Supporting Information for

Suman Das,[a] Jayeeta Bhattacharjee,[a] Tarun K. Panda*[a]

Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi – 502 285, Sangareddy, Telangana, India.

Table of contents

X-ray crystallographic analyses: Single crystals of complexes **2b, 3a, 4a** and **7** were grown from a concentrated solution of toluene or toluene/n-pentane (3:1) in an argon-filled atmosphere at -35 °C. However, single crystals of **5a** and **5k** were obtained from a solution of ethanol at room temperature. A crystal of suitable dimensions of complexes **2b, 3a, 4a** and **7** was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. The crystals of **5a** and **7k** were measured at 298 K. All measurements were made on a Rigaku Supernova X-calibur Eos CCD detector with graphite monochromatic Cu-Kα (1.54184 Å) (**2b, 4a, 7, 5a** and **5k)** or Mo-Kα (0.71073 Å) (**3a**) radiation. Crystal data and structure refinement parameters of complexes **2b, 3a, 4a, 7, 5a** and **5k** are summarized in Table TS1. The structures were solved by direct methods (SIR2004)[1] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[2] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules of **2b, 3a, 4a, 7, 5a** and **5k**. 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 1880612 (**5a**), 1880613 (**5k**), 1880614 (**4a**), 1880615 (**3a**), 1880616 (**2a**), and 1880617 (**7**). 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 1. Crystallography table of metal complexes **2b**, **3a**, **4a**, **7**, **5a** and **5k.**

Crystal Parameters	**2b**	**3a.DippNH$_2$**	**4a**	**7**	**5a**	**5k**
CCDC No.	1880616	1880615	1880614	1880617	1880612	1880613
Empirical formula	$C_{46}H_{60}N_8Ti$	$C_{48}H_{83}N_9Ti$	$C_{35}H_{47}N_3O_3Ti$	$C_{60}H_{70}N_{10}S_2Ti$	$C_{14}H_{19}N_3O$	$C_{14}H_{18}ClN_3O$
Formula weight	772.89	834.10	605.63	1043.25	245.32	279.76
T (K)	150(2) K	150(2) K	150(2) K	150(2) K	150(2)	293(2)
λ (Å)	1.54184	0.71073	1.54184	1.54184	1.54184	1.54184
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Tetragonal	Monoclinic
Space group	*P* ccn	C 2/c	*P* -1	*P* -1	*P* 4_2/n	*P* 2_1/n
a(Å)	20.4747(4)	32.9866(10)	9.2296(5)	11.9485(5)	16.6882(4)	9.1264(5)
b (Å)	20.9986(3)	10.4591(2)	11.5622(6)	12.6031(6)	16.6882(4)	15.3834(8)
c(Å)	20.8892(3)	34.4041(10)	16.0686(7)	21.2454(8)	10.0005(4)	11.2882(5)
α (°)	90.00	90.00	98.137(4)	92.364(4)	90	90
β (°)	90.00	122.401(4)	93.568(4)	97.250(3)	90	111.447(5)
γ (°)	90.00	90.00	99.629(4)	118.055(5)	90	90
V(Å^3)	8981.1(3)	10021.9(6)	1667.08(15)	2782.2(2)	2785.10(17)	1475.07(14)
Z	8	8	2	2	8	4
D_{calc} g cm^{-3}	1.143	1.106	1.207	1.245	1.170	1.260
μ (mm^{-1})	1.911	0.211	2.460	2.373	0.601	2.260
F(000)	3312	3648	648	1108	1056	592
Theta range for data collection	3.014 to 71.592 deg	1.402 to 25.955 deg.	3.925 to 71.213 deg	4.001 to 71.631 deg.	3.746 to 69.937 deg.	5.098 to 70.073 deg.
Limiting indices -	-18<=h<=24, -25<=k<=21, -14<=l<=25	-33<=h<=40, -11<=k<=12, -41<=l<=27	-11<=h<=11, -13<=k<=14, -19<=l<=14	-14<=h<=14, -15<=k<=14, -21<=l<=26	-11<=h<=19, -20<=k<=20, -11<=l<=4	-11<=h<=10, -18<=k<=18, -13<=l<=9
Reflections collected / unique	19723 / 8561 [R(int) = 0.0408]	22209 / 9540 [R(int) = 0.0297]	13316 / 6335 [R(int) = 0.0328]	18429 / 10617 [R(int) = 0.0308]	5200 / 2594 [R(int) = 0.0370]	5422 / 2741 [R(int) = 0.0275]
Completeness to theta	99.7 %	99.8 %	99.8 %	99.9 %	99.8 %	99.8 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.84474	1.00000 and 0.90125	1.00000 and 0.87063	1.00000 and 0.77592	1.00000 and 0.34873	1.00000 and 0.66840
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	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

Data / restraints / parameters	8561 / 0 / 513	9540 / 0 / 545	6335 / 0 / 391	10617 / 0 / 674	2594 / 0 / 172	2741 / 0 / 181
Goodness-of-fit on F^2	1.094	1.062	1.092	1.033	0.946	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1519	R1 = 0.0552, wR2 = 0.1528	R1 = 0.0433, wR2 = 0.1161	R1 = 0.0460, wR2 = 0.1228	R1 = 0.0487, wR2= 0.1246	R1 = 0.0468, wR2 = 0.1235
R indices (all data)	R1 = 0.0805, wR2 = 0.1679	R1 = 0.0622, wR2 = 0.1597	R1 = 0.0492, wR2 = 0.1205	R1 = 0.0526, wR2 = 0.1294	R1 = 0.0675, wR2= 0.1427	R1 = 0.0592, wR2 = 0.1382

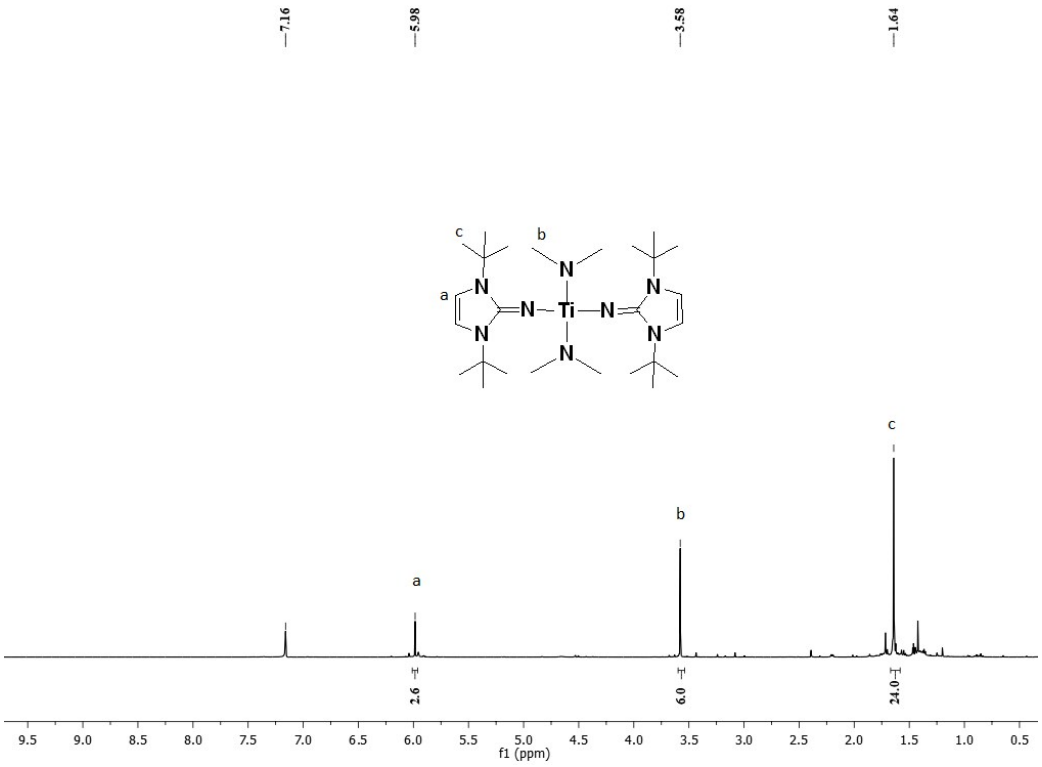


Figure FS1. [1]H NMR spectra of complex **2a.**

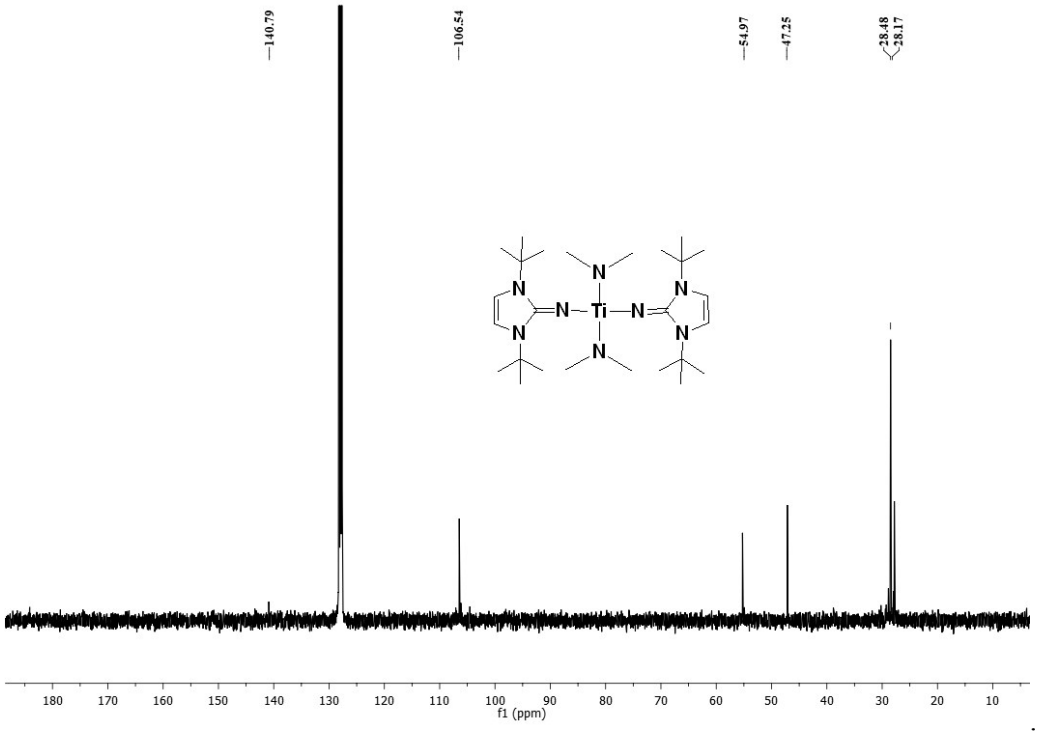


Figure FS2. [13]C NMR spectra of complex **2a.**

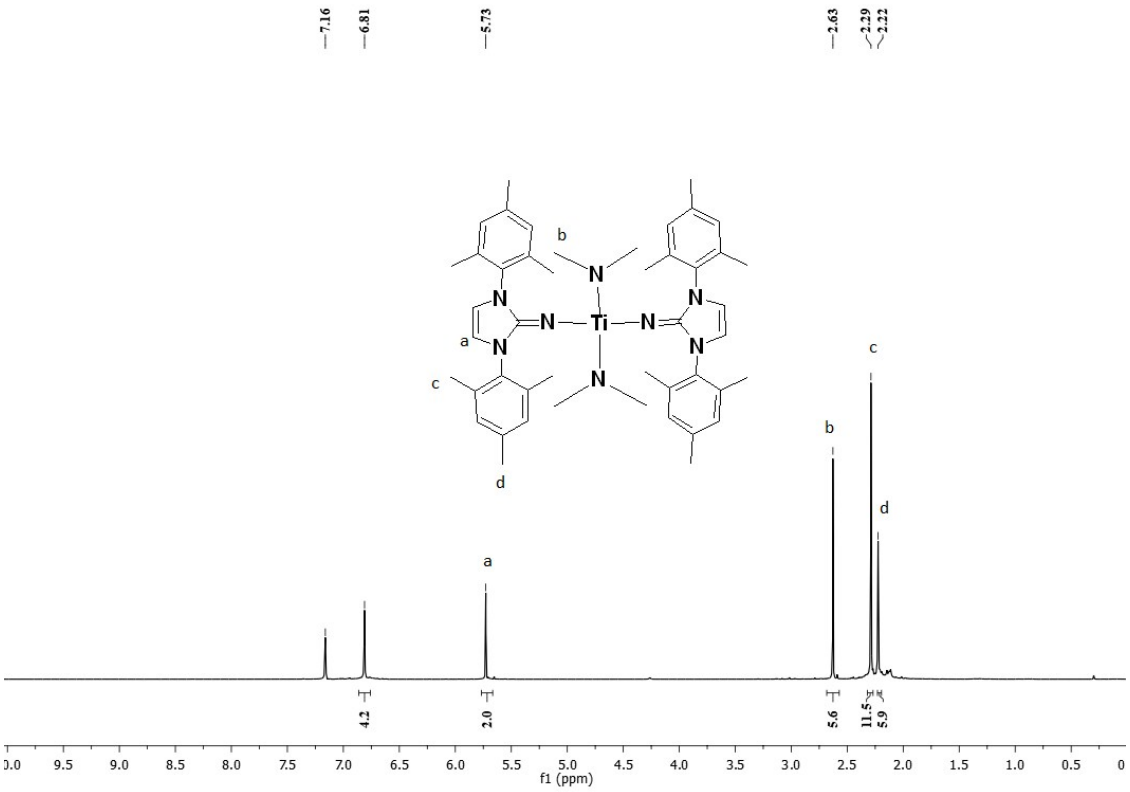


Figure FS3. ^{1}H NMR spectra of complex **2b**.

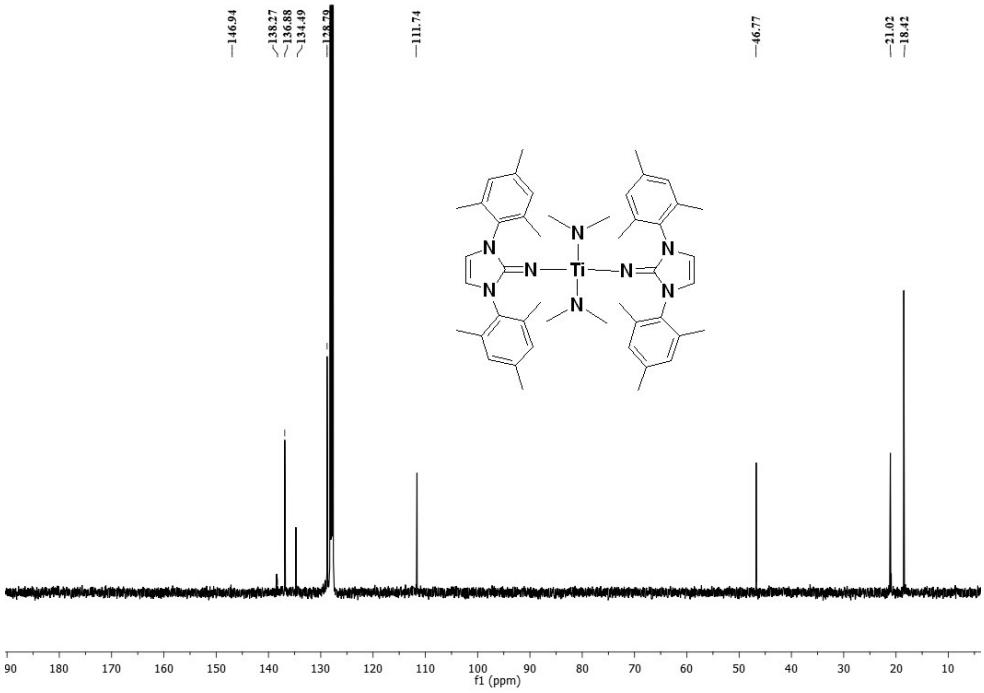


Figure FS4. ^{13}C NMR spectra of complex **2b**.

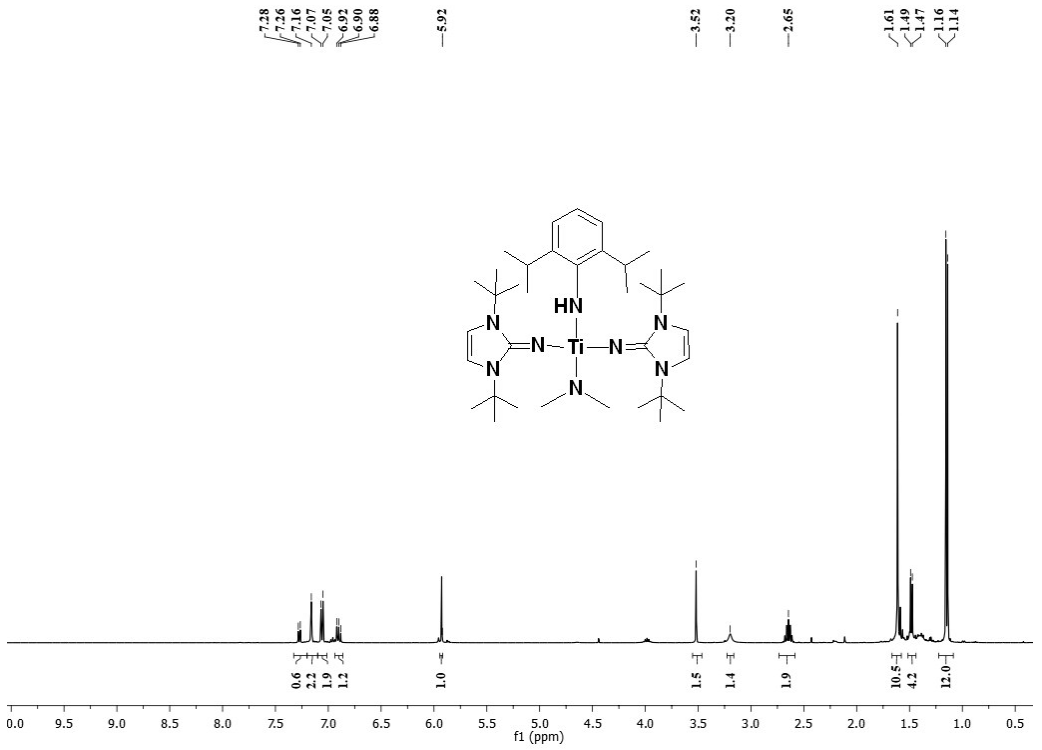


Figure FS5. ^{1}H NMR spectra of complex **3a.**

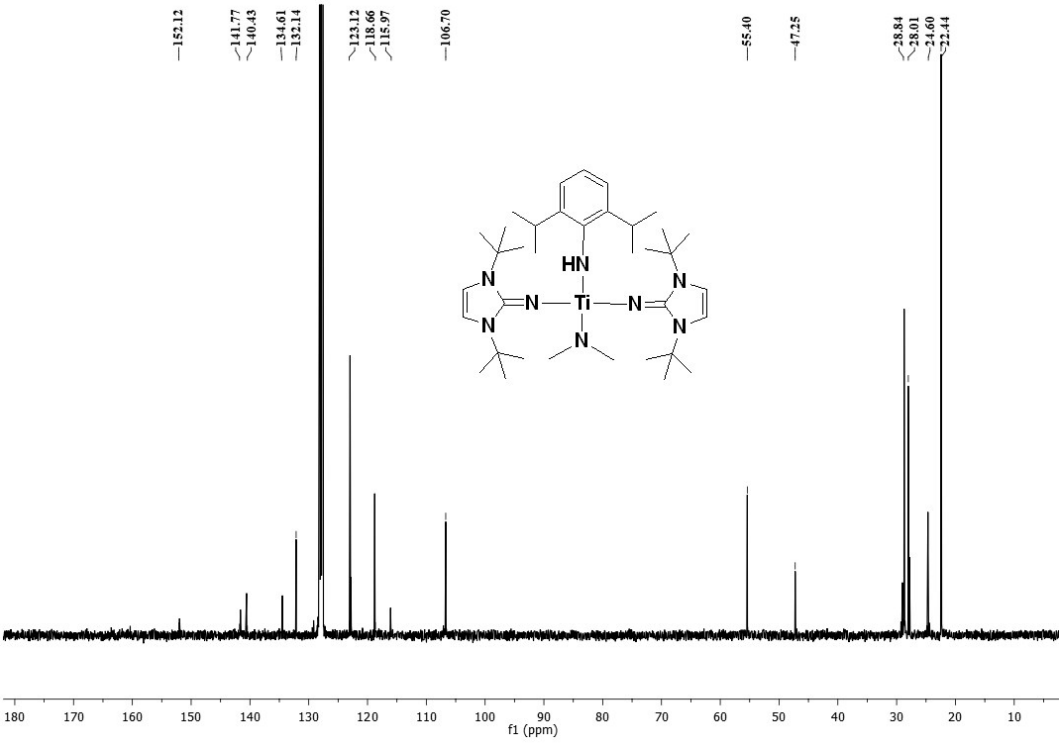


Figure FS6. ^{13}C NMR spectra of complex **3a.**

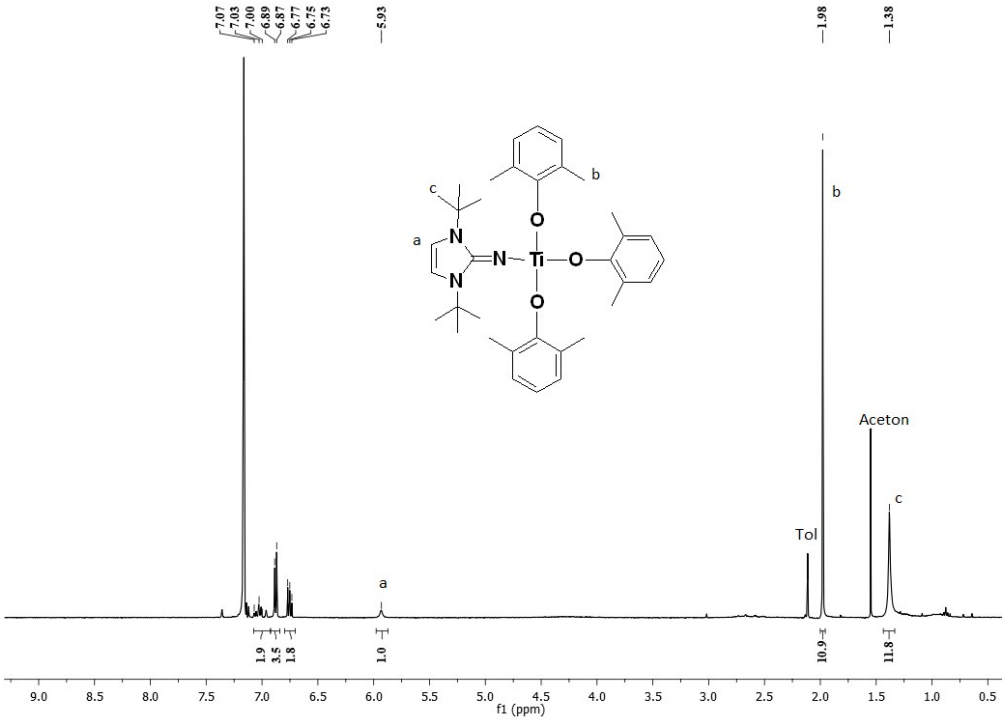


Figure FS7. ^{1}H NMR spectra of complex **4a.**

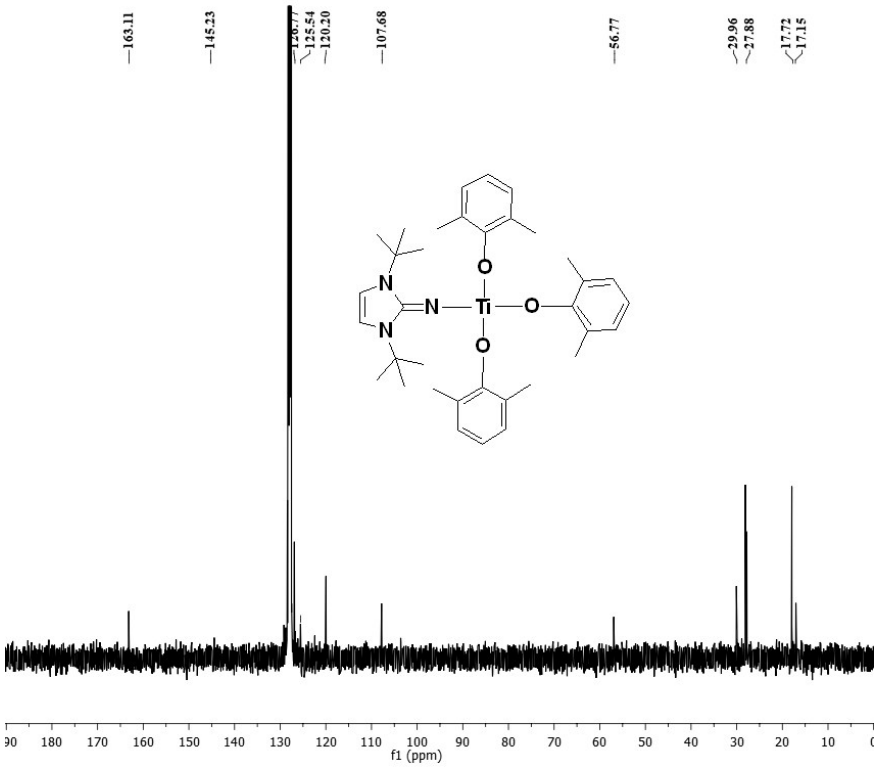


Figure FS8. ^{13}C NMR spectra of complex **4a.**

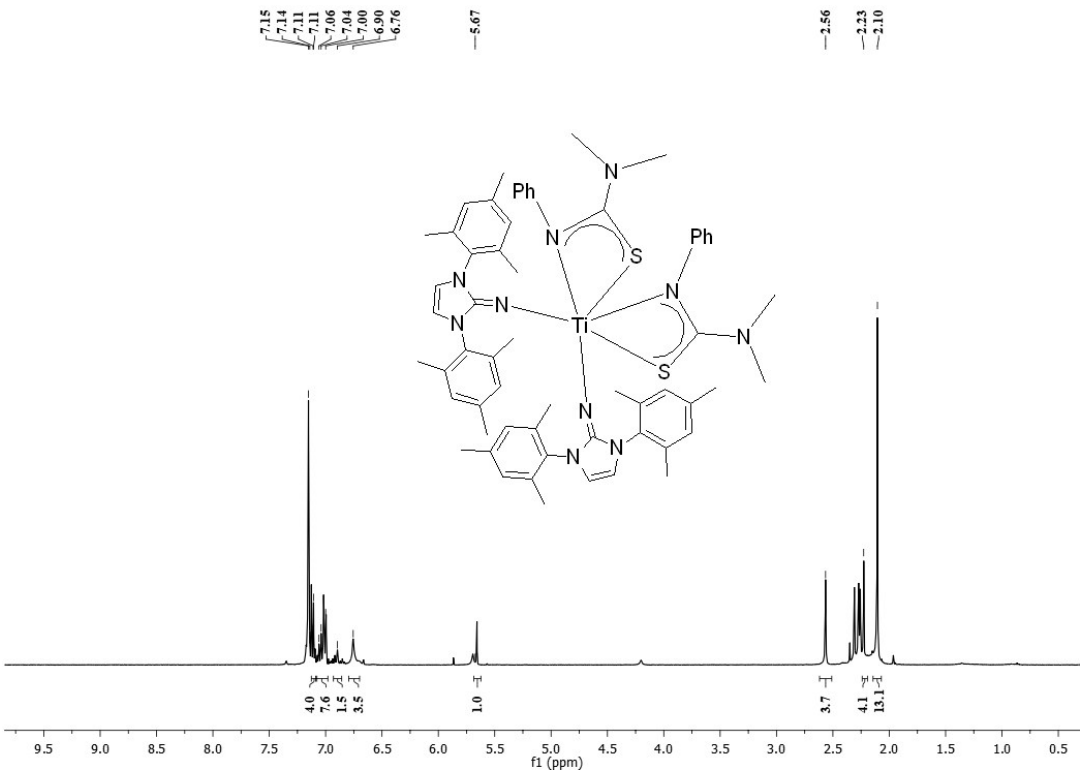


Figure FS9. ^{1}H NMR spectra of complex **7.**

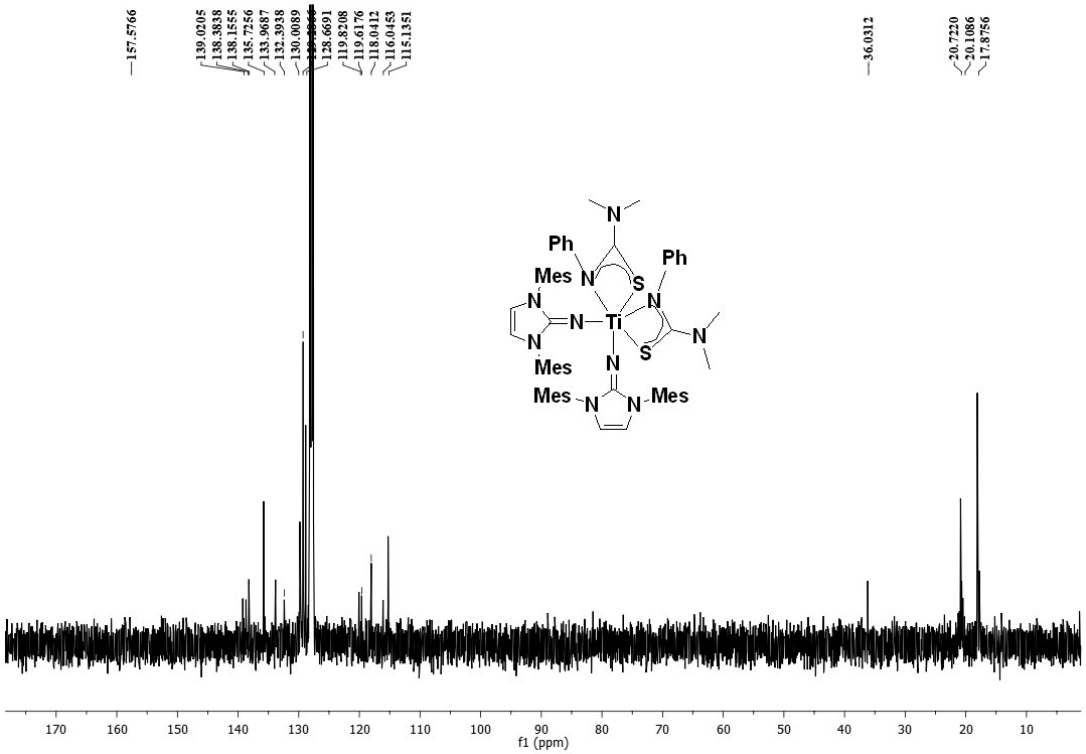
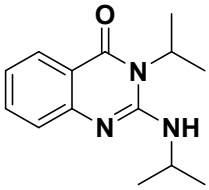


Figure FS10. ^{13}C NMR spectra of complex **7.**

General procedure for Catalytic Titanium-mediated guanylation/cyclization of amino acid ester in presence of hetarocumulene.

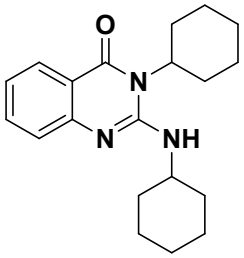
A solution of respective amino acid ester (0.606 mmol, 1equiv.) was added drop-wise into the reaction mixture of respective heterocumulene (1.212 mmol, 2 equiv.), and catalyst (**2b**) 23.39 mg (0.0303 mmol). This was done in a 25 mL dry Schlenk flask inside the glovebox. The yellow color reaction mixture was kept in room temperature or heated to 40-60 °C depending on the nature of nucleophiles. The progress of the reactions was monitored by TLC. After that reaction was quench by adding 20 mL of ethylacetate and then basic workup was carried out by adding 5 mL of saturated sodium bicarbonate solution into the reaction mixture. The product collected in the organic layer and finally purified the compound by coloum chromatography in (5:100) hexan/ethylacetate eluent solvent. The products were characterized by ^{1}H, ^{13}C, and DEPT NMR spectroscopy (where necessary), as well as MS analysis.

<u>Characterization Data</u>: (For guanylation/cyclization product).



3-isopropyl-2-(isopropylamino)quinazolin-4(3*H*)-one (5a)

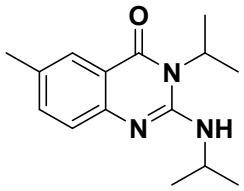
Isolated yield (142 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 - 7.95 (dd, *J* = 8.0,1.36 Hz, 1H, Ar*H*), 7.41 - 7.37 (m, 1H, Ar*H*), 7.21 - 7.19 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.99 - 6.95 (m, 1H, Ar*H*), 5.25 (s, 1H, N*H*), 4.50 - 4.48 (m, 1H, C*H*), 4.33 - 4.24 (m, 1H, C*H*), 1.42 - 1.41 (d, *J* = 7.1 Hz, 6H, CH_3), 1.18 - 1.17 (d, *J* = 6.4 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.2, 149.1, 148.9, 133.9, 126.8, 124.6, 122.0, 117.6, 43.6, 22.7, 20.1, ppm. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $[C_{14}H_{20}N_3O]$+ 246.1601; found 246.1621. Mp: 79.8 − 80.1 °C.



3-cyclohexyl-2-(cyclohexylamino)quinazolin-4(3*H*)-one (5b)

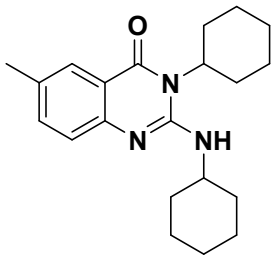
Isolated yield (187 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 - 7.95 (dd, *J* = 8.0 Hz, 1.36 Hz, 1H, Ar*H*), 7.41 - 7.37 (m, 1H, Ar*H*), 7.20 - 7.18 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.99 - 6.95 (m, 1H, Ar*H*), 4.95 (s,

1H, N*H*), 4.60 - 4.58 (d, *J* = 7.16 Hz, 1H, C*H*), 4.05 - 3.97 (m, 1H, C*H*), 2.08 - 1.97 (m, 4H, CH_2), 1.80 - 1.72 (m, 4H, CH_2) 1.62 - 1.50 (m, 4H, CH_2) 1.40 - 1.32 (m, 4H, CH_2) 1.24 - 1.06 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.3, 149.1, 149.0, 133.9, 127.0, 124.5, 121.9, 117.6, 50.0, 32.9, 30.1, 26.5, 25.7, 25.5, 24.7, ppm. HRMS (ESI-TOF) m/z: [M + H]+ calcd for [$C_{20}H_{28}N_3O$]+ 326.2227; found 326.2238.



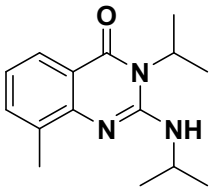
3-isopropyl-2-(isopropylamino)-6-methylquinazolin-4(3*H*)-one (3c)

Isolated yield (144 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.86 (s, 1H, Ar*H*), 7.36 - 7.34 (dd, *J* = 8.3 Hz, 2.04 Hz, 1H, Ar*H*), 7.26 - 7.21 (m, 1H, Ar*H*), 5.45 (s, 1H, N*H*), 4.40 - 4.31 (m, 2H, C*H*), 2.36 (s, 1H, CH_3), 1.54 - 1.52 (d, *J* = 7.2 Hz, 6H, CH_3), 1.30 - 1.28 (d, *J* = 6.24 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.2, 148.5, 146.9, 135.5, 131.8, 126.4, 124.4, 117.2, 43.5, 22.9, 20.9, 20.2 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{15}H_{22}N_3O]^+$ 260.1757; found 246.1759. Mp: 134 - 136 °C.



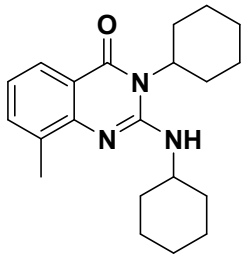
3-cyclohexyl-2-(cyclohexylamino)-6-methylquinazolin-4(3*H*)-one (5d)

Isolated yield (184 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.75 (s, 1H, Ar*H*), 7.23 - 7.18 (m, 1H, Ar*H*), 7.12 - 7.10 (d, *J* = 8.3 Hz, 1H, Ar*H*), 4.93 (s, 1H, N*H*), 4.50 - 4.48 (d, *J* = 6.88 Hz, 1H, C*H*), 4.01 - 3.94 (m, 1H, C*H*), 2.25 (s, 1H, CH_3), 2.08 - 1.98 (m, 4H, CH_2), 1.80 - 1.71 (m, 4H, CH_2) 1.61 - 1.52 (m, 4H, CH_2) 1.38 - 1.32 (m, 4H, CH_2) 1.18 - 1.07 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.3, 148.6, 146.9, 135.4, 131.5, 126.3, 124.5, 117.3, 50.0, 32.9, 30.1, 26.5, 25.7, 25.5, 24.7, ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for [$C_{22}H_{29}N_3ONa$]+ 326.2203; found 326.2246.



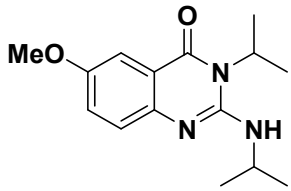
3-isopropyl-2-(isopropylamino)-8-methylquinazolin-4(3*H*)-one (5e)

Isolated yield (133 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 - 7.95 (dd, *J* = 8.0, 0.84 Hz, 1H, Ar*H*), 7.39 - 7.37 (d, *J* = 7.16, Hz 1H, Ar*H*), 7.02 - 6.98 (m, 1H, Ar*H*), 5.35 (s, 1H, N*H*), 4.70 (m, 1H, C*H*), 4.44 - 4.37 (m, 1H, C*H*), 2.47 (s, 1H, CH_3), 1.56 - 1.54 (d, *J* = 7.08 Hz, 6H, CH_3), 1.35 - 1.33 (d, *J* = 6.52 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.6, 148.1, 147.6, 134.1, 132.7, 124.5, 121.9, 117.3, 44.0, 22.5, 20.1, 17.1, ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{15}H_{21}N_3O]$+ 260.1757; found 260.1762. Mp: 127 - 128 °C.



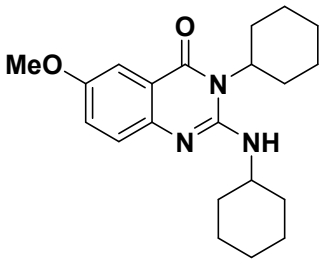
3-cyclohexyl-2-(cyclohexylamino)-8-methylquinazolin-4(3*H*)-one (5f)

Isolated yield (172 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.81 - 7.79 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.22 - 7.20 (d, *J* = 8.0 Hz, 1H, Ar*H*), 6.85 - 6.81 (m, 1H, Ar*H*), 5.06 (s, 1H, N*H*), 4.68 - 4.66 (d, *J* = 8.0 Hz, 1H, C*H*), 3.98 - 3.91 (m, 1H, C*H*), 2.30 (s, 1H, CH_3), 2.18 - 2.01 (m, 4H, CH_2), 1.76 - 1.69 (m, 4H, CH_2), 1.60 - 1.46 (m, 4H, CH_2), 1.35 - 1.27 (m, 4H, CH_2), 1.24 - 1.04 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.3, 148.1, 147.5, 134.0, 132.6, 124.6, 121.5, 117.3, 50.8, 32.6, 30.0, 26.5, 25.8, 25.5, 24.8, 16.9. HRMS (ESI-TOF) m/z: [M + K]+ calcd for $[C_{21}H_{29}N_3OK]^+$ 378.1942; found 378.1955.



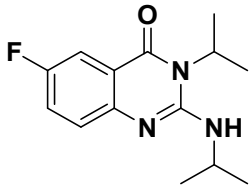
3-isopropyl-2-(isopropylamino)-6-methoxyquinazolin-4(3*H*)-one (5g)

Isolated yield (156 mg, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (s, 1H, Ar*H*), 7.20 - 7.17 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.11 - 7.09 (dd, *J* = 6.8, 1.6 Hz, 1H, Ar*H*), 5.35 (s, 1H, N*H*), 4.30 - 4.21 (m, 1H, C*H*), 3.76 (s, 3H, OCH_3), 1.48 - 1.47 (d, *J* = 5.6 Hz, 6H, CH_3), 1.22 - 1.21 (d, *J* = 6.0 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.0, 155.2, 147.8, 143.7, 126.2, 124.5, 117.7, 106.4, 55.6, 43.5 22.9, 20.2 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{15}H_{21}N_3O_2]^+$ 276.1707; found 276.1706. Mp: 123 - 124 °C.



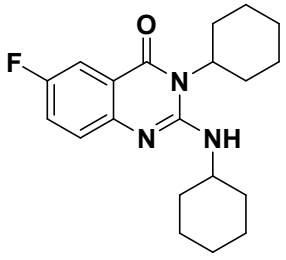
3-cyclohexyl-2-(cyclohexylamino)-6-methoxyquinazolin-4(3*H*)-one (5h)

Isolated yield (197 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.19 (m, 1H, Ar*H*), 7.10 - 7.07 (dd, *J* = 8.8, 2.9 Hz, 1H, Ar*H*), 4.95 (s, 1H, N*H*), 4.39 (s, 1H, C*H*), 3.97 - 3.95 (m, 1H, C*H*), 3.7 (s, 3H, OC*H*$_3$), 2.03 – 1.99 (m, 4H, C*H*$_2$), 1.85 - 1.74 (m, 4H, C*H*$_2$), 1.66 - 1.61 (m, 4H, C*H*$_2$), 1.41 - 1.37 (m, 4H, C*H*$_2$), 1.20 - 1.16 (m, 4H, C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.2, 156.9, 155.1, 147.9, 126.1, 124.4, 106.3, 55.2, 50.05, 33.8, 30.1, 26.5, 25.8, 25.5, 24.9. 24.7 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $[C_{21}H_{29}N_3O_2Na]^+$ 378.2152; found 378.2172.



6-fluoro-3-isopropyl-2-(isopropylamino)quinazolin-4(3*H*)-one (5i)

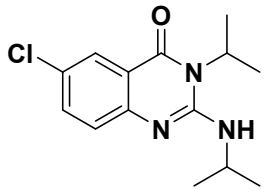
Isolated yield (111 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 - 7.61 (dd, *J* = 8.8, 2.42 Hz, 1H, Ar*H*), 7.22 -7.14 (m, 2H, Ar*H*), 5.34 (s, 1H, N*H*), 4.31 - 4.23 (m, 2H, C*H*), 1.48 - 1.46 (d, *J* = 7.16 Hz, 6H, C*H*$_3$), 1.25 - 1.21 (d, *J* = 6.26 Hz, 6H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.5, 159.3, 156.9, 148.4, 145.6, 126.6, 122.6, 118.1, 111.4, 43.6, 22.8, 20.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{14}H_{19}FN_3O]^+$ 264.1507; found 264.1508. Mp: 80.1- 81.0 °C.



3-cyclohexyl-2-(cyclohexylamino)-6-fluroquinazolin-4(3*H*)-one (5j)

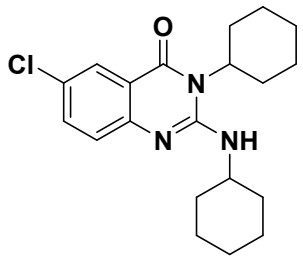
Isolated yield (149 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 - 7.58 (dd, *J* = 8.6, 2.36 Hz, 1H, Ar*H*), 7.20 - 7.14 (m, 2H, Ar*H*), 4.90 (s, 1H, N*H*), 4.52 - 4.50 (d, *J* = 6.7 Hz, 1H, C*H*), 4.00 - 3.93 (m, 1H, C*H*), 2.08 - 1.93 (m, 4H, C*H*$_2$), 1.84 - 1.73 (m, 4H, C*H*$_2$), 1.68 - 1.53 (m, 4H, C*H*$_2$), 1.42 - 1.33 (m, 4H, C*H*$_2$) 1.22 - 1.09 (m, 4H, C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.6, 159.2, 156.8, 148.5, 145.7, 126.4, 122.3,

118.0,111.4, 50.1, 32.9, 30.0, 26.5, 25.7, 25.5, 24.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{20}H_{27}FN_3O]^+$ 344.2133; found 344.2142.



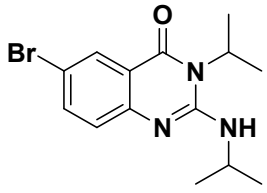
6-chloro-3-isopropyl-2-(isopropylamino)quinazolin-4(3*H*)-one (5k)

Isolated yield (128 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, *J* = 2.48 Hz, 1H, Ar*H*), 7.35 - 7.32 (dd, *J* = 8.7, 2.48 Hz, 1H, Ar*H*), 7.15 - 7.13 (d, *J* = 8.7 Hz, 1H, Ar*H*), 5.30 (s, 1H, N*H*), 4.42 - 4.41 (d, *J* = 6.9 Hz, C*H*), 4.31 - 4.23 (m, 1H, C*H*), 1.45 - 1.44 (d, *J* = 7.2 Hz, 6H, CH_3), 1.21 - 1.20 (d, *J* = 6.44 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_H 162.0, 148.9, 147.7, 134.2, 127.1, 126.5, 43.7, 22.8, 19.8 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{14}H_{19}ClN_3O]^+$ 280.1211; found 280.1209. Mp: 119 – 120 °C.



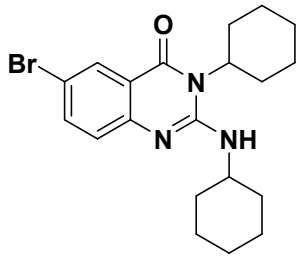
6-chloro-3-cyclohexyl-2-(cyclohexylamino)quinazolin-4(3*H*)-one (5l)

Isolated yield (169 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 (s, 1H, Ar*H*), 7.38 - 7.36 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.20 - 7.18 (d, *J* = 8.3 Hz, 1H, Ar*H*), 4.94 (s, 1H, N*H*), 4.70 - 4.68 (m, 1H, C*H*), 4.04 - 4.03 (m, 1H, C*H*), 2.14 – 2.04 (m, 4H, CH_2), 1.88 - 1.79 (m, 4H, CH_2), 1.69 - 1.58 (m, 4H, CH_2), 1.44 - 1.42 (m, 4H, CH_2), 1.31 - 1.15 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.3, 149.1, 147.7, 134.0, 134.0, 126.9, 126.2, 118.4, 50.2, 32.8, 29.9, 26.4, 25.7, 25.4, 24.7 ppm. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $[C_{20}H_{27}ClN_3O]^+$ 360.1837; found 326.1844.



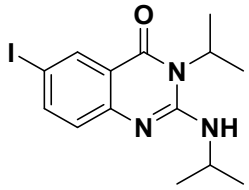
6-bromo-3-isopropyl-2-(isopropylamino)quinazolin-4(3*H*)-one (5m)

Isolated yield (157 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.07 - 8.06 (d, *J* = 2.3 Hz, 1H, Ar*H*), 7.64 - 7.61 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar*H*), 6.96 - 6.94 (d, *J* = 8.7 Hz, 1H, Ar*H*), 5.27 (s, 1H, N*H*), 4.49 - 4.48 (d, *J* = 6.96 Hz, 1H, C*H*), 4.31 - 4.23 (m, 1H, C*H*), 1.44 - 1.43 (d, *J* = 7.1 Hz, 6H, CH_3), 1.21 - 1.19 (d, *J* = 6.48 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.0, 149.1, 148.0, 142.3, 136.8, 129.3, 126.8, 118.9, 114.5, 43.7, 22.8, 20.1 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{14}H_{19}BrN_3O]^+$ 324.0706; found 324.0715. Mp: 129 - 130 °C.



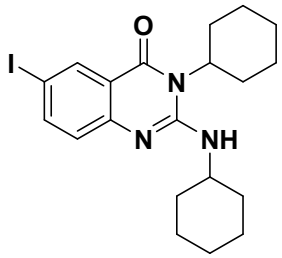
6-bromo-3-cyclohexyl-2-(cyclohexylamino)quinazolin-4(3*H*)-one (5n)

Isolated yield (190 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (d, *J* = 2.36 Hz, 1H, Ar*H*), 7.41 - 7.38 (dd, *J* = 8.7, 2.3 Hz, 1H, Ar*H*), 7.05 - 7.03 (d, *J* = 8.7 Hz, 1H, Ar*H*), 4.84 (s, 1H, N*H*), 4.68 - 4.66 (d, *J* = 8.0 Hz, 1H, C*H*), 3.97 - 3.94 (m, 1H, C*H*), 2.07 – 1.95 (m, 4H, CH_2), 1.79 - 1.70 (m, 4H, CH_2), 1.58 - 1.48 (m, 4H, CH_2), 1.32 - 1.22 (m, 4H, CH_2), 1.20 - 1.11 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.1, 149.2, 148.0, 136.7, 129.7, 126.4, 118.9, 114.3, 50.2, 32.8, 26.4, 25.7, 25.4, 24.7 ppm. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{20}H_{26}BrN_3O]^+$ 404.1285; found 404.129. Mp: 134 - 137 °C.



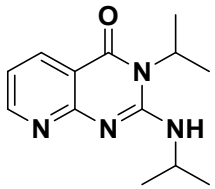
6-iodo-3-isopropyl-2-(isopropylamino)quinazolin-4(3*H*)-one (5o)

Isolated yield (190 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.26 (d, *J* = 2.2 Hz, 1H, Ar*H*), 7.47 -7.44 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar*H*), 7.09 - 7.07 (d, *J* = 8.6 Hz, 1H, Ar*H*), 5.25 (s, 1H, N*H*), 4.45 - 4.43 (d, *J* = 6.9 Hz, 1H, C*H*), 4.31 - 4.23 (m, 1H, C*H*), 1.45 - 1.43 (d, *J* = 7.2 Hz, 6H, CH_3), 1.21 - 1.19 (d, *J* = 6.5 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.8, 149.2, 148.5, 142.3, 135.5, 126.8, 119.5, 84.4, 43.7, 22.8, 20.1 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{14}H_{19}IN_3O]^+$ 372.0567; found 372.0576, Mp: 120 – 121 °C.



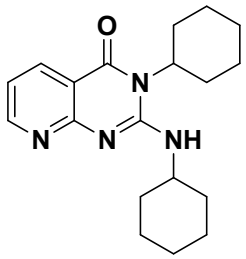
3-cyclohexyl-2-(cyclohexylamino)-6-iodoquinazolin-4(3*H*)-one (5p)

Isolated yield (226 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.23 (d, J = 4.8 Hz, 1H, Ar*H*), 7.61 - 7.57 (m, 1H, Ar*H*), 6.94 - 6.91 (m, 1H, Ar*H*), 4.83 (s, 1H, N*H*), 4.67 - 4.65 (m, 1H, C*H*), 3.97 - 3.96 (m, 1H, C*H*), 2.07 – 1.98 (m, 4H, CH_2), 1.77 - 1.73 (m, 4H, CH_2), 1.34 - 1.33 (m, 4H, CH_2), 1.20 - 1.06 (m, 4H, CH_2), 1.20 - 1.11 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 161.9, 149.3, 148.5, 142.2, 135.6, 126.7, 119.5, 84.3, 50.2, 32.8, 29.5, 26.5, 25.3, 24.7 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{20}H_{27}IN_3O]^+$ 452.1193; found 452.1209.



3-isopropyl-2-(isopropylamino)pyrido[2,3-*d*]pyrimidin-4(3*H*)-one (5q)

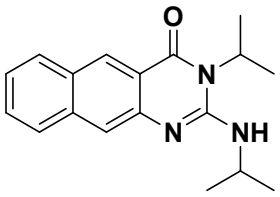
Isolated yield (107 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.63 - 8.62 (d, J = 8.0 Hz, 1H, Ar*H*), 8.30 - 8.28 (d, J = 8.0 Hz, 1H, Ar*H*), 7.0 - 6.96 (m, 1H, Ar*H*), 5.33 (s, 1H, N*H*), 4.78 (m, 1H, C*H*), 4.56 - 4.48 (m, 1H, C*H*), 1.49 - 1.47 (d, J = 7.0 Hz, 6H, CH_3), 1.25 - 1.23 (d, J = 6.36 Hz, 1H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.0, 157.8, 154.7, 150.1, 135.6, 117.0, 111.1, 42.9, 28.6, 21.8, 19.1 ppm. HRMS (ESI-TOF) m/z: $[M + K]^+$ calcd for $[C_{13}H_{18}N_4OK]^+$ 285.1112; found 285.1122. Mp: 185 - 187 °C.



3-cyclohexyl-2-(cyclohexylamino)pyrido[2,3-*d*]pyrimidin-4(3*H*)-one (5r)

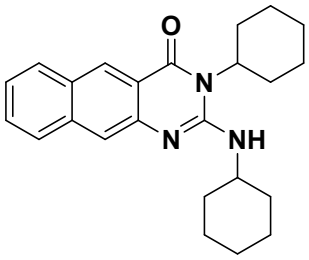
Isolated yield (138 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.81 - 7.79 (d, J = 8.0 Hz, 1H, Ar*H*), 7.22 - 7.20 (dd, J = 7.8, 2.0 Hz, 1H, Ar*H*), 6.85 - 6.81 (m, 1H, Ar*H*), 5.06 (s, 1H, N*H*), 4.68 - 4.66 (d, J = 6.96 Hz, 1H, C*H*), 3.98 - 3.91 (m, 1H, C*H*), 2.18 - 2.01 (m, 4H, CH_2), 1.76 - 1.69 (m, 4H, CH_2), 1.60 - 1.46 (m, 4H, CH_2), 1.35 - 1.27 (m, 4H, CH_2), 1.24 - 1.04 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.3,

158.8, 155.7, 151.2, 136.7, 117.3, 50.8, 33.9, 33.0, 26.5, 25.8, 25.5, 24.8, ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $[C_{19}H_{26}N_4O]^+$ 327.2179; found 327.2189.



3-isopropyl-2-(isopropylamino)benzo[g]quinazolin-4(3*H*)-one (5s)

Isolated yield (151 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.71 (s, 1H, Ar*H*), 7.93 – 7.91 (d, *J* = 8.2 Hz, 1H, Ar*H*), 7.81 - 7.79 (*J* = 8.6 Hz, 1H, Ar*H*), 7.75 (s, 1H, Ar*H*), 7.48 - 7.44 (m, 1H, Ar*H*), 7.36 - 7.32 (m, 1H, Ar*H*), 5.40 (s, 1H, N*H*), 4.47 - 4.38 (m, 2H, C*H*), 1.60 - 1.58 (d, *J* = 7.2 Hz, 6H, CH_3), 1.36 - 134 (d, *J* = 6.4 Hz, 1H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.4, 151.0, 142.6, 128.5, 126.7, 125.8, 125.6, 54.1, 43.0, 31.9, 22.2, 20.5, 19.2 ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $[C_{18}H_{22}N_3O]^+$ 296.1757; found 296.1755. Mp: 134 - 136 °C.



3-cyclohexyl-2-(cyclohexylamino)benzo[g]quinazolin-4(3H)-one (5t)

Isolated yield (186 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.69 (s, 1H, Ar*H*), 7.90 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.80 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.73 (s, 1H, Ar*H*), 7.46 (m, 1H, Ar*H*), 7.33 (m, 1H, Ar*H*), 5.03 (s, 1H, N*H*), 4.68 (s, 1H, C*H*), 4.16 (m, 1H, C*H*), 2.17 – 2.14 (m, 4H, CH_2), 1.97 - 1.89 (m, 4H, CH_2) 1.78 - 1.64 (m, 4H, CH_2), 1.51 - 1.49 (m, 4H, CH_2), 1.36 - 1.25 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 163.8, 148.1, 137.1, 129.3, 128.5, 127.8, 127.0, 124.0,120, 50.1, 33.0, 31.4, 30.2, 29.7, 26.6, 25.8. 25.6, 24.7 ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $[C_{24}H_{30}N_3O]^+$ 376.2383; found 326.2391.

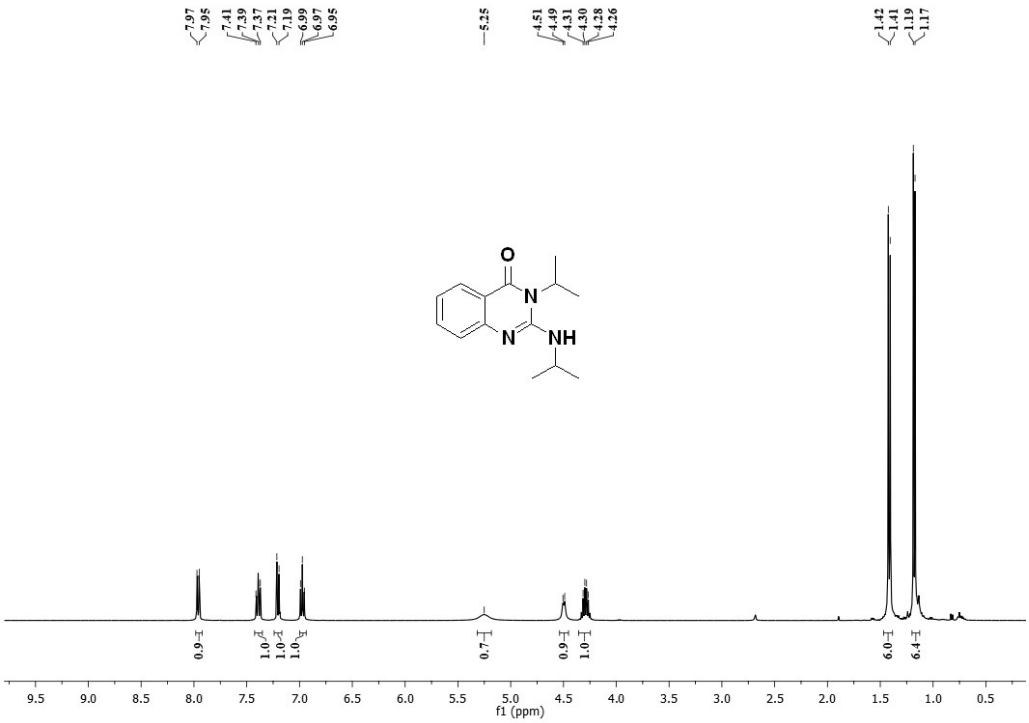


Figure FS11. ^{1}H NMR spectra of the complex **(5a).**

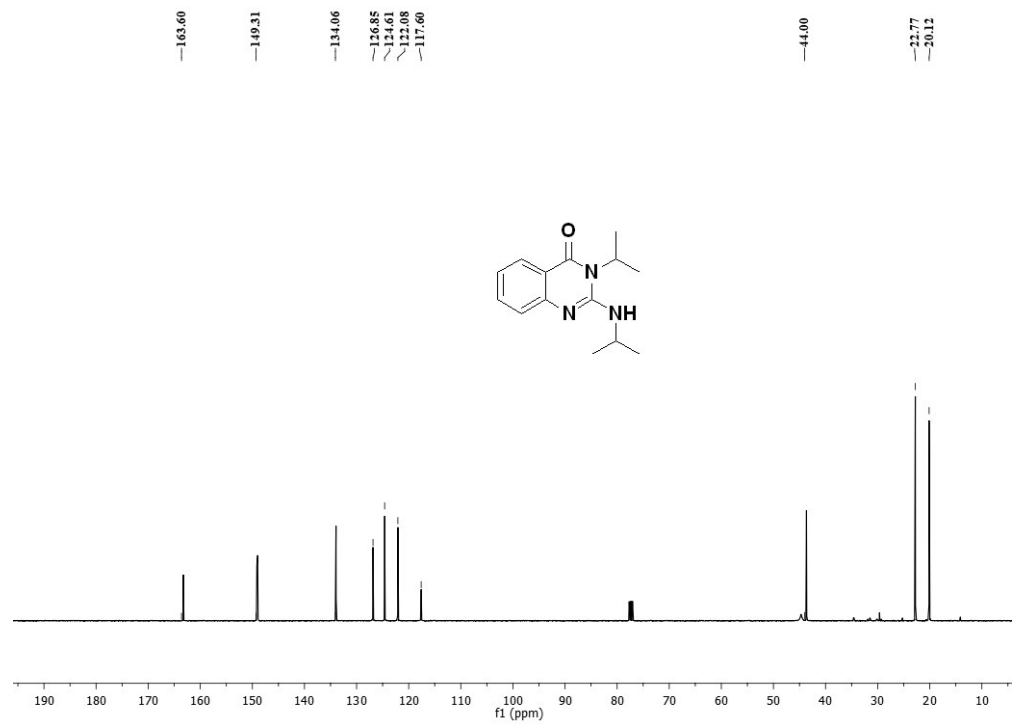


Figure FS12. ^{13}C NMR spectra of the complex **(5a).**

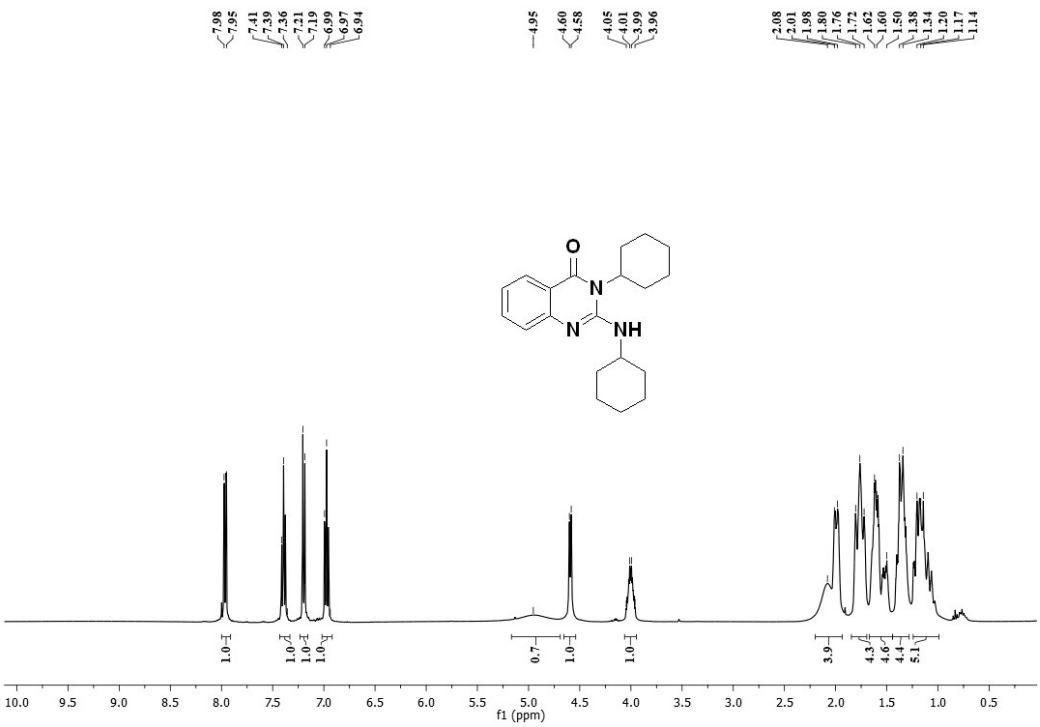


Figure FS13. ^{1}H NMR spectra of the complex **(5b).**

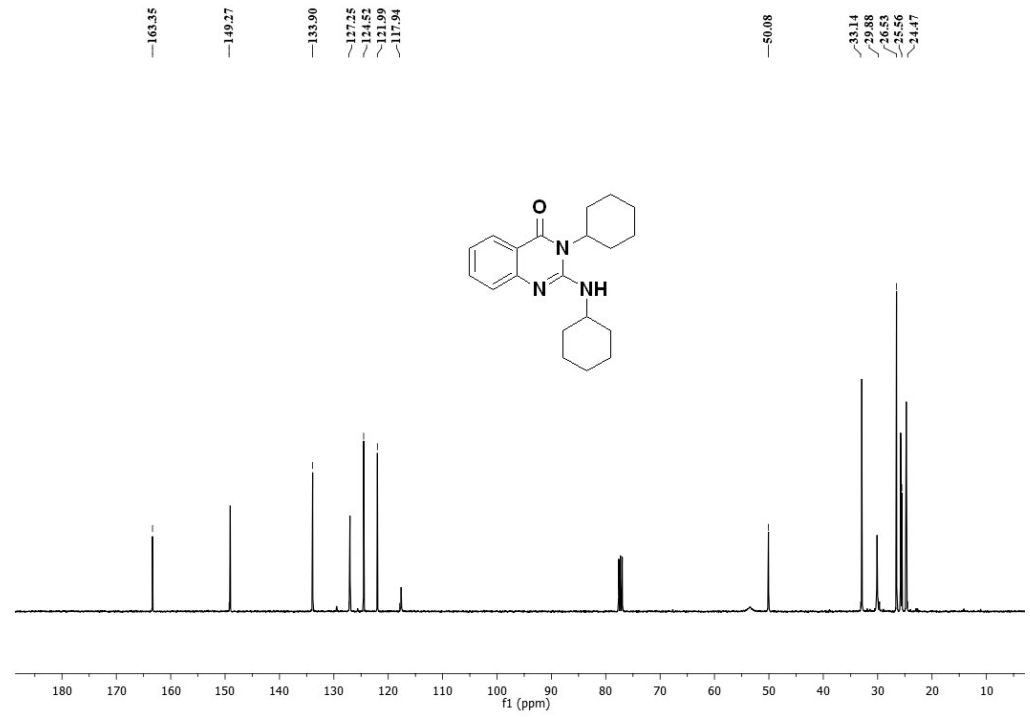


Figure FS14. ^{13}C NMR spectra of the complex **(5b).**

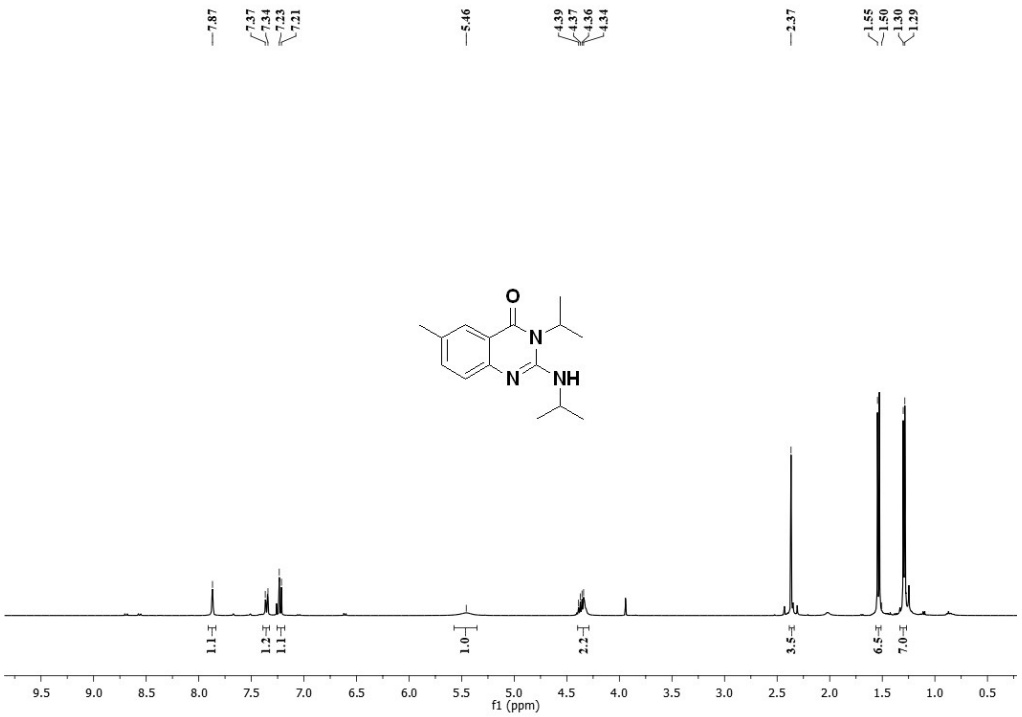


Figure FS15. ^{1}H NMR spectra of the complex **(5c).**

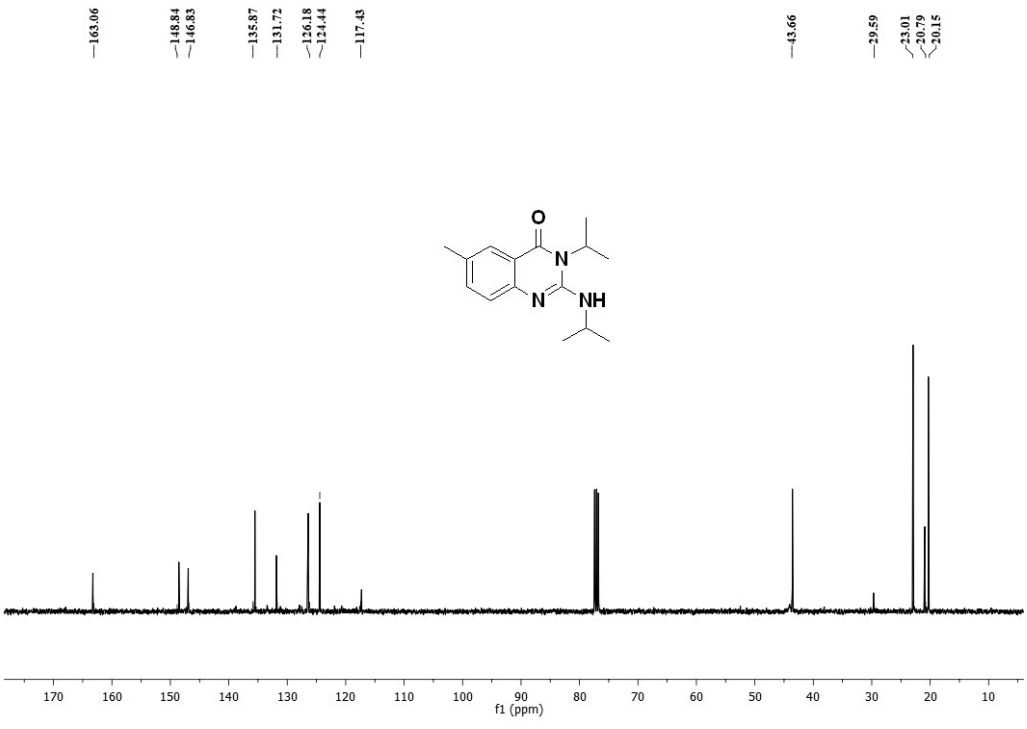


Figure FS16. ^{13}C NMR spectra of the complex **(5c).**

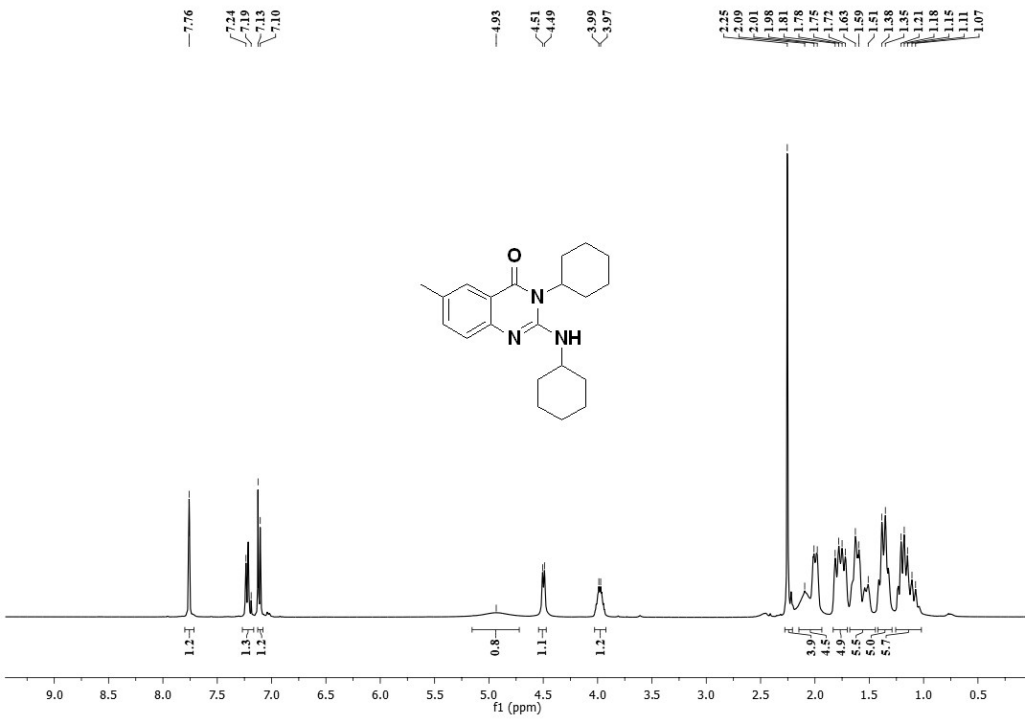


Figure FS17. ^{1}H NMR spectra of the complex **(5d).**

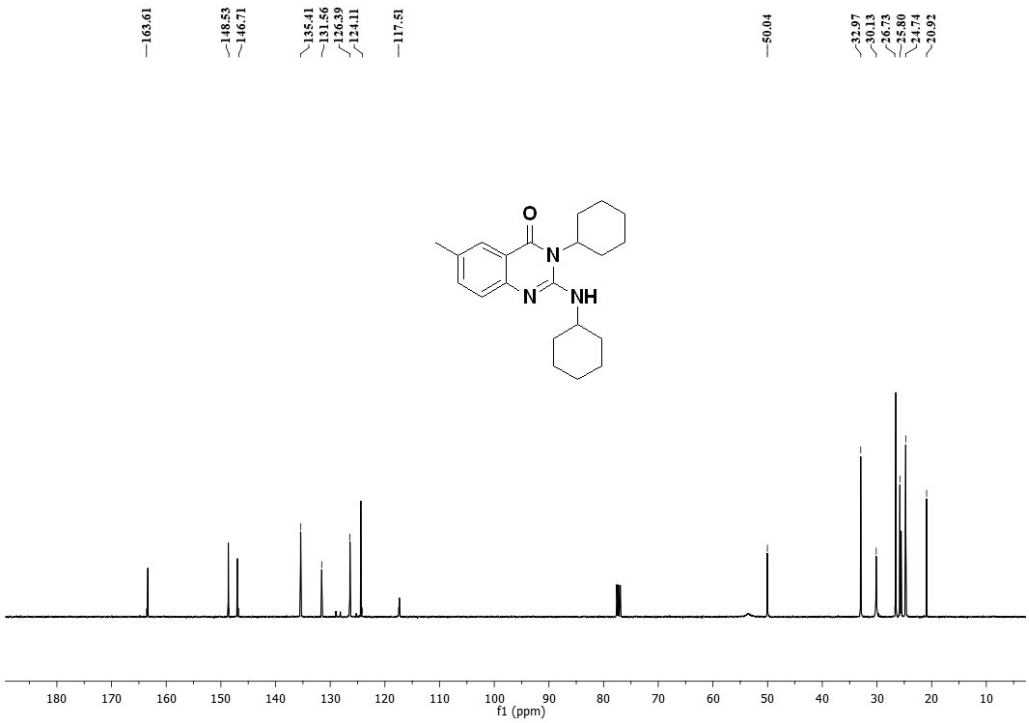


Figure FS18. ^{13}C NMR spectra of the complex **(5d).**

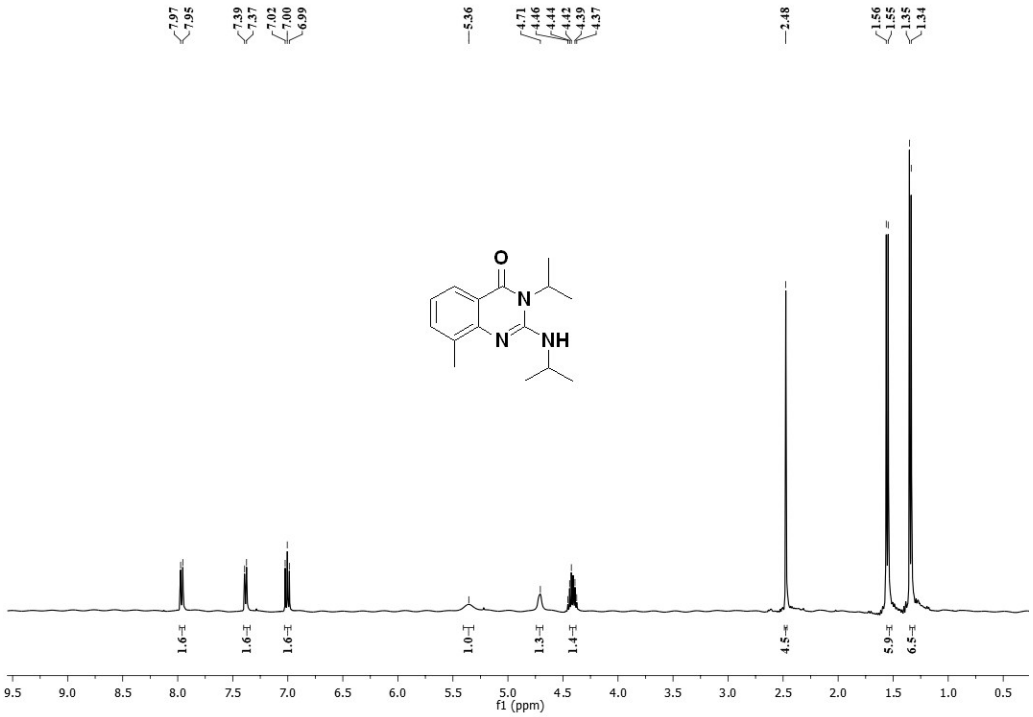


Figure FS19. ^{1}H NMR spectra of the complex **(5e).**

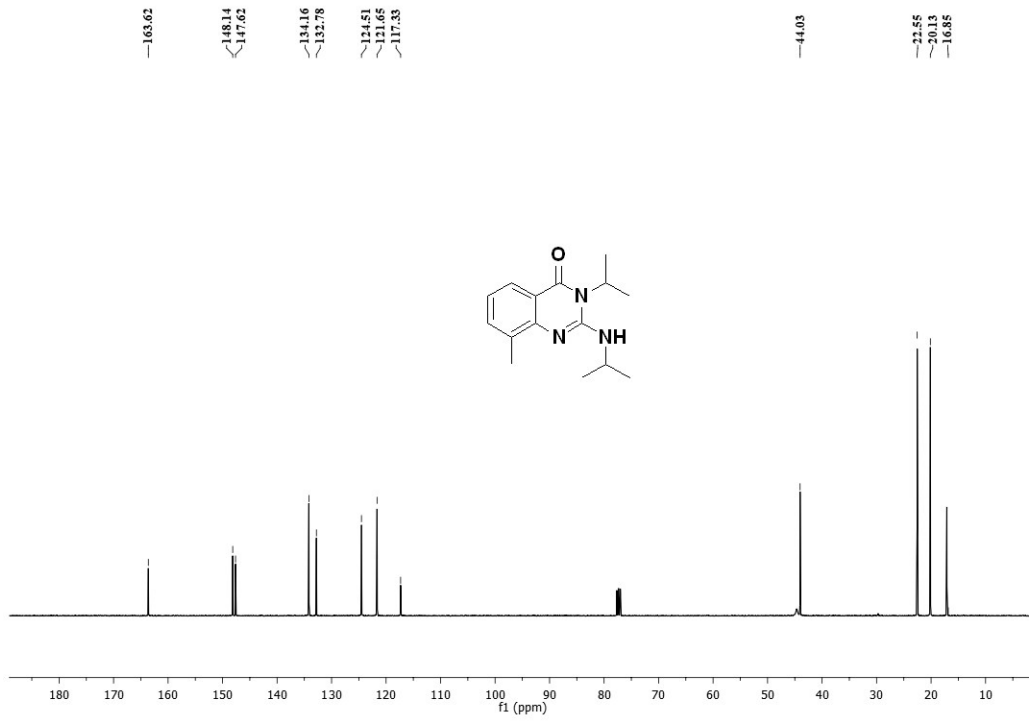


Figure FS20. ^{13}C NMR spectra of the complex **(3e).**

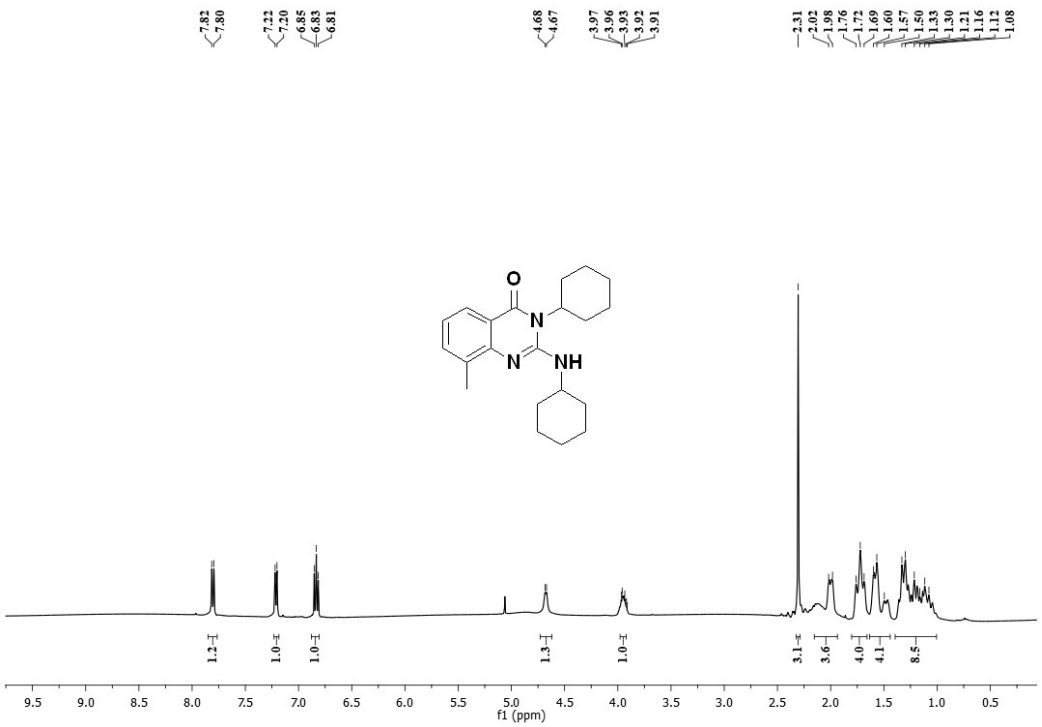


Figure FS21. [1]H NMR spectra of the complex **(3f).**

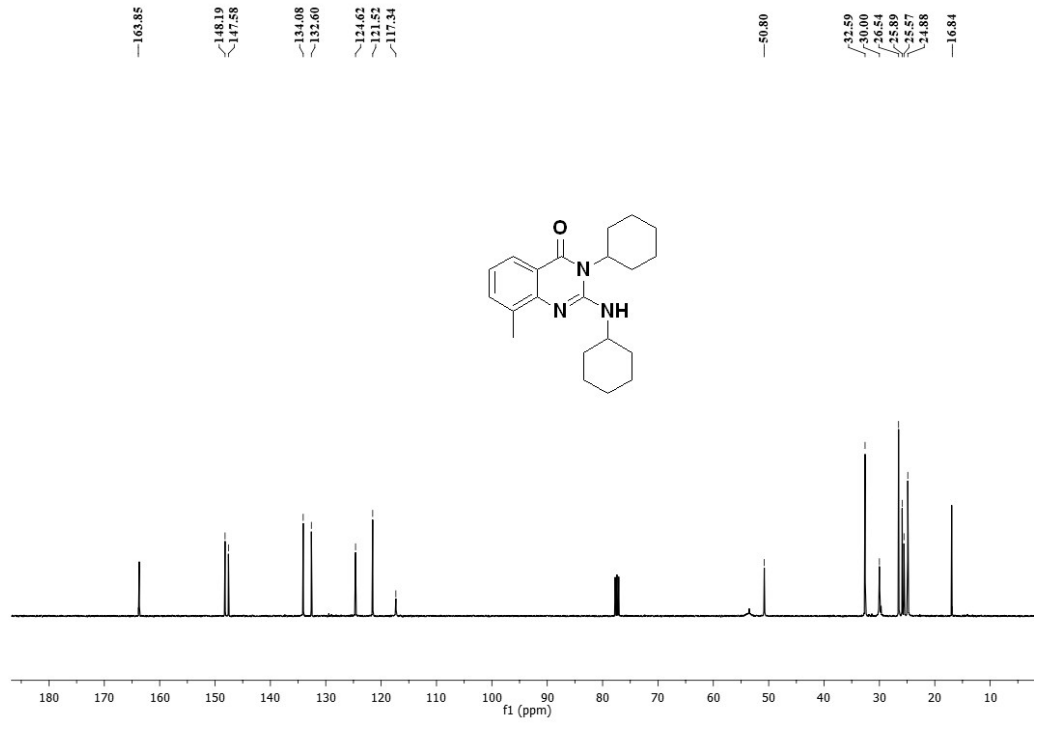


Figure FS22. [13]C NMR spectra of the complex **(3f).**

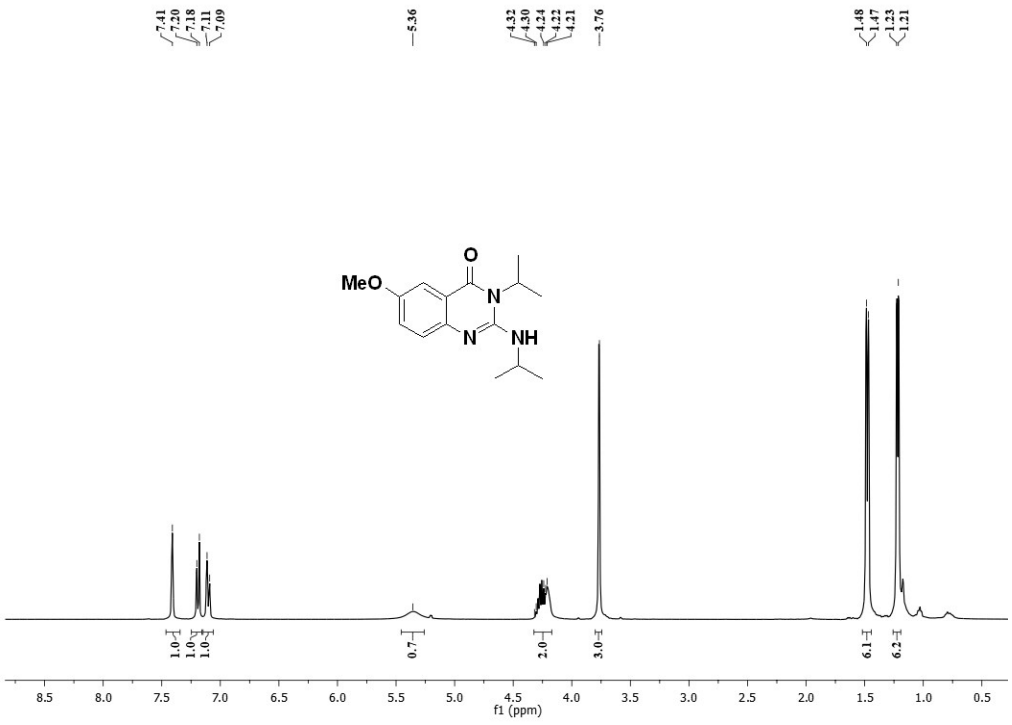


Figure FS23. ^{1}H NMR spectra of the complex **(5g).**

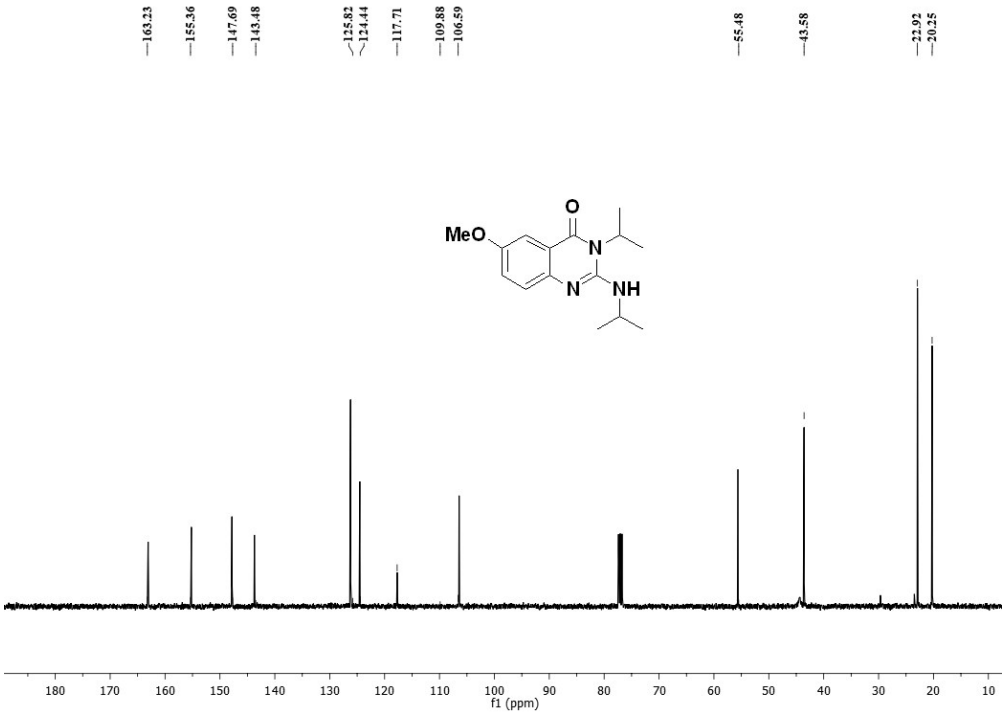


Figure FS24. ^{13}C NMR spectra of the complex **(5g).**

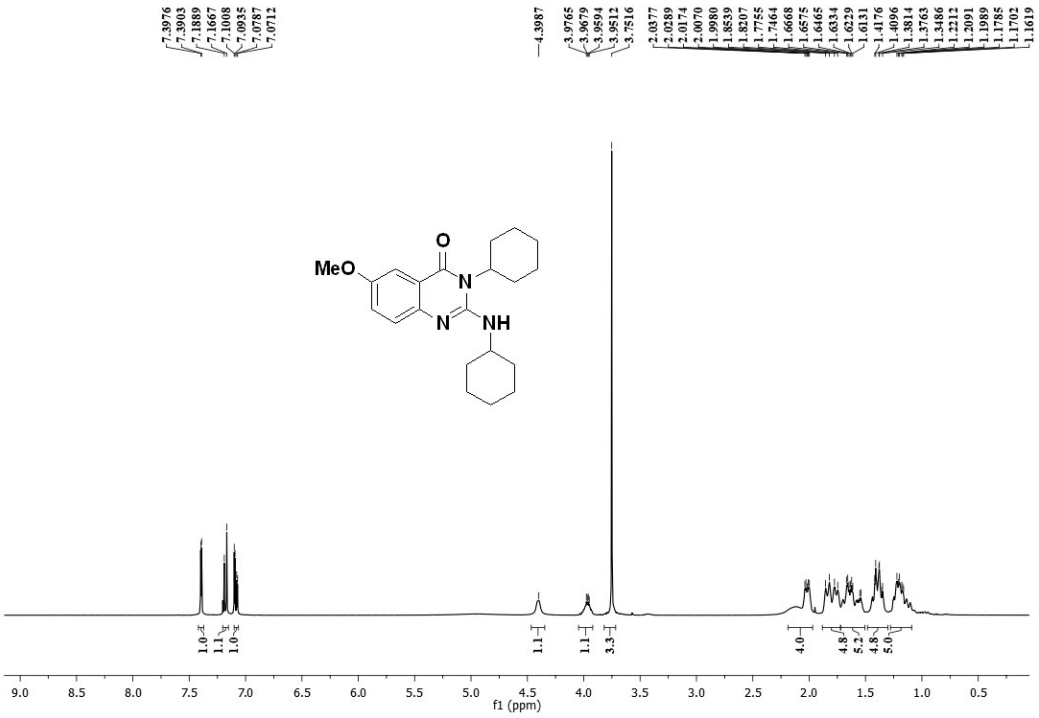


Figure FS25. ^{1}H NMR spectra of the complex **(5h).**

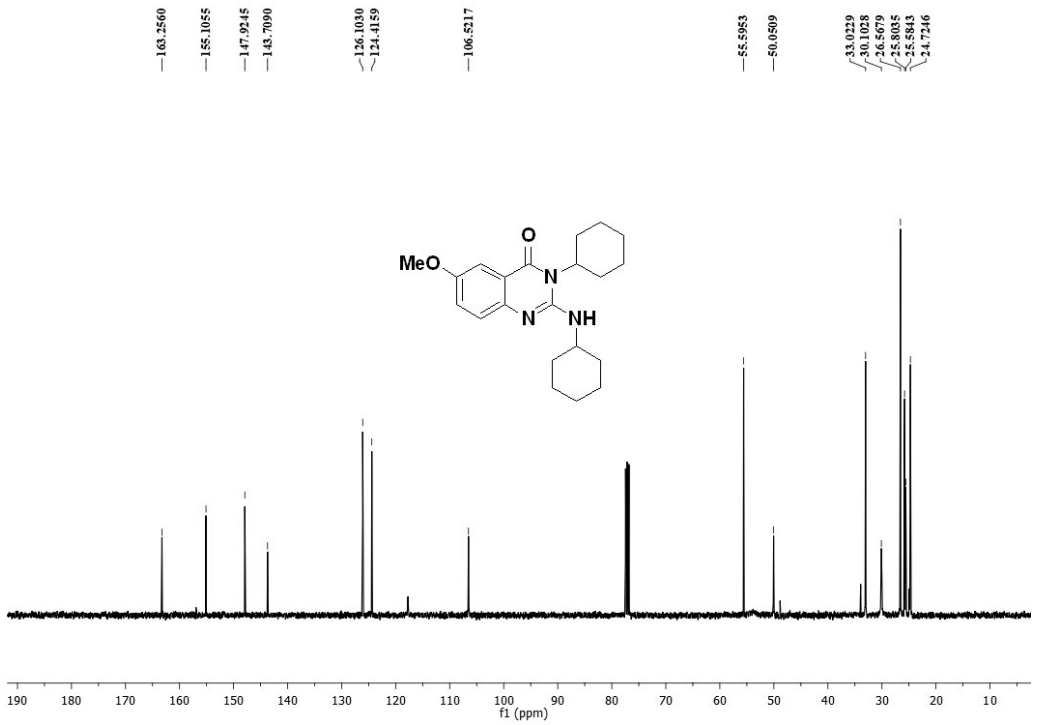


Figure FS26. ^{13}C NMR spectra of the complex **(5h).**

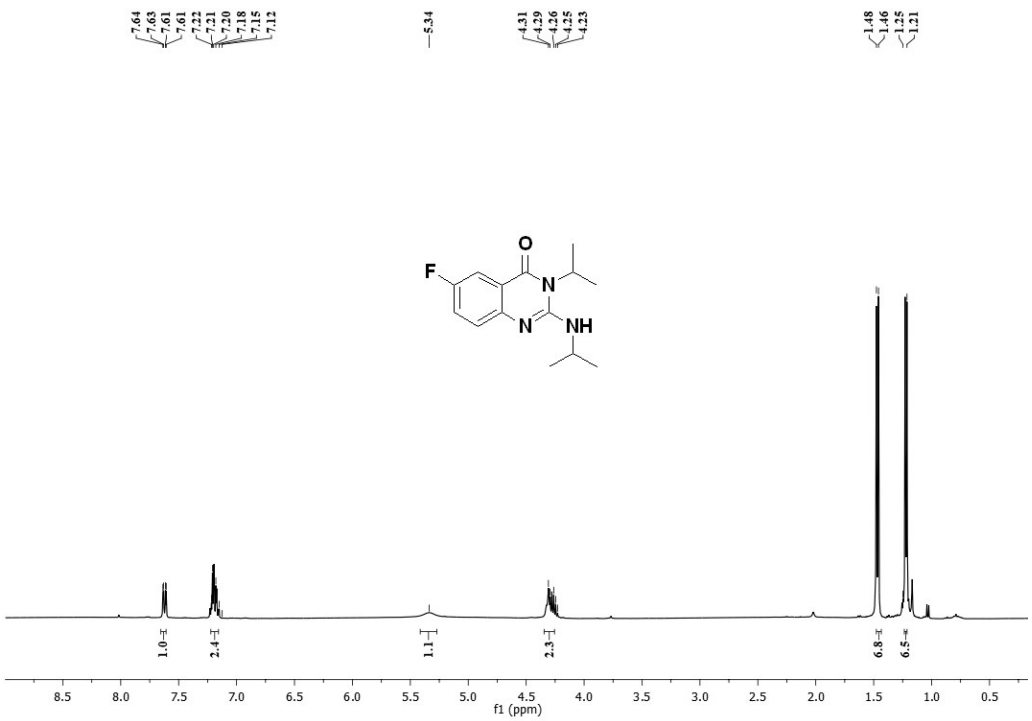


Figure FS27. ^{1}H NMR spectra of the complex **(5i).**

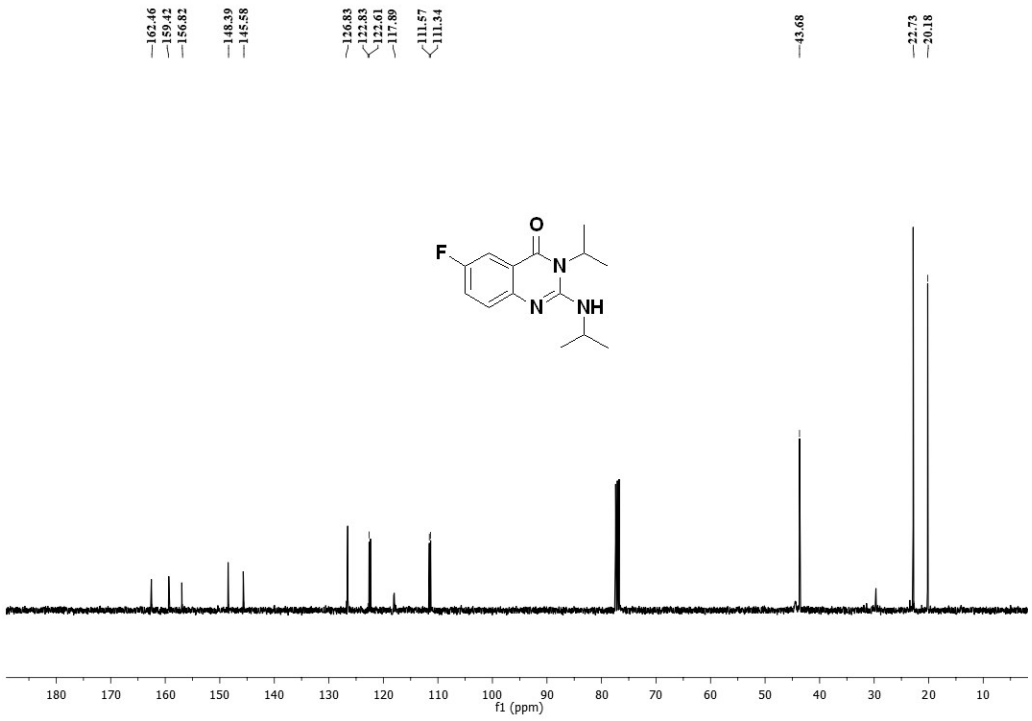


Figure FS28. ^{13}C NMR spectra of the complex **(5i).**

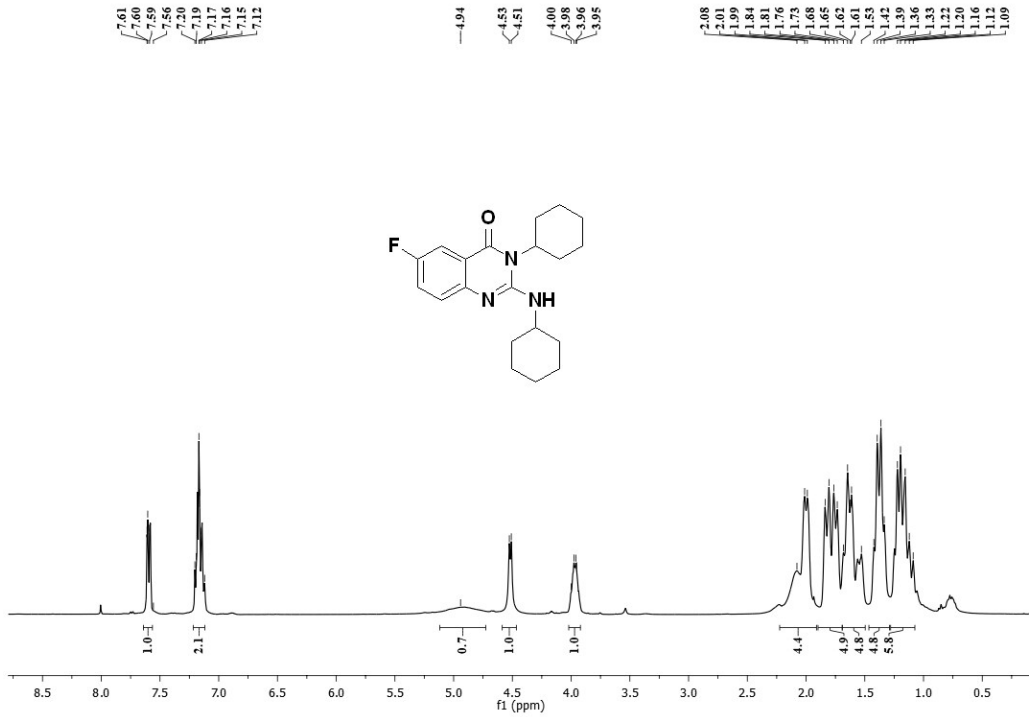


Figure FS29. [1]H NMR spectra of the complex **(5j).**

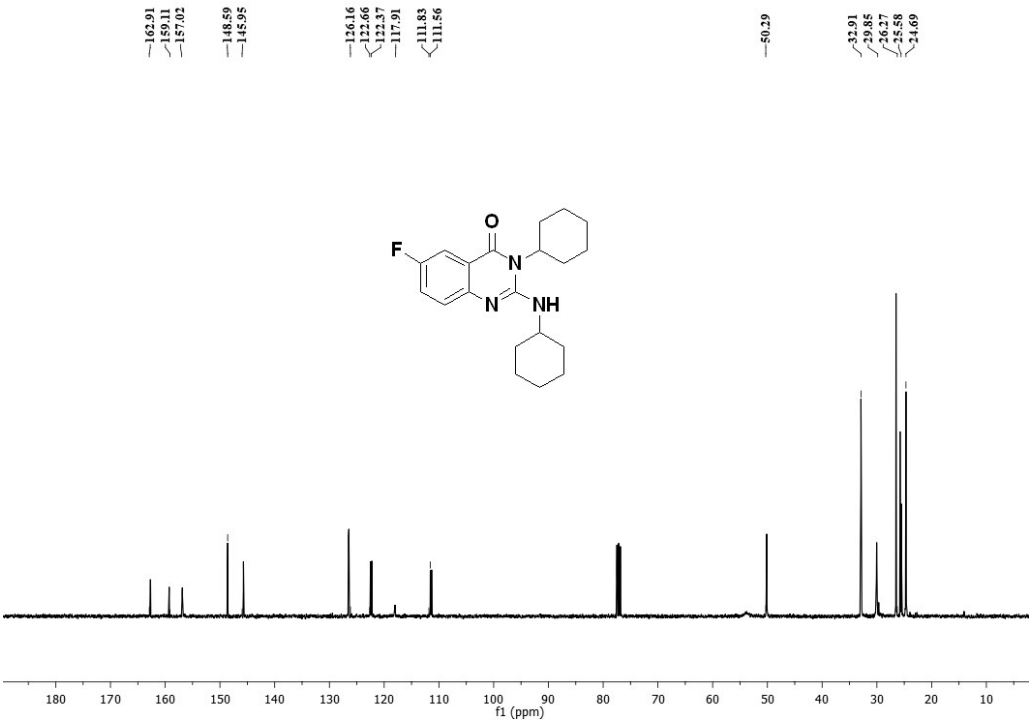


Figure FS30. [13]C NMR spectra of the complex **(5j).**

Figure FS31. ^{1}H NMR spectra of the complex **(5k).**

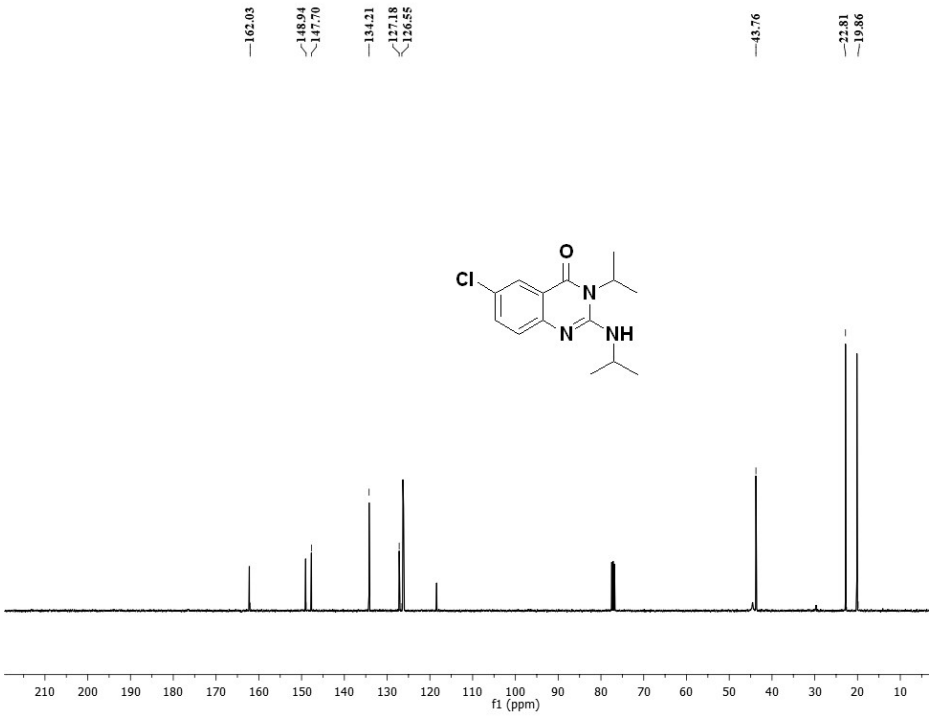


Figure FS32. ^{13}C NMR spectra of the complex **(5k).**

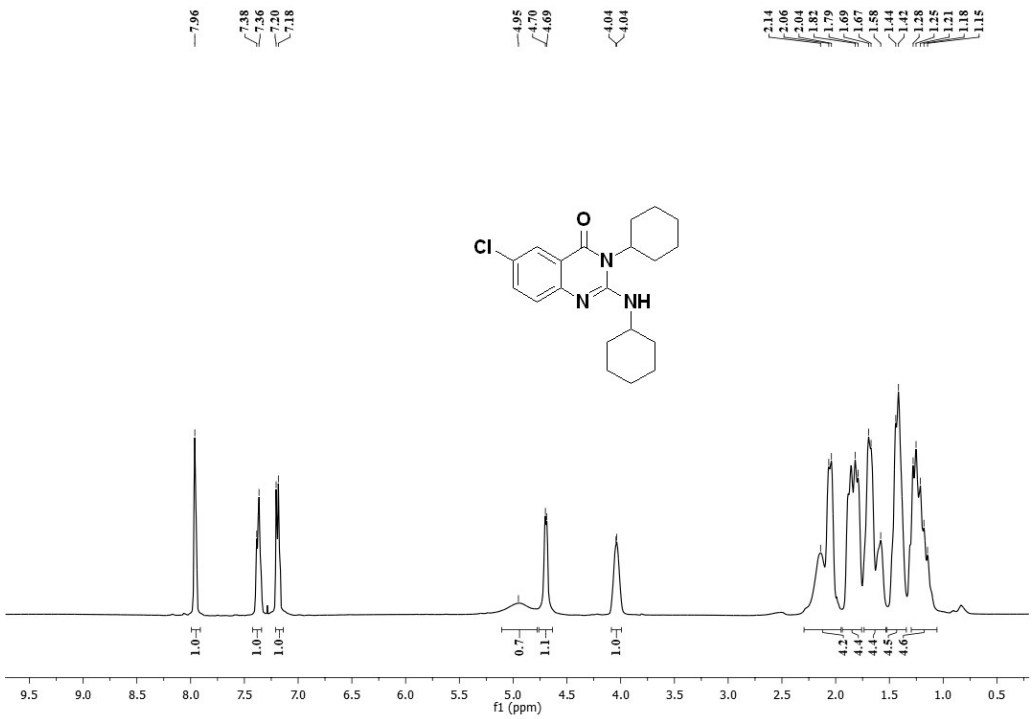


Figure FS33. ^{1}H NMR spectra of the complex **(5l).**

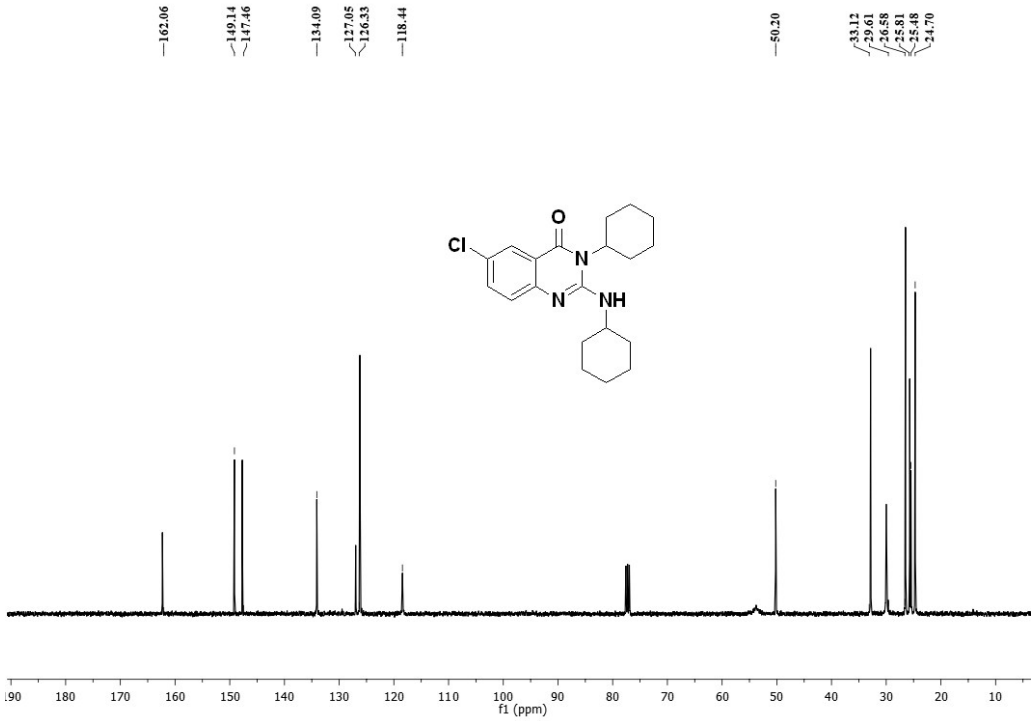


Figure FS34. ^{13}C NMR spectra of the complex **(5l).**

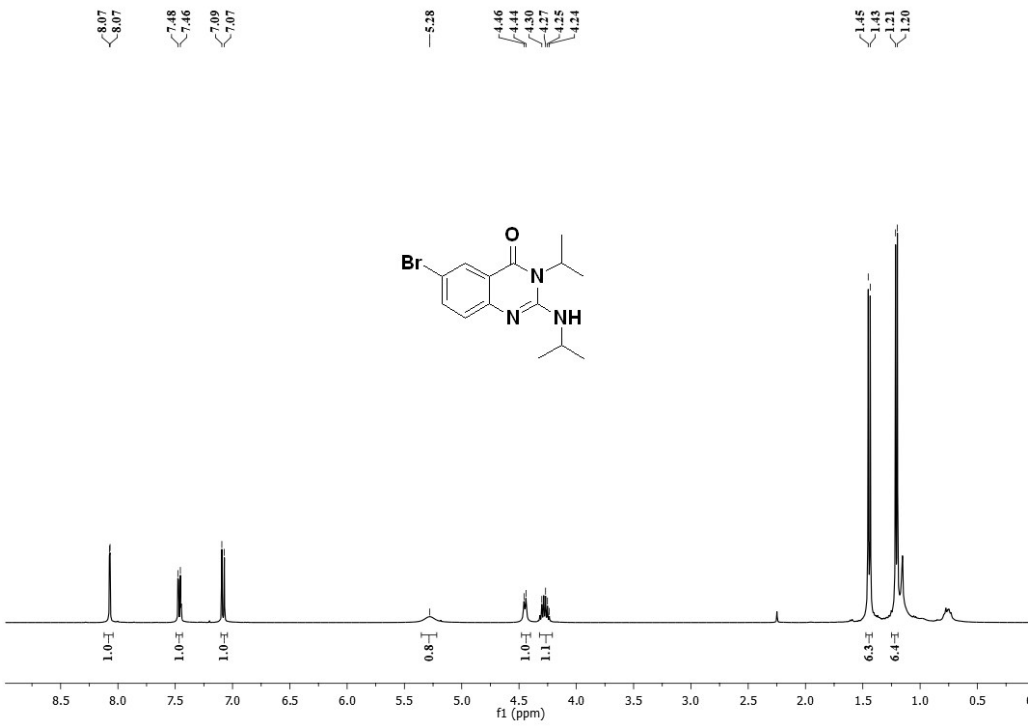


Figure FS35. ^{1}H NMR spectra of the complex **(5m).**

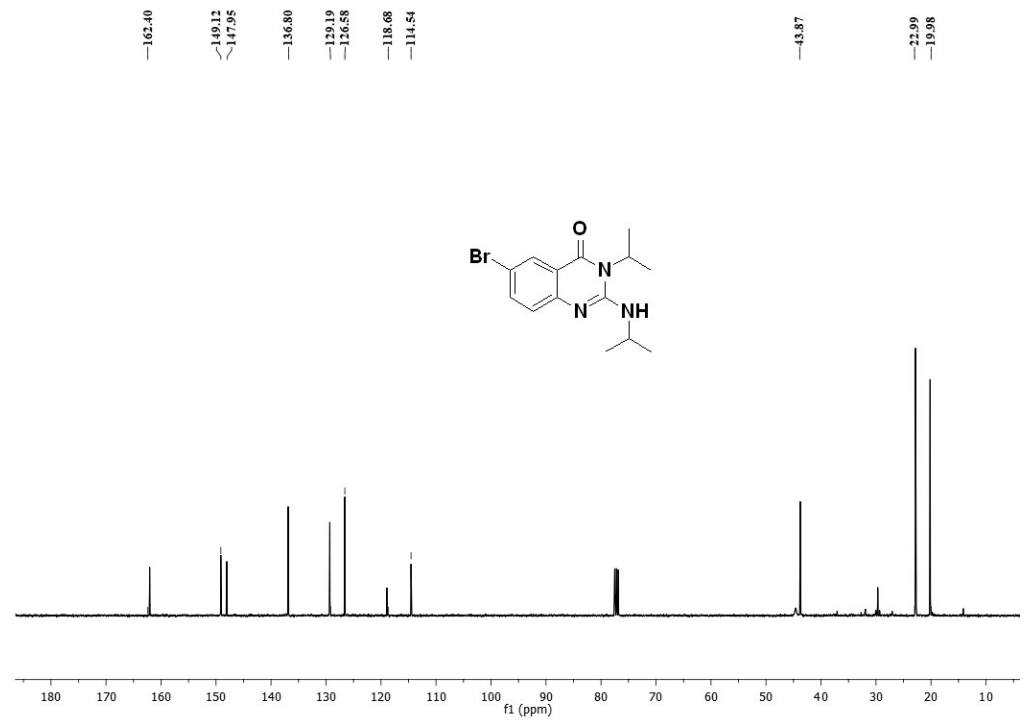


Figure FS36. ^{13}C NMR spectra of the complex **(5m).**

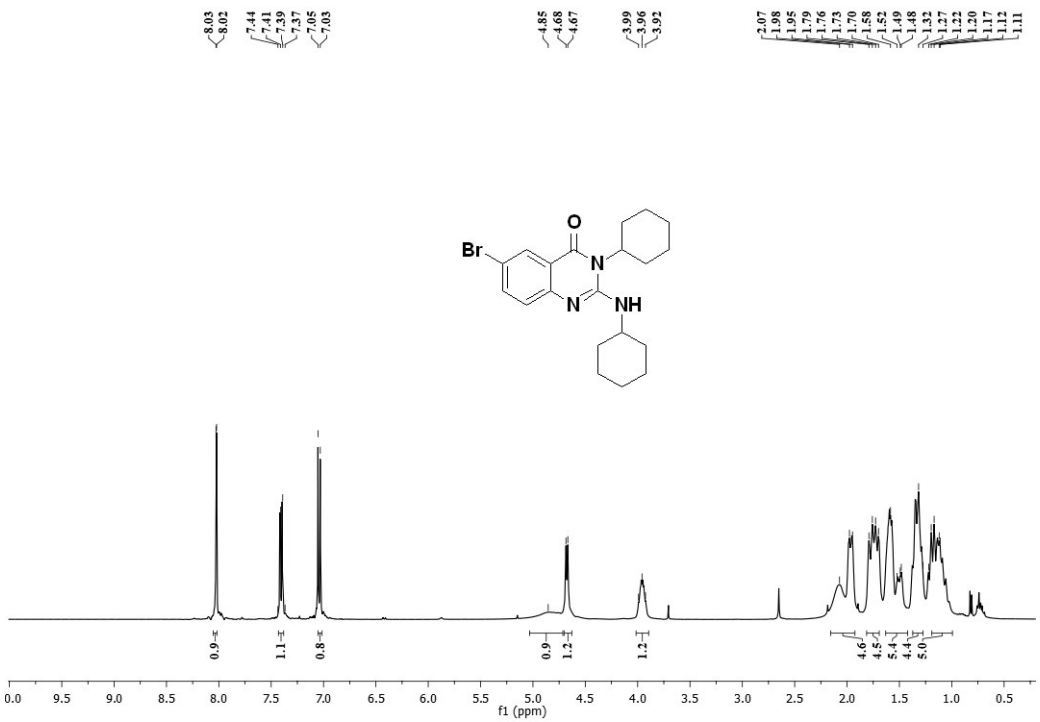


Figure FS37. [1]H NMR spectra of the complex **(5n).**

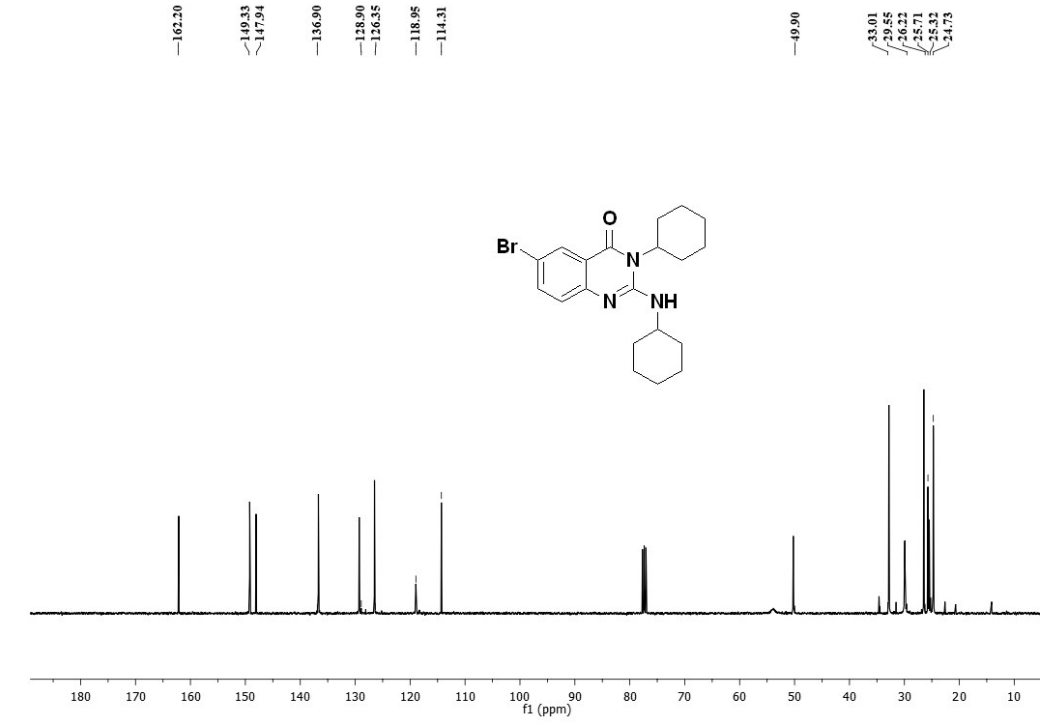


Figure FS38. [13]C NMR spectra of the complex **(5n).**

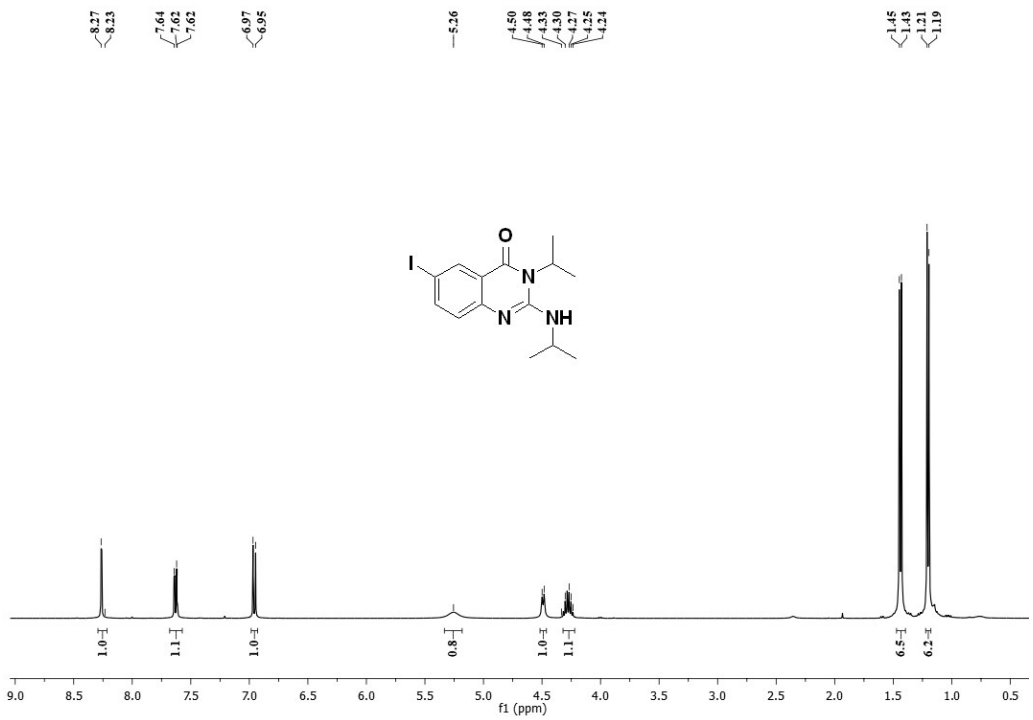


Figure FS39. [1]H NMR spectra of the complex **(5o).**

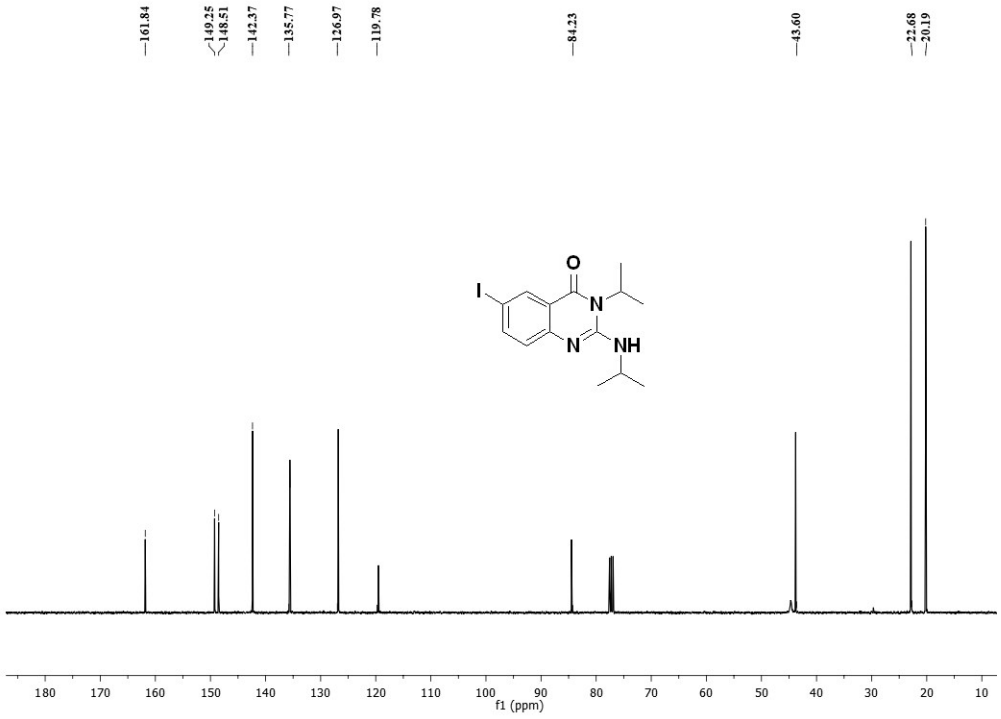


Figure FS40. [13]C NMR spectra of the complex **(5o).**

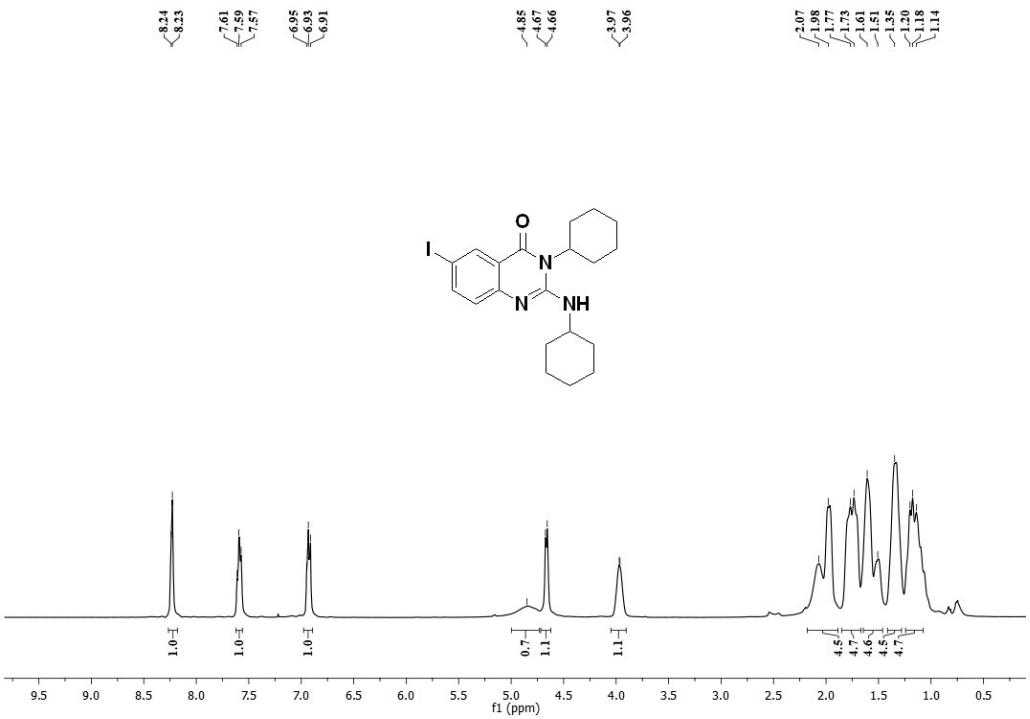


Figure FS41. ^{1}H NMR spectra of the complex **(5p).**

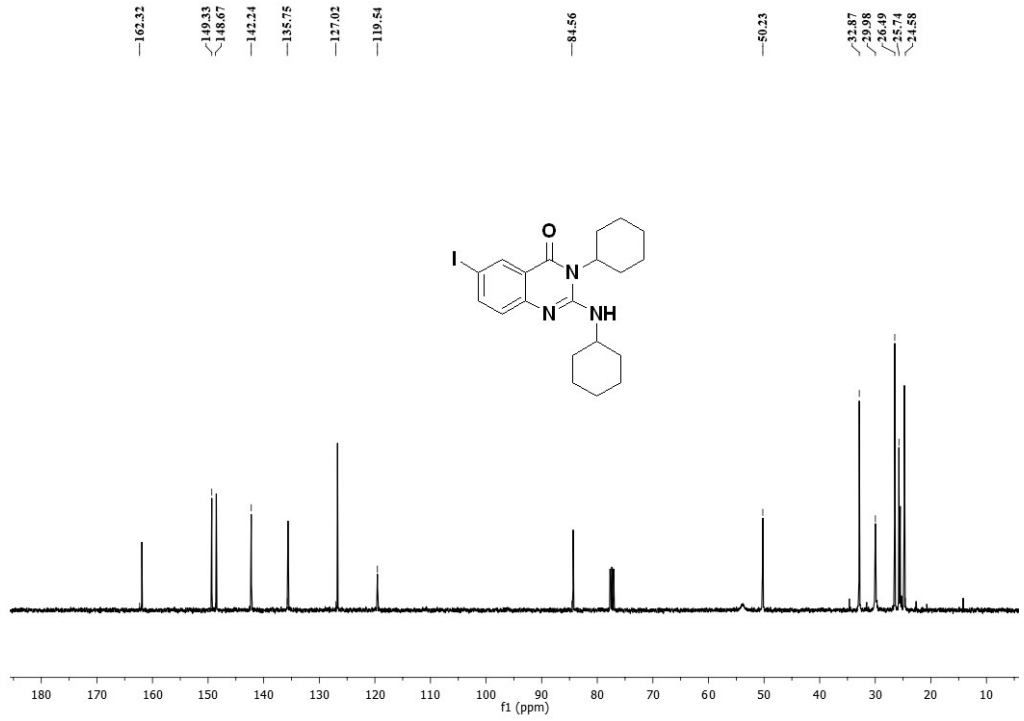


Figure FS42. ^{13}C NMR spectra of the complex **(5p).**

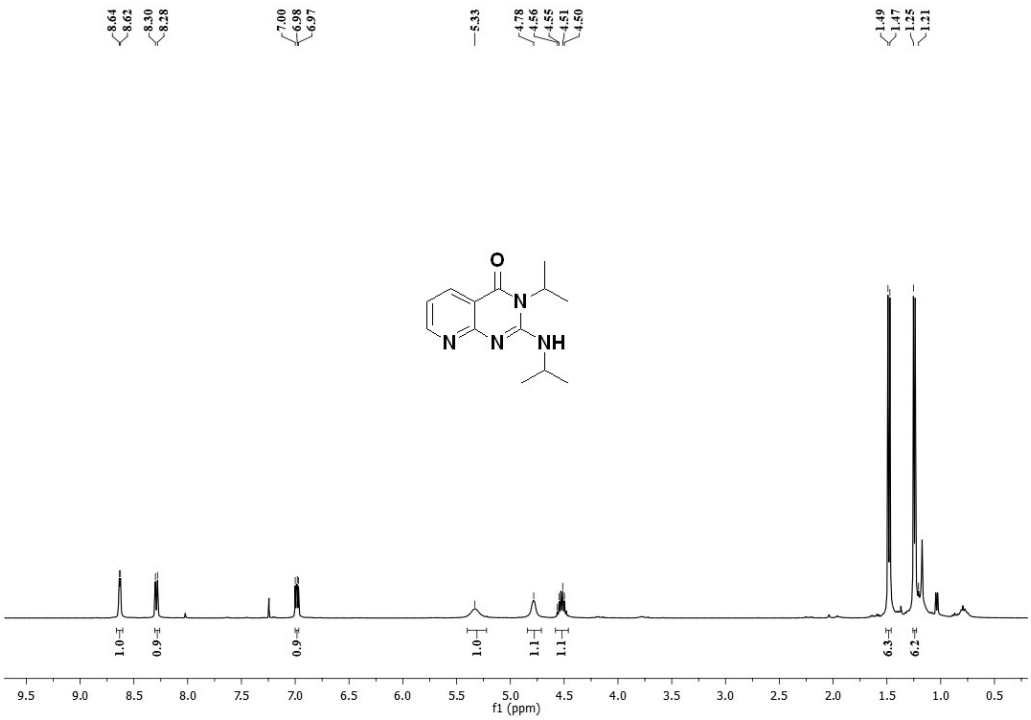


Figure FS43. ^{1}H NMR spectra of the complex **(5q).**

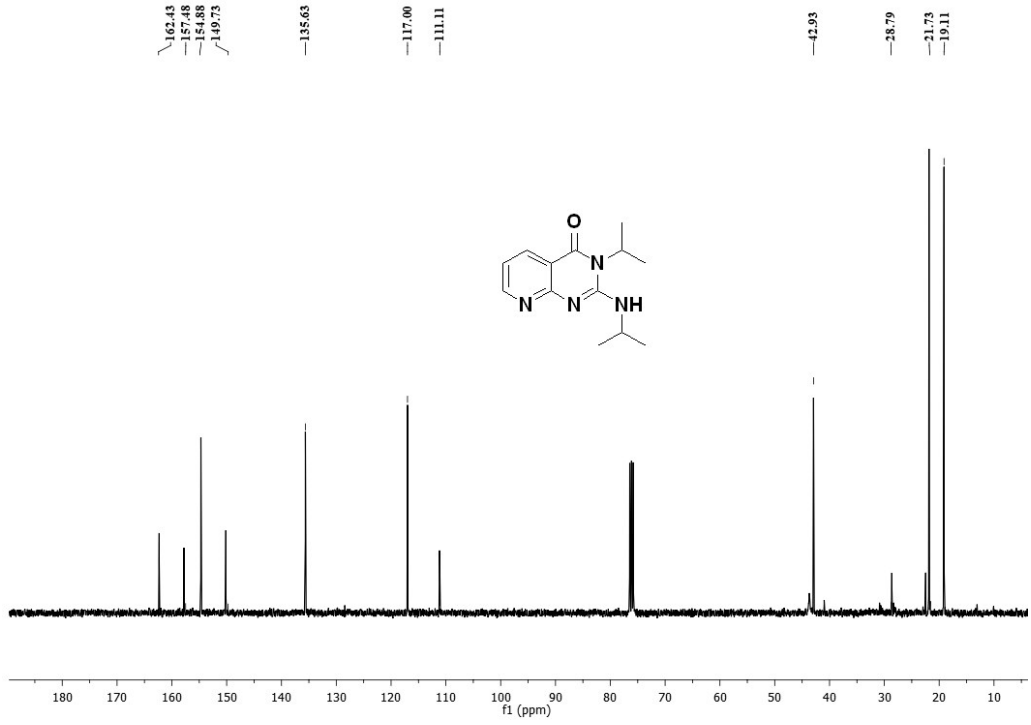


Figure FS44. ^{13}C NMR spectra of the complex **(5q).**

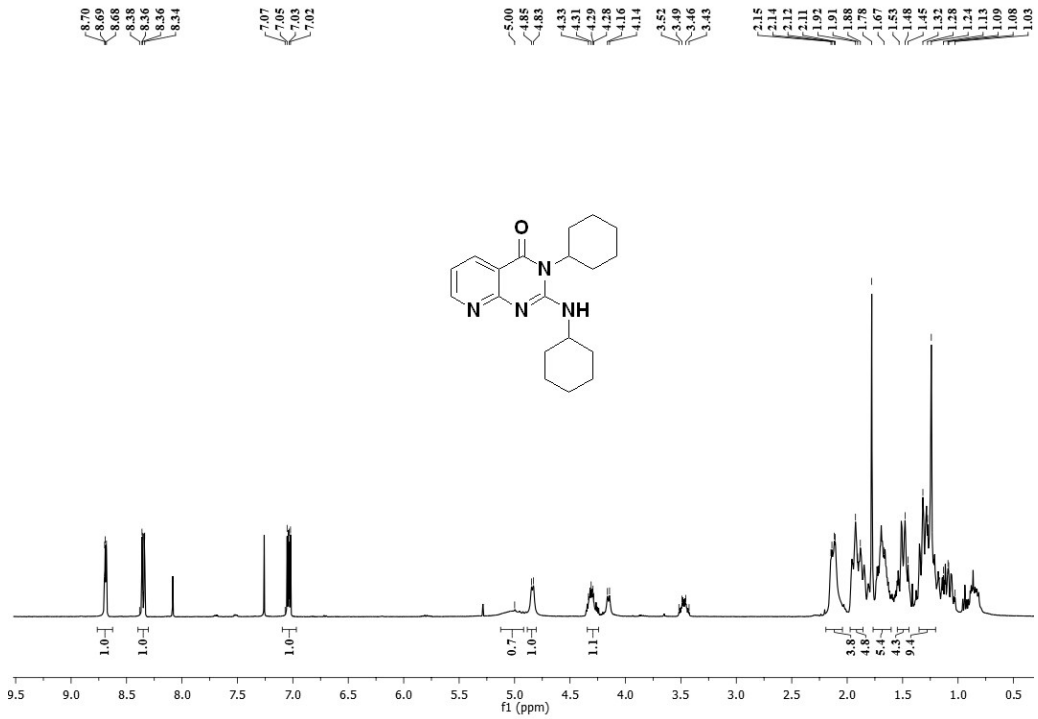


Figure FS45. ^{1}H NMR spectra of the complex **(5r).**

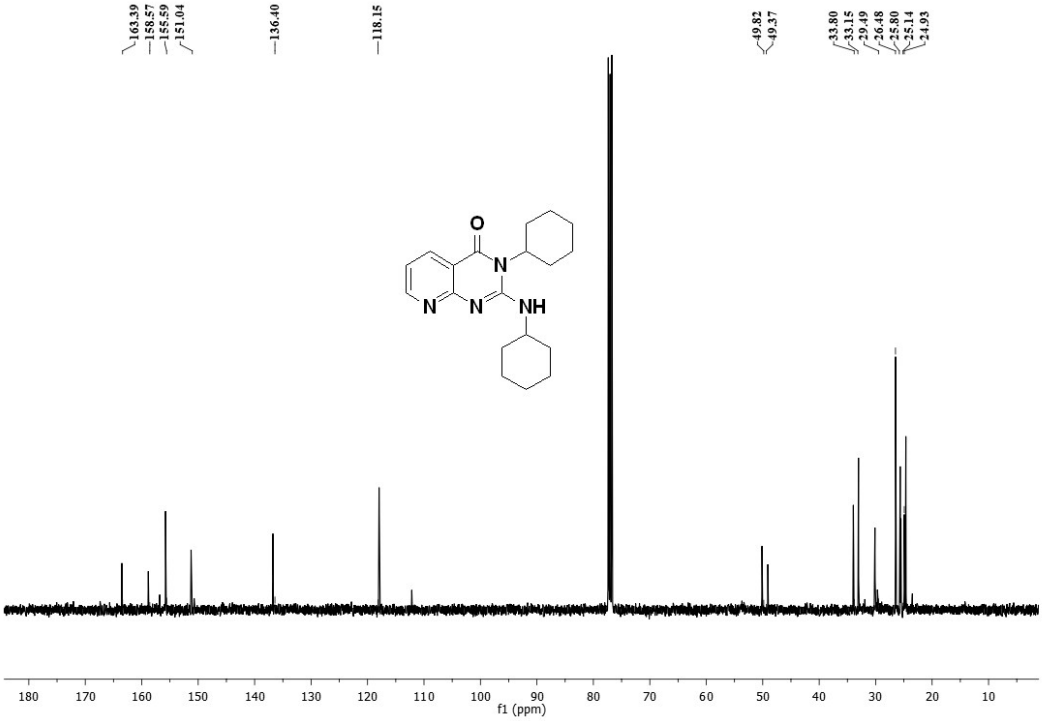


Figure FS46. ^{13}C NMR spectra of the complex **(5r).**

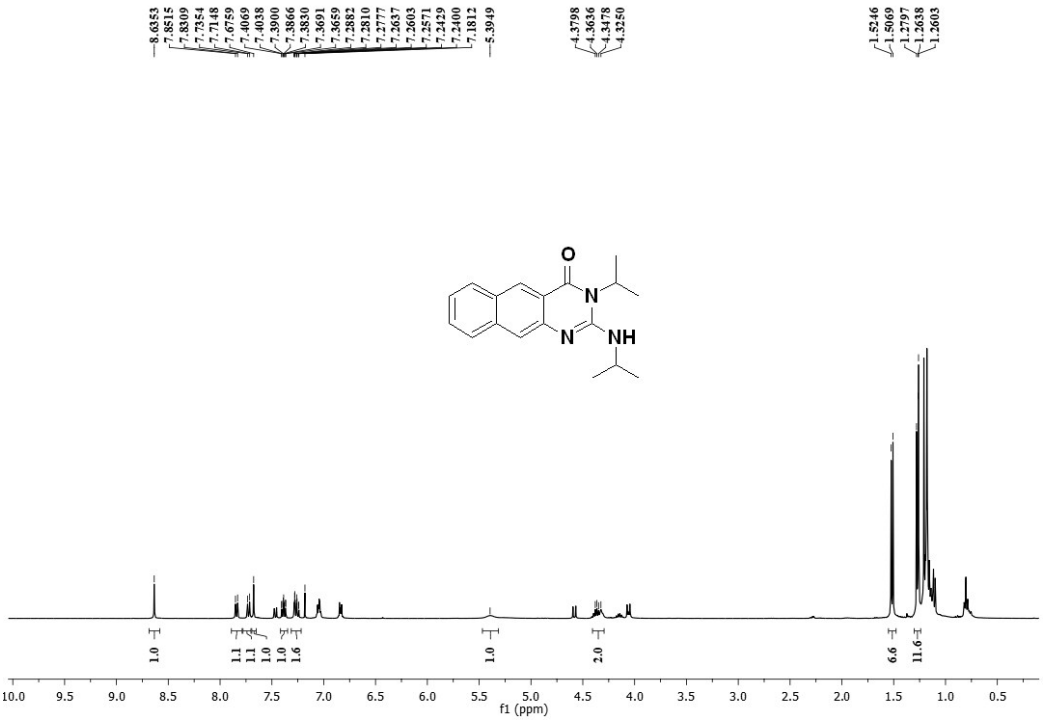


Figure FS47. [1]H NMR spectra of the complex **(5s).**

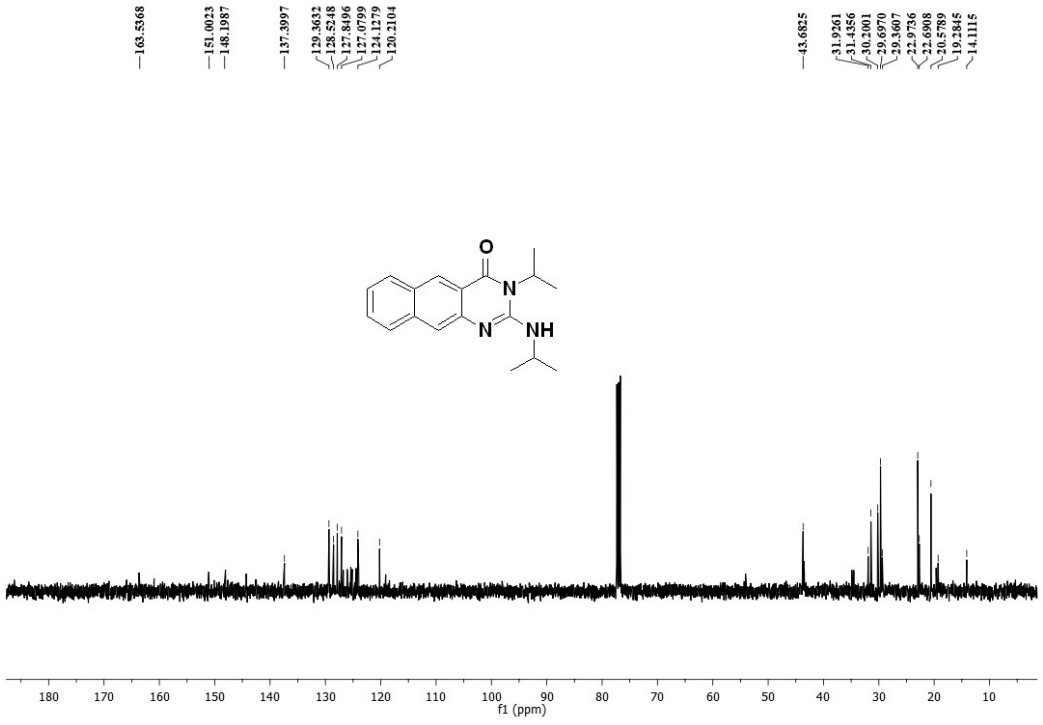


Figure FS48. [13]C NMR spectra of the complex **(5s).**

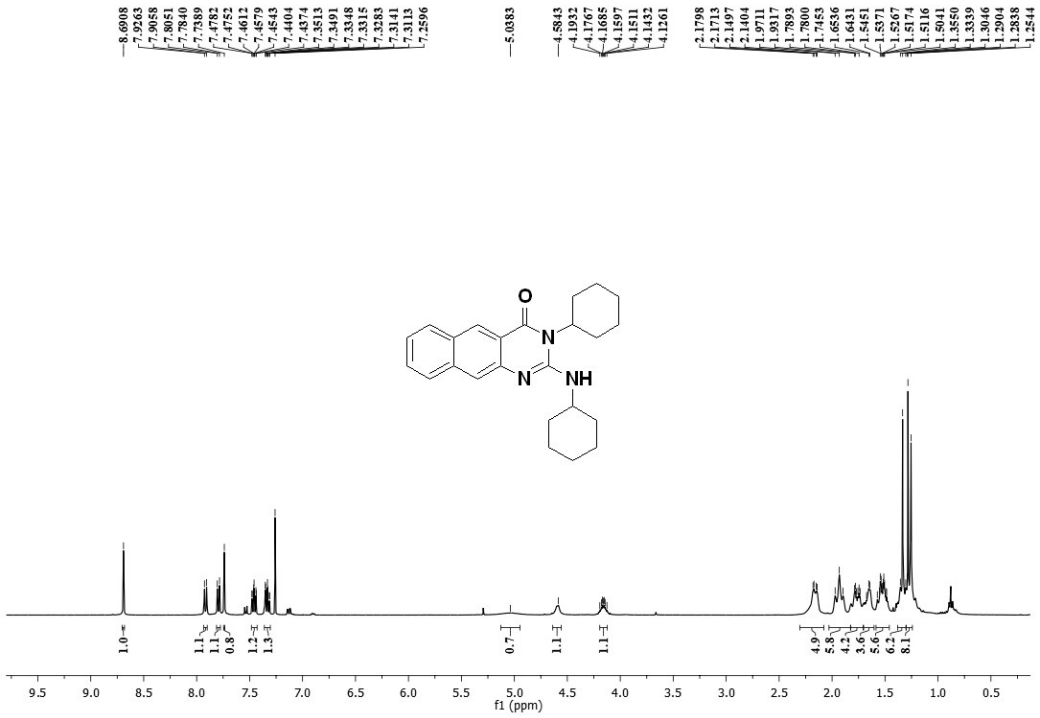


Figure FS49. ^{1}H NMR spectra of the complex **(5t).**

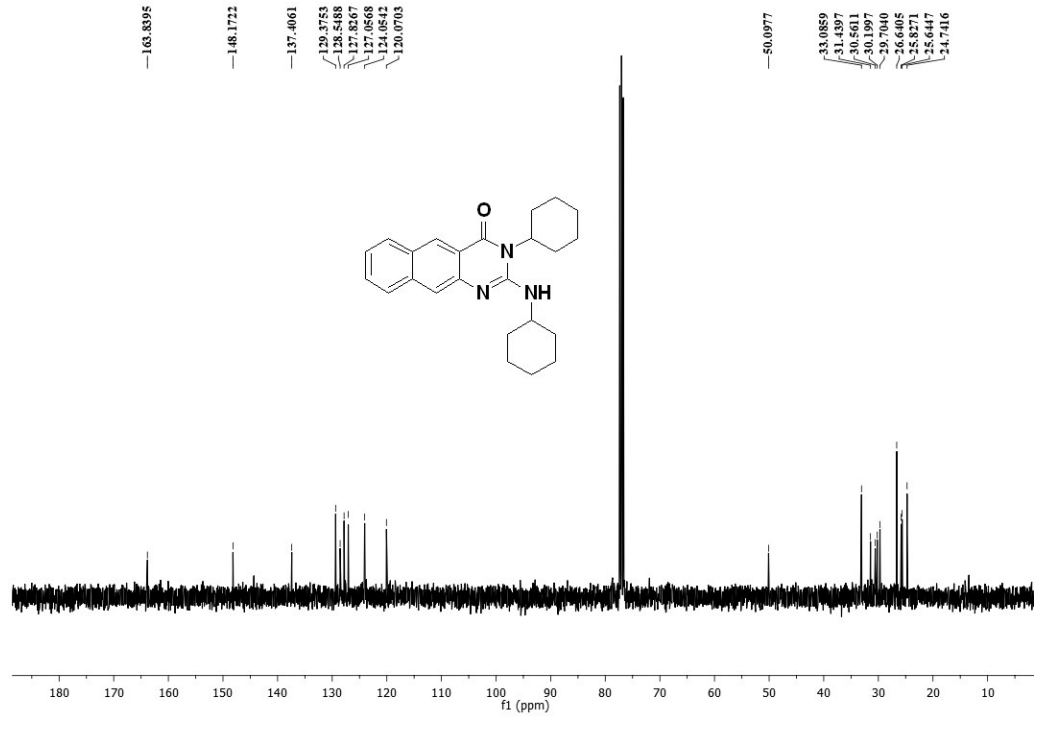
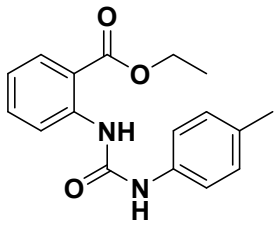


Figure FS50. ^{13}C NMR spectra of the complex **(5t).**

General procedure for Catalytic Titanium-mediated Urea derivatives for an amino acid ester in presence of isocyanates.

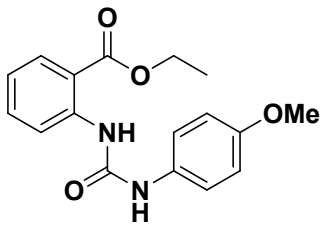
A solution of respective amino acid ester (0.606 mmol, 1equiv.) in was added drop-wise into the reaction mixture of respective heterocumulene (0.606 mmol, 1 equiv.), and catalyst (**2b**) 23.39 mg (0.0303 mmol). This was done in a 25 mL dry Schlenk flask inside the glovebox. The reaction mixture was kept in room temperature and the progress of the reactions was monitored by TLC. After that, the reaction was quench by adding 20 mL of ethyl acetate solvent and then basic workup was carried out adding 5 mL of saturated sodium bicarbonate solution into the reaction mixture. The product was collected in the organic layer and finally, the compound was purified by coloumm chromatography in (5:100) hexan/ethylacetate eluent solvent. The products were characterized according to ^{1}H, ^{13}C, and DEPT NMR spectroscopy (where necessary), as well as MS analysis.

<u>Characterization Data</u>: (For urea derivatives amino acid ester).



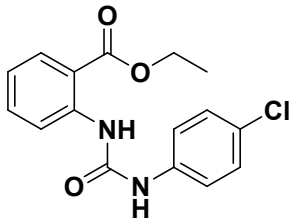
ethyl 2-(3-(*p*-tolyl)ureido)benzoate (6a).

Isolated yield (166 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.37 (s, 1H, N*H*), 8.44 - 8.42 (dd, *J* = 8.6, 0.6 Hz, 1H, Ar*H*), 7.88 - 7.86 (dd, *J* = 8.1, 1.6 Hz, 1H, Ar*H*), 7.39 - 7.34 (m, 1H, Ar*H*), 7.22 - 7.18 (m, 2H, Ar*H*), 7.01 - 6.99 (m, 2H, Ar*H*), 6.89 - 6.85 (m, 1H, Ar*H*), 4.19 - 4.14 (m, 1H, CH_2), 2.20 (s, 3H, CH_3), 1.25 - 1.22 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.5, 153.1, 142.9, 135.4, 133.9, 129.6, 121.2, 120.0, 114.6, 61.2, 20.7, 14.1 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{17}H_{19}N_2O_3]^+$ 299.139; found 299.1314. Mp: 142 - 148 °C.



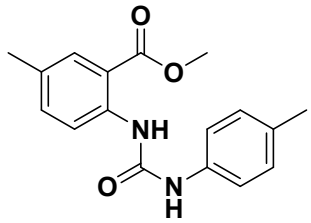
ethyl 2-(3-(4-methoxyphenyl)ureido)benzoate (6b).

Isolated yield (180 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.39 (s, 1H, N*H*), 8.47 - 8.46 (dd, *J* = 8.7, 0.6 Hz, 1H, Ar*H*), 7.91 - 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*),7.42 - 7.37 (m, 1H, Ar*H*), 7.25 - 7.22 (d, *J* = 8.9 Hz, 1H, Ar*H*), 6.91 - 6.87 (m, 1H, Ar*H*), 6.84 (s, 1H, N*H*), 6.81 – 6.74 (m, 1H, Ar*H*), 4.21 - 4.16 (m, 1H, CH_2), 3.71 (s, 3H, OCH_3), 1.28 – 1.17 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 167.3, 160.3, 156.0, 155.4, 152.8, 140.6, 134.0, 131.3, 128.8, 122.6, 121.0, 120.2, 115.4, 114.0, 61.1, 55.6, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{17}H_{19}N_2O_4]^+$ 314.1451; found 314.1452. Mp: 146 -154 °C.



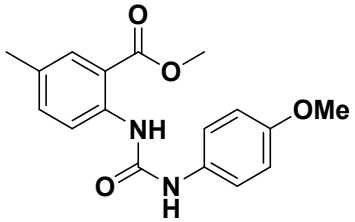
ethyl 2-(3-(4-chlorophenyl)ureido)benzoate (6c).

Isolated yield (173 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.52 (s, 1H, N*H*), 8.41 - 8.39 (dd, *J* = 8.6, 0.8 Hz, 1H, Ar*H*), 7.93 - 7.90 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 7.43 - 7.39 (m, 1H, Ar*H*), 7.31 - 7.28 (m, 1H, Ar*H*), 7.19 – 7.16 (m, 1H, Ar*H*), 6.96 (s, 1H, N*H*), 6.94 – 6.90 (m, 1H, Ar*H*), 4.25 - 4.20 (q, *J* = 7.0 Hz, 1H, CH_2), 1.31 – 1.28 (t, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.7, 152.4, 142.4, 136.8, 134.0, 130.7, 129.0, 128.8, 121.6, 119.8, 114.6, 61.1, 14.0 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{16}H_{17}ClN_2O_3]$+ 319.0844; found 319.0855. Mp: 181 - 187 °C.



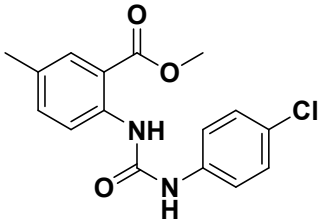
methyl 2-(3-(p-tolyl)ureido)benzoate (6d).

Isolated yield (162 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.54 (s, 1H, N*H*), 7.73 - 7.71 (dd, *J* = 7.7, 1.0 Hz, 1H, Ar*H*), 7.36 - 7.34 (d, *J* = 7.4 Hz, 1H, Ar*H*), 7.25 - 7.20 (m, 2H, Ar*H*), 7.10 - 7.03 (m, 3H, Ar*H*), 6.97 (s, 1H, N*H*), 3.81 (s, 1H, OCH_3), 2.29 (s, 1H, CH_3) 2.27 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.3, 153.6, 137.8, 135.7, 135.5, 133.3, 129.5, 124.6,123.6 120.8, 52.2, 20.8, 18.9 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{17}H_{19}N_2O_3]^+$ 299.139; found 299.1399. Mp: 176 - 180 °C.



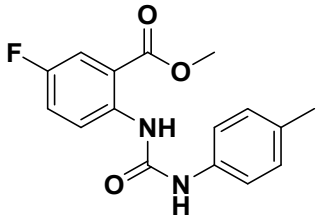
methyl 2-(3-(4-methoxyphenyl)ureido)-5-methylbenzoate (6e).

Isolated yield (176 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.55 (s, 1H, N*H*), 7.77 - 7.75 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.40 - 7.39 (d, *J* = 7.3 Hz, 1H, Ar*H*), 7.31 - 7.26 (m, 1H, Ar*H*), 7.18 - 7.10 (m, 1H, Ar*H*), 6.86 - 6.84 (m, 1H, Ar*H*), 6.71 (s, 1H, N*H*), 3.85 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 2.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.5, 153.6, 135.6, 128.8, 124.6, 114.4, 55.5, 52.2, 19.0, ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{17}H_{19}N_2O_4]^+$ 314.139; found 314.1381. Mp: 170 −172 °C.



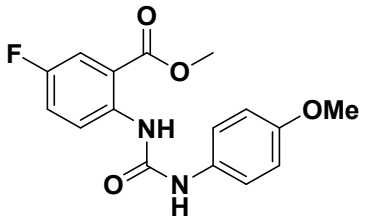
Methyl 2-(3-(4-chlorophenyl)ureido)-5-methylbenzoate (6f).

Isolated yield (171 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.39 (s, 1H, N*H*), 8.38 - 8.36 (d, *J* = 8.6 Hz, 1H, Ar*H*), 7.79 - 7.78 (s, 1H, Ar*H*), 7.39 - 7.36 (m, 2H, Ar*H*), 7.34 - 7.31 (m, 1H, Ar*H*), 7.27 – 7.25 (m, 2H, Ar*H*), 6.91 (s, 1H, N*H*), 3.87 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 169.1, 140.0, 136.9, 135.5, 130.8, 129.0, 121.4 119.8,114.2, 52.2, 20.0 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{16}H_{16}ClN_2O_3]^+$ 319.0844; found 319.083. Mp: 194 - 198 °C.



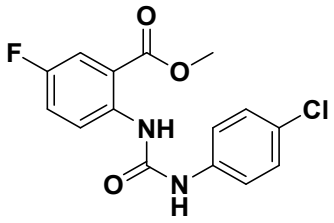
Methyl 5-fluoro-2-(3-(*p*-tolyl)ureido)benzoate (6g).

Isolated yield (157 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.28 (s, 1H, N*H*), 8.55 - 8.52 (m, 1H, Ar*H*), 7.67 - 7.63 (m, 1H, Ar*H*), 7.30 - 7.32 (m, 3H, Ar*H*), 7.16 – 7.14 (m, 2H, Ar*H*), 6.67 (s, 1H, N*H*), 3.87 (s, 1H, OCH_3), 2.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 167.6, 152.8, 141.0, 137.0, 129.7, 121.9, 115.8,113.3, 52.4, 20.8 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{16}H_{16}FN_2O_3]^+$ 303.1139; found 303.1147. Mp: 188 - 194°C.



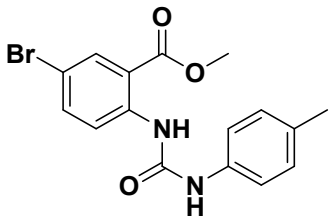
methyl 5-fluoro-2-(3-(4-methoxyphenyl)ureido)benzoate (6h).

Isolated yield (169 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_C 10.15 (s, 1H, N*H*), 8.49 - 8.45 (m, 1H, Ar*H*), 7.58 - 7.55 (m, 1H, Ar*H*), 7.25 - 7.19 (m, 3H, Ar*H*), 6.84 - 6.81 (m, 2H, Ar*H*), 6.55 (s, 1H, N*H*), 3.77 (s, 1H, OCH_3), 3.74 (s, 1H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 167.7, 156.9, 153.0, 130, 124.7, 121.4, 116.8,114.0, 52.5, 52.4 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{16}H_{16}FN_2O_4]^+$ 319.1089; found 319.1093. Mp: 179 - 182 °C.



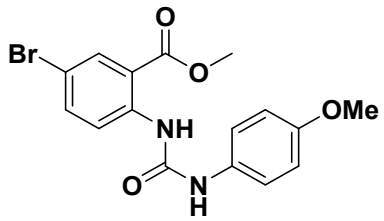
methyl 2-(3-(4-chlorophenyl)ureido)-5-flurobenzoate (6i).

Isolated yield (164 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.07 (s, 1H, N*H*), 8.51 (m, 1H, Ar*H*), 7.58 - 7.55 (m, 1H, Ar*H*), 7.25 - 7.19 (m, 3H, Ar*H*), 6.84 – 6.81 (m, 2H, Ar*H*), 6.7 (s, 1H, N*H*), 3.7 (s, 1H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 157.9, 152.0, 153.0, 138.1, 128.7, 126.7, 121.3 116.1, 115.7 52.3 . HRMS (ESI-TOF) m/z: [M + H]+ calcd for [C15H13ClFN2O3]+ 323.0597; found 323.0597. Mp: 184 - 188 °C.



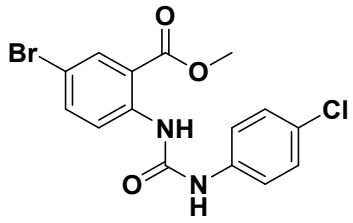
methyl 5-bromo-2-(3-(*p*-tolyl)ureido)benzoate (6j).

Isolated yield (192 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.40 (s, 1H, N*H*), 8.50 - 8.48 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.10 - 8.09 (s, 1H, Ar*H*), 7.60 -7.57 (m, 1H, Ar*H*), 7.29 – 7.26 (m, 2H, Ar*H*), 7.16 - 7.14 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.61 (s, 1H, N*H*), 3.87 (s, 1H, OCH_3), 2.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 167.6, 152.5, 141.8, 137.2, 134.2, 133.1, 129.7, 121.9, 115.7,113.3, 52.4, 20.8 ppm. HRMS (ESI-TOF) m/z: $[M + K]^+$ calcd for $[C_{16}H_{15}BrN_2O_3K]^+$ 384.9773; found 384.9779. Mp: 185 - 192 °C.



methyl 5-bromo-2-(3-(4-methoxyphenyl)ureido)benzoate (6k).

Isolated yield (206 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.35 (s, 1H, N*H*), 8.51 - 8.49 (d, *J* = 8.8 Hz, 1H, Ar*H*), 8.09 - 8.08 (s, 1H, Ar*H*), 7.60 - 7.57 (m,1H, Ar*H*), 7.31 – 7.29 (m, 2H, Ar*H*), 6.91 – 6.89 (d, *J* = 7.9 Hz, 1H, Ar*H*), 6.50 (s, 1H, N*H*), 3.87 (s, 1H, OCH_3), 3.78 (s, 1H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 167.6, 152.8, 141.5, 137.2, 133.1, 121.5, 114.7, 52.4, 52.4 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{16}H_{16}BrN_2O_4]^+$ 380.0319; found 380.0325. Mp: 176 - 178°C.



methyl 5-bromo-2-(3-(4-chlorophenyl)ureido)benzoate (6l).

Isolated yield (199 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.5 (s, 1H, N*H*), 8.48 - 8.46 (d, *J* = 8.9 Hz, 1H, Ar*H*), 8.12 (s, 1H, Ar*H*),7.62 -7.60 (m, 1H, Ar*H*), 7.39 – 7.34 (m, 2H, Ar*H*), 7.29 - 7.26 (d, *J* = 7.9, Hz 1H, Ar*H*), 6.68 (s, 1H, N*H*), 3.92 (s, 1H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 167.6, 152.8, 141.4, 137.2, 133.3, 125.2, 122.4 115.7,113.3, 52.4, ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $[C_{15}H_{13}BrClN_2O_3]^+$ 384.6324; found 384.6322 Mp: 180 - 186 °C.

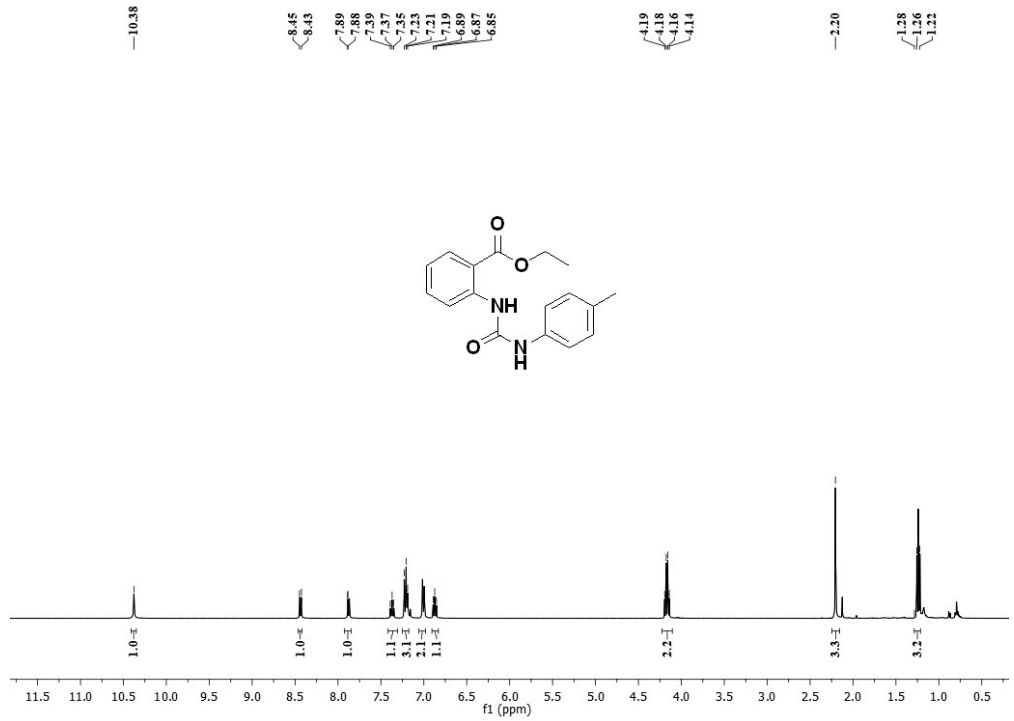


Figure FS51. ^{1}H NMR spectra of complex **(6a).**

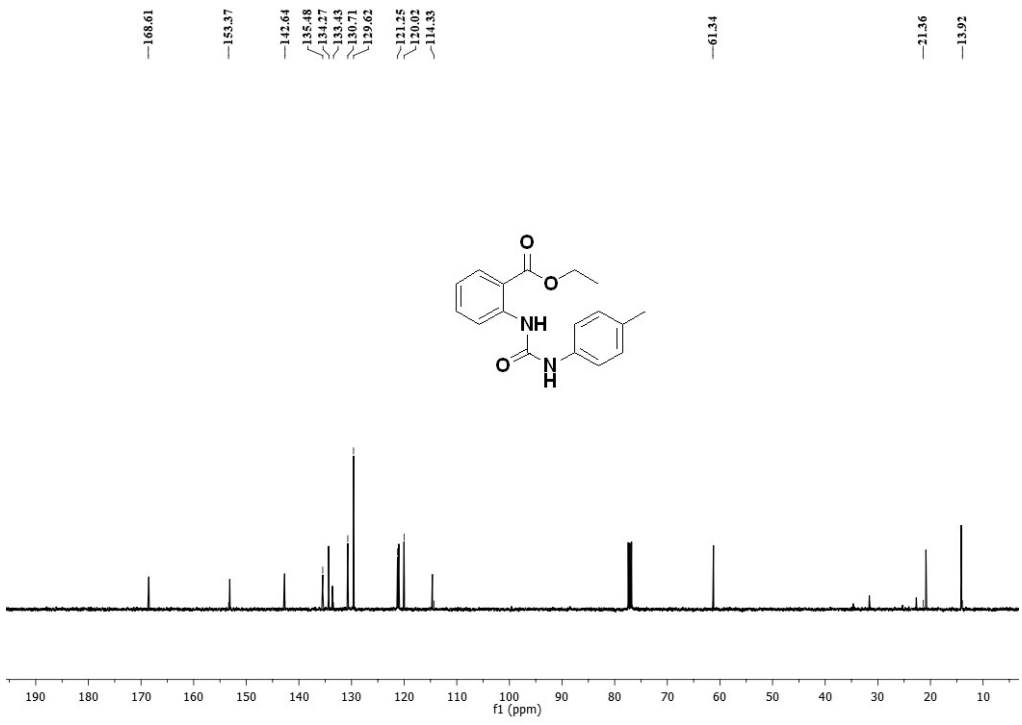


Figure FS52. ^{13}C NMR spectra of complex **(6a).**

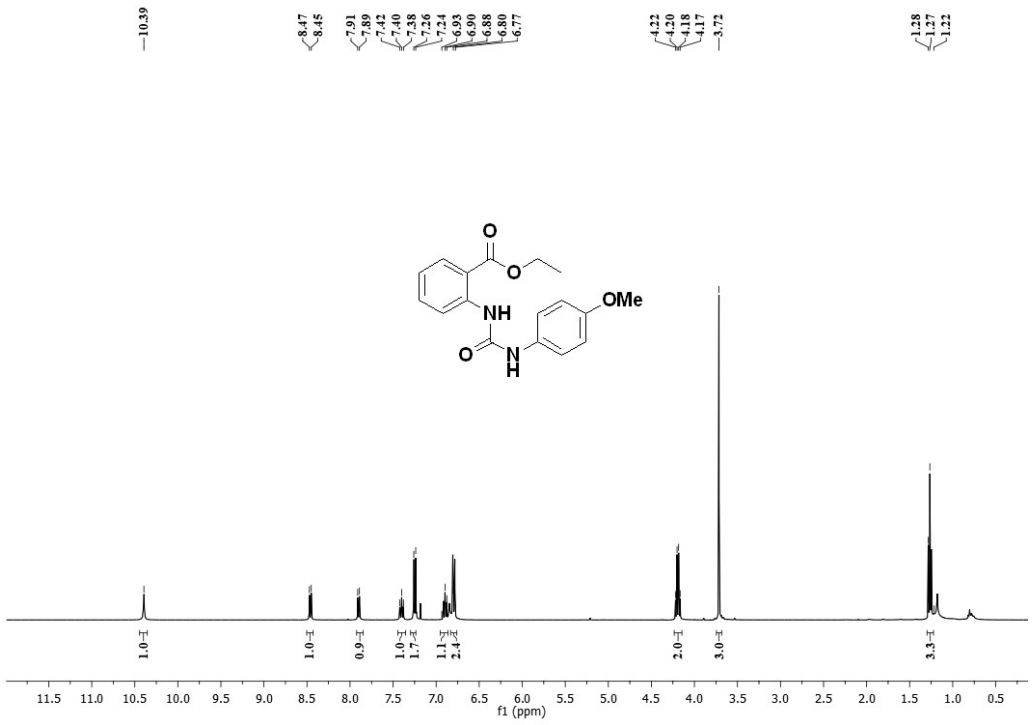


Figure FS53. ^{1}H NMR spectra of the complex **(6b).**

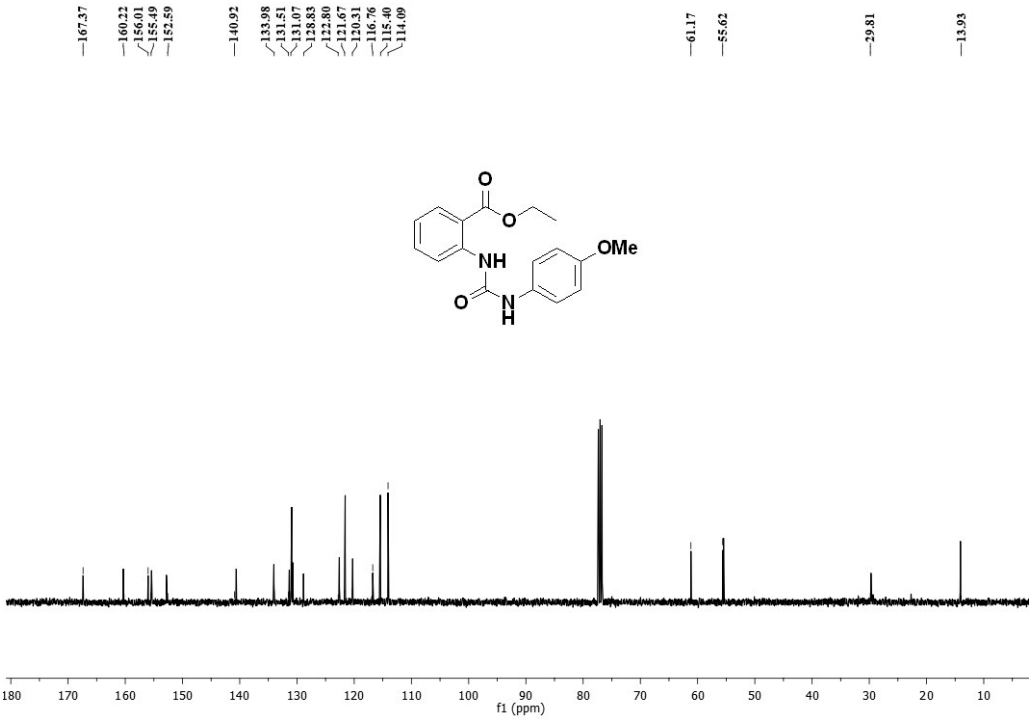


Figure FS54. ^{13}C NMR spectra of the complex **(6b).**

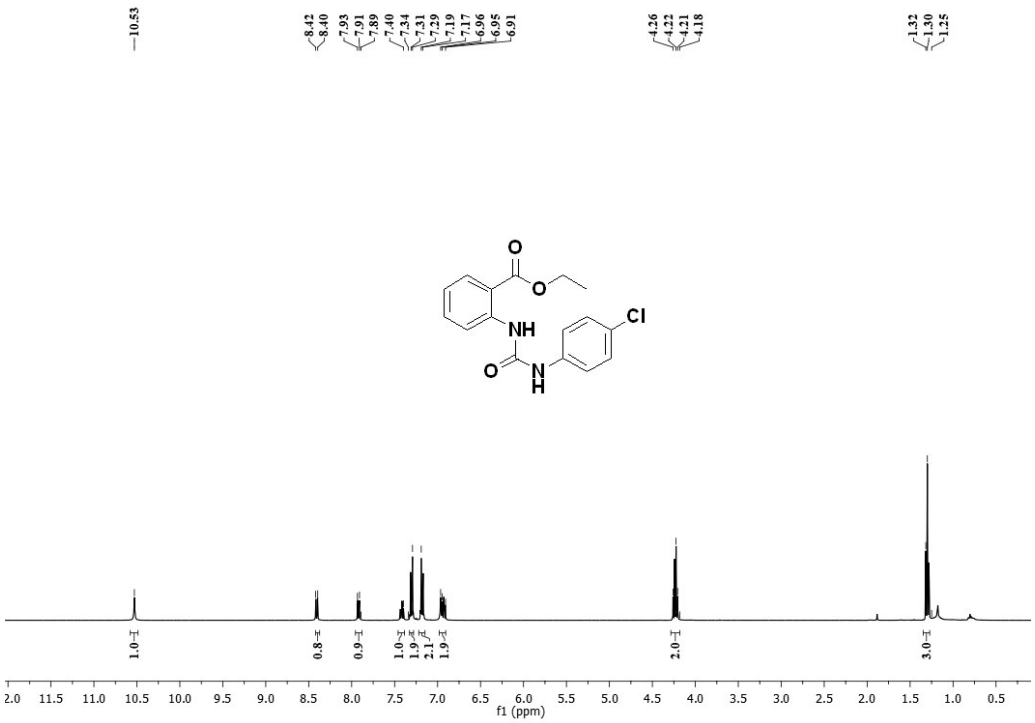


Figure FS55. [1]H NMR spectra of the complex **(6c).**

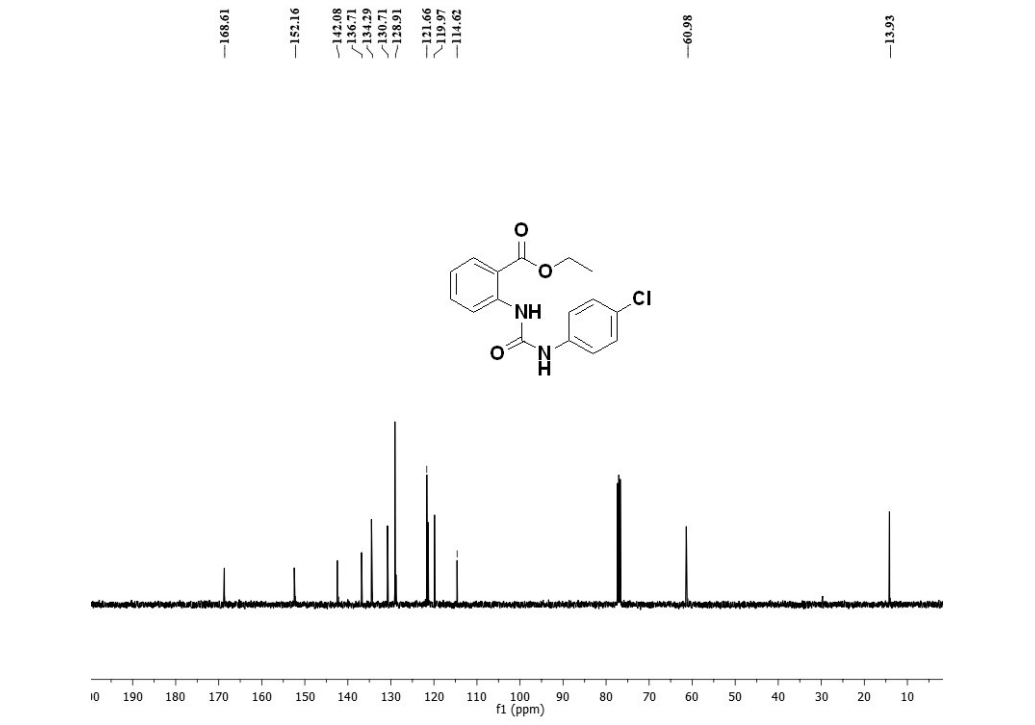


Figure FS56. [13]C NMR spectra of the complex **(6c).**

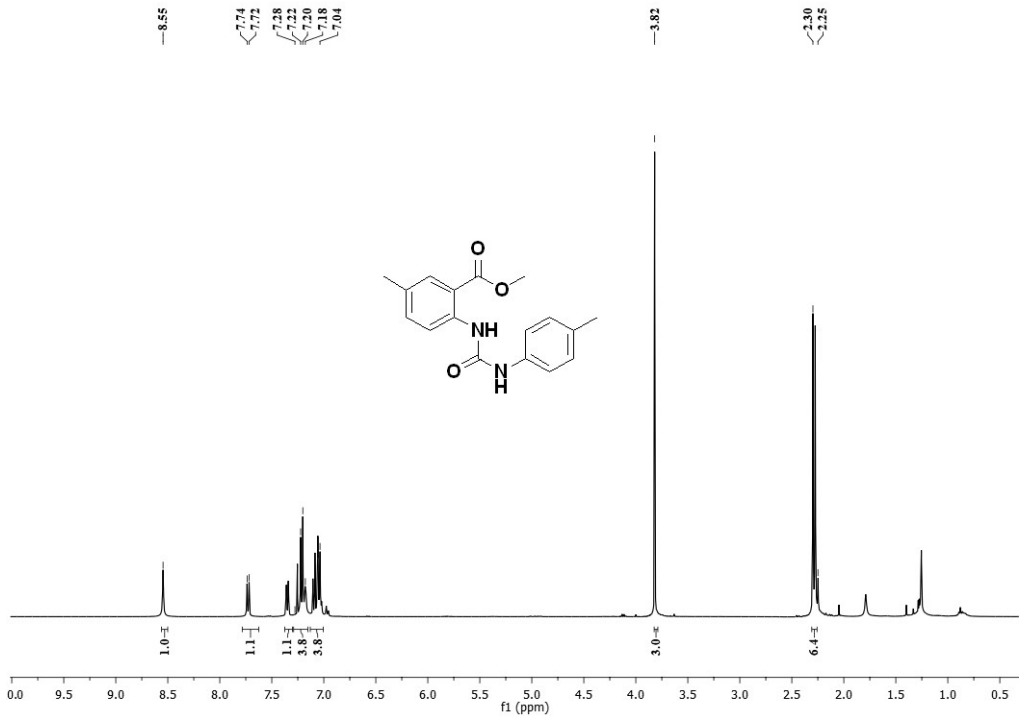


Figure FS57. ^{1}H NMR spectra of the complex **(6d).**

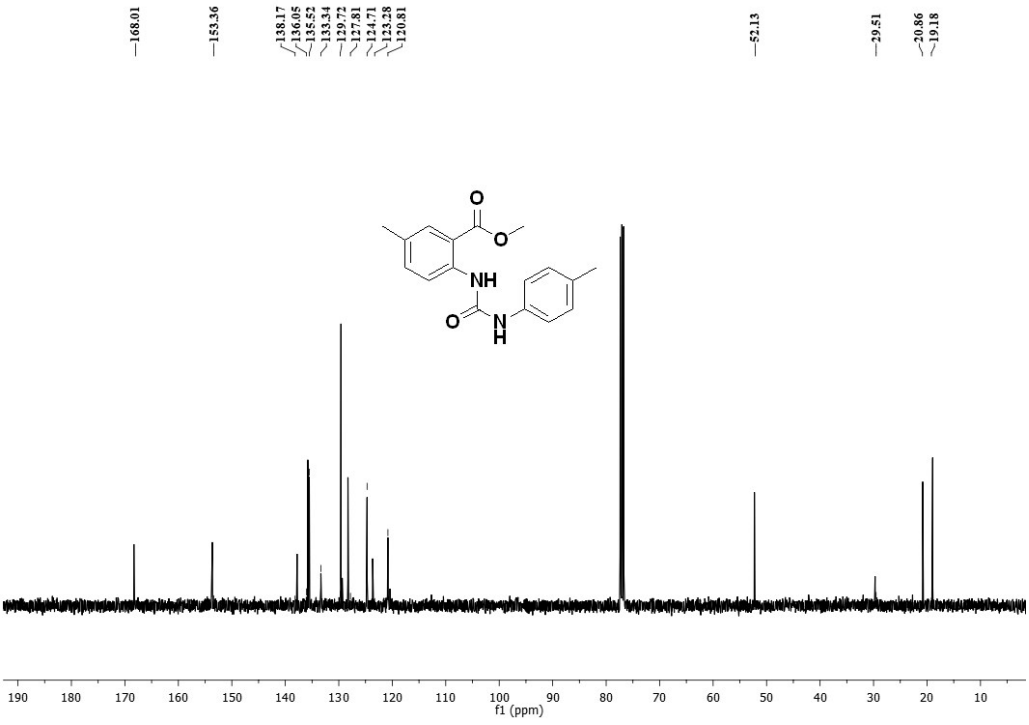


Figure FS58. ^{13}C NMR spectra of the complex **(6d).**

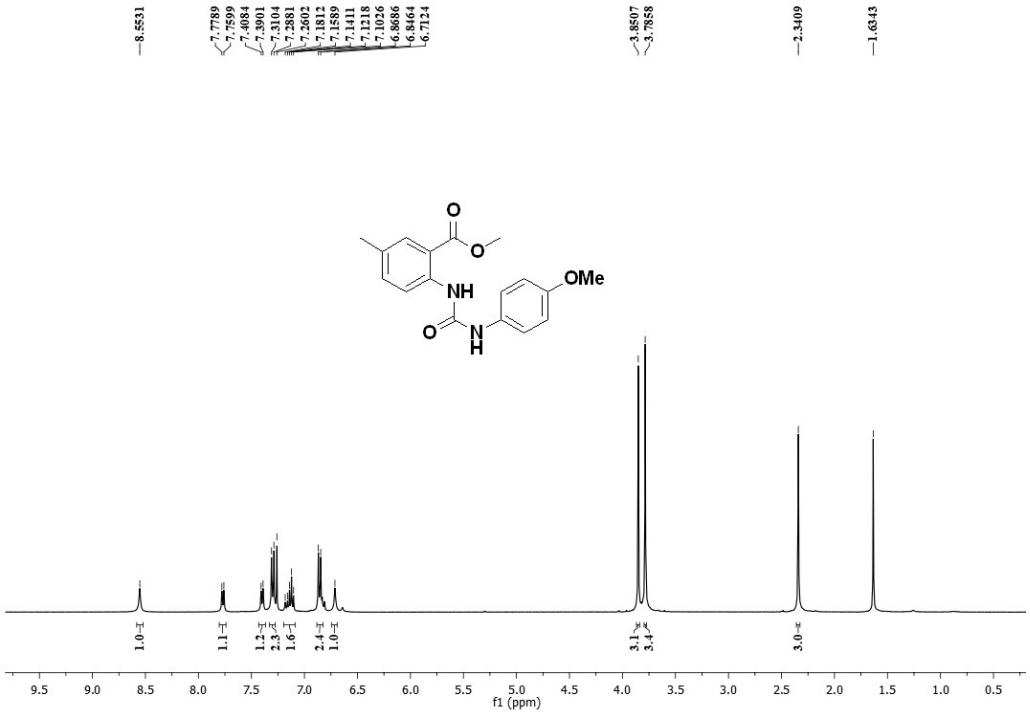


Figure FS59. ^{1}H NMR spectra of the complex **(6e).**

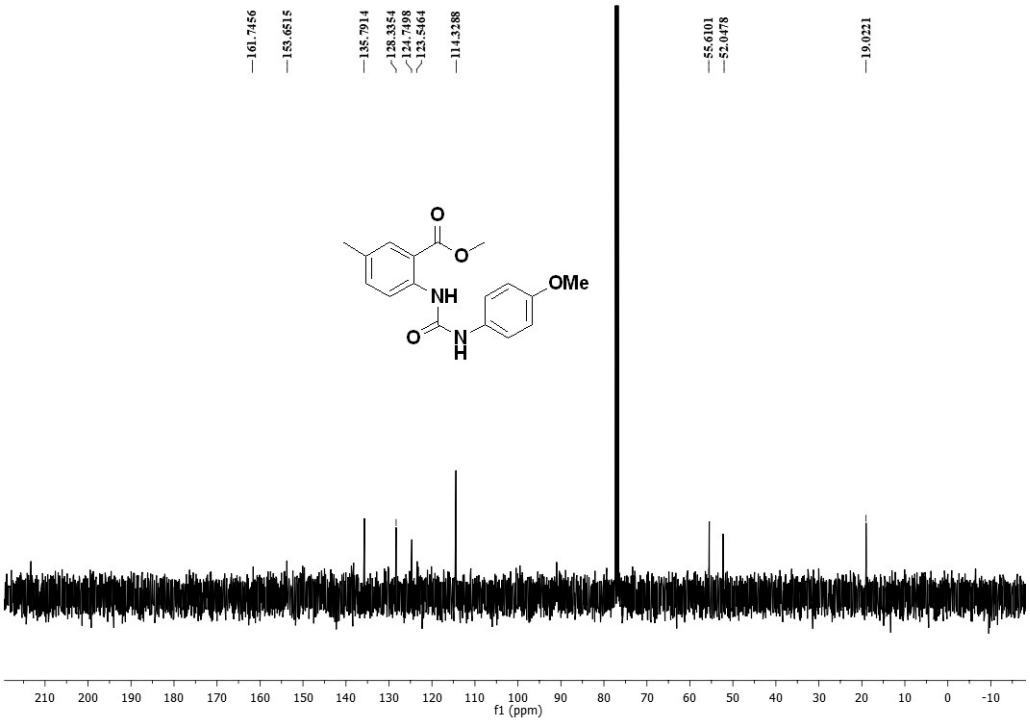


Figure FS60. ^{13}C NMR spectra of the complex **(6e).**

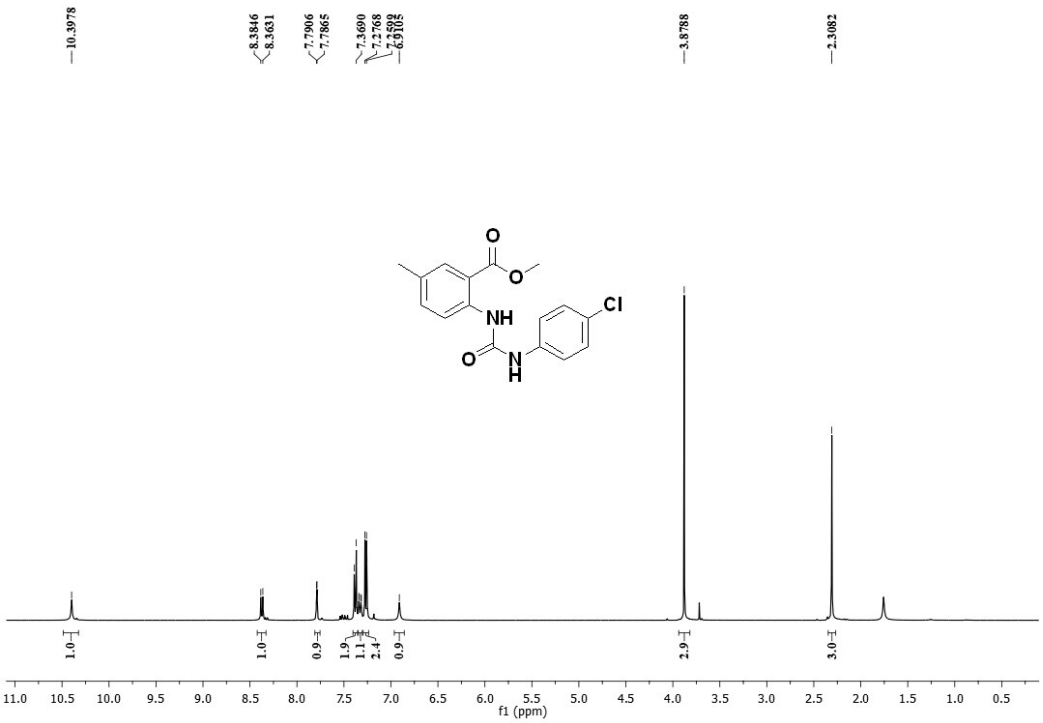


Figure FS61. [1]H NMR spectra of the complex **(6f).**

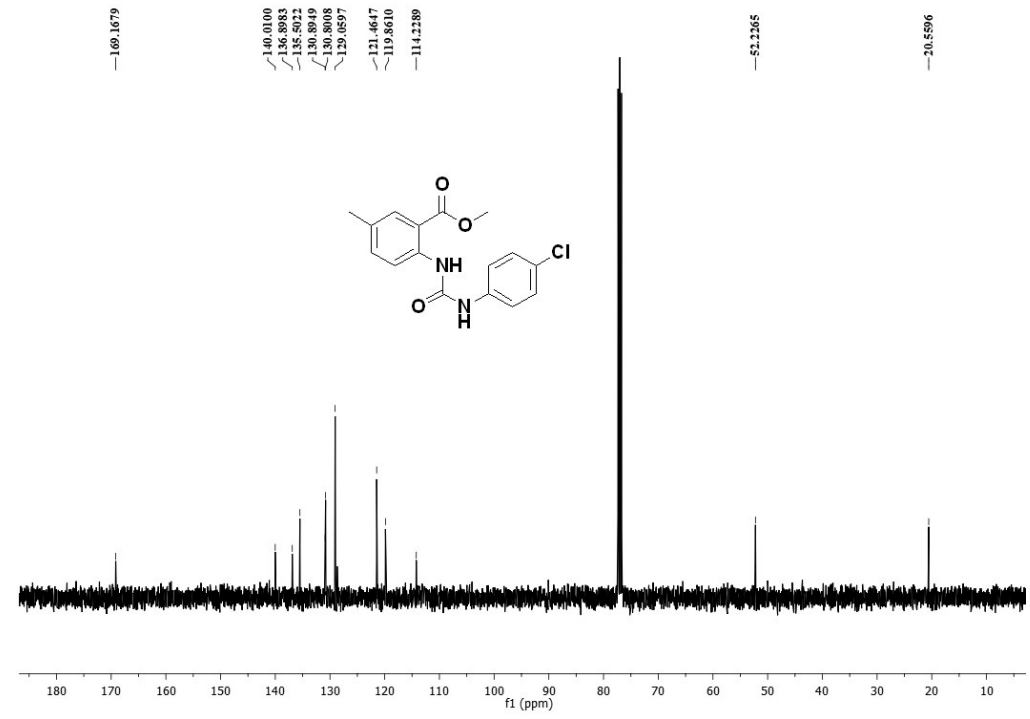


Figure FS62. [13]C NMR spectra of the complex **(6f).**

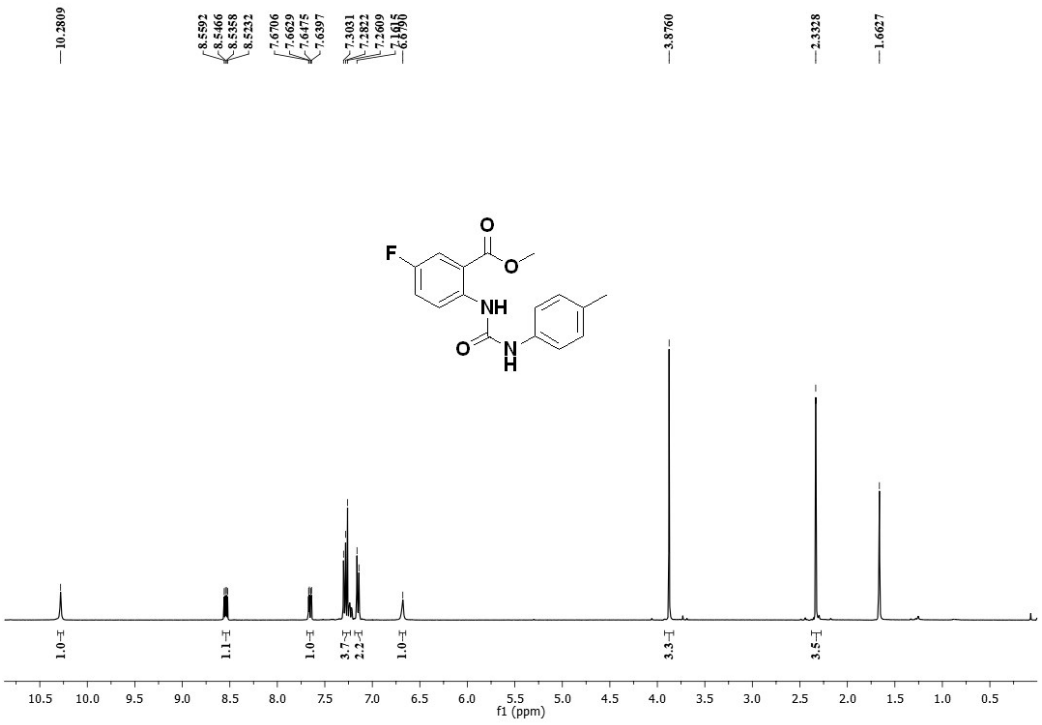


Figure FS63. [1]H NMR spectra of the complex **(6g).**

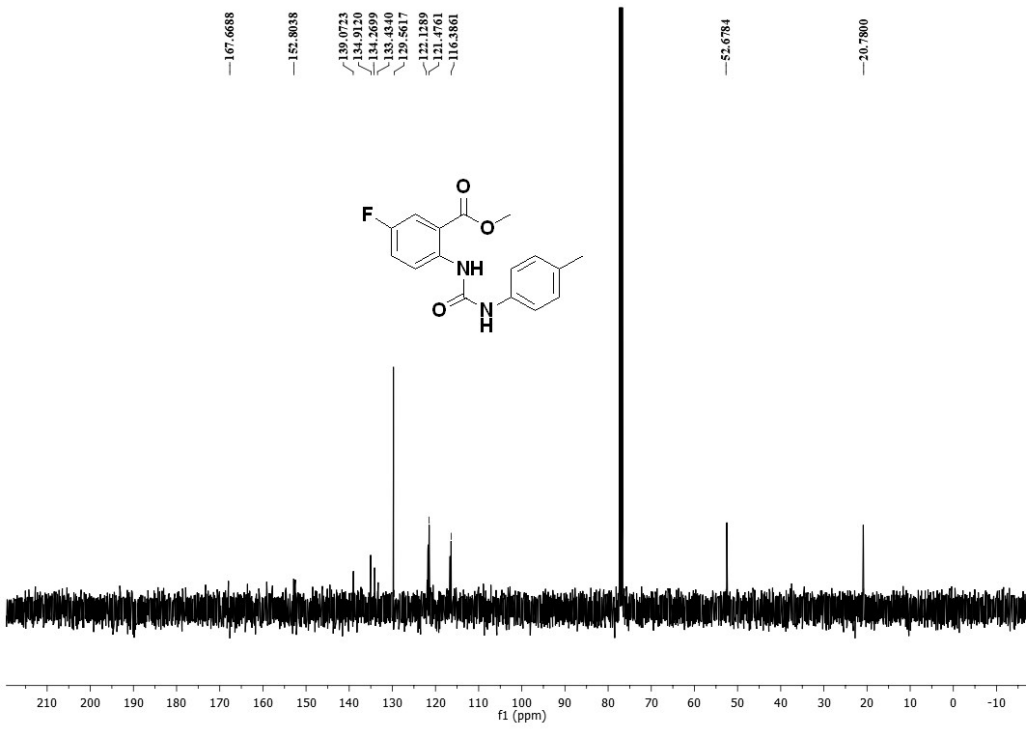


Figure FS64. [13]C NMR spectra of the complex **(6g).**

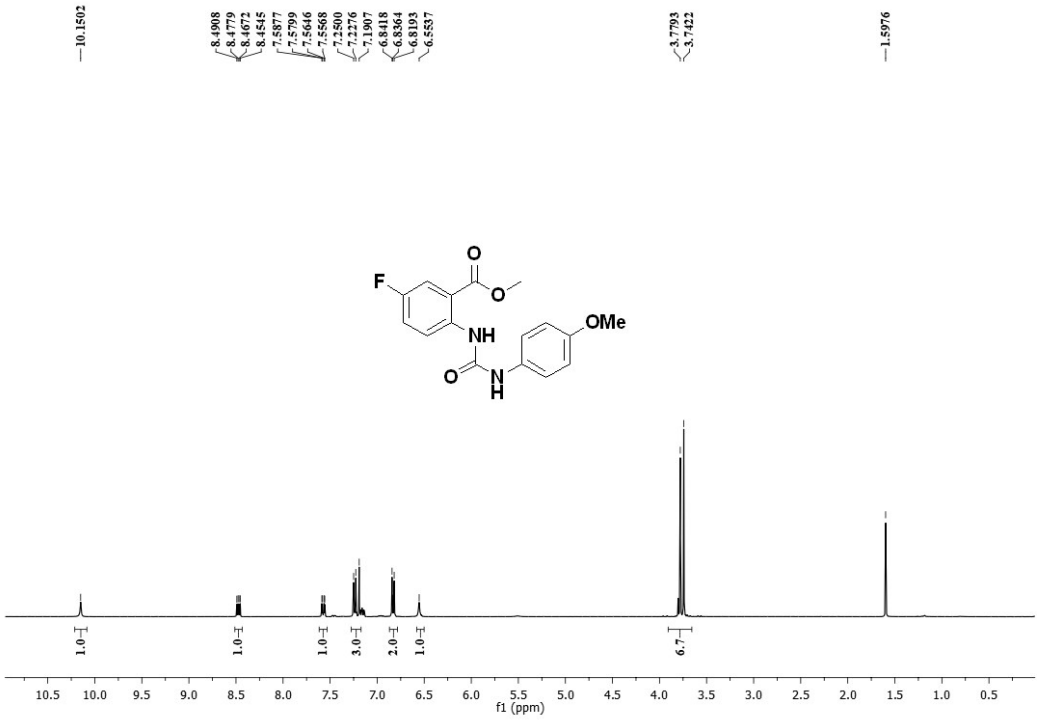


Figure FS65. [1]H NMR spectra of the complex **(6h).**

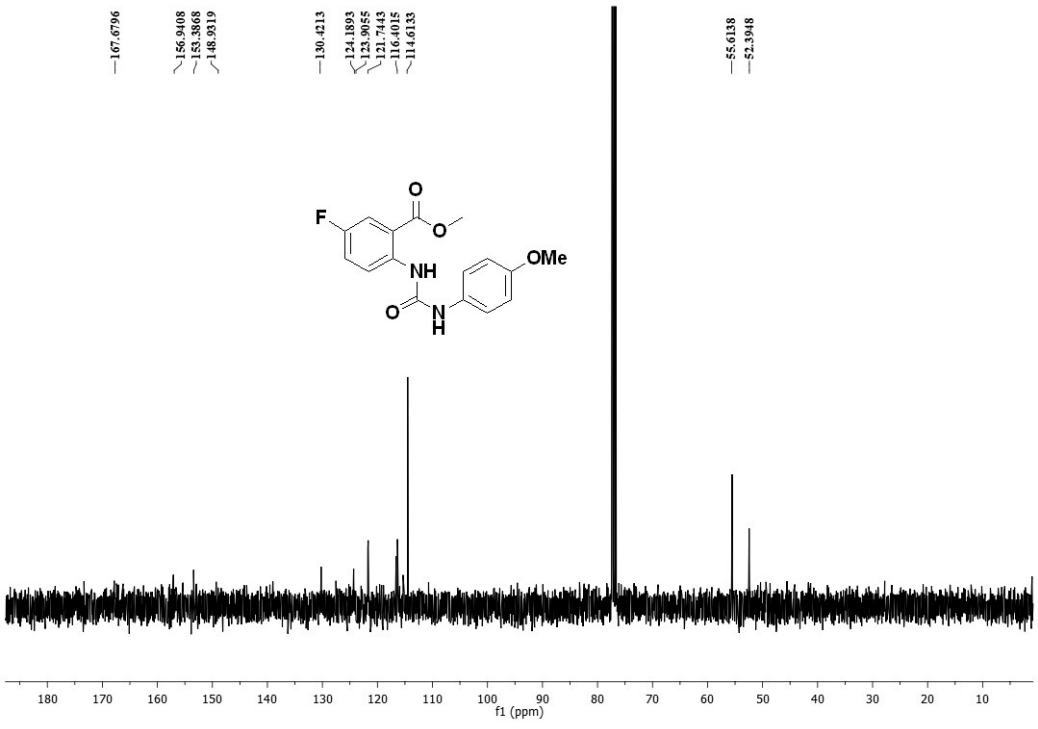


Figure FS66. [13]C NMR spectra of the complex **(6h).**

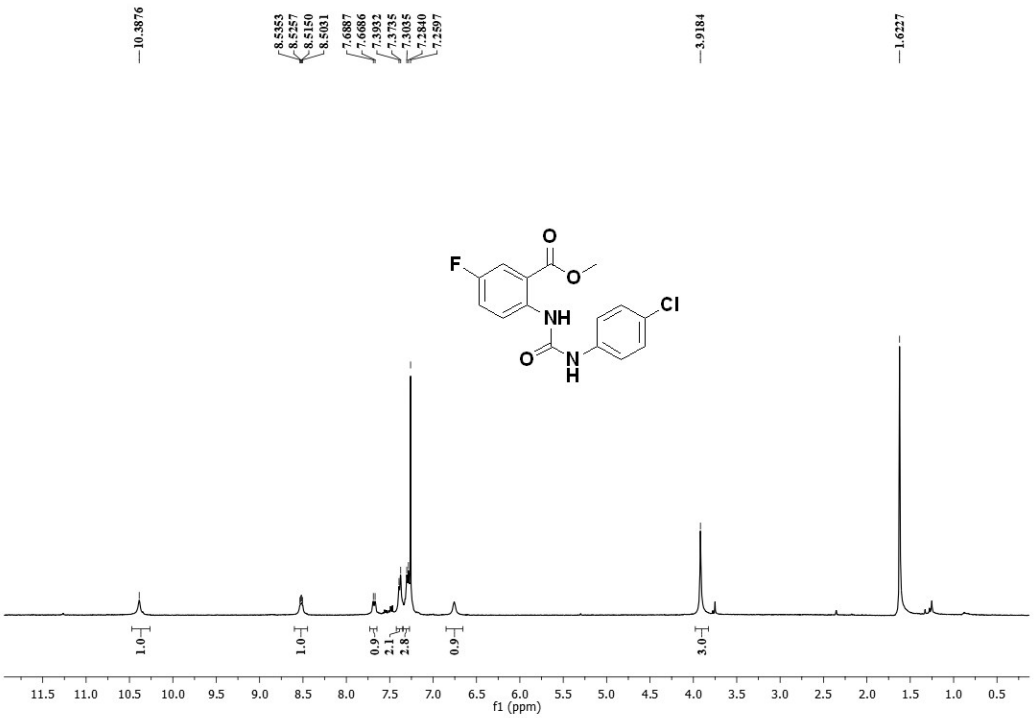


Figure FS67. [1]H NMR spectra of the complex **(6i).**

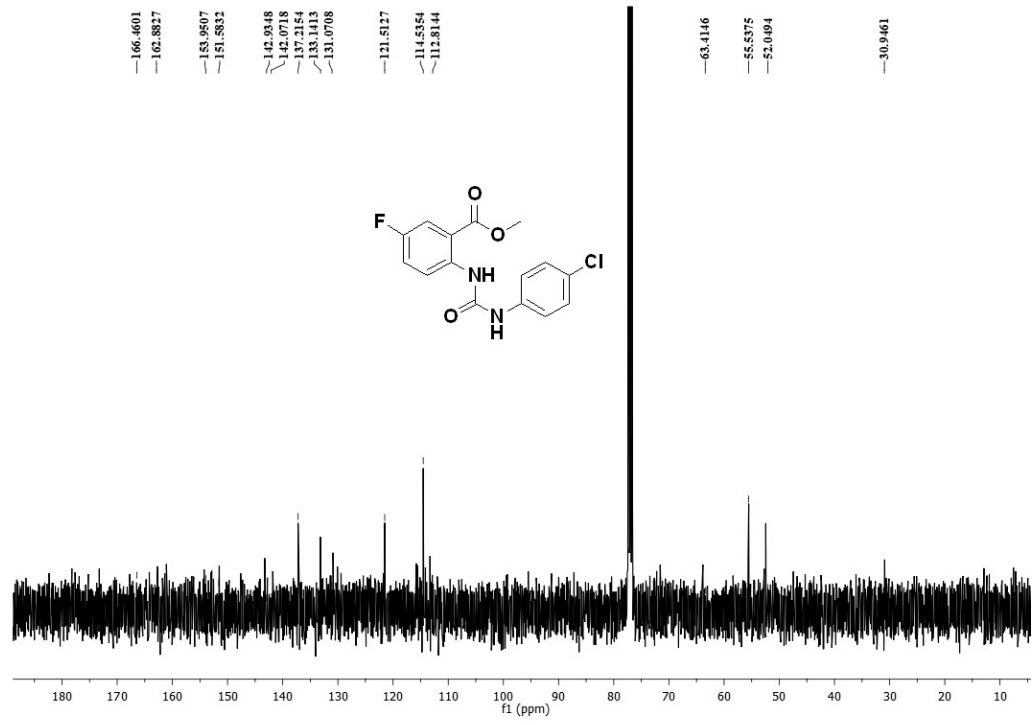


Figure FS68. [13]C NMR spectra of the complex **(6i).**

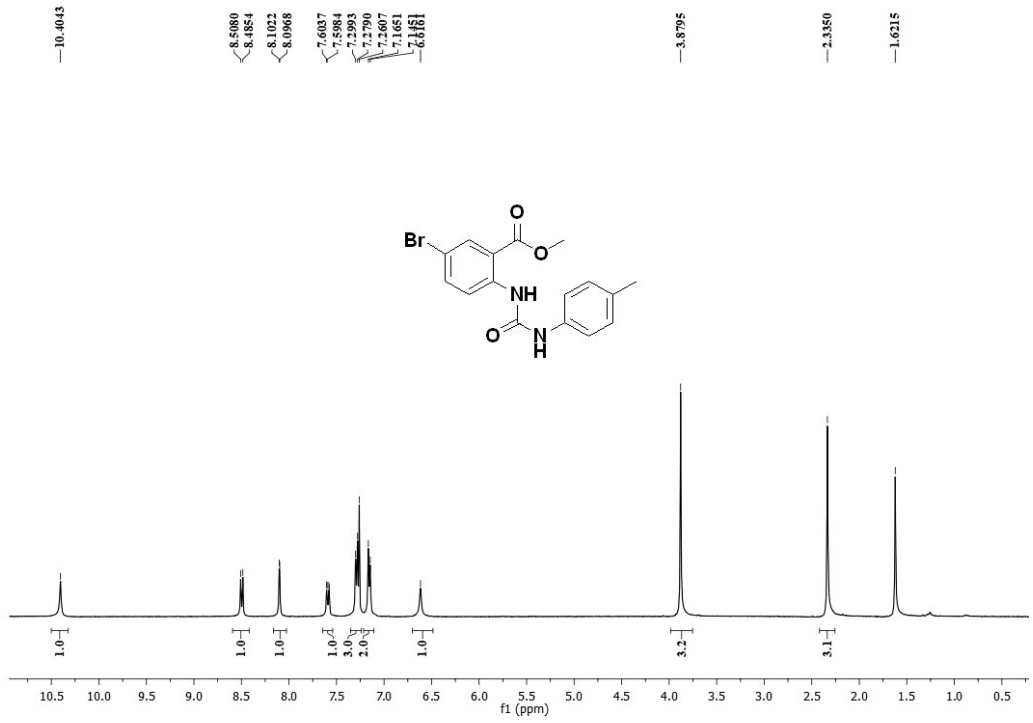


Figure FS69. [1]H NMR spectra of the complex **(6j).**

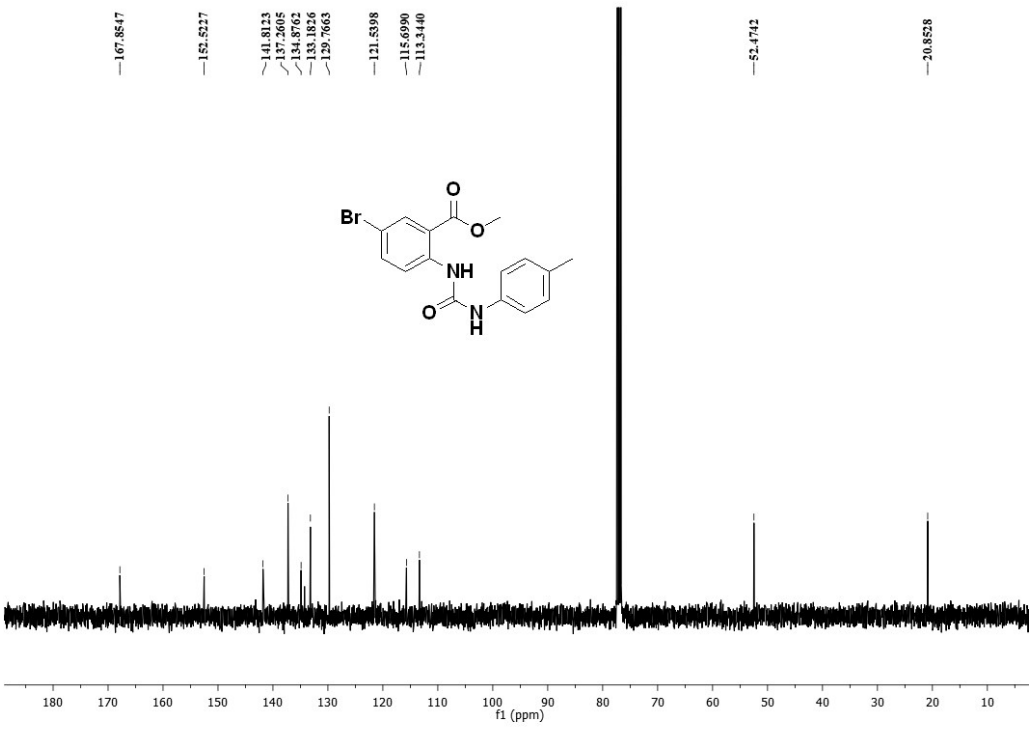


Figure FS70. [13]C NMR spectra of complex **(6j).**

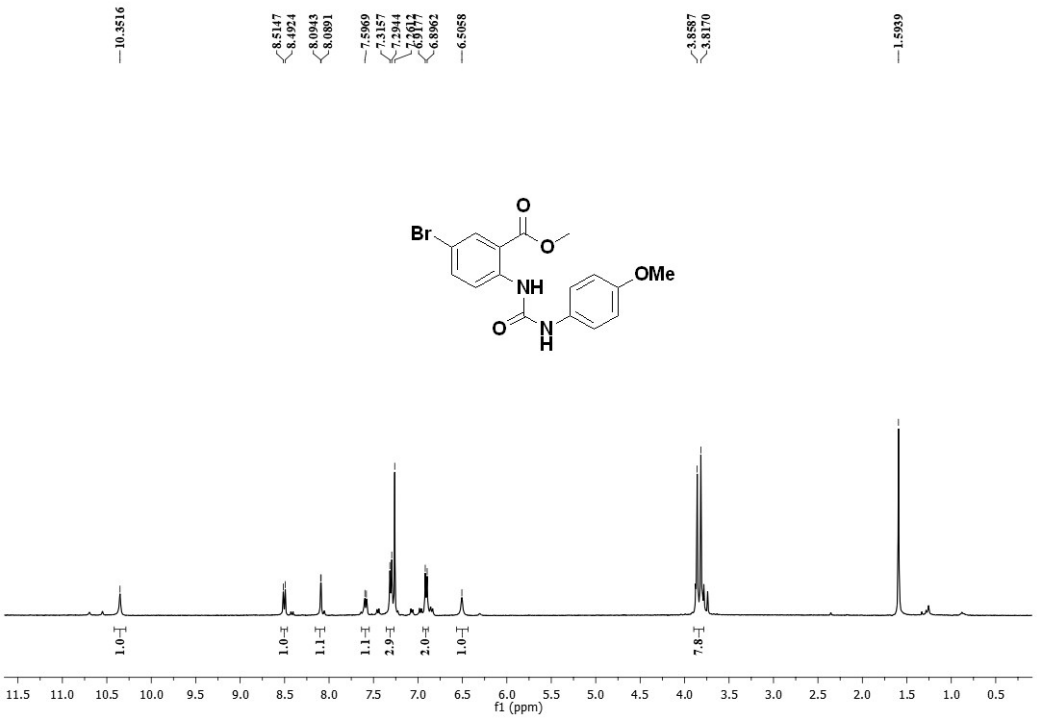


Figure FS71. [1]H NMR spectra of the complex **(6k).**

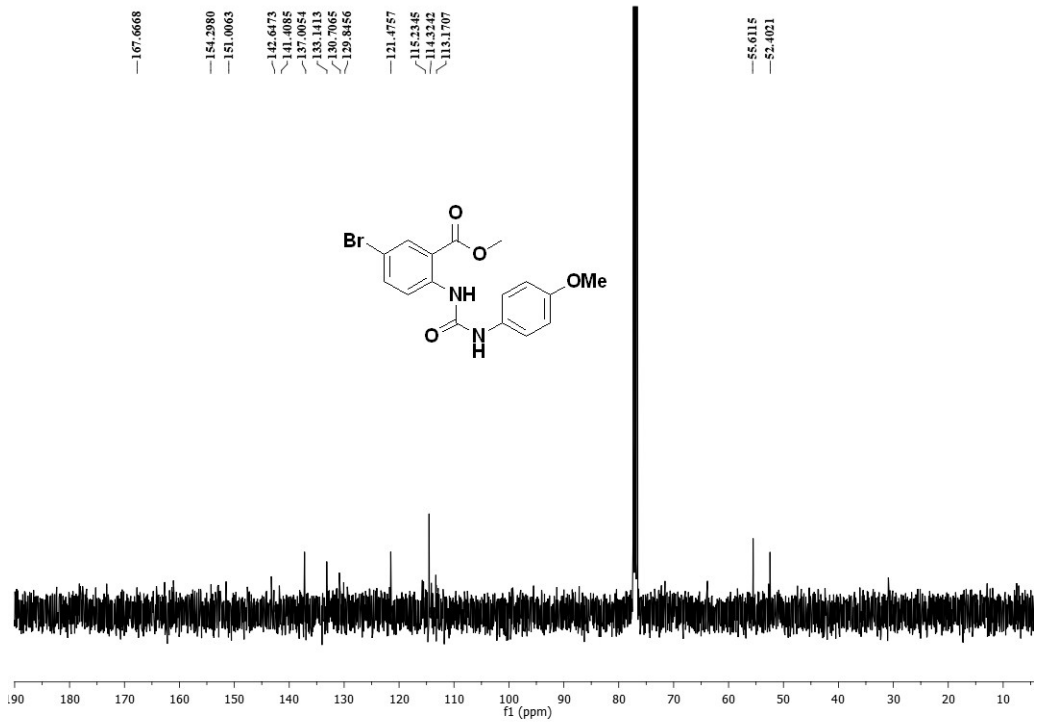


Figure FS72. [13]C NMR spectra of the complex **(6k).**

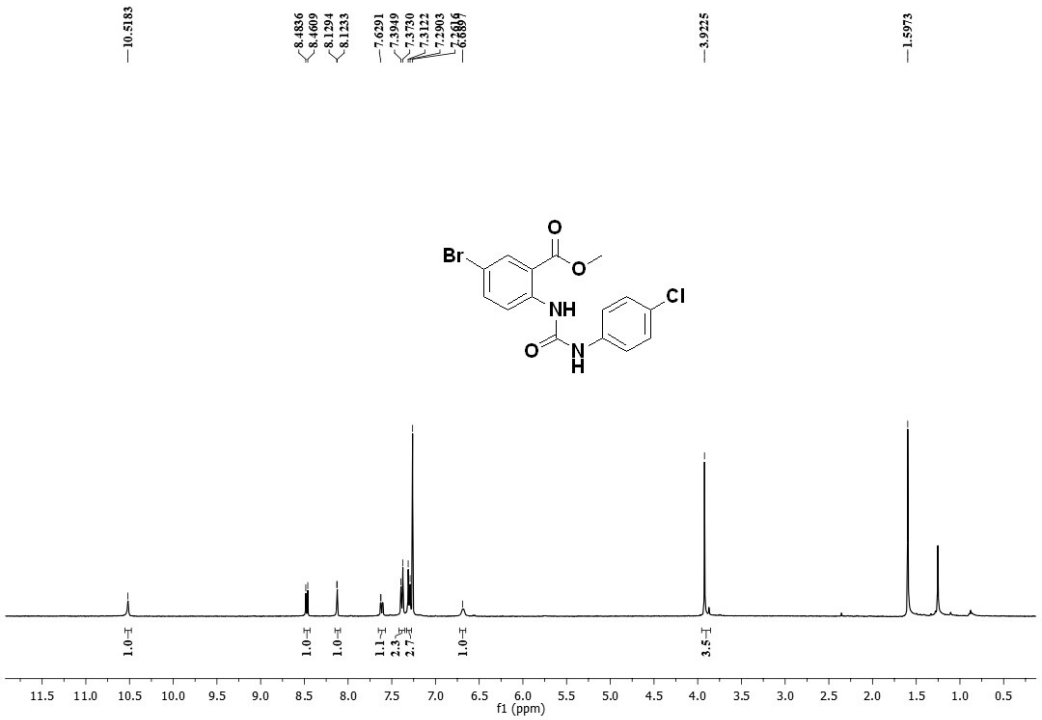


Figure FS73. [1]H NMR spectra of the complex **(6l).**

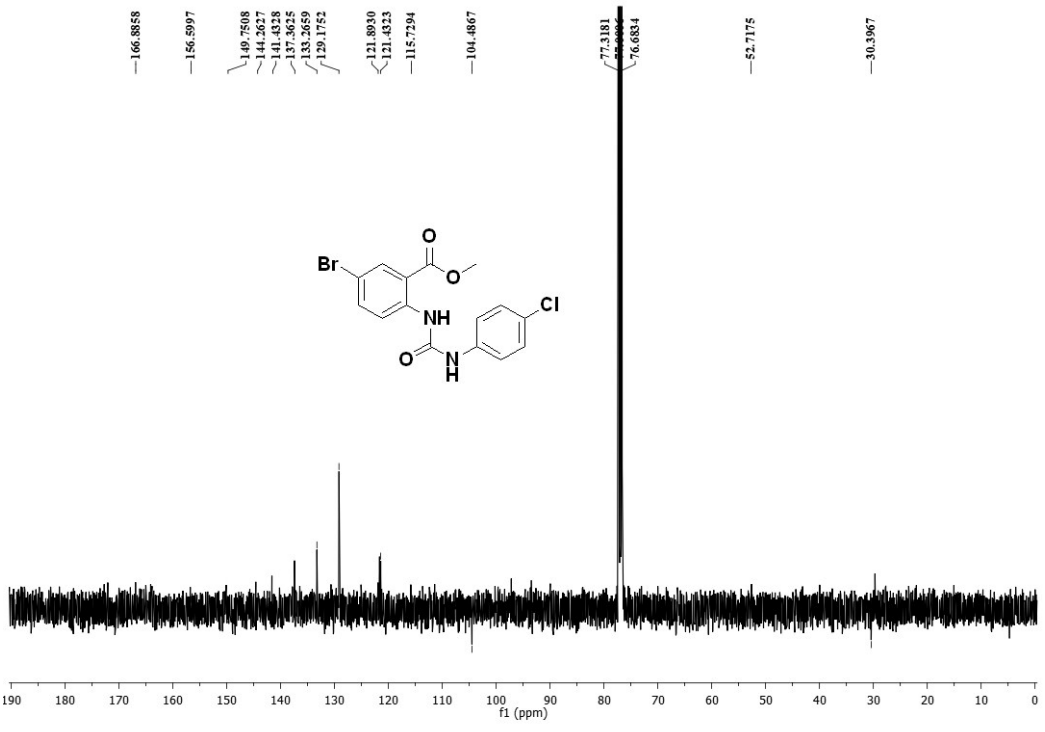


Figure FS74. [13]C NMR spectra of the complex **(6l).**

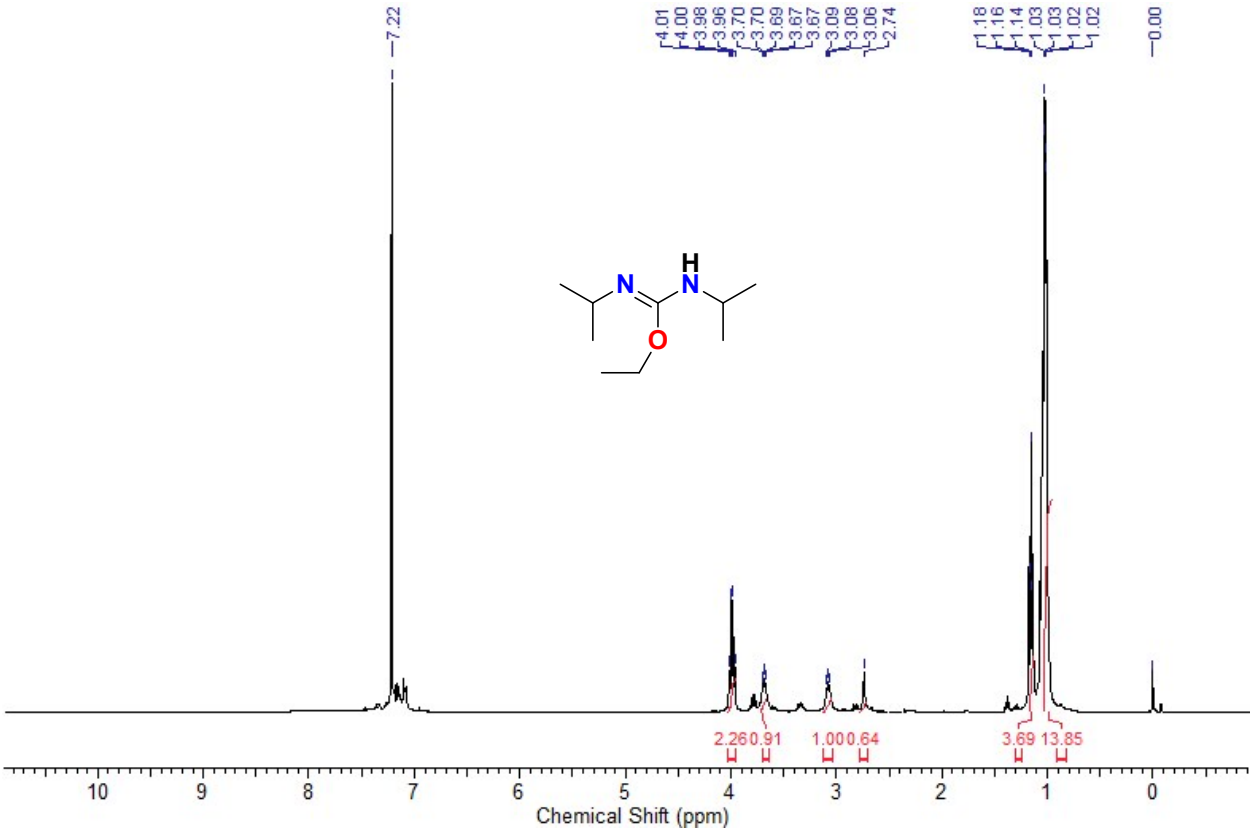


Figure FS75. ^{1}H NMR spectra of byproduct isourea species of DIC.

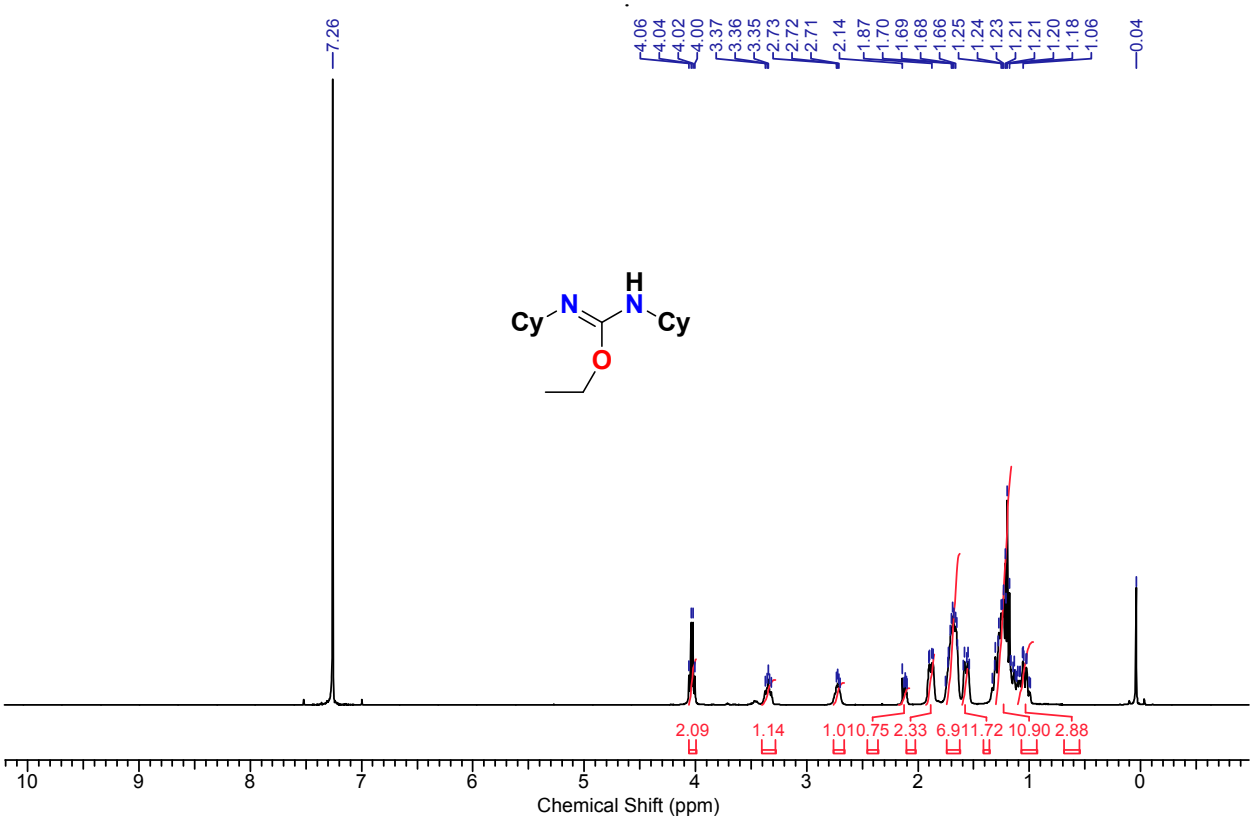


Figure FS76. [1]H NMR spectra of byproduct isourea species of DCC.

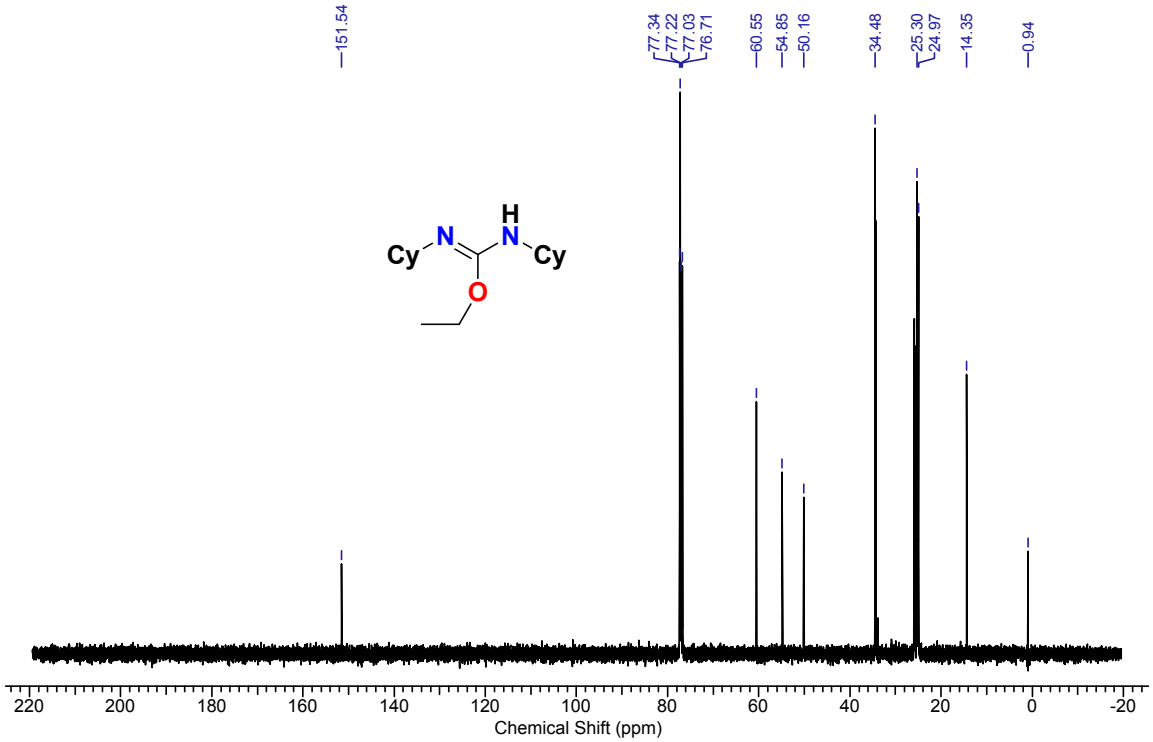


Figure FS77. [13]C NMR spectra of byproduct isourea species of DCC.

General Procedure for Kinetic NMR Experiments.

A typical kinetics study was conducted to establish the reaction order with respect to catalyst [κ^1-$(ImMesN)_2Ti(NMe_2)_2$] (**2b**). For kinetic ^1H NMR studies an NMR tube was loaded with the respective amount of complex **2b** (0.015, 0.02, 0.025, 0.03, 0.035 M) from a stock solution, ethyl 2-aminobenzoate (0.5 M) and N,N' diisopropylcarbodiimide (DIC) (1 M), $CDCl_3$ (0.4 mL) was added inside the glove box and the tube was sealed. The solution was set in the NMR tube at 90°C. At the indicated time intervals, the tube was analyzed by ^1H NMR. As expected, plots of ln[*o*-$NH_2PhCOOCH_2CH_3$]/ln[*o*-$NH_2PhCOOCH_2CH_3]_0$ vs. time for a wide range of catalyst [κ^1-$(ImMesN)_2Ti(NMe_2)_2$] are linear.(Fig FS78,). A plot of lnk_{obs} vs. ln[κ^1-$(ImMesN)_2Ti(NMe_2)_2$] (Fig FS79-80) is also linear, with slope 0.77 which indicate the rate law of the reaction follow first order dependence with respect to catalyst [κ^1-$(ImMesN)_2Ti(NMe_2)_2$].

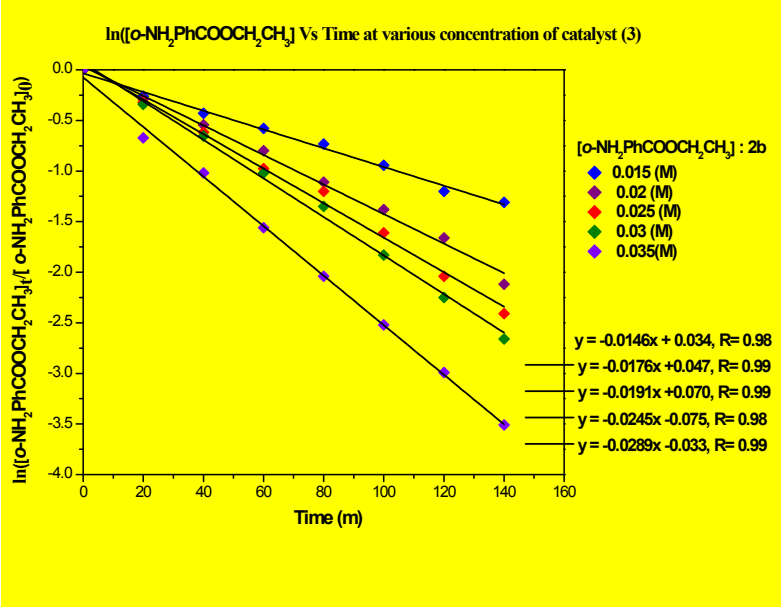


Figure **FS78**. Plots of ln[*o*-$NH_2PhCOOCH_2CH_3$] versus time for the Titanium (**2b**) catalysed [κ^1-$(ImMesN)_2Ti(NMe_2)_2$] reaction of *o*-$NH_2PhCOOCH_2CH_3$ and DIC at 90°C in $CDCl_3$ (0.4 ML). (1 equiv. of ethyl 2-aminobenzoate is present with respect to 2 equiv. DIC). The catalyst concentration was varied from 15 mM to 35 mM.

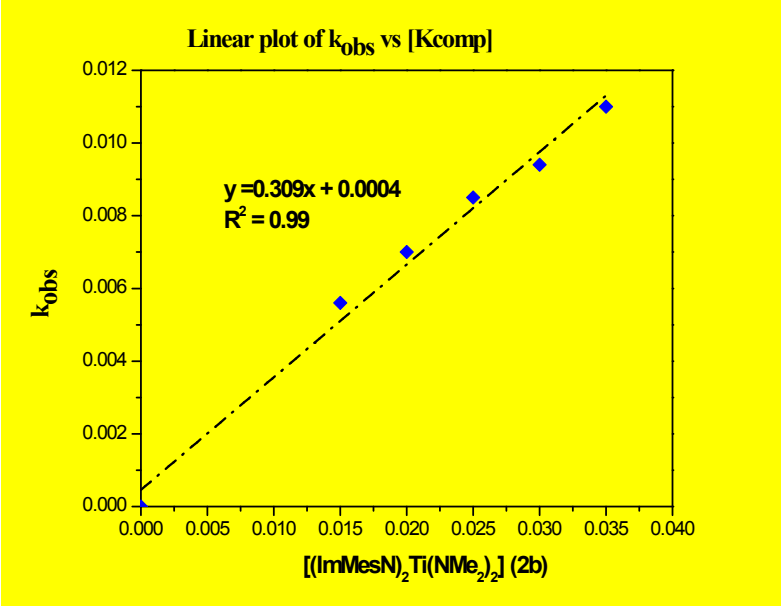


Figure **FS79**. Kinetics plots of k_{obs} vs [κ^1-(ImMesN)$_2$Ti(NMe$_2$)$_2$] for the reaction of [*o*-NH$_2$PhCOOCH$_2$CH$_3$] with [DIC] in presence of catalyst (**2b**) [κ^1-(ImMesN)$_2$Ti(NMe$_2$)$_2$]. Reaction conditions: [DIC] = 1.0 M and [*o*-NH$_2$PhCOOCH$_2$CH$_3$] =0.5 M, [κ^1-(ImMesN)$_2$Ti(NMe$_2$)$_2$] (**2b**) = [15 mM to 35 mM] in CDCl$_3$ (0.4 mL).

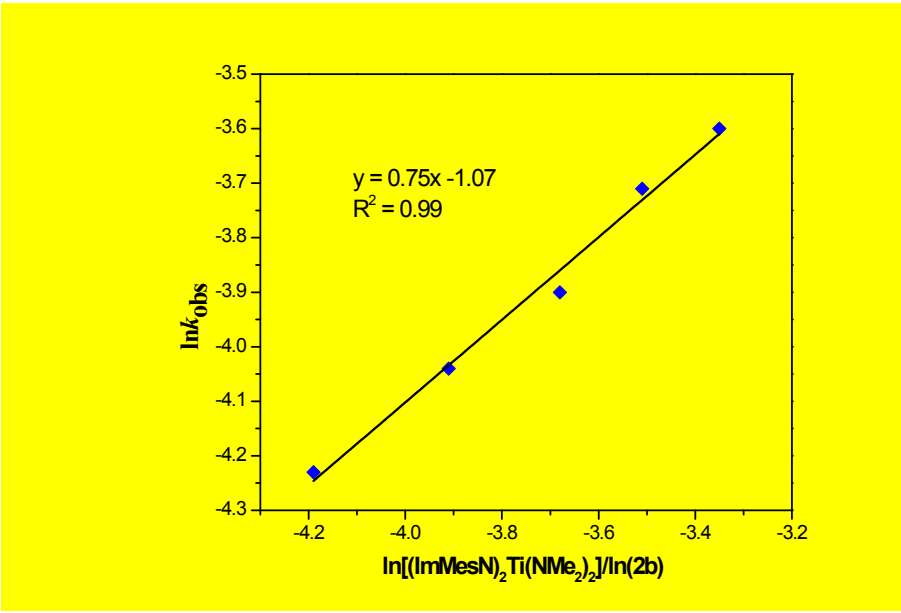


Figure F**S80**. Kinetics plots of lnk_{obs} vs ln[κ^1-(ImMesN)$_2$Ti(NMe$_2$)$_2$](**2b**) for the reaction of [*o*-NH$_2$PhCOOCH$_2$CH$_3$] with [DIC] in presence of catalyst (**2b**) [κ^1-(ImMesN)$_2$Ti(NMe$_2$)$_2$].

Reaction conditions: [DIC] = 1.0 M and [*o*-$NH_2PhCOOCH_2CH_3$]=0.5 M, [κ^1-$(ImMesN)_2Ti(NMe_2)_2$](**2b**) = [15 mM to 35 mM] in $CDCl_3$ (0.4 mL).

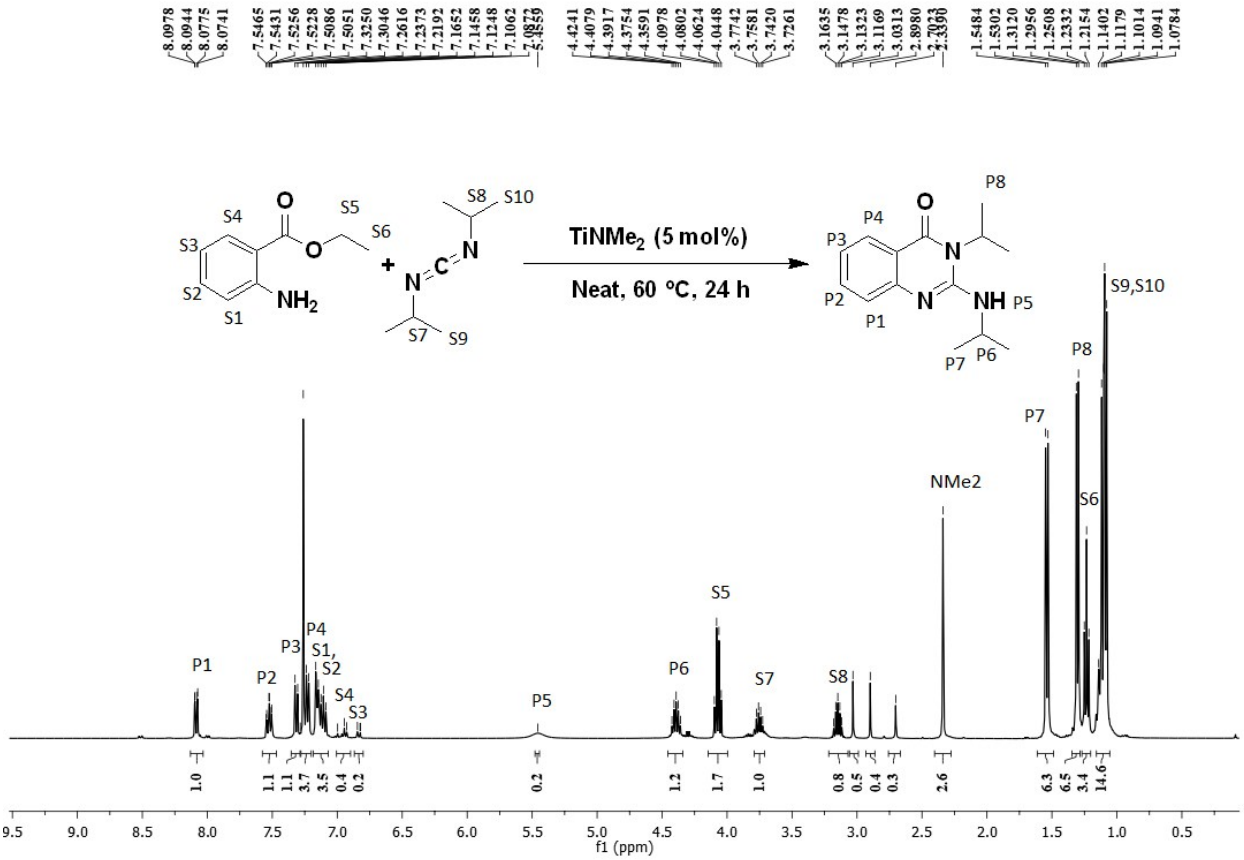


Fig FS81: ^{1}H NMR for amino ester with DIC (1:2), in presence of [$Ti(NMe_2)_4$] 5 mol% in catalytic amount in 60 °C, 24 h, neat condition measured in $CDCl_3$ as NMR solvent.

Reference.

1. A. Altomare, M. C. Burla, G. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr*. 1994, **27**, 435-436.
2. G. M. Sheldrick, *Acta Crystallogr. Sect. A*: 2008, ***A64***, 112-122.
3. T. Ishikawa and T. Kumamoto, *Synthesis*, 2006, 737–752.
4. R. J. Batrice and M. S. Eisen *Chem. Sci.*, 2016, **7**, 939–944.
5. H. Liu, N. Fridman, M. Tamm and M. S. Eisen *Organometallics*, 2017, **36**, 3896–3903.

6. I. S. R. Karmel, M. Tamm and M. S. Eisen, *Angew. Chem. Int. Ed.* 2015, **127**, 12599-12602.
7. R. J. Batrice, C. E. Kefalidis, L. Maron and M. S. Eisen, *J. Am. Chem. Soc*., 2016, **138** , 2114–2117.