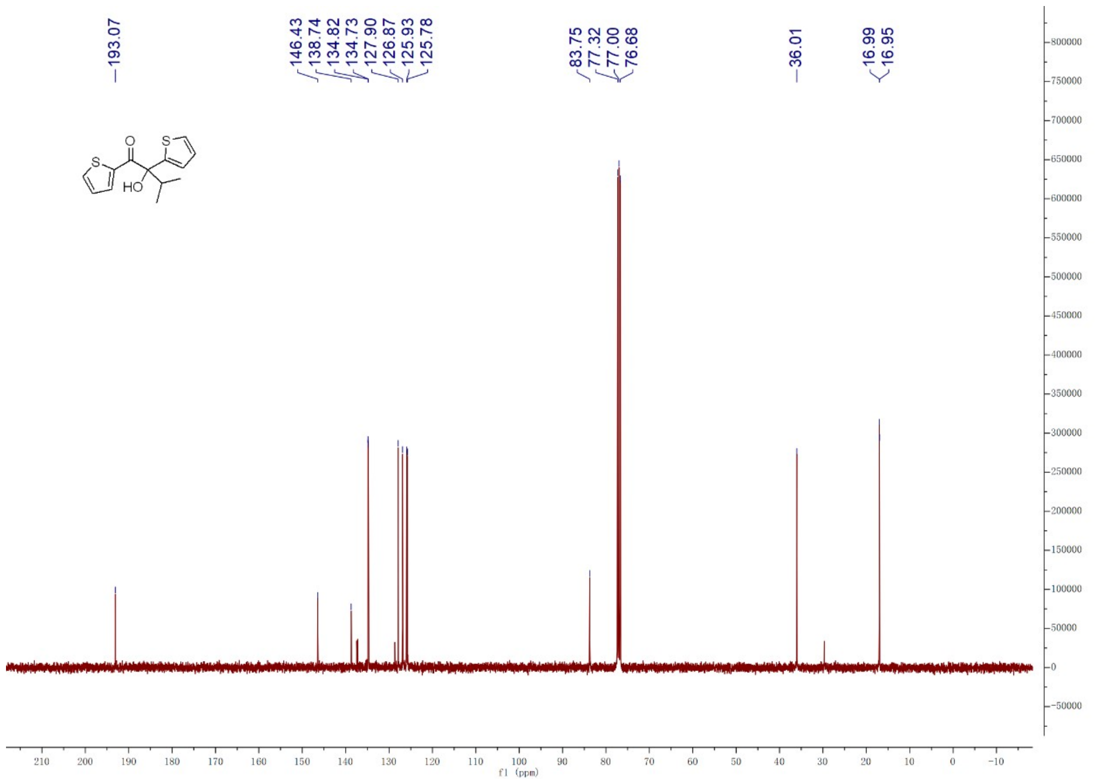

Figure S46 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4ao**

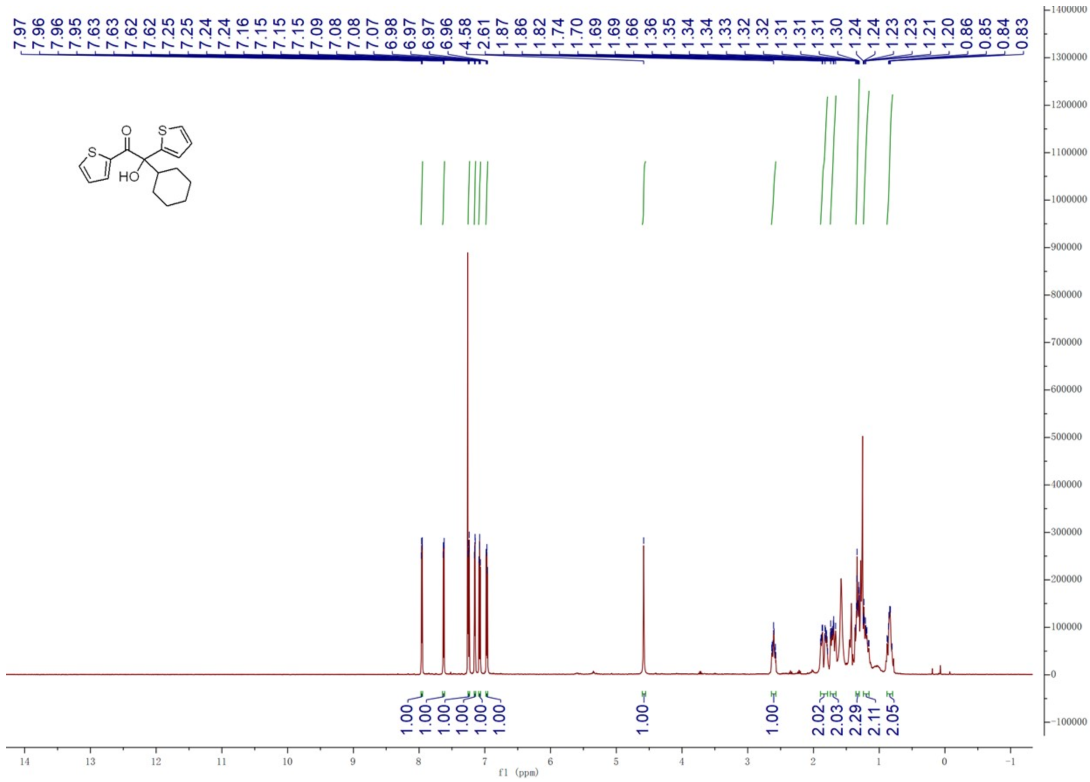

Figure S47 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4al**

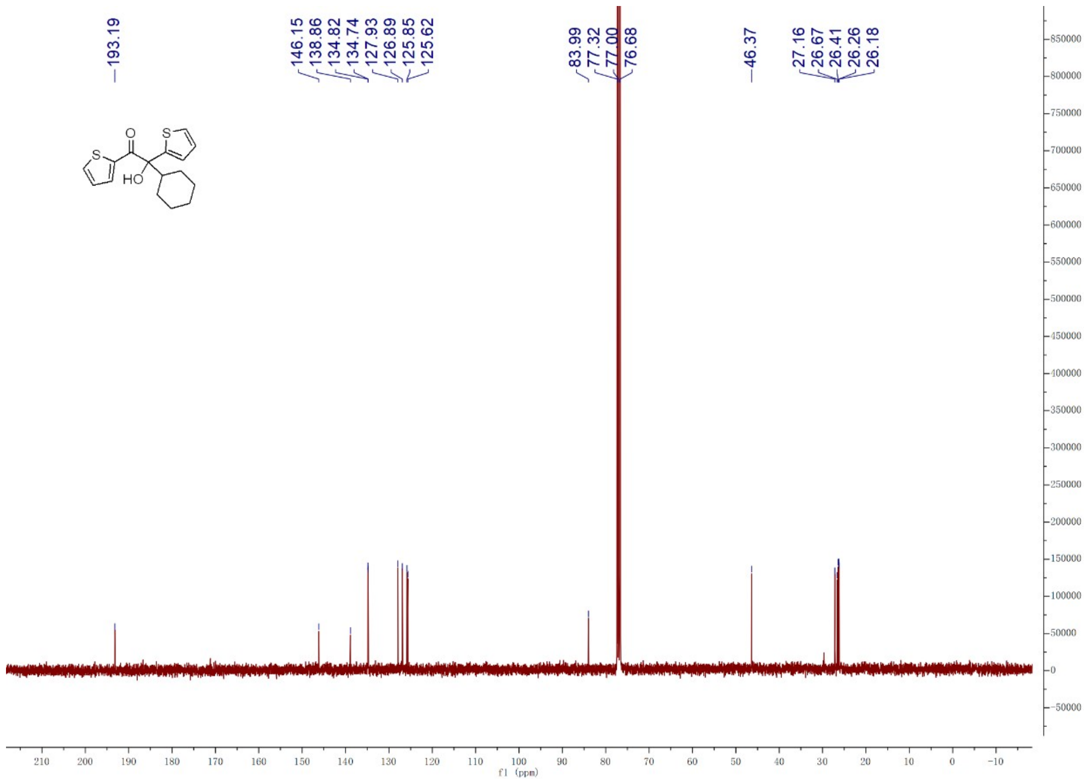

Figure S48 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4al**

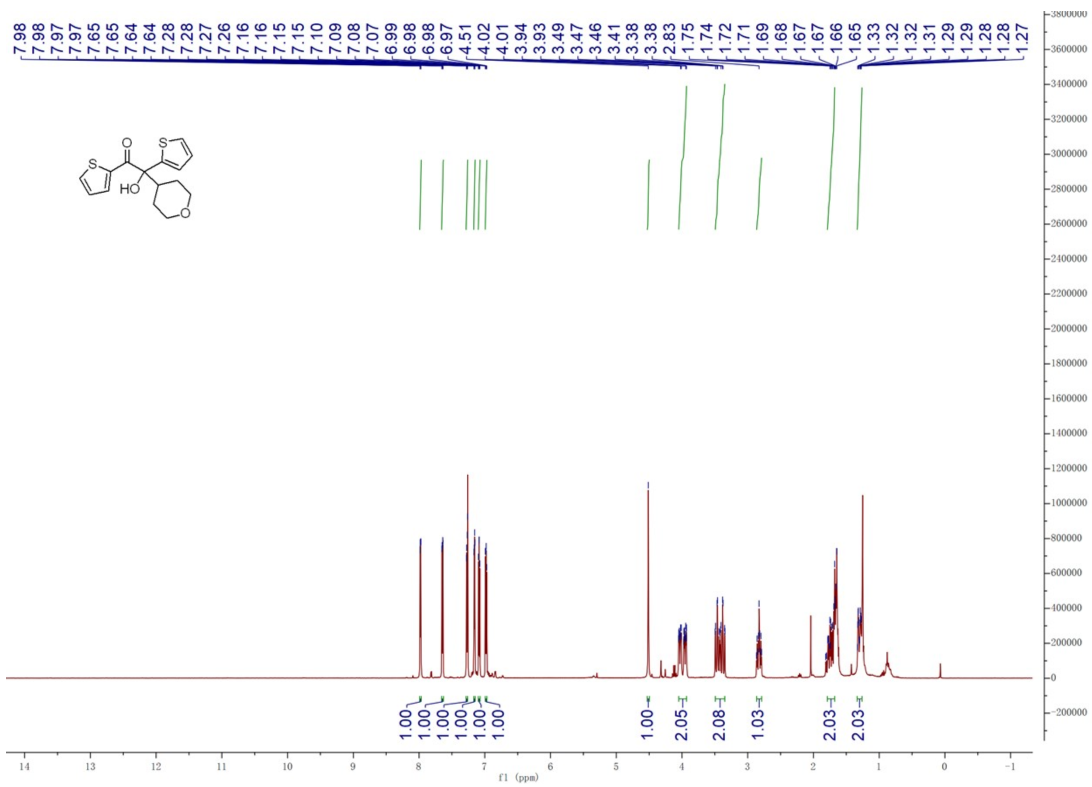

Figure S49 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4am**

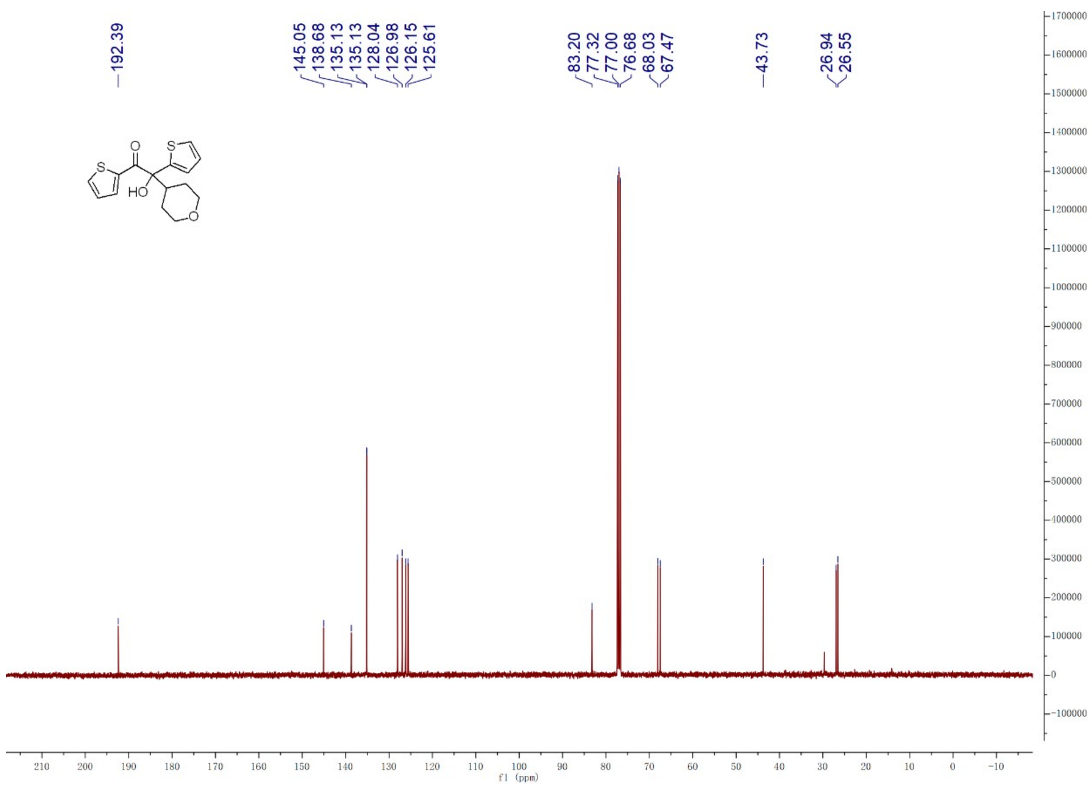

Figure S50 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4am**

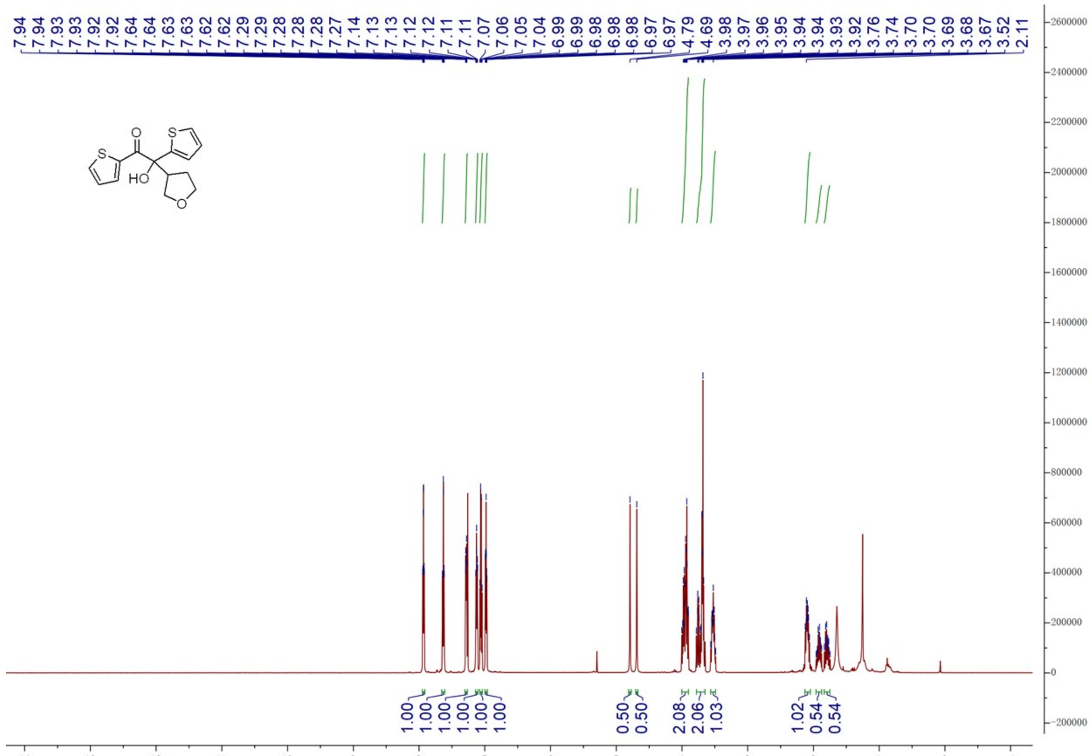

Figure S51 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4aac**

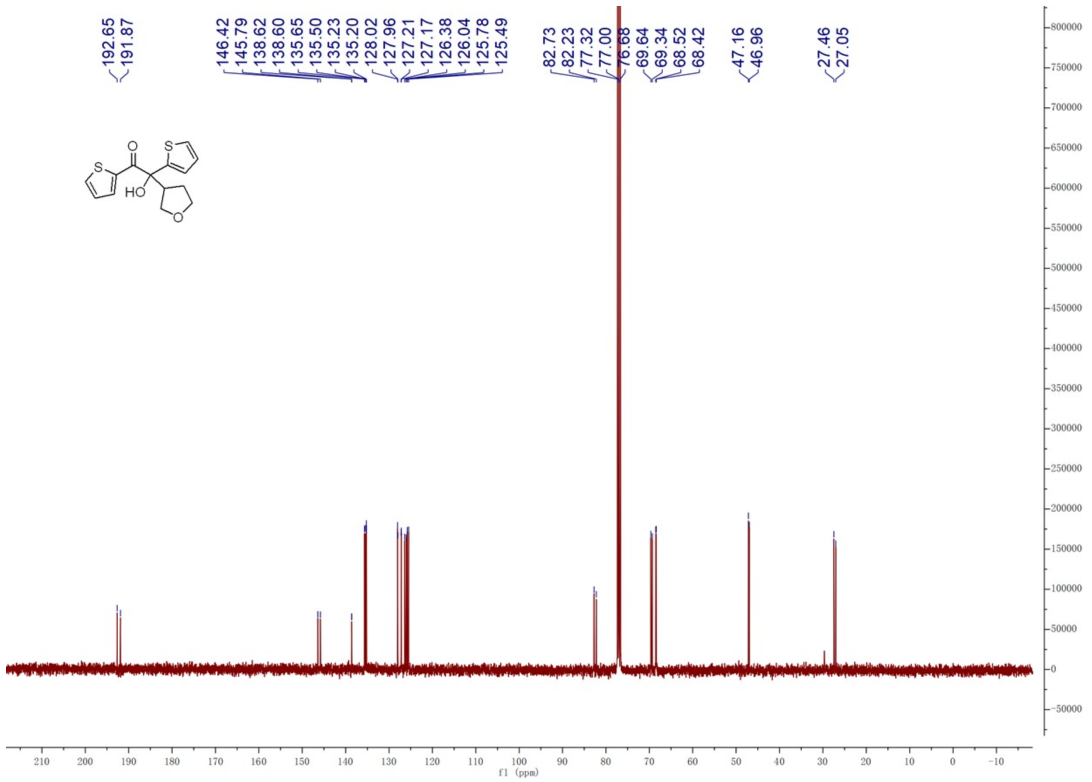

Figure S52 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4aac**

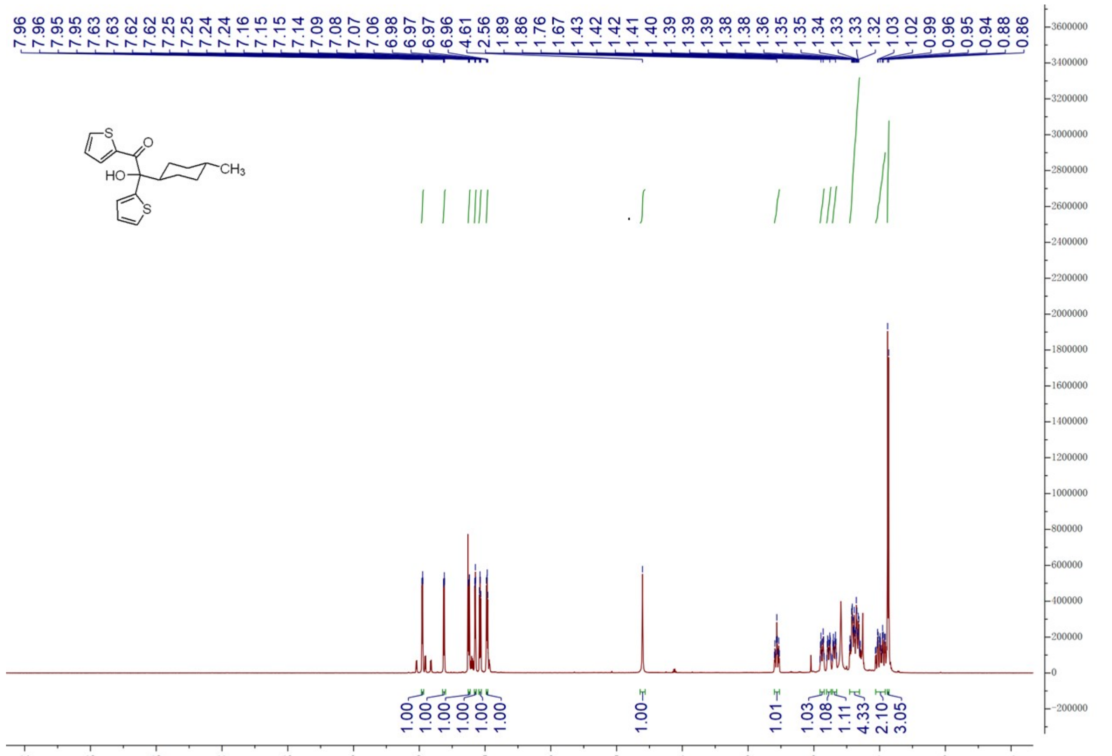

Figure S53 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4ap**

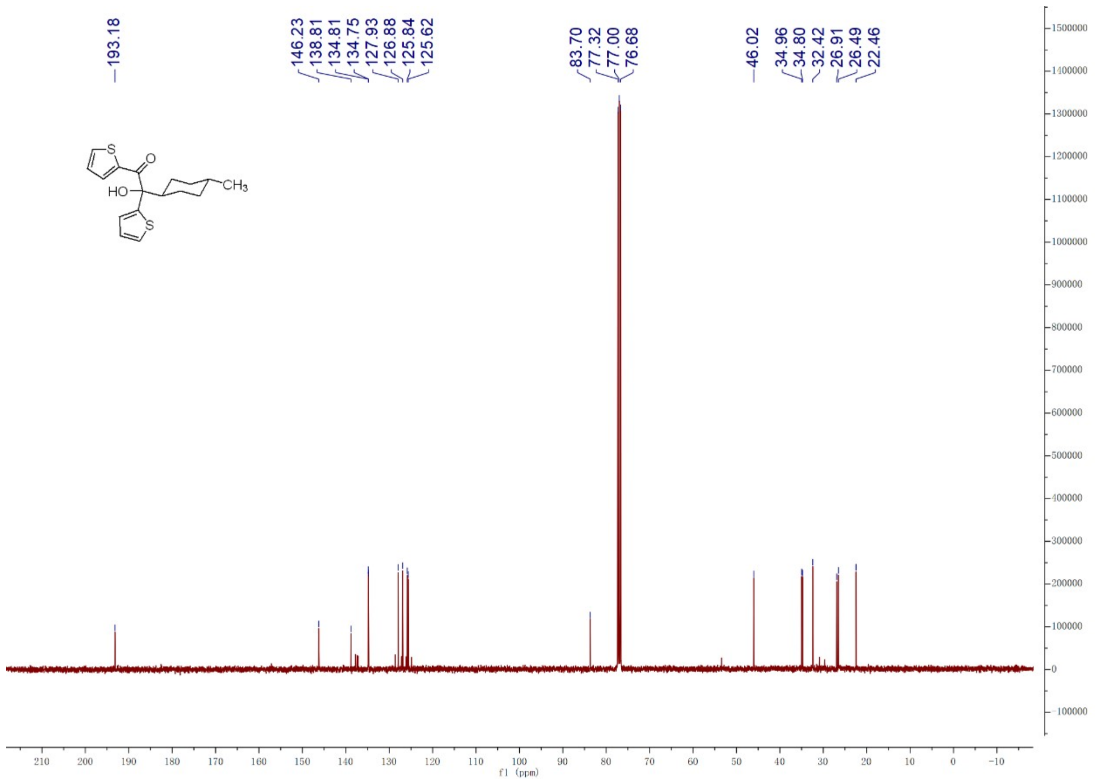

Figure S54 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4ap**

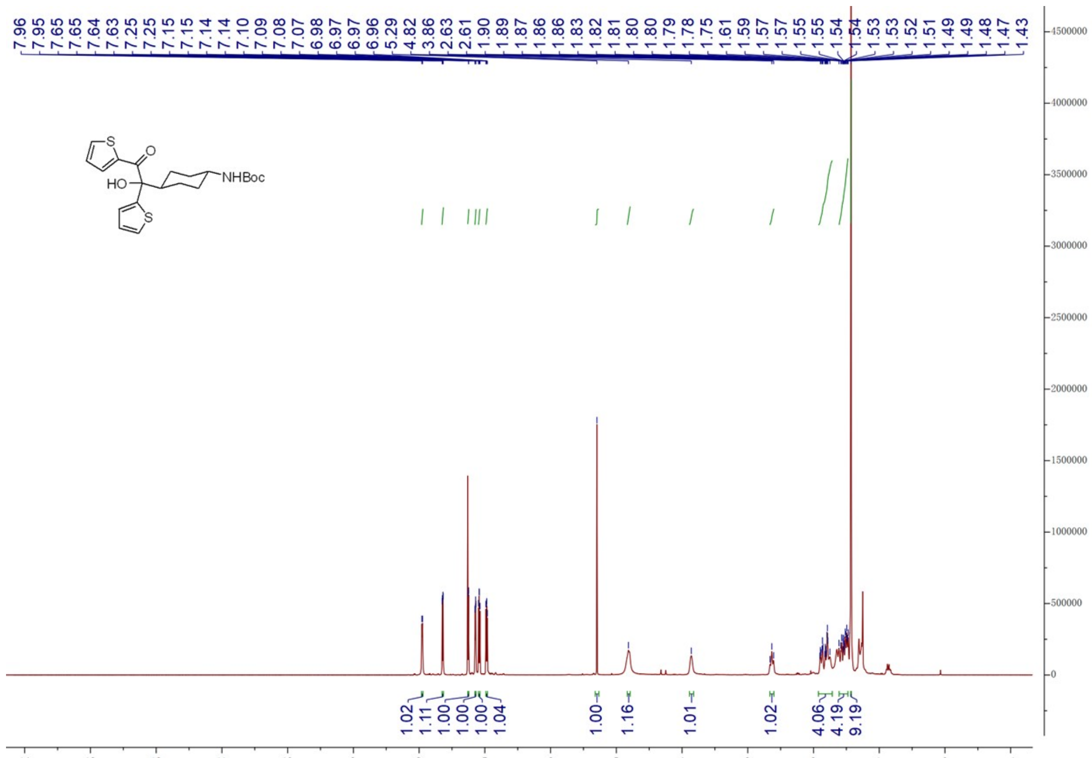

Figure S55 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4aq**

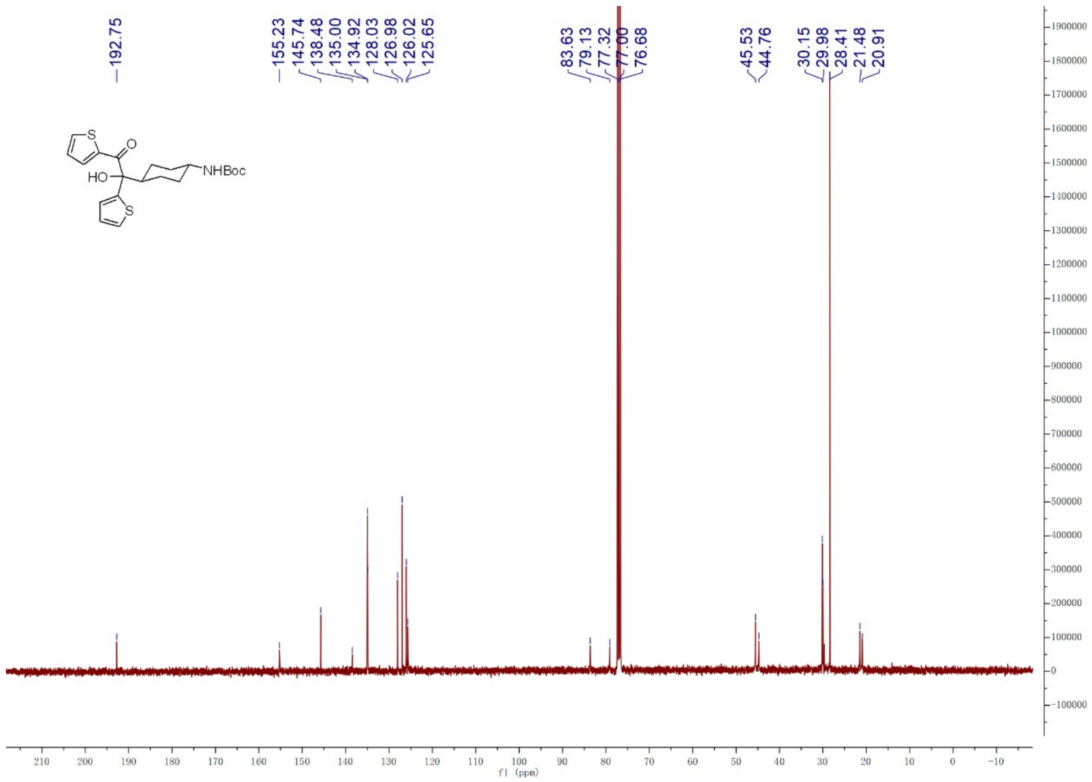

Figure S56 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4aq**

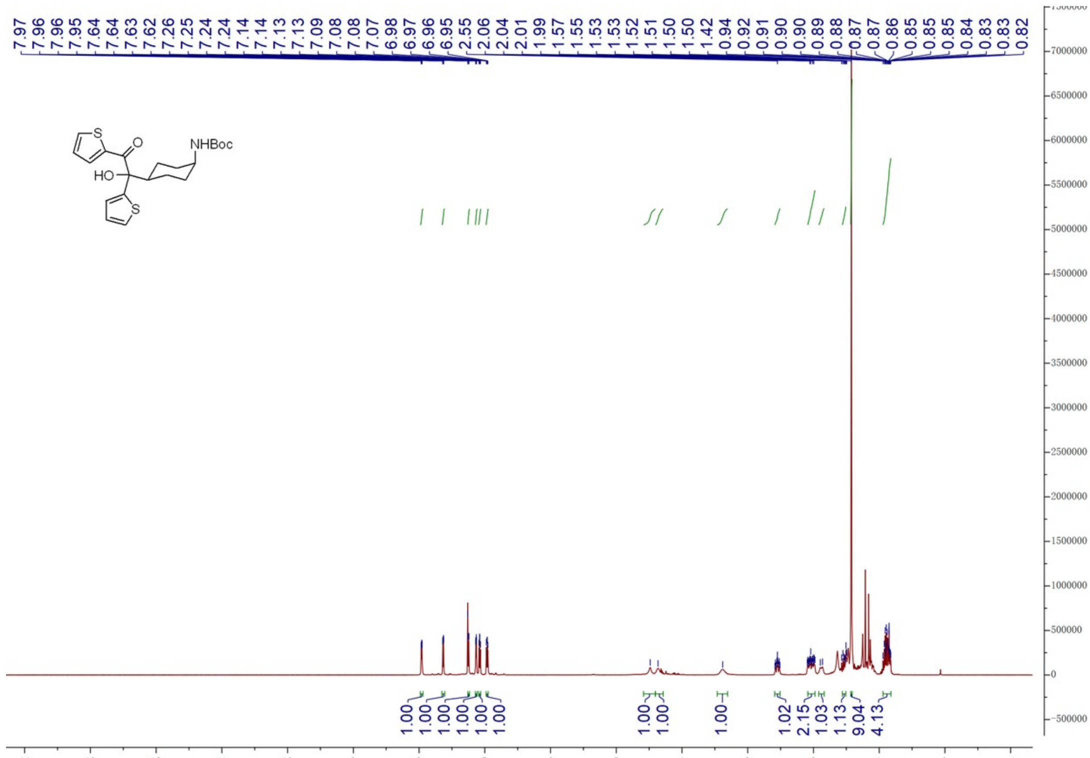

Figure S57 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4ar**

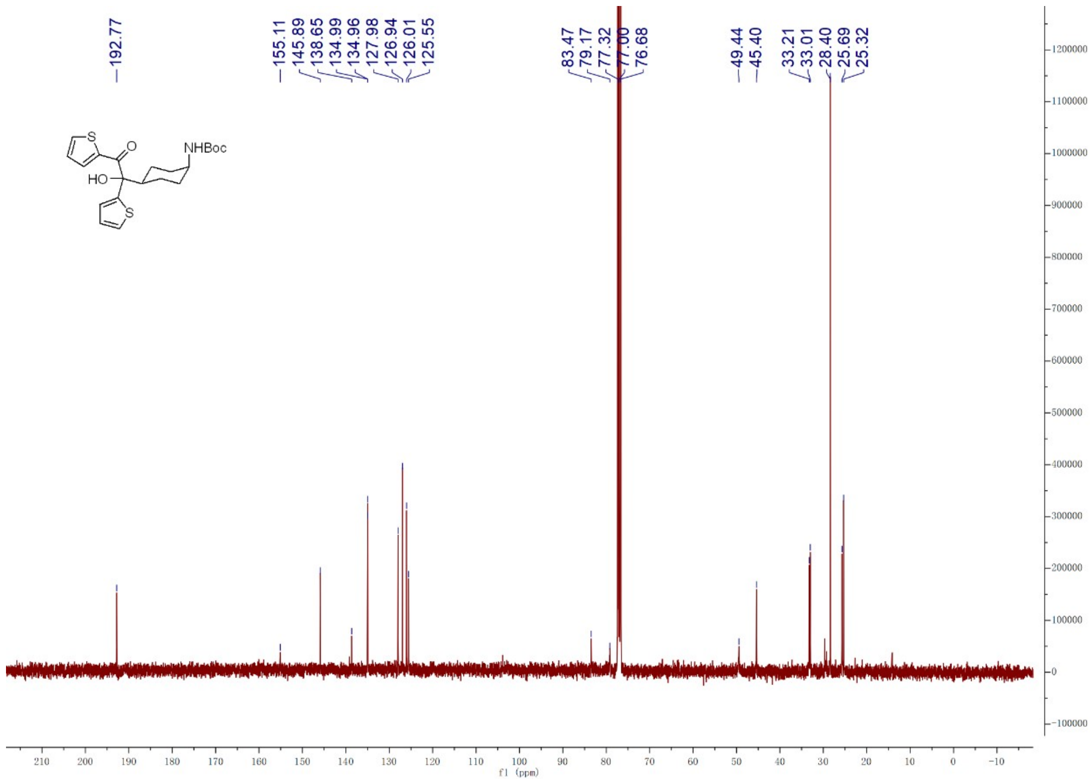

Figure S58 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4ar**

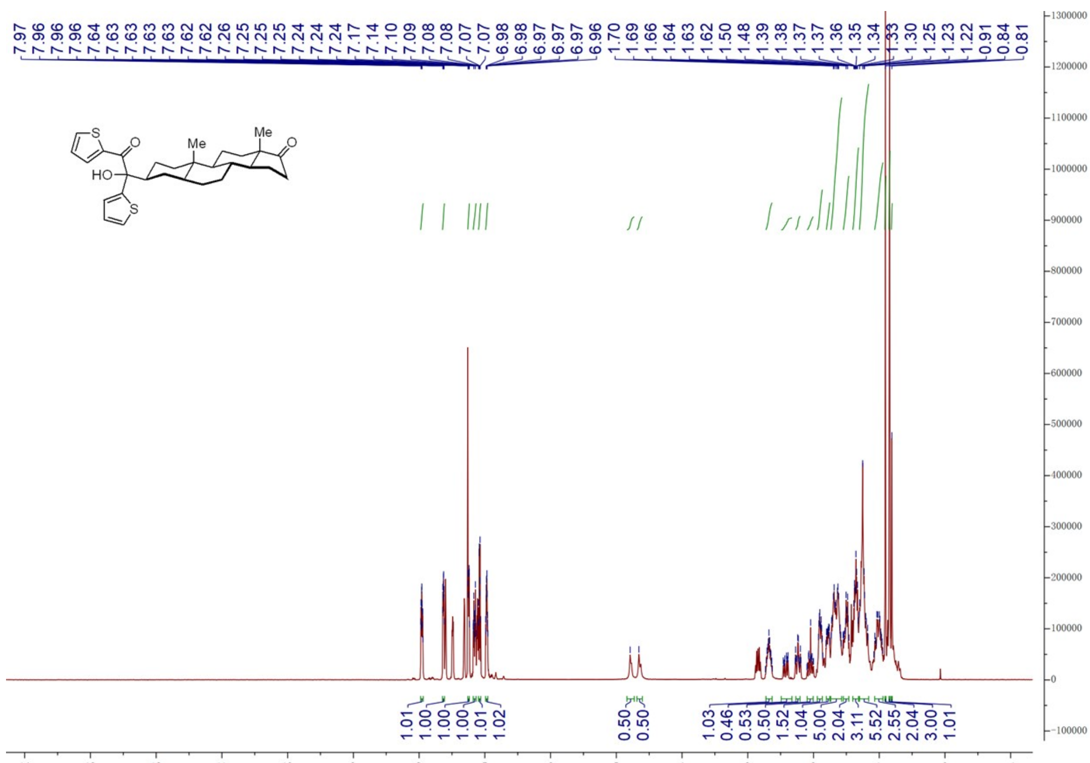

Figure S59 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4at**

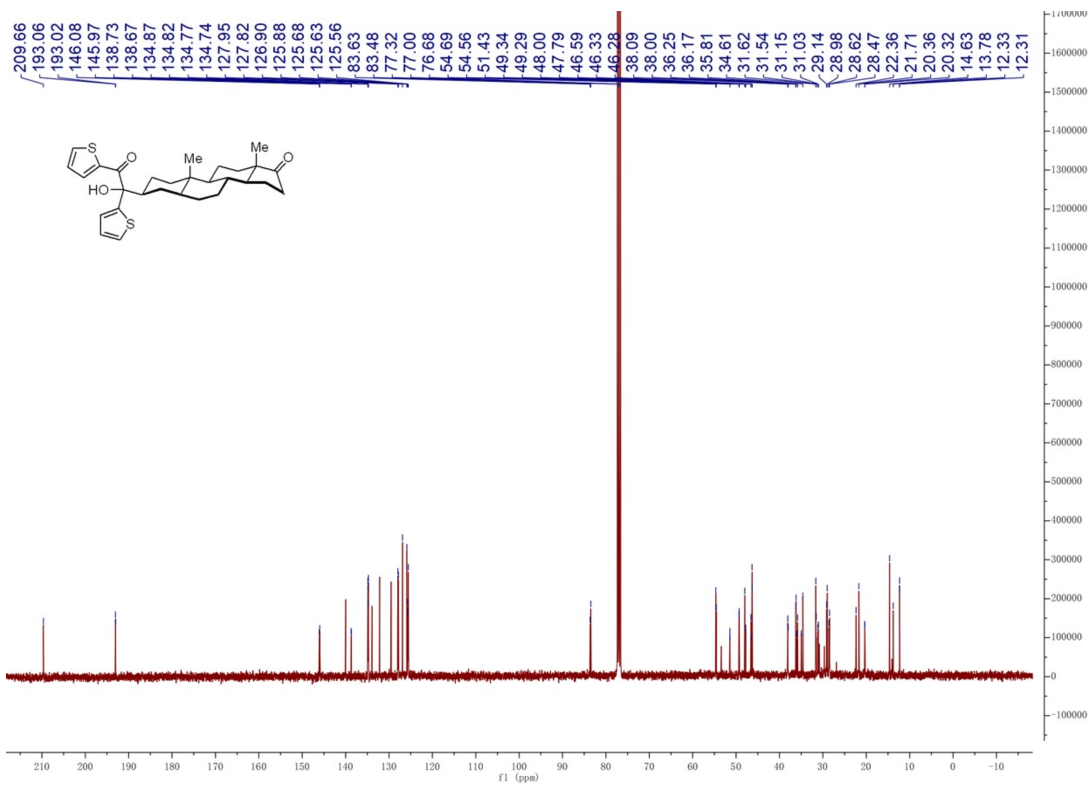

Figure S60 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4at**

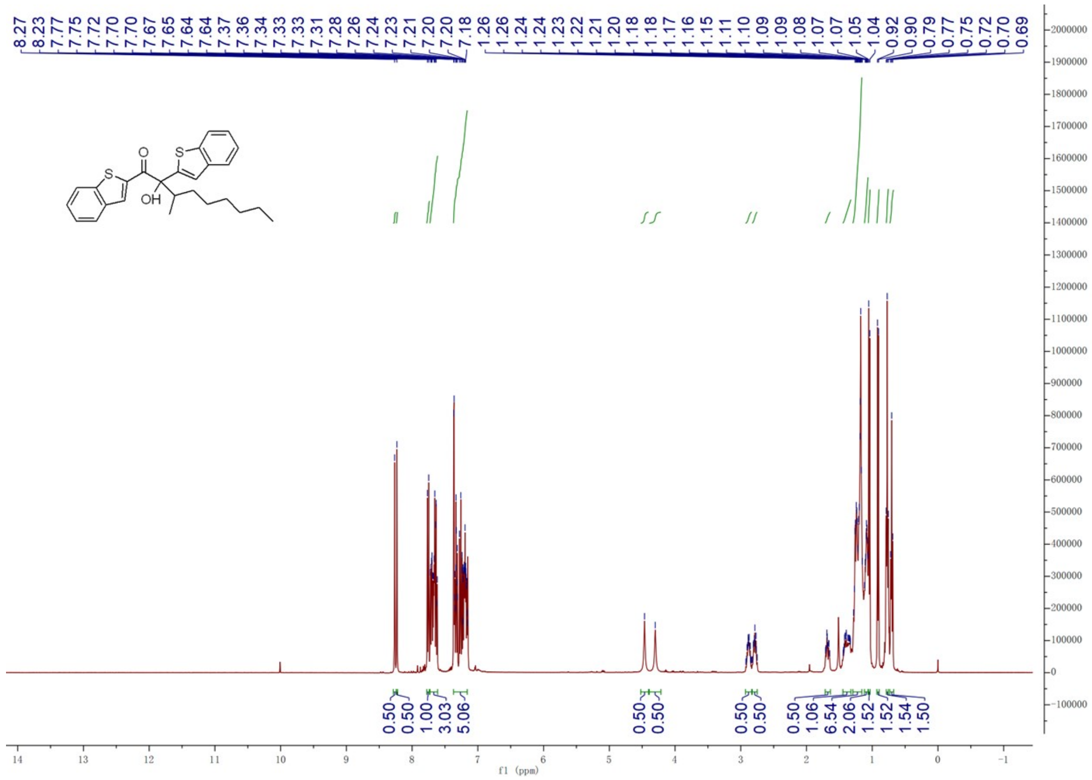

Figure S61 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **4cu**

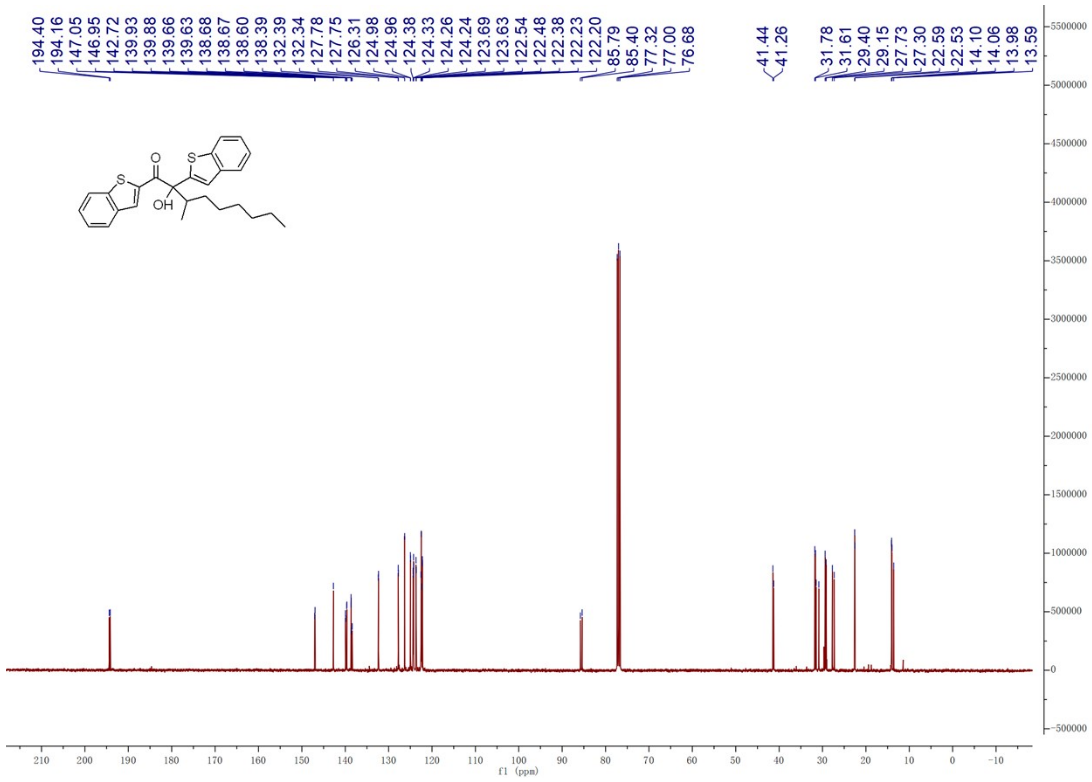

Figure S62 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **4cu**

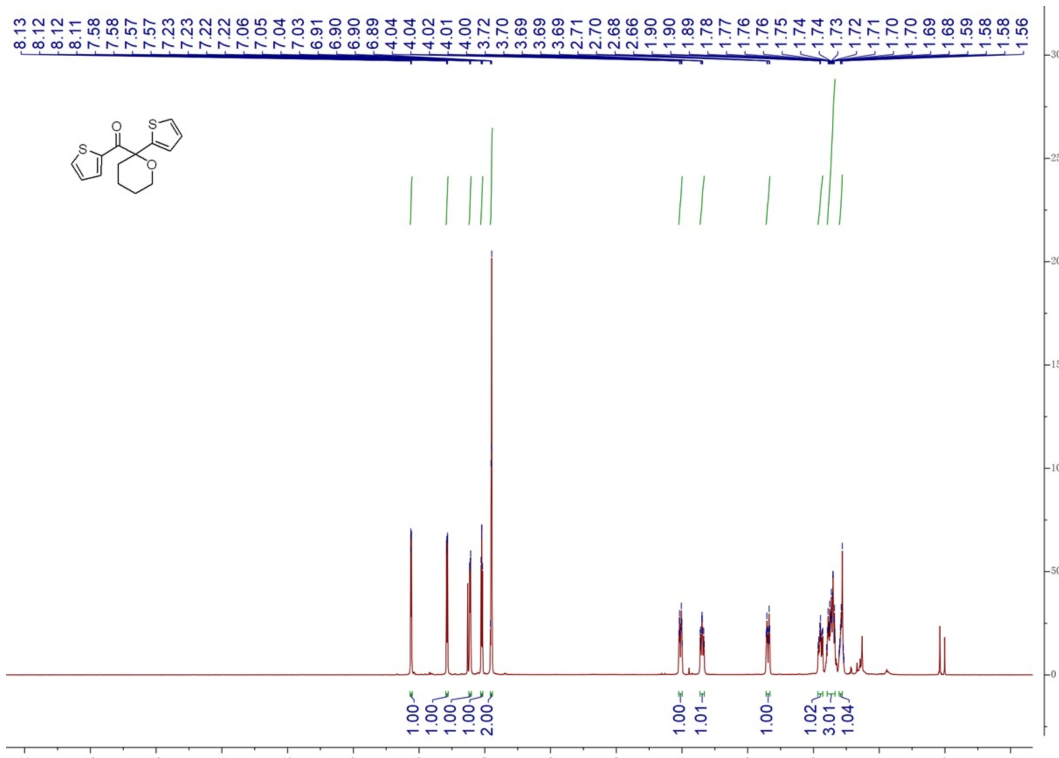

Figure S63 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **5ac**

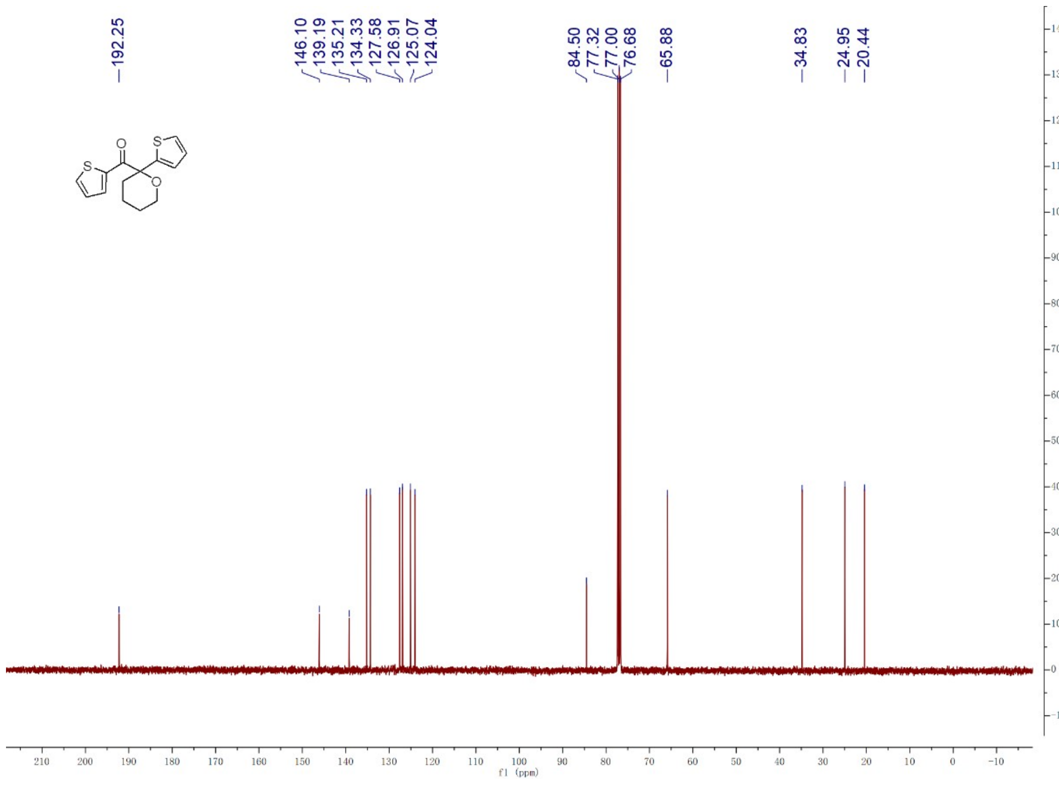

Figure S64 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **5ac**

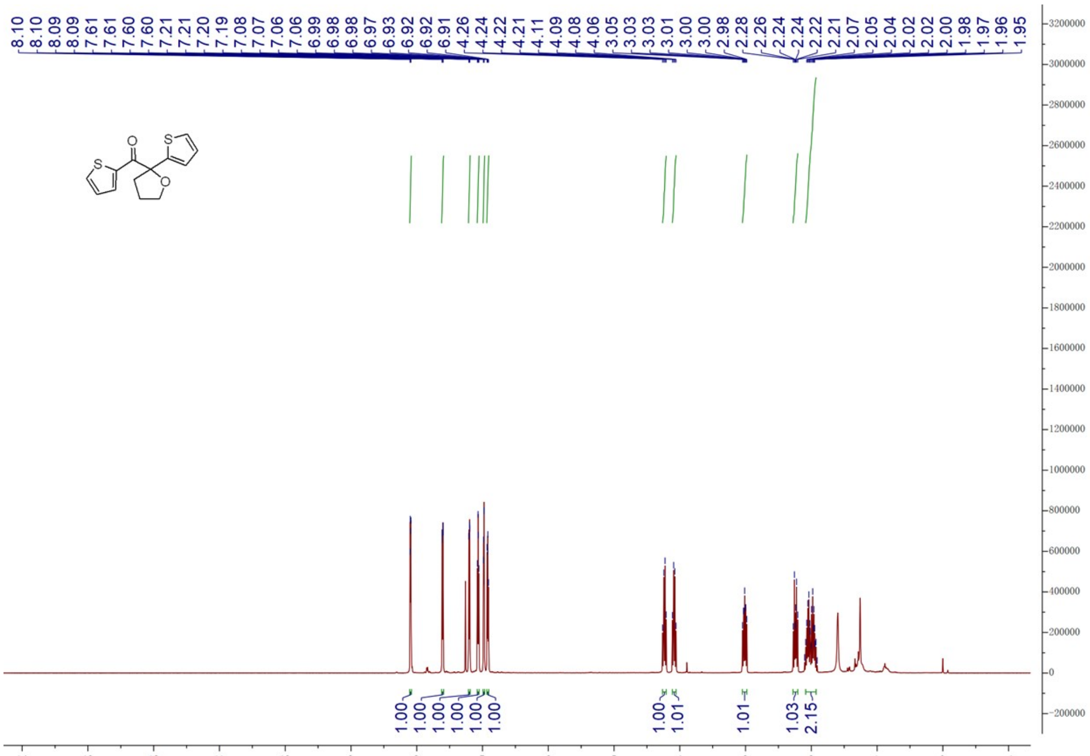

Figure S65 ^{1}H NMR (25 ^{o}C, 400 MHz, $CDCl_3$) of **5ad**

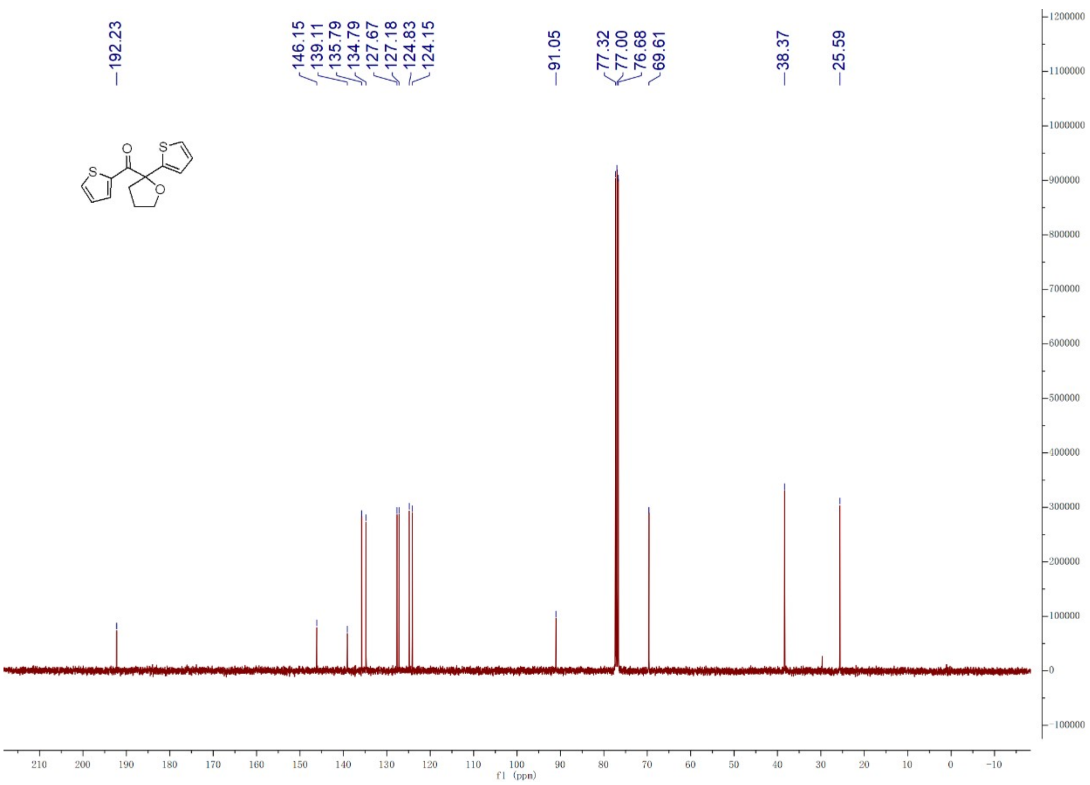

Figure S66 $^{13}C\{^{1}H\}$ NMR (25 ^{o}C, 101 MHz, $CDCl_3$) of **5ad**