Supporting Information for

Hydroamination of Carbodiimides, Isocyanates, and Isothiocyanates by Bis(phosphinoselenoic amide) Supported Titanium(IV) complex

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Table TS1. Crystallographic data and refinement parameters of titanium (IV) complex **1** and 3-(4-chlorophenyl)-1,1-dimethylurea (**B**).

Compound	**1**	**B**
CCDC No.	1470715	1495777
Empirical formula	$C_{30}H_{36}N_4P_2Se_2Ti$	$C_9H_{11}ClN_2O$
Formula weight	720.39	198.65
T (K)	150	150
λ (Å)	1.54184	1.54184
Crystal system	Monoclinic	Orthorhombic
Space group	*P c*	*P* b c a
a (Å)	8.9540(3)	9.1347(3)
b (Å)	14.1215(10)	11.3629(4)
c (Å)	14.6424(12)	18.5528(6)
α (°)	90	90
β (°)	120	90
γ (°)	90	90
V (Å^3)	1594.94(18)	1925.72(11)
Z	2	8
D_{calc} g cm^{-3}	1.500	1.370
μ (mm^{-1})	6.028	3.201
F (000)	728	832.0
Theta range for data collection	3.13 to 70.57 deg.	3.8870 to 71.4541 deg
Limiting indices	-10<=h<=10 -12<=k<=16 -17<=l<=17	-6<=h<=11 -12<=k<=13 -22<=l<=15
Reflections collected / unique	6223/ 4114 [R(int) = 0.0239]	3946/1833 [R(int) = 0.0259]
Completeness to theta = 71.25	99.3 %	99.9%
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	1.000 and 0.70975	1.00000 and 0.59522
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4114 / 2 / 357	1833/0/120
Goodness-of-fit on F^2	1.071	1.049
Final R indices [I>2σ(I)]	$R1$ = 0.0364, $wR2$ = 0.0974	$R1$ = 0.0480, $wR2$ = 0.1203
R indices (all data)	$R1$ = 0.0369, $wR2$ = 0.0981	$R1$ = 0.0584, $wR2$ = 0.1291
Absolute structure parameter	0.012	n/a

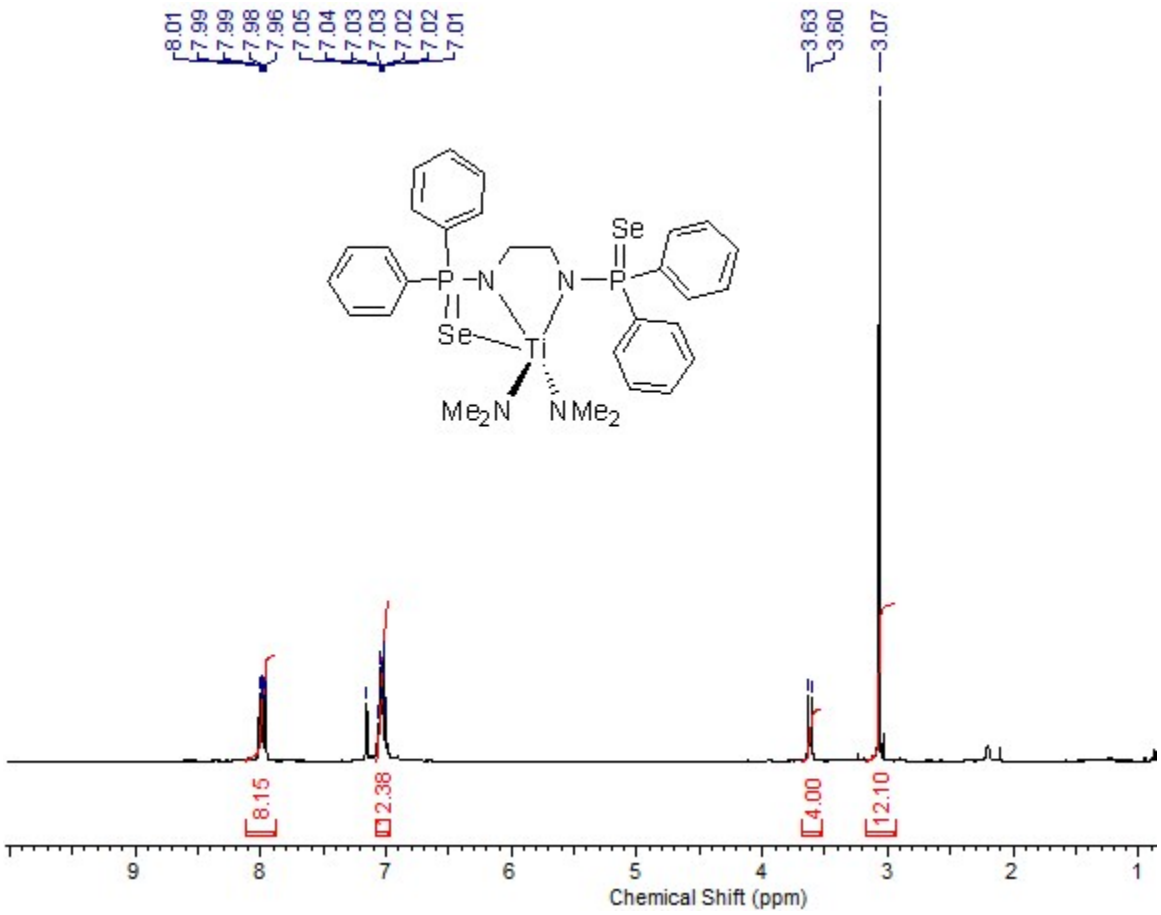


Figure S1. ^{1}H NMR spectra of complex **1**.

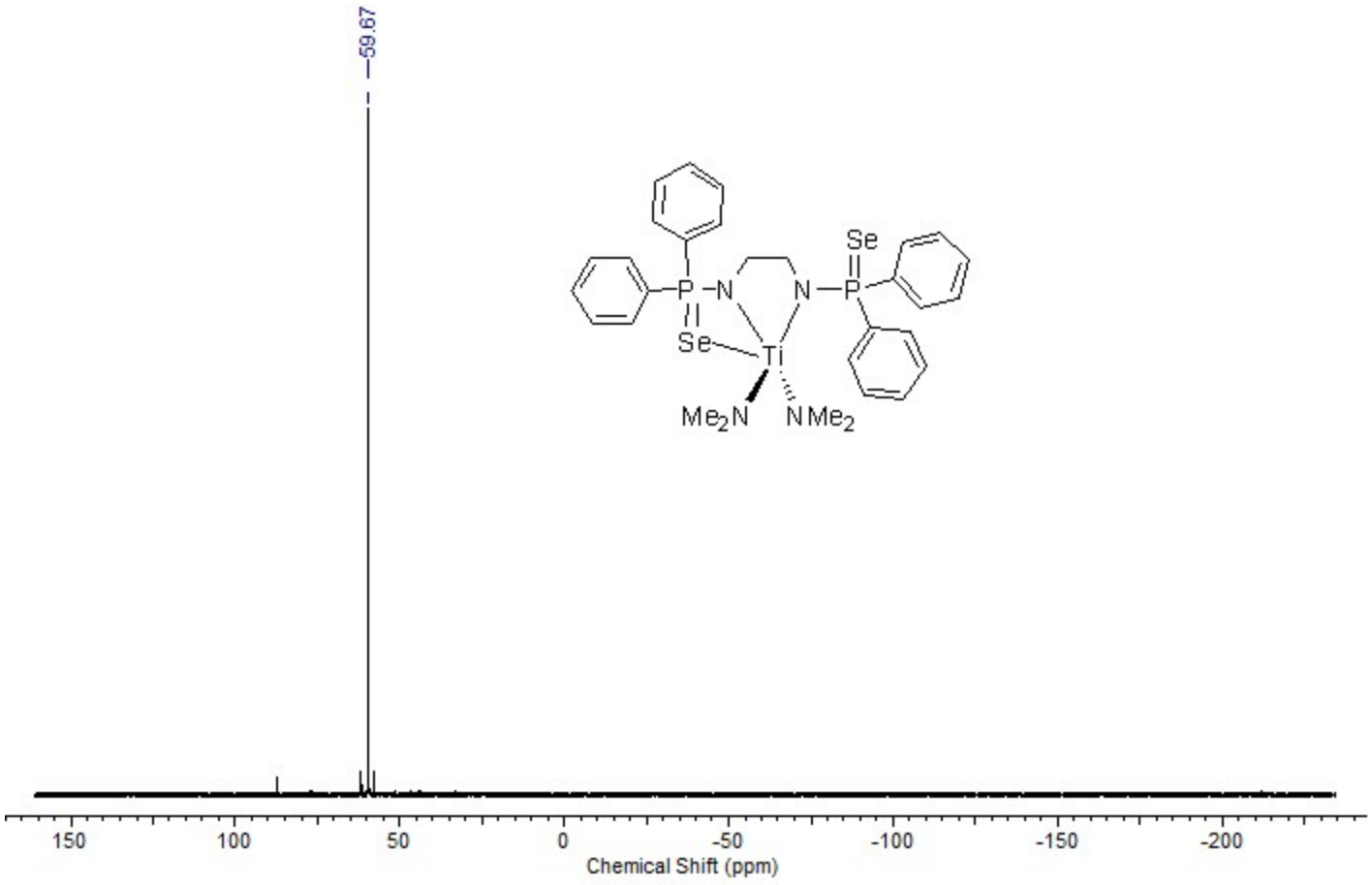


Figure S2. ^{31}P NMR spectra of complex **1.**

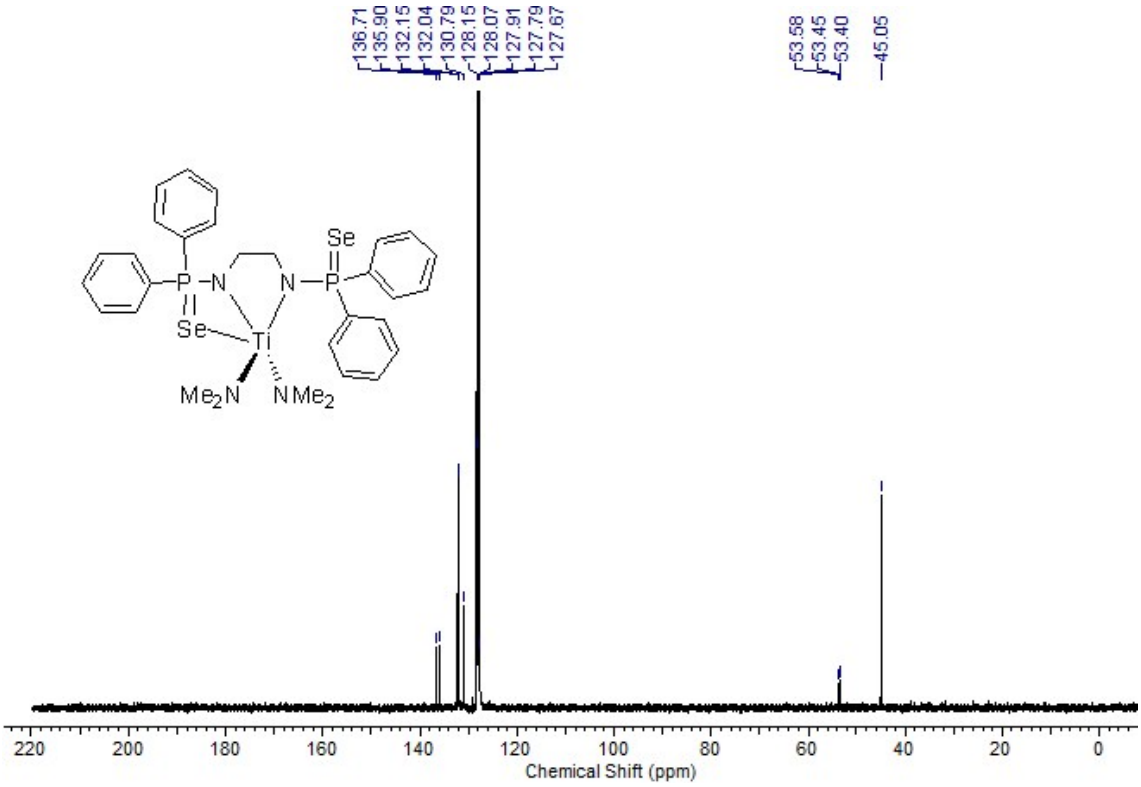


Figure S3. ^{13}C NMR spectra of complex **1**

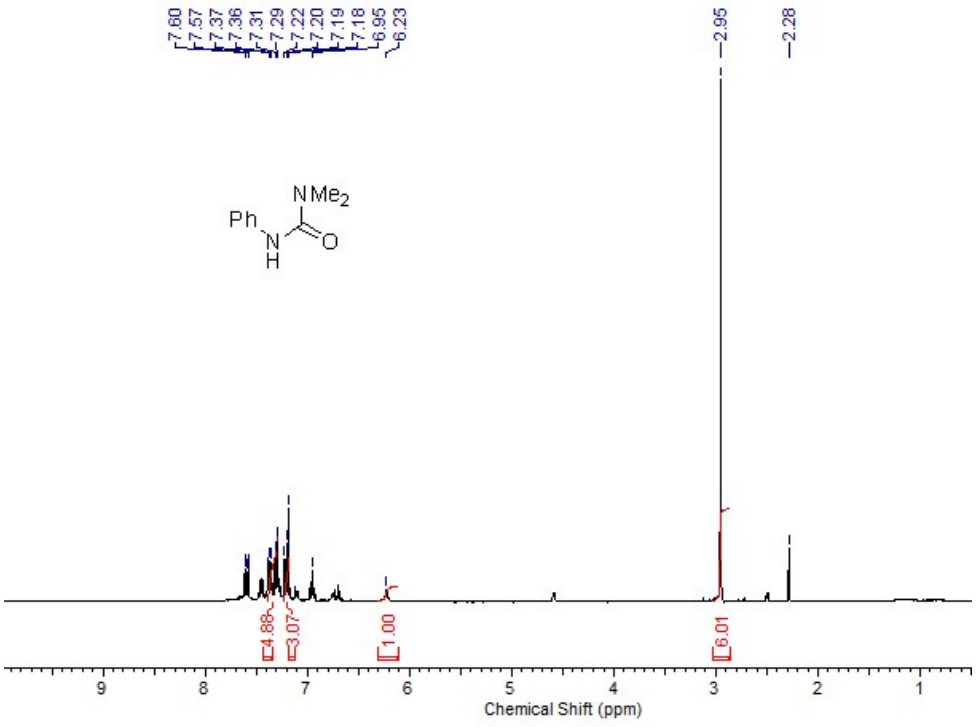


Figure S4. ^{1}H NMR spectra of compound **A.**

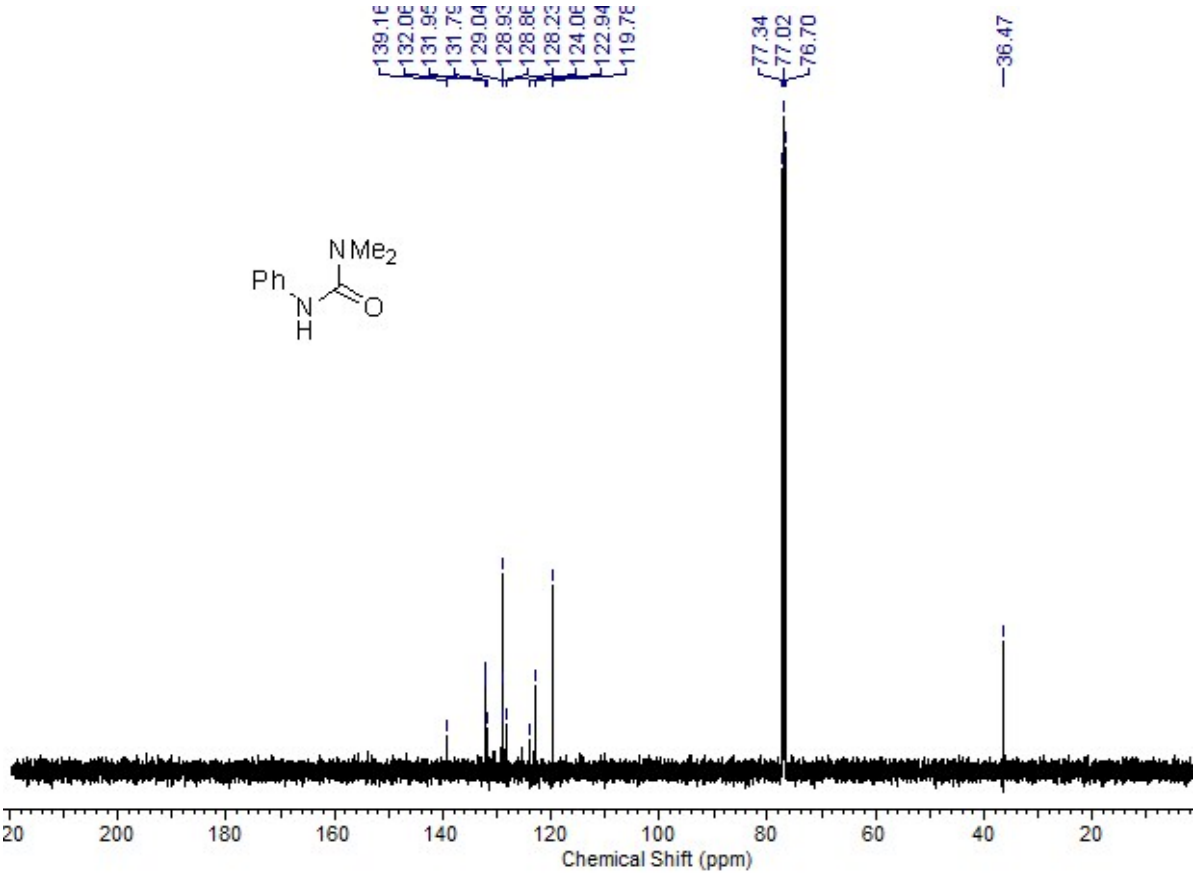


Figure S5. ^{13}C NMR spectra of compound **A.**

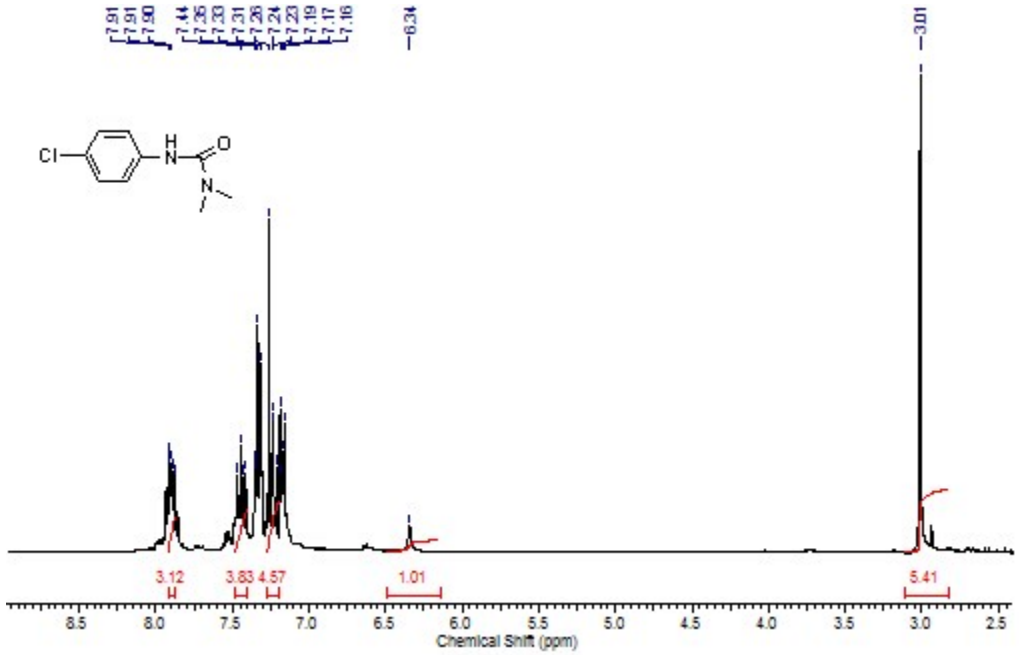


Figure S6. ^{1}H NMR spectra of compound **B**.

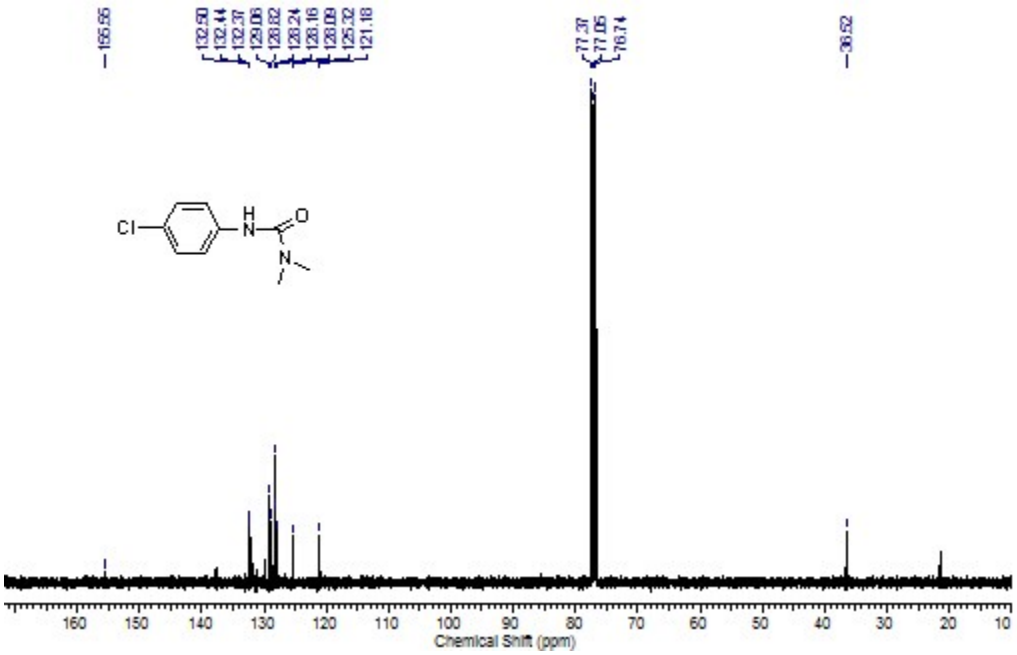


Figure S7. ^{13}C NMR spectra of compound **B**.

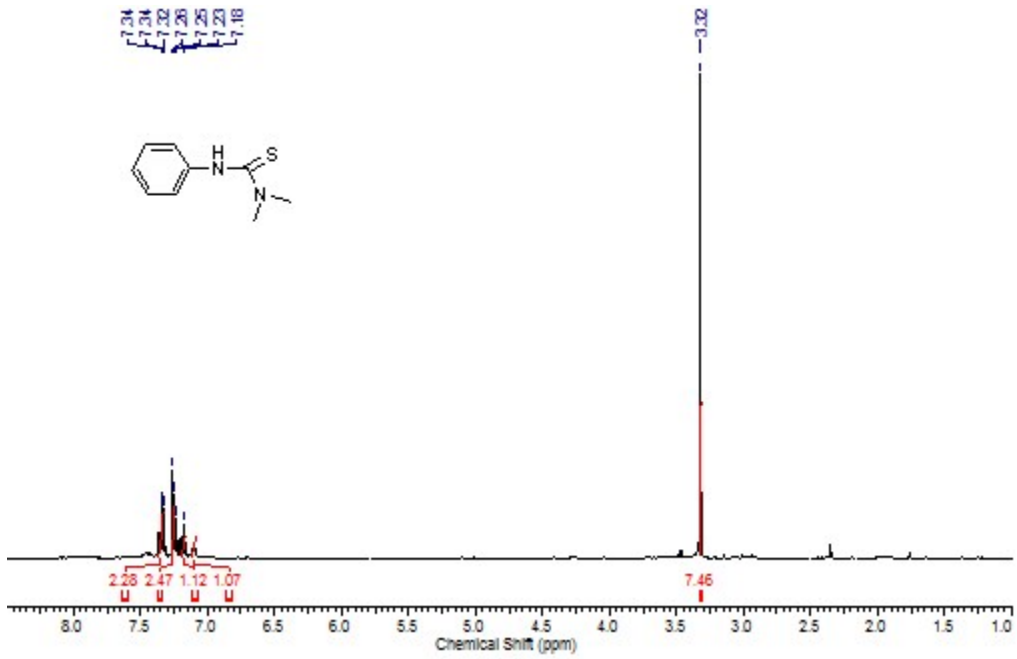


Figure S8. ^{1}H NMR spectra of compound **C**.

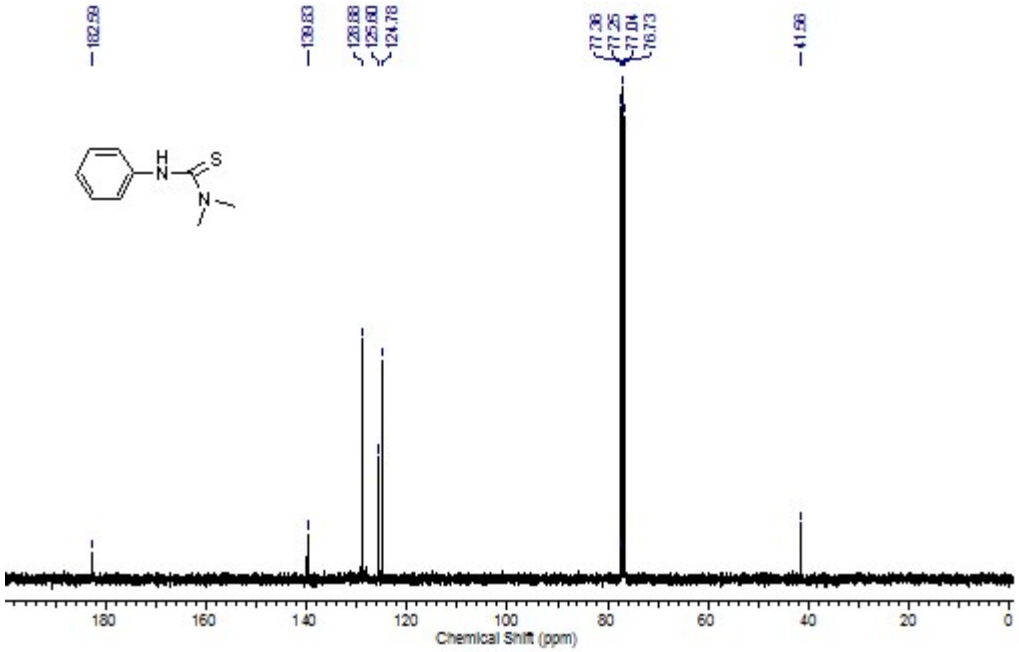


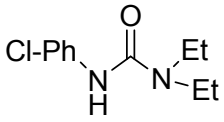
Figure S9. ^{13}C NMR spectra of compound **C**.

General Procedure for the Catalytic Addition of Amines with RNCO and RNCS.

A solution of primary or secondary amine (0.276 mmol) in toluene (1.0 mL) was added drop wise into the reaction mixture of RNCO (0.276 mmol) or RNCS (0.276 mmol) and titanium complex **1** (0.0138 mmol) to a 25 mL dry Schlenk flask inside the glove box. The dark red reaction mixture was stirred for 1 h at room temperature. Solvent was evaporated under vacuo, White solid compound obtained in each case. The conversion of amines was calculated from isolated pure products. The products were identified by ^{1}H NMR spectroscopy and MS analysis; the values were compared with previous literature.

After isolation, due to small amount of intractable $HNMe_2$ we obtained singlet signals from 3 - 4 ppm region in NMR spectra.

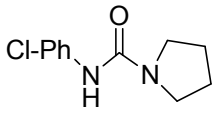
Insertion of diethylamine into 4-chlorophenylisocyanate



The insertion of diethylamine (20 mg, 0.276 mmol) into 4-chlorophenylisocyanate (40 mg, 0.276 mmol) was carried out following the general procedure described above. 1,1-diethyl-3-(4-chlorophenyl)urea (**2i**) was obtained in 99 % yield after a reaction time of 1 hours.

Yield: 59.6 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.35-7.33 (m, 2H, Ar), 7.46-7.24 (m, 2H, Ar), 6.25 (s, 1H, PhN*H*), 3.36 (q, 4H, $^{3}J_{HH}$ = 7.20 Hz, CH_2), 1.22 (t, 6H, $^{3}J_{HH}$ = 7.20 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$) δ 154.3 (*C*O), 137.8 (Ar), 128.7 (Ar), 127.7 (Ar), 120.8 (Ar), 41.6 (*C*H_2), 13.9 (*C*H_3) ppm. MS: m/z 244.0818 (M^+).

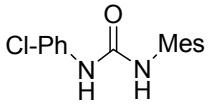
Insertion of Pyrrolidine into 4-chlorophenylisocyanate



The insertion of pyrrolidine (20 mg, 0.276 mmol) into 4-chlorophenylisocyanate (40 mg, 0.276 mmol) was carried out following the general procedure described above. N-(4-chlorophenyl)pyrrolidine-1-carboxamide (**2j**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 58.3 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.42 (d, 2H, Ar), 7.36-7.27 (t, 2H, Hz, Ar), 6.25 (s, 1H, PhN*H*), 3.42 (t, 4H, $^{3}J_{HH}$ = 6.80 Hz, CH_2), 1.94 (q, 4H, $^{3}J_{HH}$ = 6.80 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$) δ 154.0 (*C*O), 139 (Ar), 128 (Ar), 122 (Ar), 119 (Ar), 45 (*C*H_2), 25 (*C*H_2) ppm. MS: m/z 113.07 (M^+).

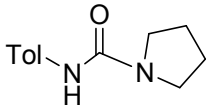
Insertion of Mesityl amine into 4-chlorophenylisocyanate



The insertion of mesityl amine (36 mg, 0.276 mmol) into 4-chlorophenylisocyanate (40 mg, 0.276 mmol) was carried out following the general procedure described above. 1-(4-chlorophenyl)-3-mesitylurea (**2k**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 75 mg, 99%.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (br, 2H, PhN*H*), 7.44-7.40 (m, 3H, Ar), 7.30-7.26 (m, 2H, Ar), 7.19-7.16 (m, 2H, Ar) 6.04 (br, 2H, PhN*H*), 1.6 (s, 9H, CH_3) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$): δ 154 (*C*O), 131.8 (Ar), 129.7 (Ar), 128.9 (Ar), 128.5 (Ar), 128.4 (Ar), 121 (Ar) 36.5 (*C*H_3), 28.5(*C*H_3) ppm. MS: m/z 288.10 (M^+).

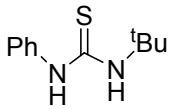
Insertion of pyrrolidine into *p*-tolylisocyanate



The insertion of pyrrolidine (20 mg, 0.276 mmol) into *p*-tolylisocyanate (34 mg, 0.276 mmol) was carried out following the general procedure described above. N-(p-tolyl)pyrrolidine-1-carboxamide (**2l**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 56 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.28 (m, 2H, Ar), 7.26-7.07 (m, 2H, Ar), 6.08 (s, 1H, PhN*H*), 3.45 (t, 4H, $^{3}J_{HH}$ = 6.80 Hz, CH_2), 2.29 (s, 3H, CH_3-OTs), 1.96 (q, 4H, $^{3}J_{HH}$ = 6.80 Hz, CH_2), ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$) δ 154.0 (*C*O), 138 (Ar), 139.3 (Ar), 128.5 (Ar), 119.6 (Ar), 45.7 (*C*H_2), 25.8 (*C*H_2), 29.7 (*C*H_2) ppm. MS: m/z 204.1266 (M^+).

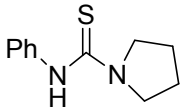
Insertion of *tert*-butylamine into phenylisothiocyanate



The insertion of *tert*-butylamine (19 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1-(tert-butyl)-3-phenylthiourea (**3a**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 54.4 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H, PhN*H*), 7.46-7.44 (m, 2H, Ar), 7.29-7.25 (m, 1H, Ar) 7.19-7.17 (m, 2H, Ar), 6.04 (s, 1H, *t*BuN*H*), 1.5 (s, 9H, CH_3) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$): δ 179.3 (*C*S), 136 (Ar), 132 (Ar), 130 (Ar), 124 (Ar), 54 (*C*$(CH_3)_3$), 28.9 (*C*H_3) ppm. MS: m/z 322.42 (M^+).

Insertion of pyrrolidine into phenylisothiocyanate

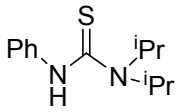


The insertion of pyrrolidine (20mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. N-phenylpyrrolidine-1-carbothioamide (**3b**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 54.87 mg, 99%. ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H, Ar), 7.28-7.24 (m, 2H, Ar), 7.02-7.00 (m, 1H, Ar*H*), 6.26 (s, 1H, PhN*H*), 3.43 (t, 4H, $^{3}J_{HH}$ = 6.80 Hz, CH_2), 1.93 (q, 4H,

$^{3}J_{HH}$ = 6.80 Hz, CH_2) ppm. $^{13}C\{^{1}H\}$ NMR (100, MHz, $CDCl_3$) δ 178.45.0 (*C*S), 139 (Ar), 128.7 (Ar), 125.8 (Ar), 125.5 (Ar), 45 (*C*H_2), 25 (*C*H_2) ppm. MS: m/z 206.09 (M^+).

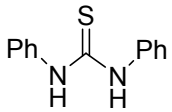
Insertion of N,N'-$^{i}Pr_2$-ethylamine into phenylisothiocyanate



The insertion of N,N'-$^{i}Pr_2$-ethylamine (30 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1,1-diisopropyl-3-phenylthiourea (**3c**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 63 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.35 (m, 2H, Ar), 7.29-7.24 (m, 3H, Ar), 6.19 (s, 1H, PhN*H*), 3.99 (sept, 2H, $^{3}J_{HH}$ = 6.40 Hz, C*H*), 1.33(d, 12H, $^{3}J_{HH}$ = 6.40 Hz, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (100, MHz, $CDCl_3$): δ 154.7 (*C*S), 139.3 (Ar), 128.8 (Ar), 122.6 (Ar), 119.7 (Ar), 45.4 (*C*H), 21.5 (*C*H_3) ppm. MS: m/z 236.13 (M^+).

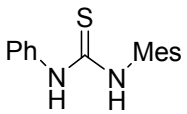
Insertion of aniline into phenylisothiocyanate



The insertion of aniline (24 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1,3-diphenylthiourea (**3d**) was obtained in 99 % yield after a reaction time of 1 hours.

Yield: 61 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (br, 2H, ArN*H*), 7.42-7.39 (m, 8H, Ar), 7.31-7.29 (m, 2H, Ar) ppm. $^{13}C\{^{1}H\}$ NMR (100, MHz, $CDCl_3$): δ 178 (*C*S),139 (Ar),128 (Ar), 125.7(Ar), 125.5(Ar) ppm. MS: m/z 228.07 (M^+).

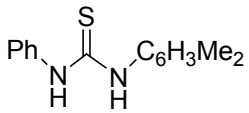
Insertion of mesityl amine into phenylisothiocyanate



The insertion of mesityl amine (36 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1-mesityl-3-phenylthiourea (**3e**) was obtained in 95 % yield after a reaction time of 1 hour.

Yield: 68 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 4H, Ar), 7.05-7.03 (m, 2H, Ar), 7.01 (br, 1H, MesN*H*), 6.97 (br, 1H, PhN*H*), 2.31 (s, 3H, CH_3), 2.29 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$): δ 167.9 (*C*S), 137.0(Ar), 132.0 (Ar), 131.9 (Ar), 129.9 (Ar), 128.9(Ar), 128.7(Ar), 125.3(Ar), 124.5(Ar), 30.9 (*C*H_3), 21.1(*C*H_3), 18.1(*C*H_3) ppm MS: m/z 270.12 (M^+).

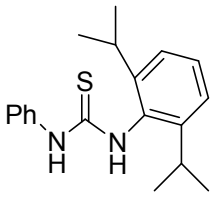
Insertion of 2,6-dimethylaniline into phenylisothiocyanate



The insertion of 2,6-dimethylaniline (32 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1-(2,6-dimethylphenyl)-3-phenylthiourea (**3f**) was obtained in 99 % yield after a reaction time of 1 hours.

Yield: 68 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (br, 1H, PhN*H*), 7.25-7.18 (m, 4H, Ar), 7.05-6.65 (m, 3H, Ar), 6.39 (br, 1H, ArN*H*), 2.25 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$): δ 179 (*C*S),138 (Ar),136 (Ar), 133 (Ar), 128 (Ar), 123 (Ar), 120 (Ar), 18 (*C*H_3) ppm. MS: m/z 256.10 (M^+).

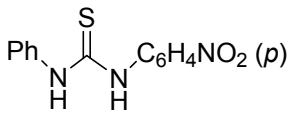
Insertion of DippNH_2 into phenylisothiocyanate



The insertion of DippNH_2 (46 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1-(2,6-diisopropylphenyl)-3-phenylthiourea (**3g**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 83 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (br, 1H, PhN*H*), 7.51-7.41 (m, 3H, Ar), 7.28-7.21 (m, 5H, Ar), 6.94 (br, 1H, ArN*H*), 3.29 (sept, 2H, C*H*), 1.25 (dd, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$): δ 181.1 (CS), 147.9 (Ar), 130.3 (Ar), 129.8 (Ar), 128.8 (Ar), 126.5 (Ar), 125.5 (Ar), 124.8 (Ar), 28.7 (C*H*), 24.3 (CH_3) ppm. MS: m/z 312.17 (M^+).

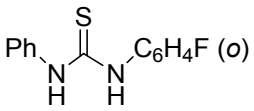
Insertion of *p*-nitroaniline into phenylisothiocyanate



The insertion of *p*-nitroaniline (36 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1-(4-nitrophenyl)-3-phenylthiourea (**3i**) was obtained in 75 % yield after a reaction time of 1 hour.

Yield: 55 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (br, 1H, ArN*H*), 7.34-7.32 (m, 3H, Ar), 7.27-7.22 (m, 4H, Ar), 6.62 (br, 1H, PhN*H*) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$) δ 182.9 (*C*S), 133.1 (Ar), 132.0 (Ar),131.9 (Ar), 128.9 (Ar), 128.6 (Ar), 126.7 (Ar), 124.6 (Ar) ppm. MS: m/z 273.06 (M^+).

Insertion of *o*-fluoroaniline into phenylisothiocyanate



The insertion of *o*-fluoroaniline (30 mg, 0.276 mmol) into phenylisothiocyanate (36 mg, 0.276 mmol) was carried out following the general procedure described above. 1-(2-fluorophenyl)-3-phenylthiourea (**3j**) was obtained in 99 % yield after a reaction time of 1 hour.

Yield: 65.5 mg, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (br, 1H, ArN*H*), 7.96 (br, 1H, PhN*H*), 7.99-7.96 (m, 1H, Ar), 7.45-7.39 (m, 5H, Ar), 7.35-7.26 (m, 3H, Ar) ppm. ^{13}C{^{1}H} NMR (100, MHz, $CDCl_3$) δ 182.6 (*C*S), 134.2 (Ar), 132.1 (Ar),132 (Ar), 131.9 (Ar), 128.9 (Ar), 128.6 (Ar), 128.5 (Ar), 125.5 (Ar) ppm. MS: m/z 246.06 (M^+).

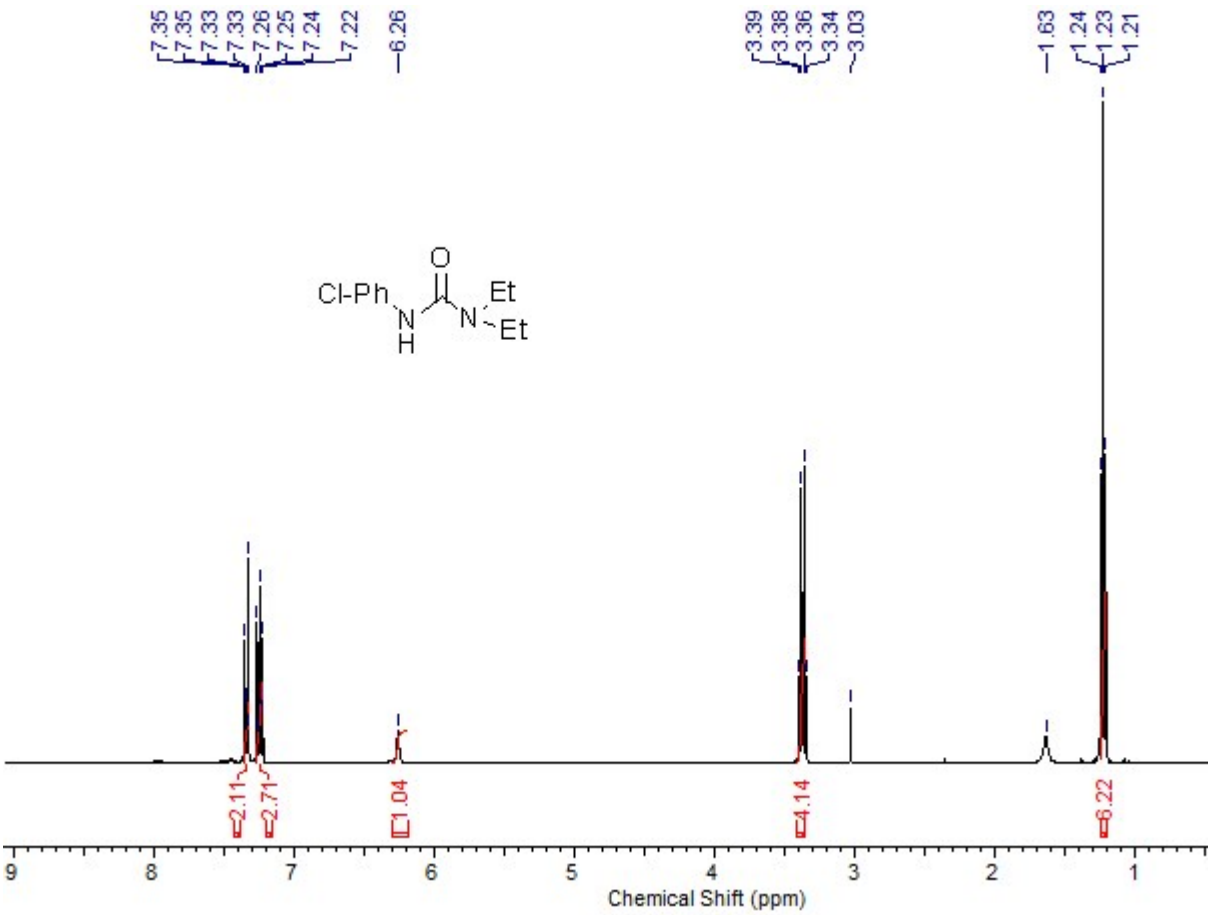


Figure S10. ^{1}H NMR spectra of compound **2i.**

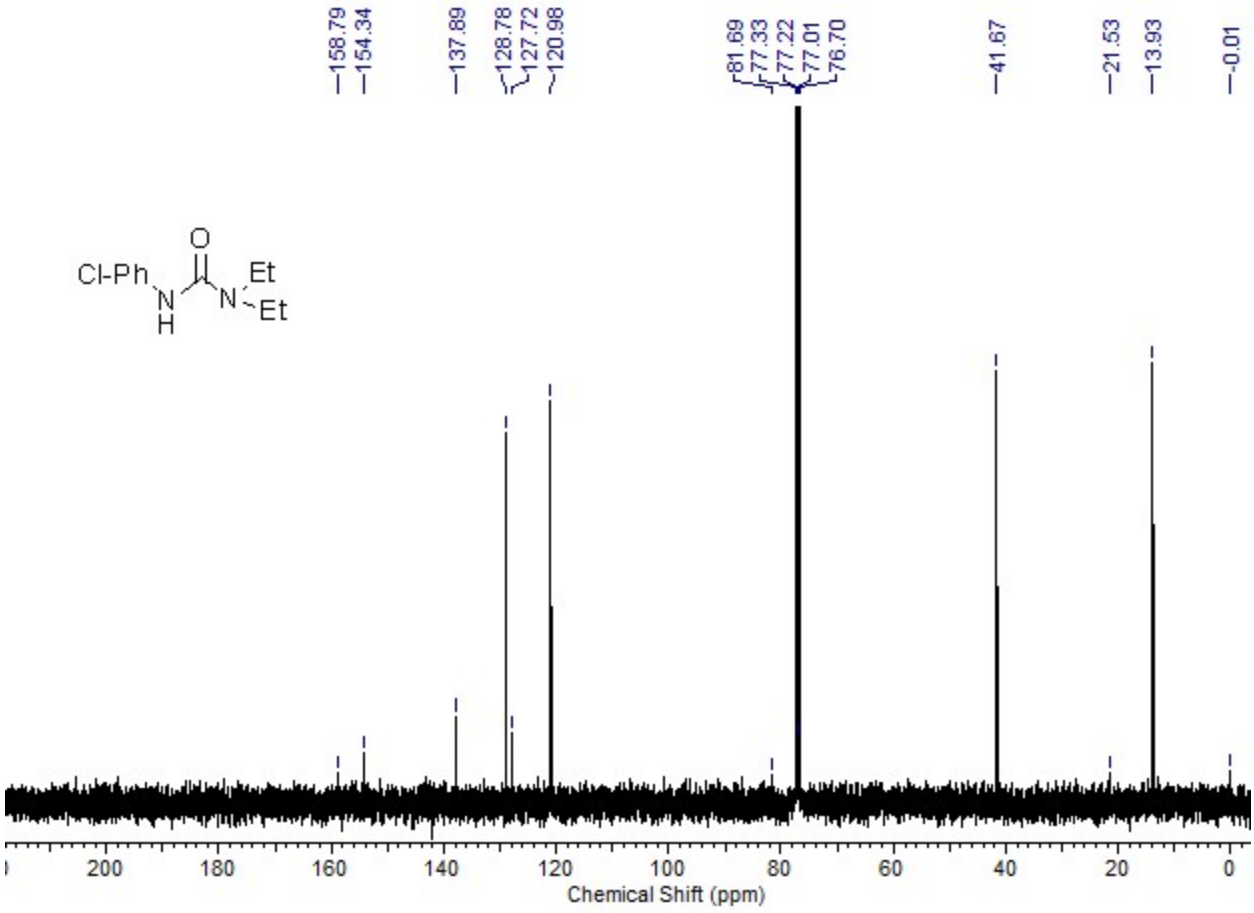


Figure S11. ^{13}C NMR spectra of compound **2i.**

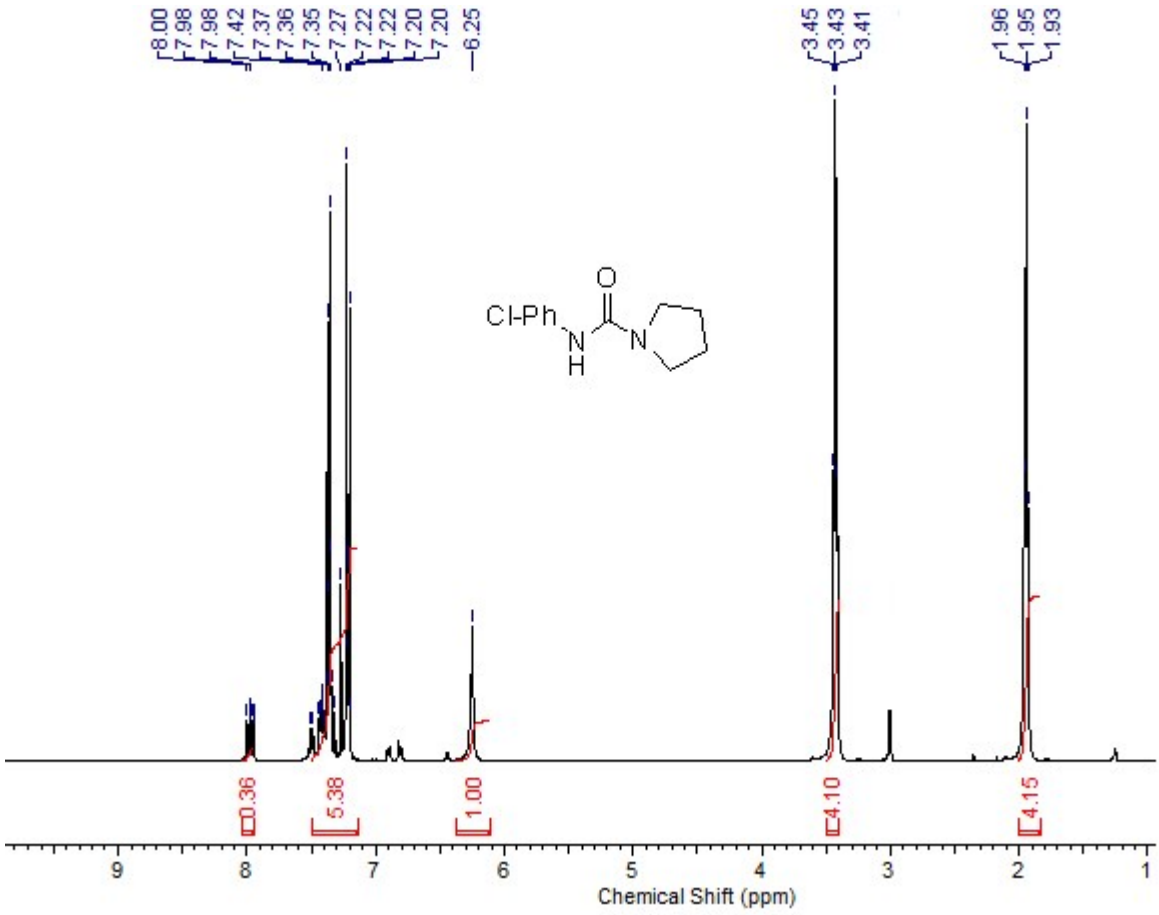


Figure S12. ^{1}H NMR spectra of compound **2j.**

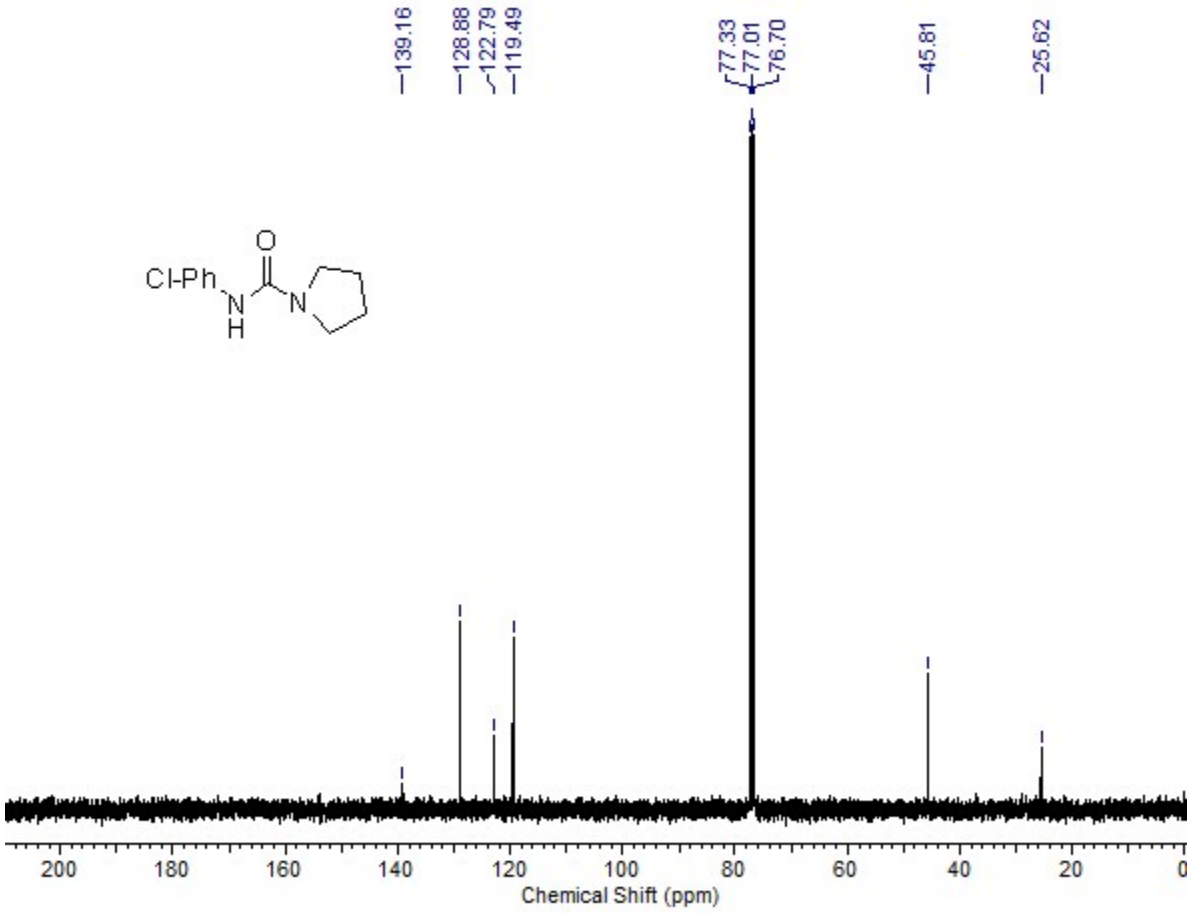


Figure S13. ^{13}C NMR spectra of compound **2j.**

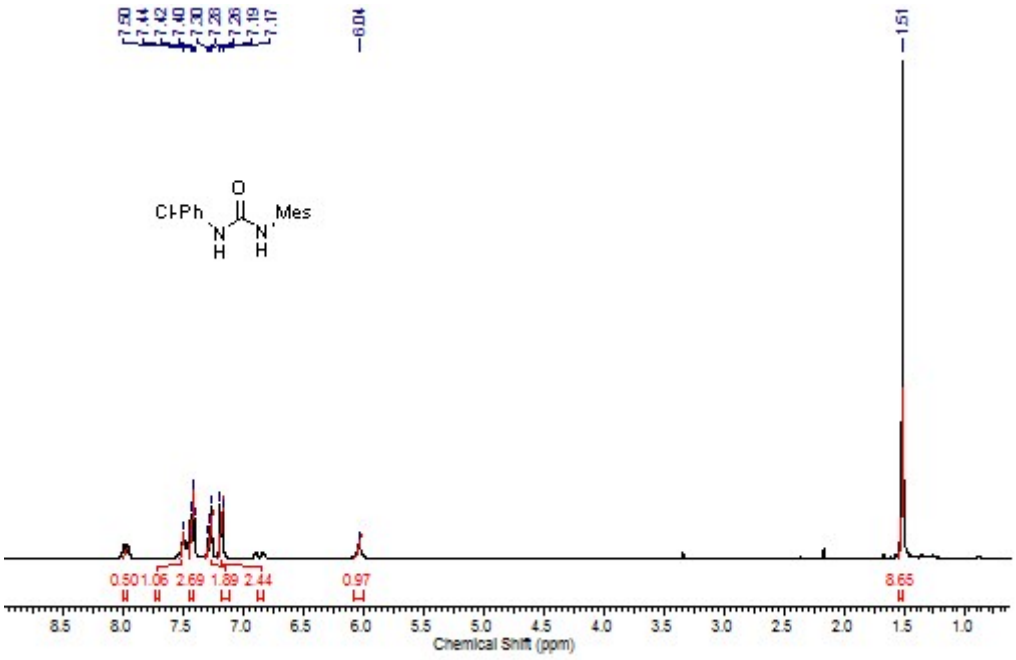


Figure S14. ^{1}H NMR spectra of compound **2k.**

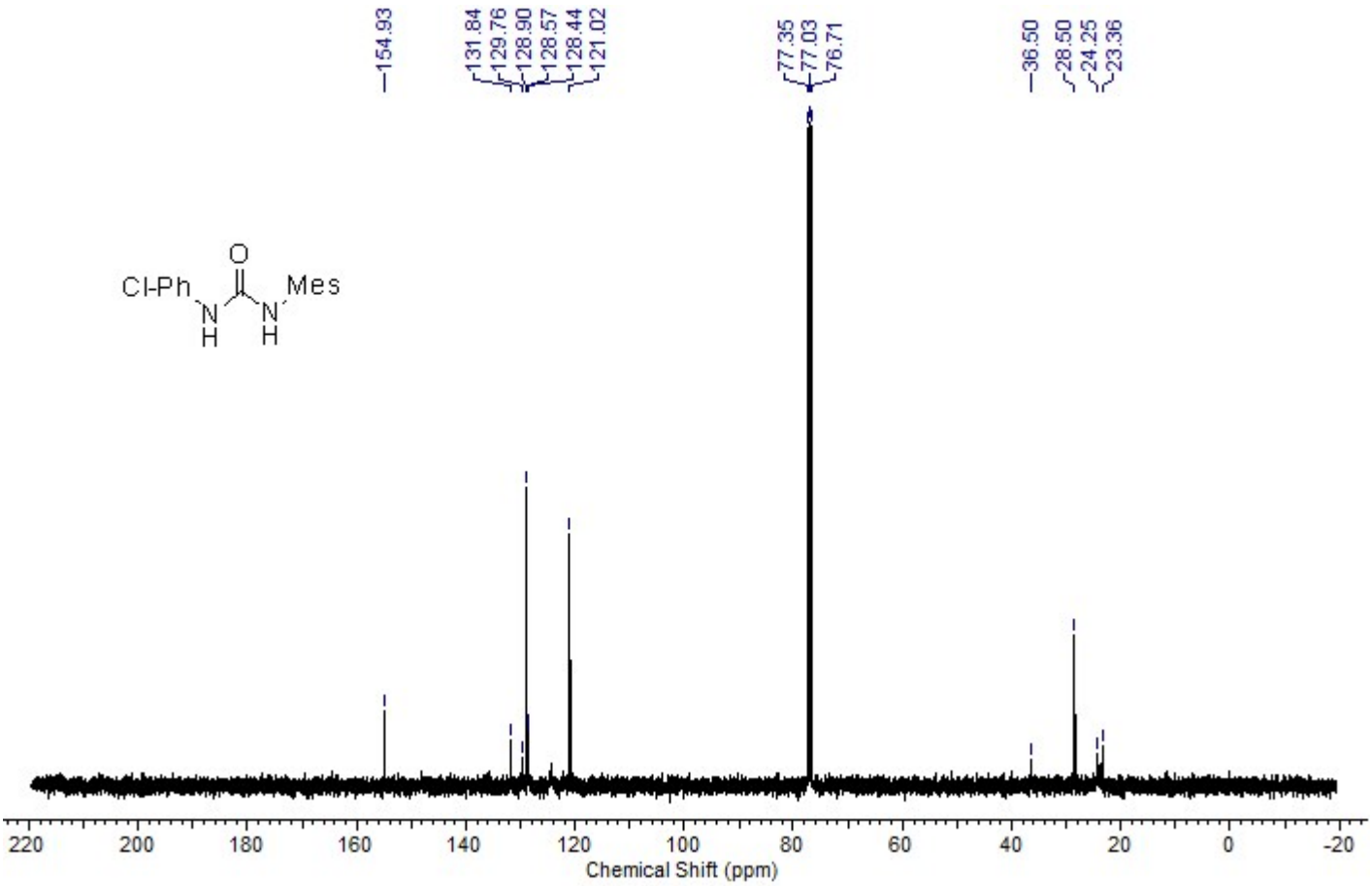


Figure S15. ^{13}C NMR spectra of compound **2k.**

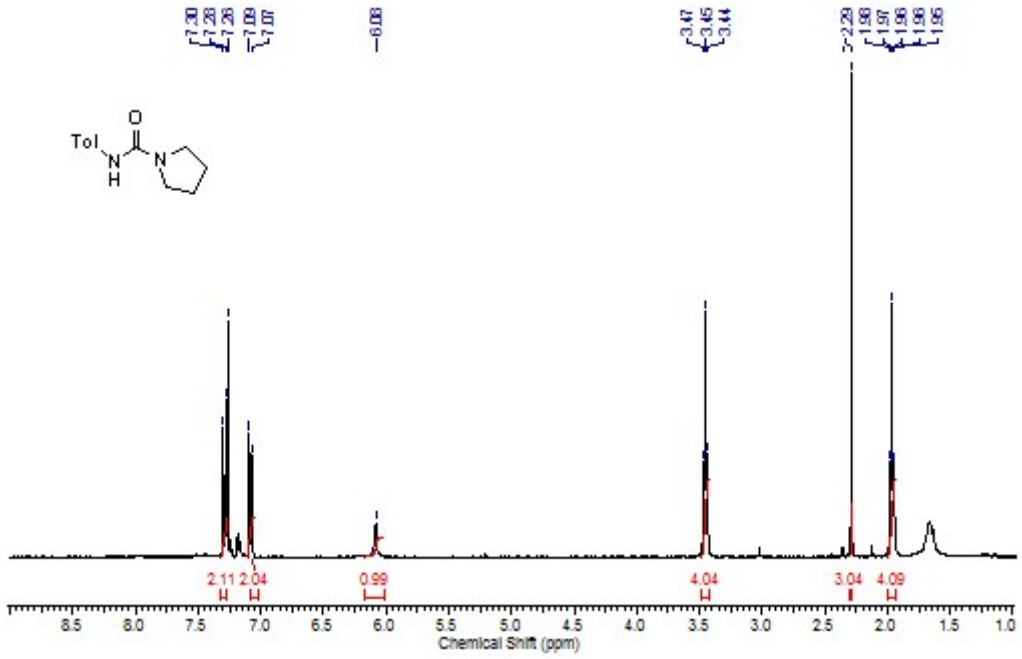


Figure S16. ^{1}H NMR spectra of compound **2l.**

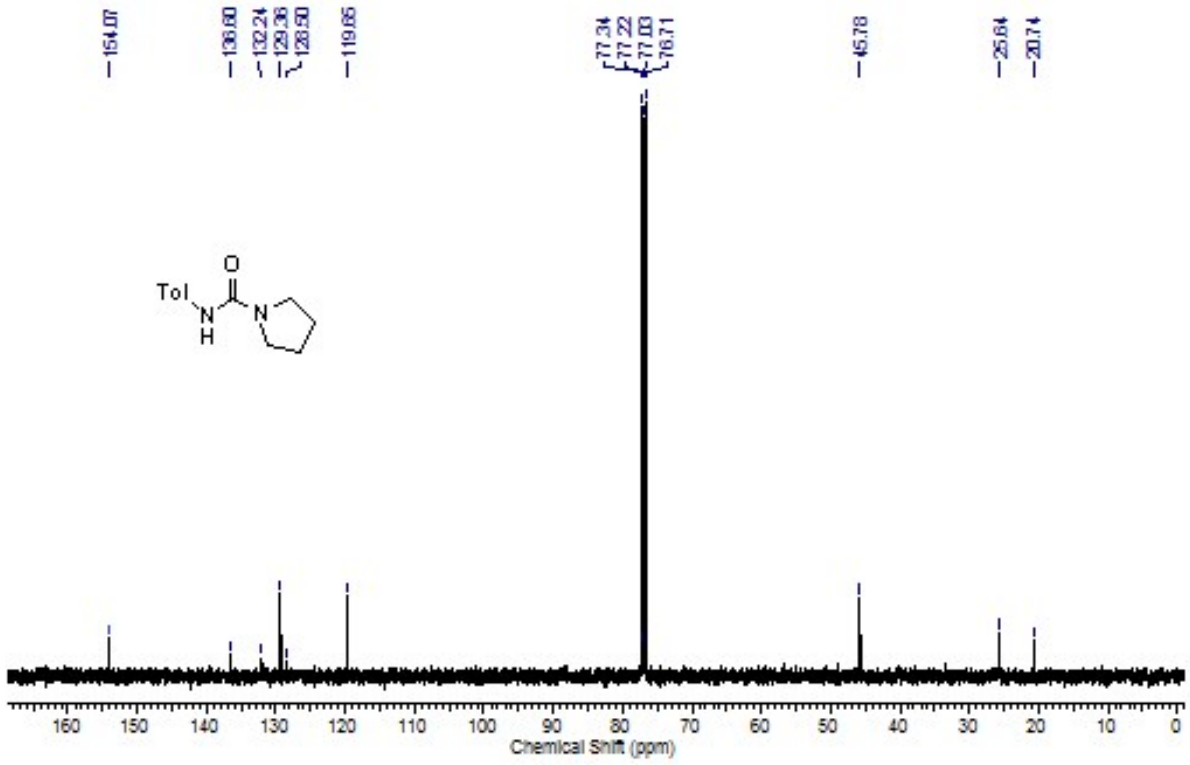


Figure S17. ^{13}C NMR spectra of compound **2l.**

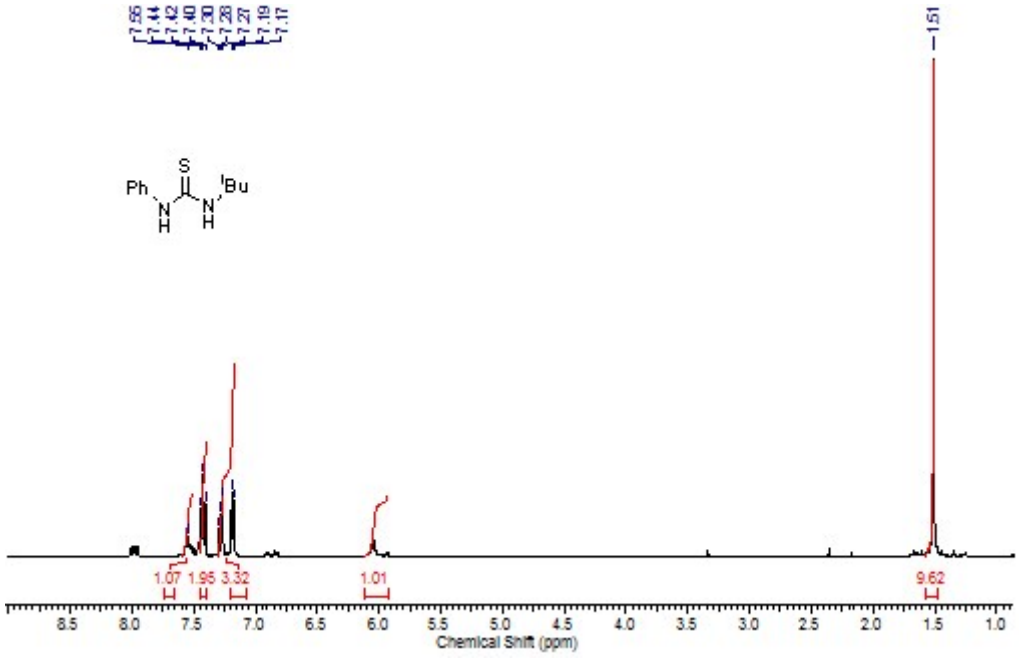


Figure S18. ^{1}H NMR spectra of compound **3a.**

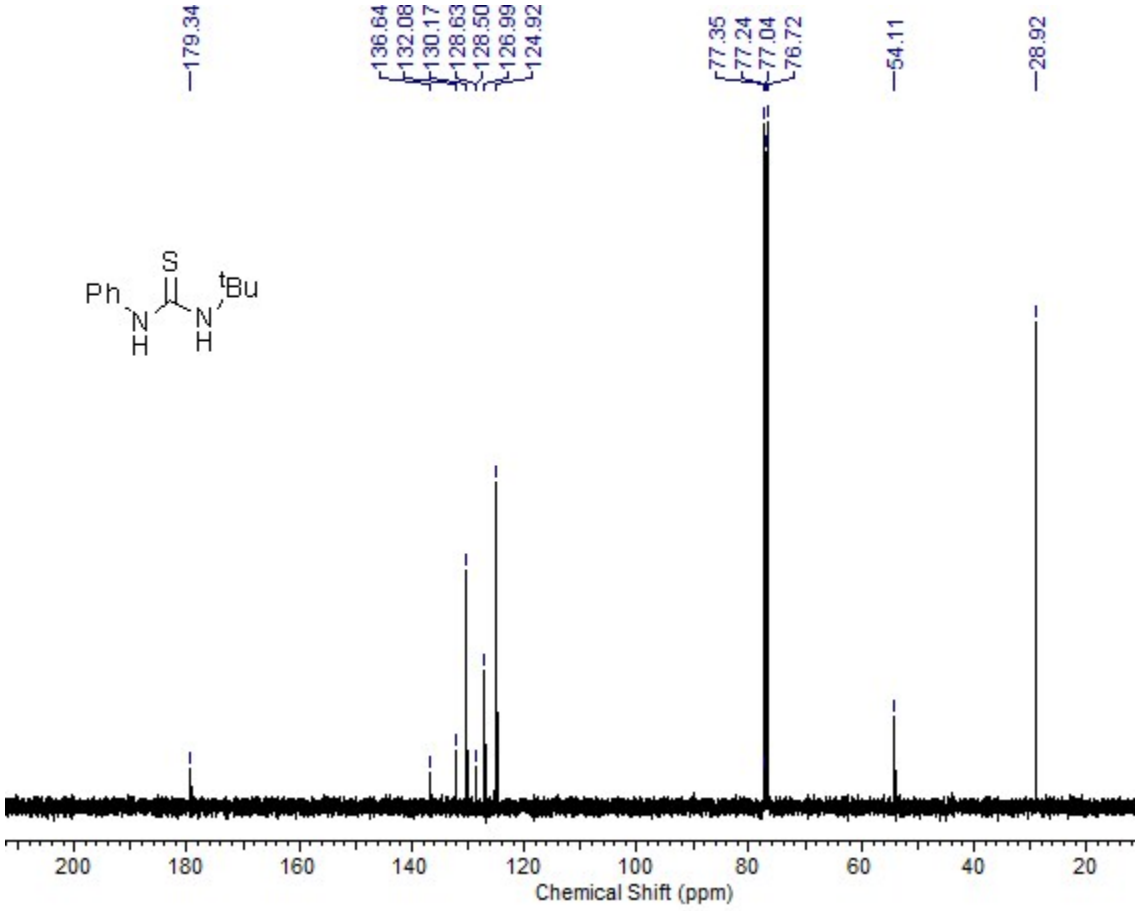


Figure S19. ^{13}C NMR spectra of compound **3a.**

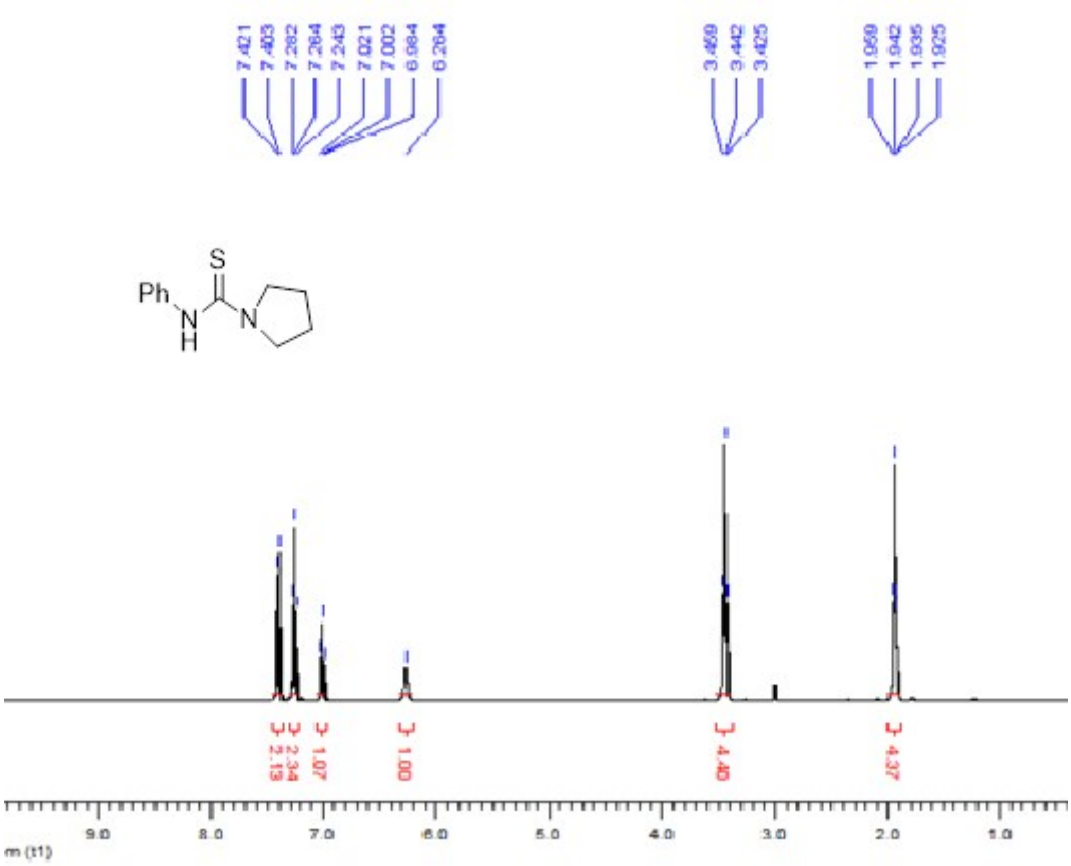


Figure S20. ^{1}H NMR spectra of compound **3b.**

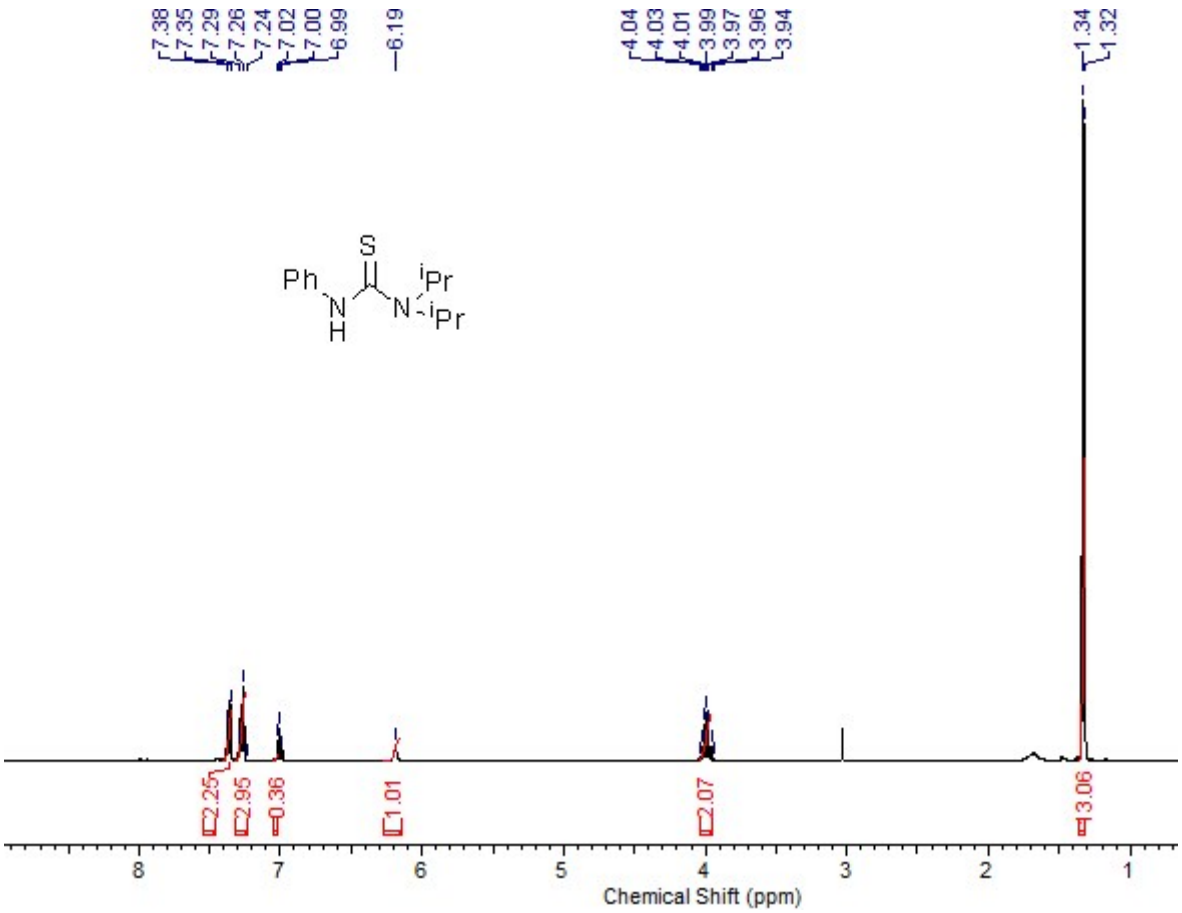


Figure S21. ^{1}H NMR spectra of compound **3c.**

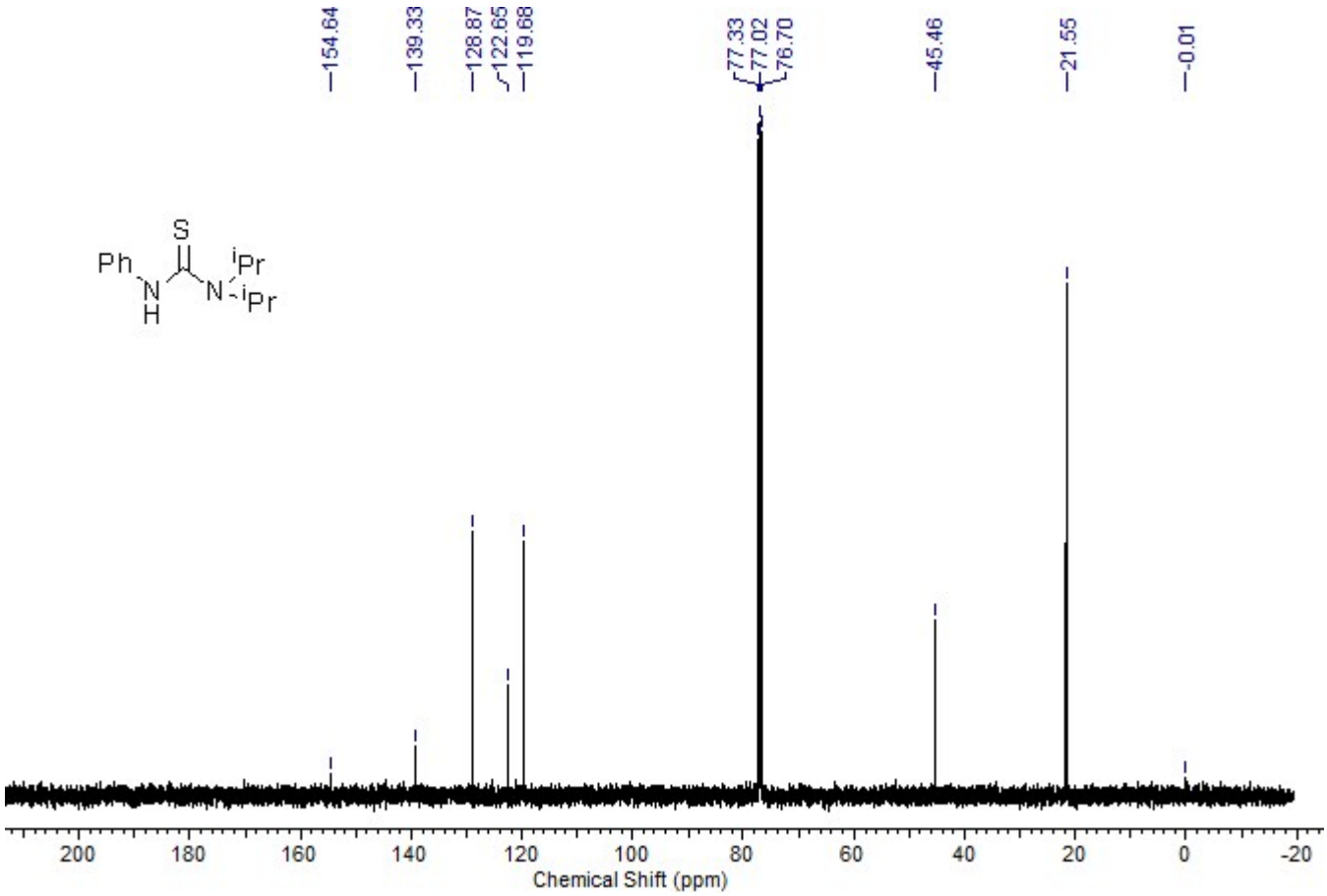


Figure S22. ^{13}C NMR spectra of compound **3c.**

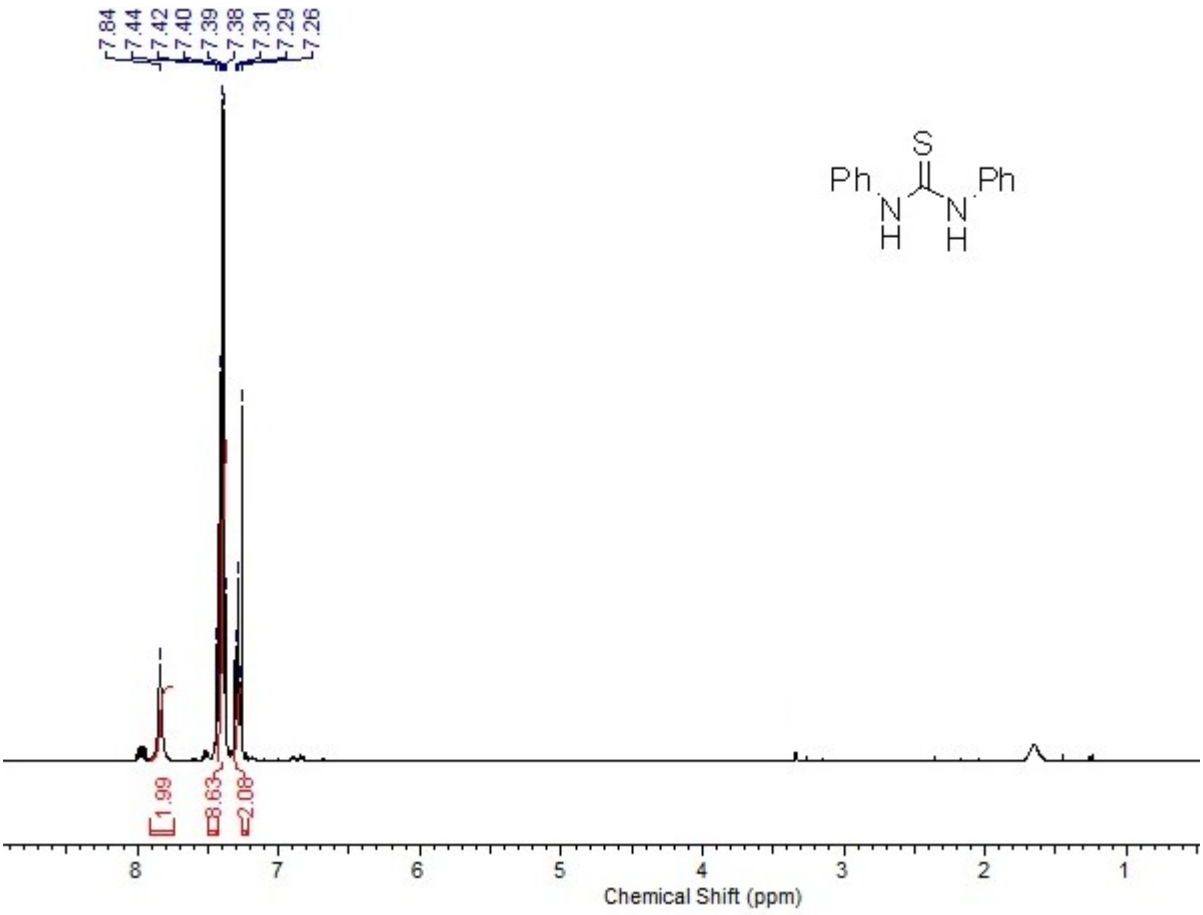


Figure S23. ^{1}H NMR spectra of compound **3d.**

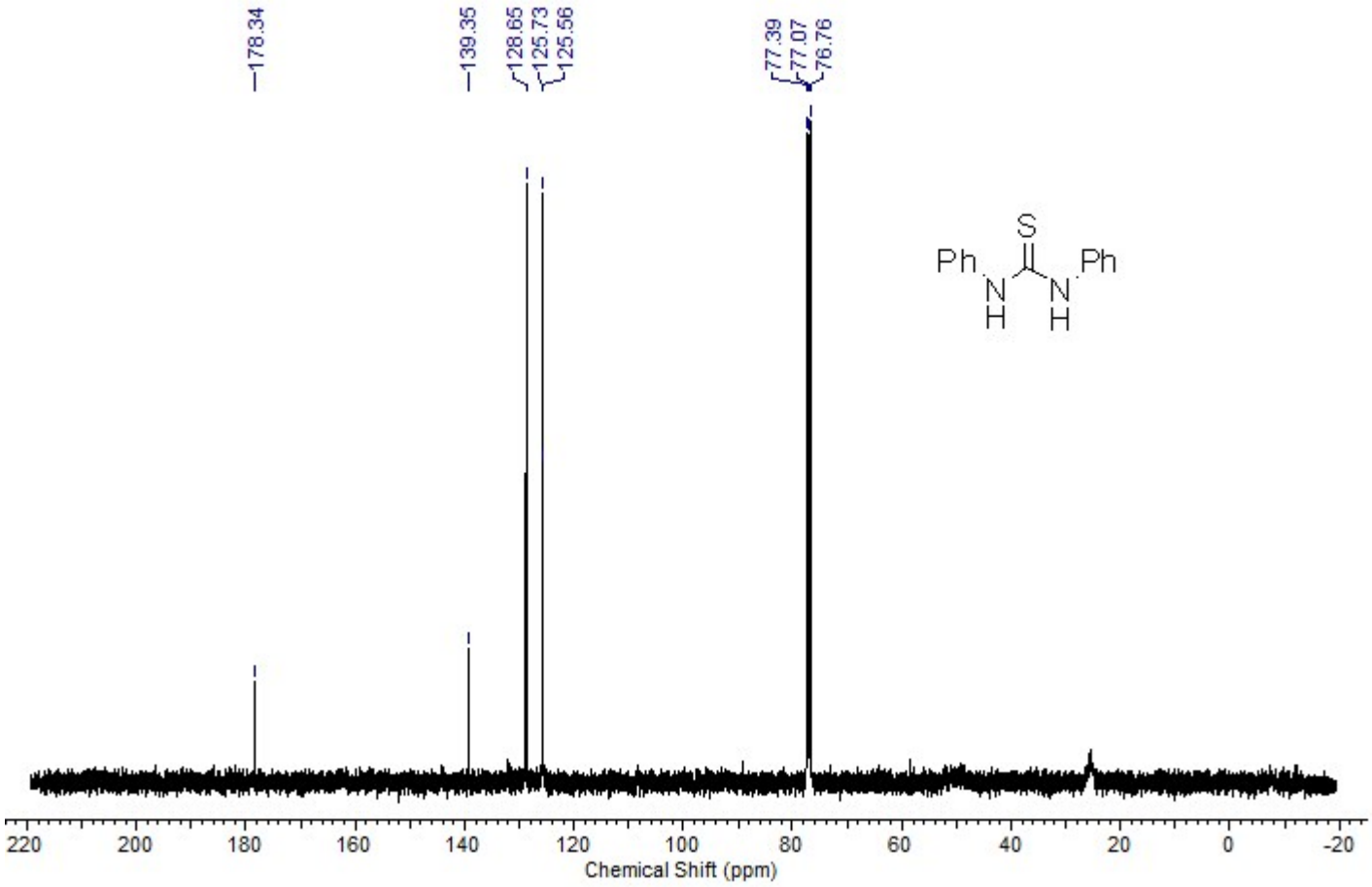


Figure S24. ^{13}C NMR spectra of compound **3d.**

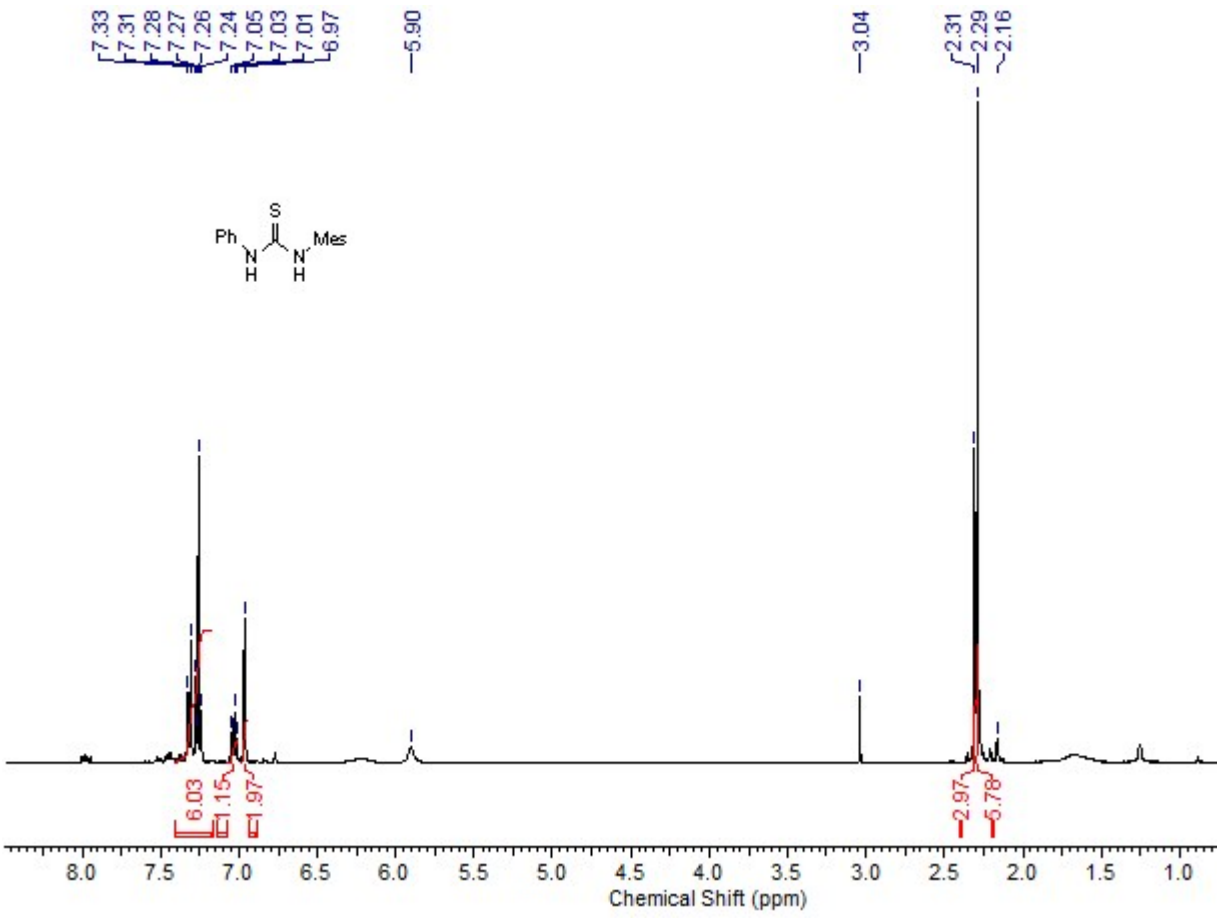


Figure S25. ^{1}H NMR spectra of compound **3e.**

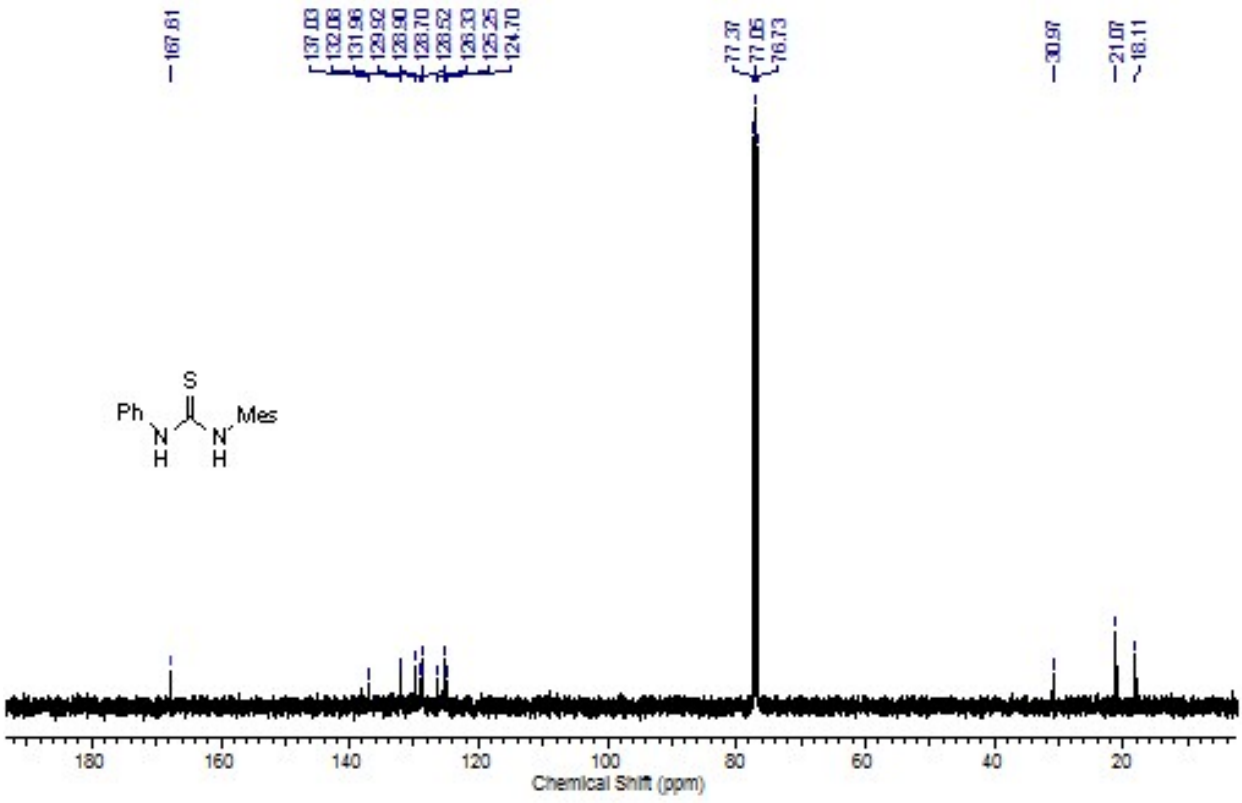


Figure S26. ^{13}C NMR spectra of compound **3e.**

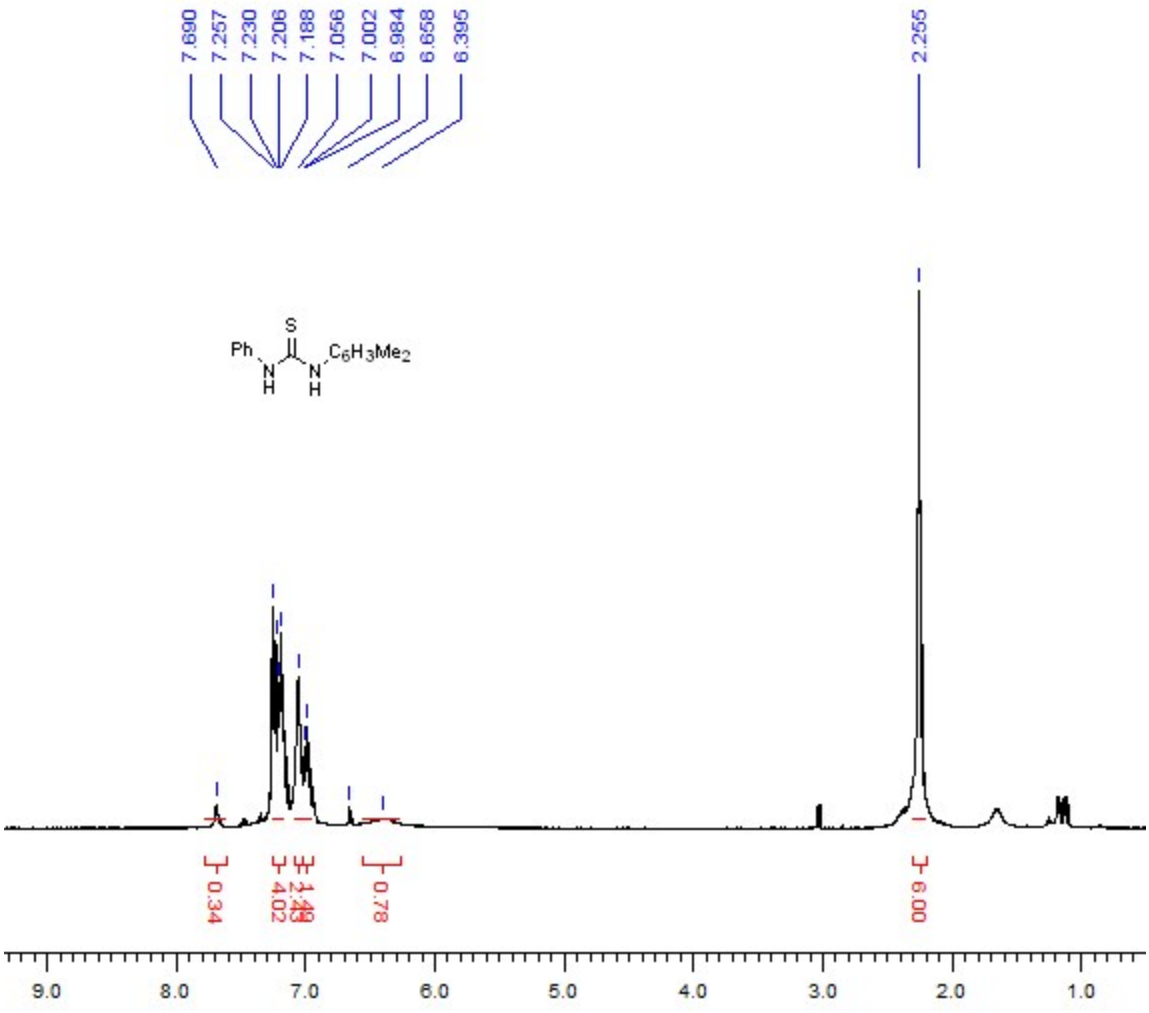


Figure S27. ^{1}H NMR spectra of compound **3f.**

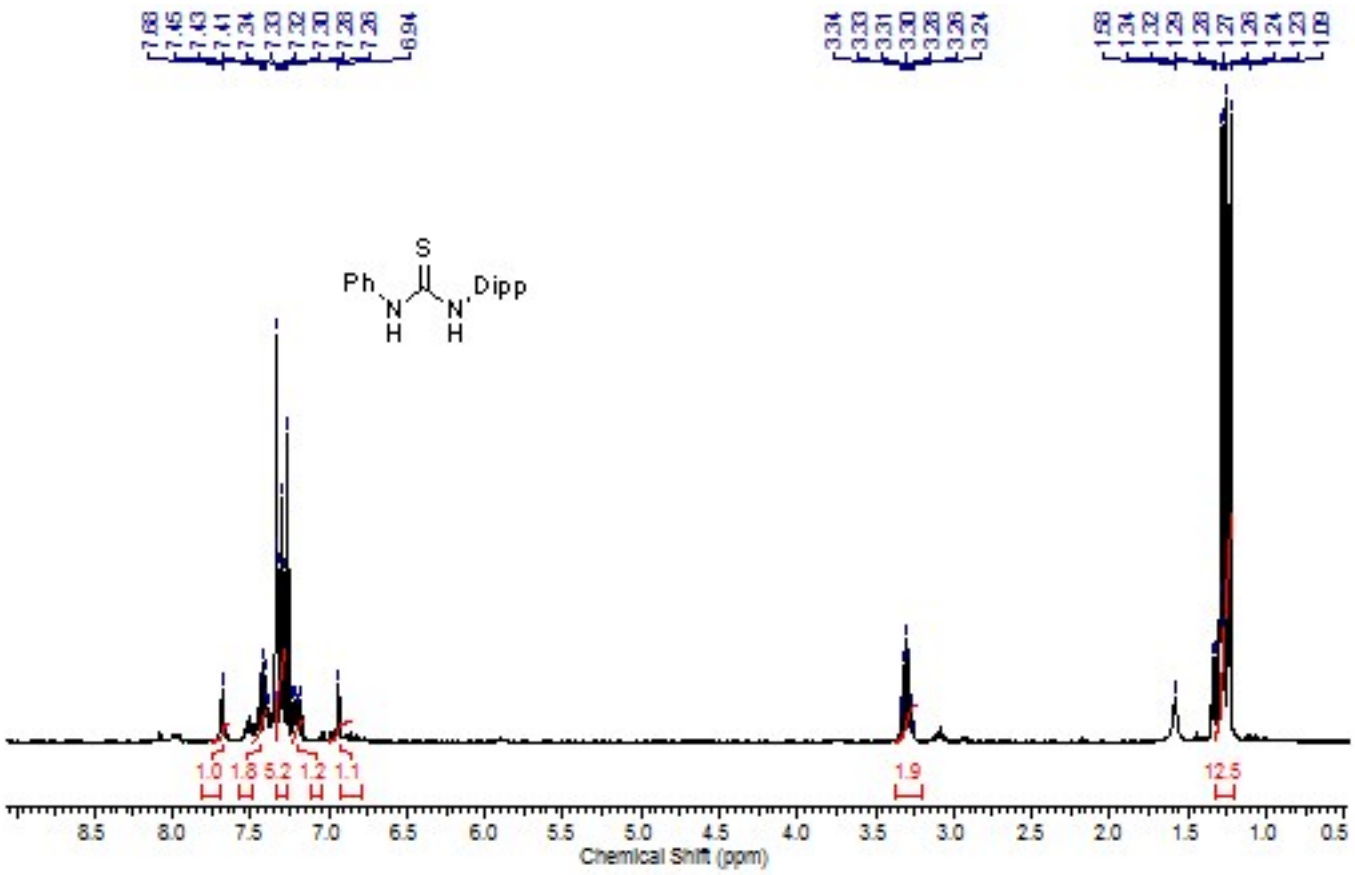


Figure S28. ^{1}H NMR spectra of compound **3g.**

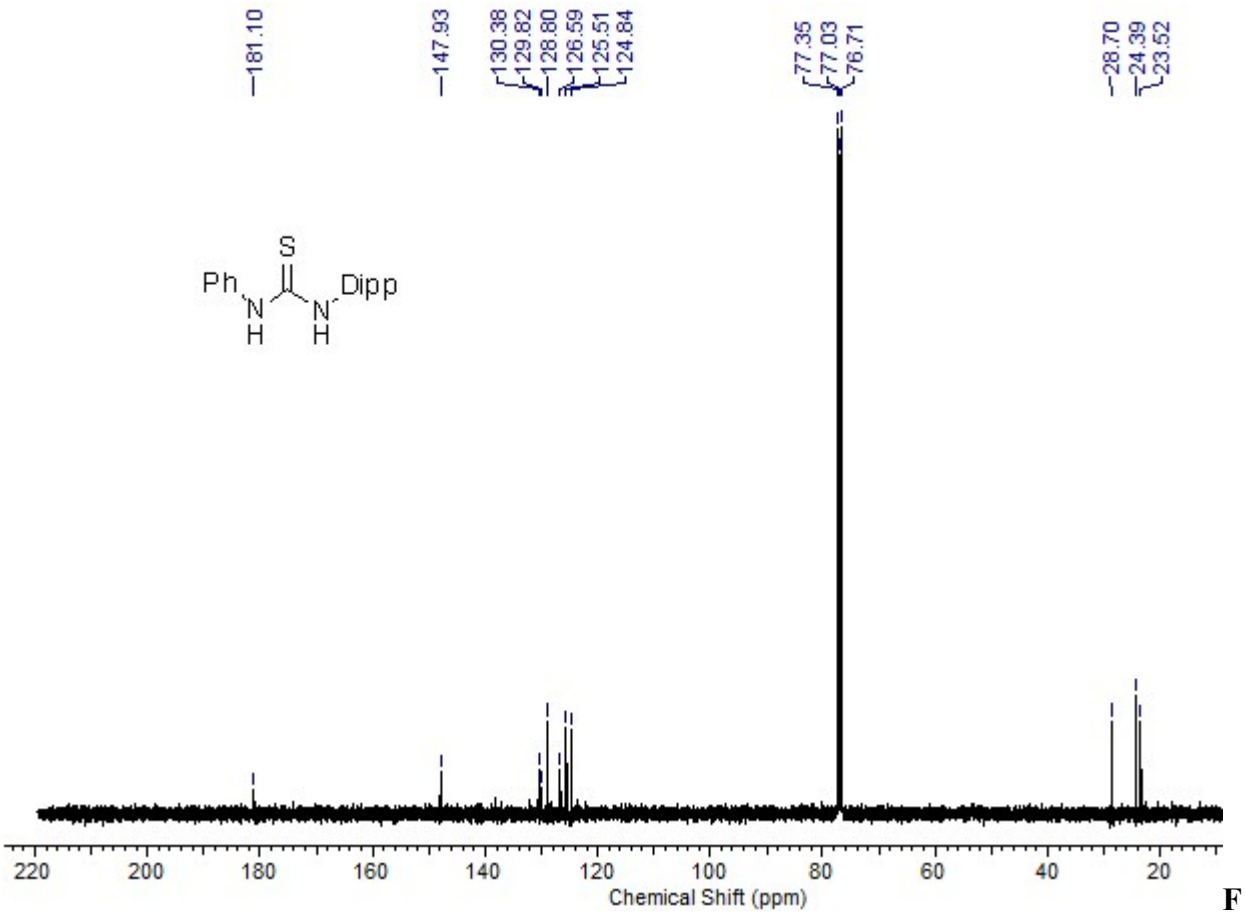


Figure S29. ^{13}C NMR spectra of compound **3g.**

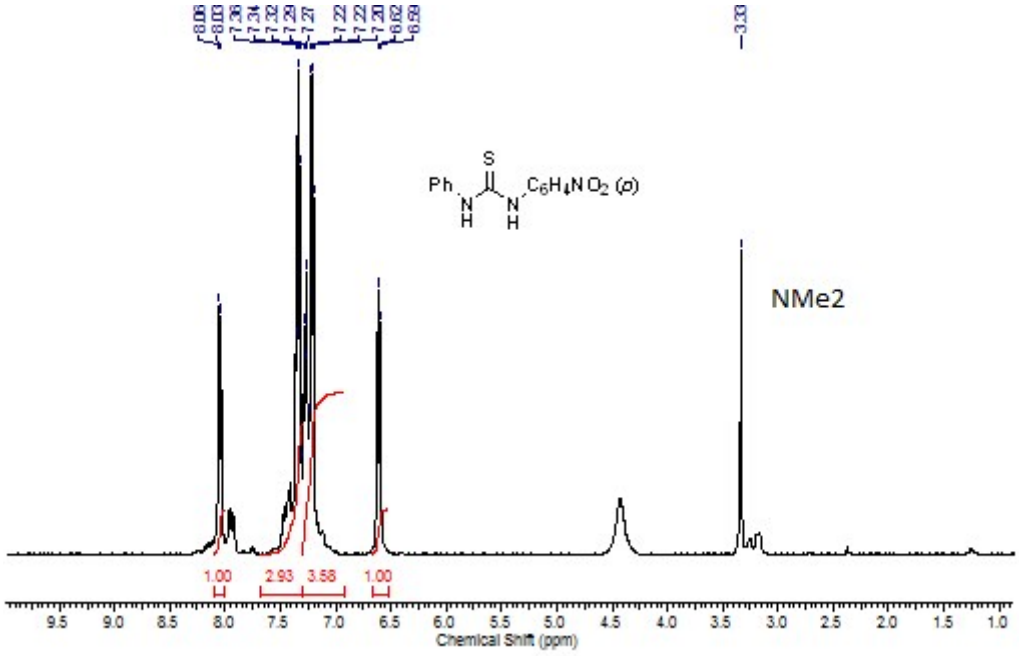


Figure S30. ^{1}H NMR spectra of compound **3i.**

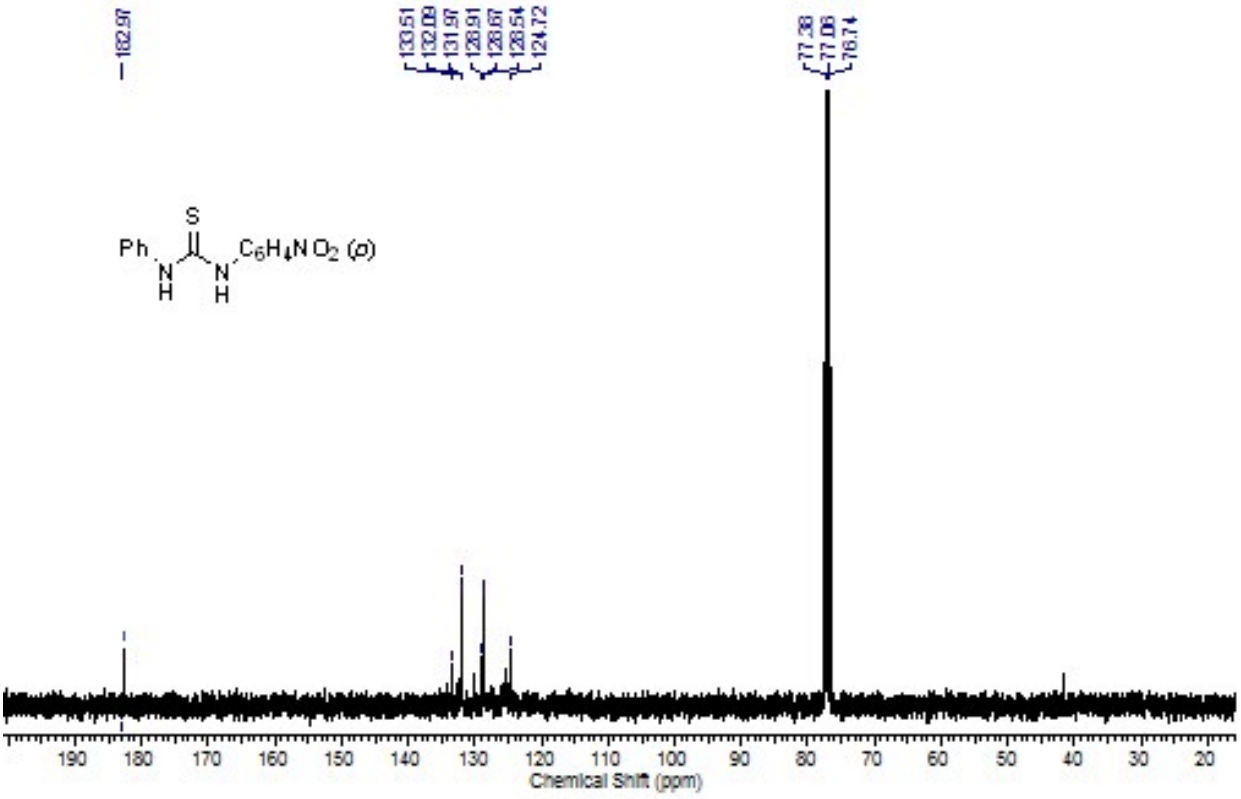


Figure S31. ^{13}C NMR spectra of compound **3i.**

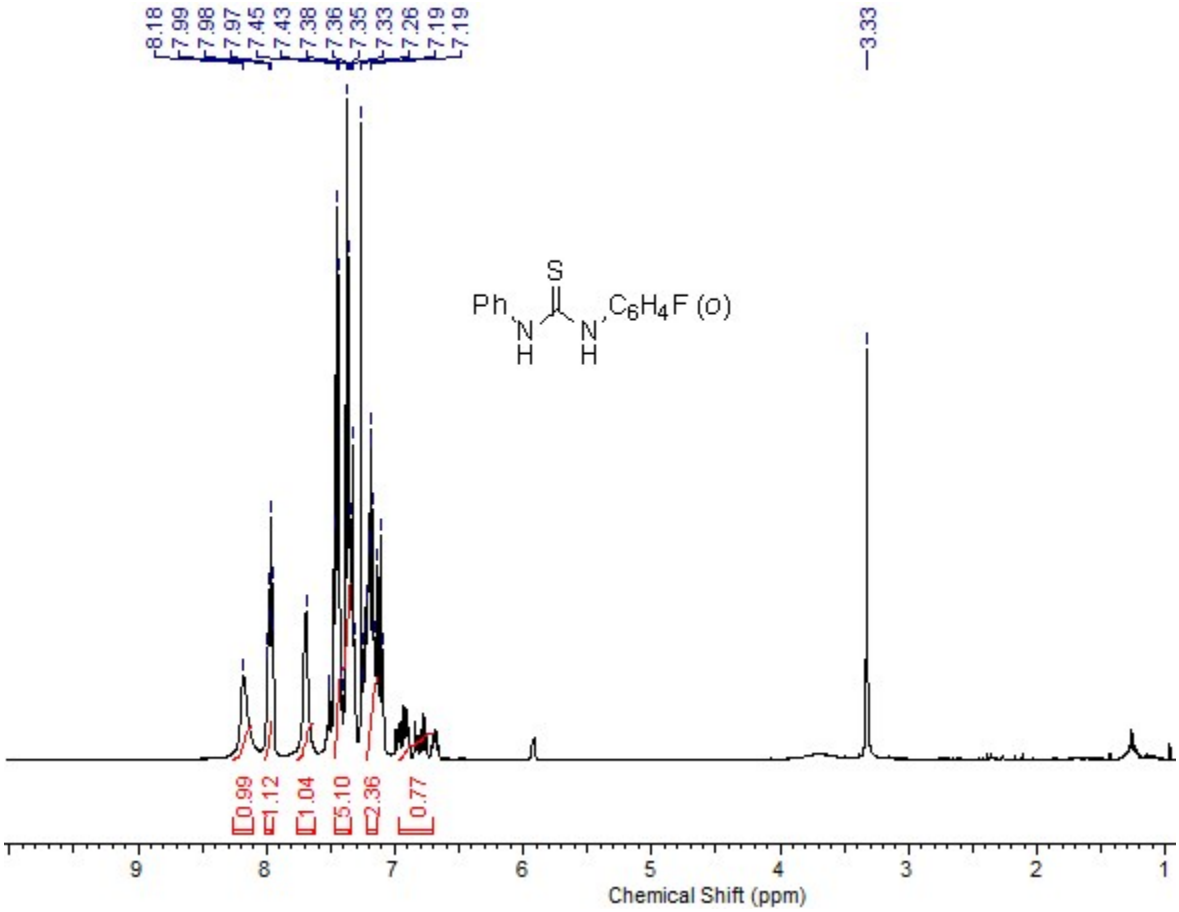


Figure S32. ^{1}H NMR spectra of compound **3j.**

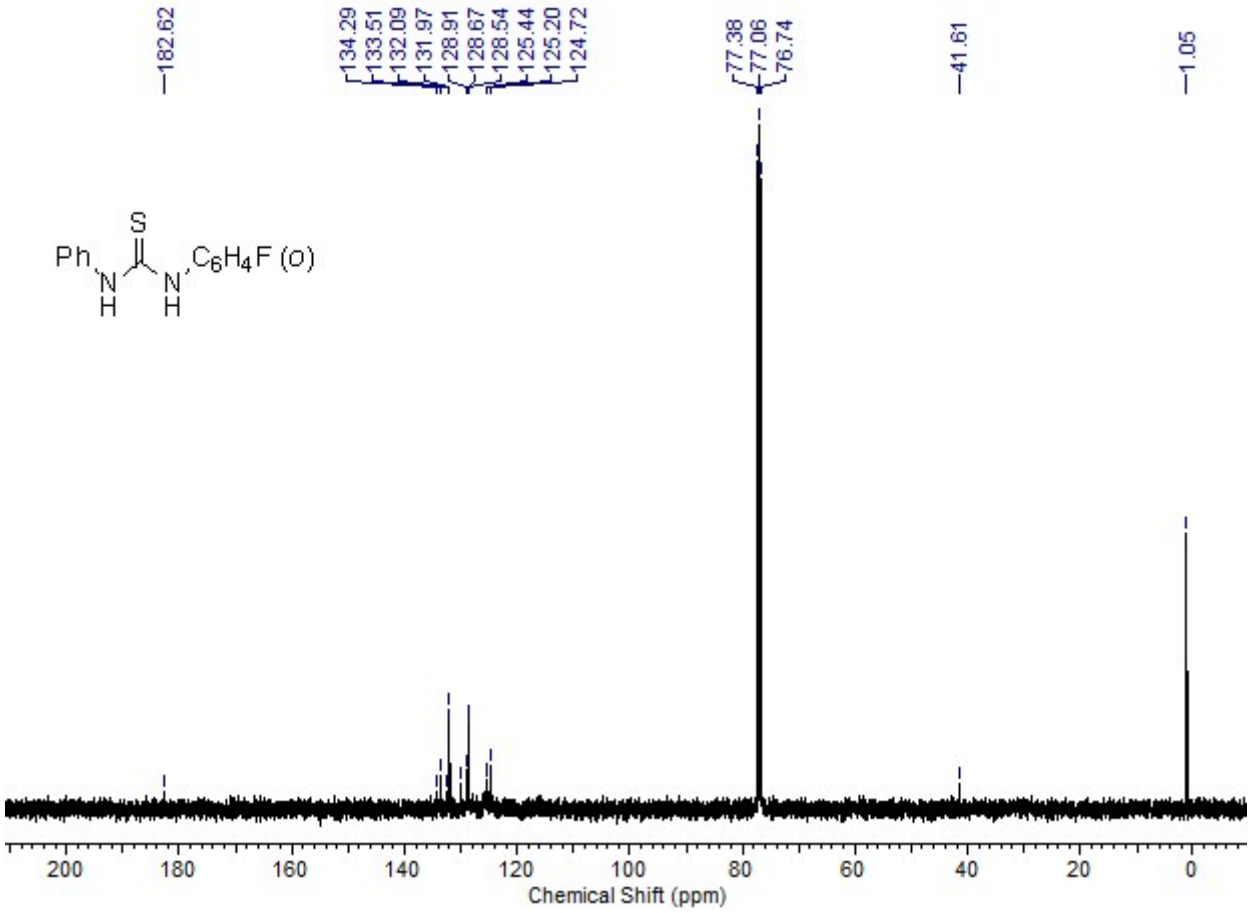
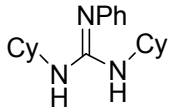


Figure S33. ^{13}C NMR spectra of compound **3j.**

General Procedure for the Catalytic Addition of Amines with Carbodiimide.

A solution of primary or secondary amine (0.276 mmol) in toluene (1.0 mL) was added drop wise into the reaction mixure of carbodiimide (0.276 mmol) an [$(NMe_2)_2$Ti{Ph_2P(Se)N-$CH_2CH_2NPPh_2$(Se)}] (**1**) (0.0138 mmol) to a 25 mL dry Schlenk flask inside the glove box. The dark red reaction mixture was stirred for 6 h at 70˚C temperature. Solvent was evaporated under vacuo, and a solid residue obtained was obtained, which was washed with *n*-pentane (5 mL). White solid compound obtained in each case. The conversion of amines was calculated from isolated pure products.

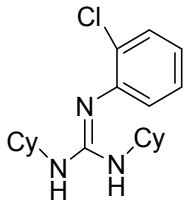
Insertion of aniline into carbodiamide



The insertion of aniline (24 mg, 0.276 mmol) into carbodiamide (54 mg, 0.276 mmol) was carried out following the general procedure described above. 1,3-dicyclohexyl-2-phenylguanidine (**4a**) was obtained in 95 % yield after a reaction time of 6 hours at 60˚C.

Yield: 78 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.24 (m, 2H, Ar-*H*), 7.03-6.95 (m, 1H, Ar-*H*), 6.92-6.90 (d, 2H, Ar-*H*), 3.40 (br, 2H, N*H*), 1.98-1.13 (m, 22H, C*H* and CH_2 of cyclohexyl) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.8 (*C*=N), 150.2, 129.9, 128.5, 127.5, 125.5, 122.9, (Ar-*C*), 50.5(*C*H), 33.7 (CH_2), 25.6 (CH_2), 24.8(CH_2). FT-IR (selected frequencies): υ = 3271 (N-H), 3062 (aromatic C-H), 2927 (sp^3 C-H), 2852 (sp^3 C-H), 1550 (aromatic C-C), 1447 (C-H bend), 1346 (C=N), 889, 862, 837, 795, 738 (aromatic C-H oop) cm^{-1}. MS: m/z 345.2898 (M^+).

Insertion of 2-chloroaniline into carbodiamide



The insertion of 2-chloroaniline (32 mg, 0.276 mmol) into carbodiamide (54mg, 0.276 mmol) was carried out following the general procedure described above. 2-(2-chlorophenyl)-1,3-dicyclohexylguanidine (**4e**) was obtained in 53 % yield after a reaction time of 6 hours at 60˚C.

Yield: 46 mg, 53%. ^{1}H NMR (400MHz,$CDCl_3$): δ 7.22-7.18 (m, 1H, Ar-*H*), 7.07-7.03 (m, 1H, Ar-*H*), 6.77-6.75 (m, 1H, Ar-*H*), 6.70-6.66 (m, 1H, Ar-*H*), 3.35 (br, 2H, N*H*), 1.96-1.12 (m, 22H, C*H* and CH_2 of cyclohexyl) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.8 (*C*=N), 150.2, 129.9, 128.5, 127.5, 125.5, 122.9, (Ar-*C*), 50.5 (*C*H), 33.7 (CH_2), 25.6 (CH_2), 24.8(CH_2).

IR(neat, cm^{-1}): υ = 3281 (N-H), 3056 (aromatic C-H), 2926 (sp^3 C-H), 2852 (sp^3 C-H), 1574 (aromatic C-C), 1470 (C-H bend), 1348 (C=N), 1058, 889, 803, 739 (aromatic C-H oop) cm^{-1}. MS: m/z 334.20 (M^+)

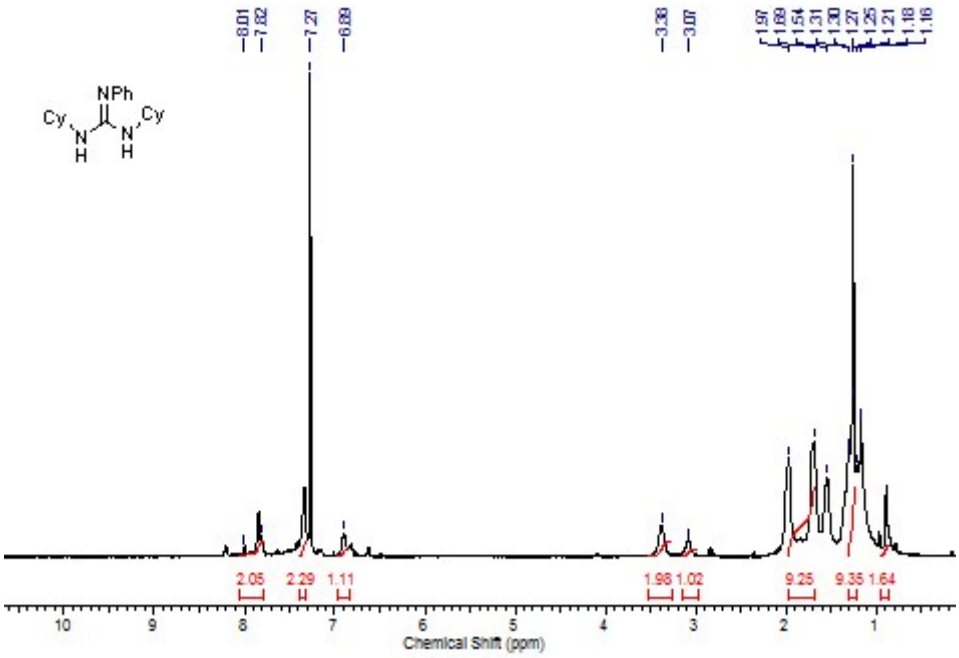


Figure S34. ^{1}H NMR spectra of compound **4a.**

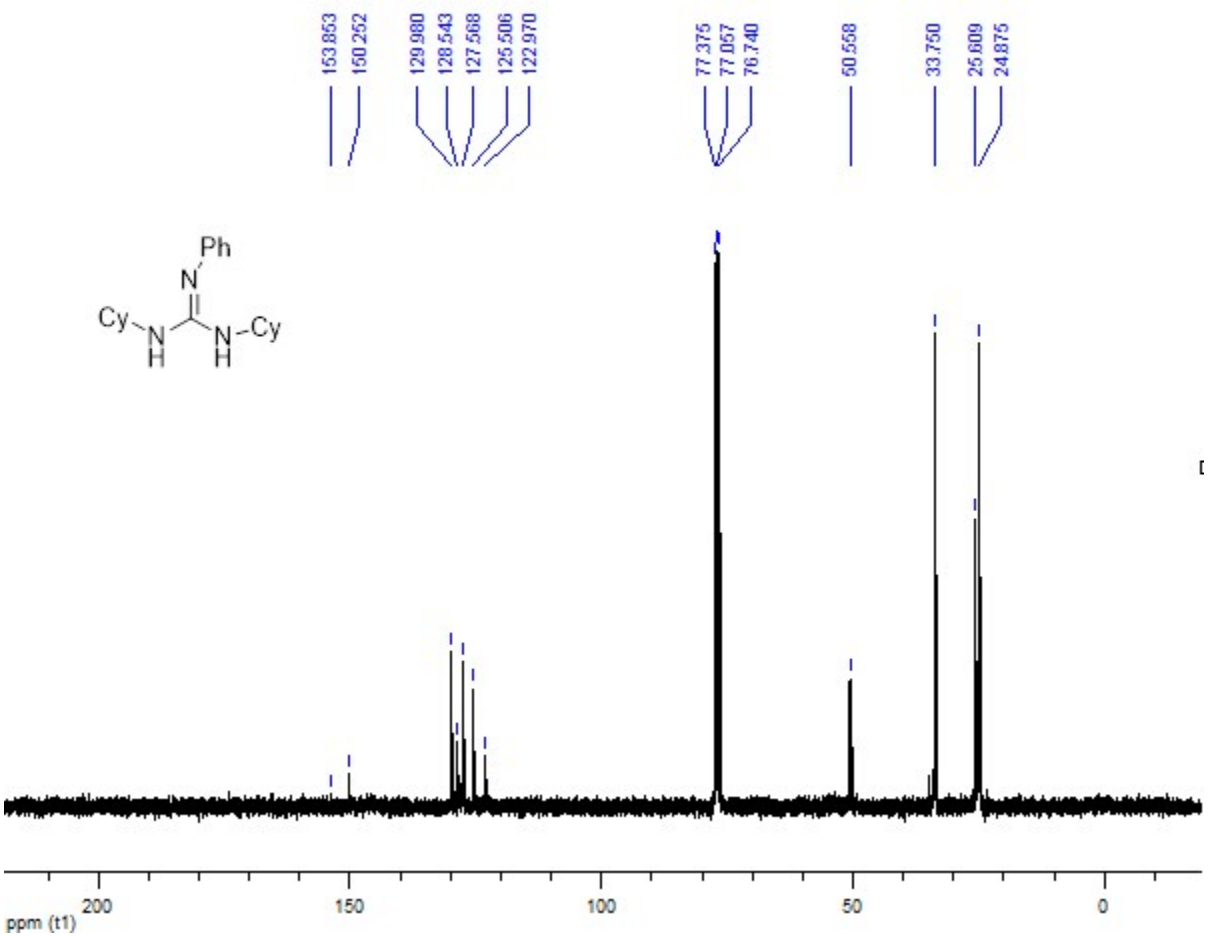


Figure S35. ^{13}C NMR spectra of compound **4a.**

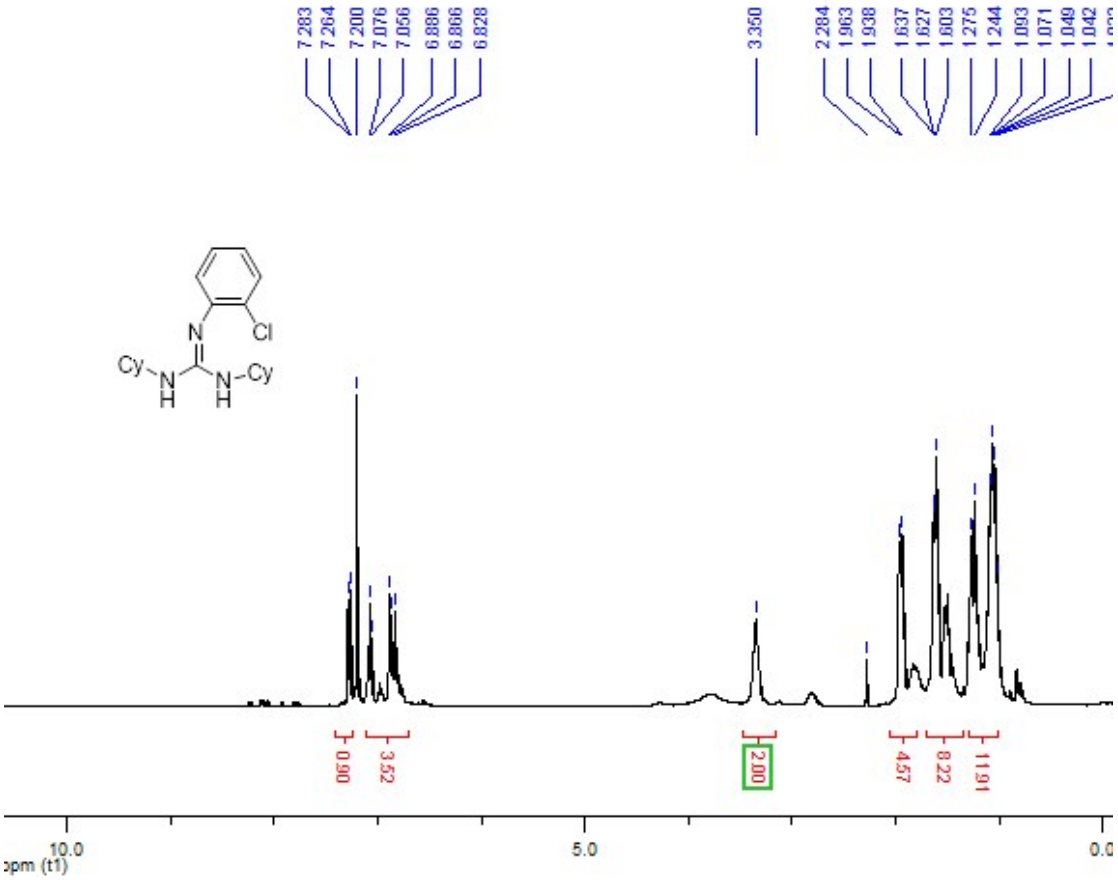


Figure S36. ^{1}H NMR spectra of compound **4e.**

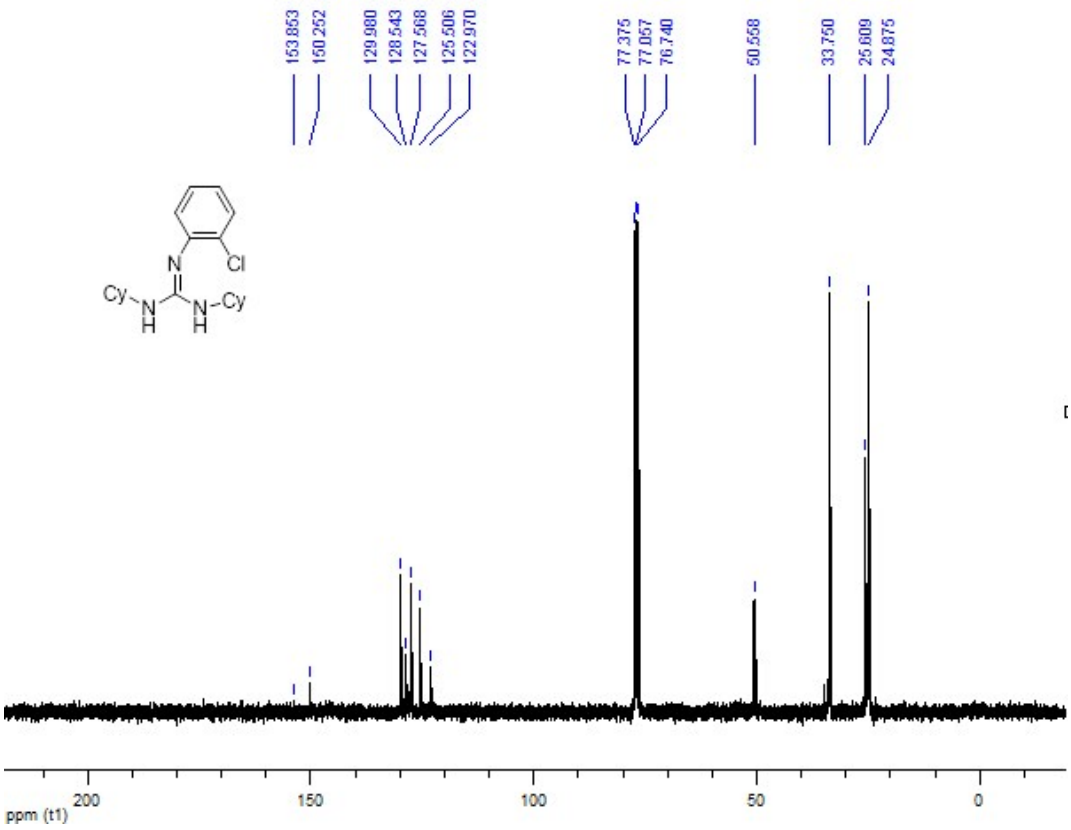


Figure S37. ^{13}C NMR spectra of compound **4e.**

General Procedure for Kinetic NMR Experiments.

A typical kinetics study was conducted to establish the reaction order with respect to catalyst $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (**1**). For kinetic ^1H NMR studies a NMR tube was loaded with the respective amount of complex 1 (0.08, 0.1, 0.12, 0.14, 0.16 M) from a stock solution, 4-chlorophenylisocyanate (0.307 g, 2.0 mmol) and *tert*-butylamine (0.146 g, 2.0 mmol), $CDCl_3$ (0.4 mL) was added inside the glove box and the tube was sealed. The solution was set in the NMR tube at 25°C. At the indicated time intervals, the tube was analyzed by ^1H NMR. As expected, plots of $\ln[(CH_3)_3CNH_2]/[(CH_3)_3CNH_2]_0$ vs. time for a wide range of catalyst $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ are linear .(Fig S35, Table S2). A plot of $\boldsymbol{k_{obs}}$ vs. $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (Fig S36, Table S2) is also linear, with slope 0.404 which indicate the rate law of the reaction follow first order dependence with respect to catalyst $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$. Same experiment also conducted varing wide range of concentration of ClPhNCO (1, 1.5, 2, 2.5, 3 M) and $(CH_3)_3CNH_2$ (1, 1.5, 2, 2.5, 3 M)

which were also linear and follows first order dependence with respect to ClPhNCO and $(CH_3)_3CNH_2$.(Fig 42, Table 5, Fig 43 , Table 6).

Table S2. First order kinetics plots for $ln[(CH_3)_3CNH_2]/[(CH_3)_3CNH_2]_0$ with time in $CDCl_3$(0.4 mL) with different concentration of $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$.

S.No	[*tert*-butylamine]/[1]	Time(m)	Conversion[a]	$[(CH_3)_3CNH_2]$[b]	$ln[(CH_3)_3CNH_2]/[(CH_3)_3CNH_2]_0$
1	100/4	0	0	0	0
2	100/4	10	22.5%	1.55	-.254
3	100/4	20	37.5%	1.25	-.470
4	100/4	30	49%	1.02	-.6733
5	100/4	40	59%	0.82	-.891
6	100/4	50	66.5%	0.67	-1.09
7	100/4	60	75.5%	0.49	-1.41
8	100/4	70	80%	0.40	-1.61
9	100/5	0	0	0	0
10	100/5	10	25.5%	1.49	-.294
11	100/5	20	42.5%	1.15	-.553
12	100/5	30	55%	0.90	.798
13	100/5	40	67%	0.66	-1.11
14	100/5	50	75.5%	0.49	-1.41
15	100/5	60	81.5%	0.37	-1.68
16	100/5	70	88%	0.244	-2.10

17	100/6	0	0	0	0
18	100/6	10	27.5	1.45	-0.315
19	100/6	20	46	1.08	-0.615
20	100/6	30	62.5	0.754	-0.975
21	100/6	40	70	0.596	-1.21
22	100/6	50	80	0.403	-1.6
23	100/6	60	87	0.257	-2.05
24	100/6	70	91	0.188	-2.36
25	100/7	0	0	0	0
26	100/7	10	28.5%	1.43	-0.335
27	100/7	20	48%	1.04	-0.653
28	100/7	30	62.5%	0.75	-.981
29	100/7	40	74%	0.52	-1.34
30	100/7	50	83.5%	0.33	-1.80
31	100/7	60	89.5%	0.21	-2.25
32	100/7	70	92.5%	0.15	-2.59
33	100/8	0	0	0	0
34	100/8	10	49%	1.04	-.654
35	100/8	20	64%	0.735	-1.00
36	100/8	30	79%	0.42	-1.56
37	100/8	40	87%	0.26	-2.04
38	100/8	50	92%	0.16	-2.52

39	100/8	60	95%	0.10	-2.99
40	100/8	70	97%	0.07	-3.4

[a] Obtained from 1H NMR analysis

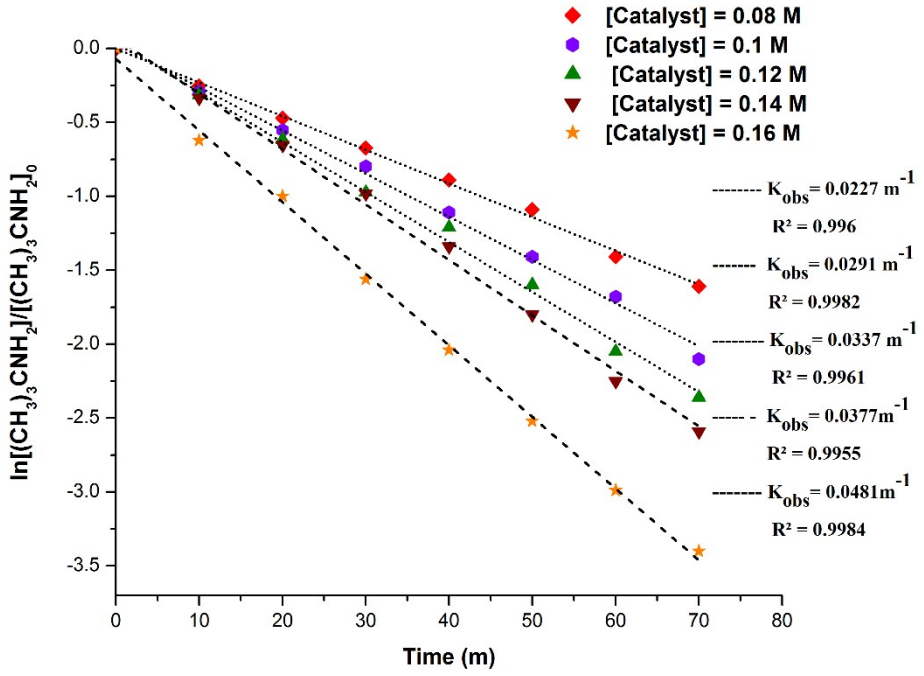


Figure S38. First order kinetics plots for $\ln[(CH_3)_3CNH_2]/[(CH_3)_3CNH_2]_0$ with time in $CDCl_3$ (0.4 mL) with different concentration of $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (**1**) at 25°C.

Table S3. Kinetics plots of K_{obs} vs $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ for the reaction of [4-chlorophenylisocyanate] = 2.0 M with [*tert*-butylamine] = 2.0 M in $CDCl_3$ (0.4 mL) at 25°C.

S.NO.	$[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$	K_{obs}
1	0.08	0.0227
2	0.1	0.029
3	0.12	0.034
4	0.14	0.0377
5	0.16	0.0492

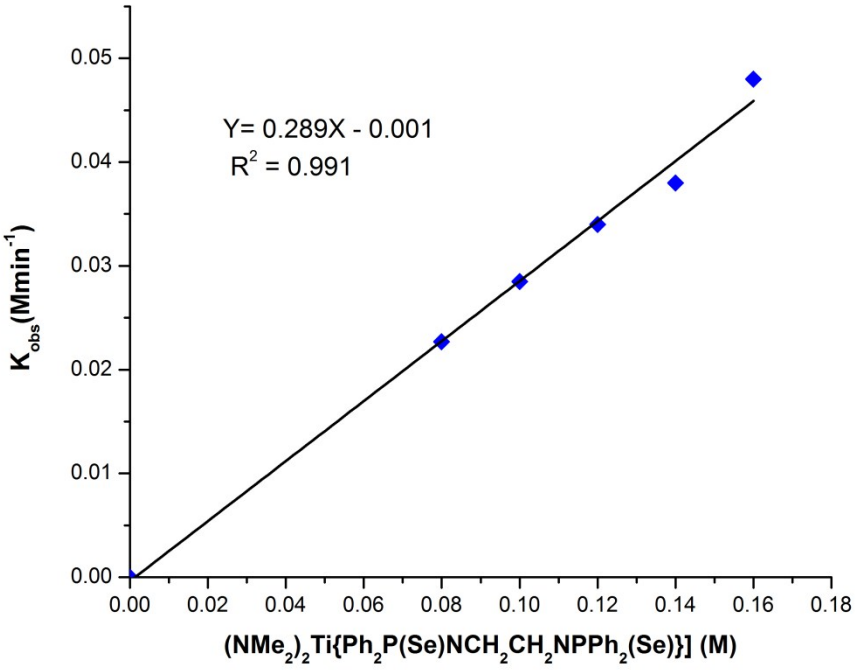


Figure S39. Kinetics plots of K_{obs} vs $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ for the reaction of [4-chlorophenylisocyanate] = 2.0 M with [*tert*-butylamine] = 2.0 M in $CDCl_3$ (0.4 mL) at 25°C.

Table S4. First order kinetics plots for $\ln[(CH_3)_3CNH_2]/[(CH_3)_3CNH_2]_0$ with time in $CDCl_3$(0.4 mL) with different concentration of [ClPhNCO].

S.No	[*tert*-butylamine]/[1]	[ClPhNCO]	Time(m)	Conversion[a]	$[(CH_3)_3CNH_2]$[b]	$ln[(CH_3)_3CNH_2]/[(CH_3)_3CNH_2]_0$
1	100/5	1	0	0	0	0
2	100/5	1	10	14%	1.72	-.151
3	100/5	1	20	25%	1.5	-.287
4	100/5	1	30	33%	1.34	-.400
5	100/5	1	40	42%	1.16	-.544
6	100/5	1	50	49%	1.02	-.673
7	100/5	1	60	57%	0.86	-.843
8	100/5	1	70	65%	0.7	-1.04
9	100/5	1.5	0	0	0	0
10	100/5	1.5	10	21%	1.58	-.235
11	100/5	1.5	20	35%	1.3	-.430
12	100/5	1.5	30	47%	1.06	-.634
13	100/5	1.5	40	56%	0.88	-.821
14	100/5	1.5	50	63%	0.74	-0.994
15	100/5	1.5	60	73%	0.54	-1.31
16	100/5	1.5	70	79%	0.42	-1.56
17	100/5	2	0	0	0	0
18	100/5	2	10	22.5%	1.55	-.254
19	100/5	2	20	37.5%	1.25	-.470
20	100/5	2	30	49%	1.02	-.6733
21	100/5	2	40	59%	0.82	-.891

22	100/5	2	50	66.5%	0.67	-1.09
23	100/5	2	60	75.5%	0.49	-1.41
24	100/5	2	70	80%	0.40	-1.61
25	100/5	2.5	0	0	0	0
26	100/5	2.5	10	26%	1.48	0.301
27	100/5	2.5	20	45%	1.1	-0.597
28	100/5	2.5	30	61%	0.78	-.941
29	100/5	2.5	40	71%	0.58	-1.23
30	100/5	2.5	50	81%	0.38	-1.66
31	100/5	2.5	60	87%	0.26	-2.04
32	100/5	2.5	70	91%	0.18	-2.40
33	100/5	3	0	0	0	0
34	100/5	3	10	45%	1.1	-.597
35	100/5	3	20	61%	0.78	-0.941
36	100/5	3	30	75%	0.50	-1.38
37	100/5	3	40	83%	0.34	-1.77
38	100/5	3	50	89%	0.22	-2.20
39	100/5	3	60	93%	0.14	-2.65
40	100/5	3	70	96%	0.036	-3.30

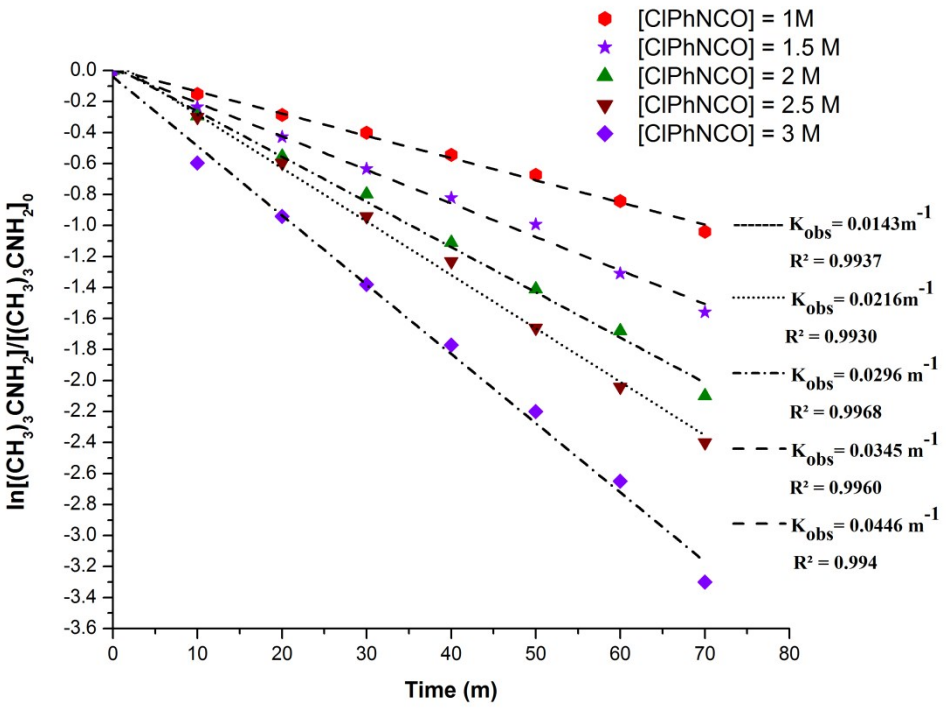


Figure S40. First order kinetics plots for $\ln[(CH_3)_3CNH_2]/[(CH_3)_3CNH_2]_0$ with time in $CDCl_3$ (0.4 mL) with different concentration of [ClPhNCO] at 25°C.

Table S5. Table for Formation rates of $ClPhNHCONHC(CH_3)_3$ versus the ratios of ClPhNCO / $(CH_3)_3CNH_2$ in $CDCl_3$ at 298 K, indicating a linear dependence. Conditions: $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (5 mol%, 0.1 mmol), $(CH_3)_3CNH_2$ (2 mmol), $CDCl_3$ (0.4 mL).

S.NO.	[ClPhNCO]	K_{obs}
1	1	0.0143
2	1.5	0.0216
3	2	0.029
4	2.5	0.0345
5	3	0.0446

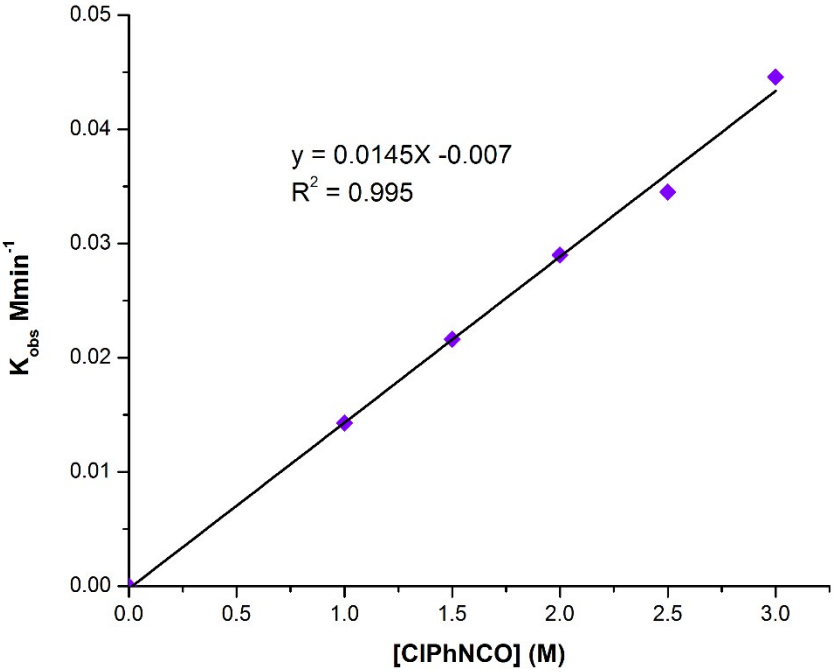


Figure 41. Kinetics plots for Formation rates of $ClPhNHCONHC(CH_3)_3$ versus the ratios of ClPhNCO / $(CH_3)_3CNH_2$ in $CDCl_3$ at 298 K, indicating a linear dependence. Conditions: $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (5 mol%, 0.1 mmol), $(CH_3)_3CNH_2$ (2 mmol), $CDCl_3$ (0.4 mL).

Table S6. Table for Formation rates of $ClPhNHCONHC(CH_3)_3$ versus the ratios of ClPhNCO / $(CH_3)_3CNH_2$ in $CDCl_3$ at 298 K, indicating a linear dependence. Conditions: $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (5 mol%, 0.1 mmol), ClPhNCO (2 mmol), $CDCl_3$ (0.4 mL).

S.NO.	$(CH_3)_3CNH_2$	K_{obs}
1	1	0.0155
2	1.5	0.0239
3	2	0.0296
4	2.5	0.0399
5	3	0.0498

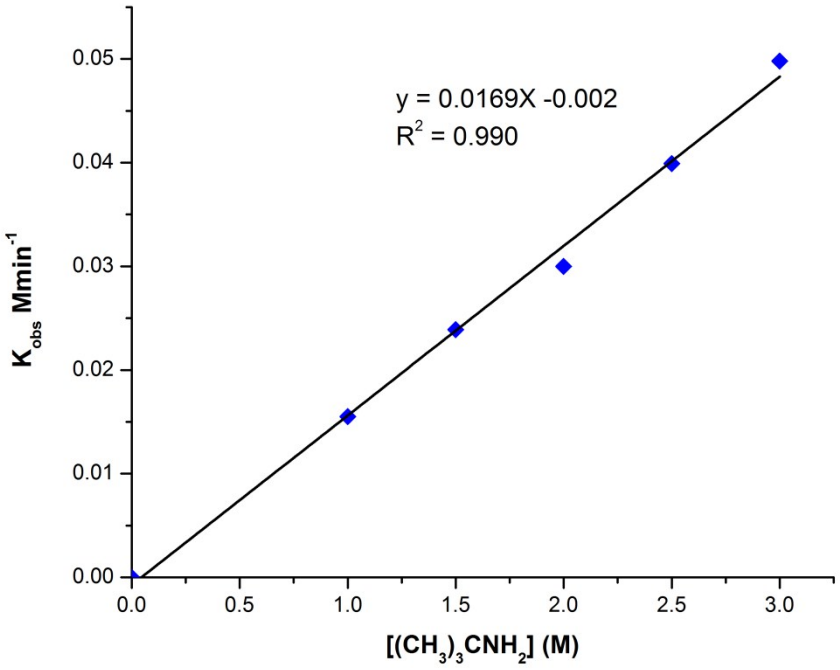


Figure 42. Kinetics plots for Formation rates of $ClPhNHCONHC(CH_3)_3$ versus the ratios of $ClPhNCO$ / $(CH_3)_3CNH_2$ in $CDCl_3$ at 298 K, indicating a linear dependence. Conditions: $[(NMe_2)_2Ti\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (5 mol%, 0.1 mmol), ClPhNCO (2 mmol), $CDCl_3$ (0.4 mL).

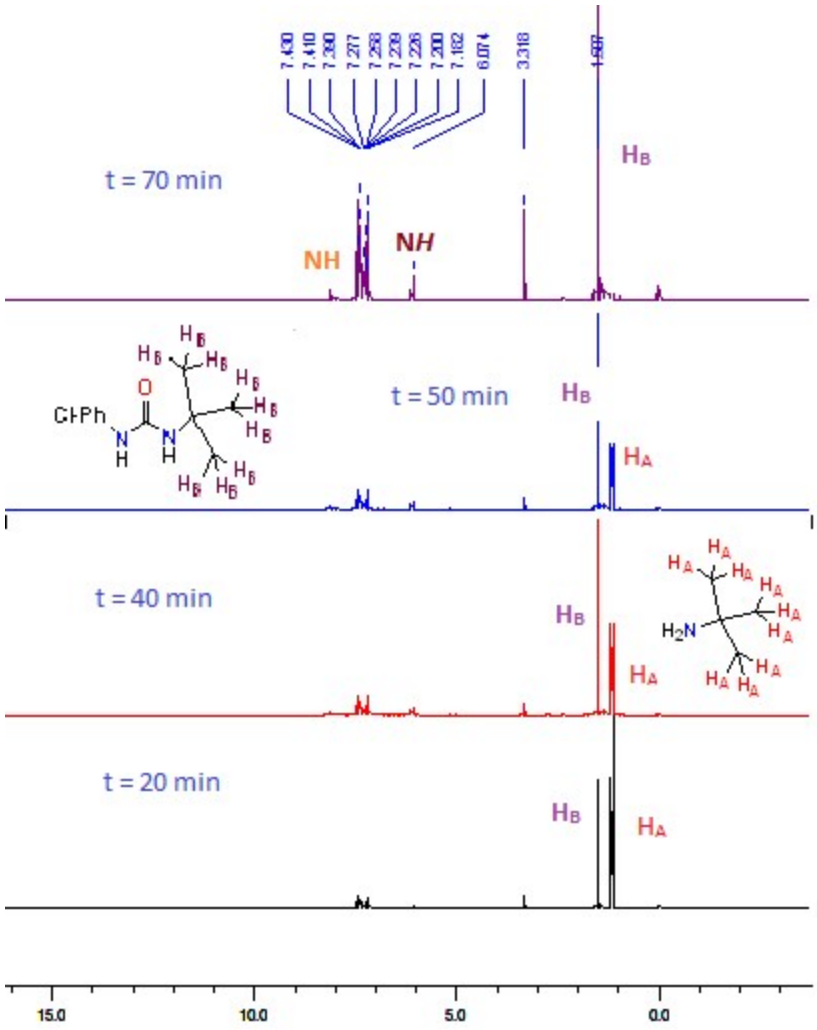


Figure 43: ^{1}H NMR spectra for the reaction of *4*-chlorophenylisocyanate with *tert*-butyl amine catalysed by complex **1**.This spectrum is shown only highlighted in a range between 1-2 ppm for clarity.

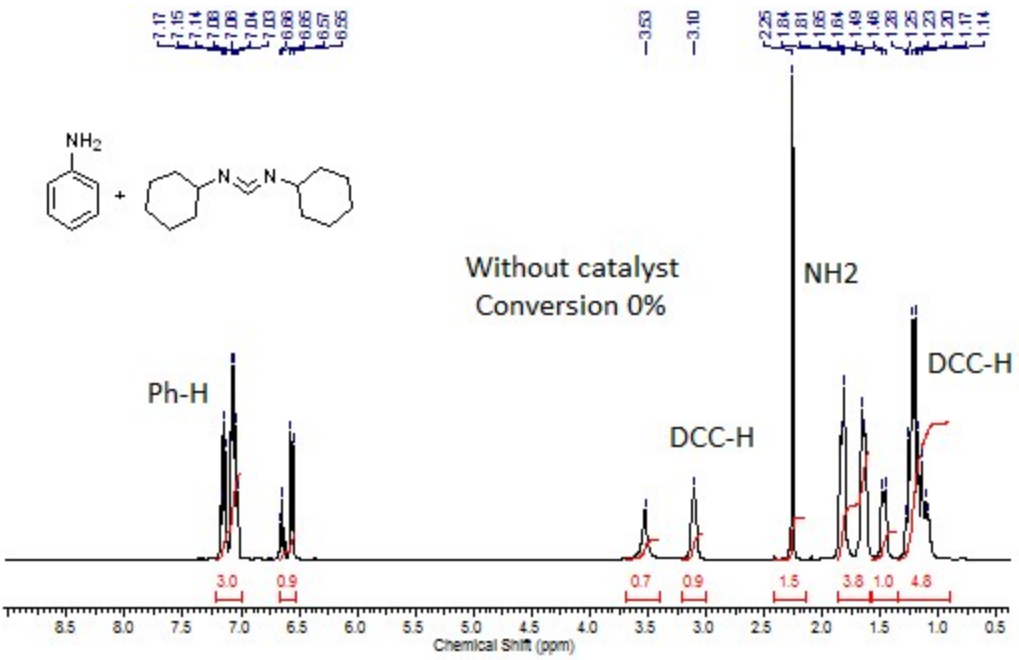


Figure S44. ^{1}H NMR spectra of DCC with aniline without Catalyst**.**

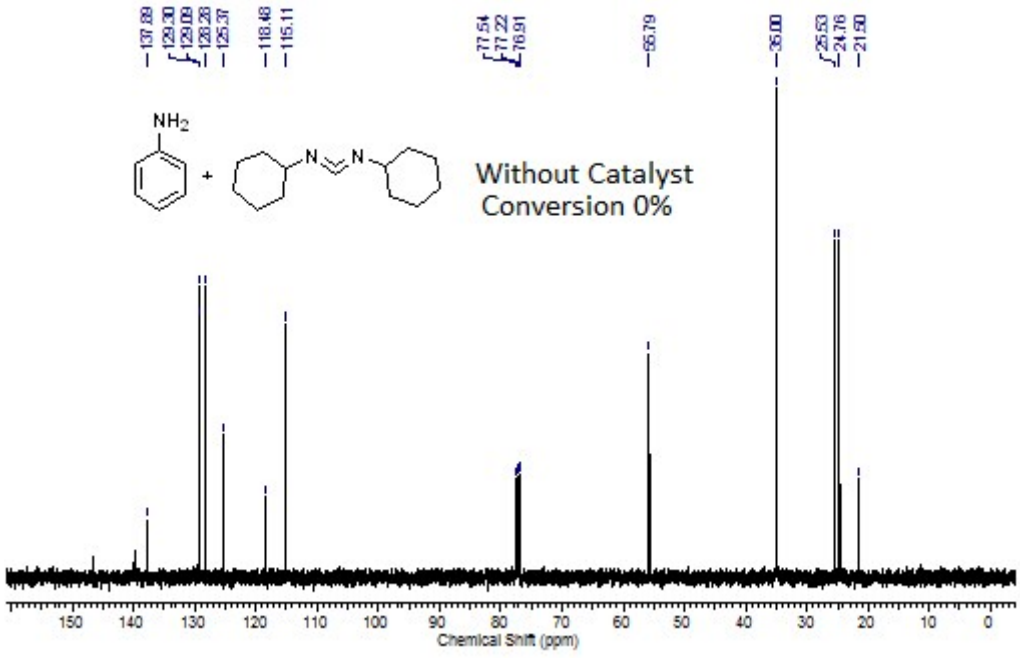


Figure S45. ^{13}C NMR spectra of DCC with aniline without Catalyst**.**

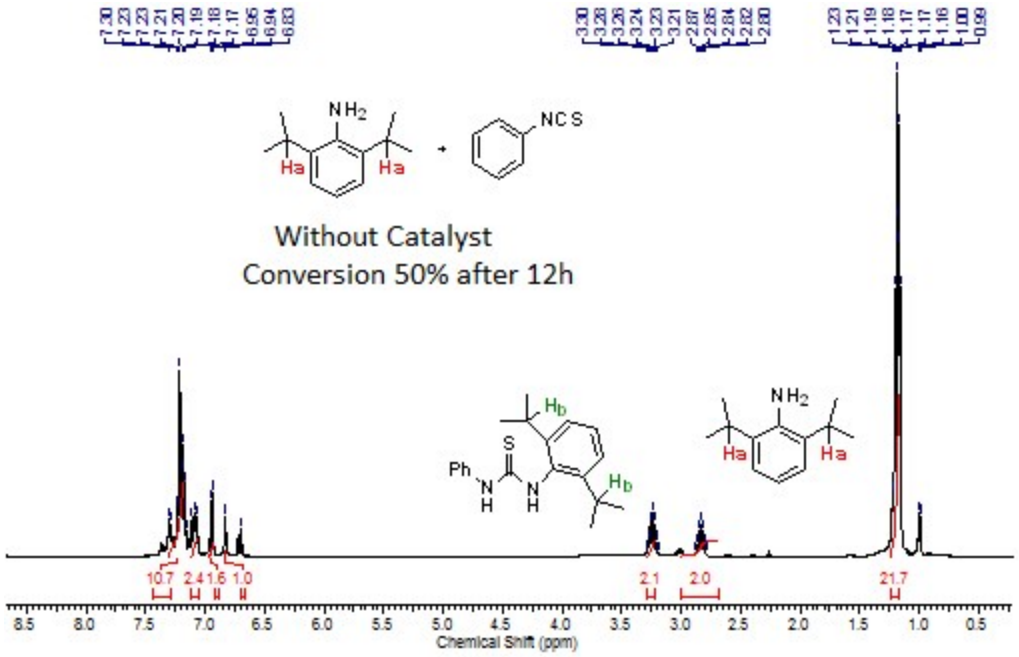


Figure S46. [1]H NMR spectra of PhNCS with Dippaniline without Catalyst**.**

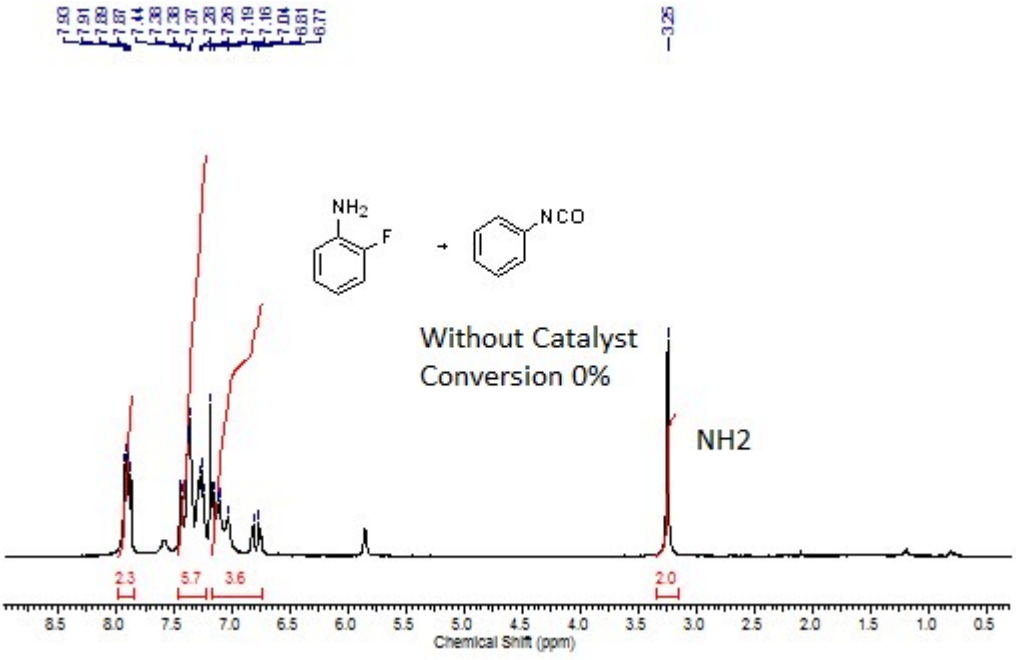


Figure S47. [1]H NMR spectra of PhNCO with 2-Fluroaniline without Catalyst**.**

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