Electronic Supplementary Information for

A *trans*-palladium dichloride complex with a bulky organosulfur ligand: syntheses, structure, and applications in catalytic alkylation of acetophenone and secondary alcohols using alcohols

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EXPERIMENTAL SECTION

General. The synthesis of the ligand precursor, ligand (**L1**), and palladium complex (**C1**) were performed using standard Schlenk line techniques. HPLC grade solvents, including DMF, MeOH, EtOAc, hexane, DCM, EtOH, $CHCl_3$,Toluene and acetone, were employed in the reactions. All solvents were used as received without further purification. 1-Naphthaldehyde (Sigma Aldrich), $CDCl_3$ (Sigma Aldrich), K^{t}OBu (Sigma Aldrich), $PdCl_2(CH_3CN)_2$ (Sigma Aldrich), Acetophenone (Sigma Aldrich), K_2CO_3 (Spectrochem), $NaBH_4$ (Spectrochem), $SOCl_2$ (Spectrochem), Sulfur powder (Spectrochem), Na_2SO_4 (Spectrochem), NaOH (Spectrochem), KOH (Spectrochem), Benzyl alcohol (Spectrochem), 3-bromoacetophenone (Molychem), 3-methoxy acetophenone (Molychem), para methoxy benzyl alcohol(Molychem), and para methyl benzyl alcohol (Molychem) were used as received. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the compounds were recorded at ambient temperature using a Bruker 500 MHz instrument. The NMR solvent peaks were referenced as follows (δ, ppm): ^1H, $CHCl_3$ (7.26); $^{13}C\{^1H\}$, $CDCl_3$ (77.00). The melting point was determined using a Buchi Melting Point B-540 instrument. Infrared spectra were recorded in the 4000–400 cm^{-1} region at room temperature using a PerkinElmer FTIR spectrometer. High-resolution mass spectrometry (HRMS) data were obtained with an Agilent Q-TOF LC-MS spectrometer using the electrospray ionization (ESI) method. The reaction progress was monitored by TLC, utilizing 0.25 mm silica gel 60-F254 plates and a UV chamber equipped with 254 nm and 395 nm lamps.

Crystallography:

A suitable yellow block-shaped crystal of **L1**, along with colorless plate-shaped crystals of **C1**, were selected using a polarizing microscope. These crystals were carefully mounted on a nylon loop using paraffin oil and placed in a cold nitrogen stream maintained at a low temperature of 110.00 K with the help of an Oxford Cryo-system. Crystal screening, unit cell determination, and data collection were conducted on a Bruker Venture diffractometer equipped with a PHOTON III detector.[s1] The diffraction pattern of the crystals was indexed, and strategy calculations from the APEX 3 software (Bruker, 2018) were used to determine the number of runs and images needed for data collection. The process involved φ and ω scans utilizing CuKα radiation, which extended to a maximum resolution of Θ = 70.115° (corresponding to a wavelength of 0.82 Å). [S2] The unit cell parameters were refined using SAINT V8.38A software (Bruker, 2018), based on 9936 reflections,[s3] which represented 33% of the observed reflections. The crystal structure solution and

final refinement parameters for the compound **C1** are detailed in Table s1, along with data for L1.[S4] Additionally, selected bond distances and angles are presented in Table s2, providing important structural insights into the molecular arrangement of these compounds.

Table s1. Summary of crystallographic data.

	L1	**C1**
empirical formula	$C_{22}H_{18}S$	$C_{44}H_{36}Cl_2PdS_2$
formula weight	314.42	806.15
temperature [K]	110.0	110.00
Diffractometer	Bruker APEX-II	Bruker Venture (PHOTON III)
wavelength [Å]	0.71073	1.54178
crystal system	orthorhombic	Monoclinic
space group	*Ibca*	*C*2/*c*
unit cell dimensions:		
a[Å]	7.7139(5)	21.9194(7)
b[Å]	15.7197(9)	6.1161(2)
c[Å]	26.6782(16)	26.6465(9)
α[°]	90.00	90
β[°]	90.00	90.928(2)
γ[°]	90.00	90
V[Å^3]	3235.0(3)	3571.8(2)
Z	8	4
ρ_{calc}[Mg/m^3]	1.291	1.499
μ[mm^{-1}]	0.197	6.898
F(000)	1328	1648
crystal size [mm^3]	0.48×0.45×0.39	0.36×0.13×0.01
θ limit[°]	2.591 to 30.593	3.317 to 70.115
index range (*h*, *k*, *l*)	-11, 10, -22, 22, -38, 37	-26, 26,-7, 7, -32, 32
reflections collected	26735	30433
independent reflections	9951	9936
R(int)	0.0445	0.0247
max. and min. transmission	0.928 and 0.911	0.910 and 0.189
data/restraints/parameters	2493/0/ 105	3400/0/ 223
goodness-of-fit on F^2	1.030	1.065
R indices (final) [$I > 2\sigma(I)$]		
R_1	0.0445	0.0247
wR_1	0.1107	0.0672
R indices (all data)		
R_1	0.0608	0.0251
wR_2	0.1202	0.0676
largest diff. peak and hole [eÅ^{-3}]	0.389 and -0.272	0.363 and -0.459

Table s2. Key crystallographic distances [Å] and angles [°].

C1	
Bond	**Length (Å)**
Pd(1)—S(1)	2.3127(4)
Pd(1)—S(2)	2.3128(4)
Pd(1)—Cl(1)	2.2930(4)
Pd(1)—Cl(2)	2.2931(4)
S(1)—Cl(1)	1.8363(19)
S(2)—Cl(2)	1.8294(18)
C1	
Bond	**Angle (deg.)**
S(2)—Pd(1)—S(1)	180.0
Cl(1)—Pd(1)—S(2)	82.975(15)
Cl(2)—Pd(1)—S(2)	97.025(15)
Cl(1)—Pd(1)—S(1)	97.026(15)
Cl(2)—Pd(1)—S(1)	82.974(15)
Cl(1)—Pd(1)—Cl(2)	180.0

Copies of spectral data

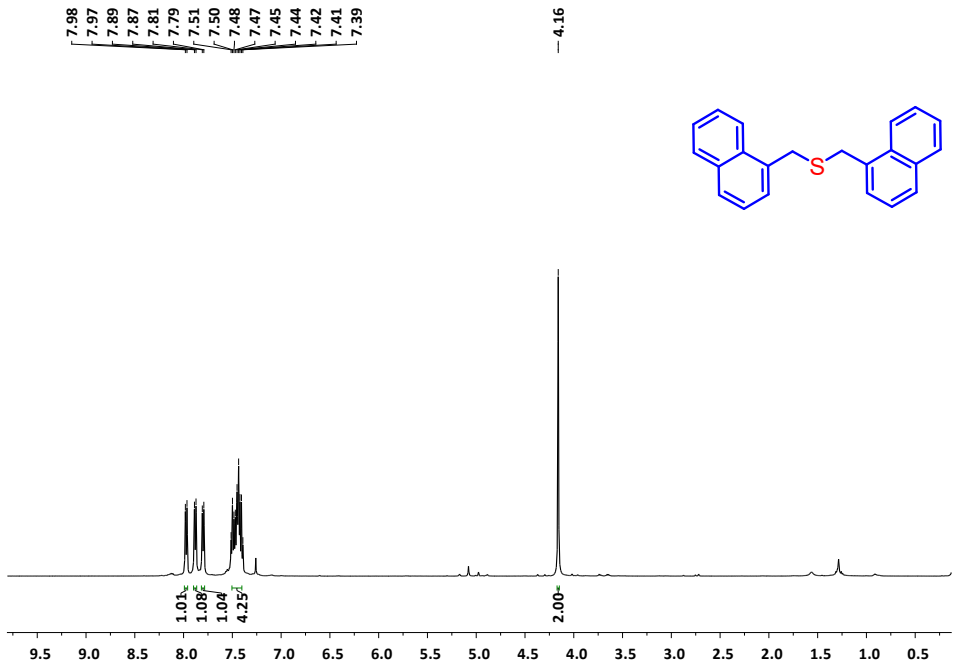


Figure s1. ^{1}H NMR spectrum of **L1**.

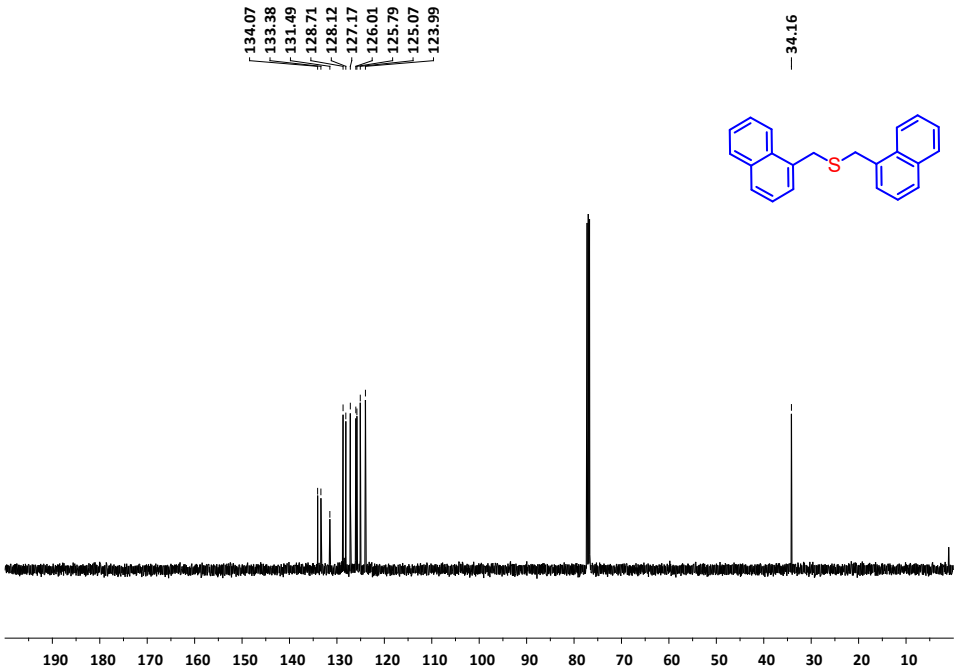


Figure s2. ^{13}C{^{1}H} NMR spectrum of **L1**.

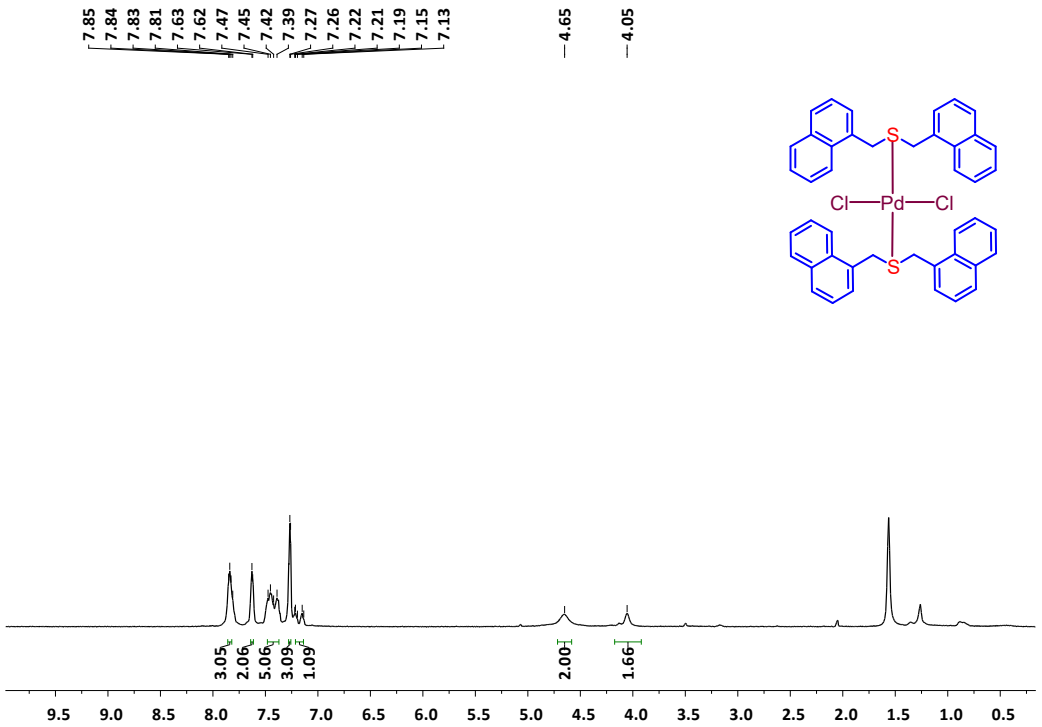


Figure s3. ^{1}H NMR spectrum of **C1**.

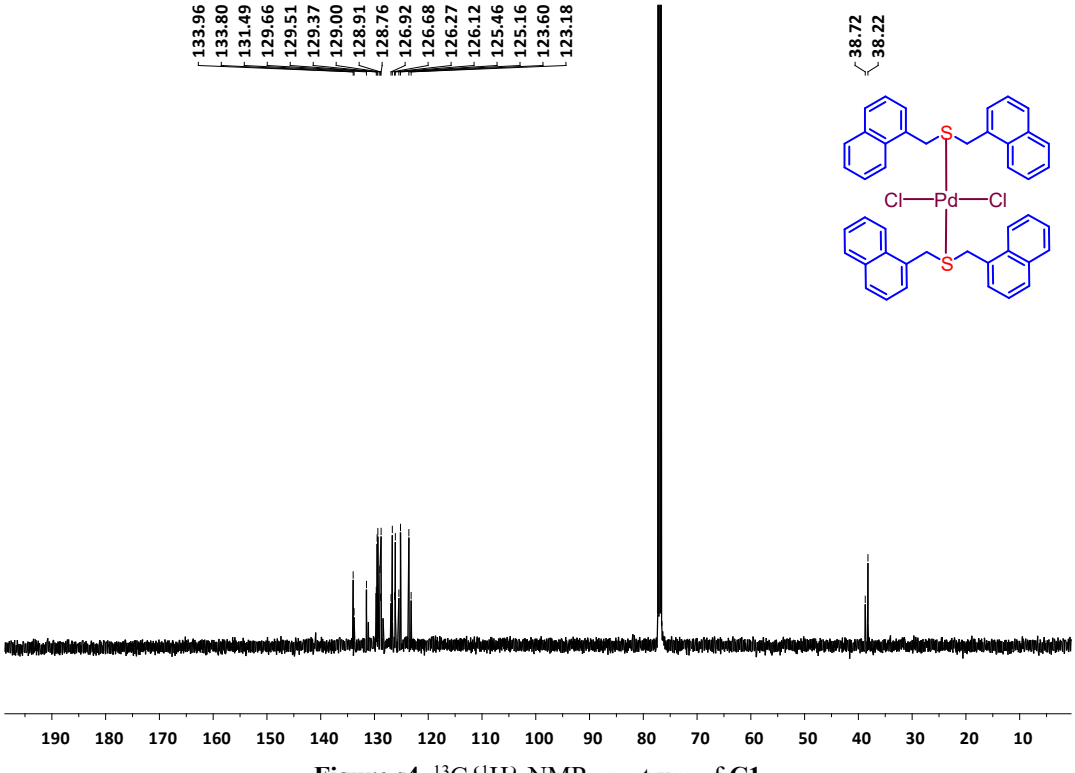


Figure s4. $^{13}C\{^{1}H\}$ NMR spectrum of **C1**.

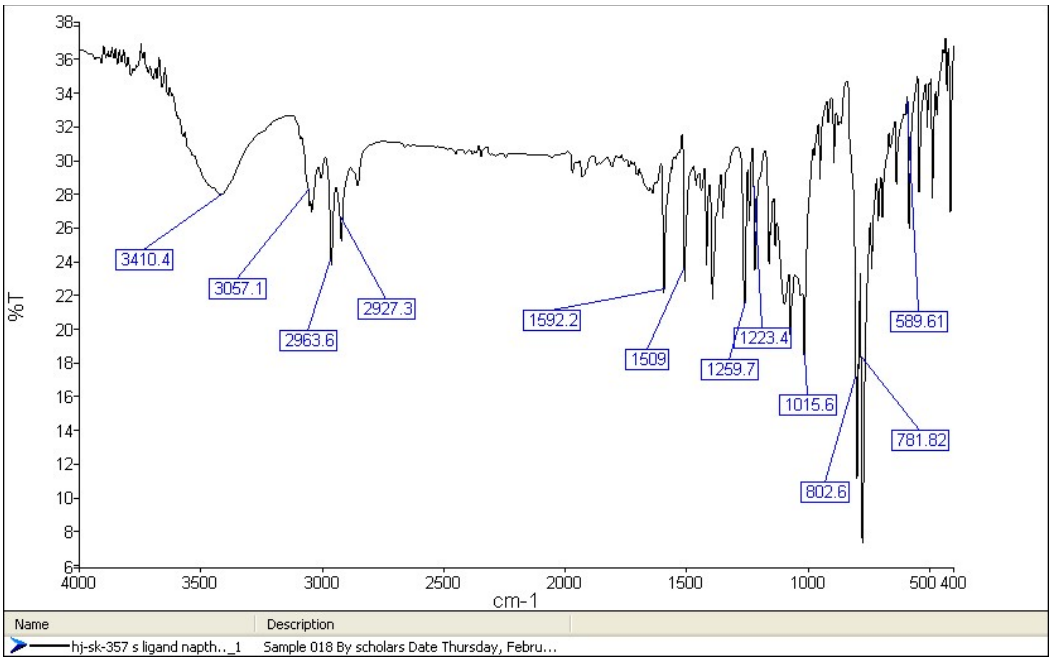


Figure s5. FTIR spectrum of **L1**.

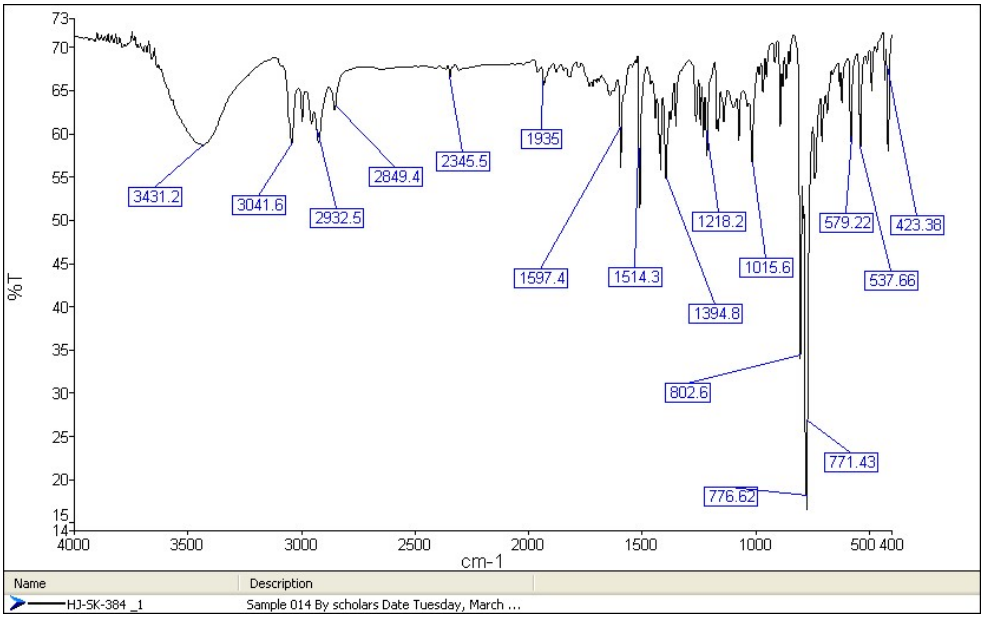


Figure s6. FTIR spectrum of **C1**.

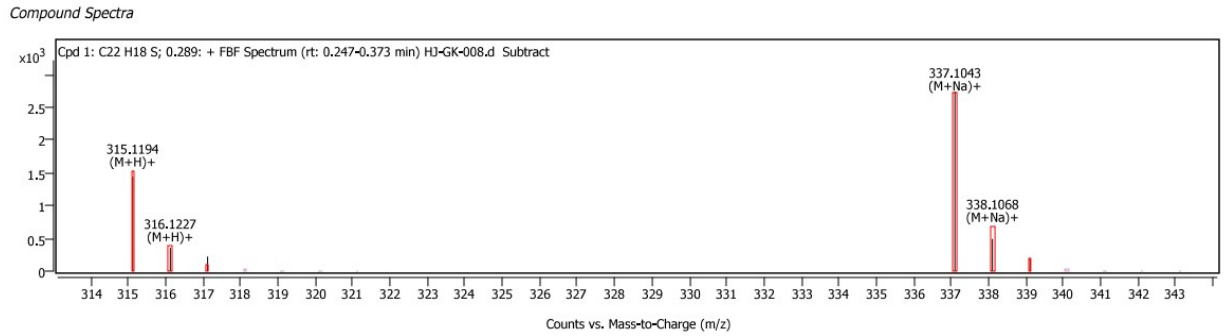


Figure s7. HRMS of **L1.**

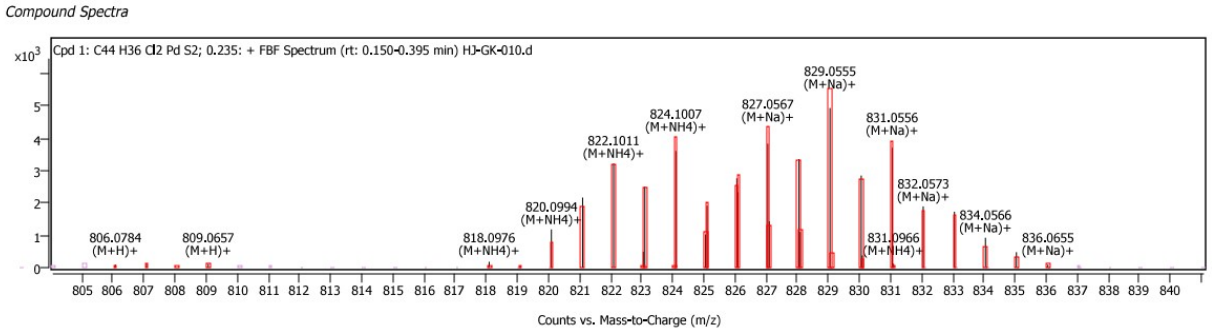
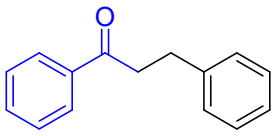
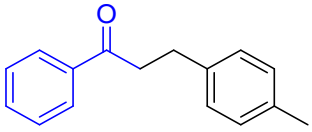


Figure s8. HRMS of **C1**.

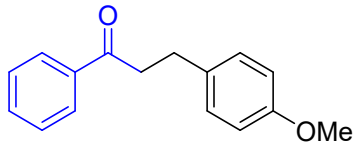
Spectroscopic Data of Products (^{1}H NMR and ^{13}C{^{1}H}) :



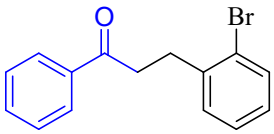
1,3-diphenylpropan-1-one (3aa)[s5, s6] Yellow liquid, 89%, **NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 7.98 (d, *J* = 7 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8 Hz, 2H), 7.22 – 7.35 (m, 5H), 3.33 (t, *J* = 7 Hz, 2H), 3.10 (t, *J* = 8 Hz 2H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 199.1 (s), 141.2 (s), 136.8 (s), 132.9 (s), 128.5 (s), 128.4 (s), 128.3 (s), 127.9 (s), 126.0 (s), 40.3 (s), 30.0 (s).



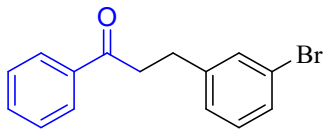
1-phenyl-3-(p-tolyl)propan-1-one (3ab)[s5, s6] Yellow liquid, 73%**, NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 7.98 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.16 (dd, *J* = 19.7, 7.8 Hz, 4H), 3.31 (t, *J* = 8 Hz, 2H), 3.06 (t, *J* = 9 Hz, 2H), 2.35 (s, 3H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 199.2 (s), 138.1 (s), 136.8 (s), 135.5 (s), 132.9 (s), 129.6 (s), 129.3 (s), 129.1 (s), 128.5 (s), 128.2 (s), 128.0, 40.5 (s), 29.7 (s), 20.9 (s).



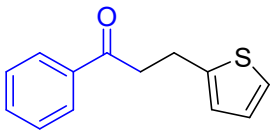
3-(4-methoxyphenyl)-1-phenylpropan-1-one (3ac)[s5, s6] Yellow liquid, 65%, **NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 7.88 (d, *J* = 8 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7 Hz, 2H), 7.19 (s, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.71 (s, 3H), 3.20 (t, *J* = 8 Hz, 2H), 2.94 (t, *J* = 7 Hz, 2H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 199.4 (s), 157.8 (s), 136.9 (s), 133.3 (s), 133.0 (s), 129.3 (s), 128.6 (s), 127.9 (s), 113.9 (s), 55.3 (s), 40.7 (s), 29.3 (s).



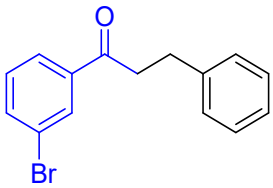
3-(2-bromophenyl)-1-phenylpropan-1-one (3ad)[s5] Yellow liquid, 76%, **NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 7.98 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 7 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.07-7.10 (m,1H), 3.32 (t, *J* = 7.5 Hz, 2H), 3.19 (t, *J* = 8 Hz, 2H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 198.9 (s), 140.5 (s), 136.7 (s), 133.1 (s), 132.9 (s), 130.8 (s), 128.6 (s), 128.0 (s), 127.9 (s), 127.6 (s), 124.3 (s), 38.6 (s), 30.8 (s).



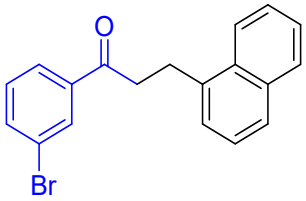
3-(3-bromophenyl)-1-phenylpropan-1-one (3ae), Yellow liquid, 81%**, NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 7.96 (d, *J* = 7 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.41 (s, 1H), 7.33-7.35 (m,1H), 7.14-7.20 (m, 2H), 3.29 (t, *J* = 8 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 198.6 (s), 143.6 (s), 136.6 (s), 133.1 (s), 131.4 (s), 130.0 (s), 129.2 (s), 128.6 (s), 127.9 (s), 127.1 (s), 122.5 (s), 39.9 (s), 29.5 (s).



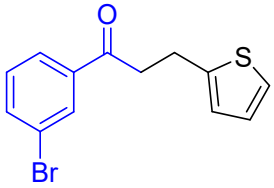
1-phenyl-3-(thiophen-2-yl)propan-1-one (3af)[s6] Yellow liquid, 77%**, NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 7.97 (d, *J* = 7 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.13 (dd, *J* = 4 Hz, *J* = 1 Hz, 1H), 6.92-6.93 (m,1H), 6.86-6.87 (m, 1H), 3.36-3.39 (m,2H), 3.29-3.32 (m,2H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 198.5 (s), 143.9 (s), 136.7 (s), 133.1 (s), 128.6 (s), 128.0 (s), 126.8 (s), 124.6 (s), 123.3 (s), 40.5 (s), 24.1 (s).



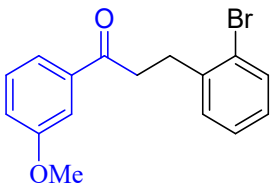
1-(3-bromophenyl)-3-phenylpropan-1-one (3ba), Yellow liquid, 82%**, NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 8.08 (t, *J* = 1.5 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.25 – 7.22 (m, 3H). 3.28 (t, *J* = 7.6 Hz 2H), 3.06 (t, *J* = 8 Hz 2H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 197.7 (s), 140.9 (s), 138.6 (s), 135.9 (s), 131.1 (s), 130.1 (s), 128.5 (s), 128.4 (s), 128.0 (s), 126.5 (s), 122.9 (s), 40.5 (s), 30.2 (s).



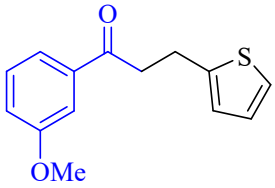
1-(3-bromophenyl)-3-(naphthalen-1-yl)propan-1-one (3bg), Yellow liquid, 73%**, NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 8.07 (t, *J* = 1.6 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.85-7.89 (m, 2H), 7.66-7.76 (m, 2H), 7.40-7.52 (m, 4H), 7.32 (t, *J* = 7.9 Hz, 1H), 3.53 (t, *J* = 7 Hz, 2H), 3.40 (t, *J* = 8.5 Hz, 2H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 197.9 (s), 138.5 (s), 136.9 (s), 135.9 (s), 134.0 (s), 131.2 (s), 130.2 (s), 129.0 (s), 128.9 (s), 127.1 (s), 126.8 (s), 126.5 (s), 126.2 (s),126.1 (s), 125.6 (s), 123.3 (s), 123.0 (s), 39.9 (s), 26.0 (s).



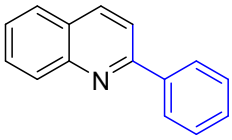
1-(3-bromophenyl)-3-(thiophen-2-yl)propan-1-one (3bf), Yellow liquid, 79%**, NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 8.09 (t, *J* = 1.6 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.68-7.70 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 3.27-3.35 (m, 4H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 197.2 (s), 143.4 (s), 138.6 (s), 136.0 (s), 131.1 (s), 130.2 (s), 126.9 (s), 126.5 (s), 124.8 (s), 123.5 (s), 123.1 (s), 40.6 (s), 24.0 (s).



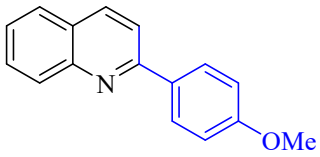
3-(2-bromophenyl)-1-(3-methoxyphenyl)propan-1-one (3ca), Yellow liquid, 84%**, NMR** ($CDCl_3$, δ/ppm): 7.70 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.53 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.43-7.47 (m, 1H), 7.27-7.30 (m, 1H), 7.23 (dd, *J* = 7.4, 6.7 Hz, 1H), 7.04-7.08 (m, 1H), 6.94-7.01 (m, 2H), 3.87 (s, 3H), 3.32 (t, *J* = 7.5 Hz, 2H), 3.14 (t, *J* = 7.7 Hz, 2H), **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$) δ: 201.5 (s), 140.9 (s), 133.5 (s), 132.9 (s), 130.7 (s), 130.2 (s), 128.4 (s), 128.3 (s), 127.7 (s), 127.5 (s), 124.5 (s), 120.8 (s), 111.4 (s), 55.4 (s), 43.3 (s), 30.9 (s).



1-(3-methoxyphenyl)-3-(thiophen-2-yl)propan-1-one (3cf), Yellow liquid, 76%**, NMR** ($CDCl_3$, δ/ppm): **^1H** (500 MHz): 7.54 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.49 (m, 1H), 7.37 (t, *J*= 7.9 Hz, 1H), 7.10-7.13 (m, 2H) 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 3.85 (s, 3H), 3.34 (t, *J* = 7 Hz, 2H), 3.29 (t, *J* = 7 Hz, 2H), **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$) δ: 198.6 (s), 160.0 (s), 144.0 (s), 138.4 (s), 129.6 (s), 126.8 (s), 124.7 (s), 123.4 (s), 120.7 (s), 119.6 (s), 112.2 (s), 55.9 (s), 39.9 (s), 24.3 (s).

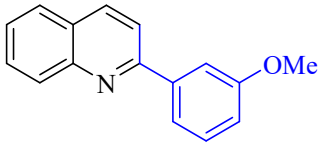


2-phenylquinoline (6aa)[s7, s8] white solid, 93%, **NMR** ($CDCl_3$, δ/ppm): **^1H** (500 MHz): 8.25 – 8.16 (m, 4H), 7.89 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.74 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.5 Hz, 3H), 7.47 (t, J = 7.3 Hz, 1H), **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$) δ: 157.3(s), 148.1 (s), 139.5 (s), 136.9 (s), 129.7 (s), 129.6 (s), 129.4 (s), 128.8 (s), 127.6 (s), 127.4 (s), 127.2 (s), 126.3 (s), 119.0 (s).

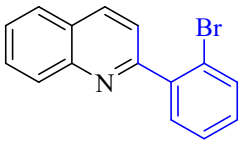


2-(4-methoxyphenyl)quinoline (6ba)[s7, s8] white solid, 89%, **NMR** ($CDCl_3$, δ/ppm): **^1H** (500 MHz): 8.19 – 8.13 (m, 4H), 7.82 (dd, *J* = 15.9, 8.4 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$) δ: 160.8 (s),

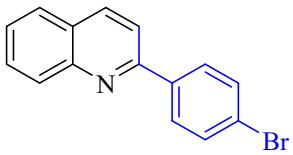
156.9 (s), 148.5 (s), 136.7 (s), 132.2 (s), 129.6 (s), 129.4 (s), 128.9 (s), 127.4 (s), 126.9 (s), 125.9 (s), 118.5 (s), 114.2 (s), 55.4 (s).



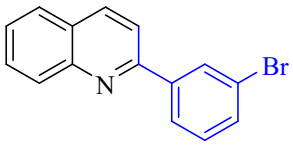
2-(3-methoxyphenyl)quinoline (6ca)[s7, s8] white solid, 87%, **NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 8.20 (t, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.75 – 7.71 (m, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.03 (dd, *J* = 8.1, 2.1 Hz, 1H), 3.93 (s, 3H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 160.0 (s), 157.0 (s), 148.1 (s), 141.0 (s), 136.7 (s), 129.7 (s), 129.6 (s), 129.5 (s), 127.4 (s), 127.1 (s), 126.2 (s), 119.9 (s), 119.0 (s), 115.3 (s), 112.6 (s), 55.3 (s).



2-(2-bromophenyl)quinoline (6da), white solid, 74%, **NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 8.23 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.74 (m, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 166.5 (s), 158.7 (s), 147.9 (s), 141.6 (s), 135.7 (s), 133.3 (s), 131.6 (s), 129.9 (s), 129.7 (s), 127.7 (s), 127.6 (s), 127.1 (s), 126.8 (s), 122.7 (s), 121.9 (s).



2-(4-bromophenyl) quinoline (6ea)[s7] white solid, 90 %, **NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz): 8.26-8.18 (m, 2H), 8.09 – 8.05 (m, 2H), 7.86-7.83 (m, 2H), 7.78-7.74 (m, 1H), 7.69-7.65 (m, 2H), 7.59-7.53 (m, 1H), **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ: 156.0 (s), 148.1 (s), 138.3 (s), 137.0 (s), 132.1 (s), 129.9 (s), 129.5 (s), 129.1 (s), 127.5 (s), 127.2 (s), 126.6 (s), 124.0 (s), 118.5 (s).



2-(3-bromophenyl)quinoline (6fa)[s7] white solid, 88%, **NMR** ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz):

8.25-8.17 (m, 4H), 7.90 – 7.88 (m, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.75-7.72 (m, 1H), 7.55-7.53 (m, 2H), 7.49-7,46 (m, 1H), **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$) δ: 157.3 (s), 148.2 (s), 145.8 (s), 139.6 (s), 138.3 (s), 136.8 (s),133.8 (s), 129.7 (s), 129.3 (s), 128.8 (s), 127.6 (s), 127.4 (s), 127.2 (s), 126.3 (s), 119.0 (s).

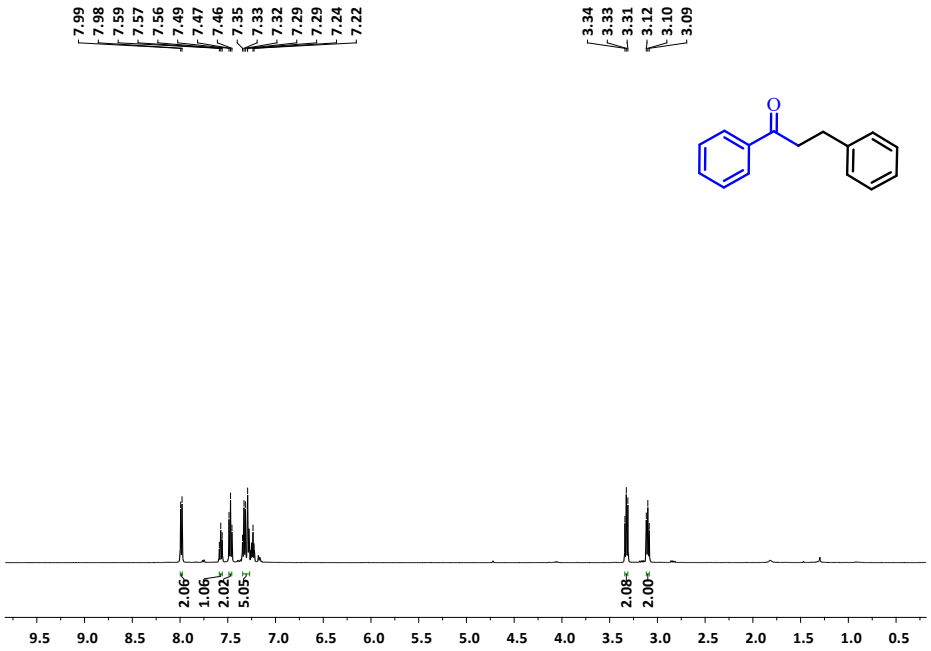


Figure s9. ^{1}H NMR spectrum of **3aa**.

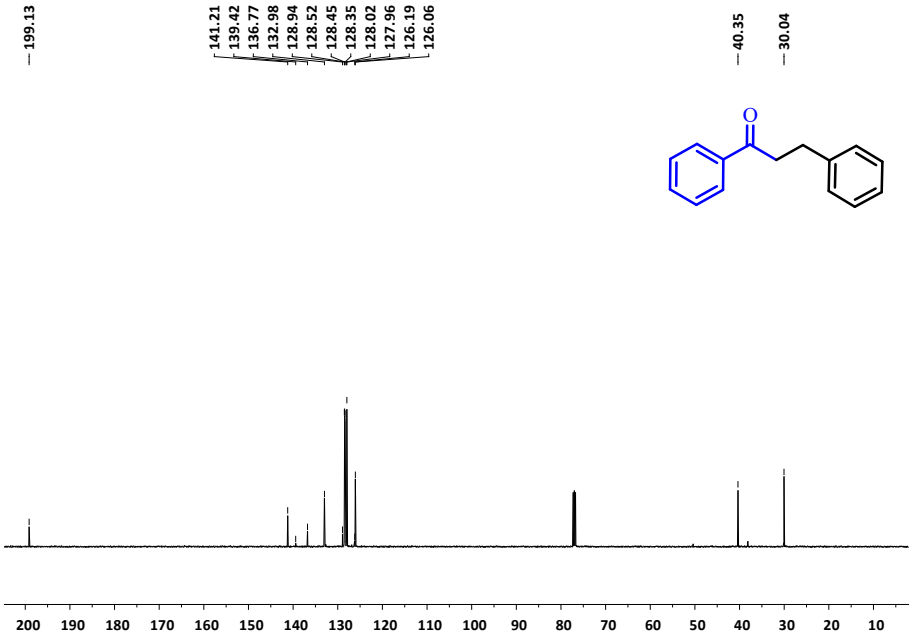


Figure s10. $^{13}C\{^{1}H\}$ NMR spectrum of **3aa.**

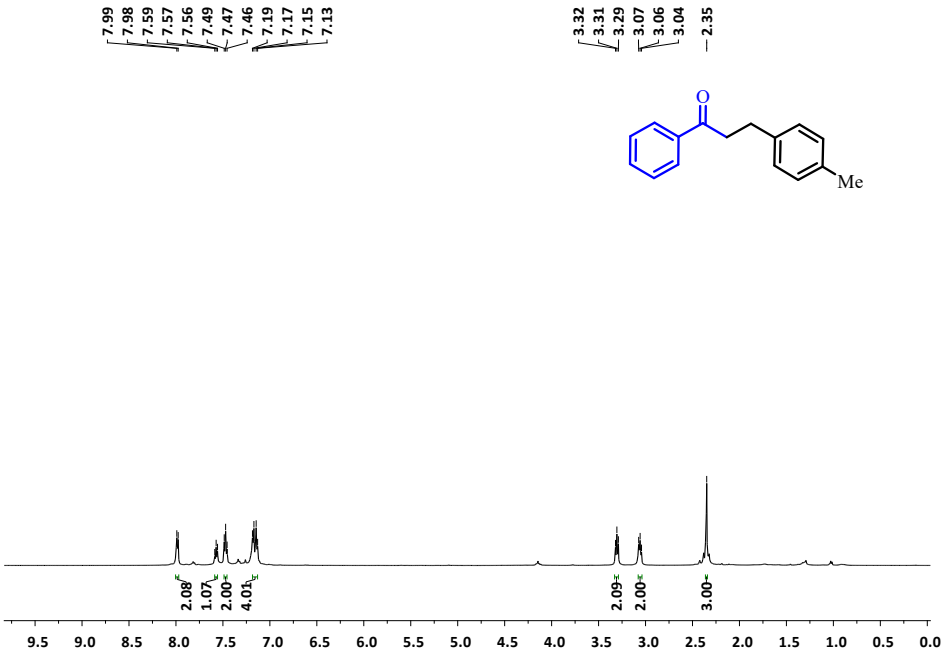


Figure s11. ^{1}H NMR spectrum of **3ab.**

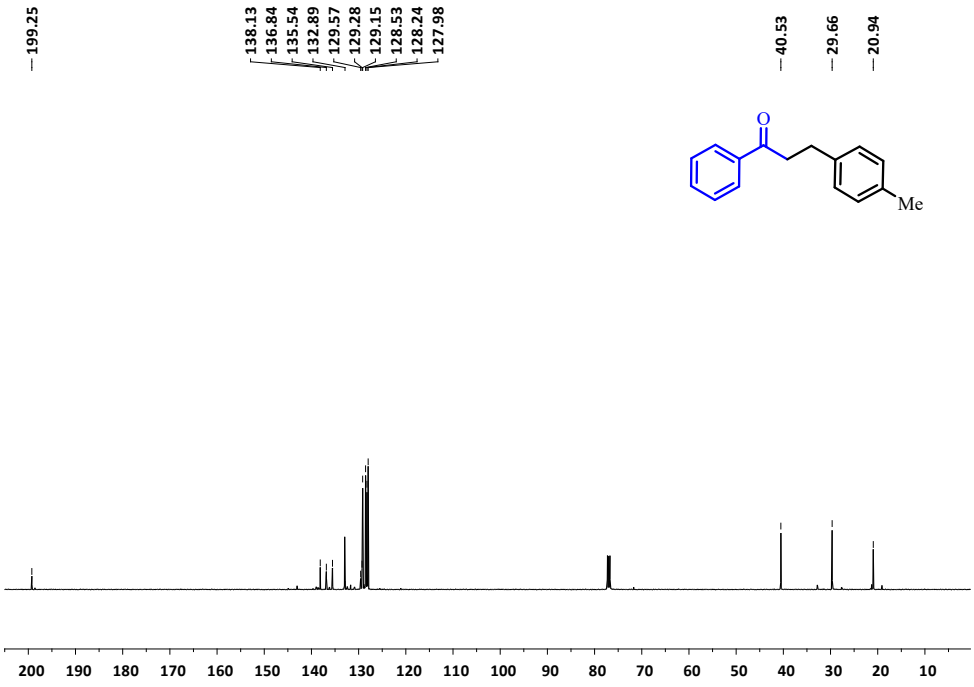


Figure s12. ^{13}C{^{1}H} NMR spectrum of **3ab.**

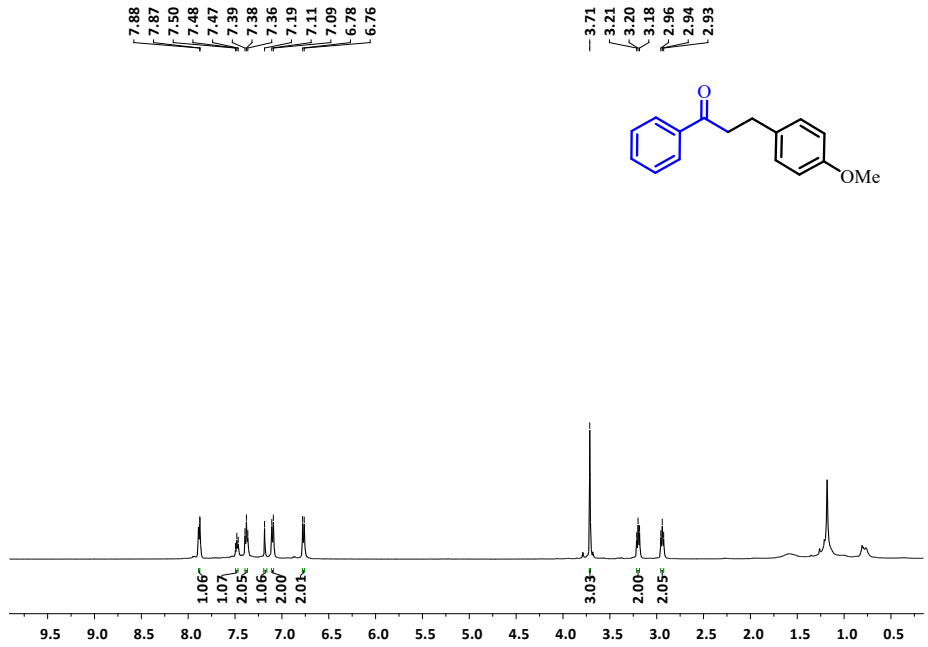


Figure s13. ^{1}H NMR spectrum of **3ac.**

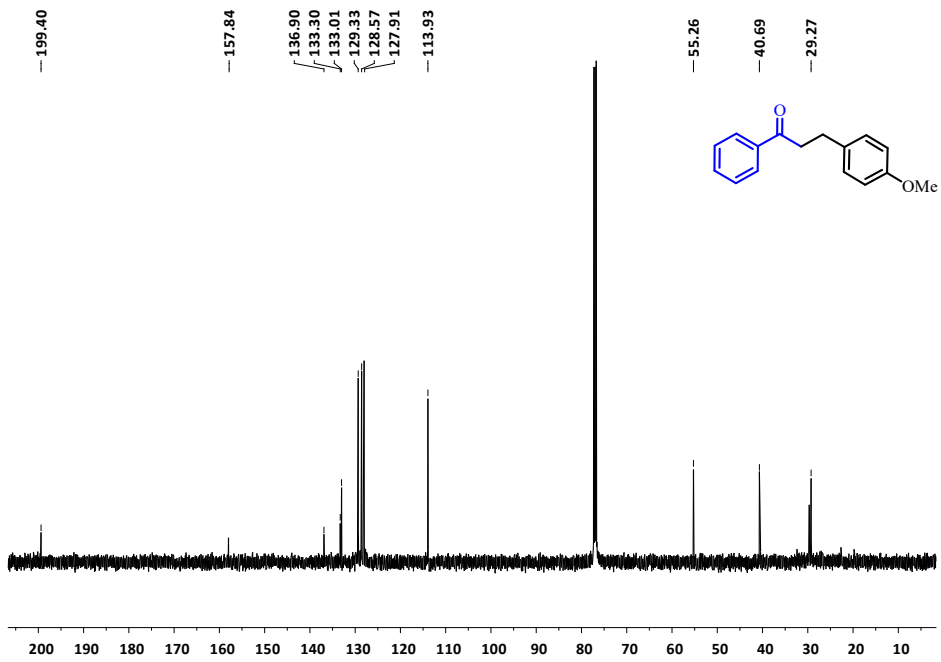


Figure s14. ^{13}C{^{1}H} NMR spectrum of **3ac.**

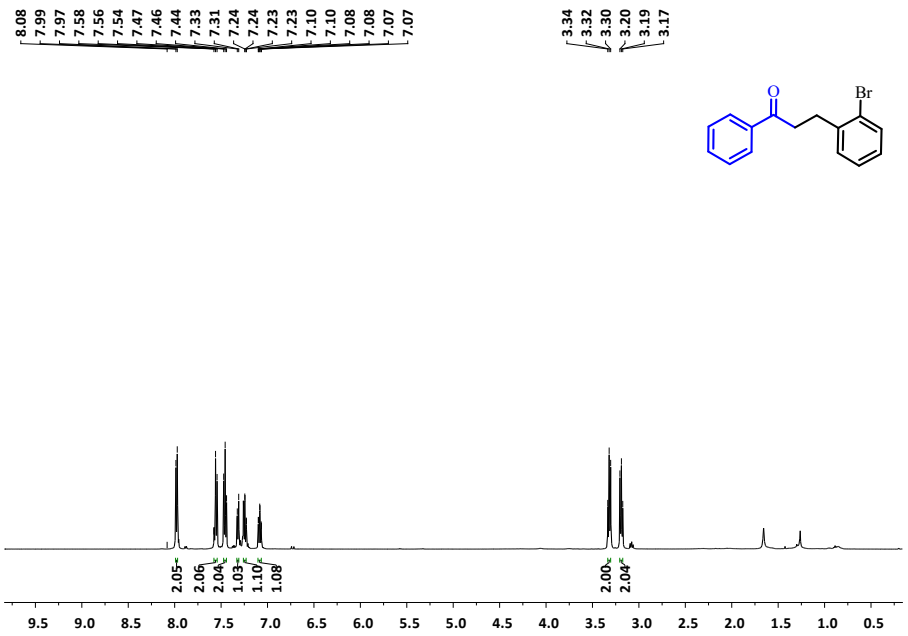


Figure s15. ^{1}H NMR spectrum of **3ad.**

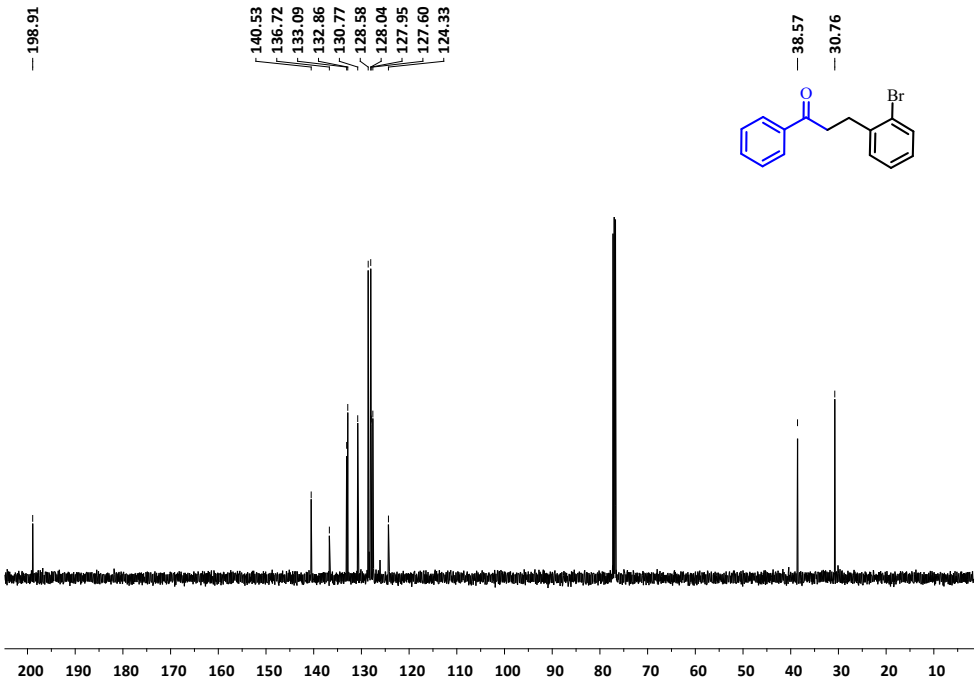


Figure s16. ^{13}C{^{1}H} NMR spectrum of **3ad.**

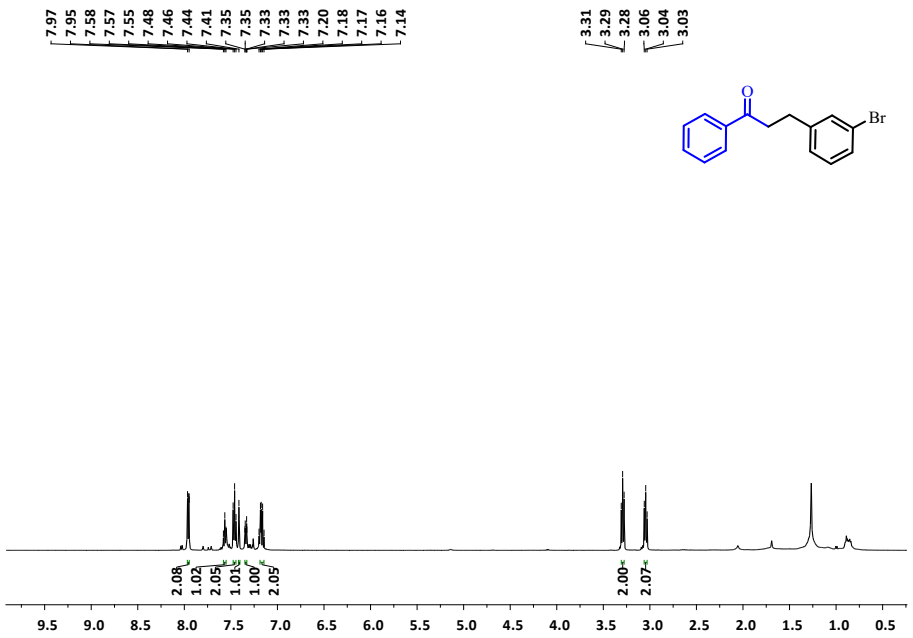


Figure s17. ^{1}H NMR spectrum of **3ae.**

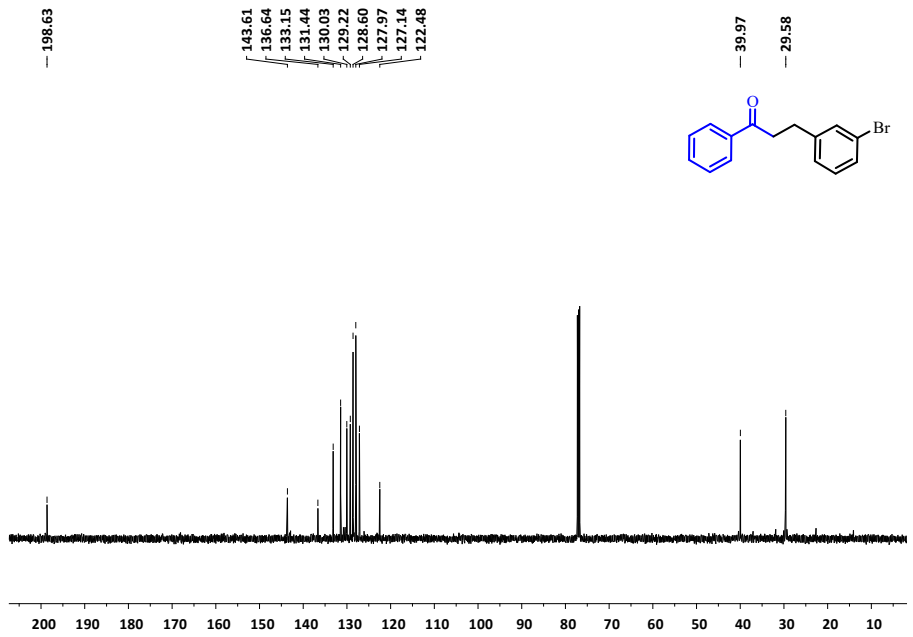


Figure s18. ^{13}C{^{1}H} NMR spectrum of **3ae.**

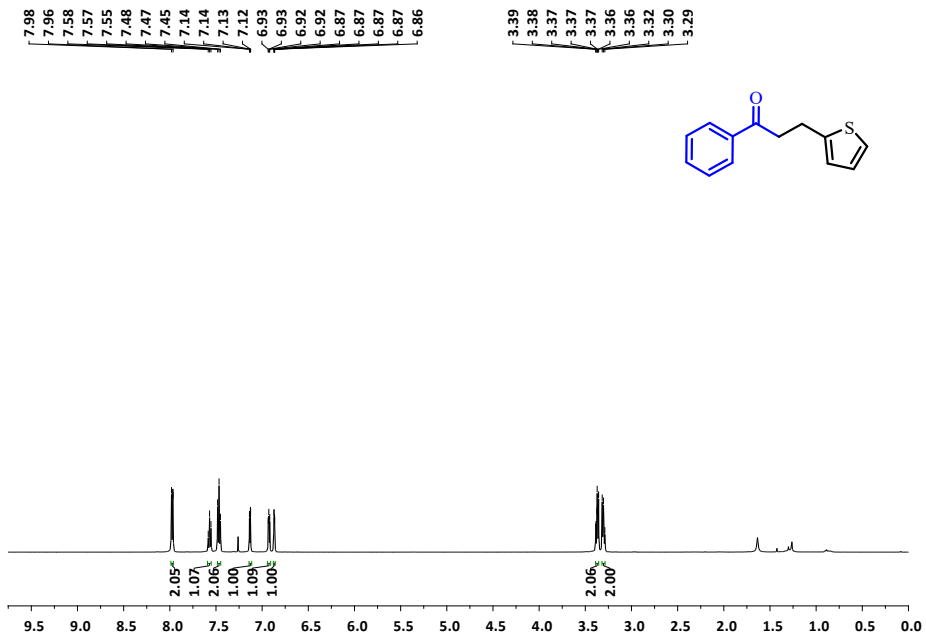


Figure s19. ^{1}H NMR spectrum of **3af.**

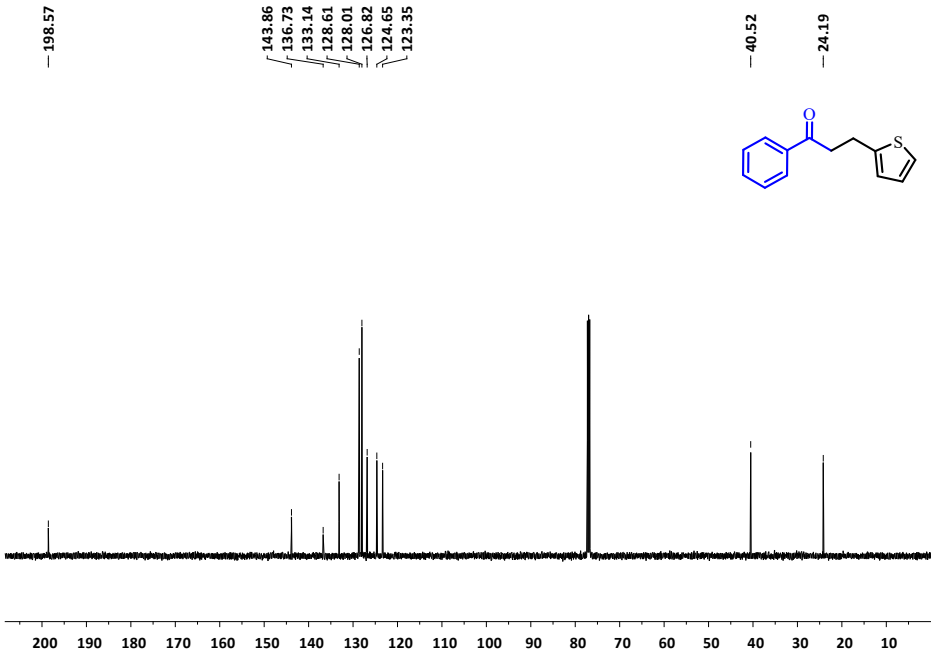


Figure s20. ^{13}C{^{1}H} NMR spectrum of **3af.**

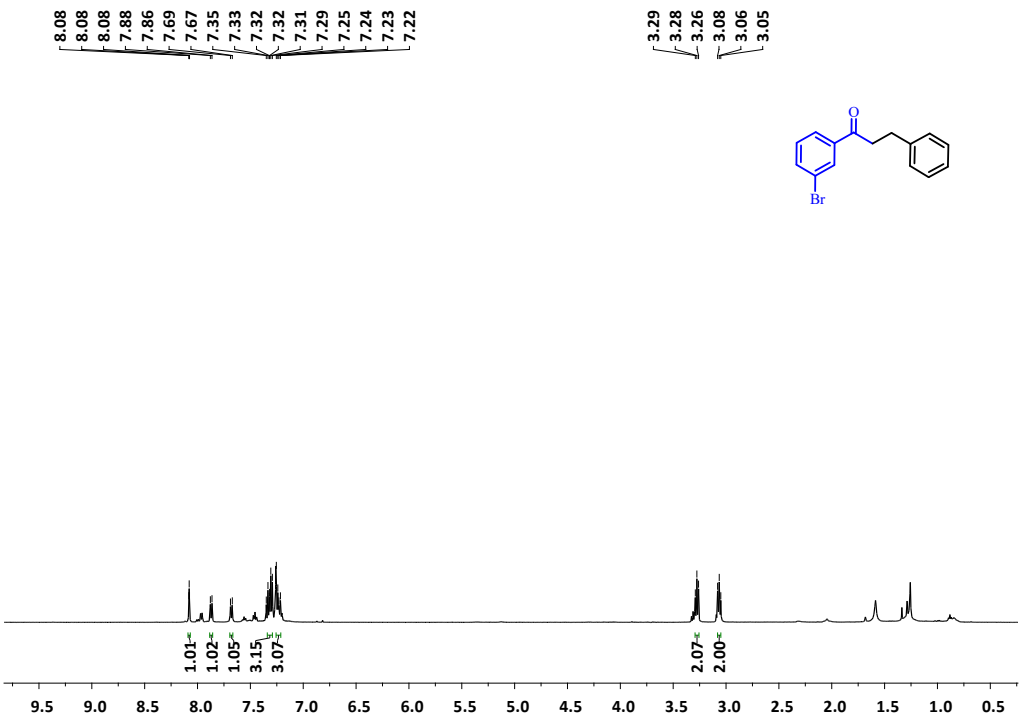


Figure s21. ^{1}H NMR spectrum of **3ba.**

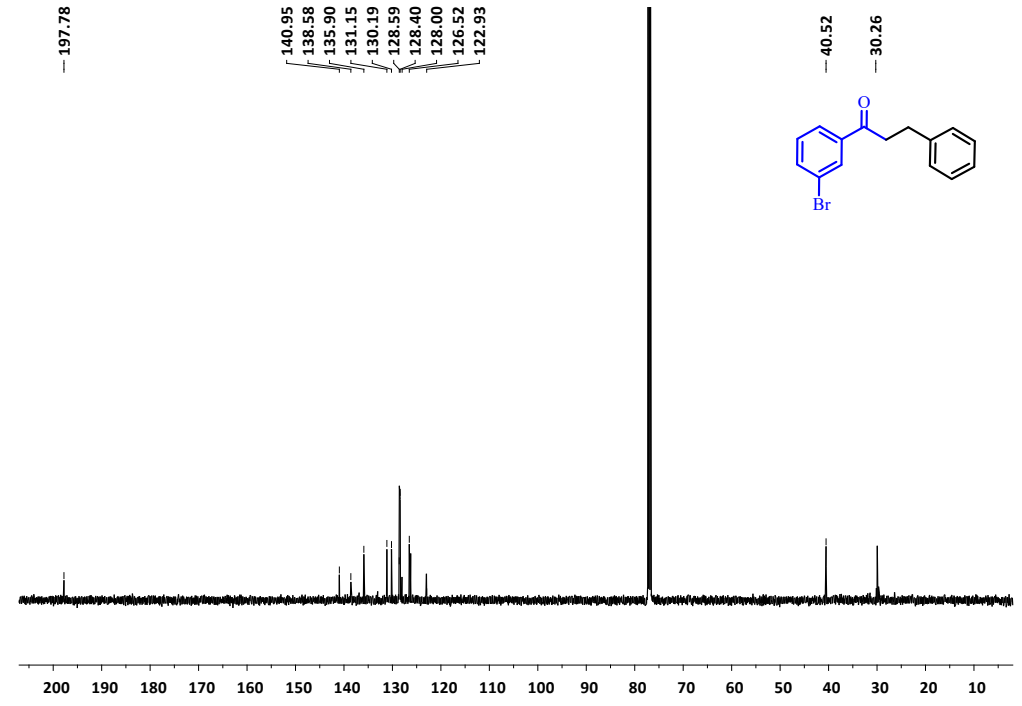


Figure s22. ^{13}C{^{1}H} NMR spectrum of **3ba.**

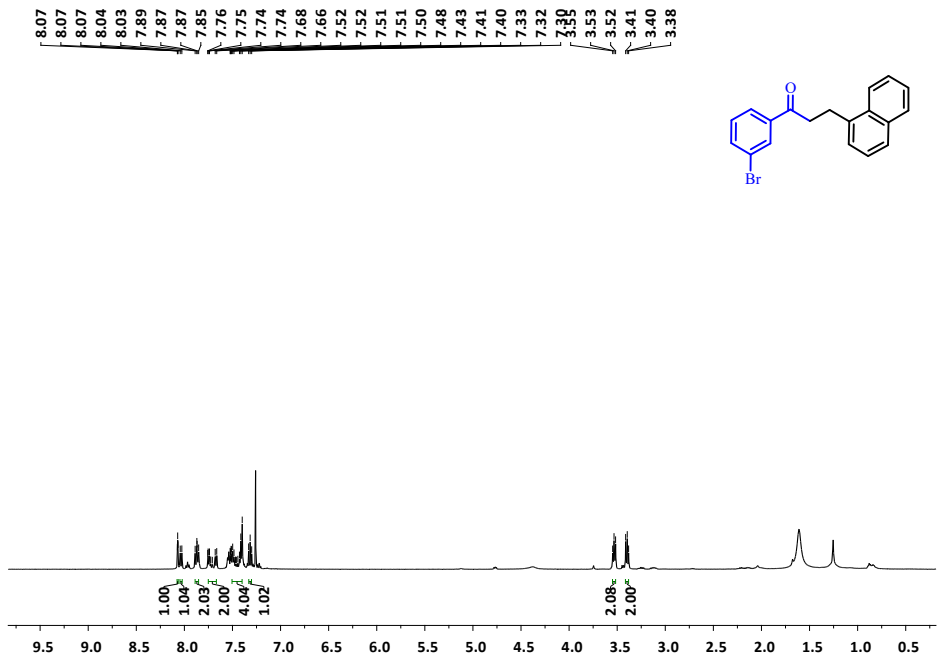


Figure s23. ^{1}H NMR spectrum of **3bg.**

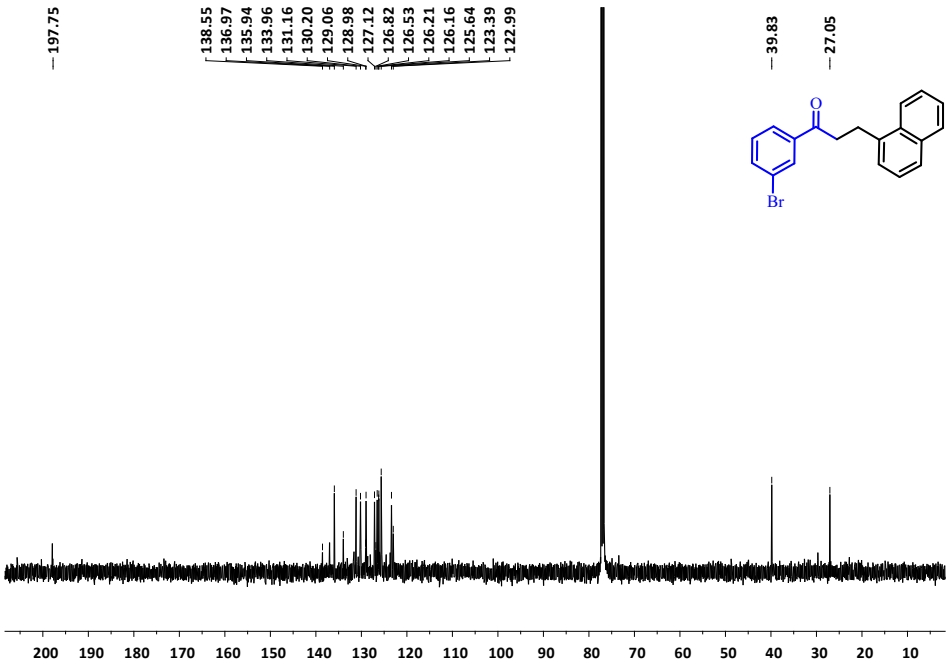


Figure s24. ^{13}C{^{1}H} NMR spectrum of **3bg.**

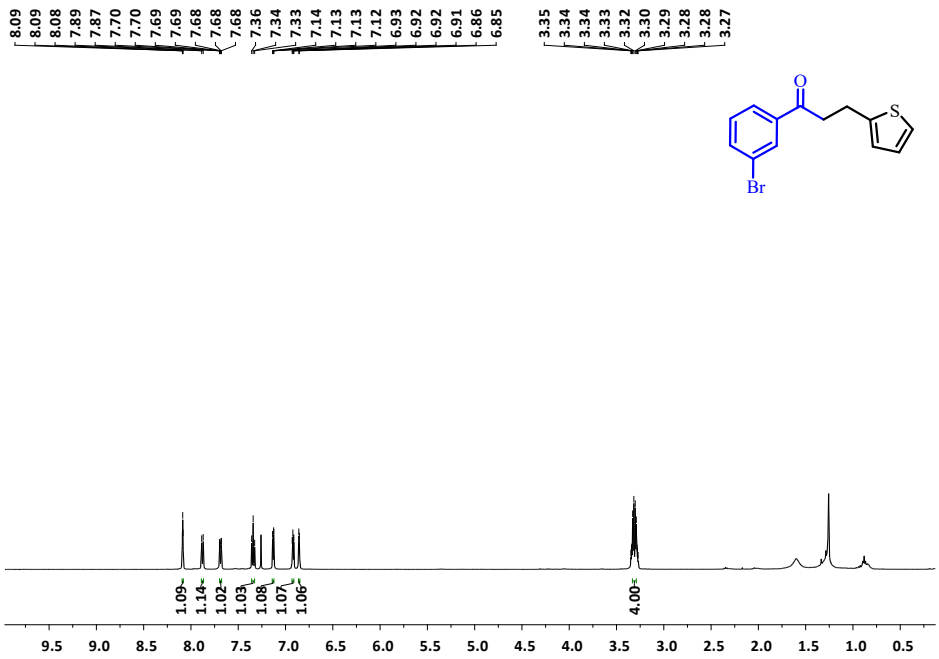


Figure s25. ^{1}H NMR spectrum of **3bf.**

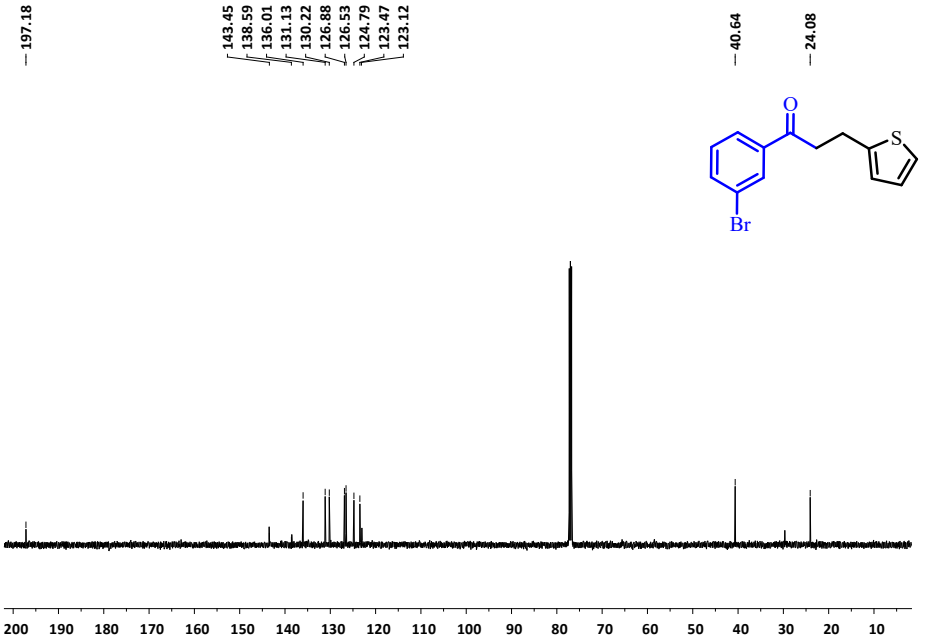


Figure s26. ^{13}C{^{1}H} NMR spectrum of **3bf.**

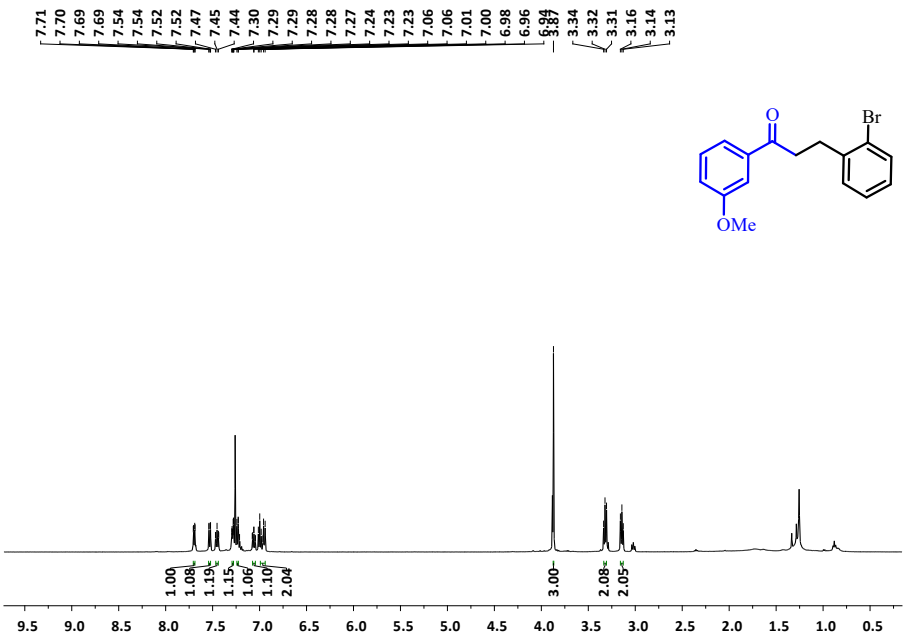


Figure s27. ^{1}H NMR spectrum of 3**ca.**

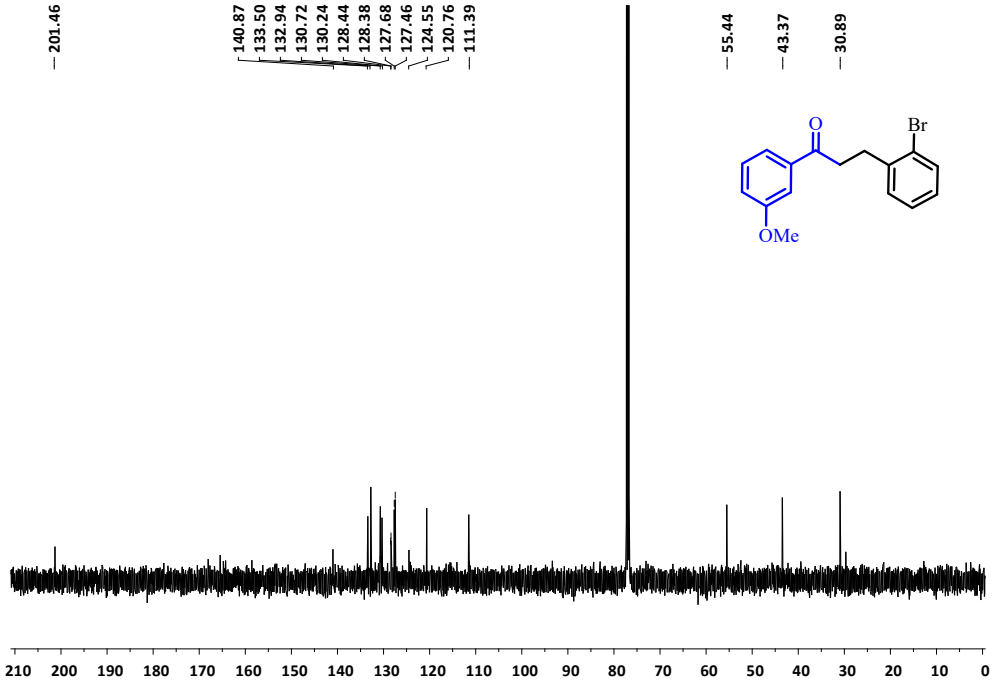


Figure s28. ^{13}C{^{1}H} NMR spectrum of **3ca.**

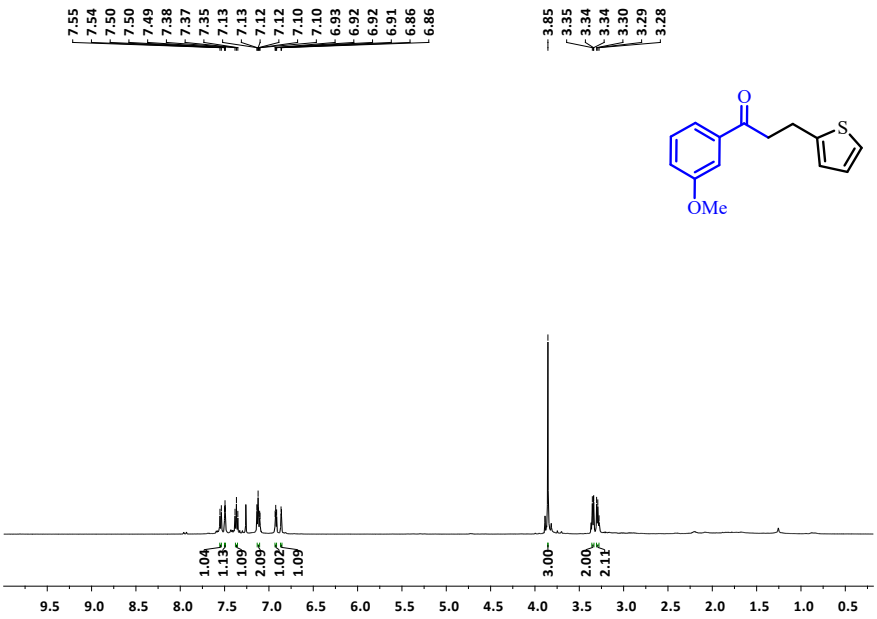


Figure s29. ^{1}H NMR spectrum of **3cf.**

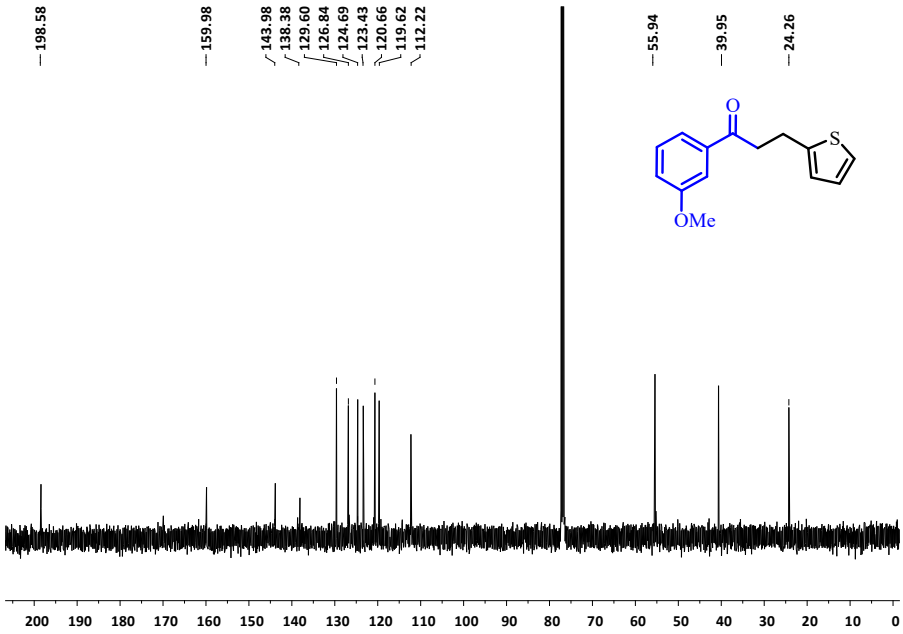


Figure s30. ^{13}C{^{1}H} NMR spectrum of **3cf.**

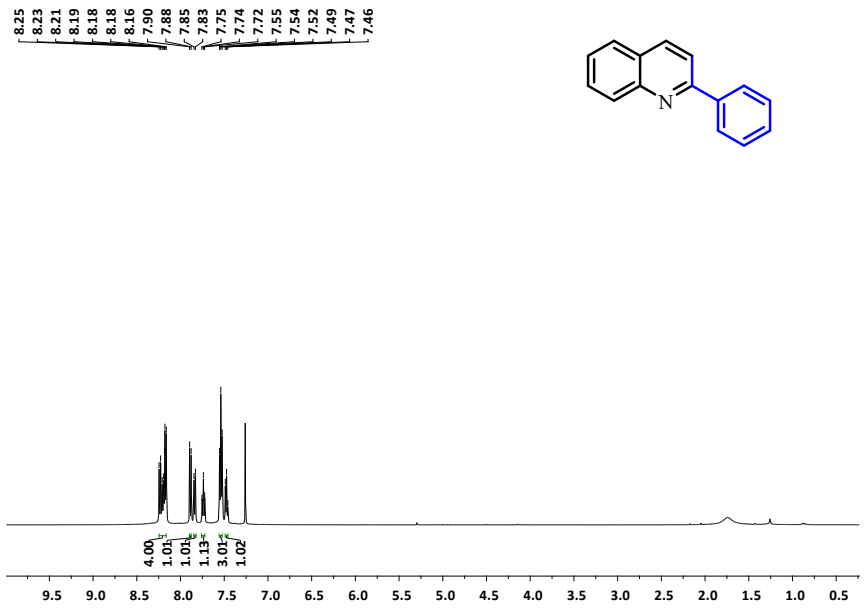


Figure s31. ^{1}H NMR spectrum of **6aa.**

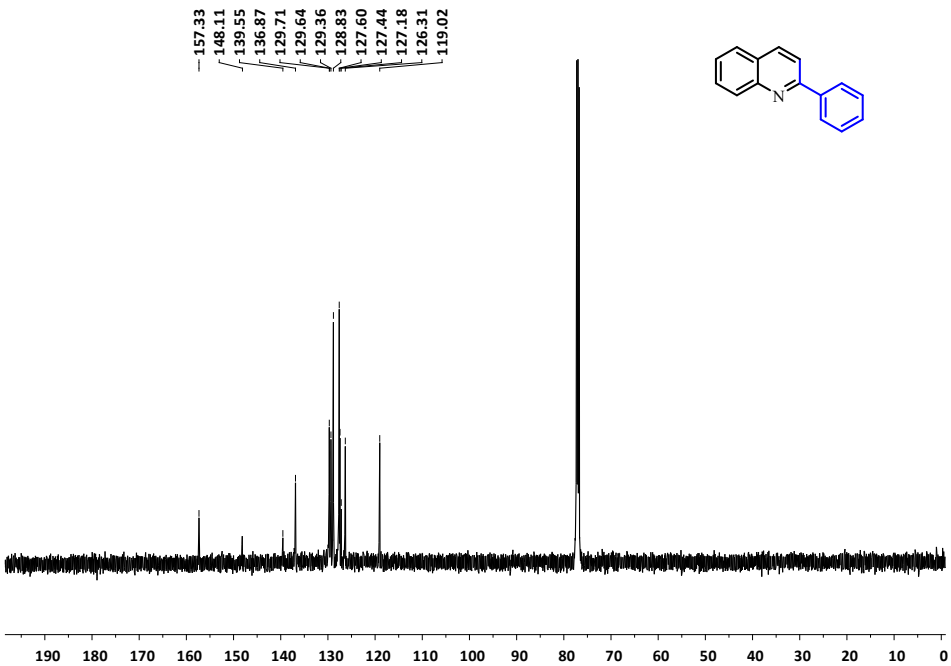


Figure s32. ^{13}C{^{1}H} NMR spectrum of **6aa.**

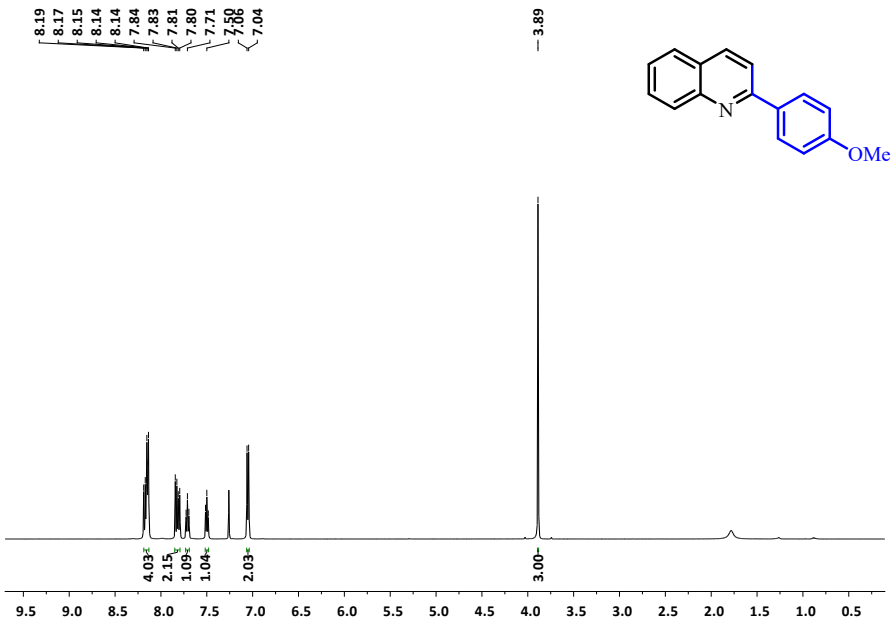


Figure s33. ^{1}H NMR spectrum of **6ba.**

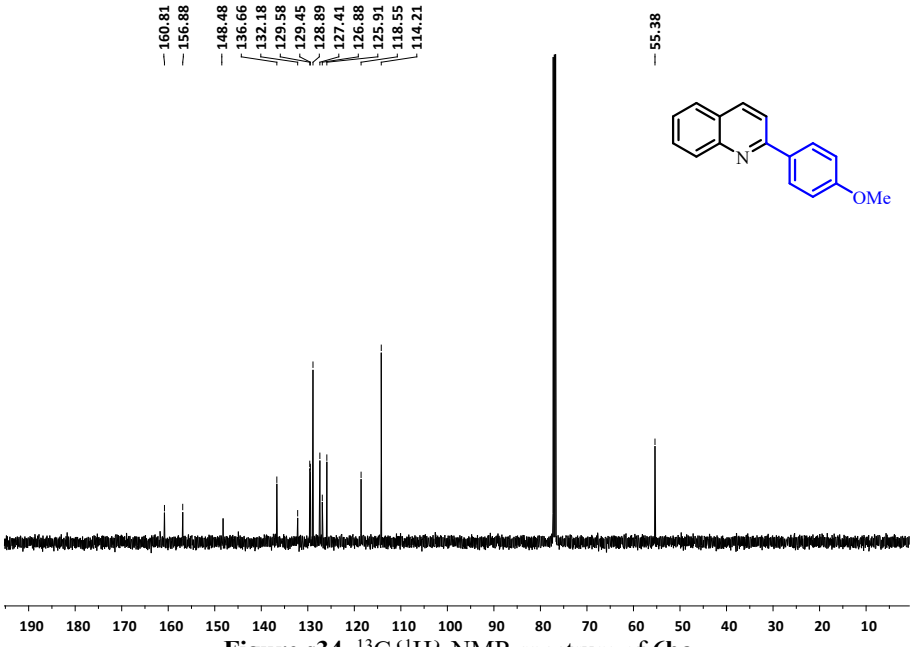


Figure s34. ^{13}C{^{1}H} NMR spectrum of **6ba.**

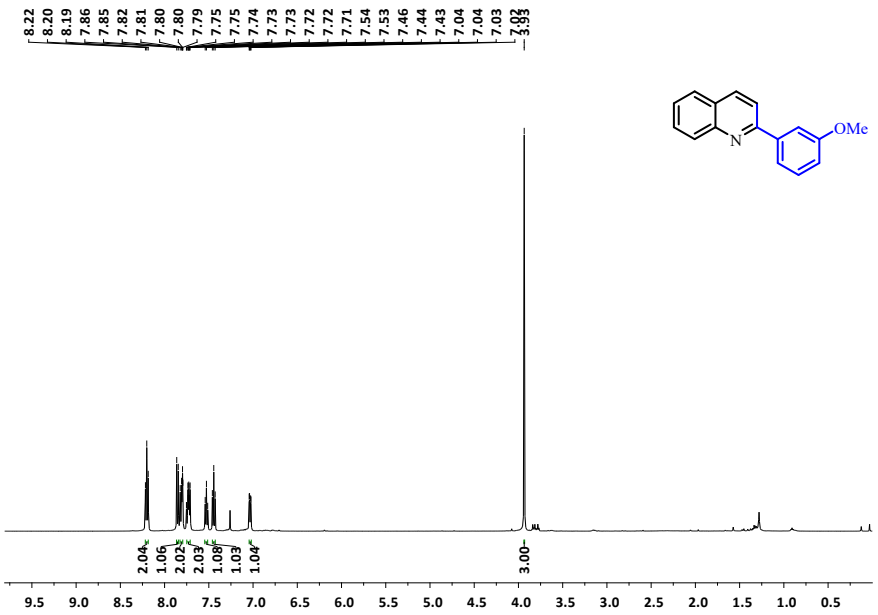


Figure s35. ^{1}H NMR spectrum of **6ca.**

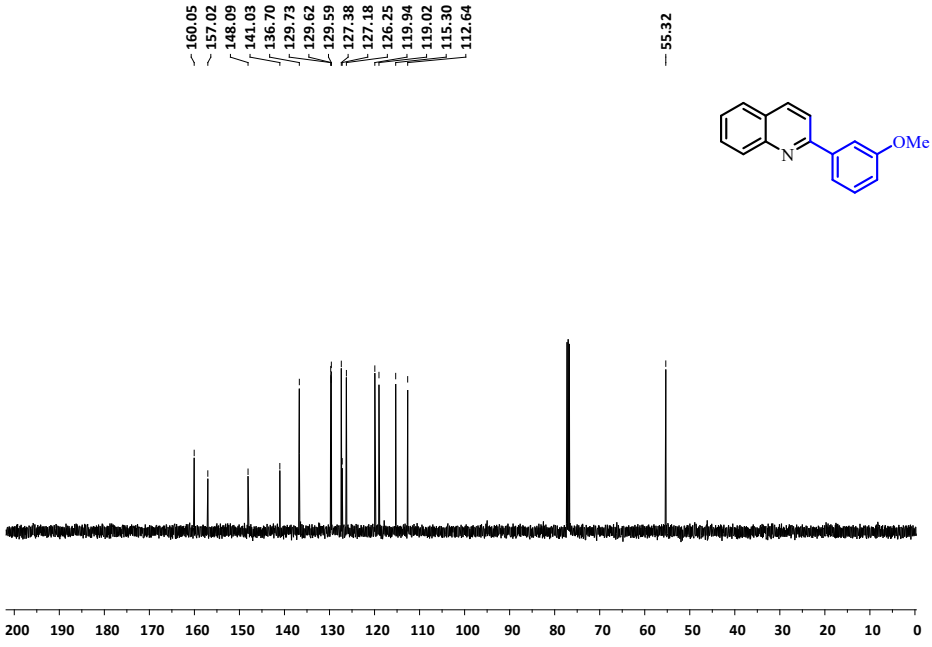


Figure s36. ^{13}C{^{1}H} NMR spectrum of **6ca.**

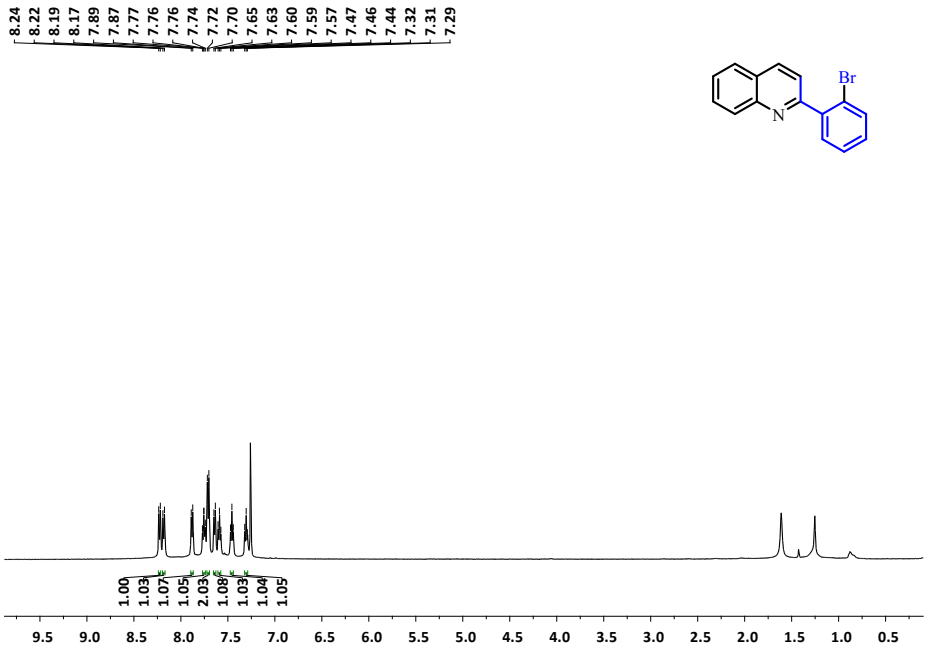


Figure s37. ^{1}H NMR spectrum of **6da.**

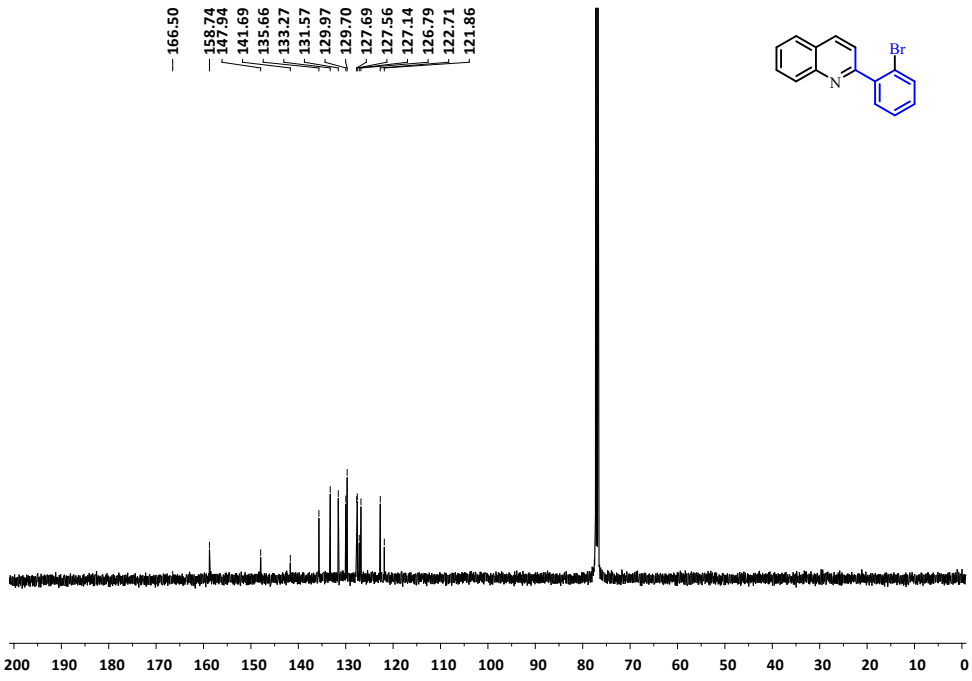


Figure s38. ^{13}C{^{1}H} NMR spectrum of **6da.**

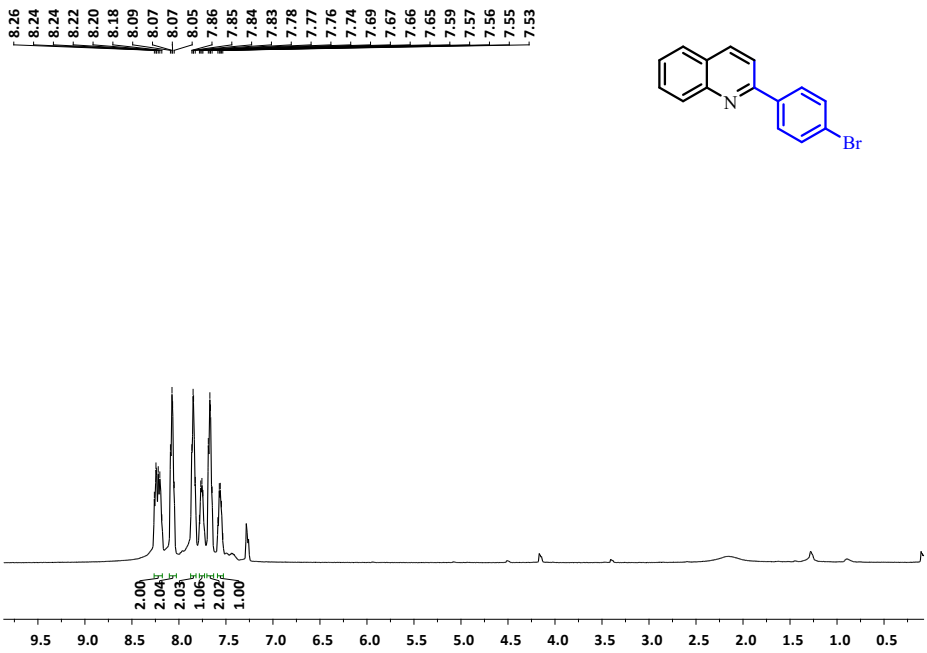


Figure s39. ^{1}H NMR spectrum of **6ea.**

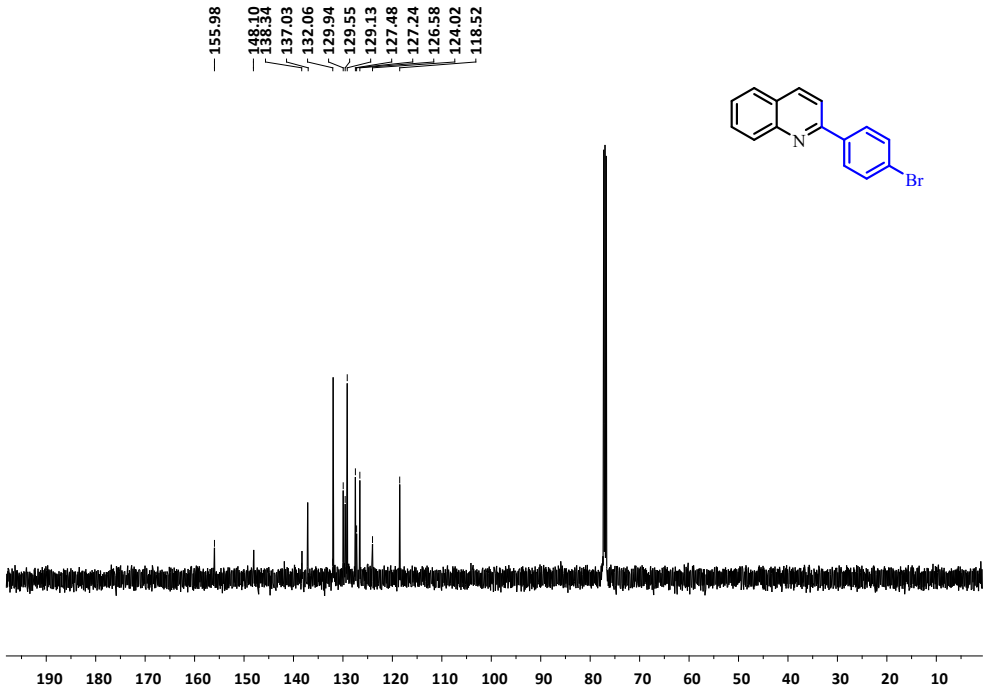


Figure s40. ^{13}C{^{1}H} NMR spectrum of **6ea.**

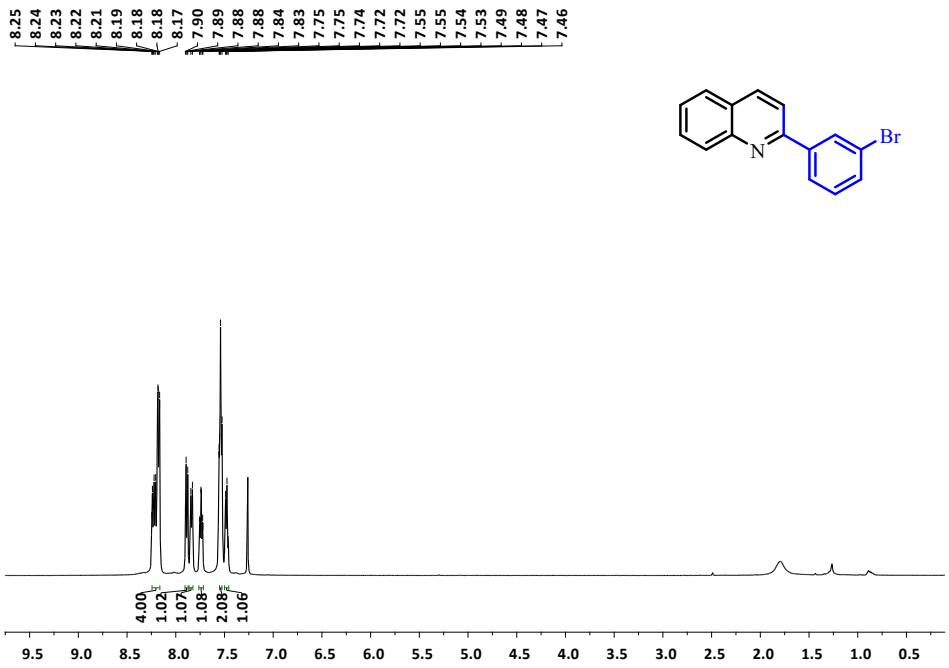


Figure s41. ^{1}H NMR spectrum of **6fa.**

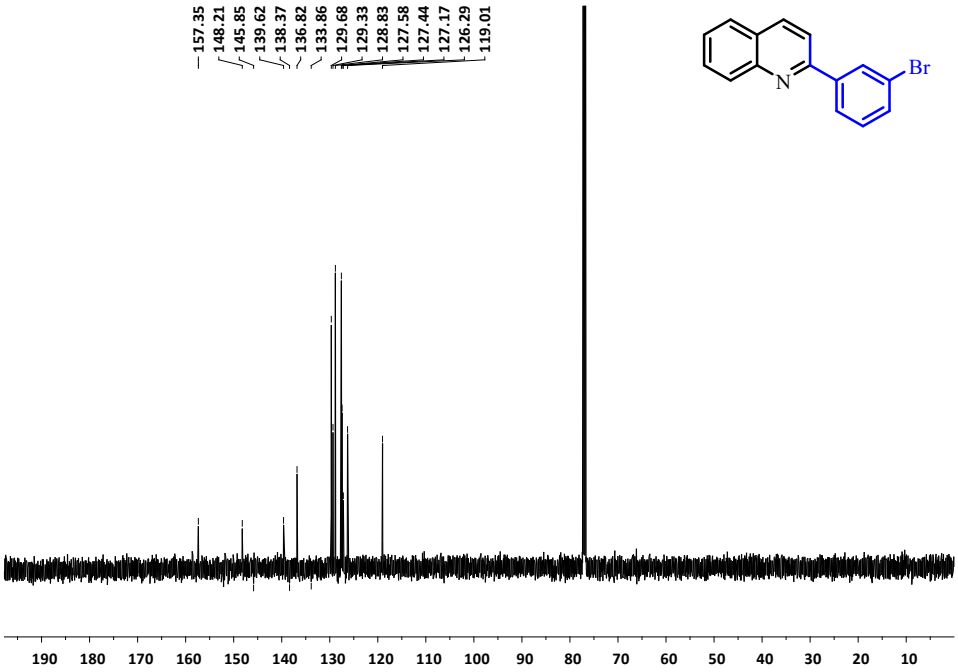


Figure s42. ^{13}C{^{1}H} NMR spectrum of **6fa.**

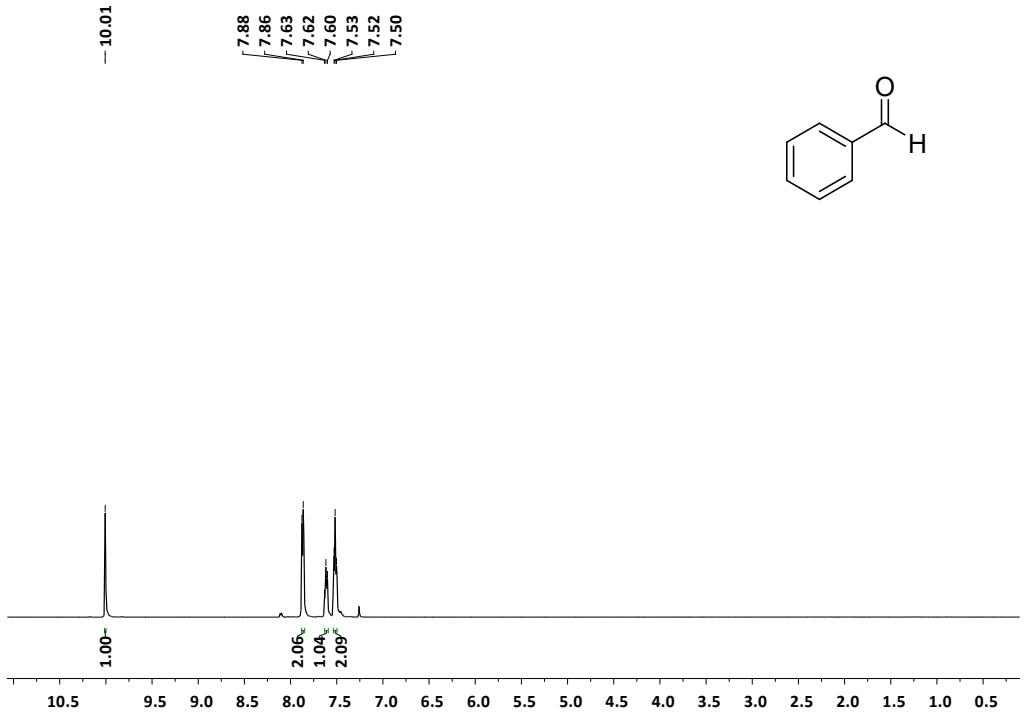


Figure s43. ^{1}H NMR spectrum of **2a'**.

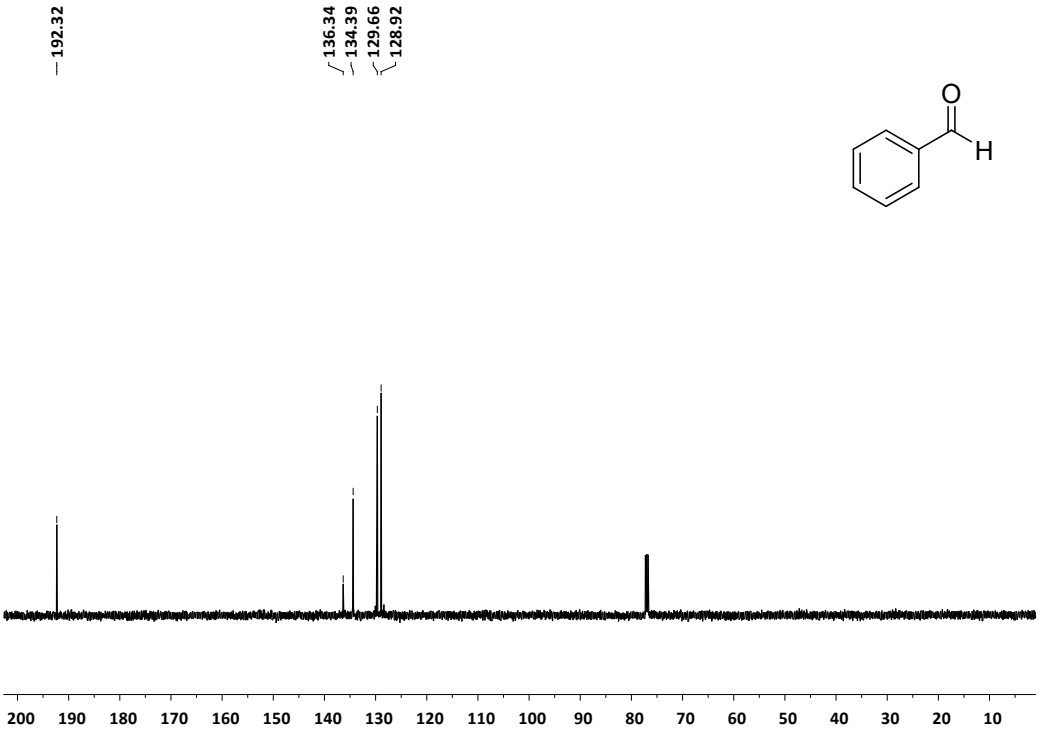


Figure s44. ^{13}C{^{1}H} NMR spectrum of **2a'.**

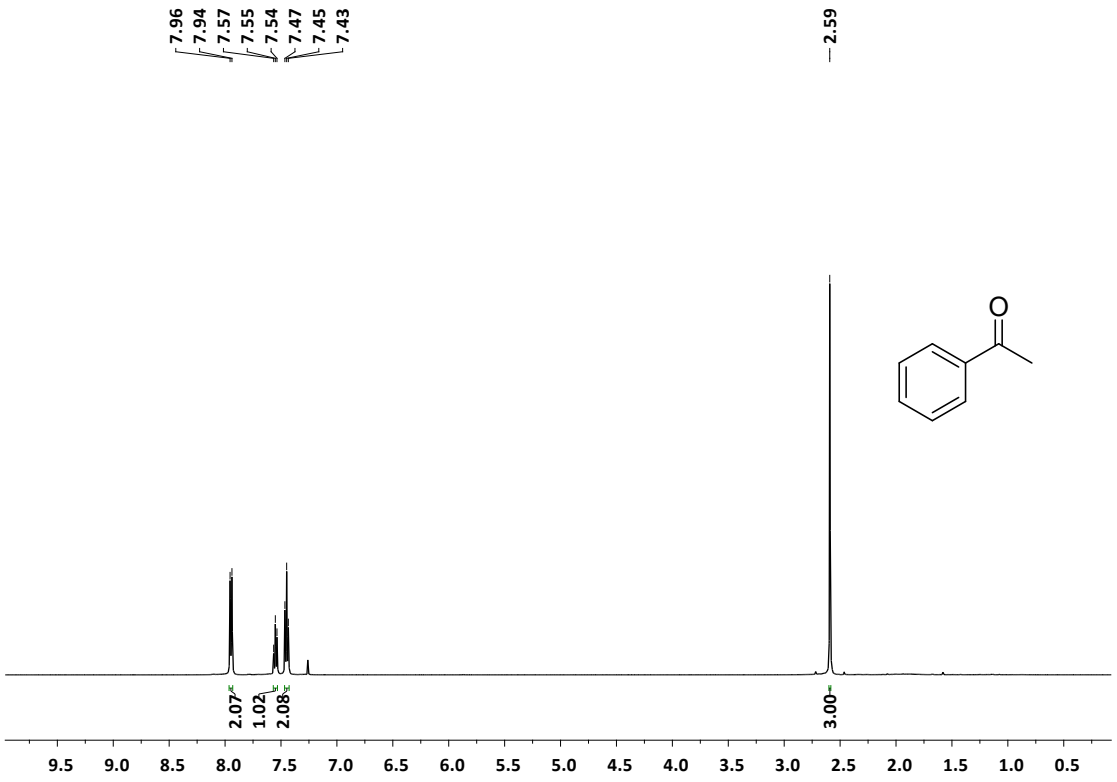


Figure s45. ^{1}H NMR spectrum of **1a.**

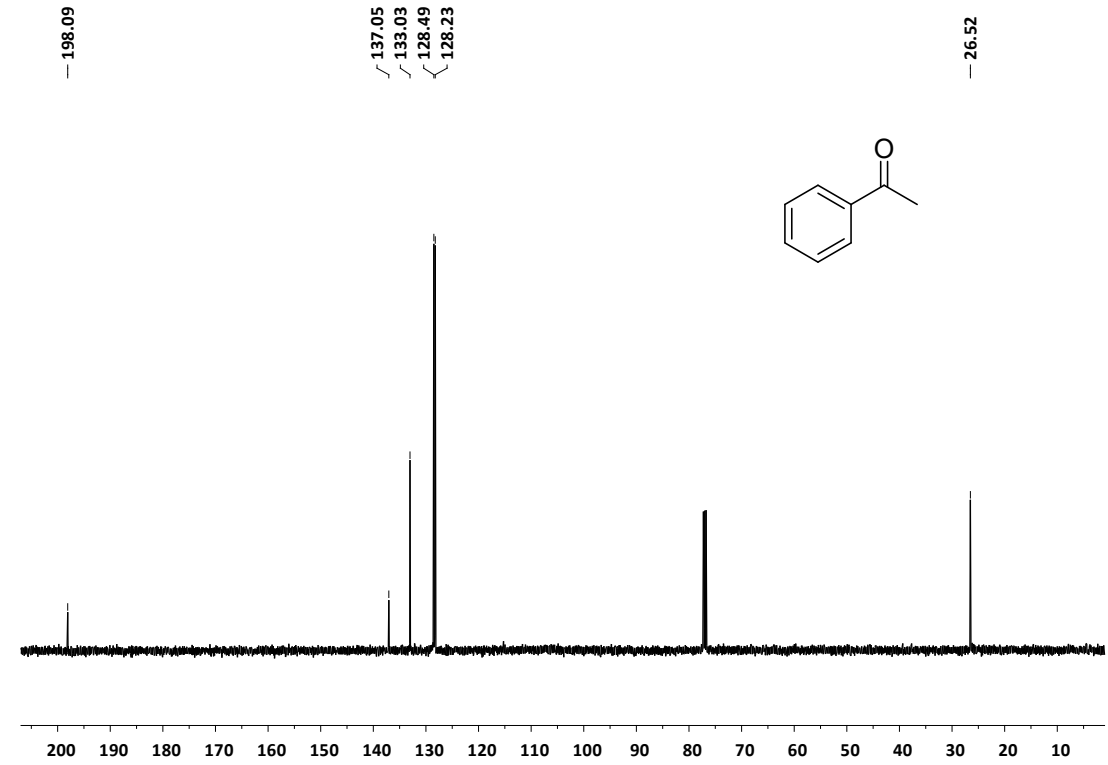


Figure s46. ^{13}C{^{1}H} NMR spectrum of **1a.**

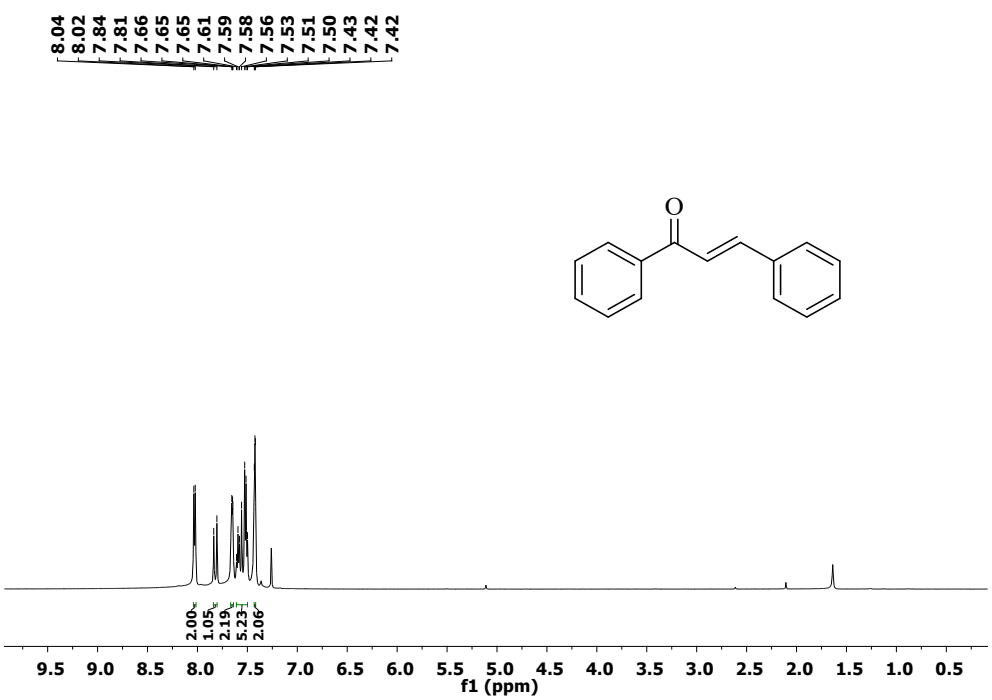


Figure s47. ^{1}H NMR spectrum of **3aa'.**

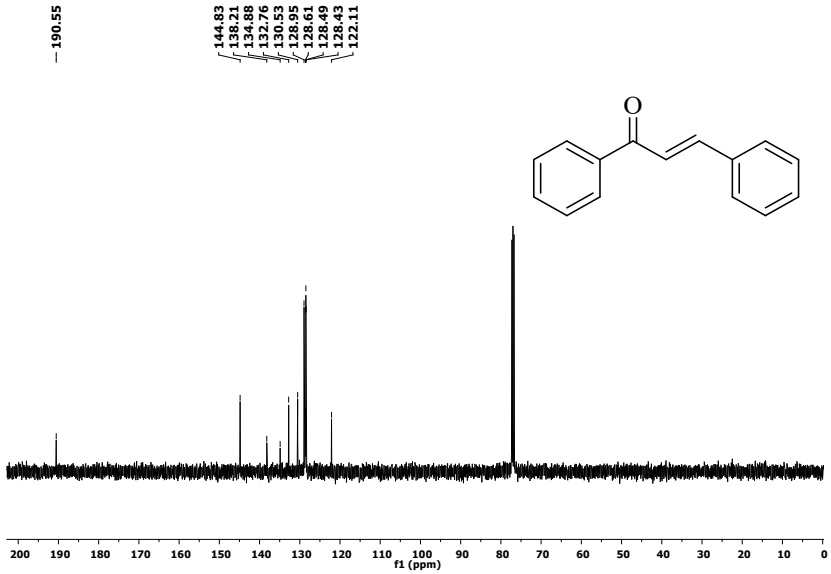


Figure s48. ^{13}C{^{1}H} NMR spectrum of **3aa'.**

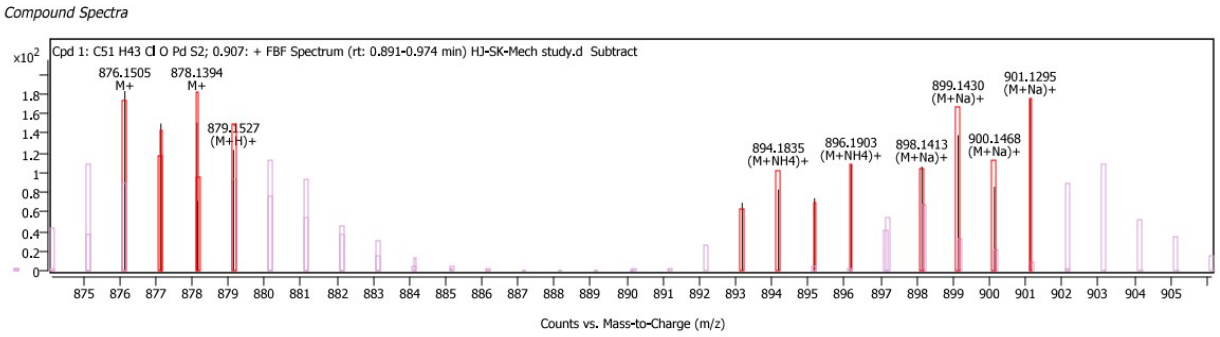


Figure s49. HRMS spectrum of intermediate **A** showing HRMS (ESI) m/z cacld for $C_{51}H_{43}ClOPdS_2$ $[M]^+$ 876.1479, found 876.1505.

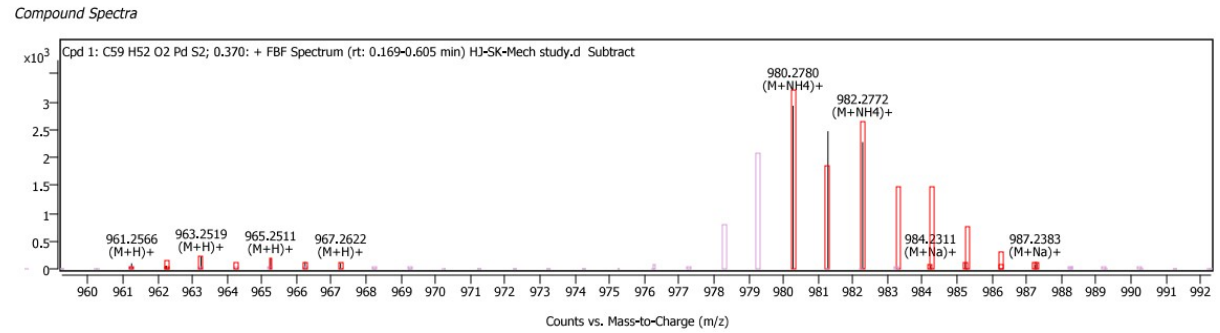


Figure s50. HRMS spectrum of intermediate **B** showing HRMS (ESI) m/z cacld for $C_{59}H_{52}O_2PdS_2$ $[M+H]^+$ 963.2522, found 963.2519.

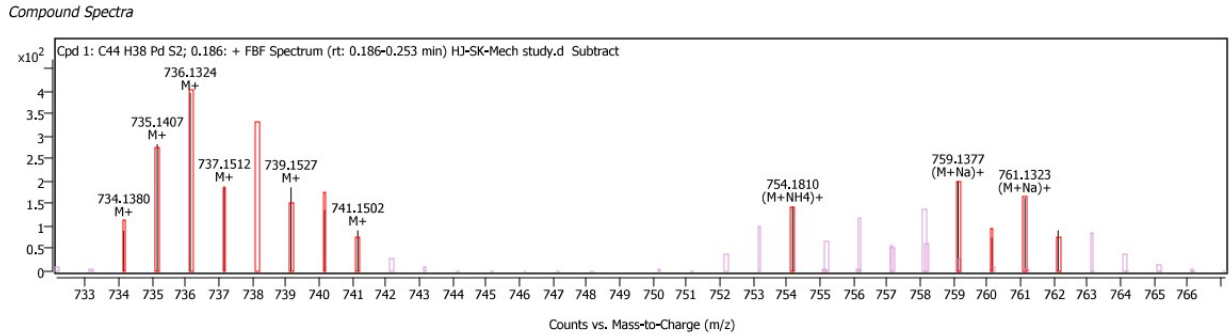


Figure s51. HRMS spectrum of intermediate **C** showing HRMS (ESI) m/z cacld for $C_{59}H_{52}O_2PdS_2$ $[M+Na]^+$ 759.1347, found 759.1377.

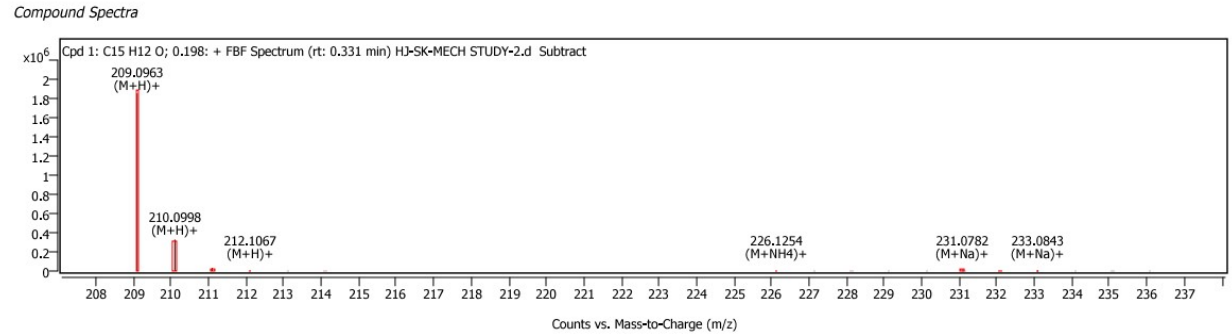


Figure s52. HRMS spectrum of intermediate **3aa'** showing HRMS (ESI) m/z cacld for $C_{15}H_{12}O$ $[M+H]^+$ 209.0966, found 209.0963.

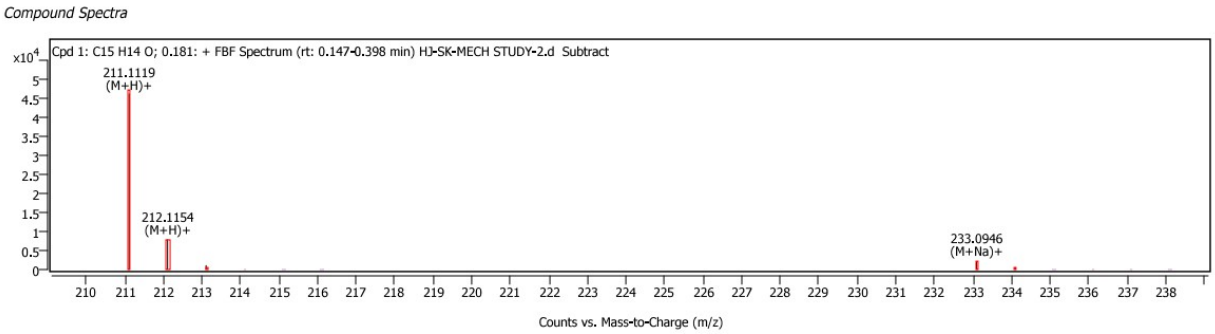


Figure s53. HRMS spectrum of product **3aa** showing HRMS (ESI) m/z cacld for $C_{15}H_{14}O$ $[M+H]^+$ 211.1123, found 211.1119.

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