Electronic Supporting Information

Synthesis and catalytic activity of tetradentate β-diketiminato rare-earth metal monoalkyl complexes in tandem Oppenauer oxidation and cross-aldol condensation

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Table S1. Crystallographic data of complexes 1a-1d

	1a (Y)	**1b (Gd)**	**1c (Yb)**	**1d (Lu)**
CCDC	2296626	2296627	2296628	2296629
Empirical formula	$C_{36}H_{52}N_3OSiY$	$C_{36}H_{52}N_3OSiGd$	$C_{36}H_{52}N_3OSiYb$	$C_{36}H_{52}N_3OSiLu$
Formula weight	659.80	728.14	743.93	745.86
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.0699(9)	12.8562(12)	11.0453(14)	11.017(7)
b (Å)	11.5878(9)	20.653(2)	11.5867(15)	11.593(7)
c (Å)	14.7859(12)	14.1698(13)	14.7165(19)	14.734(9)
α (°)	87.2450(10)	90	87.403(2)	87.665(6)
β (°)	81.8270(10)	93.4440(10)	81.877(2)	82.008(15)
γ (°)	79.6000(10)	90	79.435(2)	79.438(8)
V (Å^3)	1846.1(3)	3755.6(6)	1832.5(4)	1832(2)
Z	2	4	2	2
D_{calcd} (mg m^{-3})	1.187	1.288	1.348	1.352
μ (mm^{-1})	1.641	1.826	2.614	2.757
F (000)	700	1500	762	764
θ range (°)	1.392 to 27.580	1.745 to 27.703	1.398 to 27.490	1.396 to 27.502
Reflections collected	21694	41986	21106	21469
Data/restraints/parameters	8420/30/388	8723/6/388	8264/12/388	8291/48/376
Goodness-of-fit on F^2	0.960	1.010	1.016	1.051
R(int)	0.0515	0.0514	0.0393	0.0309
R_1,wR_2 ($I>2\sigma(I)$)	0.0512, 0.1100	0.0389, 0.0795	0.0345, 0.0803	0.0334, 0.0777
Largest diff peak/hole (e Å^{-3})	0.428 and -0.309	0.605 and -0.668	1.050 and -0.746	1.317 and -0.757

Table S2. Crystallographic data of complexes 2a-2d

	2a (Y)	**2b (Gd)**	**2c (Yb)**	**2d (Lu)**
CCDC	2296630	2296631	2296632	2296633
Empirical formula	$C_{102}H_{150}N_9O_3Si_3Y_3$	$C_{68}H_{100}N_6O_2Si_2$ Gd_2	$C_{68}H_{100}N_6O_2Si_2Yb_2$	$C_{34}H_{50}N_3OSiLu$
Formula weight	1901.30	1404.21	1435.79	719.83
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pī*	*C2/c*	*C2/c*	*C2/c*
a (Å)	14.531(4)	35.524(3)	35.46(5)	35.237(9)
b (Å)	20.424(5)	22.8423(16)	23.07(3)	22.966(6)
c (Å)	20.587(5)	23.6243(16)	23.60(3)	23.494(6)
α (°)	117.206(3)	90	90	90
β (°)	92.833(3)	129.8560(10)	129.797(13)	129.875(3)
γ (°)	100.856(3)	90	90	90
V (Å^3)	5272(2)	14716(18)	14828(33)	14592(6)
Z	2	8	8	16
D_{calcd} (mg m^{-3})	1.198	1.268	1.286	1.311
μ (mm^{-1})	1.721	1.862	2.581	2.766
F (000)	2016	5776	5872	5888
θ range (°)	1.154 to 25.499	1.163 to 27.528	1.157 to 27.730	1.163 to 27.613
Reflections collected	52223	86252	81118	81424
Data/restraints/paramet	19585/84/1099	16880/142/781	16820/169/781	16616/286/766
Goodness-of-fit on F^2	0.950	1.013	1.029	0.991
R(int)	0.1448	0.0630	0.0663	0.1559
R_1,wR_2 (I >2σ(I))	0.0620, 0.0929	0.0394, 0.0774	0.0435, 0.1007	0.0761, 0.1948
Largest diff peak/hole (e Å^{-3})	0.453 and -0.656	0.700 and -0.826	0.809 and -0.458	3.391 and -1.735

Molecular structures of complexes 1b-2d.

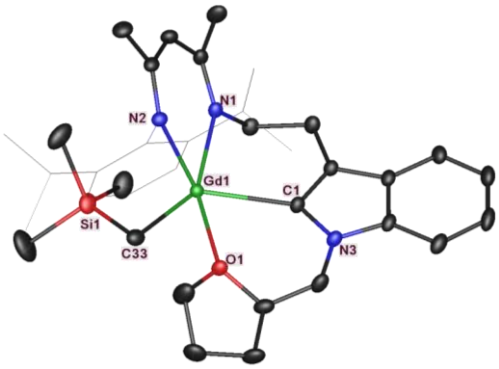


Fig S1. Molecular structure of **1b**. All the hydrogen atoms are omitted and 2,6-diisopropyl phenyl group was depicted in wireframe style for clarity. Selected bond lengths (Å) and angles (°): Gd(1)−N(1) 2.354(3), Gd(1)−N(2) 2.335(3), Gd(1)−C(1) 2.467(4), Gd(1)−C(33) 2.411(4), Gd(1)−O(1) 2.414(3), C(33)−Gd(1)−N(2) 117.77(14), C(33)−Gd(1)−C(1) 115.60(16).

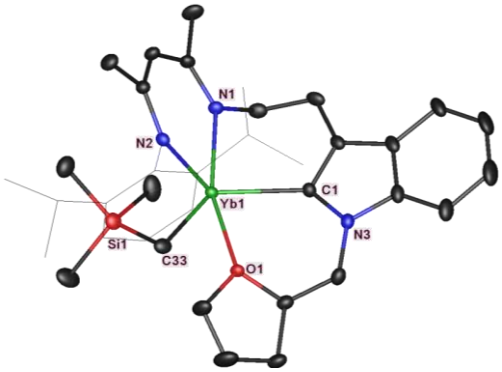


Fig S2. Molecular structure of **1c**. All the hydrogen atoms are omitted and 2,6-diisopropyl phenyl group was depicted in wireframe style for clarity. Selected bond lengths (Å) and angles (°): Yb(1)−N(1) 2.318(2), Yb(1)−N(2) 2.279(3), Yb(1)−C(1) 2.362(4), Yb(1)−C(33) 2.325(4), Yb(1)−O(1) 2.318(2), C(33)−Yb(1)−N(2) 118.55(15), C(33)−Yb(1)−C(1) 116.82(16).

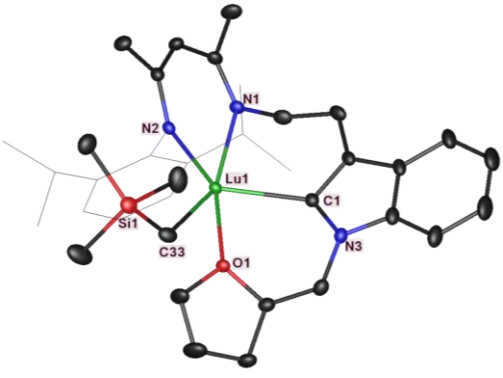


Fig S3. Molecular structure of **1d**. All the hydrogen atoms are omitted and 2,6-diisopropyl phenyl group was depicted in wireframe style for clarity. Selected bond lengths (Å) and angles (°): Lu(1)−N(1) 2.267(3), Lu(1)−N(2) 2.272(3), Lu(1)−C(1) 2.355(4), Lu(1)−C(33) 2.311(4), Lu(1)−O(1) 2.308(3), C(33)−Lu(1)−N(2) 118.70(15), C(33)−Lu(1)−C(1) 116.80(16).

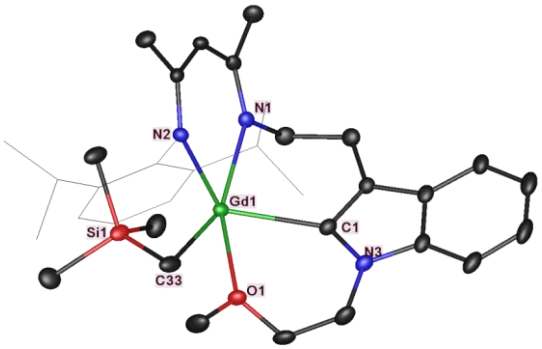


Fig S4. Molecular structure of **2b**. All the hydrogen atoms are omitted and 2,6-diisopropyl phenyl group was depicted in wireframe style for clarity. Selected bond lengths (Å) and angles (°): Gd(1)−N(1) 2.349(3), Gd(1)−N(2) 2.361(3), Gd(1)−C(1) 2.439(4), Gd(1)−C(33) 2.409(4), Gd(1)−O(1) 2.419(2), C(33)−Gd(1)−N(2) 127.33(13), C(33)−Gd(1)−C(1) 107.68(15).

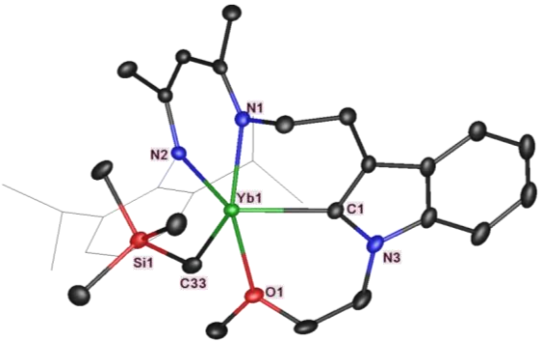


Fig S5. Molecular structure of **2c**. All the hydrogen atoms are omitted and 2,6-diisopropyl phenyl group was depicted in wireframe style for clarity. Selected bond lengths (Å) and angles (°): Yb(1)−N(1) 2.285(5), Yb(1)−N(2) 2.308(5), Yb(1)−C(1) 2.370(6), Yb(1)−C(33) 2.339(6), Yb(1)−O(1) 2.365(5), C(33)−Yb(1)−N(2) 125.8(2), C(33)−Yb(1)−C(1) 108.8(2).

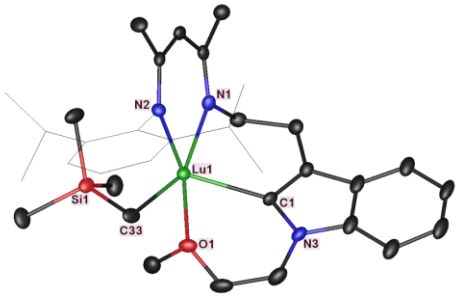
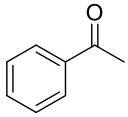
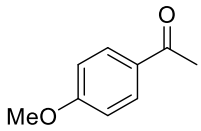


Fig S6. Molecular structure of **2d**. All the hydrogen atoms are omitted and 2,6-diisopropyl phenyl group was depicted in wireframe style for clarity. Selected bond lengths (Å) and angles (°): Lu(1)−N(1) 2.262(8), Lu(1)−N(2) 2.292(8), Lu(1)−C(1) 2.360(11), Lu(1)−C(33) 2.310(10), Lu(1)−O(1) 2.326(7), C(33)−Lu(1)−N(2) 126.3(4), C(33)−Lu(1)−C(1) 109.2(4).

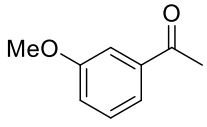
Characterization data of the catalytic products



Colorless oil.[1] 95% yield (114.09 mg, 0.95 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.96 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.57 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.47 (t, *J* = 7.5 Hz, 2H, Ar*H*), 2.61 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.6 (*C*=O), 137.5, 133.5, 129.0, 128.7 (Ar*C*), 27.1 (*C*H_3).

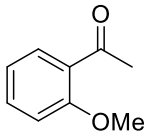


Colorless oil.[1] 91% yield (136.68 mg, 0.91 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.89 (d, *J* = 9.0 Hz, 2H, Ar*H*), 6.89 (d, *J* = 9.0 Hz, 2H, Ar*H*), 3.82 (s, 3H, OCH_3), 2.51 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 197.1 (*C*=O), 163.8, 130.9, 130.7, 114.0 (Ar*C*), 55.8 (O*C*H_3), 26.7 (*C*H_3).

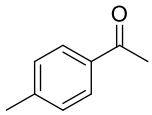


Colorless oil.[2] 87% yield (130.67 mg, 0.87 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.54 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.49 (s, 1H, Ar*H*), 7.37 (t, *J* = 8.0 Hz, 1H, Ar*H*), 7.11 (dd, *J* = 2.5, 8.0 Hz, 1H, Ar*H*), 3.86 (s, 3H, OCH_3), 2.60 (s, 3H, CH_3). ^{13}C{^{1}H} NMR

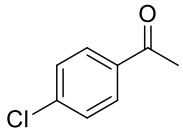
(125 MHz, $CDCl_3$, ppm): δ 198.4 (*C*=O), 160.2, 138.9, 130.0, 121.5, 120.1, 112.7 (Ar*C*), 55.8 (O*C*H_3), 27.1 (*C*H_3).



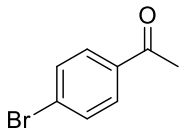
Colorless oil.[2] 76% yield (114.15 mg, 0.76 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.73 (dd, *J* = 2.0, 7.5 Hz, 1H, Ar*H*), 7.48–7.45 (m, 1H, Ar*H*), 7.01–6.96 (m, 2H, Ar*H*), 3.92 (s, 3H, OC*H*$_3$), 2.62 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 200.3 (*C*=O), 159.3, 134.0, 130.8, 128.7, 121.0, 111.9 (Ar*C*), 55.9 (O*C*H_3), 32.2 (*C*H_3).



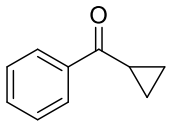
Colorless oil.[1] 93% yield (124.80 mg, 0.93 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.25 (d, *J* = 8.0 Hz, 2H, Ar*H*), 2.57 (s, 3H, C*H*$_3$), 2.41 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.3 (*C*=O), 144.3, 135.1, 129.6, 128.8 (Ar*C*), 26.9 (*C*H_3), 22.0 (*C*H_3).



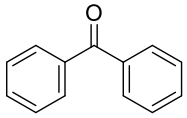
Colorless oil.[1] 89% yield (137.59 mg, 0.89 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.89 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.43 (d, *J* = 8.5 Hz, 2H, Ar*H*), 2.58 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 197.2 (*C*=O), 139.9, 135.8, 130.1, 129.3 (Ar*C*), 26.9 (*C*H_3).



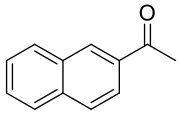
White solid.[1] M.p.: 48–50 ℃. 85% yield (169.19 mg, 0.85 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.81 (d, *J* = 8.5 Hz, 2H Ar*H*), 7.59 (d, *J* = 8.5 Hz, 2H, Ar*H*), 2.58 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 197.4 (*C*=O), 136.2, 132.3, 130.2, 128.7 (Ar*C*), 26.9 (*C*H_3).



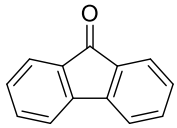
Colorless oil.[3] 95% yield (138.89 mg, 0.95 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.02 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.56 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.47 (t, *J* = 7.5 Hz, 2H, Ar*H*), 2.70–2.66 (m, 1H, C*H*), 1.26–1.23 (m, 2H, CH_2), 1.06–1.02 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 201.1 (*C*=O), 138.4, 133.1, 128.9, 128.4 (Ar*C*), 17.5 (*C*H), 12.0 (*C*H_2).



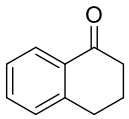
White solid.[1] M.p.: 52–53 ℃. 92% yield (167.64 mg, 0.92 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.81 (d, *J* = 7.0 Hz, 4H, Ar*H*), 7.60 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.49 (t, *J* = 7.5 Hz, 4H, Ar*H*). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, ppm): δ 197.2 (*C*=O), 138.0, 132.8, 130.5, 128.7 (Ar*C*).



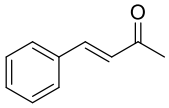
Colorless oil.[1] 90% yield (153.18 mg, 0.90 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.48 (s, 1H, Ar*H*), 8.04 (dd, *J* = 1.5, 8.5 Hz, 1H, Ar*H*), 7.97 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.89 (t, *J* = 8.5 Hz, 2H, Ar*H*), 7.62–7.55 (m, 2H, Ar*H*), 2.74 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.5 (*C*=O), 136.0, 134.9, 132.9, 130.6, 129.9, 128.9, 128.8, 128.2, 127.2, 124.3 (Ar*C*), 27.1 (*C*H_3).



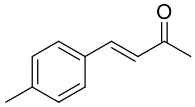
Yellow solid.[2] M.p.: 81–82 ℃. 94% yield (169.39 mg, 0.94 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 194.3 (*C*=O), 144.8, 135.1, 134.5, 129.5, 124.7, 120.7 (Ar*C*).



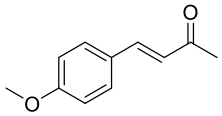
Colorless oil.[2] 96% yield (140.35 mg, 0.96 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.04 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.47 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.31 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.25 (d, *J* = 7.5 Hz, 1H, Ar*H*), 2.97 (t, *J* = 6.0 Hz, 2H, CH_2), 2.66 (t, *J* = 6.0 Hz, 2H, CH_2), 2.17–2.12 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.9 (*C*=O), 144.9, 133.8, 133.0, 129.2, 127.6, 127.0 (Ar*C*), 39.6, 30.1, 23.7 (*C*H_2).



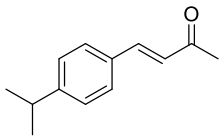
Colorless oil.[4] 84% yield (122.80 mg, 0.84 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.56–7.50 (m, 2H, Ar*H*), 7.41 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH), 7.41 (t, *J* = 3.5 Hz, 3H, Ar*H*), 6.73 (d, *J* = 16.0 Hz, 1H, C*H*), 2.39 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.5 (*C*=O), 143.5 (Ar*C*H=CH), 134.4, 130.6, 129.0, 128.3, 127.2 (*C*H), 27.6 (*C*H_3).



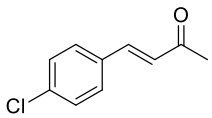
Colorless oil.[5] 81% yield (129.76 mg, 0.81 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.49 (d, *J* = 16.5 Hz, 1H, ArC*H*=CH), 7.44 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.21 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.68 (d, *J* = 16.5 Hz, 1H, C*H*), 2.38 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.9 (*C*=O), 143.9 (Ar*C*H=CH), 141.4, 132.0, 130.1, 128.7, 126.6 (*C*H), 27.8 (*C*H_3), 21.9 (*C*H_3).



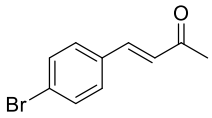
Colorless oil.[5] M.p.: 70–72 ℃. 80% yield (140.96 mg, 0.80 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.49 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.47 (d, *J* = 16.5 Hz, 1H, ArC*H*=CH), 6.91 (d, *J* = 9.0 Hz, 2H, Ar*H*), 6.60 (d, *J* = 16.5 Hz, 1H, C*H*), 3.84 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.8 (*C*=O), 162.0, 143.6 (Ar*C*H=CH), 130.3, 127.4, 125.4 (*C*H), 114.8, 55.8 (O*C*H_3), 27.8 (*C*H_3).



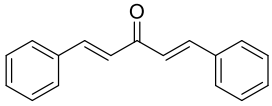
Colorless oil.[1] 78% yield (146.85 mg, 0.78 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.52–7.47 (m, 3H, ArC*H*=CH and Ar*H*), 7.26 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.69 (d, *J* = 16.5 Hz, 1H, C*H*), 2.93 (sept, *J* = 6.5 Hz, 1H, C*H*(CH_3)$_2$), 2.38 (s, 3H, CH_3), 1.26 (d, *J* = 6.5 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.9 (*C*=O), 152.3, 143.9 (Ar*C*H=CH), 132.4, 128.8, 127.5, 126.7 (*C*H), 34.5 (C*H*(CH_3)$_2$), 27.8 (*C*H_3), 24.1 (CH(CH_3)$_2$).



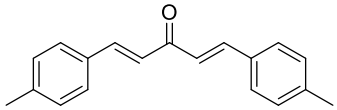
White solid.[6] M.p.: 54–56 ℃. 44% yield (79.46 mg, 0.44 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.48–7.44 (m, 3H, ArC*H*=CH and Ar*H*), 7.37 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.68 (d, *J* = 16.5 Hz, 1H, C*H*), 2.37 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.5 (*C*=O), 142.3 (Ar*C*H=CH), 136.8, 133.3, 129.8, 129.6, 127.8 (*C*H), 123.9, 28.1 (*C*H_3).



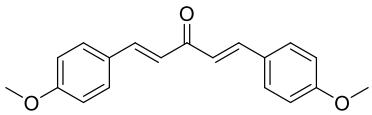
White solid.[6] M.p.: 78–79 ℃. 48% yield (108.05 mg, 0.48 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.53 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.43 (d, *J* = 16.5 Hz, 1H, ArC*H*=CH), 7.39 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.70 (d, *J* = 16.5 Hz, 1H, C*H*), 2.37 (s, 3H CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 198.5 (*C*=O), 142.3 (Ar*C*H=CH), 133.7, 132.6, 130.0, 127.9 (*C*H), 125.2, 28.1 (*C*H_3).



Yellow solid.[7] M.p.: 112–113 ℃. 62% yield (58.11 mg, 0.25 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.75 (d, *J* = 16.0 Hz, 2H, ArC*H*=CH), 7.63–7.61 (m, 4H, Ar*H*), 7.42–7.41 (m, 6H, Ar*H*), 7.10 (d, *J* = 16.0 Hz, 2H, ArCH=C*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.3 (*C*=O), 143.7 (Ar*C*=CH), 135.2, 130.9, 129.4, 128.8 (Ar*C*), 125.8 (ArC=*C*H).

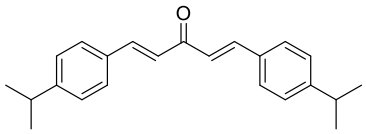


Yellow solid.[7] M.p.: 172–174 ℃. 65% yield (68.20 mg, 0.26 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.72 (d, *J* = 15.5 Hz, 2H, ArC*H*=CH), 7.52 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.04 (d, *J* = 15.5 Hz, 2H, ArCH=C*H*), 2.39 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.5 (*C*=O), 143.6 (Ar*C*=CH), 141.4, 132.5, 130.1, 128.8 (Ar*C*), 125.0 (ArC=*C*H), 21.9 (*C*H_3).

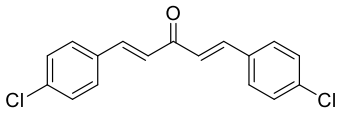


Yellow solid.[7] M.p.: 124–125 ℃. 61% yield (71.81 mg, 0.24 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.70 (d, *J* = 16.0 Hz, 2H, ArC*H*=CH), 7.57 (d, *J* = 8.5 Hz, 4H, Ar*H*), 6.95 (d, *J* = 16.0 Hz, 2H, ArCH=C*H*), 6.93 (d, *J* = 8.5 Hz, 4H, Ar*H*), 3.86 (s,

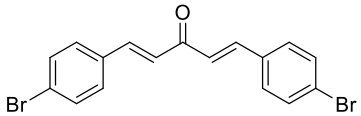
6H, C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.3 (*C*=O), 161.9, 143.1 (Ar*C*=CH), 130.5, 128.0, 123.9 (ArC=*C*H), 114.8 (Ar*C*), 55.8 (O*C*H$_3$).



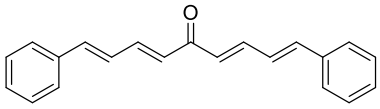
Yellow solid. M.p.: 73–75 ℃. 38% yield (48.41 mg, 0.15 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.72 (d, *J* = 16.0 Hz, 2H, ArC*H*=CH), 7.56 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.27 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.04 (d, *J* = 16.0 Hz, 4H, ArCH=C*H*), 2.94 (sept, *J* = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 1.27 (d, *J* = 7.0 Hz, 12H, C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.5 (*C*=O), 152.2, 143.6 (Ar*C*=CH), 132.9, 128.9, 127.5 (Ar*C*), 125.1 (ArC=*C*H), 34.5 (*C*H(CH$_3$)$_2$), 24.2 (*C*H$_3$). HRMS (APCI): calcd for $C_{23}H_{26}O$ $[M+H]^+$: 319.2056, found 319.2055.



Yellow solid.[8] M.p.: 171–172 ℃. 43% yield (52.15 mg, 0.17 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.67 (d, *J* = 16.0 Hz, 2H, ArC*H*=CH), 7.55 (d, *J* = 8.5 Hz, 4H, Ar*H*), 7.47 (d, *J* = 8.5 Hz, 4H, Ar*H*), 7.05 (d, *J* = 16.0 Hz, 2H, ArCH=C*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 188.7 (*C*=O), 142.5 (Ar*C*=CH), 134.0, 132.6, 130.1, 126.1 (ArC=*C*H), 125.3 (Ar*C*).

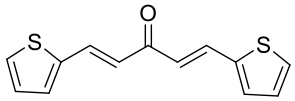


Yellow solid.[8] M.p.: 189–191 ℃. 45% yield (70.58 mg, 0.18 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.69 (d, *J* = 16.0 Hz, 2H, ArC*H*=CH), 7.55 (d, *J* = 8.5 Hz, 4H, Ar*H*), 7.39 (d, *J* = 8.5 Hz, 4H, Ar*H*), 7.03 (d, *J* = 16.0 Hz, 2H, ArCH=C*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 188.7 (*C*=O), 142.5 (Ar*C*=CH), 134.0, 132.6, 130.1, 126.1 (ArC=*C*H), 125.3 (Ar*C*).

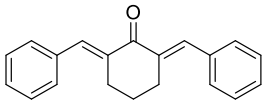


Yellow solid. M.p.: 134–136 ℃. 50% yield (57.28 mg, 0.20 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.48 (t, *J* = 7.0 Hz, 6H, Ar*H*), 7.39–7.31 (m, 6H, Ar*H* and C*H*), 7.01–6.92 (m, 4H, C*H*), 6.57 (d, *J* = 15.5 Hz, 2H, C*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.4 (*C*=O), 143.4 (*C*H), 141.8 (*C*H), 136.5 (*C*H), 129.6, 129.4

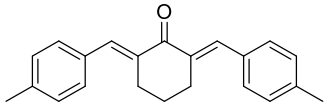
(*C*H), 129.2, 127.6 (Ar*C*), 127.4 (*C*H). HRMS (APCI): calcd for $C_{21}H_{18}O$ $[M+H]^+$: 287.1430, found 287.1426.



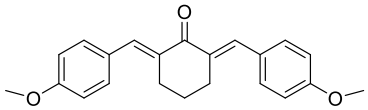
Yellow solid.[8] M.p.: 116–117 ℃. 47% yield (46.30 mg, 0.19 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 16.0 Hz, 2H, C*H*=CHCO), 7.41 (d, *J* = 5.0 Hz, 2H,), 7.34 (d, *J* = 3.0 Hz, 2H), 7.08 (dd, *J* = 3.0, 5.0 Hz, 2H, thiophene*H*), 6.82 (d, *J* = 16.0 Hz, 2H, CH=C*H*CO). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 188.1 (*C*=O), 140.7, 136.0 (*C*H), 132.2, 129.2, 128.7 (thiophene*C*), 124.8 (*C*H).



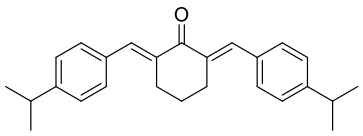
Yellow solid.[9] M.p.: 116–118 ℃. 86% yield (94.37 mg, 0.34 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.81 (s, 2H, C*H*), 7.47 (d, *J* = 7.5 Hz, 4H), 7.41 (t, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 2H, Ar*H*), 2.94 (t, *J* = 5.0 Hz, 4H, CH_2), 1.82–1.77 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 190.8 (*C*=O), 137.3 (*C*H), 136.6 (CH=*C*), 136.4, 130.8, 129.0, 128.8 (Ar*C*), 28.9 (*C*H_2), 23.4 (*C*H_2).



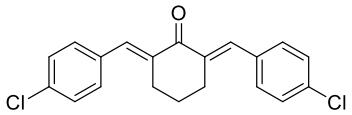
Yellow solid.[9] M.p.: 168–170 ℃. 83% yield (100.39 mg, 0.33 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.78 (s, 2H, C*H*), 7.38 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 4H, Ar*H*), 2.93 (t, *J* =5.0 Hz, 4H, CH_2), 2.39 (s, 6H, CH_3), 1.81–1.76 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 190.8 (*C*=O), 139.2, 137.3 (*C*H), 135.9 (CH=*C*), 133.6, 130.9, 129.5 (Ar*C*), 28.9 (*C*H_2), 23.4 (*C*H_2), 21.8 (*C*H_3).



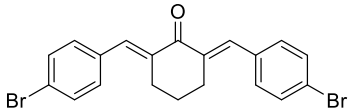
Yellow solid.[9] M.p.: 160–162 ℃. 81% yield ((108.34 mg, 0.32 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.76 (s, 2H, C*H*), 7.46 (d, *J* = 8.5 Hz, 4H, Ar*H*), 6.94 (d, *J* = 8.5 Hz, 4H, Ar*H*), 3.85 (s, 6H, CH_3), 2.92 (t, *J* = 5.0 Hz, 4H, CH_2), 1.83–1.78 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 190.7 (*C*=O), 160.3 (*C*OMe), 136.9 (*C*H), 134.7 (CH=*C*), 132.6, 129.1, 114.3 (Ar*C*), 55.7 (O*C*H_3), 28.9 (*C*H_2), 23.4 (*C*H_2).



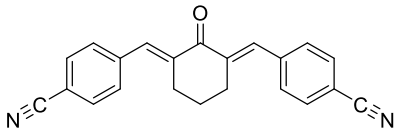
Yellow solid. M.p.: 149–150 ℃. 65% yield (93.21 mg, 0.26 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.80 (s, 2H, C*H*), 7.43 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.27 (d, *J* = 8.0 Hz, 4H, Ar*H*), 2.95–2.93 (m, 6H, CH_2 and C*H*$(CH_3)_2$), 1.81–1.76 (m, 2H, CH_2), 1.27 (d, *J* = 7.0 Hz, 12H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 190.8 (*C*=O), 150.1, 137.3, 135.9 (*C*H), 134.0 (CH=*C*), 131.0, 126.9 (Ar*C*), 34.4, 28.9, 24.2, 23.5. HRMS (APCI): calcd for $C_{26}H_{30}O$ $[M+H]^+$: 359.2369, found 359.2360.



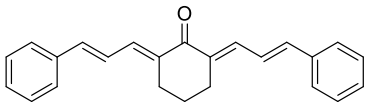
Yellow solid.[9] M.p.: 146–147 ℃. 72% yield (98.84 mg, 0.29 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.73 (s, 2H, C*H*), 7.40–7.35 (m, 8H, Ar*H*), 2.89 (t, *J* = 5.0 Hz, 4H, CH_2), 1.83–1.78 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 190.3 (*C*=O), 136.8 (CH=*C*), 136.2 (*C*H), 135.0, 134.7, 132.0, 129.1 (Ar*C*), 28.8 (*C*H_2), 23.2 (*C*H_2).



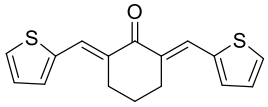
Yellow solid.[10] M.p.: 145–146 ℃. 74% yield (127.90 mg, 0.30 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.71 (s, 2H, C*H*), 7.53 (d, *J* = 8.5 Hz, 4H, Ar*H*), 7.32 (d, *J* = 8.5 Hz, 4H, Ar*H*), 2.88 (t, *J* = 5.0 Hz, 4H, CH_2), 1.82–1.77 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 190.3 (*C*=O), 136.9 (CH=*C*), 136.2 (*C*H), 135.1, 132.2, 132.0, 123.3 (Ar*C*Br), 28.8 (*C*H_2), 23.2 (*C*H_2).



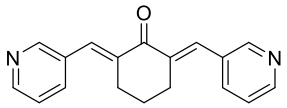
Yellow solid.[10] M.p.: 227–228 ℃. 75% yield (97.32 mg, 0.30 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.75 (s, 2H, C*H*), 7.70 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.53 (d, *J* = 8.0 Hz, 4H, Ar*H*), 2.91 (t, *J* = 5.0 Hz, 4H, CH_2), 1.85–1.80 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.7 (*C*=O), 140.6, 138.6 (CH=*C*), 135.6 (*C*H), 132.5, 131.0 (Ar*C*), 118.9 (*C*N), 112.4, 28.7 (*C*H_2), 23.0 (*C*H_2).



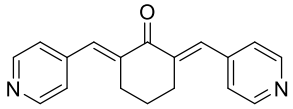
Yellow solid.[9] M.p.: 125–126 ℃. 82% yield (107.06 mg, 0.33 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.50 (t, *J* = 7.0 Hz, 6H, Ar*H*), 7.36 (t, *J* = 7.0 Hz, 4H, Ar*H*), 7.30 (t, *J* = 7.0 Hz, 2H, C*H*), 7.11–7.06 (m, 2H, C*H*), 6.98 (d, *J* = 15.5 Hz, 2H, C*H*), 2.81 (t, *J* = 5.5 Hz, 4H, CH_2), 1.91–1.86 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.3 (*C*=O), 141.2, 137.1, 136.7, 135.8, 129.2, 129.1, 127.6 (Ar*C*), 124.1, 27.0 (*C*H_2), 22.5 (*C*H_2).



Yellow solid. M.p.: 153–154 ℃. 79% yield (90.50 mg, 0.32 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.00 (s, 2H, C*H*=C), 7.53 (d, *J* = 5.0 Hz, 2H, 5-thiophene*H*), 7.38 (d, *J* = 3.5 Hz, 2H, 3-thiophene*H*), 7.14 (t, *J* = 5.0 Hz, 2H, 4-thiophene*H*), 2.93 (t, *J* = 5.5 Hz, 4H, CH_2), 2.00–1.95 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.5 (*C*=O), 139.9 (CH=*C*), 133.4 (*C*H), 133.2, 130.3, 130.1, 128.0 （thiophene*C*）, 28.5 (*C*H_2), 22.0 (*C*H_2). HRMS (APCI): calcd for $C_{16}H_{14}OS_2$ $[M+H]^+$: 287.0559, found 289.0557.

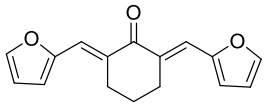


Yellow solid.[11] M.p.: 143–144 ℃. 54% yield (59.68 mg, 0.22 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.71 (s, 2H, C*H*=C), 8.57–8.56 (m, 2H), 7.62–7.76 (m, 4H), 7.36–7.34 (m, 2H, pyridine*H*), 2.94 (t, *J* = 5.0 Hz, 4H, CH_2), 1.86–1.78 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.6 (*C*=O), 151.6 (2-pyridine*C*), 149.7 (6-pyridine*C*), 138.1 (CH=*C*), 137.4 (*C*H), 134.0, 132.0, 123.7 (pyridine*C*), 28.7 (*C*H_2), 23.1 (*C*H_2).



Yellow solid.[11] M.p.: 147–149 ℃. 67% yield (74.05 mg, 0.27 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.65 (d, *J* = 5.5 Hz, 4H, 2-pyridine*H*), 7.65 (s, 2H, C*H*), 7.27 (d, *J* = 5.5 Hz, 4H, 3-pyridine*H*), 2.91 (t, *J* = 5.0 Hz, 4H, CH_2), 1.84–1.79 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.7 (*C*=O), 150.5 (2-pyridine*C*), 143.4

(4-pyridine*C*), 139.5 (CH=*C*), 134.8 (*C*H), 124.4 (3-pyridine*C*), 28.6 (*C*H_2), 22.8 (*C*H_2). HRMS (APCI): calcd for $C_{18}H_{16}N_2O$ $[M+H]^+$: 277.1335, found 277.1345.



Yellow solid.[9] M.p.: 143–145 ℃. 76% yield (77.30 mg, 0.30 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.56 (d, *J* = 5.5 Hz, 4H, furan*H*), 6.67 (d, *J* = 3.5 Hz, 2H, furan*H*), 6.52 (s, 2H, C*H*=C), 3.01 (t, *J* = 5.5 Hz, 4H, CH_2), 1.91–1.86 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, ppm): δ 189.5 (*C*=O), 153.2 (2-furan*C*), 144.9 (5-furan*C*), 133.4 (CH=*C*), 123.7 (*C*H), 116.5, 112.7 (furan*C*), 28.4 (*C*H_2), 22.0 (*C*H_2).

Copies of NMR spectra

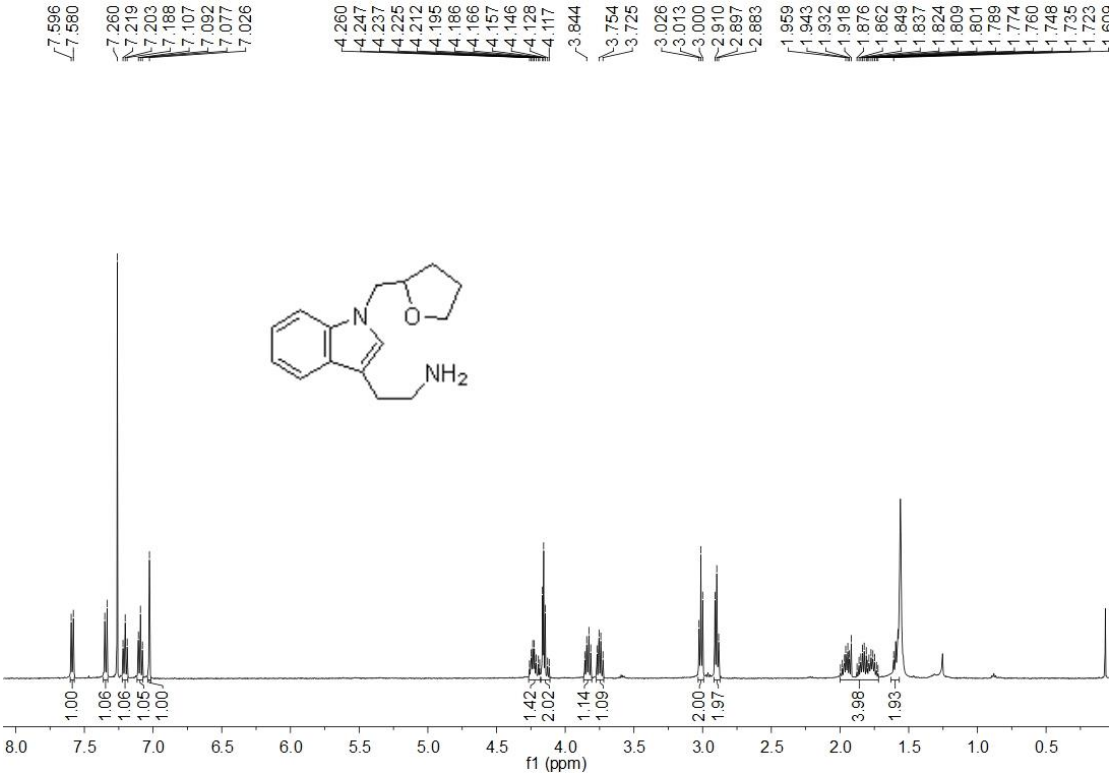


Fig. S7 ^{1}H NMR spectrum of [1-CH_2-(2-C_4H_7O)]-tryptamine (500 MHz, $CDCl_3$)

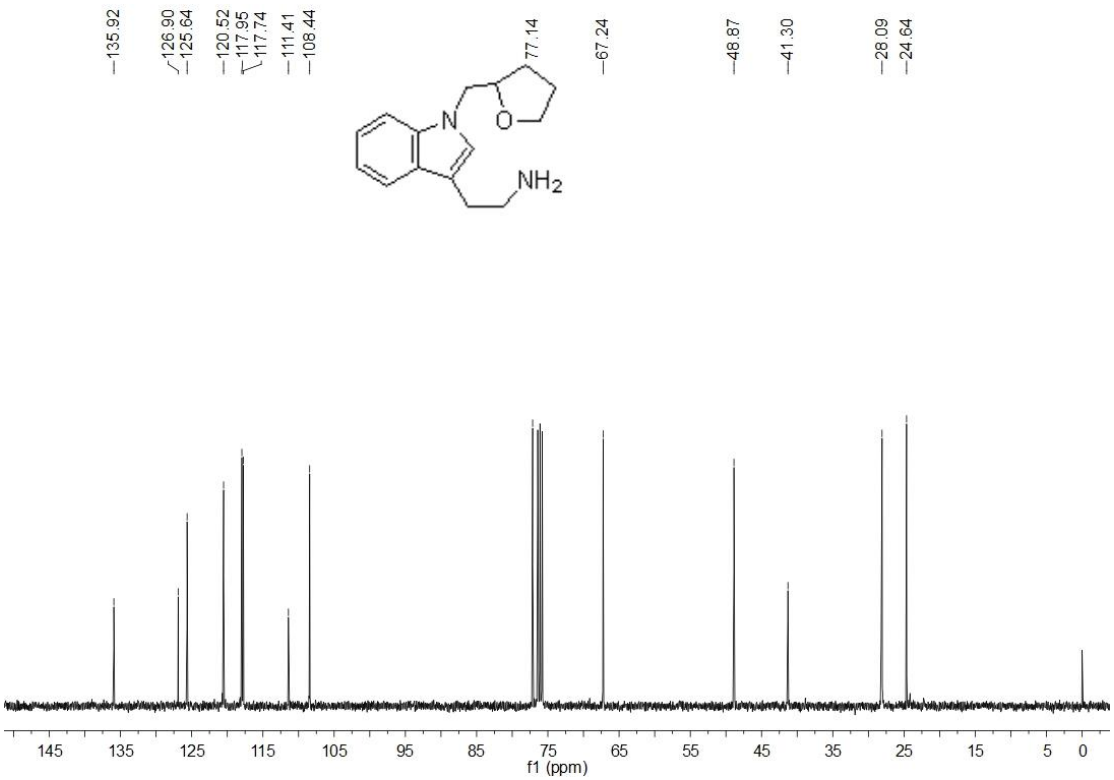


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of [1-CH_2-(2-C_4H_7O)]-tryptamine (125 MHz, $CDCl_3$)

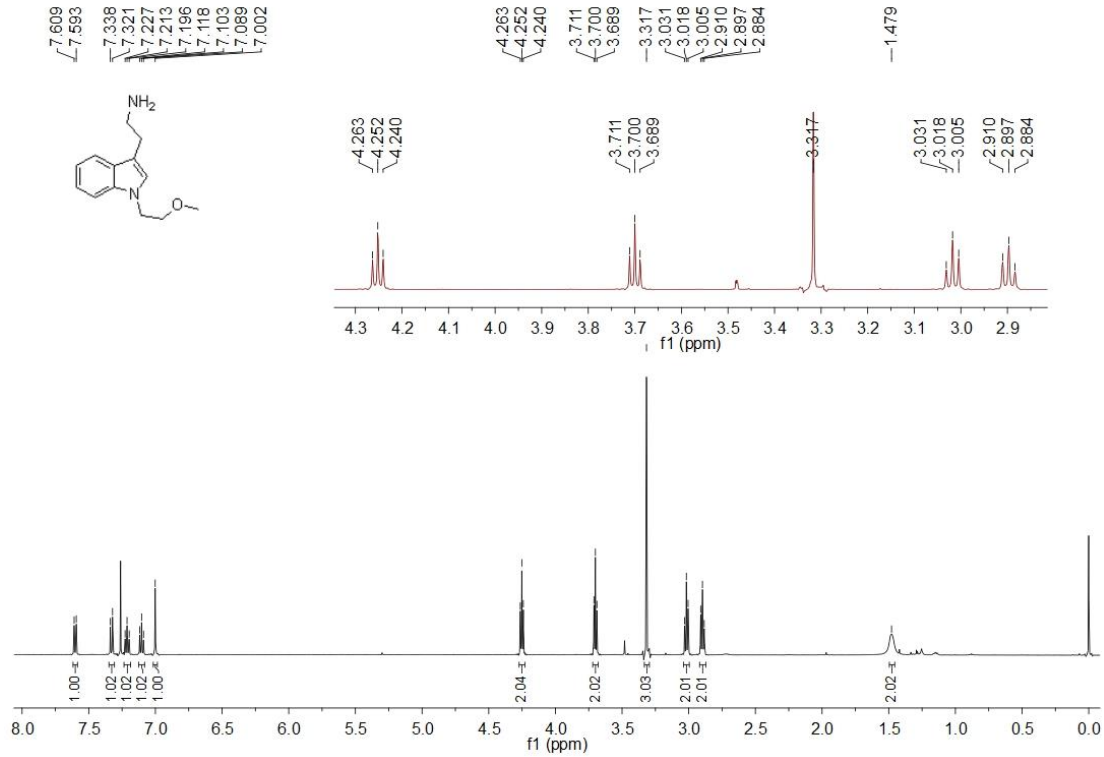


Fig. S9 ^{1}H NMR spectrum of [1-$(CH_2)_2$OMe)]-tryptamine (500 MHz, $CDCl_3$)

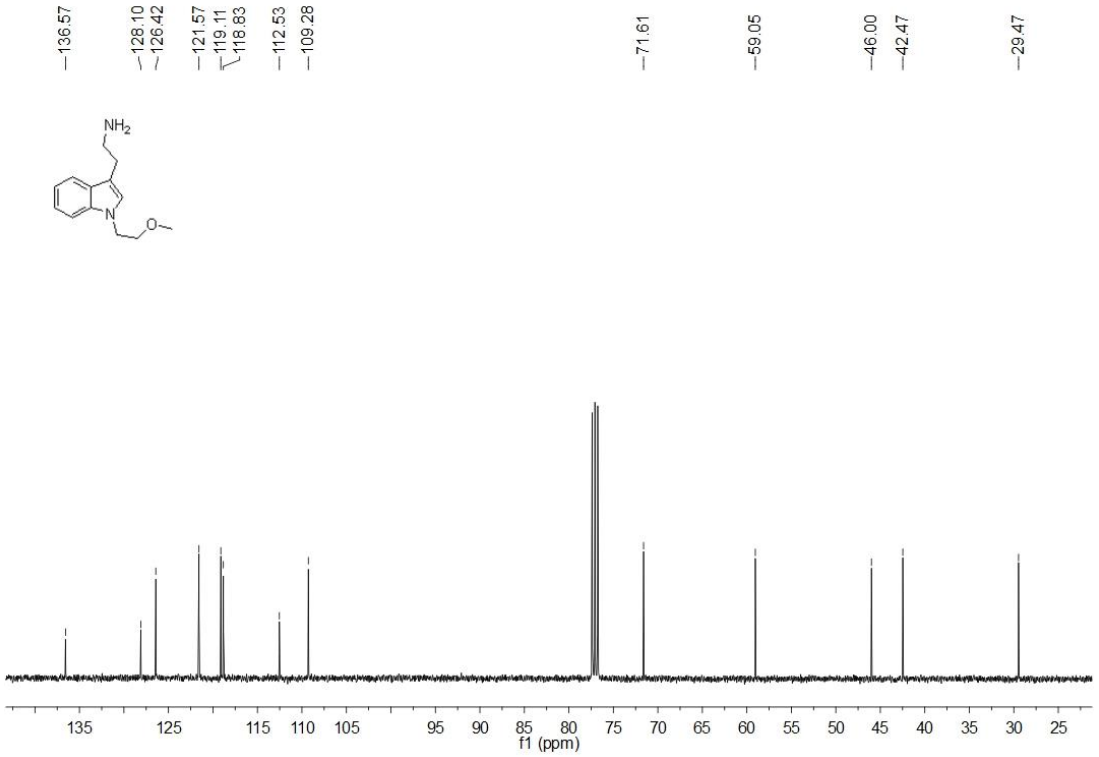


Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of [1-$(CH_2)_2$OMe)]-tryptamine (125 MHz, $CDCl_3$)

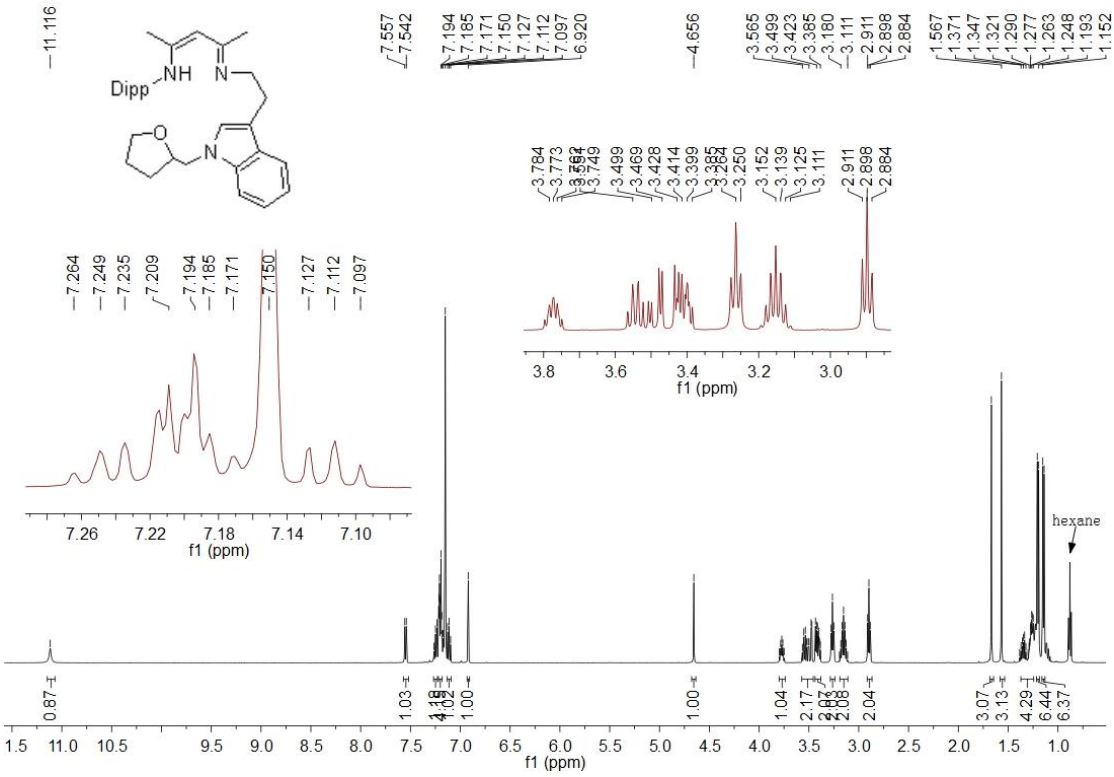


Fig. S11 ^{1}H NMR spectrum of the proligand $H_2\mathbf{L^1}$ (500 MHz, C_6D_6)

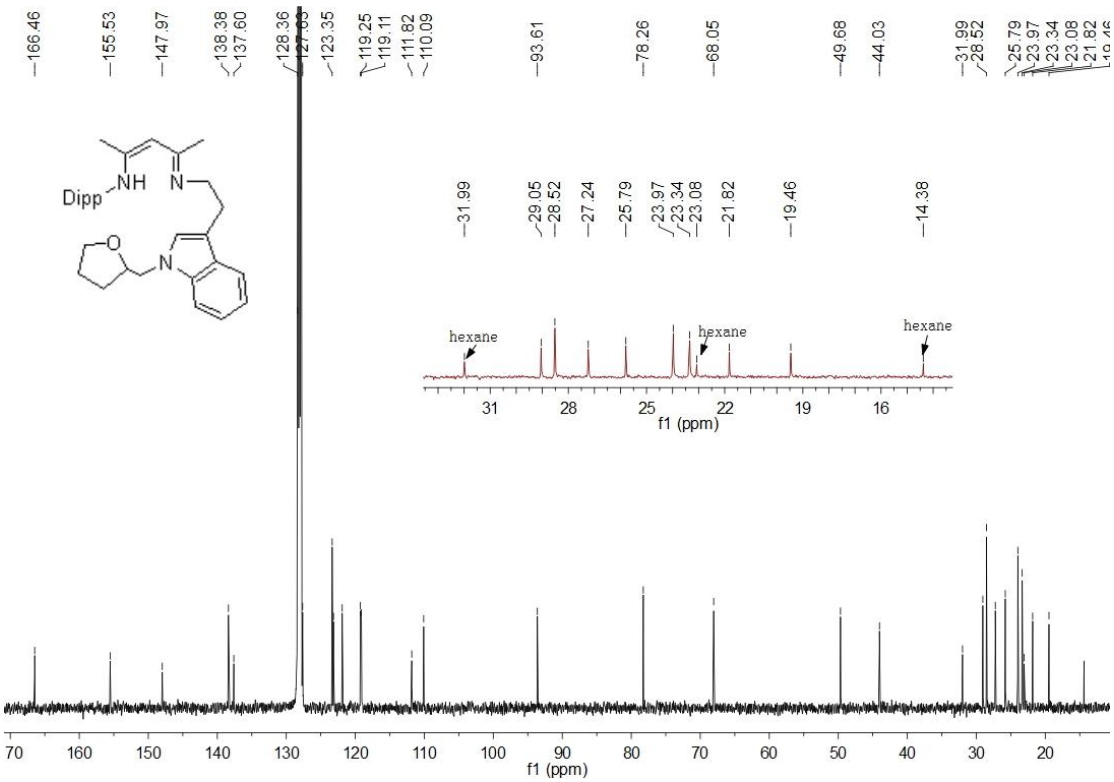


Fig. S12 $^{13}C\{^{1}H\}$ NMR spectrum of the proligand $H_2\mathbf{L^1}$ (125 MHz, C_6D_6)

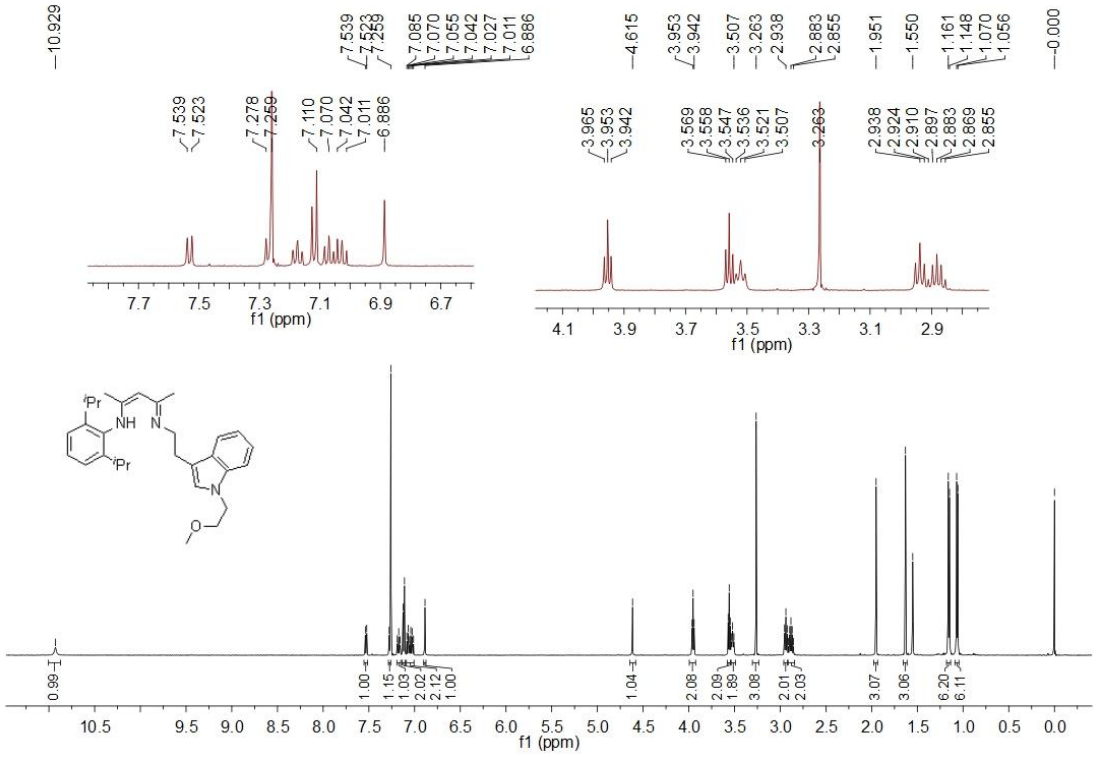


Fig. S13 ^{1}H NMR spectrum of the proligand $H_2\mathbf{L^2}$ (500 MHz, $CDCl_3$)

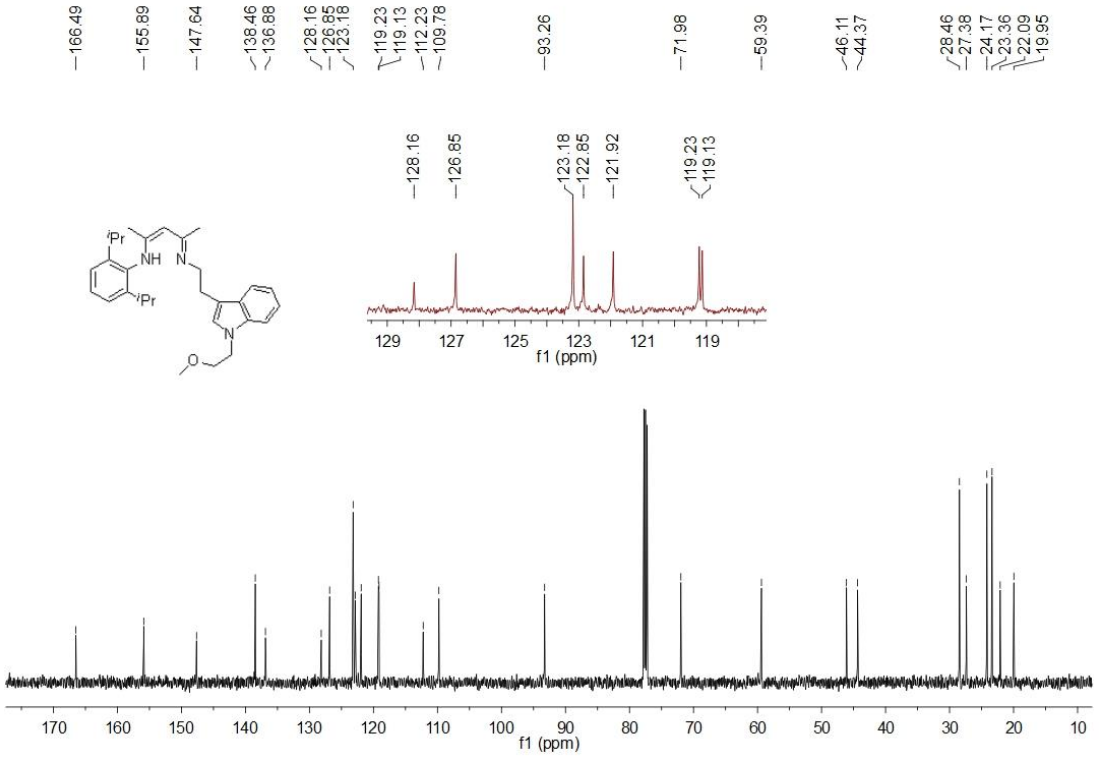


Fig. S14 $^{13}C\{^{1}H\}$ NMR spectrum of the proligand $H_2\mathbf{L^2}$ (125 MHz, $CDCl_3$)

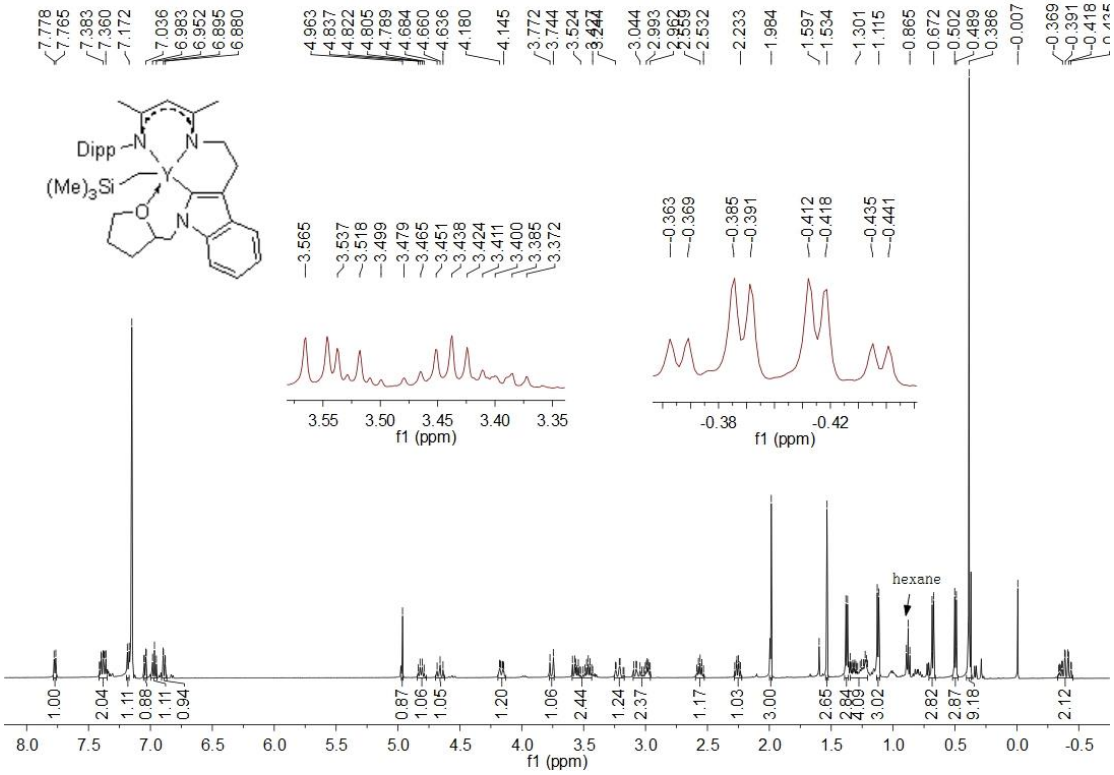


Fig. S15 ^{1}H NMR spectrum of the complex **1a** (500 MHz, C_6D_6)

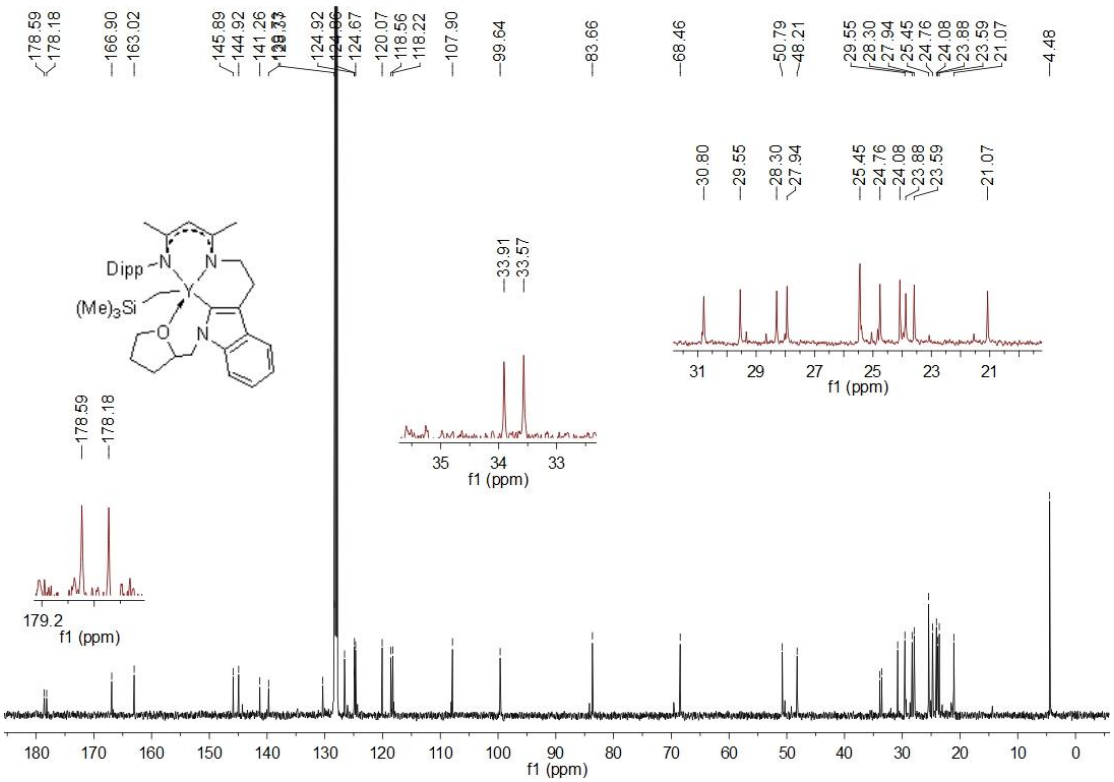


Fig. S16 $^{13}C\{^{1}H\}$ NMR spectrum of the complex **1a** (125 MHz, C_6D_6)

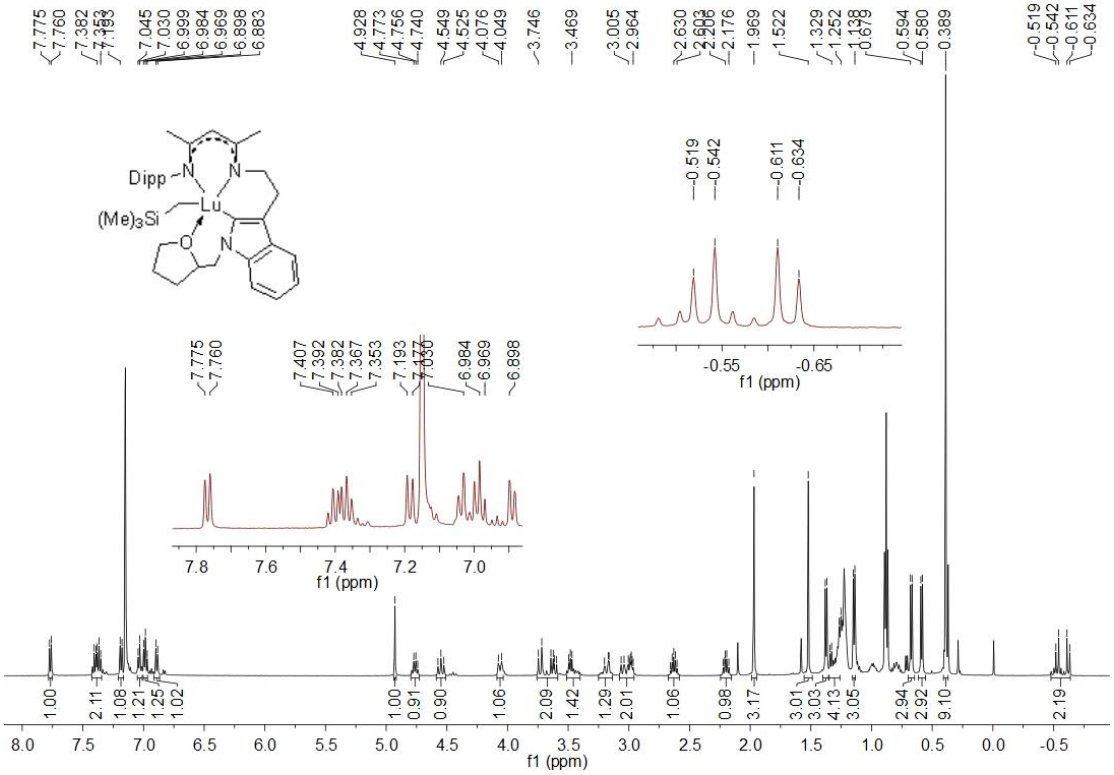


Fig. S17 ^{1}H NMR spectrum of the complex **1d** (500 MHz, C_6D_6)

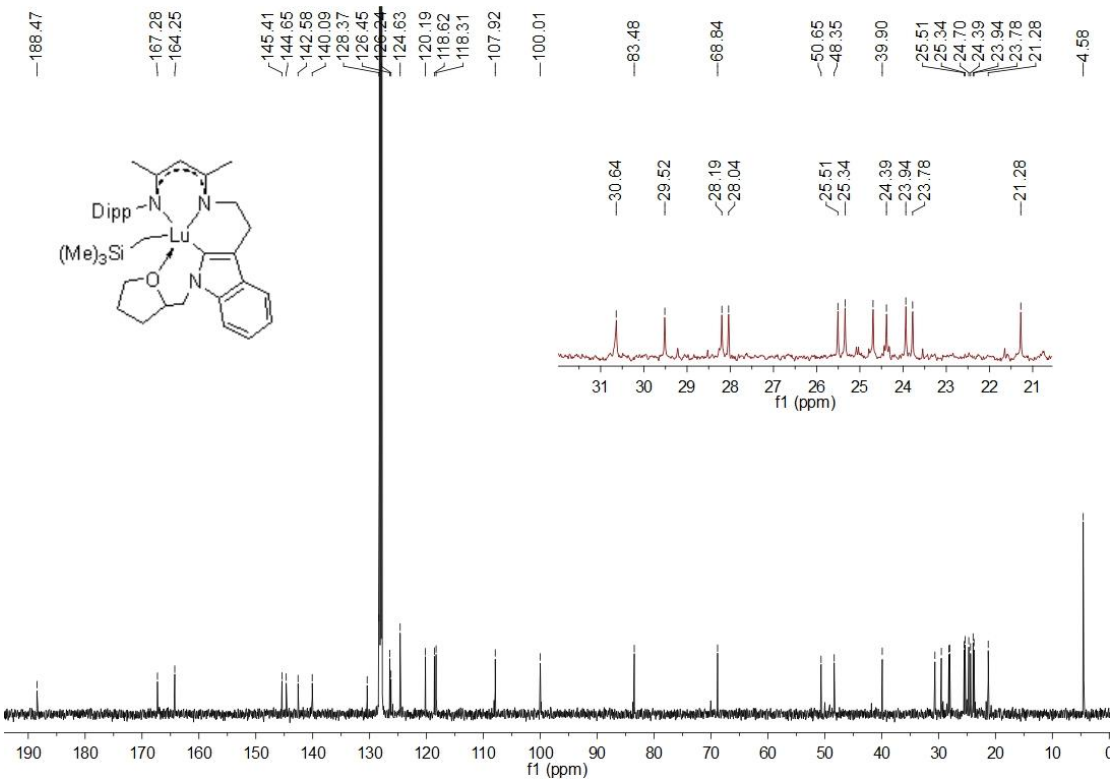


Fig. S18 $^{13}C\{^{1}H\}$ NMR spectrum of the complex **1d** (125 MHz, C_6D_6)

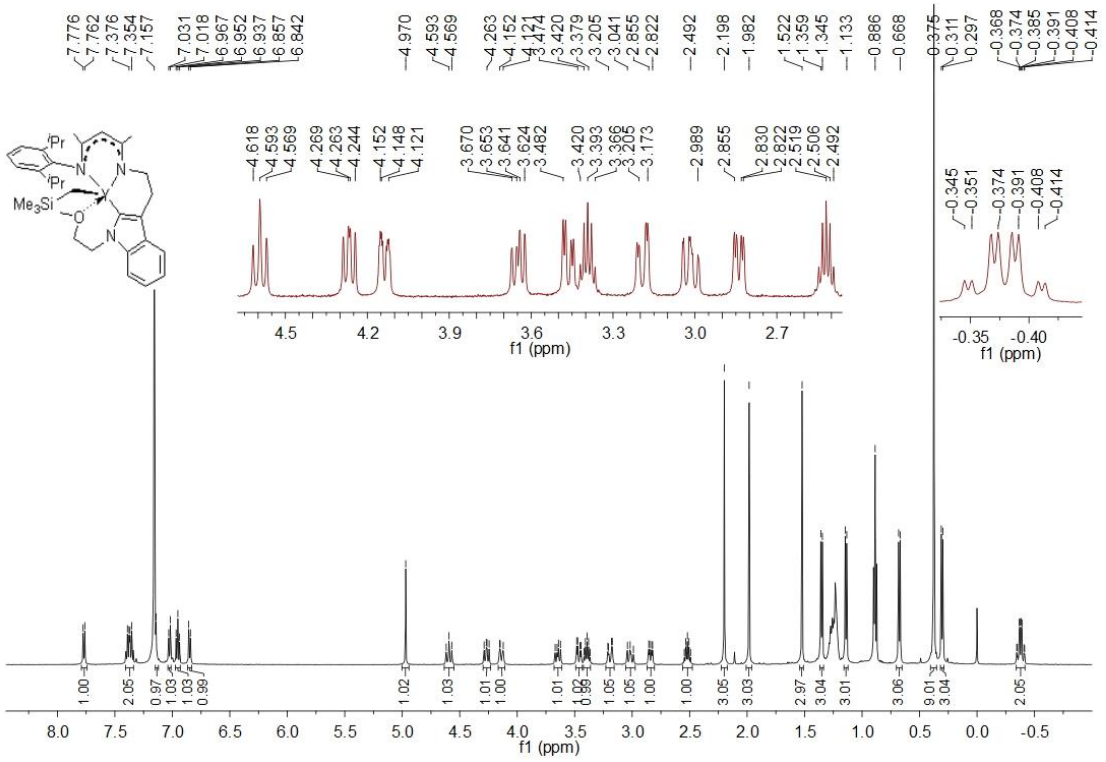


Fig. S19 ^{1}H NMR spectrum of the complex **2a** (500 MHz, C_6D_6)

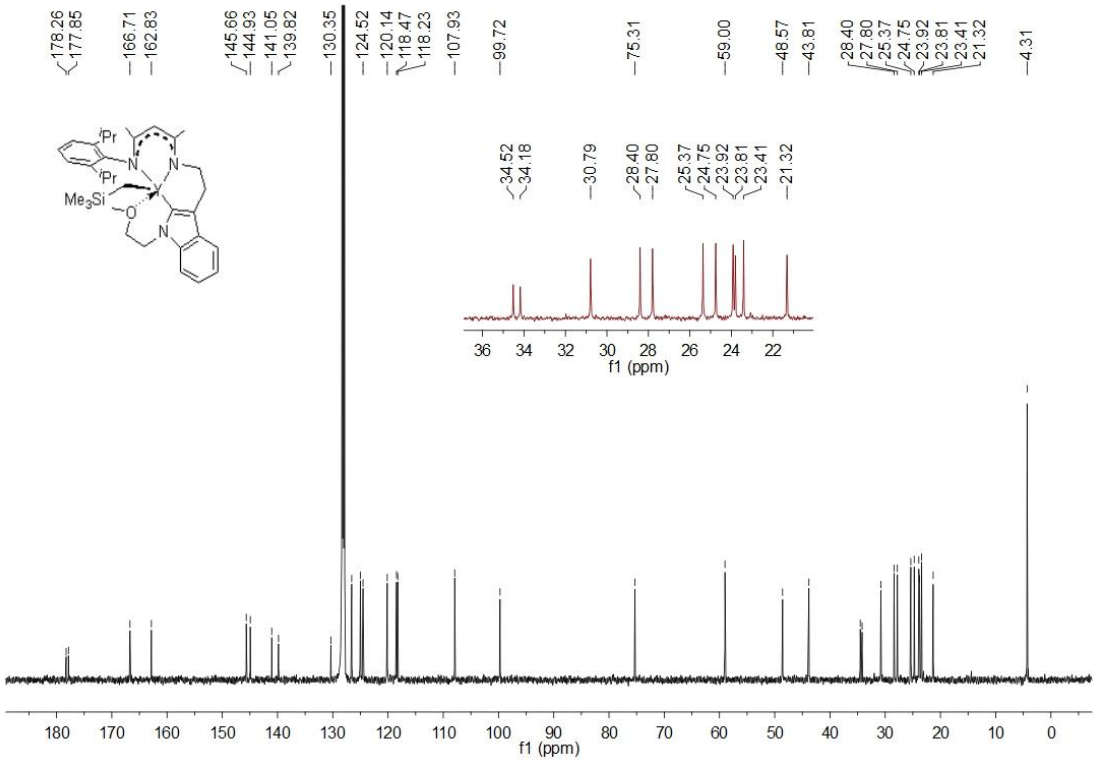


Fig. S20 $^{13}C\{^{1}H\}$ NMR spectrum of the complex **2a** (125 MHz, C_6D_6)

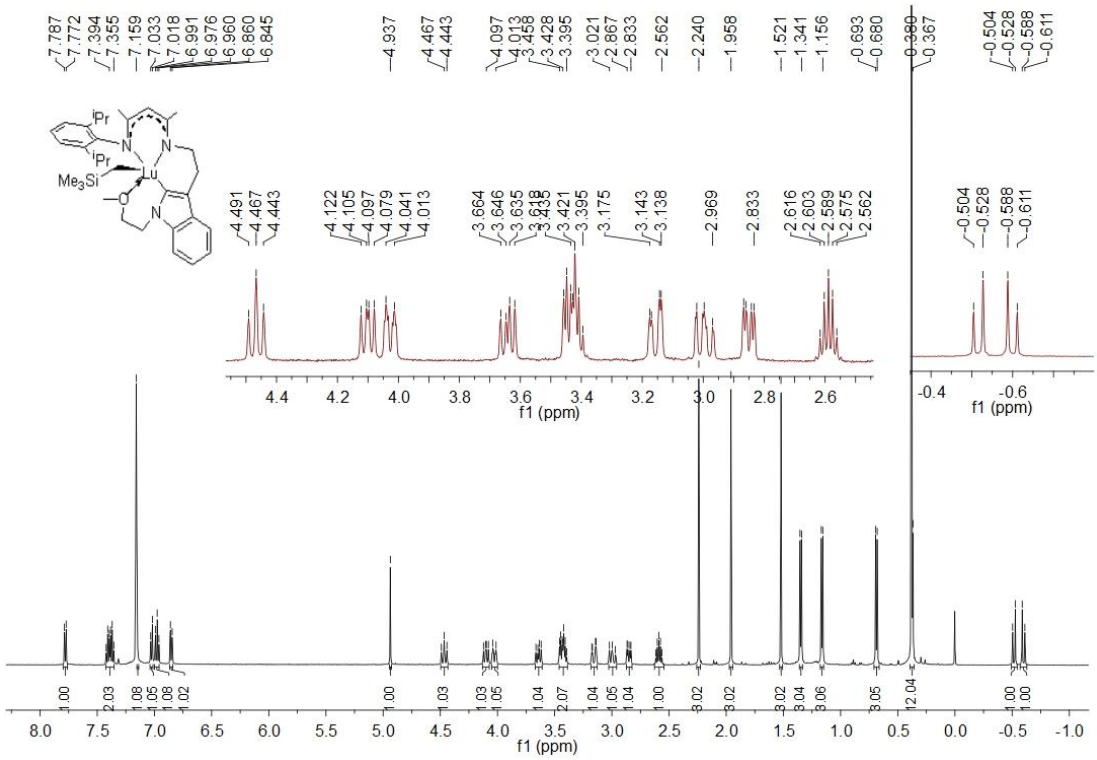


Fig. S21 ^{1}H NMR spectrum of the complex **2d** (500 MHz, C_6D_6)

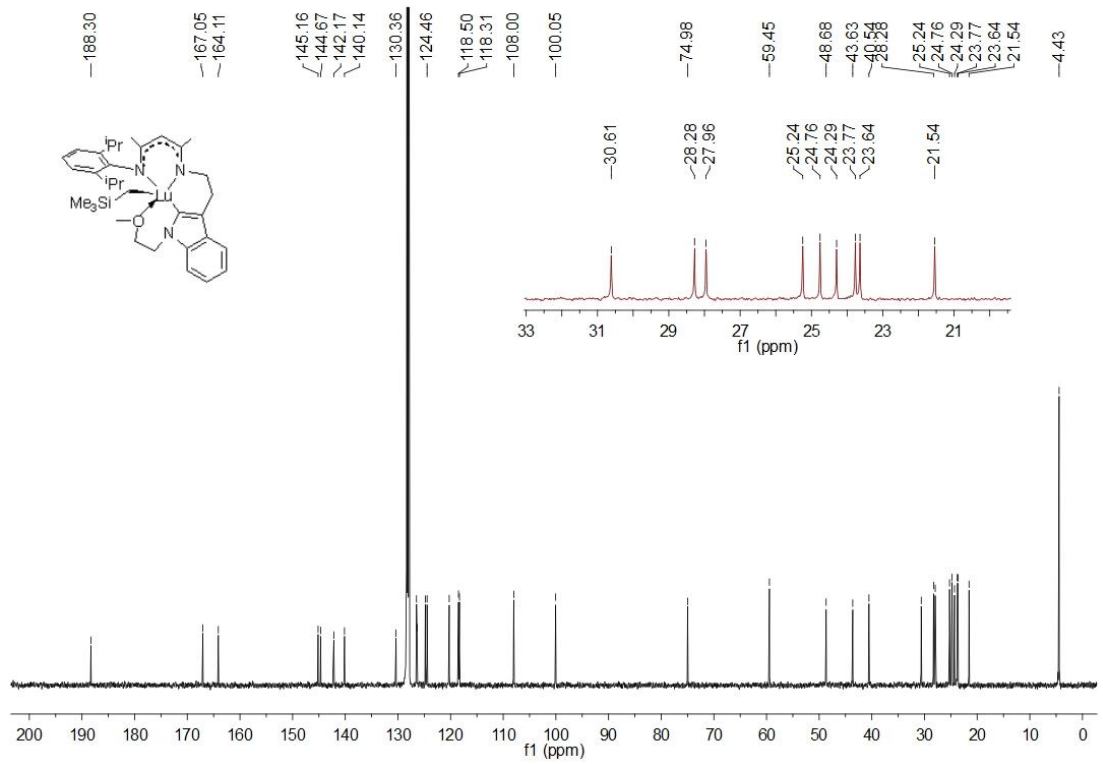


Fig. S22 $^{13}C\{^{1}H\}$ NMR spectrum of the complex **2d** (125 MHz, C_6D_6)

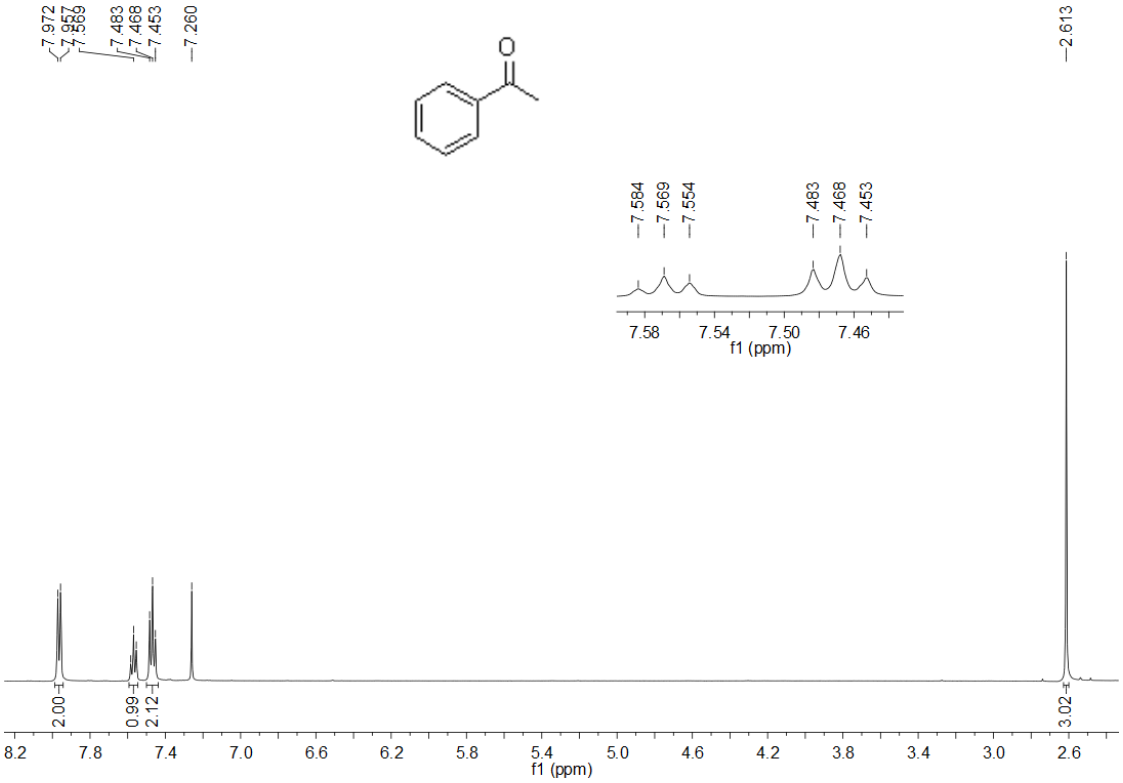


Fig. S23 ^{1}H NMR spectrum of **4a** (500 MHz, $CDCl_3$)

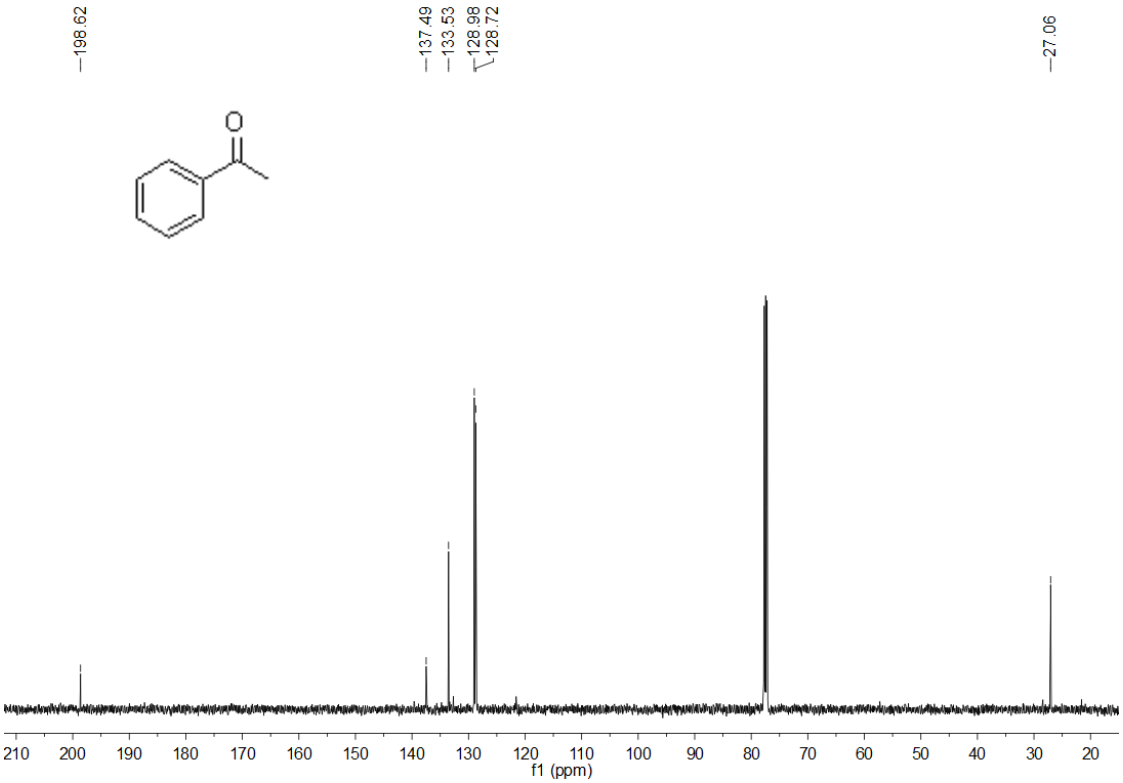


Fig. S24 $^{13}C\{^{1}H\}$ NMR spectrum of **4a** (125 MHz, $CDCl_3$)

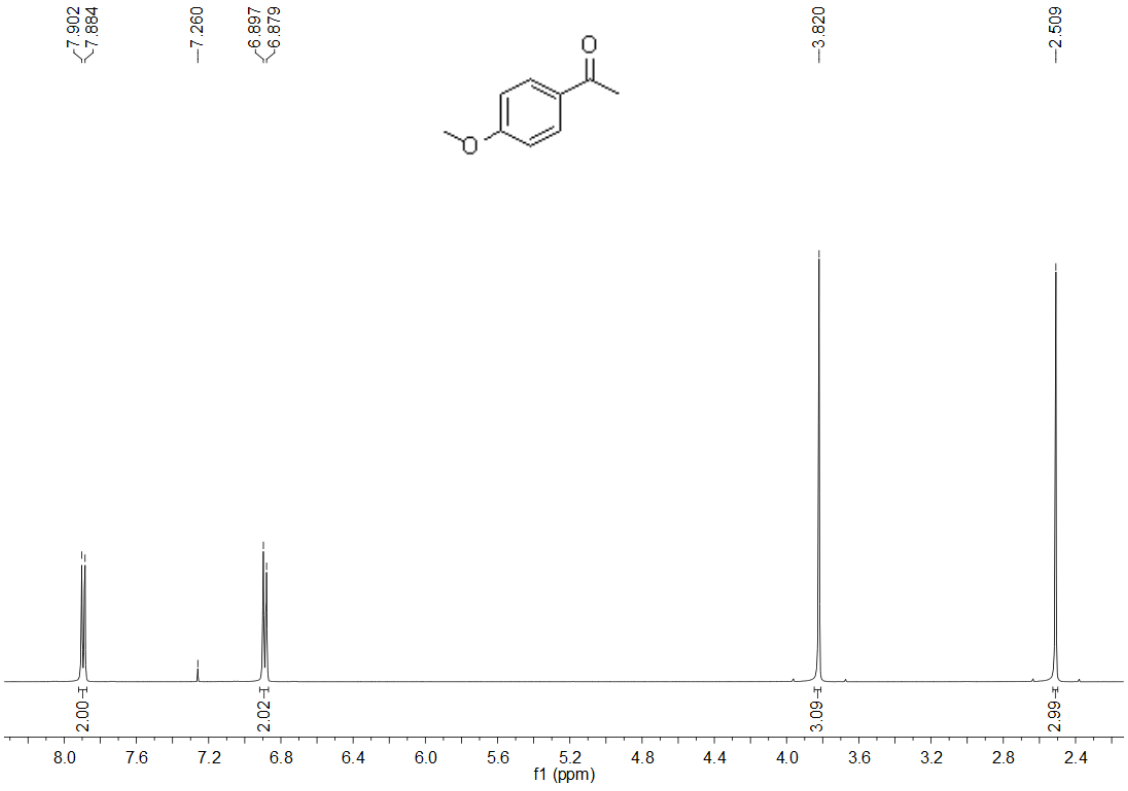


Fig. S25 ^{1}H NMR spectrum of **4b** (500 MHz, $CDCl_3$)

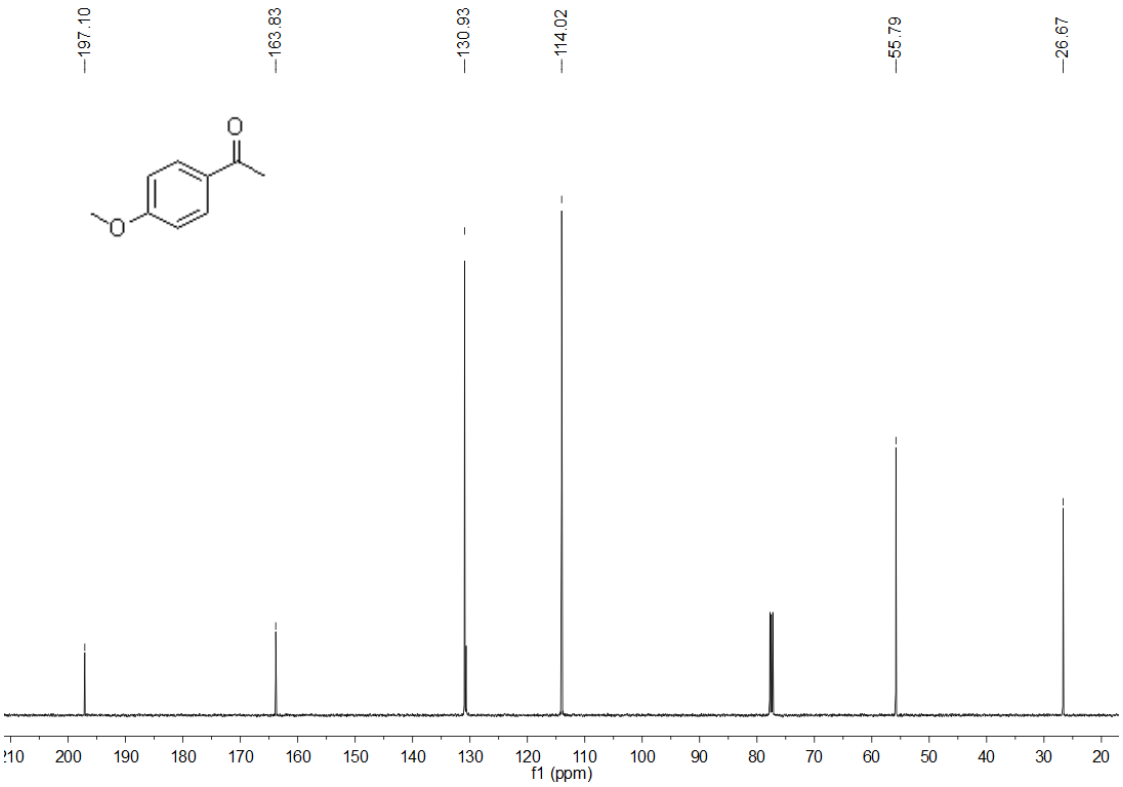


Fig. S26 $^{13}C\{^{1}H\}$ NMR spectrum of **4b** (125 MHz, $CDCl_3$)

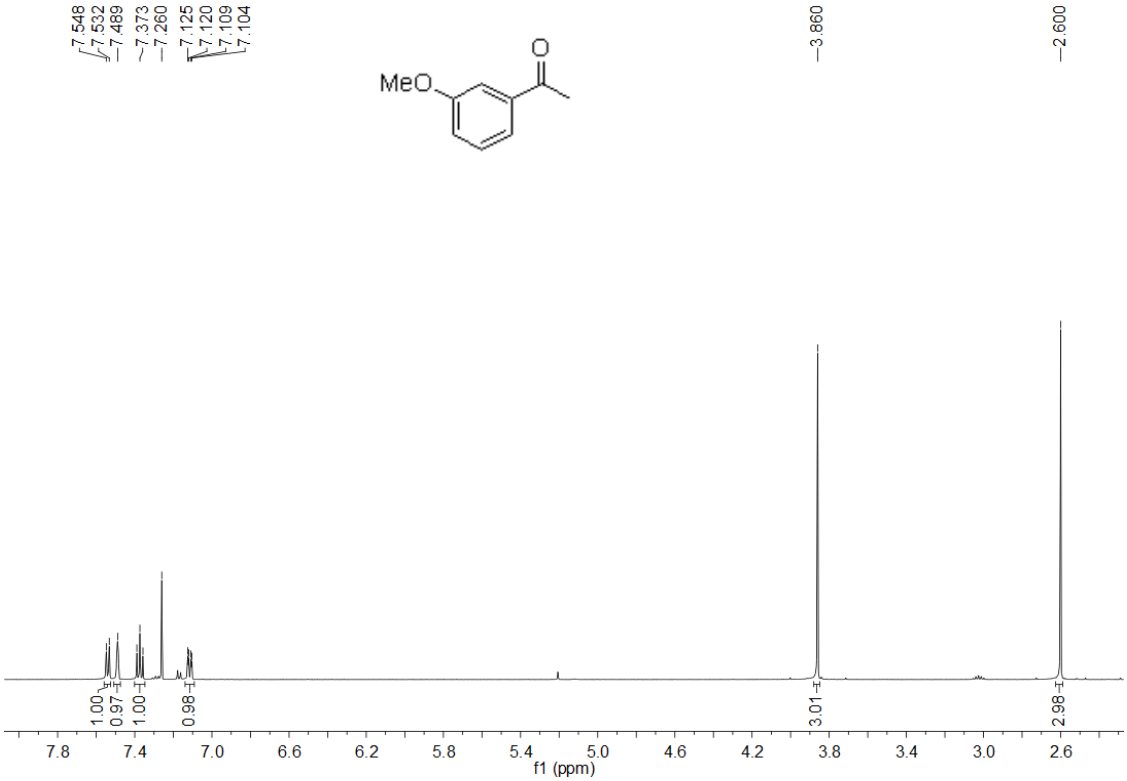


Fig. S27 ^{1}H NMR spectrum of **4c** (500 MHz, $CDCl_3$)

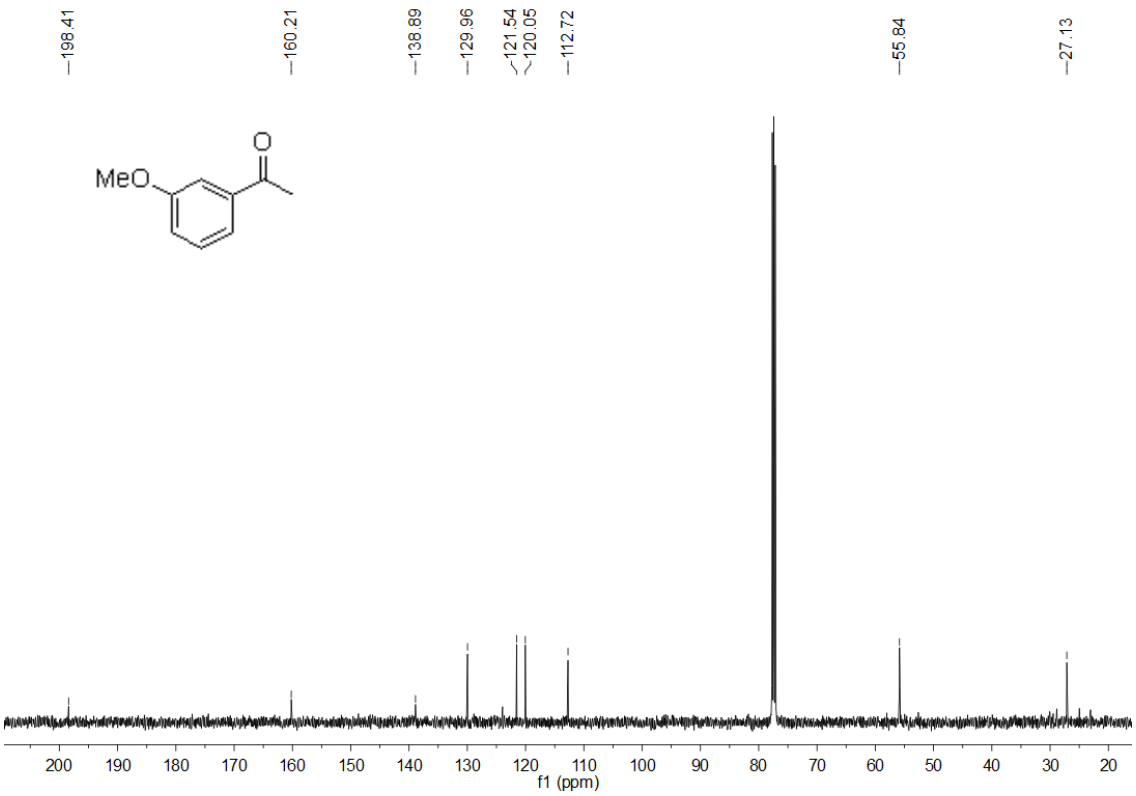


Fig. S28 $^{13}C\{^{1}H\}$ NMR spectrum of **4c** (125 MHz, $CDCl_3$)

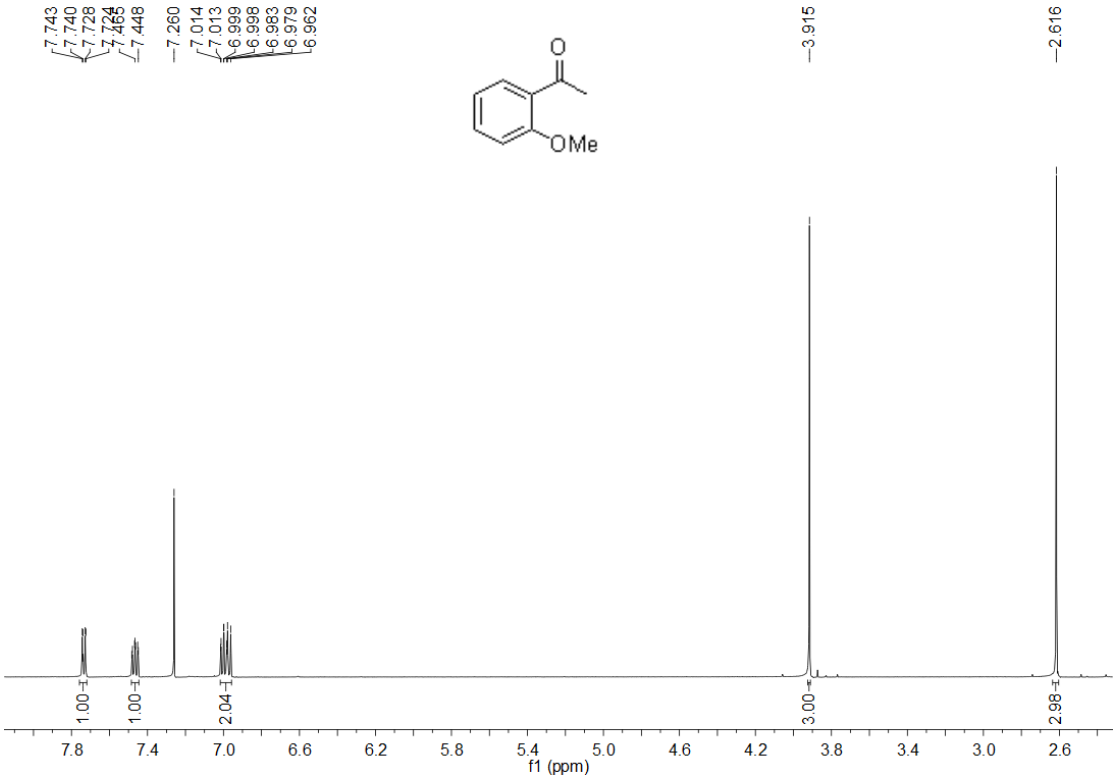


Fig. S29 ^{1}H NMR spectrum of **4d** (500 MHz, $CDCl_3$)

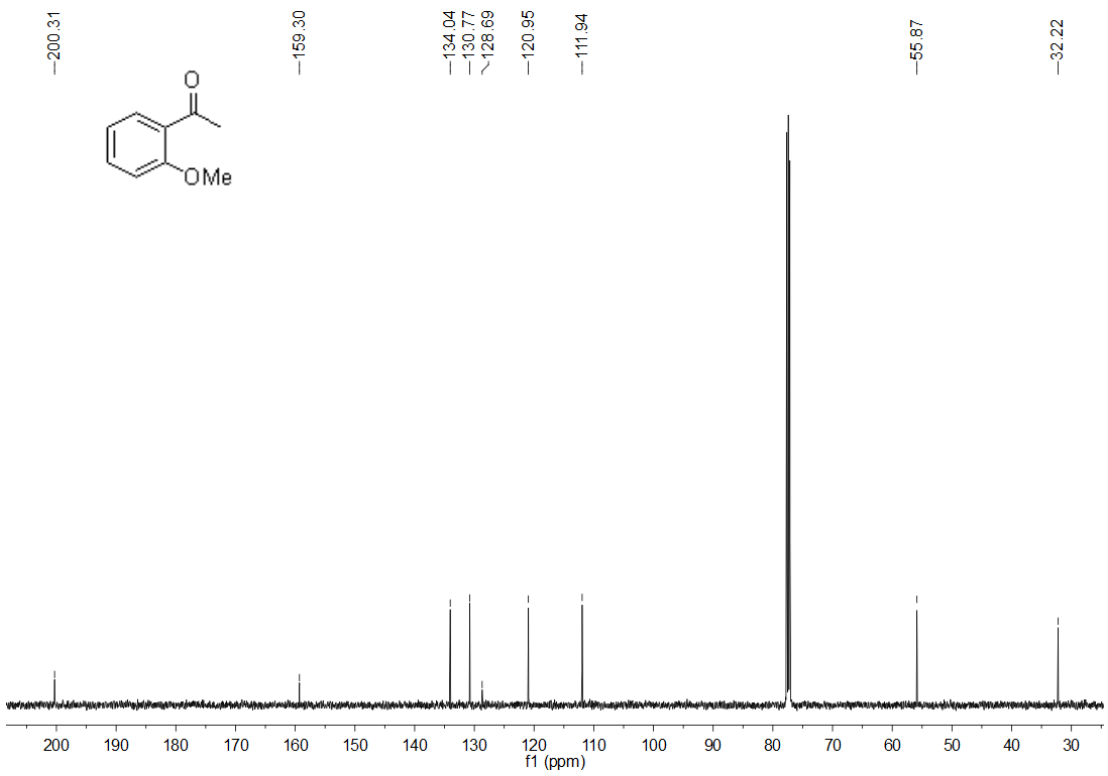


Fig. S30 $^{13}C\{^{1}H\}$ NMR spectrum of **4d** (125 MHz, $CDCl_3$)

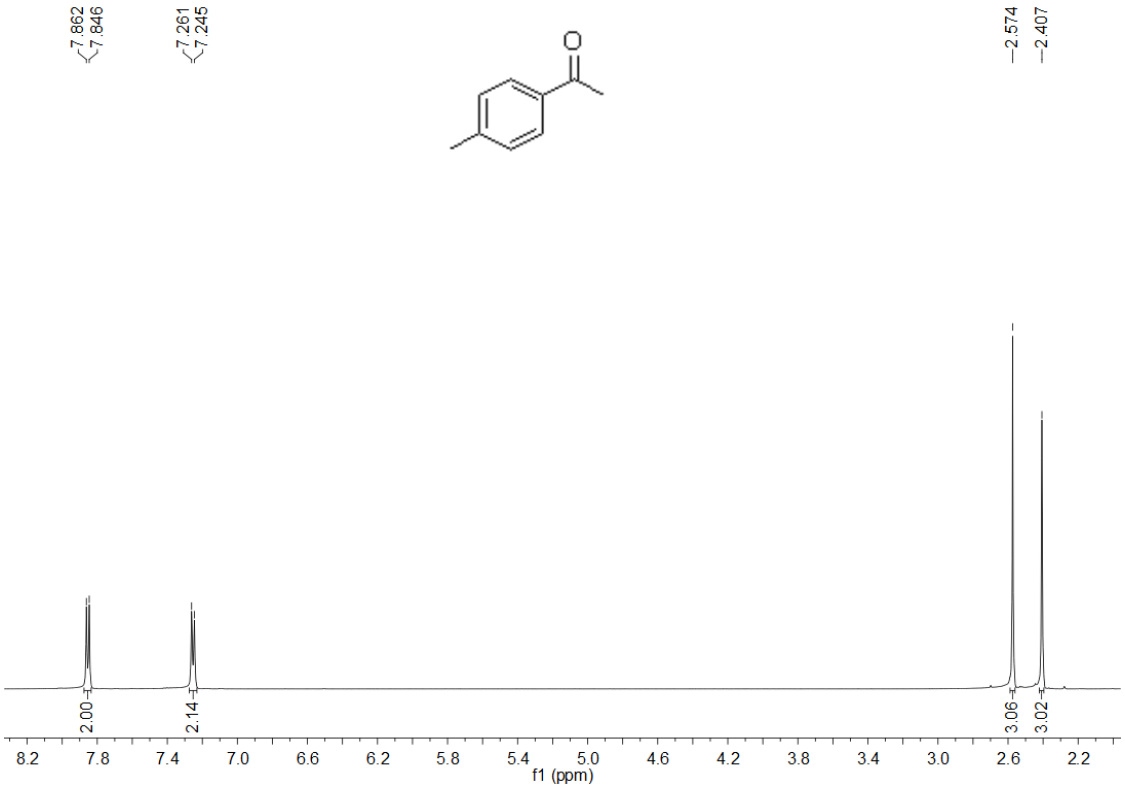


Fig. S31 ^{1}H NMR spectrum of **4e** (500 MHz, $CDCl_3$)

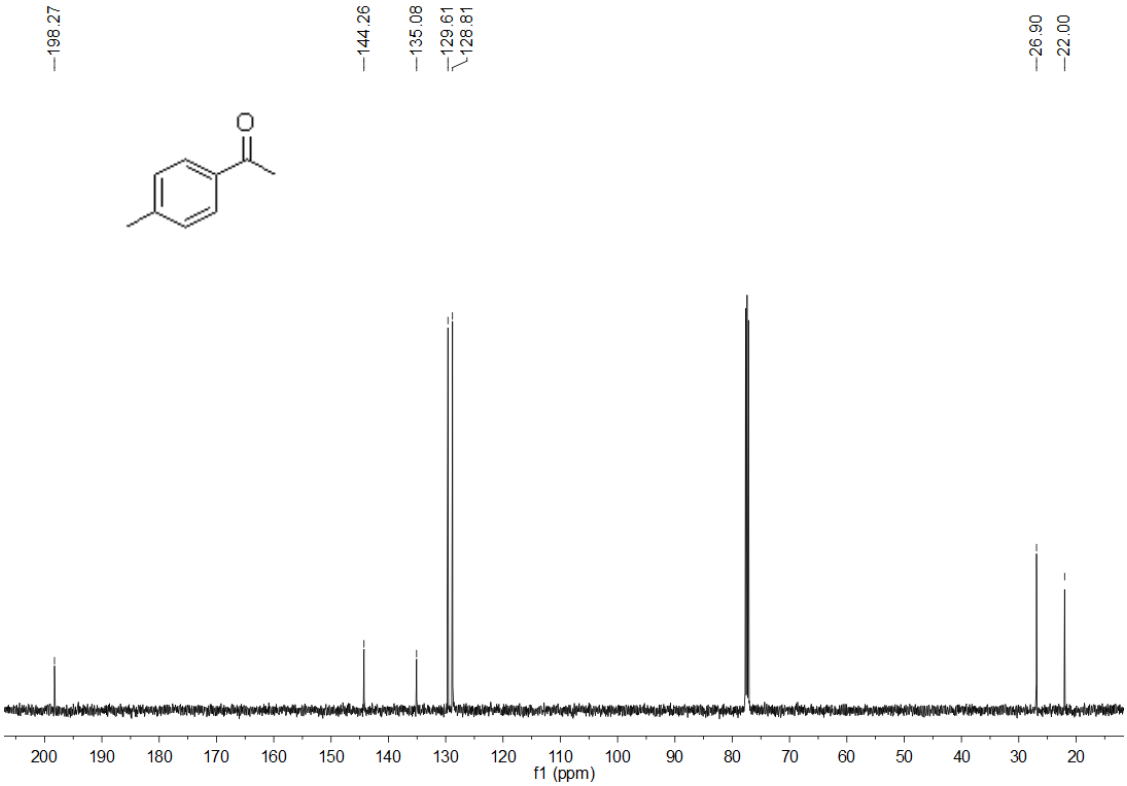


Fig. S32 $^{13}C\{^{1}H\}$ NMR spectrum of **4e** (125 MHz, $CDCl_3$)

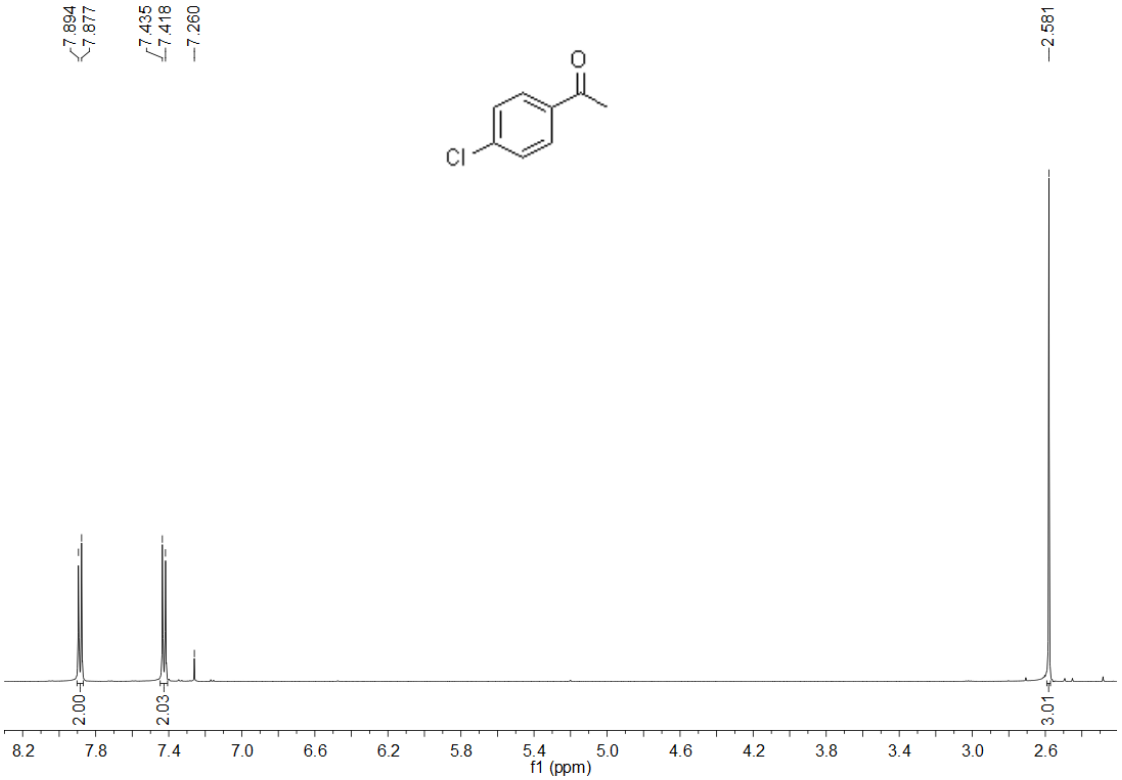


Fig. S33 ^{1}H NMR spectrum of **4f** (500 MHz, $CDCl_3$)

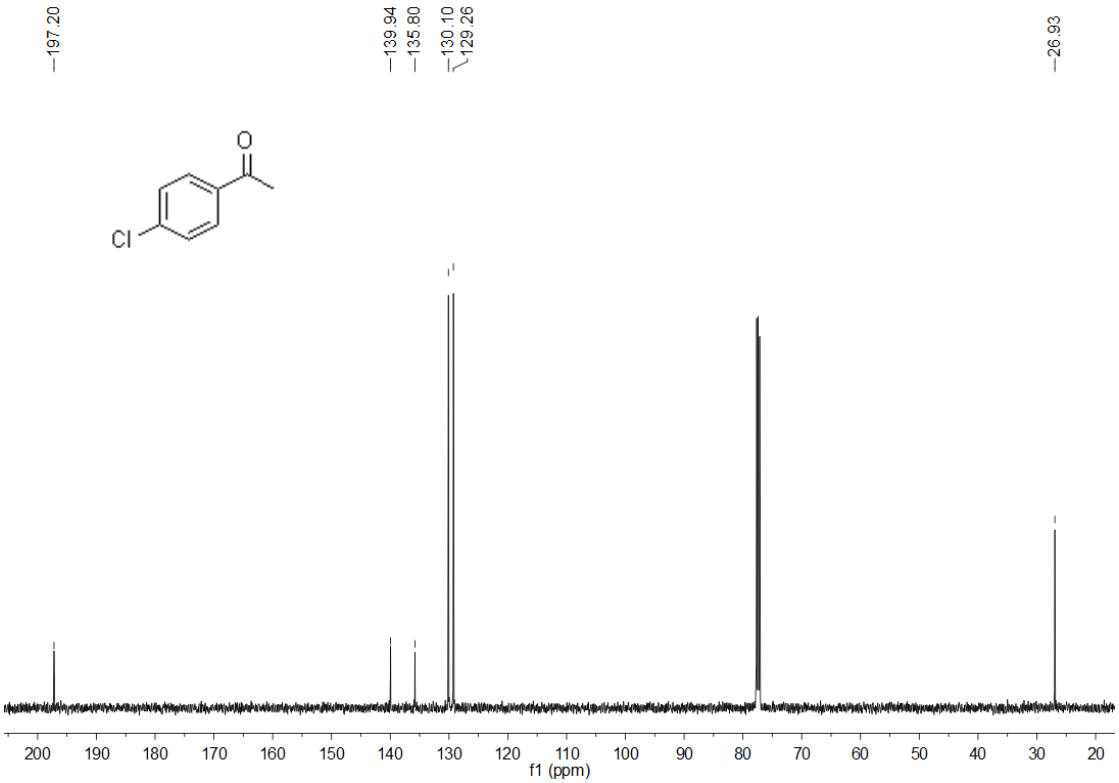


Fig. S34 $^{13}C\{^{1}H\}$ NMR spectrum of **4f** (125 MHz, $CDCl_3$)

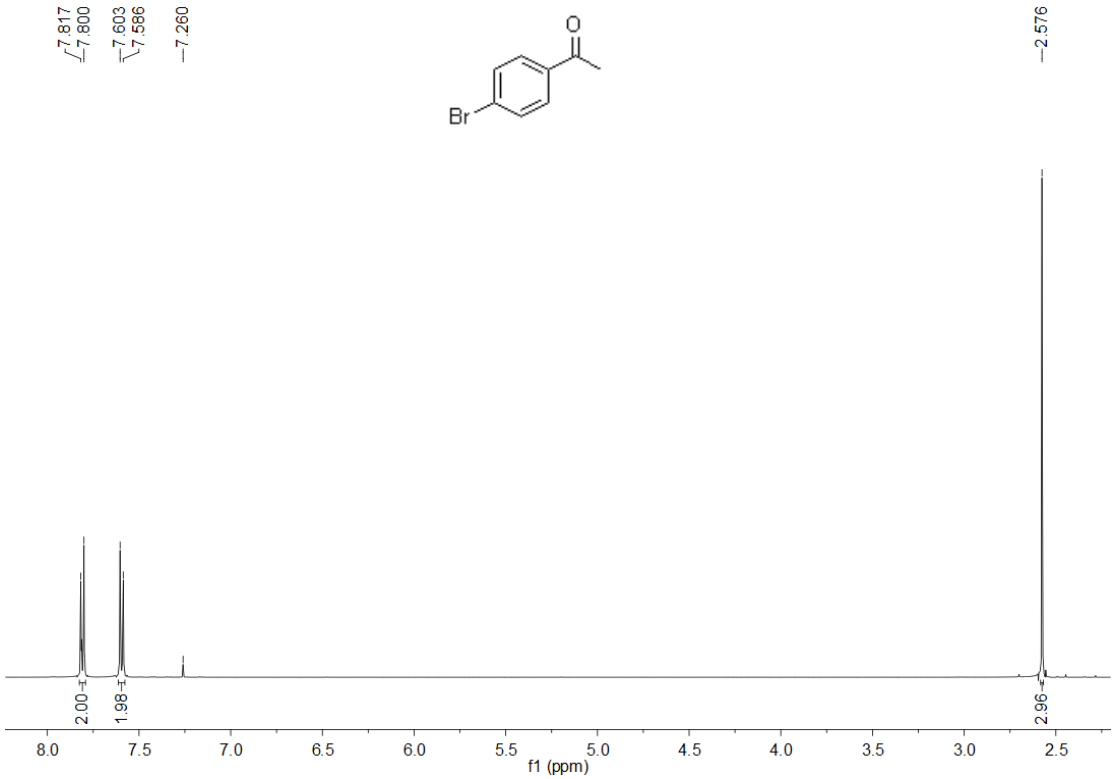


Fig. S35 ^{1}H NMR spectrum of **4g** (500 MHz, $CDCl_3$)

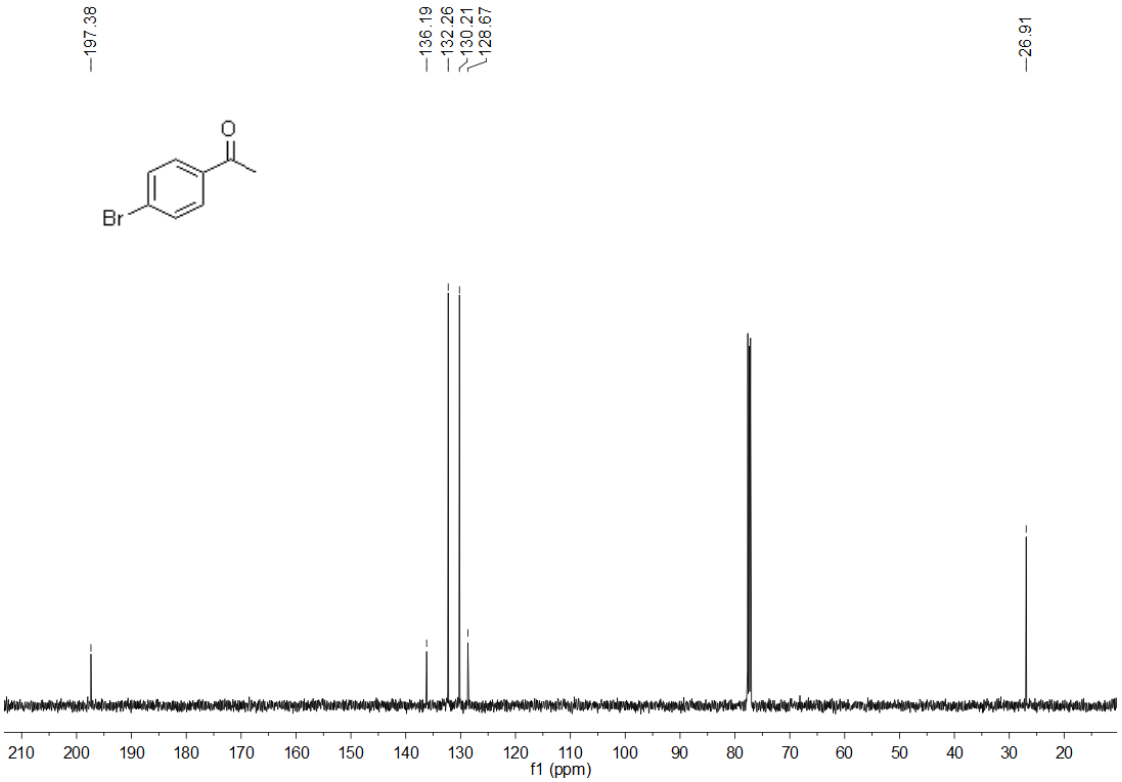


Fig. S36 $^{13}C\{^{1}H\}$ NMR spectrum of **4g** (125 MHz, $CDCl_3$)

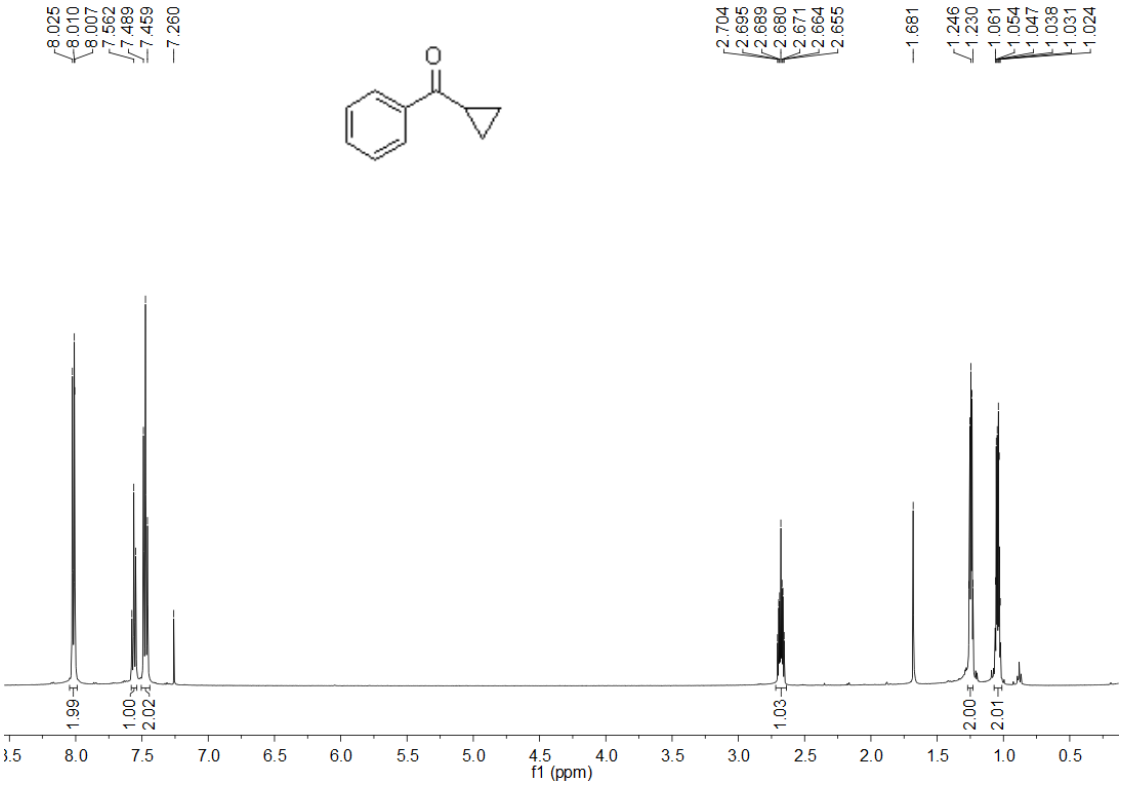


Fig. S37 ^{1}H NMR spectrum of **4h** (500 MHz, $CDCl_3$)

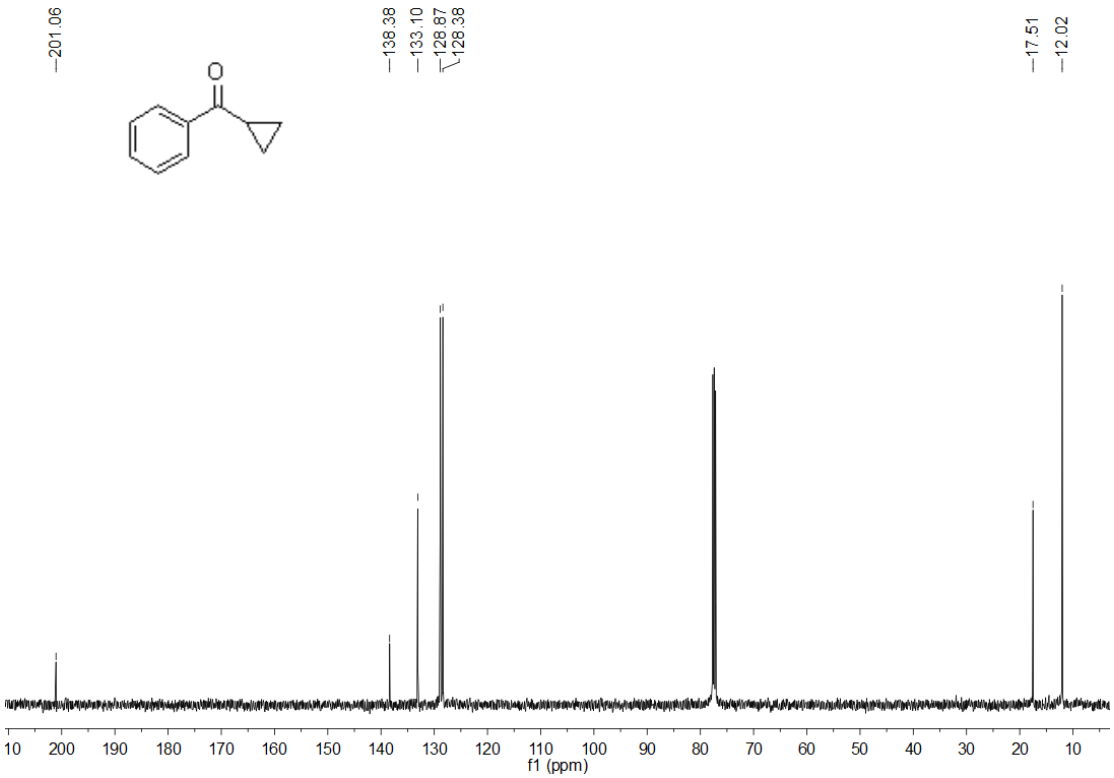


Fig. S38 $^{13}C\{^{1}H\}$ NMR spectrum of **4h** (125 MHz, $CDCl_3$)

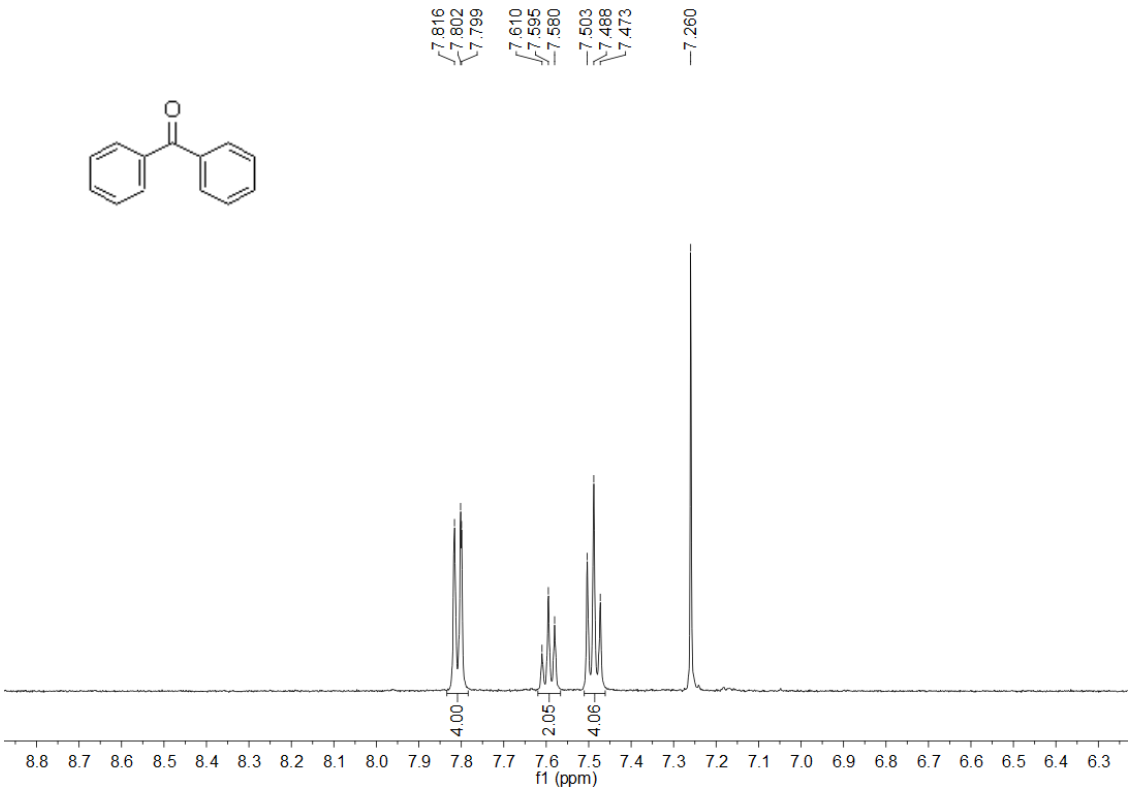


Fig. S39 ^{1}H NMR spectrum of **4i** (500 MHz, $CDCl_3$)

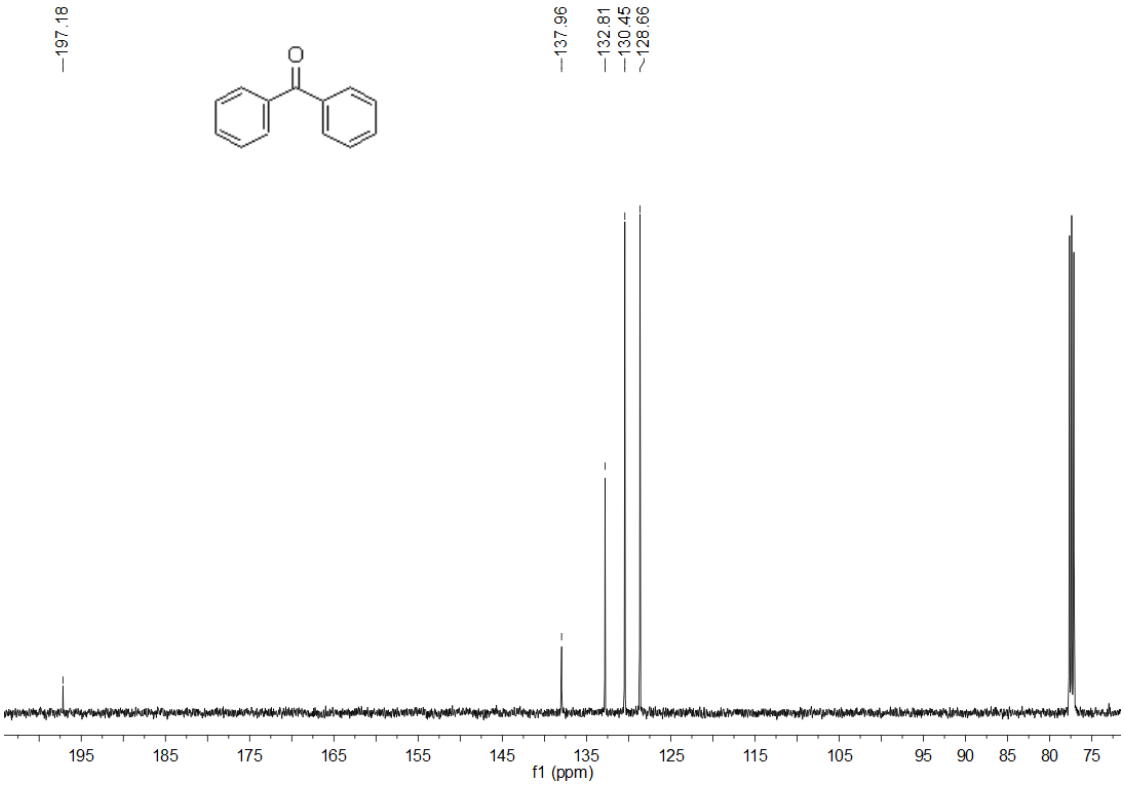


Fig. S40 $^{13}C\{^{1}H\}$ NMR spectrum of **4i** (125 MHz, $CDCl_3$)

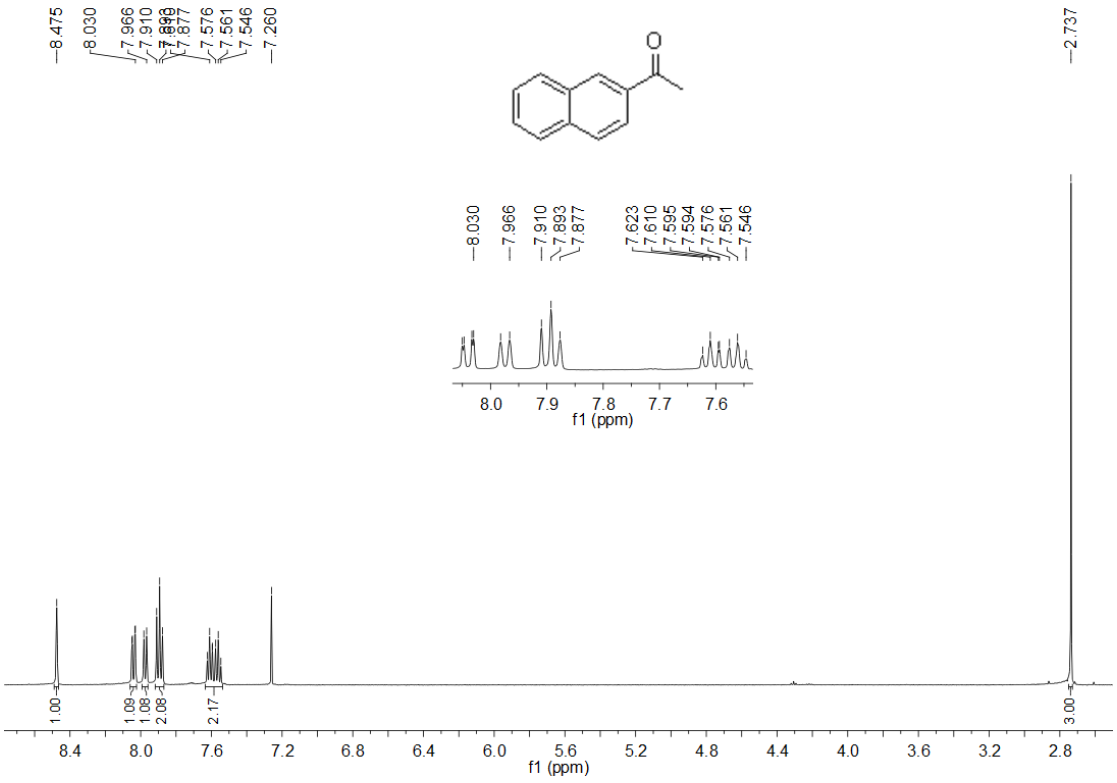


Fig. S41 ^{1}H NMR spectrum of **4j** (500 MHz, $CDCl_3$)

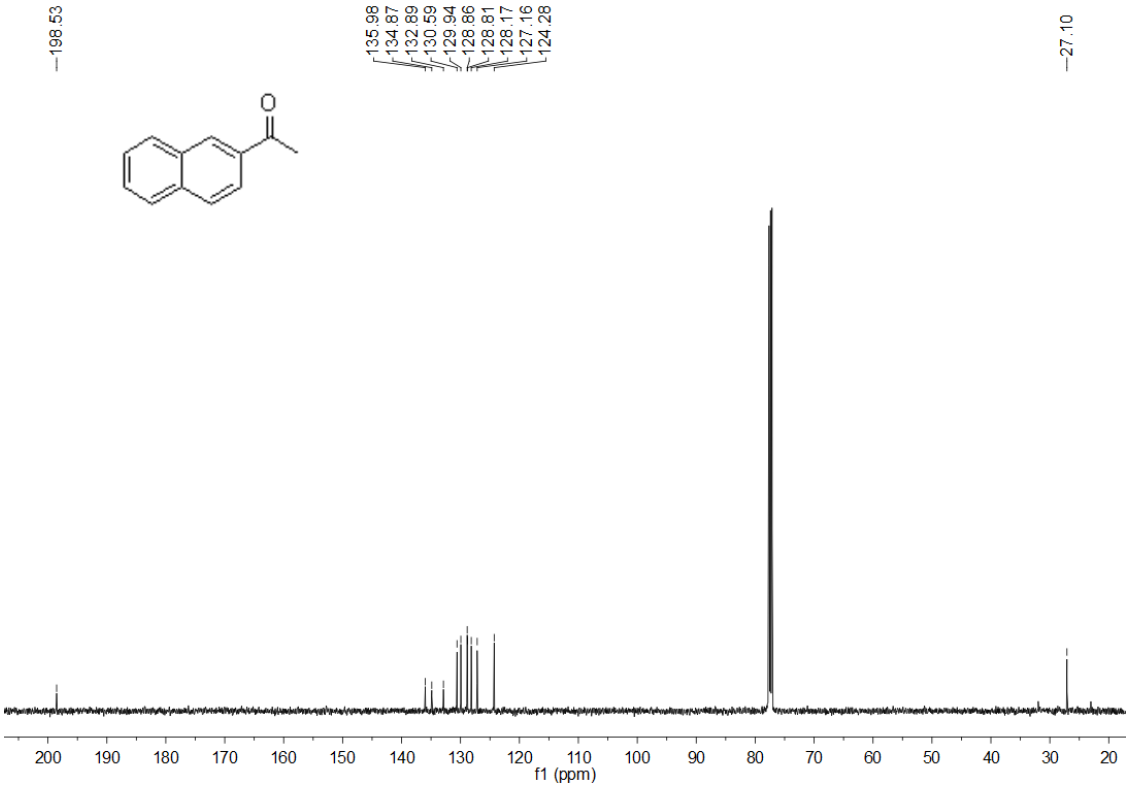


Fig. S42 $^{13}C\{^{1}H\}$ NMR spectrum of **4j** (125 MHz, $CDCl_3$)

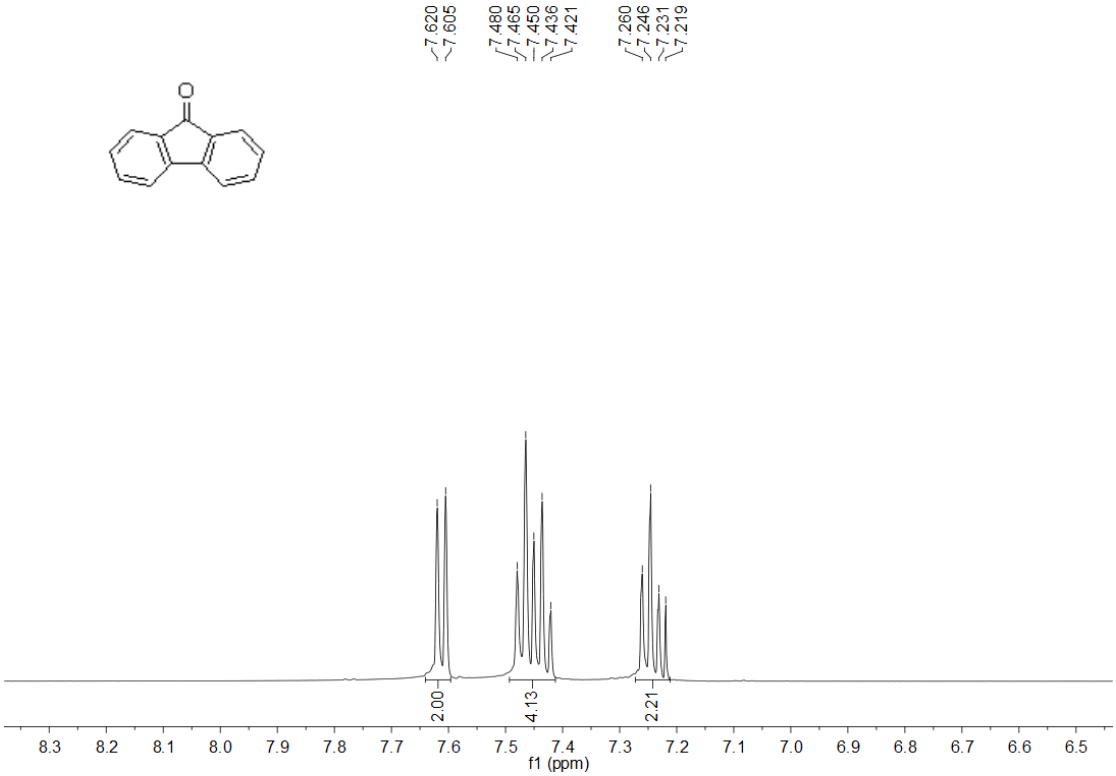


Fig. S43 ^{1}H NMR spectrum of **4k** (500 MHz, $CDCl_3$)

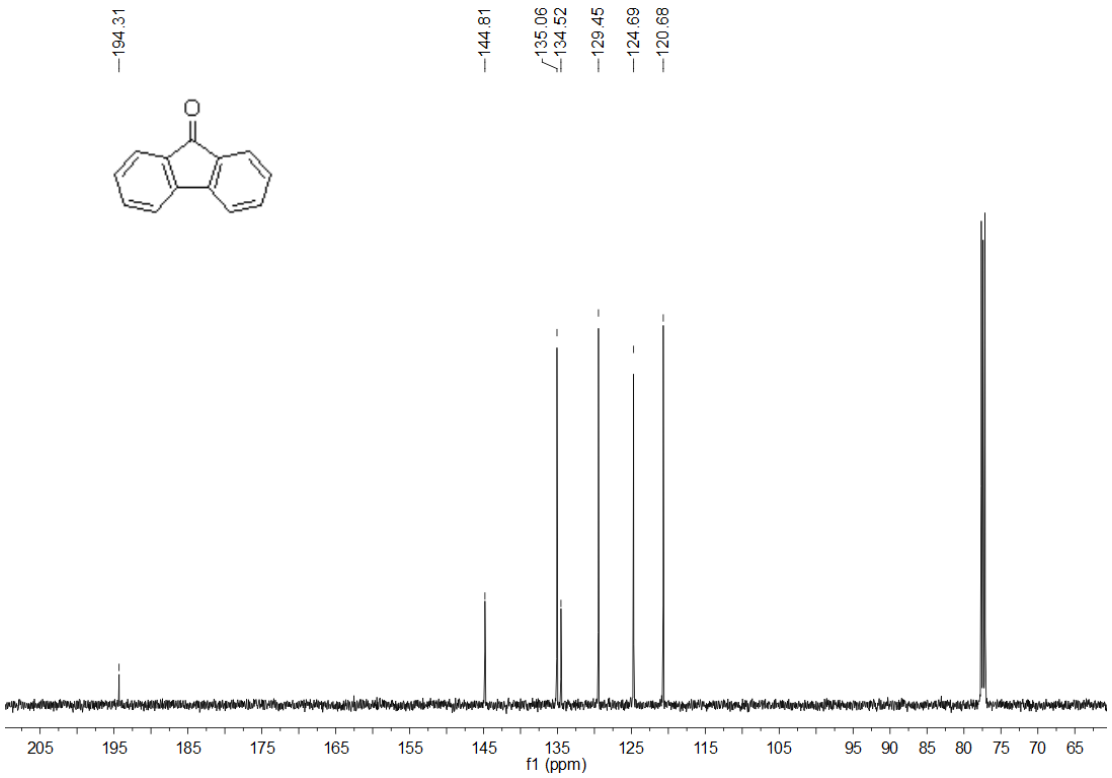


Fig. S44 $^{13}C\{^{1}H\}$ NMR spectrum of **4k** (125 MHz, $CDCl_3$)

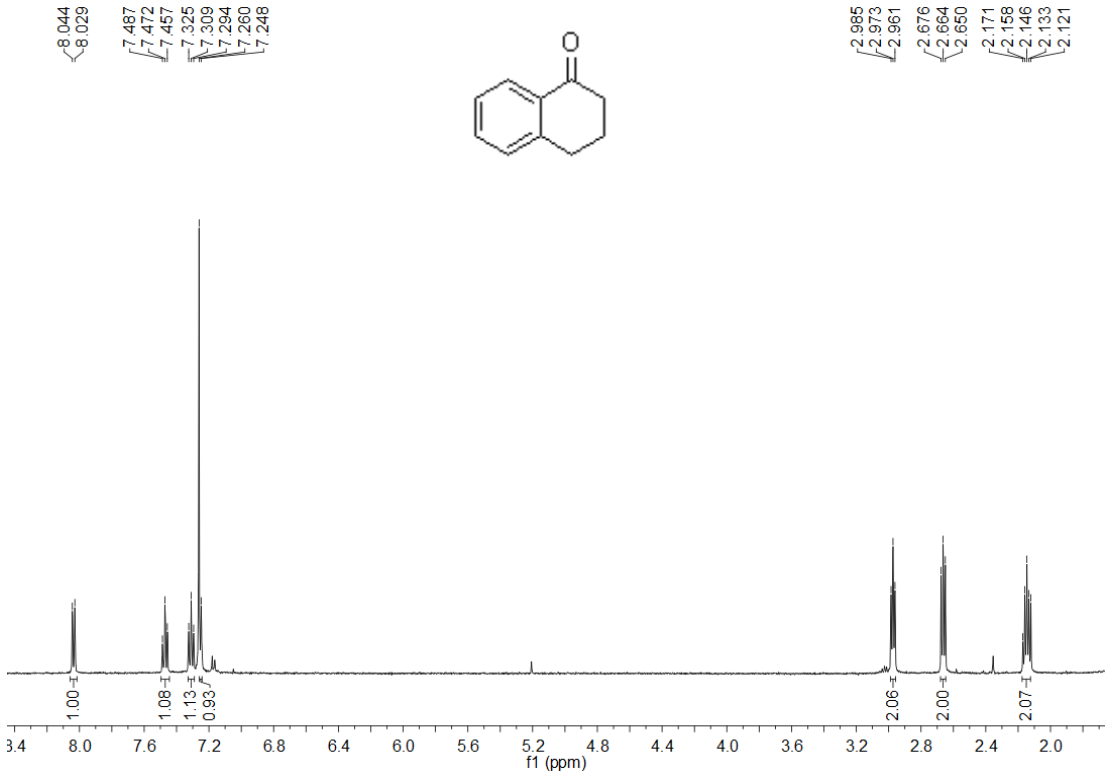


Fig. S45 ^{1}H NMR spectrum of **4l** (500 MHz, $CDCl_3$)

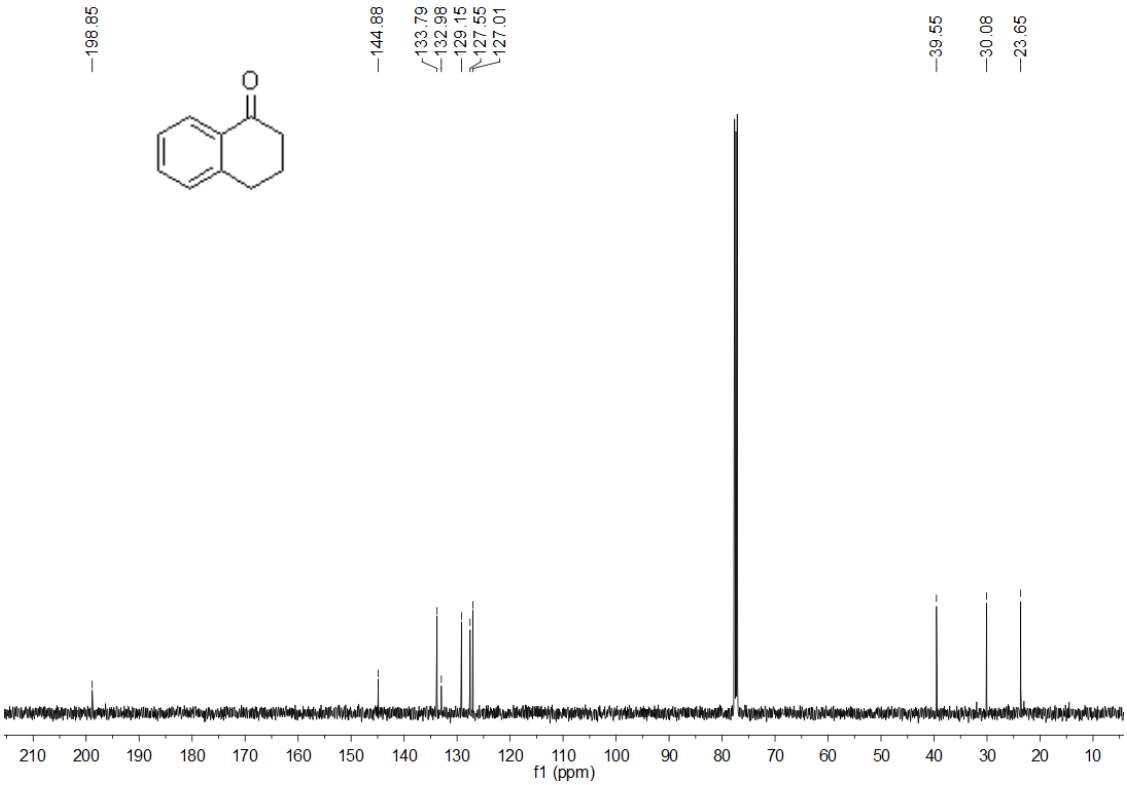


Fig. S46 $^{13}C\{^{1}H\}$ NMR spectrum of **4l** (125 MHz, $CDCl_3$)

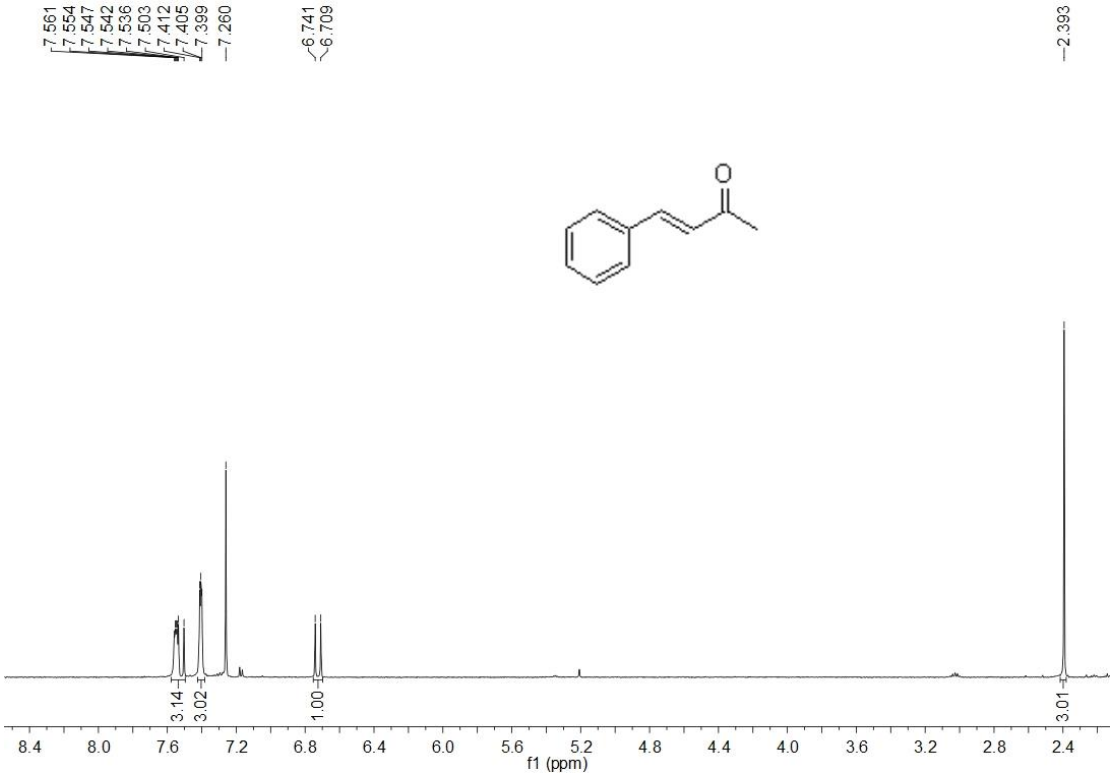


Fig. S47 ^{1}H NMR spectrum of **6a** (500 MHz, $CDCl_3$)

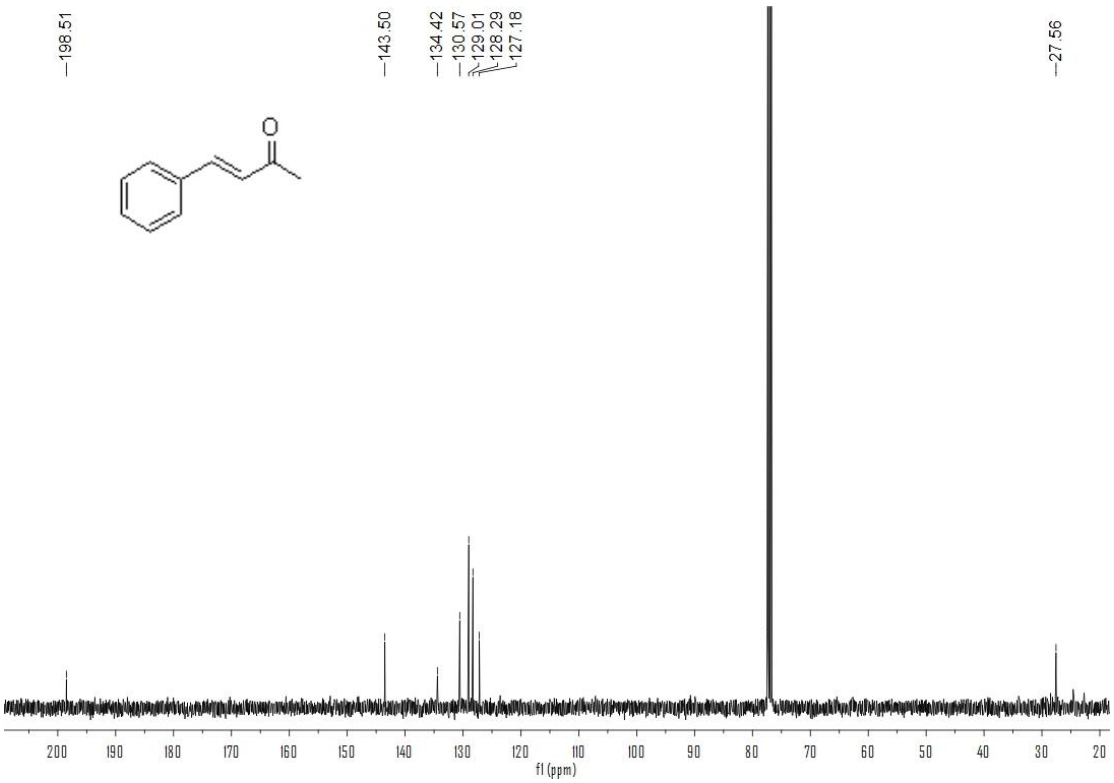


Fig. S48 $^{13}C\{^{1}H\}$ NMR spectrum of **6a** (125 MHz, $CDCl_3$)

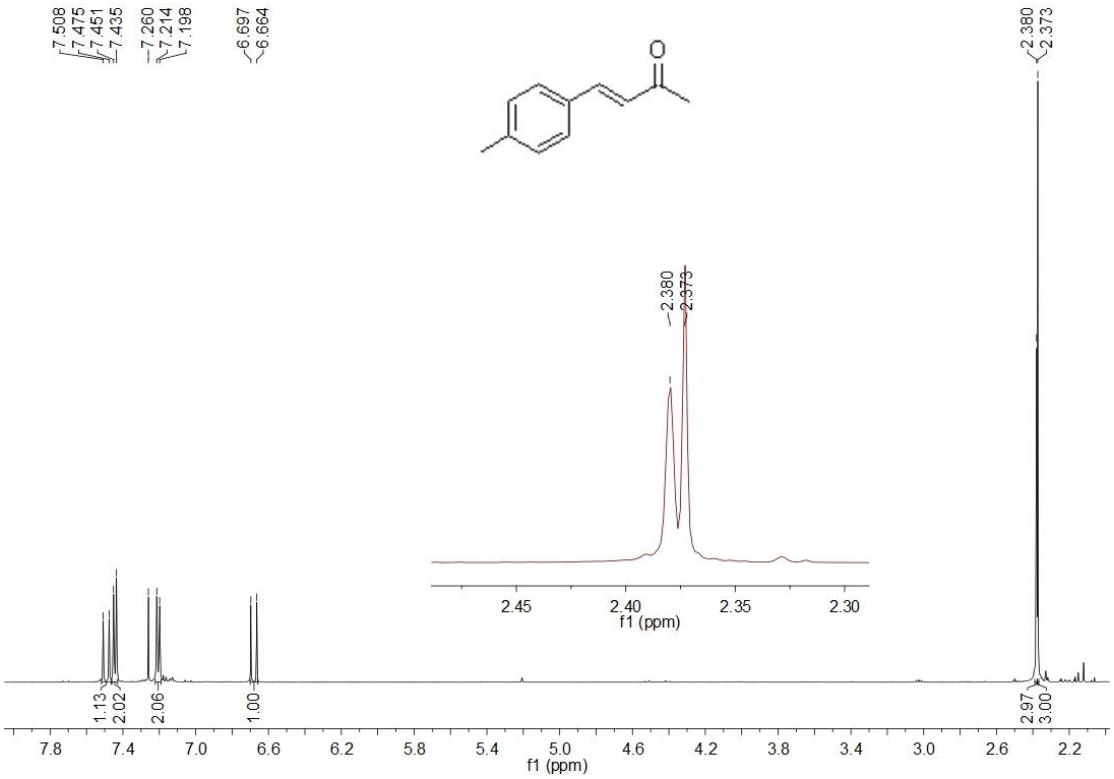


Fig. S49 ^{1}H NMR spectrum of **6b** (500 MHz, $CDCl_3$)

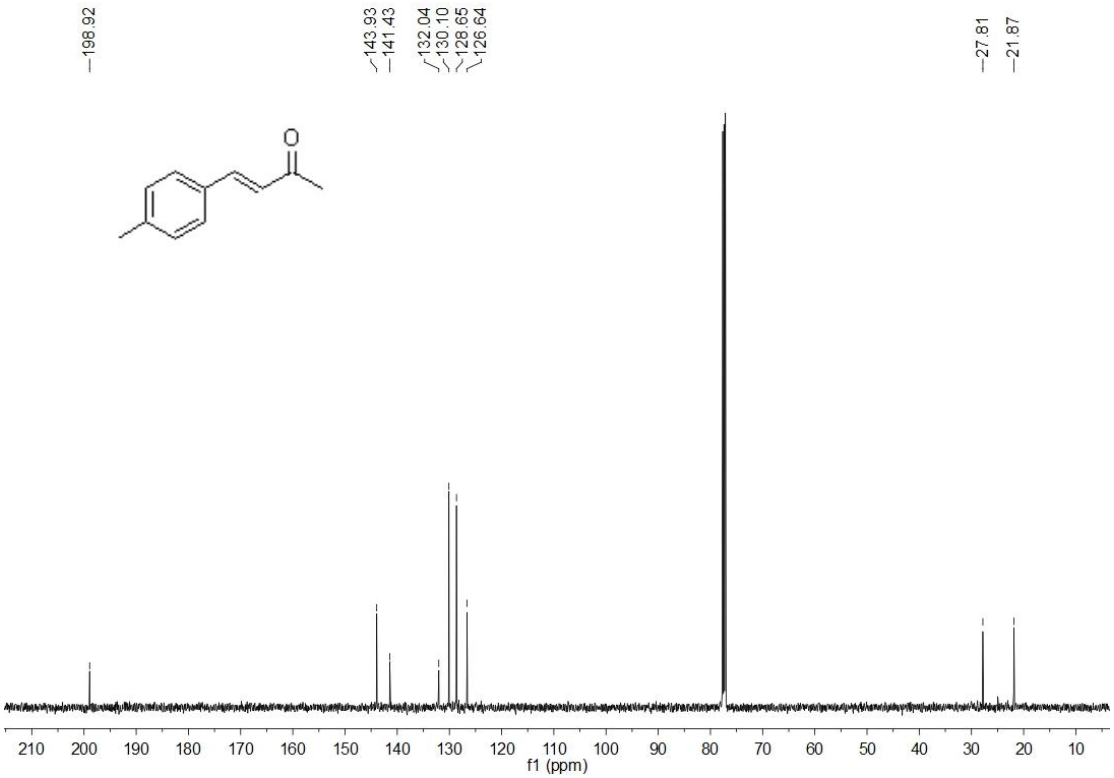


Fig. S50 $^{13}C\{^{1}H\}$ NMR spectrum of **6b** (125 MHz, $CDCl_3$)

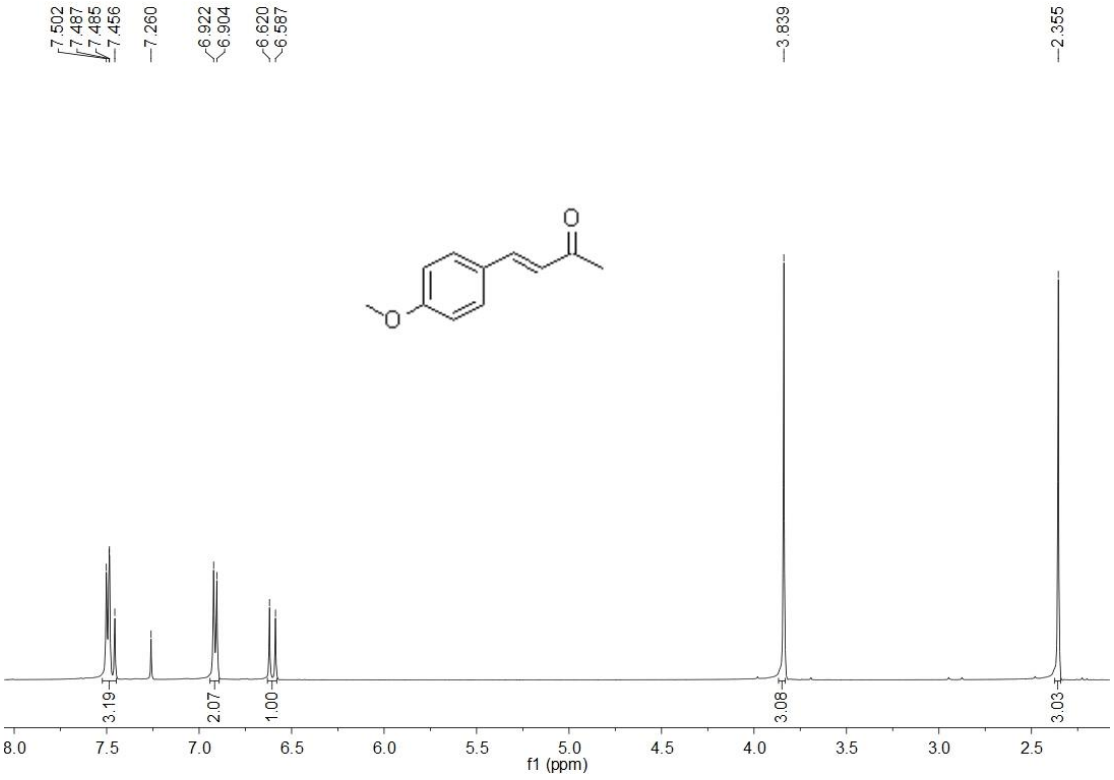


Fig. S51 ^{1}H NMR spectrum of **6c** (500 MHz, $CDCl_3$)

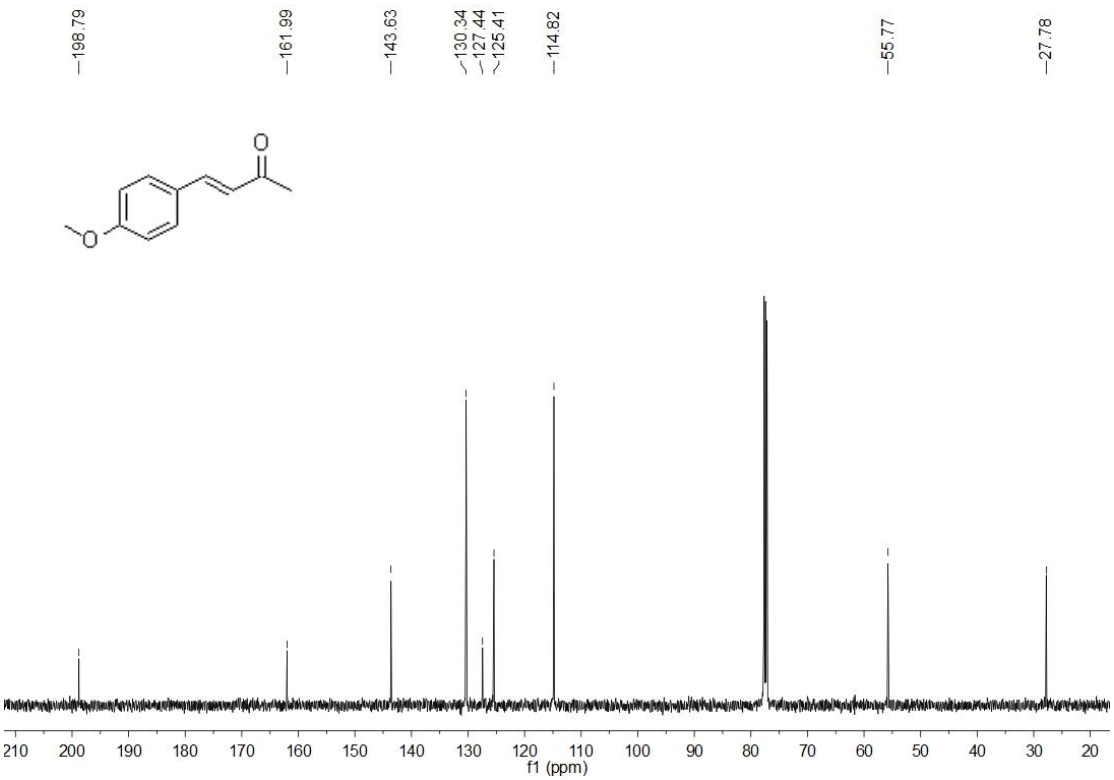


Fig. S52 $^{13}C\{^{1}H\}$ NMR spectrum of **6c** (125 MHz, $CDCl_3$)

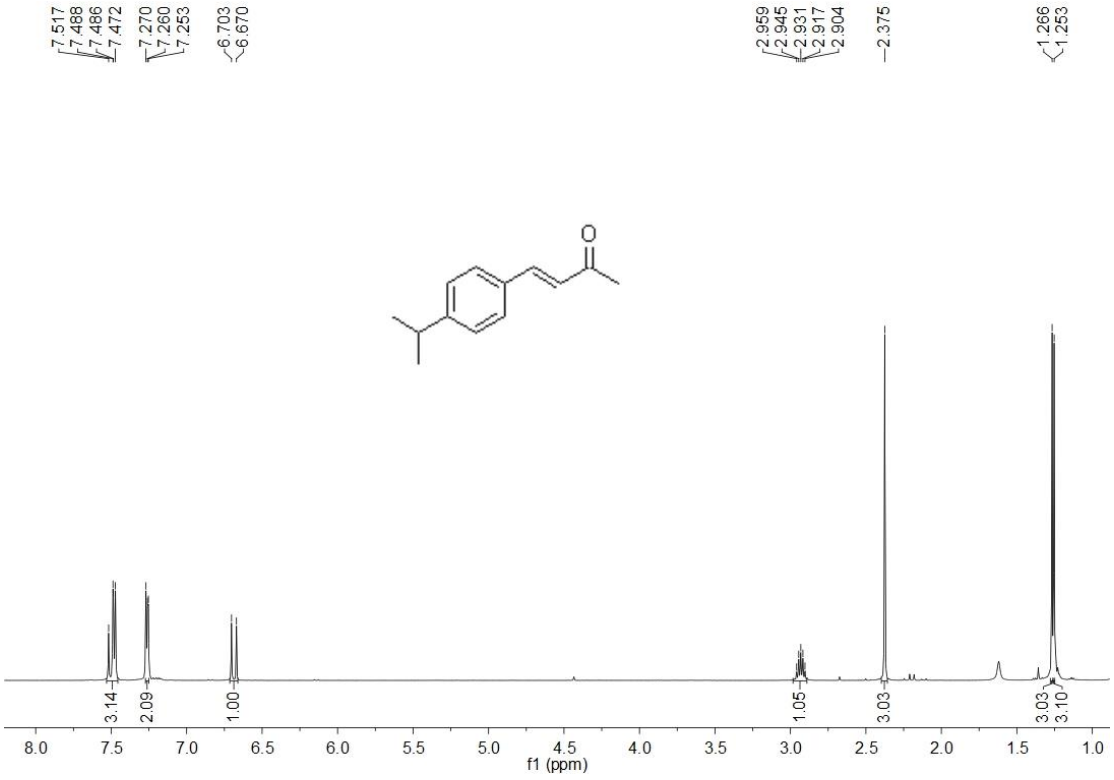


Fig. S53 ^{1}H NMR spectrum of **6d** (500 MHz, $CDCl_3$)

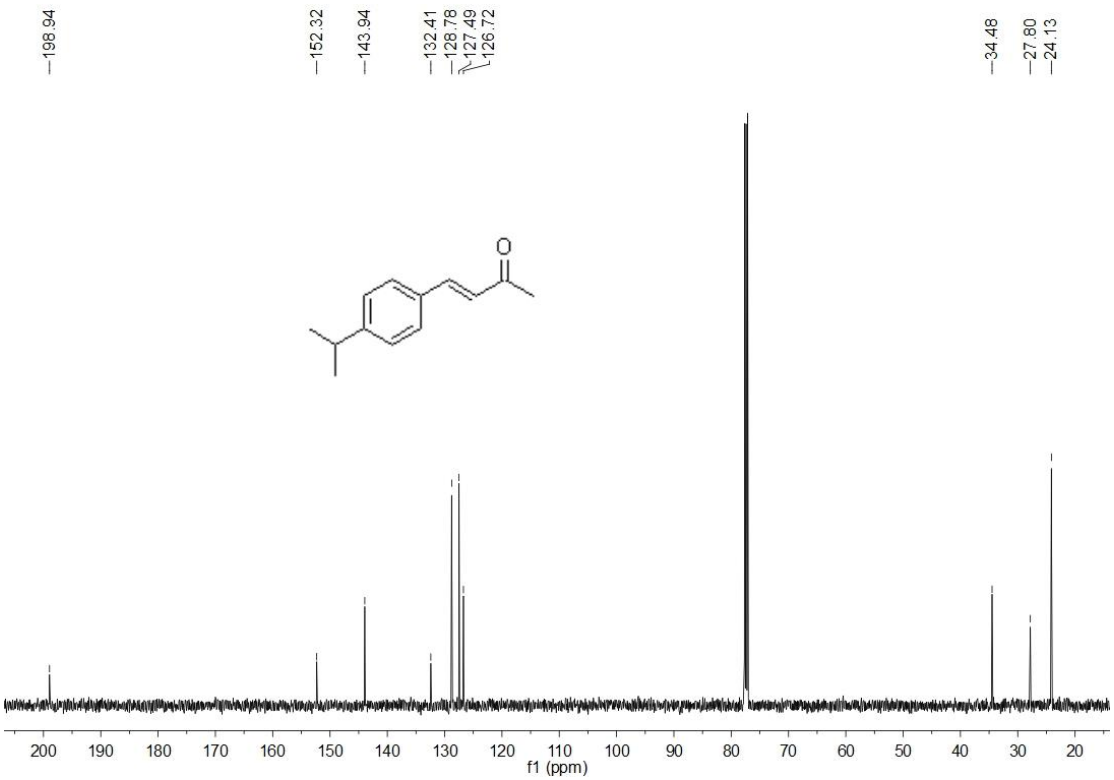


Fig. S54 $^{13}C\{^{1}H\}$ NMR spectrum of **6d** (125 MHz, $CDCl_3$)

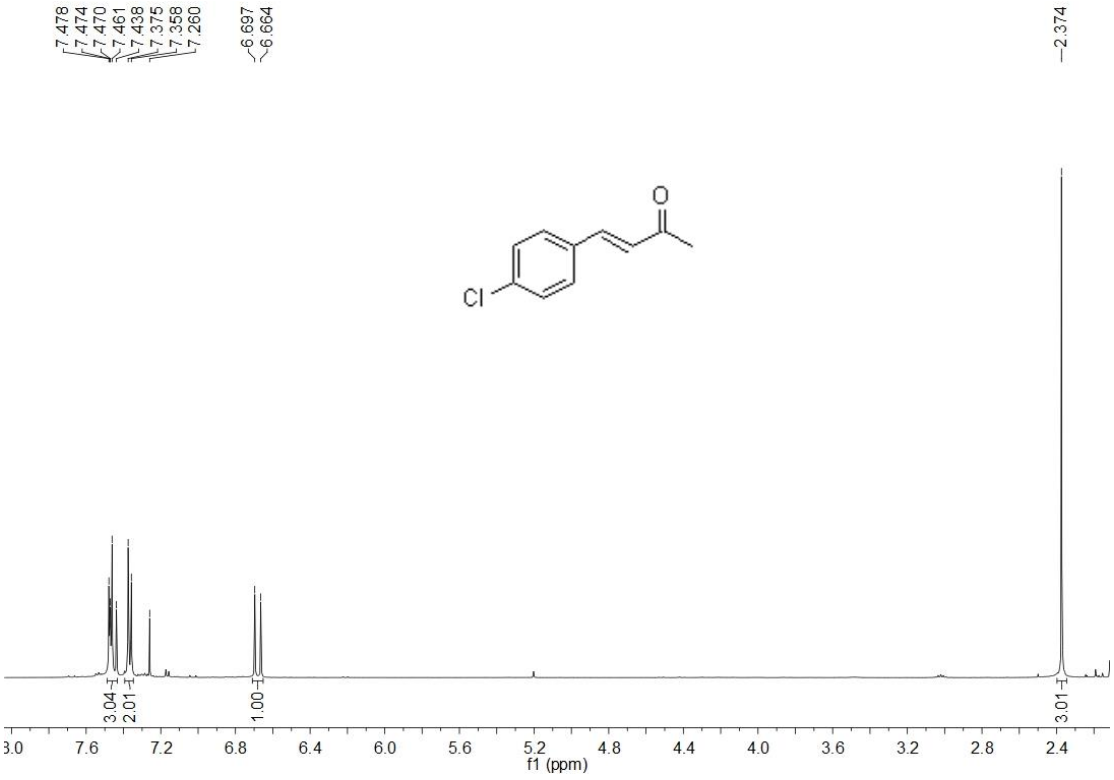


Fig. S55 ^{1}H NMR spectrum of **6e** (500 MHz, $CDCl_3$)

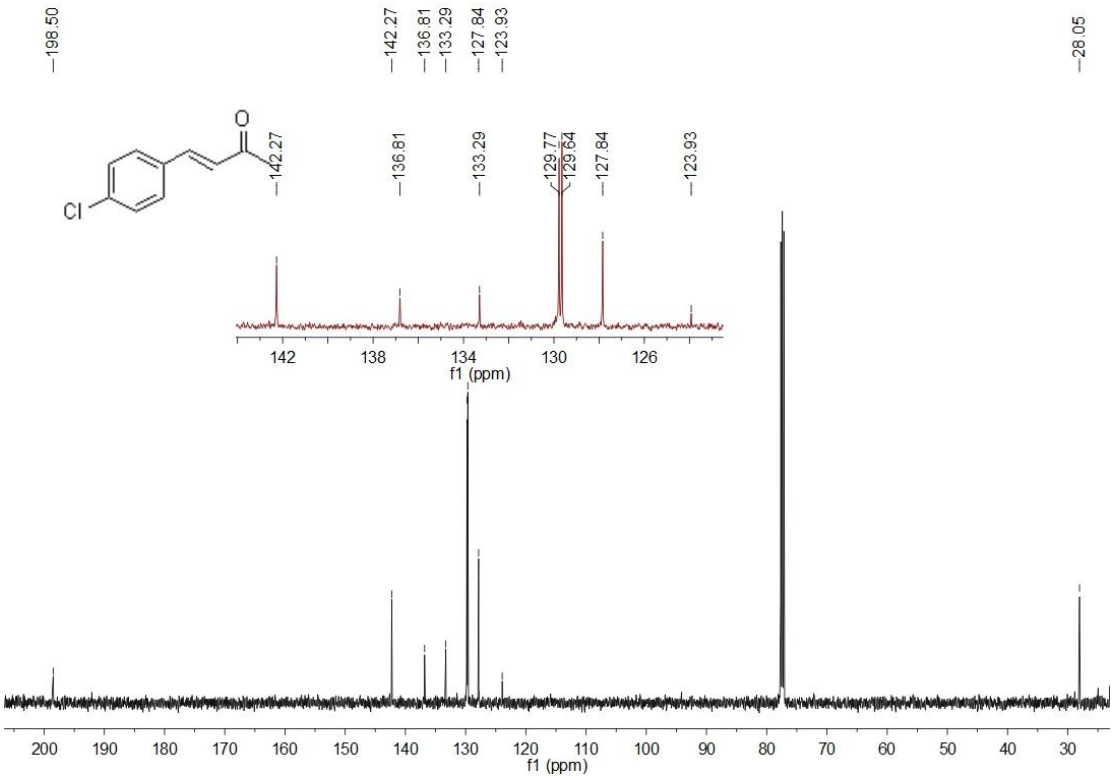


Fig. S56 $^{13}C\{^{1}H\}$ NMR spectrum of **6e** (125 MHz, $CDCl_3$)

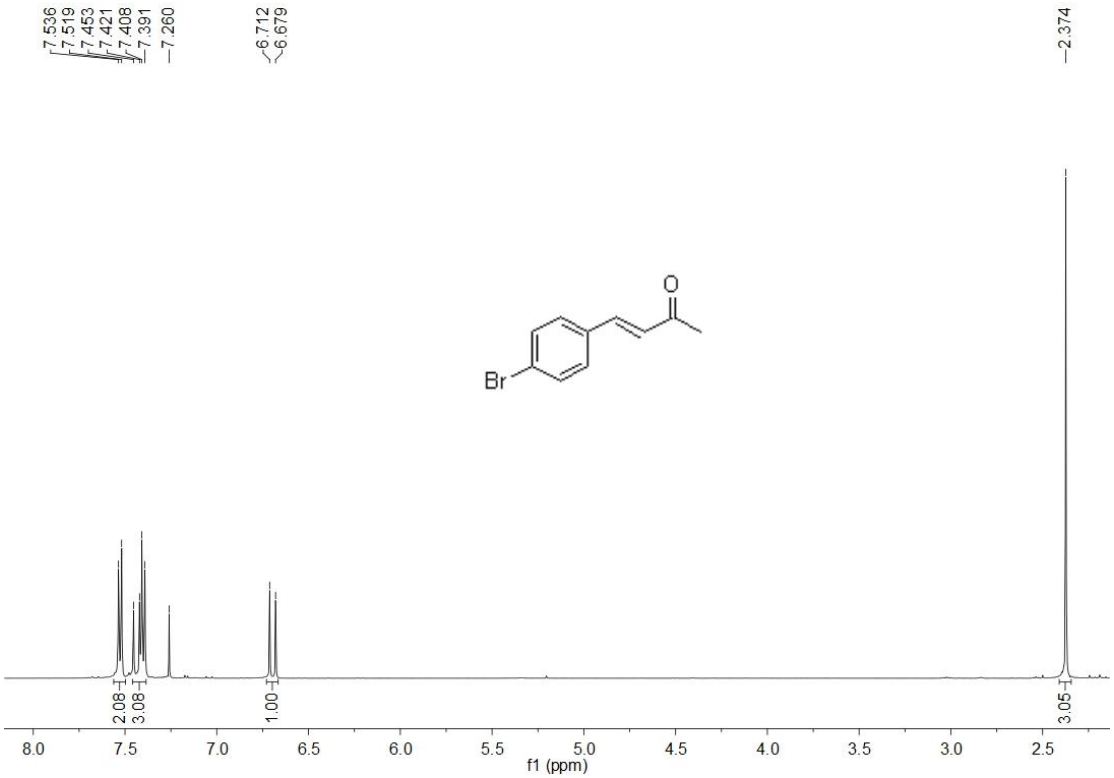


Fig. S57 ^{1}H NMR spectrum of **6f** (500 MHz, $CDCl_3$)

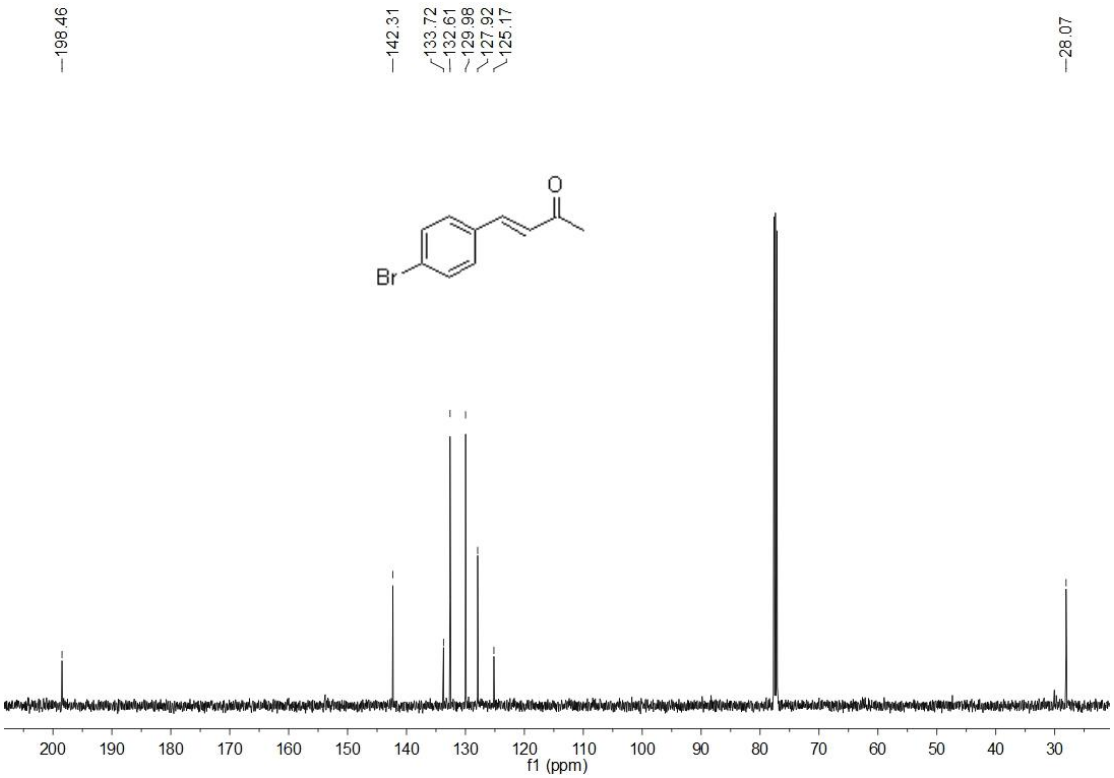


Fig. S58 $^{13}C\{^{1}H\}$ NMR spectrum of **6f** (125 MHz, $CDCl_3$)

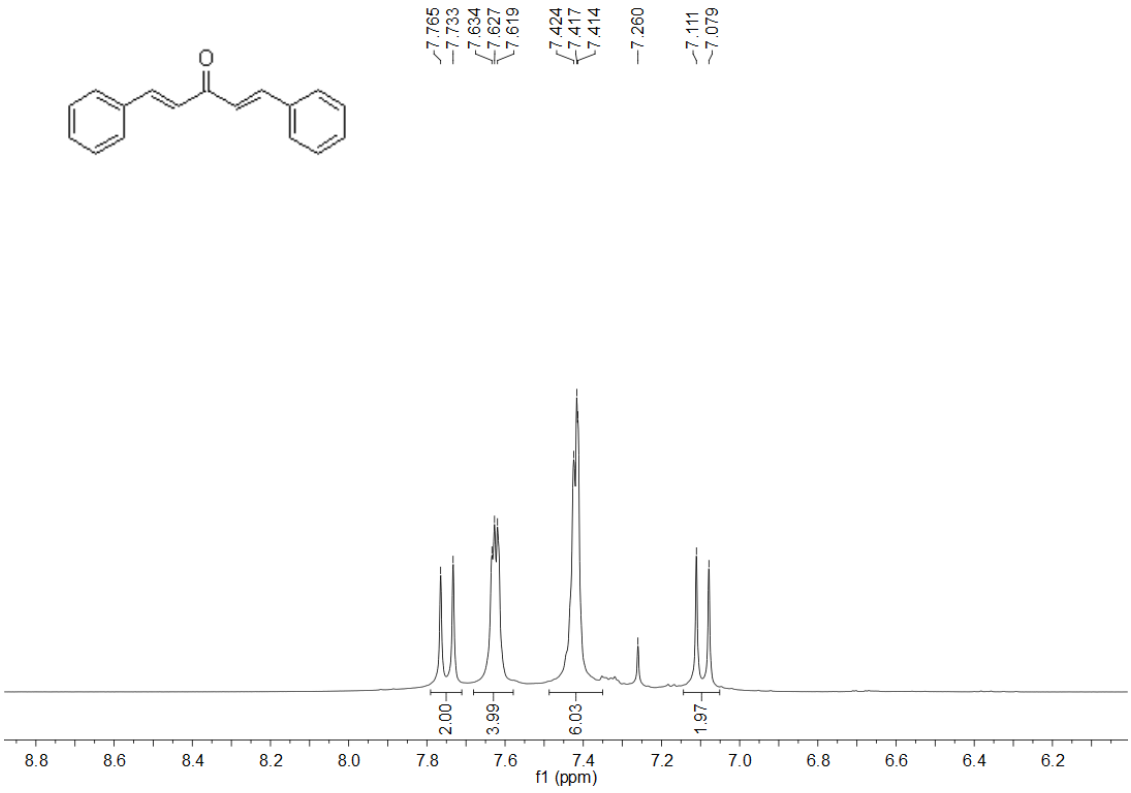


Fig. S59 ^{1}H NMR spectrum of **7aa** (500 MHz, $CDCl_3$)

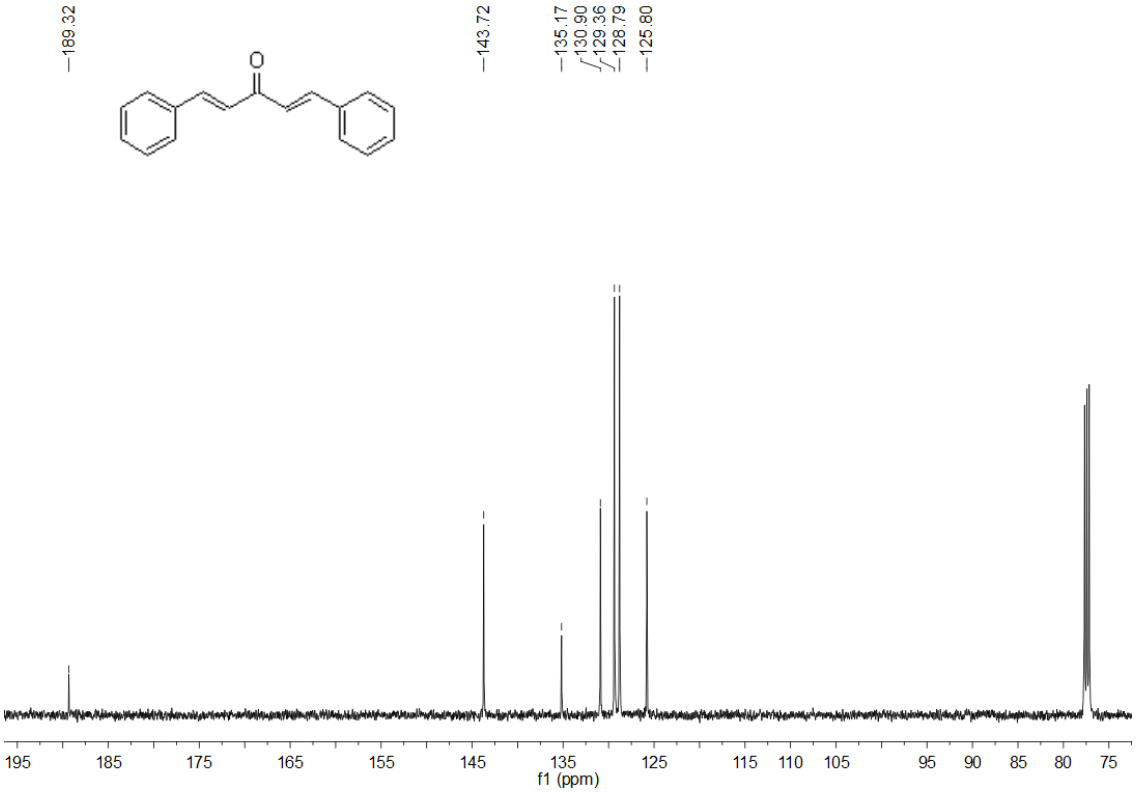


Fig. S60 $^{13}C\{^{1}H\}$ NMR spectrum of **7aa** (125 MHz, $CDCl_3$)

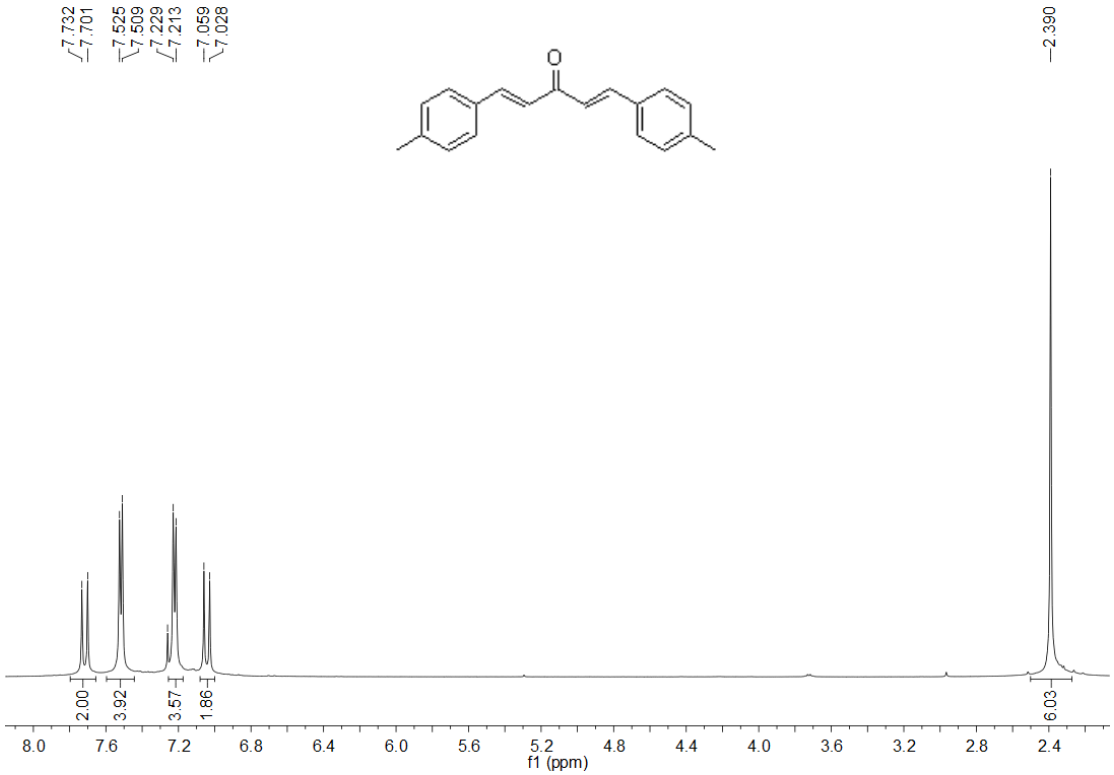


Fig. S61 ^{1}H NMR spectrum of **7bb** (500 MHz, $CDCl_3$)

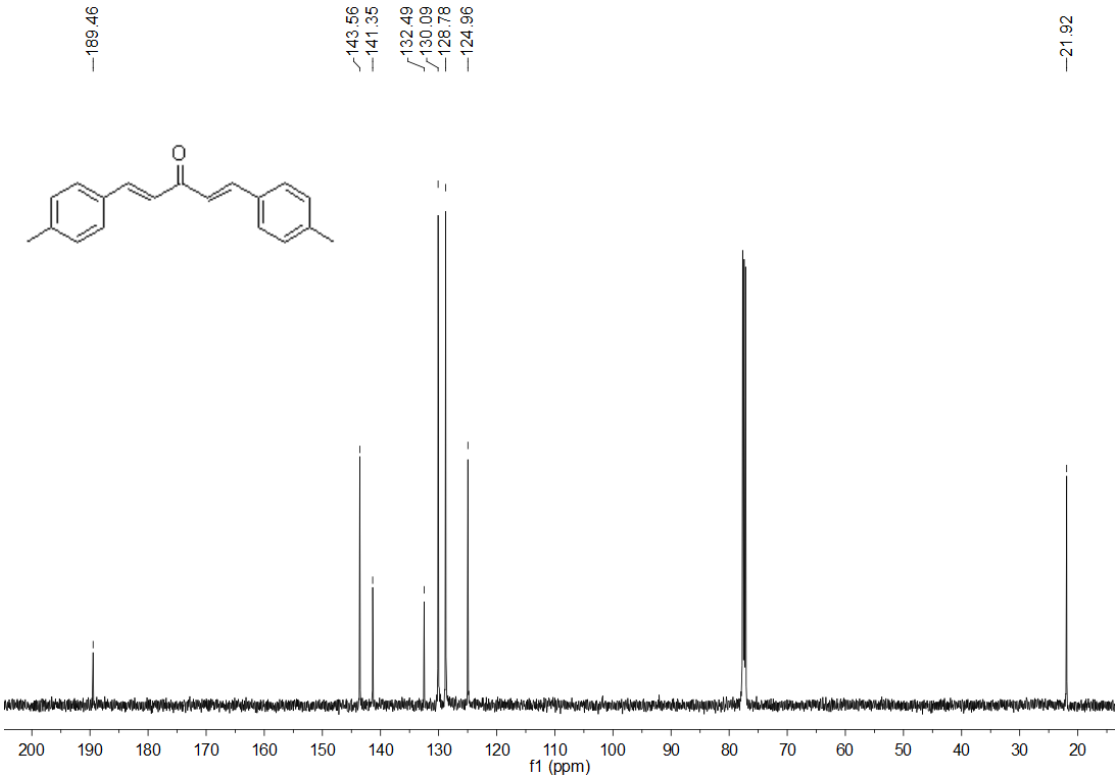


Fig. S62 $^{13}C\{^{1}H\}$ NMR spectrum of **7bb** (125 MHz, $CDCl_3$)

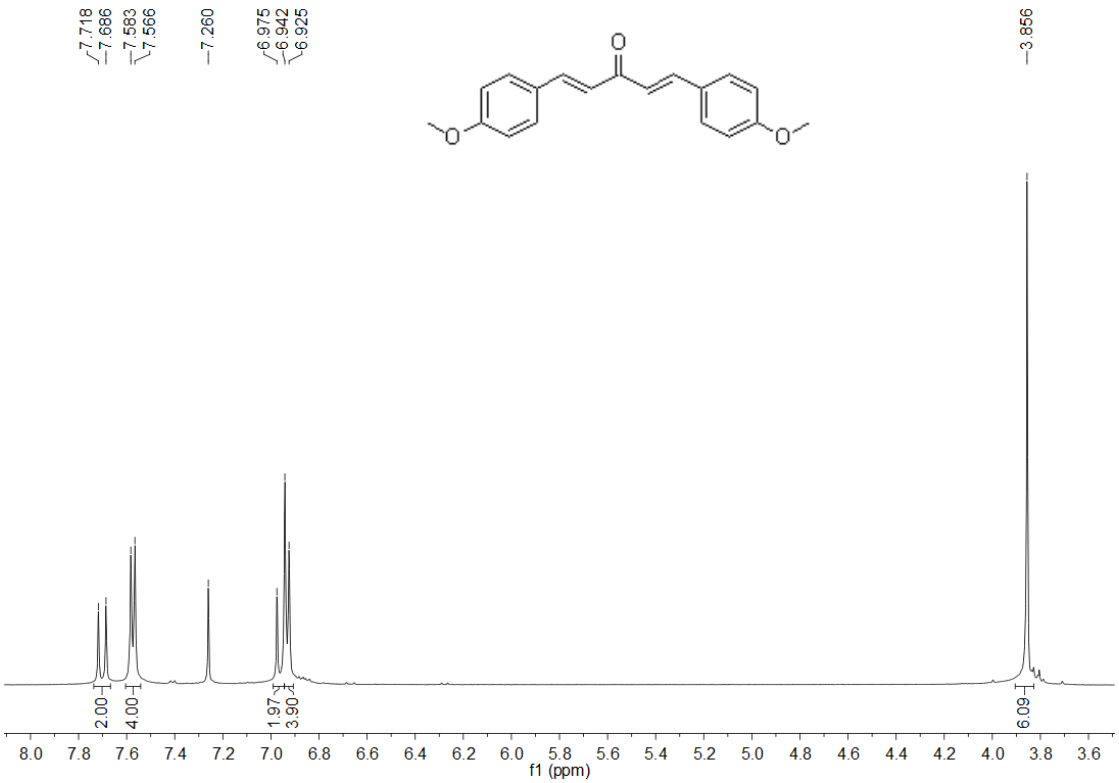


Fig. S63 ^{1}H NMR spectrum of **7cc** (500 MHz, $CDCl_3$)

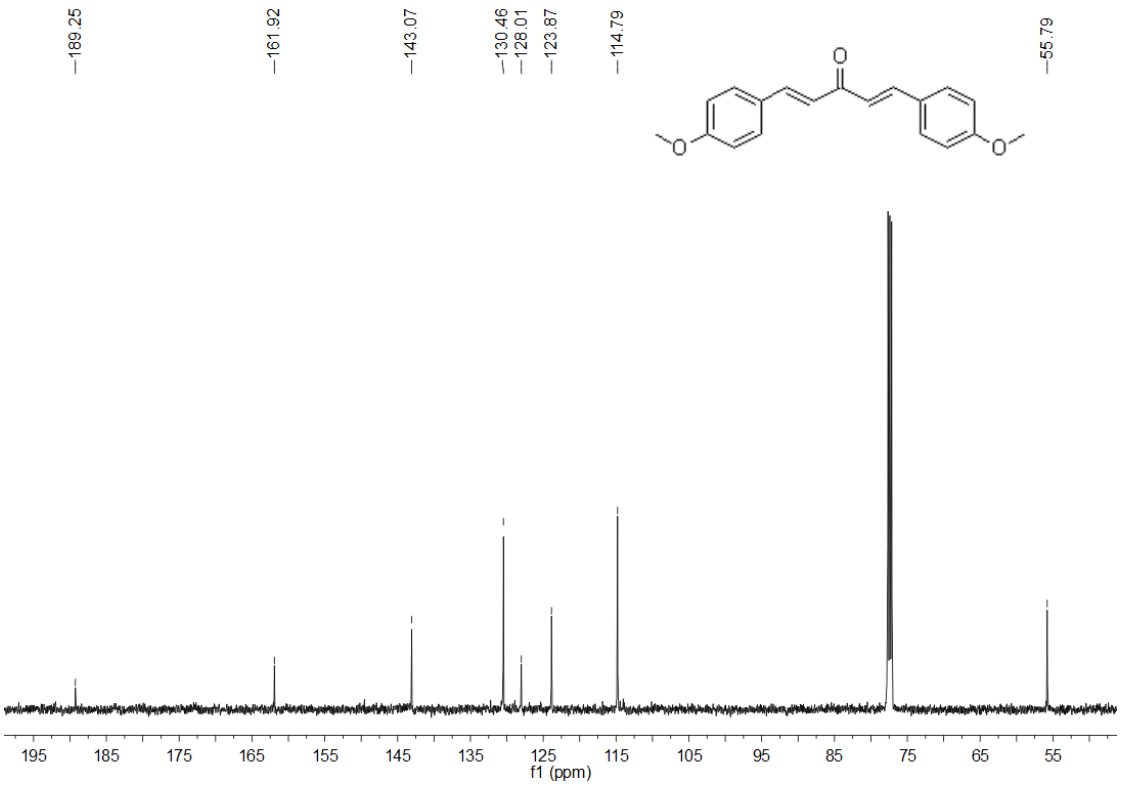


Fig. S64 $^{13}C\{^{1}H\}$ NMR spectrum of **7cc** (125 MHz, $CDCl_3$)

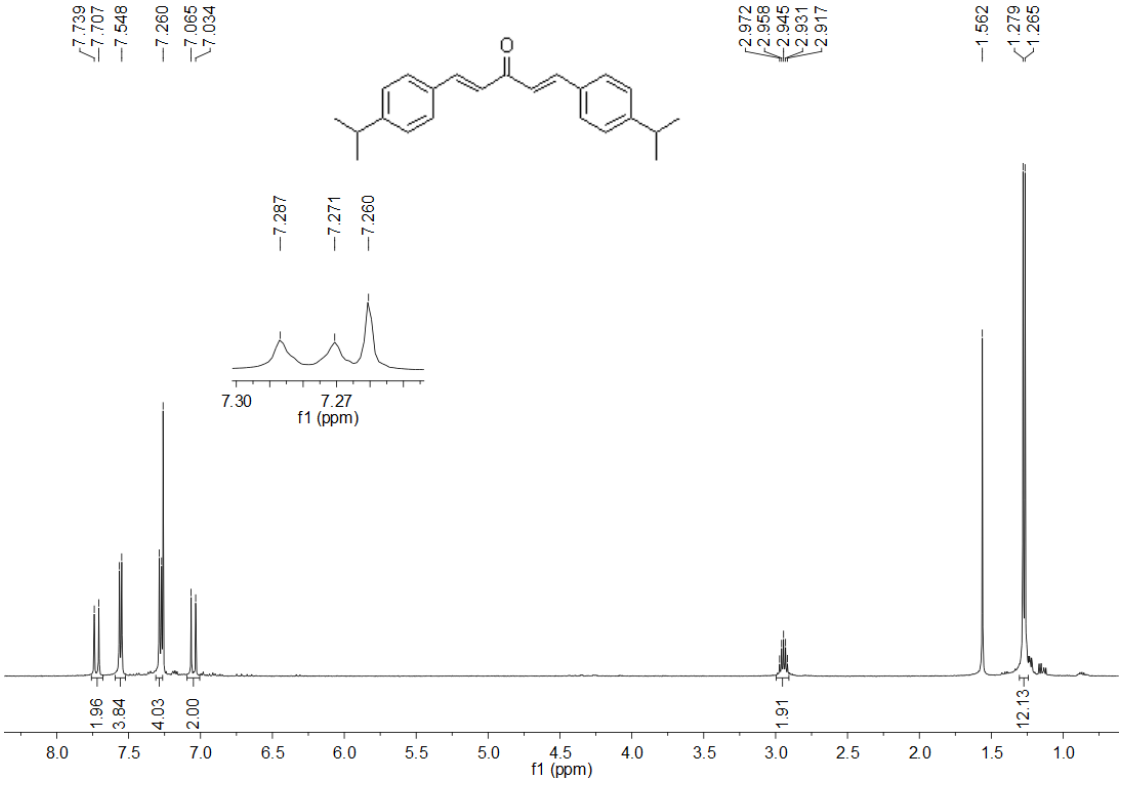


Fig. S65 ^{1}H NMR spectrum of **7dd** (500 MHz, $CDCl_3$)

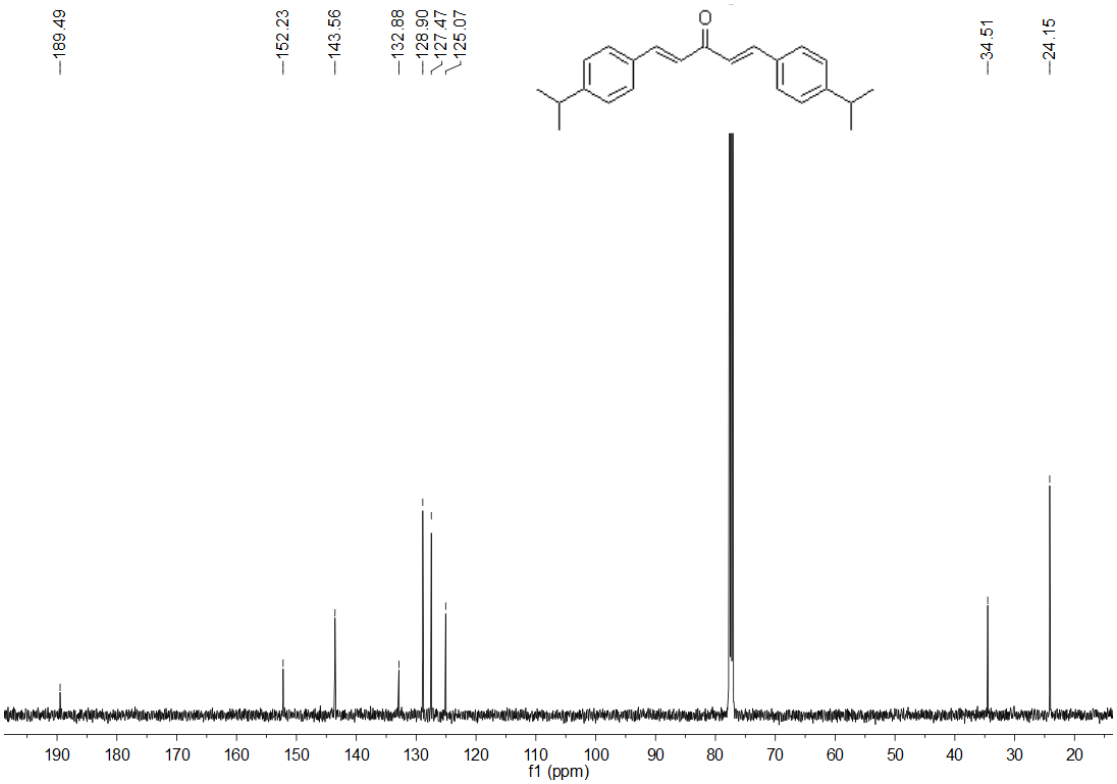


Fig. S66 $^{13}C\{^{1}H\}$ NMR spectrum of **7dd** (125 MHz, $CDCl_3$)

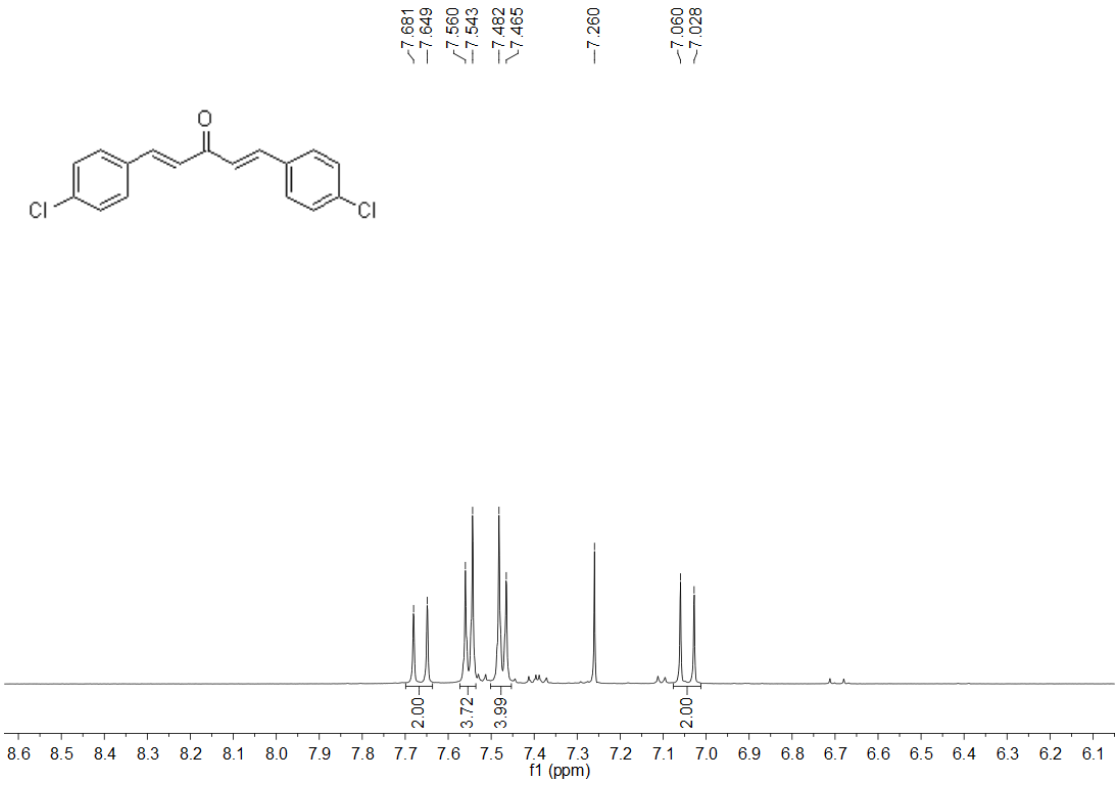


Fig. S67 ^{1}H NMR spectrum of **7ee** (500 MHz, $CDCl_3$)

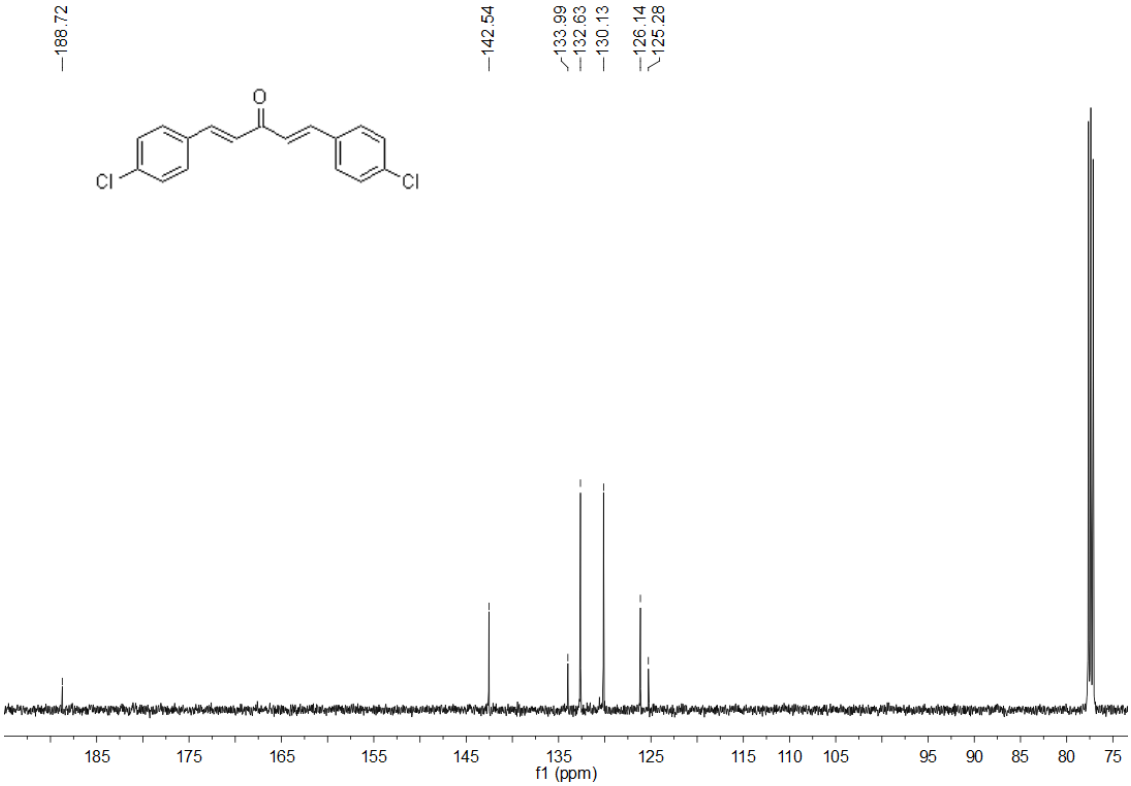


Fig. S68 $^{13}C\{^{1}H\}$ NMR spectrum of **7ee** (125 MHz, $CDCl_3$)

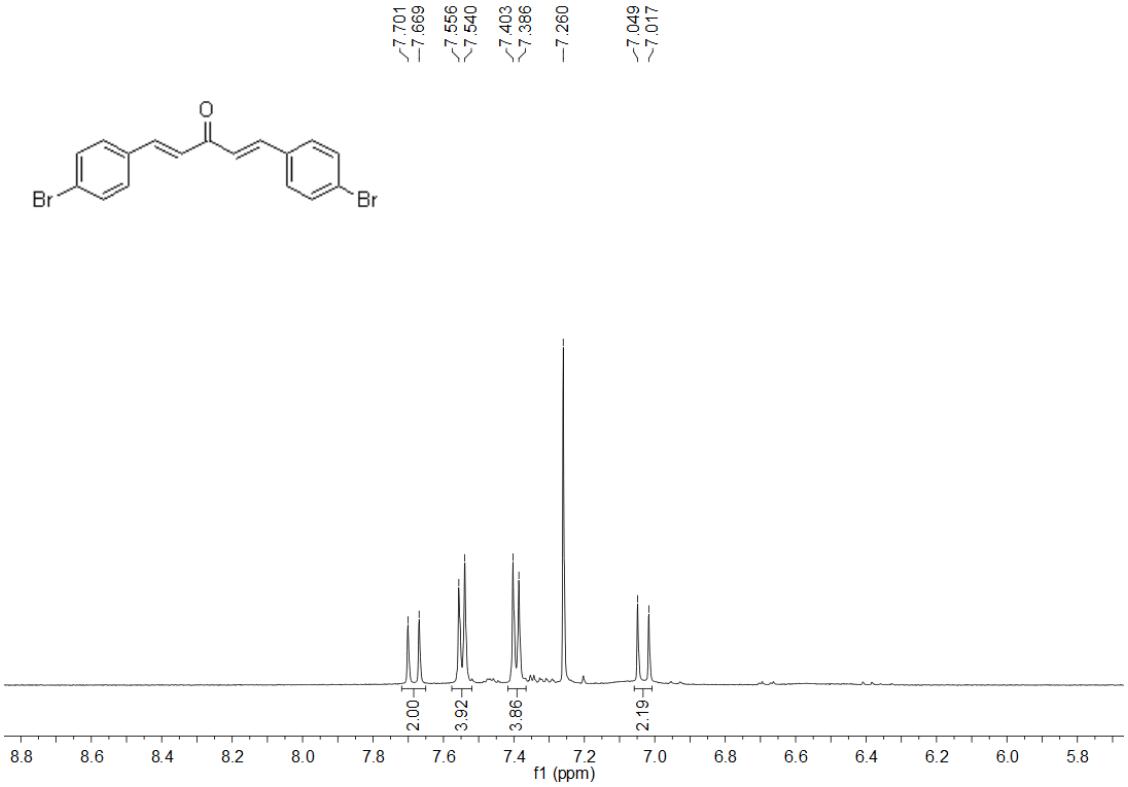


Fig. S69 ^{1}H NMR spectrum of **7ff** (500 MHz, $CDCl_3$)

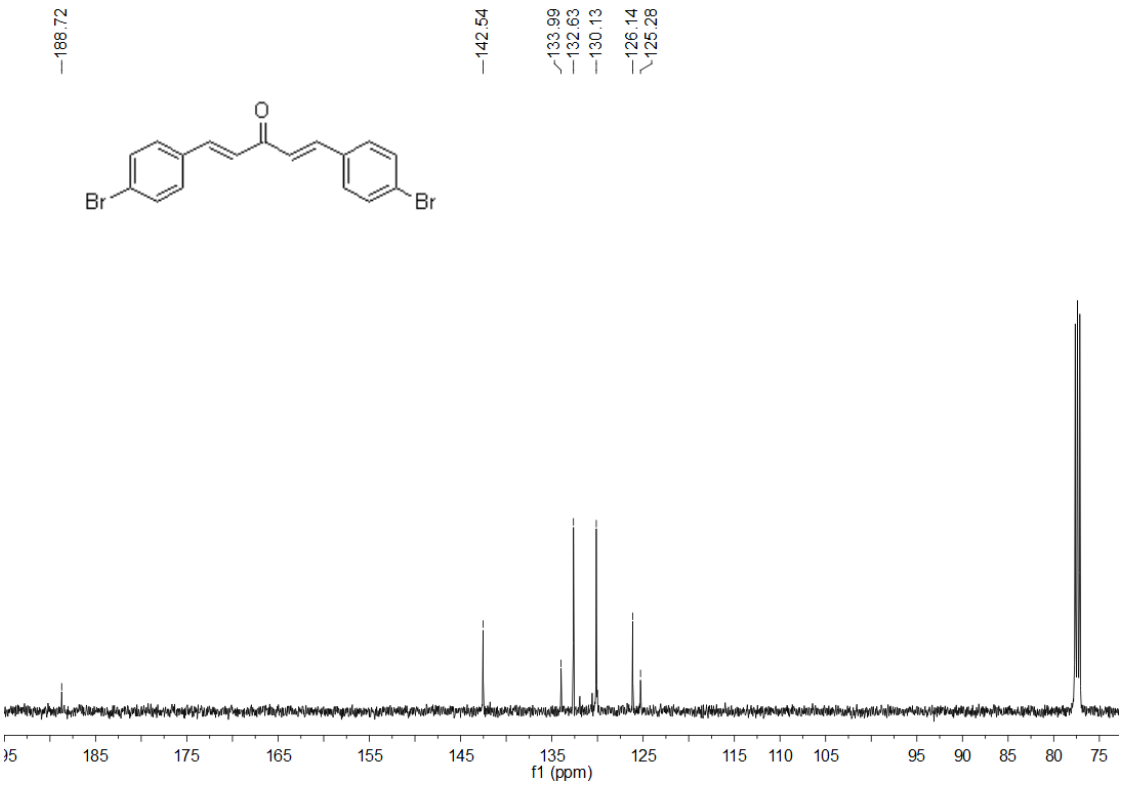


Fig. S70 $^{13}C\{^{1}H\}$ NMR spectrum of **7ff** (125 MHz, $CDCl_3$)

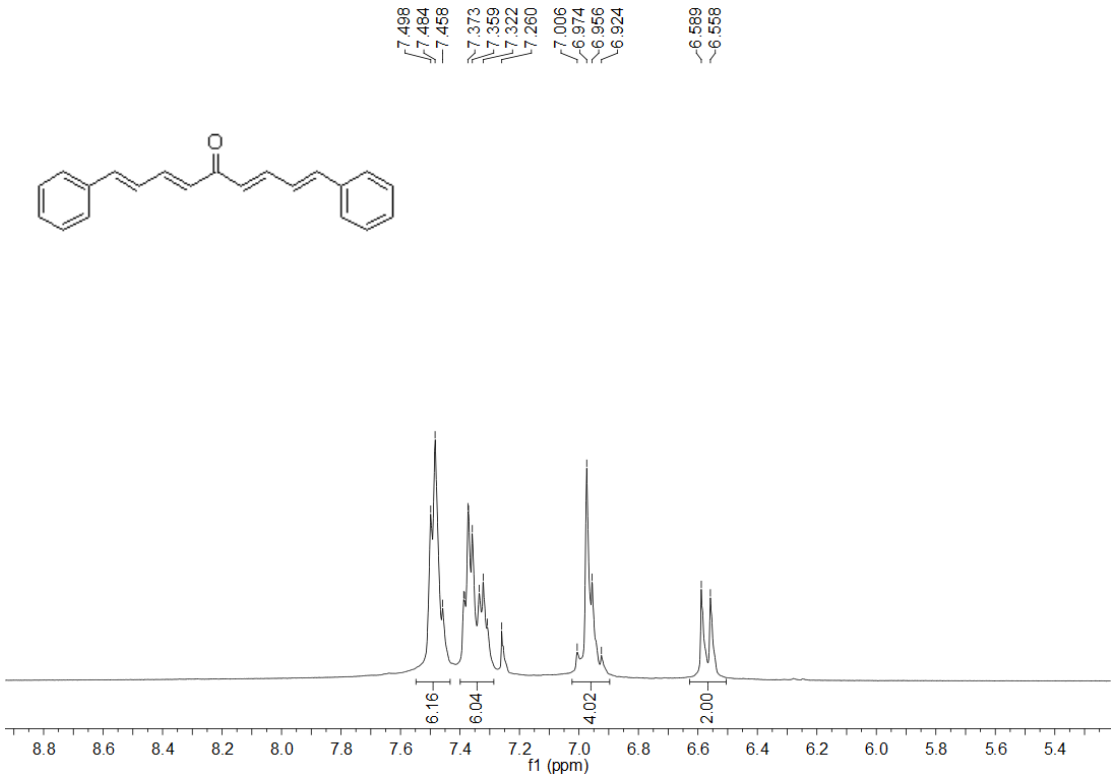


Fig. S71 ^{1}H NMR spectrum of **7gg** (500 MHz, $CDCl_3$)

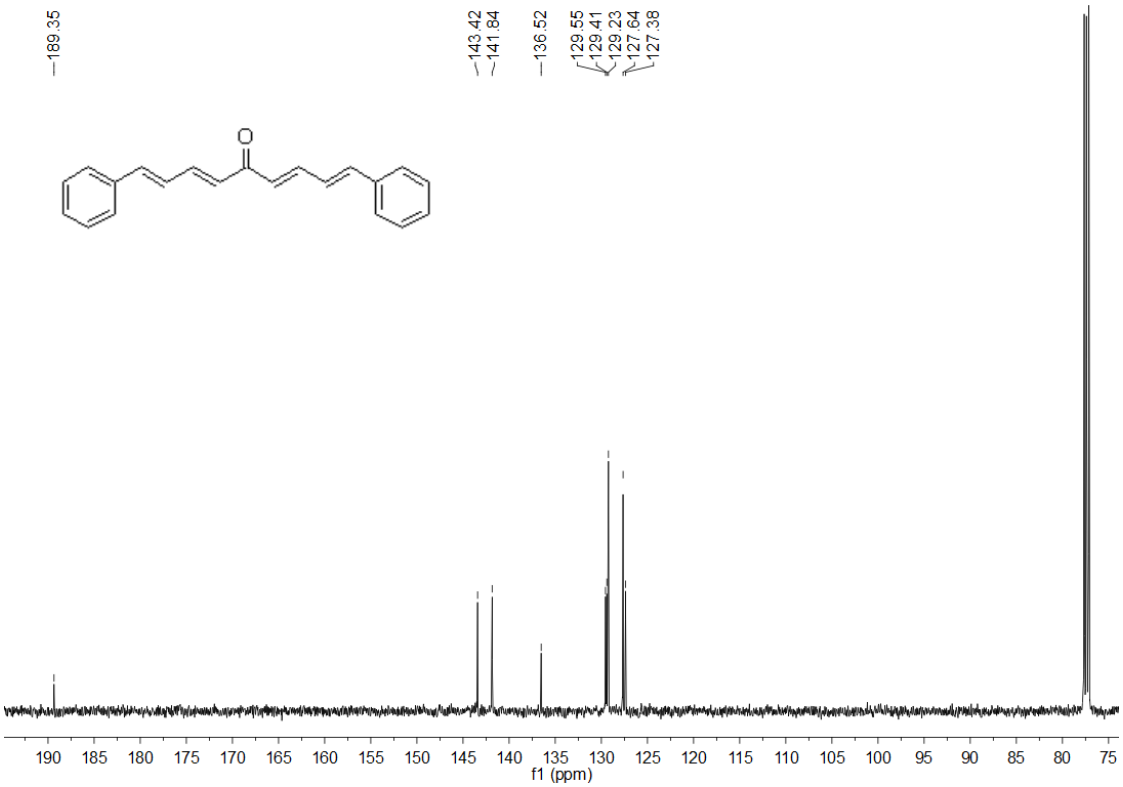


Fig. S72 $^{13}C\{^{1}H\}$ NMR spectrum of **7gg** (125 MHz, $CDCl_3$)

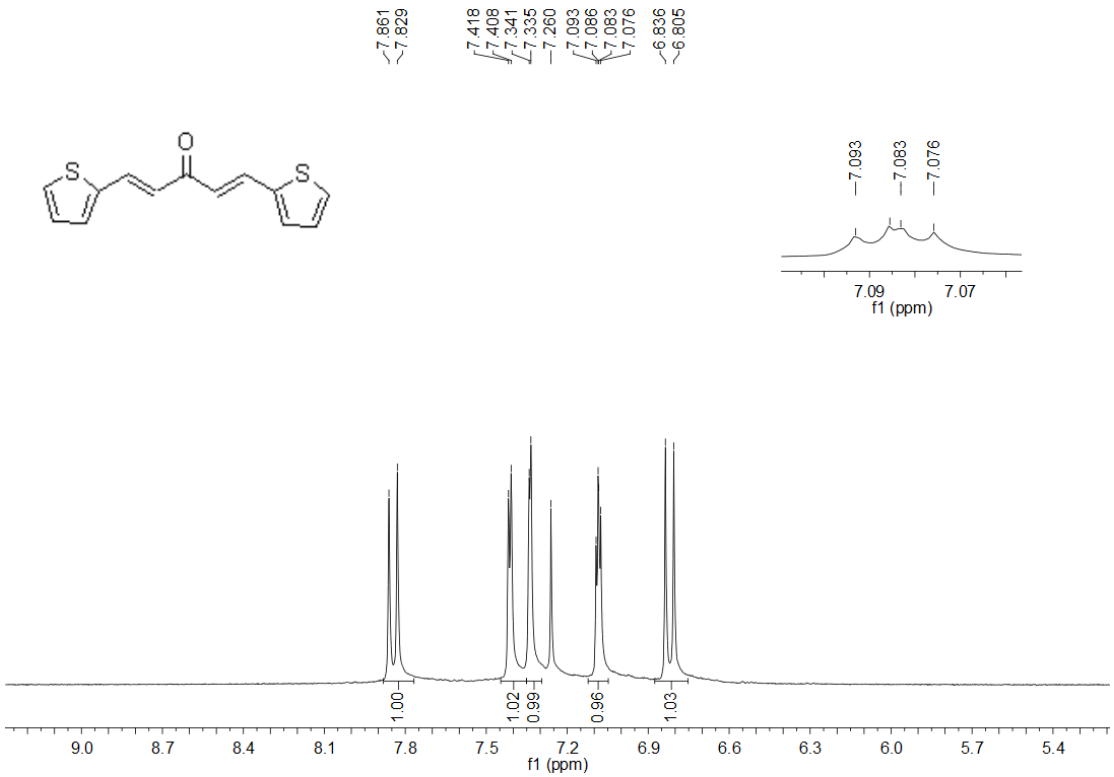


Fig. S73 ^{1}H NMR spectrum of **7hh** (500 MHz, $CDCl_3$)

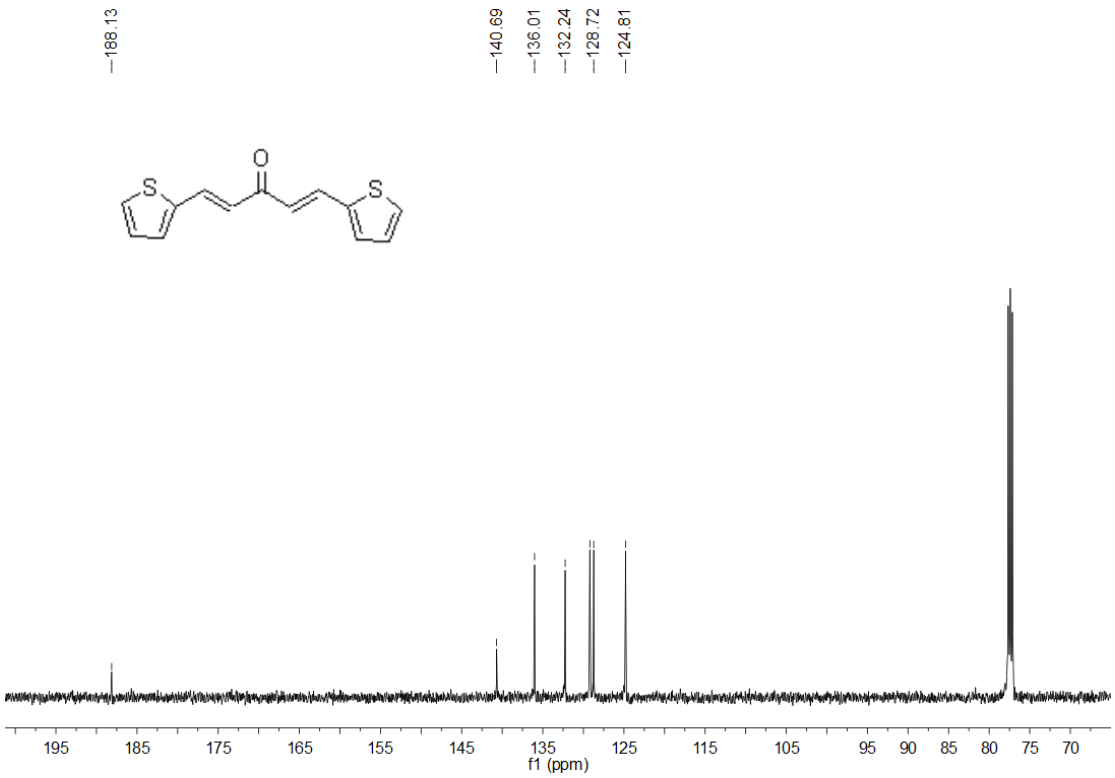


Fig. S74 $^{13}C\{^{1}H\}$ NMR spectrum of **7hh** (125 MHz, $CDCl_3$)

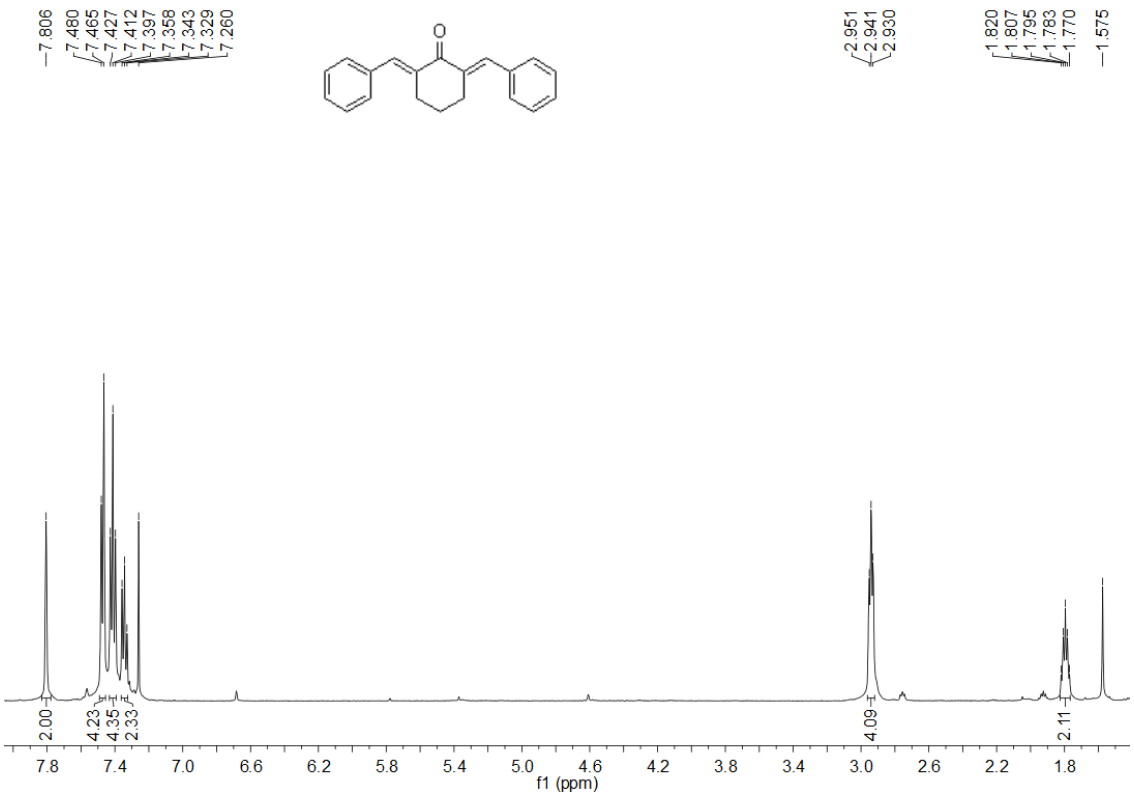


Fig. S75 ^{1}H NMR spectrum of **8aa** (500 MHz, $CDCl_3$)

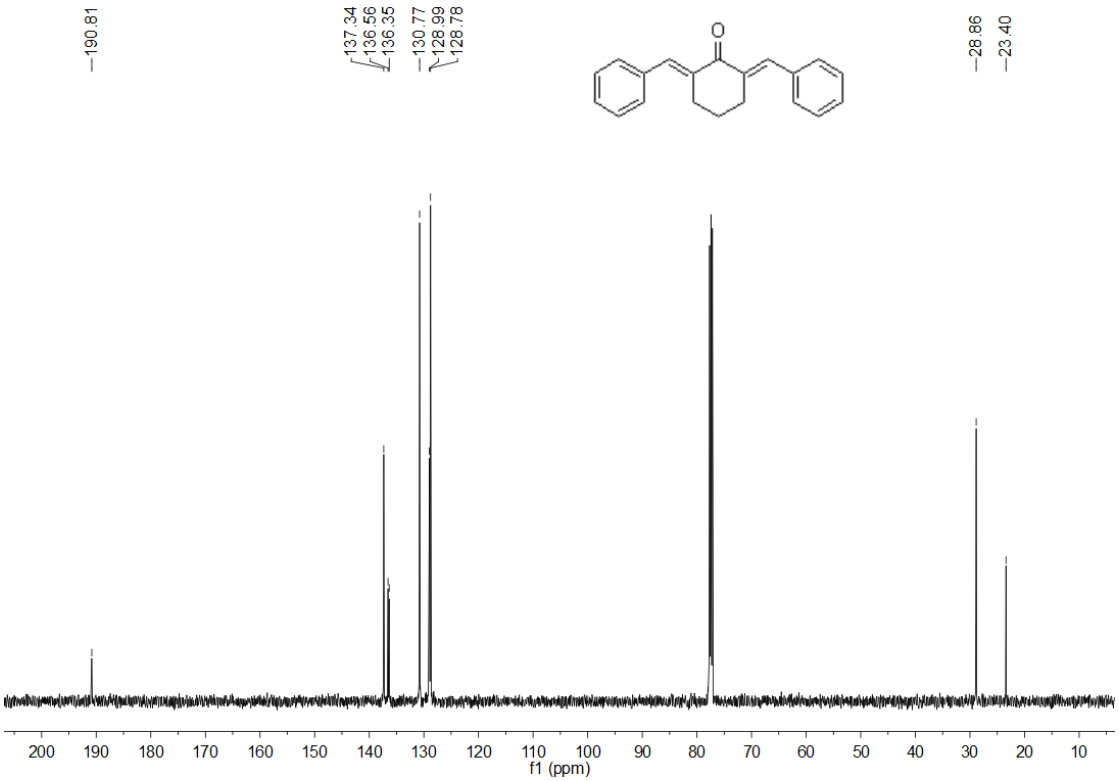


Fig. S76 $^{13}C\{^{1}H\}$ NMR spectrum of **8aa** (125 MHz, $CDCl_3$)

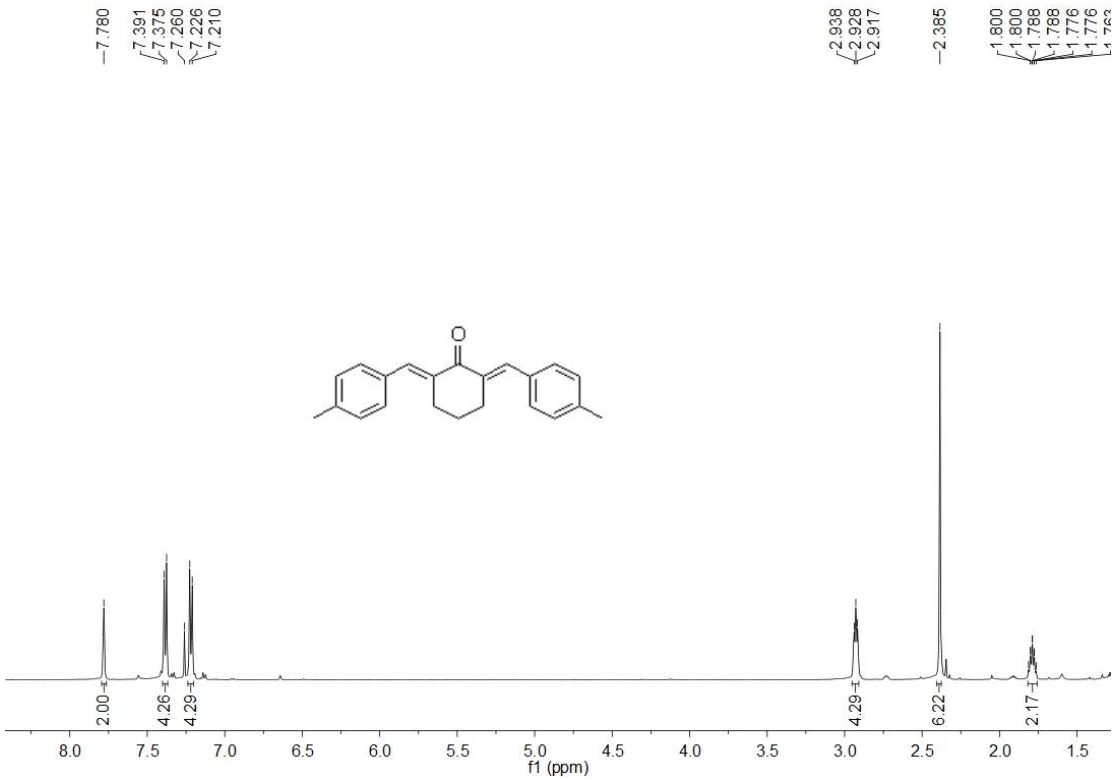


Fig. S77 ^{1}H NMR spectrum of **8bb** (500 MHz, $CDCl_3$)

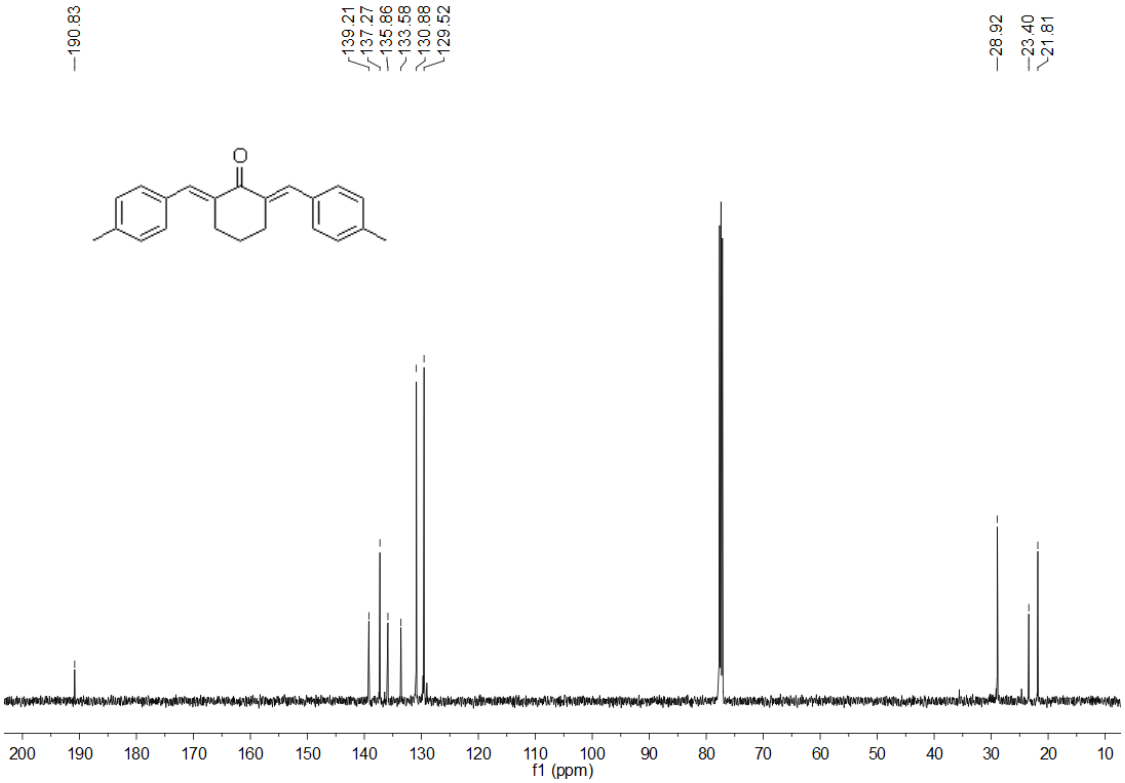


Fig. S78 $^{13}C\{^{1}H\}$ NMR spectrum of **8bb** (125 MHz, $CDCl_3$)

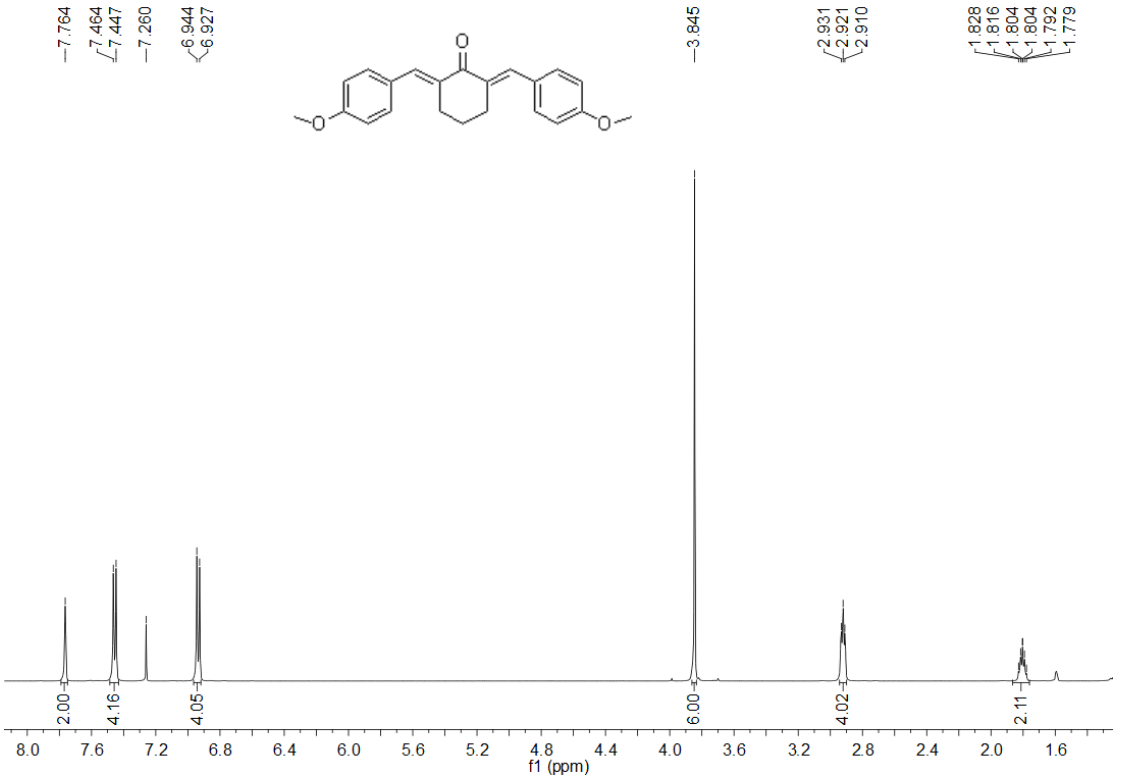


Fig. S79 ^{1}H NMR spectrum of **8cc** (500 MHz, $CDCl_3$)

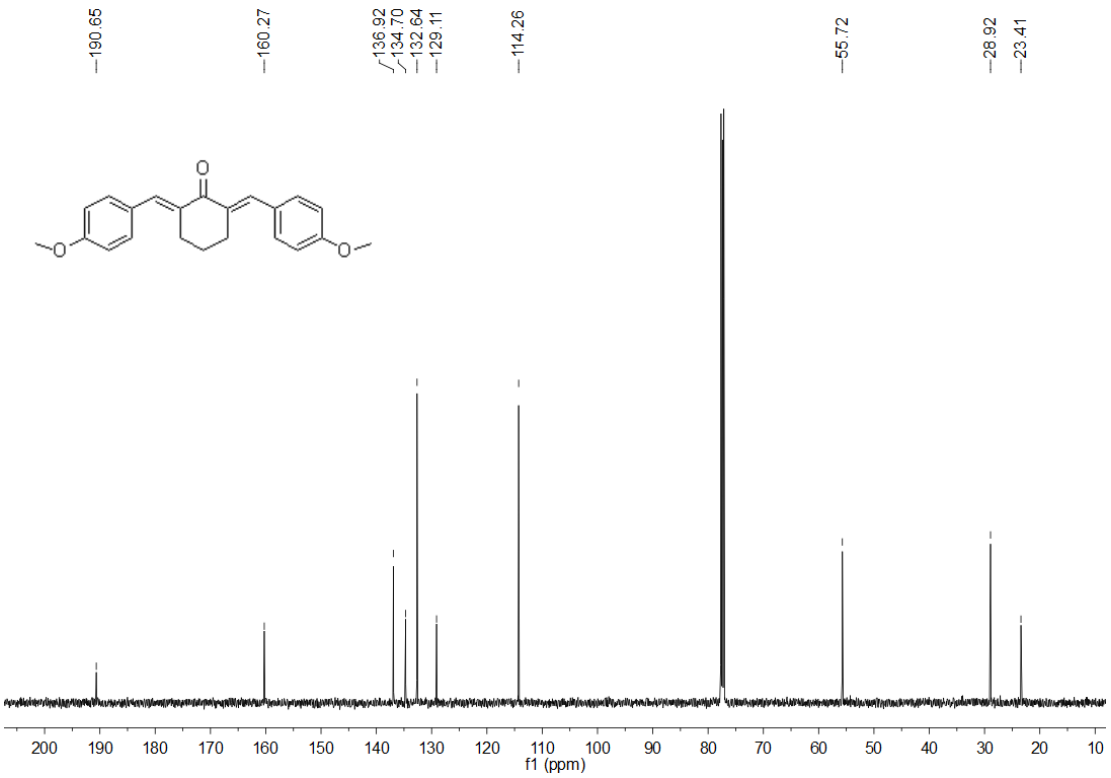


Fig. S80 $^{13}C\{^{1}H\}$ NMR spectrum of **8cc** (125 MHz, $CDCl_3$)

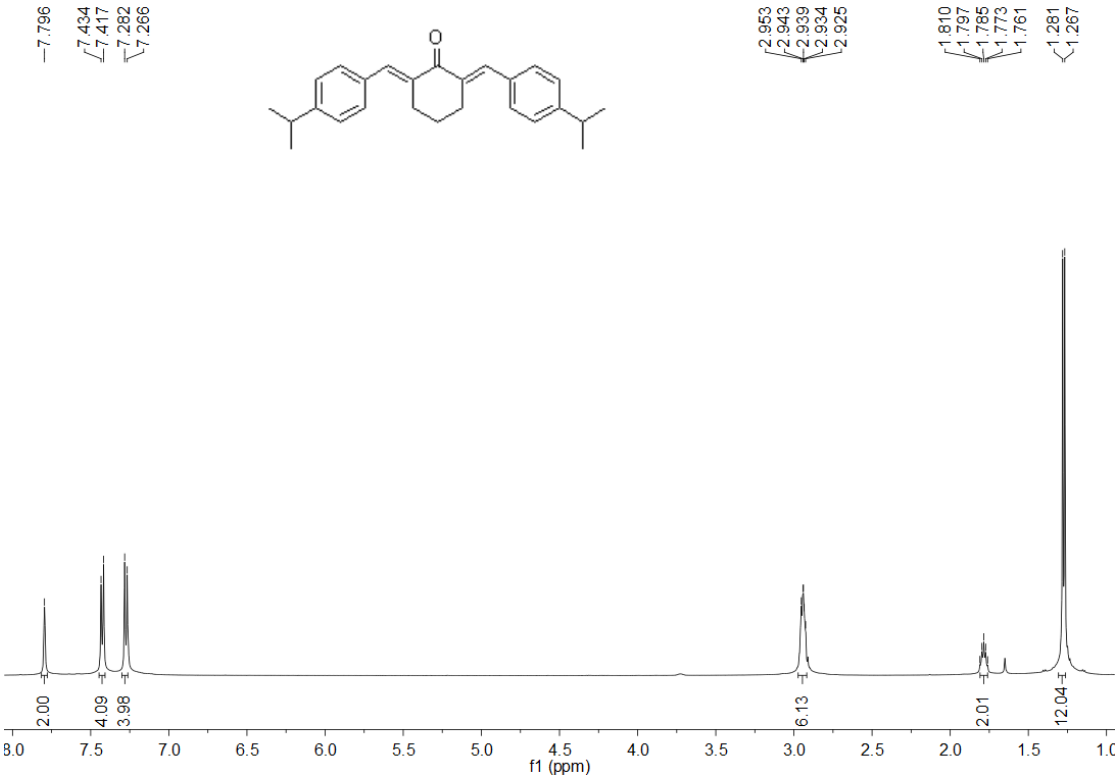


Fig. S81 ^{1}H NMR spectrum of **8dd** (500 MHz, $CDCl_3$)

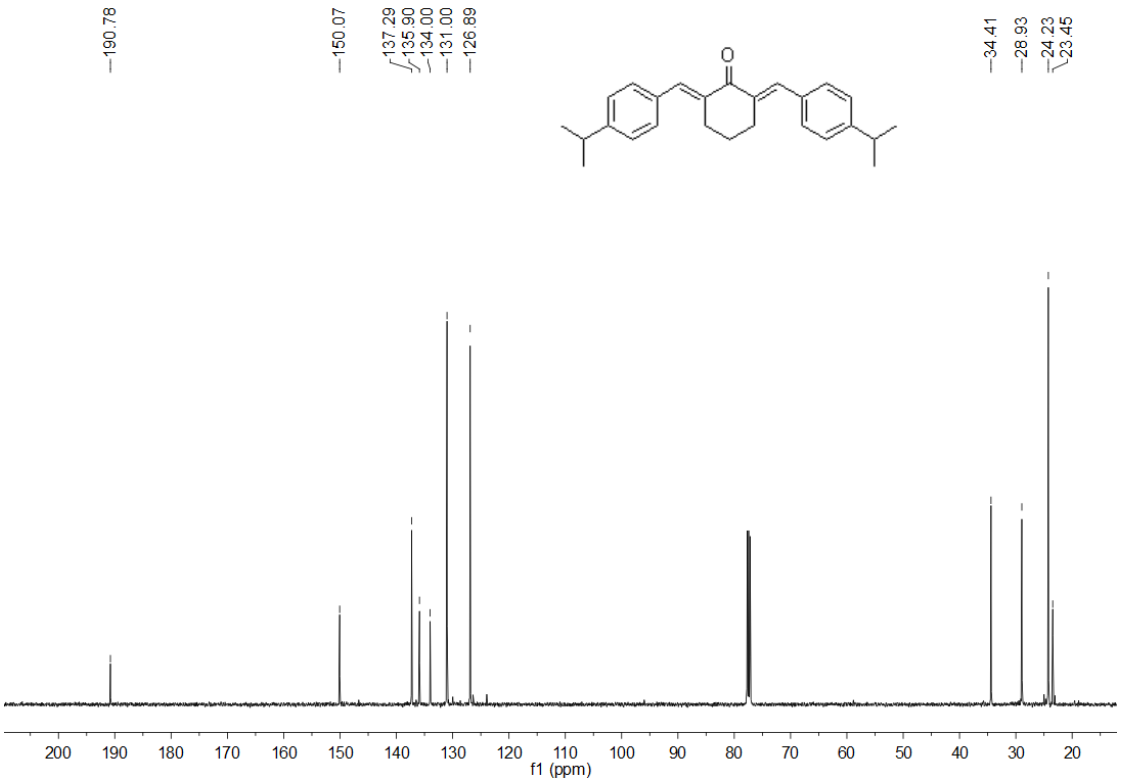


Fig. S82 $^{13}C\{^{1}H\}$ NMR spectrum of **8dd** (125 MHz, $CDCl_3$)

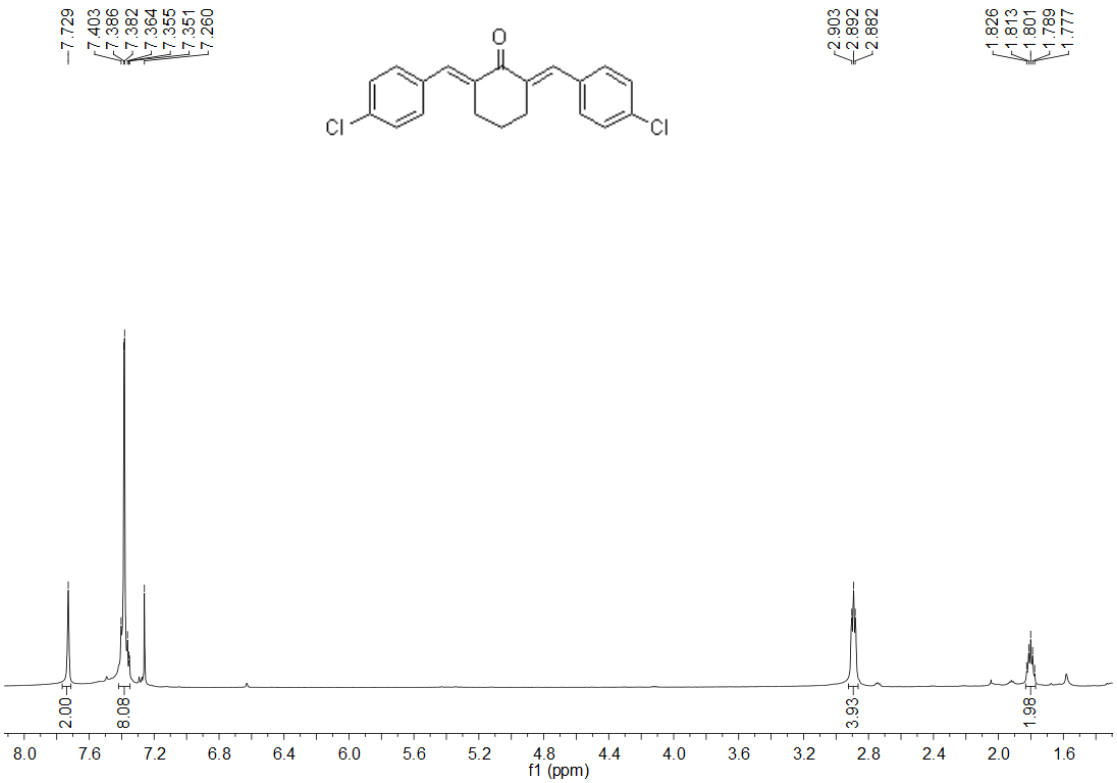


Fig. S83 ^{1}H NMR spectrum of **8ee** (500 MHz, $CDCl_3$)

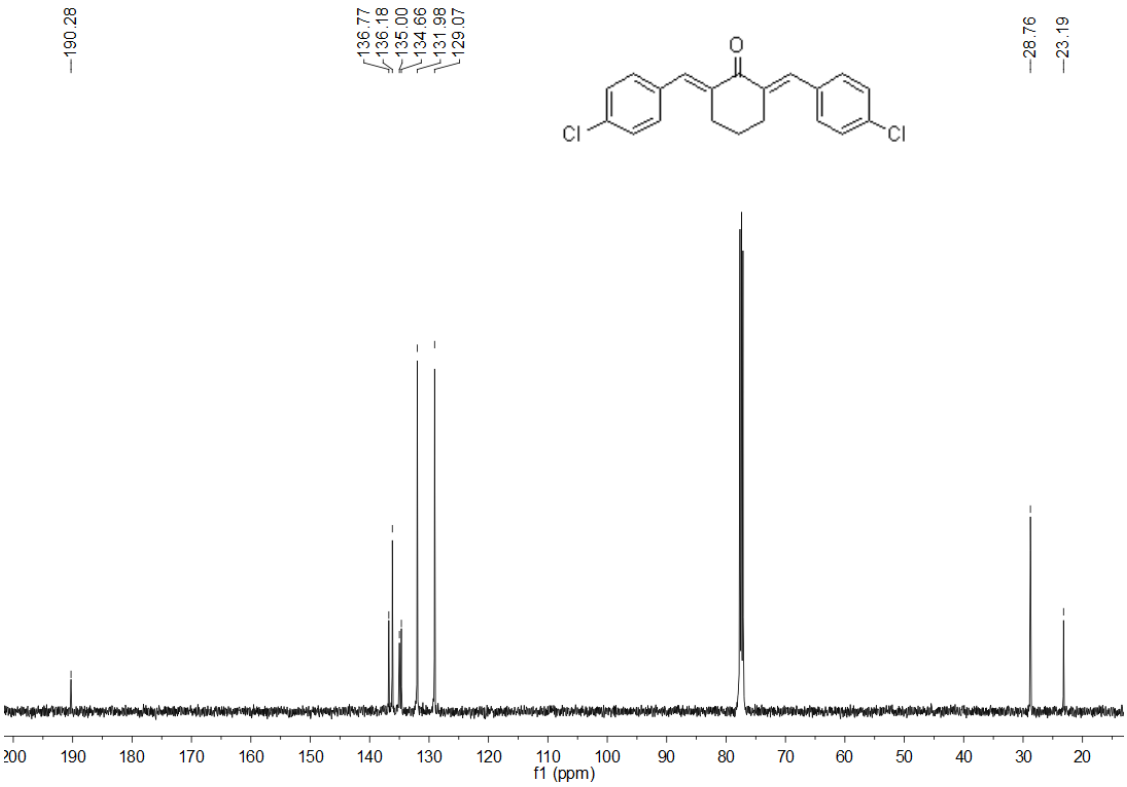


Fig. S84 $^{13}C\{^{1}H\}$ NMR spectrum of **8ee** (125 MHz, $CDCl_3$)

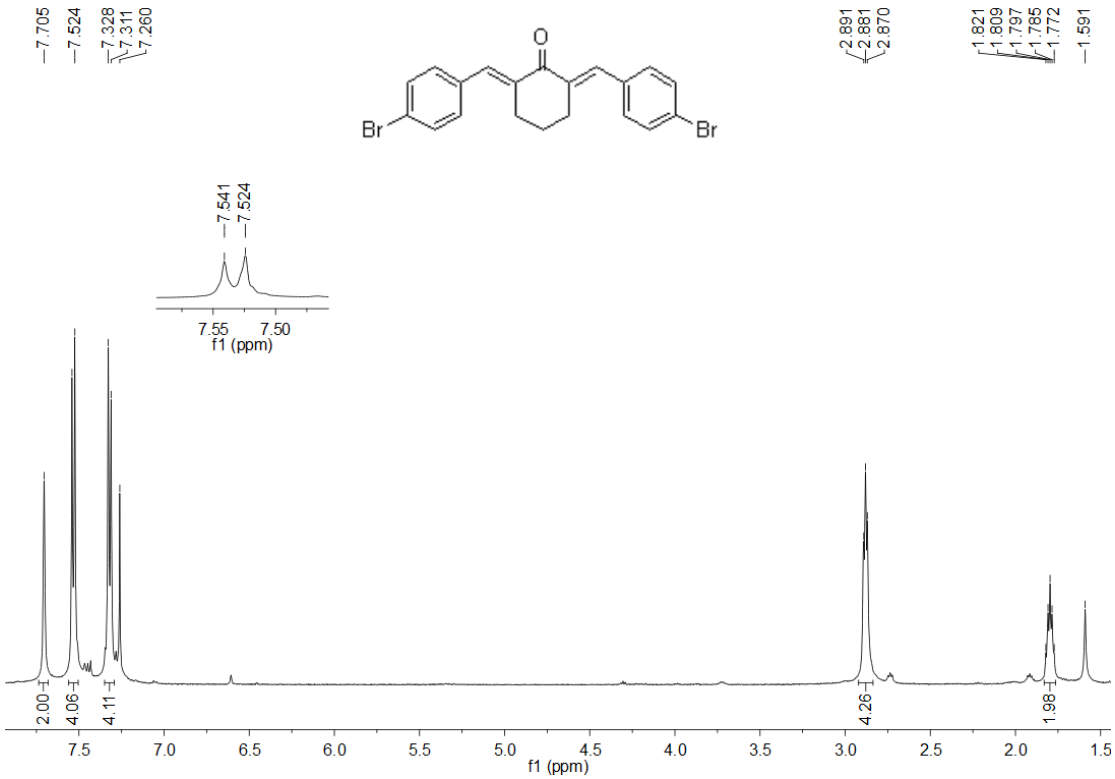


Fig. S85 ^{1}H NMR spectrum of **8ff** (500 MHz, $CDCl_3$)

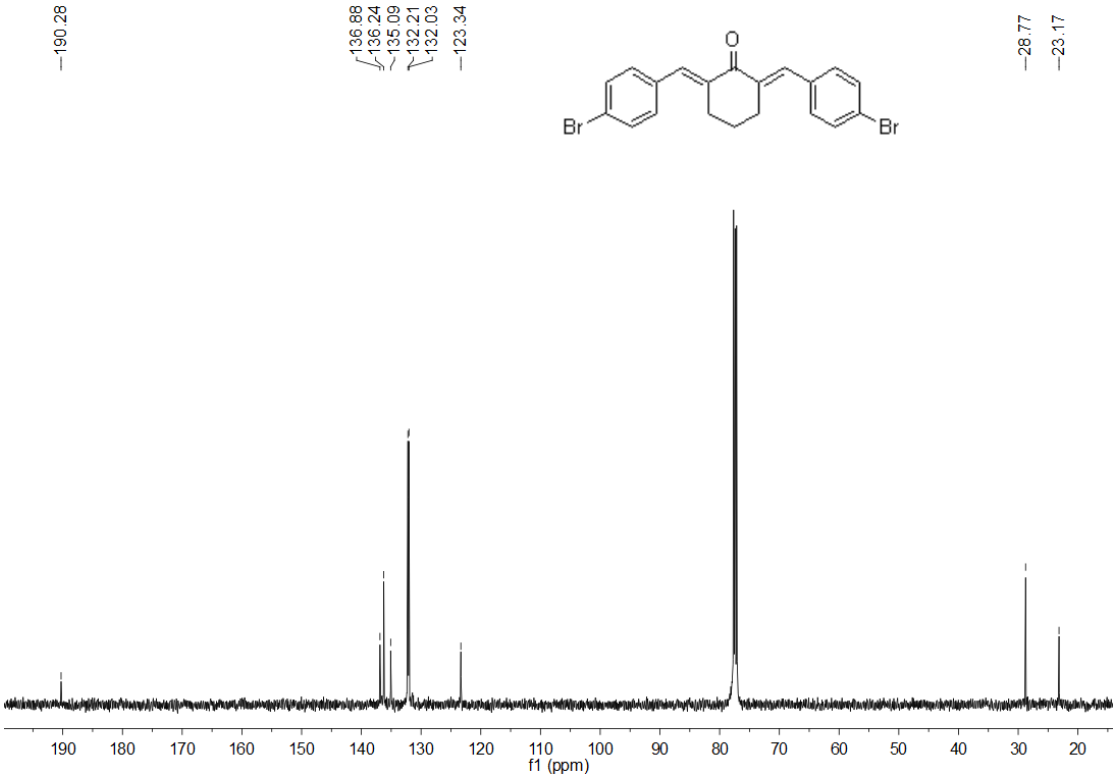


Fig. S86 $^{13}C\{^{1}H\}$ NMR spectrum of **8ff** (125 MHz, $CDCl_3$)

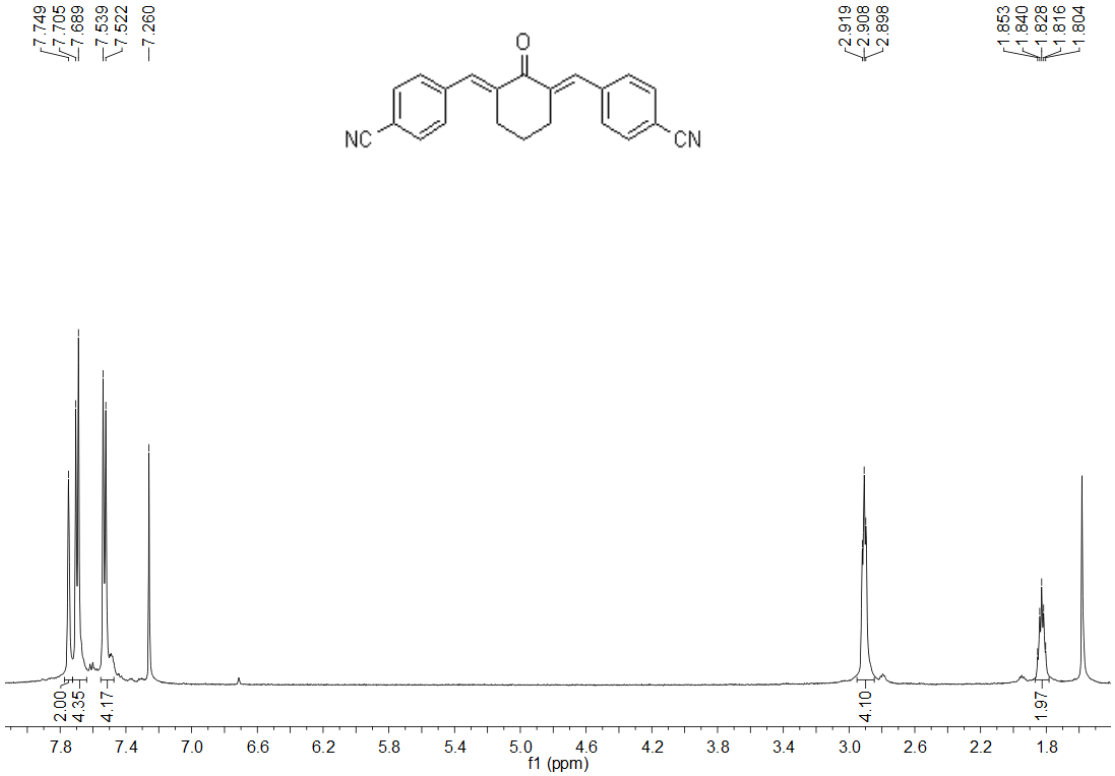


Fig. S87 ^{1}H NMR spectrum of **8gg** (500 MHz, $CDCl_3$)

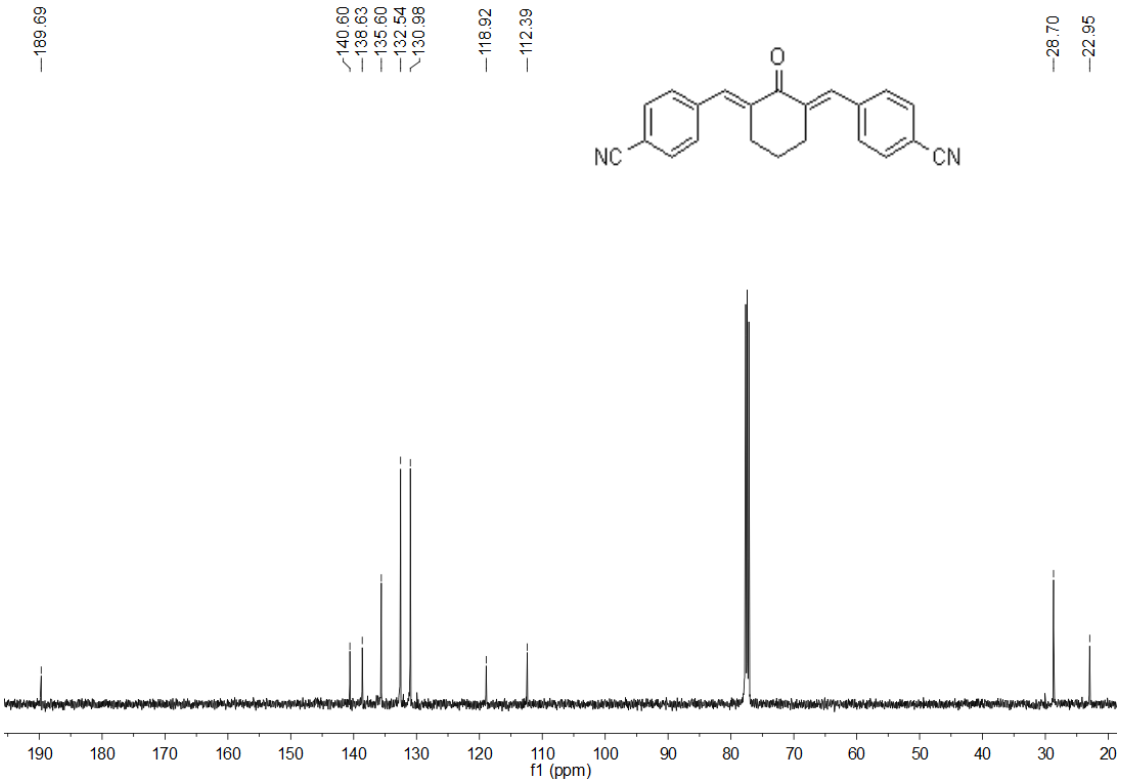


Fig. S88 $^{13}C\{^{1}H\}$ NMR spectrum of **8gg** (125 MHz, $CDCl_3$)

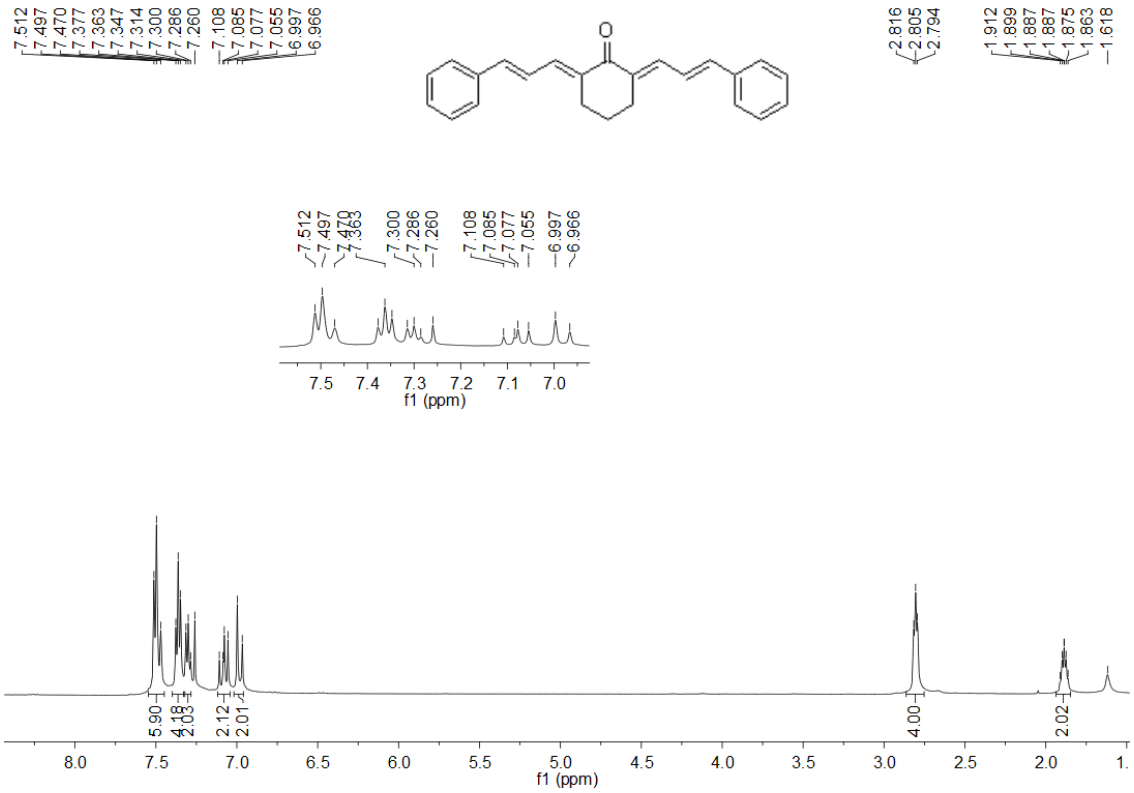


Fig. S89 ^{1}H NMR spectrum of **8hh** (500 MHz, $CDCl_3$)

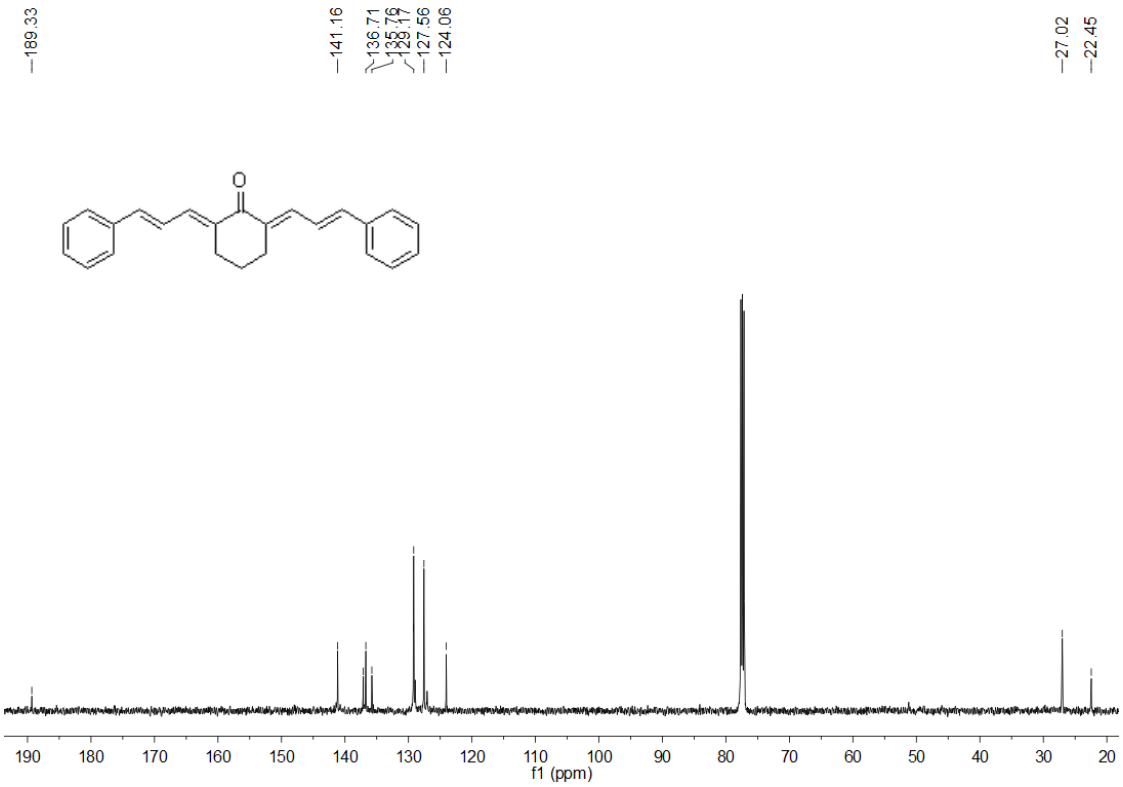


Fig. S90 $^{13}C\{^{1}H\}$ NMR spectrum of **8hh** (125 MHz, $CDCl_3$)

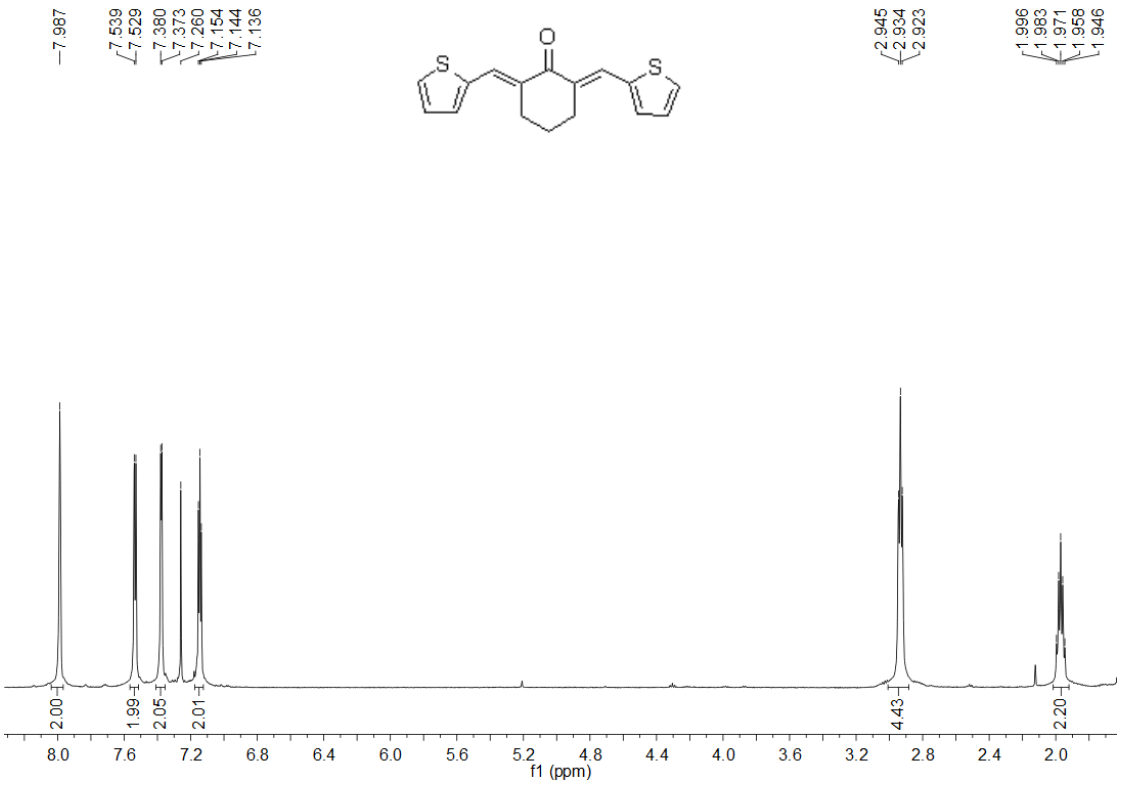


Fig. S91 ^{1}H NMR spectrum of **8ii** (500 MHz, $CDCl_3$)

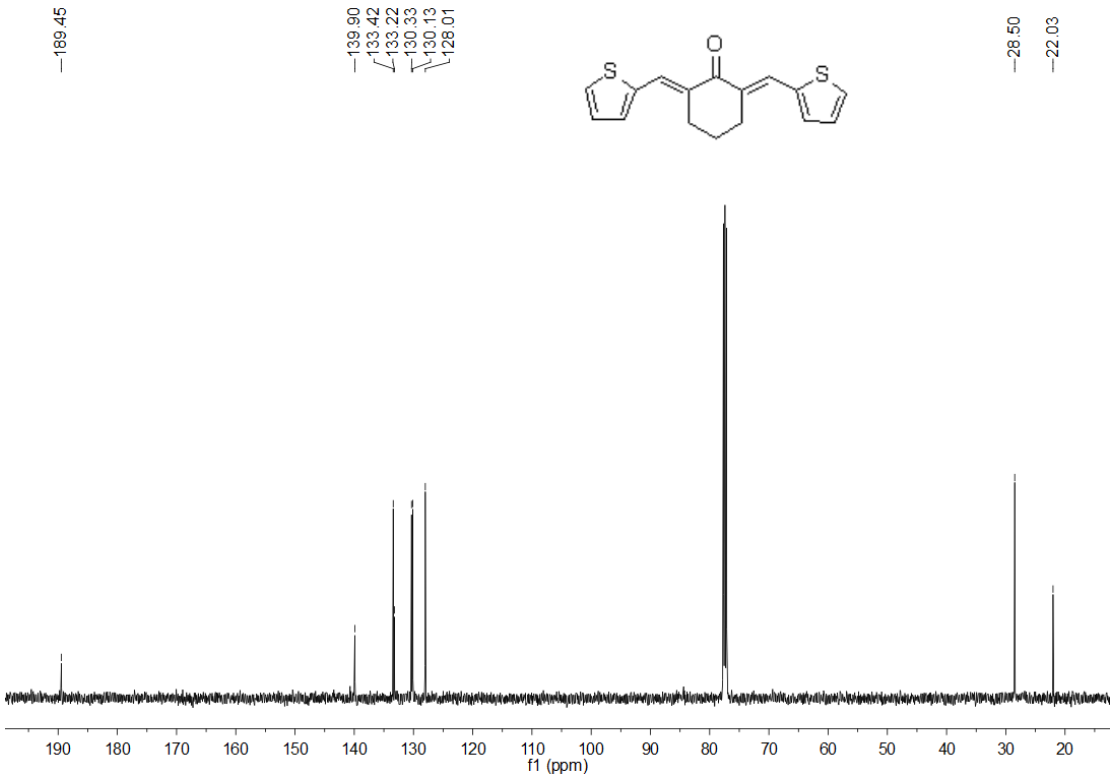


Fig. S92 $^{13}C\{^{1}H\}$ NMR spectrum of **8ii** (125 MHz, $CDCl_3$)

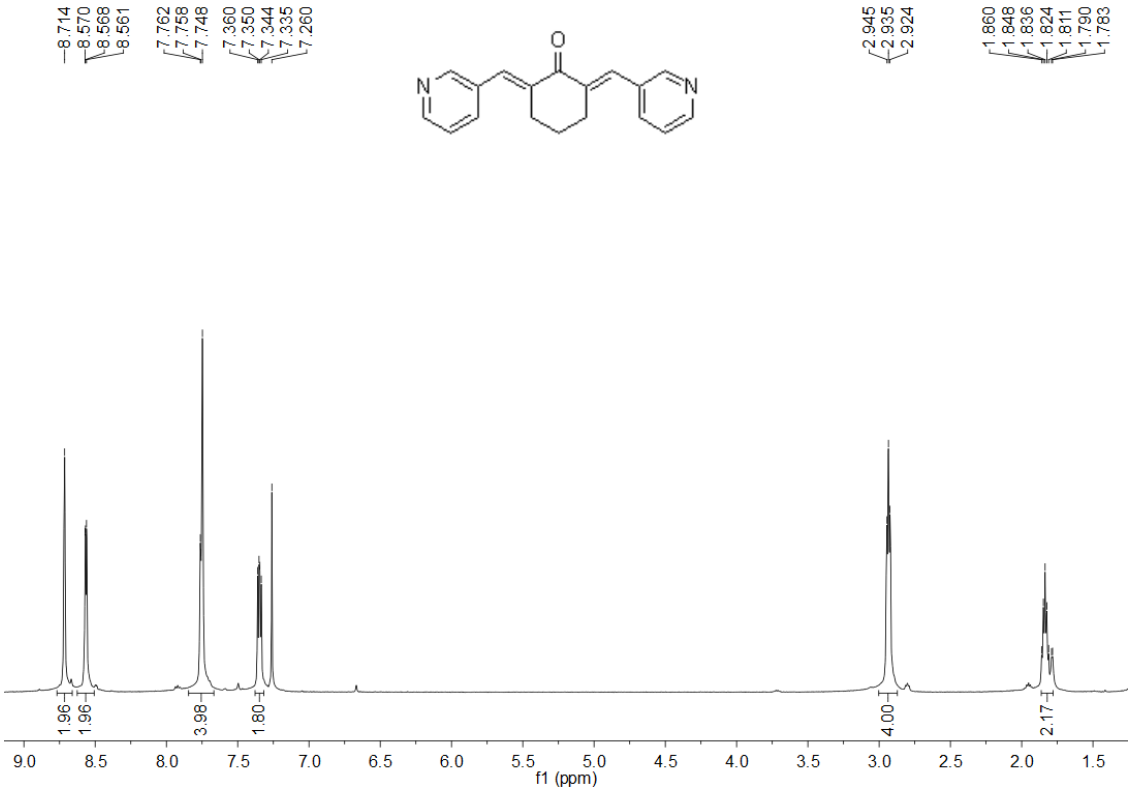


Fig. S93 ^{1}H NMR spectrum of **8jj** (500 MHz, $CDCl_3$)

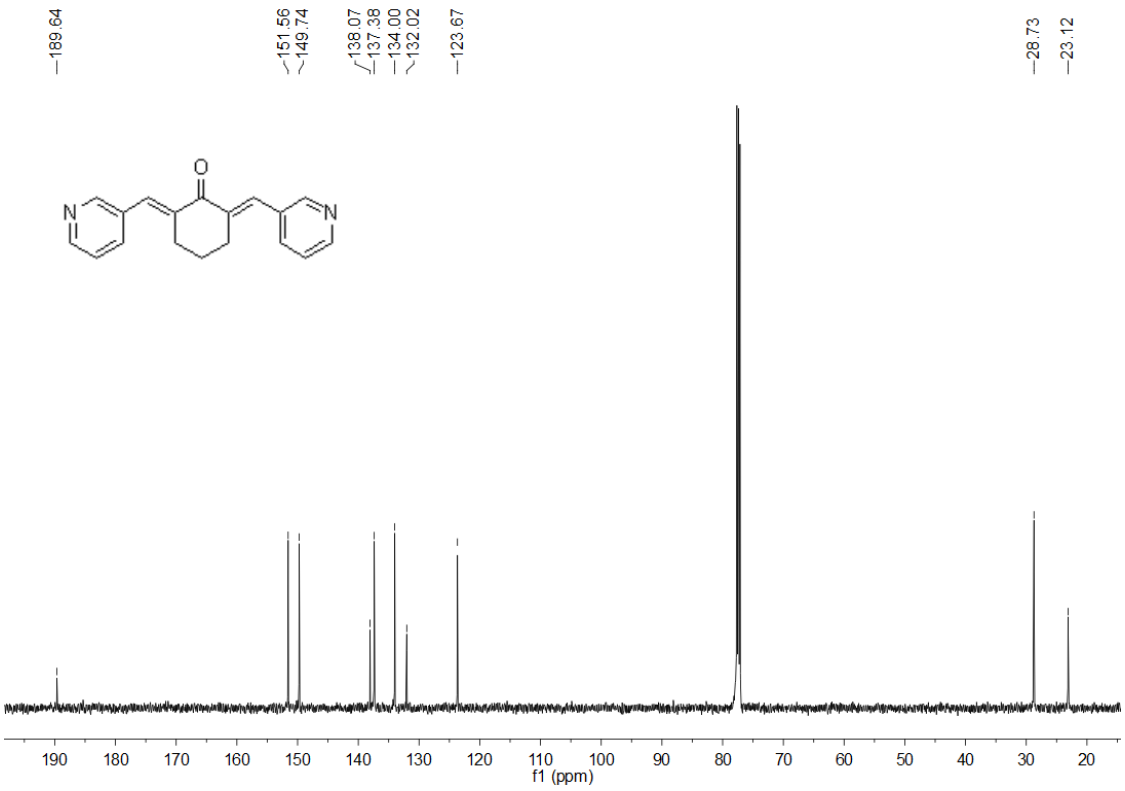


Fig. S94 $^{13}C\{^{1}H\}$ NMR spectrum of **8jj** (125 MHz, $CDCl_3$)

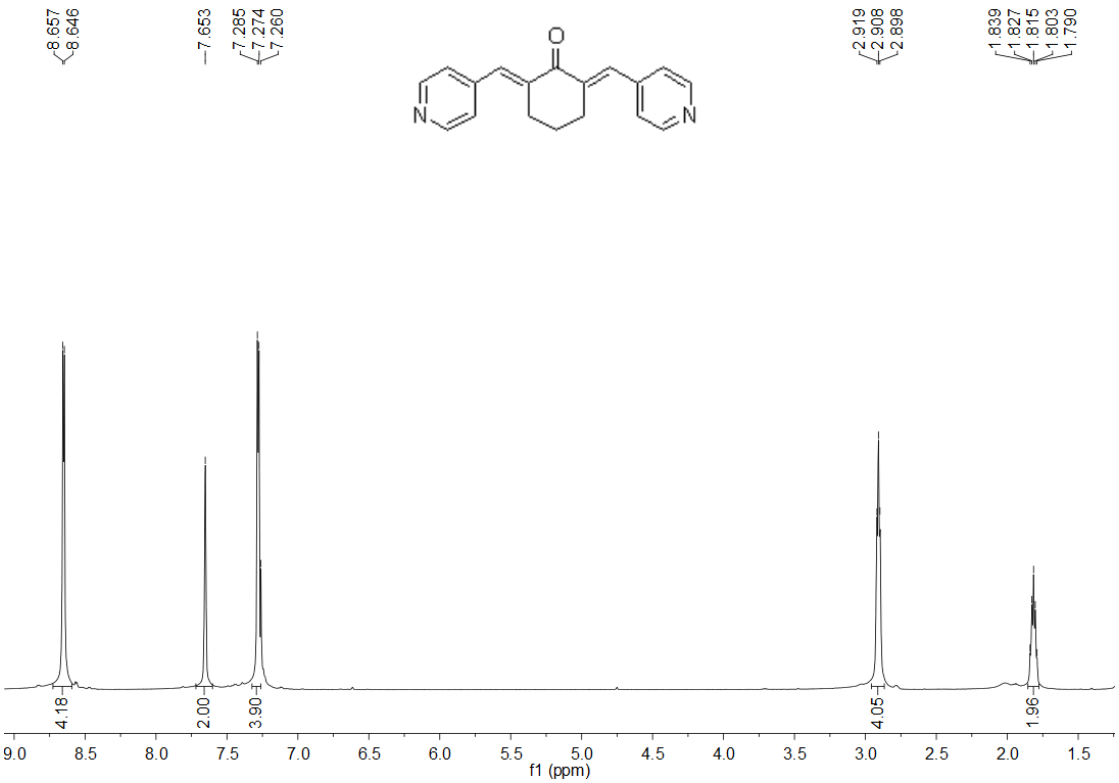


Fig. S95 ^{1}H NMR spectrum of **8kk** (500 MHz, $CDCl_3$)

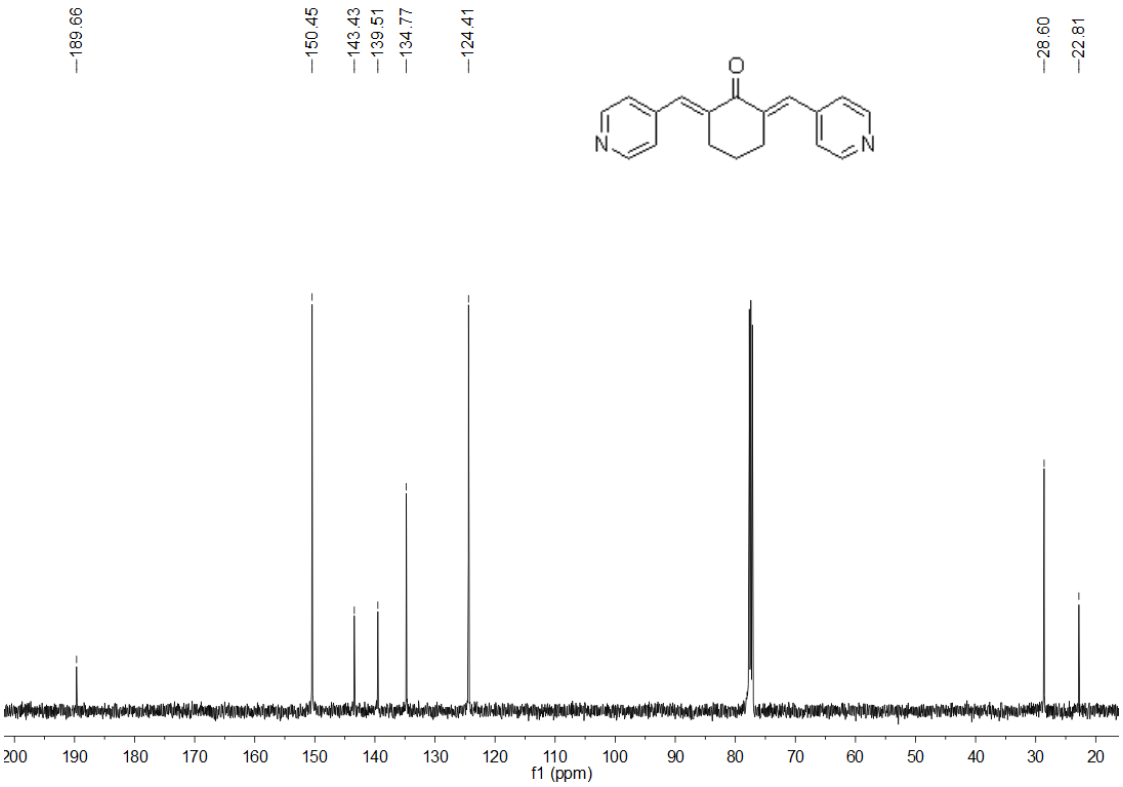


Fig. S96 $^{13}C\{^{1}H\}$ NMR spectrum of **8kk** (125 MHz, $CDCl_3$)

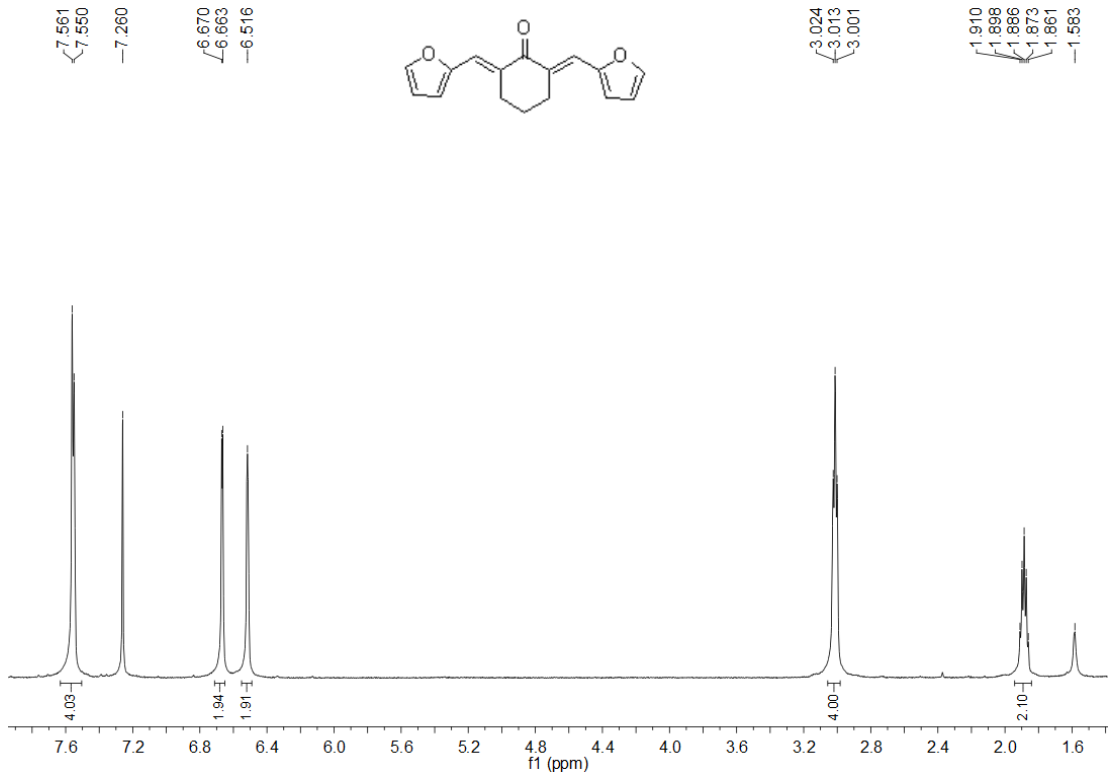


Fig. S97 ^{1}H NMR spectrum of **8ll** (500 MHz, $CDCl_3$)

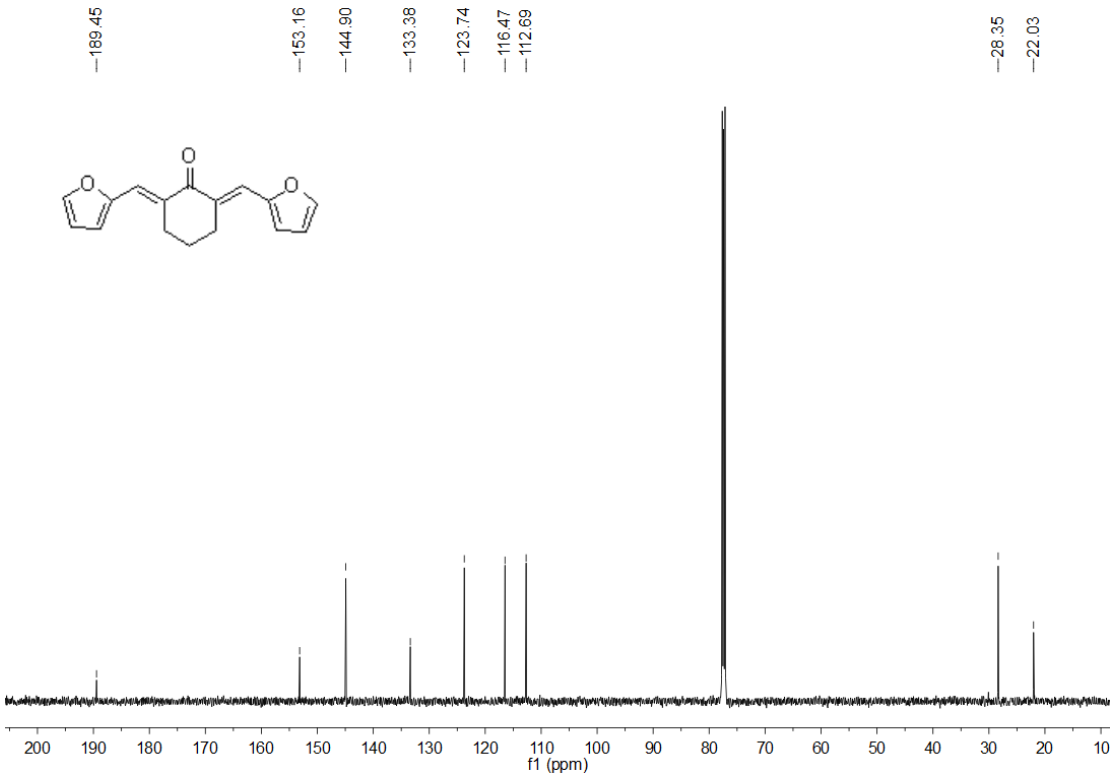


Fig. S98 $^{13}C\{^{1}H\}$ NMR spectrum of **8ll** (125 MHz, $CDCl_3$)

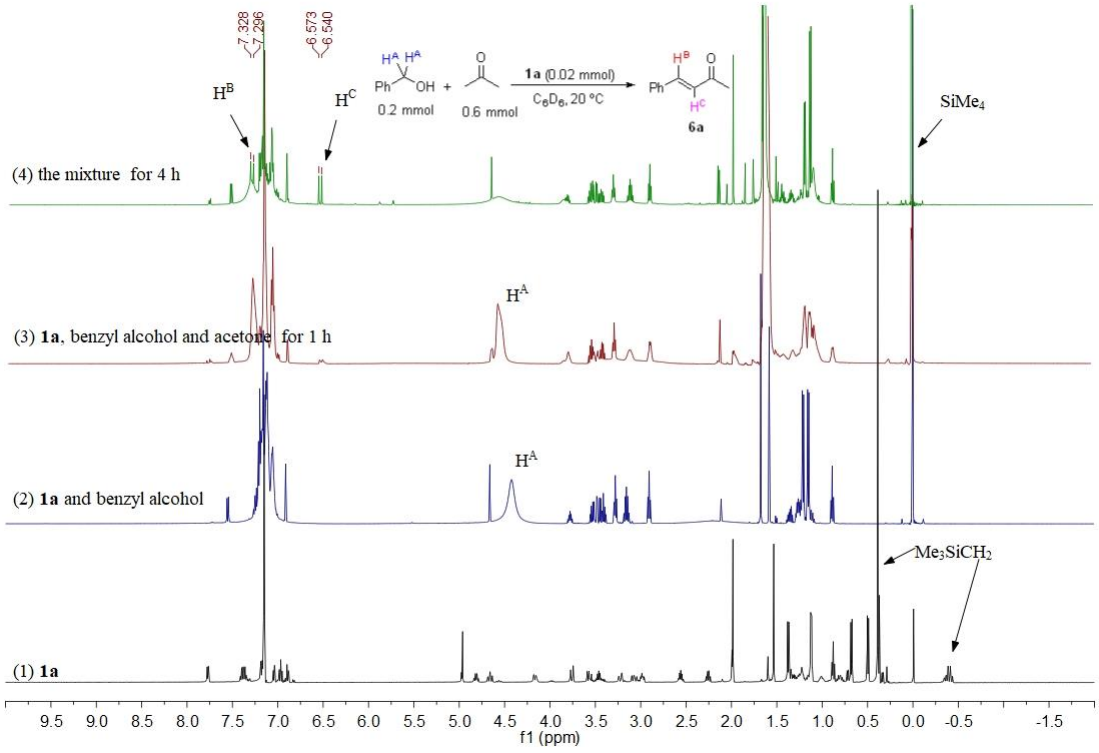


Fig. S99 ^{1}H NMR Monitoring the catalytic reaction of benzyl alcohol (0.2 mmol) and acetone (0.6 mmol) catalyzed by **1a** (0.02 mmol) in C_6D_6 at room temperature.

A gram-scale preparation of 4k

9-Fluorenol (7.0 mmol) and **1a** (0.23 g, 0.35 mmol) were mixed in 10 mL of toluene, and then 1.54 mL of acetone (21.0 mmol) was added. The mixture was stirred at room temperature for 3 h. After that, volatiles of the mixture were removed under reduced pressure. The product was purified by silica gel column chromatography (ethyl acetate:petroleum ether = 1:6) to give the yellow solid **4k** (1.08 g, 86% yield).

Fig. S100 Samples of the catalytic product of 9-fluorenone.

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