

Supporting Information

Synthesis of rare-earth metal complexes with a morpholine-functionalized β -diketiminato ligand and their catalytic activities towards C–O and C–N bond formation

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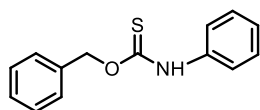
Table S1. Crystallographic data of complexes 1a-c

	1a (Y)	1b (Yb)	1c (Lu)
CCDC	2181769	2181770	2181771
Empirical formula	C ₃₁ H ₅₂ Cl ₃ LiN ₃ O ₃ Y	C ₃₁ H ₅₂ Cl ₃ LiN ₃ O ₃ Yb	C ₃₁ H ₅₂ Cl ₃ LiN ₃ O ₃ Lu
Formula weight	717.98	801.08	803.01
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.0084(8)	10.9753(17)	10.896(8)
<i>b</i> (Å)	11.5337(8)	11.5275(16)	11.454(7)
<i>c</i> (Å)	17.1823(11)	17.147(3)	17.044(10)
α (°)	103.679(2)	103.943(5)	103.77(3)
β (°)	94.344(2)	94.042(6)	94.20(3)
γ (°)	116.617(2)	116.603(5)	117.04(3)
<i>V</i> (Å ³)	1853.2(2)	1842.3(5)	1799(2)
<i>Z</i>	2	2	2
<i>D</i> _{calcd} (mg m ⁻³)	1.2848	1.444	1.482
μ (mm ⁻¹)	1.839	2.788	2.999
<i>F</i> (000)	747	814	816
θ range (°)	2.92 to 27.59	3.138 to 27.484	2.946 to 27.886
Reflections collected	75295	23047	75464
Data/restraints/parameters	8492/82/431	7900/192/422	8400/548/431
Goodness-of-fit on F ²	1.0916	1.076	1.146
R(int)	0.0604	0.0381	0.0388
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0511, 0.1002	0.0373, 0.0741	0.0261, 0.0617
Largest diff peak/hole (e Å ⁻³)	0.7432 and -0.9134	1.351 and -1.181	0.654 and -1.045

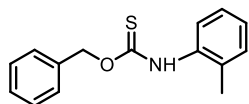
Table S2. Crystallographic data of complexes 2a-c and 5a

	2a (Y)	2b (Yb)	2c (Lu)	5a (Y)
CCDC	2181772	2181773	2181774	2181775
Empirical formula	C ₃₁ H ₅₈ N ₃ OSi ₂ Y	C ₃₁ H ₅₈ N ₃ OSi ₂ Yb	C ₃₁ H ₅₈ N ₃ OSi ₂ Lu	C ₃₉ H ₆₅ N ₄ OSiY
Formula weight	633.89	718.02	719.95	722.95
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P$\bar{1}$</i>
<i>a</i> (Å)	11.519(2)	11.5135(6)	11.5104(10)	11.1438(11)
<i>b</i> (Å)	17.466(3)	17.4563(10)	17.4656(15)	11.2147(12)
<i>c</i> (Å)	19.217(4)	19.1193(10)	19.0773(16)	21.504(2)
α (°)	90	90.00	90	86.101(2)
β (°)	99.326(3)	99.0470(10)	98.9440(10)	84.965(2)
γ (°)	90	90.00	90	69.8760(10)
<i>V</i> (Å ³)	3815.2(12)	3794.9(4)	3788.6(6)	2511.6(4)
Z	4	4	4	2
<i>D</i> _{calcd} (mg m ⁻³)	1.104	1.257	1.262	0.956
μ (mm ⁻¹)	1.615	2.551	2.693	1.211
<i>F</i> (000)	1360	1484	1488	776
θ range (°)	1.585 to 25.000	1.589 to 27.487	1.590 to 27.499	1.903 to 27.480
Reflections collected	27593	33002	32809	22403
Data/restraints/parameters	6733/201/425	8678/171/425	8668/105/386	11332/49/428
Goodness-of-fit on F ²	1.049	1.012	1.050	0.964
R(int)	0.1611	0.0437	0.0557	0.1144
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0722, 0.1703	0.0343, 0.0733	0.0434, 0.1174	0.0722, 0.1830
Largest diff peak/hole (e Å ⁻³)	0.883 and -0.730	0.831 and -0.749	1.337 and -1.524	0.688 and -0.718

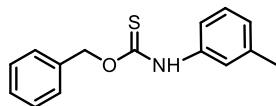
Data of thiocarbamates



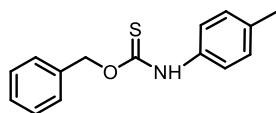
White solid.¹ M.P.: 78–80 °C. ¹H NMR (500 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.28 (br, 1H, *NH*), 7.74 (s, 1H, *ArH*), 7.39–7.20 (m, 9H, *ArH*), 5.64 (s, 1H, *CH*₂), 5.56 (s, 1H, *CH*₂). ¹³C NMR (125 MHz, DMSO-*d*₆, ppm, 20 °C): δ 188.3, 187.9 (*C=S*), 139.5, 138.5, 136.8, 136.5, 129.6, 129.3, 129.1, 126.0, 125.7, 123.8, 122.8 (*ArC*), 73.0, 71.3 (*CH*₂). ¹H NMR (500 MHz, DMSO-*d*₆, ppm, 60 °C): δ 11.10 (br, 1H, *NH*), 7.48–7.37 (m, 9H, *ArH*), 7.19 (d, *J* = 6.5 Hz, 1H, *ArH*), 5.62 (s, 2H, *CH*₂). ¹³C NMR (125 MHz, DMSO-*d*₆, ppm, 60 °C): δ 188.4 (*C=S*), 139.1, 136.7, 129.4, 129.2, 128.9, 125.8, 123.3 (*ArC*), 72.1 (*CH*₂). HRMS (ESI): *m/z* calcd. for C₁₄H₁₃NOS [M+H]⁺: 244.0791, found: 244.0801.



Light yellow solid. M.P.: 79–81 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 10.90, 10.79 (br, 1H, *NH*), 7.52–7.21 (m, 9H, *ArH*), 5.57 (s, 2H, *CH*₂), 2.24, 2.20 (s, 3H, *CH*₃). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 190.1 (*C=S*), 137.6, 136.6, 135.1, 130.8, 128.9, 128.6, 128.4, 128.0, 127.5, 126.7 (*ArC*), 71.9, 71.3 (*CH*₂), 18.0 (*CH*₃). HRMS (ESI): *m/z* calcd. for C₁₅H₁₅NOS [M+H]⁺: 258.0947, found: 258.0948.

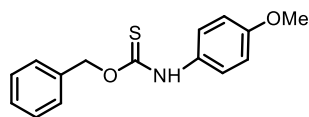


White solid. M.P.: 77–79 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.18 (br, 1H, *NH*), 7.49–7.37 (m, 6H, *ArH*), 7.18 (s, 2H, *ArH*), 6.98 (s, 1H, *ArH*), 5.60 (s, 1H, *CH*₂), 5.54 (s, 1H, *CH*₂), 2.31, 2.26 (s, 3H, *CH*₃). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 187.5 (*C=S*), 139.0, 138.4, 138.2, 136.4, 136.0, 128.9, 128.6, 126.2, 125.9, 123.9, 123.0, 120.6, 119.5 (*ArC*), 72.7, 70.8 (*CH*₂), 21.5 (*CH*₃). HRMS (APCI): *m/z* calcd. for C₁₅H₁₅NOS [M+H]⁺: 258.0947, found: 258.0941.

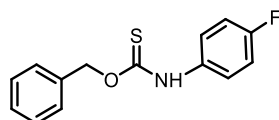


White solid. M.P.: 76–78 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.15 (br, 1H, *NH*), 7.57–7.43 (m, 6H, *ArH*), 7.21–7.13 (m, 3H, *ArH*), 5.61 (s, 1H, *CH*₂), 5.52 (s, 1H, *CH*₂), 2.31, 2.27 (s, 3H, *CH*₃). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 187.9, 187.3 (*C=S*), 136.5, 136.1, 135.6, 134.8, 134.5, 129.3, 128.9, 128.8, 128.6,

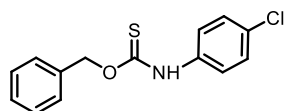
128.5, 123.54, 122.4 (ArC), 72.6, 70.8 (CH₂), 20.9 (CH₃). HRMS (ESI): *m/z* calcd. for C₁₅H₁₅NOS [M+H]⁺: 258.0947, found: 258.0942.



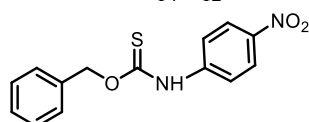
White solid. M.P.: 76–77 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.11, 11.07 (br, 1H, NH), 7.55 (d, *J* = 8.8 Hz, 1H, ArH), 7.51 (d, *J* = 7.2 Hz, 1H, ArH), 7.46–7.39 (m, 4H, ArH), 7.27 (d, *J* = 8.8 Hz, 1H, ArH), 6.96 (d, *J* = 8.8 Hz, 1H, ArH), 6.89 (d, *J* = 8.8 Hz, 1H, ArH), 5.61 (s, 1H, CH₂), 5.53 (s, 1H, CH₂), 3.78, 3.74 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 188.3, 187.2 (C=S), 157.2, 156.9, 136.5, 136.2, 131.9, 131.1, 128.9, 128.8, 128.6, 128.4, 125.3, 124.1, 114.4, 114.1 (ArC), 72.4, 70.9 (CH₂), 55.7 (OCH₃). HRMS (ESI): *m/z* calcd. for C₁₅H₁₅NO₂S [M+H]⁺: 274.0896, found: 274.0890.



White solid. M.P.: 85–87 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.26 (br, 1H, NH), 7.70 (s, 1H, ArH), 7.50–7.40 (m, 6H, ArH), 7.23–7.21 (m, 2H, ArH), 5.62 (s, 1H, CH₂), 5.53 (s, 1H, CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 188.4 (C=S), 159.6 (d, ¹*J*_{F-C} = 259.0 Hz), 136.4, 136.0, 135.4, 134.5, 129.0, 128.7, 128.5, 125.6 (d, ³*J*_{F-C} = 7.0 Hz), 124.6, 124.5, 116.1, 115.6 (d, ²*J*_{F-C} = 21.0 Hz), 72.6, 71.1 (CH₂). HRMS (APCI): *m/z* calcd. for C₁₄H₁₂FNOS [M+H]⁺: 262.0696, found: 262.0697.

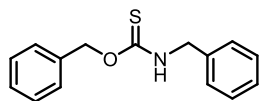


White solid. M.P.: 99–101 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.35 (br, 1H, NH), 7.77 (s, 1H, ArH), 7.44–7.39 (m, 8H, ArH), 5.62 (s, 1H, CH₂), 5.54 (s, 1H, CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 187.8 (C=S), 138.0, 137.0, 136.1, 136.0, 129.0, 128.7, 124.7, 124.0 (ArC), 72.8, 71.1 (CH₂). HRMS (ESI): *m/z* calcd. for C₁₄H₁₂ClNOS [M+H]⁺: 278.0401, found: 278.0404.

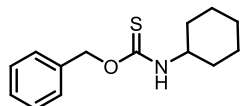


Yellow solid. M.P.: 144–146 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.80 (br, 1H, NH), 8.24 (d, *J* = 8.8 Hz, 2H, ArH), 7.91 (s, 2H, ArH), 7.52 (d, *J* = 6.8 Hz, 2H, ArH), 7.47–7.39 (m, 3H, ArH), 5.62 (s, 2H, CH₂). ¹³C NMR (100 MHz,

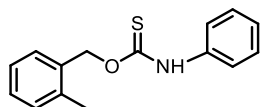
DMSO-*d*₆, ppm, 20 °C): δ 187.8 (C=S), 144.6, 143.5, 135.7, 129.0, 129.0, 128.9, 125.0, 121.6 (ArC), 72.3 (CH₂). HRMS (APCI): *m/z* calcd. for C₁₄H₁₂N₂O₃S [M+H]⁺: 289.0641, found: 289.0646.



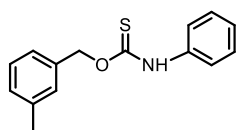
White solid. M.P.: 67–69 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 9.85 (br, 1H, NH), 7.47–7.23 (m, 10H, ArH), 5.50 (s, 2H, CH₂), 4.70 (d, *J* = 5.6 Hz, 1H, CH₂), 4.38 (d, *J* = 5.6 Hz, 1H, CH₂). ¹³C NMR (101 MHz, DMSO-*d*₆, ppm, 20 °C): δ 190.5 (C=S), 138.6, 138.3, 136.7, 128.8, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 127.7, 127.5 (ArC), 71.7, 71.1 (CH₂), 48.4, 46.2 (CH₂). HRMS (ESI): *m/z* calcd. for C₁₅H₁₅NOS [M+H]⁺: 258.0947, found: 258.0957.



Yellow solid. M.P.: 64–66 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 9.20 (d, *J* = 8.4 Hz, 1H, NH), 7.40–7.33 (m, 5H, ArH), 5.50 (s, 1H, CH₂), 5.40 (s, 1H, CH₂), 3.93–3.82 (m, 1H, CyH), 1.88 (d, *J* = 10.0 Hz, 2H, CyH), 1.77–1.51 (m, 3H, CyH), 1.27–1.04 (m, 5H, CyH). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 188.3, 187.3 (C=S), 136.8, 128.9, 128.8, 128.6, 128.4, 128.3, 127.9 (ArC), 71.3, 70.6 (OCH₂), 54.4, 52.4 (NCH), 32.4, 31.7, 25.5, 25.4, 25.1, 25.0 (CH₂). HRMS (APCI): *m/z* calcd. for C₁₄H₁₉NOS [M+H]⁺: 250.1260, found: 250.1265.

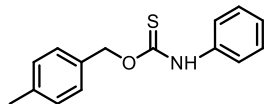


White solid. M.P.: 96–98 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.24 (br, 1H, NH), 7.73 (s, 1H, ArH), 7.46–7.29 (m, 8H, ArH), 5.63 (s, 1H, CH₂), 5.53 (s, 1H, CH₂), 2.37 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 187.8 (C=S), 139.1, 137.3, 134.4, 130.6, 129.8, 129.0, 126.3, 125.4, 123.2, 122.3 (ArC), 71.2, 69.6 (CH₂), 19.0 (CH₃). HRMS (ESI): *m/z* calcd. for C₁₅H₁₅NOS [M+H]⁺: 258.0947, found: 258.0952.

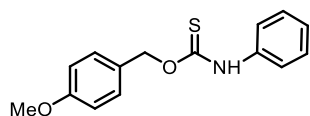


White solid. M.P.: 78–80 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.24 (br, 1H, NH), 7.72 (s, 1H, ArH), 7.36–7.20 (m, 8H, ArH), 5.59 (s, 1H, CH₂), 5.50 (s, 1H,

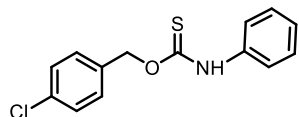
CH_2), 2.35 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ 187.9 (C=S), 139.1, 138.1, 136.2, 136.0, 129.3, 128.8, 125.9, 125.5, 123.3, 122.4 (ArC), 72.6, 70.9 (CH_2), 21.4 (CH_3). HRMS (ESI): m/z calcd. for $\text{C}_{15}\text{H}_{15}\text{NOS}$ $[\text{M}+\text{H}]^+$: 258.0947, found: 258.0941.



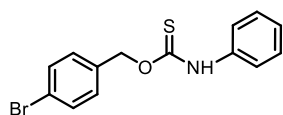
White solid. M.P.: 130–132 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ 11.22 (br, 1H, NH), 7.70 (s, 1H, ArH), 7.35 (s, 5H, ArH), 7.24–7.23 (m, 3H, ArH), 5.57 (s, 1H, CH_2), 5.49 (s, 1H, CH_2), 2.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ 187.6 (C=S), 139.1, 138.1, 133.3, 129.5, 128.9, 125.2, 123.4, 122.3 (ArC), 72.7, 70.9 (CH_2), 21.3 (CH_3). HRMS (ESI): m/z calcd. for $\text{C}_{15}\text{H}_{15}\text{NOS}$ $[\text{M}+\text{H}]^+$: 258.0947, found: 258.0938.



White solid. M.P.: 110–112 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ 11.18 (br, 1H, NH), 7.69 (s, 1H, ArH), 7.43–7.17 (s, 6H, ArH), 6.98 (d, $J = 7.6$ Hz, 2H, ArH), 5.54 (s, 1H, CH_2), 5.46 (s, 1H, CH_2), 3.79 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ 188.0 (C=S), 159.8, 138.2, 130.7, 129.2, 127.9, 125.2, 123.4, 122.2, 114.3 (ArC), 72.7, 71.0 (CH_2), 55.6 (OCH_3). HRMS (APCI): m/z calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 274.0896, found: 274.0888.

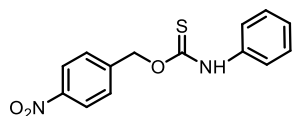


White solid. M.P.: 117–119 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ 11.28 (br, 1H, NH), 7.70 (s, 1H, ArH), 7.49 (s, 4H, ArH), 7.35 (s, 3H, ArH), 7.18 (s, 1H, ArH), 5.61 (s, 1H, CH_2), 5.54 (s, 1H, CH_2). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, ppm, 20 °C) δ 187.8 (C=S), 139.0, 135.5, 133.3, 130.5, 129.3, 129.0, 125.6, 123.4, 122.5 (ArC), 71.7, 69.9 (CH_2). HRMS (APCI): m/z calcd. for $\text{C}_{14}\text{H}_{12}\text{ClNOS}$ $[\text{M}+\text{H}]^+$: 278.0401, found: 278.0407.



White solid. M.P.: 122–124 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ 11.25 (br, 1H, NH), 7.67–7.59 (m, 3H, ArH), 7.43–7.32 (m, 5H, ArH), 7.16 (s, 1H, ArH), 5.56 (s, 1H, CH_2), 5.49 (s, 1H, CH_2). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, ppm, 20 °C): δ

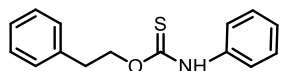
187.8 (C=S), 139.0, 138.0, 136.0, 135.5, 131.9, 130.9, 129.3, 129.0, 125.6, 125.4, 123.4, 122.5, 121.9 (ArC), 71.7, 69.9 (CH₂). HRMS (APCI): *m/z* calcd. for C₁₄H₁₂BrNOS [M+H]⁺: 321.9896, found: 321.9903.



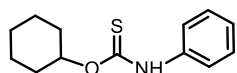
White solid. M.P.: 136–138 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.39 (br, 1H, NH), 8.29 (s, 2H, ArH), 7.75–7.70 (m, 3H, ArH), 7.39 (s, 3H, ArH), 7.20 (s, 1H, ArH), 5.77 (s, 1H, CH₂), 5.71 (s, 1H, CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 187.6 (C=S), 147.5, 144.5, 138.9, 129.0, 125.7, 124.0, 123.4, 122.7 (ArC), 71.0, 69.2 (CH₂). HRMS (ESI): *m/z* calcd. for C₁₄H₁₂N₂O₃S [M+H]⁺: 289.0641, found: 289.0645.



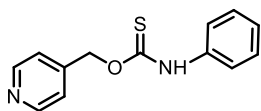
White solid. M.P.: 149–151 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.39 (br, 1H, NH), 7.91 (s, 2H, ArH), 7.70–7.61 (m, 3H, ArH), 7.37–7.20 (m, 4H, ArH), 5.72 (s, 1H, CH₂), 5.64 (s, 1H, CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 187.2 (C=S), 142.3, 141.9, 138.9, 137.9, 132.9, 129.3, 128.9, 125.7, 123.3, 122.6, 119.1, 111.1 (ArC), 71.3, 69.5 (OCH₂). HRMS (ESI): *m/z* calcd. for C₁₅H₁₂N₂OS [M+H]⁺: 269.0743, found: 269.0747.



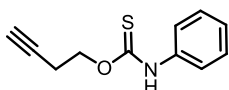
White solid.¹ M.P.: 86–88 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.10 (br, 1H, NH), 7.67 (s, 1H, ArH), 7.34–7.26 (m, 7H, ArH), 7.18 (s, 2H, ArH), 4.73 (s, 2H, CH₂), 3.08 (t, *J* = 6.4 Hz, 2H, CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 187.6 (C=S), 138.4, 129.4, 129.1, 128.9, 126.9, 125.1, 123.6, 122.2 (ArC), 72.3 (OCH₂), 34.6 (CH₂). HRMS (ESI): *m/z* calcd. for C₁₅H₁₅NOS [M+H]⁺: 258.0947, found: 258.0955.



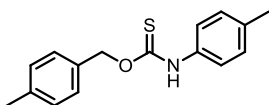
Yellow solid.¹ M.P.: 78–80 °C. ¹H NMR (400 MHz, DMSO-*d*₆, ppm, 20 °C): δ 11.00 (br, 1H, NH), 7.65 (s, 1H, ArH), 7.34 (s, 3H, ArH), 7.14 (s, 1H, ArH), 5.34 (s, 1H, OCH), 1.94 (s, 2H, CyH), 1.72–1.29 (m, 8H, CyH). ¹³C NMR (100 MHz, DMSO-*d*₆, ppm, 20 °C): δ 186.8 (C=S), 138.2, 129.2, 125.0, 122.2 (ArC), 79.8 (OCH), 31.6, 31.1, 25.3, 23.5 (CyC). HRMS (APCI): *m/z* calcd. for C₁₃H₁₇NOS [M+H]⁺: 236.1104, found: 236.1102.



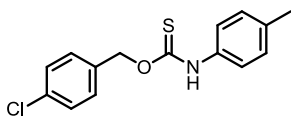
Light yellow solid. M.P.: 144–146 °C. ^1H NMR (400 MHz, DMSO- d_6 , ppm, 20 °C): δ 11.39 (br, 1H, NH), 8.61 (s, 2H, PydH), 7.71 (s, 1H, PydH), 7.47–7.40 (m, 5H, ArH), 7.22 (s, 1H, PydH), 5.68 (s, 1H, CH₂), 5.61 (s, 1H, CH₂). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm, 20 °C): δ 187.3 (C=S), 150.2, 145.7, 137.9, 129.4, 129.0, 125.8, 123.4, 122.8, 122.4 (ArC), 70.5, 68.7 (CH₂). HRMS (APCI): m/z calcd. for C₁₃H₁₂N₂OS [M+H]⁺: 245.0743, found: 245.0738.



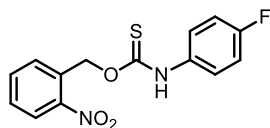
Yellow oil. ^1H NMR (400 MHz, DMSO- d_6 , ppm, 20 °C): δ 11.23 (br, 1H, NH), 7.67 (s, 1H, ArH), 7.45–7.37 (m, 3H, ArH), 7.17 (s, 1H, ArH), 4.57 (s, 2H, OCH₂), 2.98 (t, J = 6.4 Hz, 1H, CH), 2.68 (dt, J = 2.8, 6.4 Hz, 2H, CH₂). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm, 20 °C): δ 187.2 (C=S), 138.1, 129.2, 125.1, 123.5, 122.1 (ArC), 81.4 (C≡CH), 73.1 (C≡CH), 69.4, 67.4 (OCH₂), 18.7 (CH₂). HRMS (ESI): m/z calcd. for C₁₁H₁₁NOS [M+H]⁺: 206.0634, found: 206.0625.



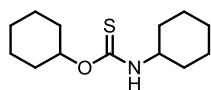
White solid. M.P.: 108–110 °C. ^1H NMR (400 MHz, DMSO- d_6 , ppm, 20 °C): δ 11.14 (br, 1H, NH), 7.58 (d, J = 6.0 Hz, 1H, ArH), 7.38–7.33 (m, 2H, ArH), 7.23–7.12 (m, 5H, ArH), 5.57 (s, 1H, CH₂), 5.48 (s, 1H, CH₂), 2.34 (s, 3H, CH₃), 2.27 (s, 3H, CH₃). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm, 20 °C): δ 187.9, 187.3 (C=S), 138.0, 135.6, 134.4, 133.0, 129.6, 129.4, 129.3, 128.9, 128.7, 123.4, 122.3 (ArC), 72.5, 70.7 (CH₂), 21.2 (CH₃), 20.9 (CH₃). HRMS (ESI): m/z calcd. for C₁₆H₁₇NOS [M+H]⁺: 272.1104, found: 272.1098.



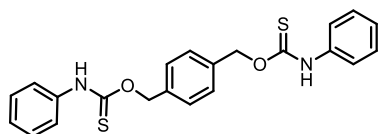
White solid. M.P.: 130–132 °C. ^1H NMR (400 MHz, DMSO- d_6 , ppm, 20 °C): δ 11.20 (br, 1H, NH), 7.58–7.47 (m, 5H, ArH), 7.24–7.14 (m, 3H, ArH), 5.60 (s, 1H, CH₂), 5.53 (s, 1H, CH₂), 2.31, 2.27 (s, 3H, CH₃). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm, 20 °C): δ 187.7 (C=S), 136.4, 135.9, 135.6, 135.1, 134.9, 134.6, 133.6, 133.2, 132.6, 130.5, 130.4, 129.6, 129.3, 128.9, 123.4, 122.4 (ArC), 71.5, 69.7 (CH₂), 20.9 (CH₃). HRMS (ESI): m/z calcd. for C₁₅H₁₄ClNOS [M+H]⁺: 292.0557, found: 292.0562.



Light yellow solid. M.P.: 114–116 °C. ^1H NMR (400 MHz, DMSO- d_6 , ppm, 20 °C): δ 11.41 (br, 1H, NH), 8.20–8.16 (m, 1H, ArH), 7.87–7.59 (m, 4H, ArH), 7.39 (s, 1H, ArH), 7.24 (d, $J = 8.4$ Hz, 2H, ArH), 5.93 (s, 1H, CH₂), 5.90 (s, 1H, CH₂). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm, 20 °C): δ 187.9, 187.1 (C=S), 159.8 (d, $^1J_{\text{F-C}} = 242.0$ Hz), 147.7, 135.2, 134.6, 134.2, 132.4, 131.7, 129.8, 129.7, 125.5 (d, $^3J_{\text{F-C}} = 8.0$ Hz), 125.0, 116.1, 115.6 (d, $^2J_{\text{F-C}} = 21.0$ Hz), 69.2, 67.2 (CH₂). HRMS (ESI): m/z calcd. for C₁₄H₁₁FN₂O₃S [M+H]⁺: 307.0547, found: 307.0549.

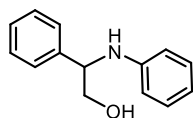


White solid. M.P.: 106–108 °C. ^1H NMR (400 MHz, DMSO- d_6 , ppm, 20 °C): δ 8.97–8.92 (m, 1H, NH), 5.26–5.13 (m, 1H, OCH), 3.89–3.54 (m, 1H, NHCH), 1.91–1.51 (m, 10H, CyH), 1.36–1.05 (m, 10H, CyH). ^{13}C NMR (125 MHz, DMSO- d_6 , ppm, 20 °C): δ 188.0 (C=S), 78.0, 77.4 (OCH), 54.4, 52.7 (NCH), 32.7, 32.3, 32.2, 31.6, 25.9, 25.7, 25.6, 25.5, 24.3, 23.8 (CyC). HRMS (ESI): m/z calcd. for C₁₃H₂₃NOS [M+H]⁺: 242.1573, found: 242.1567.



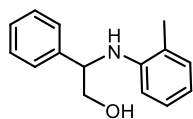
White solid. M.P.: 187–189 °C. ^1H NMR (400 MHz, DMSO- d_6 , ppm, 20 °C): δ 11.26 (br, 2H, NH), 7.71 (s, 2H, ArH), 7.52–7.36 (m, 10H, ArH), 7.18 (s, 2H, ArH), 5.63 (s, 2H, CH₂), 5.55 (s, 2H, CH₂). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm, 20 °C): δ 187.8 (C=S), 138.9, 137.9, 136.0, 128.9, 125.5, 123.3, 122.5 (ArC), 72.2, 70.5 (CH₂). HRMS (ESI): m/z calcd. for C₂₂H₂₀N₂O₂S₂ [M+H]⁺: 409.1039, found: 409.1032.

Data of β -amino alcohols

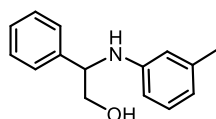


Yellow oil.² ^1H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.38–7.32 (m, 4H, ArH), 7.29–7.27 (m, 1H, ArH), 7.10 (t, $J = 8.0$ Hz, 2H, ArH), 6.69 (t, $J = 7.6$ Hz, 1H, ArH), 6.58 (dd, $J = 8.4, 0.8$ Hz, 2H, ArH), 4.52 (dd, $J = 4.0, 6.4$ Hz, 1H, CH), 3.95 (d, $J = 10.4$ Hz, 1H, CH₂), 3.76 (t, $J = 8.0$ Hz, 1H, CH₂), 1.73 (br, 1H, NH). ^{13}C NMR (100

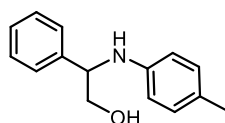
MHz, CDCl₃, ppm, 20 °C): δ 147.3, 140.2, 129.2, 128.8, 127.6, 126.8, 117.9, 113.9 (ArC), 67.3 (CHOH), 59.9 (CH₂NH). HRMS (ESI): m/z calcd. for C₁₄H₁₅NO [M+H]⁺: 214.1226, found: 214.1225.



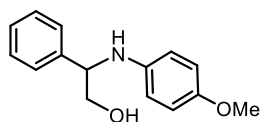
White solid. M.p.: 79–81 °C. ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.38–7.27 (m, 5H, ArH), 7.10 (d, J = 7.2 Hz, 1H, ArH), 6.98 (t, J = 7.6 Hz, 1H, ArH), 6.67 (t, J = 7.2 Hz, 1H, ArH), 6.40 (d, J = 8.0 Hz, 1H, ArH), 4.56 (dd, J = 4.0, 6.4 Hz, 1H, CH), 4.42 (br, 1H, OH), 3.99–3.97 (m, 1H, CH₂), 3.81–3.80 (m, 1H, CH₂), 2.31 (s, 3H, CH₃), 1.88 (br, 1H, NH). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 145.1, 140.2, 130.1, 128.8, 127.6, 127.0, 126.7, 122.6, 117.5, 111.5 (ArC), 67.5 (CHOH), 59.8 (CH₂NH), 17.7 (Me). HRMS (ESI): m/z calcd. for C₁₅H₁₇NO [M+H]⁺: 228.1383, found: 228.1386.



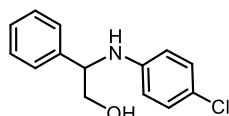
Yellow oil. ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.38–7.32 (m, 4H, ArH), 7.29–7.27 (m, 1H, ArH), 6.99 (t, J = 7.6 Hz, 1H, ArH), 6.51 (d, J = 7.2 Hz, 1H, ArH), 6.44 (s, 1H, ArH), 6.37 (dd, J = 8.0, 2.0 Hz, 1H, ArH), 4.51 (dd, J = 4.4, 6.8 Hz, 1H, CH), 3.94 (dd, J = 4.0, 11.2 Hz, 1H, CH₂), 3.76 (dd, J = 6.8, 11.2, Hz, 1H, CH₂), 2.22 (s, 3H, CH₃), 1.61 (br, 1H, NH). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 147.2, 140.2, 138.9, 129.0, 128.8, 127.6, 126.7, 118.9, 114.7, 110.8 (ArC), 67.3 (CHOH), 59.8 (CH₂NH), 21.6 (Me). HRMS (ESI): m/z calcd. for C₁₅H₁₇NO [M+H]⁺: 228.1383, found: 228.1384.



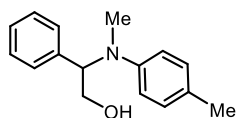
White solid. M.p.: 72–74 °C. ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.40–7.34 (m, 4H, ArH), 7.31–7.28 (m, 1H, ArH), 6.94 (d, J = 8.4 Hz, 2H, ArH), 6.53 (d, J = 8.4 Hz, 2H, ArH), 4.51 (dd, J = 4.0, 6.8 Hz, 1H, CH), 3.96 (dd, J = 4.0, 10.8 Hz, 1H, CH₂), 3.76 (dd, J = 7.2, 11.2 Hz, 1H, CH₂), 2.22 (s, 3H, Me), 1.85 (br, 1H, NH). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 144.8, 140.2, 129.6, 128.8, 127.5, 127.1, 126.7, 114.0 (ArC), 67.4 (CHOH), 60.1 (CH₂NH), 20.4 (Me). HRMS (ESI): m/z calcd. for C₁₅H₁₇NO [M+H]⁺: 228.1383, found: 228.1389.



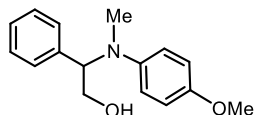
Yellow oil.² ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.35–7.31 (m, 4H, ArH), 7.28–7.26 (m, 1H, ArH), 6.70 (d, *J* = 8.8 Hz, 2H, ArH), 6.54 (d, *J* = 8.8 Hz, 2H, ArH), 4.43 (dd, *J* = 4.4, 7.6 Hz, 1H, CH), 3.92 (dd, *J* = 4.0, 11.2 Hz, 1H, CH₂), 3.71 (dd, *J* = 7.6, 11.2 Hz, 1H, CH₂), 3.69 (s, 3H, Me). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 152.3, 141.3, 140.3, 128.8, 127.6, 126.7, 115.3, 114.7 (ArC), 67.3 (CHOH), 60.8 (CHNH), 55.7(OMe). HRMS (ESI): *m/z* calcd. for C₁₅H₁₇NO₂ [M+H]⁺: 244.1332, found: 244.1329.



White solid. M.p.: 78–80 °C. ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.36–7.28 (m, 5H, ArH), 7.03 (d, *J* = 8.8 Hz, 2H, ArH), 6.47 (d, *J* = 8.8 Hz, 2H, ArH), 4.59 (br, 1H, OH), 4.45 (dd, *J* = 4.0, 6.8 Hz, 1H, CH), 3.94 (d, *J* = 10.8 Hz, 1H, CH₂), 3.77–3.72 (m, 1H, CH₂), 1.79 (br, 1H, NH). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 145.7, 139.6, 129.0, 128.9, 127.8, 126.7, 122.4, 114.9 (ArC), 67.3 (CHOH), 59.9 (CH₂NH). HRMS (ESI): *m/z* calcd. for C₁₄H₁₄NOCl [M+H]⁺: 248.0837, found: 248.0830.

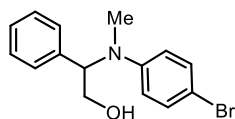


Yellow oil. ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.45–7.32 (m, 5H, ArH), 7.10 (d, *J* = 8.0 Hz, 2H, ArH), 6.81 (d, *J* = 8.0 Hz, 2H, ArH), 4.98 (dd, *J* = 4.4, 8.4 Hz, 1H, CH), 3.48–3.37 (m, 2H, CH₂N), 2.93 (s, 3H, NMe), 2.71 (br, 1H, NH), 2.30 (s, 3H, Me). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 148.1, 142.0, 129.8, 128.5, 127.7, 127.2, 125.9, 114.0 (ArC), 71.5 (CHOH), 62.6 (CH₂N), 39.6 (NMe), 20.3 (Me). HRMS (ESI): *m/z* calcd. for C₁₆H₁₉NO [M+H]⁺: 242.1539, found: 242.1546.

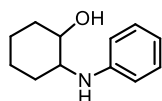


Yellow oil. ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.28–7.26 (m, 3H, ArH), 7.06–7.04 (m, 2H, ArH), 6.91–6.82 (m, 4H, ArH), 4.81 (dd, *J* = 5.2, 10.0 Hz, 1H, CH), 4.12 (t, *J* = 10.8 Hz, 1H, CH₂N), 3.99 (s, 1H, CH₂N), 3.78 (s, 3H, Me), 2.59 (s, 3H, NMe), 2.45 (br, 1H, NH). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 153.4, 145.3, 136.8, 128.4, 127.6, 127.5, 118.3, 114.5 (ArC), 67.0 (CHOH), 61.2 (CHN), 55.6

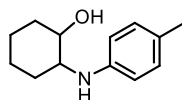
(OMe), 32.9 (NMe). HRMS (ESI): m/z calcd. for $C_{16}H_{19}NO_2$ $[M+H]^+$: 258.1489, found: 258.1494.



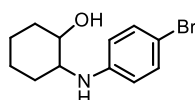
Yellow oil. 1H NMR (400 MHz, $CDCl_3$, ppm, 20 °C): δ 7.34–7.27 (m, 5H, ArH), 7.11 (d, J = 8.0 Hz, 2H, ArH), 6.78 (d, J = 8.4 Hz, 2H, ArH), 5.01 (t, J = 6.8 Hz, 1H, CH), 4.13–4.11 (m, 2H, CH₂N), 2.71 (s, 3H, Me), 2.02 (br, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 20 °C): δ 150.1, 137.1, 131.9, 128.7, 127.8, 127.0, 116.2, 110.2 (ArC), 64.6 (CHOH), 61.7 (CHN), 32.2 (NMe). HRMS (ESI): m/z calcd. for $C_{15}H_{16}NOBr$ $[M+H]^+$: 306.0488, found: 306.0489.



White solid.² M.p.: 57–59 °C. 1H NMR (400 MHz, $CDCl_3$, ppm, 20 °C): δ 7.20–7.16 (m, 2H, ArH), 6.76–6.71 (m, 3H, ArH), 3.35 (dt, J = 4.0, 9.6 Hz, 1H, CHOH), 3.18–3.11 (m, 1H, CHN), 2.76 (br, 1H, OH), 2.13–2.20 (m, 2H, CyH), 1.80–1.70 (m, 2H, CyH), 1.63 (br, 1H, NH), 1.45–1.01 (m, 4H, CyH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 20 °C): δ 147.8, 129.3, 118.4, 114.4 (ArC), 74.5 (CHOH), 60.1 (CHNH), 33.1, 31.6, 25.0, 24.2 (CyC). HRMS (ESI): m/z calcd. for $C_{12}H_{17}NO$ $[M+H]^+$: 192.1383, found: 192.1389.

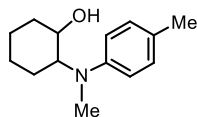


Yellow oil.³ 1H NMR (400 MHz, $CDCl_3$, ppm, 20 °C): δ 7.00 (d, J = 8.0 Hz, 2H, ArH), 6.65 (d, J = 8.0 Hz, 2H, ArH), 3.33 (dt, J = 4.4, 9.6 Hz, 1H, CHOH), 3.12–3.06 (m, 1H, CHN), 2.95 (br, 1H, OH), 2.25 (s, 3H, Me), 2.13–2.09 (m, 2H, CyH), 1.79–1.69 (m, 2H, CyH), 1.44–1.27 (m, 3H, CyH), 1.07–0.97 (m, 1H, CyH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, 20 °C): δ 145.5, 129.8, 127.6, 114.7 (ArC), 74.4 (CHOH), 60.6 (CHNH), 33.2, 31.5, 25.0, 24.3 (CyC), 20.4 (Me). HRMS (ESI): m/z calcd. for $C_{13}H_{19}NO$ $[M+H]^+$: 206.1539, found: 206.1540.

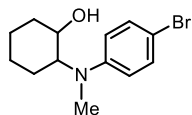


White solid.³ M.p.: 124–126 °C. 1H NMR (400 MHz, $CDCl_3$, ppm, 20 °C): δ 7.25 (d, J = 8.8 Hz, 2H, ArH), 6.59 (d, J = 8.8 Hz, 2H, ArH), 3.38–3.32 (m, 2H, CHOH and CHN), 3.10–3.06 (m, 1H, CyH), 2.58 (br, 1H, OH), 2.12–2.06 (m, 2H, CyH), 1.61 (br,

1H, *NH*), 1.79–1.71 (m, 2H, *CyH*), 1.40–1.27 (m, 2H, *CyH*), 1.09–0.99 (m, 1H, *CyH*).
¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 146.9, 132.0, 115.8, 109.8 (*ArC*), 74.5 (*CHOH*), 60.2 (*NHCH*), 33.2, 31.5, 24.9, 24.2 (*CyC*).



Yellow oil.⁴ ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.08 (d, *J* = 8.4 Hz, 2H, *ArH*), 6.89 (d, *J* = 8.4 Hz, 2H, *ArH*), 3.65 (dt, *J* = 4.4, 10.4 Hz, 1H, *CHO*), 3.36–3.30 (m, 1H, *CHN*), 2.96 (s, 1H, *OH*), 2.74 (s, 3H, *NCH*₃), 2.29 (s, 3H, *CH*₃), 2.24–2.19 (m, 1H, *CyH*), 1.77–1.69 (m, 3H, *CyH*), 1.42–1.26 (m, 4H, *CyH*). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 149.3, 129.6, 128.1, 116.3 (*ArC*), 69.9 (*COH*), 67.7 (*CHN*), 33.3, 31.3, 25.6, 25.5, 24.3, 20.3 (*CyC*).



Yellow oil.⁵ ¹H NMR (400 MHz, CDCl₃, ppm, 20 °C): δ 7.29 (d, *J* = 9.2 Hz, 2H, *ArH*), 6.78 (d, *J* = 9.2 Hz, 2H, *ArH*), 3.65 (dt, *J* = 4.4, 10.0 Hz, 1H, *CHO*), 3.36–3.29 (m, 1H, *CHN*), 2.72 (s, 3H, *NCH*₃), 2.63 (s, 1H, *OH*), 2.18–2.15 (m, 1H, *CyH*), 1.76–1.65 (m, 3H, *CyH*), 1.42–1.23 (m, 4H, *CyH*). ¹³C NMR (100 MHz, CDCl₃, ppm, 20 °C): δ 150.4, 131.7, 116.9, 110.2 (*ArC*), 70.7 (*COH*), 66.9 (*CHN*), 33.4, 31.1, 26.2, 25.4, 24.3 (*CyC*).

Copies of the ligand

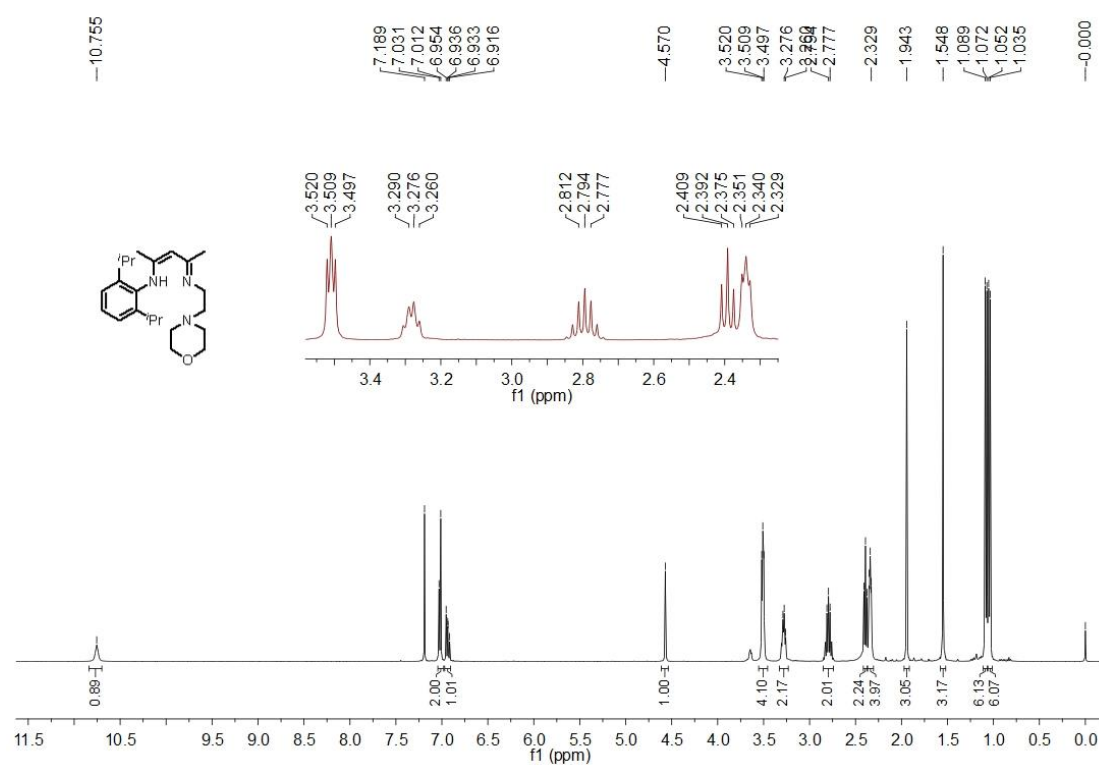


Fig. S1. ¹H NMR spectrum of **HL** (400 MHz, CDCl₃, 20 °C)

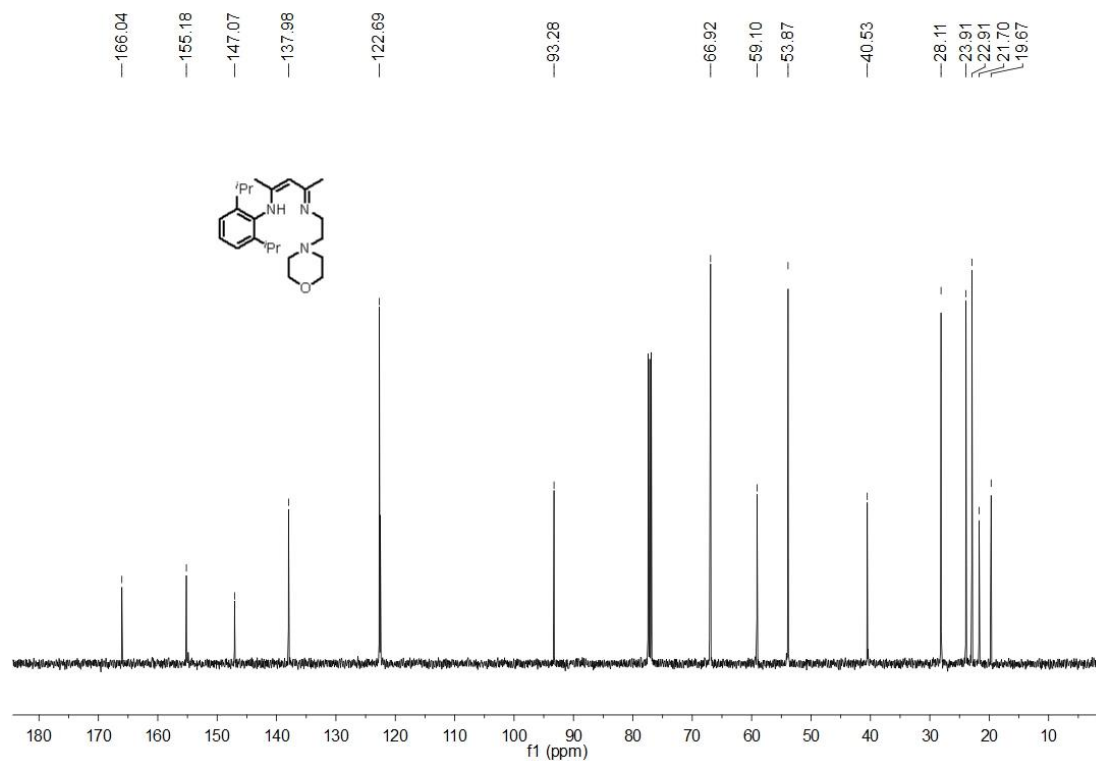


Fig. S2. ¹³C NMR spectrum of **HL** (100 MHz, CDCl₃, 20 °C)

Copies of rare-earth metal complexes

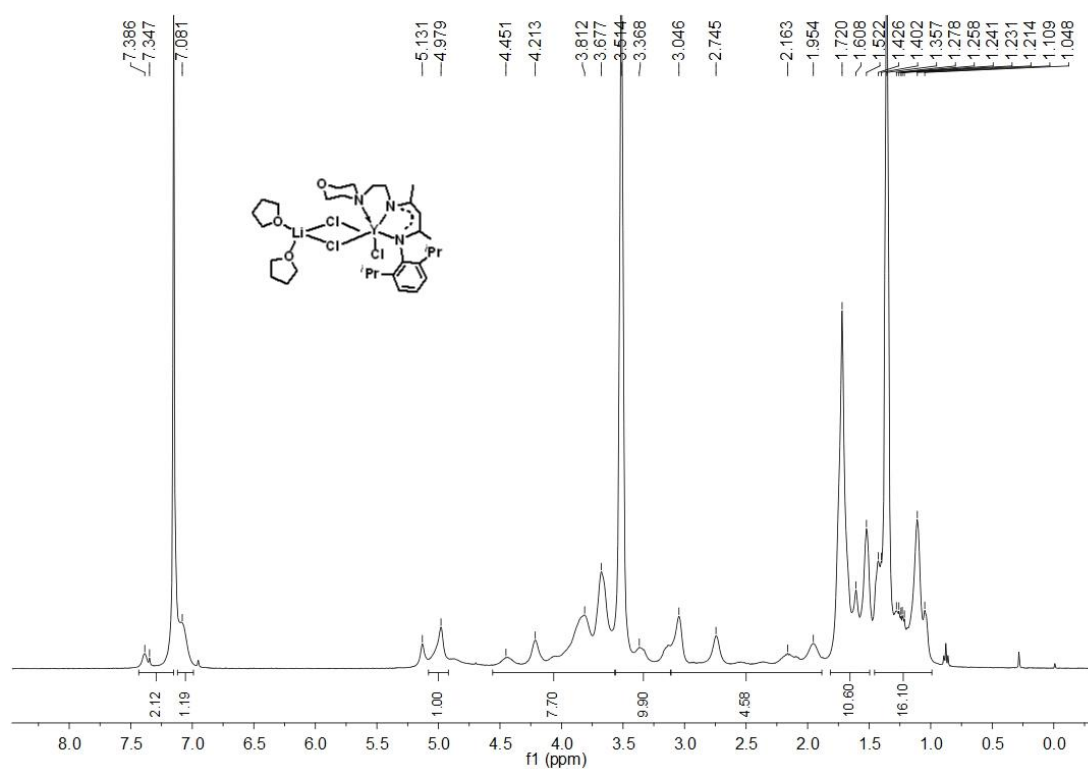


Fig. S3. ^1H NMR spectrum of **1a** (400 MHz, C_6D_6 , 20 °C)

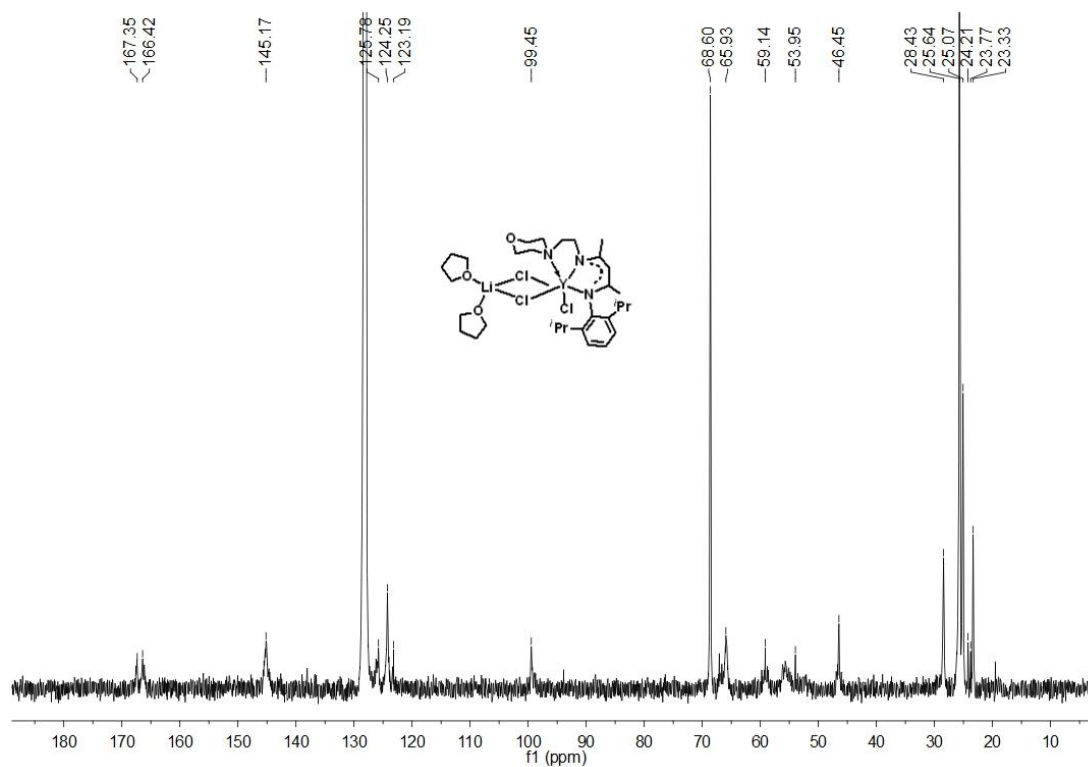


Fig. S4. ^{13}C NMR spectrum of **1a** (100 MHz, C_6D_6 , 20 °C)

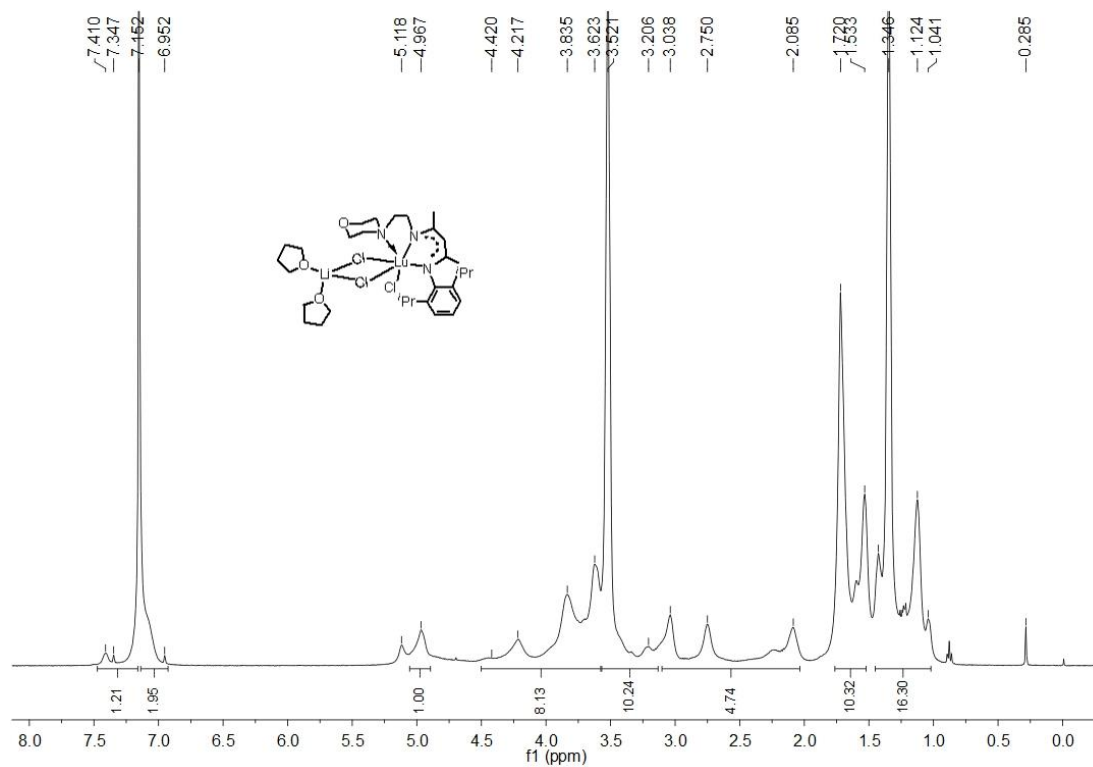


Fig. S5. ^1H NMR spectrum of **1c** (400 MHz, C_6D_6 , 20 $^\circ\text{C}$)

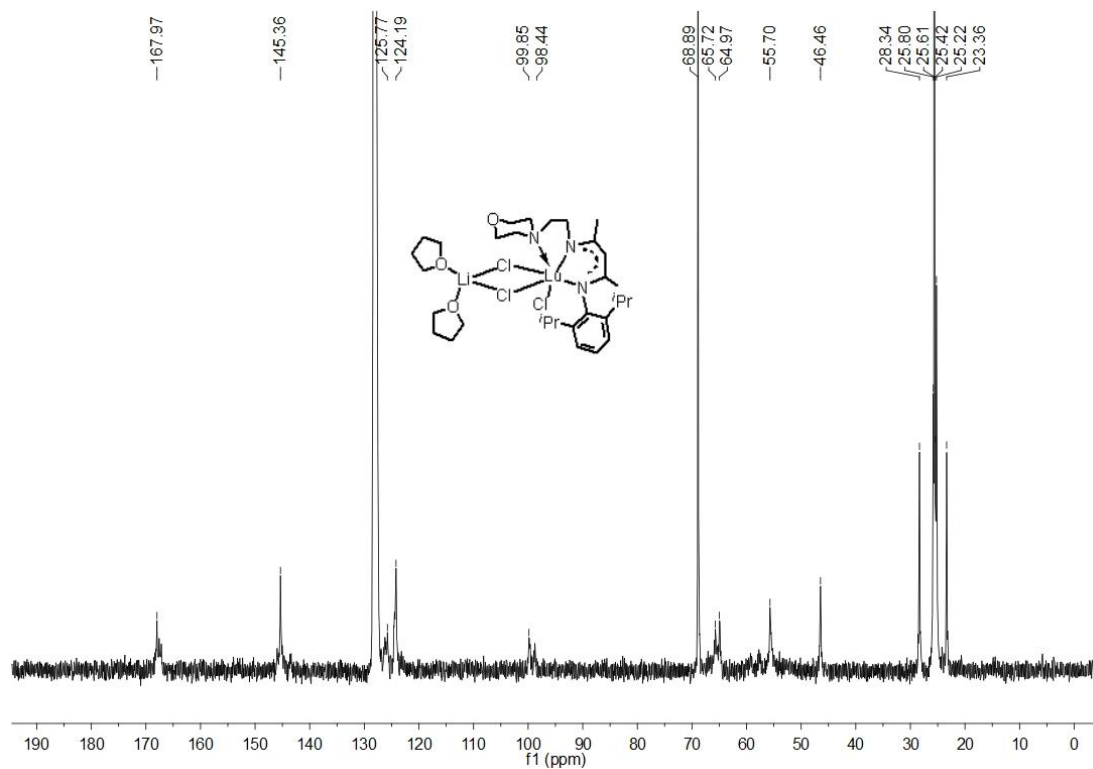


Fig. S6. ^{13}C NMR spectrum of **1c** (100 MHz, C_6D_6 , 20 $^\circ\text{C}$)

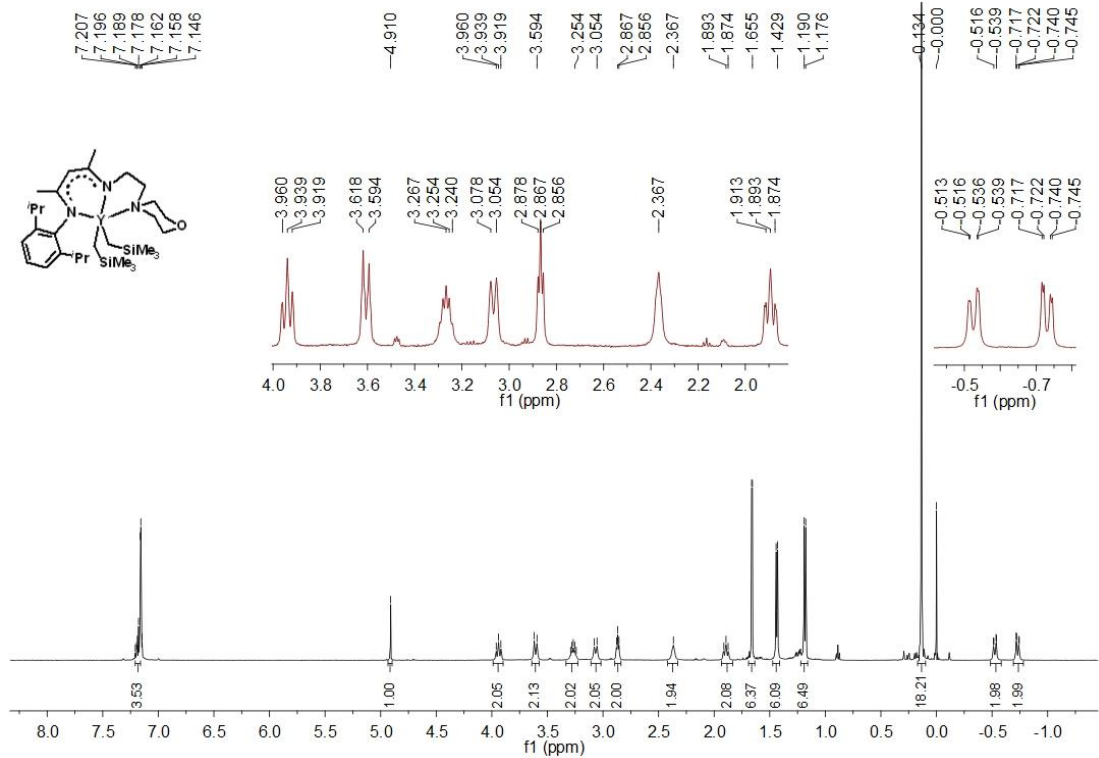


Fig. S7. ¹H NMR spectrum of **2a** (500 MHz, C₆D₆, 20 °C)

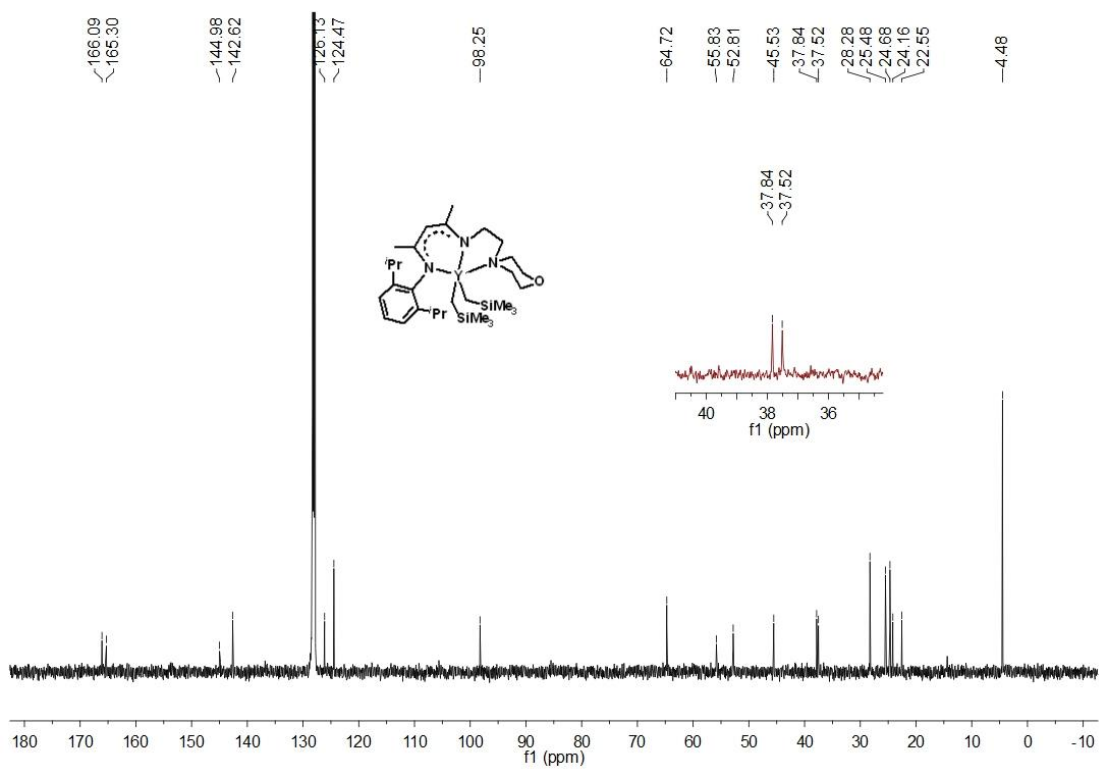


Fig. S8. ¹³C NMR spectrum of **2a** (125 MHz, C₆D₆, 20 °C)

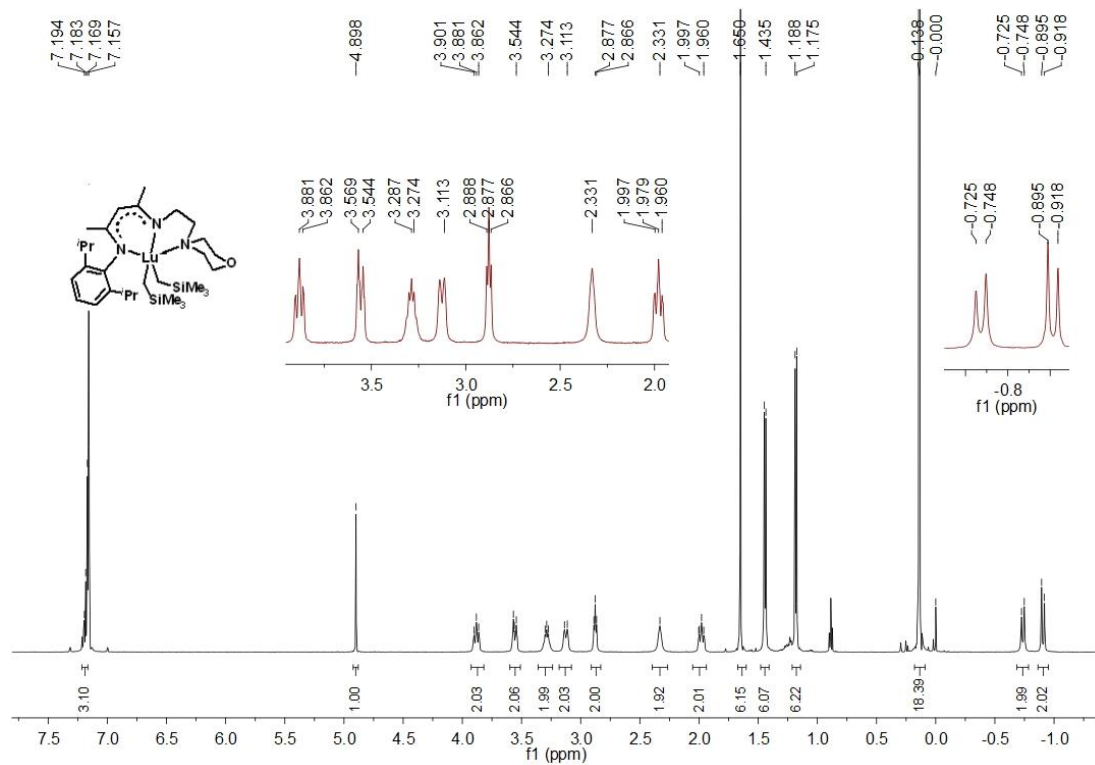


Fig. S9. ^1H NMR spectrum of **2c** (500 MHz, C_6D_6 , 20 $^\circ\text{C}$)

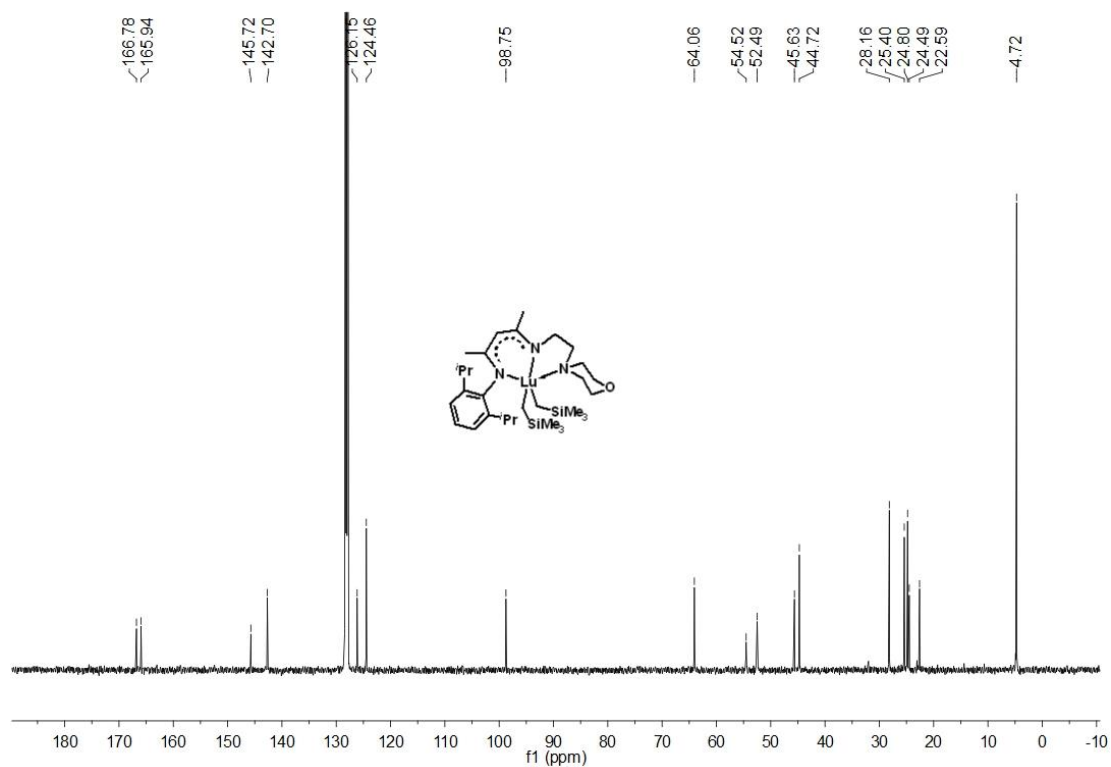


Fig. S10. ^{13}C NMR spectrum of **2c** (125 MHz, C_6D_6 , 20 $^\circ\text{C}$)

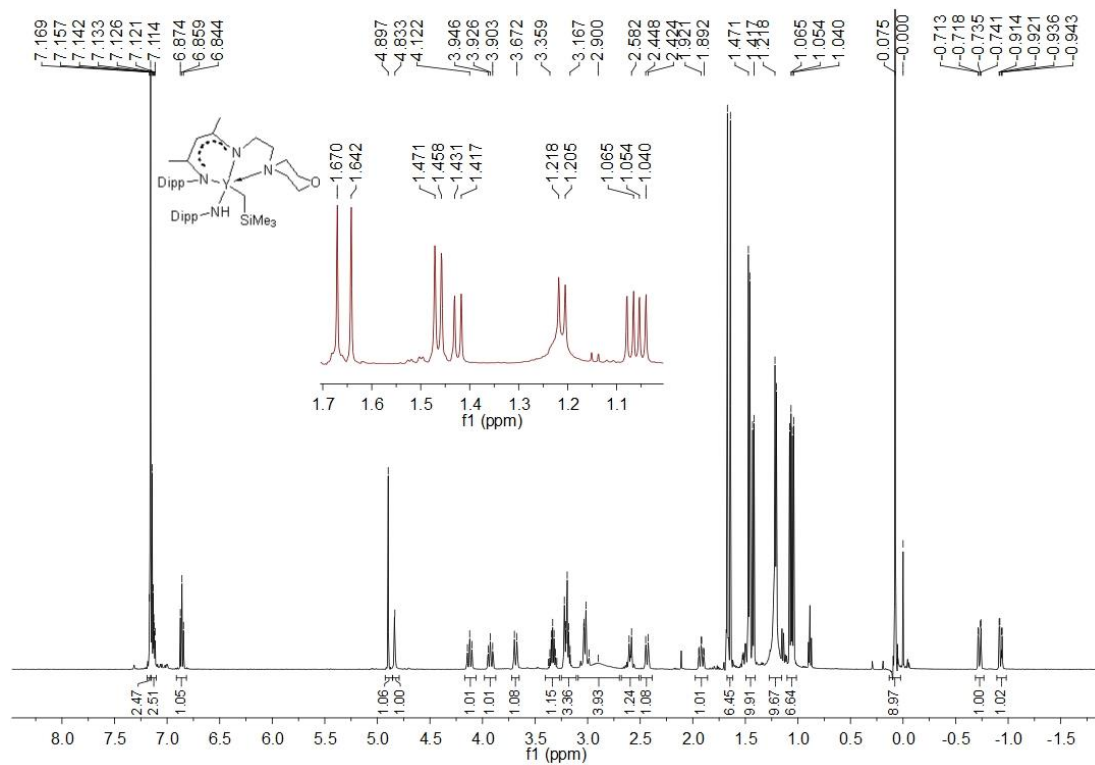


Fig. S11. ¹H NMR spectrum of **5a** (500 MHz, C₆D₆, 20 °C)

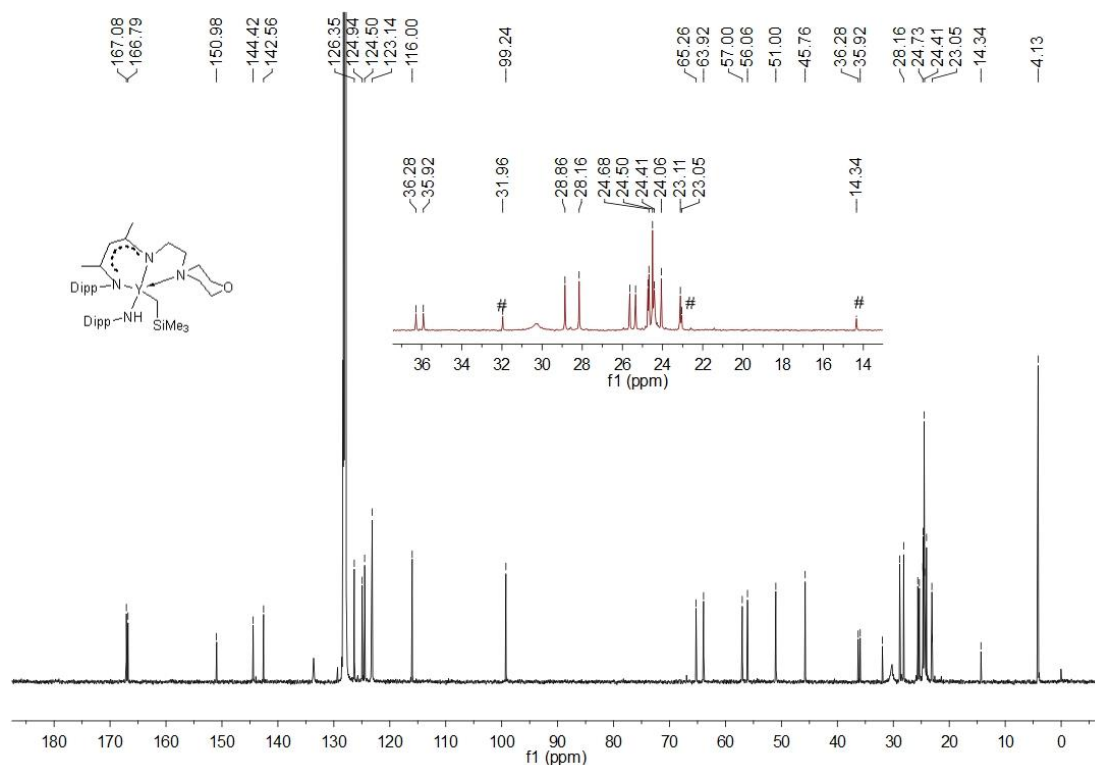


Fig. S12. ¹³C NMR spectrum of **5a** (125 MHz, C₆D₆, 20 °C). The peaks labelled with # represent residual *n*-hexane.

Copies of thiocarbamates

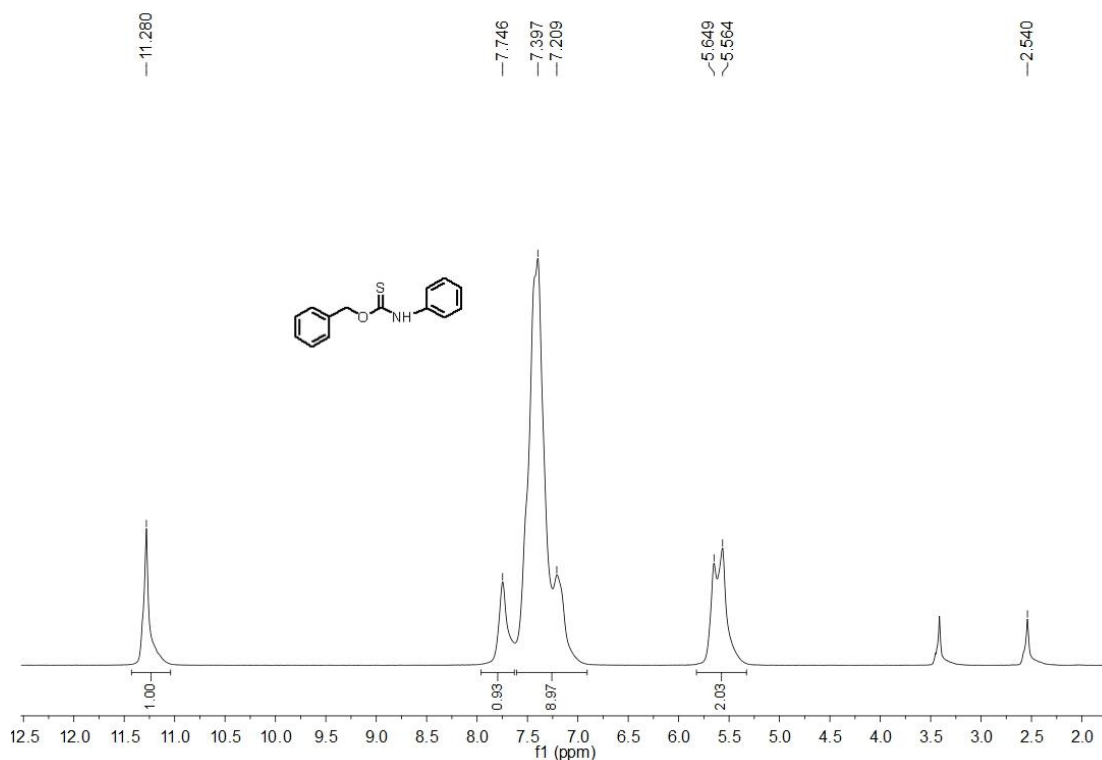


Fig. S13. ^1H NMR spectrum of 3aa (400 MHz, DMSO- d_6 , 20 °C)

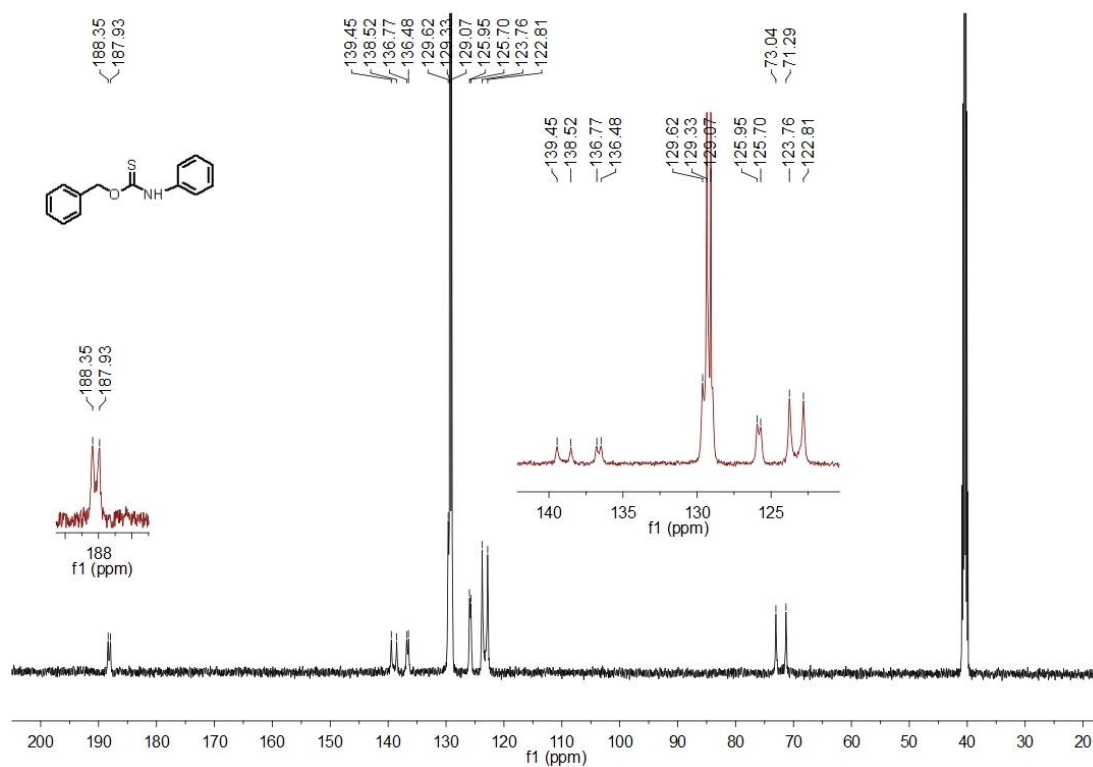


Fig. S14. ^{13}C NMR spectrum of 3aa (100 MHz, DMSO- d_6 , 20 °C)

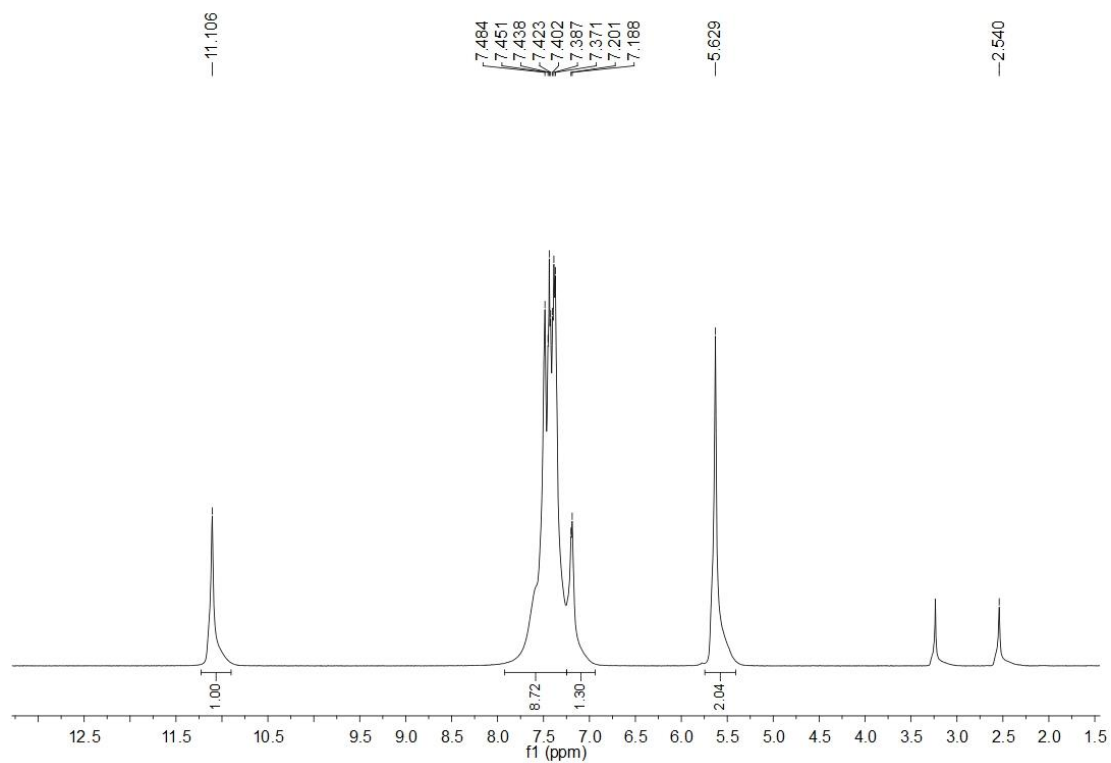


Fig. S15. ¹H NMR spectrum of 3aa (500 MHz, DMSO-*d*₆, 60 °C)

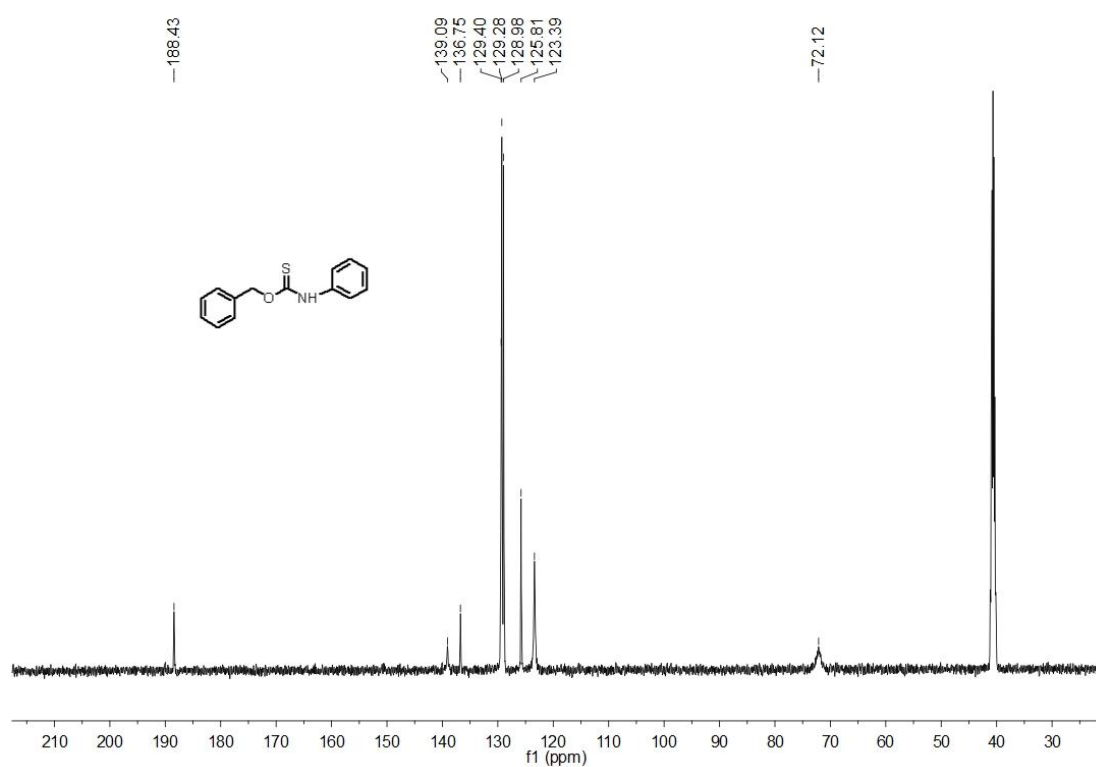


Fig. S16. ¹³C NMR spectrum of 3aa (125 MHz, DMSO-*d*₆, 60 °C)

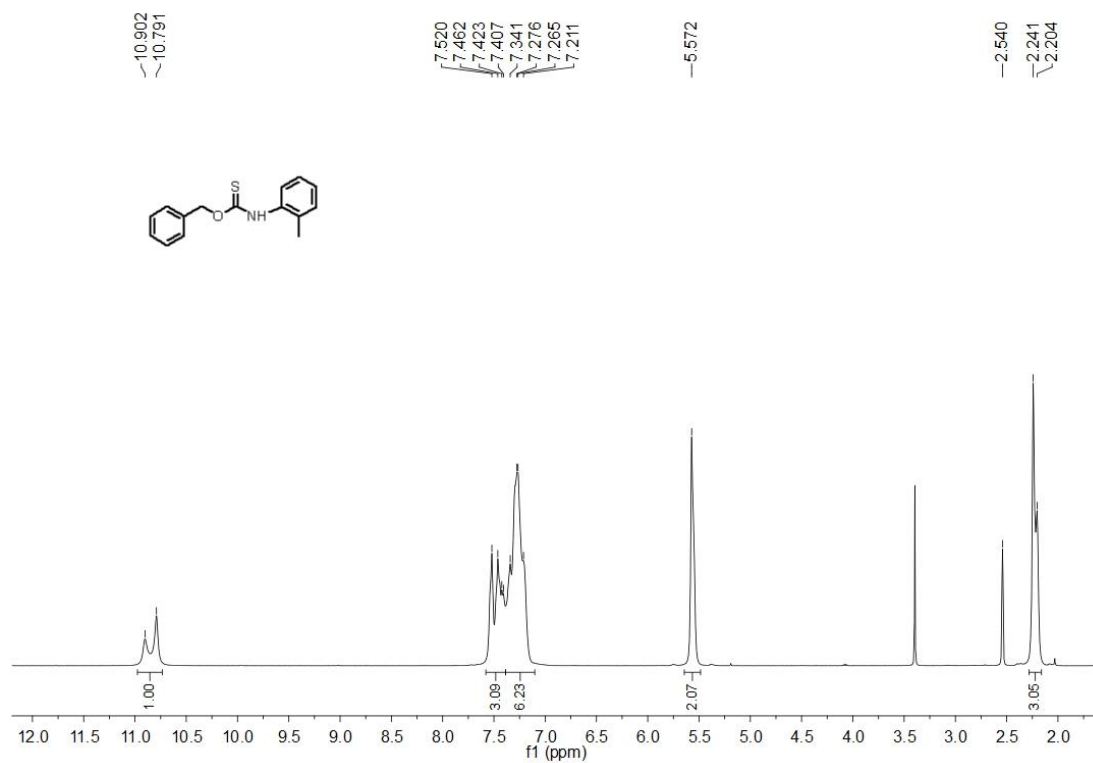


Fig. S17. ¹H NMR spectrum of 3ab (400 MHz, DMSO-*d*₆, 20 °C)

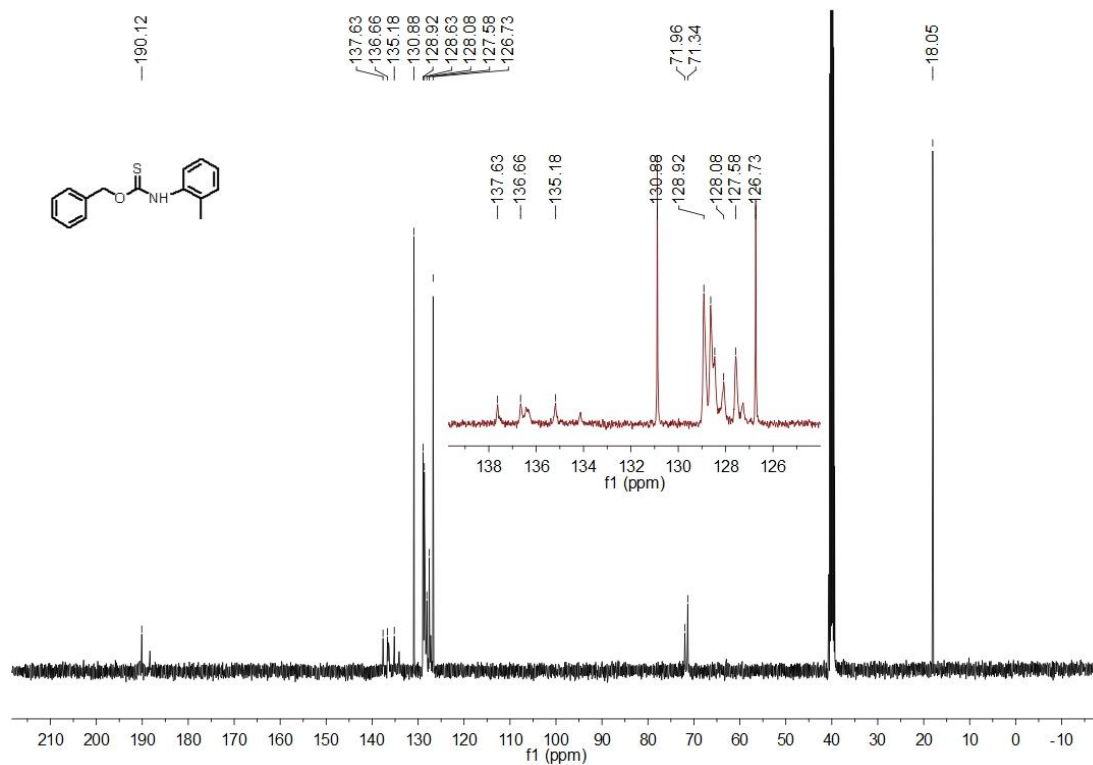


Fig. S18. ¹³C NMR spectrum of 3ab (100 MHz, DMSO-*d*₆, 20 °C)

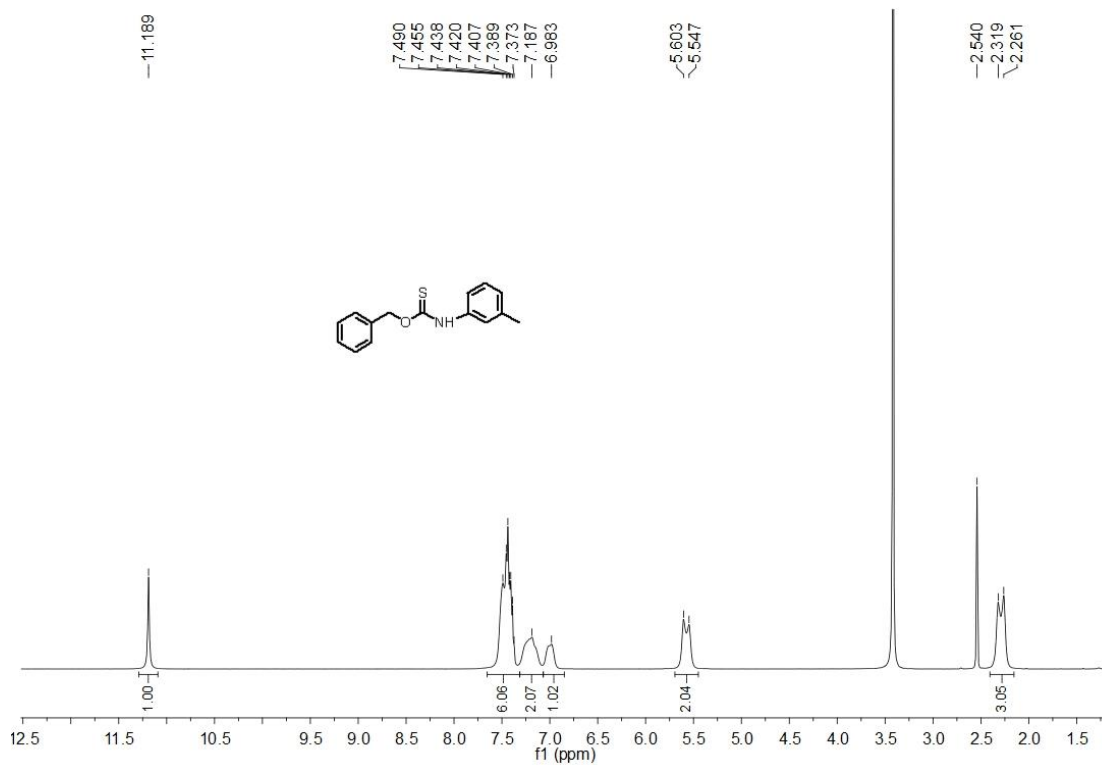


Fig. S19. $^1\text{H NMR}$ spectrum of 3ac (400 MHz, $\text{DMSO-}d_6$, 20 °C)

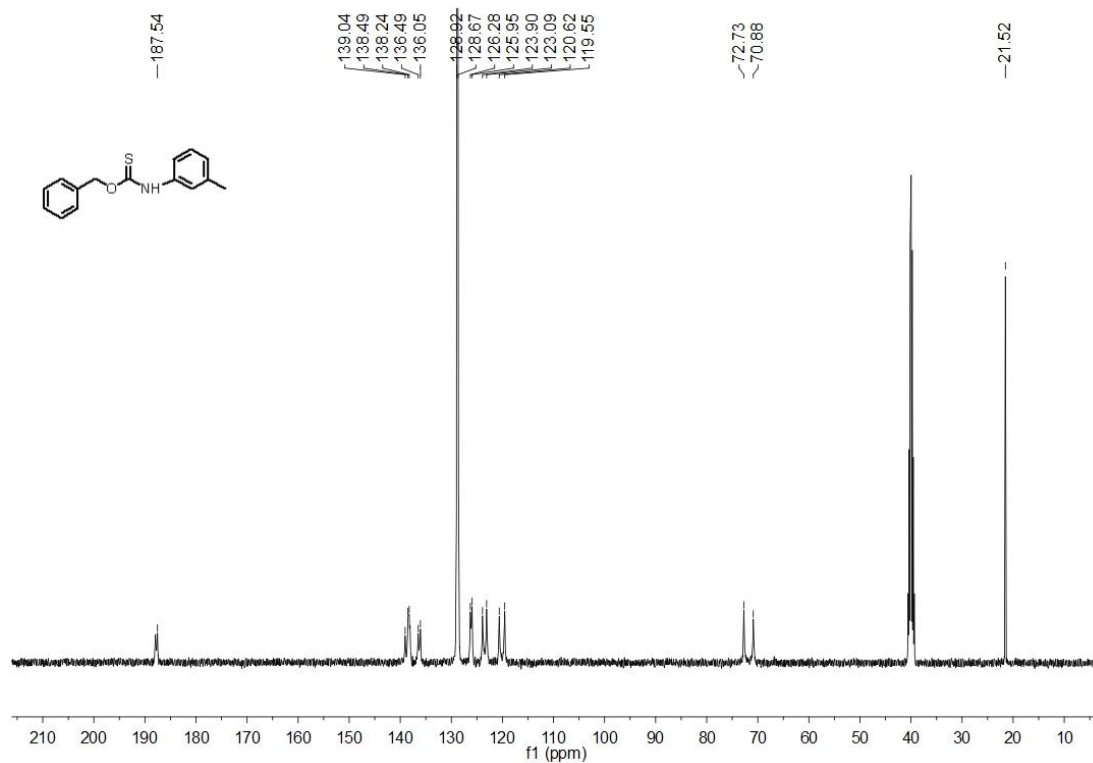


Fig. S20. $^{13}\text{C NMR}$ spectrum of 3ac (100 MHz, $\text{DMSO-}d_6$, 20 °C)

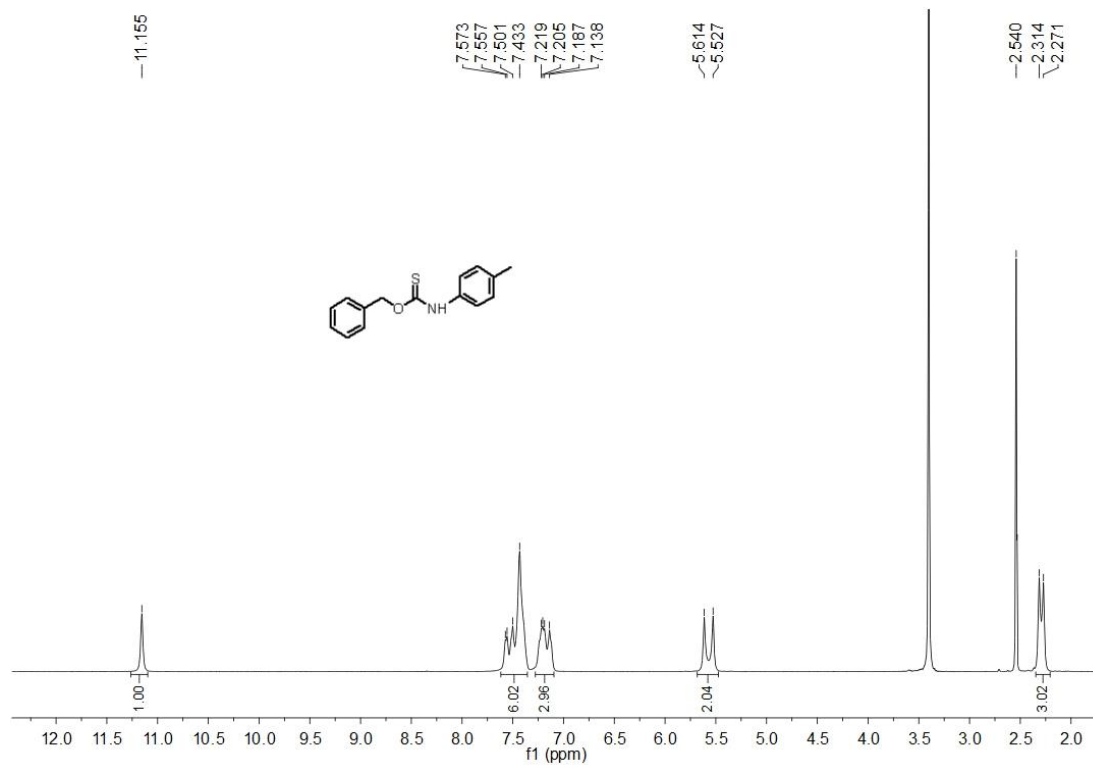


Fig. S21. ^1H NMR spectrum of **3ad** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

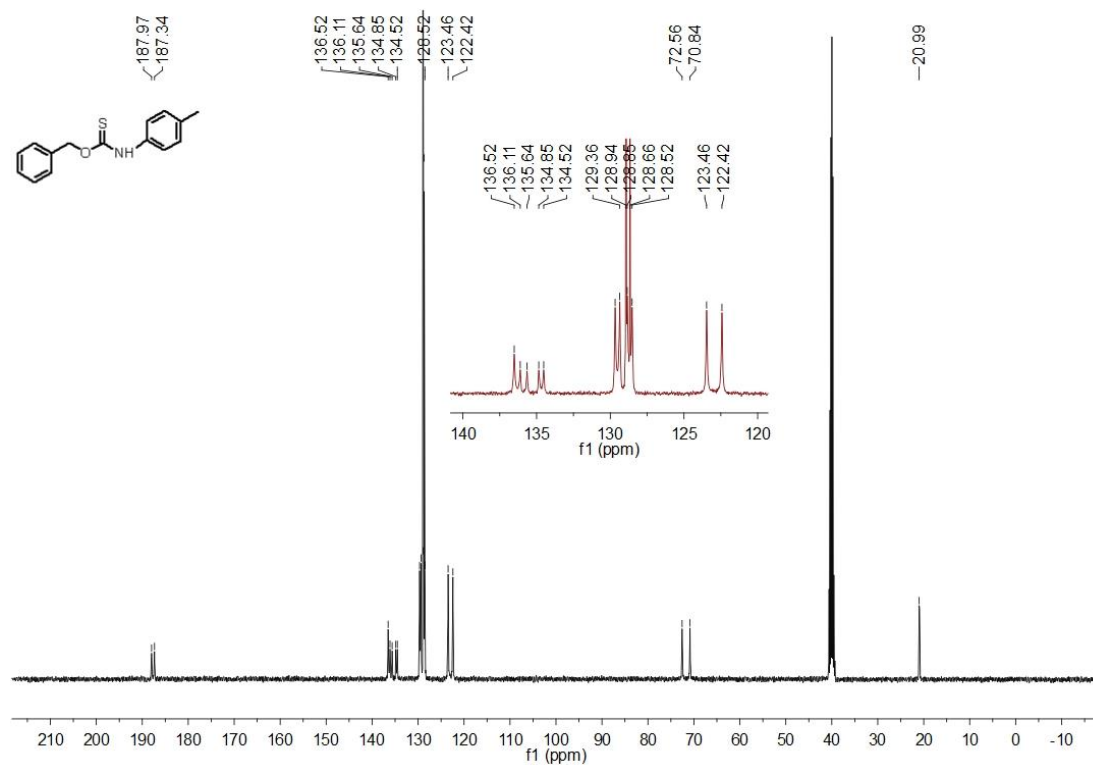


Fig. S22. ^{13}C NMR spectrum of **3ad** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

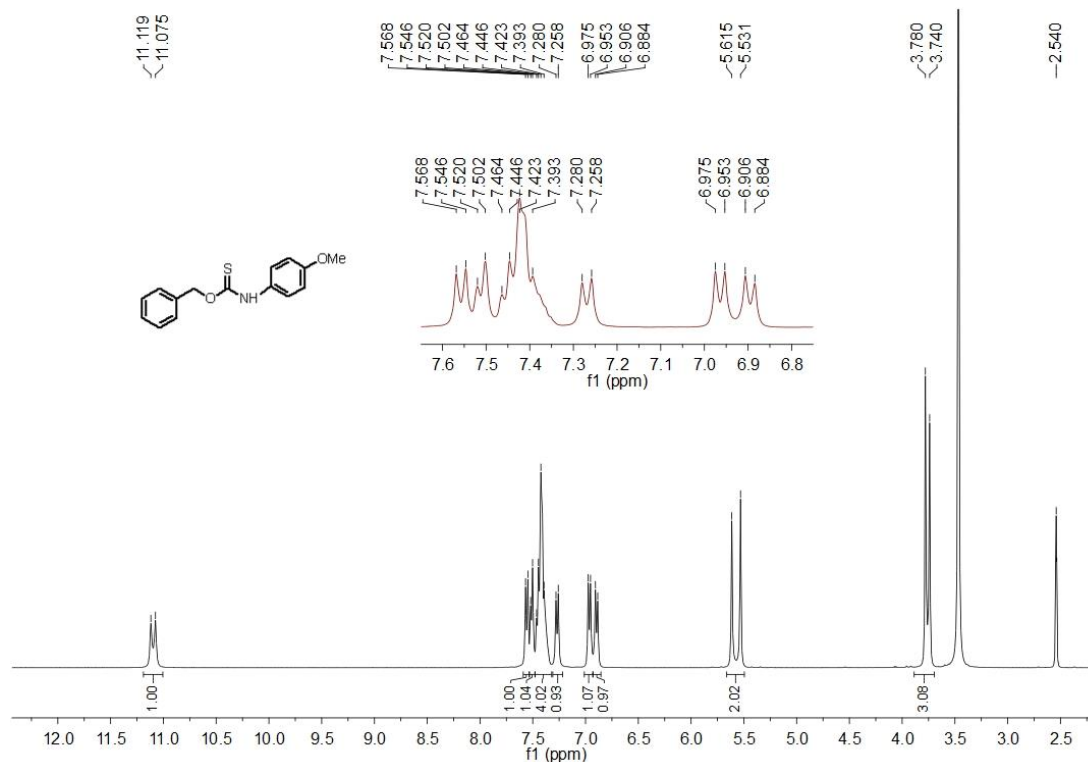


Fig. S23. ¹H NMR spectrum of **3ae** (400 MHz, DMSO-*d*₆, 20 °C)

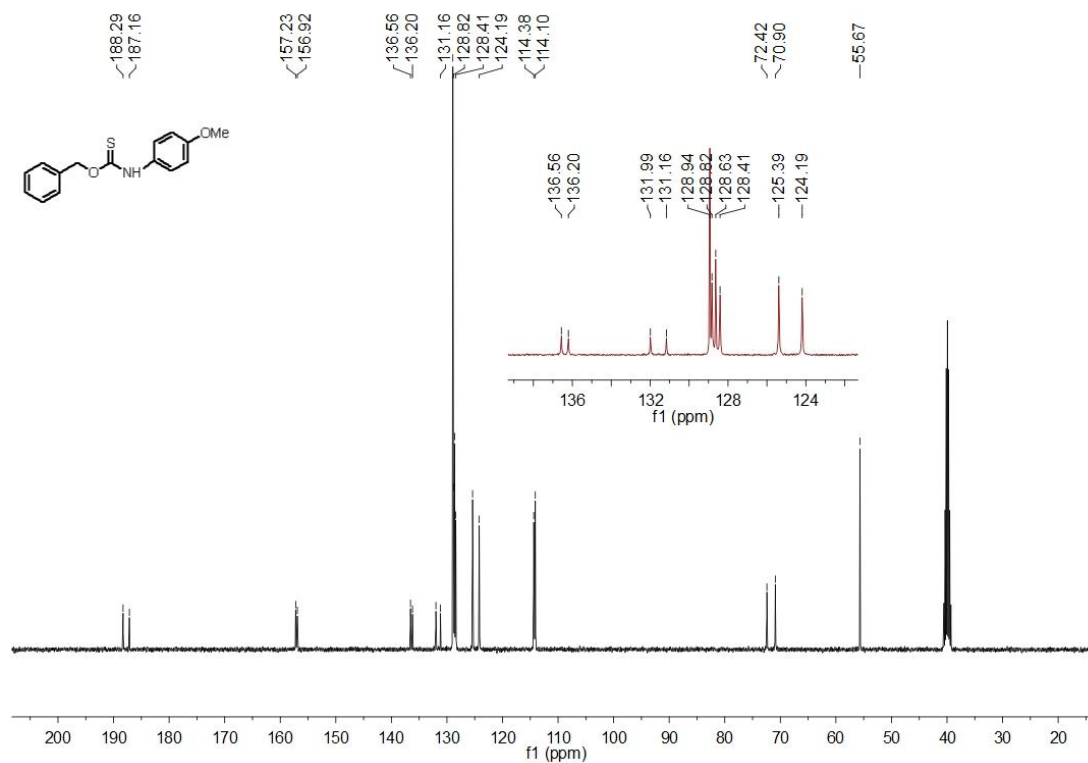


Fig. S24. ¹³C NMR spectrum of **3ae** (100 MHz, DMSO-*d*₆, 20 °C)

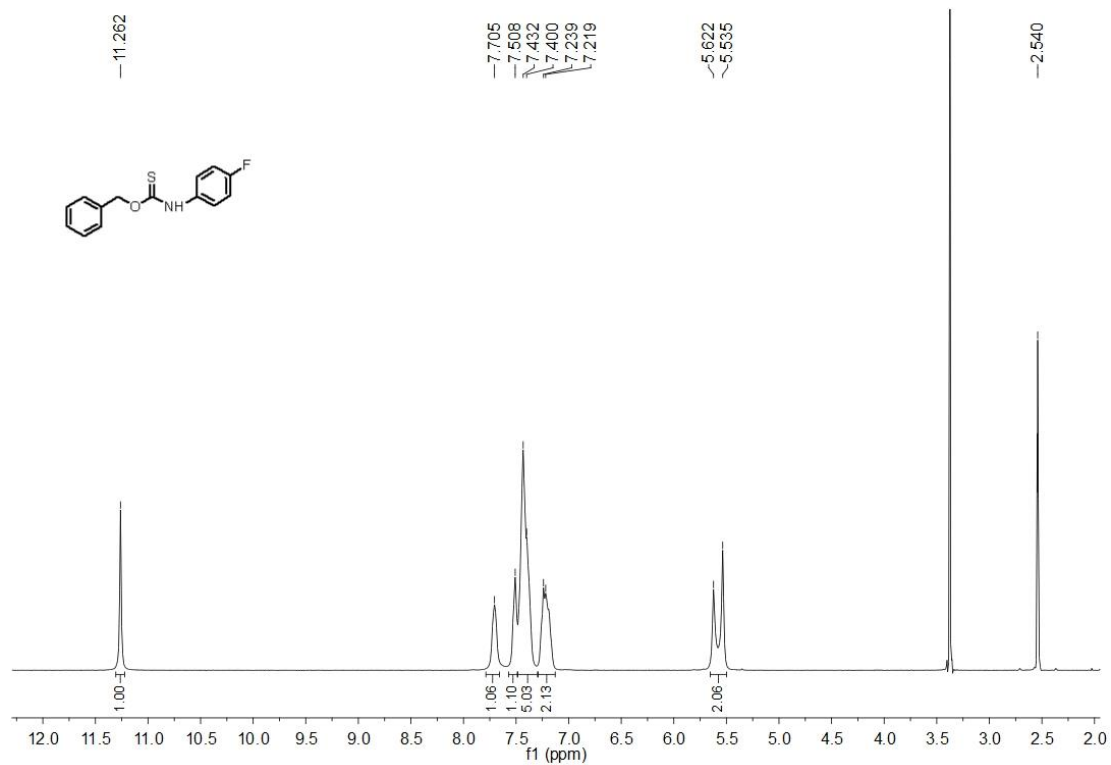


Fig. S25. ¹H NMR spectrum of 3af (400 MHz, DMSO-*d*₆, 20 °C)

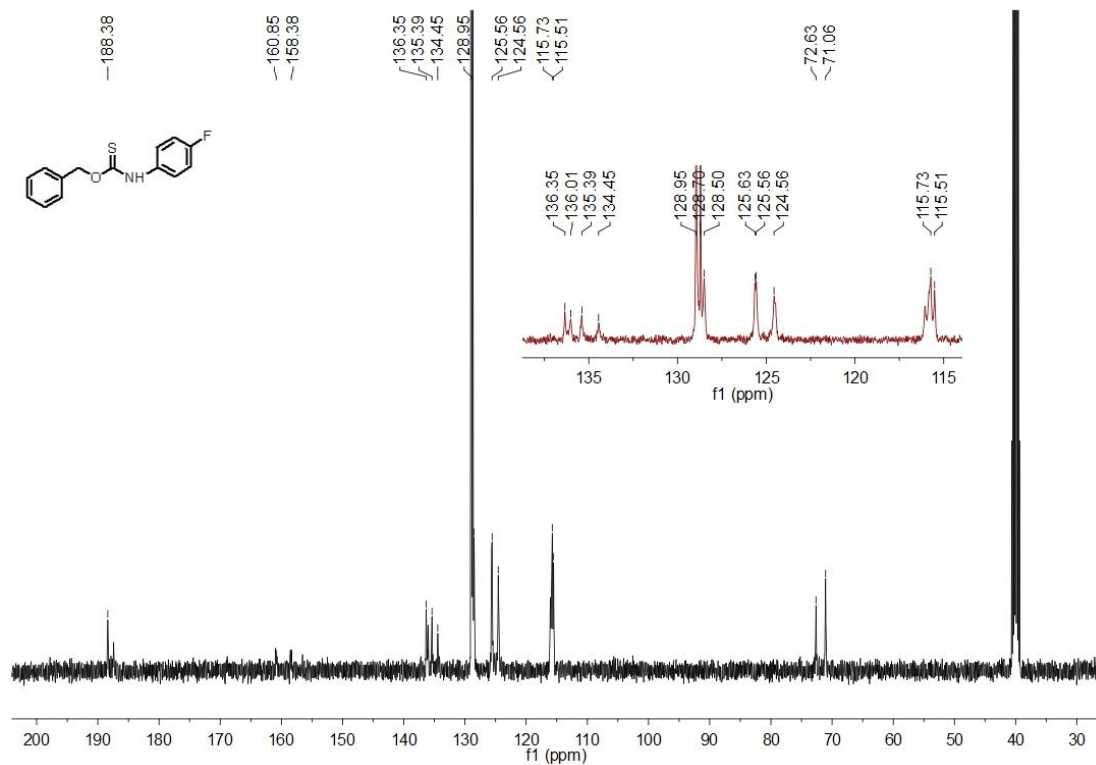


Fig. S26. ¹³C NMR spectrum of 3af (100 MHz, DMSO-*d*₆, 20 °C)

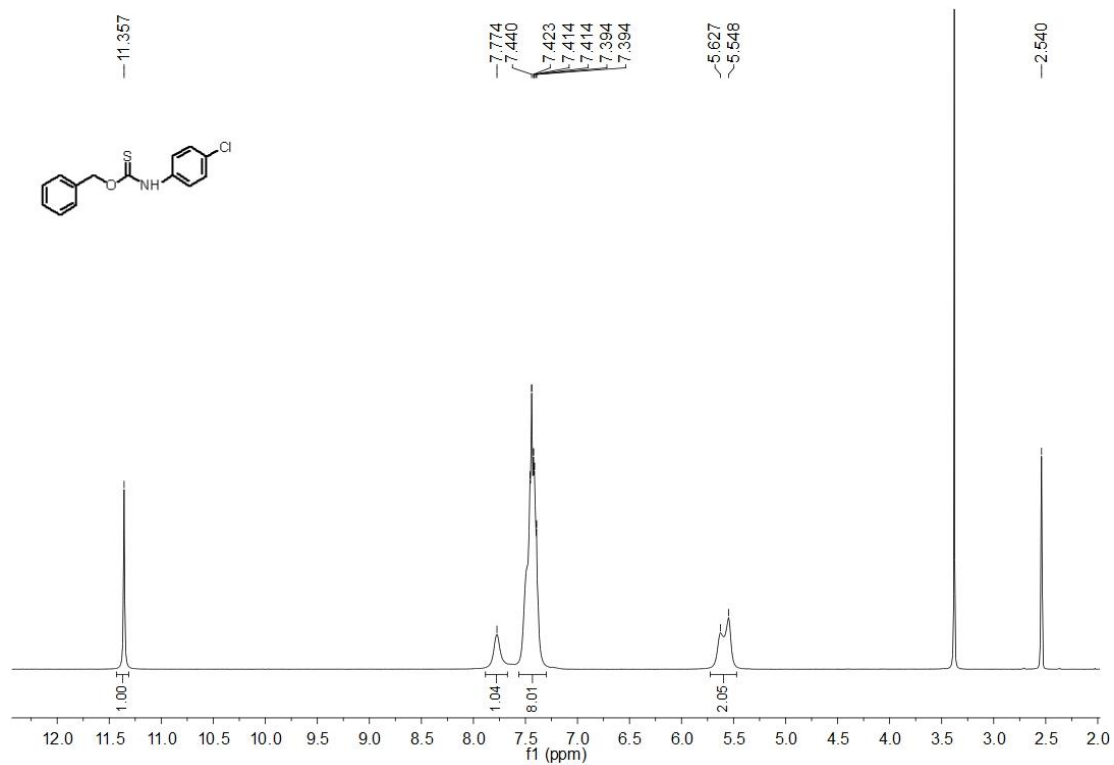


Fig. S27. ¹H NMR spectrum of 3ag (400 MHz, DMSO-*d*₆, 20 °C)

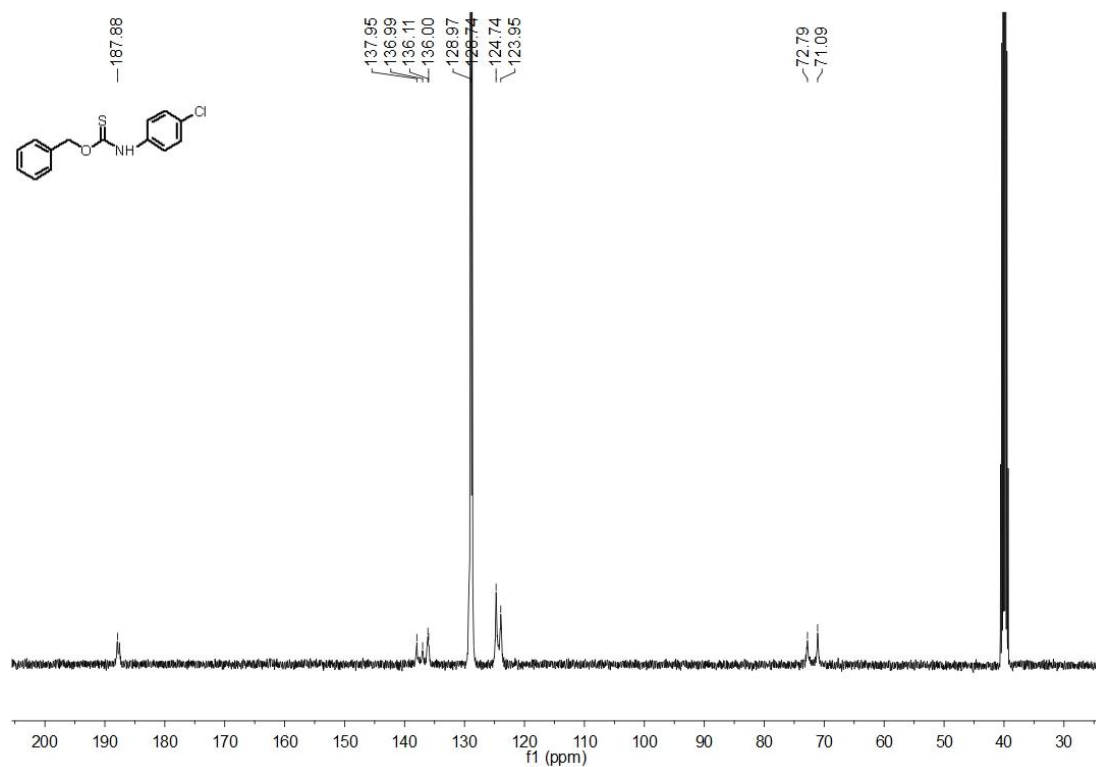


Fig. S28. ¹³C NMR spectrum of 3ag (100 MHz, DMSO-*d*₆, 20 °C)

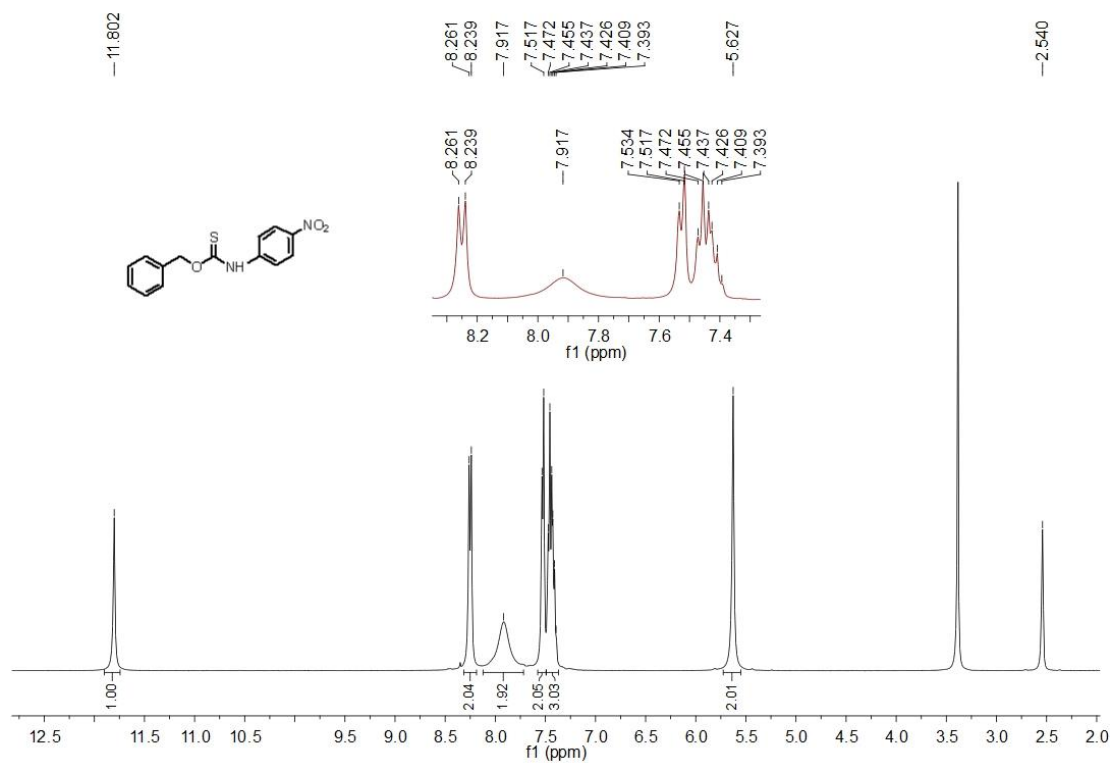


Fig. S29. ¹H NMR spectrum of **3ah** (400 MHz, DMSO-*d*₆, 20 °C)

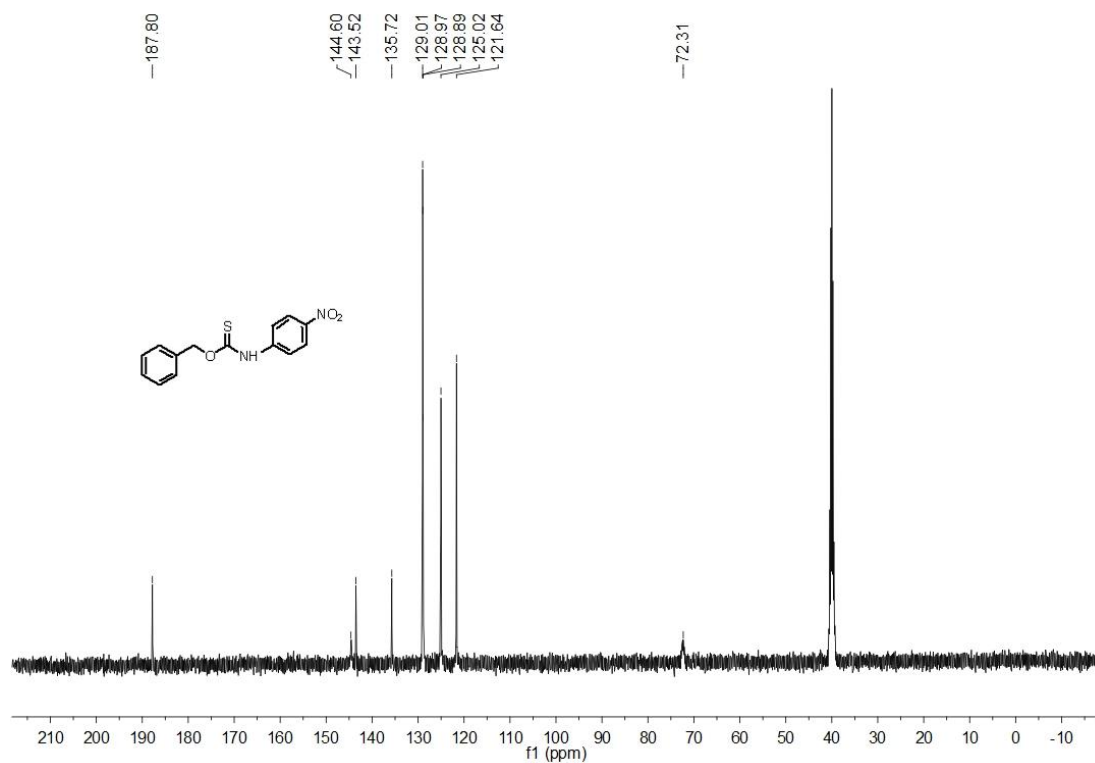


Fig. S30. ¹³C NMR spectrum of **3ah** (100 MHz, DMSO-*d*₆, 20 °C)

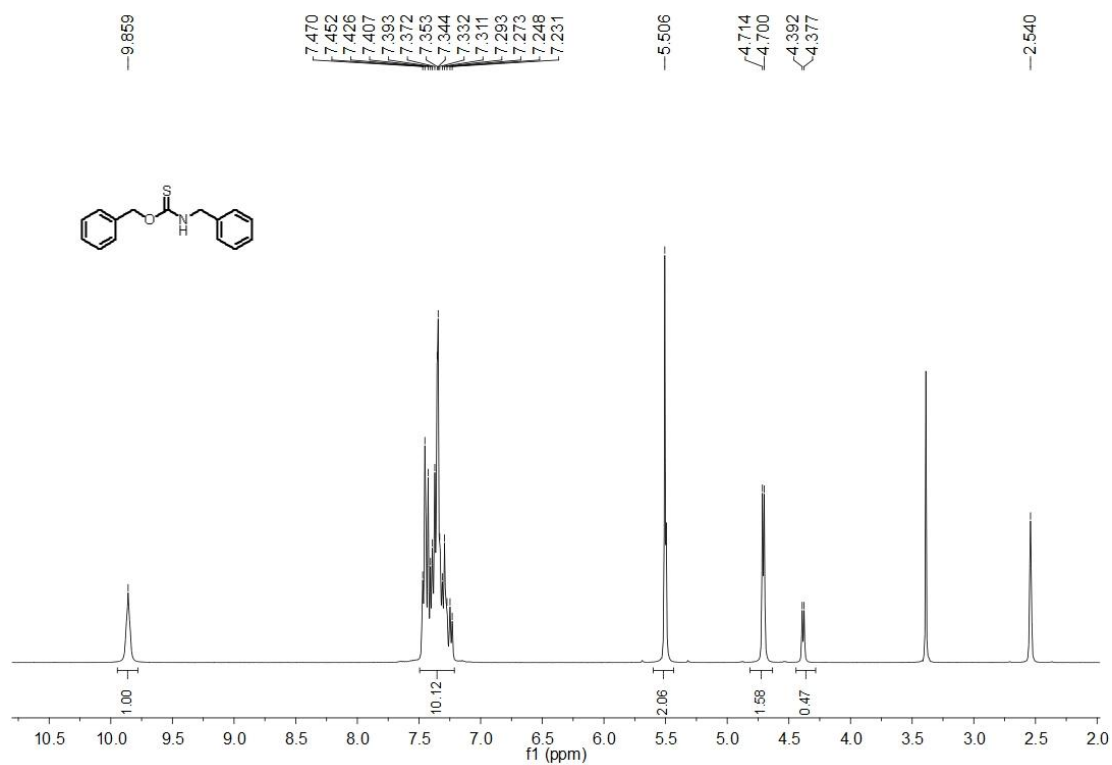


Fig. S31. ¹H NMR spectrum of 3ai (400 MHz, DMSO-*d*₆, 20 °C)

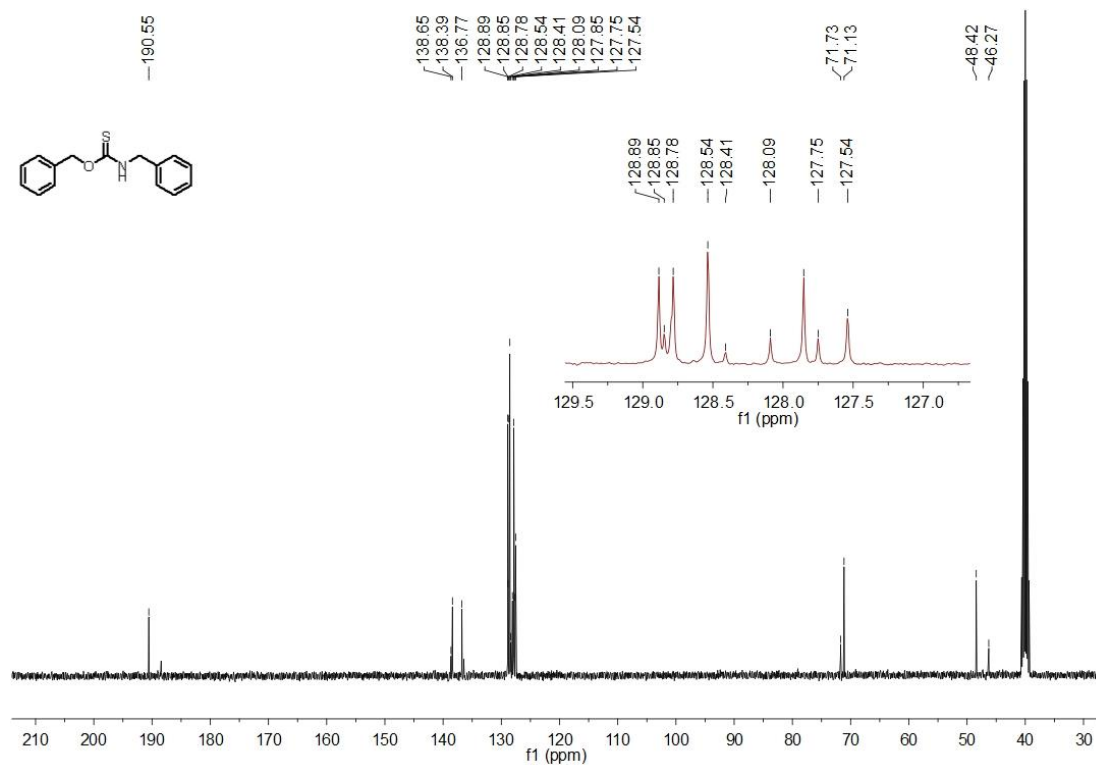


Fig. S32. ¹³C NMR spectrum of 3ai (100 MHz, DMSO-*d*₆, 20 °C)

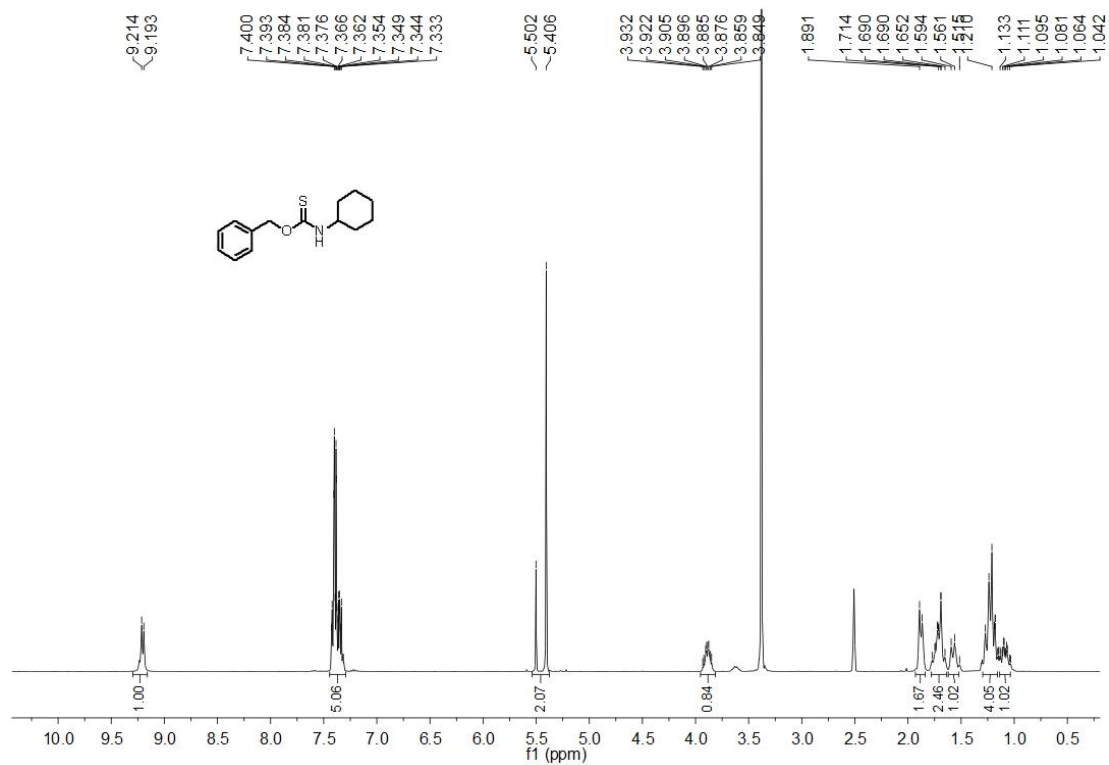


Fig. S33. ¹H NMR spectrum of **3aj** (400 MHz, DMSO-*d*₆, 20 °C)

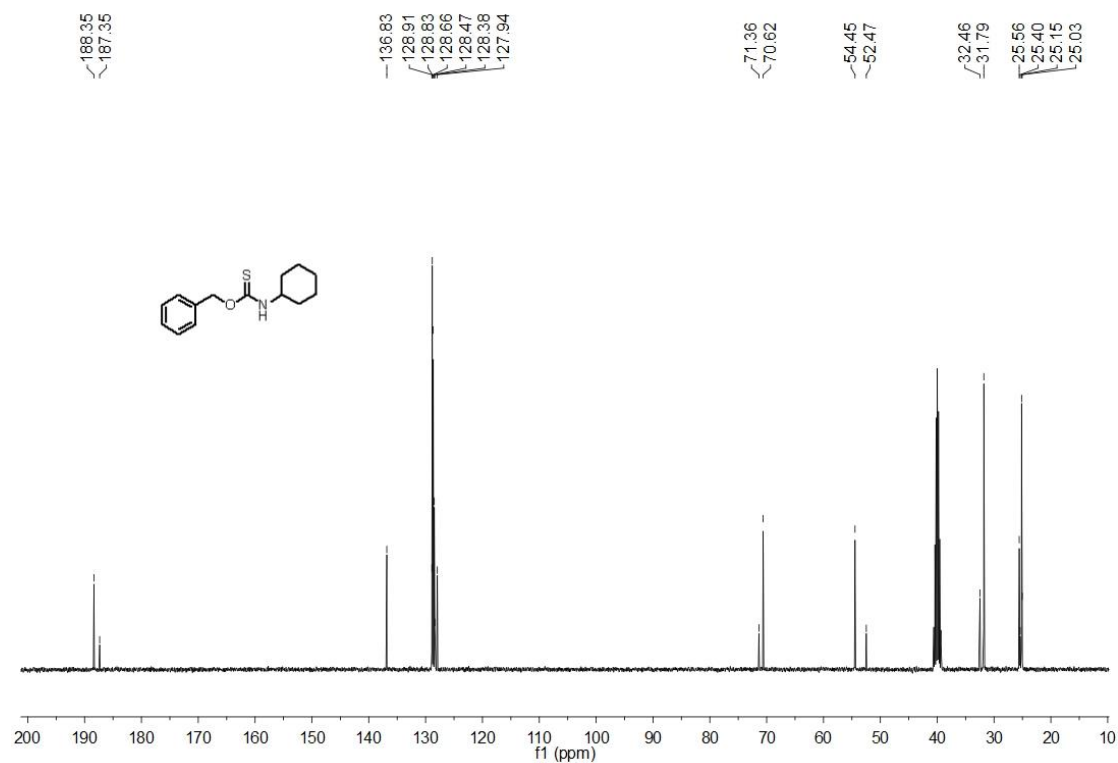


Fig. S34. ¹³C NMR spectrum of **3aj** (100 MHz, DMSO-*d*₆, 20 °C)

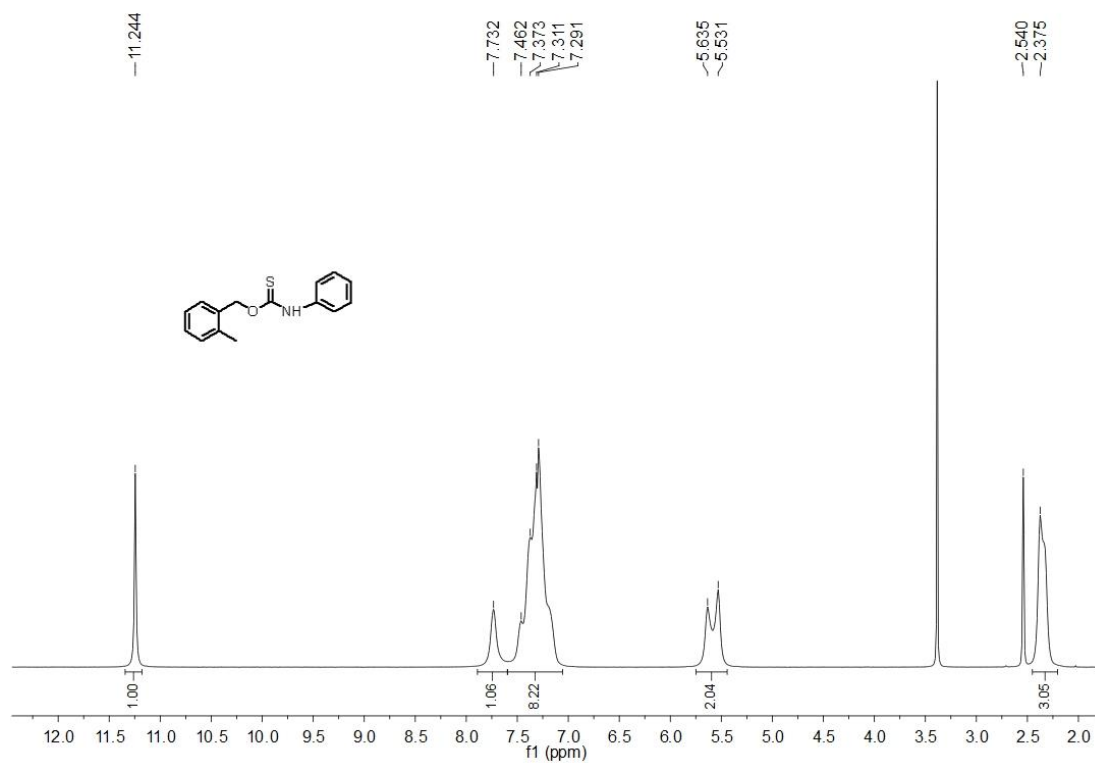


Fig. S35. ^1H NMR spectrum of **3ba** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

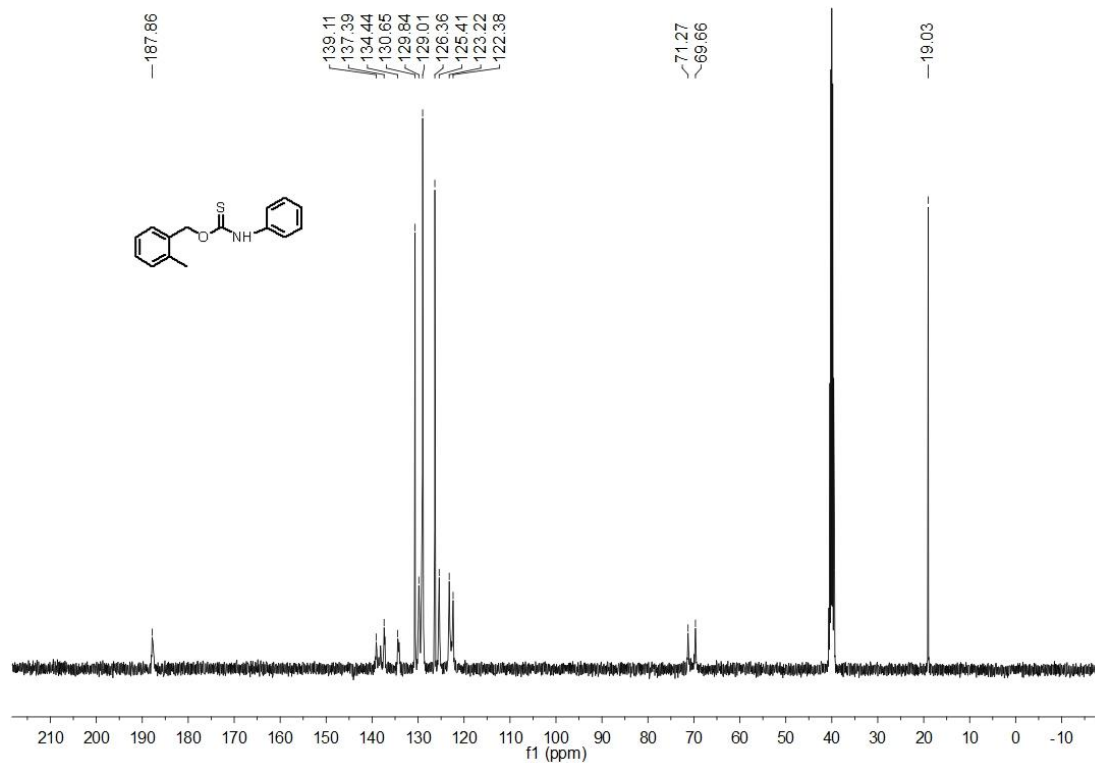


Fig. S36. ^{13}C NMR spectrum of **3ba** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

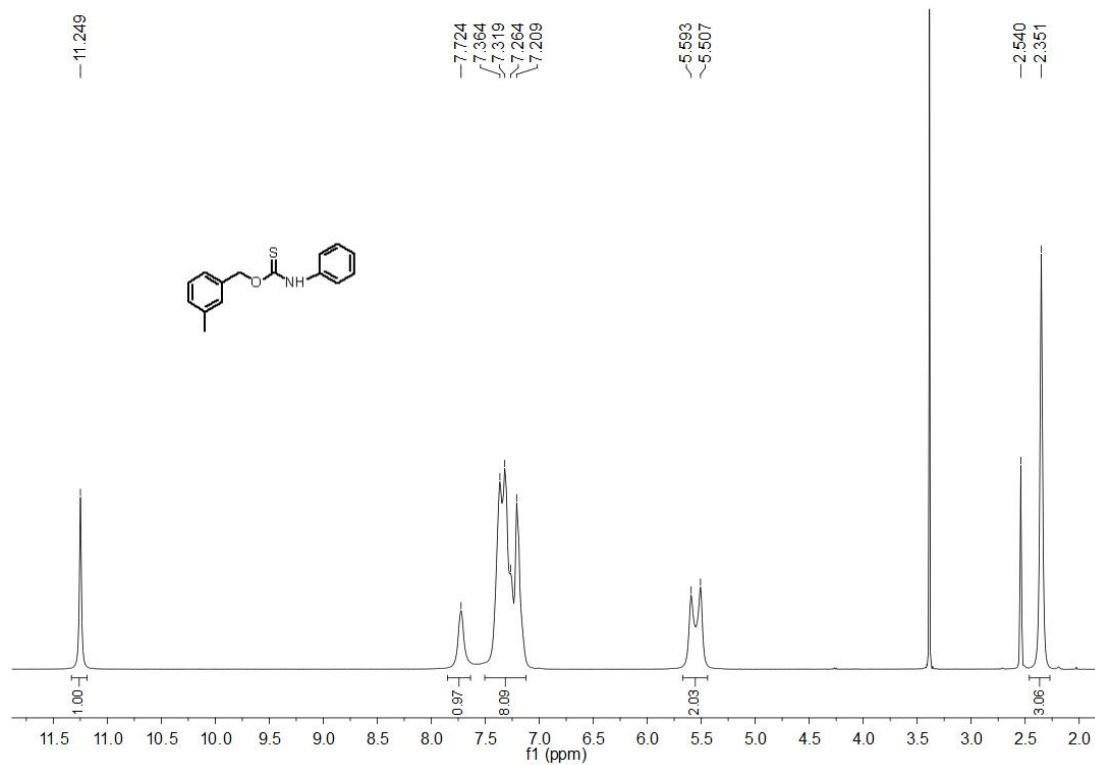


Fig. S37. ^1H NMR spectrum of **3ca** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

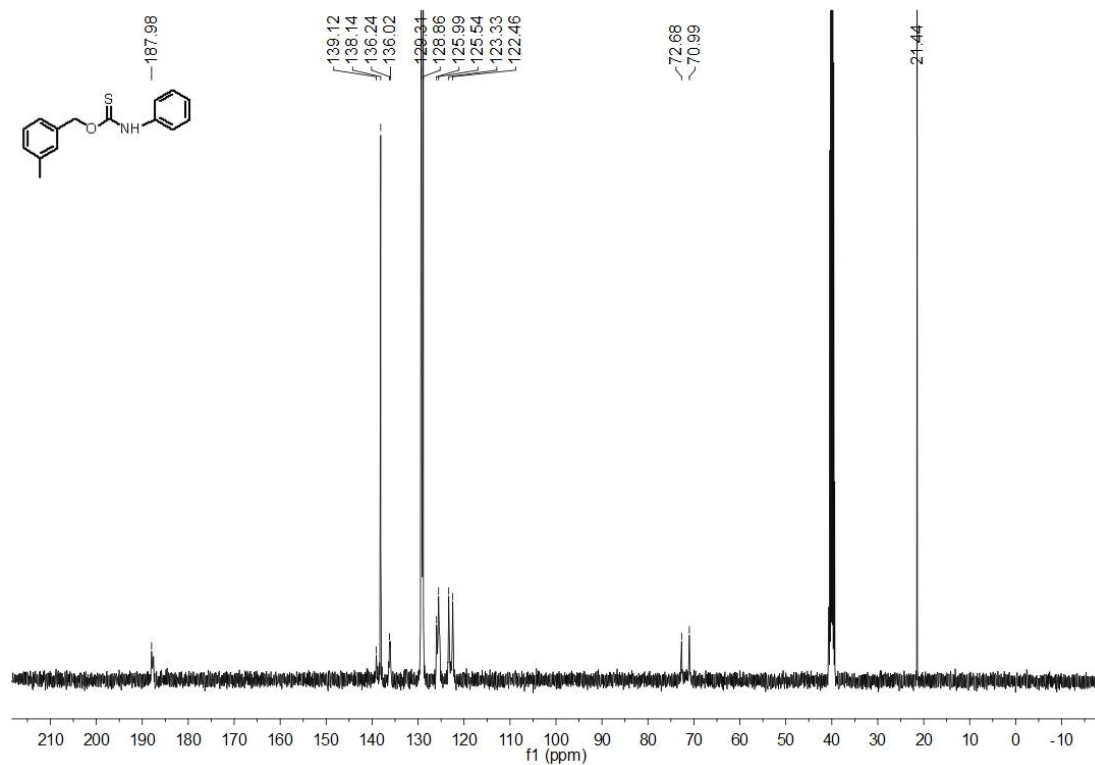


Fig. S38. ^{13}C NMR spectrum of **3ca** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

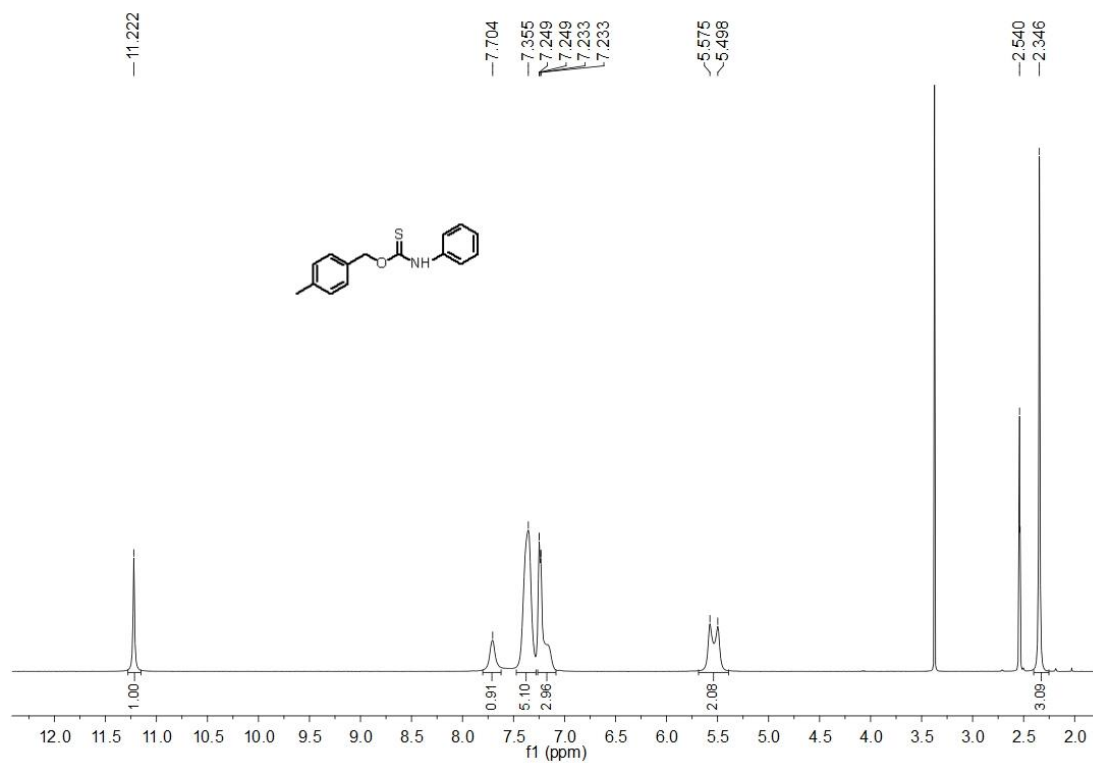


Fig. S39. ^1H NMR spectrum of **3da** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

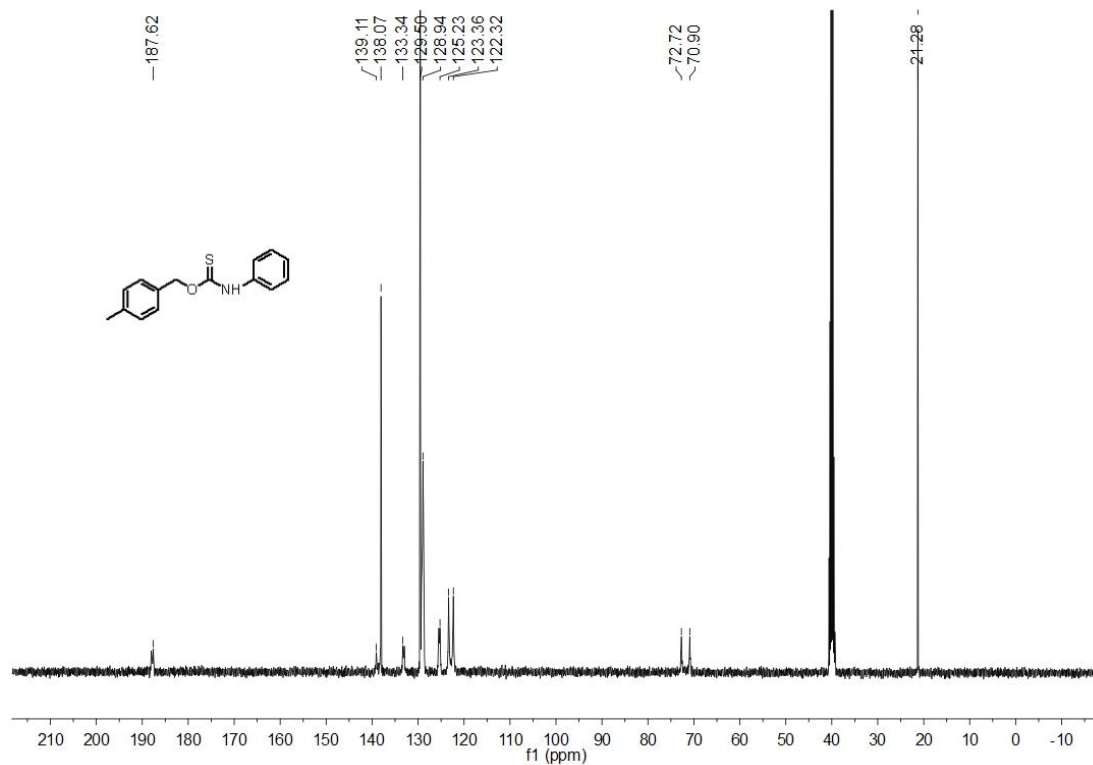


Fig. S40. ^{13}C NMR spectrum of **3da** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

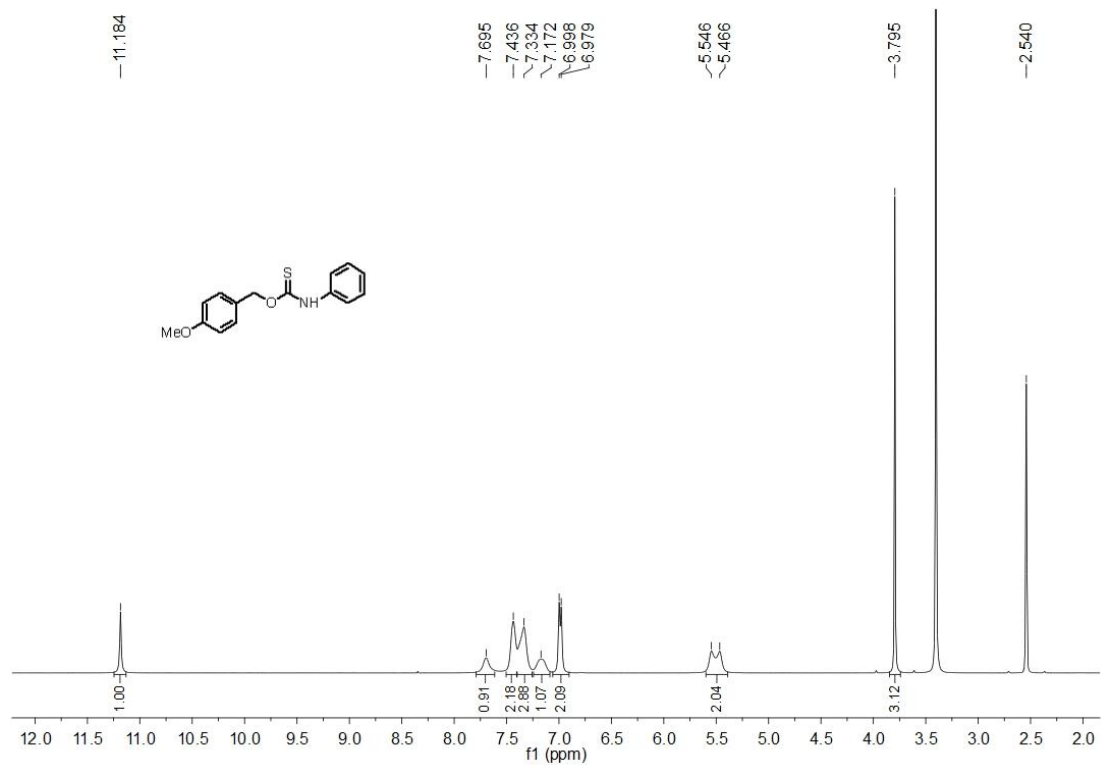


Fig. S41. ¹H NMR spectrum of 3ea (400 MHz, DMSO-*d*₆, 20 °C)

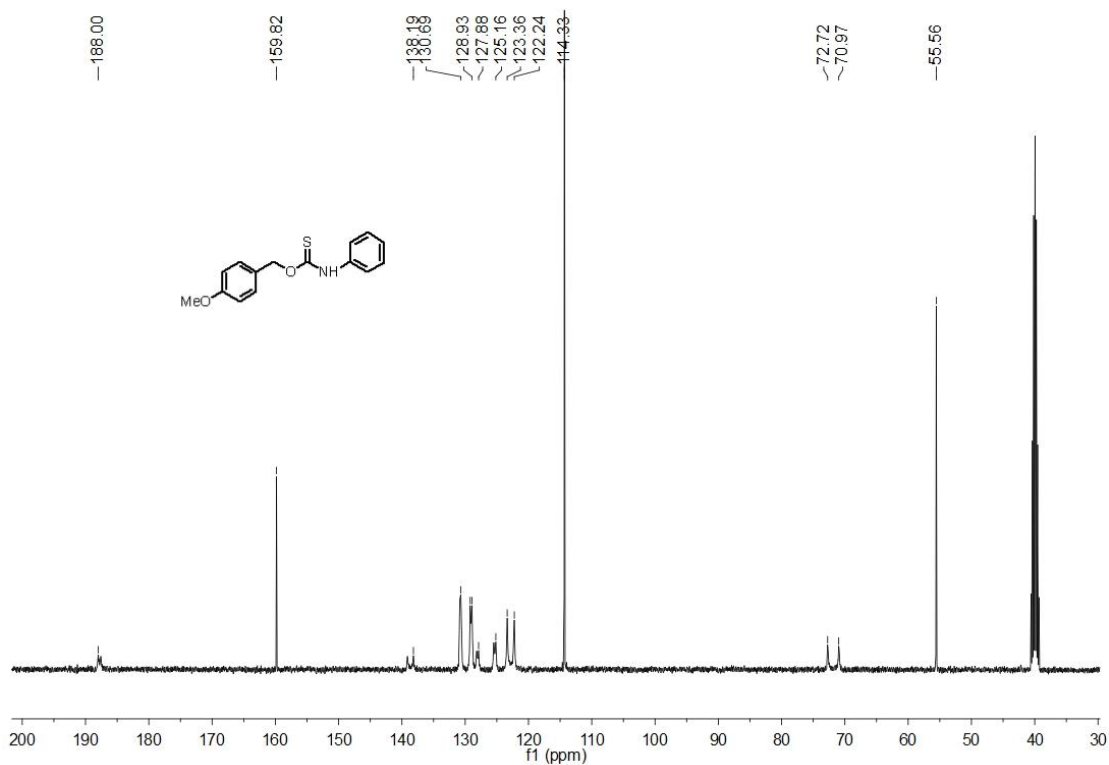


Fig. S42. ¹³C NMR spectrum of 3ea (100 MHz, DMSO-*d*₆, 20 °C)

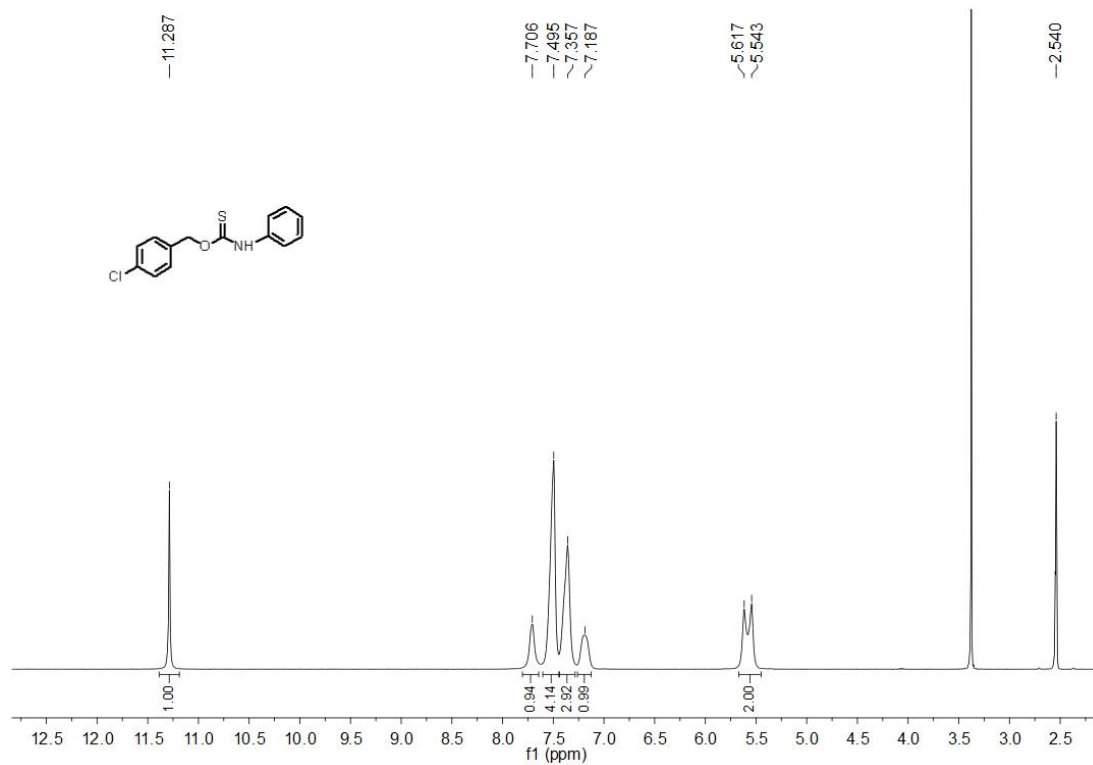


Fig. S43. ^1H NMR spectrum of 3fa (400 MHz, DMSO- d_6 , 20 °C)

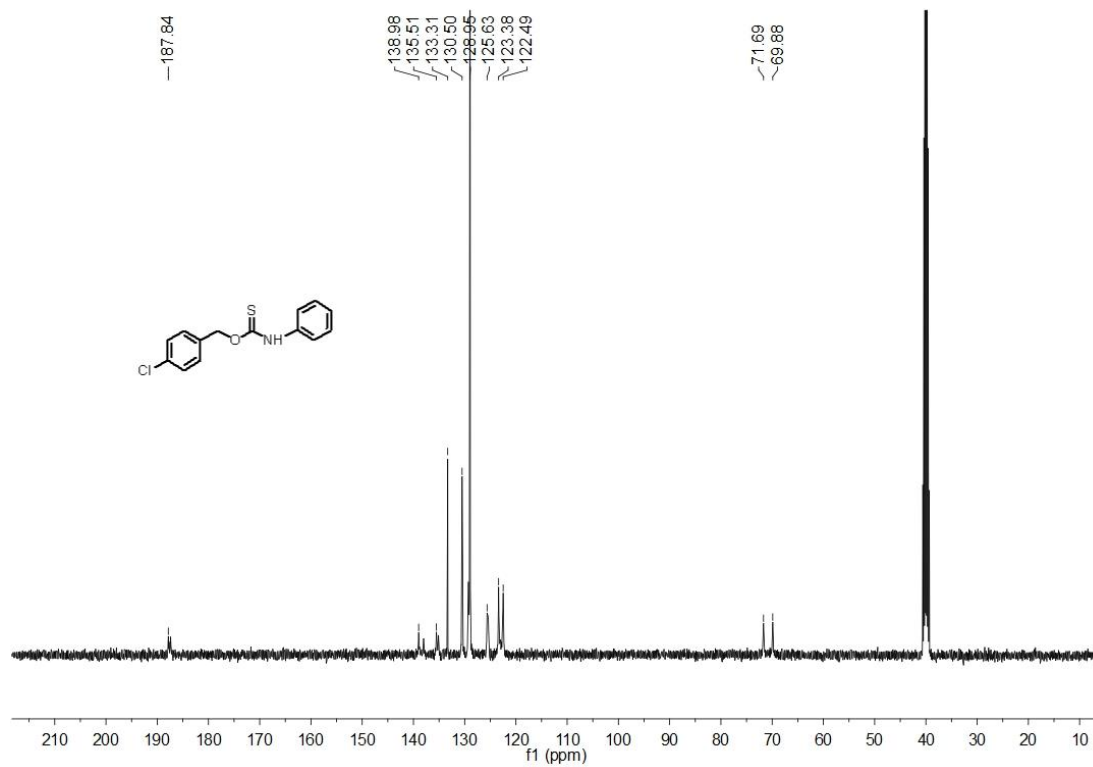


Fig. S44. ^{13}C NMR spectrum of 3fa (100 MHz, DMSO- d_6 , 20 °C)

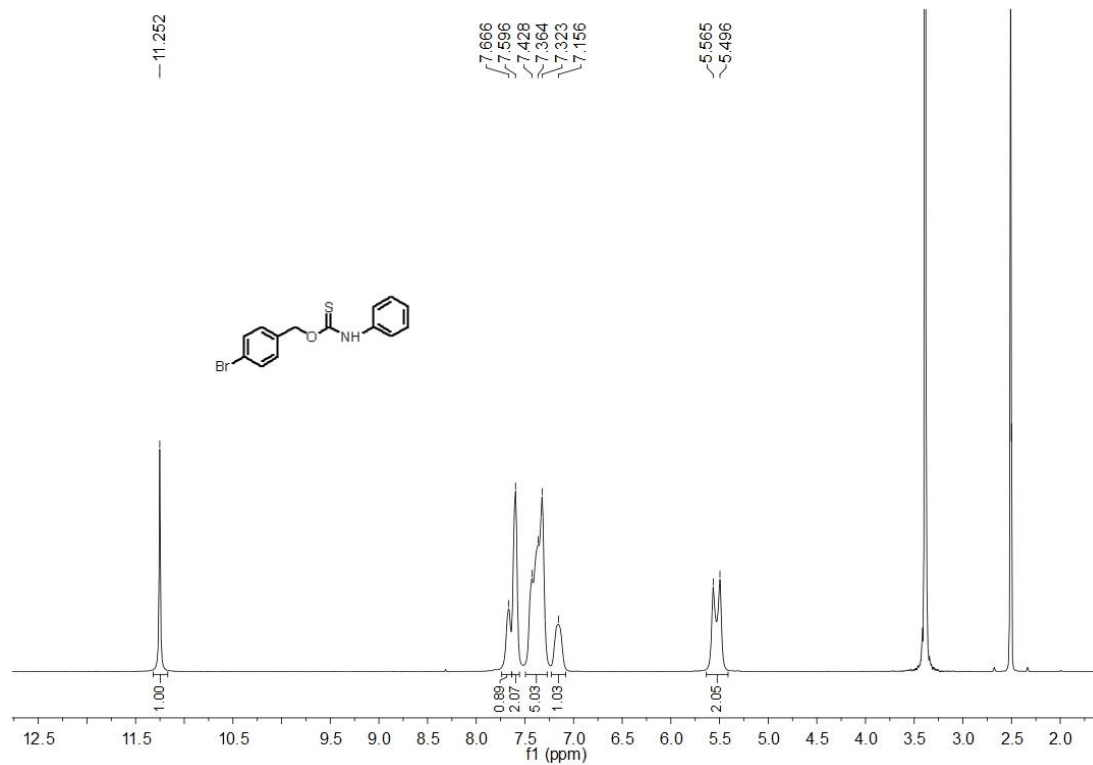


Fig. S45. $^1\text{H NMR}$ spectrum of 3ga (400 MHz, $\text{DMSO-}d_6$, 20 °C)

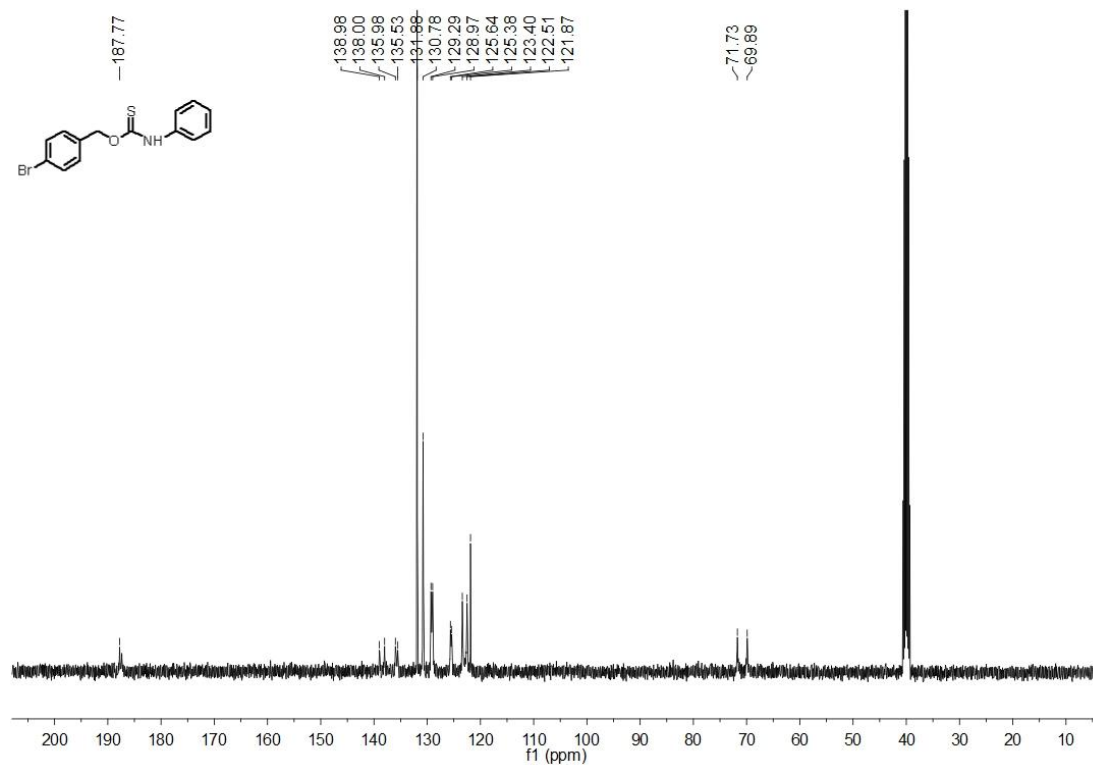


Fig. S46. $^{13}\text{C NMR}$ spectrum of 3ga (100 MHz, $\text{DMSO-}d_6$, 20 °C)

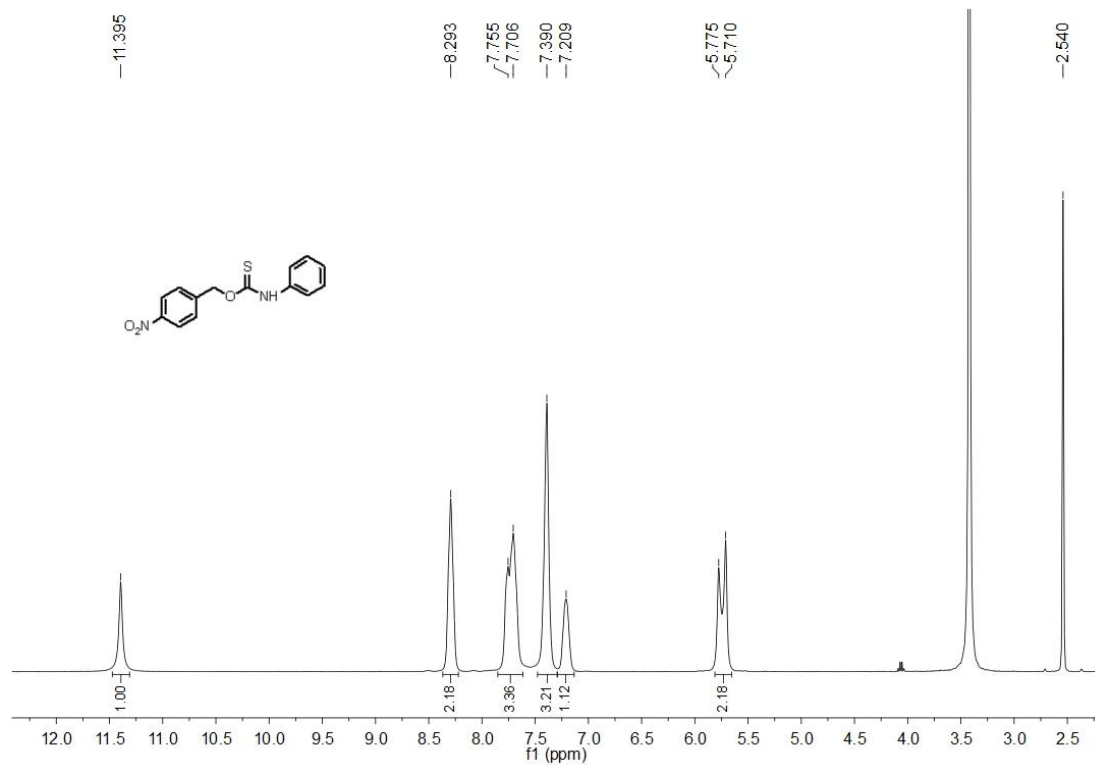


Fig. S47. ^1H NMR spectrum of **3ha** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

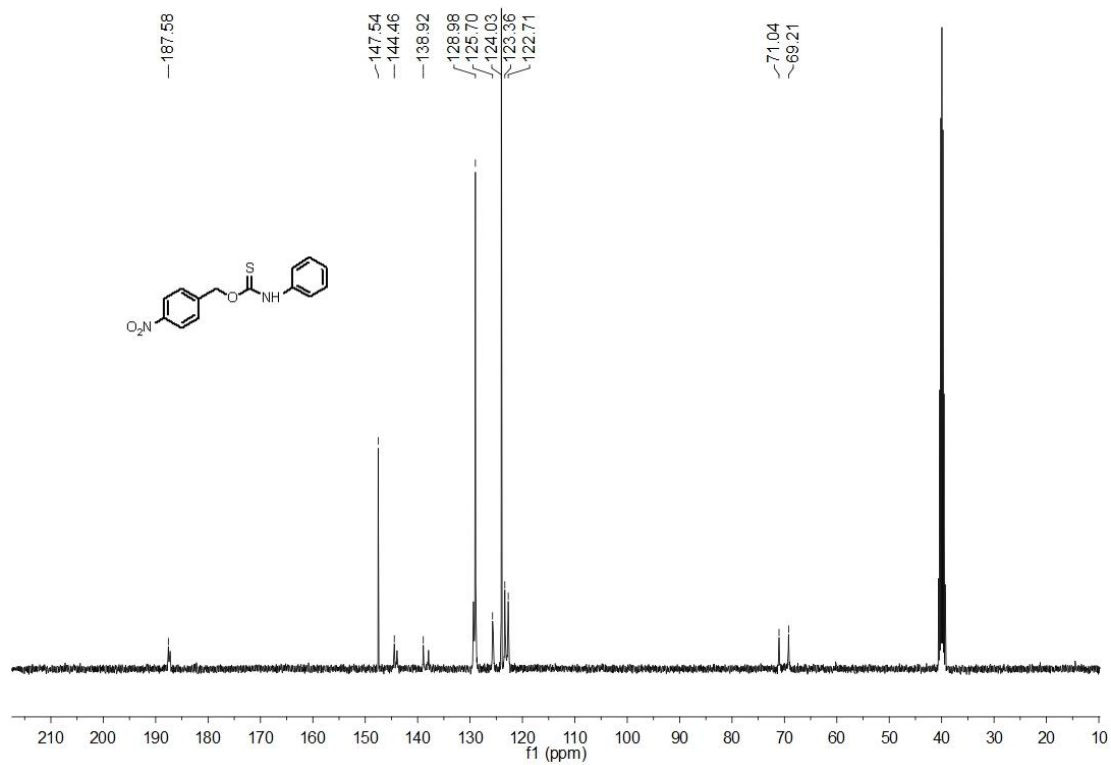


Fig. S48. ^{13}C NMR spectrum of **3ha** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

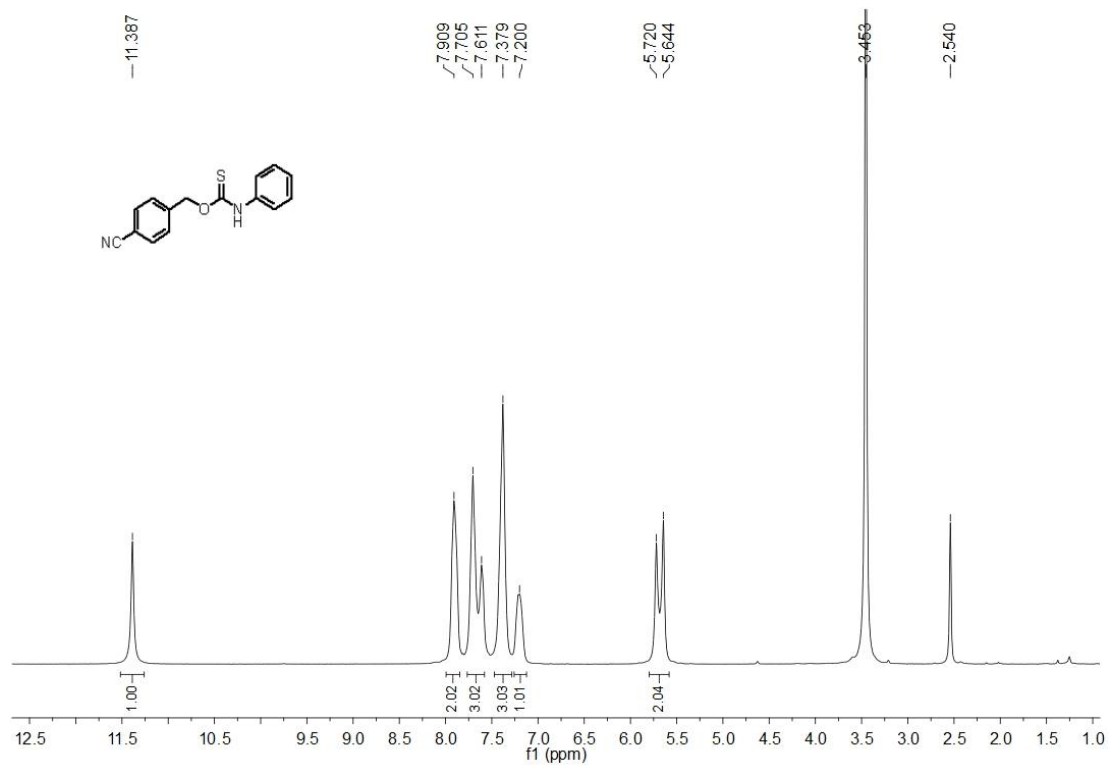


Fig. S49. ¹H NMR spectrum of 3ia (400 MHz, DMSO-*d*₆, 20 °C)

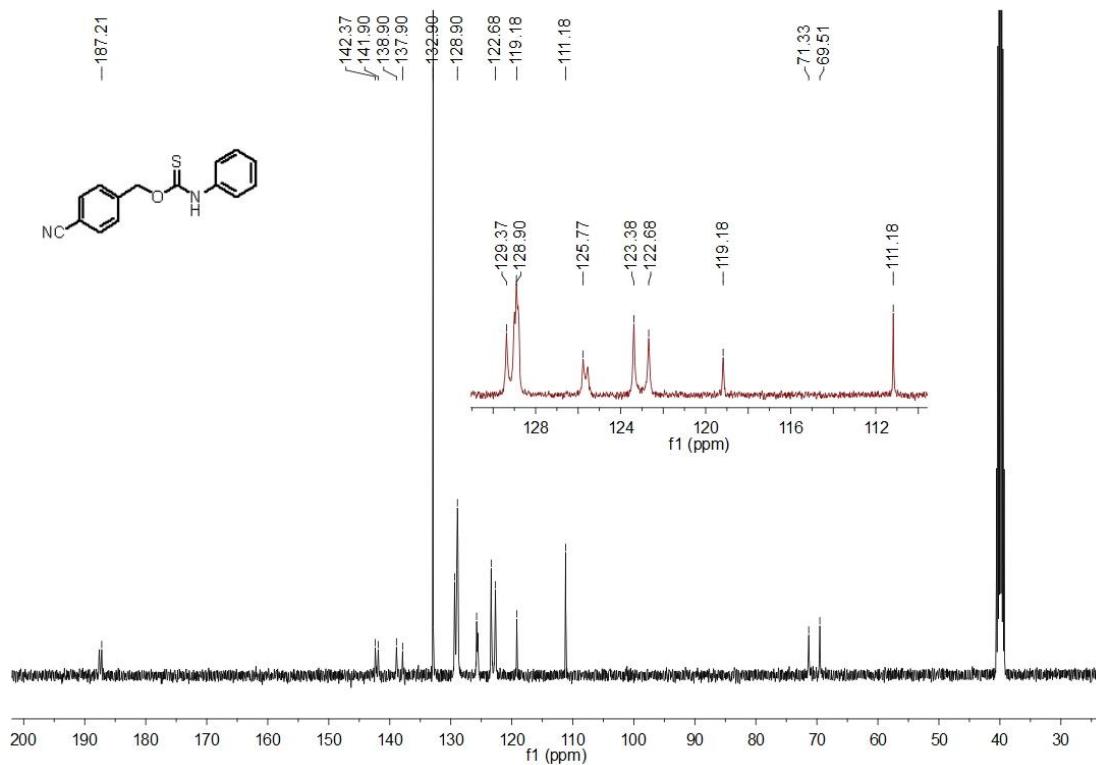


Fig. S50. ¹³C NMR spectrum of 3ia (100 MHz, DMSO-*d*₆, 20 °C)

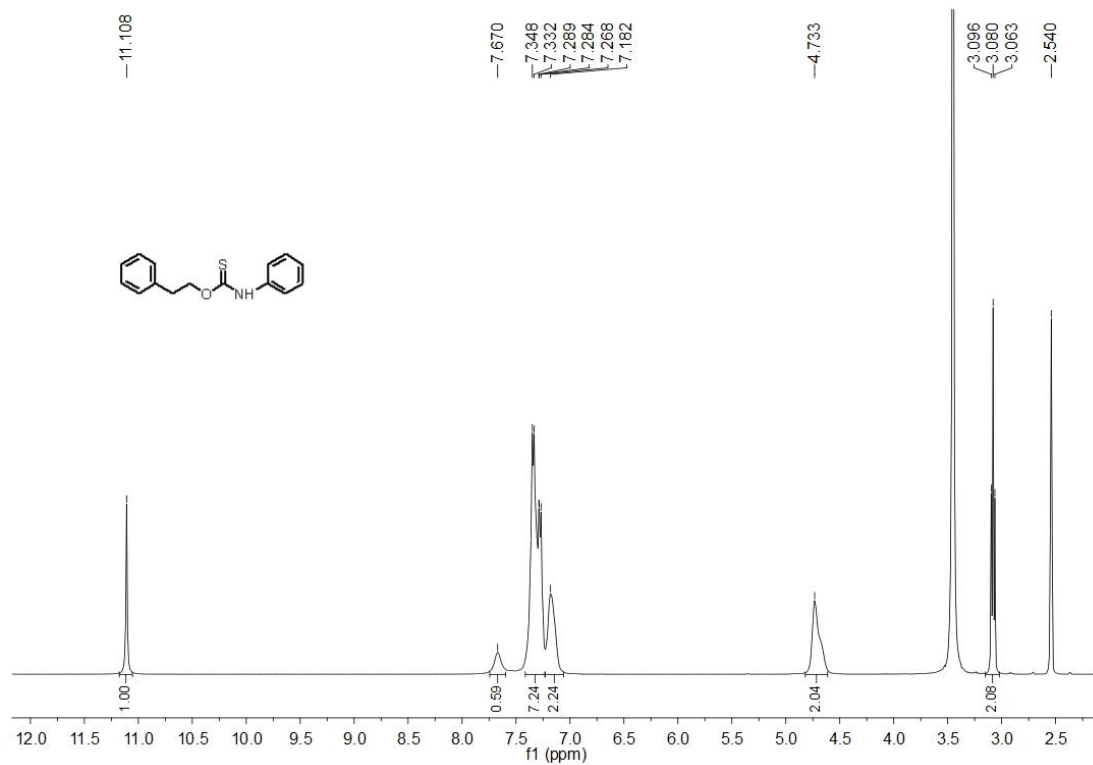


Fig. S51. ^1H NMR spectrum of **3ja** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

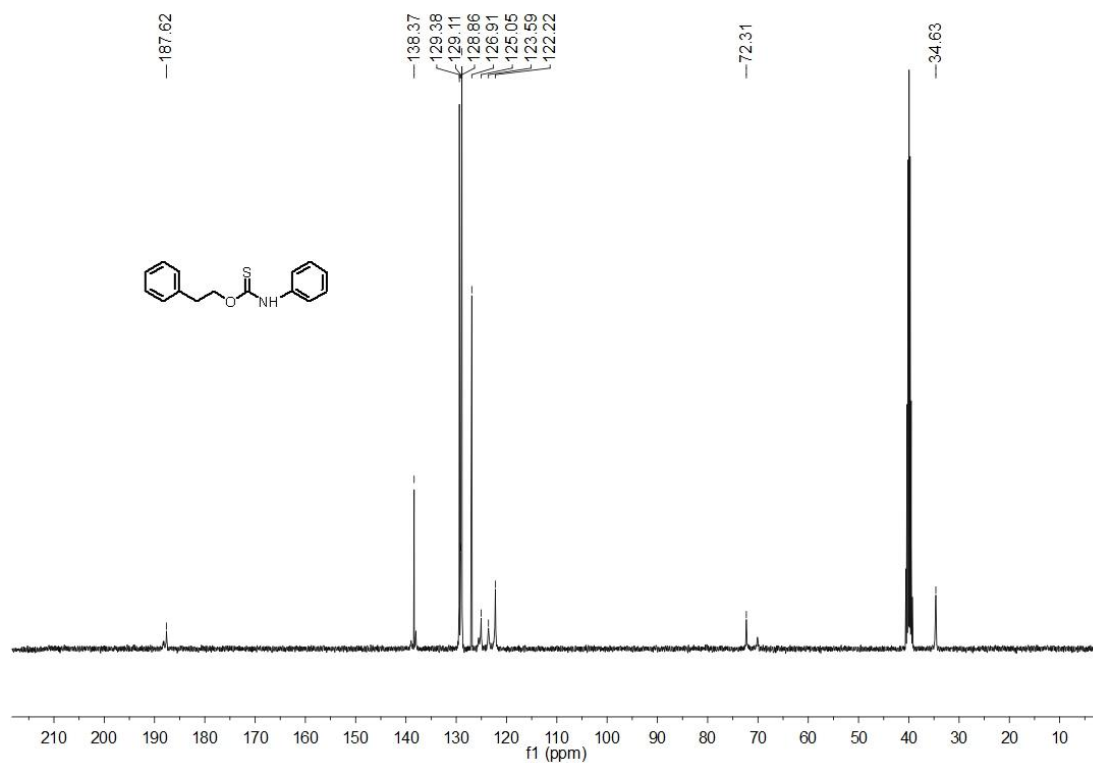


Fig. S52. ^{13}C NMR spectrum of **3ja** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

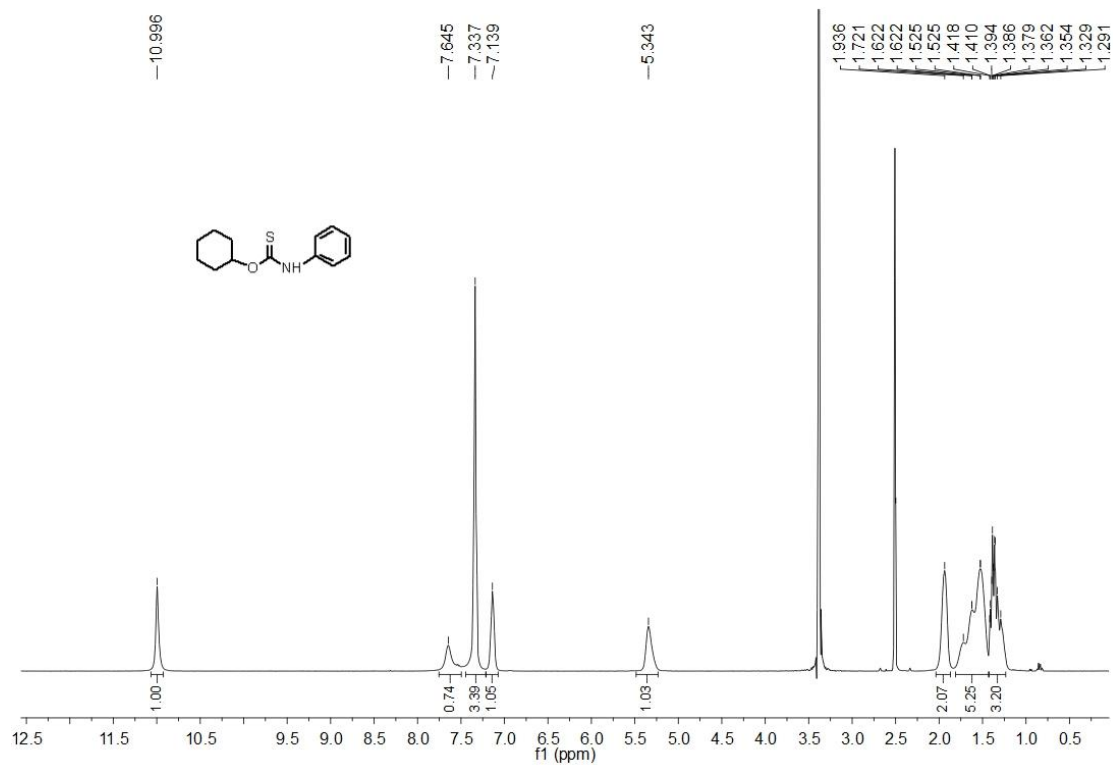


Fig. S53. ^1H NMR spectrum of **3ka** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

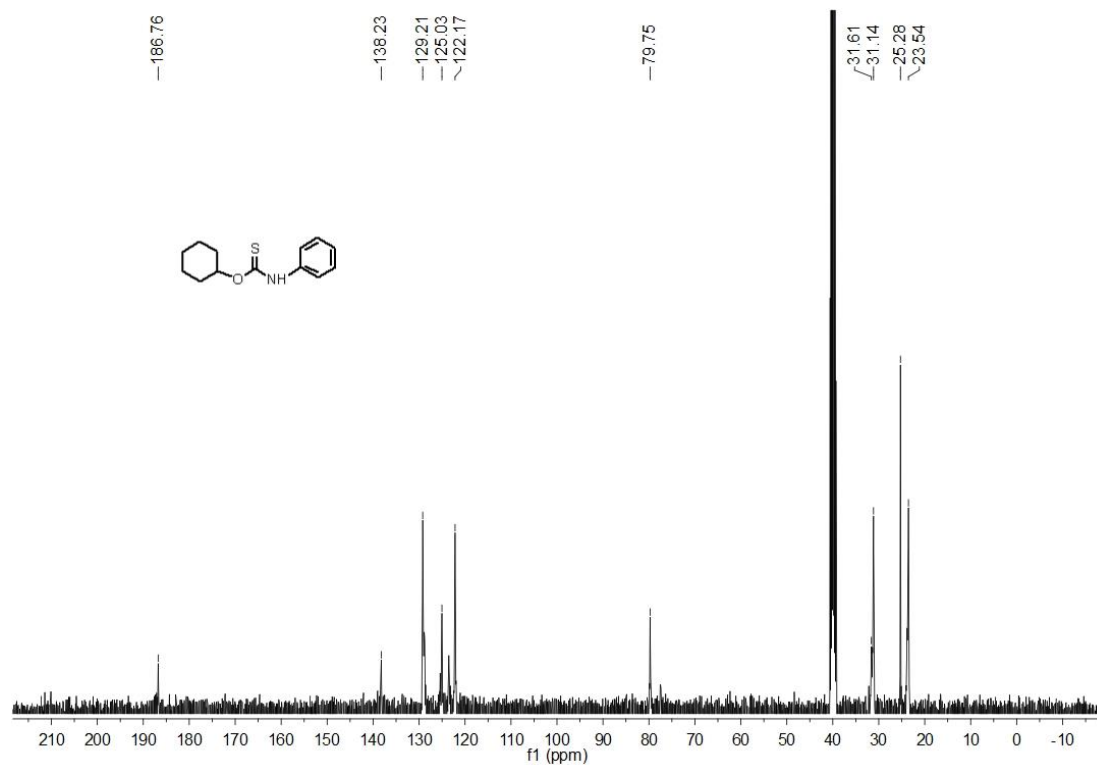


Fig. S54. ^{13}C NMR spectrum of **3ka** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

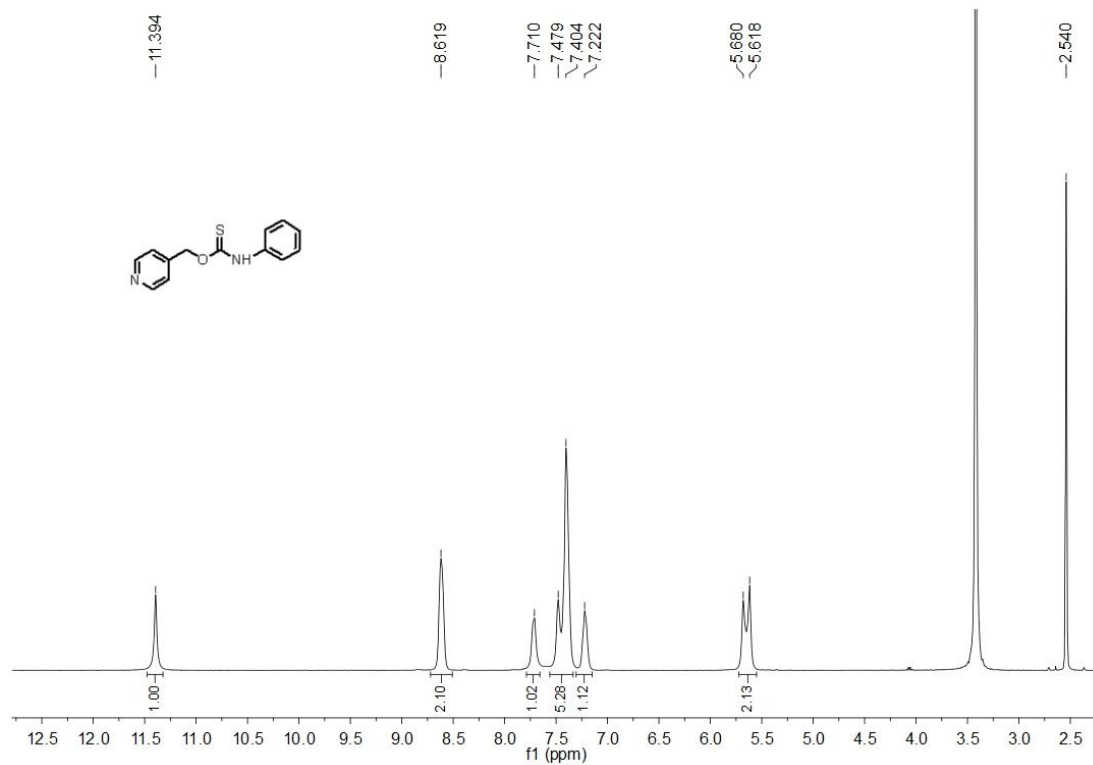


Fig. S55. ^1H NMR spectrum of **3ma** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

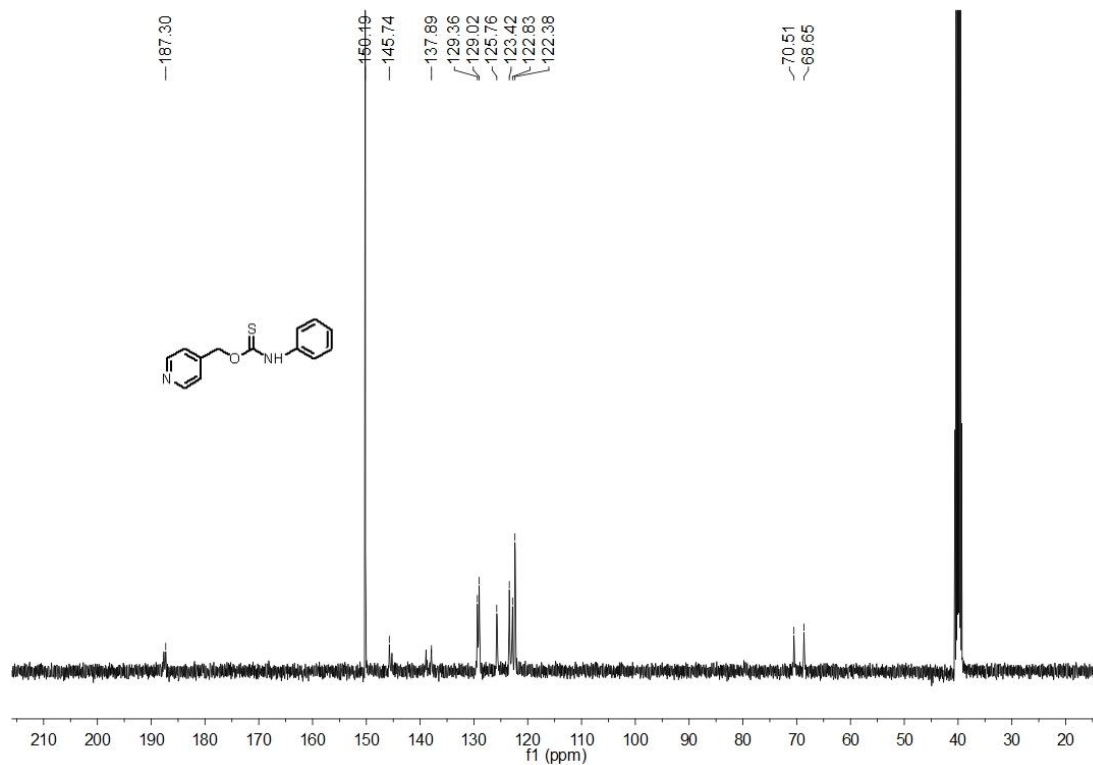


Fig. S56. ^{13}C NMR spectrum of **3ma** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

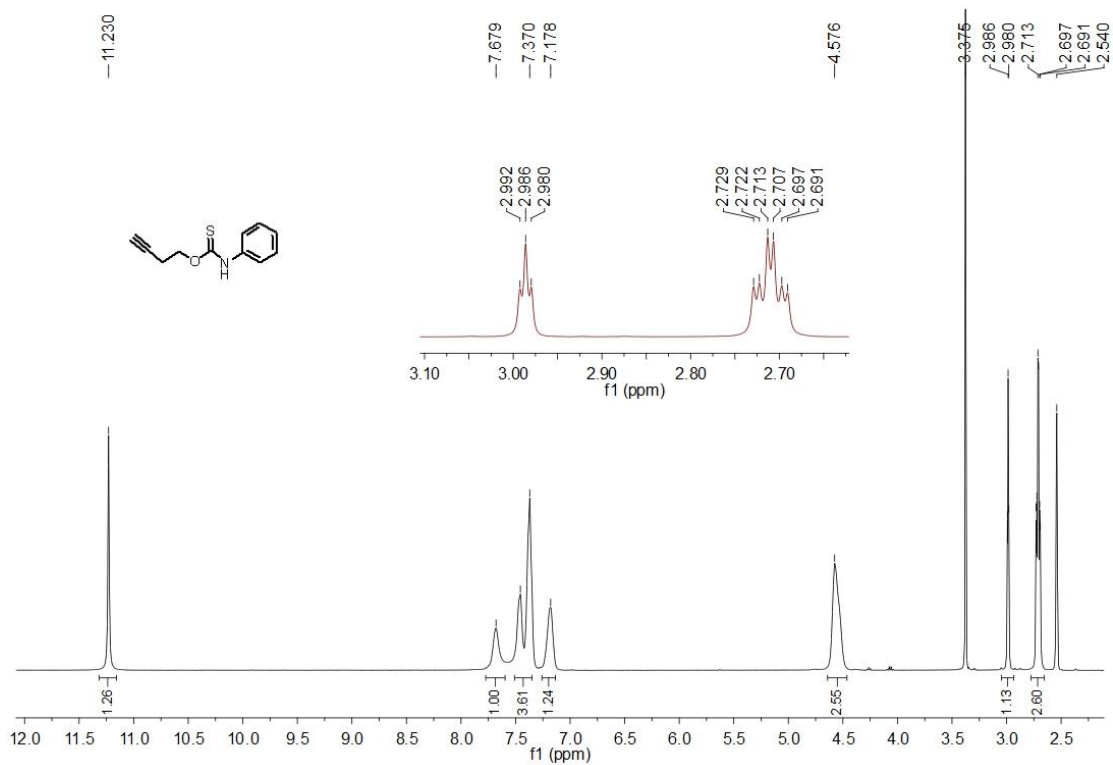


Fig. S57. ¹H NMR spectrum of **3na** (400 MHz, DMSO-*d*₆, 20 °C)

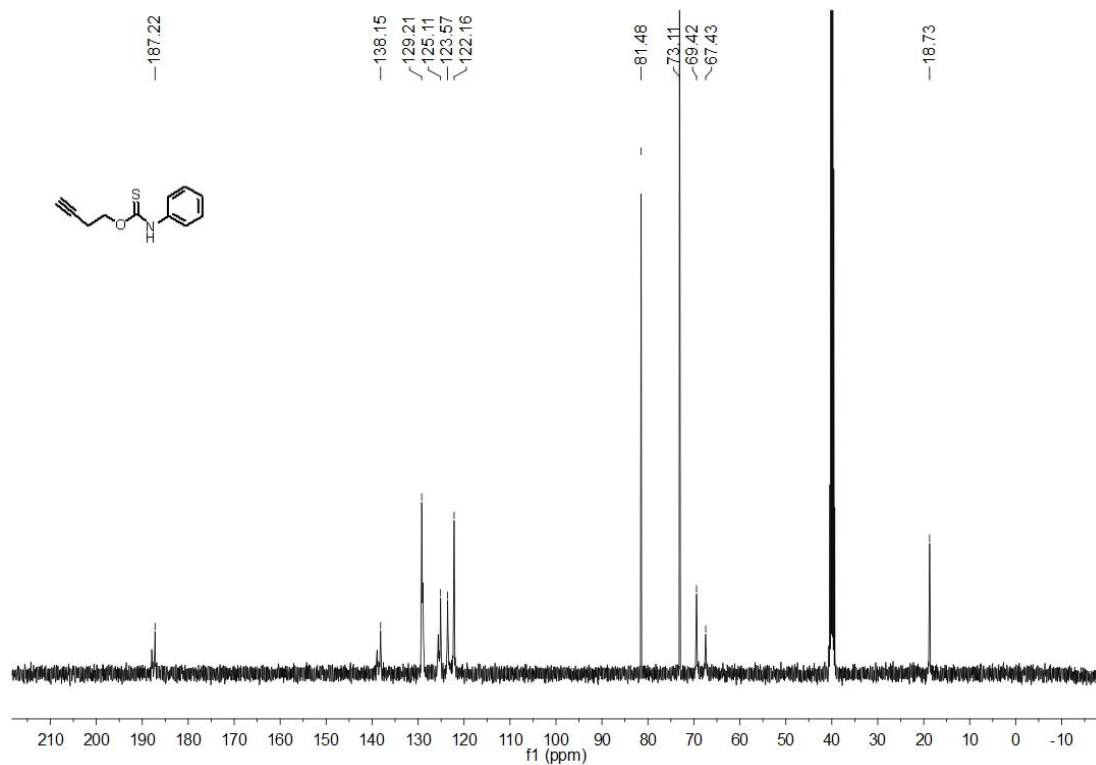


Fig. S58. ¹³C NMR spectrum of **3na** (100 MHz, DMSO-*d*₆, 20 °C)

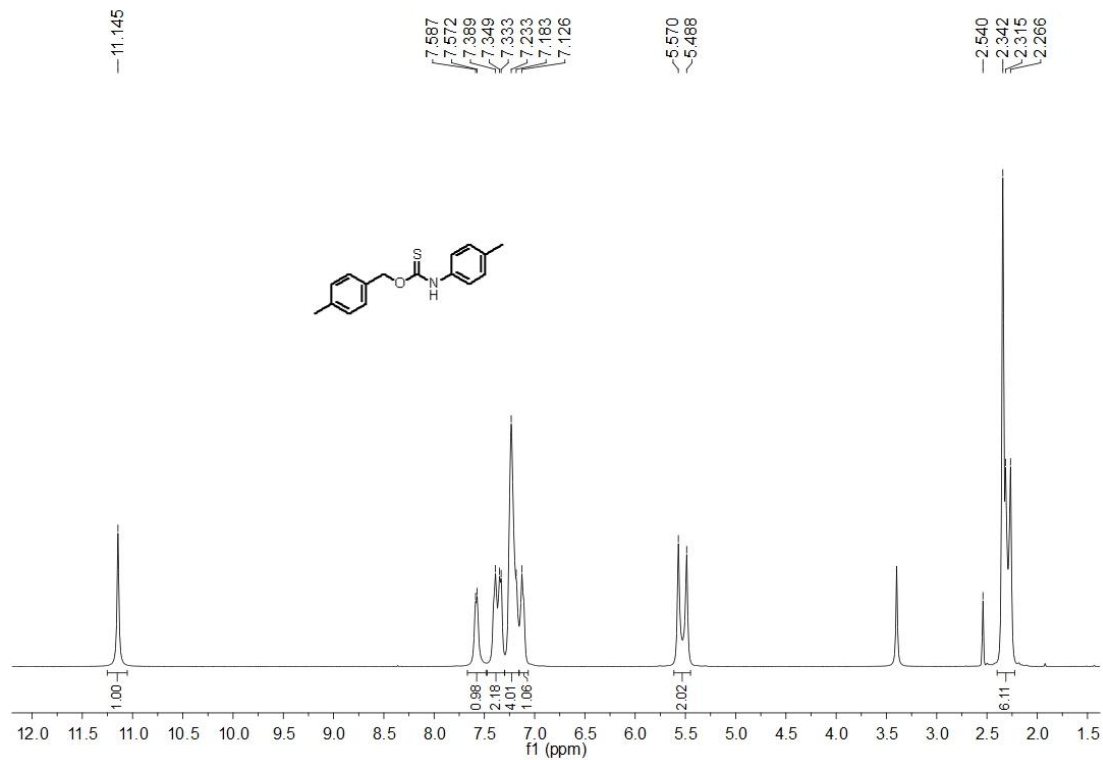


Fig. S59. ^1H NMR spectrum of **3dd** (400 MHz, $\text{DMSO-}d_6$, 20 °C)

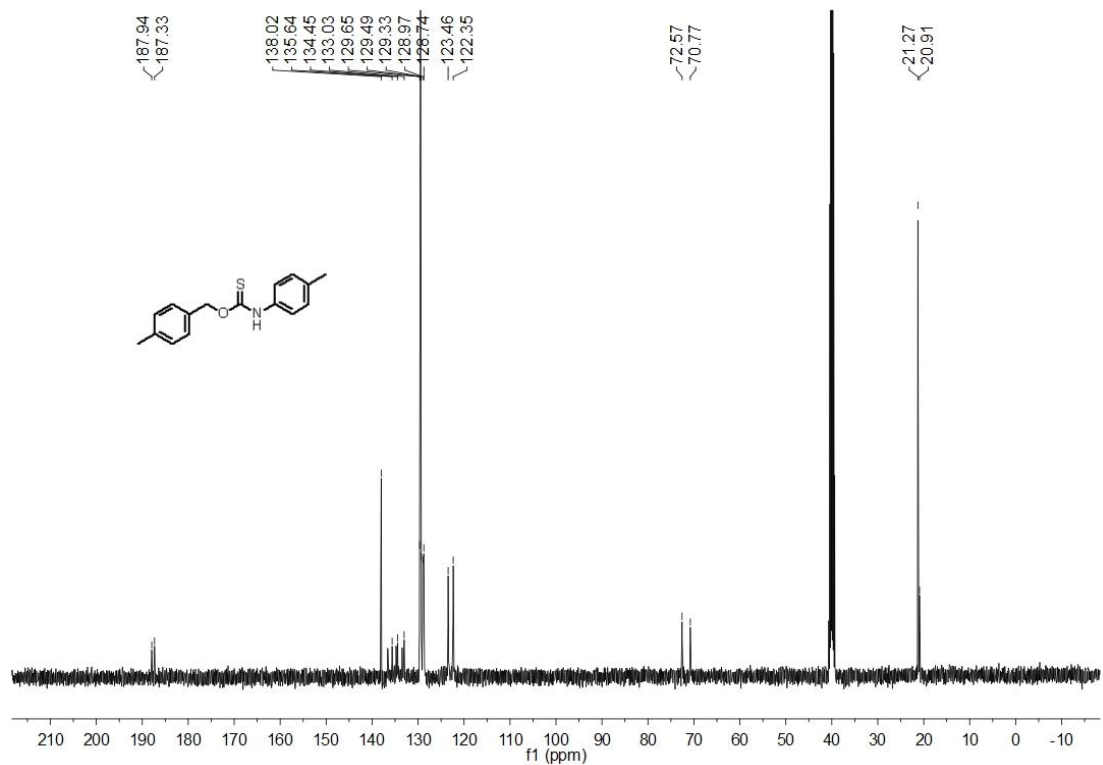


Fig. S60. ^{13}C NMR spectrum of **3dd** (100 MHz, $\text{DMSO-}d_6$, 20 °C)

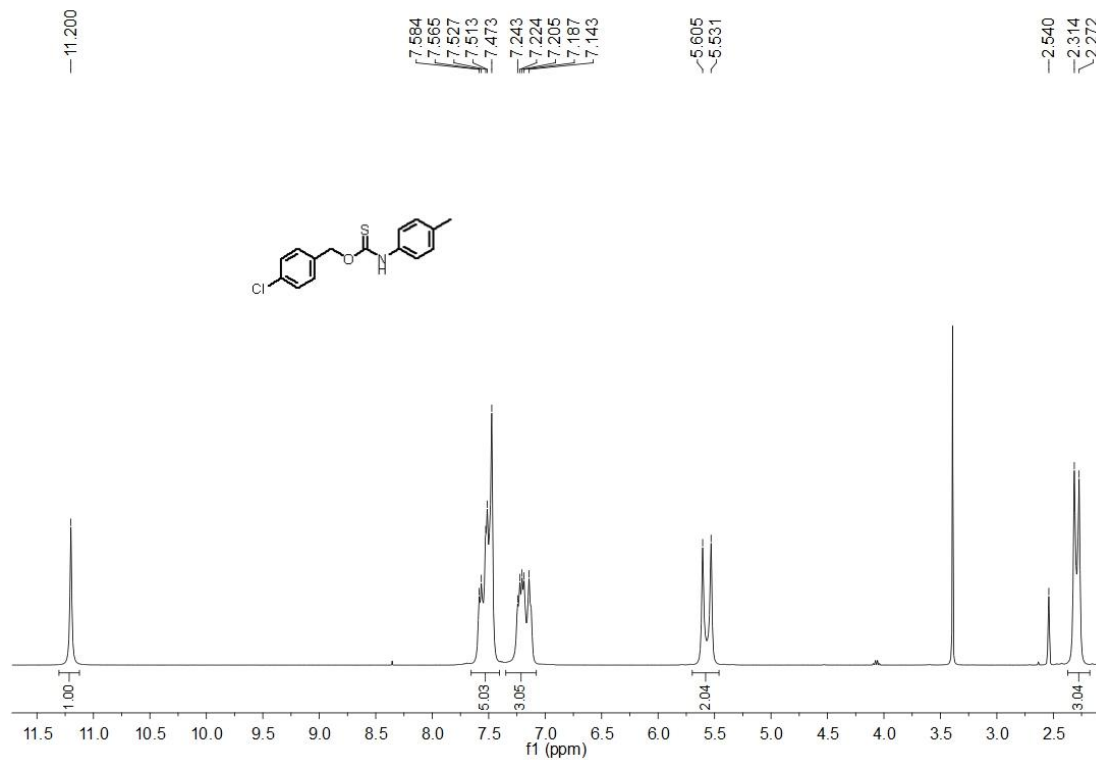


Fig. S61. $^1\text{H NMR}$ spectrum of 3fd (400 MHz, DMSO- d_6 , 20 °C)

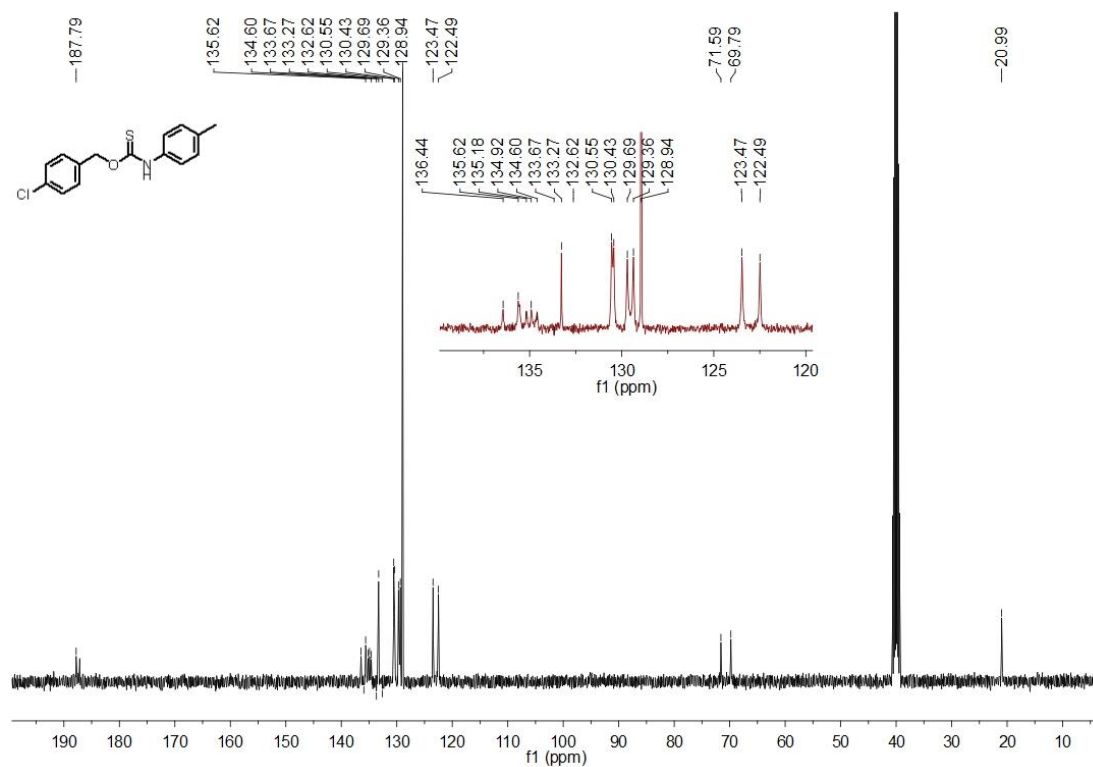


Fig. S62. $^{13}\text{C NMR}$ spectrum of 3fd (100 MHz, DMSO- d_6 , 20 °C)

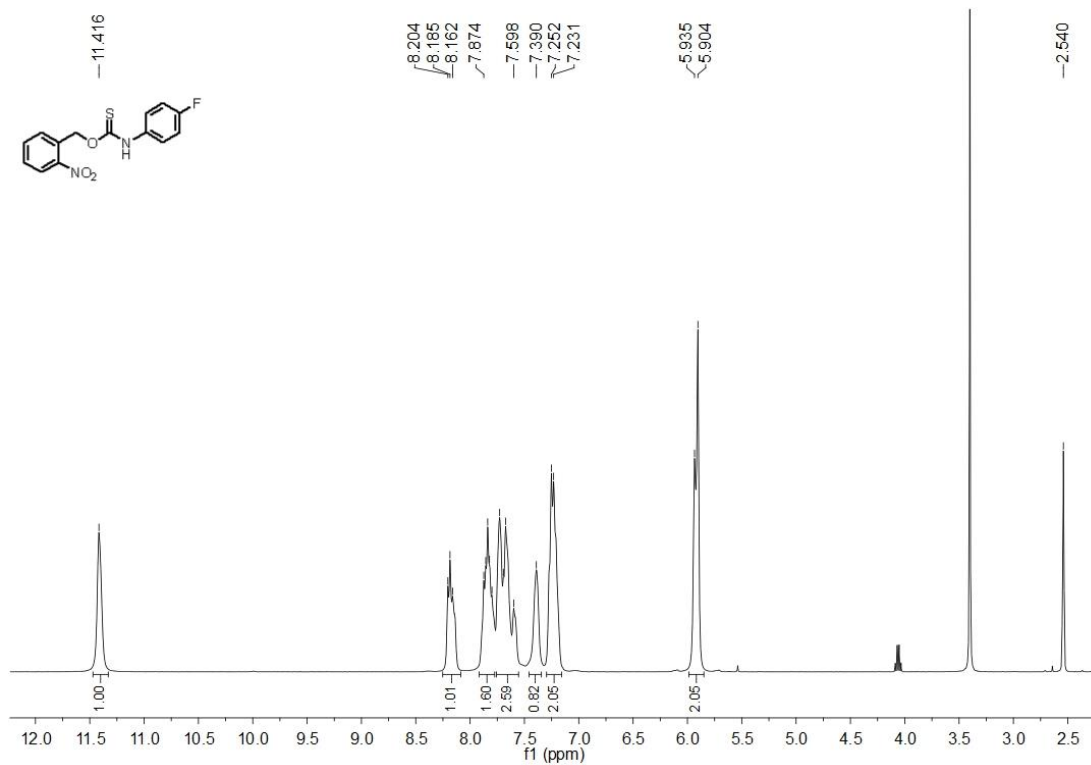


Fig. S63. ¹H NMR spectrum of 3of (400 MHz, DMSO-*d*₆, 20 °C)

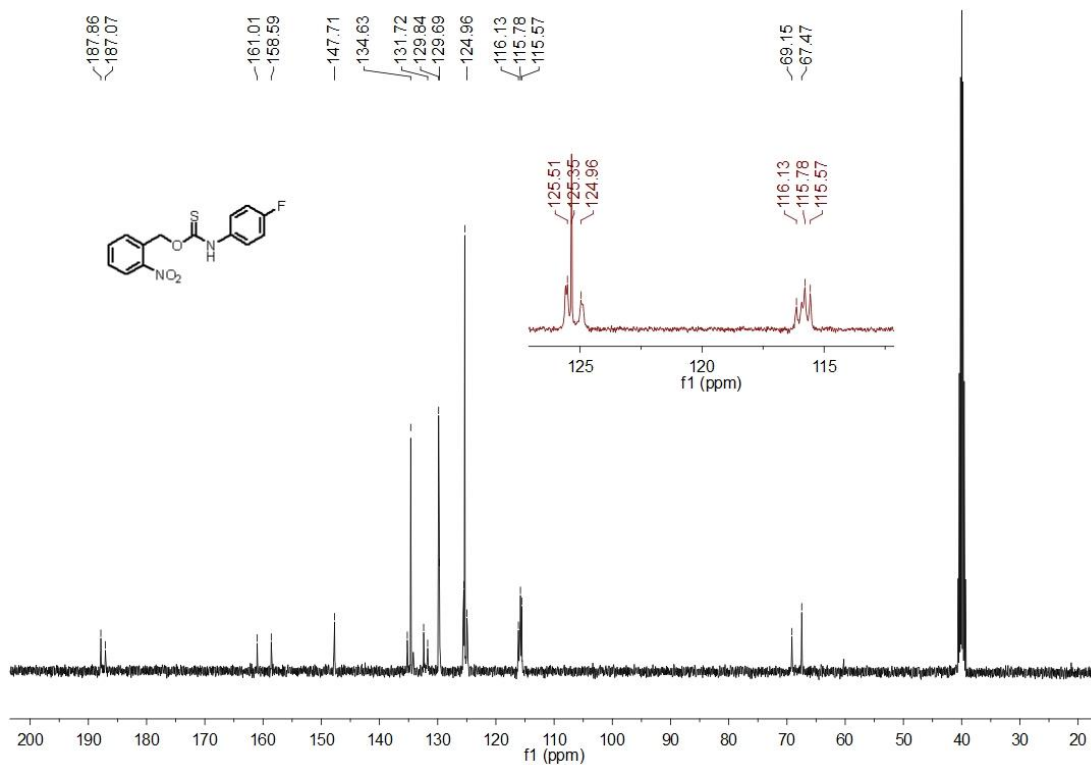


Fig. S64. ¹³C NMR spectrum of 3of (100 MHz, DMSO-*d*₆, 20 °C)

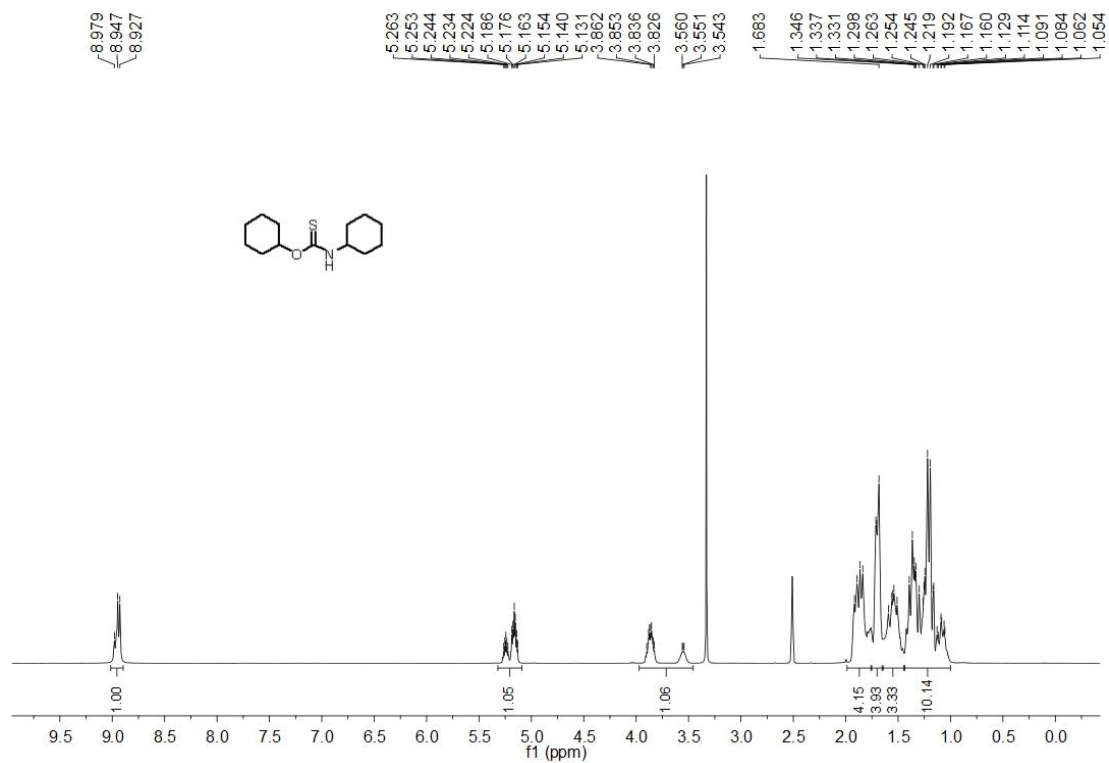


Fig. S65. ¹H NMR spectrum of 3kj (400 MHz, DMSO-*d*₆, 20 °C)

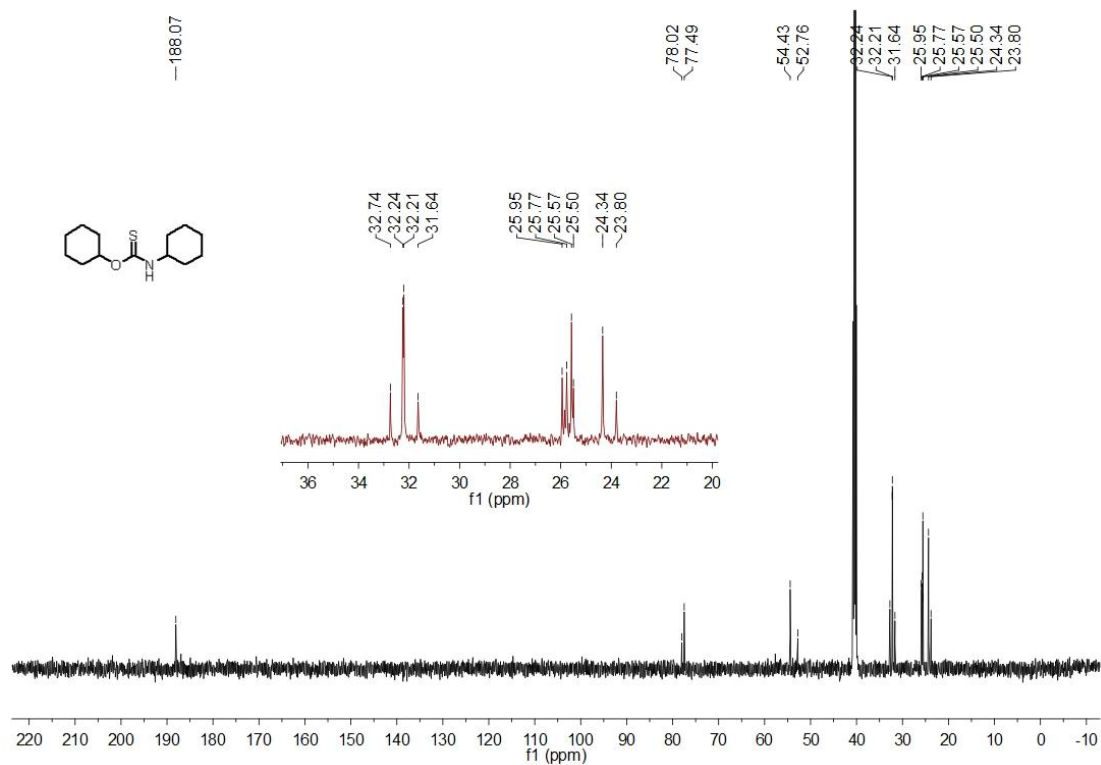


Fig. S66. ¹³C NMR spectrum of 3kj (100 MHz, DMSO-*d*₆, 20 °C)

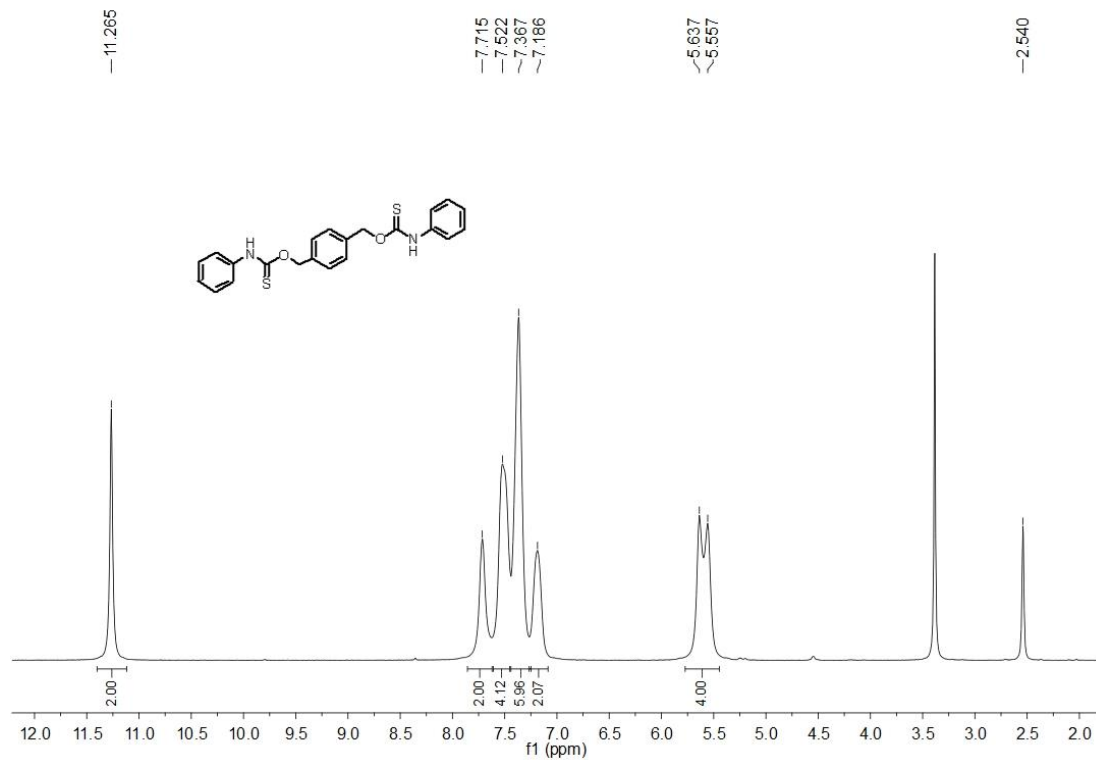


Fig. S67. ^1H NMR spectrum of 3pa (400 MHz, DMSO- d_6 , 20 °C)

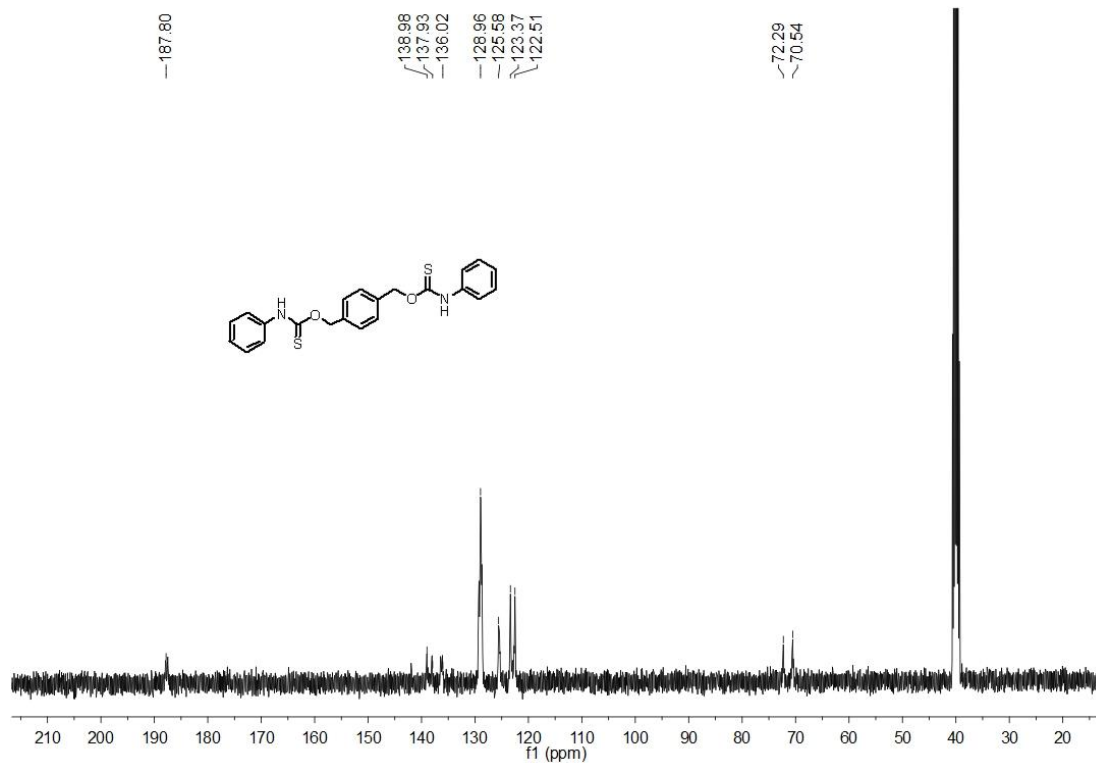


Fig. S68. ^{13}C NMR spectrum of 3pa (100 MHz, DMSO- d_6 , 20 °C)

Copies of β -amino alcohols

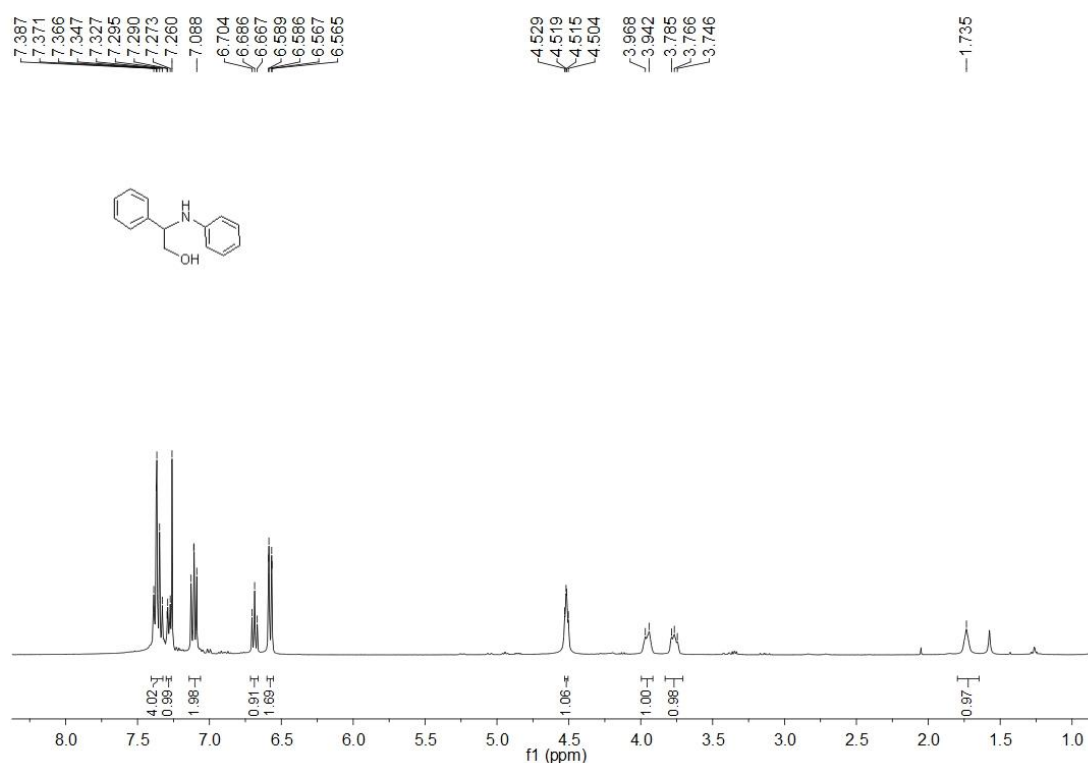


Fig. S69. ^1H NMR spectrum of **4aa** (400 MHz, CDCl_3 , 20 $^\circ\text{C}$)

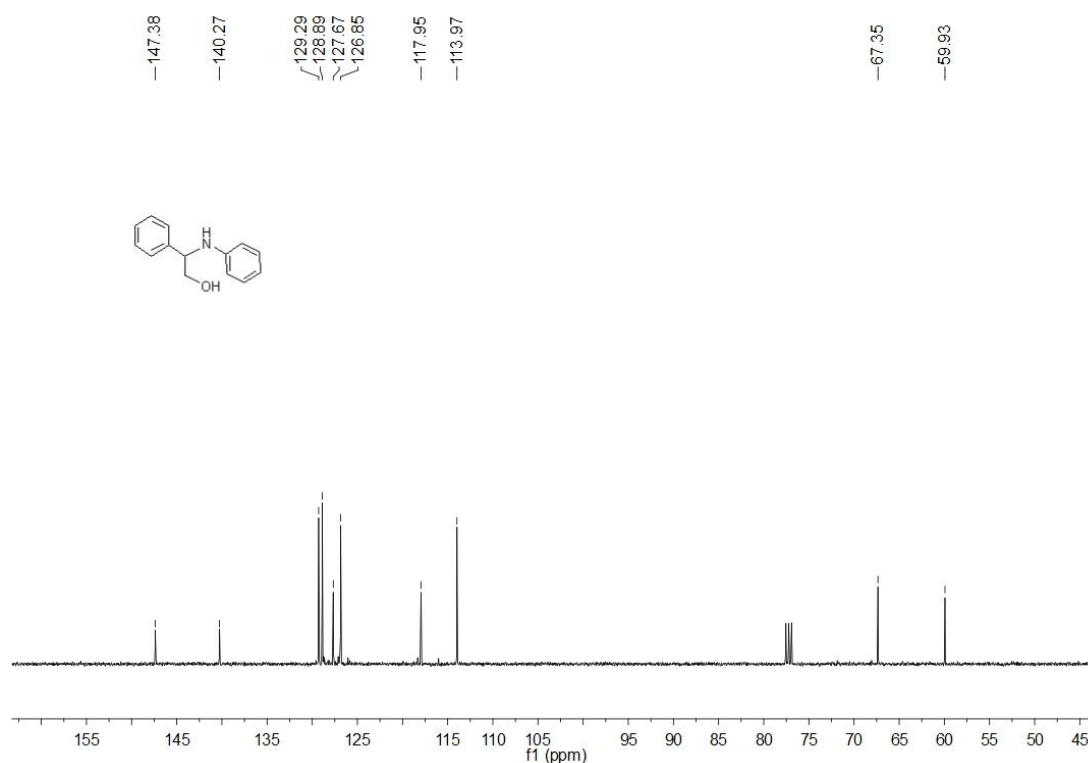


Fig. S70. ^{13}C NMR spectrum of **4aa** (100 MHz, CDCl_3 , 20 $^\circ\text{C}$)

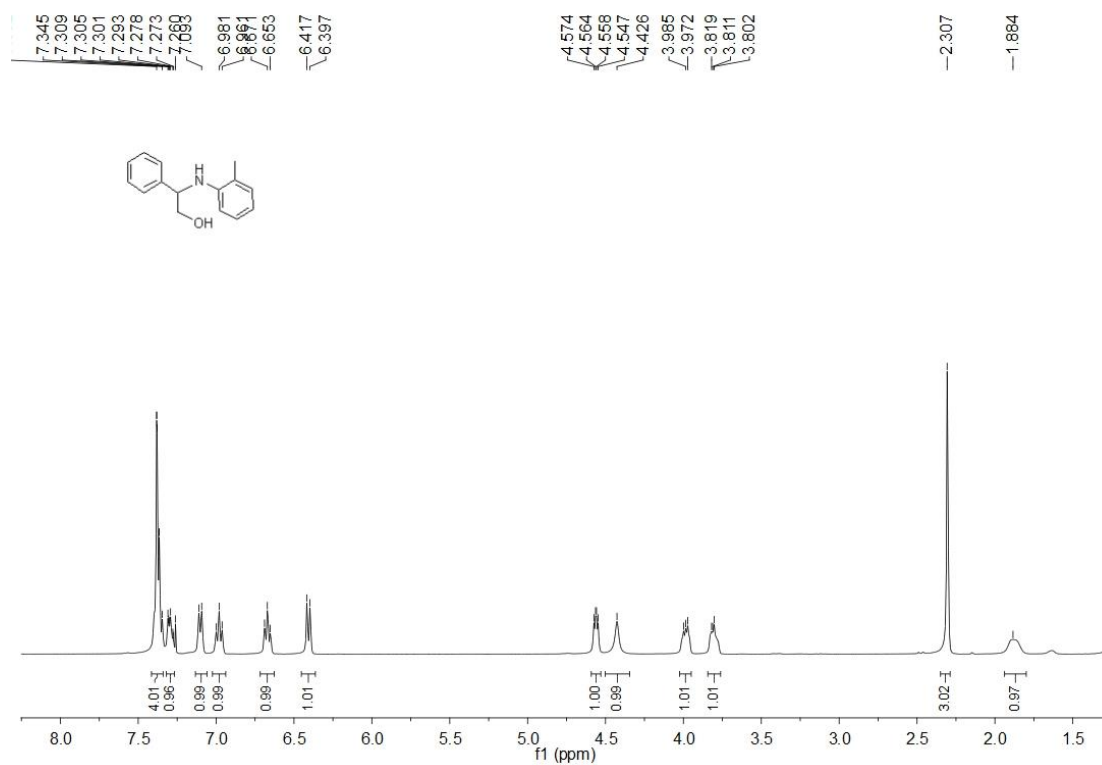


Fig. S71. ¹H NMR spectrum of **4ab** (400 MHz, CDCl₃, 20 °C)

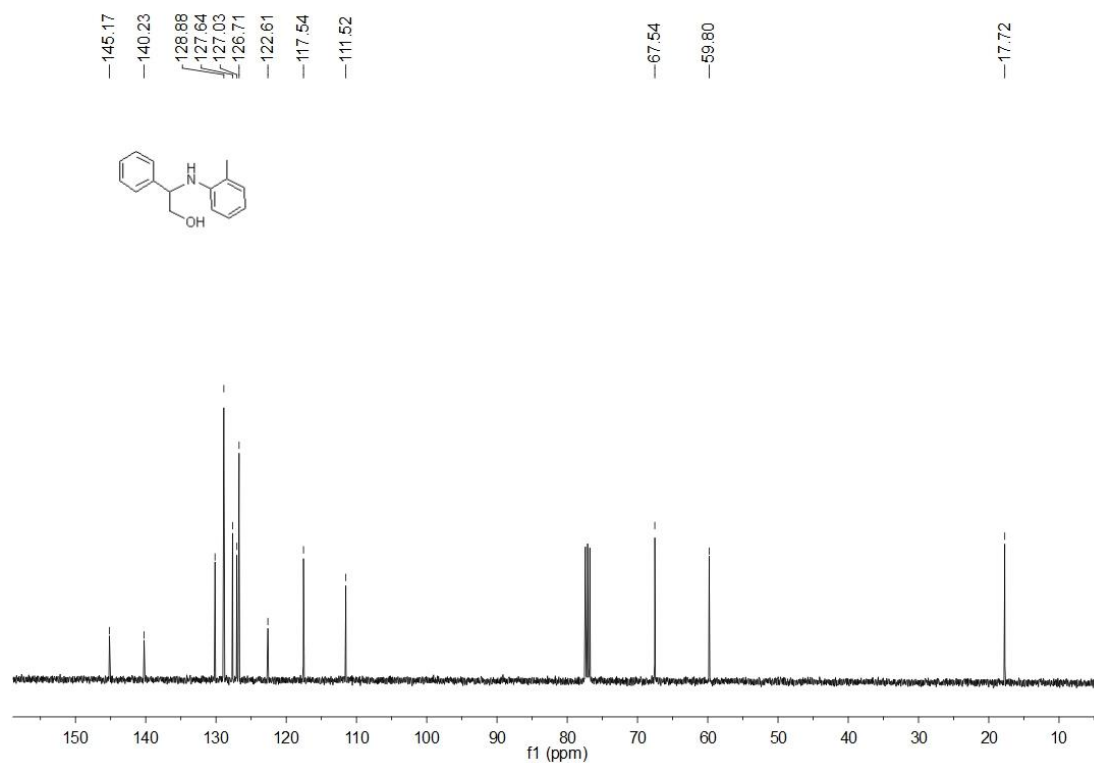


Fig. S72. ¹³C NMR spectrum of **4ab** (100 MHz, CDCl₃, 20 °C)

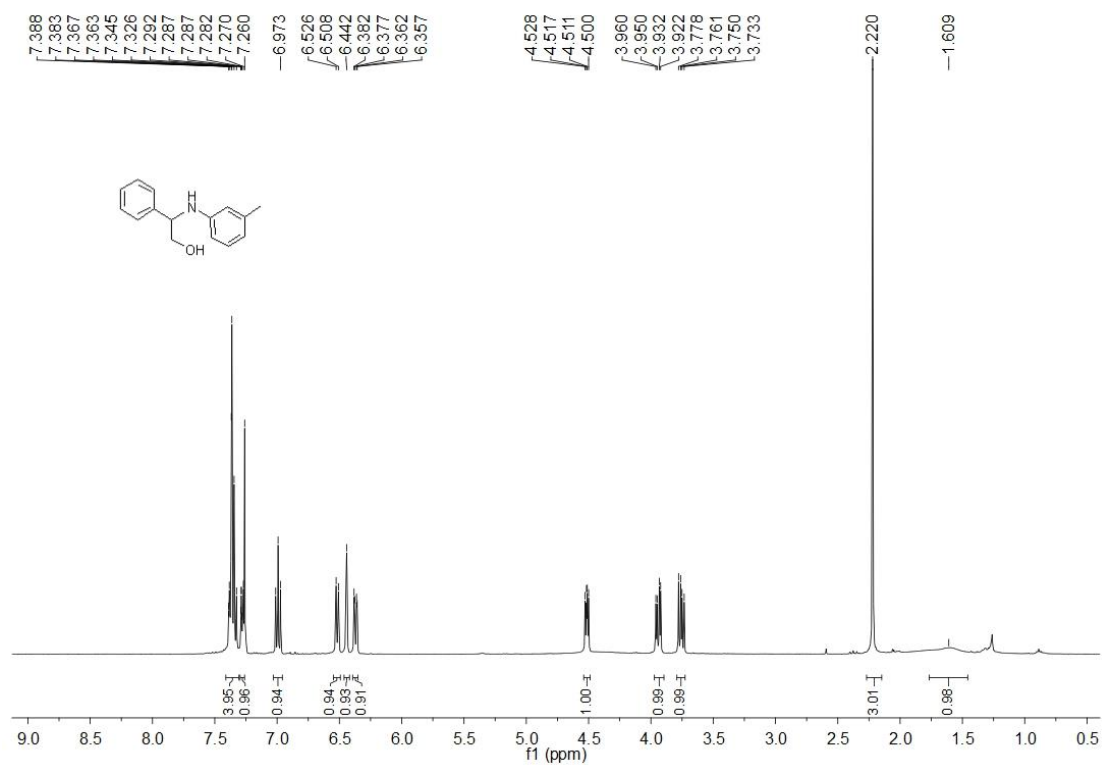


Fig. S73. ¹H NMR spectrum of 4ac (400 MHz, CDCl₃, 20 °C)

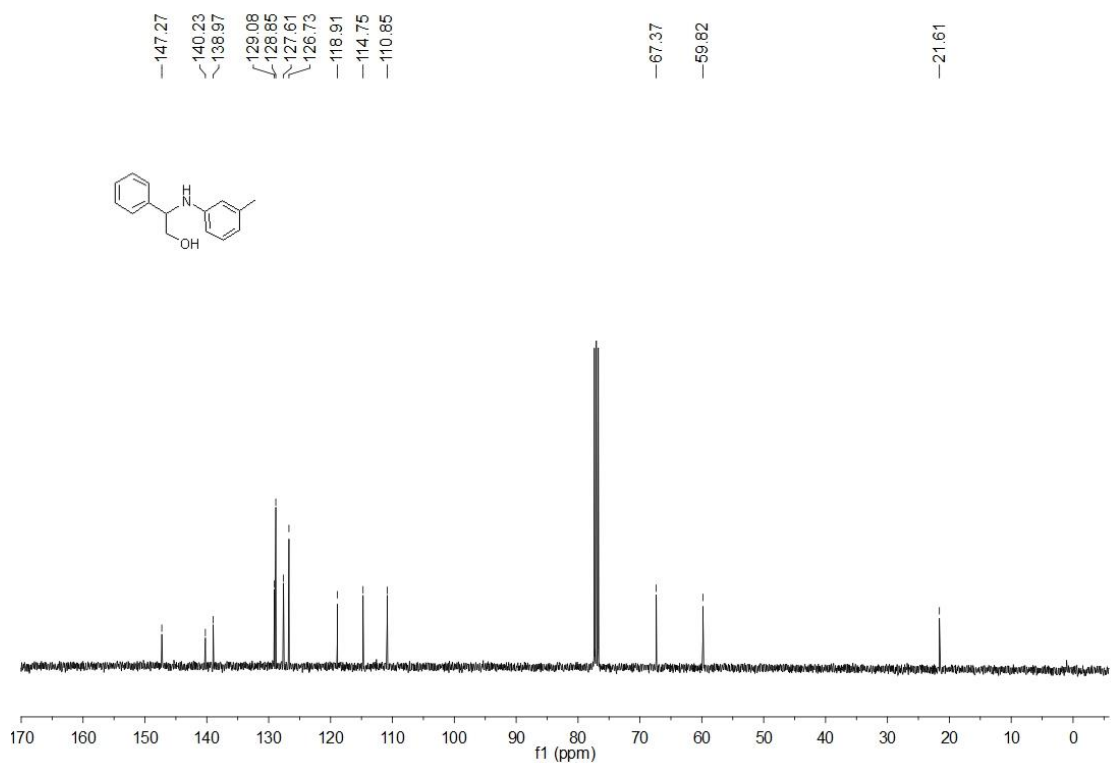


Fig. S74. ¹³C NMR spectrum of 4ac (100 MHz, CDCl₃, 20 °C)

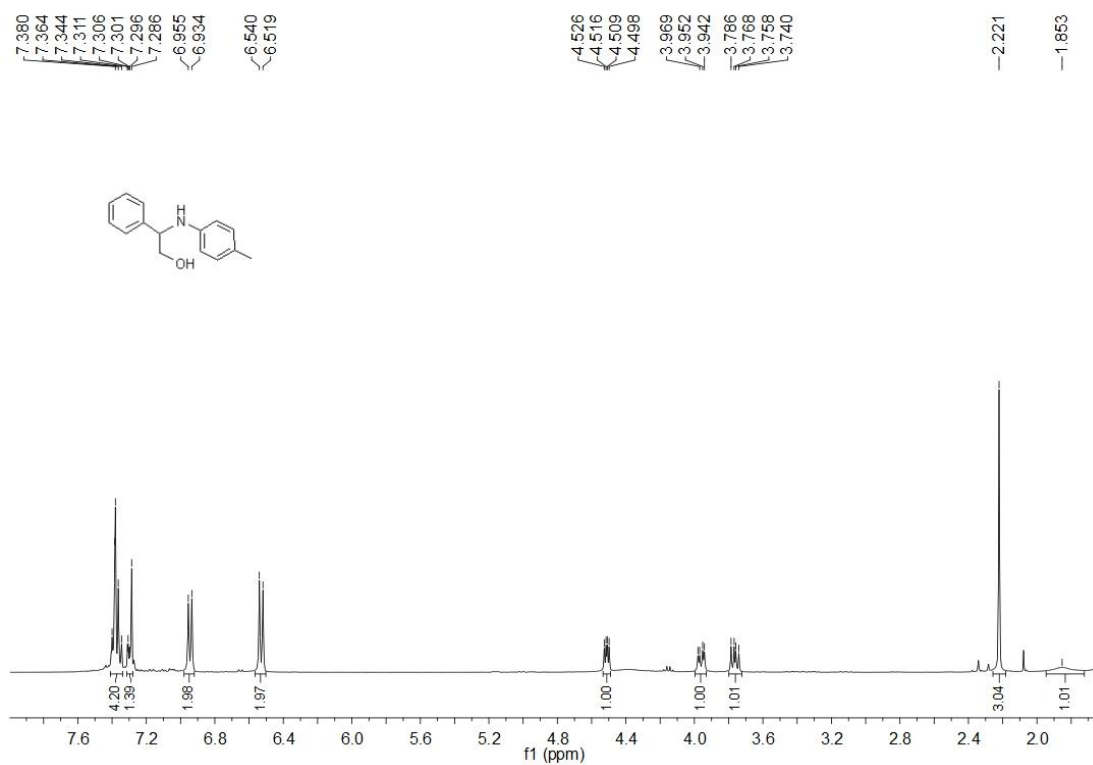


Fig. S75. ¹H NMR spectrum of **4ad** (400 MHz, CDCl₃, 20 °C)

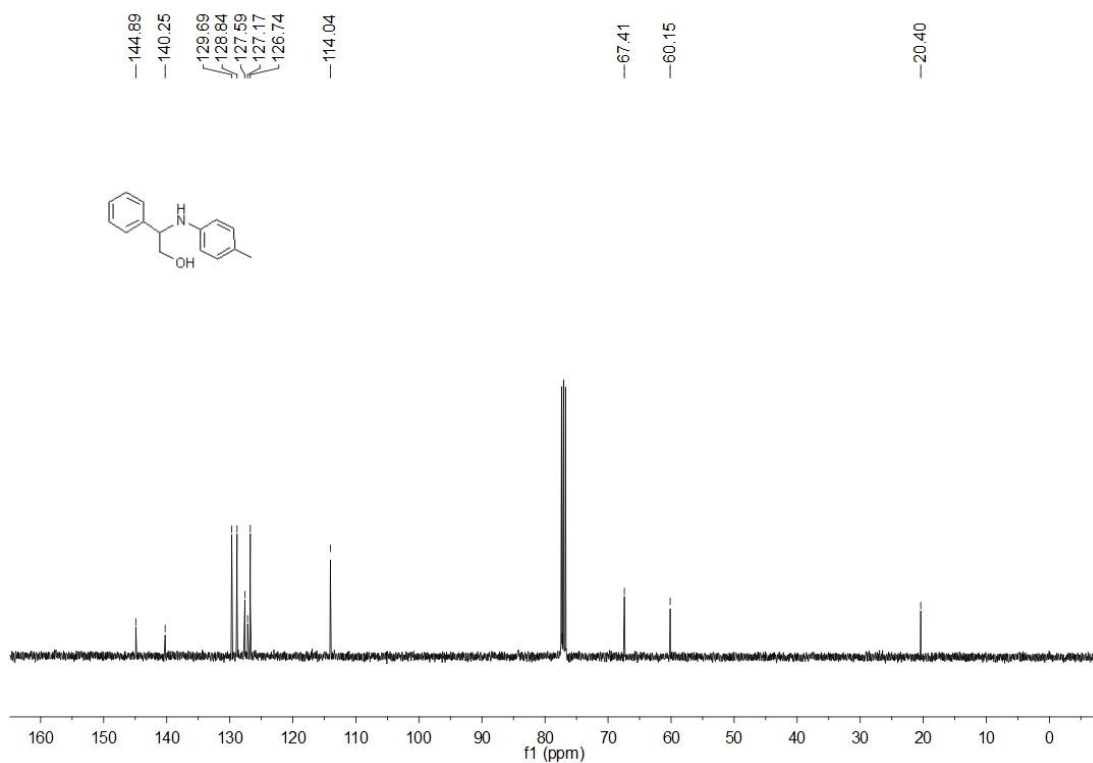


Fig. S76. ¹³C NMR spectrum of **4ad** (100 MHz, CDCl₃, 20 °C)

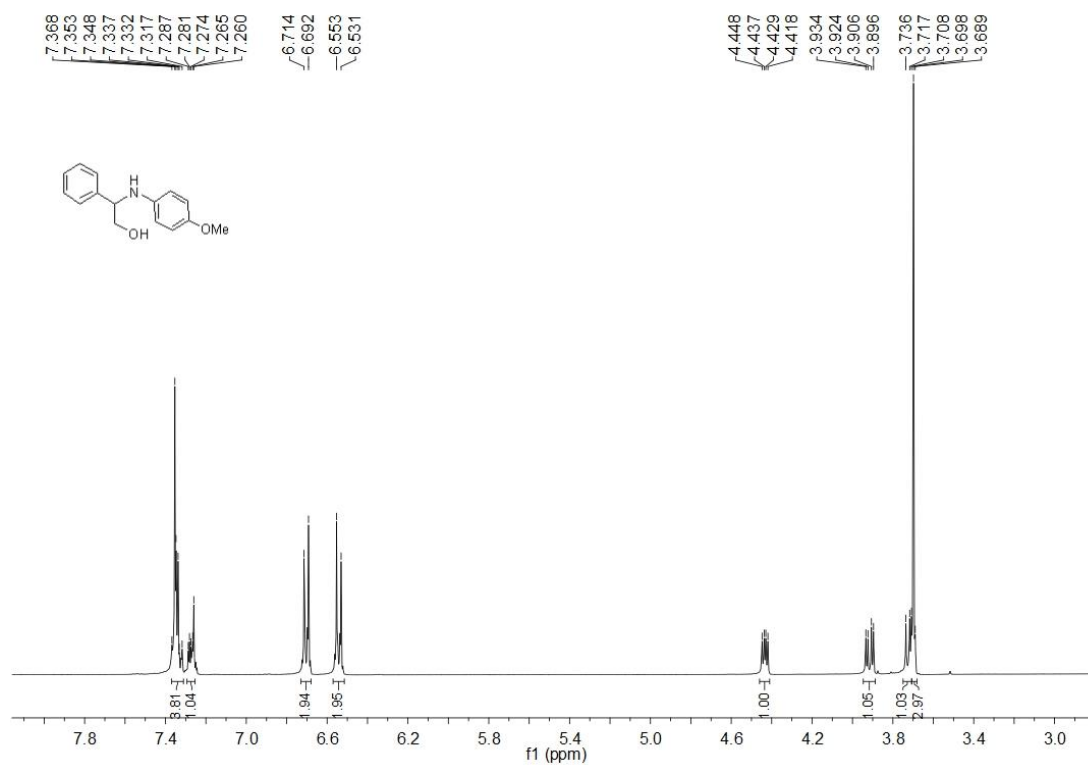


Fig. S77. ¹H NMR spectrum of 4ae (400 MHz, CDCl₃, 20 °C)

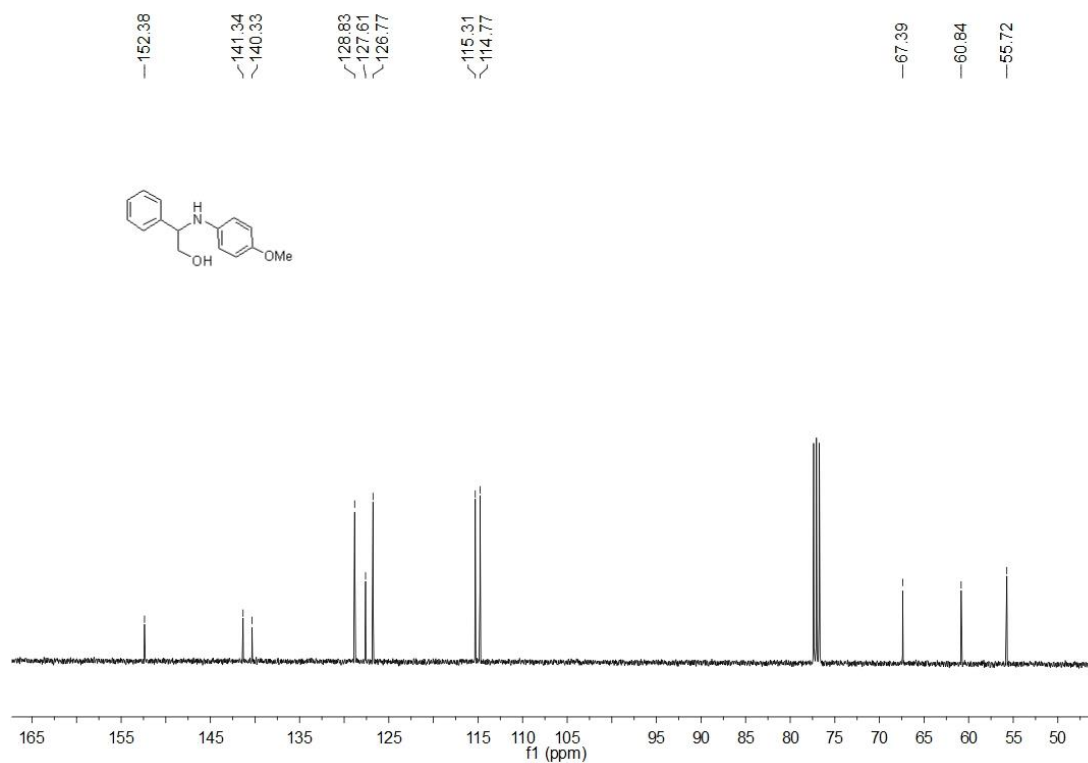


Fig. S78. ¹³C NMR spectrum of 4ae (100 MHz, CDCl₃, 20 °C)

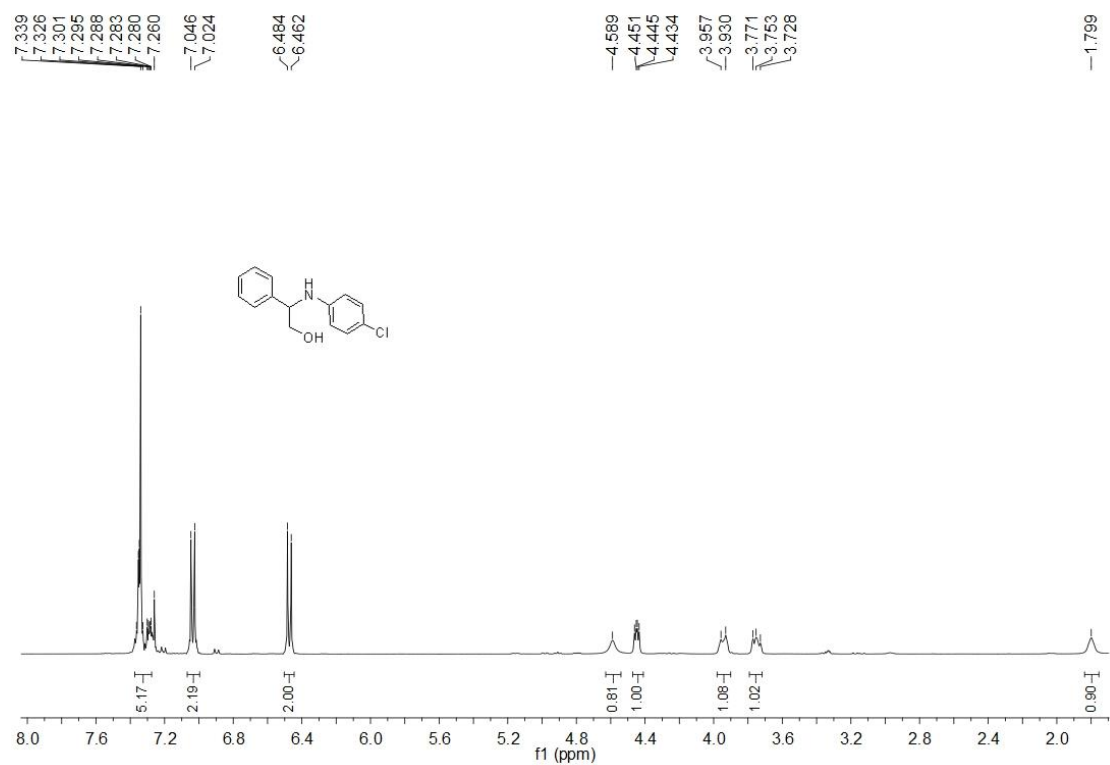


Fig. S79. ¹H NMR spectrum of **4af** (400 MHz, CDCl₃, 20 °C)

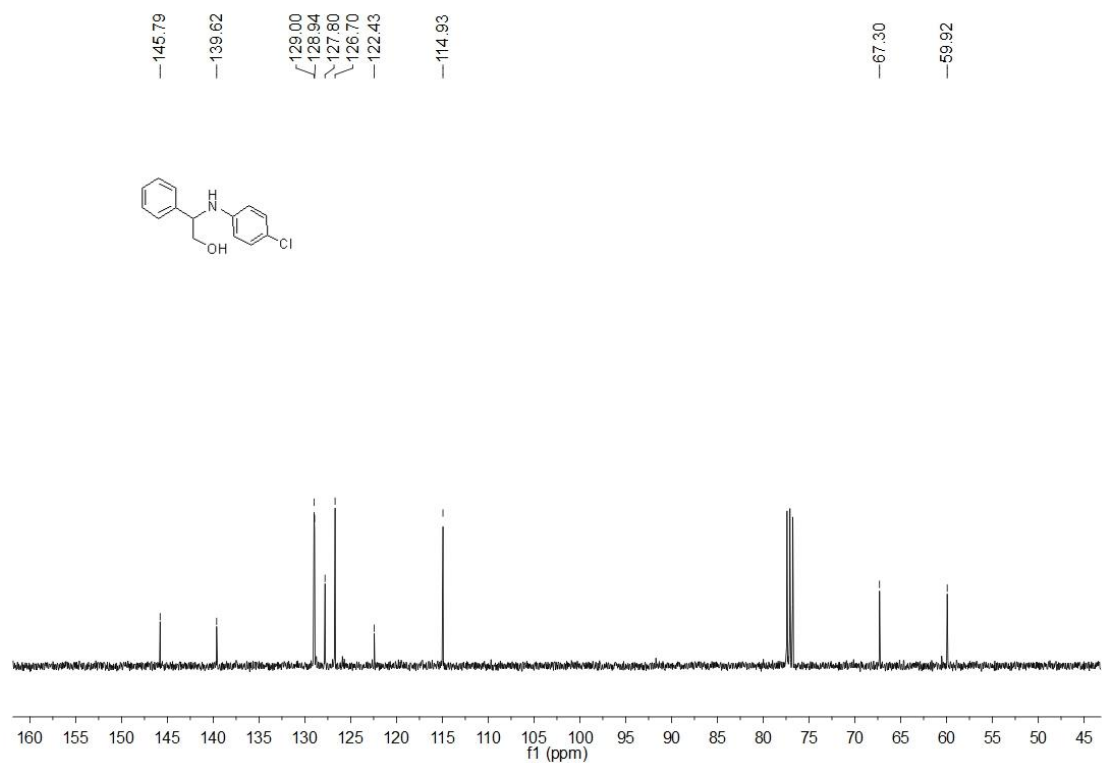


Fig. S80. ¹³C NMR spectrum of **4af** (100 MHz, CDCl₃, 20 °C)

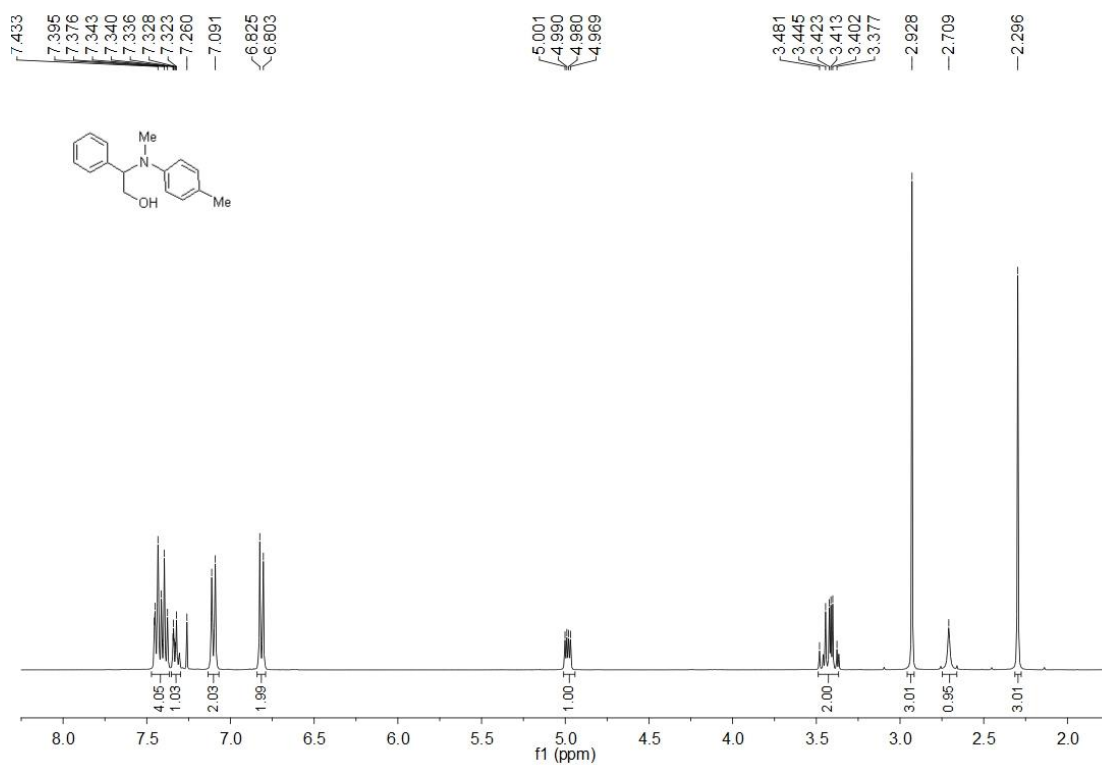


Fig. S81. ¹H NMR spectrum of **4ah** (400 MHz, CDCl₃, 20 °C)

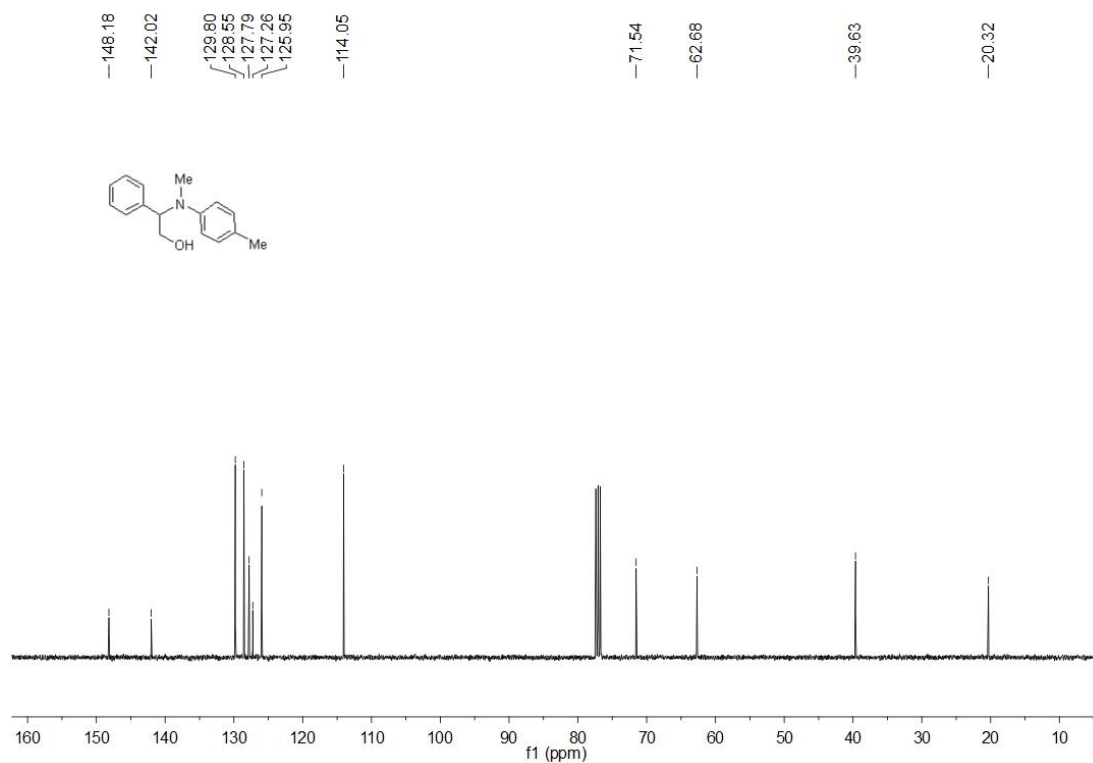
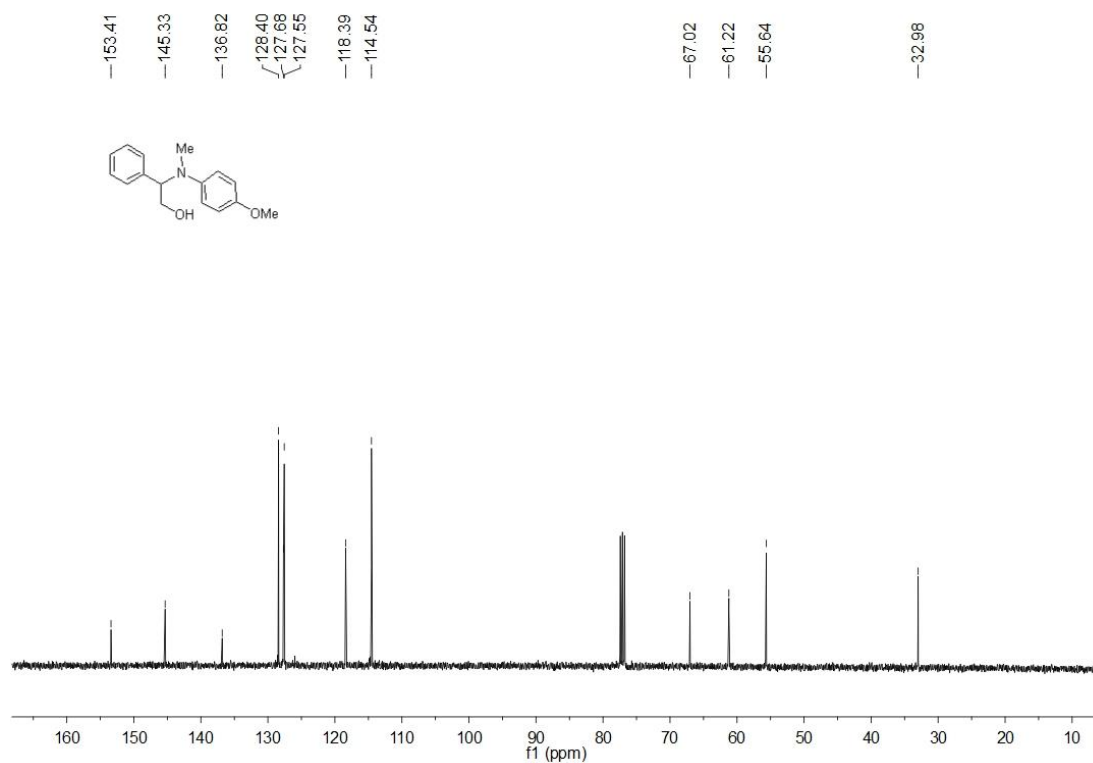
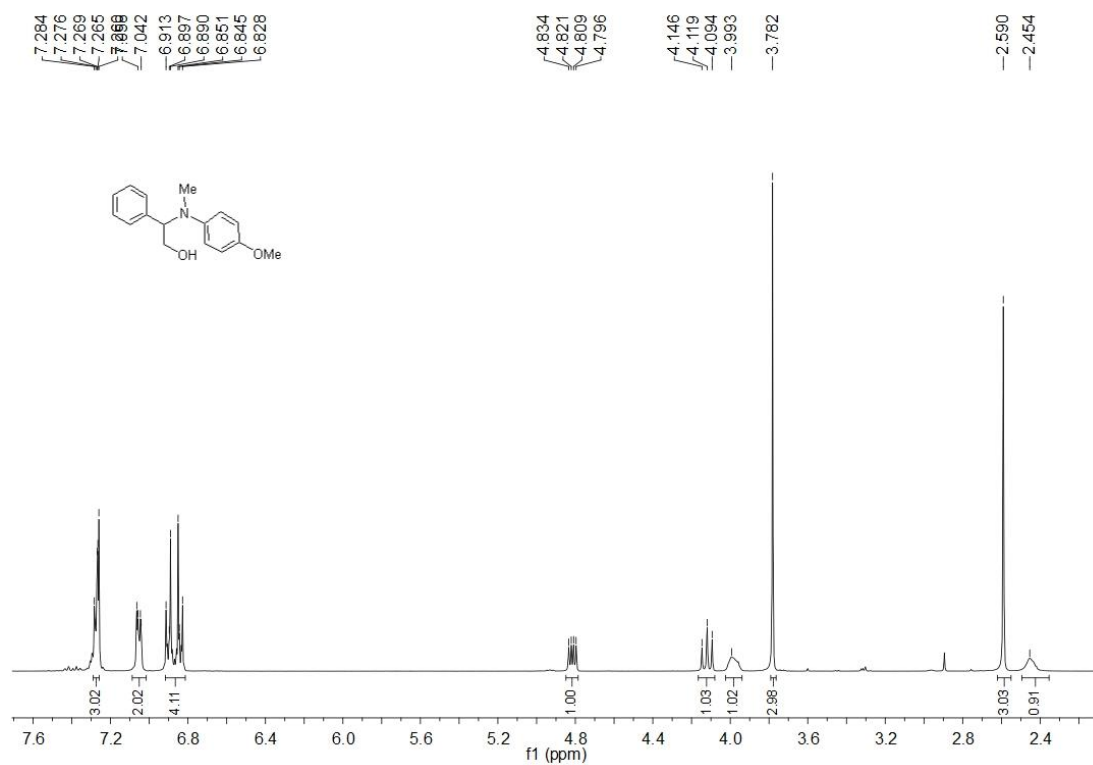
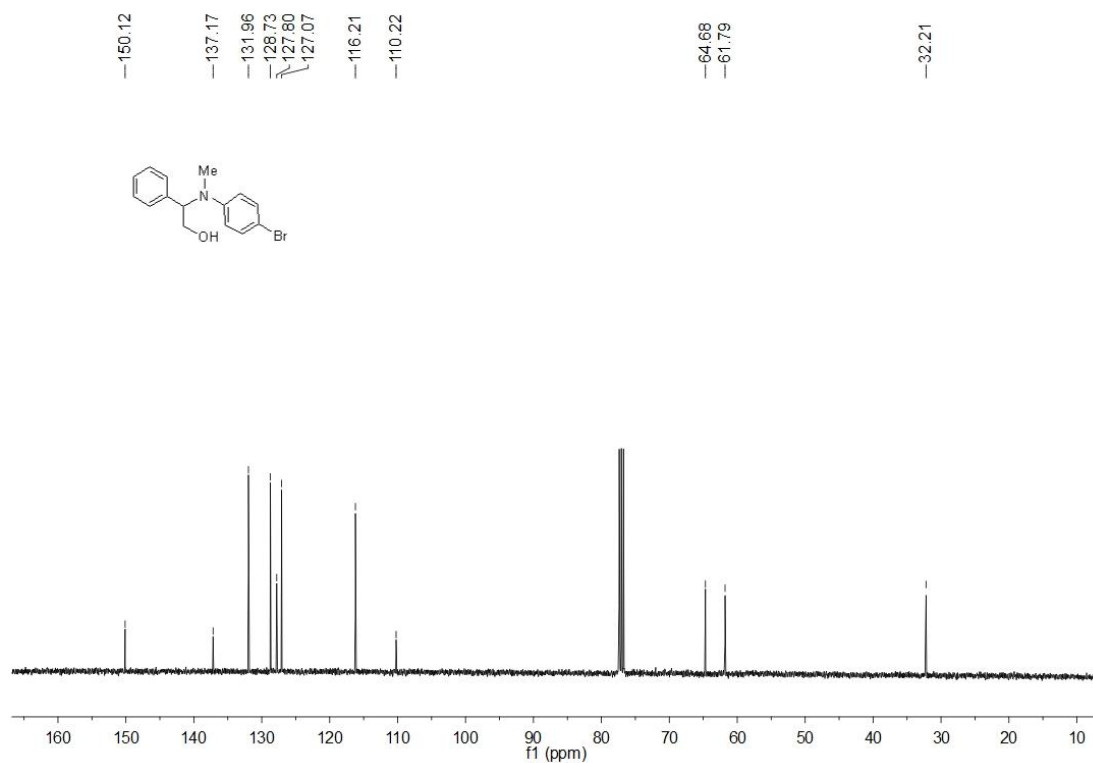
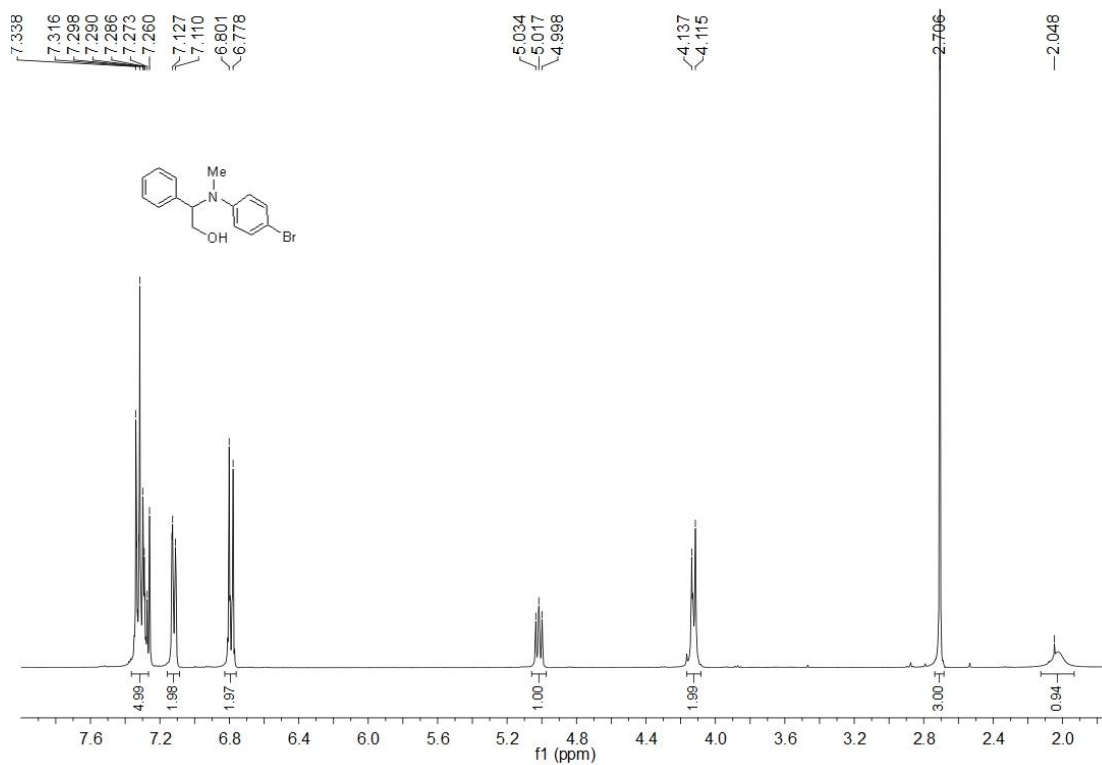


Fig. S82. ¹³C NMR spectrum of **4ah** (100 MHz, CDCl₃, 20 °C)





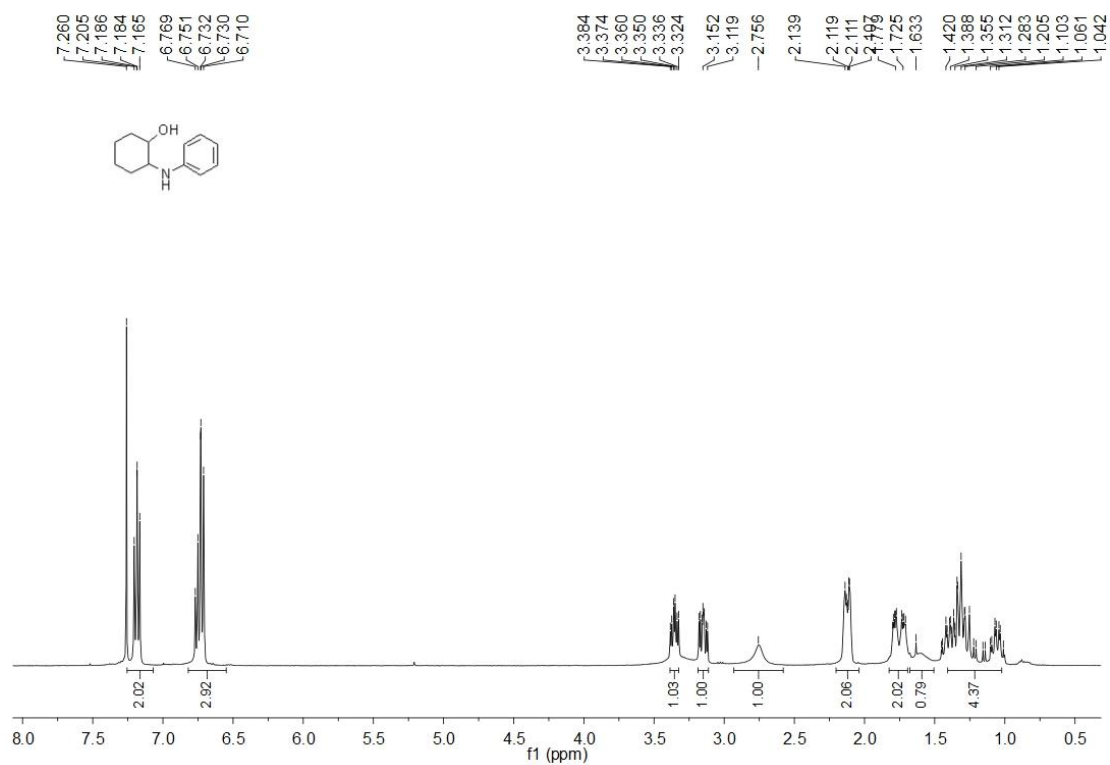


Fig. S87. ¹H NMR spectrum of 4ba (400 MHz, CDCl₃, 20 °C)

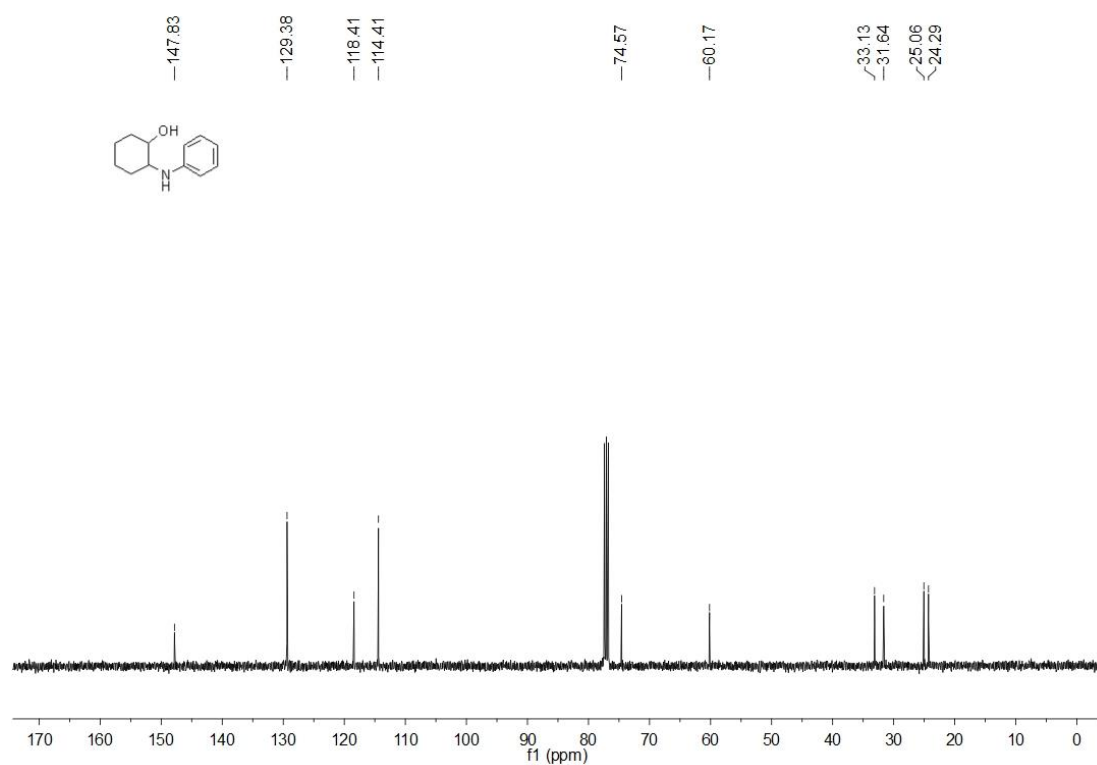


Fig. S88. ¹³C NMR spectrum of 4ba (100 MHz, CDCl₃, 20 °C)

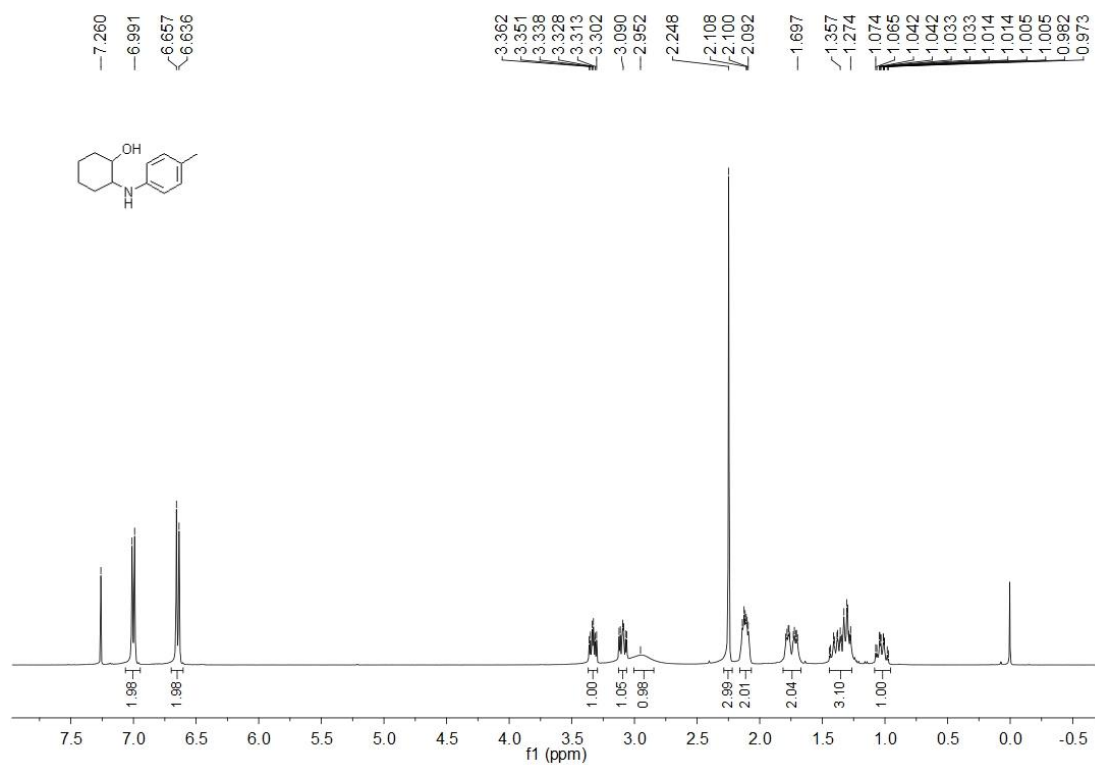


Fig. S89. ¹H NMR spectrum of **4bd** (400 MHz, CDCl₃, 20 °C)

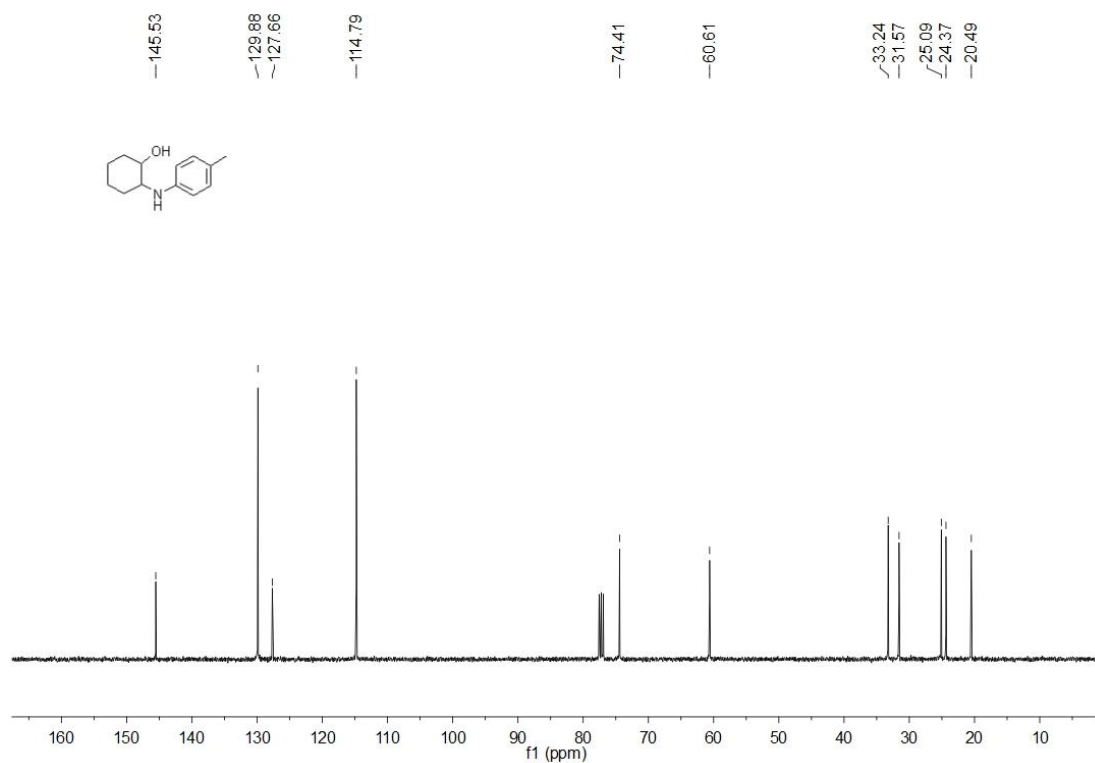


Fig. S90. ¹³C NMR spectrum of **4bd** (100 MHz, CDCl₃, 20 °C)

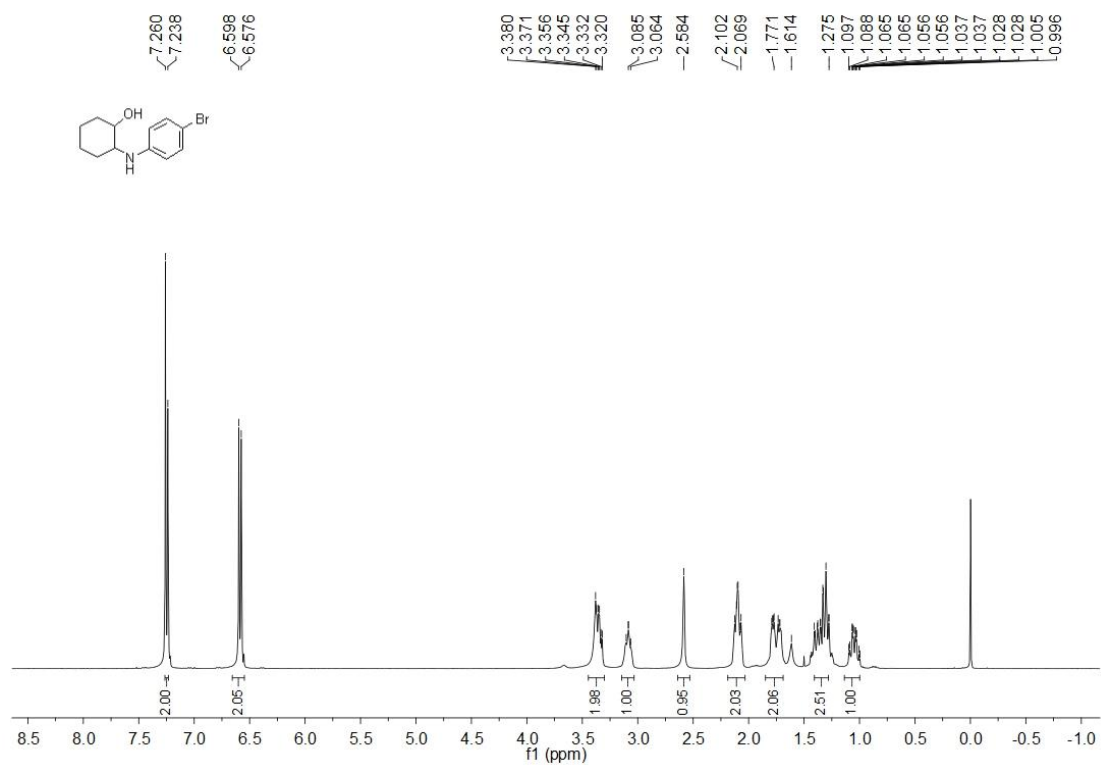


Fig. S91. ¹H NMR spectrum of **4bg** (400 MHz, CDCl₃, 20 °C)

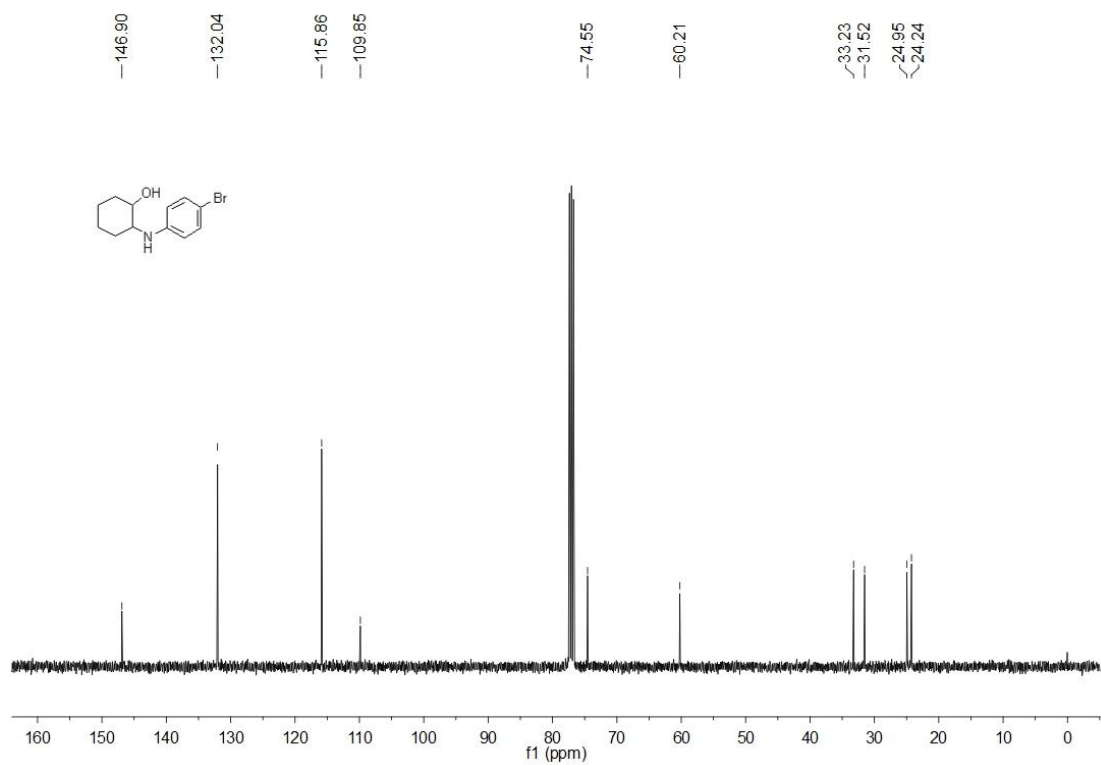


Fig. S92. ¹³C NMR spectrum of **4bg** (100 MHz, CDCl₃, 20 °C)

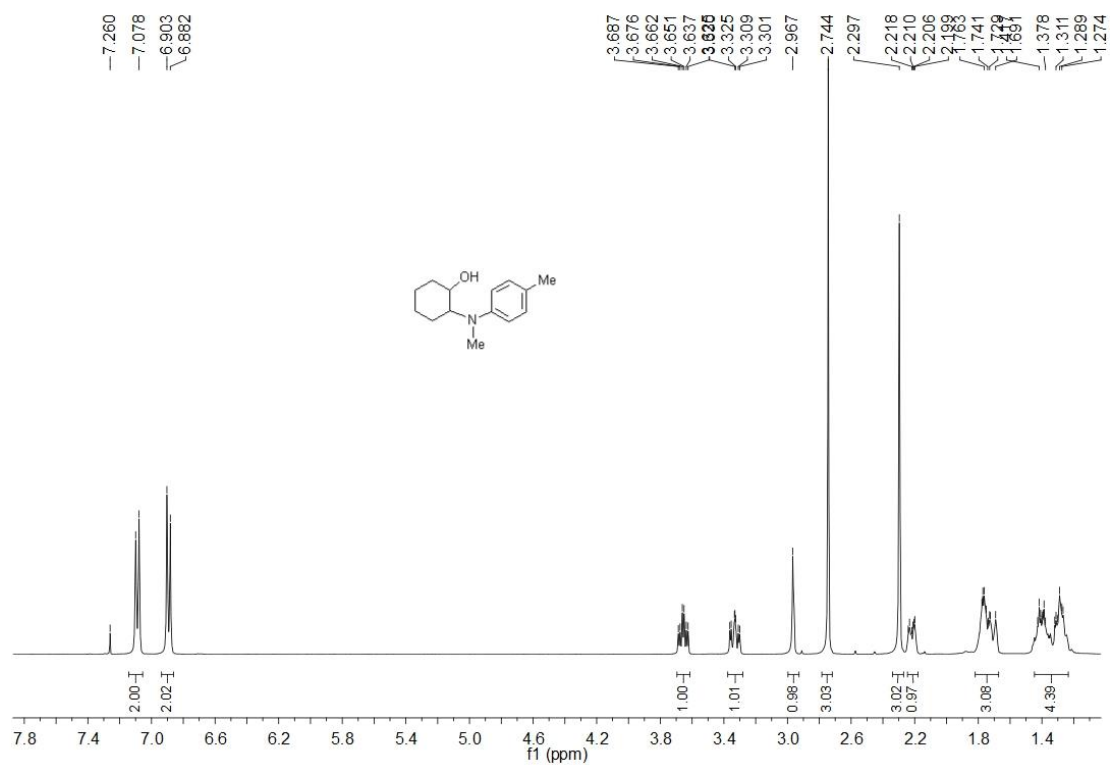


Fig. S93. ¹H NMR spectrum of **4bh** (400 MHz, CDCl₃, 20 °C)

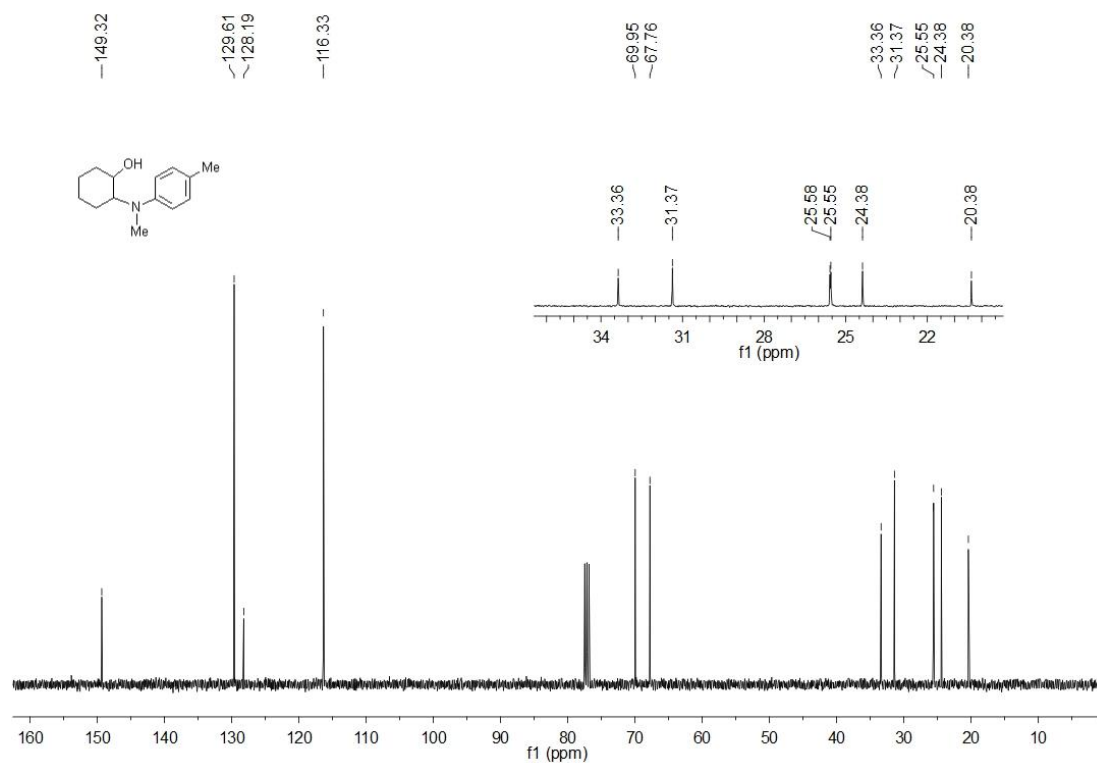


Fig. S94. ¹³C NMR spectrum of **4bh** (100 MHz, CDCl₃, 20 °C)

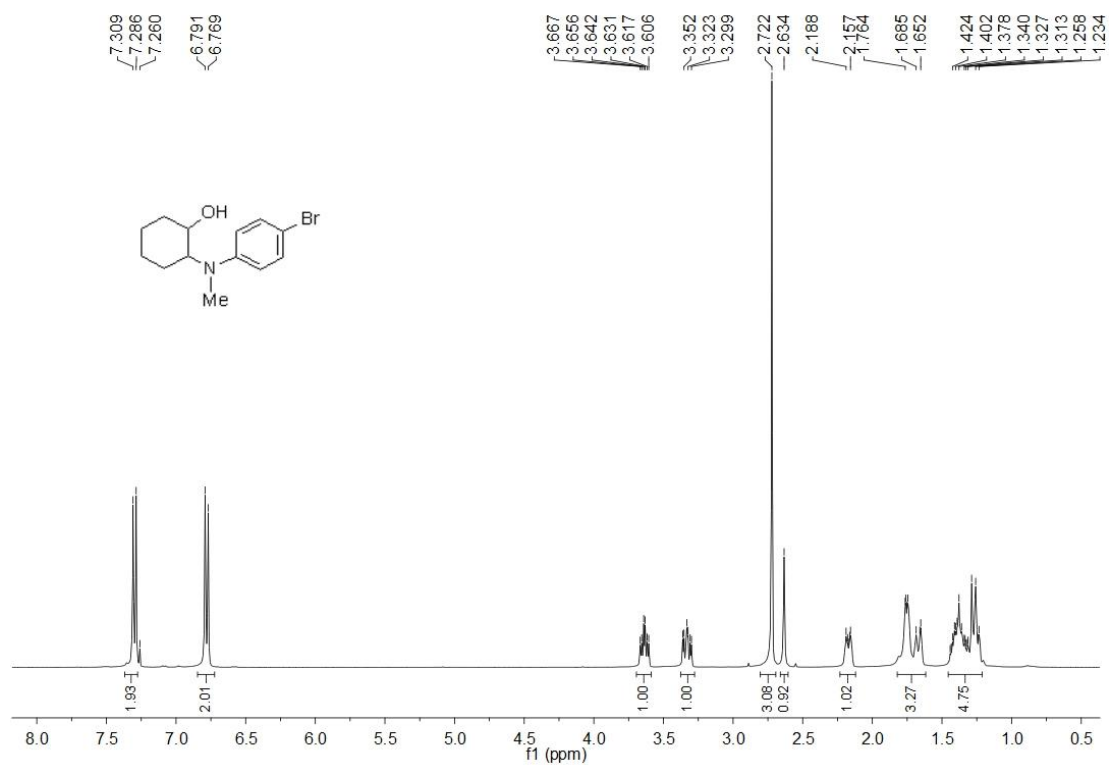


Fig. S95. ¹H NMR spectrum of 4bj (400 MHz, CDCl₃, 20 °C)

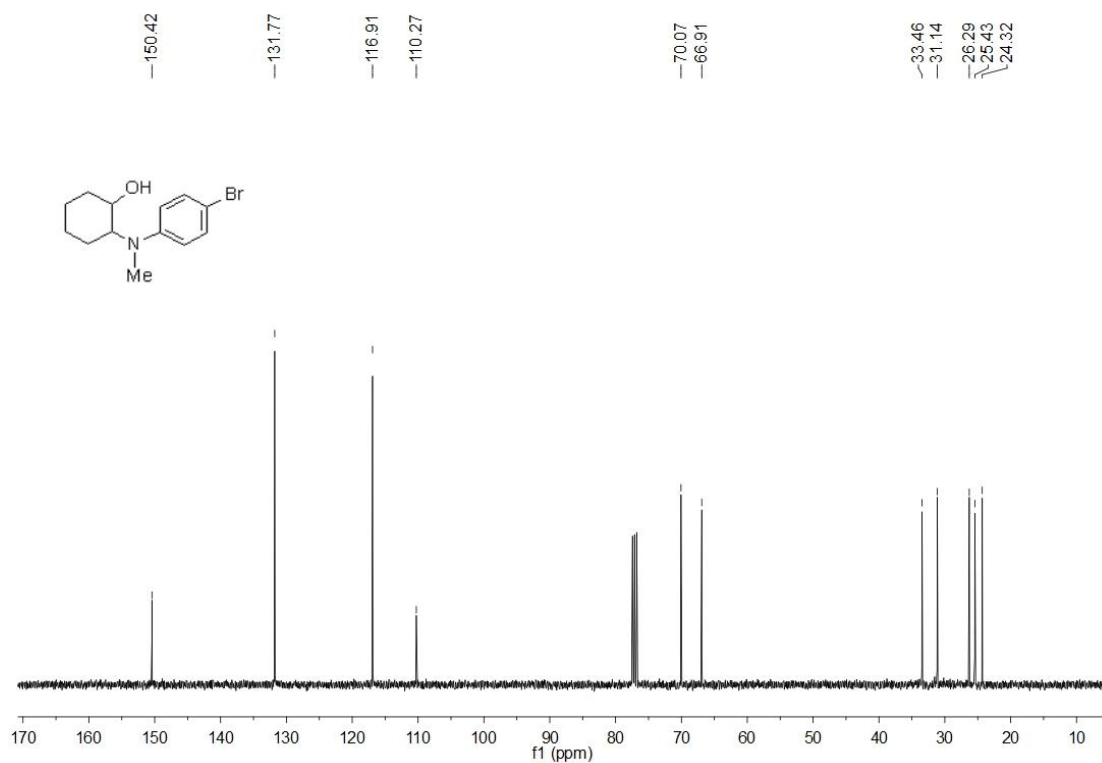


Fig. S96. ¹³C NMR spectrum of 4bj (100 MHz, CDCl₃, 20 °C)

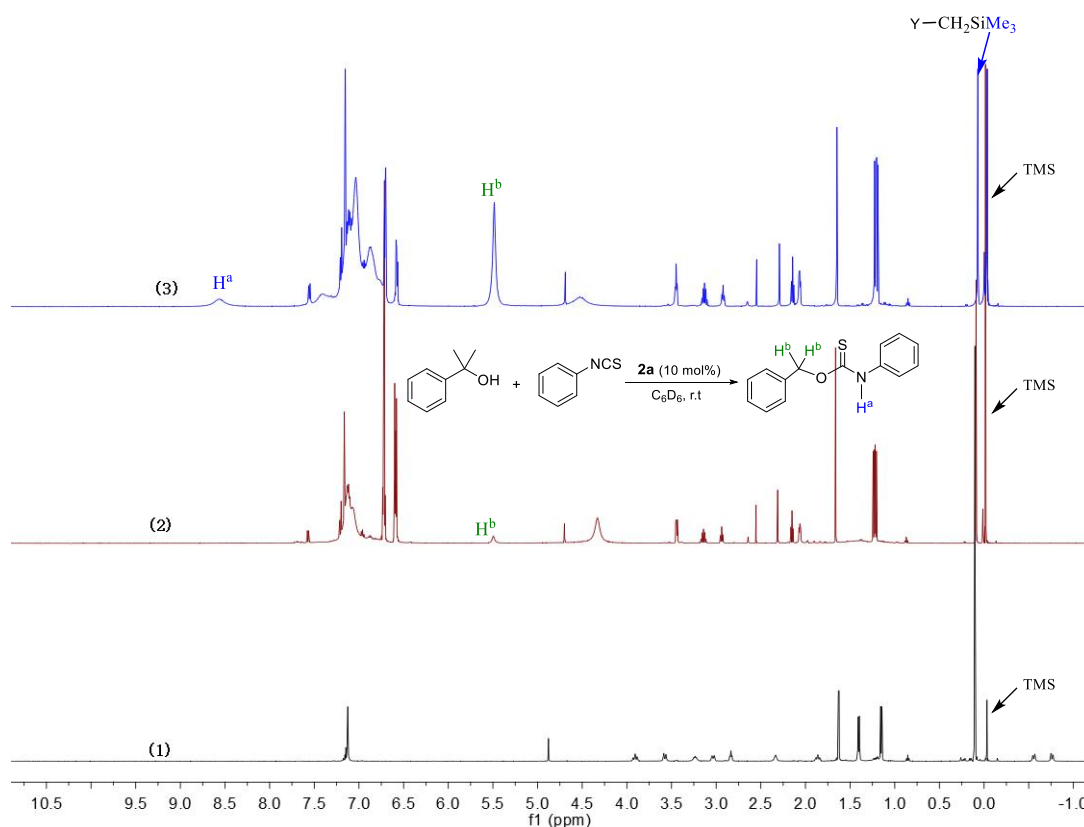


Fig. S97 ^1H NMR (500 MHz, C_6D_6) monitoring the reaction of benzyl alcohol (0.1 mmol) and phenyl isothiocyanate (0.1 mmol) in the presence of 10 mol% of **2a** at room temperature. (1) **2a** in C_6D_6 . (2) The catalytic reaction runs 3 h. (3) The catalytic reaction runs 12 h.

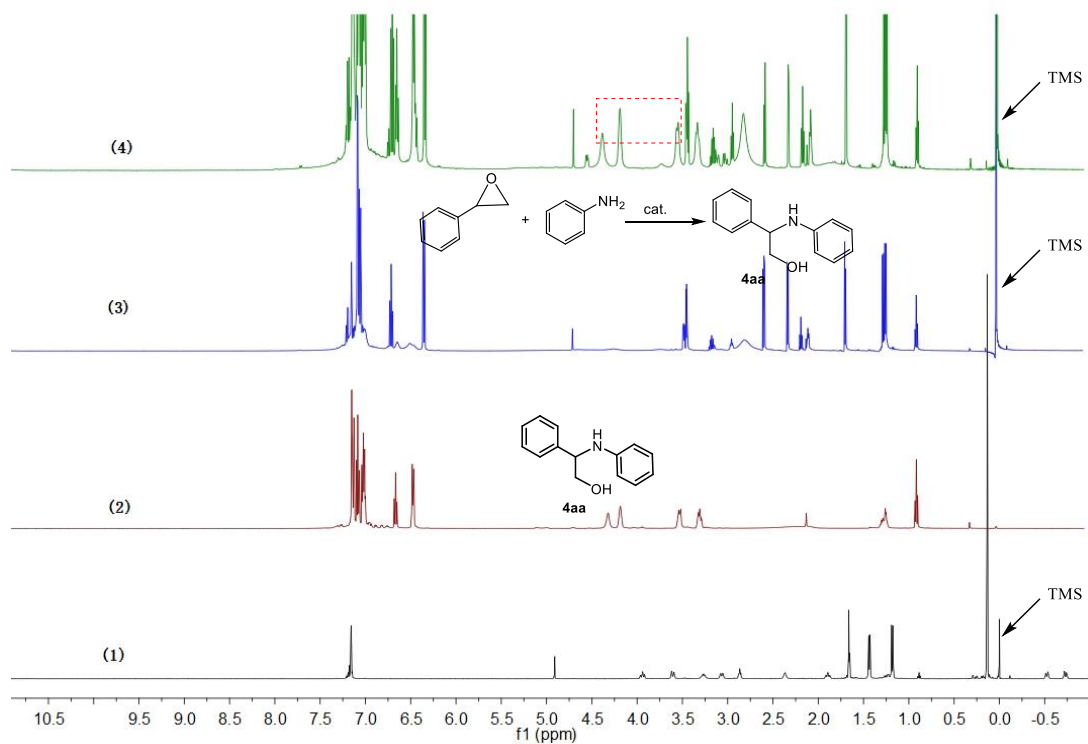


Fig. S98 ^1H NMR (500 MHz, C_6D_6) monitoring the catalytic reaction of styrene oxide (0.2 mmol) and aniline (0.1 mmol) in the presence of 10 mol% of **2a** at room temperature. (1) **2a** in C_6D_6 . (2) **4aa** in C_6D_6 . (3) The catalytic reaction runs 20 min. (4) The catalytic reaction runs 7 h.

Note after first publication

This electronic supplementary information replaces the version published on 28th July 2022, which contained errors in the crystallographic data for compound 5a.

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- (2) D. Li, J. Wang, S. Yu, S. Ye, W. Zou, H. Zhang and J. Chen, *Chem. Commun.*, 2020, **56**, 2256–2259.
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