Electronic Supporting Information for

Binuclear aluminium complex as a single competent catalyst for efficient synthesis of urea, biuret, isourea, isothiourea, phosphorylguanidine, and quinazolinones

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Table of contents

X-ray crystallographic studies of complexes 1a-H, 2a, 3a, and **4o.**

Single crystals of complexes **1a-H**, **2a**, and **3a** were grown from a concentrated toluene solution in an argon-filled atmosphere at -35 °C, and the single crystals of guanidine product **4o** were grown from the dichloromethane at ambient temperature *via* slow evaporation crystallisation technique. A crystal of suitable dimensions of compounds **1a-H**, **2a**, **3a**, and **4o** was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil. The crystals **1a-H**, **2a**, and **3a** were measured at 293 K, whereas crystals **4o** were measured at 273 K. The measurements were made on a Rigaku Supernova X-Calibur Eos CCD detector with graphite monochromatic Cu-κα (1.54184 Å) radiation for the crystals (**1a-H**, and **2a**), and Mo-Kα (0.71073 Å) radiation for the crystals **3a**, **4o**). Crystal data and structure refinement parameters of complexes **1a-H**, **2a**, **3a**, and **4o** summarised in Table TS1. The structures were solved by direct methods (SIR2004)[1,2] and refined on F^2 by full-matrix least-squares methods, using SHELXL-2016/6.[3] Non-hydrogen atoms are anisotropically refined. H-atoms are included in the refinement of calculated positions riding on their carrier atoms. The ORTEP-3 program was used to draw the molecules of **1a-H**, **2a**, **3a**, and **4o**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2151760 (**1a-H**), 2151762 (**2a**), 2209321 (**3a**), and 2209322 (**4o**). The molecular structure of **8f** in the solid state is shown in Figure FS179 and is already known.[12] Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table TS1: Crystallographic and refinement parameters for the compounds **1a-H, 2a, 3a,** and **4o.**

Crystal Parameters	**1a-H**	**2a**	**3a**	**4o**
Identification code	8952	9399	9646	TKP-KB-24
CCDC No.	2151760	2151762	2209321	2209322
Empirical formula	$C_{18}H_{23}N_2OPSe$	$C_{20}H_{28}AlN_2OPSe$	$C_{23}H_{37}Al_2N_2OPSe$	$C_{22}H_{22}N_2O$
Formula weight	393.31	449.35	521.44	330.41
T (K)	293(2) K	293(2) K	293(2) K	273(2) K
λ (Å)	1.54184 A	1.54184 A	0.71073	0.71073 A
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\ 2_1/c$	$P\ 2_1/n$	$P\ 2_1/c$	$P\ na2_1$
a(Å)	6.8367(3)	7.6068(2)	14.1432(5)	10.2479(15)
b (Å)	28.7426(13)	19.9624(7)	7.1641(2)	15.516(2)
c(Å)	9.8648(6)	14.6284(5)	27.1954(16)	11.7406(16)
α (°)	90	90	90	90
β (°)	109.255(5)	91.245(3)	94.638(4)	90
γ (°)	90	90	90	90
V(Å^3)	1830.04(17)	2220.80(12)	2746.5(2)	1866.8(5)
Z	4	4	4	4
D_{calc} g cm^{-3}	1.428	1.344	1.261	1.176
μ (mm^{-1})	3.642	3.434	1.506	0.073
F(000)	808	928	1088	704
Theta range for data collection	3.075 to 70.109	3.747 to 69.904	2.890 to 29.178	2.175 to 27.092
Limiting indices	-8<=h<=5, -25<=k<=34, -11<=l<=11	-9<=h<=8, -23<=k<=24, -16<=l<=17	-19<=h<=12, -9<=k<=8, -27<=l<=36	-13<=h<=13, -19<=k<=19, -15<=l<=14
Reflections collected / unique	3911 / 2720 [R(int) = 0.0176]	11354 / 4169 [R(int) = 0.0344]	6274 / 4036 [R(int) = 0.0414]	26554 / 4059 [R(int) = 0.0569]
Completeness to theta	80.3 %	99.9 %	99.9%	100.0 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2720 / 0 / 208	4169 / 0 / 237	6274 / 0 / 276	4059 / 1 / 228
Goodness-of-fit on F^2	1.198	1.008	1.028	1.025

Final R indices [I>2sigma(I)]	R_1 = 0.0474, wR_2 = 0.1177	R_1 = 0.0373, wR_2 = 0.0930	R_1 = 0.0484, wR_2 = 0.0925	R_1 = 0.0459, wR_2 = 0.0982
R indices (all data)	R_1 = 0.0564, wR_2 = 0.1227	R_1 = 0.0530, wR_2 = 0.1000	R_1 = 0.0919, wR_2 = 0.1094	R_1 = 0.0905, wR_2 = 0.1147
Largest diff. peak and hole	0.487 and -0.367 e.Å^{-3}	0.442 and -0.278 e.Å^{-3}	0.60 and -0.54 e.Å^{-3}	0.180 and -0.189 e.Å^{-3}

NMR Spectra for the ligands (1a-H & 1b-H) and aluminum metal complexes (2a, 2b, 3a, and 3b).

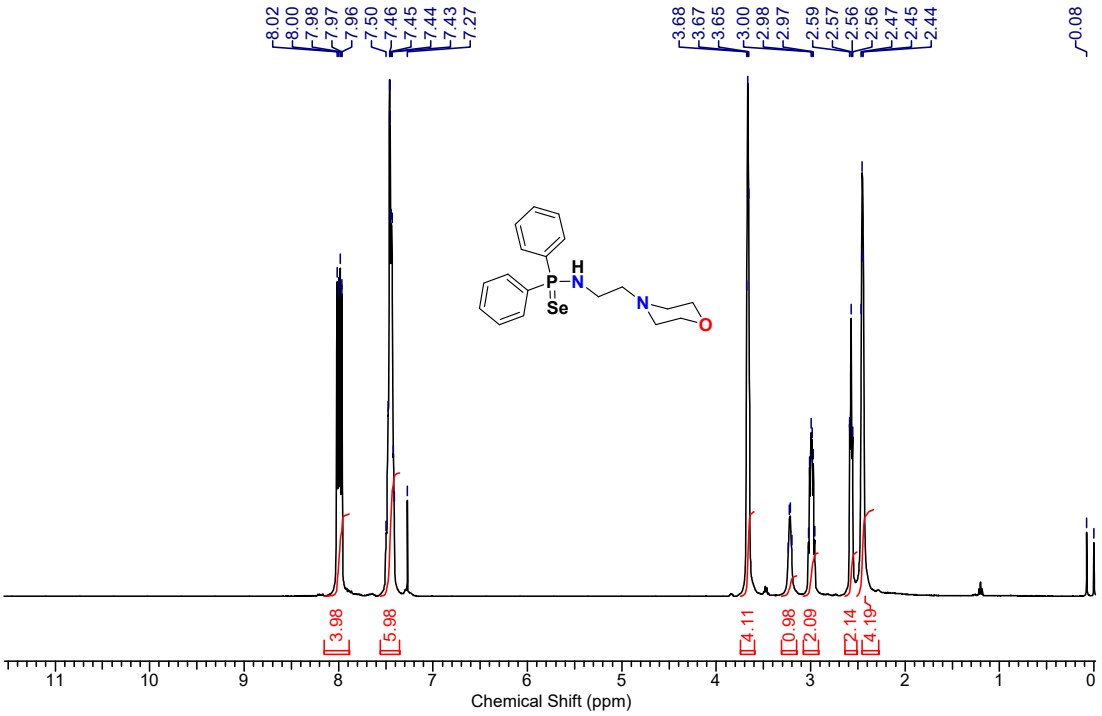


Figure FS1. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **1a-H.**

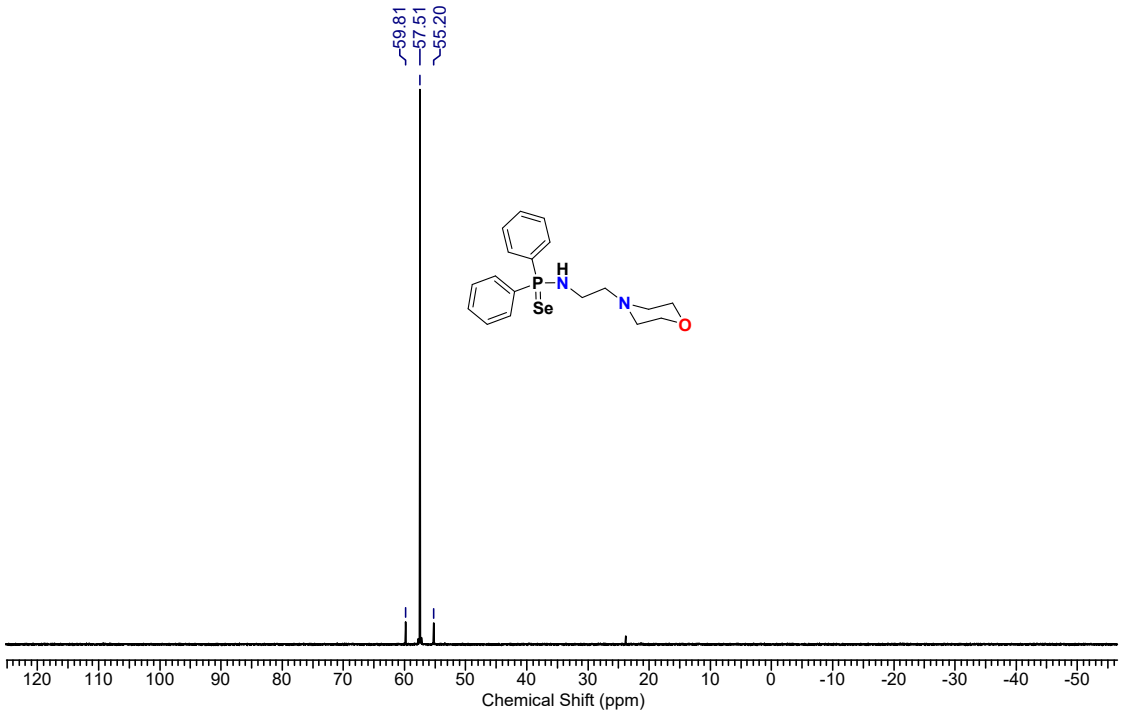
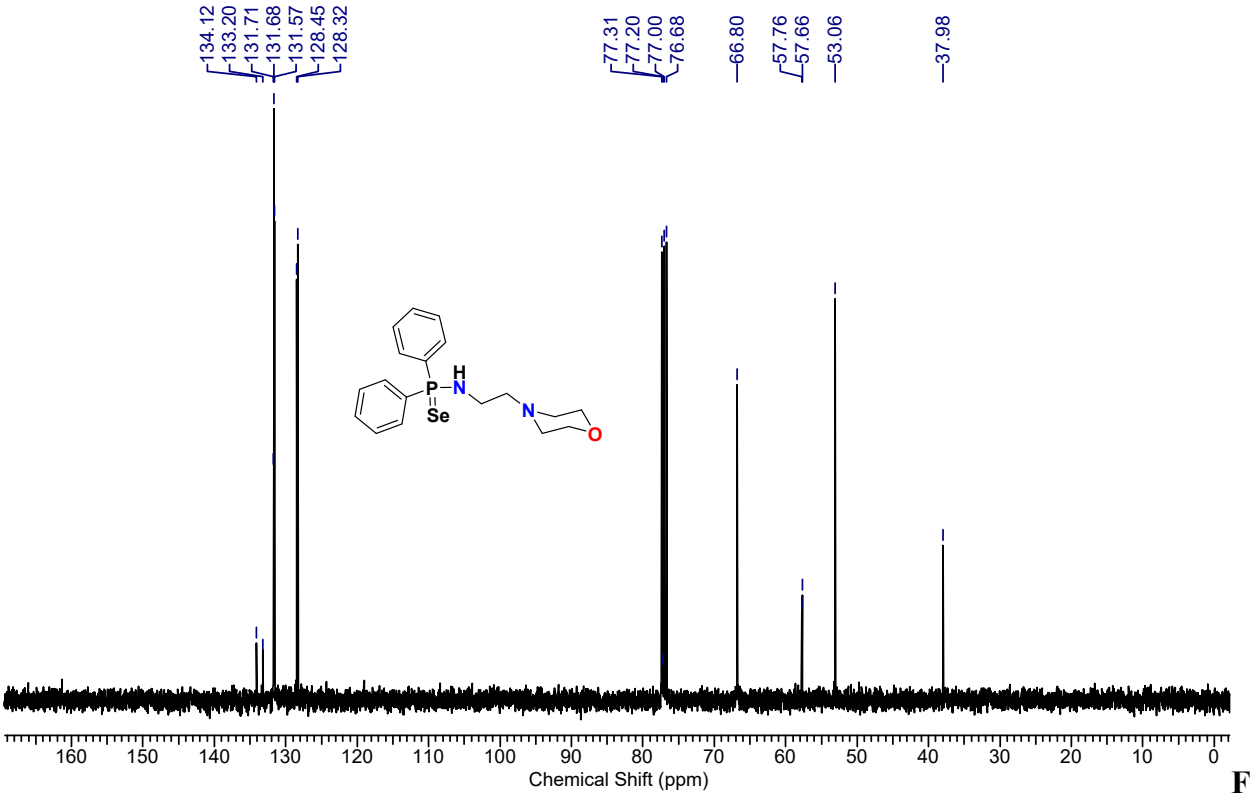
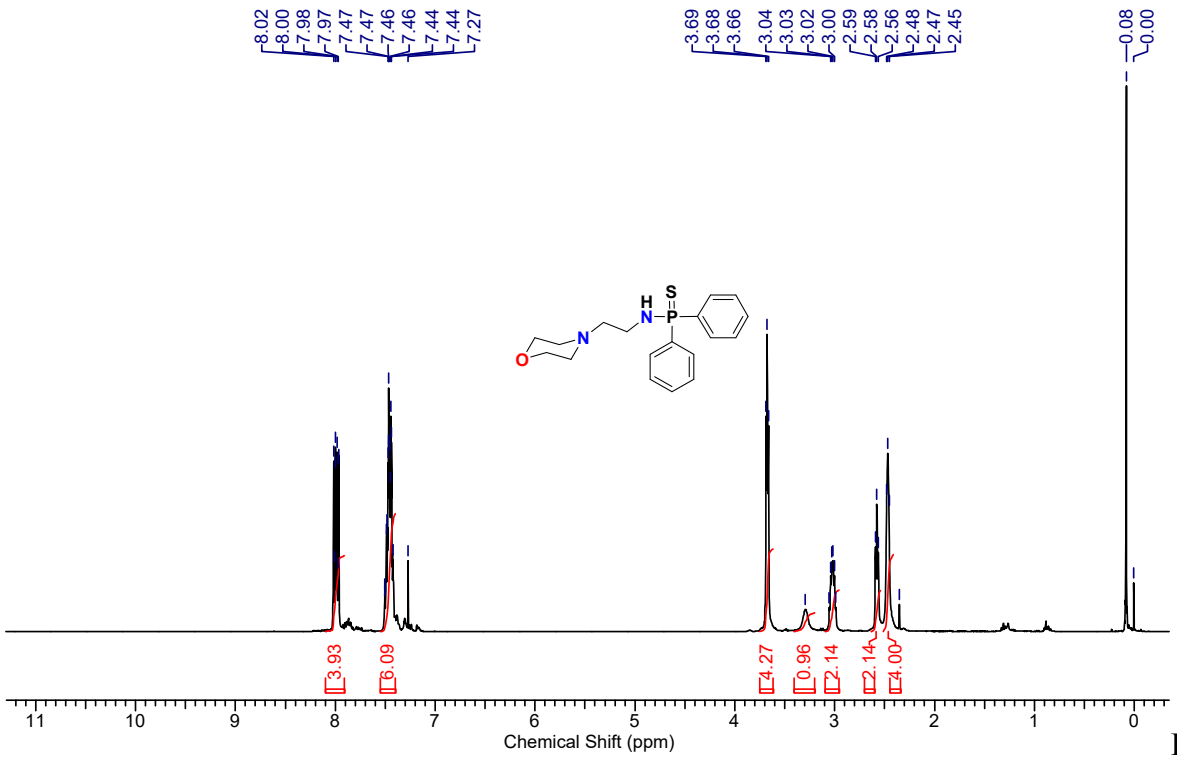


Figure FS2. $^{31}P\{^{1}H\}$- NMR ($CDCl_3$, 161.9 MHz, 25 ˚C) of **1a-H.**

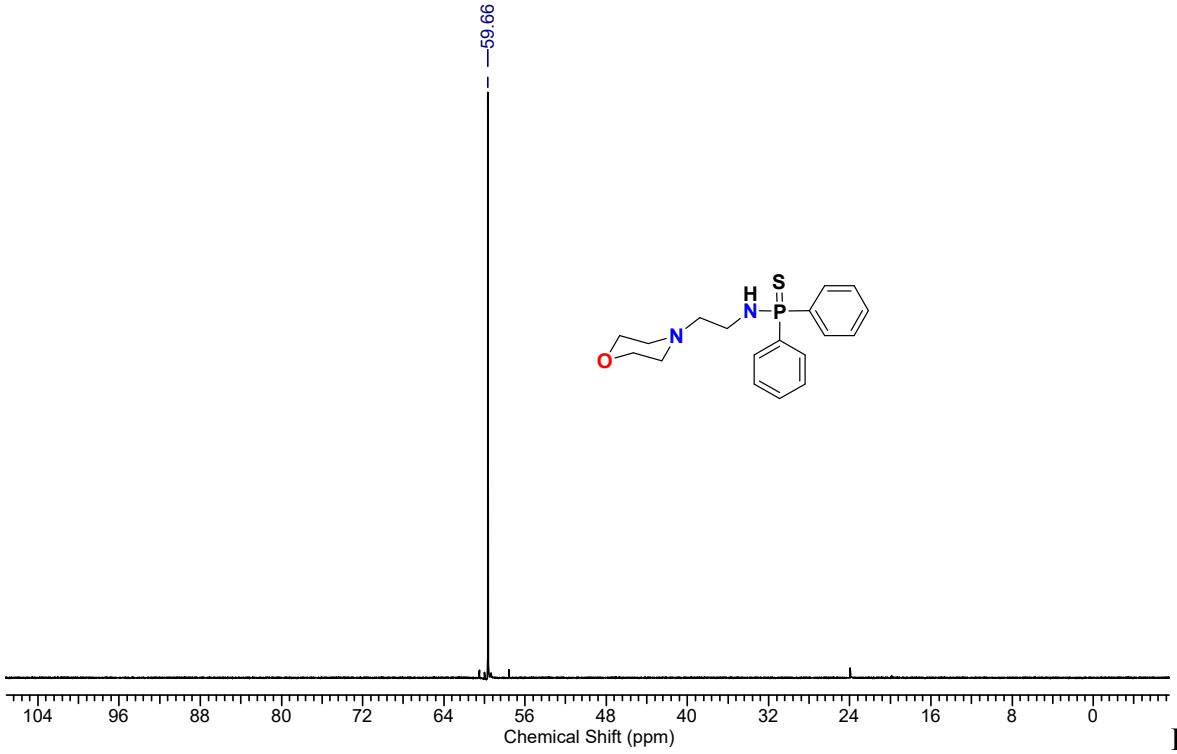


F igure FS3. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **1a-H.**



Figur

e FS4. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **1b-H.**



Figur

e FS5. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.9 MHz, 25 ˚C) of **1b-H.**

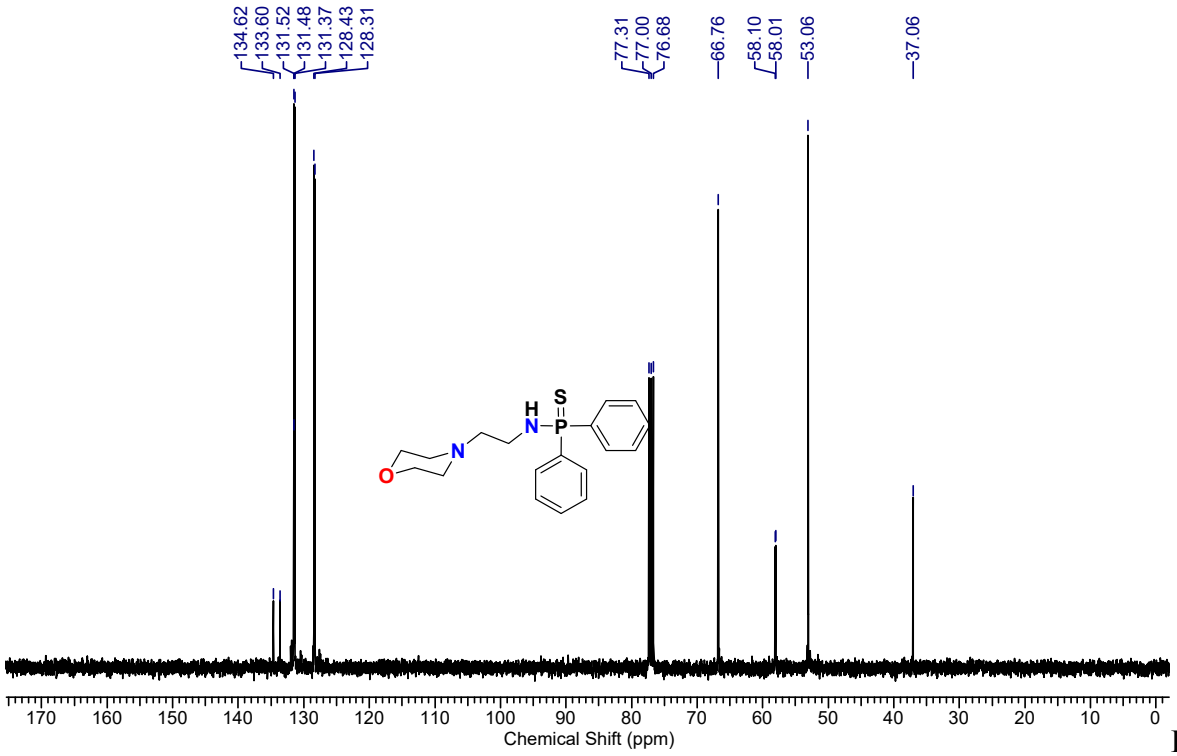


Figure FS6. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **1b-H.**

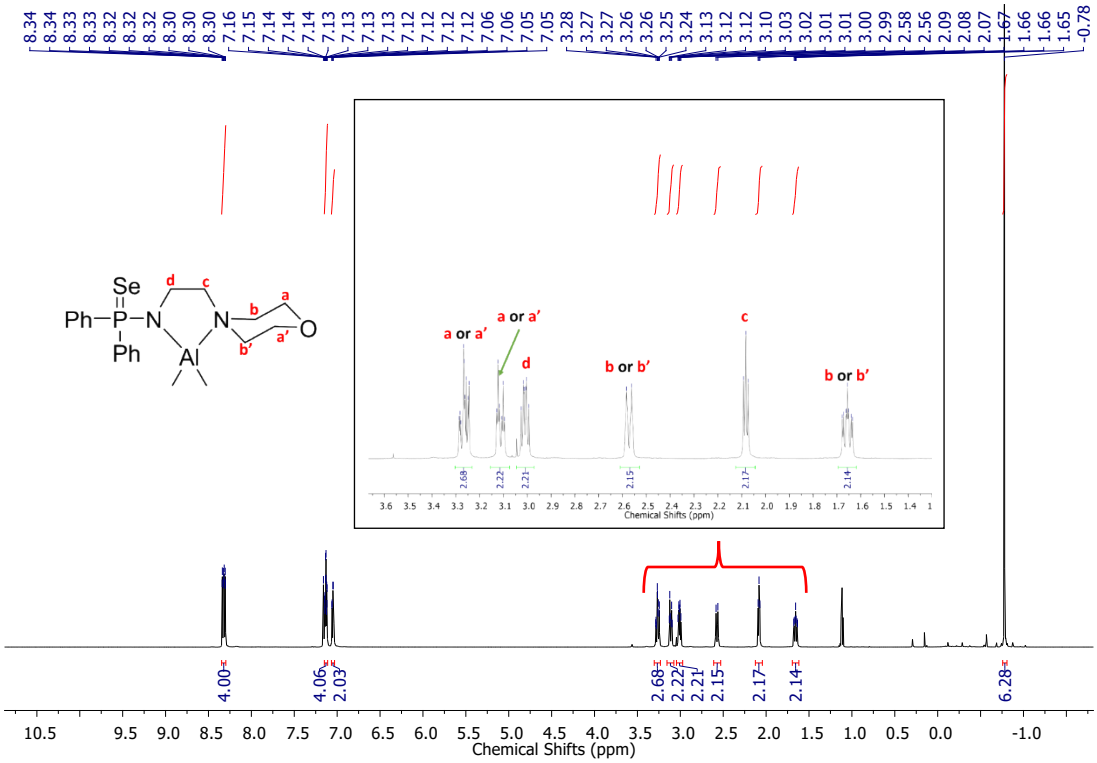


Figure FS7. ^{1}H NMR (C_6D_6, 600 MHz, 25 ˚C) of **2a.**

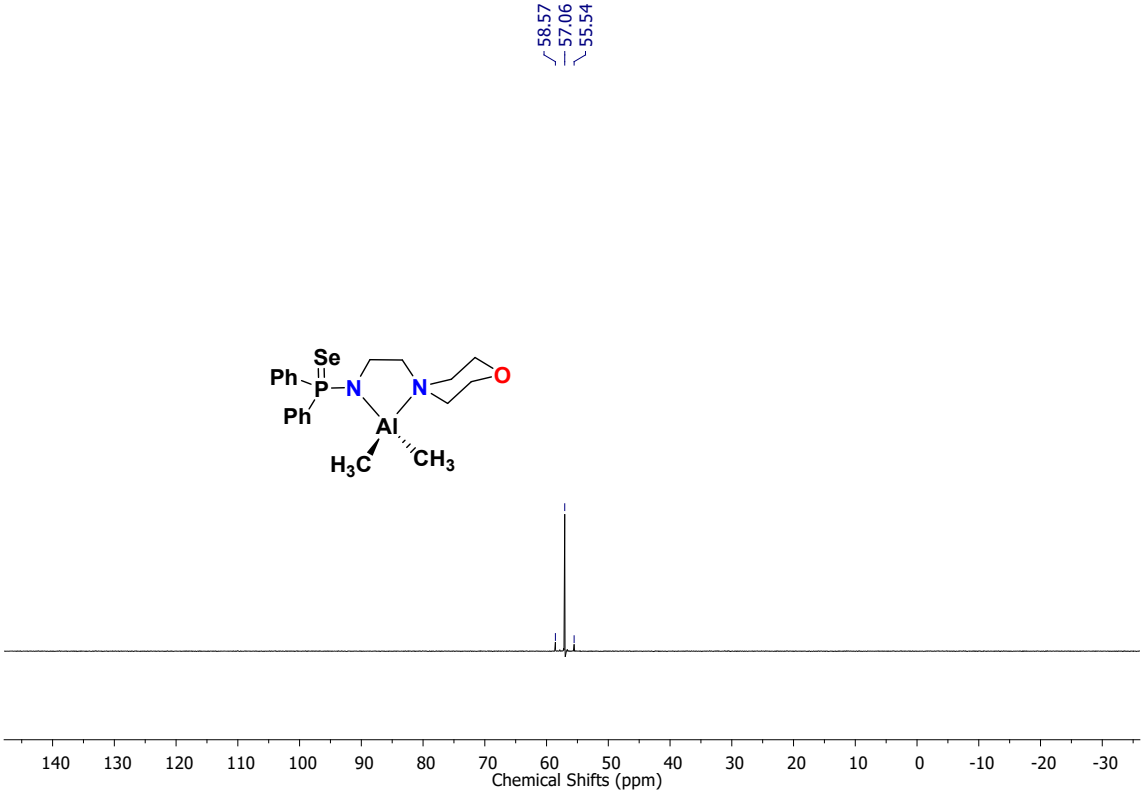


Figure FS8. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz, 25 ˚C) of **2a.**

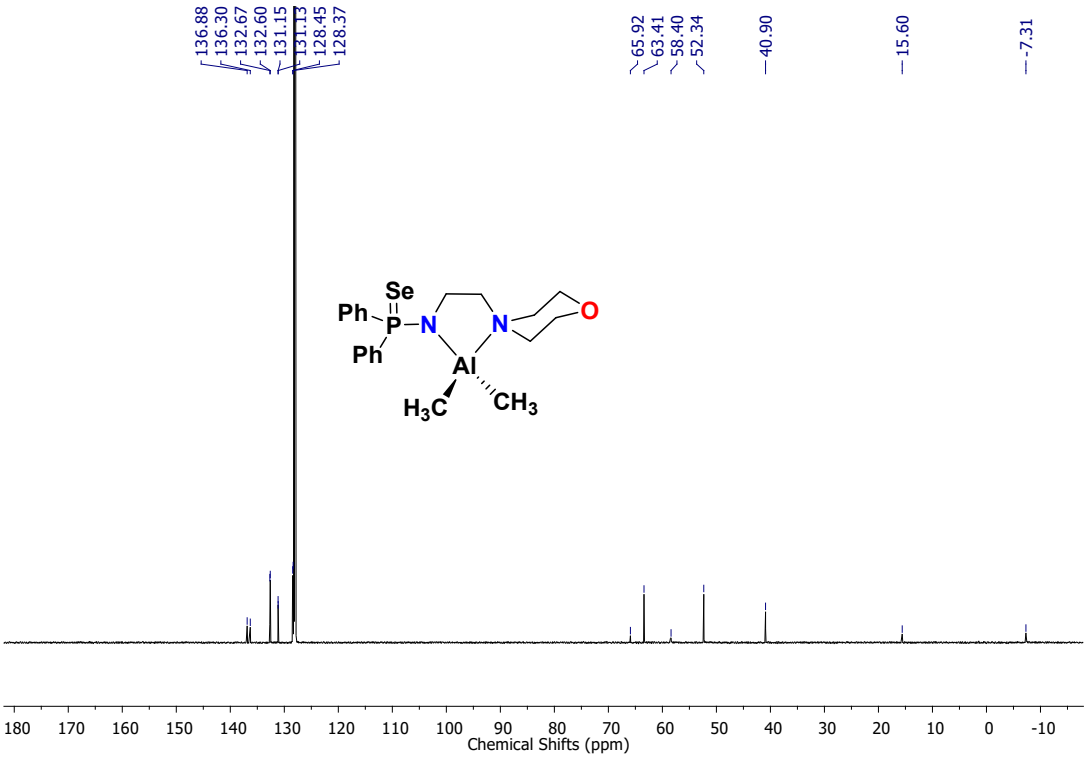


Figure FS9. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100 MHz, 25 ˚C) of **2a.**

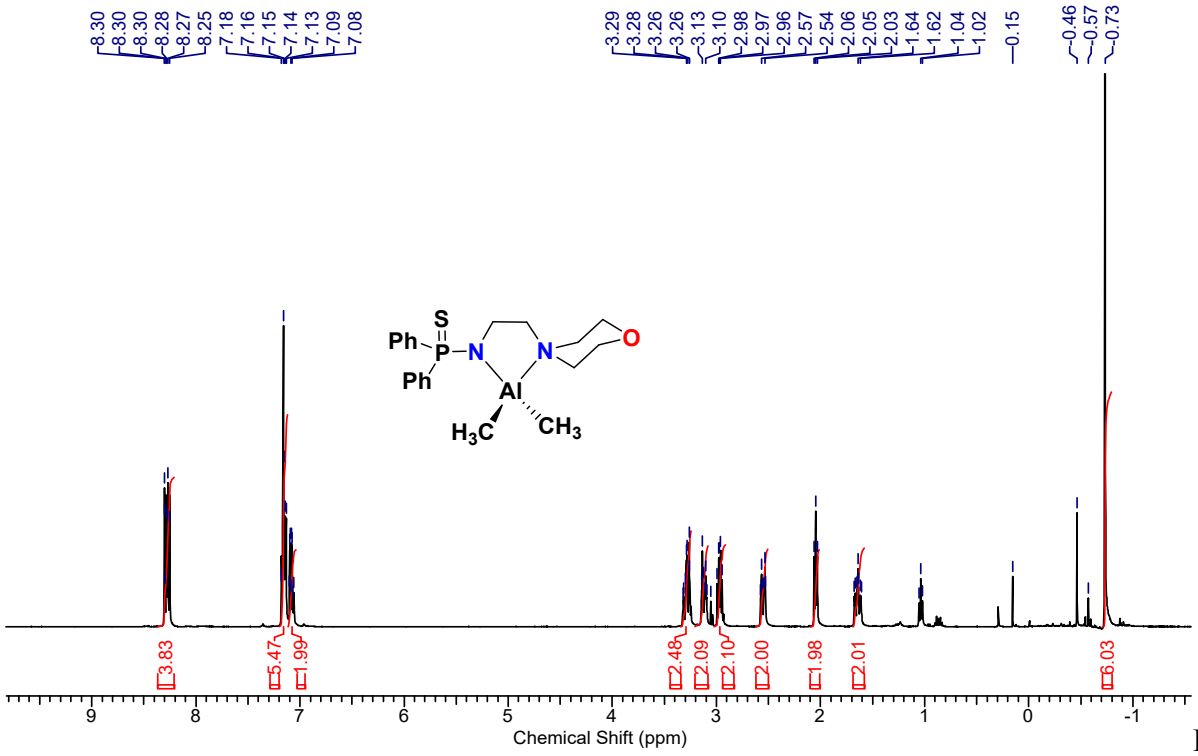


Figure FS10. ^{1}H NMR (C_6D_6, 400 MHz, 25 ˚C) of **2b.**

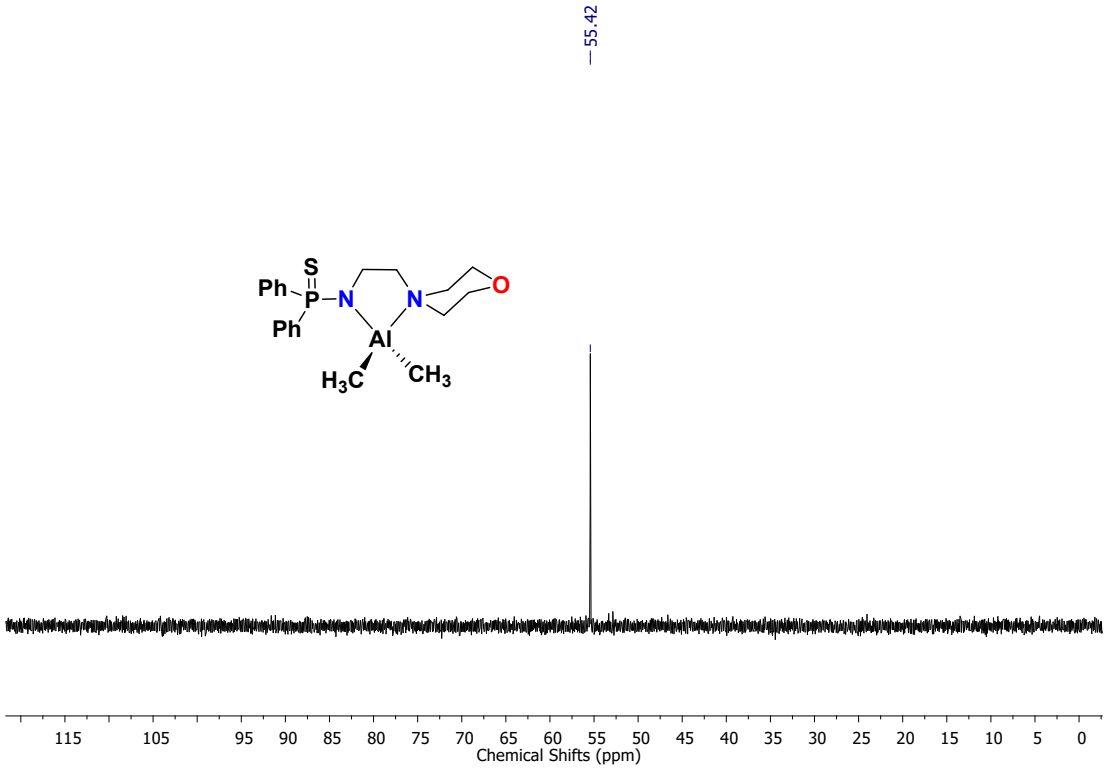


Figure FS11. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz, 25 ˚C) of **2b.**

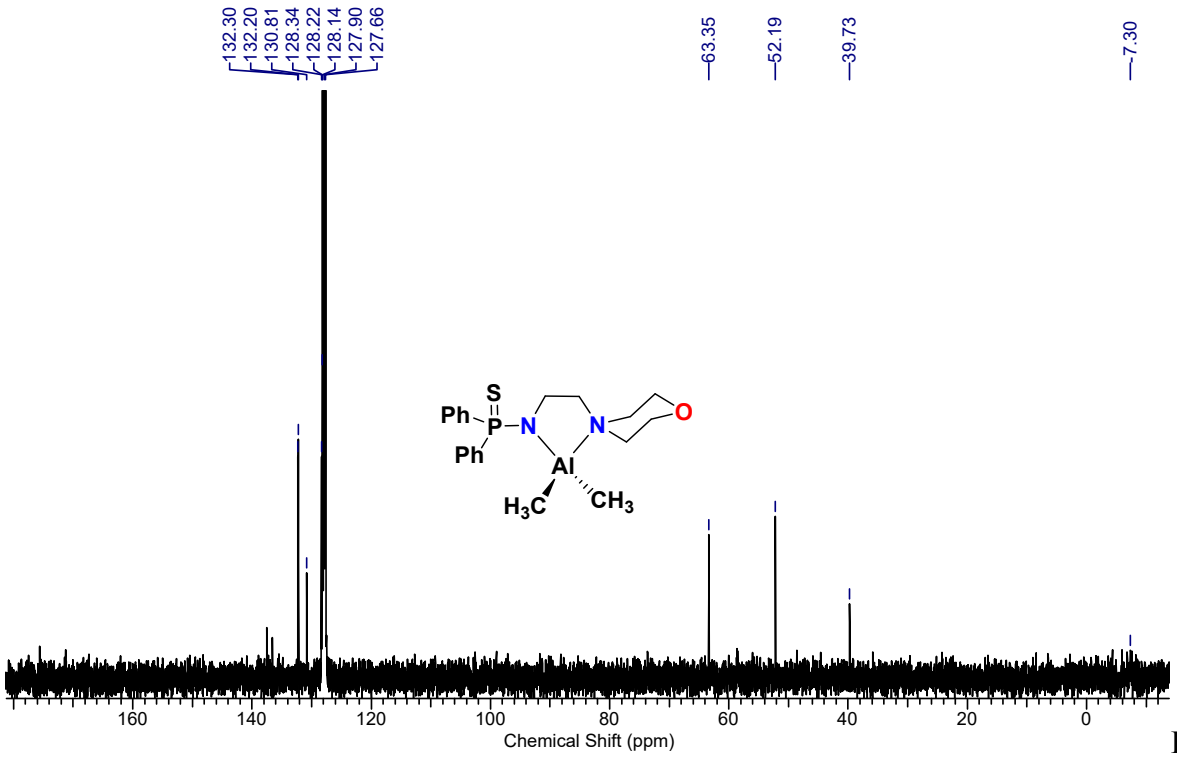


Figure FS12. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100 MHz, 25 ˚C) of **2b.**

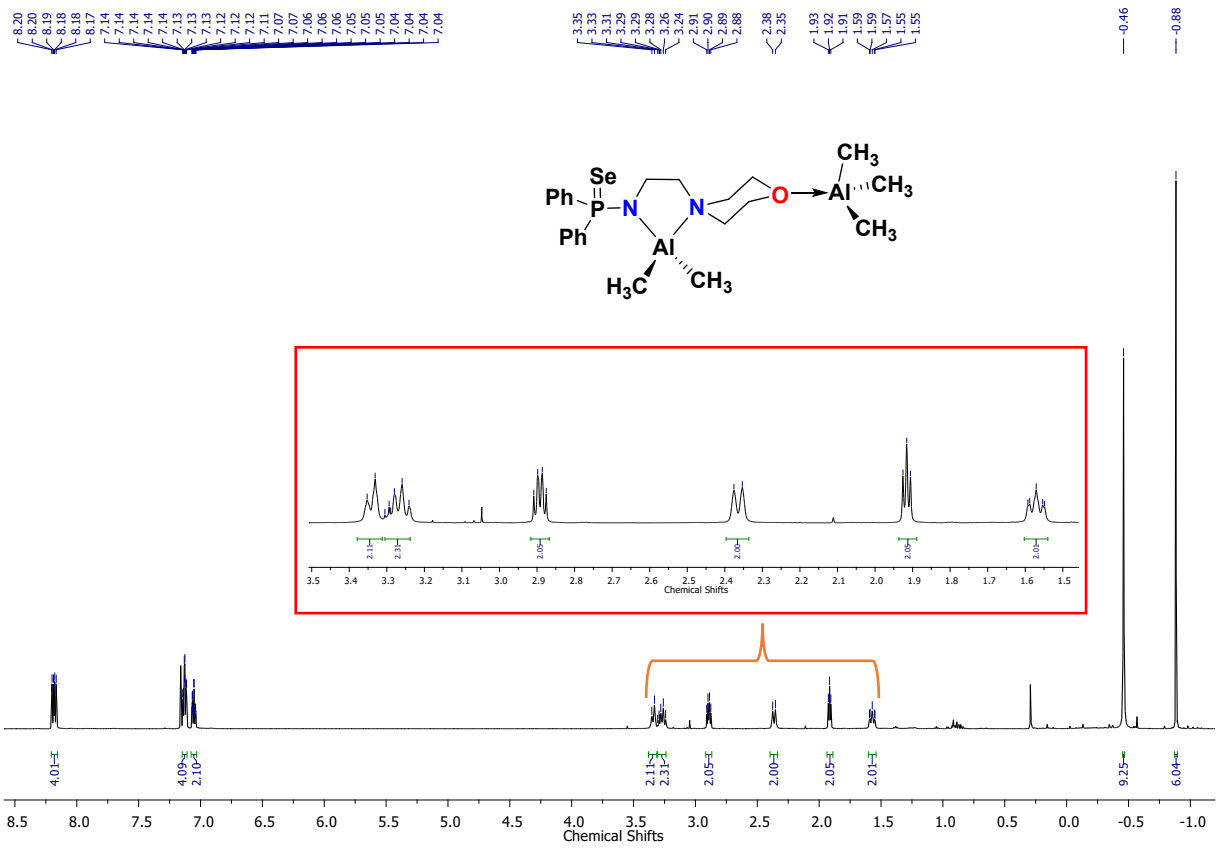


Figure FS13. ^{1}H NMR (C_6D_6, 400 MHz, 25 ˚C) of **3a.**

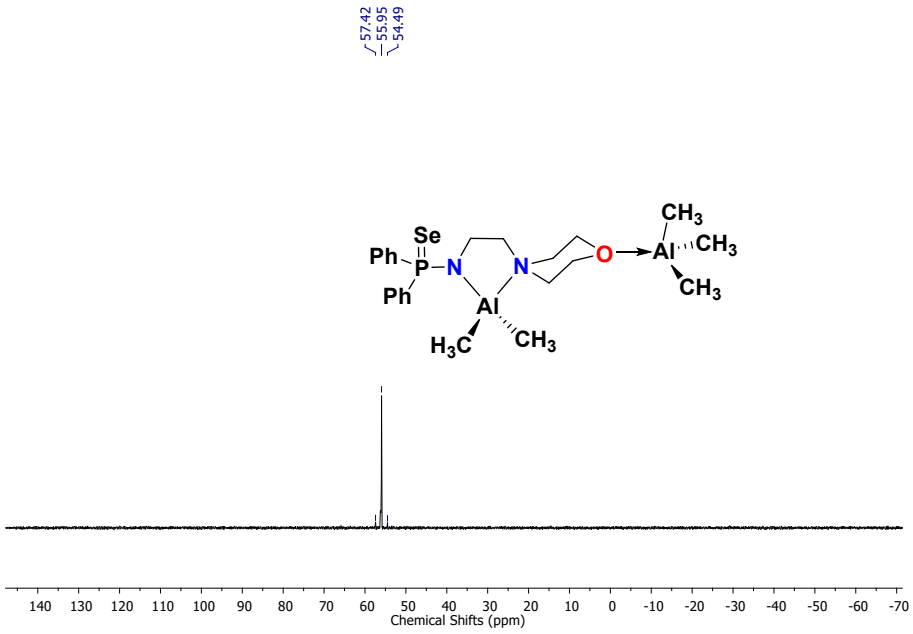


Figure FS14. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 243 MHz, 25 ˚C,) of **3a.**

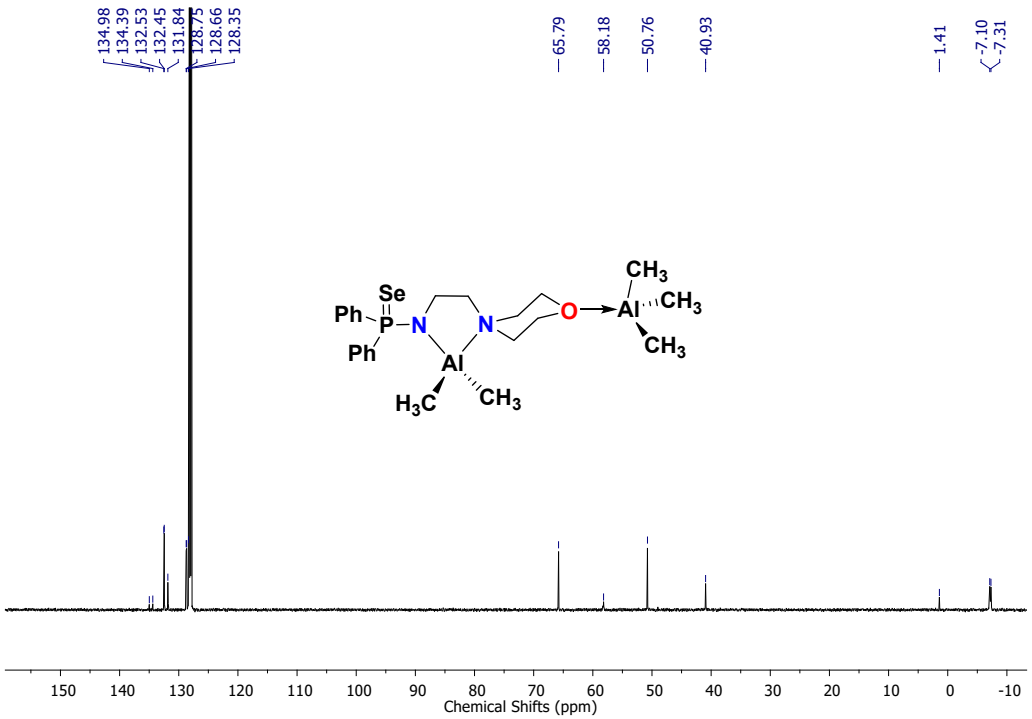


Figure FS15. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100 MHz, 25 ˚C) of **3a.**

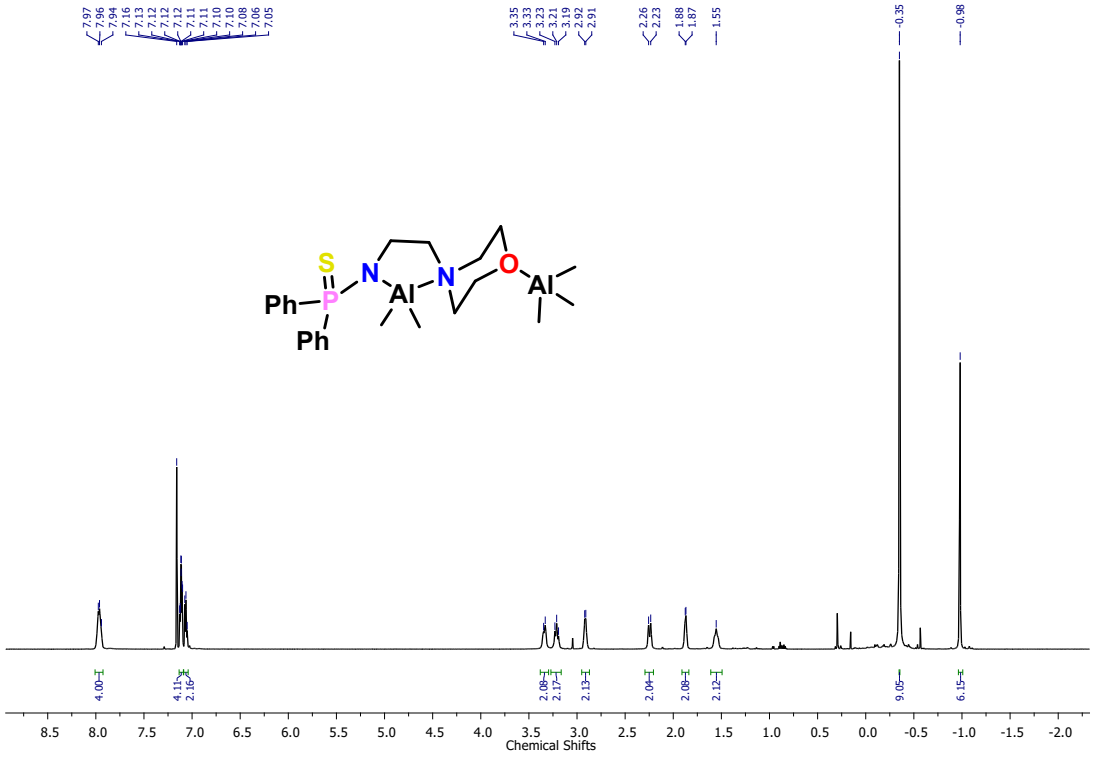


Figure FS16: ^{1}H NMR (C_6D_6, 600 MHz, 25^{o} C,) spectrum of **3b**

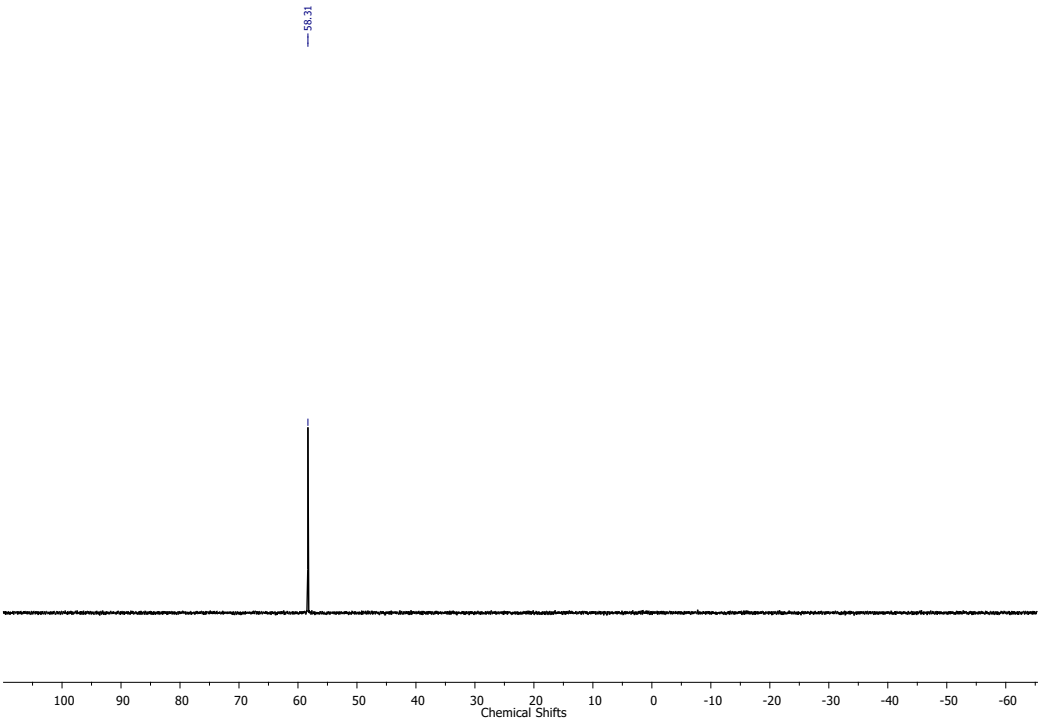


Figure FS17: $^{31}P\{^{1}H\}$ NMR (C_6D_6, 243 MHz, 25° C) spectrum of **3b.**

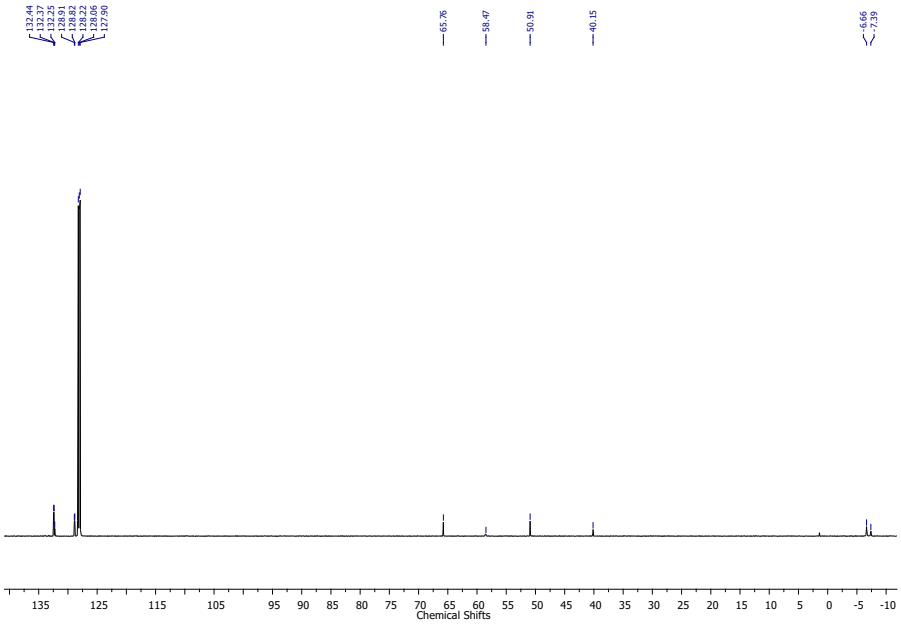
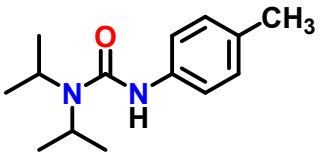


Figure FS18: $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100 MHz, 25° C,) spectrum of **3b**

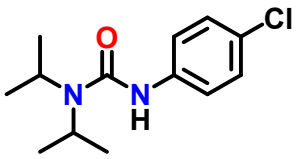
Experimental Section:

NMR data for mono urea derivatives.



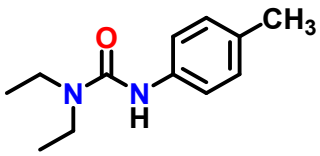
(4a)

Isolated yield: (89 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.88 (s, 1H), 7.32 (d, 2H, J = 8.3 Hz), 7.00 (d, 2H, J = 8.4 Hz), 3.99 – 3.61 (m, 2H), 2.22 (s, 3H), 1.23 (d, 12H, J = 6.7 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 153.9 (C=O), 138.3 (C_{Ar}), 129.9 (C_{Ar}), 128.5 (C_{Ar}), 120.1 (C_{Ar}), 45.4 (C_{ipr}), 21.2 (C_{ipr}), 20.3 (CH$_3$) ppm.[4]



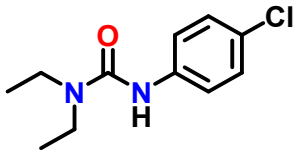
(4b)

Isolated yield: (97 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.32 – 7.29 (m, 2H), 7.23 – 7.20 (m, 2H), 6.22 (s, 1H), 3.94 (dq, 2H, J = 13.7 Hz, 6.9 Hz), 1.31 (d, 12H, J = 6.9 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 154.4 (C=O), 137.9 (C_{Ar}), 128.7 (C_{Ar}), 127.4 (C_{Ar}), 120.9 (C_{Ar}), 45.6 (C_{ipr}), 21.5 (C_{ipr}) ppm. [4]



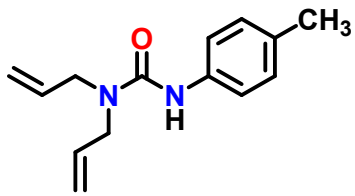
(4c)

Isolated yield: (77 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.29 – 7.24 (m, 2H), 7.07 (d, 2H, J = 8.1 Hz), 6.24 (s, 1H), 3.36 (q, 4H, J = 7.2 Hz), 2.28 (s, 3H), 1.21 (t, 6H, J = 7.2 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δc 154.9 (C=O), 136.7 (C_{Ar}), 132.4 (C_{Ar}), 129.4 (C_{Ar}), 120.1 (C_{Ar}), 41.6 (CH_2), 20.8 (CH_3), 14.1 (CH_3) ppm. [4]



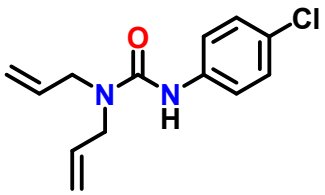
(4d)

Isolated yield: (86 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.36 – 7.31 (m, 2H), 7.25 – 7.20 (m, 2H), 6.29 (s, 1H), 3.36 (q, 4H, J = 7.2 Hz), 1.21 (t, 6H, J = 7.2 Hz) ppm.^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 154.4 (C=O), 137.9 (C_{Ar}), 128.7 (C_{Ar}), 127.7 (C_{Ar}), 121.0 (C_{Ar}), 41.6 (CH_2), 13.9 (CH_3) ppm. [4]



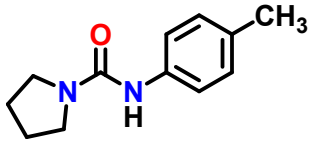
(4e)

Isolated yield: (86 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.21 (d, 2H, J = 8.3 Hz), 7.07 (d, 2H, J = 8.2 Hz), 6.41 (s, 1H), 5.89 (ddd, 2H, J = 22.6 Hz, 10.6 Hz, 5.5 Hz), 5.29 (dd, 4H, J = 19.5 Hz, 5.0 Hz), 3.96 (d, 4H, J = 5.4 Hz), 2.28 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 155.8 (C=O), 136.6 (C_{Ar}), 134.2 (C_{Ar}), 132.6 (CH_{allyl}), 129.5 (C_{Ar}), 119.9 ($CH_{2\text{-allyl}}$), 117.4 (C_{Ar} –H), 49.9 ($CH_{2\text{-allyl}}$), 20.8 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{19}N_2O^+$ 230.1419. Found: 231.1496. [5]



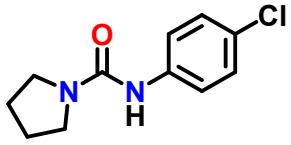
(4f)

Isolated yield: (95 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.23 – 7.18 (m, 2H), 7.17 – 7.12 (m, 2H), 6.43 (s, 1H), 5.88 – 5.74 (m, 2H), 5.27 – 5.17 (m, 4H), 3.89 (dt, 4H, J = 5.4 Hz, 1.4 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 155.5 (C=O), 137.8 (C_{Ar}), 134.0 (CH_{allyl}), 128.9 (C_{Ar}), 127.9 (C_{Ar}), 120.8 ($CH_{2\text{-}allyl}$), 117.6 (C_{Ar}), 49.7 ($CH_{2\text{-}allyl}$) ppm. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{16}ClN_2O^+$ 250.0873. Found: 251.0946. [5]



(4g)

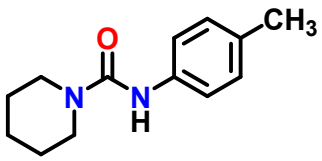
Isolated yield: (77 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.98 (s, 1H), 7.40 – 7.36 (m, 2H), 7.02 (d, 2H, J = 8.2 Hz), 3.39 – 3.30 (m, 4H), 2.22 (s, 3H), 1.88 – 1.79 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 154.0 (C=O), 138.1 (C_{Ar}), 130.2 (C_{Ar}), 128.6 (C_{Ar}), 119.6 (C_{Ar}), 45.6 (C_{py}), 25.0 (C_{py}), 20.3 (CH_3) ppm. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{17}N_2O^+$ 204.1263. Found: 205.1338. [6]



(4h)

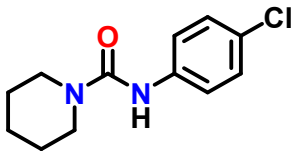
Isolated yield: (85 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.39 – 7.33 (m, 2H), 7.24 – 7.19 (m, 2H), 6.23 (s, 1H), 3.43 (t, 4H, J = 6.7 Hz), 1.98 – 1.92 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100

MHz, 25 °C, $CDCl_3$): δ_C 153.8 (*C*=O), 137.9 (C_{Ar}), 128.8 (C_{Ar}), 127.7 (C_{Ar}), 120.8 (C_{Ar}), 45.9 (C_{py}), 25.7 (C_{py}) ppm. [6]



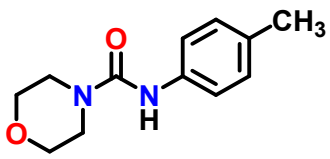
(4i)

Isolated yield: (82 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.24 – 7.20 (m, 2H), 7.07 (d, 2H, *J* = 8.2 Hz), 6.38 (s, 1H), 3.46 – 3.39 (m, 4H), 2.28 (s, 3H), 1.62 – 1.57 (m, 6H) ppm.^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 155.3 (*C*=O), 136.7 (C_{Ar}), 132.4 (C_{Ar}), 129.4 (C_{Ar}), 120.2 (C_{Ar}), 45.3 (C_{pyH}), 25.8 (C_{pyH}), 24.5 (C_{pyH}), 20.8 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{19}N_2O^+$ 218.1419. Found: 219.1495. [7]



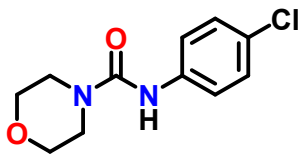
(4j)

Isolated yield: (91 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.30 (d, 2H, *J* = 8.9 Hz), 7.22 (d, 2H, *J* = 8.9 Hz), 6.40 (s, 1H), 3.48 – 3.39 (m, 4H), 1.61 (dd, 6H, *J* = 9.5 Hz, 3.7 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 154.8 (*C*=O), 138.0 (C_{Ar}), 128.9 (C_{Ar}), 127.8 (C_{Ar}), 121.1 (C_{Ar}), 45.4 ($CH_{2\text{-}Pi}$), 25.8 ($CH_{2\text{-}Pi}$), 24.5 ($CH_{2\text{-}Pi}$) ppm. [7]



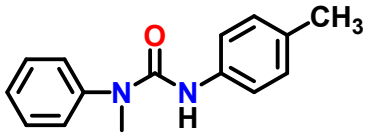
(4k)

Isolated yield: (83 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.25 – 7.19 (m, 2H), 7.09 (d, 2H, J = 8.2 Hz), 6.44 (s, 1H), 3.70 (dd, 4H, J = 6.2 Hz, 3.6 Hz), 3.44 (dd, 4H, J = 6.4 Hz, 3.5 Hz), 2.30 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 155.5 (C=O), 136.2 (C_{Ar}), 133.1 (C_{Ar}), 129.5 (C_{Ar}), 120.6 (C_{Ar}), 66.6 (CH_2), 44.3 (CH_2), 20.8 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{16}N_2O_2K_2^{2+}$ 220.1212. Found: 149.0231. [8]



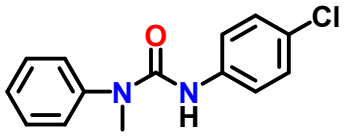
(4l)

Isolated yield: (91 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.32 – 7.28 (m, 6H), 7.26 – 7.22 (m, 7H), 6.38 (s, 3H), 3.78 – 3.70 (m, 12H), 3.50 – 3.44 (m, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 154.8 (C=O), 137.3 (C_{Ar}), 128.9 (C_{Ar}), 128.4 (C_{Ar}), 121.3 (C_{Ar}), 66.5 (CH_2), 44.2 (CH_2) ppm. [8]



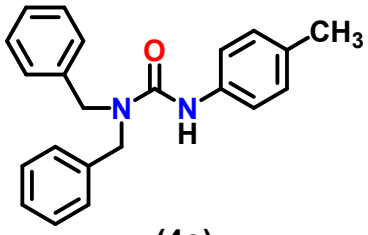
(4m)

Isolated yield: (90 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 8.04 (s, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.29 (m, 4H), 7.24 (d, 1H, J = 7.3 Hz), 7.03 (d, 2H, J = 8.3 Hz), 3.26 (s, 3H), 2.22 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 154.7 (C=O), 144.2 (C_{Ar}), 137.5 (C_{Ar}), 130.8 (C_{Ar}), 129.2 (C_{Ar}), 128.7 (C_{Ar}), 126.2 (C_{Ar}), 125.6 (C_{Ar}), 120.1 (C_{Ar}), 37.5 (CH_3), 20.3 (CH_3) ppm. [9]



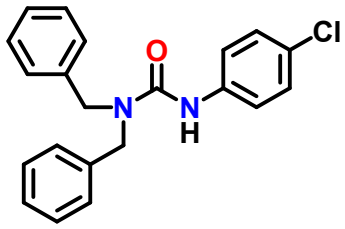
(4n)

Isolated yield: (99 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.49 (dd, 2H, J = 10.5 Hz, 4.8 Hz), 7.38 (dd, 1H, J = 8.3 Hz, 6.6 Hz), 7.32 (d, 2H, J = 7.4 Hz), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 6.25 (s, 1H), 3.32 (s, 3H) ppm.^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 154.2 (C=O), 142.6 (C_{Ar}), 137.5 (C_{Ar}), 130.4 (C_{Ar}), 128.7 (C_{Ar}), 128.1 (C_{Ar}), 127.7 (C_{Ar}), 127.5 (C_{Ar}), 120.4 (C_{Ar}), 37.3 (CH_3) ppm. [9]



(4o)

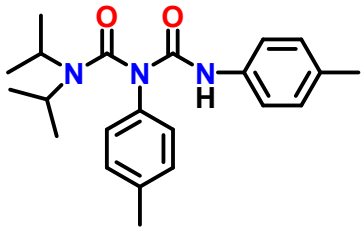
Isolated yield: (124 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.49 – 7.42 (m, 4H), 7.42 – 7.32 (m, 6H), 7.21 – 7.17 (m, 2H), 7.11 (d, 2H, J = 8.3 Hz), 6.41 (d, 1H, J = 4.1 Hz), 4.68 (s, 4H), 2.35 (s, 3H) ppm.^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 156.1 (C=O), 137.3 (C_{Ar}), 136.4 (C_{Ar}), 132.7 (C_{Ar}), 129.3 (C_{Ar}), 129.0 (C_{Ar}), 128.7 (C_{Ar}), 127.7 (C_{Ar}), 127.4 (C_{Ar}), 120.2 (C_{Ar}), 50.7 (CH_2), 20.7 (CH_3) ppm. [4]



(4p)

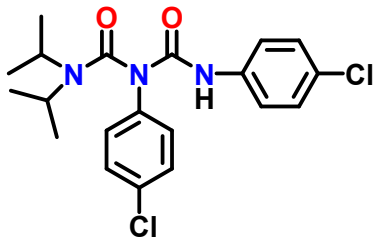
Isolated yield: (133 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.41 – 7.33 (m, 7H), 7.33 – 7.30 (m, 5H), 7.20 – 7.13 (m, 5H), 6.34 (s, 1H), 4.60 (s, 5H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 155.8 (*C*=O), 137.6 (C_{Ar}), 137.1 (C_{Ar}), 129.2 (C_{Ar}), 128.8 (C_{Ar}), 128.1 (C_{Ar}), 127.4 (C_{Ar}), 121.2 (C_{Ar}), 50.9 (CH_2) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{20}ClN_2O^+$ 350.1187. Found: 351.1261. [4]

NMR Data for biuret products (5a-5n).



(5a)

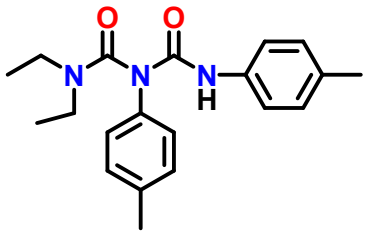
Isolated yield: (133 mg, 80%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.22 (s, 1H), 7.34 – 7.30 (m, 2H), 7.27 (dd, 3H, *J* = 6.7 Hz, 1.7 Hz), 7.20 (d, 2H, *J* = 8.1 Hz), 7.08 (d, 2H, *J* = 8.2 Hz), 3.75 (d, 2H, *J* = 4.3 Hz), 2.35 (s, 3H), 2.29 (s, 3H), 1.13 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 156.3 (*C*=O), 152.7 (*C*=O), 137.1 (C_{Ar}), 136.3 (C_{Ar}), 135.7 (C_{Ar}), 132.9 (C_{Ar}), 129.8 (C_{Ar}), 129.4 (C_{Ar}), 127.2 (C_{Ar}), 119.9 (C_{Ar}), 21.1 (*C*H), 20.8 (*C*H), 20.0 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{30}N_3O_2^+$ 367.2260. Found: 368.2336.



(5b)

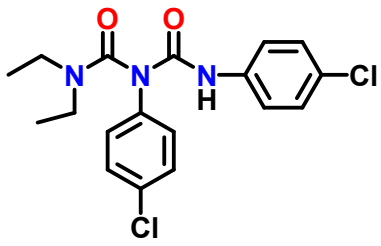
Isolated yield: (134 mg, 85%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.71 (s, 1H), 7.31 (ddd, 4H, *J* = 9.3 Hz, 5.8 Hz, 2.3 Hz), 7.26 – 7.23 (m, 2H), 7.19 – 7.15 (m, 2H), 3.64 (s, 2H), 1.03 (s, 12H)

ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 156.3 (*C*=O), 152.2 (*C*=O), 137.5 (C_{Ar}), 136.7 (C_{Ar}), 132.9 (C_{Ar}), 129.2 (C_{Ar}), 128.9 (C_{Ar}), 128.5 (C_{Ar}), 121.2 (C_{Ar}), 29.7 (*C*H), 19.9 (*C*H_3) ppm. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{23}Cl_2N_3O_2Na^+$ 407.1167. Found: 390.2146.



(5c)

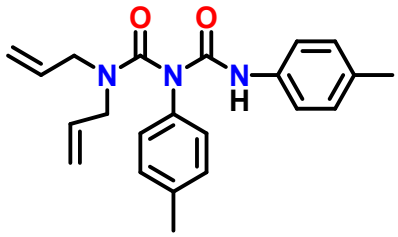
Isolated yield: (113 mg, 87%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.64 (s, 1H), 7.36 – 7.30 (m, 2H) , 7.28 – 7.23 (m, 2H), 7.20 (d, 2H, *J* = 8.2 Hz), 7.08 (d, 2H, *J* = 8.2 Hz), 3.29 (q, 4H, *J* = 7.1 Hz), 2.36 (s, 3H), 2.29 (s, 3H), 0.92 (t, 6H, *J* = 7.1 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 158.3 (*C*=O), 152.7 (*C*=O), 137.4 (C_{Ar}), 136.4 (C_{Ar}), 135.7 (C_{Ar}), 133.1 (C_{Ar}), 129.9 (C_{Ar}), 129.5 (C_{Ar}), 127.6 (C_{Ar}), 120.1 (C_{Ar}), 42.7 (*C*H_2), 21.2 (*C*H_3), 20.9 (*C*H_3), 12.5 (*C*H_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{26}N_3O_2^+$ 339.1947. Found: 340.2021.



(5d)

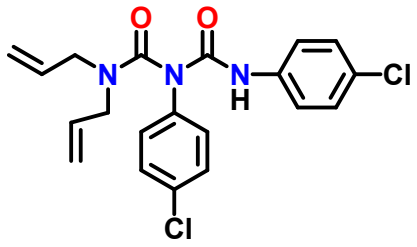
Isolated yield: (131 mg, 90%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 9.11 (s, 1H), 7.35 – 7.30 (m, 4H), 7.26 – 7.22 (m, 2H), 7.20 – 7.16 (m, 2H), 3.18 (t, 4H, *J* = 7.1 Hz), 0.84 (t, 6H, *J* = 7.0 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 158.3 (*C*=O), 152.1 (*C*=O), 137.5 (C_{Ar}), 136.7 (C_{Ar}), 133.1 (C_{Ar}), 129.3 (C_{Ar}), 129.0 (C_{Ar}), 128.9 (C_{Ar}), 128.7 (C_{Ar}), 121.3 (C_{Ar}), 42.8 (*C*H_2),

12.4 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{20}Cl_2N_3O_2^+$ 379.0854. Found: 380.0932.



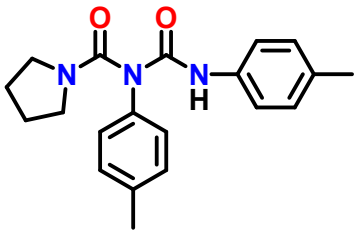
(5e)

Isolated yield: (113 mg, 82%). ^1H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.45 (s, 1H), 7.33 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.20 (m, 2H), 7.08 (d, 2H, J = 8.0 Hz), 5.43 (ddd, 2H, J = 16.3 Hz, 11.5 Hz, 5.9 Hz), 5.16 – 5.07 (m, 4H), 3.86 (d, 4H, J = 5.9 Hz), 2.38 (s, 3H), 2.29 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 158.6 (*C*=O), 152.6 (*C*=O), 137.8 (C_{Ar}), 136.2 (C_{Ar}), 134.2 (C_{Ar}), 133.3 (C_{Ar}), 132.3 (C_{Ar}), 130.1 (C_{Ar}), 129.5 (C_{Ar}), 128.1 (C_{Ar}), 120.8 (C_{Ar}), 120.1 (*C*H), 118.5 (*C*H), 50.1 (CH_2), 21.2 (CH_2), 20.9 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}N_3O_2^+$ 363.1947. Found: 364.2024.



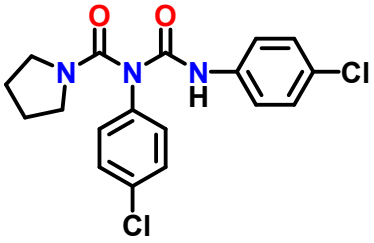
(5f)

Isolated yield: (132 mg, 86%). ^1H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 9.07 (s, 1H), 7.42 – 7.37 (m, 4H), 7.31 (d, 2H, J = 8.8 Hz), 7.27 – 7.24 (m, 2H), 5.37 (ddd, 2H, J = 16.1 Hz, 10.9 Hz, 5.8 Hz), 5.12 (ddd, 4H, J = 18.4 Hz, 13.6 Hz, 1.3 Hz), 3.81 (d, 4H, J = 5.9 Hz) ppm.$^{13}C\{^1H\}$ NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 158.6 (*C*=O), 152.1 (*C*=O), 137.2 (C_{Ar}), 136.6 (C_{Ar}), 133.5 (C_{Ar}), 131.5 (C_{Ar}), 129.5 – 128.8 (C_{Ar}), 121.5 (*C*H), 119.1 (*C*H), 50.2 (CH_2) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{19}Cl_2N_3O_2^+$ 403.0854. Found: 404.0932.



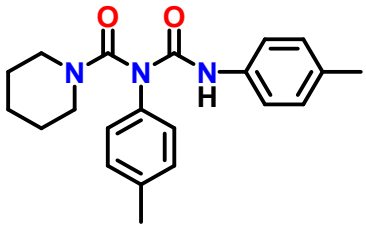
(5g)

Isolated yield: (111 mg, 87%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 9.36 (s, 1H), 7.36 (d, 2H, J = 8.4 Hz), 7.19 (d, 2H, J = 8.1 Hz), 7.11 – 7.02 (m, 4H), 3.20 (s, 4H), 2.31 (s, 3H), 2.24 (s, 3H), 1.74 (t, 4H, J = 6.7 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 157.1 (C=O), 152.1 (C=O), 136.7 (C_{Ar}), 133.1 (C_{Ar}), 129.9 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (C_{Ar}), 128.5 (C_{Ar}), 121.2 (C_{Ar}), 48.4 (CH_2), 25.2 (CH_2), 20.8 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}N_3O_2^+$ 337.1790. Found: 338.1863.



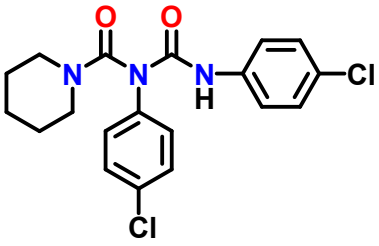
(5h)

Isolated yield: (132 mg, 92%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 10.2 (s, 1H), 7.41 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.23 – 7.16 (m, 4H), 3.03 (s, 4H), 1.70 – 1.69 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 157.1 (C=O), 152.1 (C=O), 136.7 (C_{Ar}), 133.1 (C_{Ar}), 129.9 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (C_{Ar}), 128.5 (C_{Ar}), 121.2 (C_{Ar}), 48.5 (CH_2), 25.2 (CH_2) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}Cl_2N_3O_2^+$ 377.0698. Found: 378.0775.



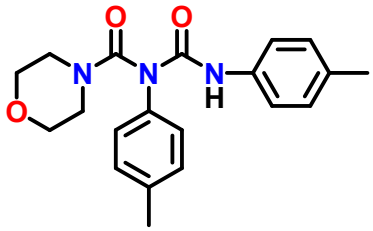
(5i)

Isolated yield: (120 mg, 88%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.53 (s, 1H), 7.32 (d, 2H, J = 8.4 Hz), 7.25 – 7.19 (m, 4H), 7.08 (d, 2H, J = 8.3 Hz), 3.42 – 3.36 (m, 4H), 2.36 (s, 3H), 2.29 (s, 3H), 1.53 – 1.48 (dt, 2H, J = 11.5 Hz, 5.6 Hz), 1.36 – 1.31 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 157.6 (*C*=O), 152.6 (*C*=O), 137.3 (C_{Ar}), 136.5 (C_{Ar}), 135.6 (C_{Ar}), 133.2 (C_{Ar}), 129.8 (C_{Ar}), 129.5 (C_{Ar}), 127.7 (C_{Ar}), 120.0 (C_{Ar}), 46.9 (CH_2), 29.8 (CH_2), 25.2 (CH_2), 24.2 (CH_2), 21.2 (CH_3), 20.9 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{26}N_3O_2^+$ 351.1947. Found: 352.2024.



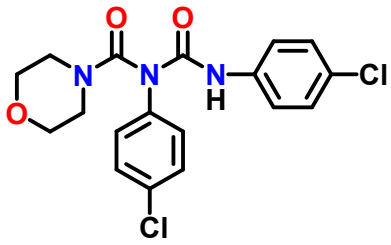
(5j)

Isolated yield: (141 mg, 93%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 9.17 (s, 1H), 7.42 – 7.35 (m, 4H), 7.31 – 7.27 (m, 2H), 7.24 (dd, 2H, J = 8.7 Hz, 1.6 Hz), 3.34 – 3.31 (m, 4H), 1.49 (d, 2H, J = 5.0 Hz), 1.32 (dd, 4H, J = 10.1 Hz, 6.1 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 157.6 (*C*=O), 152.1 (*C*=O), 137.7 (C_{Ar}), 136.7 (C_{Ar}), 132.9 (C_{Ar}), 129.2 (C_{Ar}), 128.9 (C_{Ar}), 121.2 (C_{Ar}), 46.9 (CH_2), 25.0 (CH_2), 24.0 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{20}Cl_2N_3O_2^+$ 391.0854. Found: 392.0928.



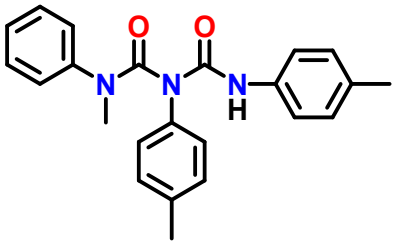
(5k)

Isolated yield: (119 mg, 89%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.36 (s, 1H), 7.32 – 7.28 (m, 2H), 7.24 (s, 4H), 7.09 (d, 2H, J = 8.2 Hz), 3.55 – 3.53 (m, 4H), 3.46 – 3.43 (m, 4H), 2.38 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 157.4 (*C*=O), 152.3 (*C*=O), 137.8 (C_{Ar}), 135.9 (C_{Ar}), 135.3 (C_{Ar}), 133.4 (C_{Ar}), 130.0 (C_{Ar}), 129.4 (C_{Ar}), 127.8 (C_{Ar}), 119.9 (C_{Ar}), 66.2 (CH_2), 46.0 (CH_2), 21.1 (CH_3), 20.8 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}N_3O_3^+$ 353.1739. Found: 354.1830.



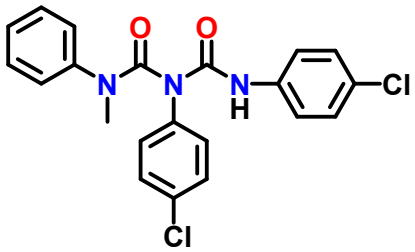
(5l)

Isolated yield: (143 mg, 96%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 9.08 (s, 1H), 7.41 (dd, 4H, J = 8.8 Hz, 6.6 Hz), 7.31 – 7.25 (m, 5H), 3.53 – 3.51 (m, 4H), 3.39 – 3.37 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 133.6 (*C*=O), 129.5 (C_{Ar}), 129.1 (C_{Ar}), 121.4 (C_{Ar}), 66.1 (CH_2), 46.2 (CH_2) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}N_3O_3^+$ 393.0647. Found: 394.0717.



(5m)

Isolated yield: (117 mg, 82%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 9.52 (s, 1H), 7.45 – 7.38 (m, 3H), 7.35 – 7.29 (m, 2H), 7.24 (dd, 2H, J = 4.7 Hz, 3.5 Hz), 7.24 – 7.16 (m, 4H), 7.12 (d, 2H, J = 8.0 Hz), 6.87 – 6.81 (m, 2H), 3.37 (s, 3H), 2.36 (s, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 157.7 (C=O), 153.9 (C=O), 143.7 (C_{Ar}), 137.4 (C_{Ar}), 136.6 (C_{Ar}), 136.3 (C_{Ar}), 133.2 (C_{Ar}),129.7 (C_{Ar}), 127.1 (C_{Ar}), 126.5 (C_{Ar}), 122.0 (C_{Ar}), 121.1 (C_{Ar}), 120.7 (C_{Ar}), 39.4 (CH_3), 38.2 (CH_3), 21.1 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{24}N_3O_2^+$ 373.1790. Found: 374.1867.



(5n)

Isolated yield: (141 mg, 89%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 10.21 (s, 1H), 7.49 – 7.44 (m, 2H), 7.31 – 7.25 (m, 2H), 7.19 – 7.11 (m, 3H), 7.04 – 6.98 (m, 2H), 6.74 – 6.62 (m, 4H), 3.27 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 159.3 (C=O), 151.9 (C=O), 143.0 (C_{Ar}), 136.6 (C_{Ar}), 132.6 (C_{Ar}), 129.6 (C_{Ar}), 129.4 (C_{Ar}), 129.0 (C_{Ar}), 128.7 (C_{Ar}), 128.1 (C_{Ar}), 127.1 (C_{Ar}), 126.2 (C_{Ar}), 121.2 (C_{Ar}), 116.2 (C_{Ar}), 40.1 (CH_3) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{18}Cl_2N_3O_2^+$ 413.0698. Found: 414.0774.

NMR Spectra for the urea derivatives:

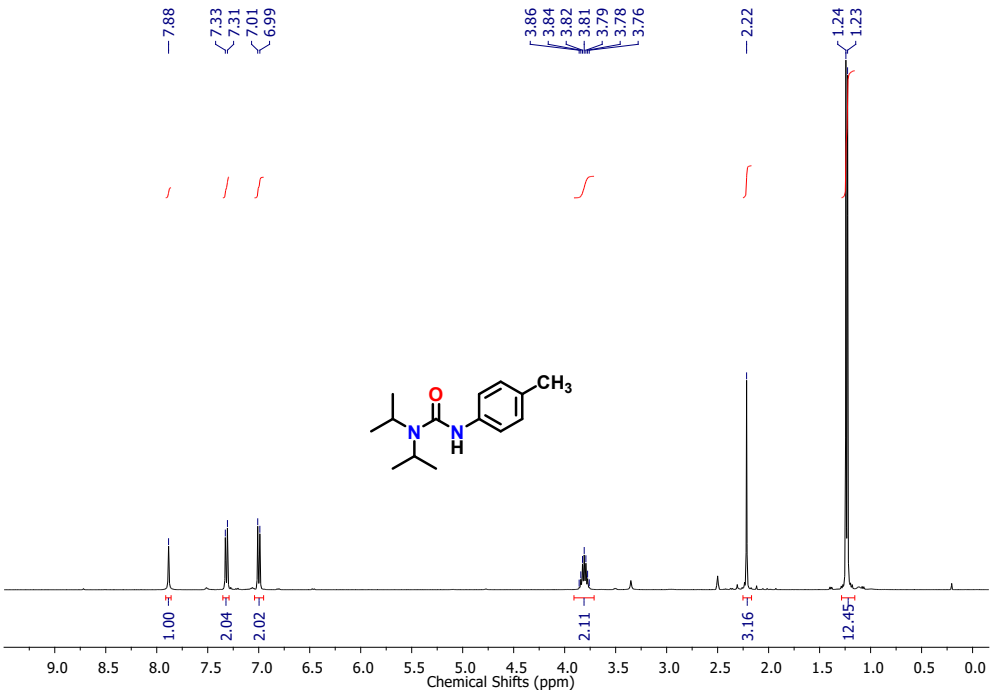


Figure FS19. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **4a.**

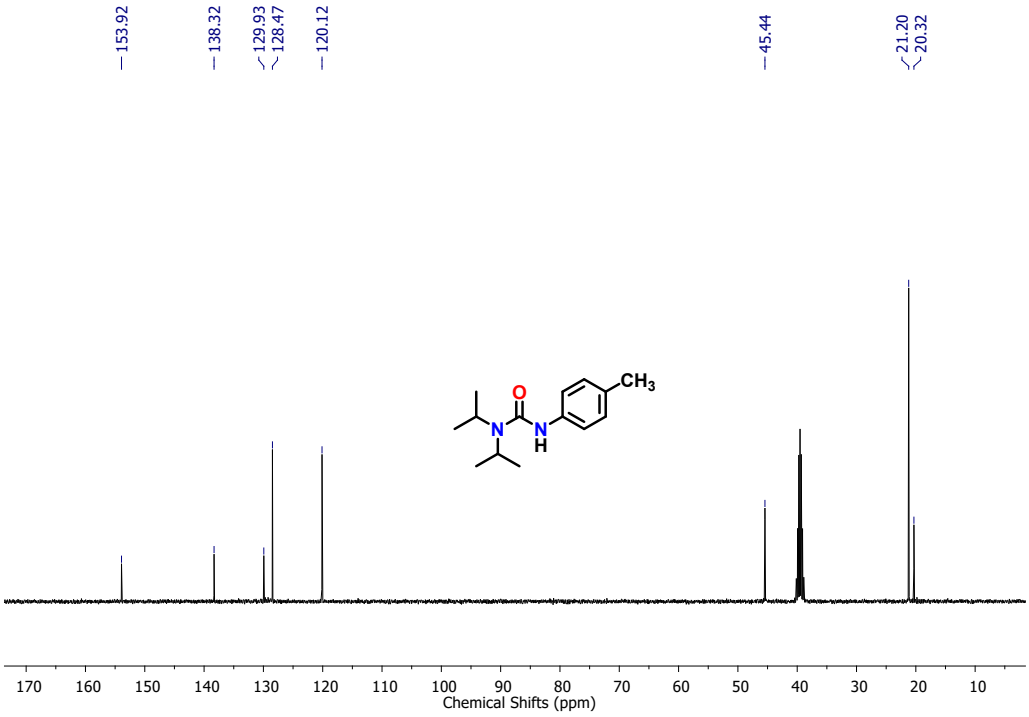


Figure FS20. ^{13}C{ ^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **4a.**

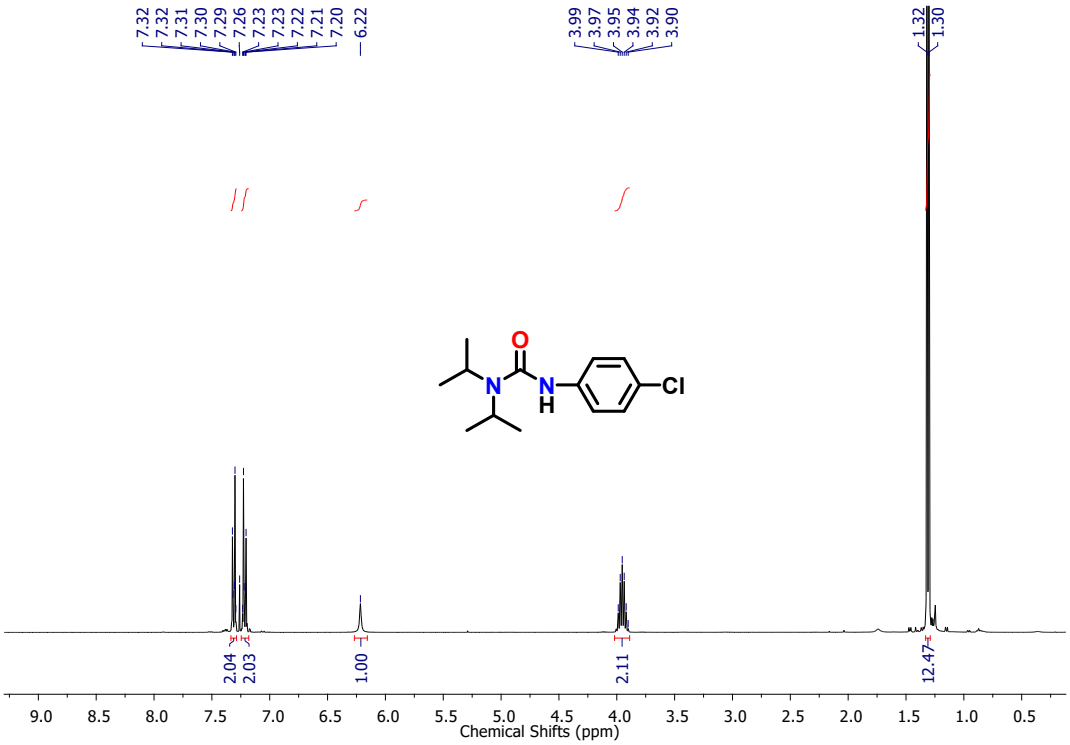


Figure FS21. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4b.**

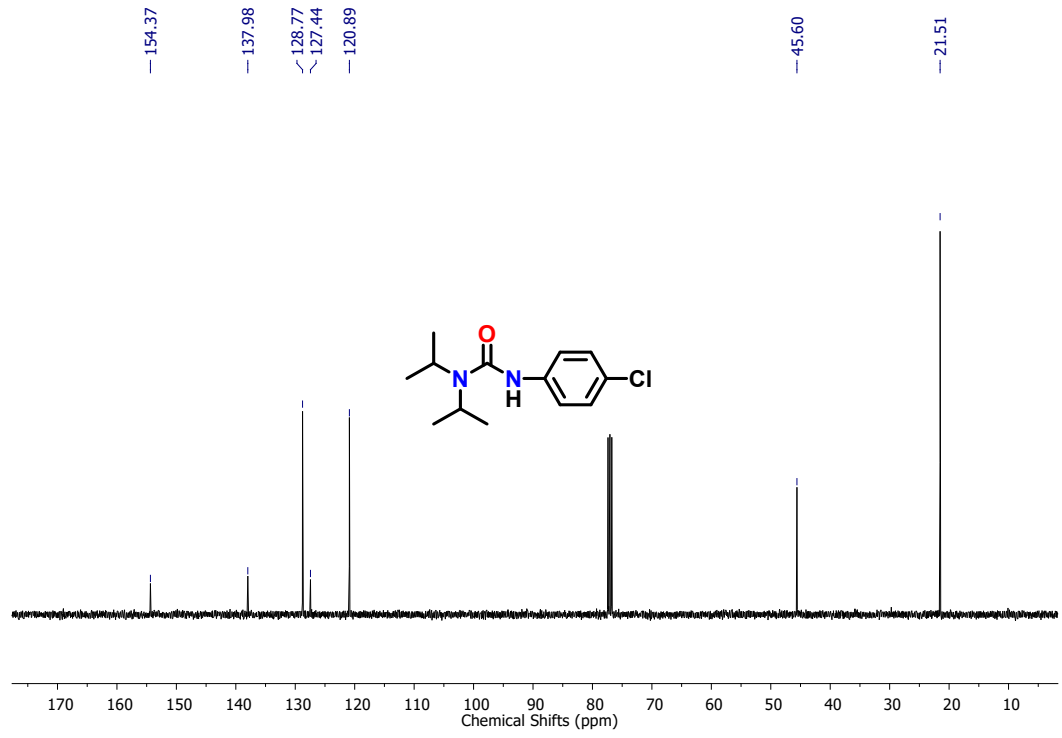


Figure FS22. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4b.**

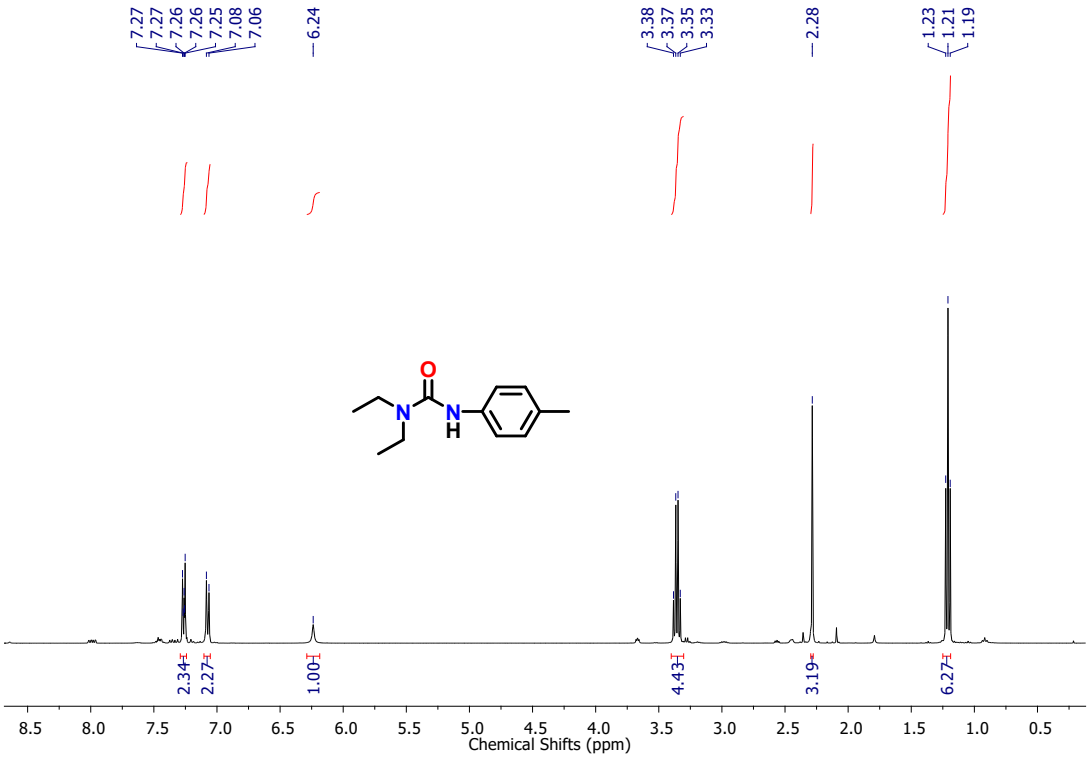


Figure FS23. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4c.**

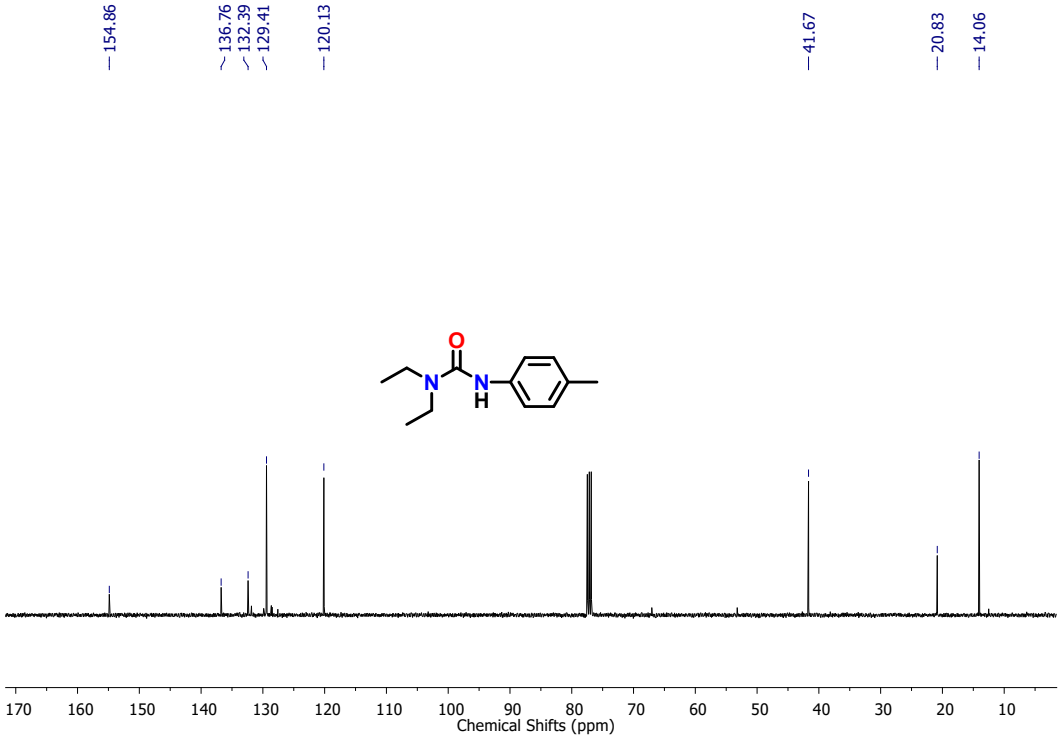


Figure FS24. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4c.**

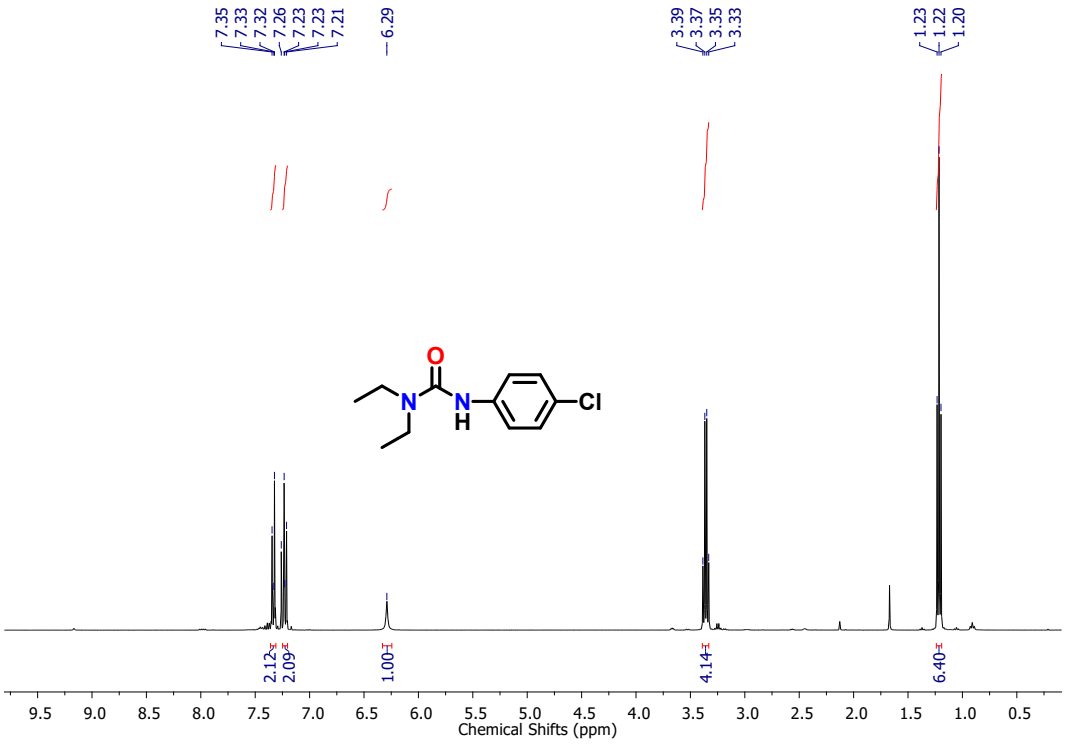


Figure FS25. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4d.**

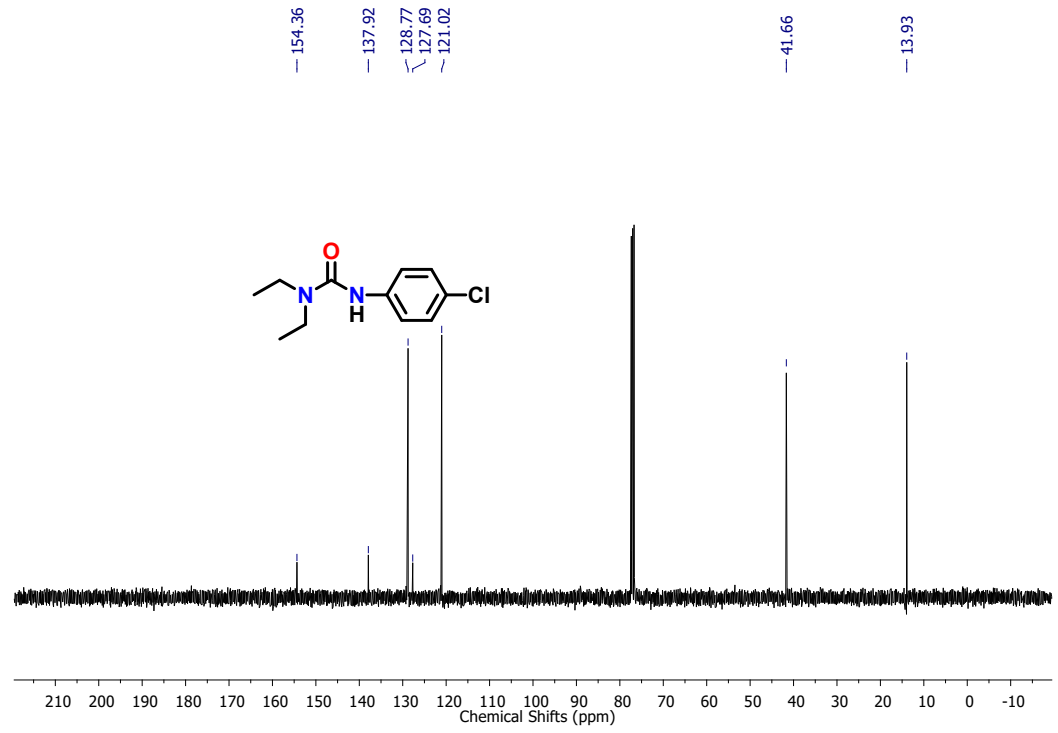


Figure FS26. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4d.**

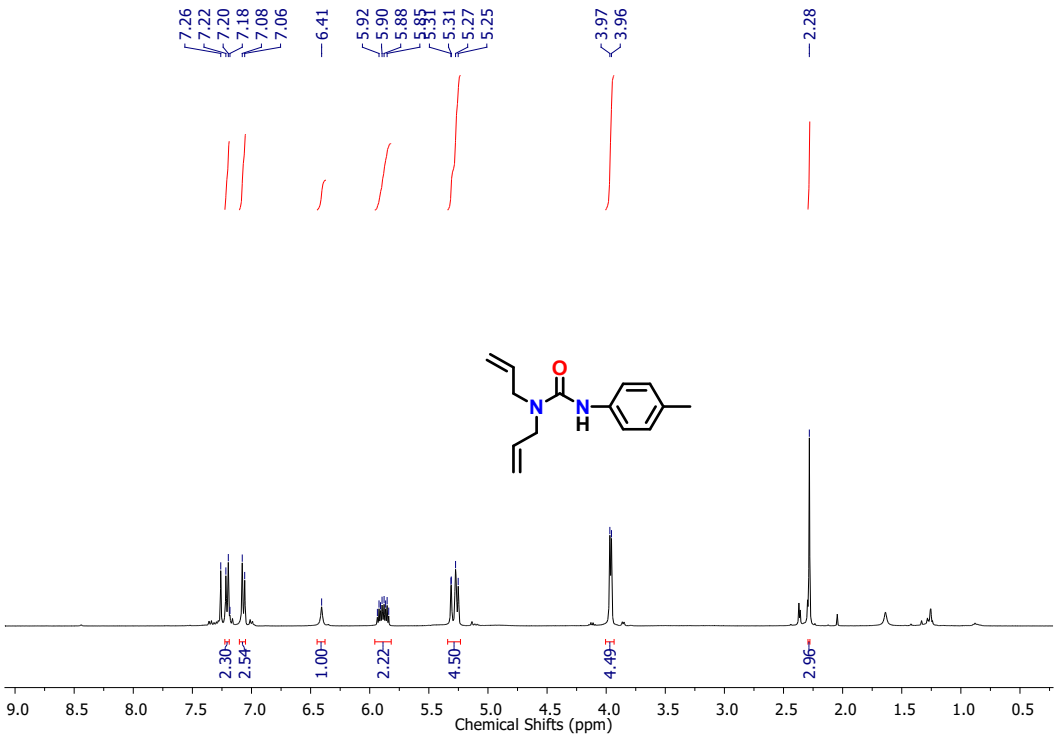


Figure FS27. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4e.**

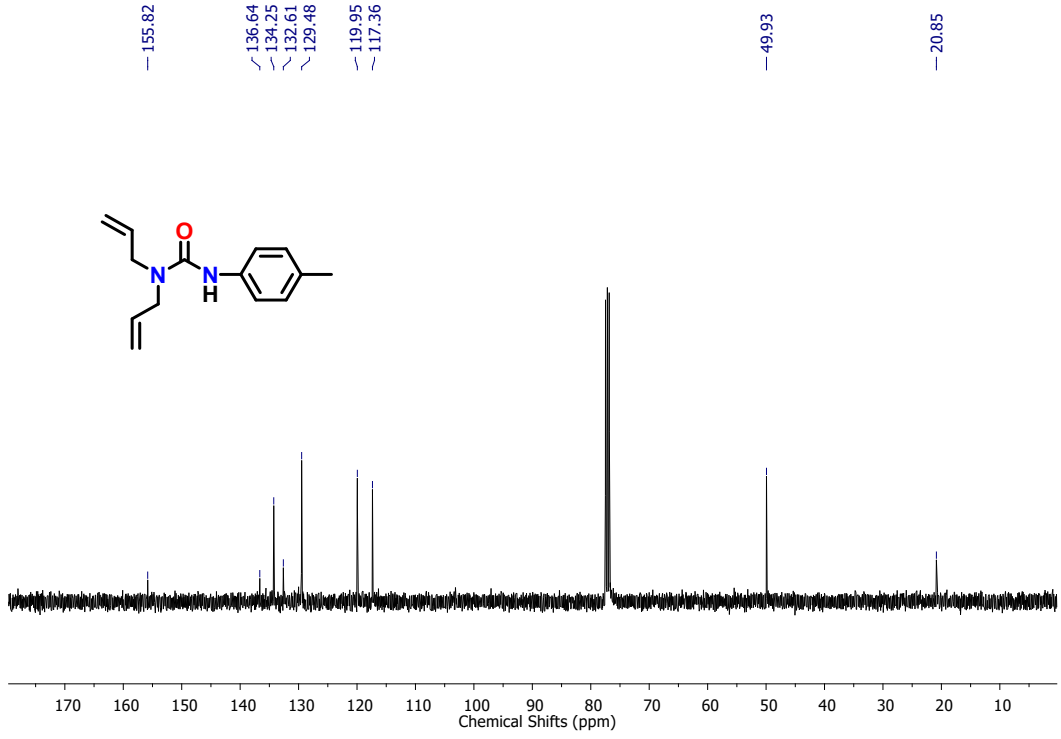


Figure FS28. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4e.**

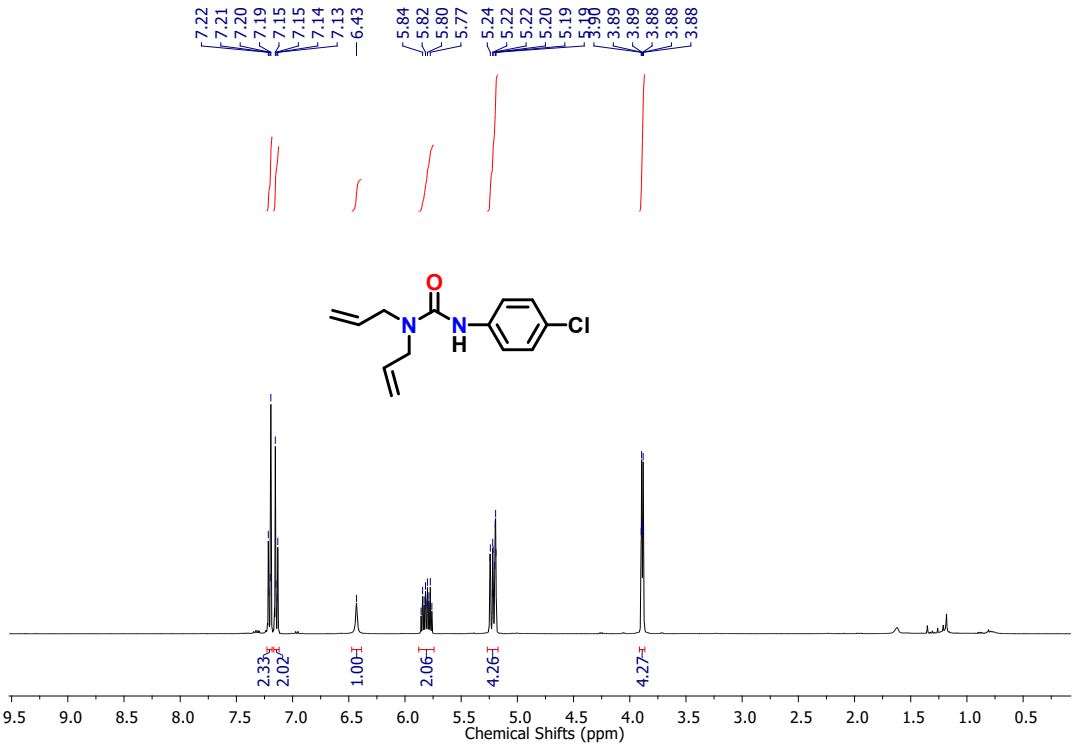


Figure FS29. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4f.**

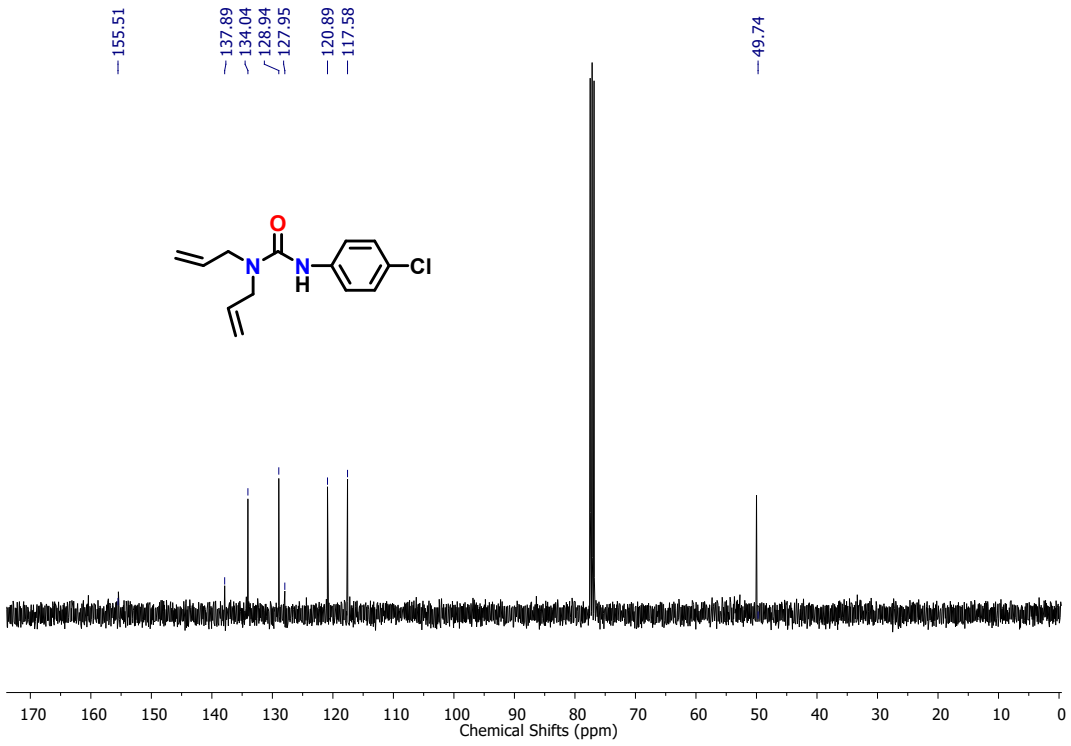


Figure FS30. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4f.**

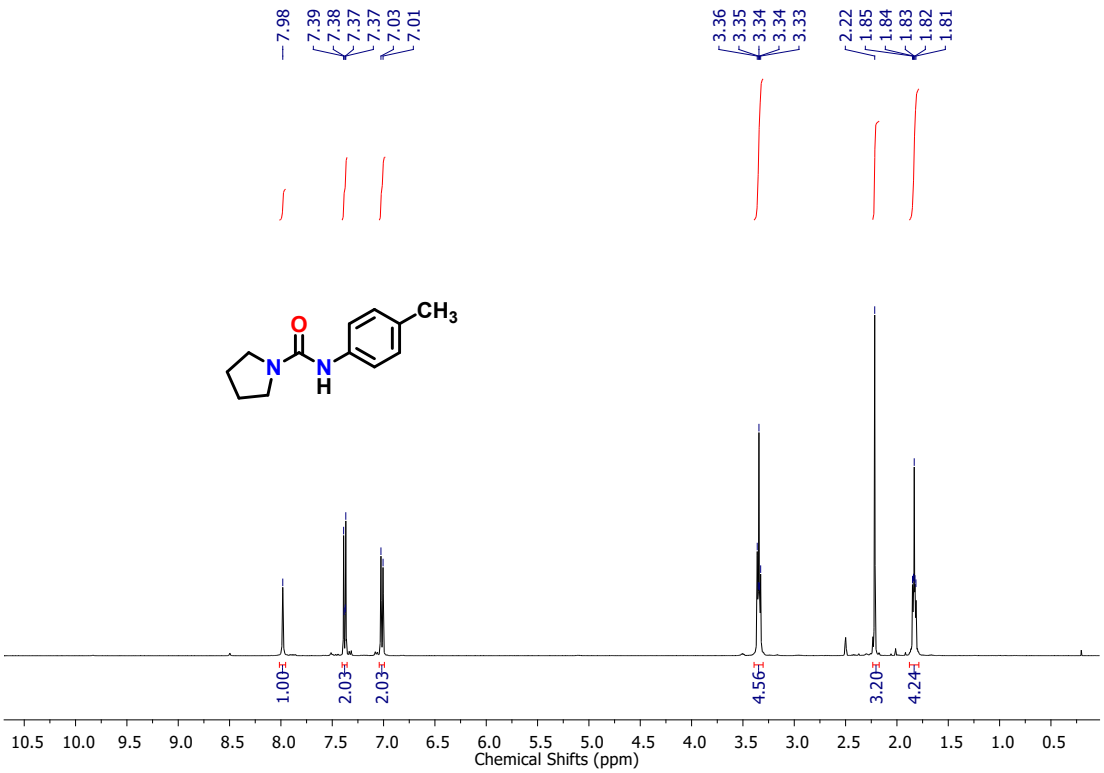


Figure FS31. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4g.**

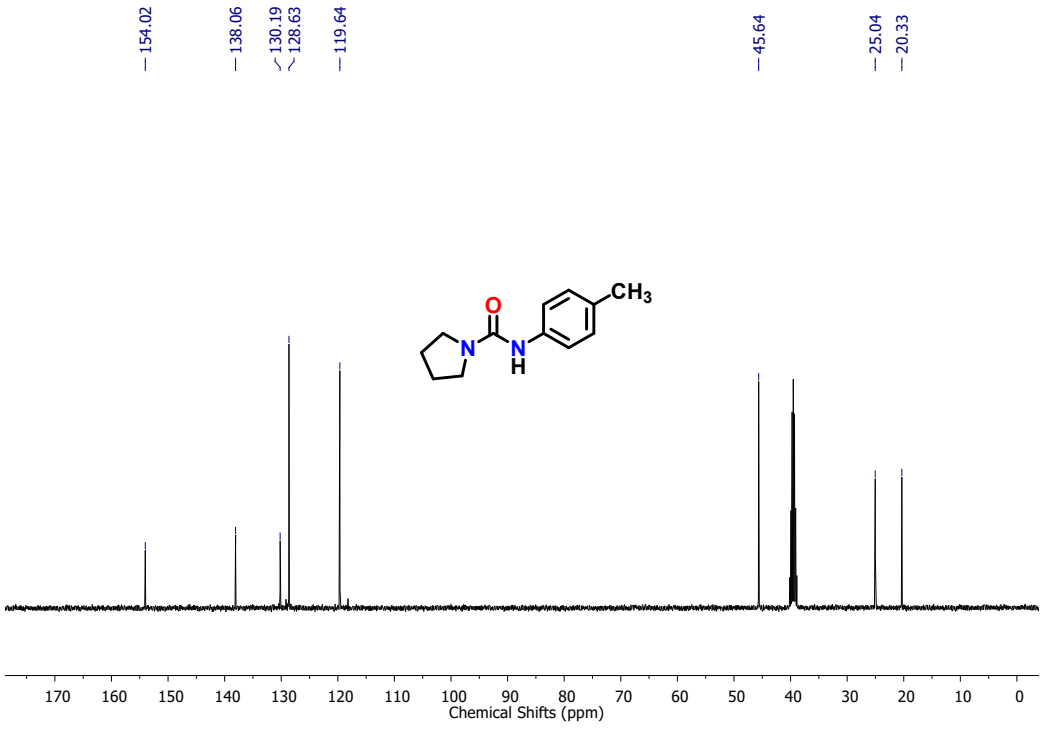


Figure FS32. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4g.**

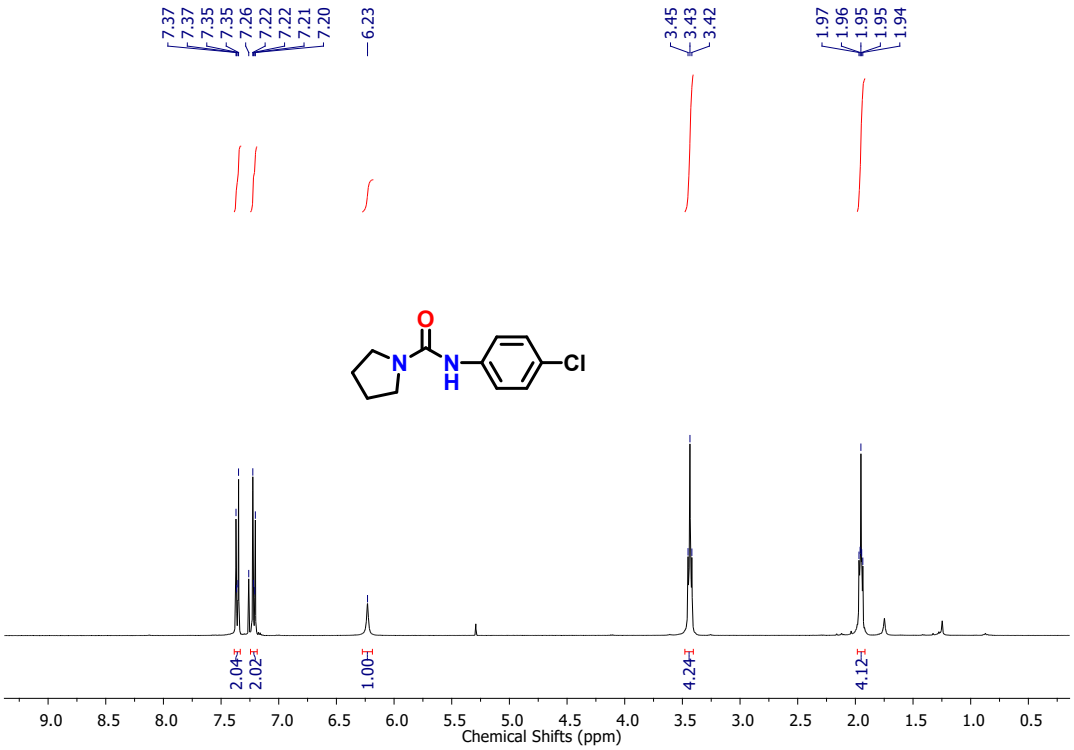


Figure FS33. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4h.**

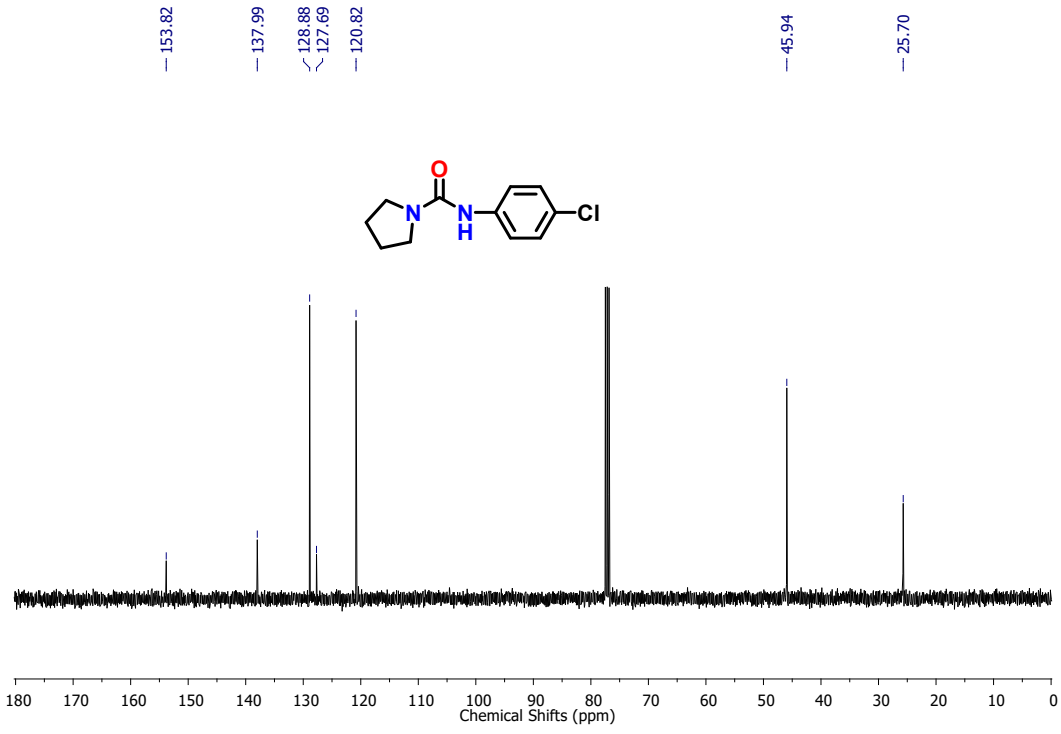


Figure FS34. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4h.**

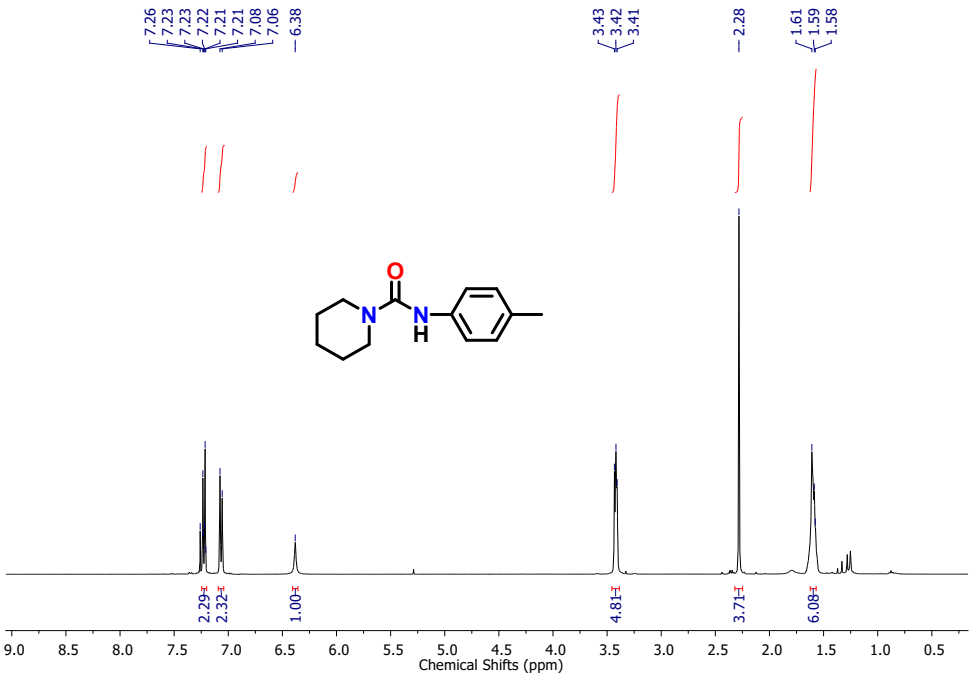


Figure FS35. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4i.**

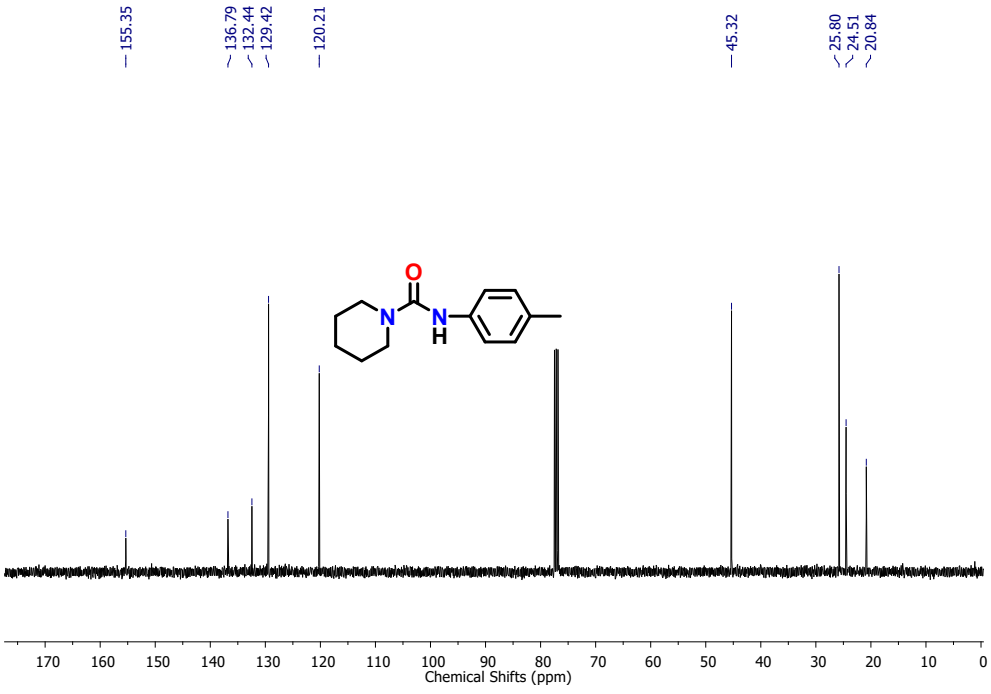


Figure FS36. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4i.**

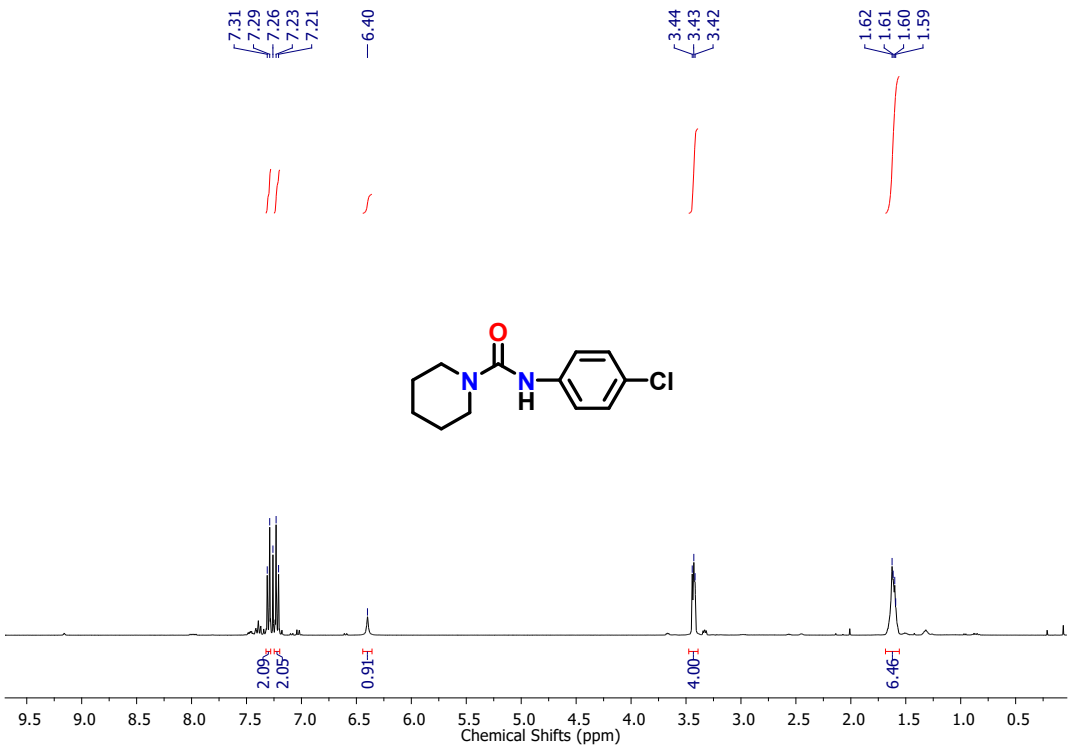


Figure FS37. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4j.**

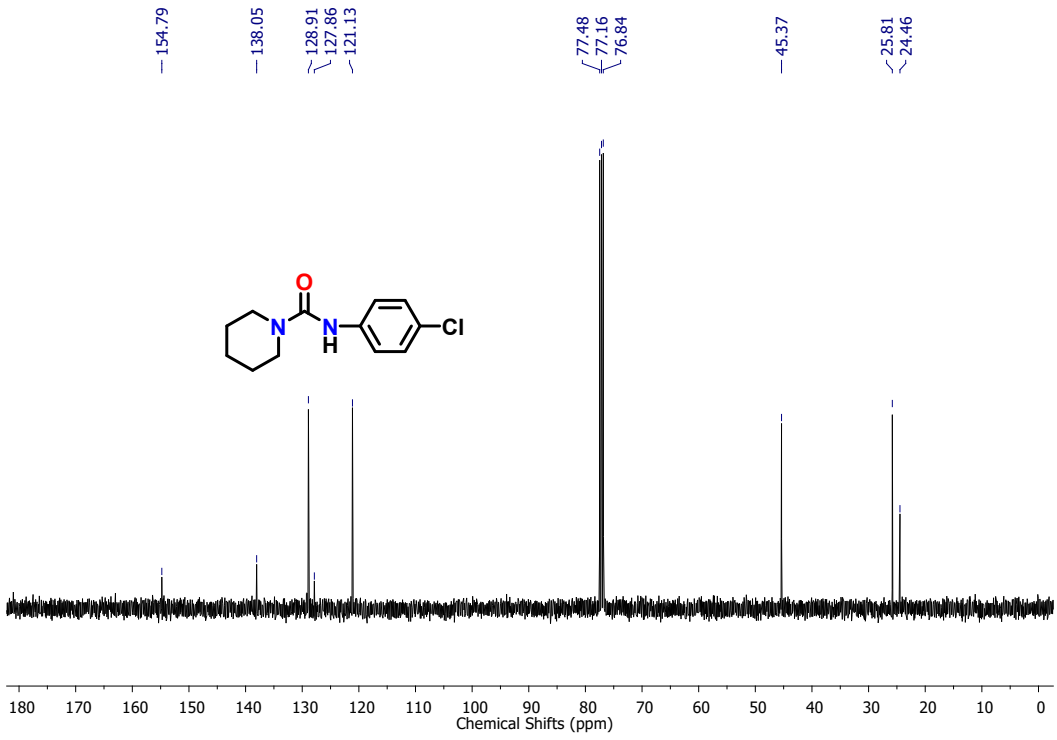


Figure FS38. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4j.**

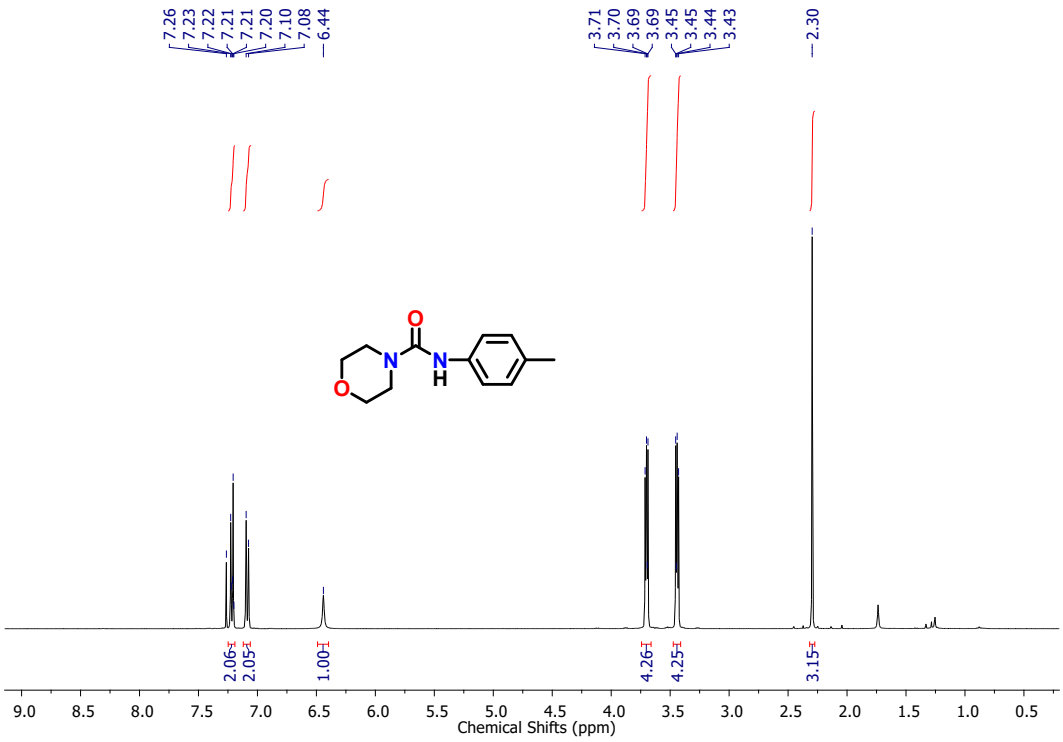


Figure FS39. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4k.**

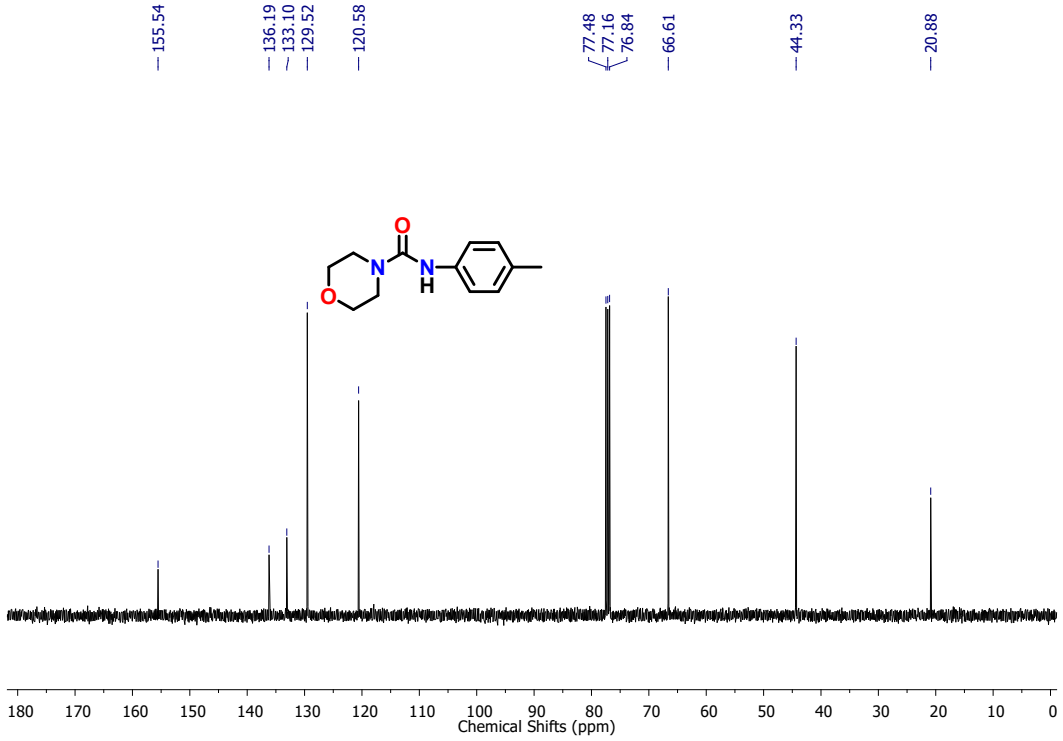


Figure FS40. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4k.**

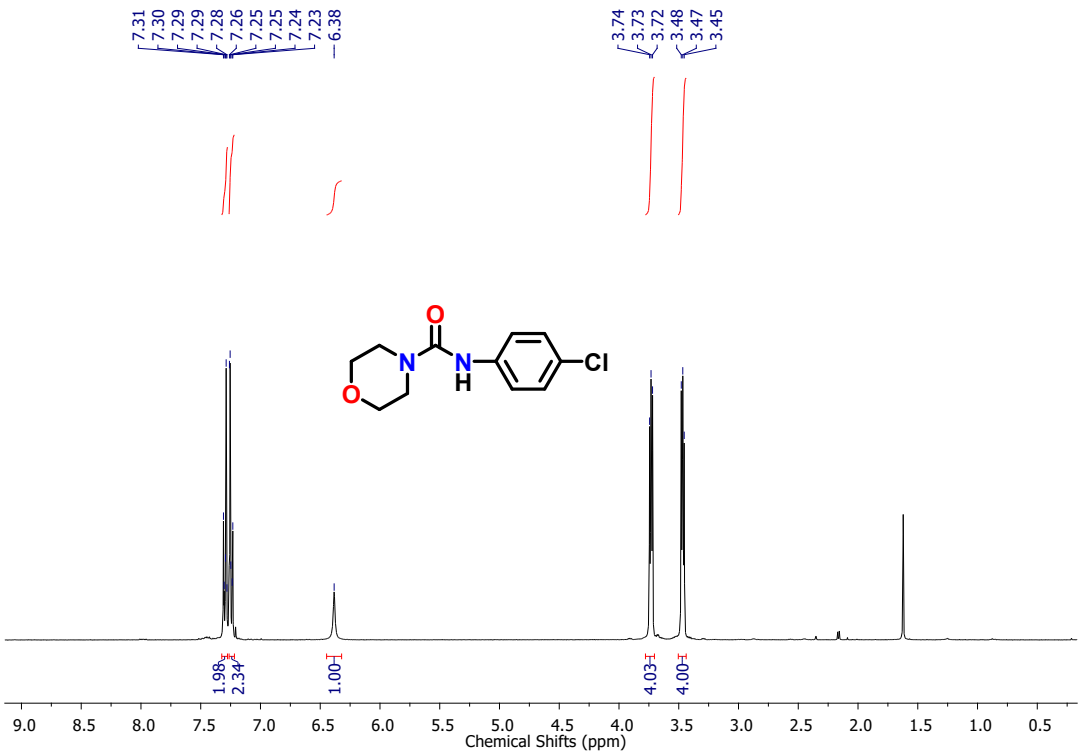


Figure FS41. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4l.**

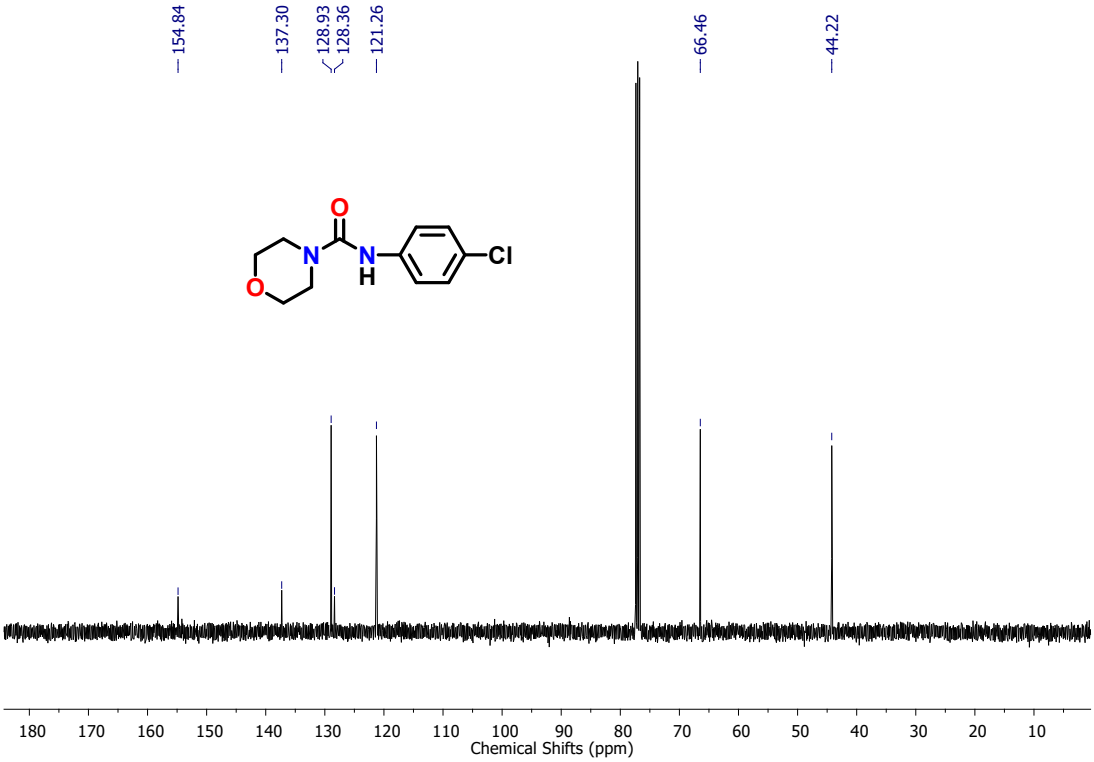


Figure FS42. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4l.**

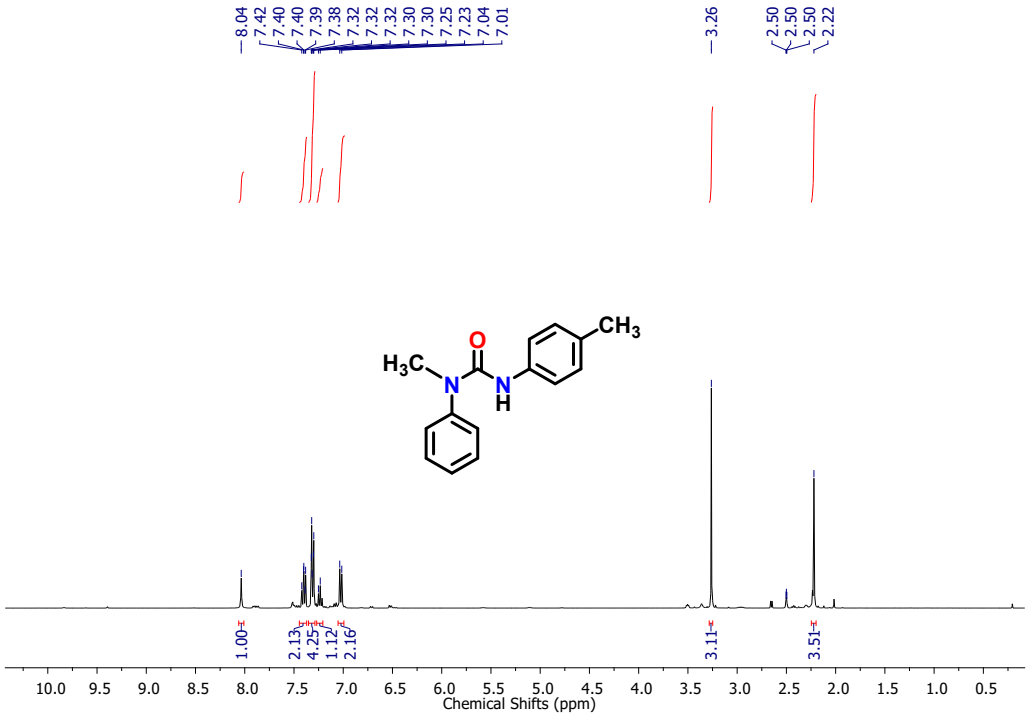


Figure FS43. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4m.**

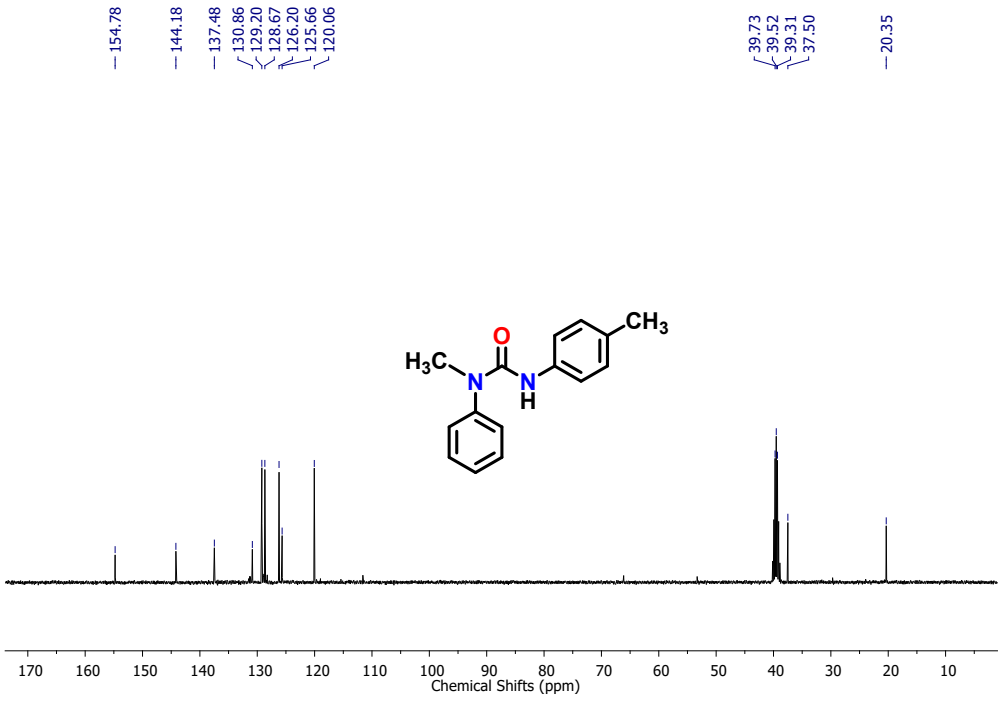


Figure FS44. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4m.**

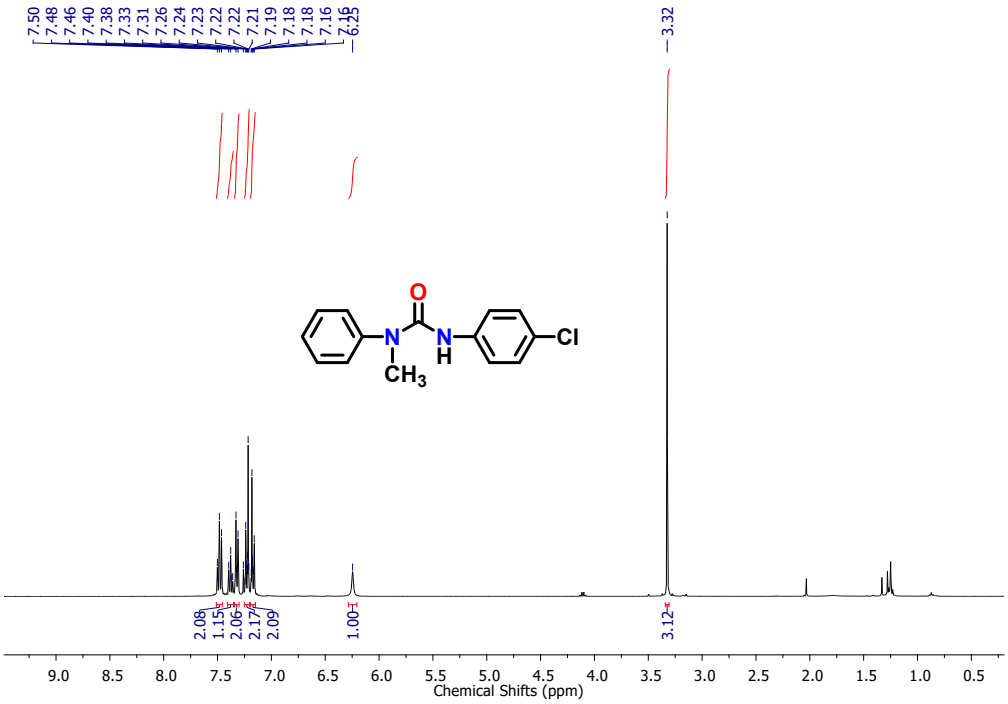


Figure FS45. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4n.**

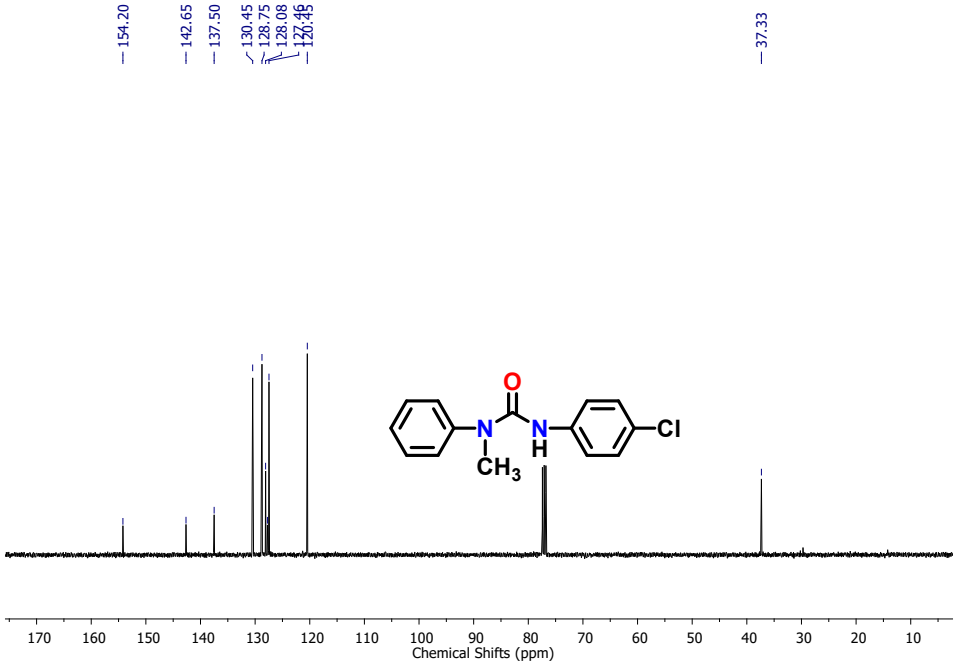


Figure FS46. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4n.**

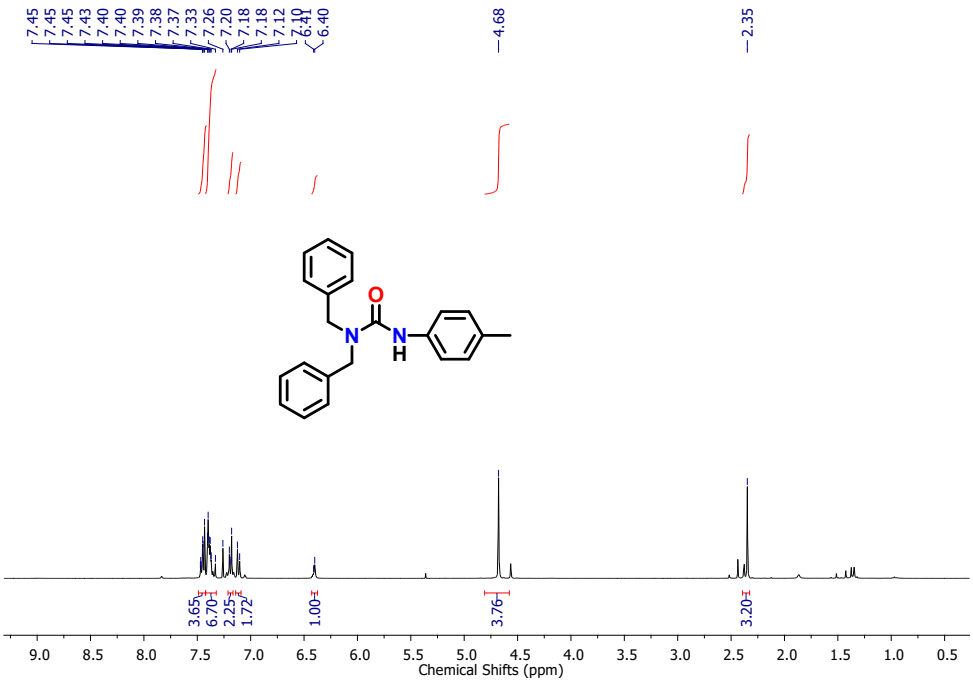


Figure FS47. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4o.**

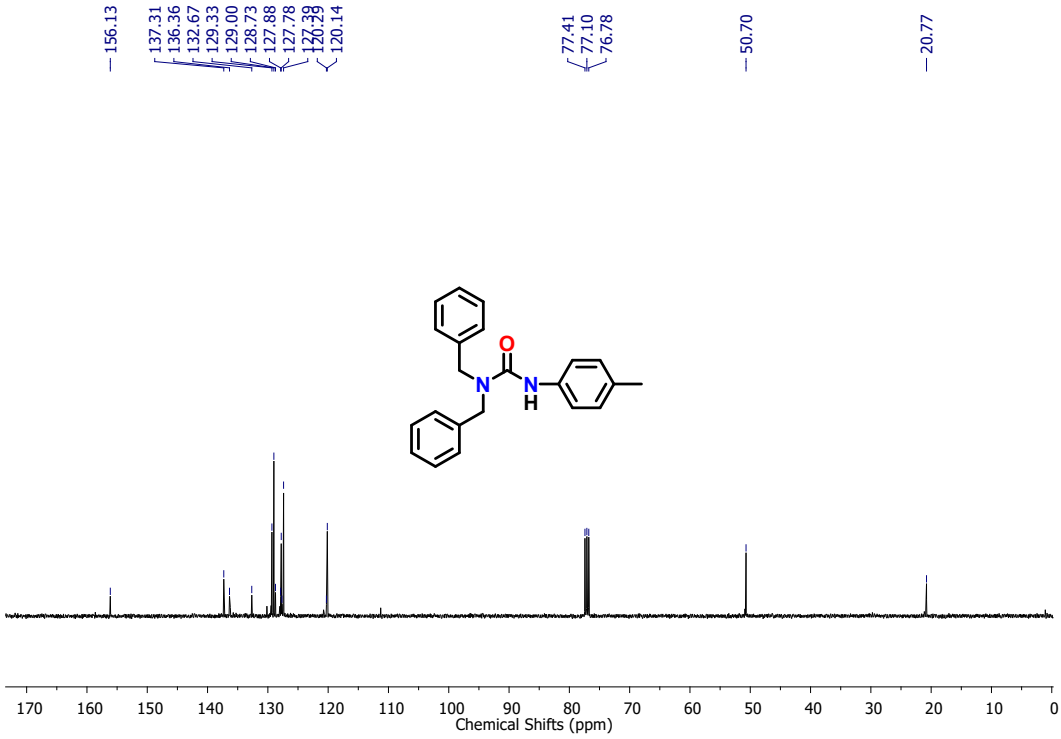


Figure FS48. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4o.**

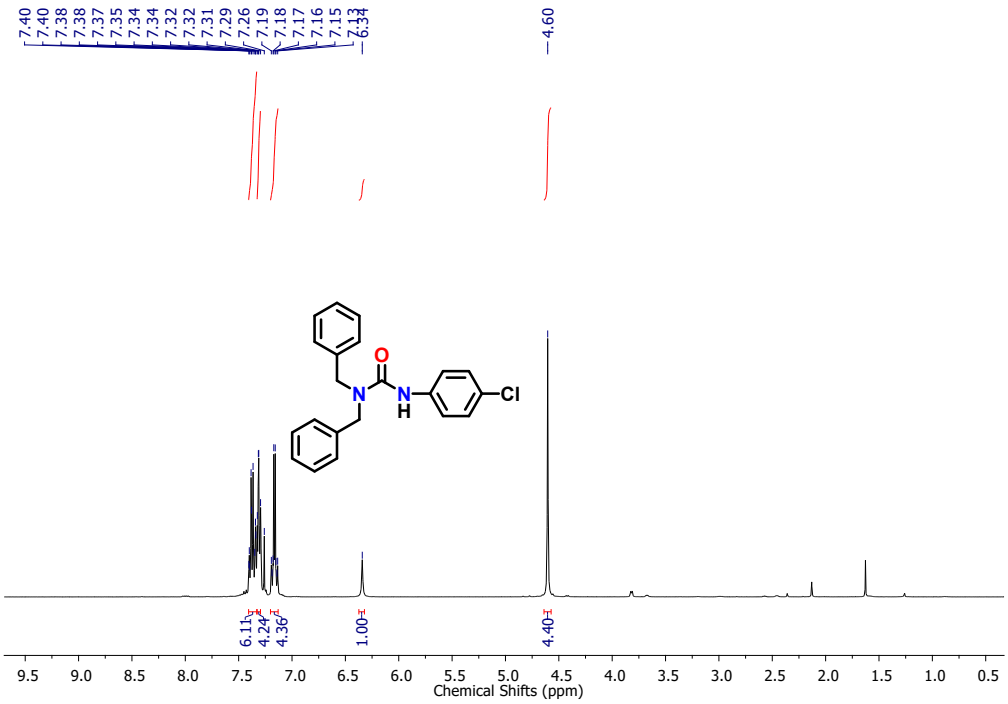


Figure FS49. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **4p.**

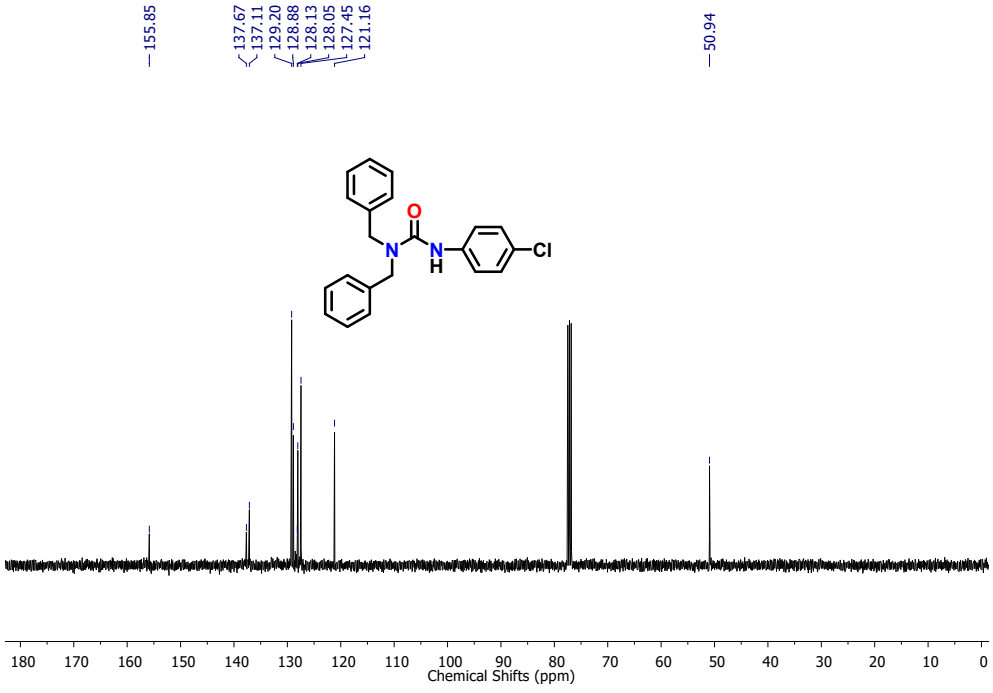


Figure FS50. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **4p.**

NMR Spectra for the biuret derivatives:

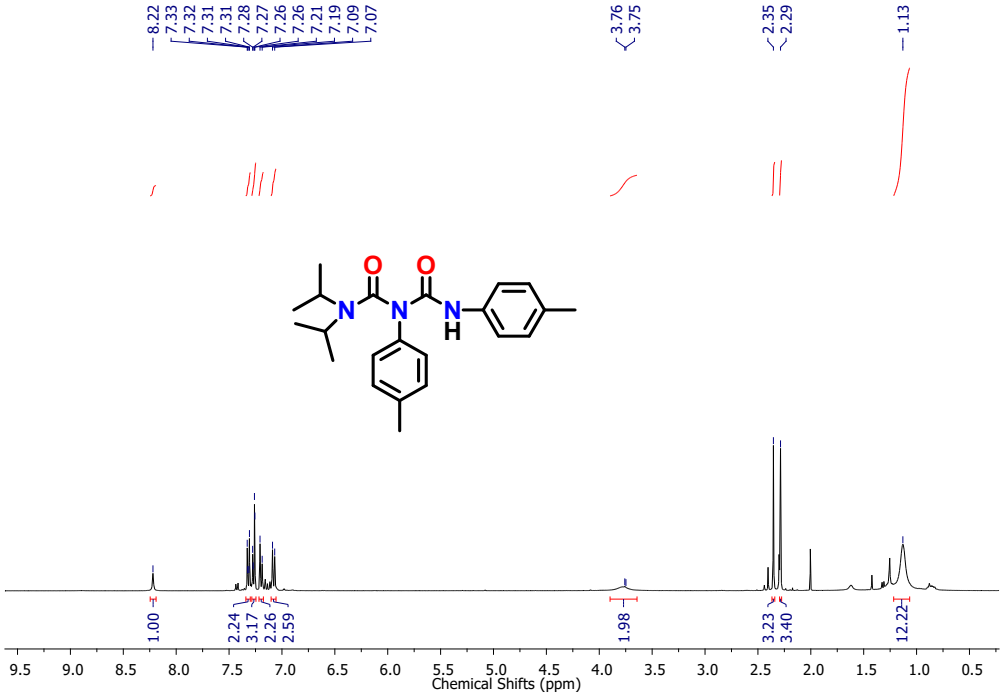


Figure FS51. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5a.**

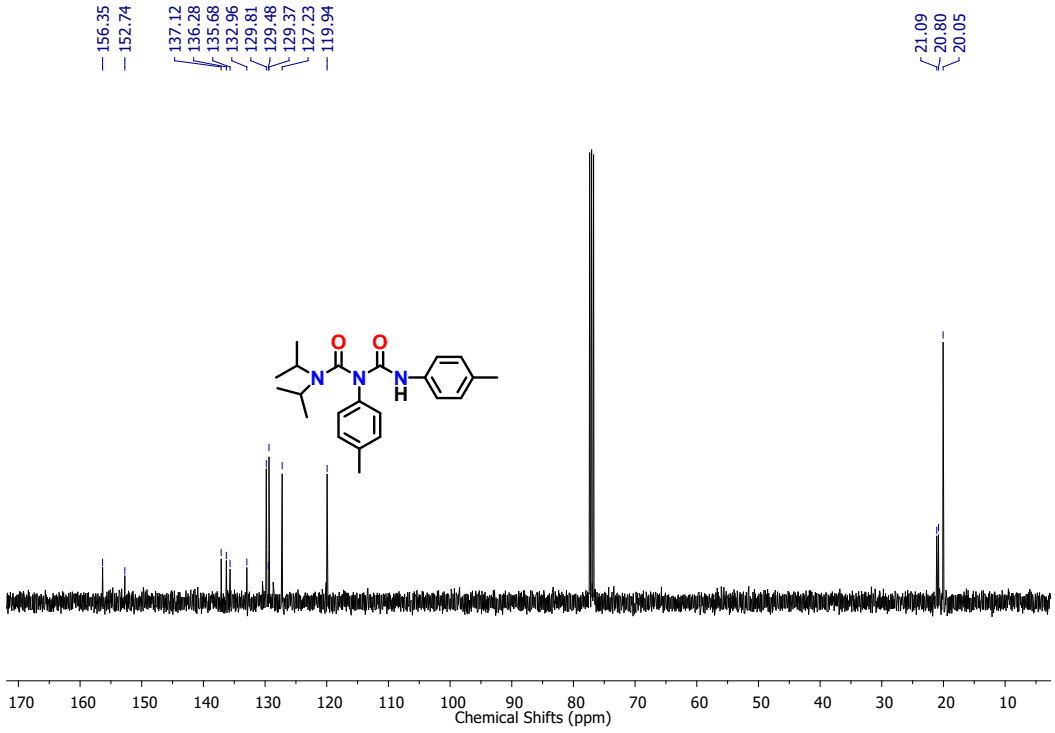


Figure FS52. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5a.**

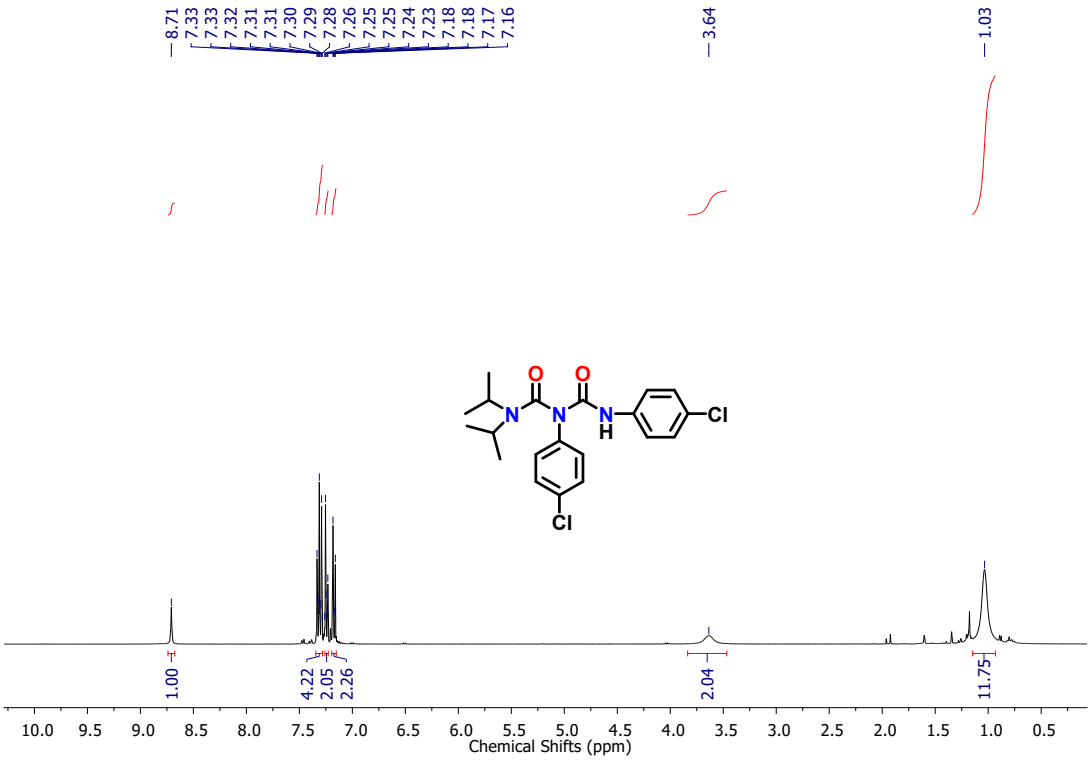


Figure FS53. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5b.**

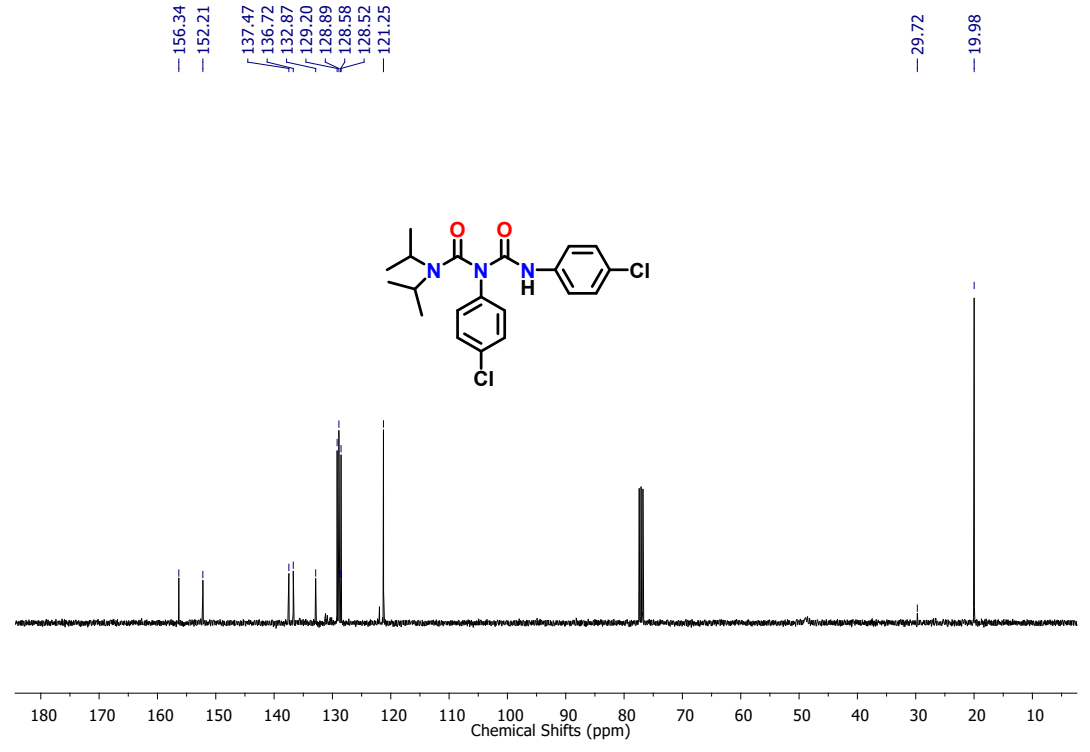


Figure FS54. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5b.**

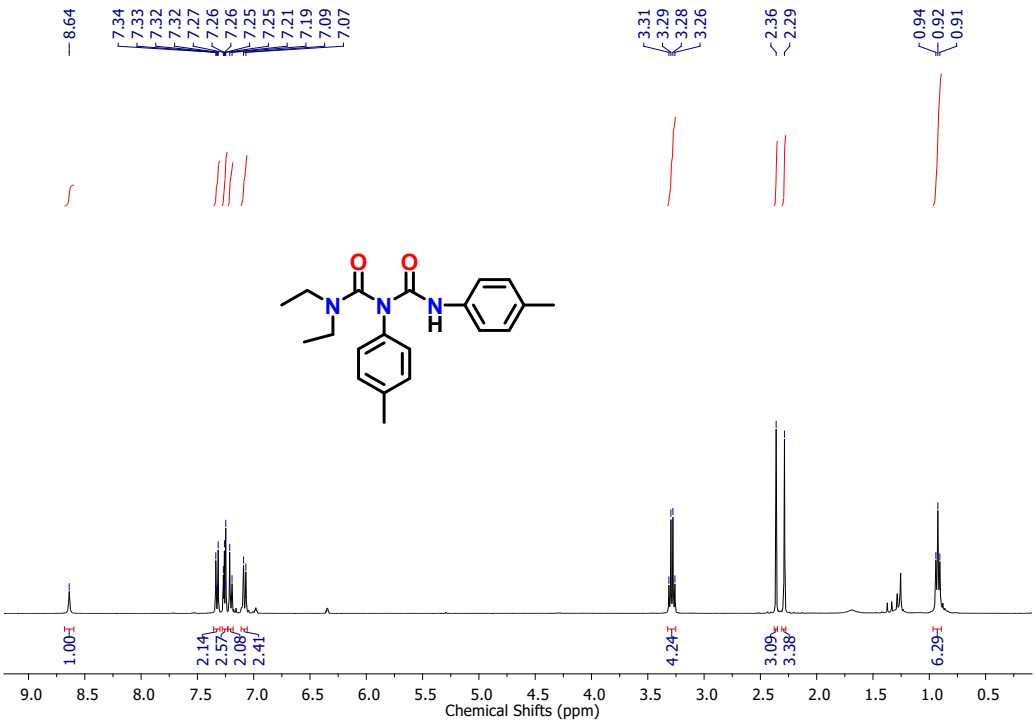


Figure FS55. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5c.**

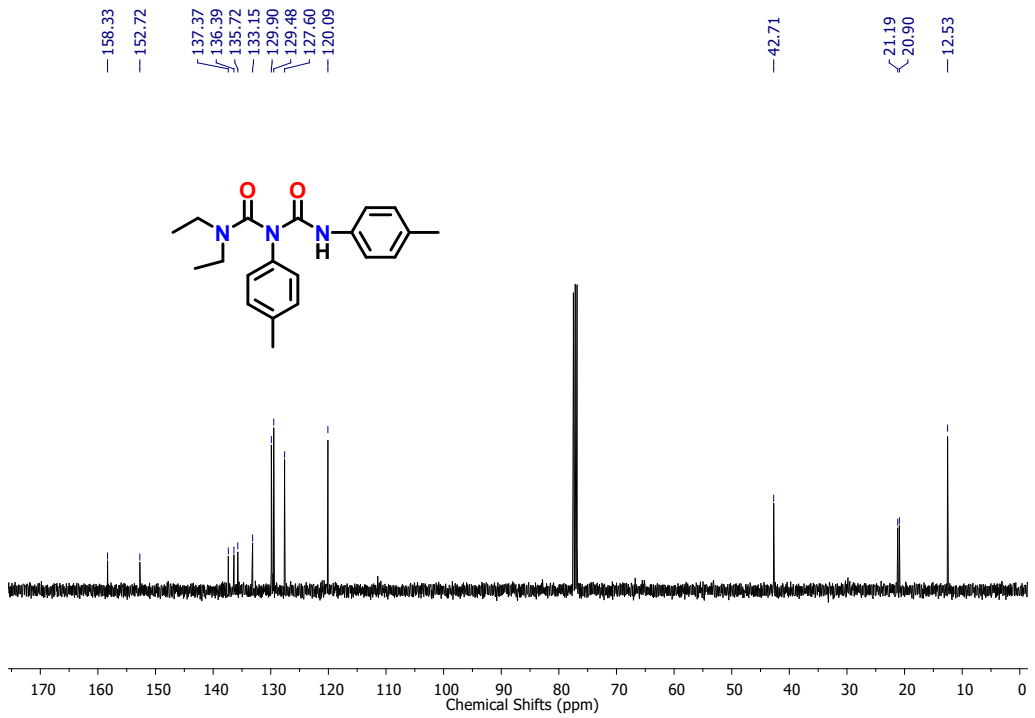


Figure FS56. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5c.**

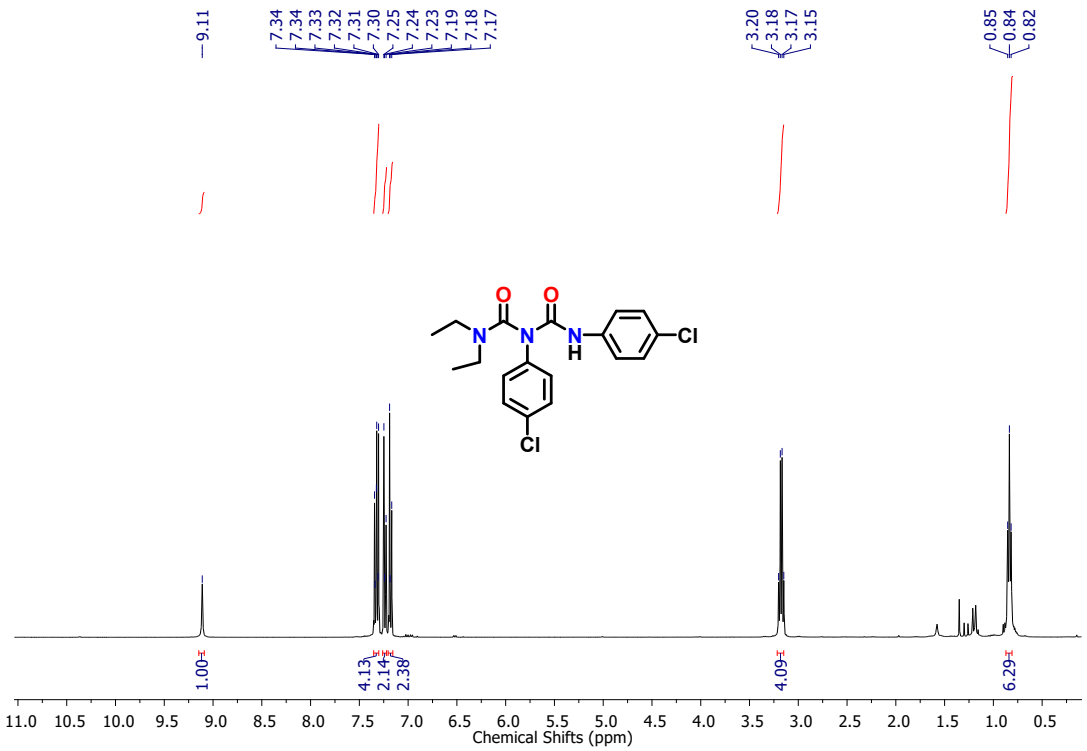


Figure FS57. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5d.**

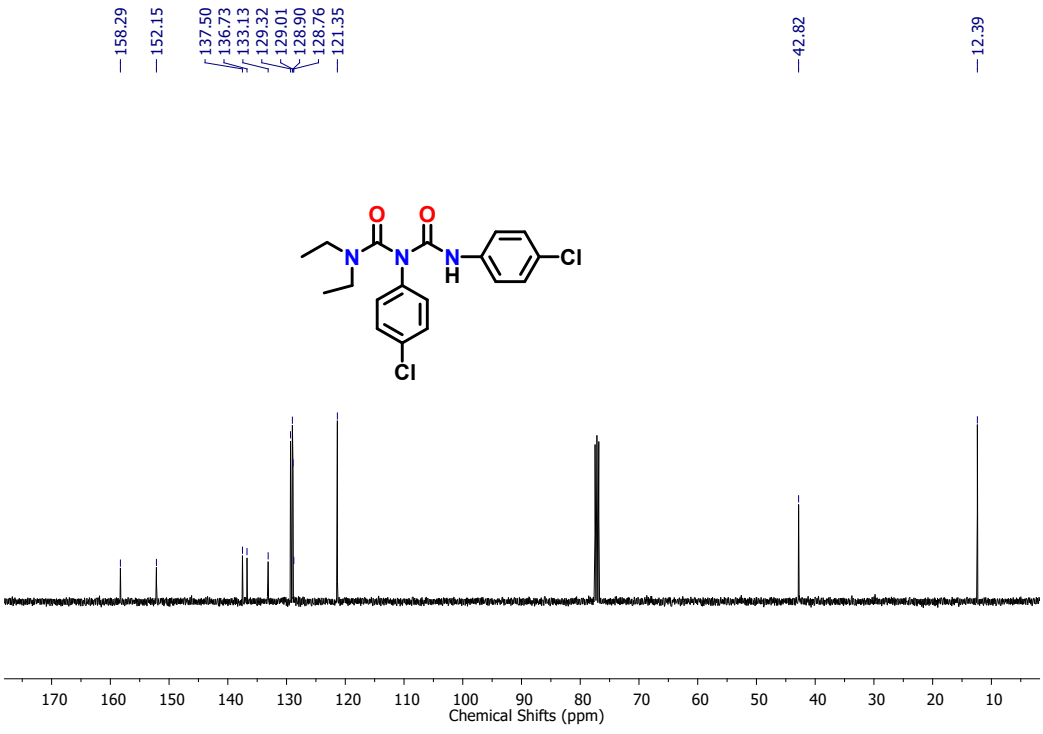


Figure FS58. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5d.**

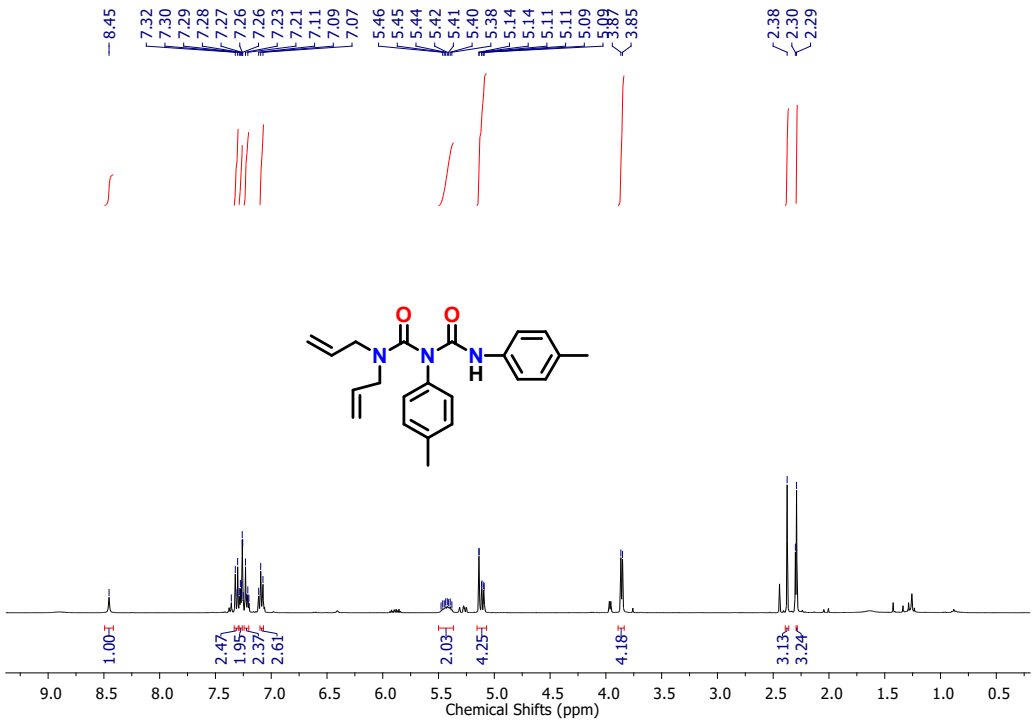


Figure FS59. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5e.**

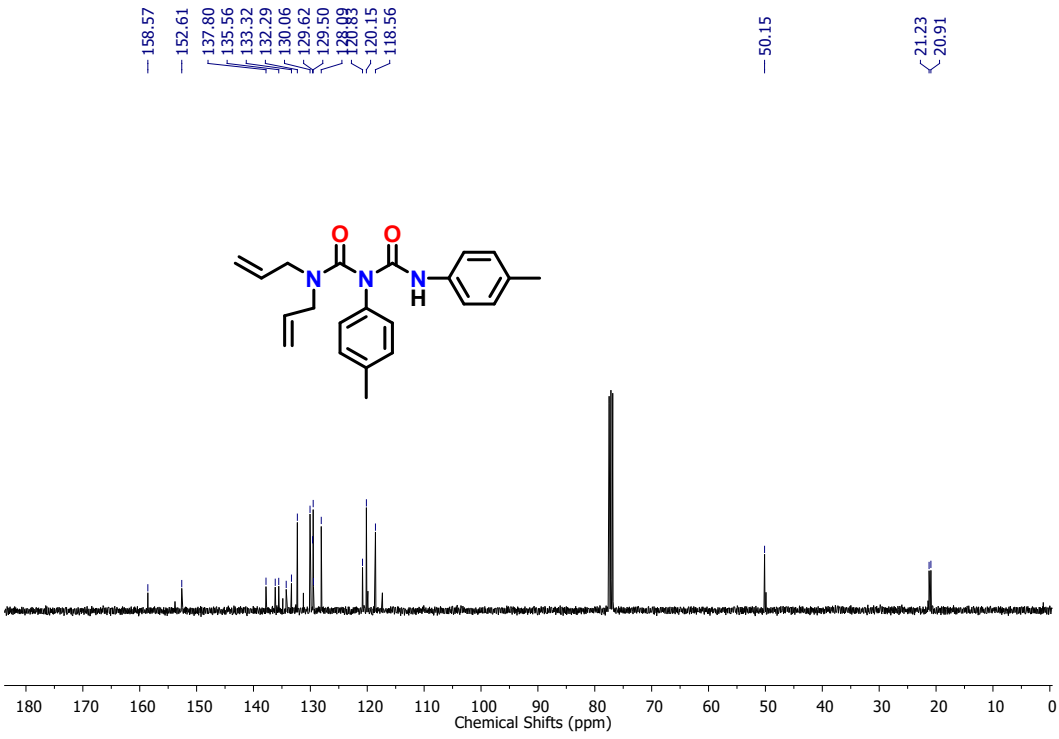


Figure FS60. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5e.**

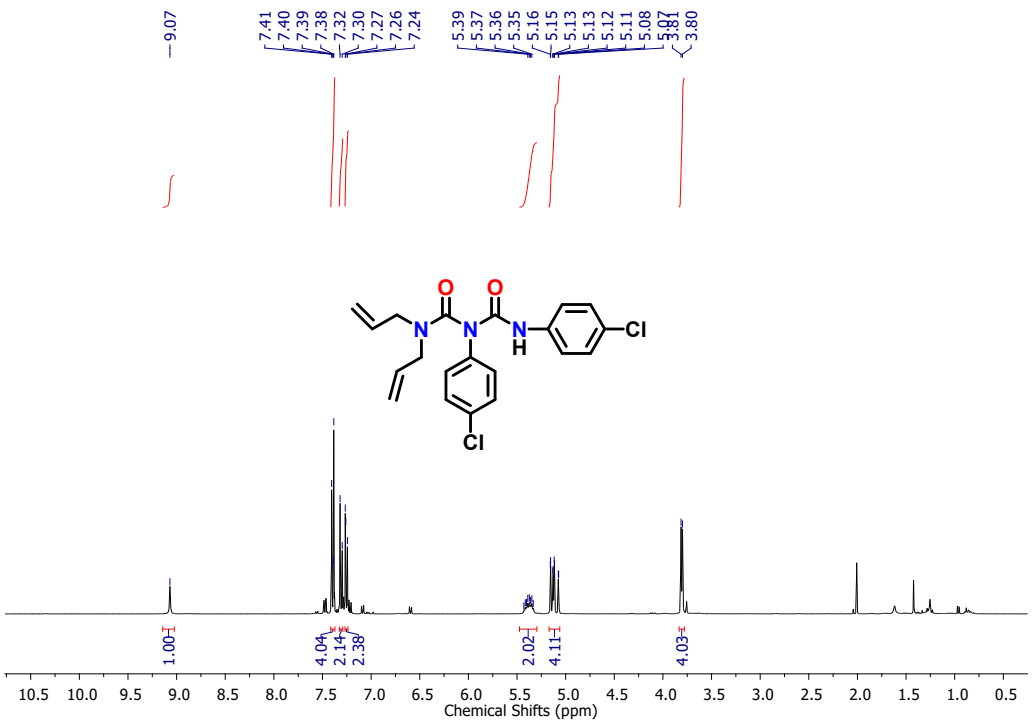


Figure FS61. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5f.**

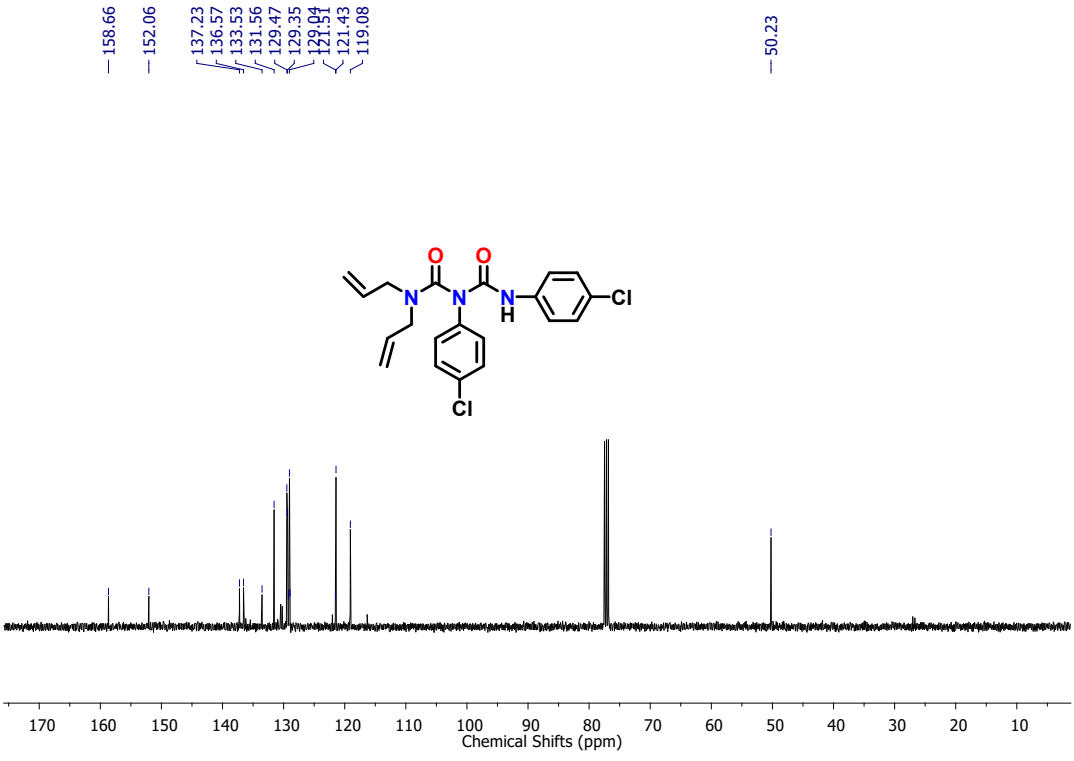


Figure FS62. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5f.**

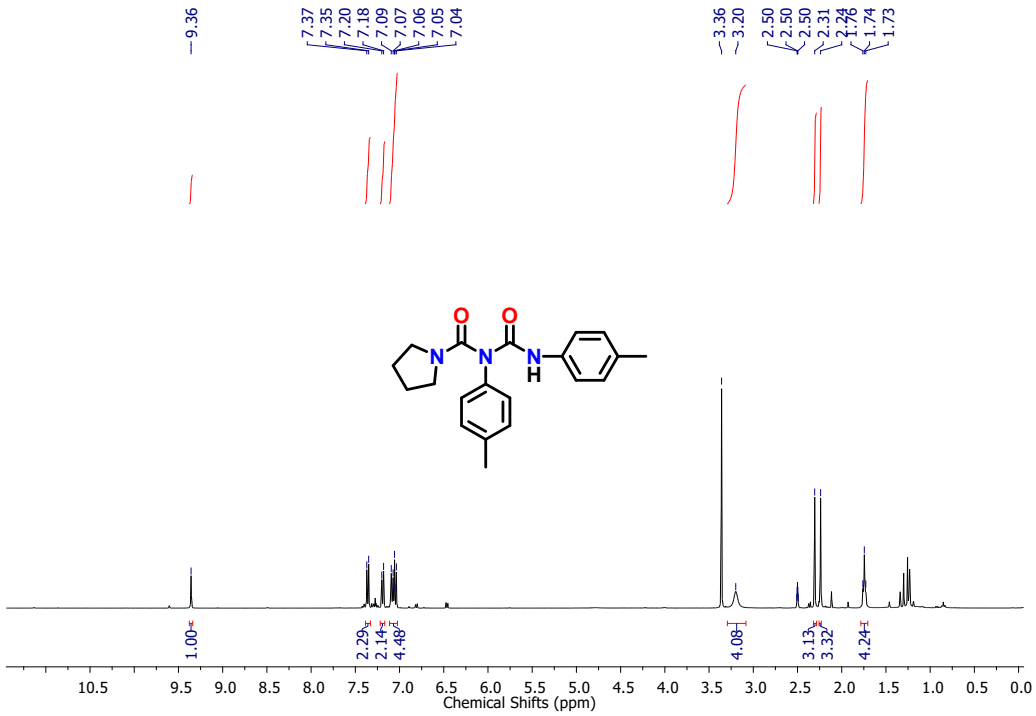


Figure FS63. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5g.**

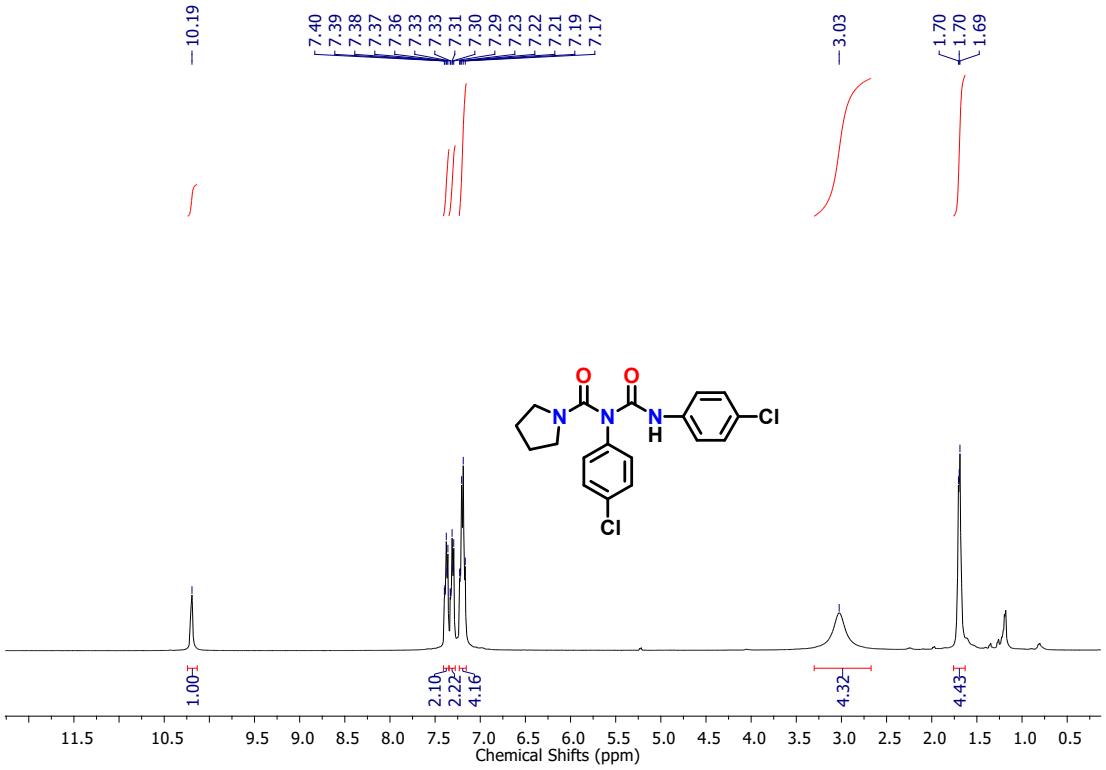


Figure FS64. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5h.**

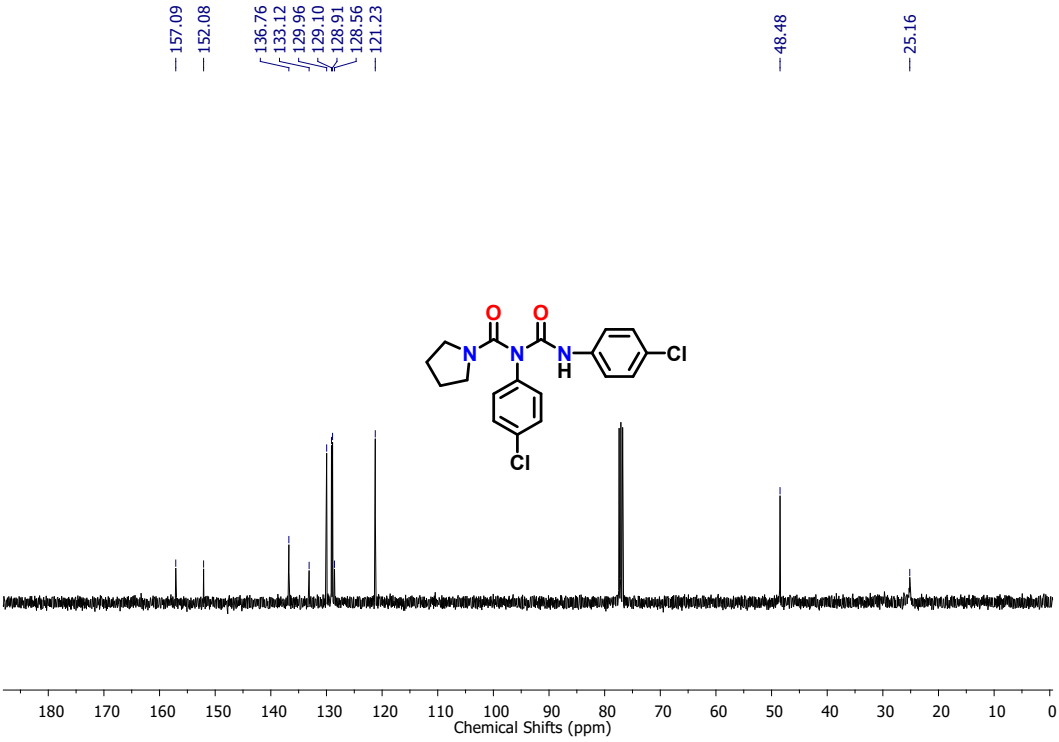


Figure FS65. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5h.**

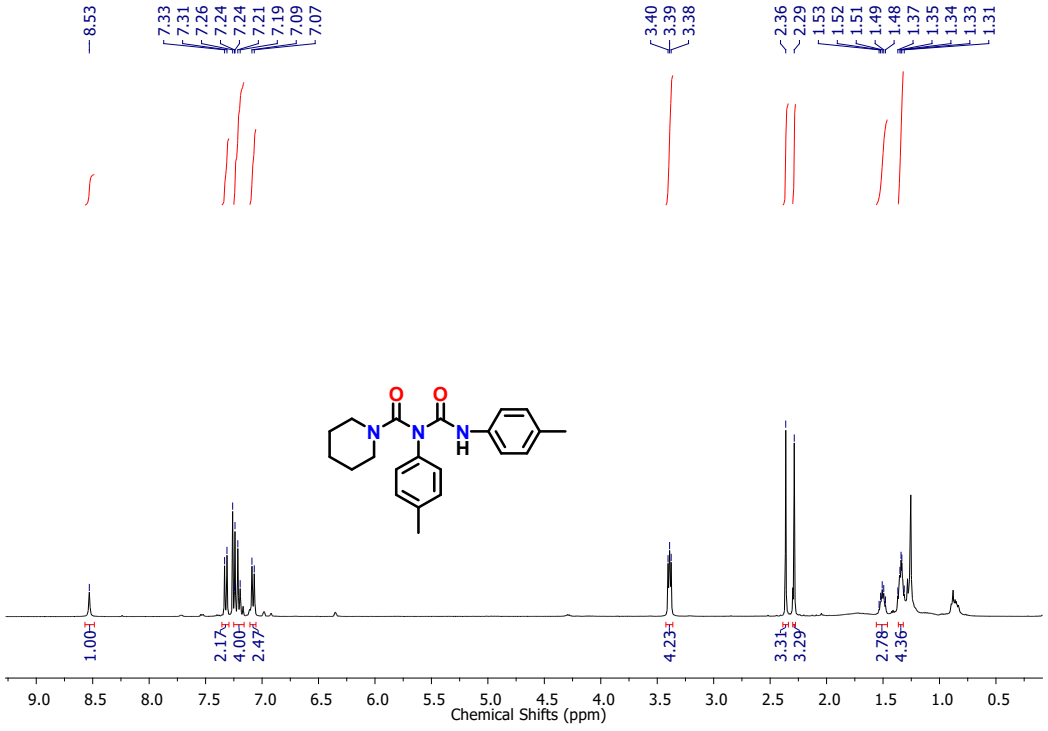


Figure FS66. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5i.**

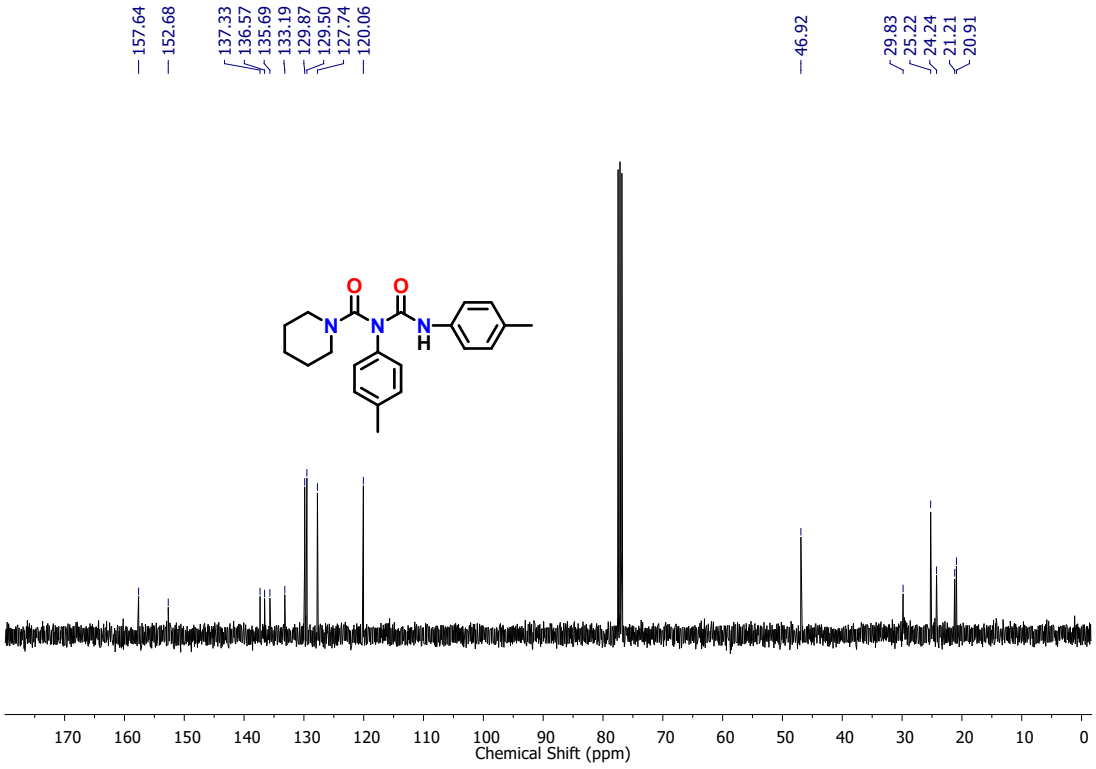


Figure FS67. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5i.**

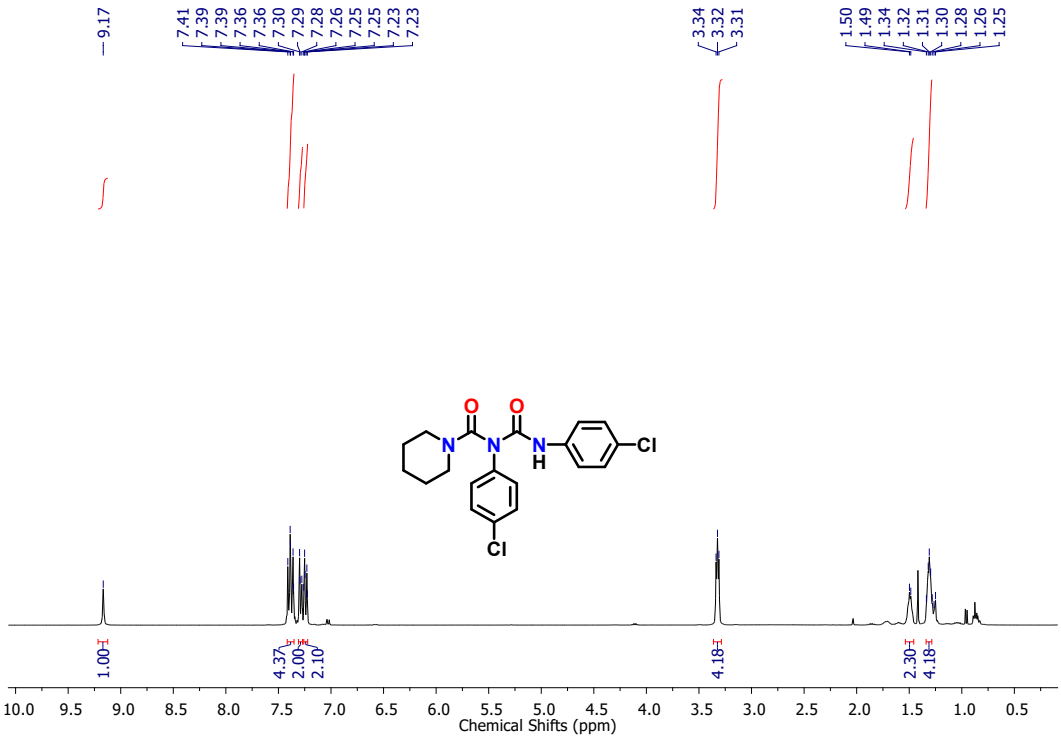


Figure FS68. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5j.**

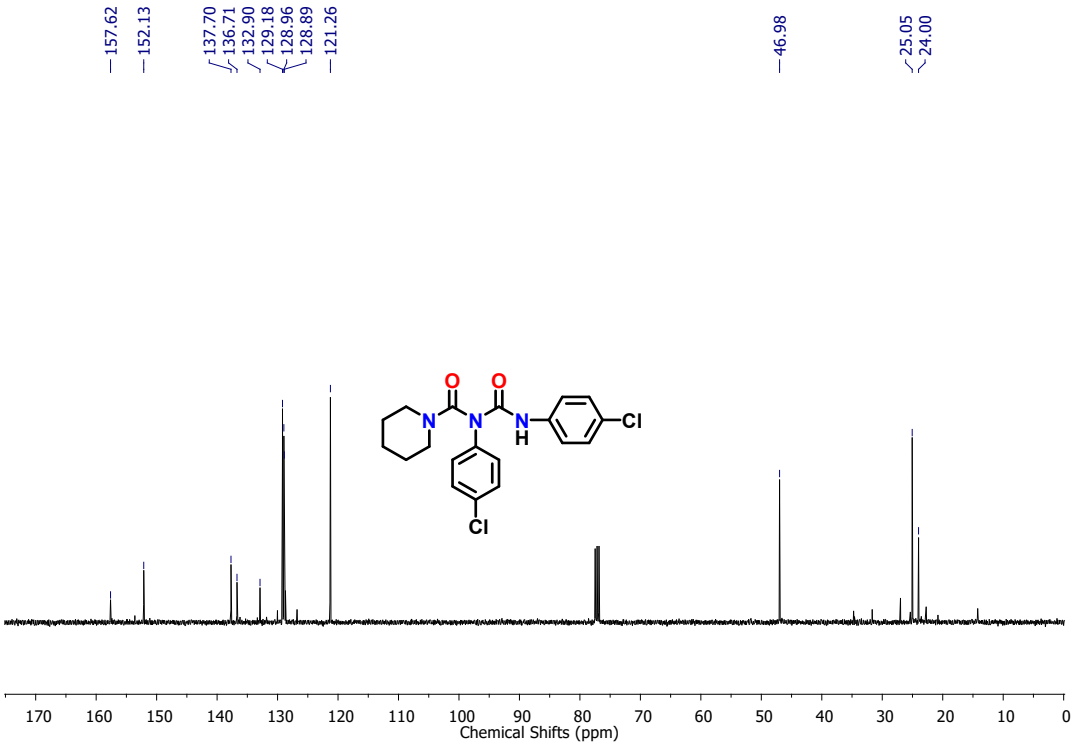


Figure FS69. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5j.**

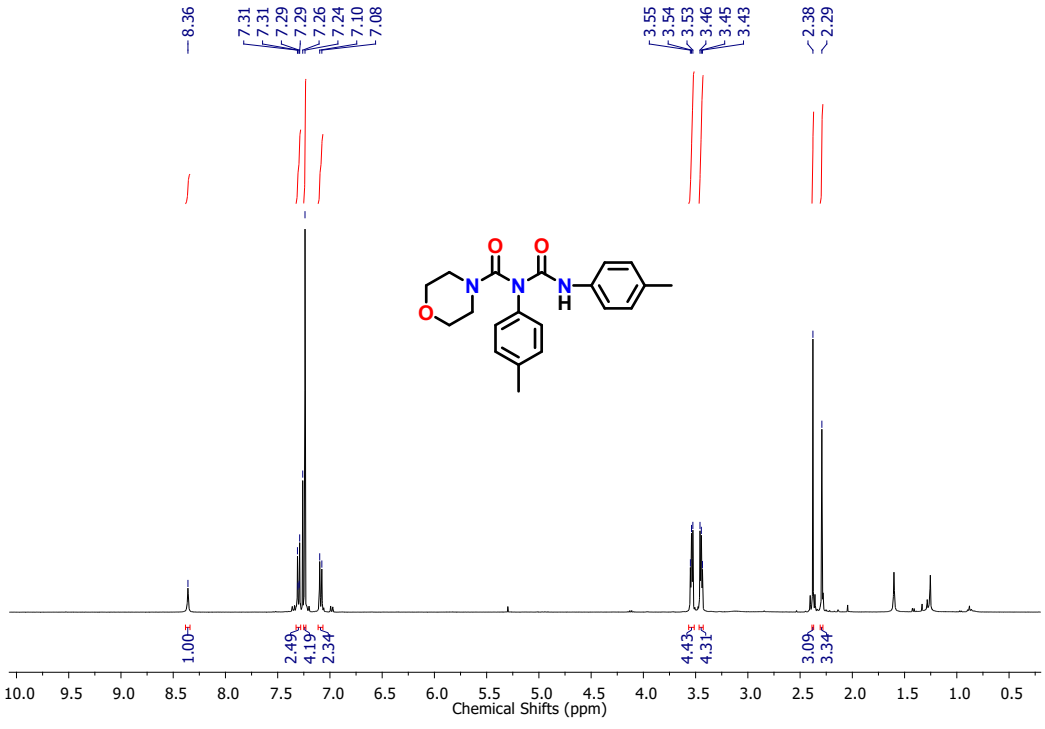


Figure FS70. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5k.**

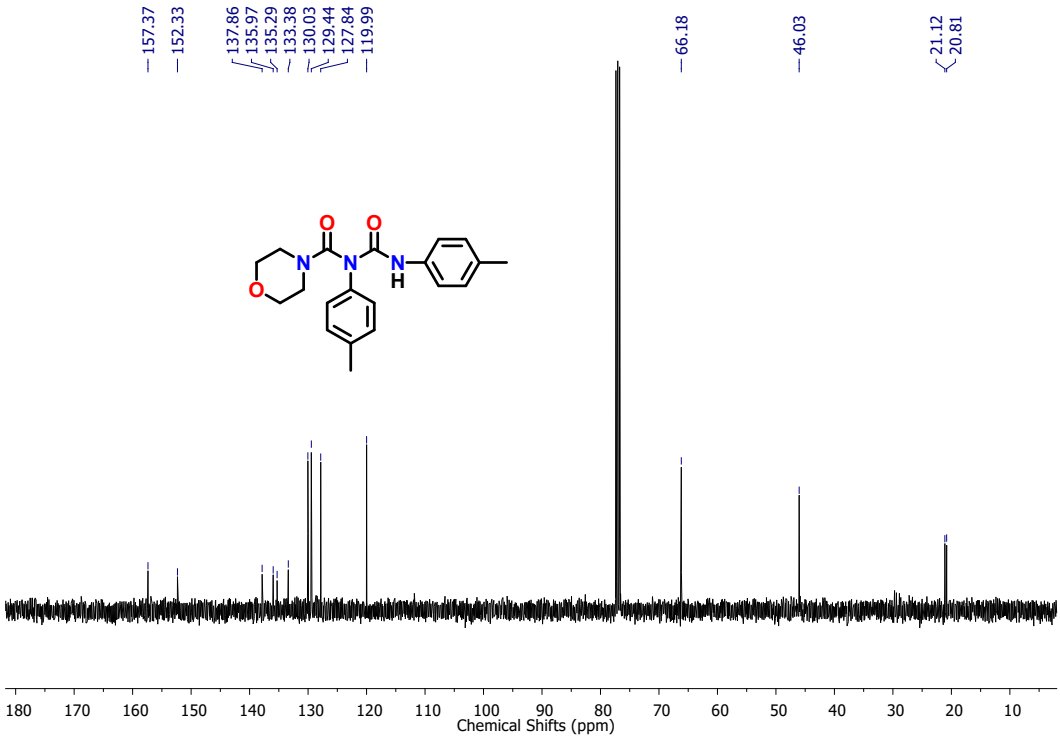


Figure FS71. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5k.**

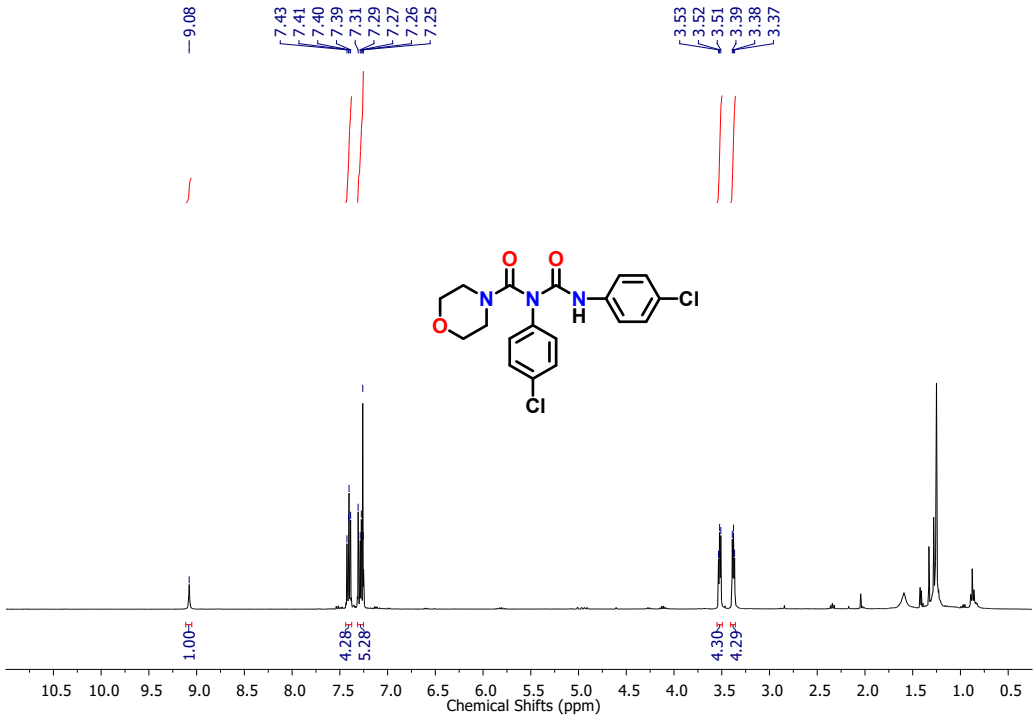


Figure FS72. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5l.**

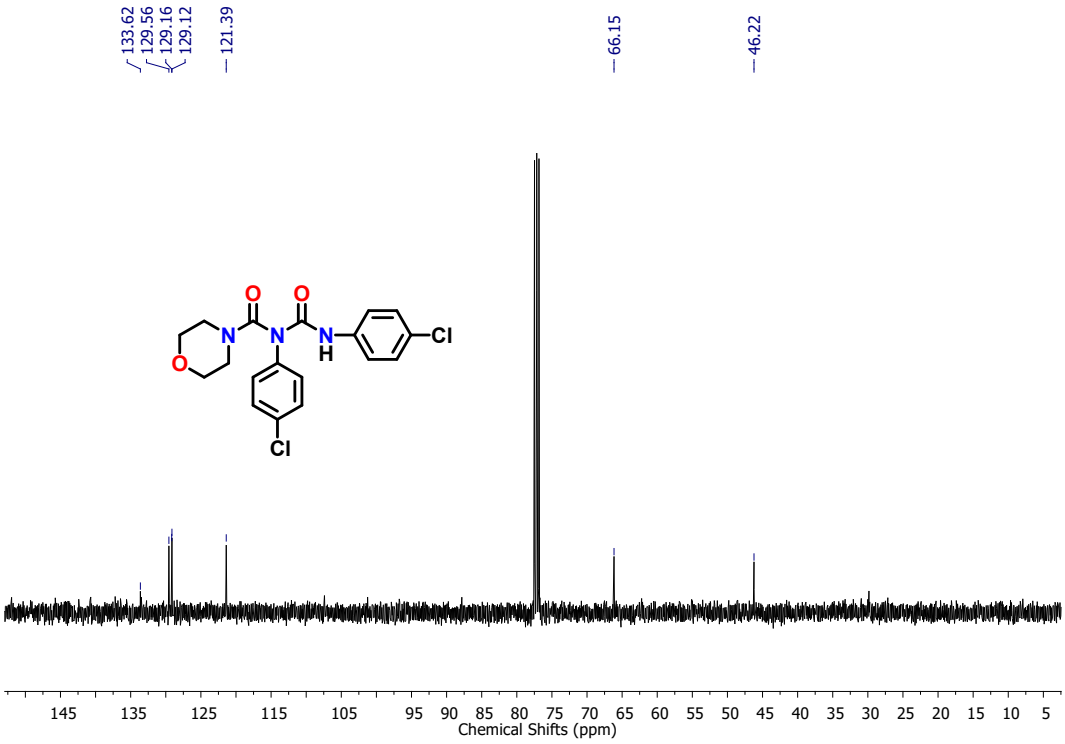


Figure FS73. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5l.**

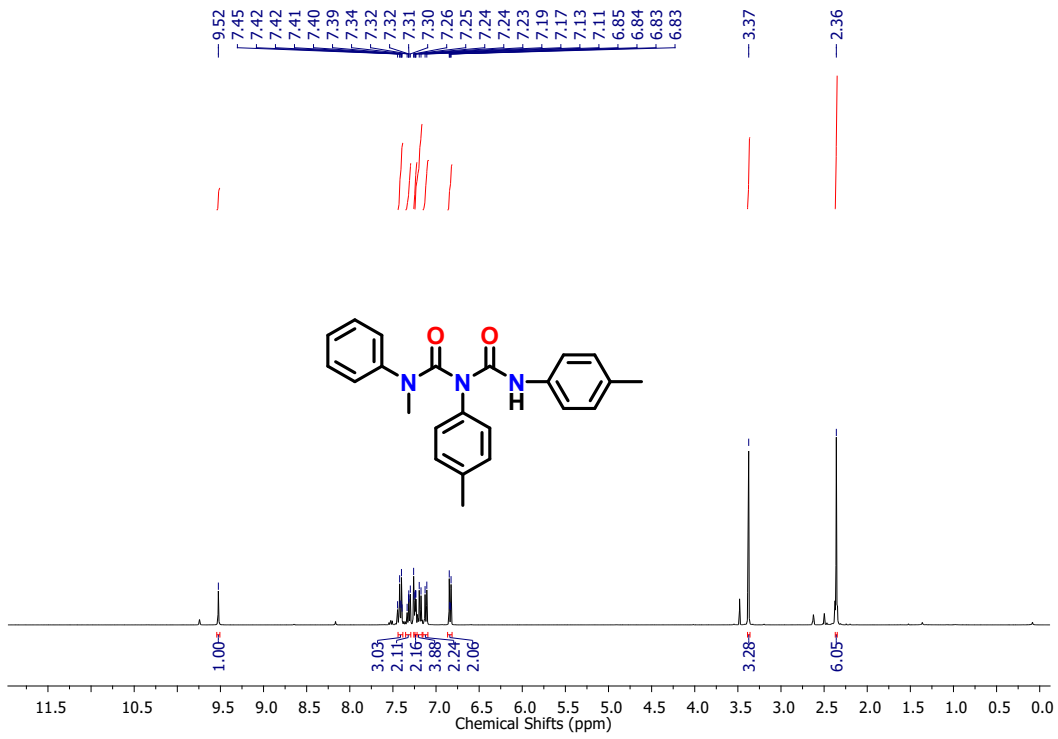


Figure FS74. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5m.**

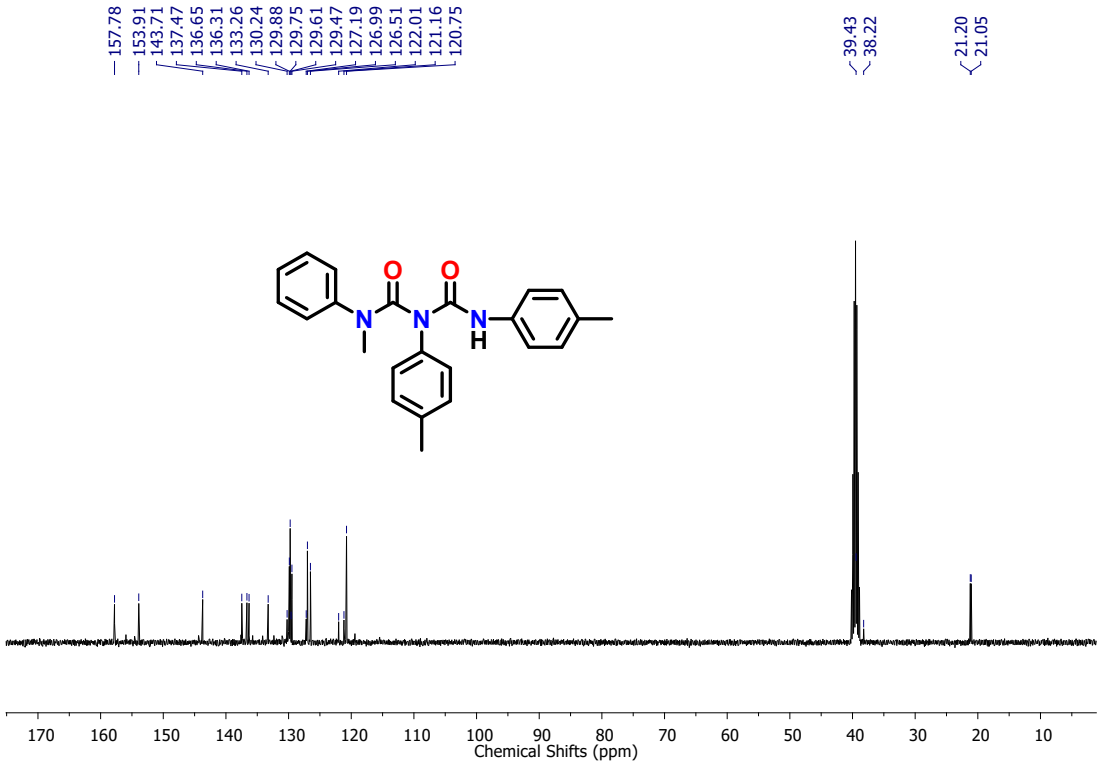


Figure FS75. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5m.**

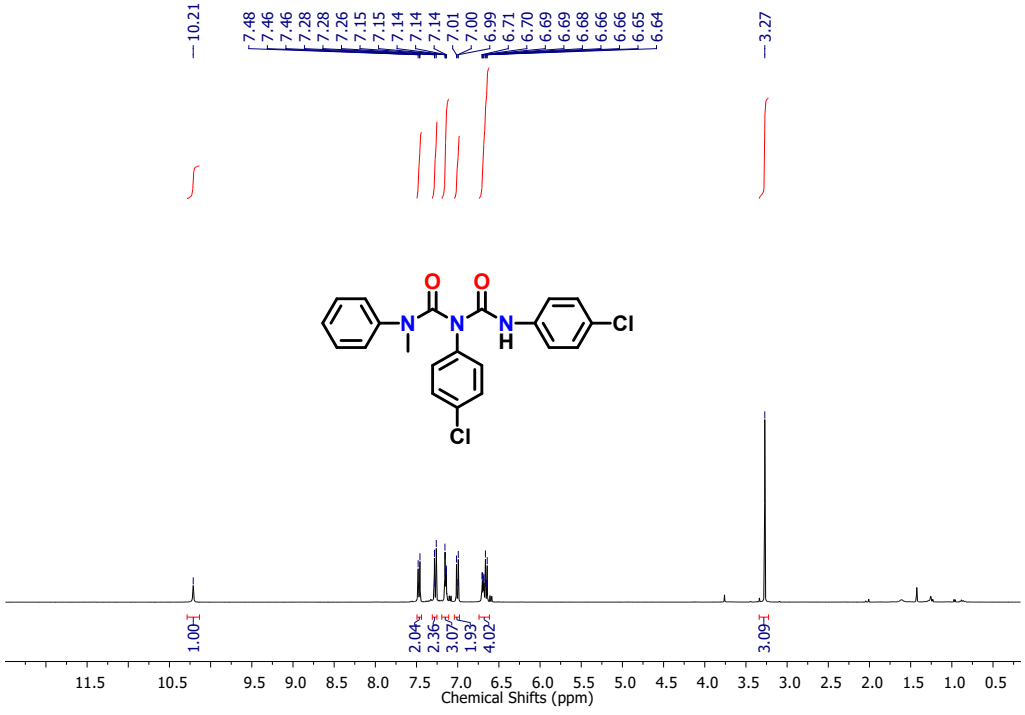


Figure FS76. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **5n.**

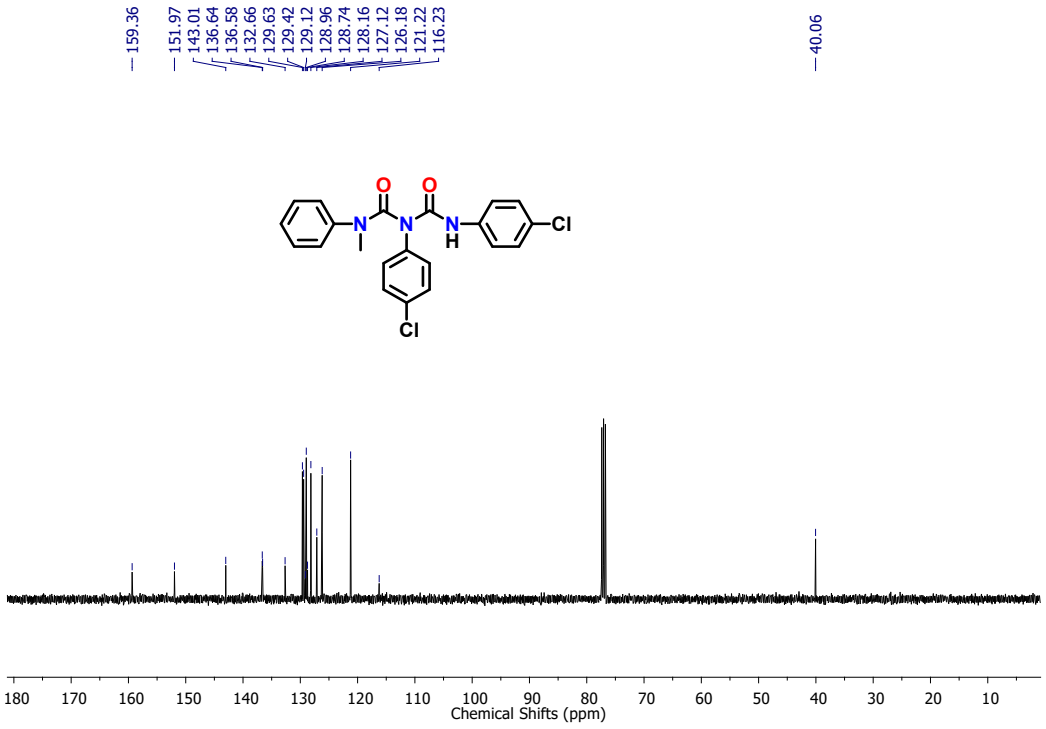
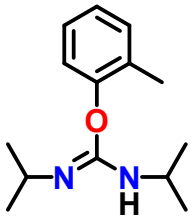


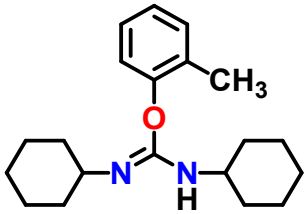
Figure FS77. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **5n.**

NMR data for isourea derivatives (6c-6s)



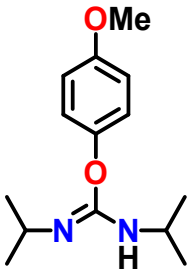
(6c)

Isolated yield: (82 mg, 92 %). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.20 – 7.13 (m, 1H, CH_{Ar}), 7.09 – 6.96 (m, 1H, CH_{Ar}), 6.94 (d, 1H, J = 7.9 Hz, CH_{Ar}), 6.78 (d, 1H, J = 6.8 Hz, CH_{Ar}), 5.76 (s, 1H, N*H*), 3.76 (s, 1H, C*H*), 3.57 (dt, 1H, J = 12.9 Hz, 6.5 Hz, C*H*), 2.26 (s, 3H, CH_3), 1.24 (d, 6H, J = 6.5 Hz, ^{i}pr), 1.11 (s, 6H, ^{i}pr) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 154.8 (*C*=N), 131.8 (C_{Ar}), 131.4 (C_{Ar}), 130.9 (C_{Ar}), 128.6 (C_{Ar}), 126.8 (C_{Ar}), 123.8 (C_{Ar}), 119.8 (C_{Ar}), 115.1 (C_{Ar}), 67.0 (*C*H), 53.2 (*C*H), 24.7 (CH_3), 23.8 (CH_3), 16.2 (*C*H$_3$) ppm. [10]



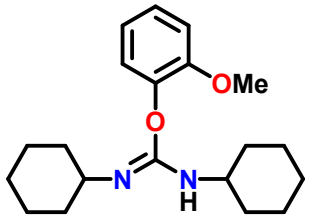
(6d)

Isolated yield: (106 mg, 88%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.11 (d, 1H, J = 8.3 Hz, CH_{Ar}), 6.94 (d, 1H, J = 8.1 Hz, CH_{Ar}), 6.80 (d, 1H, J = 8.5 Hz, CH_{Ar}), 6.63 (d, 1H, J = 8.4 Hz, CH_{Ar}), 3.25 (s, 1H, NH), 3.21 – 3.16 (m, 2H, CH), 2.17 (s, 2H, CH_2), 1.85 – 1.79 (m, 4H, CH_2), 1.67 – 1.63 (m, 4H, CH_2), 1.50 (dd, 2H, J = 8.0 Hz, 3.5 Hz, CH_2), 1.25 (dt, 10H, J = 11.4 Hz, 5.1 Hz, CH_2) ppm.^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 165.8 (C–O) 155.5 (C–N), 130.3 (C_{Ar}), 130.2 – 130.1 (C_{Ar}), 115.7 (C_{Ar}), 115.5 (C_{Ar}), 55.2 (CH), 34.9 (CH$_2$), 25.4 (CH$_2$), 25.0 (CH$_2$), 24.4 (CH$_2$), 20.5 (CH$_3$) ppm. [10]



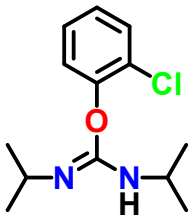
(6e)

Isolated yield: (89 mg, 94%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 6.95 – 6.91 (m, 2H, CH_{Ar}), 6.82 (d, 2H, J = 9.1 Hz, CH_{Ar}), 6.76 (s, 1H, NH), 3.75 (d, 5H, J = 1.8 Hz, OCH_3, and CH), 1.11 (d, 12H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 156.2 (C–O), 152.9 (C–N), 150.7 (C–O), 147.3 (C_{Ar}), 119.5 (C_{Ar}), 116.4 (C_{Ar}), 114.8 (C_{Ar}), 55.8 (OCH$_3$), 55.6 (CH), 45.3 (CH), 23.6 (CH_3) ppm. [10]



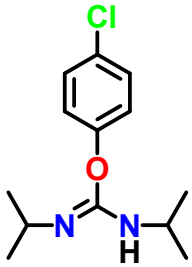
(6f)

Isolated yield: (114 mg, 90%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.47 – 7.45 (m, 1H, CH_{Ar}), 7.36 – 7.32 (m, 1H, CH_{Ar}), 6.97 – 6.90 (m, 2H, CH_{Ar}), 3.89 (s, 3H, OCH_3), 3.61 – 3.56 (m, 1H, CH), 1.79 (m, 1H, CH), 1.76 – 1.60 (m, 4H, CH_2), 1.59 – 1.57 (m, 4H, CH_2), 1.55 – 1.51 (m, 1H, CH_2), 1.34 – 1.25 (m, 6H, CH_2), 1.18 – 1.11 (m, 5H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 158.8 (*C*–O), 135.8 (*C*–N), 130.4 (C_{Ar}), 121.3 (C_{Ar}), 111.1 (C_{Ar}), 77.3 (C_{Ar}), 55.7 (O*C*H$_3$), 34.9 (*C*H), 33.6 (*C*H), 25.9 (*C*H$_2$), 25.5 (*C*H$_2$), 24.7 (CH_2) ppm. [10]



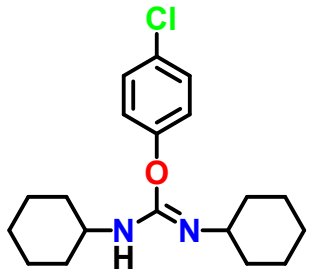
(6g)

Isolated yield: (86 mg, 89%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.35-7.33 (m, 1H, CH_{Ar}), 7.17 – 7.15 (m, 2H, CH_{Ar}), 6.94 (br.s, 1H, N*H*), 6.76-7.74 (m, 1H, CH_{Ar}), 3.51-3.44 (m, 2H, C*H*), 1.13 – 1.11 (d, 8H, CH_3), 0.99 – 0.95 (m, 4H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 156.5 (*C*–O), 129.3 (C_{Ar}), 122.5 (C_{Ar}), 117.2 (C_{Ar}), 66.3 (*C*H), 48.4 (*C*H), 34.9 (*C*H), 24.6 (*C*H$_3$) ppm. [10]



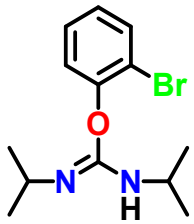
(6h)

Isolated yield: (86 mg, 89%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.32 (dd, 1H, CH_{Ar}), 7.20 – 7.08 (m, 1H, CH_{Ar}), 6.98 (ddd, 1H, J = 26.8 Hz, 8.0 Hz, 1.4 Hz, CH_{Ar}), 6.81 (td, 1H, J = 7.9 Hz, 1.4 Hz, CH_{Ar}), 5.83 (s, 1H, N*H*), 3.71 (tt, 1H, J =9.8 Hz, 4.9 Hz, C*H*), 3.57 (dq, 1H, J = 12.9 Hz, 6.4 Hz, C*H*), 1.22 (d, 6H, J = 6.4 Hz, CH_3), 1.13 (d, 6H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 152.4 (*C*–N), 131.8 (C_{Ar}), 130.6 (C_{Ar}), 129.3 (C_{Ar}), 128.2 (C_{Ar}), 127.9 (C_{Ar}), 124.8 (C_{Ar}), 120.7 (C_{Ar}), 120.4 (C_{Ar}), 116.7 (C_{Ar}), 49.1 (*C*H), 45.4 (*C*H), 24.8 (CH_3), 23.8 (CH_3) ppm. [10]



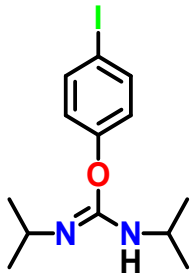
(6i)

Isolated yield: (113 mg, 88%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.37 (d, 1H, J = 8.9 Hz, CH_{Ar}), 7.21 – 7.15 (m, 1H, CH_{Ar}), 6.93 (d, 1H, J = 8.8 Hz, CH_{Ar}), 6.80 – 6.73 (m,1H, CH_{Ar}), 3.34 (s, 1H, N*H*), 3.28 – 3.14 (m, 2H, C*H*), 1.87 – 1.78 (m, 2H, CH_2), 1.72 – 1.61 (m, 6H, CH_2), 1.50 (dd, 2H, J = 7.2 Hz, 4.1 Hz, CH_2), 1.24 (dd, 5H, J = 8.0 Hz, 4.6 Hz, CH_2), 1.14 (d, 5H, J = 7.6 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 156.3 (*C*=N), 144.3 (*C*–O), 129.5 (C_{Ar}), 129.1 (C_{Ar}), 117.1 (C_{Ar}), 116.9 (C_{Ar}), 54.7 (*C*H), 34.5 (*C*H$_2$), 25.5 (*C*H$_2$), 24.9 (*C*H$_2$), 24.2 (*C*H$_2$), 24.04 (*C*H$_2$) ppm. [10]



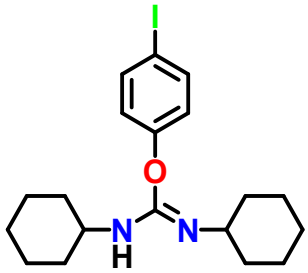
(6j)

Isolated yield: (100 mg, 88%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.47 – 7.44 (m, 1H, CH_{Ar}), 7.17 (d, 1H, J = 7.2 Hz, CH_{Ar}), 6.99 – 6.97 (m, 1H, CH_{Ar}), 6.77 (s, 1H, CH_{Ar}), 6.03 (s, 1H, N*H*), 3.71 (m, 2H, C*H*), 1.14 (d, 12H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 153.1 (*C*–O), 150.7 (*C*–N), 133.7 (C_{Ar}), 129.1 (C_{Ar}), 121.3 (C_{Ar}), 116.5 (C_{Ar}), 110.6 (C_{Ar}), 67.0 (C_{Ar}),53.2 (*C*H), 45.6 (*C*H), 24.7 (CH_3), 23.7 (CH_3) ppm. [10]



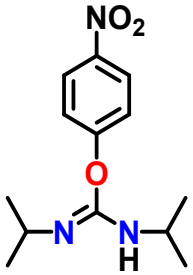
(6k)

Isolated yield: (115 mg, 87%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.56 (d, 1H, J = 8.9 Hz, CH_{Ar}), 7.42 (d, 1H, J = 8.8 Hz, CH_{Ar}), 6.77 – 6.74 (m, 1H, CH_{Ar}), 6.74 (d, 1H, J = 3.1 Hz, N*H*), 6.55 – 6.52 (m, 1H, CH_{Ar}), 3.70 – 3.53 (m, 2H, C*H*), 1.23 (d, 3H, J = 6.5 Hz, CH_3), 1.11 (d, 9H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 157.3 (*C*–O), 154.1 (*C*–N), 149.7 (C_{Ar}), 138.7 (C_{Ar}), 138.2 (C_{Ar}) 120.2 (C_{Ar}), 118.5 (C_{Ar}), 86.9 (C_{Ar}), 80.8 (C_{Ar}), 49.2 (*C*H), 45.5 (*C*H), 24.7 (CH_3), 23.7 (CH_3) ppm. [10]



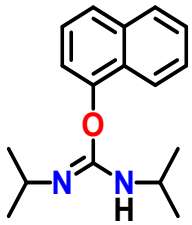
(6l)

Isolated yield: (139 mg, 85%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.64 (d, 1H, J = 8.2 Hz, CH_{Ar}), 7.45 (d, 1H, J = 8.5 Hz, CH_{Ar}), 6.76 (d, 1H, J = 8.2 Hz, CH_{Ar}), 6.61 (d, 1H, J = 8.5 Hz, CH_{Ar}), 3.34 (s, 1H, N*H*), 3.20 (d, 2H, J = 9.4 Hz, C*H*), 1.82 (d, 2H, J = 5.8 Hz, CH_2), 1.63 (d, 6H, J = 9.2 Hz, CH_2), 1.50 (s, 2H, CH_2), 1.24 (d, 5H, J = 7.3 Hz, CH_2), 1.13 (s, 5H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 157.3 (*C*=N), 138.2 (C_{Ar}), 137.8 (C_{Ar}), 118.2 (C_{Ar}), 118.0 (C_{Ar}), 80.6 (C_{Ar}–I), 54.6 (*C*H), 34.5 (*C*H$_2$), 25.4 (*C*H$_2$), 24.9 (*C*H$_2$), 24.7 (*C*H$_2$), 24.0 (*C*H$_2$) ppm. [10]



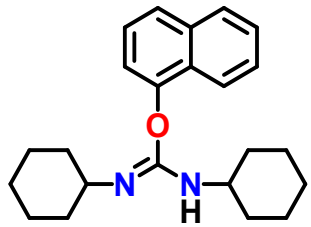
(6m)

Isolated yield: (86 mg, 85%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 8.10 (s, 2H, CH_{Ar}), 6.90 (s, 2H, CH_{Ar}), 3.89 – 3.59 (m, 1H, N*H*), 3.50 (dt, 2H, J = 12.8 Hz, 6.4 Hz, C*H*), 1.14 (d, 12H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 164.3 (*C*–O), 139.3 (C_{Ar}), 126.2 (C_{Ar}), 115.8 (C_{Ar}), 48.2 (*C*H), 24.5 (CH_3) ppm. [10]



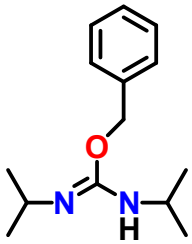
(6n)

Isolated yield: (85 mg, 83%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.18 (d, 1H, J = 7.0 Hz, CH_{Ar}), 7.71 (ddd, 1H, J = 21.4 Hz, 11.6 Hz, 4.3 Hz, CH_{Ar}), 7.37 – 7.31 (m, 2H, CH_{Ar}), 7.19 – 7.13 (m, 1H, CH_{Ar}), 6.95 (d, 1H, J = 7.5 Hz, CH_{Ar}), 6.75 (d, 1H, J = 7.2 Hz, CH_{Ar}), 3.71 (dt, 2H, J = 12.7 Hz, 6.3 Hz, N*H* and C*H*), 3.52 – 3.42 (m, 1H, C*H*), 1.13 (d, 6H, J = 6.5 Hz, CH_3), 1.02 (d, 6H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 153.3 (*C*–O), 149.9 (*C*=N), 134.9 (C_{Ar}), 129.1 (C_{Ar}), 127.9 (C_{Ar}), 126.8 (C_{Ar}), 126.1 (C_{Ar}), 124.6 (C_{Ar}), 123.7 (C_{Ar}), 122.5 (C_{Ar}), 110.9 (C_{Ar}), 108.7 (C_{Ar}), 49.2 (*C*H), 45.5 (*C*H), 24.7 (*C*H$_3$), 23.7 (*C*H$_3$) ppm. [10]



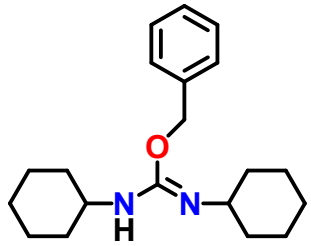
(6o)

Isolated yield: (105 mg, 78%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 8.13 (dd, 1H, J = 8.5 Hz, 4.3 Hz, CH_{Ar}), 7.90 – 7.78 (m, 1H, CH_{Ar}), 7.58 – 7.54 (m, 1H, CH_{Ar}), 7.51 – 7.42 (m, 2H, CH_{Ar}), 7.33 – 7.28 (m, 1H, CH_{Ar}), 6.89 (dd, 1H, J = 24.2 Hz, 7.3 Hz, CH_{Ar}), 3.28 (s, 2H, N*H* and C*H*), 3.17 (s, 1H, C*H*), 1.85 – 1.69 (m, 4H, CH_2), 1.64 (t, 4H, J = 10.4 Hz, CH_2), 1.49 (d, 2H, J = 15.3 Hz, CH_2), 1.26 – 1.07 (m, 10H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 153.7 (*C*=N), 151.8 (*C*–O), 134.8 (C_{Ar}), 127.8 (C_{Ar}), 126.8 (C_{Ar}), 126.5 (C_{Ar}), 124.9 (C_{Ar}), 122.4 (C_{Ar}), 118.7 (C_{Ar}), 108.5 (C_{Ar}), 55.2 (*C*H), 34.9 (*C*H), 25.9 (*C*H$_2$), 25.4 (*C*H$_2$), 25.0 (*C*H$_2$), 24.5 (*C*H$_2$) ppm. [10]



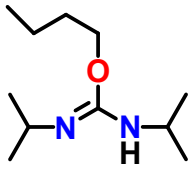
(6p)

Isolated yield: (77 mg, 86%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.38 (s, 3H, CH_{Ar}), 7.35 (s, 1H, CH_{Ar}), 7.31 (dd, 1H, J = 4.9 Hz, 1.8 Hz, CH_{Ar}), 5.11 (s, 1H, NH), 4.57 (s, 2H, CH_2), 3.85 (dd, 1H, J = 12.3 Hz, 5.6 Hz, CH), 3.56 (dt, 1H, J = 12.8 Hz, 6.4 Hz, CH), 1.23 (d, 6H, J = 6.4 Hz, CH_3), 1.15 – 1.13 (m, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 138.3 (C=N), 128.4 (C_{Ar}), 127.9 (C_{Ar}), 127.5 (C_{Ar}), 66.8 (CH$_2$), 49.1 (CH), 46.4 (CH), 24.4 (CH$_3$), 23.6 (CH$_3$) ppm. [10]



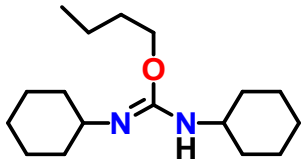
(6q)

Isolated yield: (97 mg, 81%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.35 (dd, 5H, J =8.5 Hz, 4.3 Hz, CH_{Ar}), 5.58 (d, 1H, J = 8.0 Hz, NH), 5.00 (s, 2H, CH), 4.53 (s, 2H, CH_2), 1.75 – 1.70 (m, 2H, CH_2), 1.68 – 1.58 (m, 6H, CH_2), 1.52 (s, 2H, CH_2), 1.25 – 1.05 (dd, 10H, J = 15.9 Hz, 10.4 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 153.7 (C=N), 138.8 (C_{Ar}), 128.7 (C_{Ar}), 127.9 (C_{Ar}), 71.8 (CH$_2$–O), 34.9 (CH$_2$), 33.8 (CH$_2$), 25.7 (CH$_2$), 24.9 (CH$_2$) ppm. [10]



(6r)

Isolated yield: (73 mg, 96%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 4.83 (d, 1H, J = 8.1 Hz, N*H*), 4.32 (t, 1H, J = 5.0 Hz, CH_2), 3.87 (t, 1H, J = 6.4 Hz, CH_2), 3.50 (dt, 1H, J = 12.8 Hz, 6.4 Hz, C*H*), 3.38 (dd, 2H, J = 11.4 Hz, 6.3 Hz, C*H*), 1.38 (dd, 4H, J = 9.0 Hz, 4.3 Hz, CH_2), 1.15 (d, 8H, J = 6.4 Hz, CH_3), 1.05 (d, 2H, J = 6.5 Hz, CH_3), 0.94 (d, 2H, J = 6.1 Hz, CH_3), 0.87 (d, 3H, J = 7.3 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 150.7 (*C*=N), 60.4 (*C*H$_2$), 48.1 (*C*H), 44.5 (*C*H), 42.7 (*C*H$_2$), 34.7 (*C*H$_2$), 30.7 (*C*H$_2$), 24.7 (*C*H$_3$), 23.4 (*C*H$_3$), 18.9 (*C*H$_2$), 13.8 (*C*H$_3$) ppm. [10]



(6s)

Isolated yield: (102 mg, 95%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 4.79 (d, 1H, J = 8.2 Hz, N*H*), 3.87 (t, 2H, J = 6.5 Hz, CH_2), 3.21 – 3.16 (m, 3H, CH_2 and C*H*), 3.09 – 2.90 (m, 1H, C*H*), 1.84 – 1.80 (m, 4H, CH_2), 1.68 – 1.64 (m, 6H, CH_2), 1.53 – 1.49 (m, 4H, CH_2), 1.28 – 1.24 (m, 6H, CH_2), 1.18 (dd, 5H, J = 8.2 Hz, 4.0 Hz, CH_2), 0.88 (t, 3H, J = 7.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 150.7 (*C*=N), 139.4 (*C*–O), 63.8 (*C*H), 55.2 (*C*H), 52.7 (*C*H$_2$), 50.7 (*C*H$_2$), 34.9 (*C*H$_2$), 34.1 (*C*H$_2$), 31.1 (*C*H$_2$), 26.3 (*C*H$_2$), 25.8 (*C*H$_2$), 25.5 (*C*H$_2$), 24.9 (*C*H$_2$), 24.5 (*C*H$_2$), 19.4 (*C*H$_2$), 14.2 (*C*H$_3$) ppm. [10]

NMR Spectra of Isourea Derivatives.

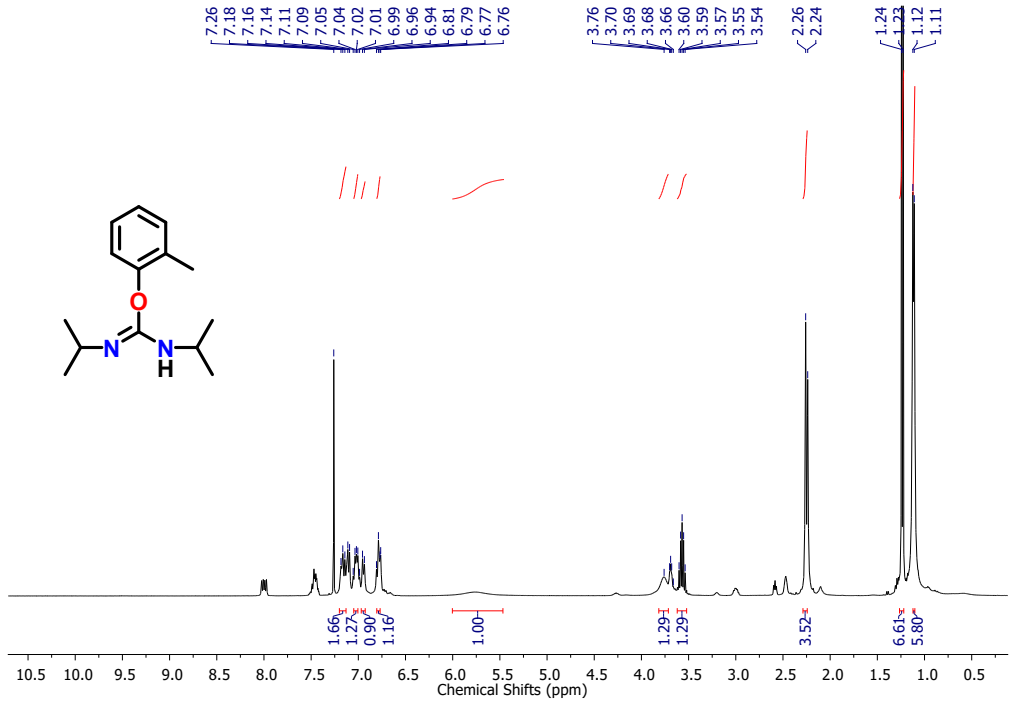


Figure FS78. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6c.**

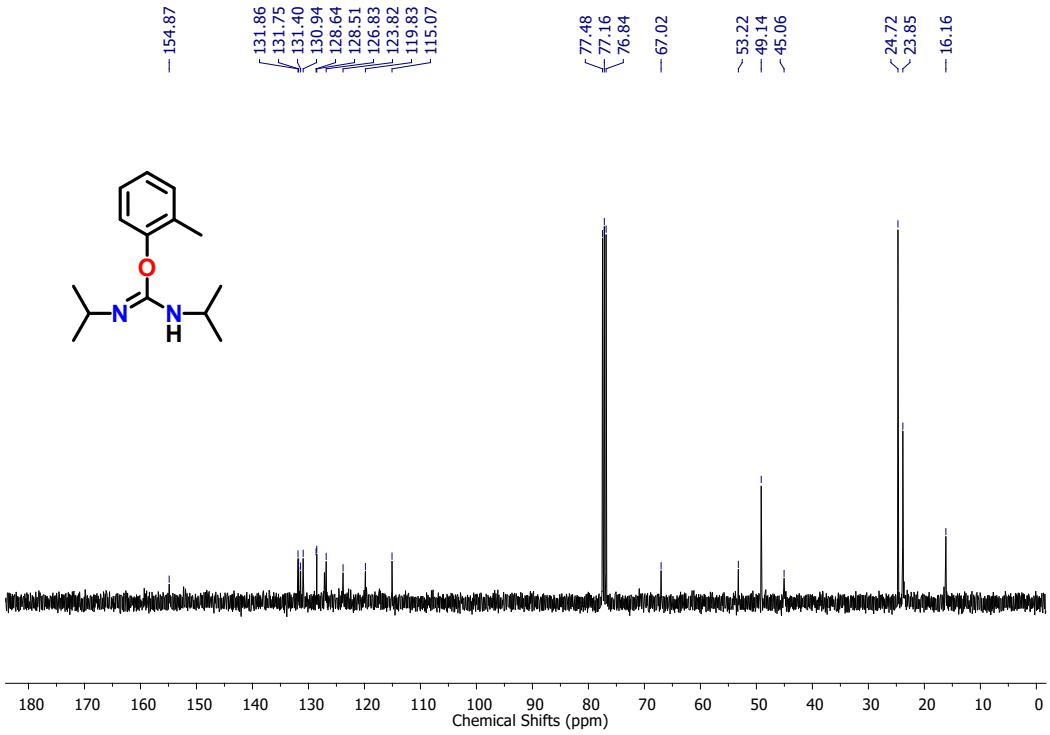


Figure FS79. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6c.**

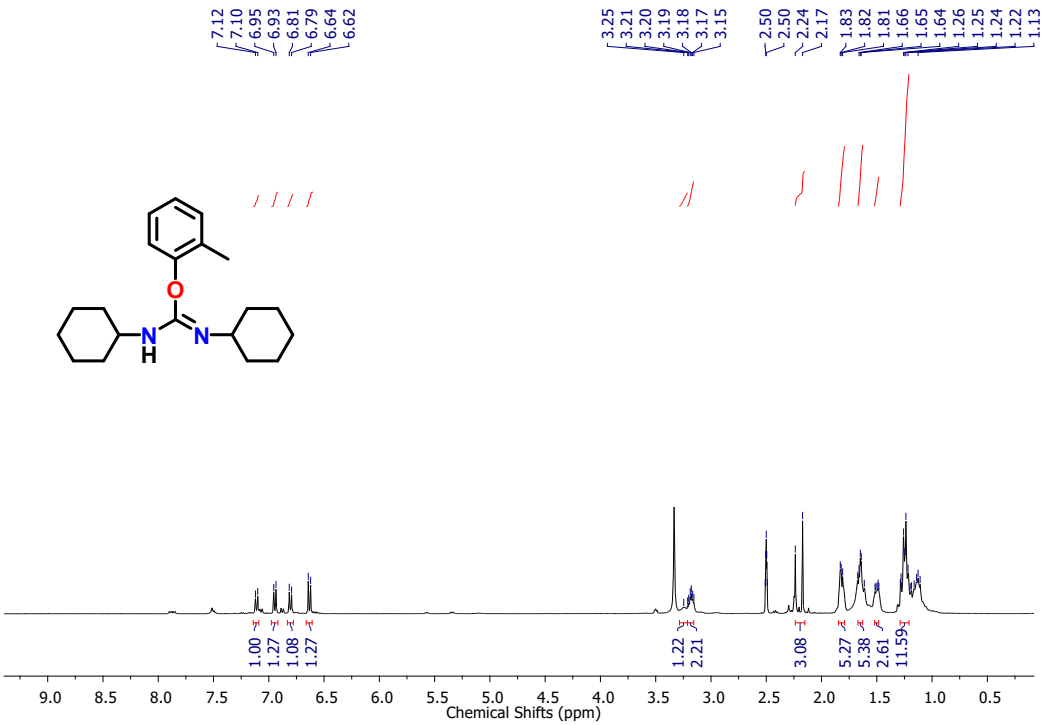


Figure FS80. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6d.**

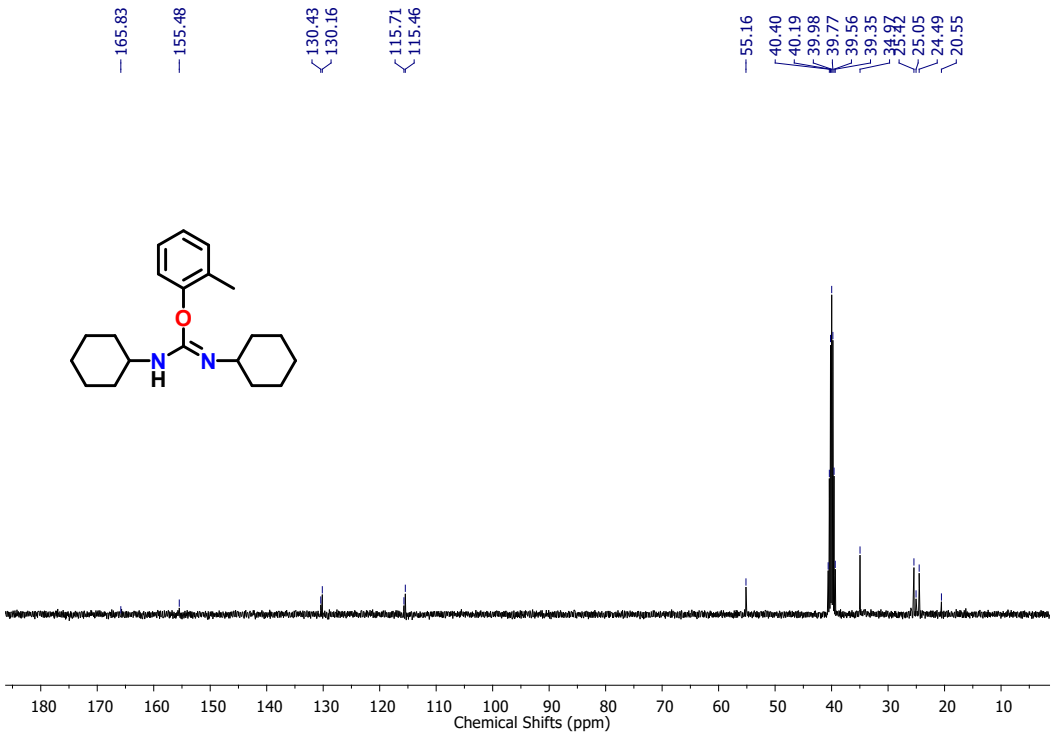


Figure FS81. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6d.**

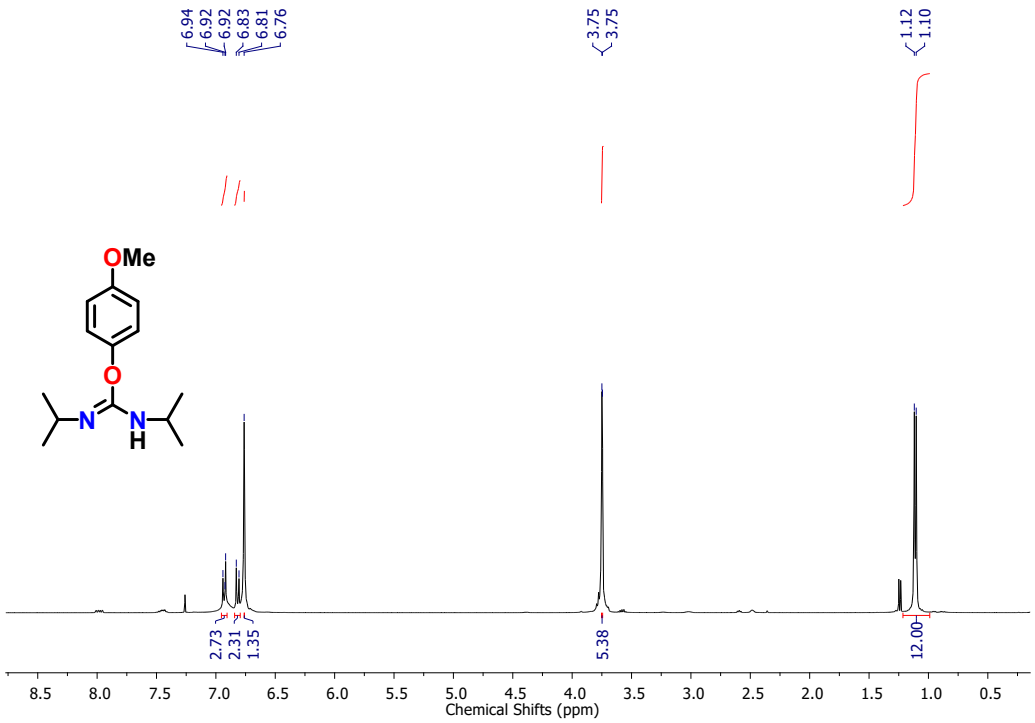


Figure FS82. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6e.**

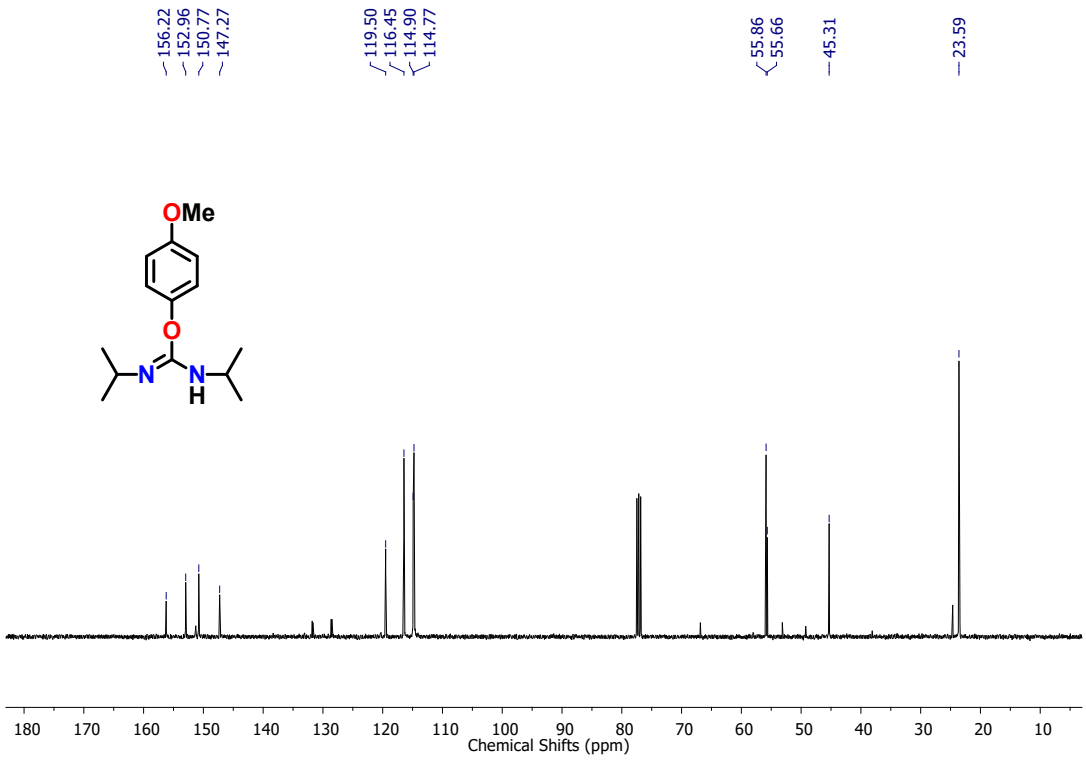


Figure FS83. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6e.**

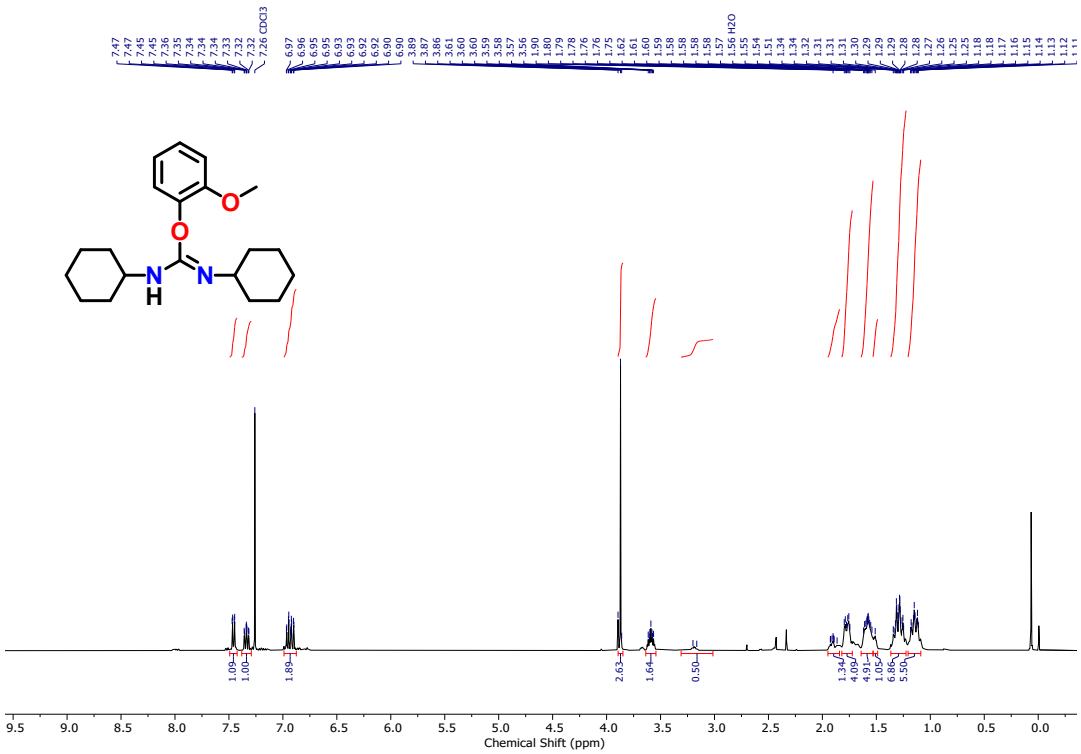


Figure FS84. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6f.**

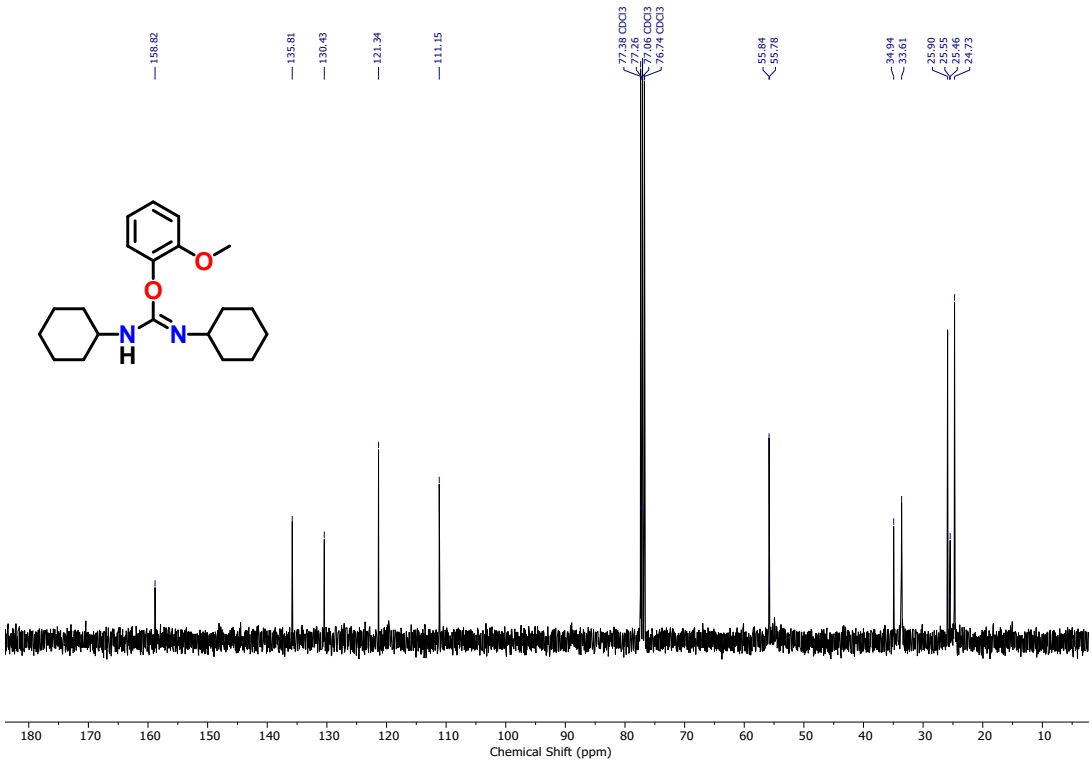


Figure FS85. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6f.**

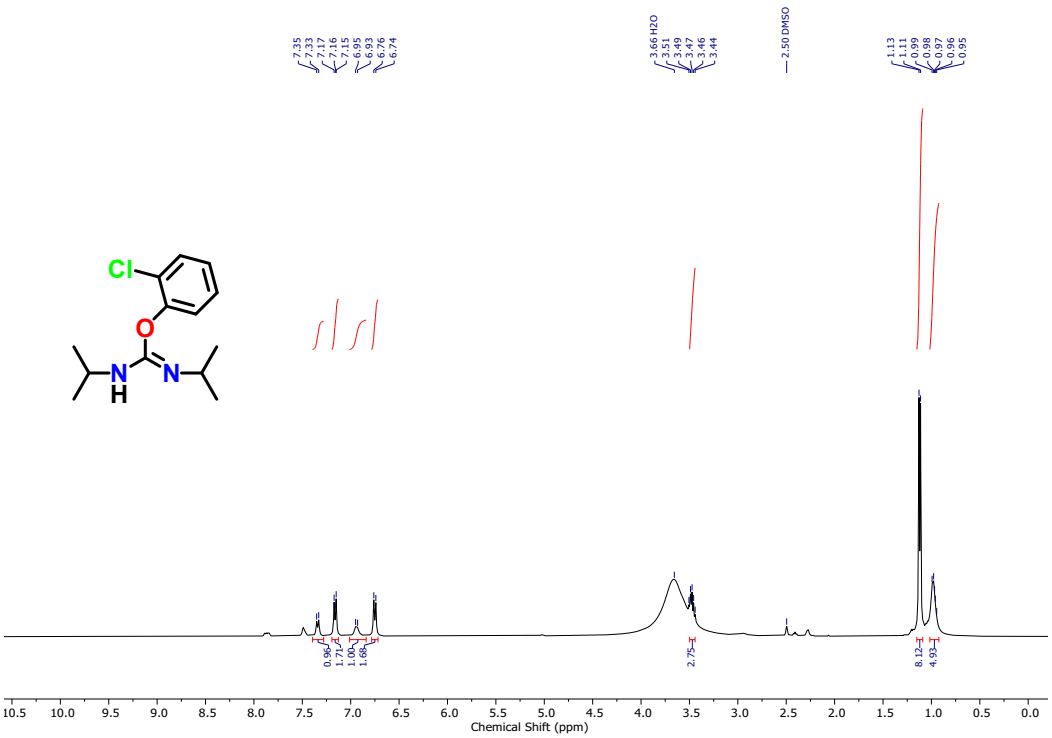


Figure FS86. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6g.**

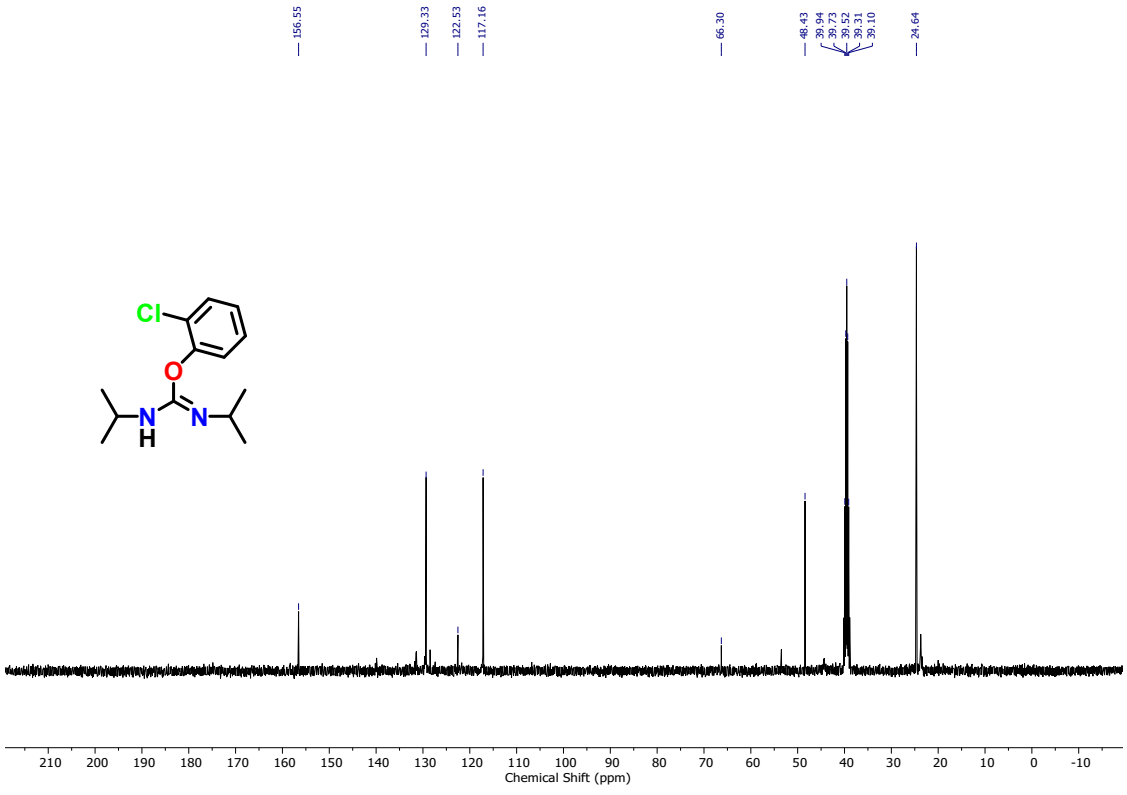


Figure FS87. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6g.**

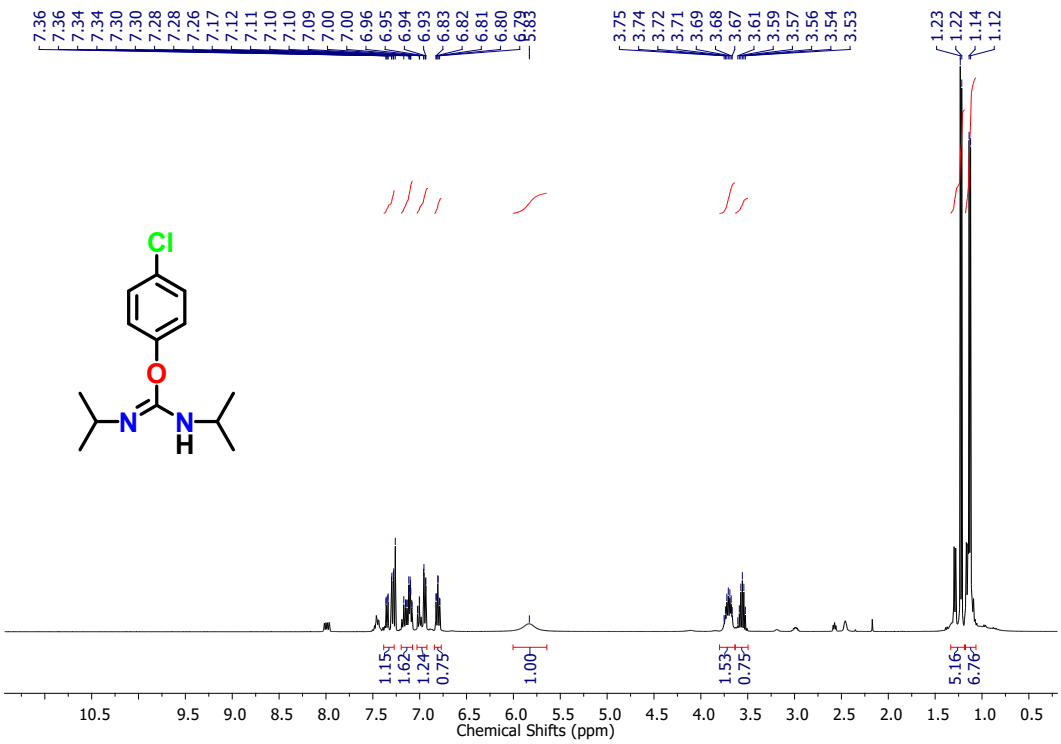


Figure FS88. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6h.**

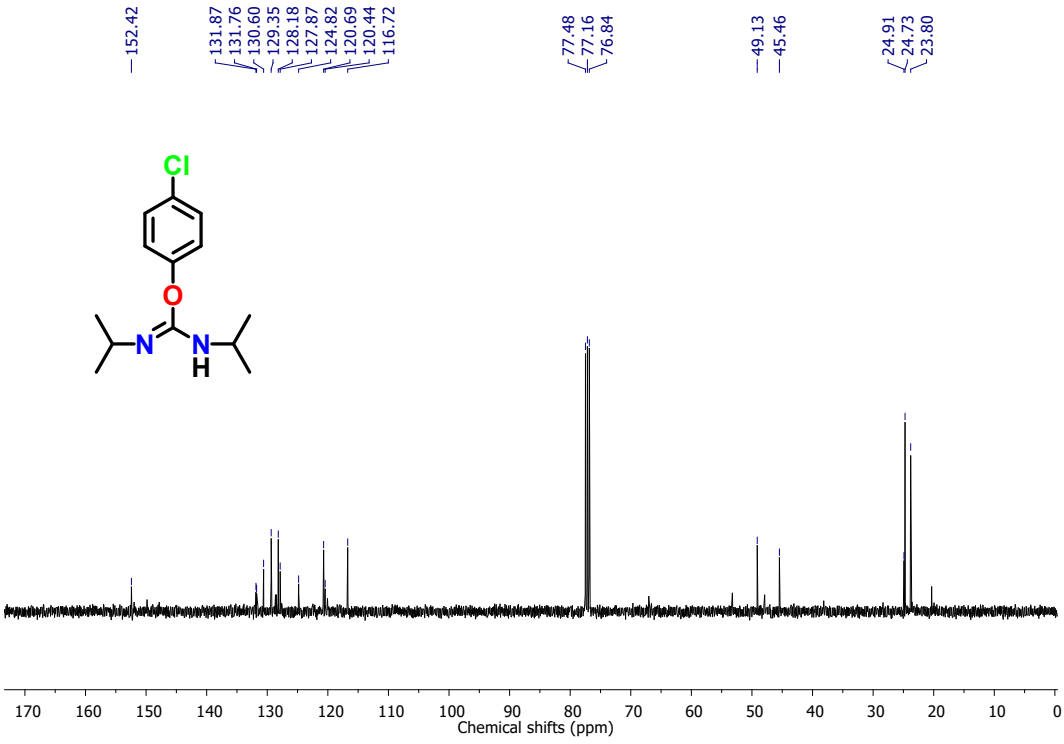


Figure FS89. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6h.**

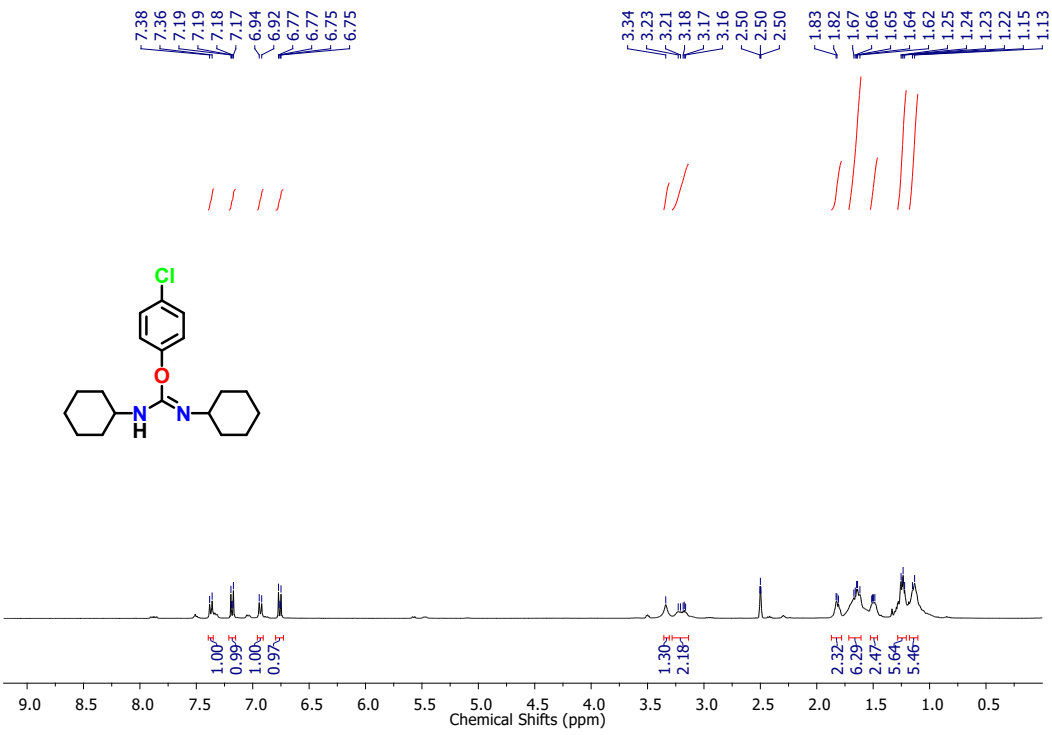


Figure FS90. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6i.**

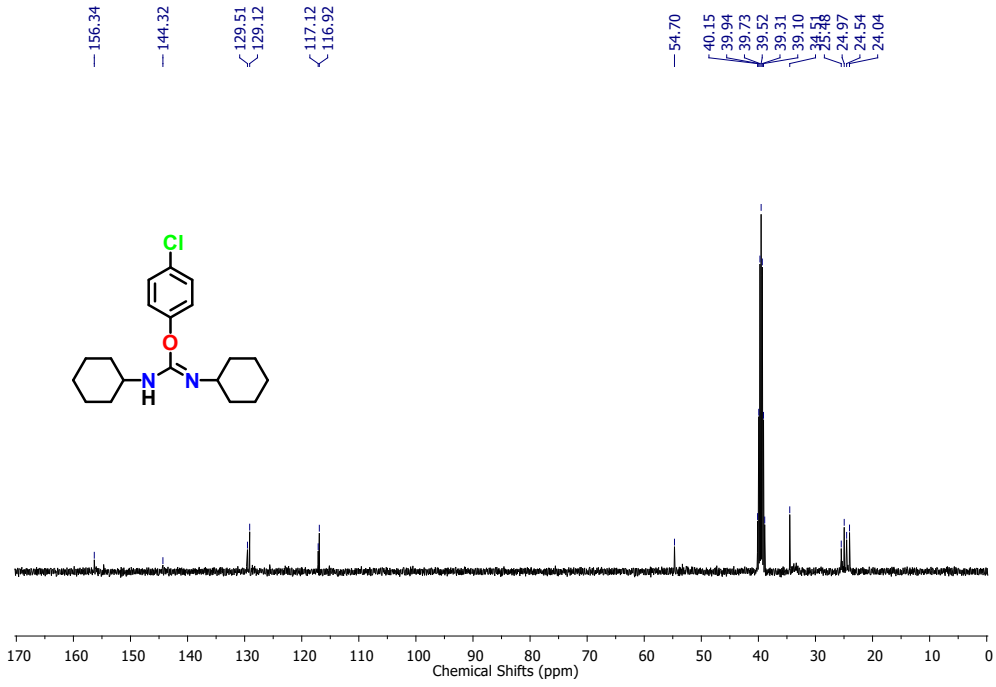


Figure FS91. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6i.**

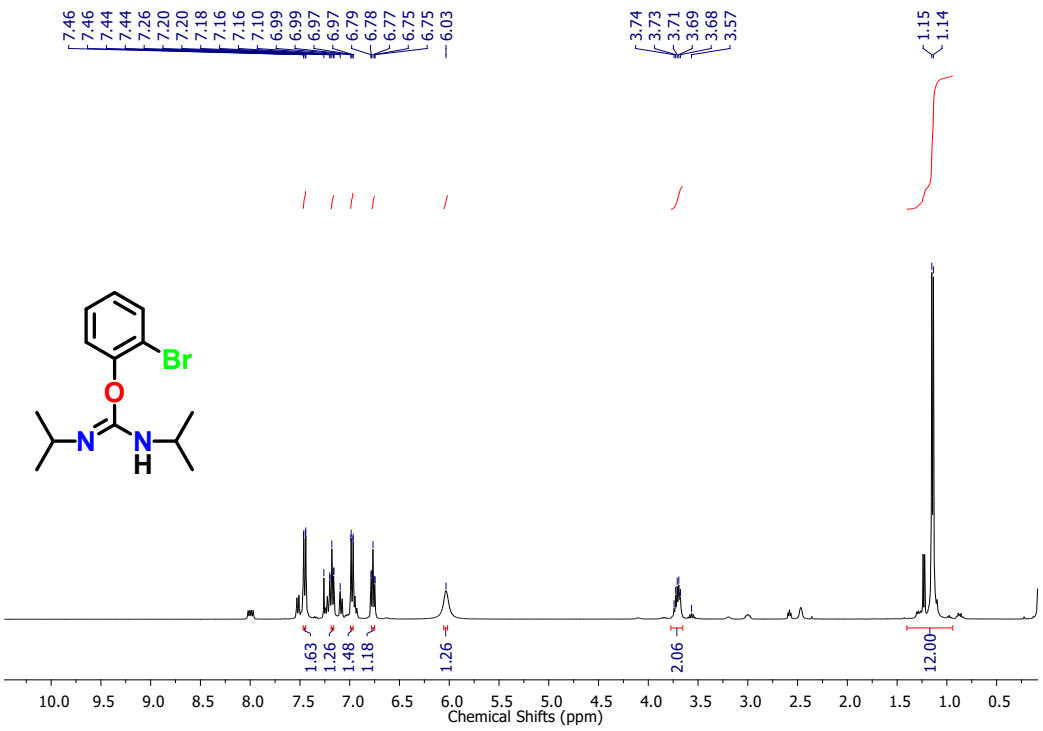


Figure FS92. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6j.**

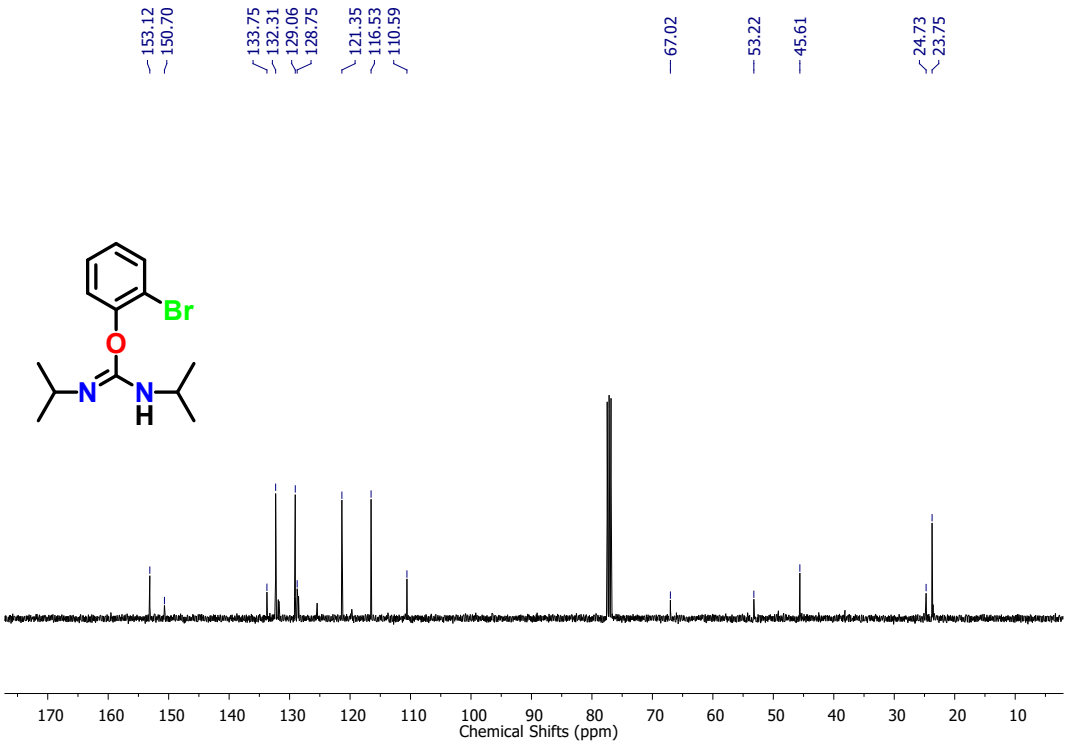


Figure FS93. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6j.**

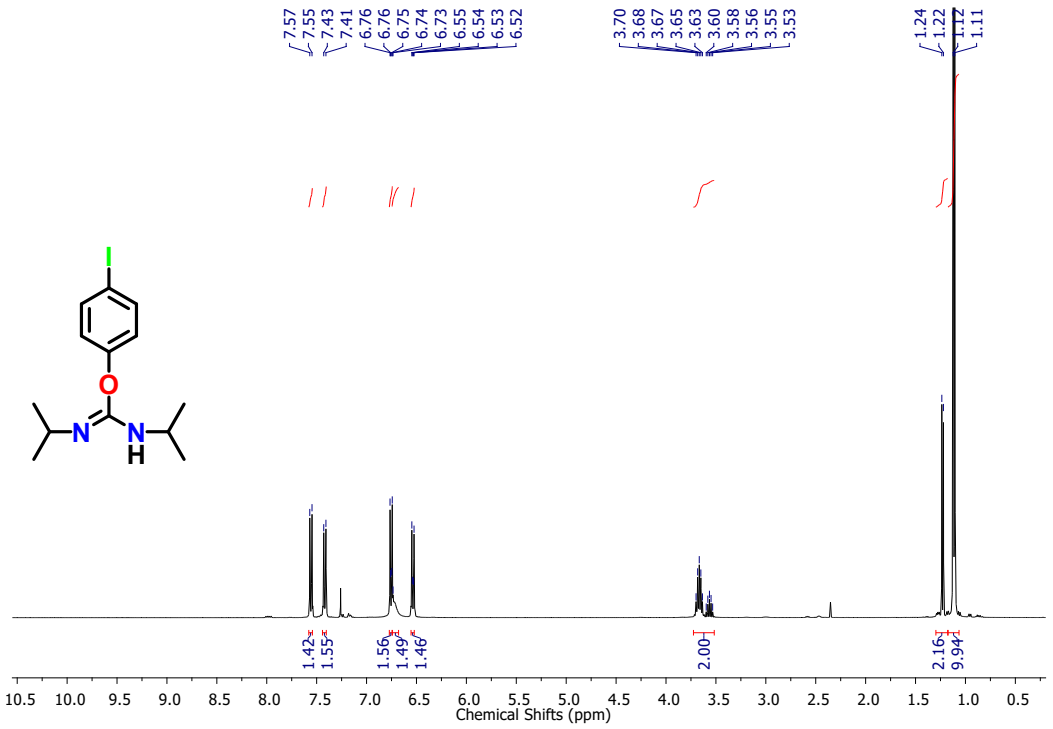


Figure FS94. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6k.**

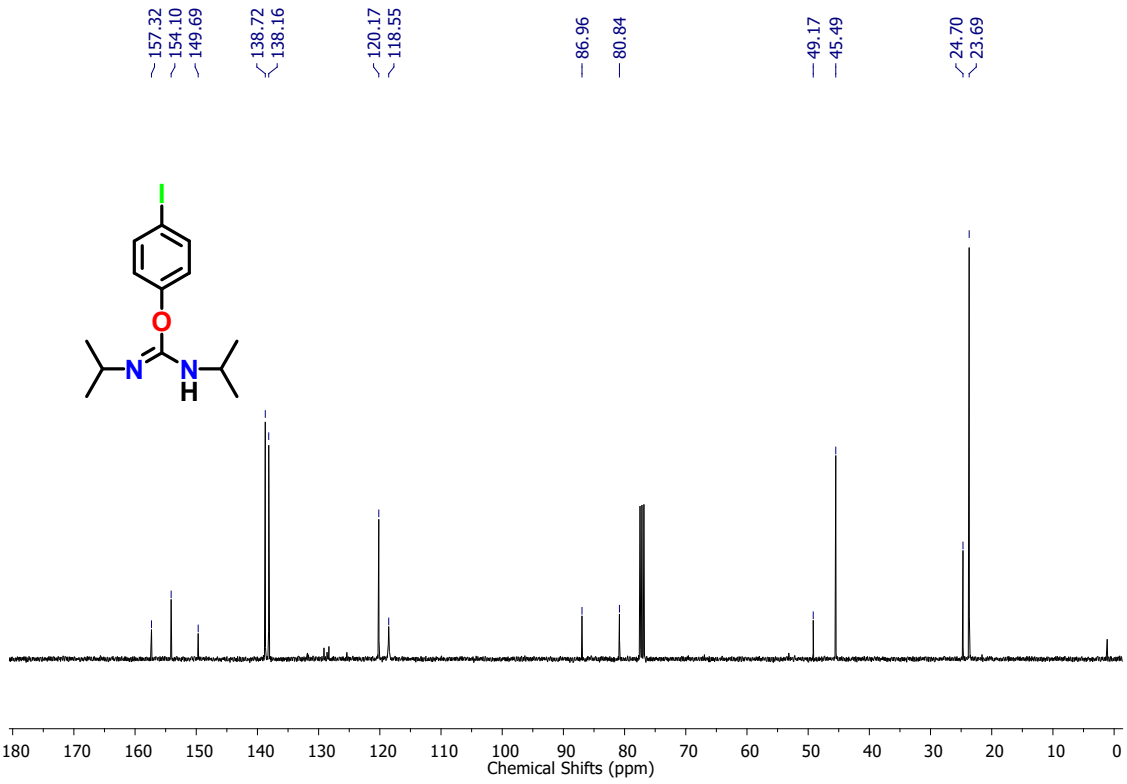


Figure FS95. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6k.**

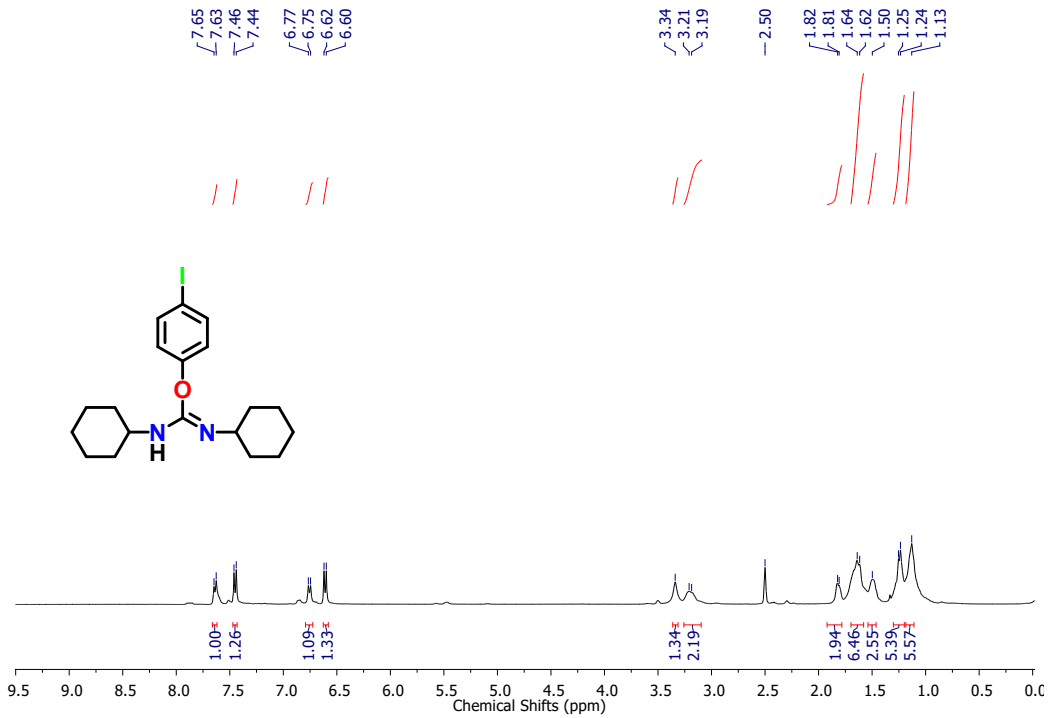


Figure FS96. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6l.**

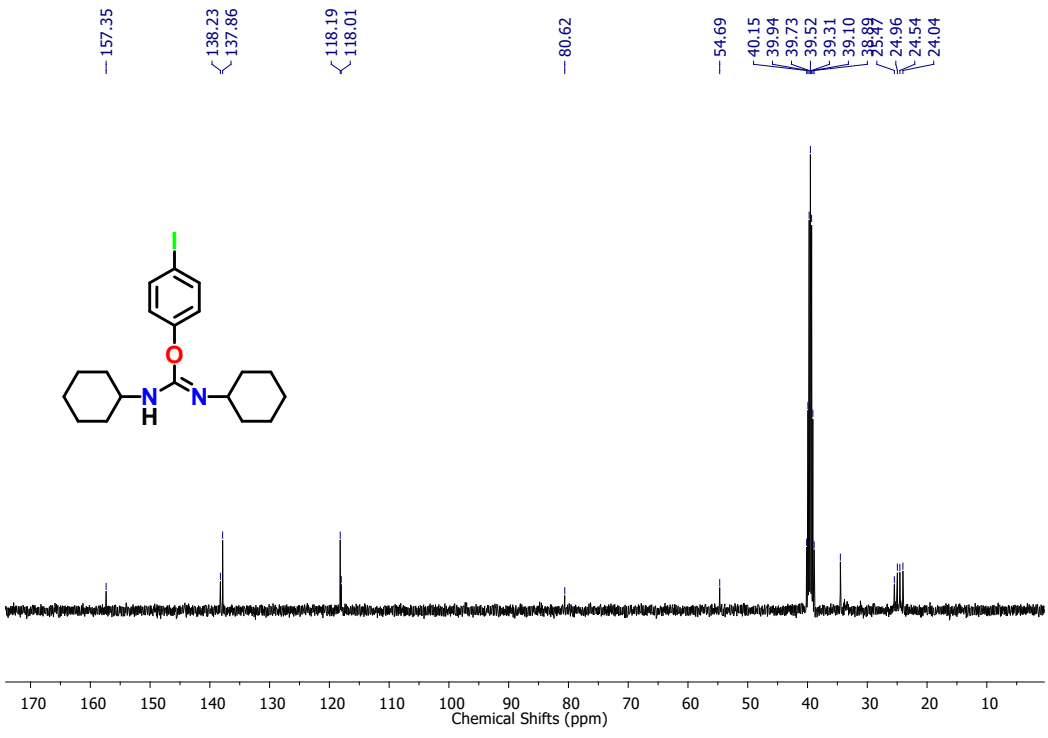


Figure FS97. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6l.**

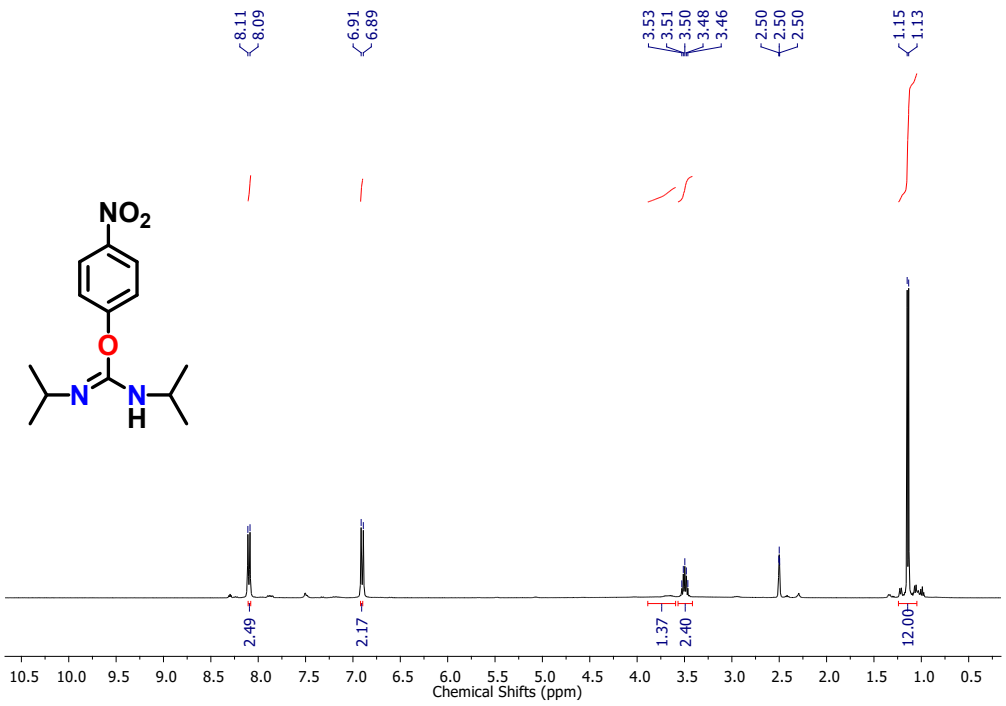


Figure FS98. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6m.**

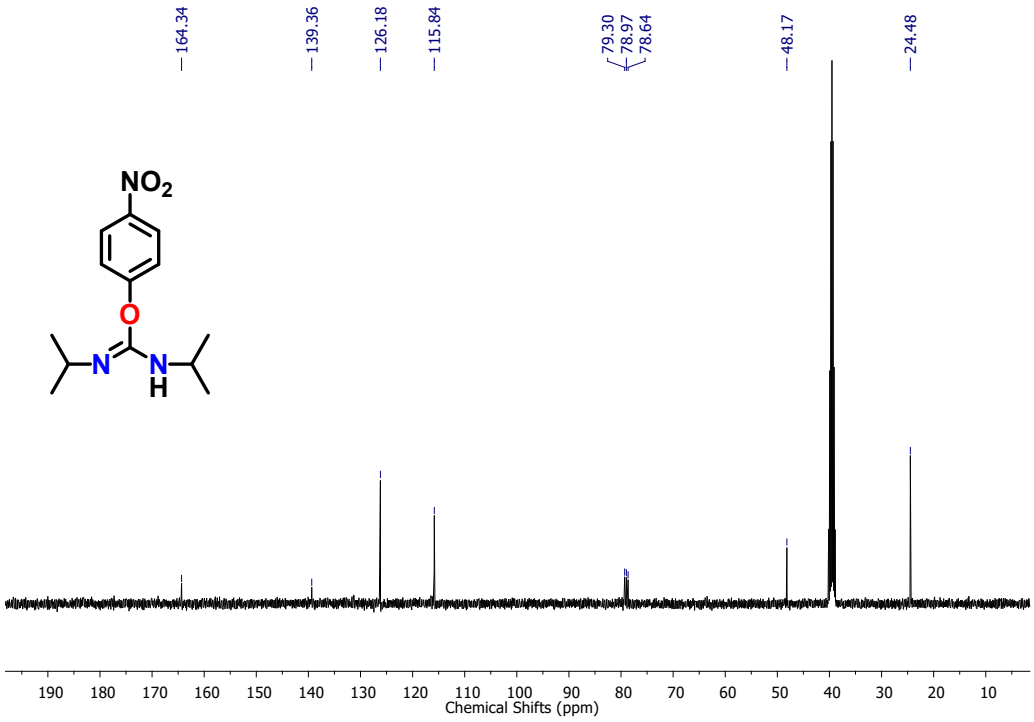


Figure FS99. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6m.**

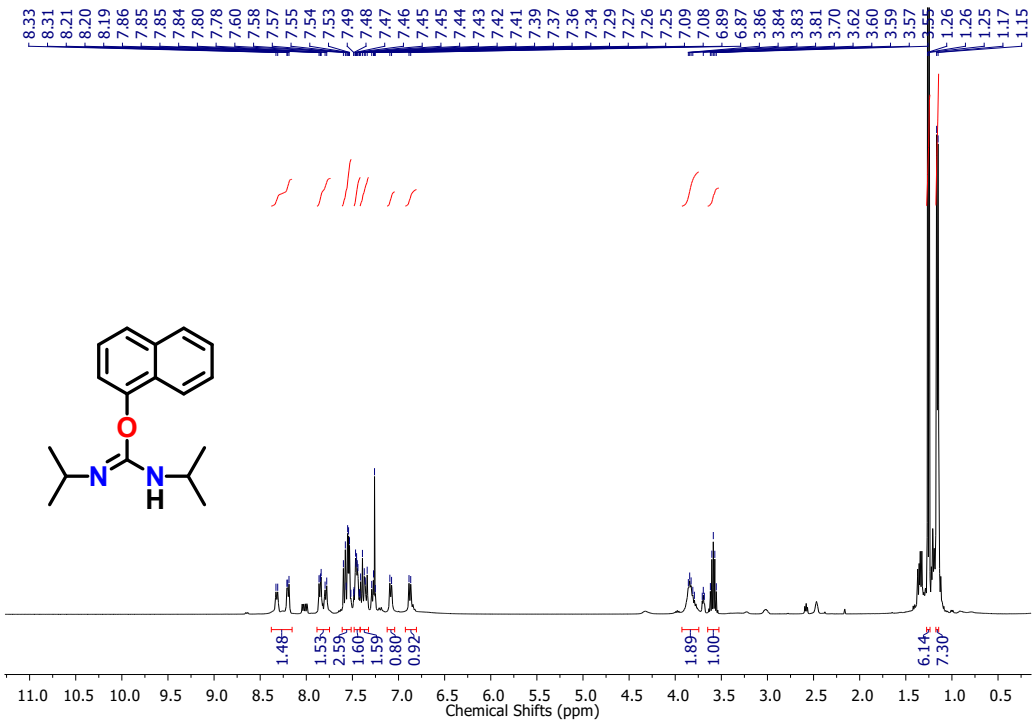


Figure FS100. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6n.**

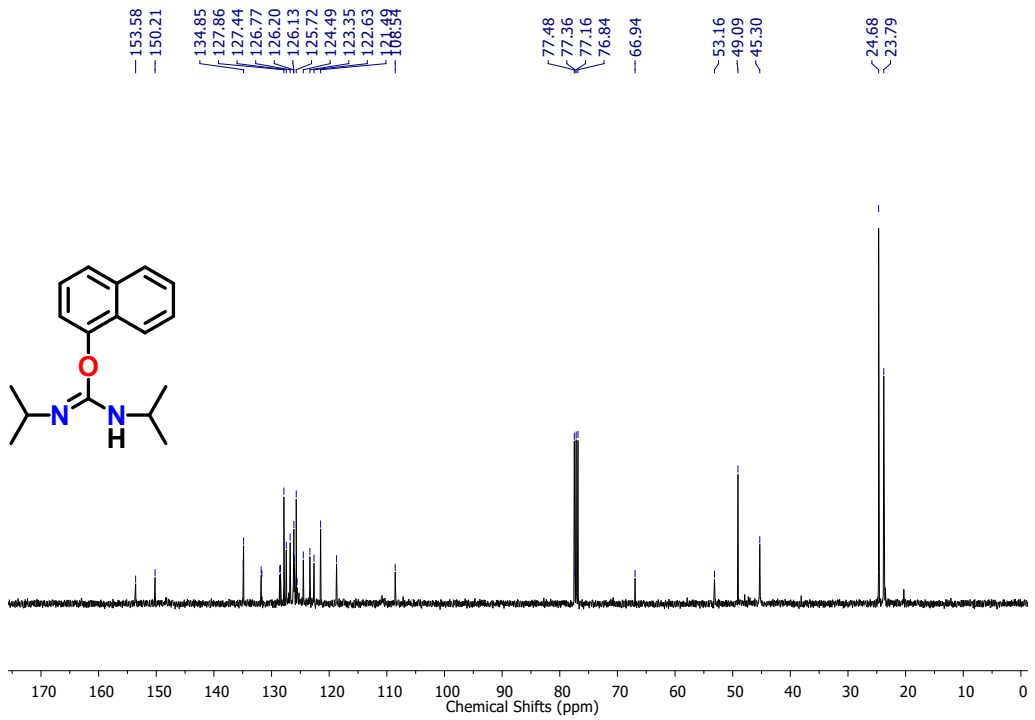


Figure FS101. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6n.**

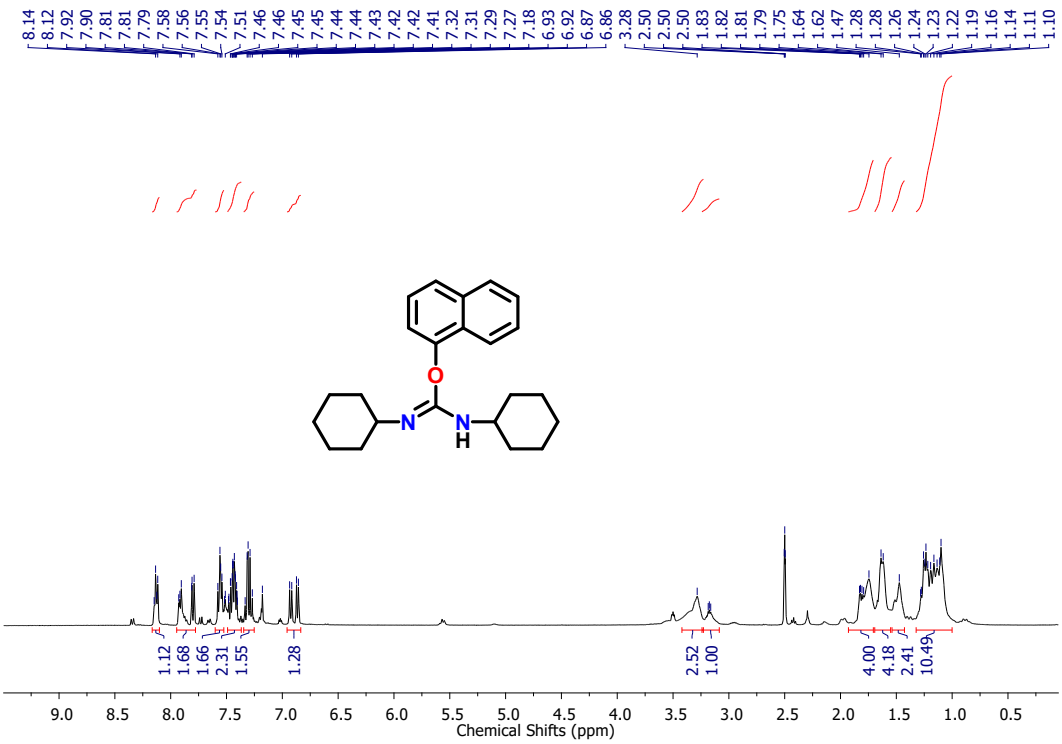


Figure FS102. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6o.**

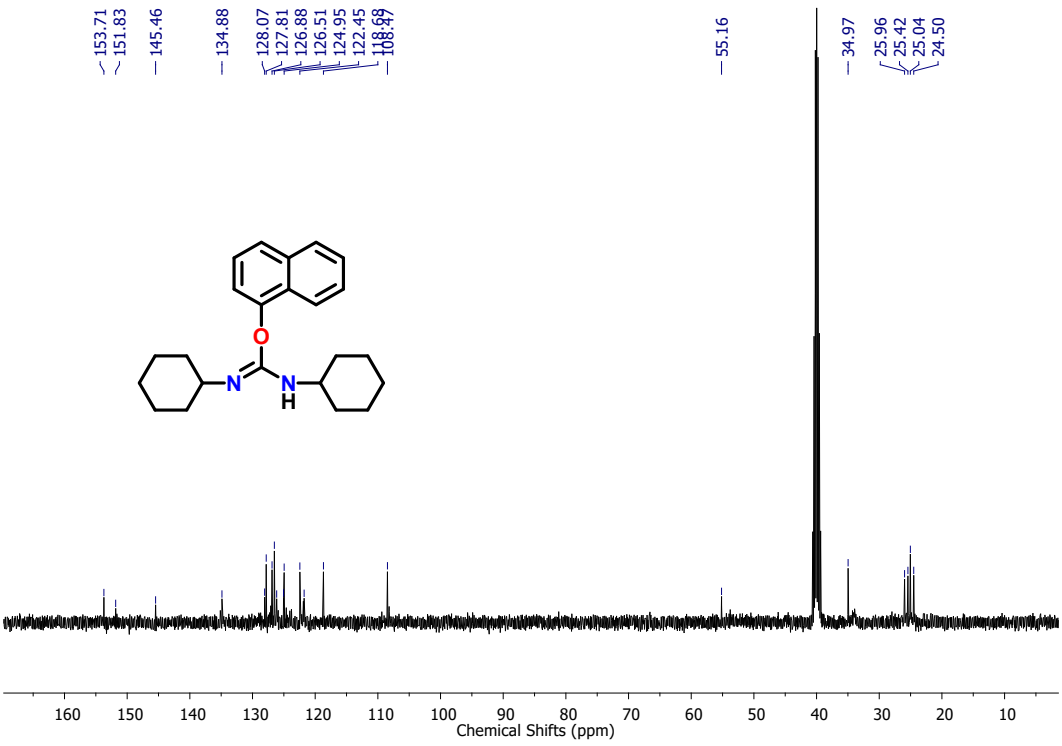


Figure FS103. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6o.**

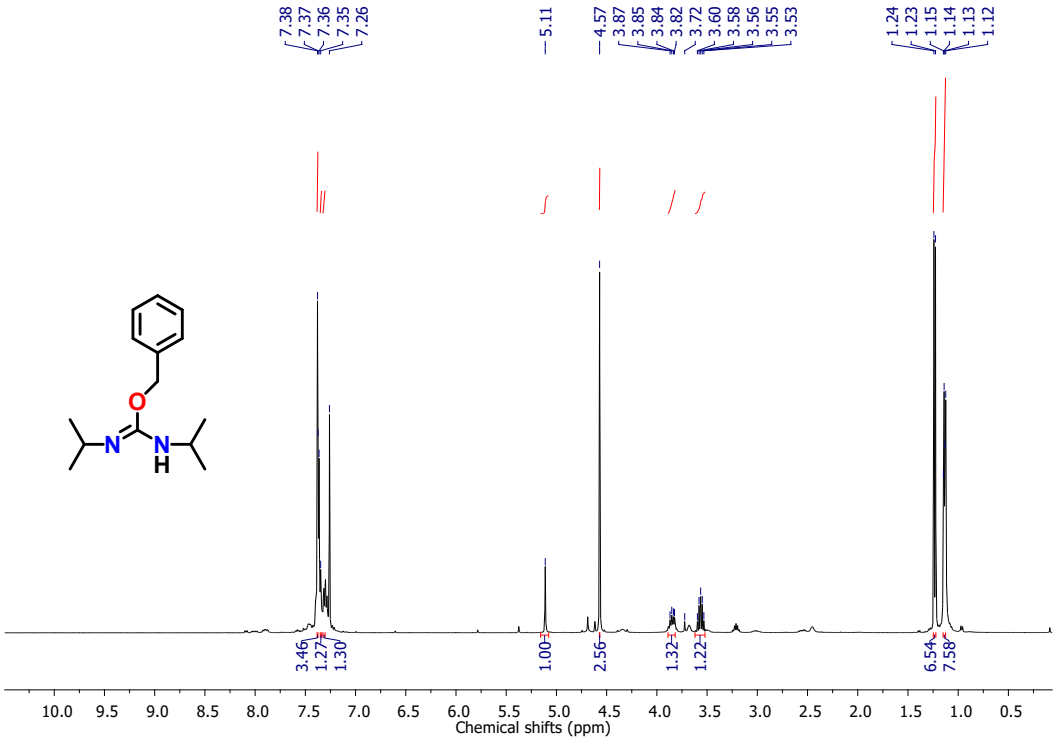


Figure FS104. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **6p.**

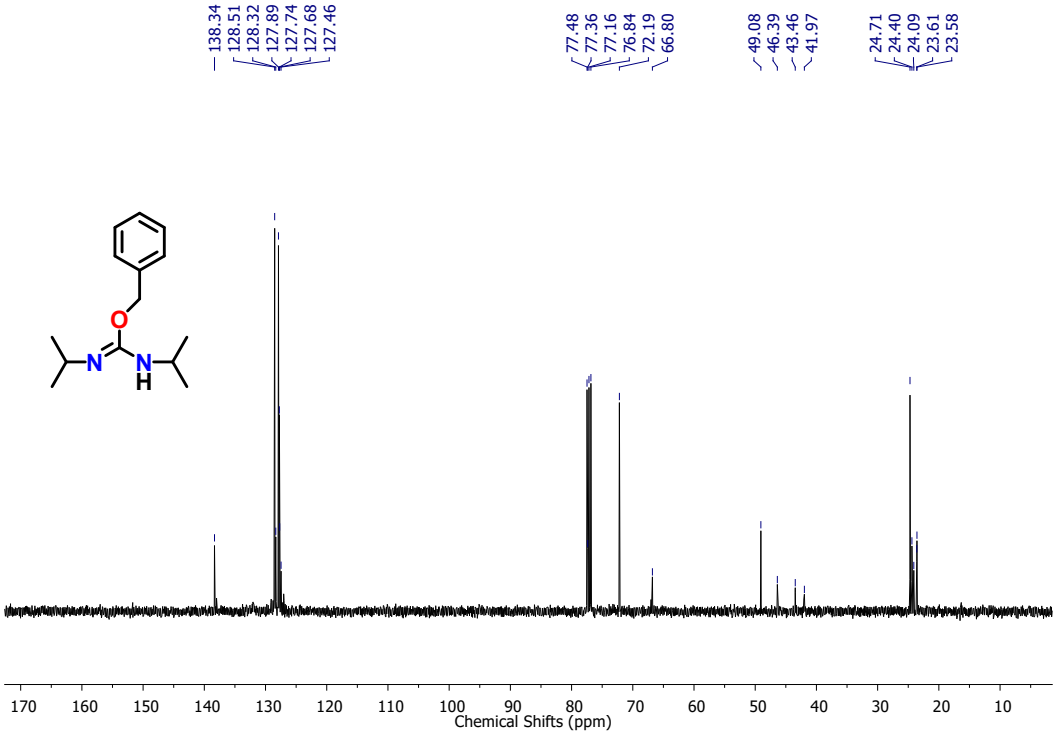


Figure FS105. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **6p.**

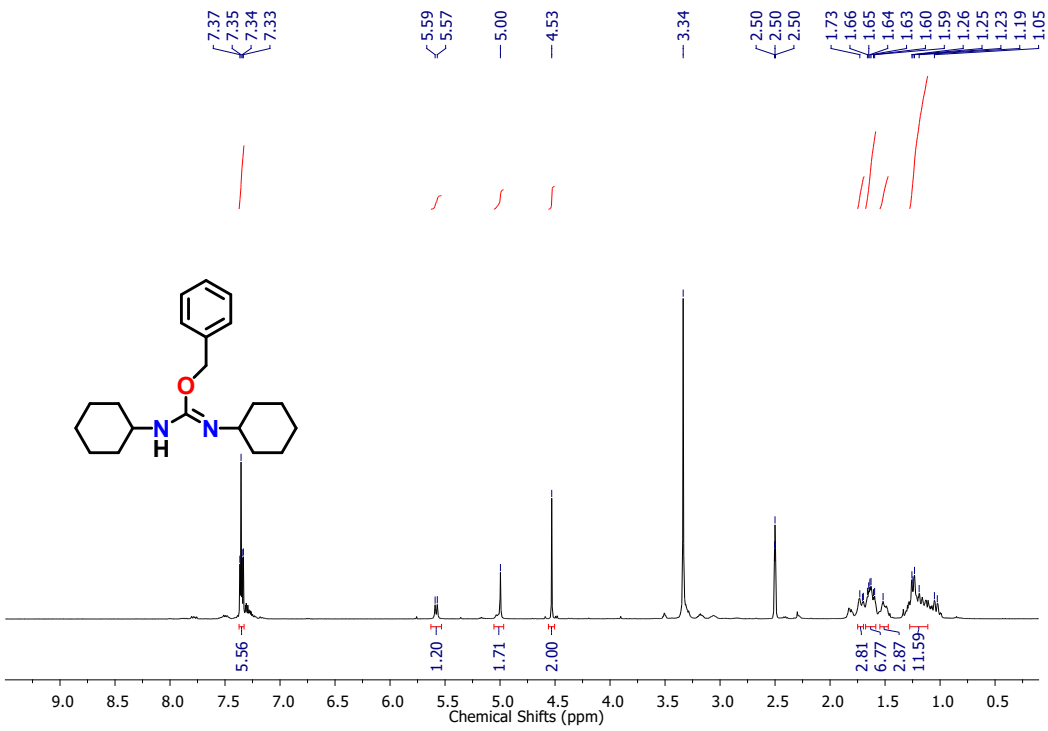


Figure FS106. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6q.**

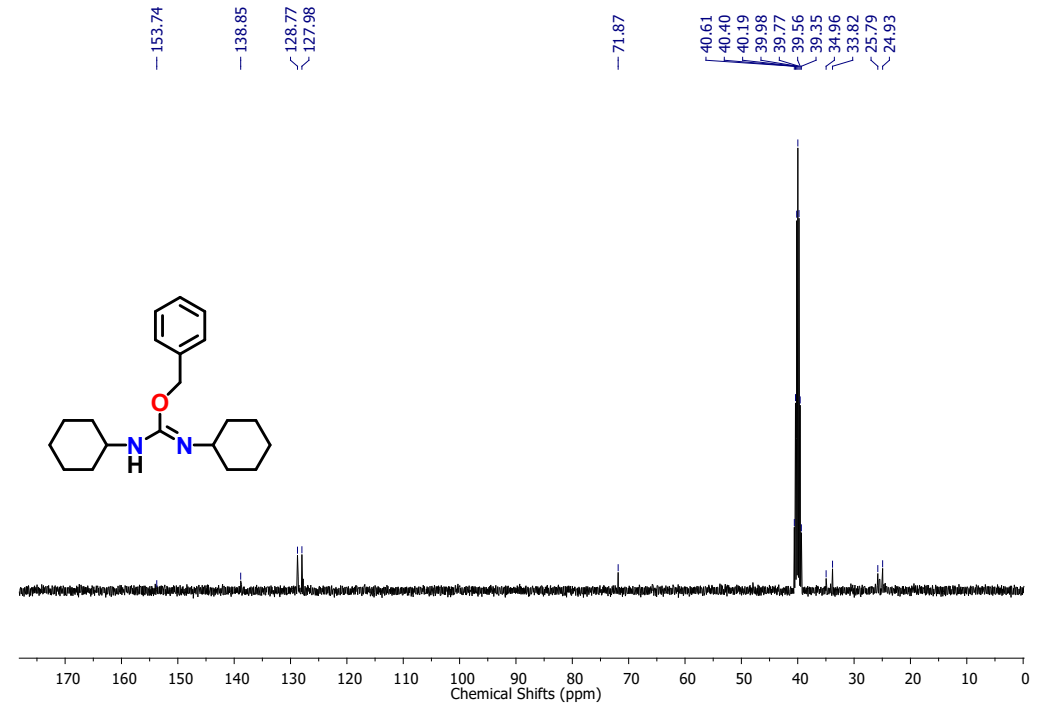


Figure FS107. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6q.**

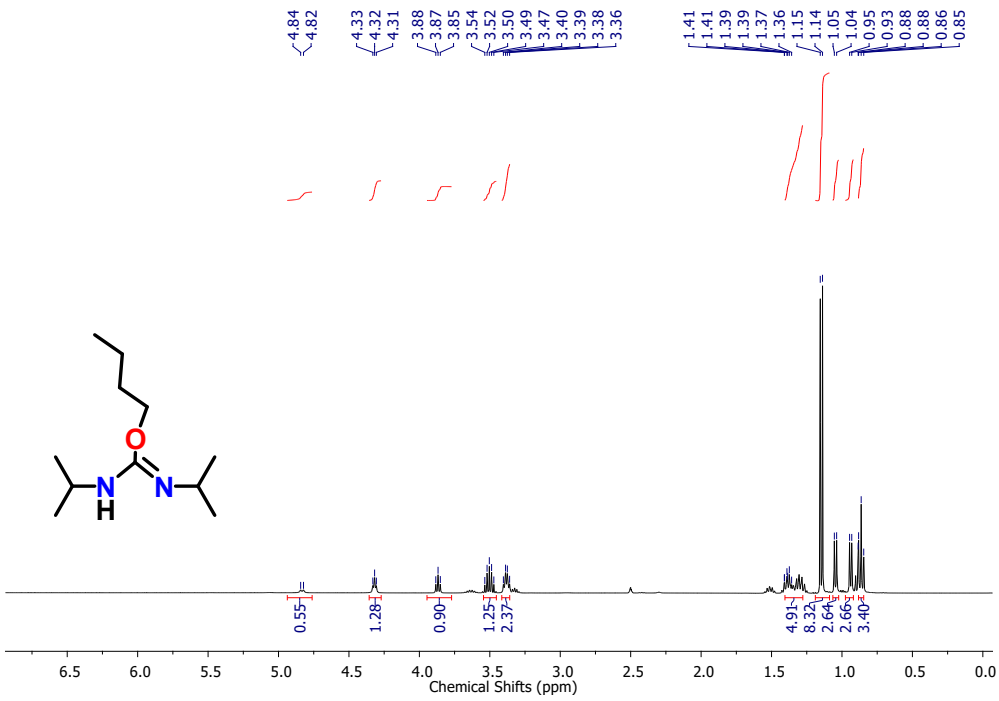


Figure FS108. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6r.**

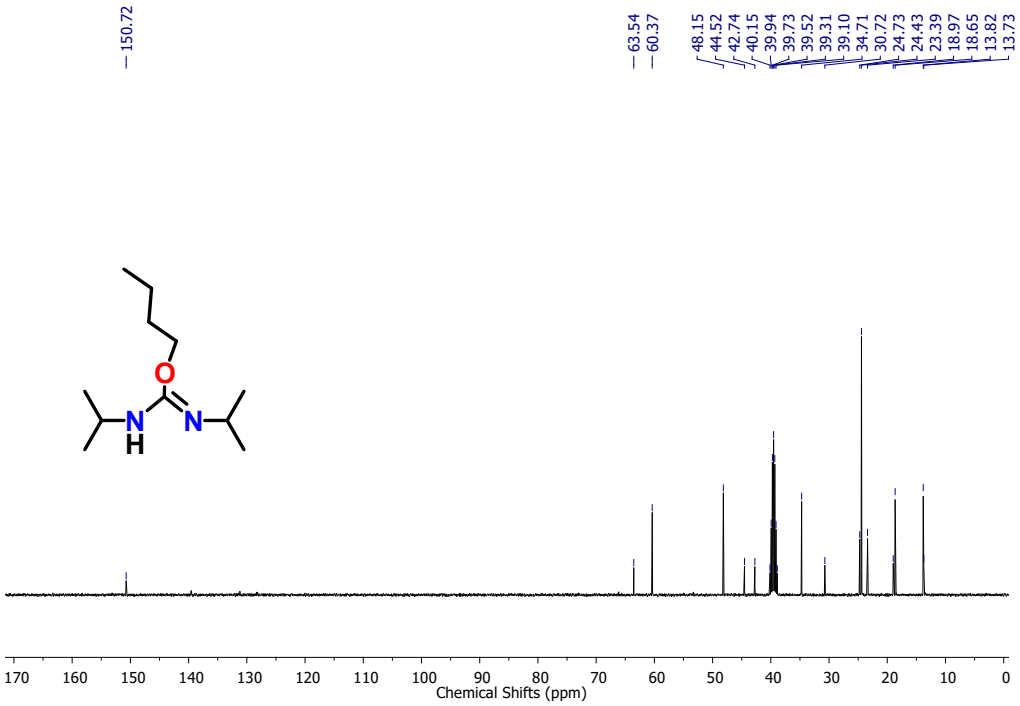


Figure FS109. ^{13}C{^{1}H}- NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6r**.

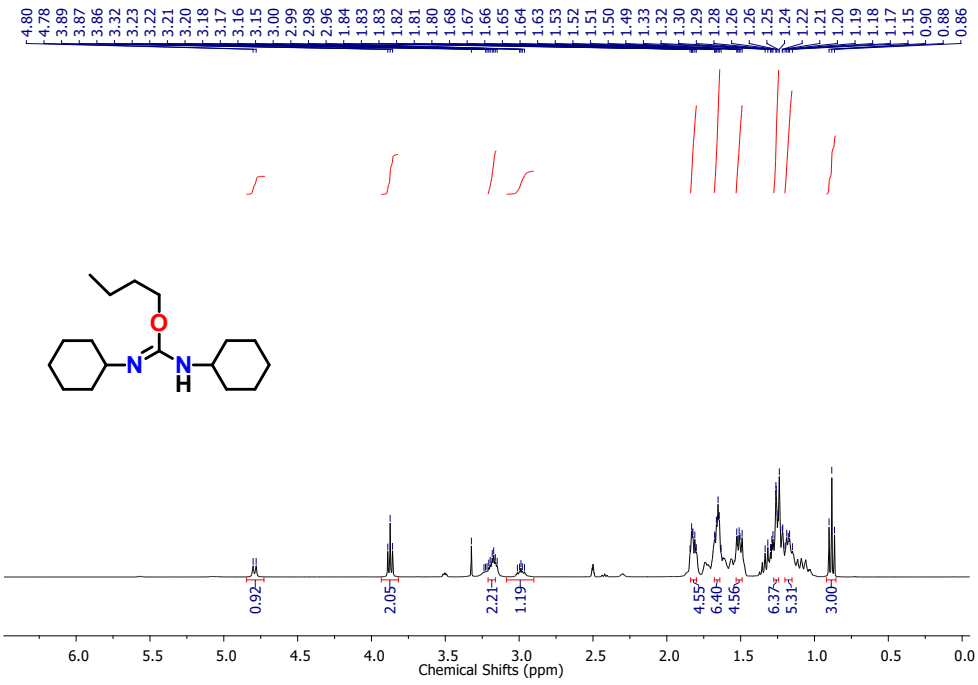


Figure FS110. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **6s**.

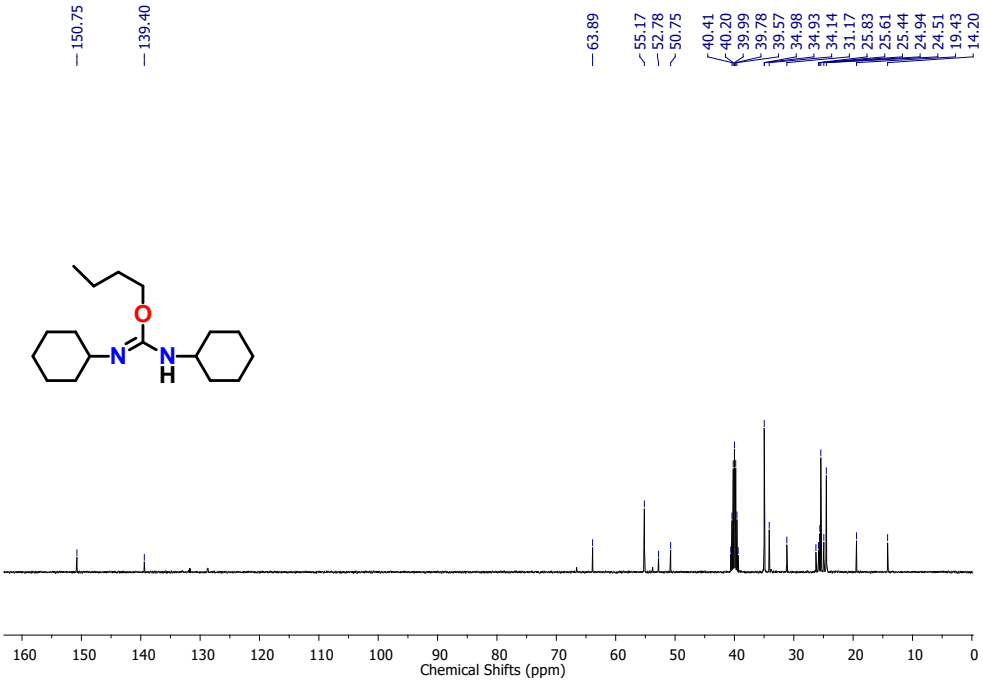
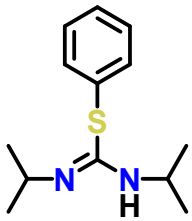


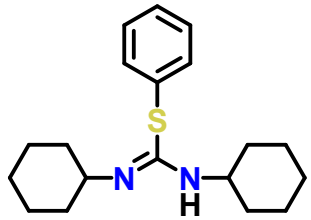
Figure FS111. ^{13}C{^{1}H}- NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **6s**.

NMR Data for isothiourea derivatives (7a-7k).



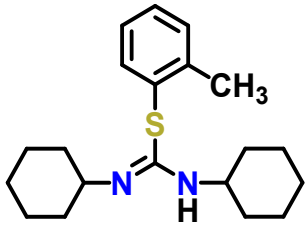
(7a)

Isolated yield: (84 mg, 95%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.36 (d, 4H, J = 4.3 Hz, CH_{Ar}), 7.27 (dd, 1H, J = 8.7 Hz, 4.4 Hz, CH_{Ar}), 5.54 (s, 1H, NH), 3.88 – 3.69 (m, 2H, CH), 0.99 (d, 12H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 142.5 (C=N), 133.2 (C_{Ar}–S), 130.2 (C_{Ar}), 129.3 (C_{Ar}), 126.9 (C_{Ar}), 66.1 (CH), 23.3 (CH$_3$) ppm. [10]



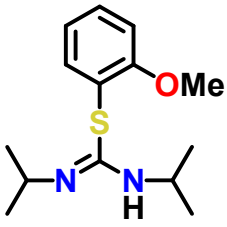
(7b)

Isolated yield: (115 mg, 95%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.41 – 7.34 (m, 4H, CH_{Ar}), 7.28 (ddd, 1H, J = 7.5 Hz, 5.2 Hz, 3.0 Hz, CH_{Ar}), 5.28 (s, 1H, NH), 3.61 – 3.38 (m, 2H, CH), 1.81 (dd, 2H, J = 10.0 Hz, 4.5 Hz, CH_2), 1.58 (s, 6H, CH_2), 1.48 (d, 4H, J = 9.1 Hz, CH_2), 1.25 – 1.01 (m, 11H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 142.3 (C=N), 132.9 (C_{Ar}–S), 130.9 (C_{Ar}), 129.3 (C_{Ar}), 127.2 (C_{Ar}), 54.7 (CH), 34.5 (CH$_2$), 25.5 (CH$_2$), 24.4 (CH$_2$) ppm. [10]



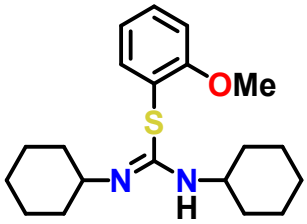
(7c)

Isolated yield: (123 mg, 97%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.45 (d, 1H, J = 8.3 Hz, CH_{Ar}), 7.16 (d, 1H, J = 8.1 Hz, CH_{Ar}), 6.96 (d, 1H, J = 8.5 Hz, CH_{Ar}), 6.70 (d, 1H, J = 8.4 Hz, CH_{Ar}), 3.25 (s, 1H, CH_3), 3.17 (m, 2H, CH), 2.17 (s, 2H, CH_2), 1.84 (m, 2H, CH_2), 1.67 (m, 6H, CH_2), 1.64 (dd, H, J = 8.0 Hz, 3.5 Hz, CH_2), 1.25 (dt, 5H, J = 11.4 Hz, 5.1 Hz, CH_2), 1.16 (dt, 5H, J = 11.4 Hz, 5.1 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 154.5 (C–S), 152.8 (C=N), 133.3 (C_{Ar}), 129.1 (C_{Ar}), 120.8 (C_{Ar}), 116.8 (C_{Ar}), 55.2 (CH), 34.9 (CH$_2$), 25.4 (CH$_2$), 24.5 (CH$_2$), 20.5 (CH$_3$) ppm. [10]



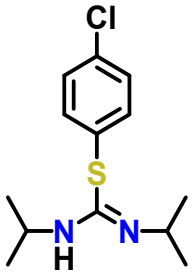
(7d)

Isolated yield: (99 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.31 – 7.22 (m, 2H, CH_{Ar}), 7.04 (dd, 1H, J = 8.1 Hz, 0.8 Hz, CH_{Ar}), 6.95 (td, 1H, J = 7.6 Hz, 1.2 Hz, CH_{Ar}), 3.81 (s, 3H, OCH_3), 3.76 (d, 2H, J = 1.7 Hz, CH), 3.34 (s, 1H, NH), 0.99 (d, 12H, J = 6.4 Hz, CH_3) ppm. [10]



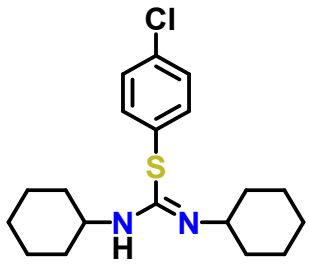
(7e)

Isolated yield: (127 mg, 96%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.46 (dd, 1H, J = 7.6 Hz, 1.7 Hz, CH_{Ar}), 7.34 (ddd, 1H, J = 8.3 Hz, 7.6 Hz, 1.7 Hz, CH_{Ar}), 6.99 – 6.87 (m, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 3.66 – 3.51 (m, 2H, CH), 1.82 – 1.65 (m, 5H, CH_2), 1.66 – 1.48 (m, 6H, CH_2), 1.34 – 1.24 (m, 6H, CH_2), 1.20 – 1.09 (m, 6H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 170.3 (C-O), 158.8 (C=N), 135.8 (C_{Ar}), 130.4 (C_{Ar}), 121.3 (C_{Ar}), 111.1 (C_{Ar}), 55.8 (CH), 34.9 (CH), 33.6 (CH$_2$), 25.8 (OCH$_3$), 25.4 (CH$_2$), 24.7 (CH$_2$) ppm. [10]



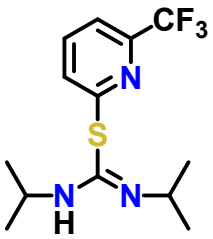
(7f)

Isolated yield: (95 mg, 92%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.44 – 7.39 (m, 2H, CH_{Ar}), 7.36 – 7.32 (m, 2H, CH_{Ar}), 5.84 (s, 1H, NH), 3.78 (dt, 2H, J = 12.7 Hz, 6.3 Hz, CH), 0.99 (d, 11H, J = 6.4 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 142.1 (C=N), 132.6 (C_{Ar}), 131.5 (C_{Ar}), 129.8 (C_{Ar}), 129.2 (C_{Ar}), 129.1 (C_{Ar}), 50.7 (CH), 23.3 (CH$_3$) ppm. [10]



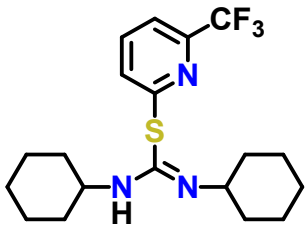
(7g)

Isolated yield: (121 mg, 90%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.38 (dd, 4H, J = 24.2 Hz, 7.3 Hz, CH_{Ar}), 5.66 (s, 1H, NH), 3.45 (s, 2H, CH), 1.82 (s, 2H, CH_2), 1.60 (s, 4H, CH_2), 1.49 (d, 4H, J = 5.8 Hz, CH_2), 1.17 (s, 10H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 141.8 (C=N), 132.6 (C_{Ar}), 131.8 (C_{Ar}), 131.6 (C_{Ar}), 129.2 (C_{Ar}), 59.6 (CH), 25.5 (CH$_2$), 24.5 (CH$_2$) ppm. [10]



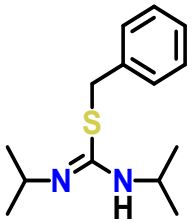
(7h)

Isolated yield: (100 mg, 86%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 8.11 (s, 1H, NH), 7.57 (d, 1H, J = 8.3 Hz, CH_{Ar}), 7.36 (d, 1H, J = 9.1 Hz, CH_{Ar}), 7.02 (d, 1H, J = 7.7 Hz, CH_{Ar}), 4.23 (d, 1H, J = 5.8 Hz, CH), 3.50 (dt, 1H, J = 12.8 Hz, 6.4 Hz, CH), 1.14 (d, 6H, J = 6.4 Hz, CH_3), 1.08 (d, 6H, J = 6.5 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 182.2 (CF$_3$), 158.6 (C=N), 137.7 (C_{Ar}), 134.1 (C_{Ar}), 131.9 (C_{Ar}), 125.3 (C_{Ar}), 48.6 (CH), 24.9 (CH$_3$), 22.8 (CH$_3$) ppm. [10]



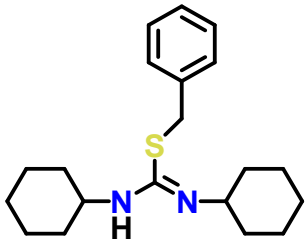
(7i)

Isolated yield: (122 mg, 83%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 8.07 (s, 1H, CH_{Ar}), 7.58 (dd, 1H, J = 9.2 Hz, 2.1 Hz, CH_{Ar}), 7.37 (d, 1H, J = 9.1 Hz, CH_{Ar}), 3.49 (d, 1H, J = 4.4 Hz, N*H*), 3.23 – 3.10 (m, 2H, C*H*), 1.81 (d, 4H, J = 8.5 Hz, CH_2), 1.65 (dd, 4H, J = 8.5 Hz, 3.8 Hz, CH_2), 1.49 (dd, 2H, J = 7.9 Hz, 3.5 Hz, CH_2), 1.23 (dd, 10H, J = 10.0 Hz, 6.5 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 181.7 (*C*=N), 139.0 (C_{Ar}), 137.0 (C_{Ar}), 133.9 (C_{Ar}), 131.7 (C_{Ar}), 54.7 (*C*H), 34.5 (*C*H$_2$), 24.9 (*C*H$_2$), 24.1 (*C*H$_2$) ppm. [10]



(7j)

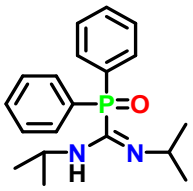
Isolated yield: (79 mg, 95%). ^{1}H NMR (400 MHz, 25 °C, DMSO-d_6): δ_H 7.40 – 7.10 (m, 5H, CH_{Ar}), 5.50 (t, 1H, J = 9.2 Hz, N*H*), 4.15 (s, 1H, CH_2), 3.73 (s, 1H, CH_2), 3.63 (ddd, 2H, J = 13.9 Hz, 9.7 Hz, 5.2 Hz, C*H*), 1.04 (dd, 12H, J = 33.1 Hz, 6.5, Hz CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, DMSO-d_6): δ_C 156.7 (*C*=N), 129.3 (*C*–S), 128.8 (C_{Ar}), 128.3 (C_{Ar}), 127.3 (C_{Ar}), 126.9 (C_{Ar}), 53.3 (*C*H), 50.3 (*C*H), 40.6 (*C*H$_2$), 35.2 (*C*H$_2$), 24.9 (*C*H$_3$), 23.3 (*C*H$_3$) ppm. [10]



(7k)

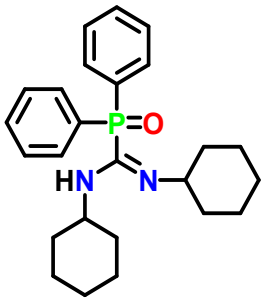
Isolated yield: (113 mg, 89%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.35 – 7.26 (m, 5H, CH_{Ar}), 4.21 (br., 1H, N*H*), 4.00 (s, 2H, CH_2), 3.53 – 3.43 (m, 2H, C*H*), 1.73 (d, 4H, *J* = 11.0 Hz, CH_2), 1.68 – 1.60 (m, 6H, CH_2), 1.55 (dd, 2H, *J* = 8.5 Hz, 3.9 Hz, CH_2), 1.36 – 1.23 (m, 5H, CH_2), 1.14 (dd, 5H, *J* = 16.0 Hz, 7.4 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 145.7 (*C*=N), 138.2 (C_{Ar}), 131.8 (C_{Ar}), 129.3 (C_{Ar}), 128.8 (C_{Ar}), 128.3 (C_{Ar}), 127.5 (C_{Ar}), 67.1 (*C*H$_2$), 53.2 (*C*H), 37.0 (*C*H$_2$), 34.9 (*C*H$_2$), 34.6 *C*H$_2$), 33.9 (*C*H$_2$), 26.0 (*C*H$_2$), 25.6 (*C*H$_2$), 24.7 (*C*H$_2$) ppm. [10]

NMR Data for phosphorylguanidine derivatives (8a-8f).



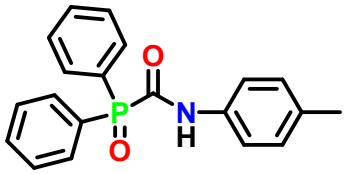
(8a)

Isolated yield: (120 mg, 96%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.87 – 7.76 (m, 4H, CH_{Ar}), 7.57 – 7.37 (m, 6H, CH_{Ar}), 4.11 (p, 2H, *J* = 7.1 Hz, C*H*), 1.37 (t, 3H, *J* = 7.1 Hz, CH_3), 1.30 – 1.21 (m, 9H, CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$): δ_P 31.48 (s) ppm. [10]



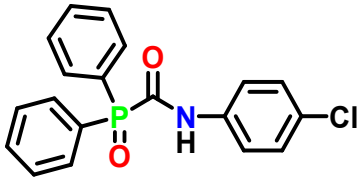
(8b)

Isolated yield: (144 mg, 92%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.82 – 7.73 (m, 3H, CH_{Ar}), 7.51 – 7.44 (m, 1H, CH_{Ar}), 7.44 – 7.37 (m, 3H, CH_{Ar}), 7.32 – 7.24 (m, 3H, CH_{Ar}), 4.06 (p, 1H, J = 7.1 Hz, C*H*), 3.02 (s, 1H, N*H*), 1.88 (d, 2H, J = 9.4 Hz, CH_2), 1.78 (d, 4H, J = 10.4 Hz, CH_2), 1.70 (d, 4H, J = 9.2 Hz, CH_2), 1.55 (d, 2H, J = 10.2 Hz, CH_2), 1.39 – 1.20 (m, 11H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 151.1 (*C*=N), 132.2 (C_{Ar}), 132.1 – 131.9 (C_{Ar}), 131.6 (C_{Ar}), 131.3 (C_{Ar}), 130.9 (C_{Ar}), 129.4 (C_{Ar}), 128.5 (C_{Ar}), 127.6 (C_{Ar}), 61.1 (*C*H), 55.7 (*C*H), 34.9 (*C*H$_2$), 34.3 (*C*H$_2$), 25.4 (*C*H$_2$), 24.9 (*C*H$_2$), 24.7 (*C*H$_2$), 16.5 (*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$): δ_P 33.28 (s), 31.37 (s) ppm. [10]



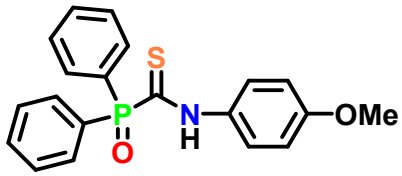
(8c)

Isolated yield: (126 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 9.38 (s, 1H, N*H*), 8.02 – 7.90 (m, 4H, CH_{Ar}), 7.62 – 7.54 (m, 4H, CH_{Ar}), 7.54 – 7.48 (m, 4H, CH_{Ar}), 7.14 (d, 2H, J = 8.3 Hz, CH_{Ar}), 2.32 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 161.2 (*C*=O), 135.5 (C_{Ar}), 132.9 (C_{Ar}), 131.9 (C_{Ar}), 129.7 (C_{Ar}), 128.9 (C_{Ar}), 119.9 (C_{Ar}), 21.1 (*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$) δ_P 15.57 (s) ppm. [10]



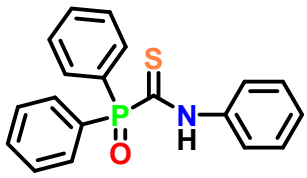
(8d)

Isolated yield: (134 mg, 98%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 10.09 (s, 1H, N*H*), 7.90 (dd, 4H, *J* = 12.0 Hz, 7.5 Hz, CH_{Ar}), 7.69 (d, 2H, *J* = 7.7 Hz, CH_{Ar}), 7.56 (t, 2H, *J* = 6.9 Hz, CH_{Ar}), 7.46 (td, 4H, *J* = 7.5 Hz, 3.1 Hz, CH_{Ar}), 7.31 – 7.20 (m, 2H, CH_{Ar}) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 168.9 (*C*=O), 135.7 (C_{Ar}), 133.0 (C_{Ar}), 131.8 (C_{Ar}), 130.6 (C_{Ar}), 128.7 (C_{Ar}), 128.3 (C_{Ar}), 121.5 (C_{Ar}) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$): δ_P 15.82 (s) ppm. [10]



(8e)

Isolated yield: (124 mg, 96%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 11.25 (s, 1H, N*H*), 8.07 – 7.97 (m, 6H, CH_{Ar}), 7.58 (td, 2H, *J* = 7.3 Hz, 1.4 Hz, CH_{Ar}), 7.53 – 7.45 (m, 4H, CH_{Ar}), 6.97 – 6.89 (m, 2H, CH_{Ar}), 3.81 (s, 3H, OCH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 192.7 (*C*=O), 191.8 (*C*–O), 158.4 (C_{Ar}), 132.8 (C_{Ar}), 131.8 (C_{Ar}), 129.7 (C_{Ar}), 128.5 (C_{Ar}), 123.4 (C_{Ar}), 114.1 (C_{Ar}), 55.6 (O*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$): δ_P 21.53 (s) ppm. [10]



(8f)

Isolated yield: (139 mg, 99%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 11.30 (d, 1H, J = 4.9 Hz, N*H*), 8.12 – 8.07 (m, 2H, CH_{Ar}), 8.06 – 7.98 (m, 4H, CH_{Ar}), 7.63 – 7.56 (m, 2H, CH_{Ar}), 7.53 – 7.46 (m, 4H, CH_{Ar}), 7.45 – 7.38 (m, 2H, CH_{Ar}), 7.32 – 7.26 (m, 1H, CH_{Ar}) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 194.6 (*C*=S), 193.7 (*C*–N), 138.5 (C_{Ar}), 132.8 (C_{Ar}), 129.6 (C_{Ar}), 129.1 (C_{Ar}), 128.5 (C_{Ar}), 127.5 (C_{Ar}), 121.7 (C_{Ar}) ppm. ^{31}P{^{1}H} NMR (162 MHz, 25 °C, $CDCl_3$): δ_P 21.57 (s) ppm.[10]

NMR Spectra for isothiourea derivatives (7a-7k).

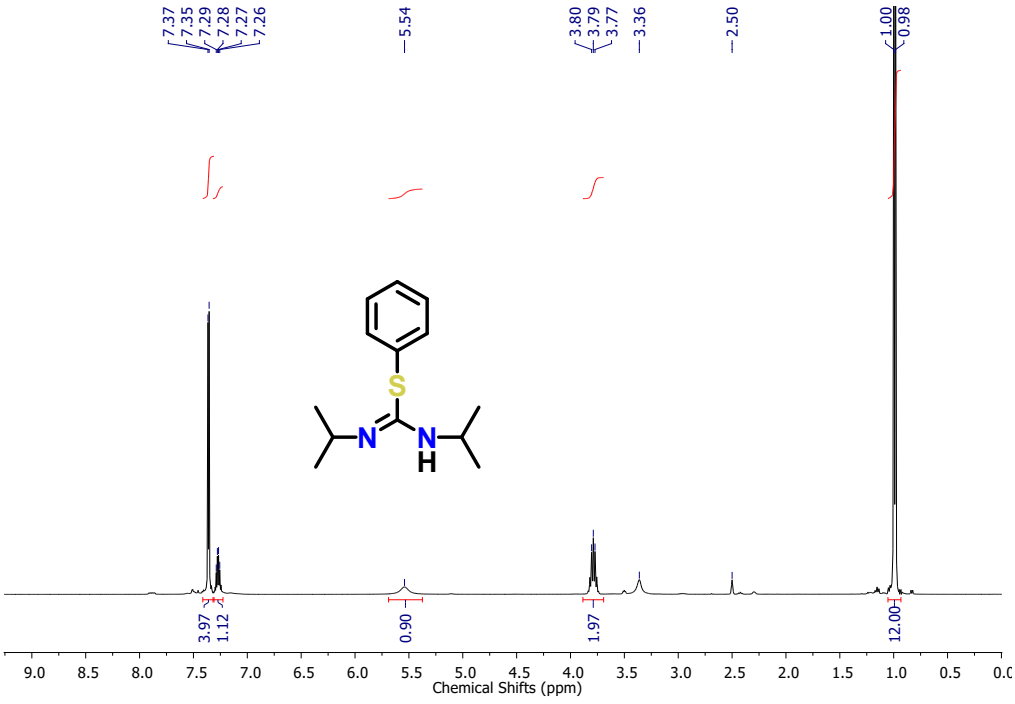


Figure FS112. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7a.**

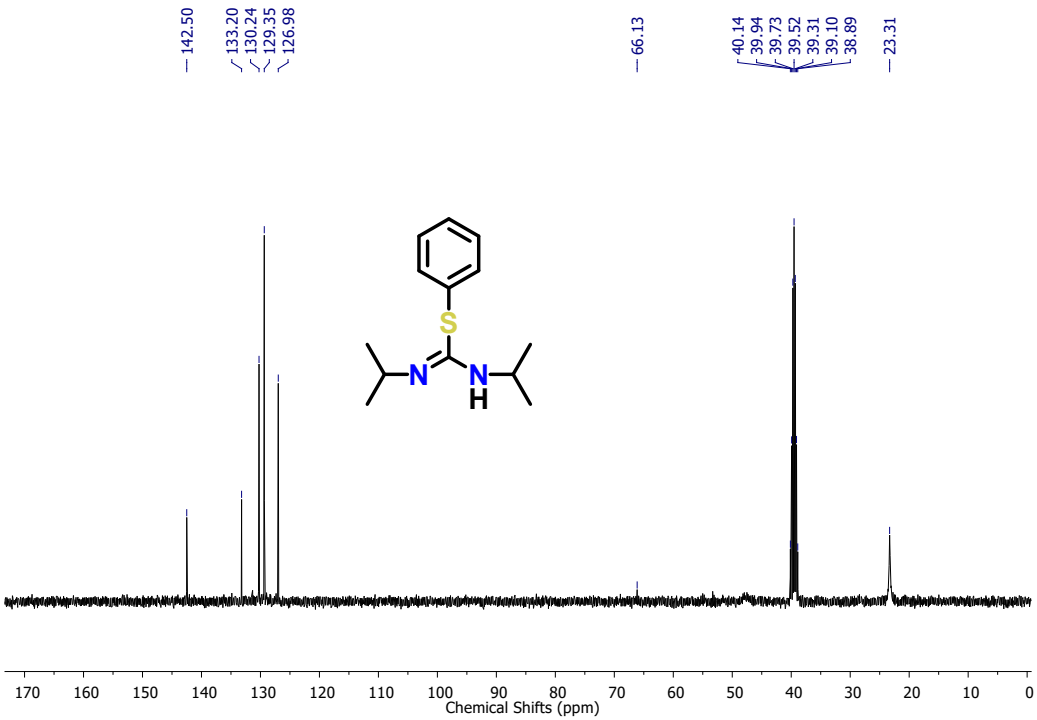


Figure FS113. $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **7a.**

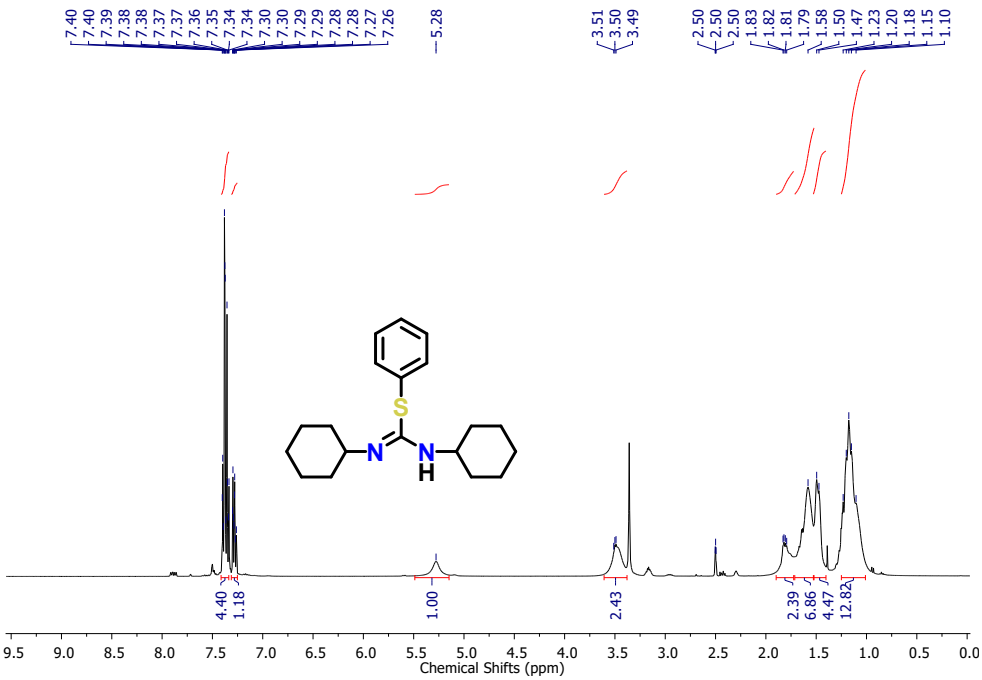


Figure FS114. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7b.**

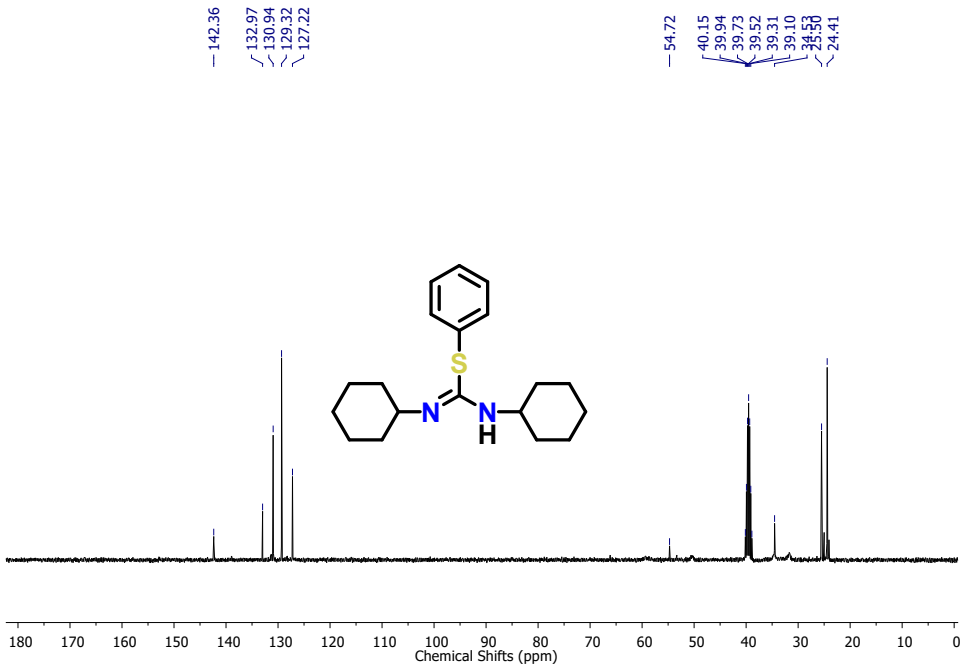


Figure FS115. $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **7b.**

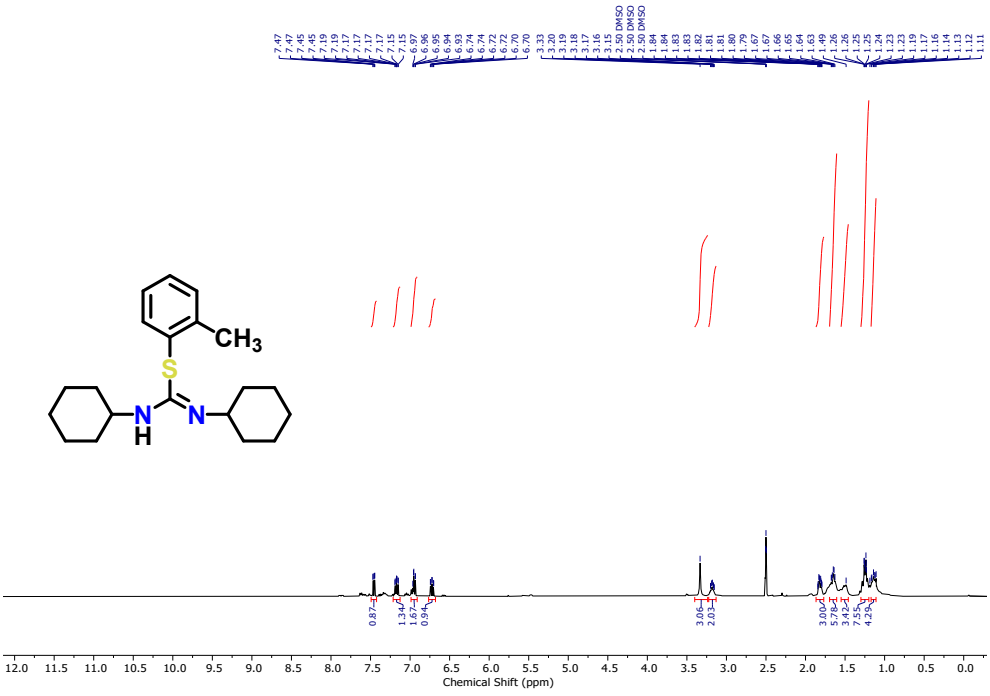


Figure FS116. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7c.**

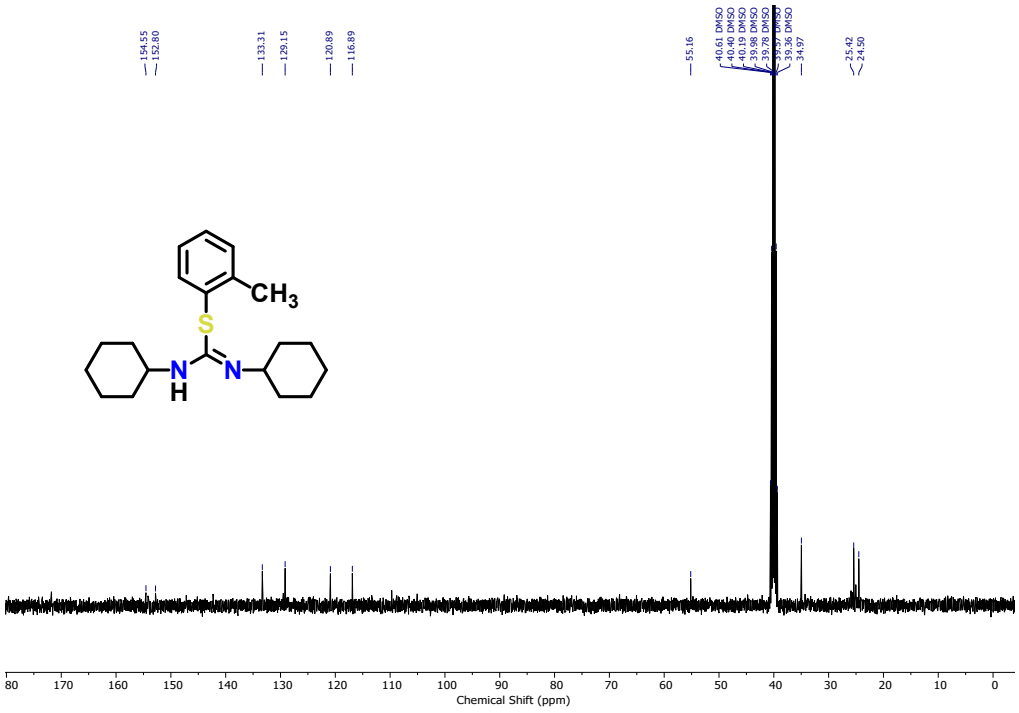


Figure FS117. $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **7c.**

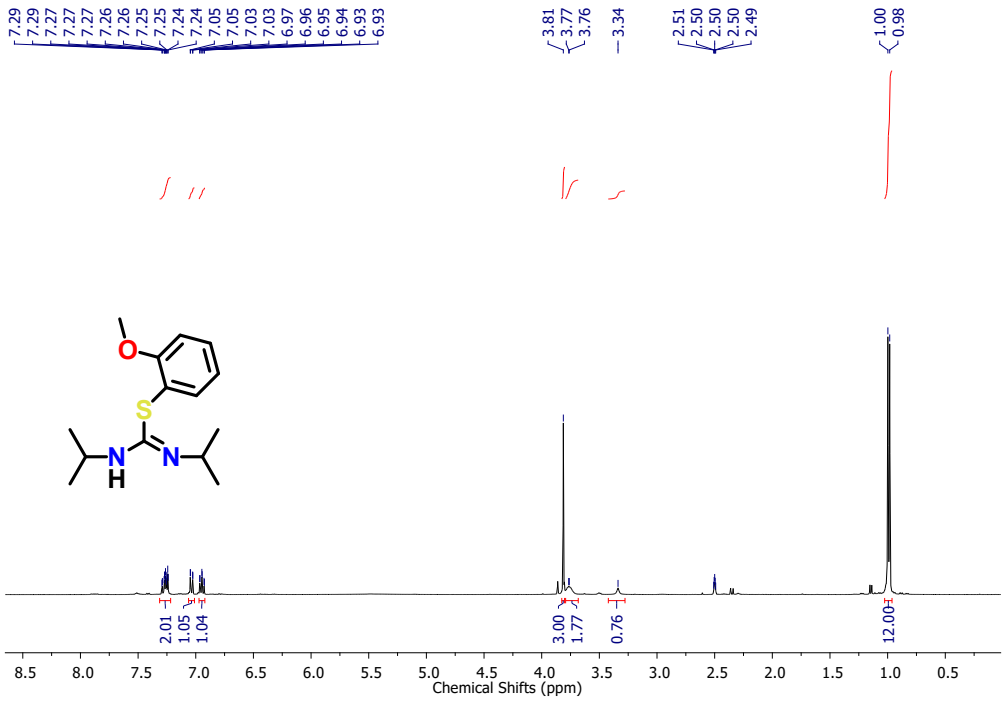


Figure FS118. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7d.**

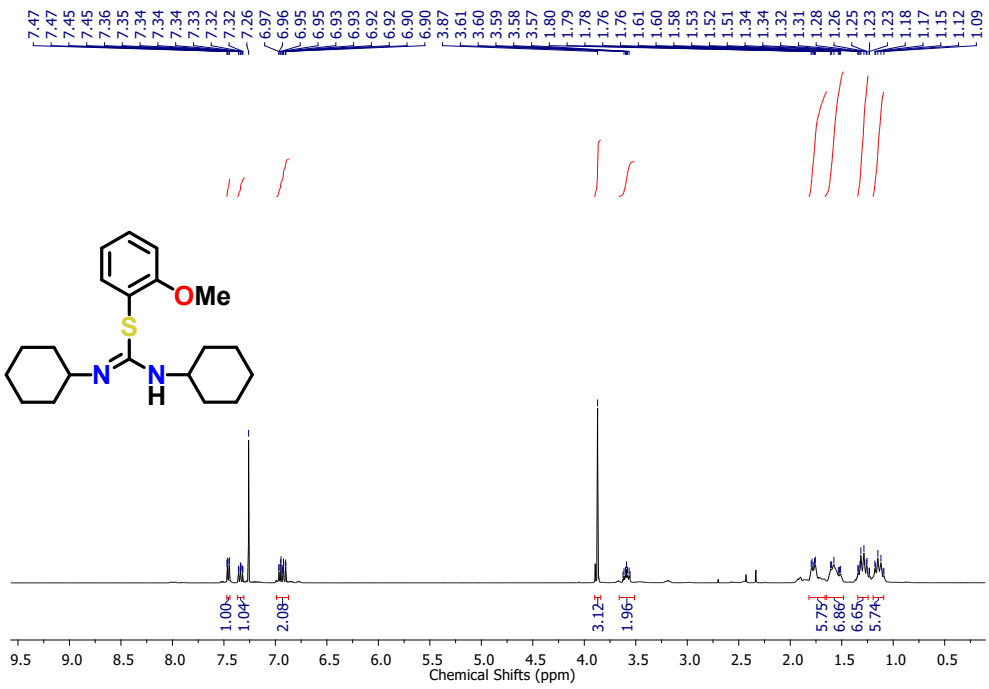


Figure FS119. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **7e.**

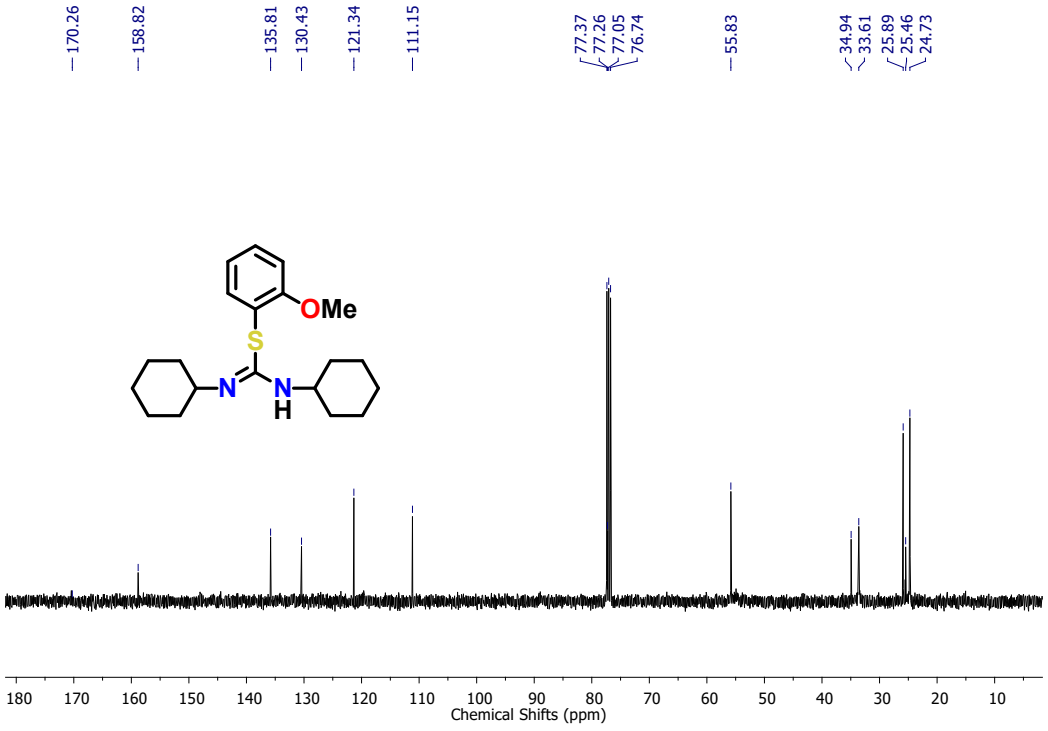


Figure FS120. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **7e.**

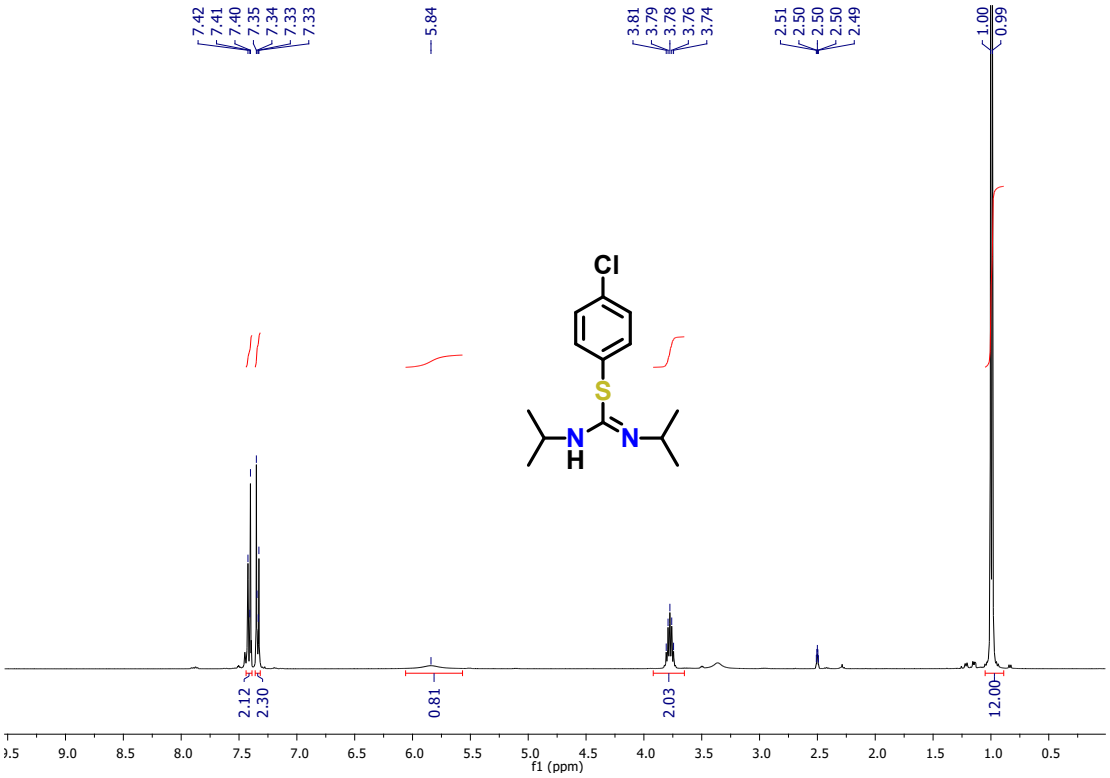


Figure FS121. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7f.**

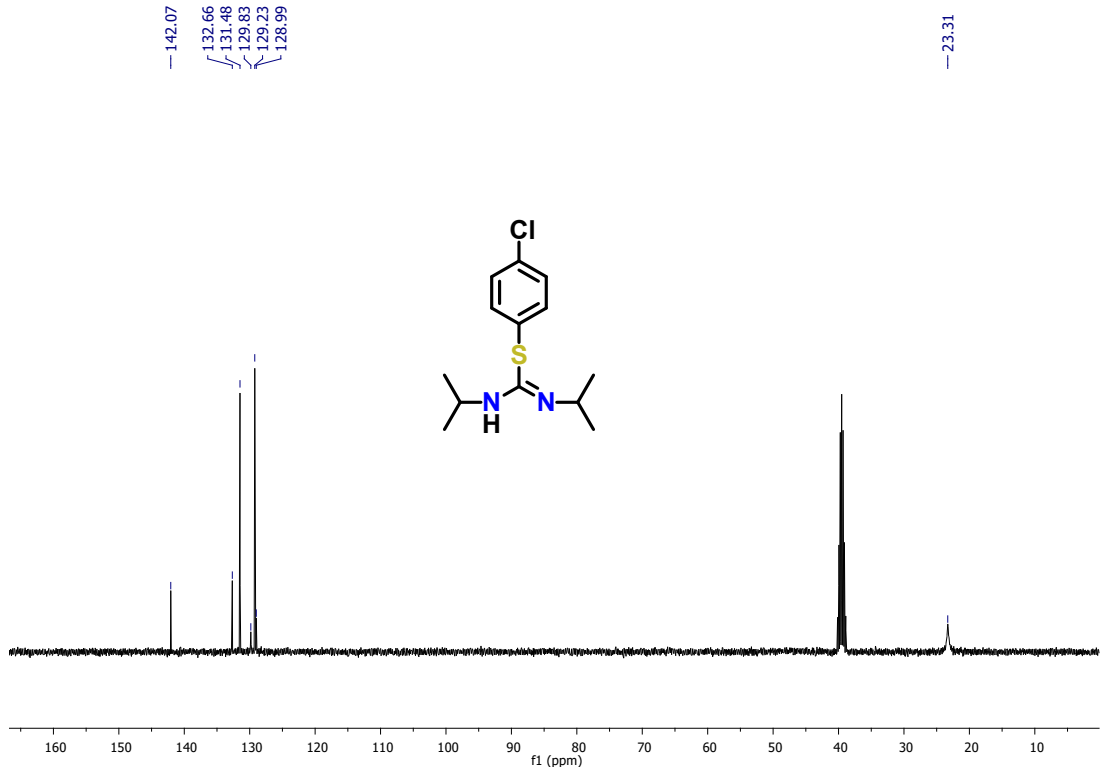


Figure FS122. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **7f.**

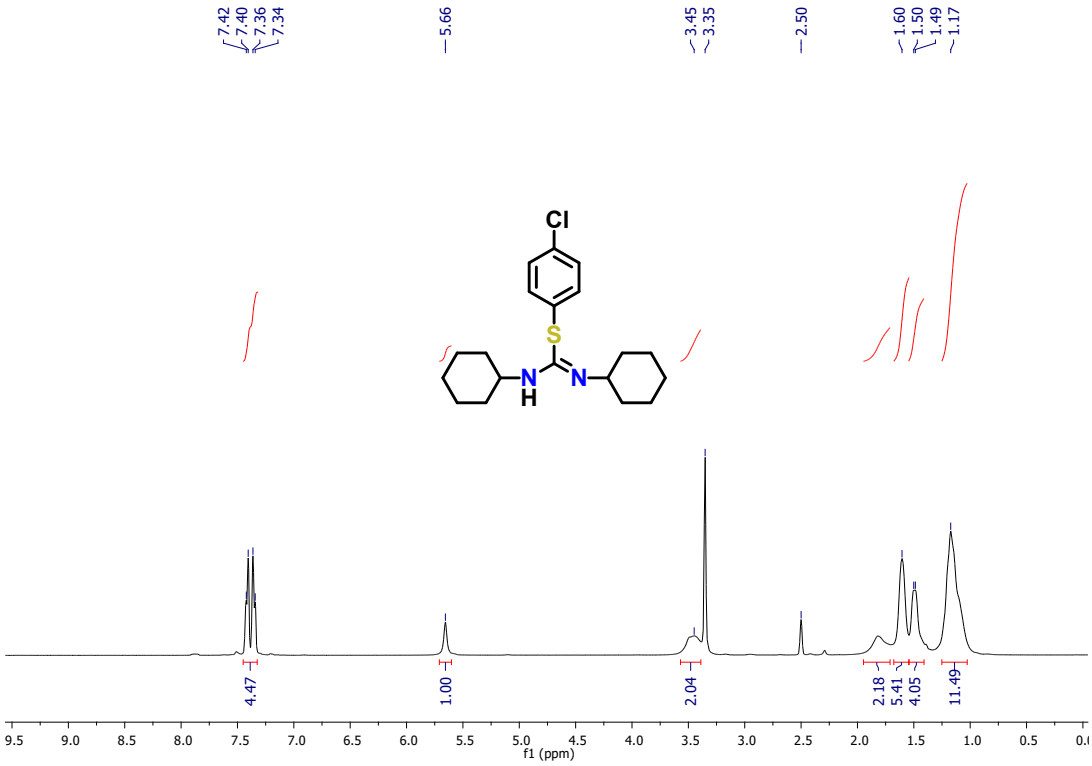


Figure FS123. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7g.**

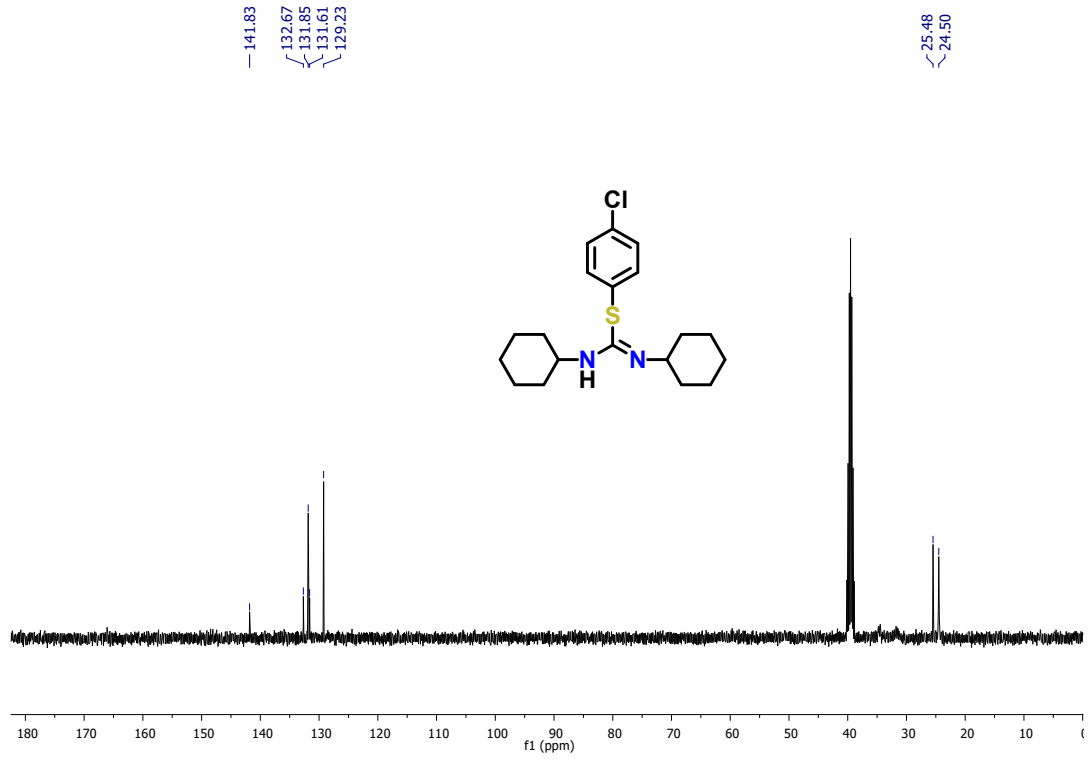


Figure FS124. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **7g**.

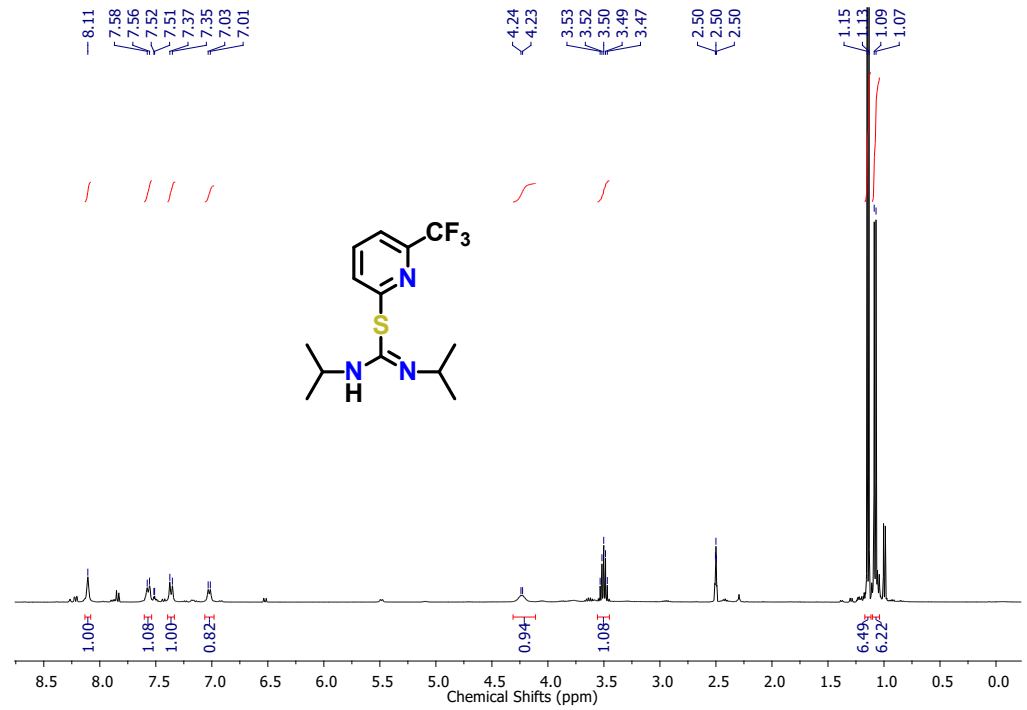


Figure FS125. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7h**.

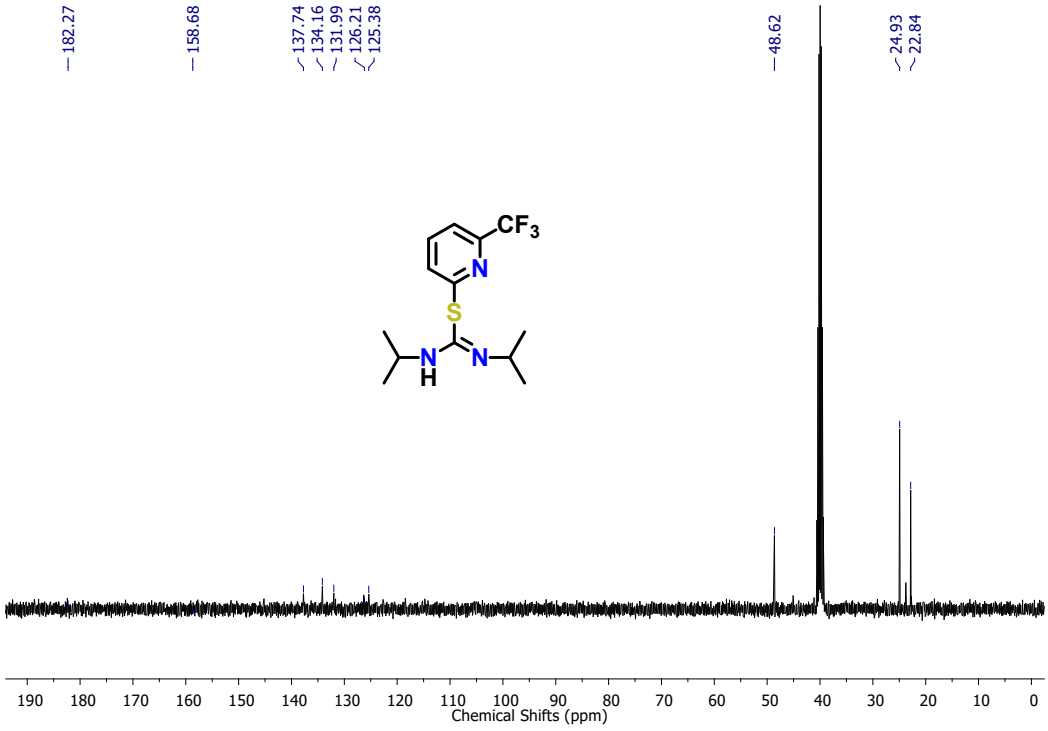


Figure FS126. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **7h**.

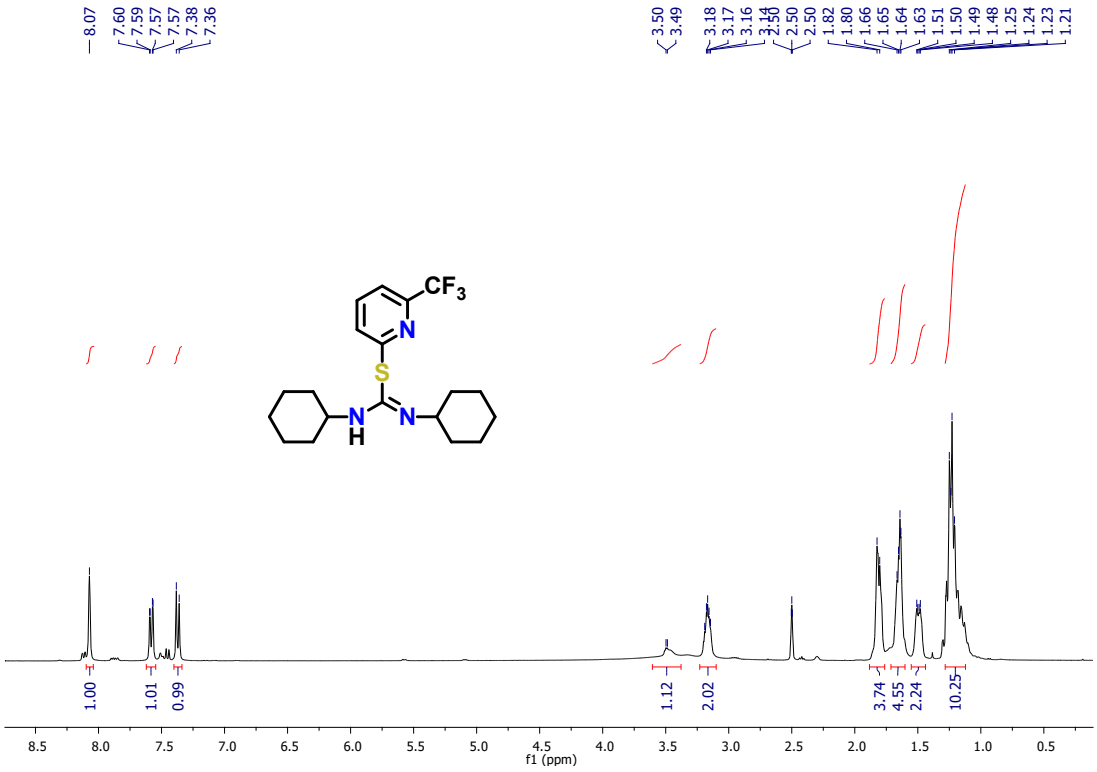


Figure FS127. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7i**.

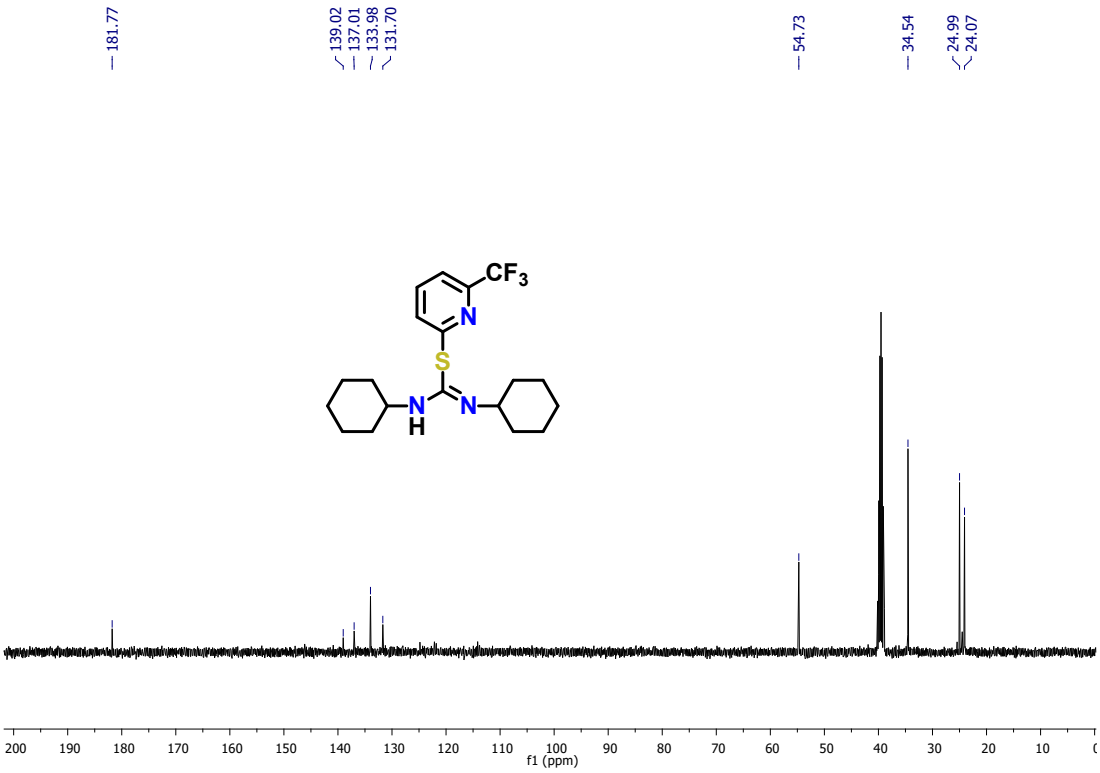


Figure FS128. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 25 ˚C) of **7i**.

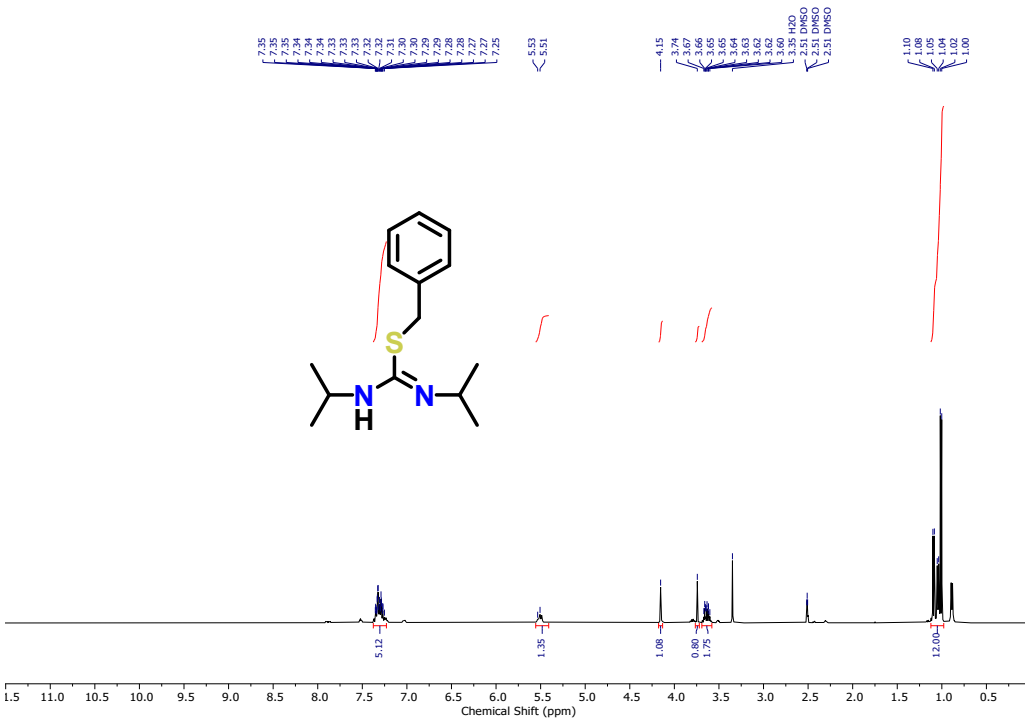


Figure FS129. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ˚C) of **7j**.

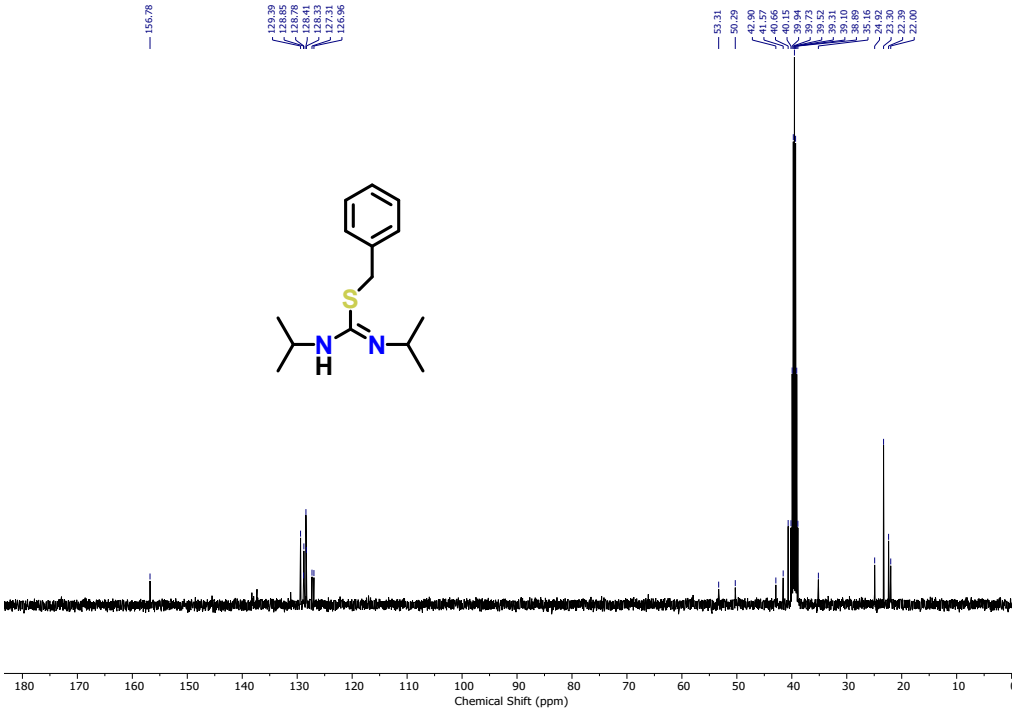


Figure FS130. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **7j.**

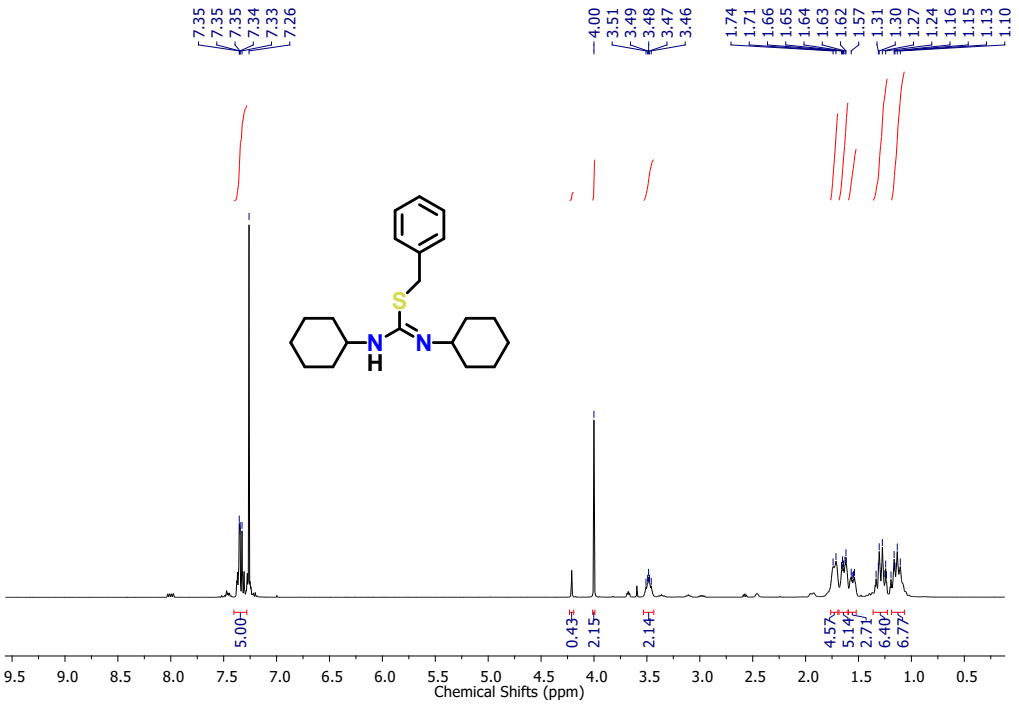


Figure FS131. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **7k.**

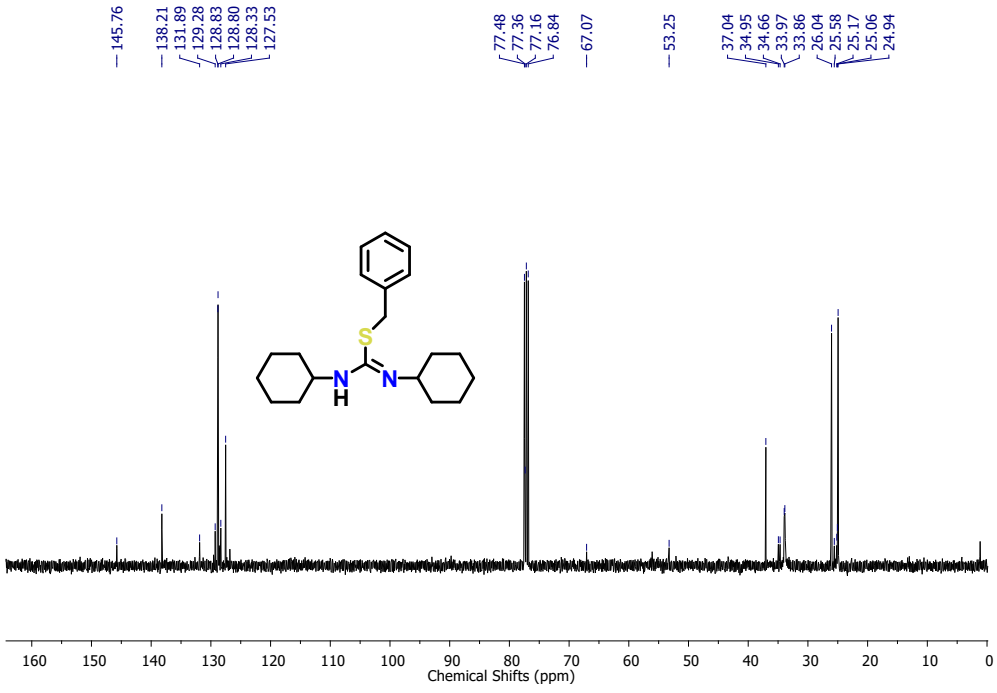


Figure FS132. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **7k.**

NMR Spectra for phosphorylguanidine derivatives (8a-8f).

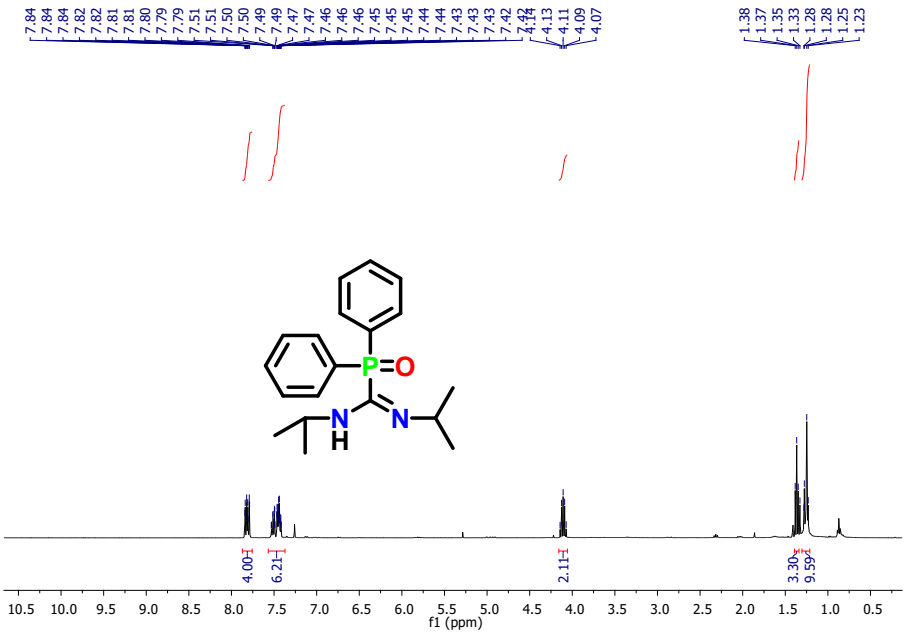


Figure FS133. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8a.**

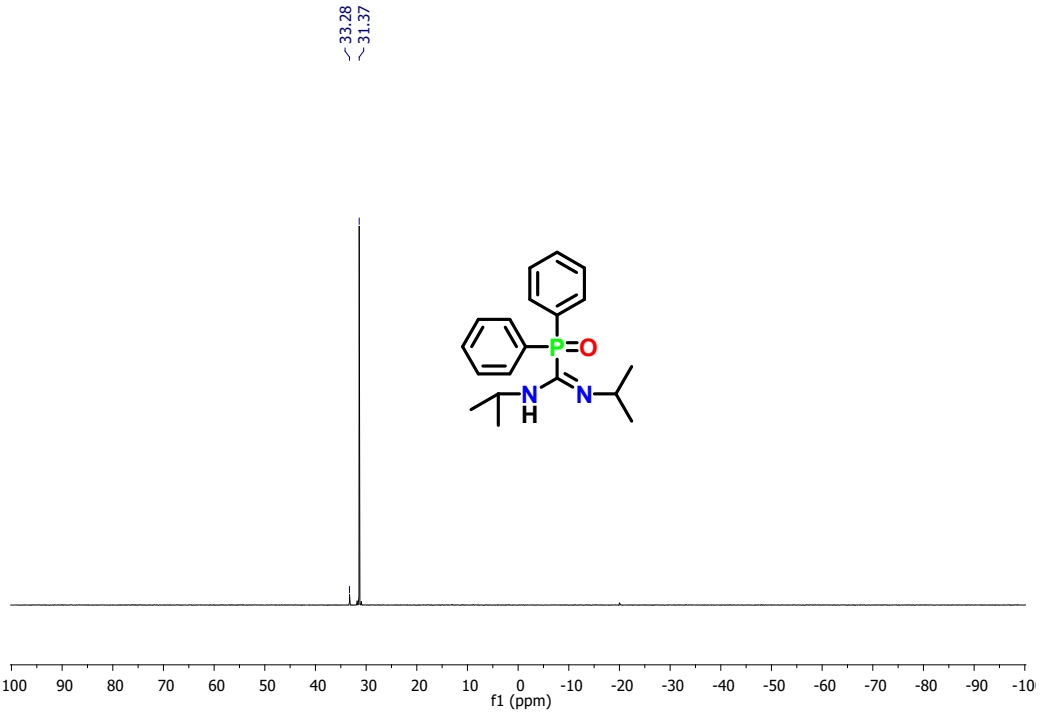


Figure FS134. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.9 MHz, 25 ˚C) of **8a.**

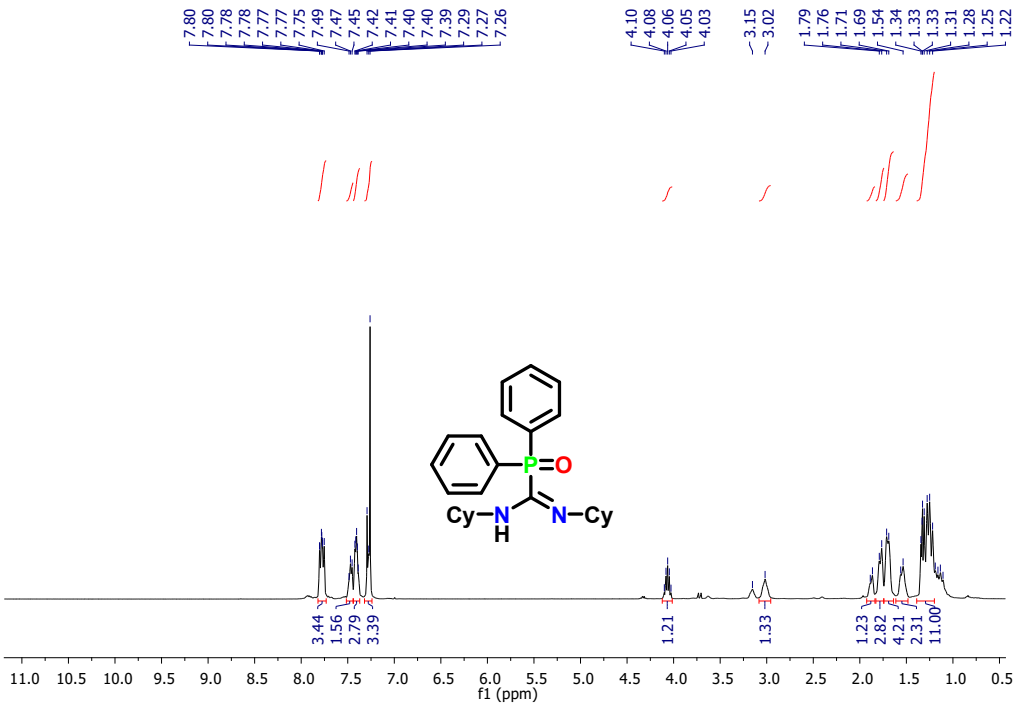


Figure FS135. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8b.**

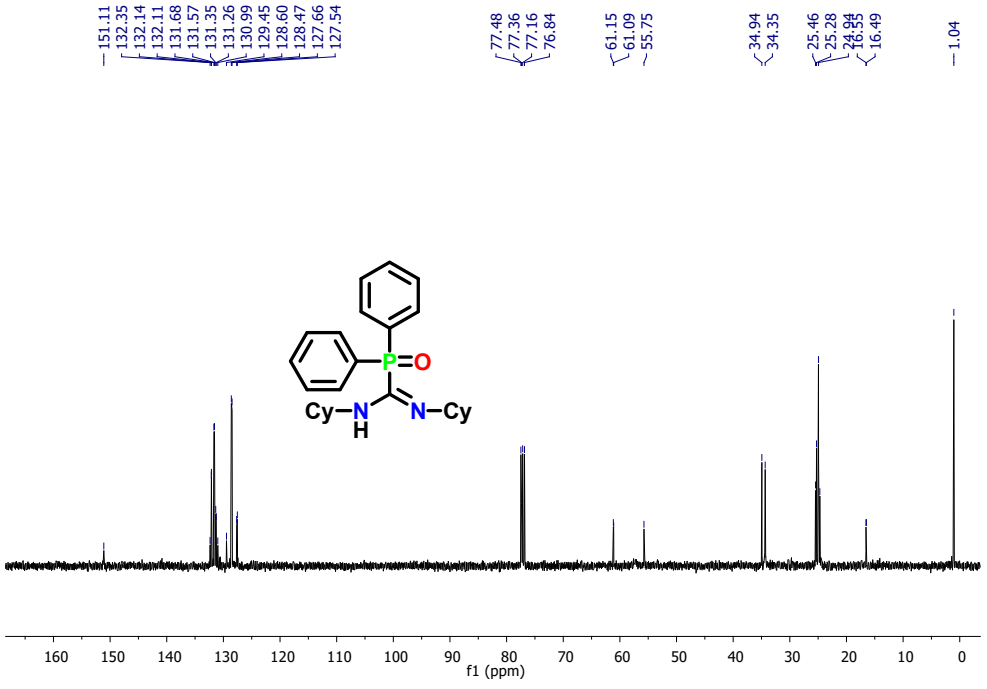


Figure FS136. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **8b.**

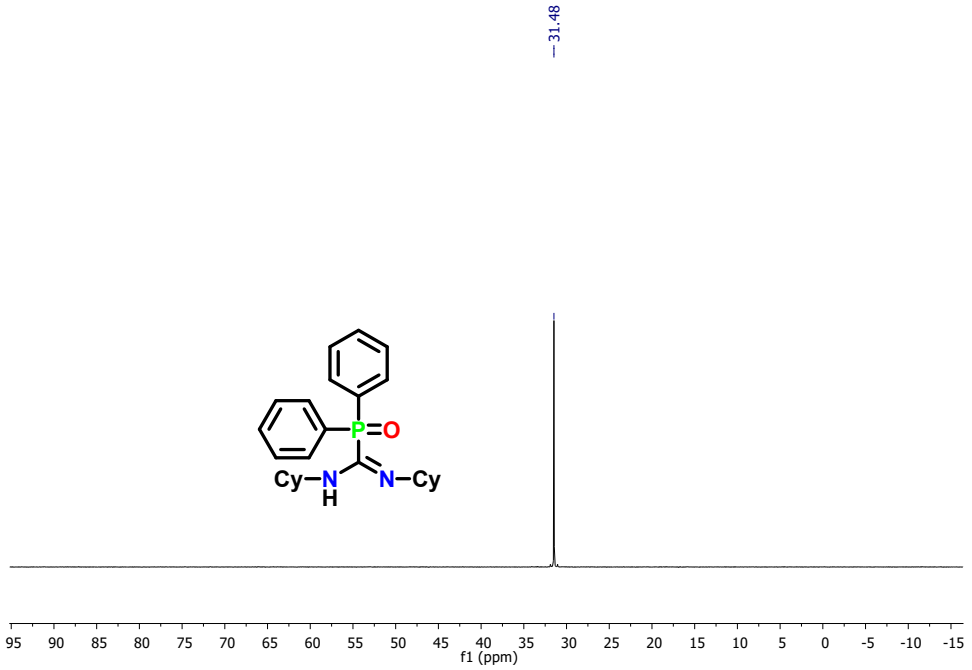


Figure FS137. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.9 MHz, 25 ˚C) of **8b.**

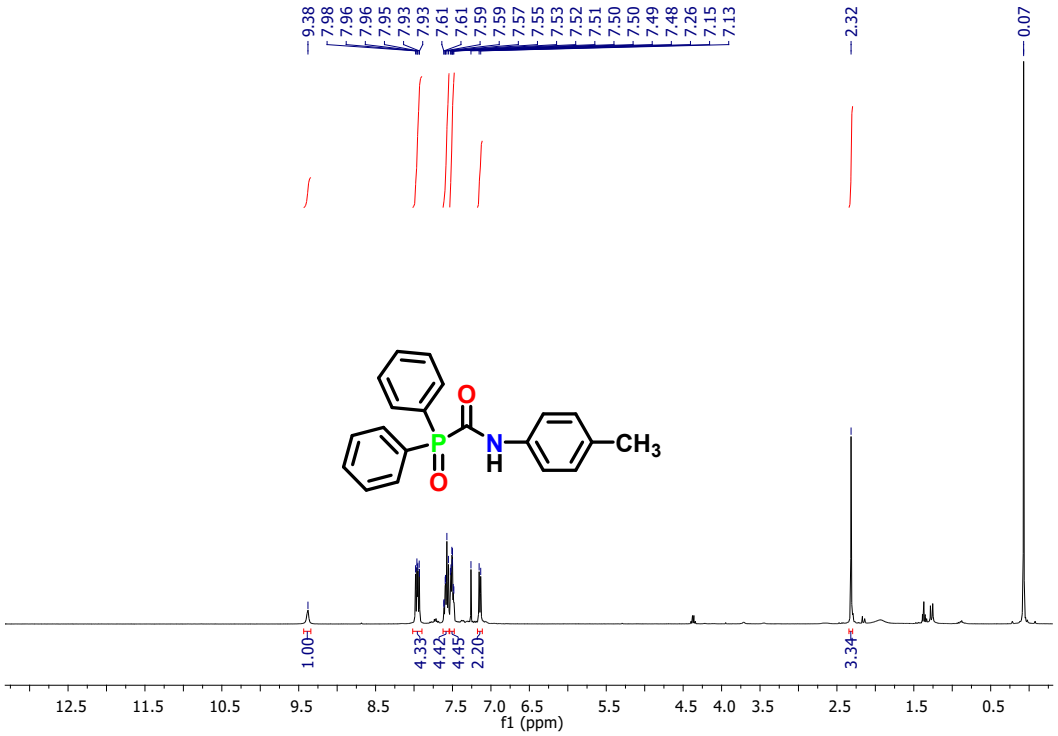


Figure FS138. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8c.**

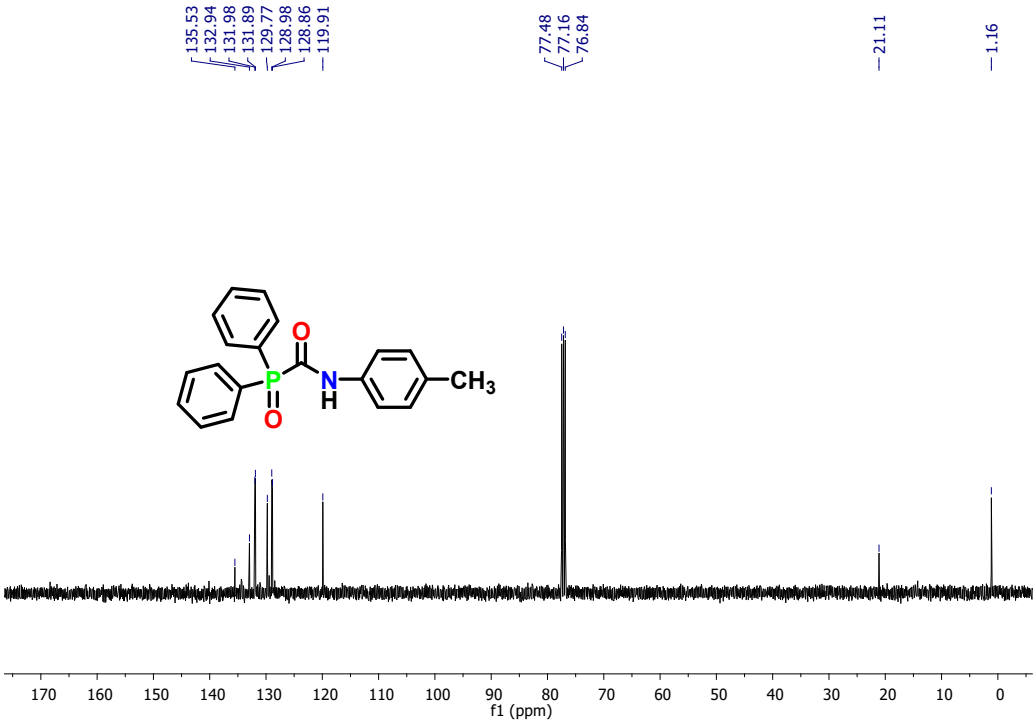


Figure FS139. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **8c.**

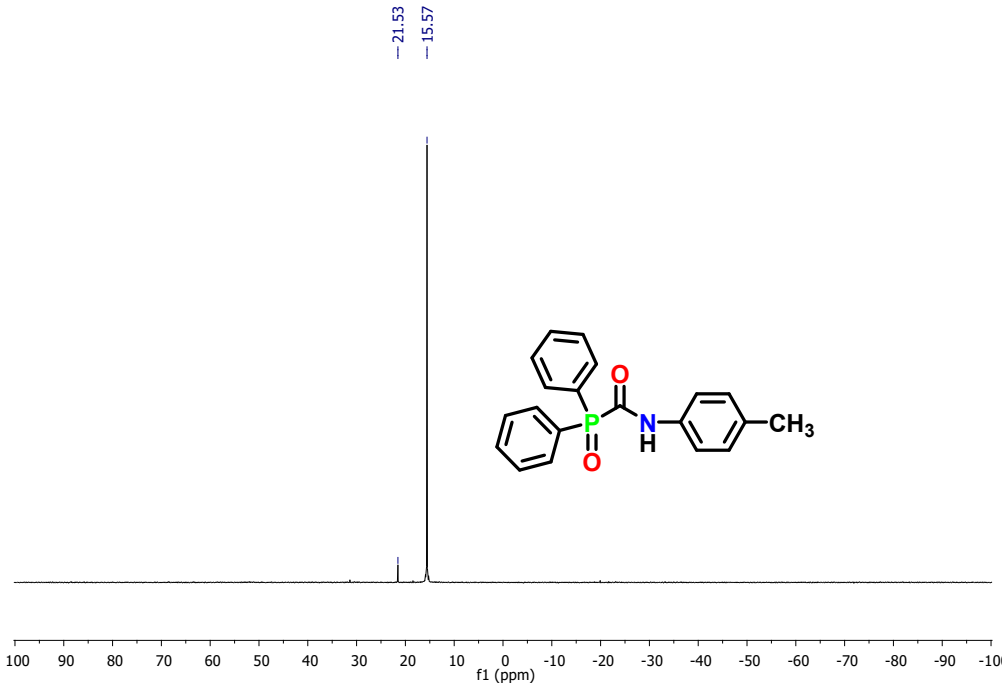


Figure FS140. ^{1}H NMR ($CDCl_3$, 161.9 MHz, 25 ˚C) of **8c.**

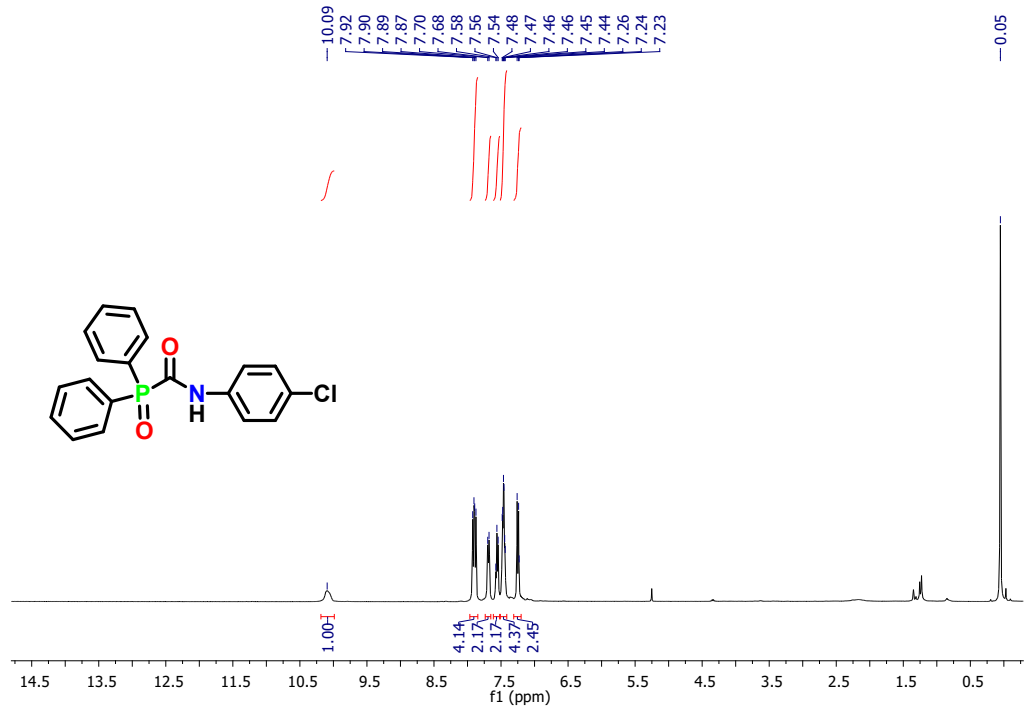


Figure FS141. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8d.**

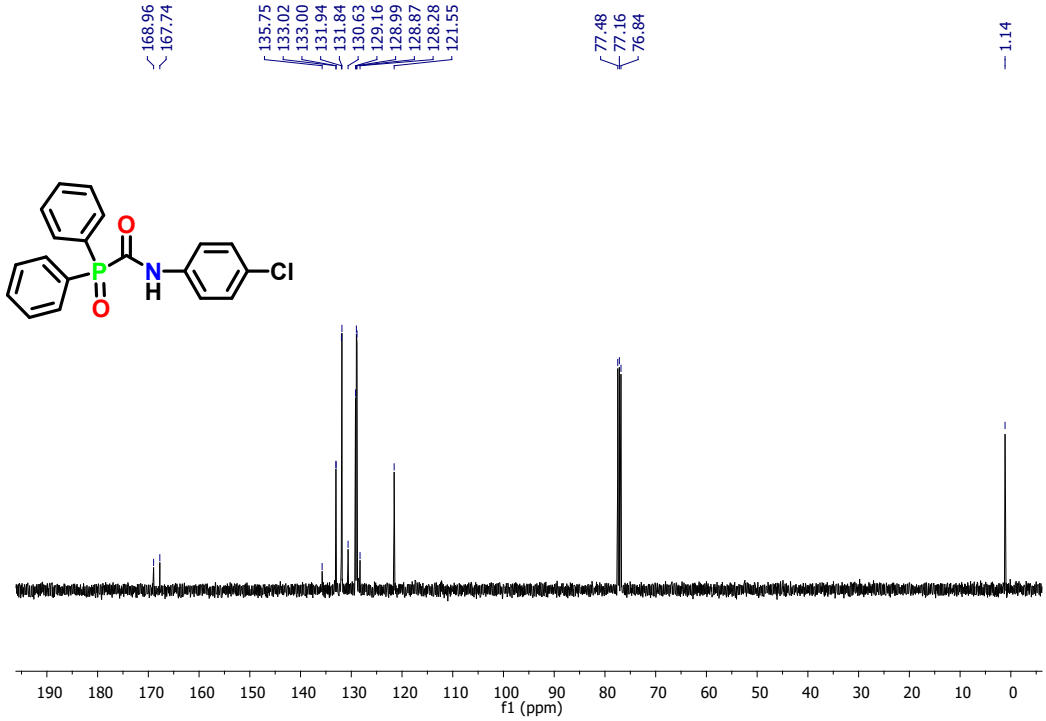


Figure FS142. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **8d.**

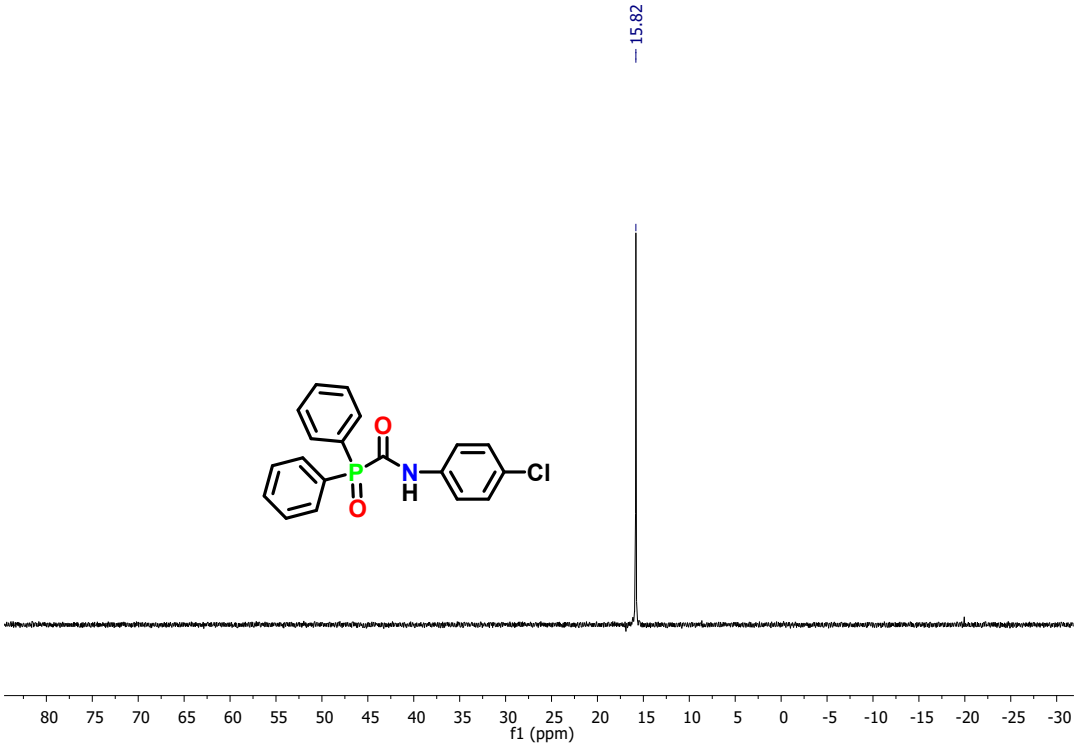


Figure FS143. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.9 MHz, 25 ˚C) of **8d.**

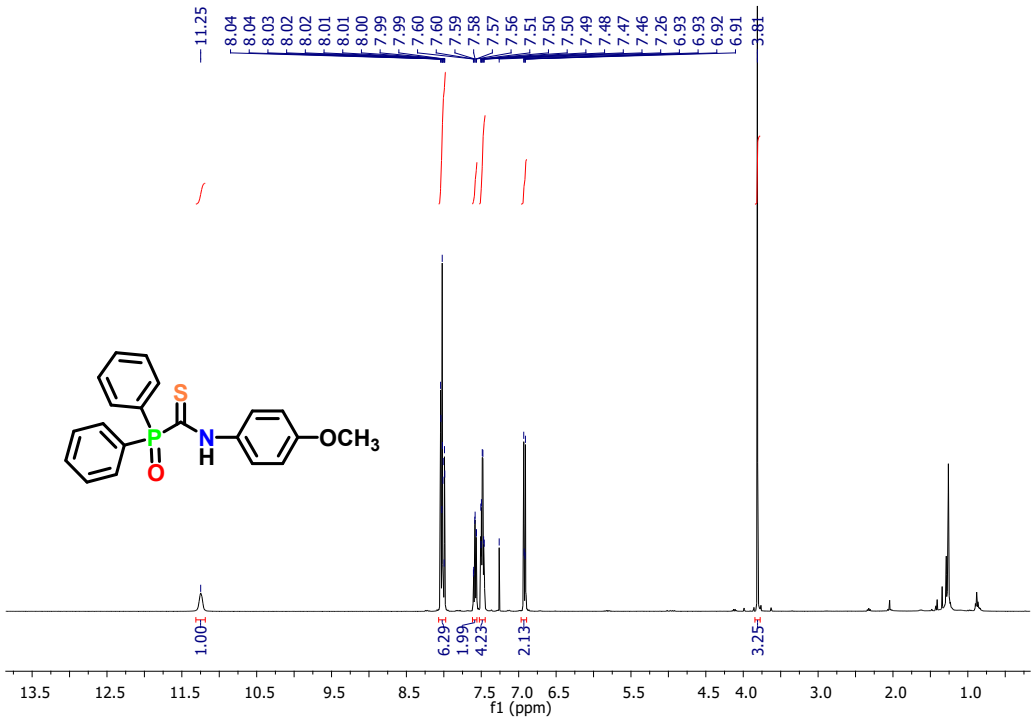


Figure FS144. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8e.**

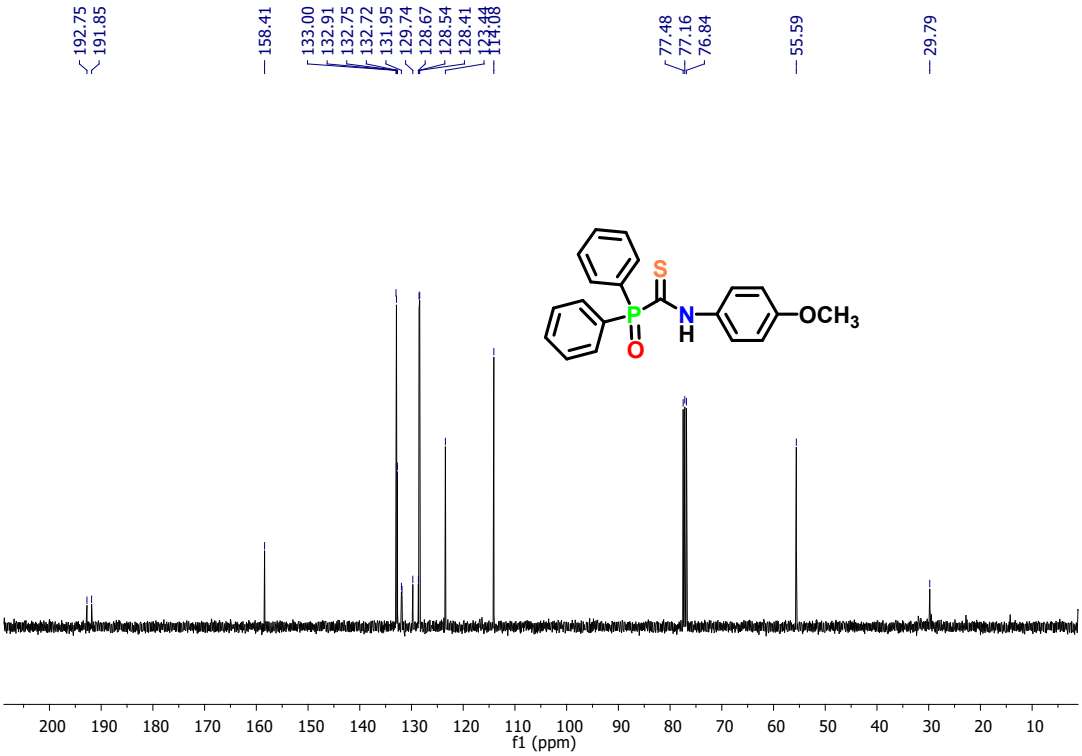


Figure FS145. $^{13}C\{^{1}H\}$- NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **8e.**

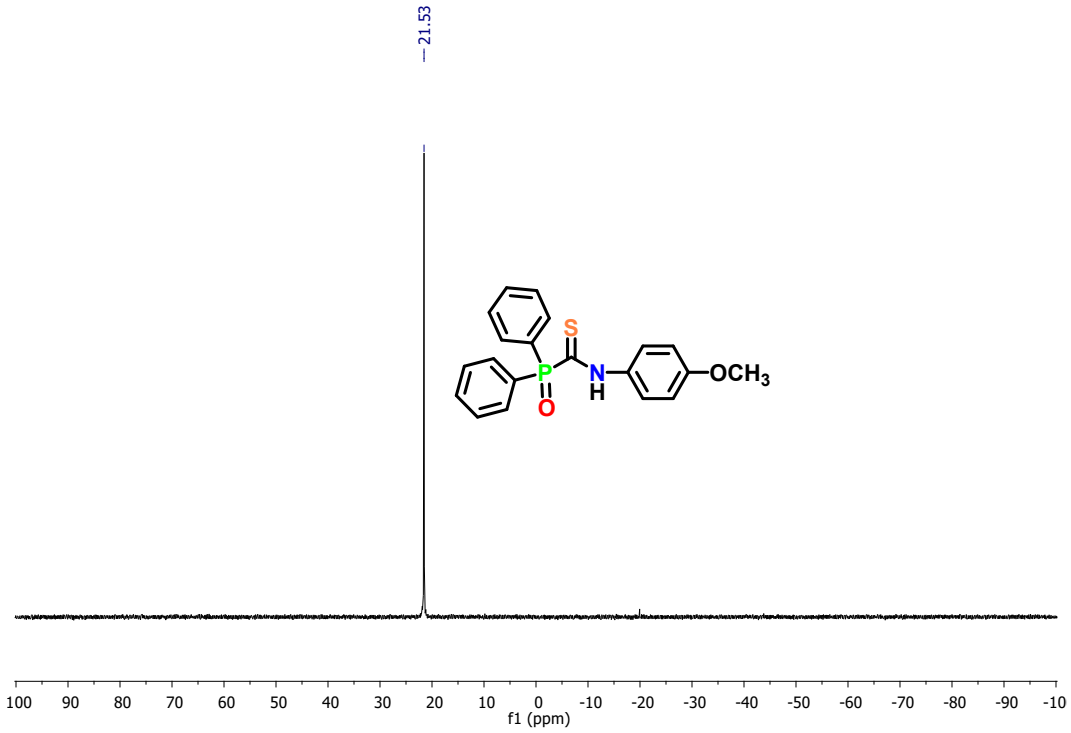


Figure FS146. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8e.**

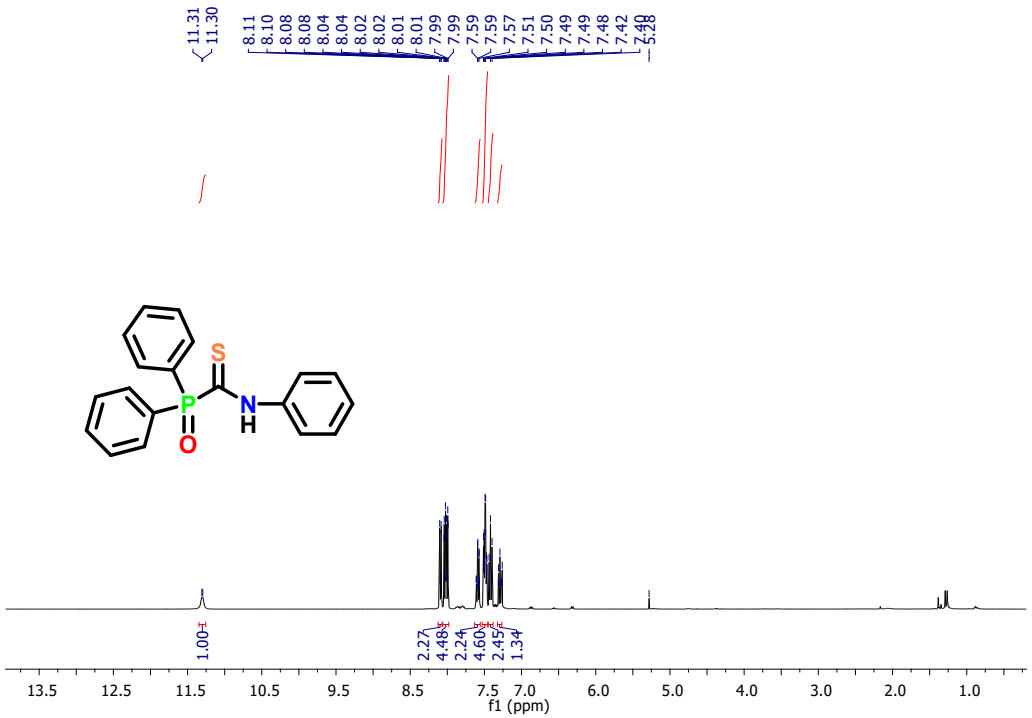


Figure FS147. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8f.**

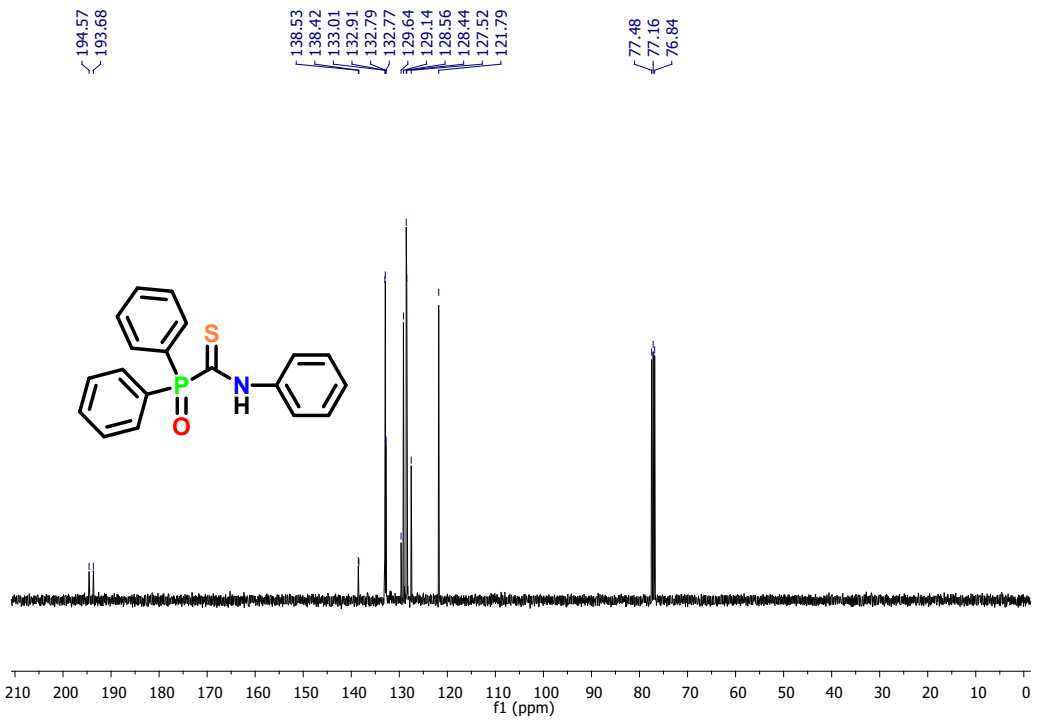


Figure FS148. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **8f.**

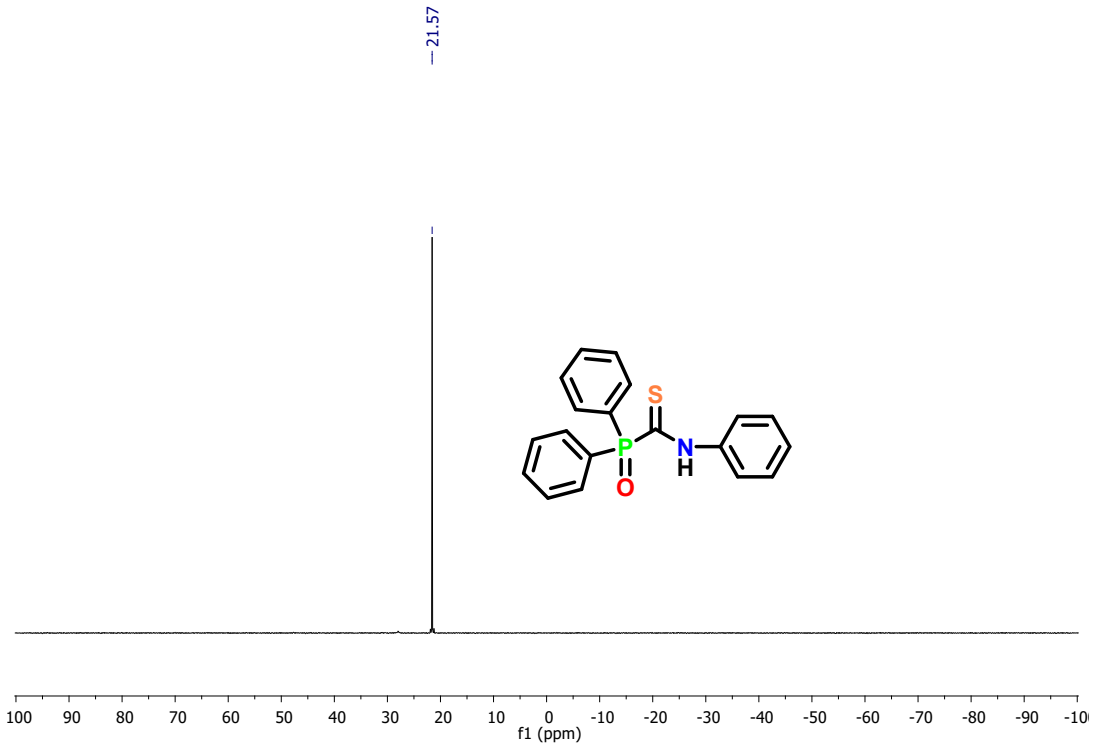
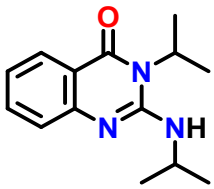


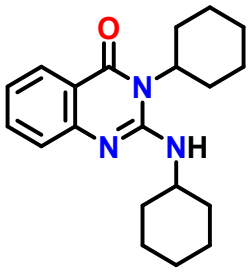
Figure FS149. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **8f.**

NMR Data for quinazolinones (9a-9p).



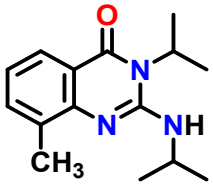
(9a)

Isolated yield: (45 mg, 95%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.11 – 8.05 (m, 1H, CH_{Ar}), 7.54 (ddd, 1H, J = 8.5 Hz, 7.1 Hz, 1.6 Hz, CH_{Ar}), 7.31 (dd, 1H, J = 8.2 Hz, 0.5 Hz, CH_{Ar}), 7.12 (ddd, 1H, J = 8.1 Hz, 7.1 Hz, 1.1 Hz, CH_{Ar}), 5.50 (s, 1H, N*H*), 4.49 – 4.30 (m, 2H, C*H*), 1.55 (d, 6H, J = 7.2 Hz, CH_3), 1.31 (d, 6H, J = 6.2 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.4 (*C*=O), 149.1 (*C*=N), 134.2 (C_{Ar}), 127.2 (C_{Ar}), 124.7 (C_{Ar}), 122.4 (C_{Ar}), 43.7 (*C*H), 29.8 (*C*H), 23.0 (*C*H$_3$), 20.4 (*C*H$_3$) ppm. [11]



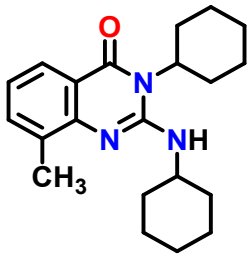
(9b)

Isolated yield: (59 mg, 94%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.07 (dd, 1H, J = 7.9Hz, 1.3 Hz, CH_{Ar}), 7.52 (ddd, 1H, J = 8.5 Hz, 7.1 Hz, 1.6 Hz, CH_{Ar}), 7.34 – 7.28 (m, 1H, CH_{Ar}), 7.10 (ddd, 1H, J = 8.1 Hz, 7.2 HZ, 1.1 Hz, CH_{Ar}), 5.11 (s, 1H, N*H*), 4.57 (s, 1H, C*H*), 4.17 – 4.03 (m, 1H, C*H*), 2.15 – 2.06 (m, 3H, CH_2), 1.89 (dd, 4H, J = 27.6 Hz, 12.4 Hz, CH_2), 1.79 – 1.69 (m, 3H, CH_2), 1.56 – 1.40 (m, 5H, CH_2), 1.38 – 1.13 (m, 5H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.5 (*C*=O), 149.2 (*C*=N), 134.1 (C_{Ar}), 127.2 (C_{Ar}), 124.6 (C_{Ar}), 122.2 (C_{Ar}), 50.1 (*C*H), 33.1 (*C*H), 30.3 (*C*H$_2$), 27.0 (*C*H$_2$), 26.6 (*C*H$_2$), 25.8 (*C*H$_2$), 24.8 (*C*H$_2$) ppm. [11]



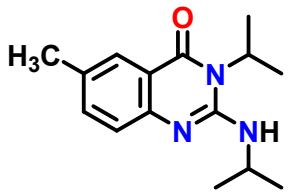
(9c)

Isolated yield: (46 mg, 92%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.87 (s, 1H, J = 1.3 Hz, 0.6 Hz, CH_{Ar}), 7.35 – 7.33 (dd, 1H, CH_{Ar}), 6.98 (d, 1H, J = 8.3 Hz, CH_{Ar}), 5.40 (br., 1H, N*H*), 4.31 (dq, 2H, J = 12.2 Hz, 6.6 Hz, CH_{ipr}), 2.38 (s, 3H, CH_3), 1.48 (d, 6H, J = 7.2 Hz, *CH*$_{3\ (ipr)}$), 1.26 (d, 6H, J = 6.3 Hz, *CH*$_{3(ipr)}$) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.7 (*C*=O), 148.1 (*C*=N), 147.6 (C_{Ar}), 134.3 (C_{Ar}), 132.8 (C_{Ar}), 124.8 (C_{Ar}), 121.9 (C_{Ar}), 117.3 (C_{Ar}), 44.1 (*C*H), 29.8 (*C*H$_{3\ (ipr)}$), 22.8 (*C*H$_3$), 20.4 (*C*H$_{3(ipr)}$), 17.2 (*C*H$_{3(ipr)}$) ppm. [11]



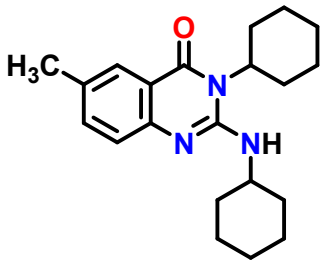
(9d)

Isolated yield: (58 mg, 89%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.93 (dd, 1H, J = 8.0 Hz, 0.9 Hz, CH_{Ar}), 7.42 – 7.39 (m, 1H, CH_{Ar}), 7.01 (d, 1H, J = 7.7 Hz, CH_{Ar}), 5.08 (s, 1H, N*H*), 4.56 (s, 1H, C*H*), 4.12 – 4.07 (m, 1H, C*H*), 2.44 (s, 3H, CH_2), 2.14 (d, 4H, J = 12.3 Hz, CH_2), 1.91 – 1.61 (m, 3H, CH_2), 1.51 (dd, 3H, J = 9.5 Hz, 4.1 Hz, CH_2), 1.48 – 1.33 (m, 5H, CH_2), 1.25 (dd, 5H, J = 24.0 Hz, 11.2 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.9 (*C*=O), 148.2 (*C*=N), 147.6 (C_{Ar}), 134.3 (C_{Ar}), 132.7 (C_{Ar}), 124.8 (C_{Ar}), 121.8 (C_{Ar}), 50.7 (*C*H), 32.8 (*CH*), 30.3 (CH_2), 26.6 (CH_2), 26.0 (CH_2), 25.7 (CH_2), 24.8 (CH_2), 17.1 (CH_3) ppm. [11]



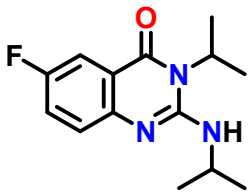
(9e)

Isolated yield: (41 mg, 82%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.87 (dd, 1H, J = 1.3 Hz, 0.6 Hz, CH_{Ar}), 7.40 – 7.33 (m, 1H, CH_{Ar}), 7.28 – 7.19 (m, 1H, CH_{Ar}), 5.48 (s, 1H, N*H*), 4.35 (dq, 2H, J = 12.2 Hz, 6.6 Hz, CH_2), 2.38 (s, 3H, CH_3), 1.54 (d, 6H, J = 7.2 Hz, CH_3), 1.30 (d, 6H, J = 6.3 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.3 (*C*=O), 148.6 (*C*=N), 147.0 (C_{Ar}), 135.6 (C_{Ar}), 131.9 (C_{Ar}), 126.5 (C_{Ar}), 124.5 (C_{Ar}), 43.7 (*C*H), 23.1 (*C*H_3), 21.1 (*C*H_3), 20.4 (*C*H_3) ppm. [11]



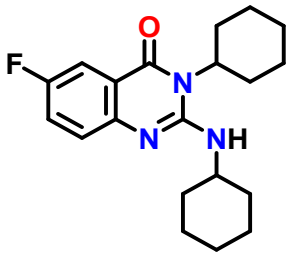
(9f)

Isolated yield: (53 mg, 81%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.85 (d, 1H, J = 0.7 Hz, CH_{Ar}), 7.35 (dd, 1H, J = 8.3 Hz, 2.1 Hz, CH_{Ar}), 7.22 – 7.20 (m, 1H, CH_{Ar}), 5.08 (s, 1H, N*H*), 4.50 (s, 1H, C*H*), 4.11 – 4.06 (m, 1H, C*H*), 2.37 (s, 3H, CH_3), 2.13 – 2.09 (m, 3H, CH_2), 1.76 – 1.71 (m, 4H, CH_2), 1.51 – 1.48 (m, 3H, CH_2), 1.47 – 1.28 (m, 5H, CH_2), 1.25 (dd, 6H, J = 21.9 Hz, 10.4 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.5 (*C*=O), 148.7 (*C*=N), 147.0 (C_{Ar}), 135.6 (C_{Ar}), 131.8 (C_{Ar}), 126.6 (C_{Ar}), 124.5 (C_{Ar}), 50.1 (C*H*), 33.1 (*C*H$_2$), 30.3 (*C*H$_2$), 26.6 (*C*H$_2$), 25.7 (*C*H$_2$), 24.8 (*C*H$_2$), 21.1 (*C*H$_3$) ppm. [11]



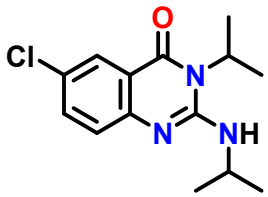
(9g)

Isolated yield: (35 mg, 70%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.75 – 7.70 (m, 1H, CH_{Ar}), 7.30 – 7.24 (m, 2H, CH_{Ar}), 5.45 (br., 1H, N*H*), 4.42 – 4.27 (m, 2H, C*H*), 1.55 (d, 6H, J = 7.2 Hz, CH_3), 1.30 (d, 6H, J = 6.2 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 162.7 (*C*=O), 159.5 (*C*–N), 157.1 (C_{Ar}), 148.6 (C_{Ar}), 145.7 (C_{Ar}), 126.7 (C_{Ar}), 122.8 (C_{Ar}), 122.6 (C_{Ar}), 111.8 (C_{Ar}), 111.6 (C_{Ar}), 43.8 (*C*H), 23.0 (*C*H$_3$), 20.4 (*C*H$_3$) ppm. [11]



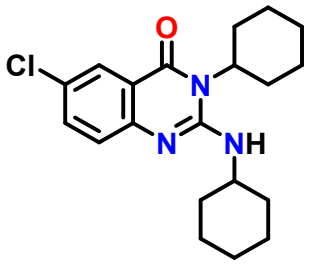
(9h)

Isolated yield: (47 mg, 72%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 7.65 – 7.62 (m, 1H, CH_{Ar}), 7.21 – 7.19 (m, 2H, CH_{Ar}), 5.00 (s, 1H, N*H*), 4.46 (s, 1H, C*H*), 4.03 – 3.95 (m, 1H, C*H*), 2.05 – 2.01 (m, 2H, CH_2), 1.89 – 1.78 (m, 6H, CH_2), 1.67 (dd, 2H, J = 9.4 Hz, 4.4 Hz, CH_2), 1.47 – 1.37 (m, 5H, CH_2), 1.29 – 1.18 (m, 5H, CH_2) ppm. ^{13}C{^{1}H} NMR (400 MHz, 25 °C, $CDCl_3$): δ_C 162.7 (*C*=O), 159.3 (*C*=N), 156.9 (*C*=N), 148.6 (C_{Ar}), 145.7 (C_{Ar}), 126.5 (C_{Ar}), 122.6 (C_{Ar}), 122.4 (C_{Ar}), 111.5 (C_{Ar}), 50.1 (*C*H), 33.0 (*C*H), 30.2 (*C*H_2), 26.7 (*C*H_2), 25.7 (*C*H_2), 24.7 (*C*H_2) ppm. [11]



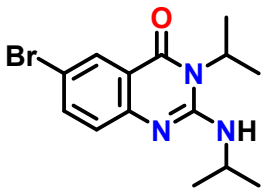
(9i)

Isolated yield: (41 mg, 75%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.03 (d, 1H, J = 2.5 Hz, CH_{Ar}), 7.45 (ddd, 1H, J = 8.8 Hz, 2.5 Hz, 0.5 Hz, CH_{Ar}), 7.28 – 7.22 (m, 1H, CH_{Ar}), 5.45 (br., 1H, N*H*), 4.37 (m, 2H, J = 19.7 Hz, 6.7 Hz, , CH_{ipr}), 1.54 (d, 6H, J = 7.2 Hz, CH_3), 1.30 (d, 6H, J = 6.2 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 162.4 (*C*=O), 149.1 (*C*=N), 147.7 (C_{Ar}), 134.4 (C_{Ar}), 127.4 (C_{Ar}), 126.4 (C_{Ar}), 118.5 (C_{Ar}–Cl), 43.8 (*C*H), 23.0 (*C*H_3), 20.4 (*C*H_3) ppm. [11]



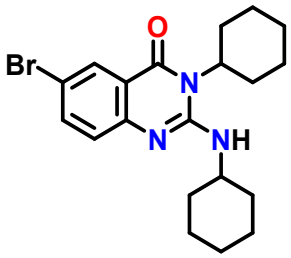
(9j)

Isolated yield: (53 mg, 76%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.01 (d, 1H, J = 2.4 Hz, CH_{Ar}), 7.44 (dd, 1H, J = 8.7 Hz, 2.6 Hz, CH_{Ar}), 7.23 (d, 1H, J = 8.7 Hz, CH_{Ar}), 5.06 (s, 1H, N*H*), 4.60 (s, 1H, C*H*), 4.13 – 4.00 (m, 1H, C*H*), 2.14 – 2.07 (m, 2H, CH_2), 1.98 – 1.76 (m, 6H, CH_2), 1.76 – 1.66 (m, 2H, CH_2), 1.59 – 1.39 (m, 5H, CH_2), 1.37 – 1.16 (m, 5H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 162.5 (*C*=O), 149.3 (*C*=N), 147.8 (C_{Ar}), 134.4 (C_{Ar}), 127.3 (C_{Ar}), 126.4 (C_{Ar}), 50.2 (*C*H), 33.1 (*C*H_2), 30.3 (*C*H_2), 26.6 (*C*H_2), 25.7 (*C*H_2), 24.8 (*C*H_2) ppm. [11]



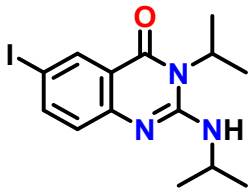
(9k)

Isolated yield: (49 mg, 79%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.18 (d, 1H, J = 2.3 Hz, CH_{Ar}), 7.58 (dd, 1H, J = 8.7 Hz, 2.4 Hz, CH_{Ar}), 7.18 (d, 1H, J = 8.7 Hz, CH_{Ar}), 5.45 (br., 1H, N*H*), 4.37 (dq, 2H, J = 19.8 Hz, 6.8 Hz, C*H*), 1.54 (d, 6H, J = 7.2 Hz, CH_3), 1.30 (d, 6H, J = 6.3 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 162.2 (*C*=O), 149.2 (*C*–N), 148.1 (C_{Ar}), 137.1 (C_{Ar}), 129.6 (C_{Ar}), 126.6 (C_{Ar}), 119.0 (C_{Ar}), 114.8 (C_{Ar}), 43.8 (*C*H), 23.0 (*C*H_3), 20.4 (*C*H_3) ppm. [11]



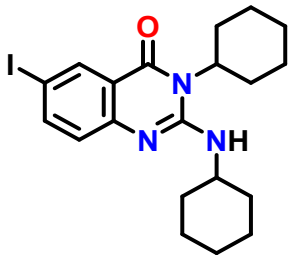
(9l)

Isolated yield: (59 mg, 76%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.16 (d, 1H, J = 2.4 Hz, CH_{Ar}), 7.57 (d, 1H, J = 6.3 Hz, CH_{Ar}), 7.17 (d, 1H, J = 8.7 Hz, CH_{Ar}), 5.08 (s, 1H, N*H*), 4.61 (s, 1H, C*H*), 4.07 (dd, 1H, J = 6.8 Hz, 3.3 Hz, C*H*), 2.09 (d, 3H, J = 8.6 Hz, CH_2), 1.91 (s, 2H, CH_2), 1.86 (d, 4H, J = 11.5 Hz, CH_2), 1.72 (t, 5H, J = 8.8 Hz, CH_2), 1.51 – 1.46 (m, 4H, CH_2), 1.42 – 1.28 (m, 5H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 162.4 (*C*=O), 149.3 (*C*=N), 148.1 (C_{Ar}), 137.1 (C_{Ar}), 129.6 (C_{Ar}), 126.5 (C_{Ar}), 114.6 (C_{Ar}), 50.2 (*C*H), 33.1 (*C*H), 30.2 (*C*H$_2$), 26.5 (*C*H$_2$), 25.7 (*C*H$_2$), 24.8 (*C*H$_2$) ppm. [11]



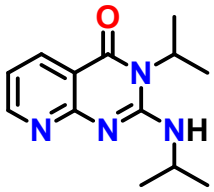
(9m)

Isolated yield: (58 mg, 82%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.38 (d, 1H, J = 2.1 Hz, CH_{Ar}), 7.75 (dd, 1H, J = 8.7 Hz, 2.2 Hz, CH_{Ar}), 7.05 (d, 1H, J = 8.7 Hz, CH_{Ar}), 5.44 (s, 1H, N*H*), 4.37 (ddt, 2H, J = 19.9 Hz, 13.4 Hz, 6.6 HZ, C*H*), 1.54 (d, 6H, J = 7.2 Hz, CH_3), 1.30 (d, 6H, J = 6.3 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 161.9 (*C*=O), 149.3 (*C*=N), 148.6 (C_{Ar}), 142.6 (C_{Ar}), 135.9 (C_{Ar}), 126.8 (C_{Ar}), 119.6 (C_{Ar}), 84.7 (C_{Ar}–I), 43.9 (*C*H$_{ipr}$), 23.0 (*C*H$_3$), 20.4 (*C*H$_3$) ppm. [11]



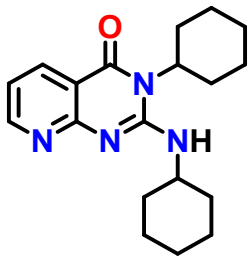
(9n)

Isolated yield: (70 mg, 81%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.36 (d, 1H, J = 2.1 Hz, CH_{Ar}), 7.74 (dd, 1H, J = 8.6 Hz, 2.2 Hz, CH_{Ar}), 7.05 (d, 1H, J = 8.6 Hz, CH_{Ar}), 5.16 (d, 1H, J = 12.6 Hz, N*H*), 4.62 (s, 1H, C*H*), 4.20 – 3.96 (m, 1H, C*H*), 2.09 (dd, 3H, J = 12.2 Hz, 3.7 Hz, CH_2), 1.89 (dd, 4H, J = 35.2 Hz, 13.4 Hz, CH_2), 1.78 – 1.62 (m, 4H, CH_2), 1.57 – 1.42 (m, 4H, CH_2), 1.37 – 1.16 (m, 5H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 161.9 (*C*=O), 149.5 (*C*–N), 148.6 (C_{Ar}), 142.5 (C_{Ar}), 135.9 (C_{Ar}), 131.4 (C_{Ar}), 129.3 (C_{Ar}), 126.8 (C_{Ar}), 50.4 (*C*H), 32.9 (*C*H), 30.2 (*C*H$_2$), 26.7 (*C*H$_2$), 25.8 (*C*H$_2$), 24.8 (*C*H$_2$) ppm. [11]



(9o)

Isolated yield: (38 mg, 82%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.70 (dd, 1H, J = 4.6 Hz, 2.1 Hz, CH_{Ar}), 8.36 (dd, 1H, J = 7.8 Hz, 2.1 Hz, CH_{Ar}), 7.05 (dd, 1H, J = 7.8 Hz, 4.6 Hz, CH_{Ar}), 5.44 (s, 1H, N*H*), 4.61 (ddt, 2H, J = 20.1 Hz, 13.6 Hz, 6.7 Hz, C*H*), 1.55 (d, 6H, J = 7.2 Hz, CH_3), 1.32 (d, 6H, J = 6.3 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.4 (*C*=O), 158.8 (*C*=N), 155.9 (C_{Ar}), 151.2 (C_{Ar}), 136.8 (C_{Ar}), 131.9 (C_{Ar}), 128.6 (C_{Ar}), 118.2 (C_{Ar}), 112.2 (C_{Ar}), 67.0 (*C*H), 53.2 (*C*H), 44.05 (*C*H$_3$), 29.8 (*C*H$_3$), 23.0 (*C*H$_3$), 20.3 (*C*H$_3$) ppm. [11]



(9p)

Isolated yield: (50 mg, 81%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ_H 8.67 (dd, 1H, J = 4.6 Hz, 1.9 Hz, CH_{Ar}), 8.36 – 8.33 (m, 1H, CH_{Ar}), 7.04 (dd, 1H, J = 7.8 Hz, 4.6 Hz, CH_{Ar}), 5.00 (s, 1H, N*H*), 4.85 (d, 1H, J = 6.6 Hz, C*H*), 4.34 – 4.27 (m, 1H, C*H*), 2.13 (dd, 3H, J = 12.2 Hz, 3.5 Hz, CH_2), 1.90 (d, 5H, J = 17.3 Hz, CH_2), 1.67 – 1.57 (m, 4H, CH_2), 1.47 (d, 2H, J = 13.3 Hz, CH_2), 1.24 (dd, 6H, J = 18.6 Hz, 13.0 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, 25 °C, $CDCl_3$): δ_C 163.6 (*C*=O), 158.9 (*C*=N), 155.9 (C_{Ar}), 151.3 (C_{Ar}), 136.8 (C_{Ar}), 118.1 (C_{Ar}), 50.2 (*C*H), 34.0 (*C*H), 33.1 (*C*H$_2$), 30.2 (*C*H$_2$), 26.6 (*C*H$_2$), 25.0 (*C*H$_2$), 24.7 (*C*H$_2$) ppm. [11]

NMR Spectra for quinazolinones (9a-9p).

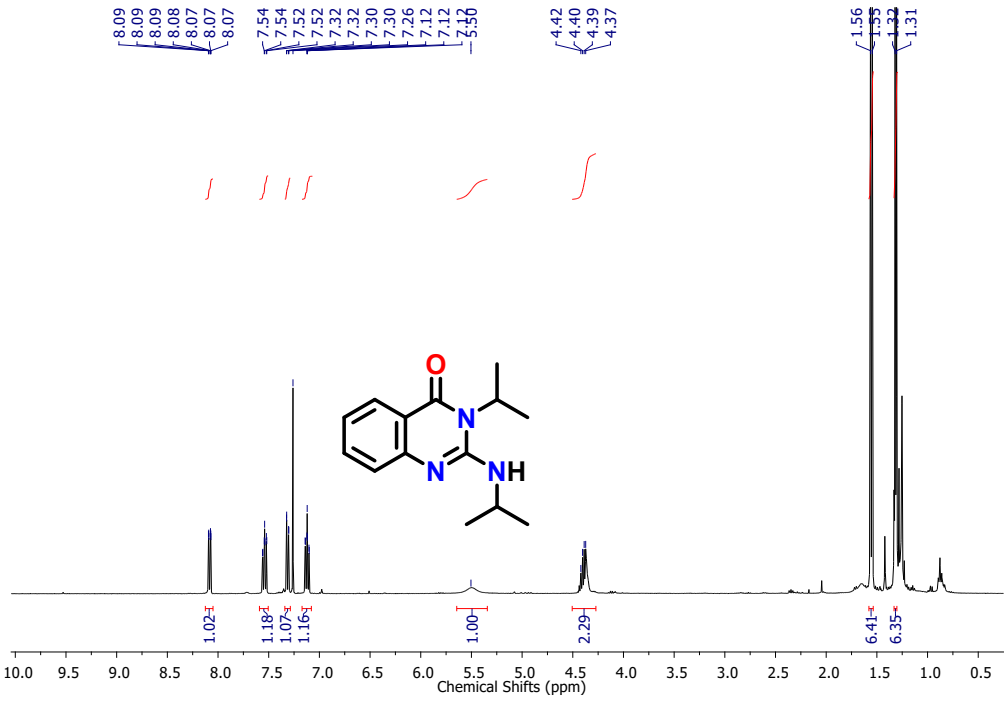


Figure FS150. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9a.**

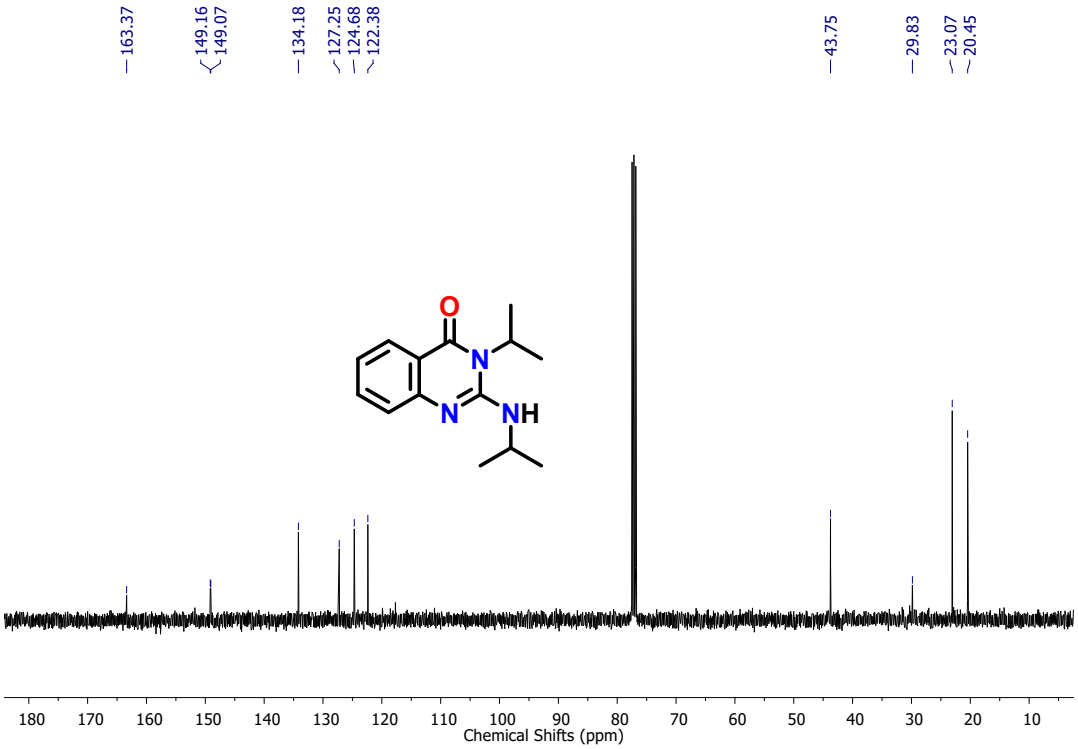


Figure FS151. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9a.**

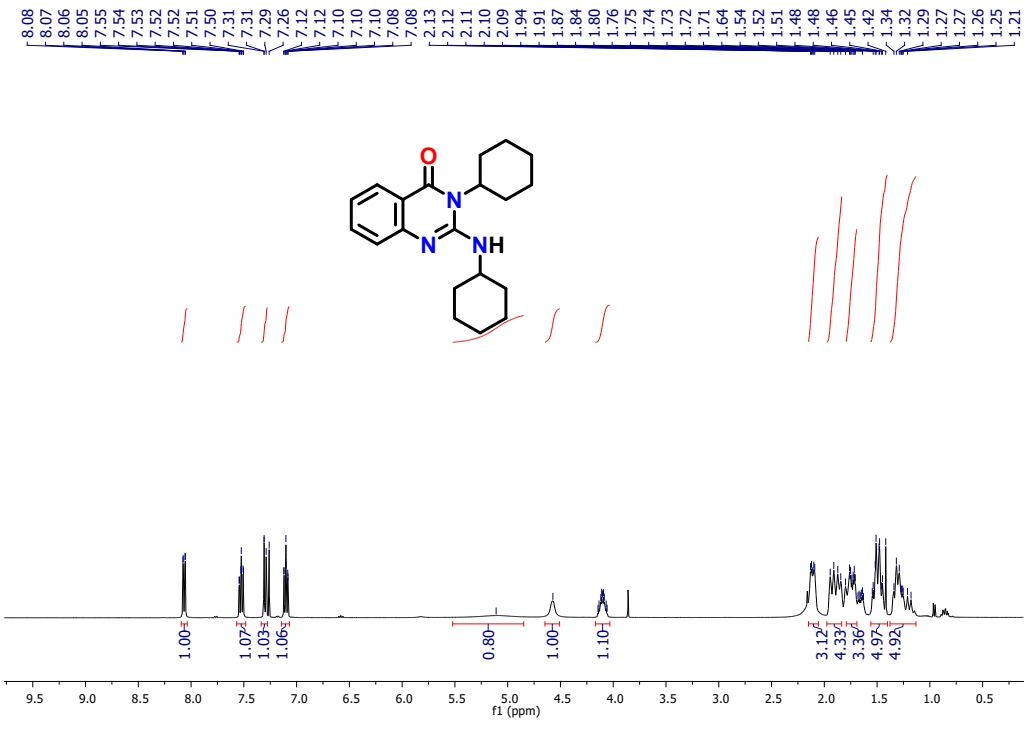


Figure FS152. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9b.**

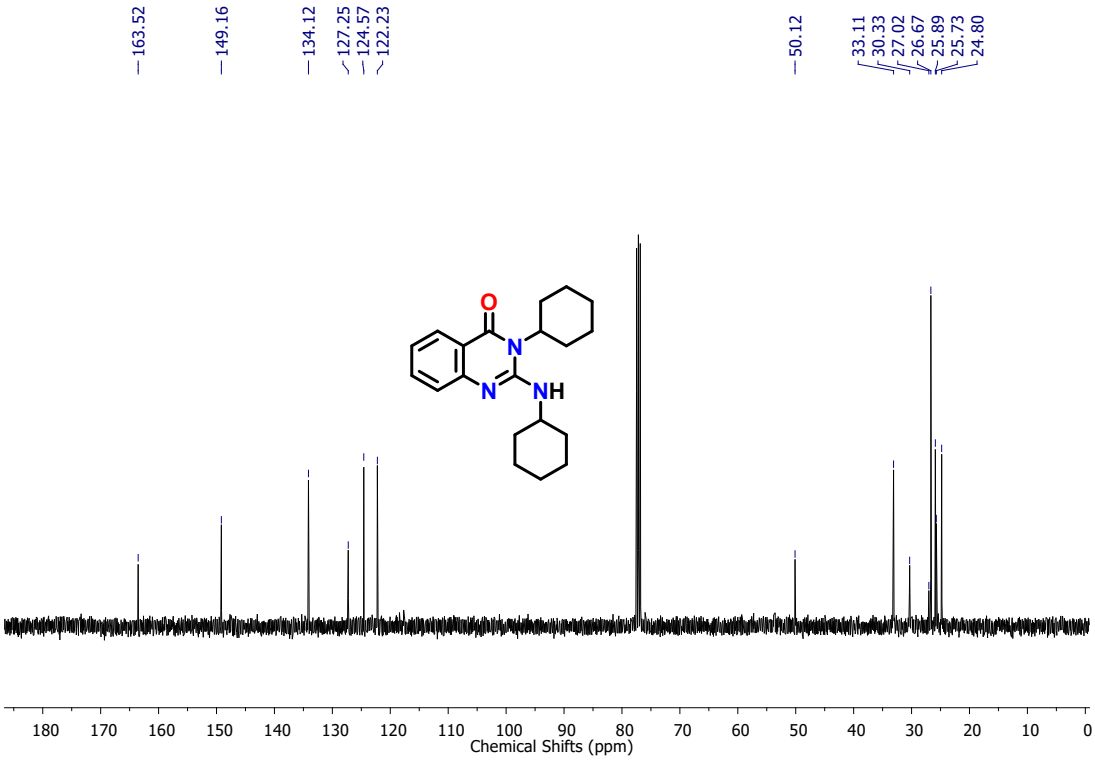


Figure FS153. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9b.**

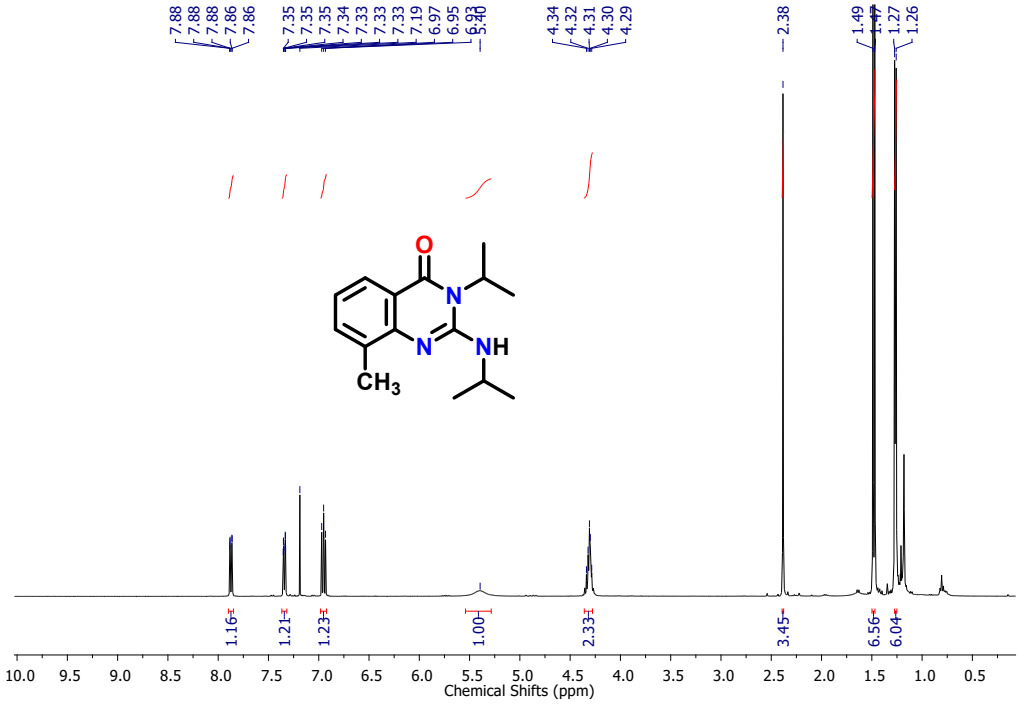


Figure FS154. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9c.**

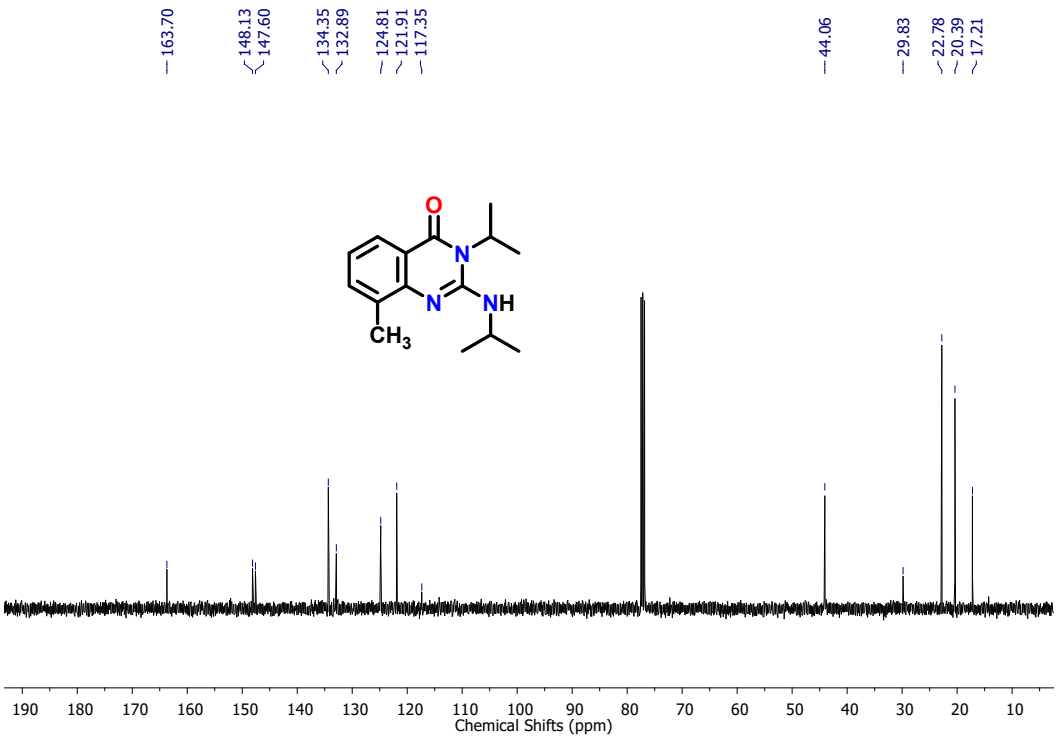


Figure FS155. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9c.**

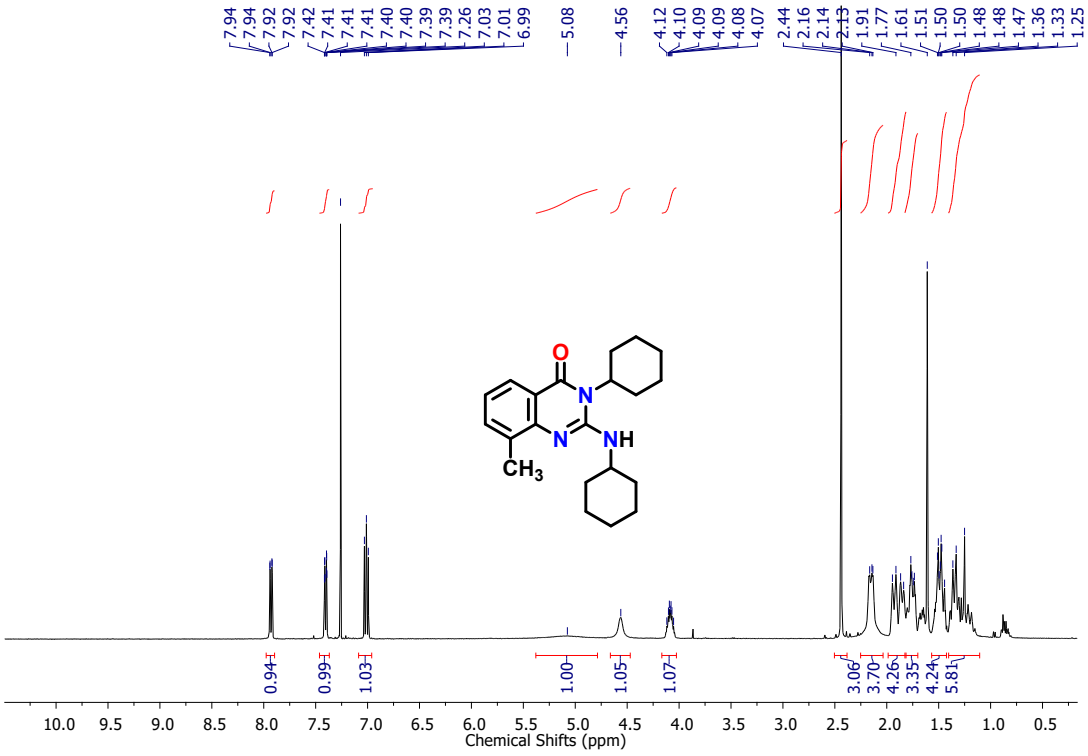


Figure FS156. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9d.**

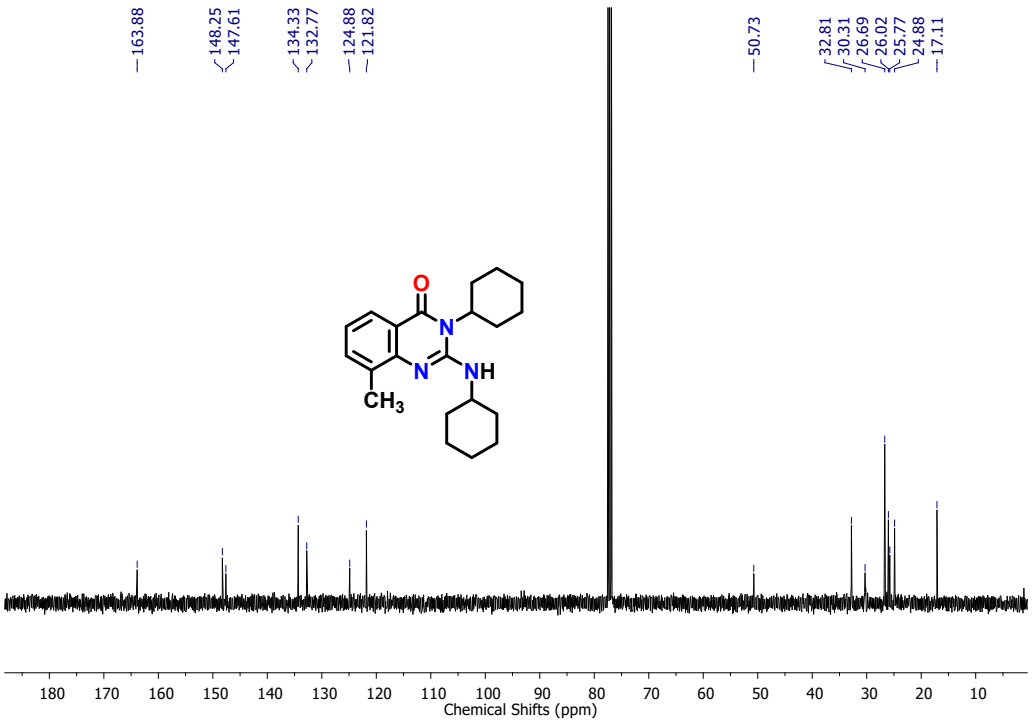


Figure FS157. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9d.**

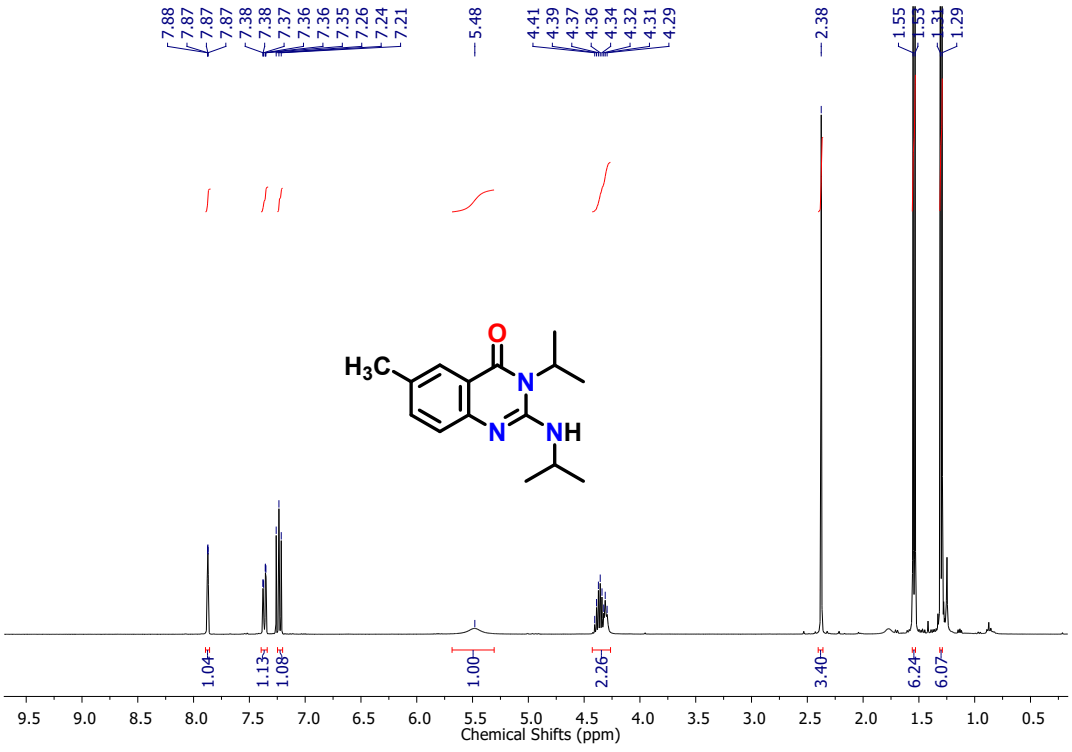


Figure FS158. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9e.**

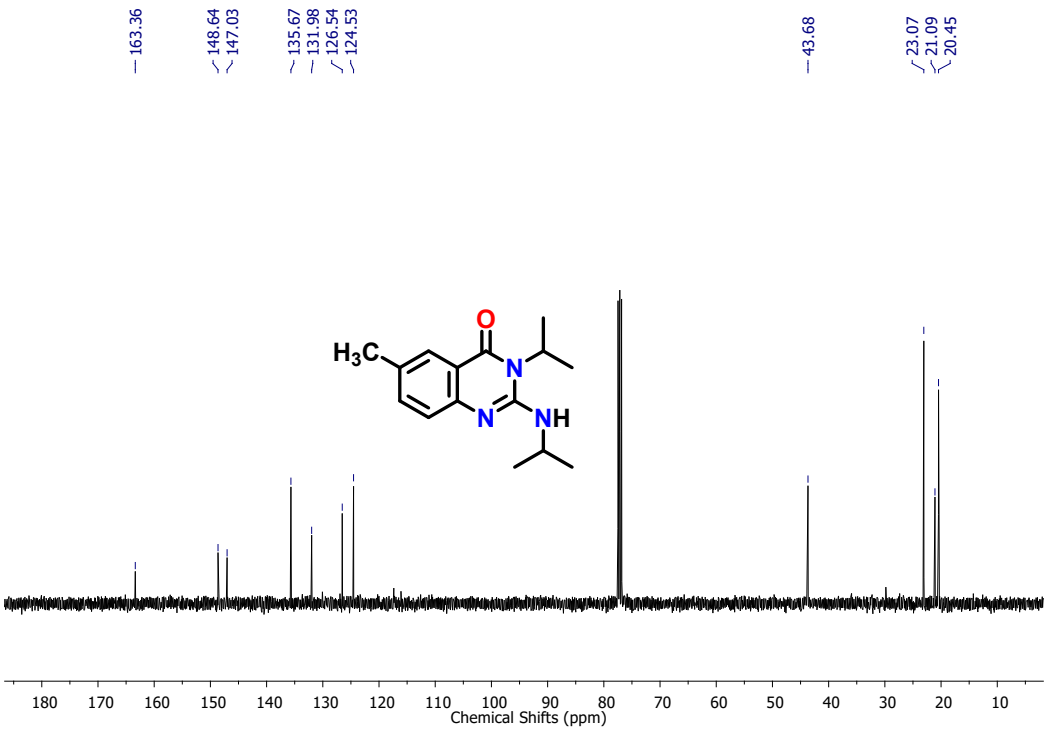


Figure FS159. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9e.**

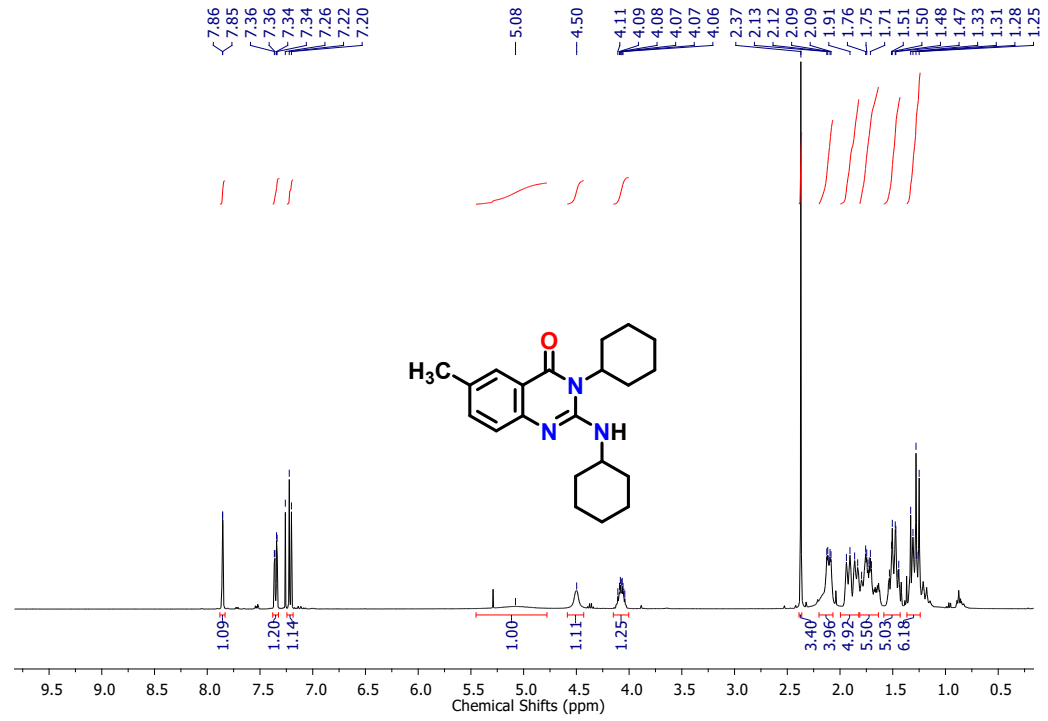


Figure FS160. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9f.**

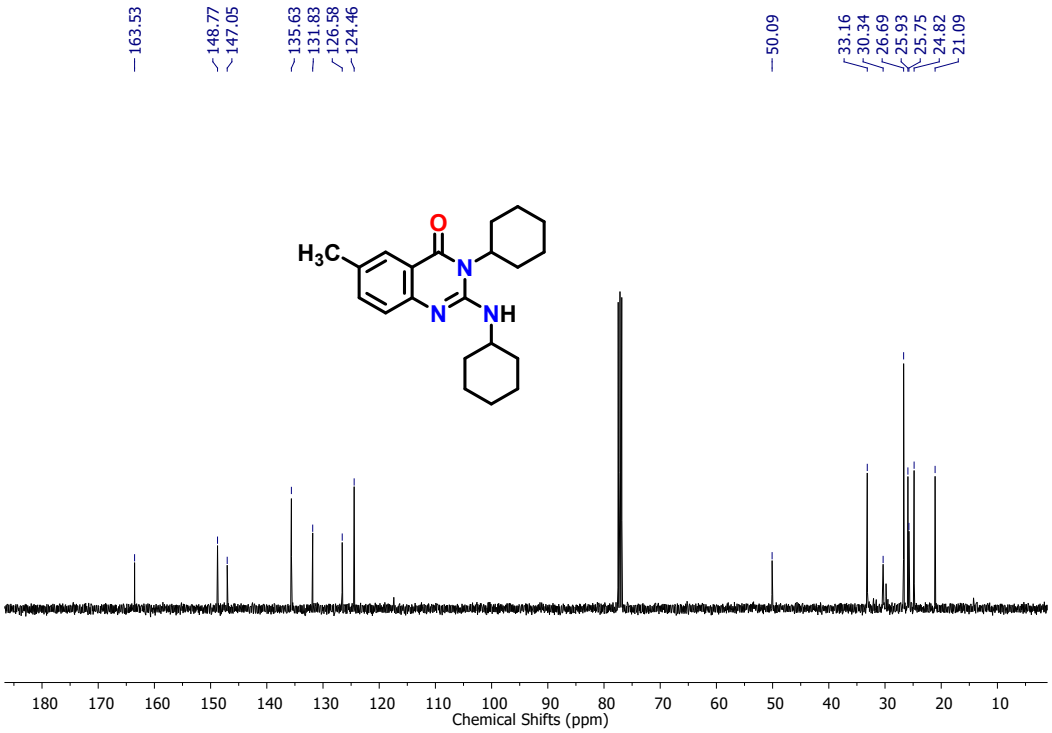


Figure FS161. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9f.**

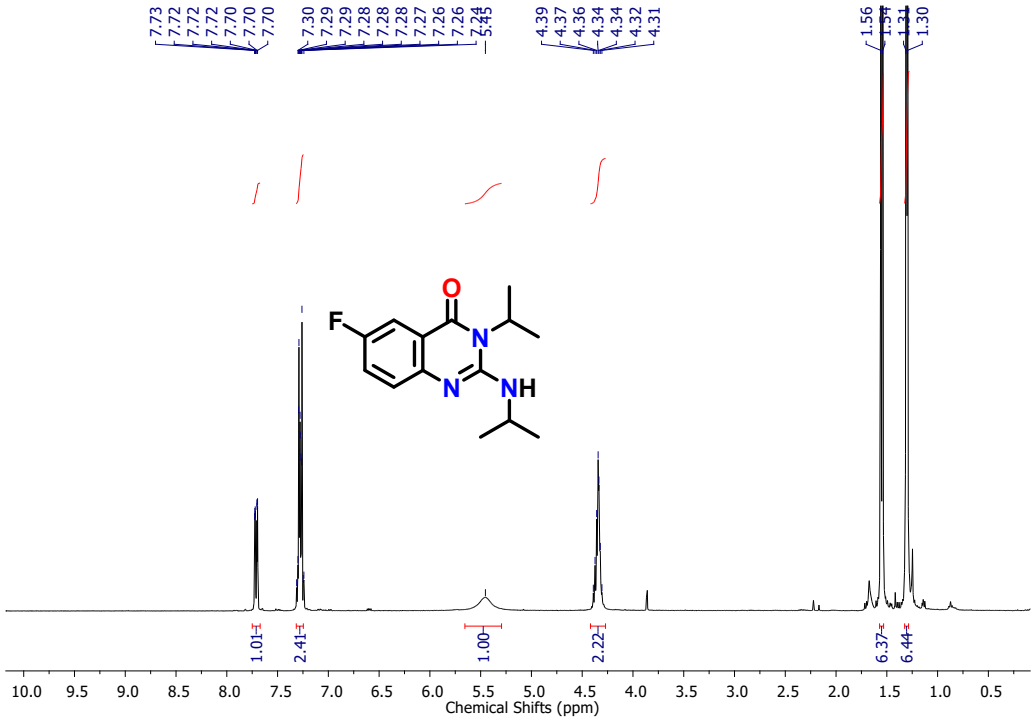


Figure FS162. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9g.**

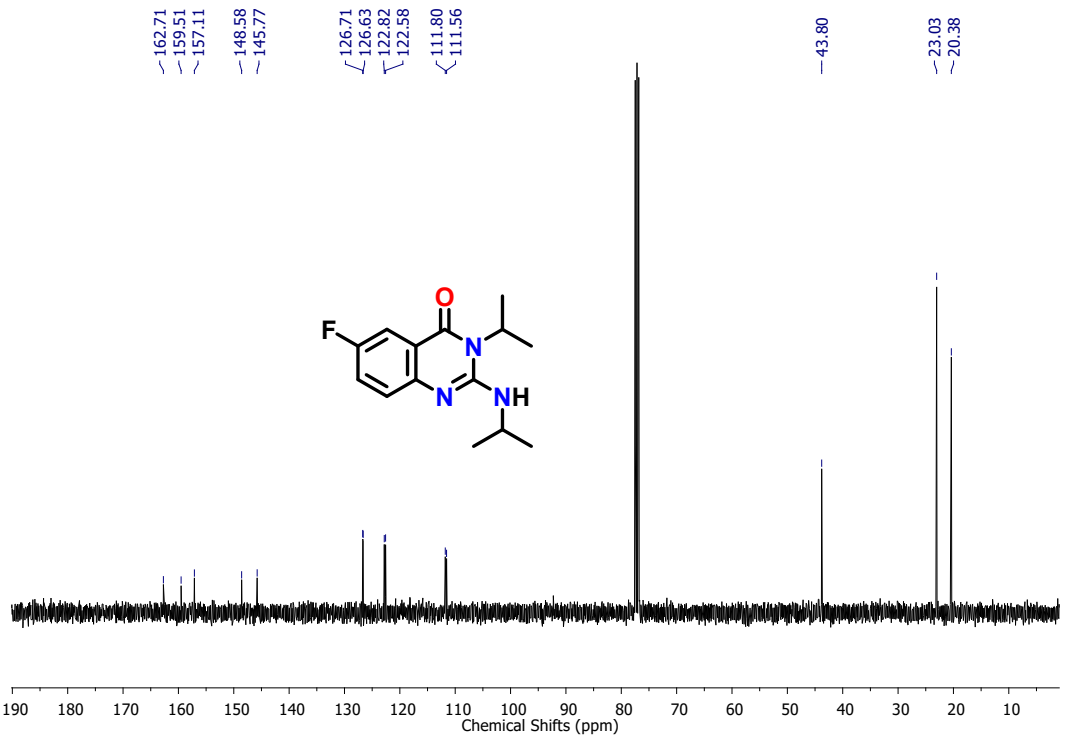


Figure FS163. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9g.**

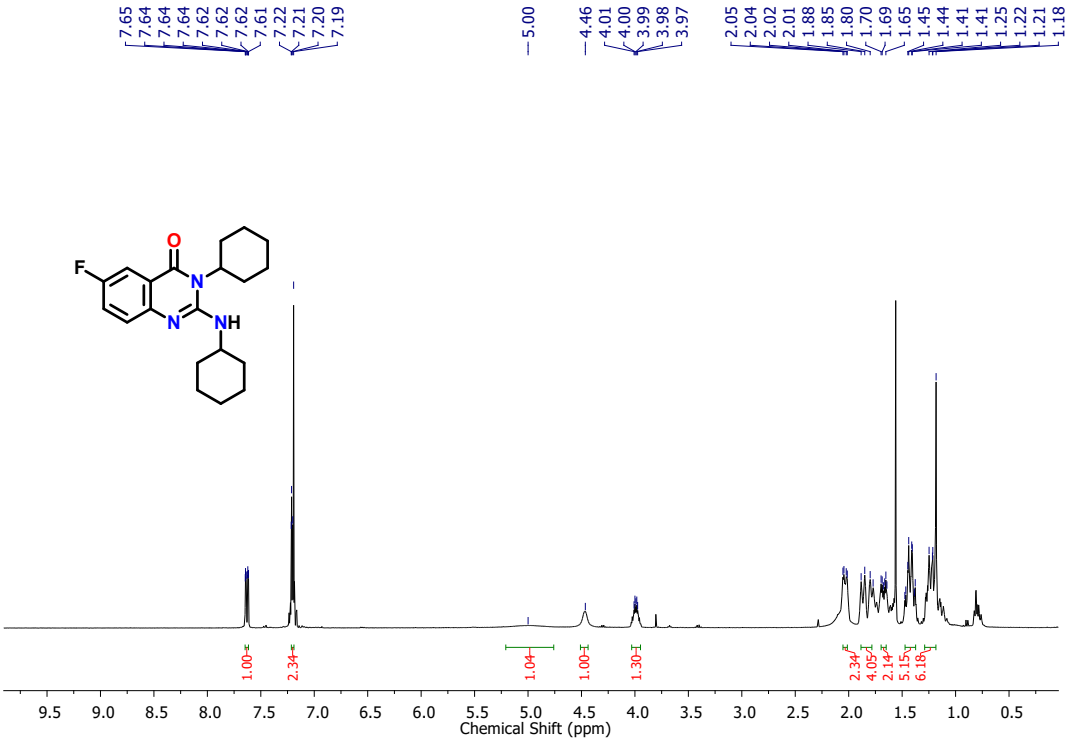


Figure FS164. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9h.**

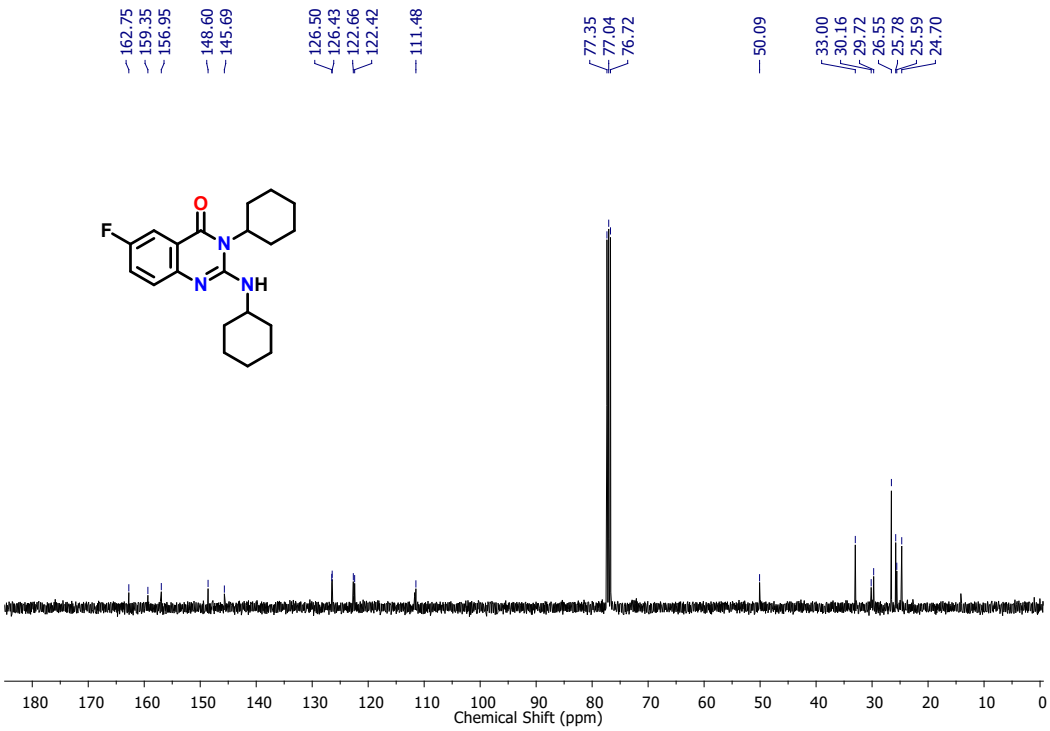


Figure FS165. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9h.**

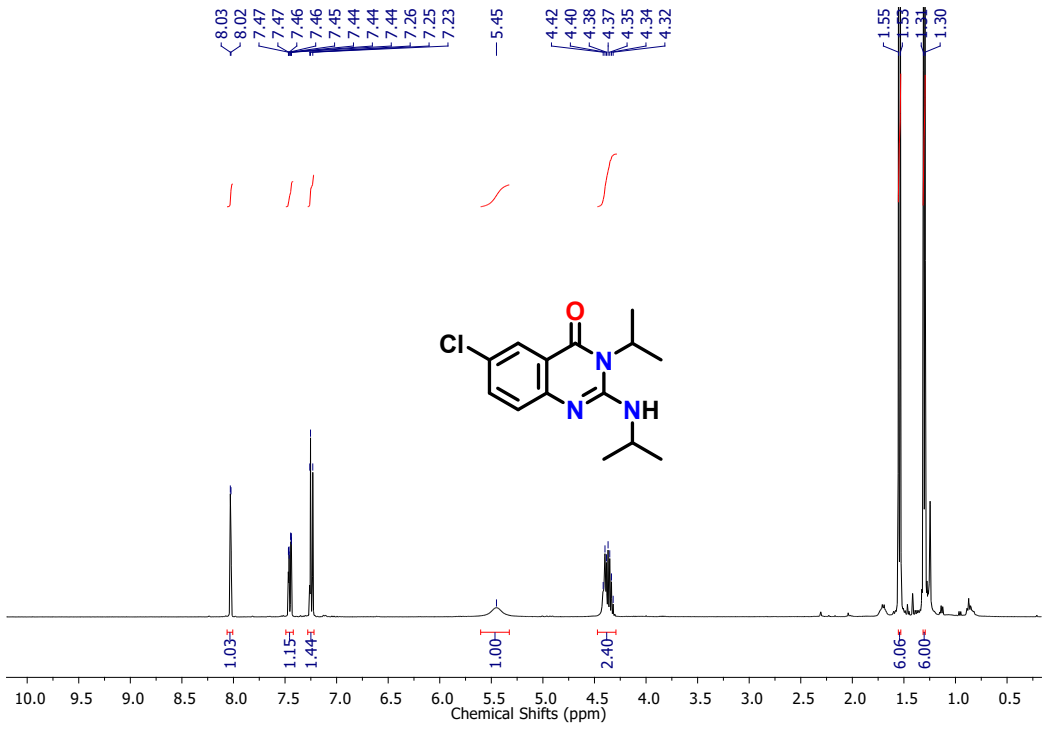


Figure FS166. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9i.**

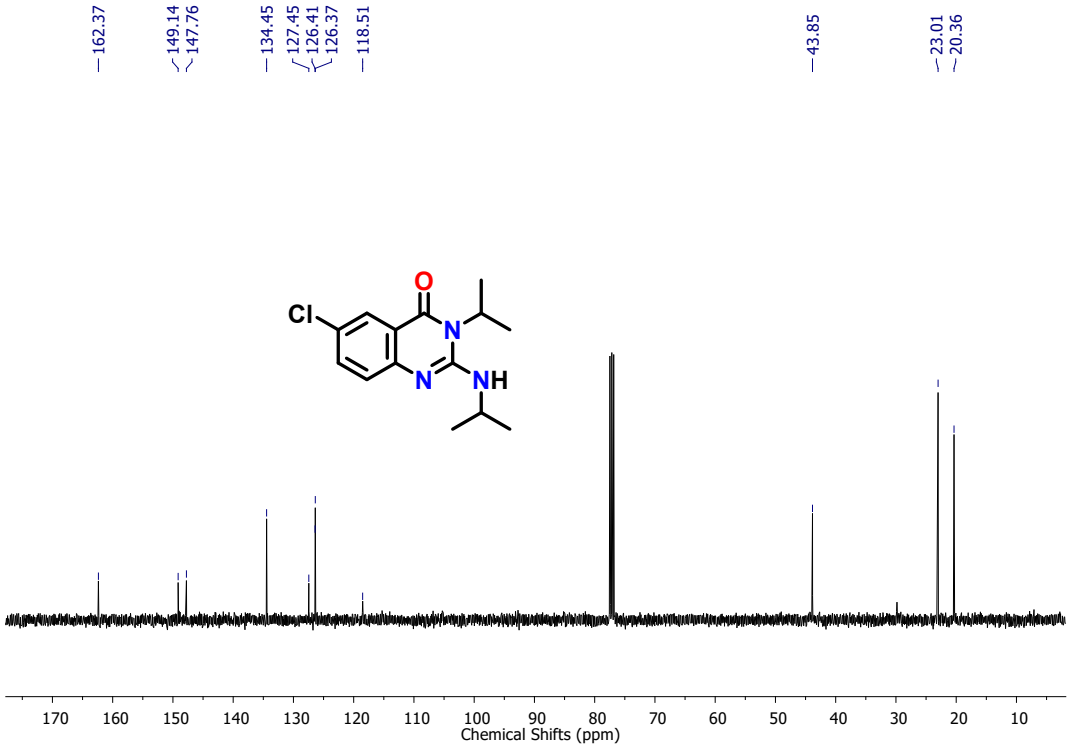


Figure FS167. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9i.**

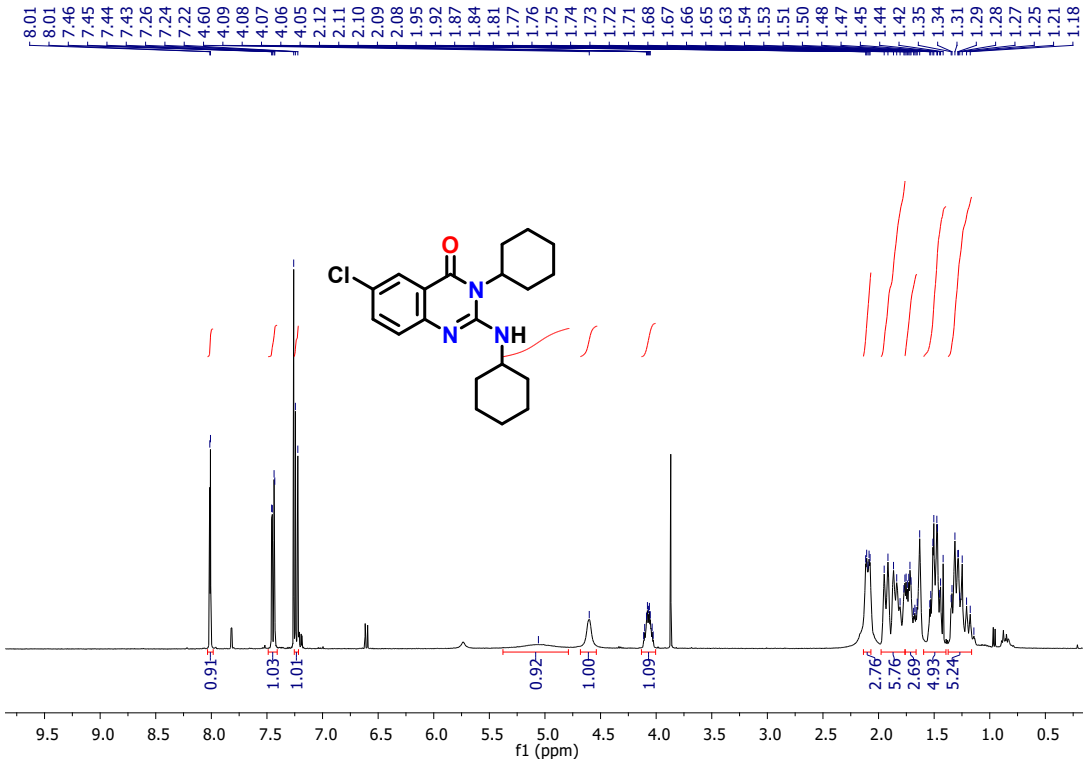


Figure FS168. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9j.**

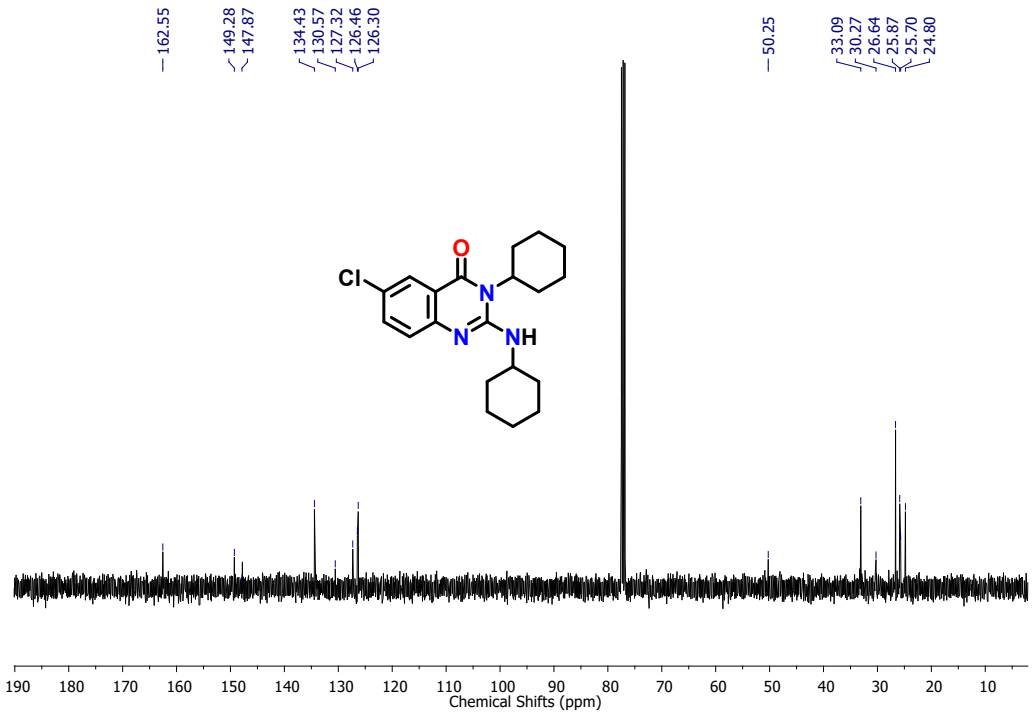


Figure FS169. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9j.**

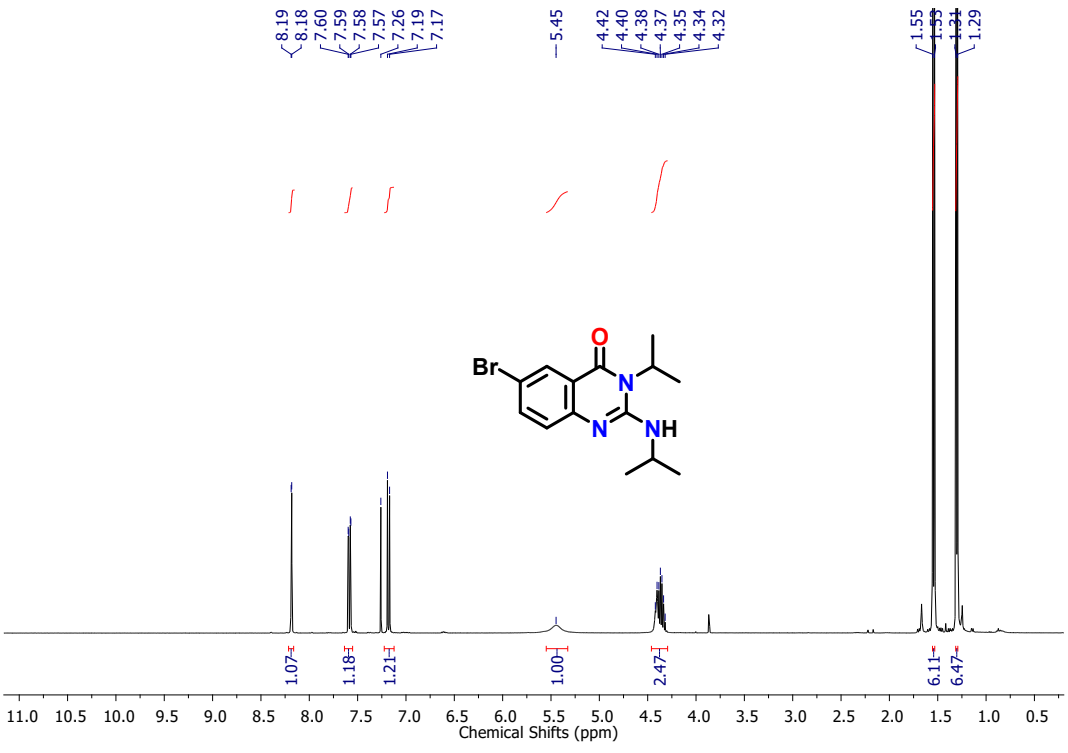


Figure FS170. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9k.**

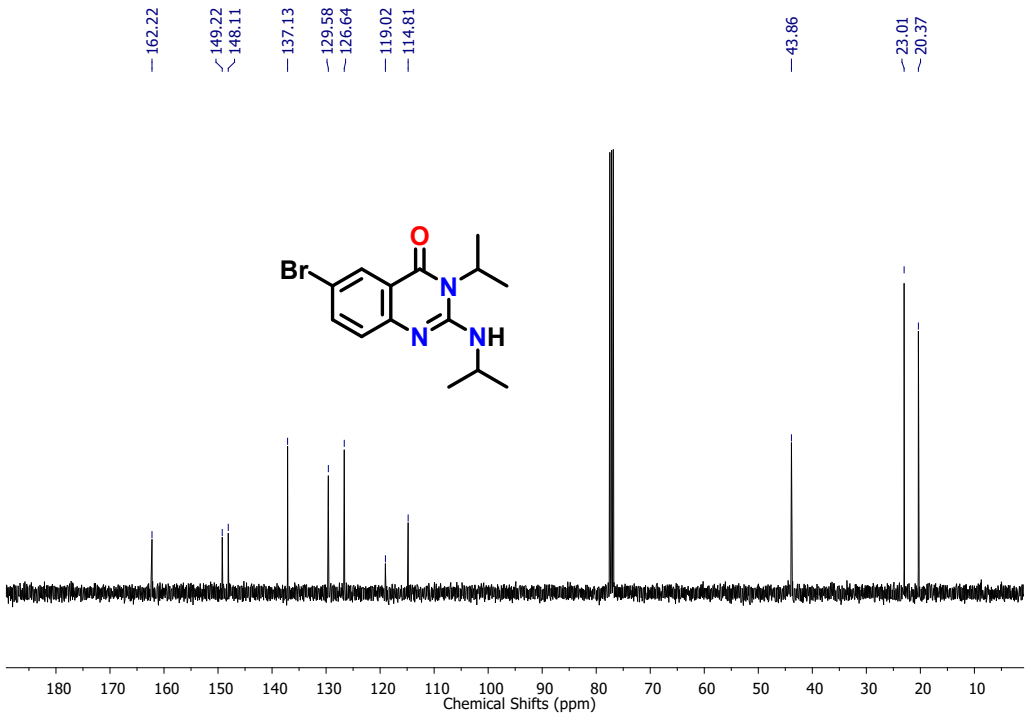


Figure FS171. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9k.**

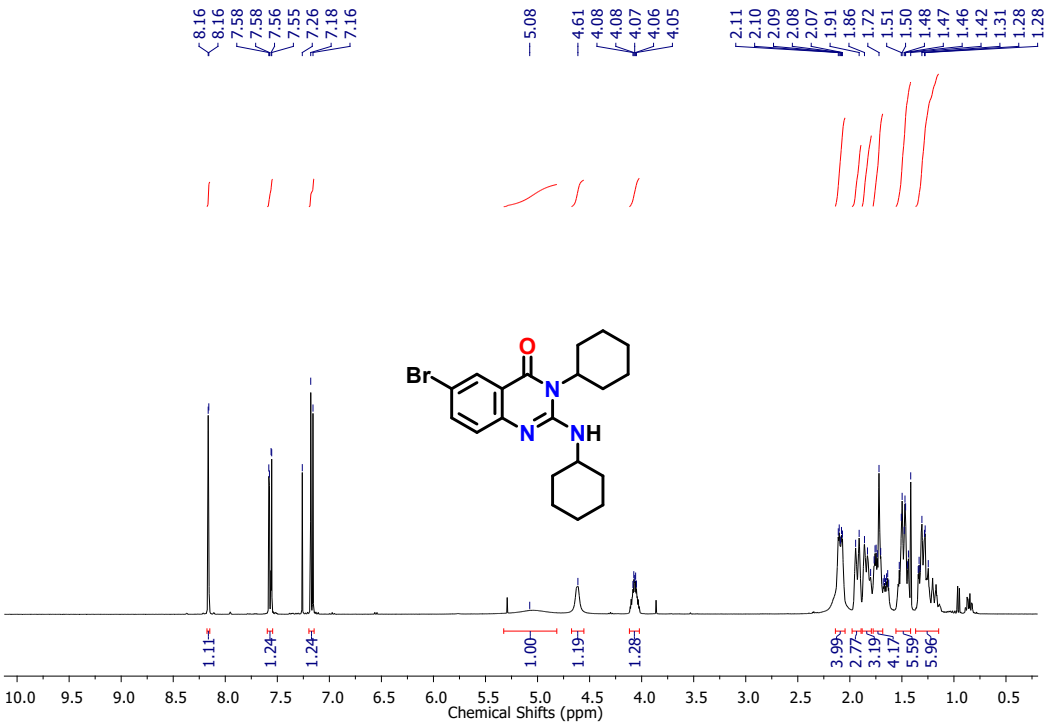


Figure FS172. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9l.**

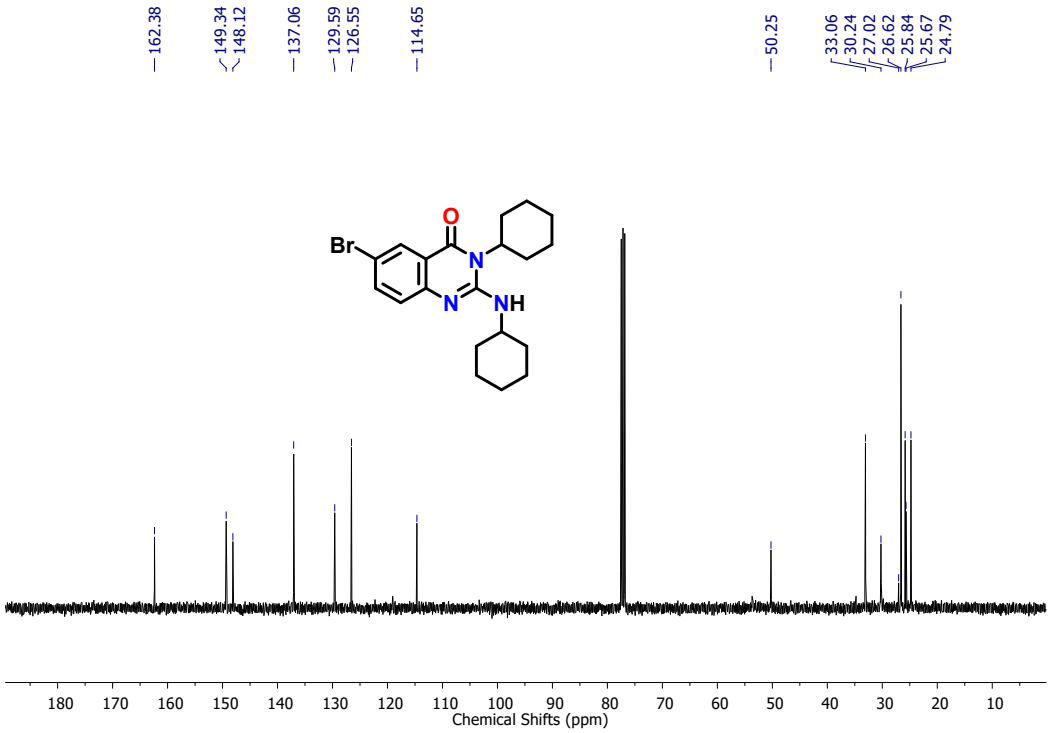


Figure FS173. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9l.**

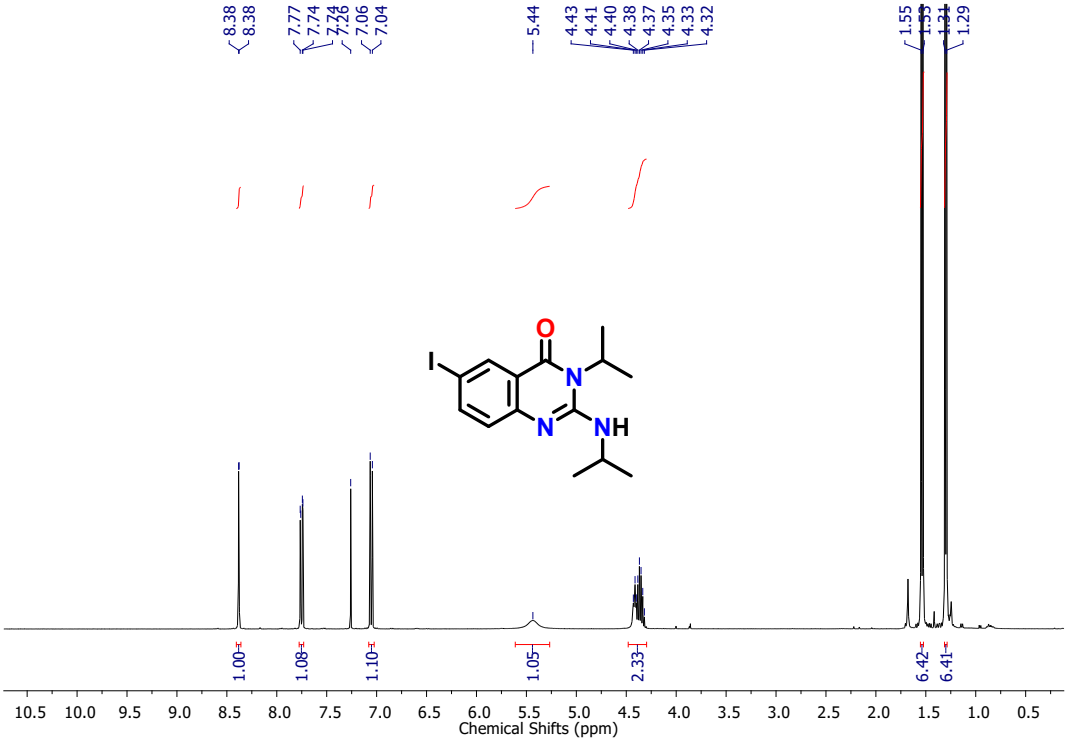


Figure FS174. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9m.**

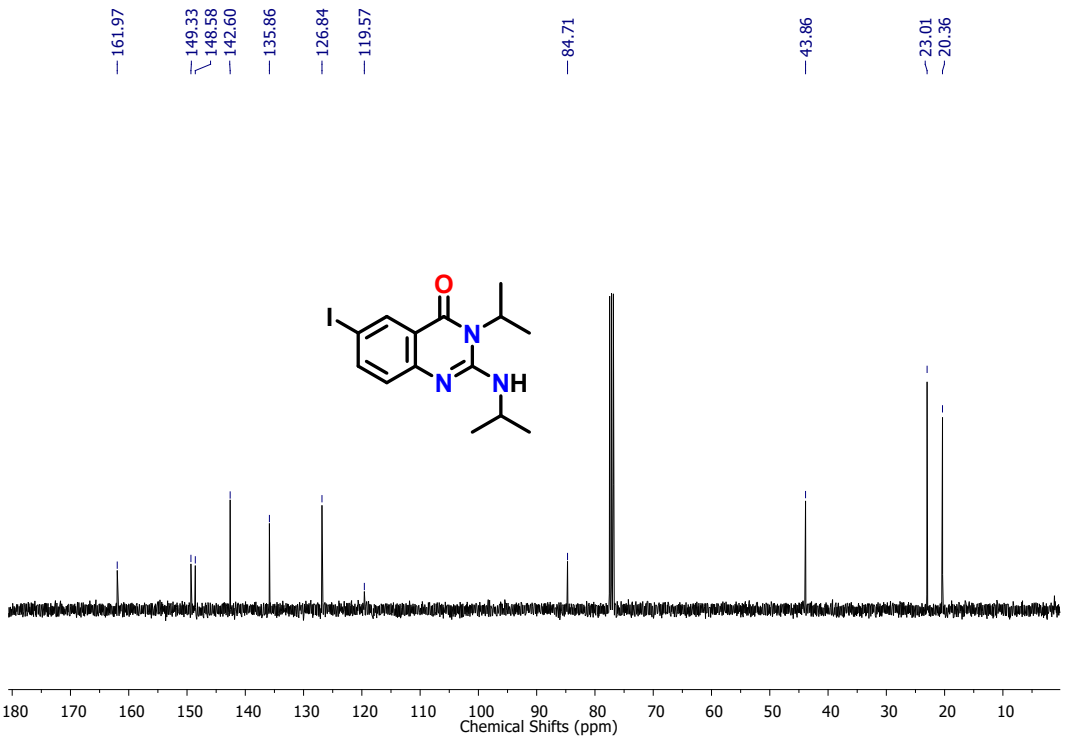


Figure FS175. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9m.**

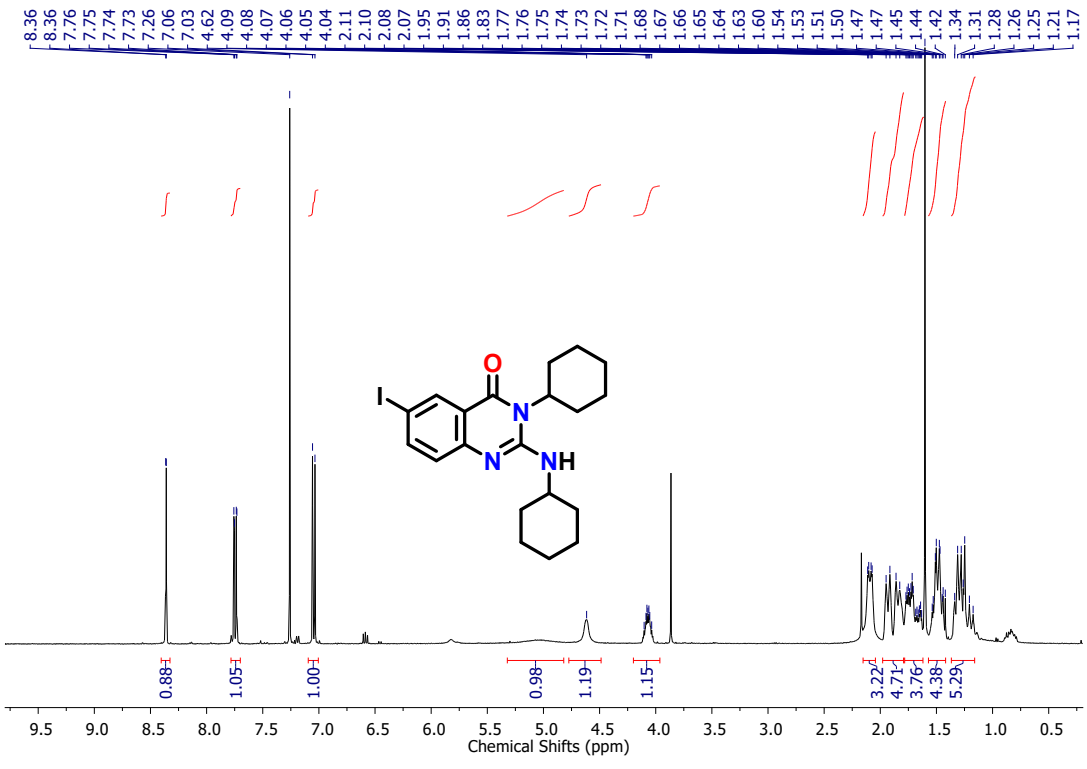


Figure FS176. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9n.**

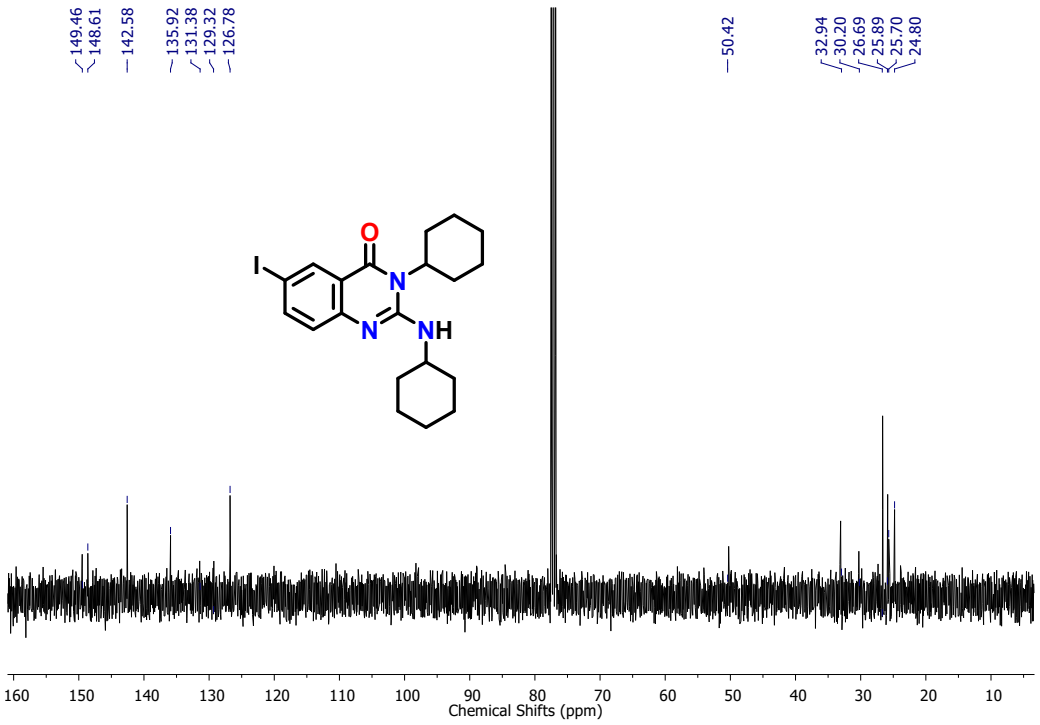


Figure FS177. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9n.**

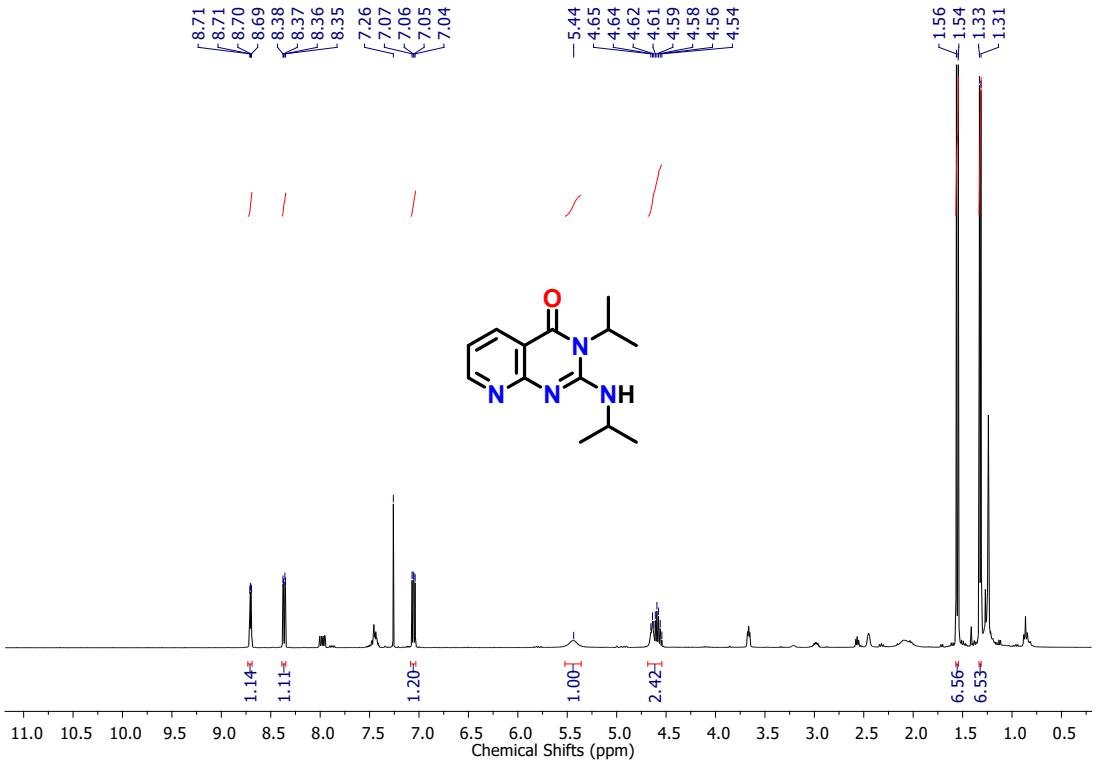


Figure FS178. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9o.**

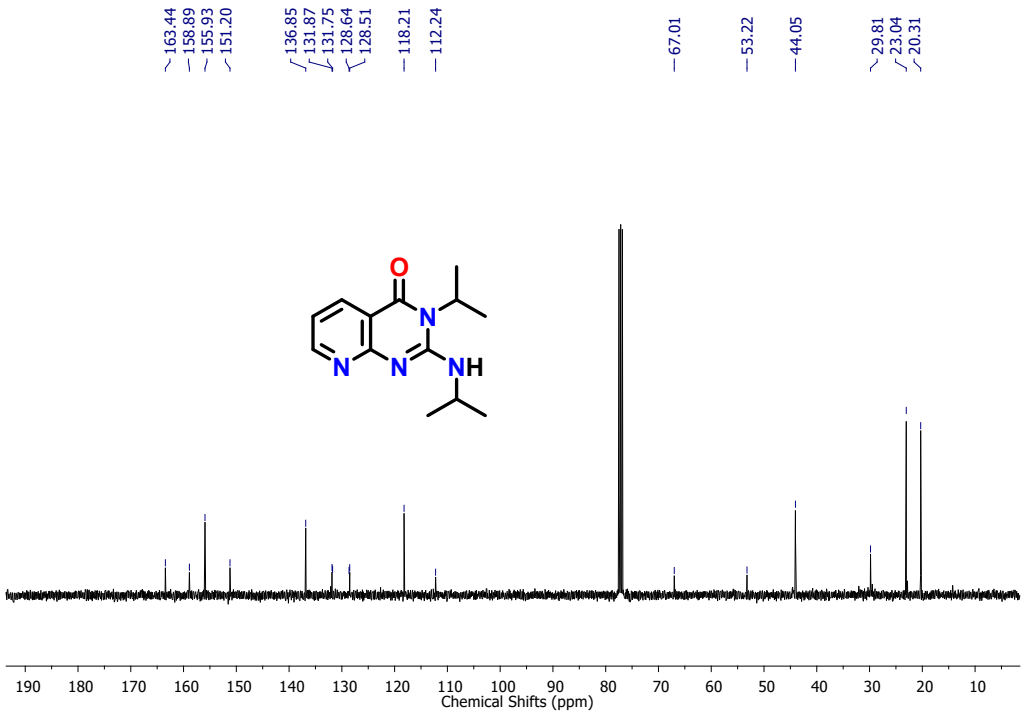


Figure FS179. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9o.**

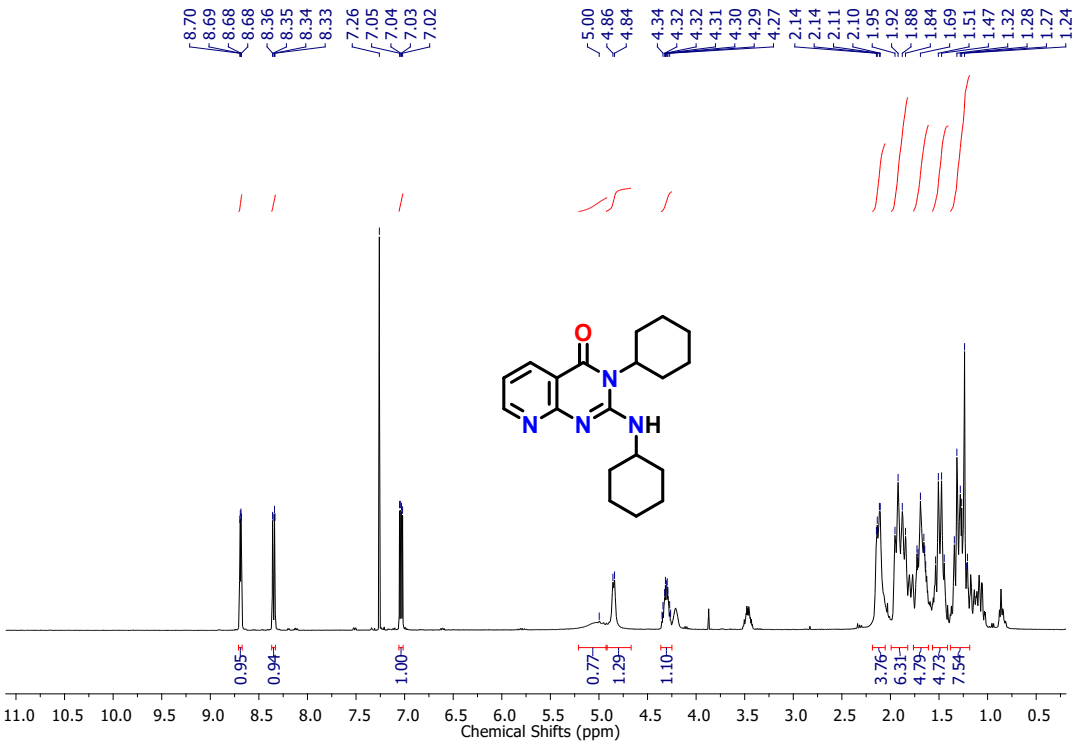


Figure FS180. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ˚C) of **9p.**

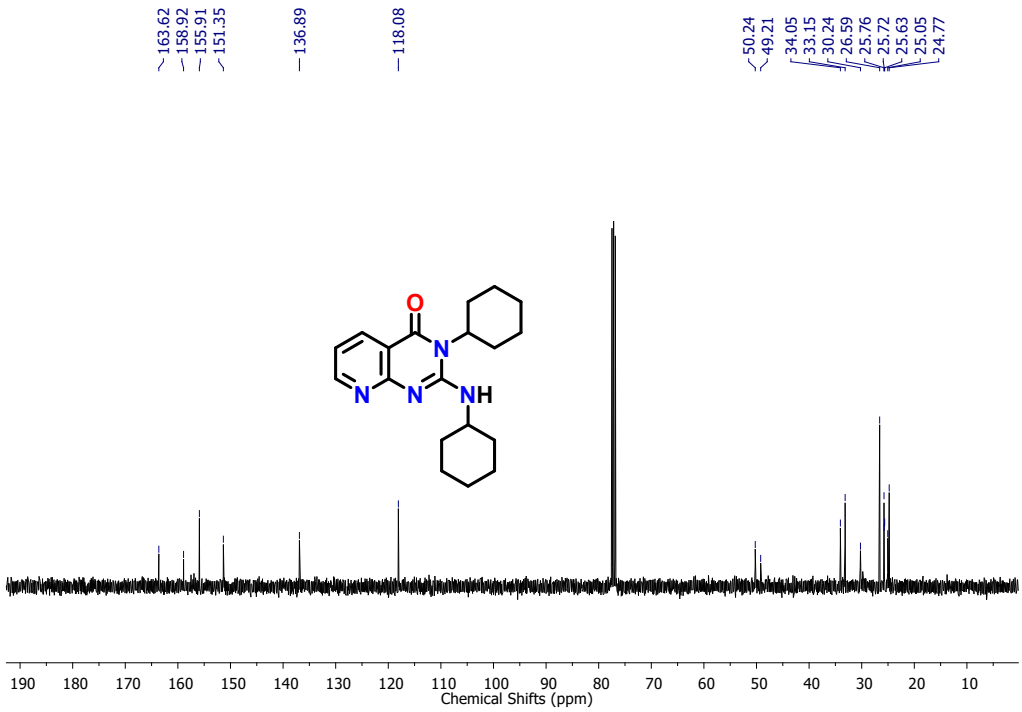


Figure FS181. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 25 ˚C) of **9p.**

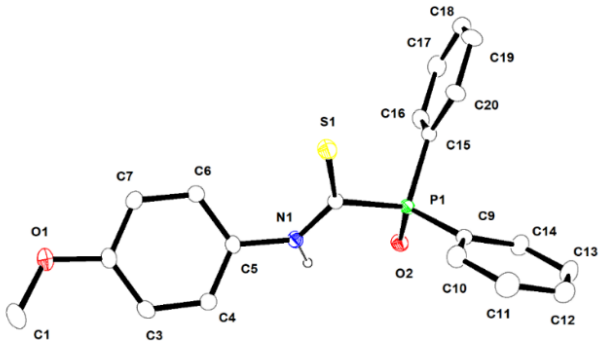
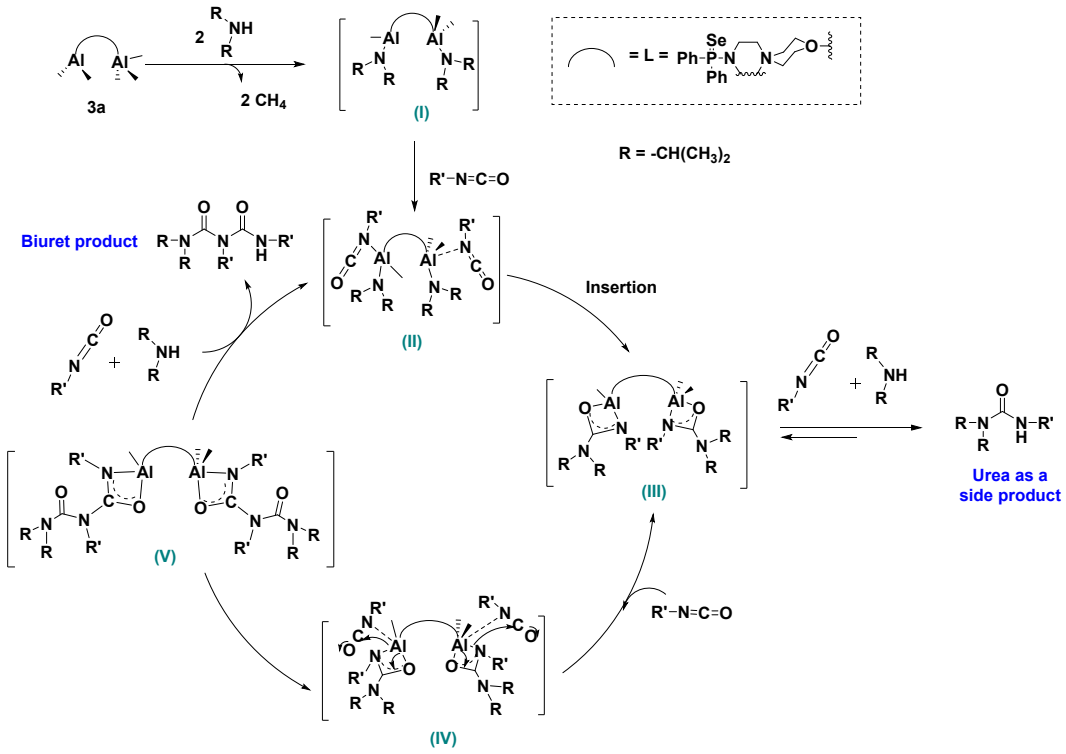


Figure FS182. Molecular structure of **8f** in its solid state.[12] Selected bond lengths (Å) and angles (°) are given. P(1)-O(1) 1.481(5), P(1)-C(7) 1.819(7), P(1)-C(1) 1.824(8), P(1)-C(13) 1.845(7), P(2)-O(2) 1.473(4); O(1)-P(1)-C(7) 111.3(3), O(1)-P(1)-C(1) 114.9(4), C(7)-P(1)-C(1) 107.4(3), O(1)-P(1)-C(13) 112.7(3), C(7)-P(1)-C(13) 107.4(3).

Plausible mechanism for the formation of biuret.

The most plausible mechanism for the catalytic synthesis of biuret derivatives from secondary amines and isocyanates is depicted in scheme 1 based on previous studies.[13] Initially, the attack of more nucleophilic secondary amine takes place on both the Al-centers of electrophilic pre-catalyst to form an intermediate I with the elimination of two methane molecules, which was previously proved as a rate-determining step.[1] The formation of intermediate I is supported by NMR studies of the product obtained in the control reaction of the Al-complex **3a** with secondary amine, diisopropyl amine in a 1 : 2 molar ratio at room temperature. In the ^{1}H NMR spectrum of the product, we detected two sharp singlets in 1:2 ratios at δ_H -0.78 and – 0.34 ppm for two types of methyl protons attached to the two Al centers (while in **3a** in 2:3 ratio at δ_H -0.89 and -0.45 ppm). In addition, two new broad signals in 1:6 ratio at δ_H 2.83 and 0.86 ppm also appeared, which are ascribed to CH protons and CH_3 protons of isopropyl amine moieties attached to the two Al centers (Fig. FS183). In the second step, formation of intermediate II takes place with the insertion of isocyanate molecules, which further gives the four - membered metallacycle intermediate III. Intermediate III gives the mono urea as a side product with the addition of another molecule of isocyanate and secondary amine. Additionally, intermediate III undergoes oligomerization or chain propagation with insertion of additional molecule of isocyanates to give intermediate IV. The final product biuret formed with the addition of corresponding isocyanate and secondary amines to the intermediate IV.



Scheme S1. Plausible mechanism for the formation of biuret.

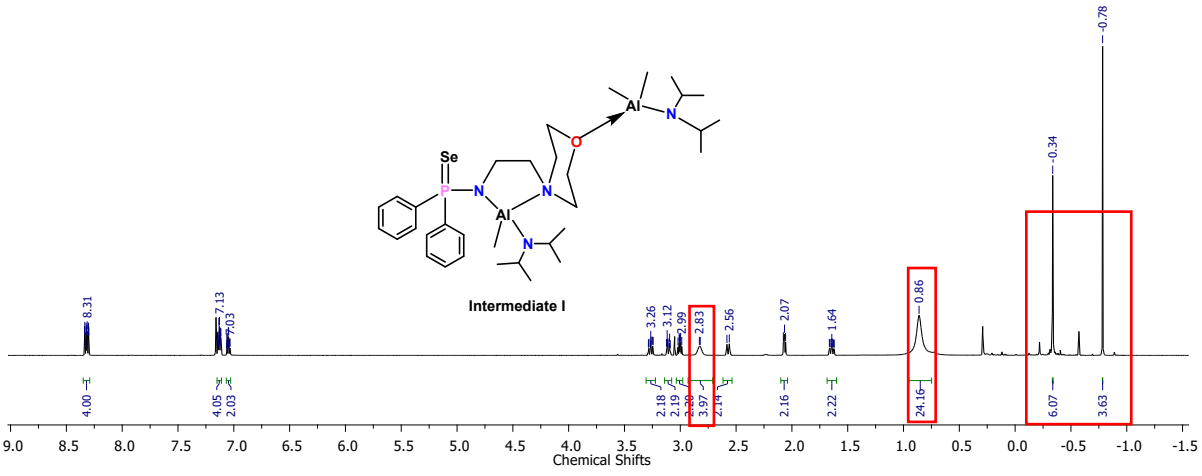


Figure FS183. ^{1}H NMR (600 MHz, 25ºC, C_6D_6) spectrum of intermediate I.

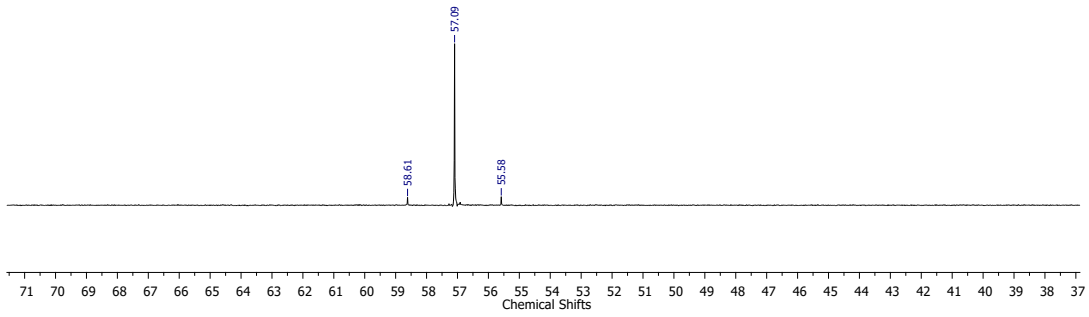
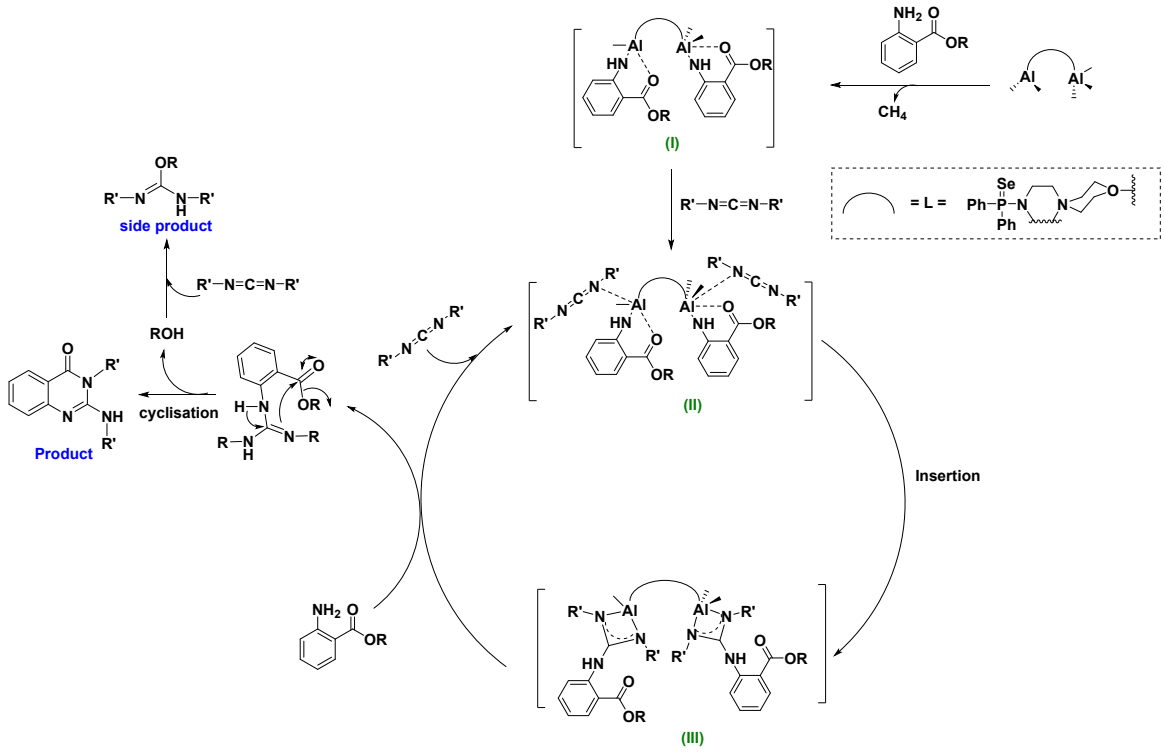


Figure FS181. $^{31}P\{^{1}H\}$ NMR (243 MHz, 25° C, C_6D_6) spectrum of intermediate I.

Plausible mechanism for the formation of quinazolinones.

Based on the previous reports from our group and other research groups[11,14], a most plausible mechanism for the catalytic guanylation/cyclization of amino acid esters is described in Scheme 2. In the first step, aminolysis of the Al-alkyl complex with aminobenzoate takes place to generate an intermediate **(I)** with the elimination of two volatile methane molecules. In the next step, intermediate **I** undertake migratory insertion of two carbodiimide into the corresponding Al-guanidinate species **III**. Then, a protonolytic cleavage occurs in the intermediate product **(III)** followed by the addition of another molecule of the aminobenzoate ester to give the uncyclized product and regenerate active species intermediate **I**. Finally, the desired cyclised product is obtained through an intramolecular nucleophilic amidation of the uncyclised product under the reaction condition with the release of a molecule of alcohol as a by-product at the same time. The second molecule of carbodiimide consumes the by-product alcohol in the presence of aluminum catalyst **3a** to yield the corresponding isourea as a side product under the same reaction conditions.



Scheme S2. Plausible mechanism of formation of quinazolinones.

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