iClick reactions of square-planar palladium(II) and platinum(II) azido complexes with electron-poor alkynes: Metal-dependent preference for N1 *vs*. N2 triazolate coordination and kinetic studies with ^{1}H and ^{19}F NMR spectroscopy

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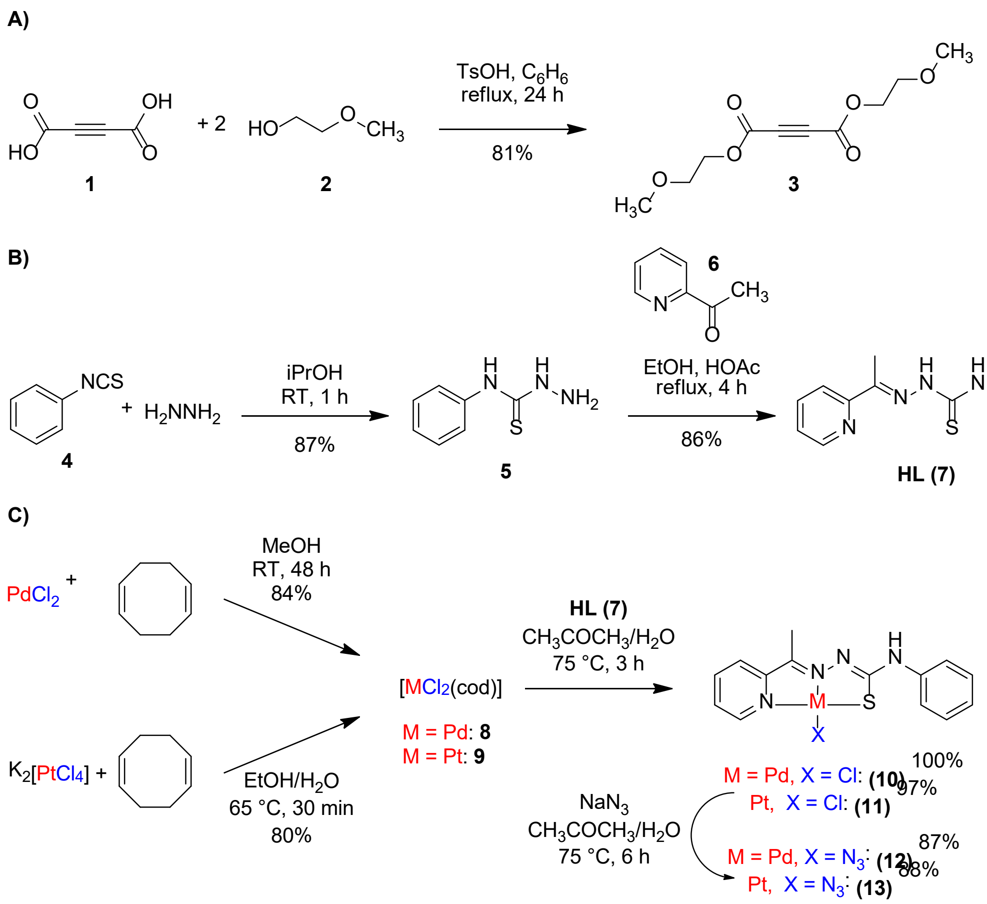
* ulrich.schatzschneider@uni-wuerzburg.de

Supporting Information



Scheme S1. Synthesis of ligand and metal complex precursors: A) alkyne **3**, B) ligand **HL** (**7**), and C) palladium(II) and platinum(II) complexes **8**–**13** (cod = 1,5-1,5-cyclooctadiene).

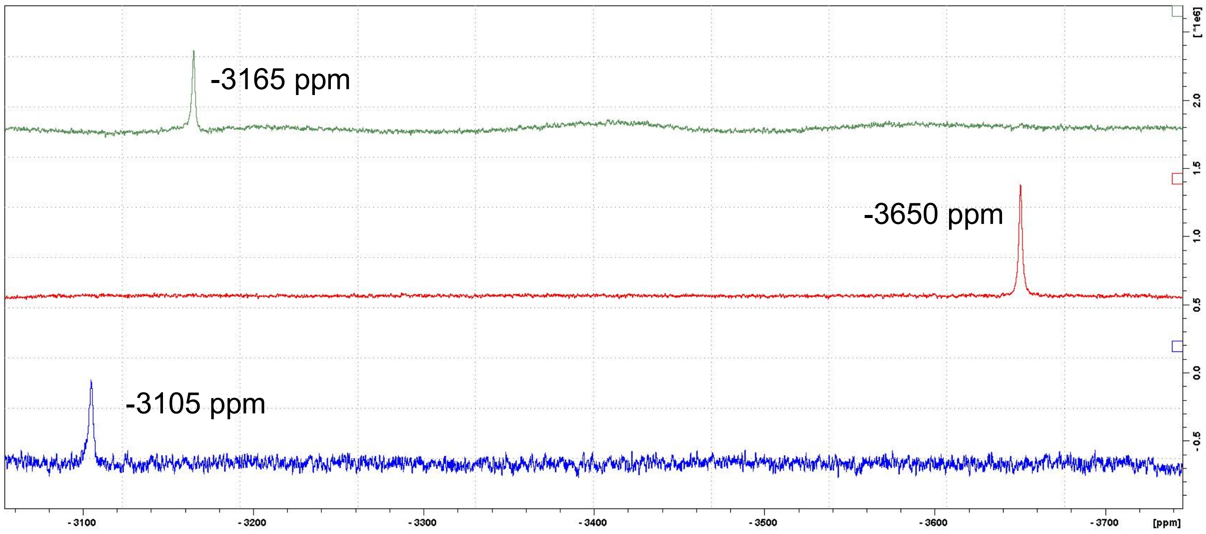


Figure S1. 107.51 MHz ^{195}Pt NMR in DMSO-d_6 solution of (top) [PtCl(L)] (**11**, green trace) and (centre) [Pt(L)(dmso)]OTf (red trace) recorded immediately after dissolution as well as (bottom) [Pt(L)(triazolate^{COOCH3,COOCH3}-N^2)] (**25**, blue trace) obtained after heating a solution of [Pt(L)(triazolate^{COOCH3,COOCH3}-N^1)] (**22**) to 50 °C for 2 d.

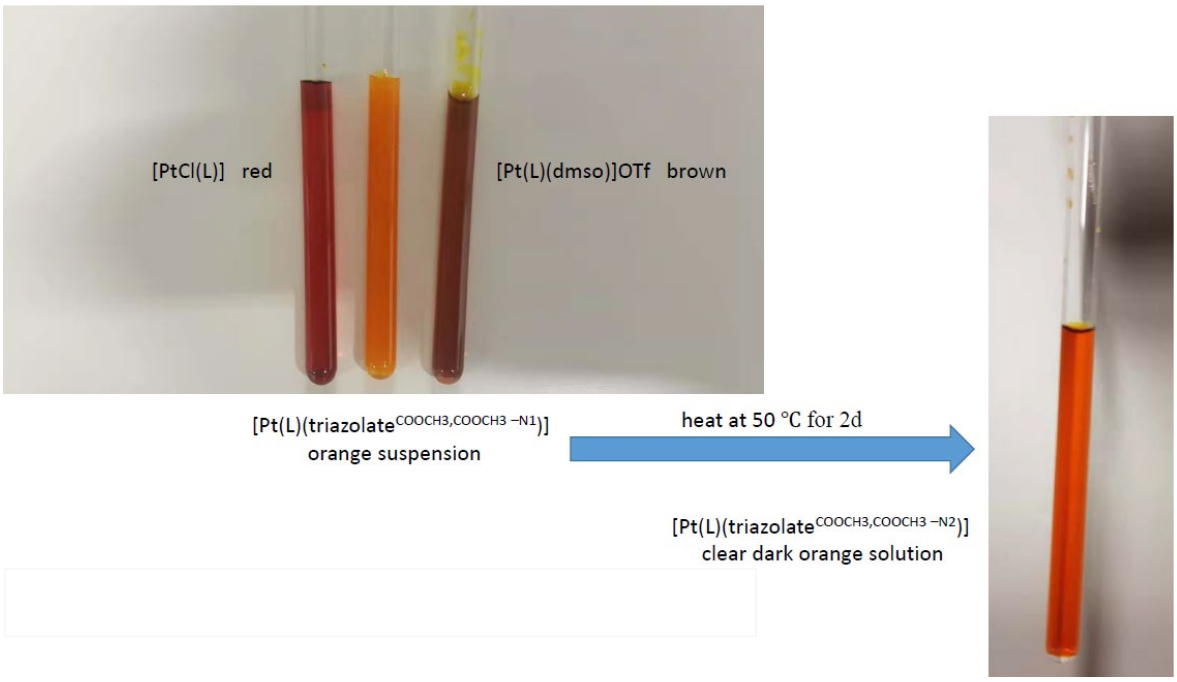
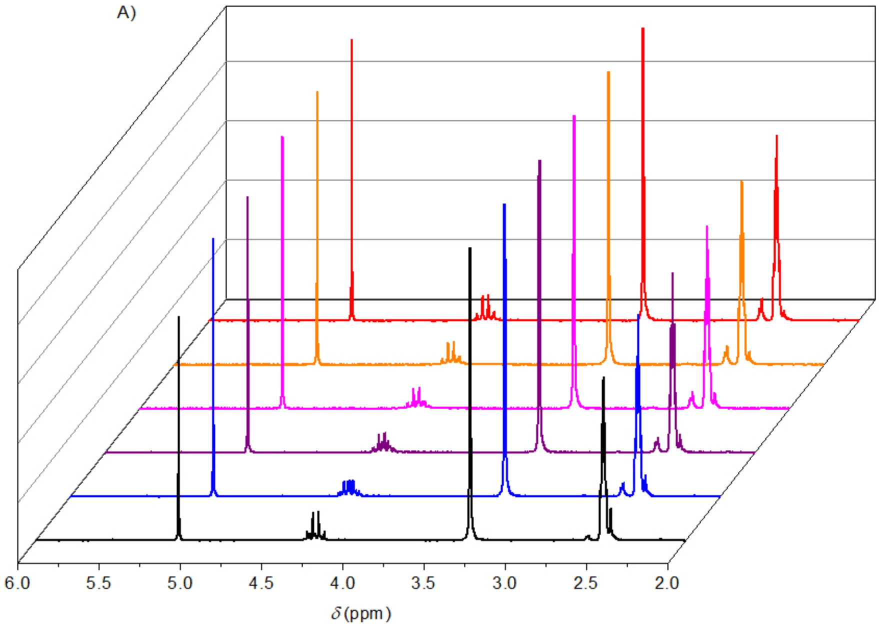


Figure S2. Colours of NMR samples of (left) complexes [PtCl(L)] **11**, [Pt(L)(triazolate^{COOCH3,COOCH3}-N^1] **22**, and [Pt(L)(dmso)]OTf immediately after dissolution in DMSO-d_6, and (right) of [Pt(L)(triazolate^{COOCH3,COOCH3}-N^2] **25** obtained after heating a solution of **22** to 50 °C for 2 d.



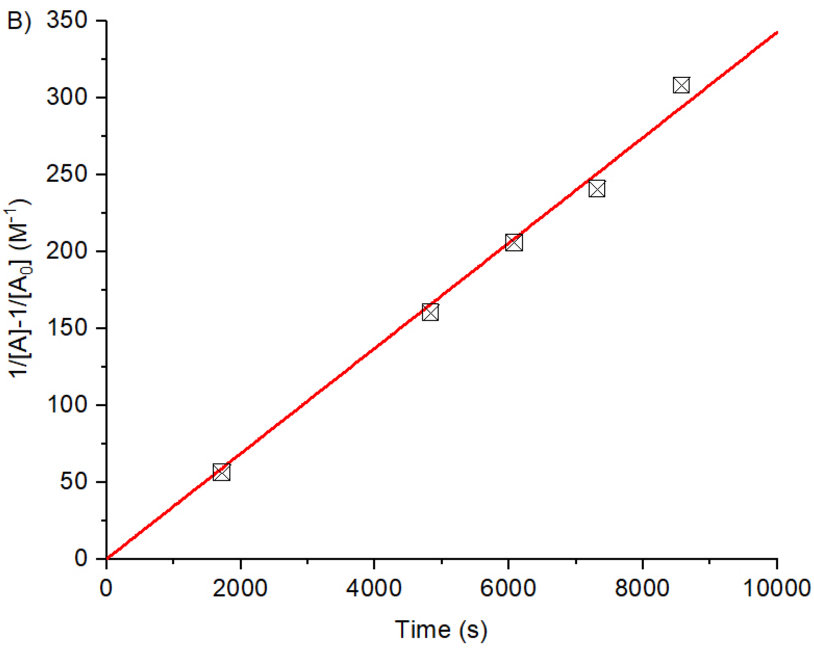


Figure S3. A) Changes in the 200 MHz [1]H NMR spectra of a mixture of platinum(II) azido complex **13** (6.7 mM), diethyl acetylene dicarboxylate (**16** (DEAD), 6.7 mM), and 1,3,5-trioxane (6.7 mM) in DMSO-d_6 at room temperature for up to 2.5 h and B) linear fit of the change of the intensity of the semithiocarbazone methyl proton signal at 2.46 ppm in the azido complex **13** to the second order rate law (see main text for details). Due to a lag time between mixing of the reactants and recording of the first spectrum, no data was collected during the initial 5 min.

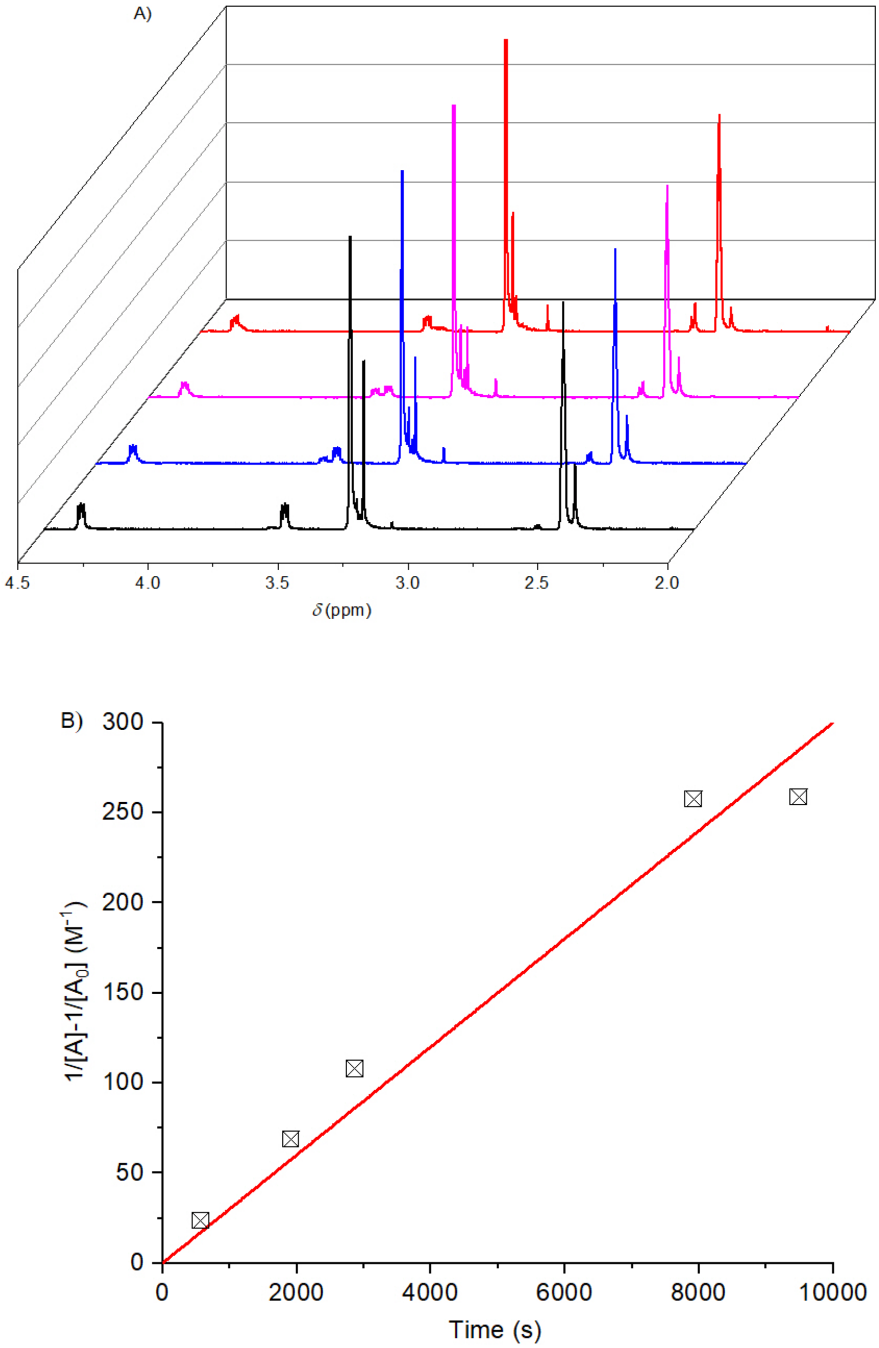
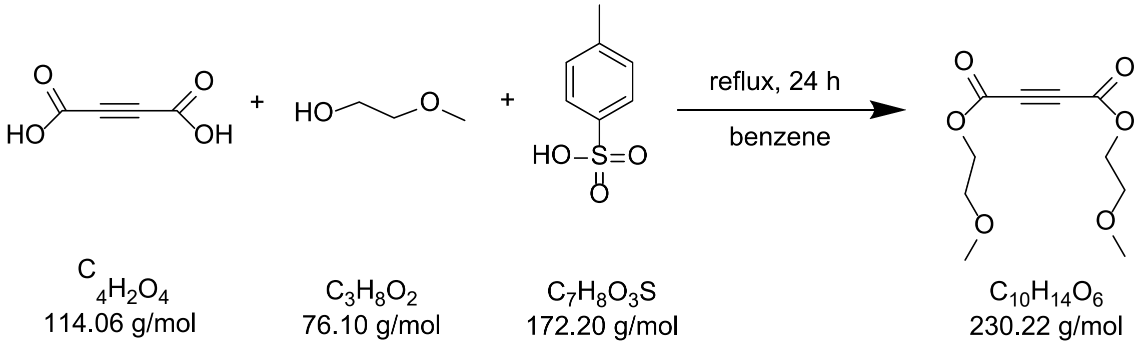


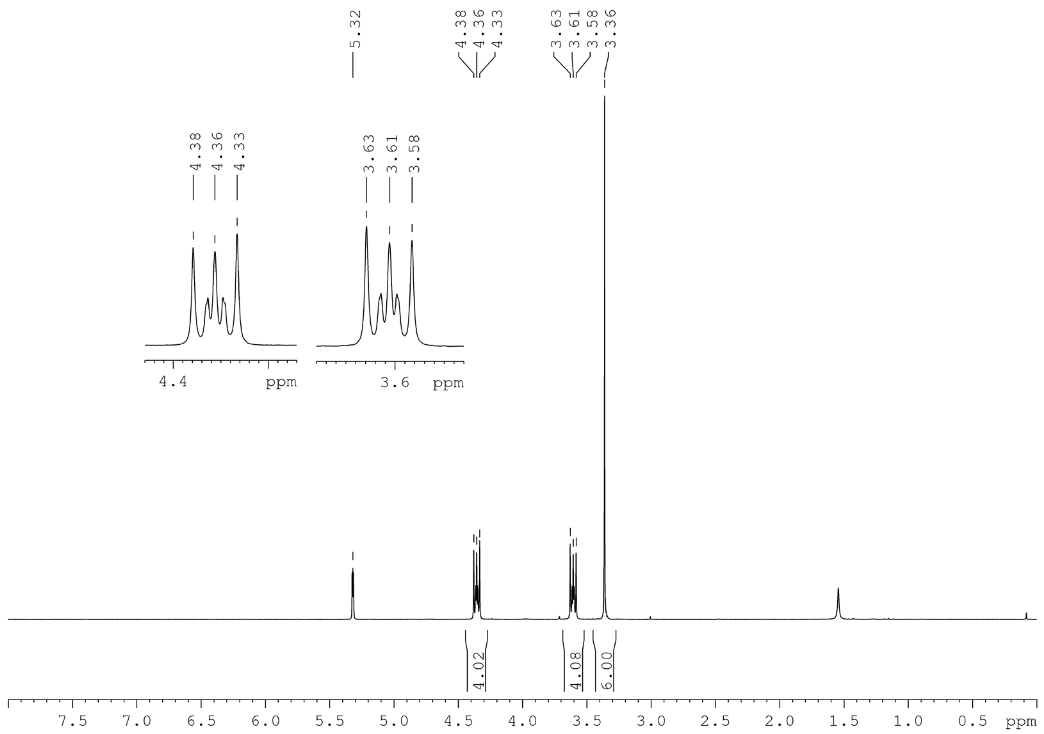
Figure S4. A) Changes in the 400 MHz ^{1}H NMR spectra of a mixture of platinum(II) azido complex **13** (6.7 mM), 2-butynedioic acid 1,4-bis(2-methoxyethyl) ester (**3**, 6.7 mM), and 1,3,5-trioxane (6.7 mM) in DMSO-d_6 at room temperature for up to 2.5 h and B) linear fit of the change of the intensity of the semithiocarbazone methyl proton signal at 2.46 ppm in the azido complex **13** to the second order rate law (see main text for details). Due to a lag time between mixing of the reactants and recording of the first spectrum, no data was collected during the initial 5 min.

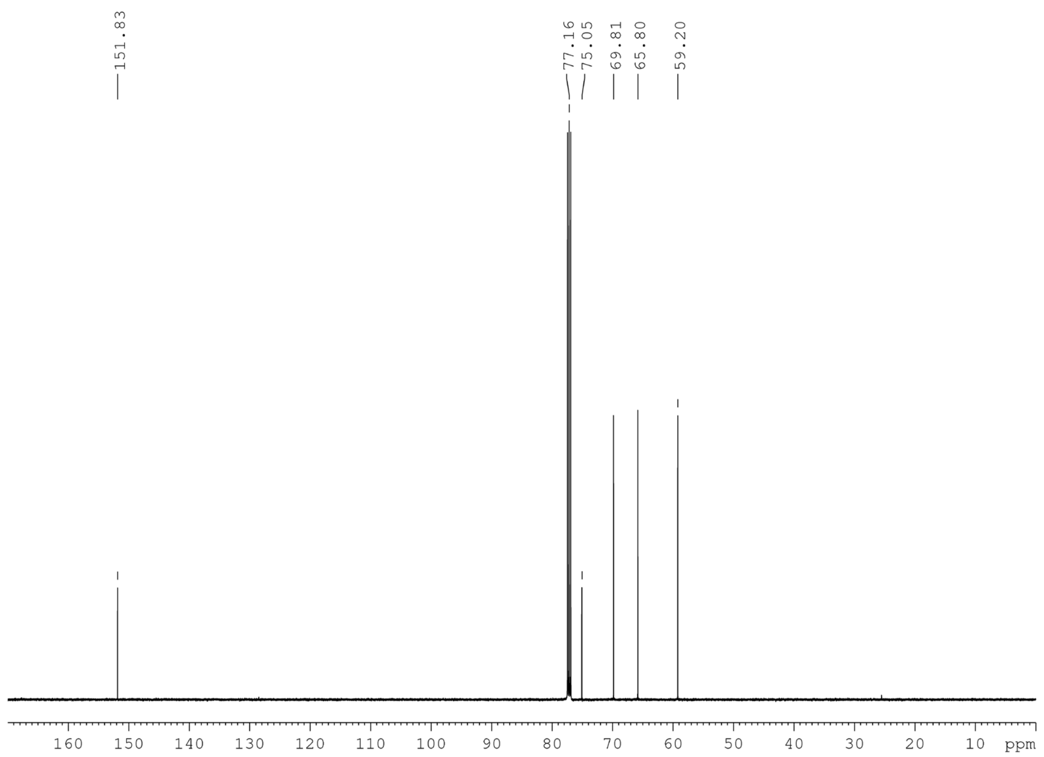
1. Synthesis of ligands and metal complex precursors

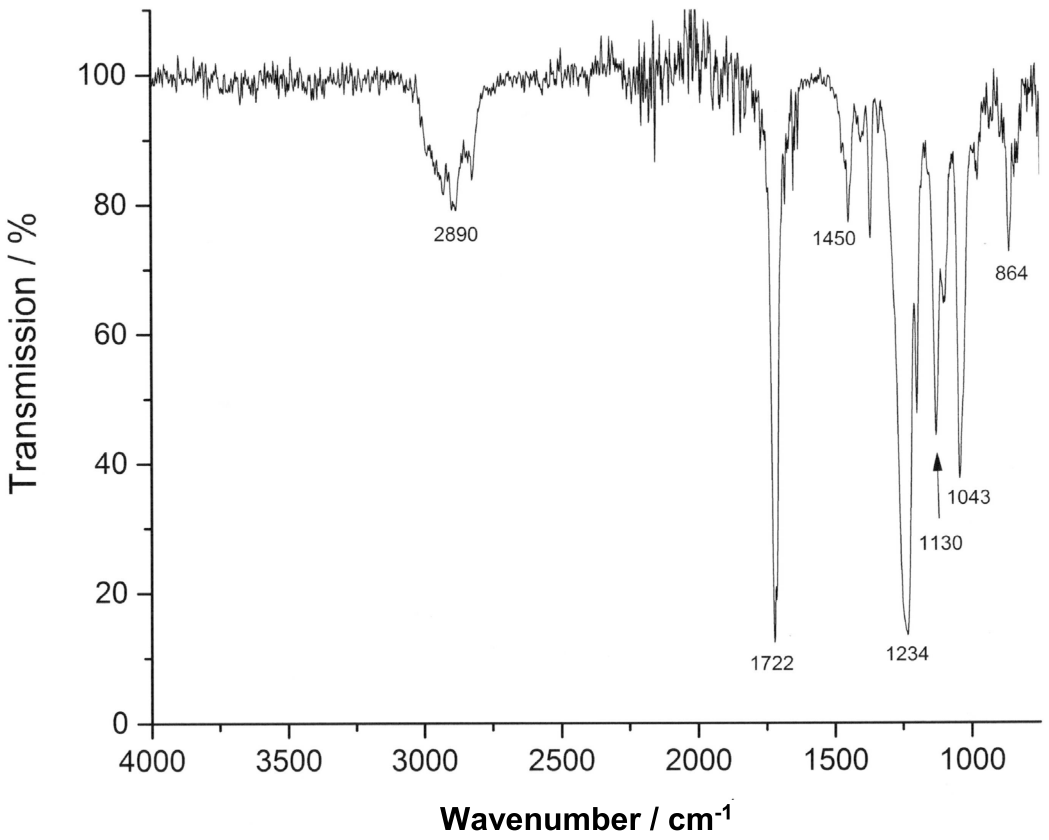
1.1 Synthesis of 2-butynedioic acid 1,4-bis(2-methoxyethyl) ester (3)



Acetylenedicarboxylic acid (2.00 g, 17.5 mmol) was suspended in benzene (35 mL) in a one-neck flask. Then, 2-methoxyethanol (3 mL, 2.90 g, 38.1 mmol) and *p*-toluene sulfonic acid monohydrate (334 mg, 1.8 mmol) were added. The suspension was heated to reflux for 24 h, during which the acetylene dicarboxylic acid dissolved. Then, the solution was cooled to room temperature and the solvent completely removed under vacuum. The resulting residue was dissolved in diethyl ether (40 mL) and washed with saturated aqueous sodium hydrogen carbonate solution (5 mL) and water (5 mL). The organic phase was dried over sodium sulphate and the solvent removed under vacuum to give the product as a colourless oil. Yield: 81% (3.24 g, 14.1 mmol). **IR** (ATR): $\tilde{\nu}$ = 2890, 1722, 1450, 1234, 1130, 1043, 864 cm^{-1}; **^{1}H NMR** (200.13 MHz, CD_2Cl_2): δ = 4.38–4.33 (m, 4H, $OCH_2CH_2OCH_3$), 3.63–3.58 (m, 4H, $OCH_2CH_2OCH_3$), 3.36 (s, 6H, OCH_3) ppm; **^{13}C NMR** (125.76 MHz, $CDCl_3$): δ = 151.83 (*C*=O), 75.05 (*C*≡*C*), 69.81 ($OCH_2CH_2OCH_3$), 65.80 ($OCH_2CH_2OCH_3$), 59.20 (OCH_3) ppm; **Elemental analysis** (%) calcd. for $C_{10}H_{14}O_6$ (230.22 g mol^{-1}): C 52.17 H 6.13; found (%): C 52.04 H 6.20.

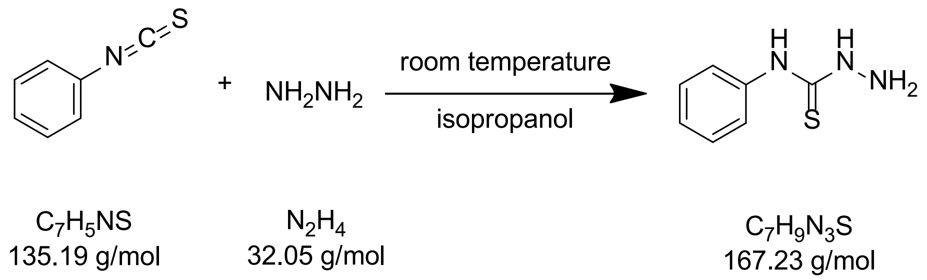

5.32
4.38
4.36
4.33
3.63
3.61
3.58
3.36
4.4
ppm
3.6
ppm
4.02
4.08
6.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


151.83
77.16
75.05
69.81
65.80
59.20
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

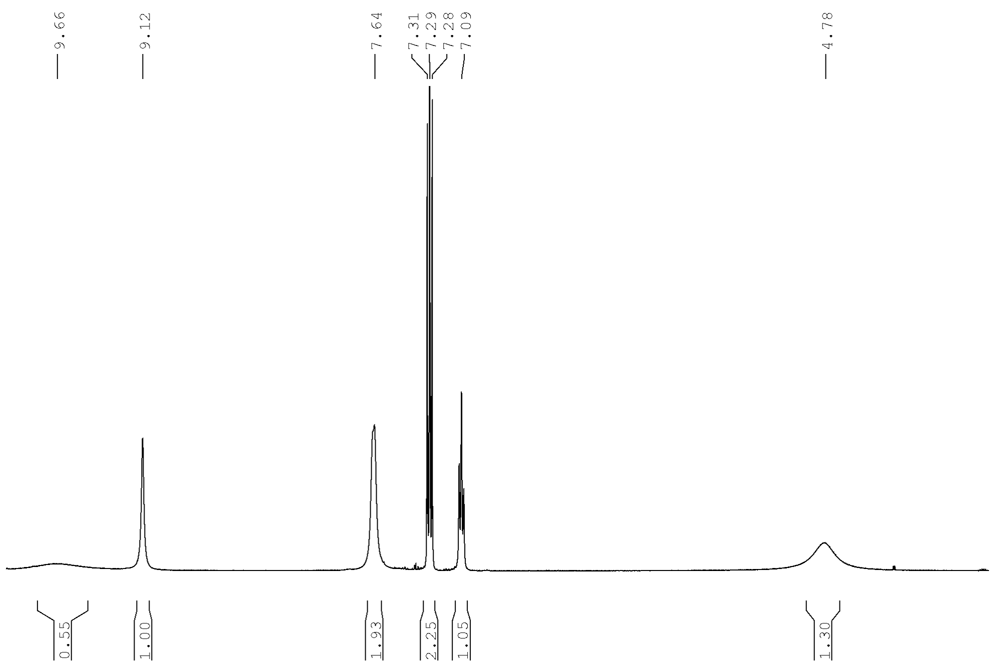


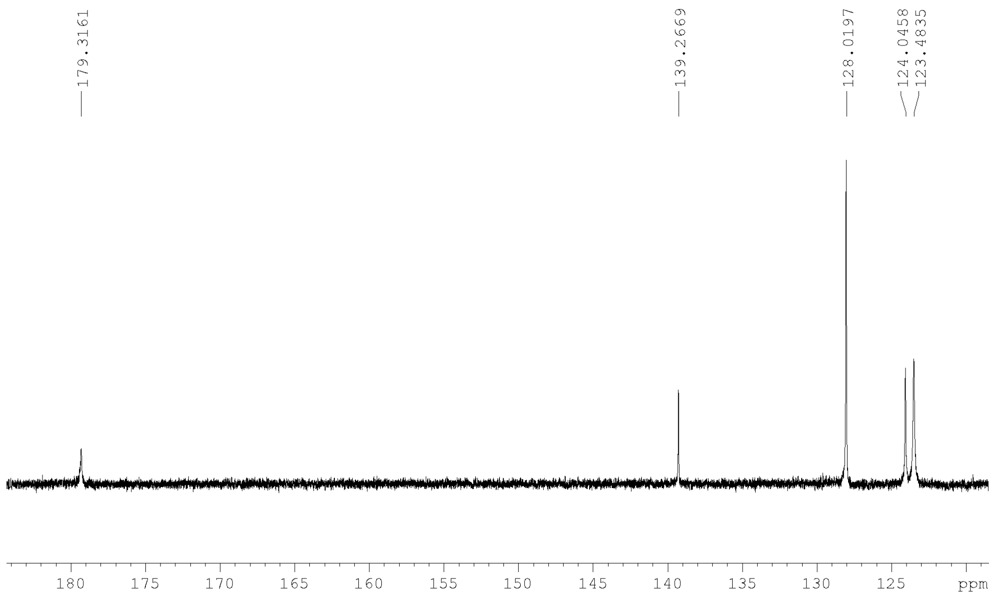
Transmission / %
100
80
60
40
20
0
2890
1722
1450
1234
1130
1043
864
4000
3500
3000
2500
2000
1500
1000
Wavenumber / cm-1

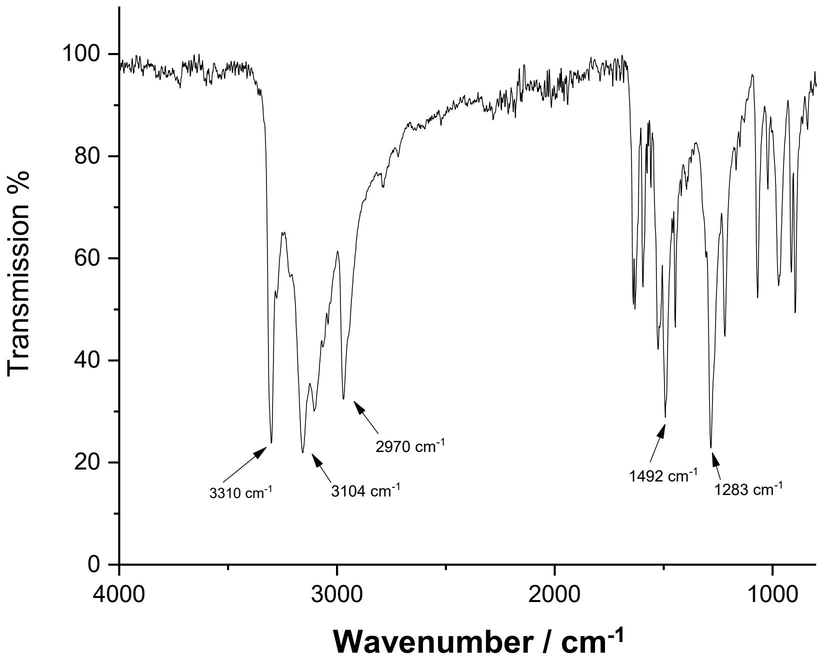
1.2 Synthesis of *N*-phenyl hydrazine carbothioamide (5)



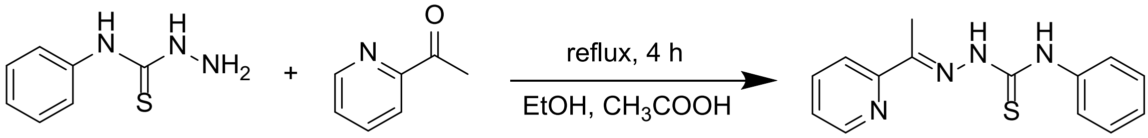
To a solution of hydrazine (8.0 mL, 8.23 g, 168 mmol) in isopropanol (80 mL), phenyl isothiocyanate (10.0 mL, 11.3 g, 84 mmol) was added dropwise with stirring at room temperature for 1 h. During that time, a white solid precipitated, which was filtered off, washed with isopropanol (4×15 mL), and dried under vacuum for 1 d. Yield: 87% (12.2 g, 73 mmol). **IR** (ATR): $\tilde{\nu}$ = 3310, 3104, 2970, 1492, 1283 cm^{-1}; **^{1}H NMR** (500.13 MHz, DMSO-d_6): δ = 9.66 (s, 1H, N*H*-phenyl), 9.12 (s, 1H, N*H*-NH_2), 7.64 (d, 2H, $^3J_{H2/H6,H3/H5}$ = 5.9 Hz, phenyl-H2/H6), 7.31–7.28 (m, 2H, phenyl-H3/H5), 7.09 (t, 1H, $^3J_{H4,H3/H5}$ = 7.3 Hz, phenyl-H4), 4.78 (s, 2H, N*H₂*) ppm; **^{13}C NMR** (125.76 MHz, DMSO-d_6): δ = 179.31 (*C*=S), 139.27 (phenyl-C1), 128.02 (phenyl-C2/C6), 124.05 (phenyl-C3/C5), 123.48 (phenyl-C4) ppm; **Elemental analysis** (%) calcd. for $C_7H_9N_3S$ (167.23 g mol^{-1}): C 50.28 H 5.42 N 25.13 S 19.17; found (%): C 50.33 H 5.64 N 24.90 S 18.95.



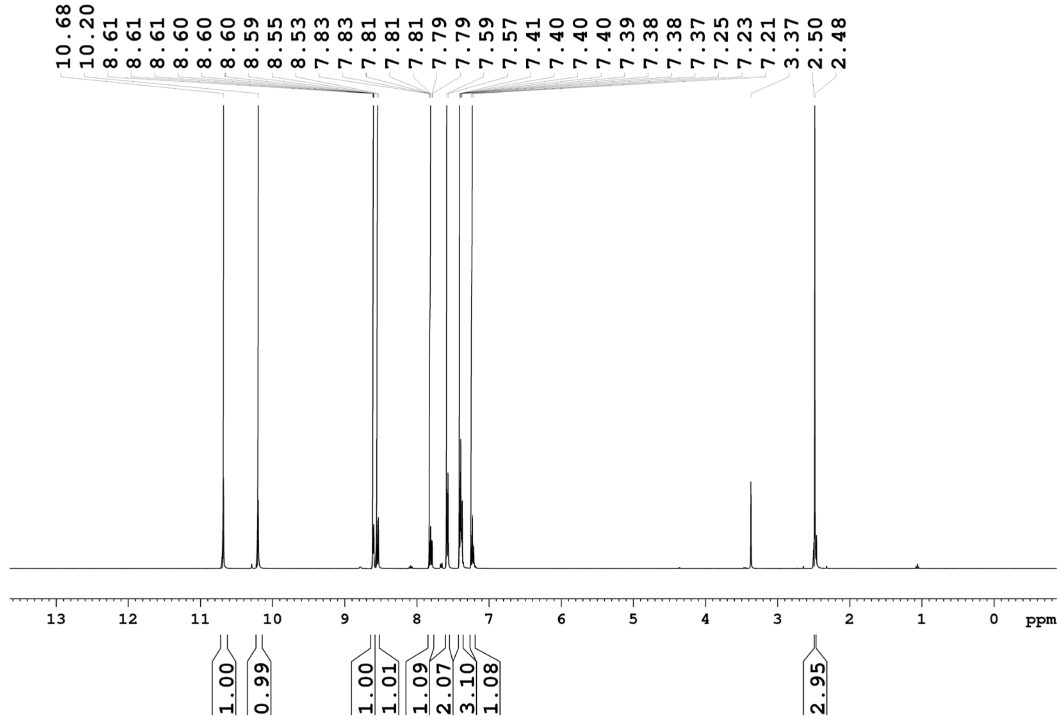

179.3161
139.2669
128.0197
124.0458
123.4835
180
175
170
165
160
155
150
145
140
135
130
125
ppm

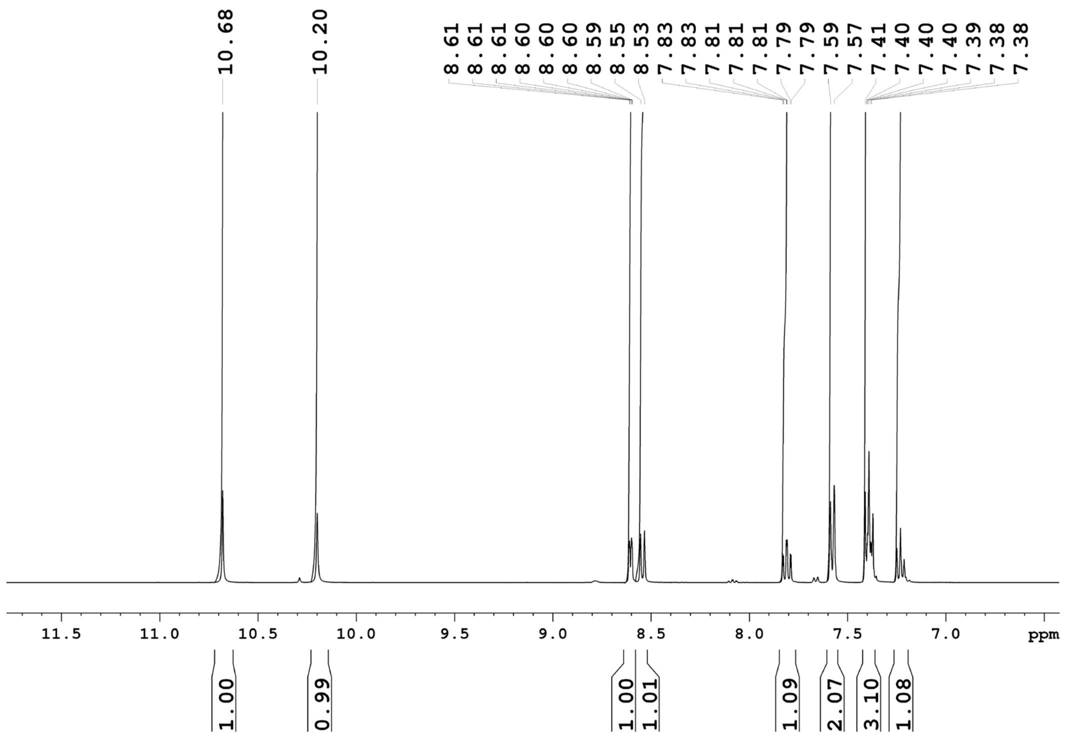

Transmission %
Wavenumber / cm-1
3310 cm-1
3104 cm-1
2970 cm-1
1492 cm-1
1283 cm-1
4000
3000
2000
1000
0
20
40
60
80
100

1.3 Synthesis of *N*-phenyl-2-[1-(2-pyridinyl)ethylidene]hydrazine carbothioamide (HL, 7)



In a 250 mL flask, *N*-phenyl hydrazine carbothioamide (2.01 g, 12.0 mmol) was dissolved in ethanol (60 mL) at 60 °C. Then, 2-acetylpyridine (1.51 g, 12.5 mmol) in acetic acid (1 mL) was added to the clear yellow solution, which was then heated to reflux. After about 1 h, a light yellow solid started to precipitate. Refluxing was continued for another 3 h and then, the solution was cooled to room temperature. The resulting light yellow solid was filtered off, washed with ethanol (3 x 10 mL), and dried under vacuum for 1 d. Yield: 86% (2.80 g, 10.4 mmol). **IR** (ATR): $\tilde{\nu}$ = 3297, 3240, 3052, 1514, 1485, 1466, 1435, 1360, 1300, 1263, 1186, 781, 740 cm^{-1}; **^{1}H NMR** (400.40 MHz, DMSO-d_6): δ = 10.68 (s, 1H, N*H*), 10.20 (s, 1H, N*H*-phenyl), 8.60 (ddd, 1H, $^3J_{H6,H5}$ = 4.8 Hz, $^4J_{H6,H4}$ = 1.6 Hz, $^5J_{H6,H3}$ = 0.9 Hz, py-H6), 8.54 (d, 1H, $^3J_{H3,H4}$ = 8.1 Hz, py-H3), 7.81 (dt, 1H, $^3J_{H4,H3/H5}$ = 7.8 Hz, $^4J_{H4,H6}$ = 1.6 Hz, py-H4), 7.58 (d, 2H, $^3J_{H2'/H6',H3'/H5'}$ = 7.5 Hz, phenyl-H2'/H6'), 7.41–7.37 (m, 3H, py-H5, phenyl-H3'/H5'), 7.23 (t, 1H, $^3J_{H4',H3'/H5'}$ = 7.4 Hz, phenyl-H4'), 2.48 (s, 3H, C*H*$_3$) ppm; **^{13}C NMR** (100.68 MHz, DMSO-d_6, ppm): δ 177.26 (*C*=S), 154.52 (*C*=N), 149.18 (py-C2), 148.46 (py-C6), 139.14 (phenyl-C1'), 136.34 (py-C4), 128.11 (phenyl-C2'/C6'), 126.13 (phenyl-C3'/C5'), 125.54 (py-C5), 124.09 (py-C3), 121.23 (phenyl-C4'), 12.49 (*C*H$_3$) ppm; **Elemental analysis** (%) calcd. for $C_{14}H_{14}N_4S$ (270.35 g mol^{-1}): C 62.20 H 5.22 N 20.72 S 11.86; found (%): C 62.23 H 5.24 N 20.80 S 11.78.


10.68
10.20
8.61
8.61
8.61
8.60
8.60
8.60
8.59
8.55
8.53
7.83
7.83
7.81
7.81
7.81
7.79
7.79
7.59
7.57
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.37
7.25
7.23
7.21
3.37
2.50
2.48
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.00
1.01
1.09
2.07
3.10
1.08
2.95


10.68
10.20
8.61
8.61
8.61
8.60
8.60
8.60
8.59
8.55
8.53
7.83
7.83
7.81
7.81
7.81
7.79
7.79
7.59
7.57
7.41
7.40
7.40
7.40
7.39
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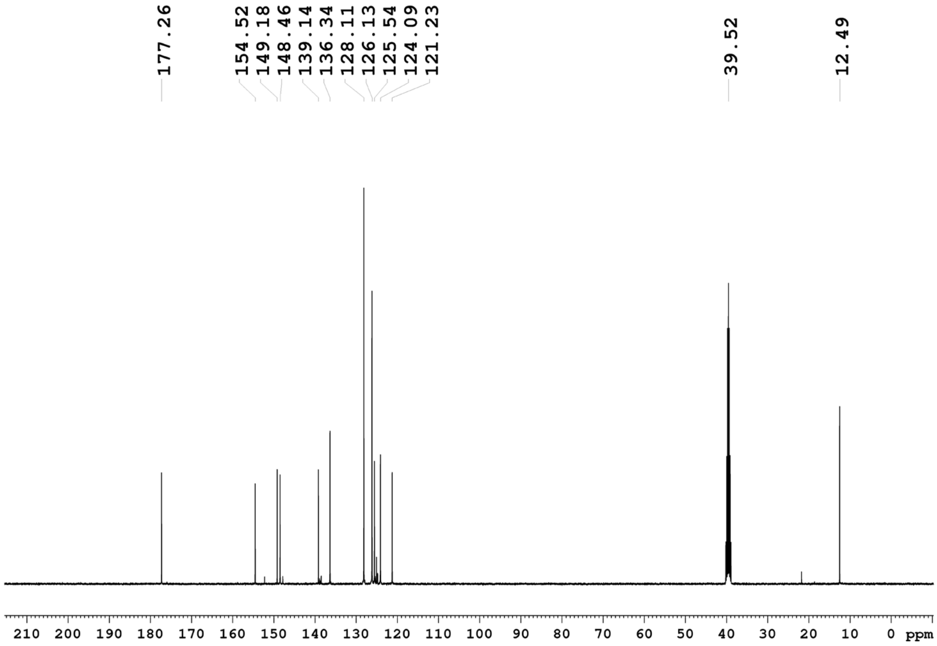
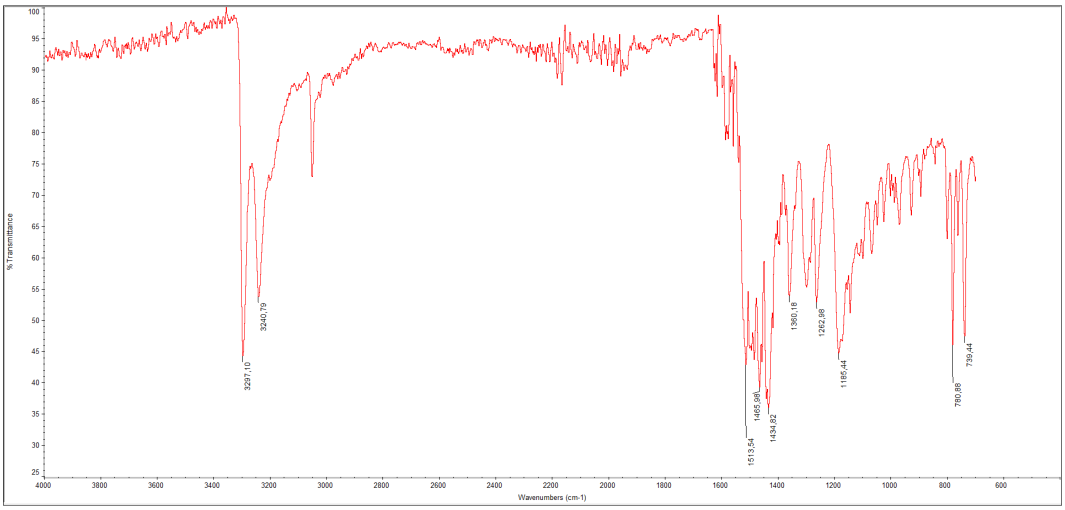
7.38
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
1.00
0.99
1.00
1.01
1.09
2.07
3.10
1.08


177.26
154.52
149.18
148.46
139.14
136.34
128.11
126.13
125.54
124.09
121.23
39.52
12.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


% Transmittance
Wavenumbers (cm-1)
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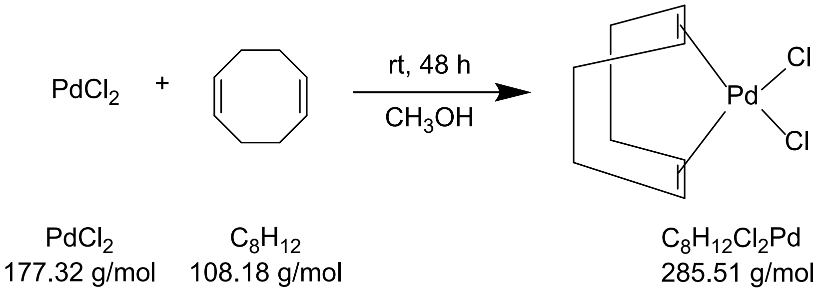
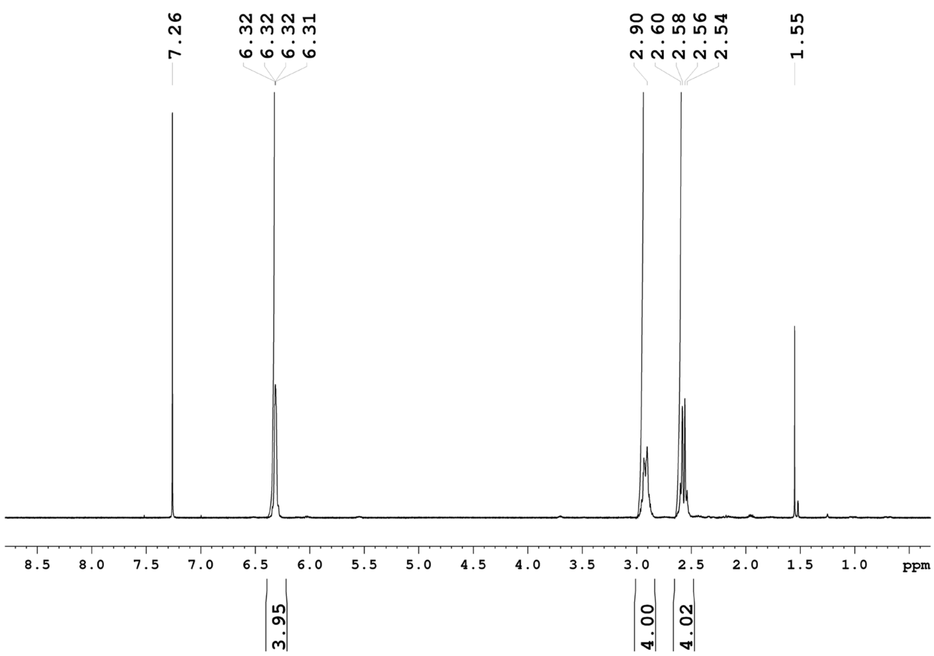
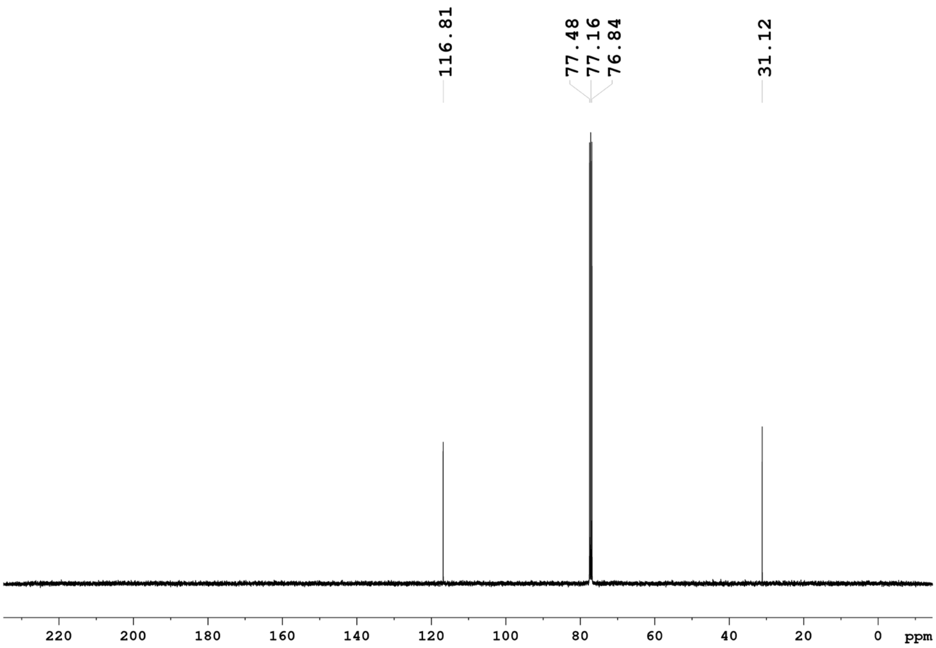
3240,79
1513,54
1465,98
1434,82
1360,18
1262,98
1185,44
780,88
739,44

1.4 Synthesis of [PdCl$_2$(cod)] (8)



To a suspension of palladium(II) chloride (1.00 g, 5.6 mmol) in methanol (50 mL), 1,5-cyclooctadiene (2.1 mL, 1.85 g, 16.9 mmol) was added and the mixture stirred for 48 h at room temperature. During that time, the colour of the reaction mixture changed from dark red to yellow and a precipitate formed. This was filtered off, washed with methanol (3 x 5 mL), and dried under vacuum for 1 d. Yield: 84% (1.35 g, 4.7 mmol). **IR** (ATR): $\tilde{\nu}$ = 2937, 2889, 1524, 1510, 1492, 1453, 1418, 1348, 1310, 1247, 1178, 1082, 1002, 915, 867, 822, 786, 778 cm^{-1}; **^{1}H NMR** (400.40 MHz, $CDCl_3$): δ = 6.34–6.29 (m, 4H, C*H*), 2.97–2.86 (m, 4H, C*H*$_2$), 2.60–2.54 (m, 4H, C*H*$_2$) ppm; **^{13}C NMR** (100.68 MHz, $CDCl_3$): δ = 116.81 (*C*H), 31.12 (*C*H$_2$) ppm; **Elemental analysis** (%) calcd. for $C_8H_{12}Cl_2Pd$ (285.51 g mol^{-1}): C 33.66, H 4.24; found (%): C 33.44, H 4.23.




116.81
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76.84
31.12
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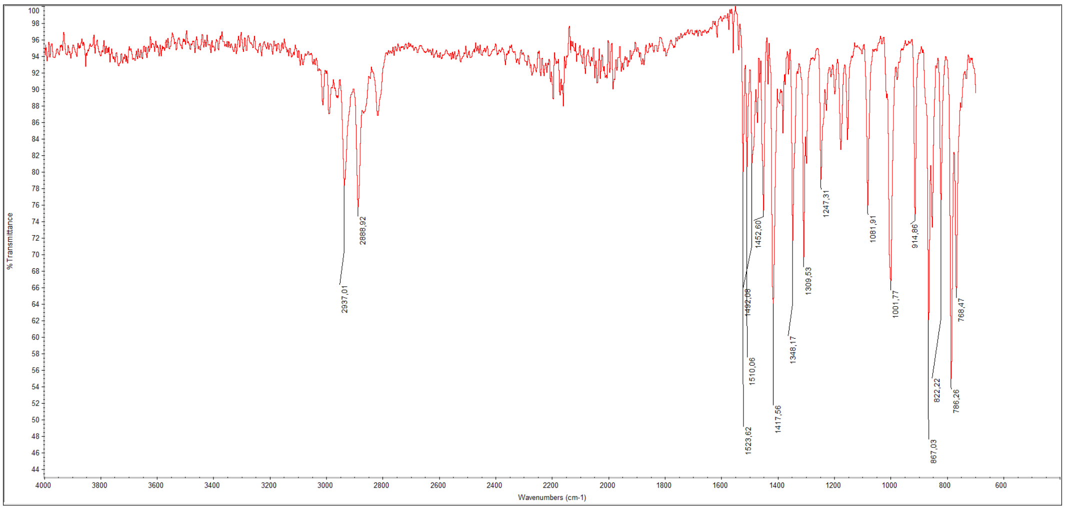
200
180
160
140
120
100
80
60
40
20
0
ppm


% Transmittance
Wavenumbers (cm-1)
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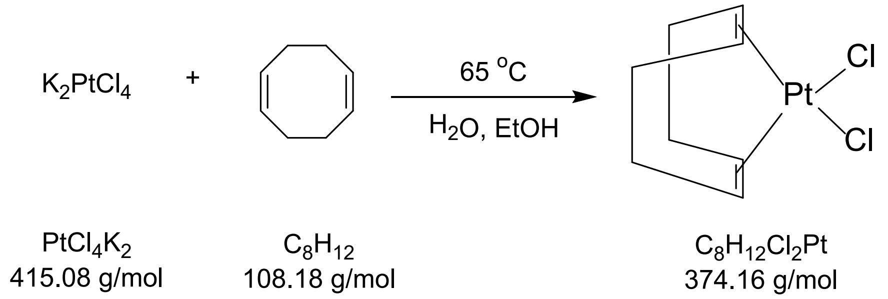
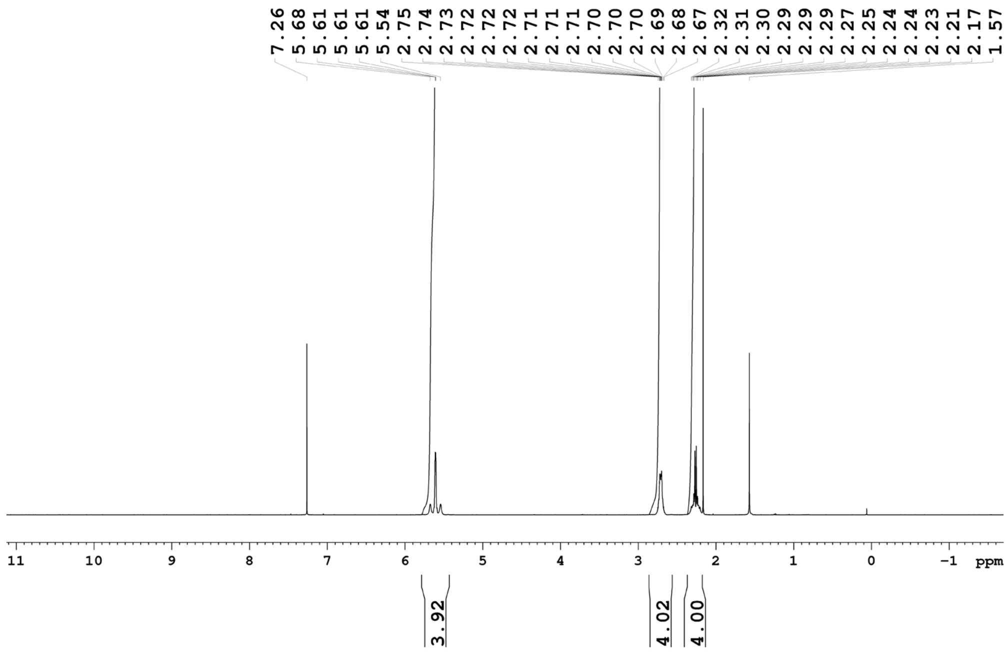
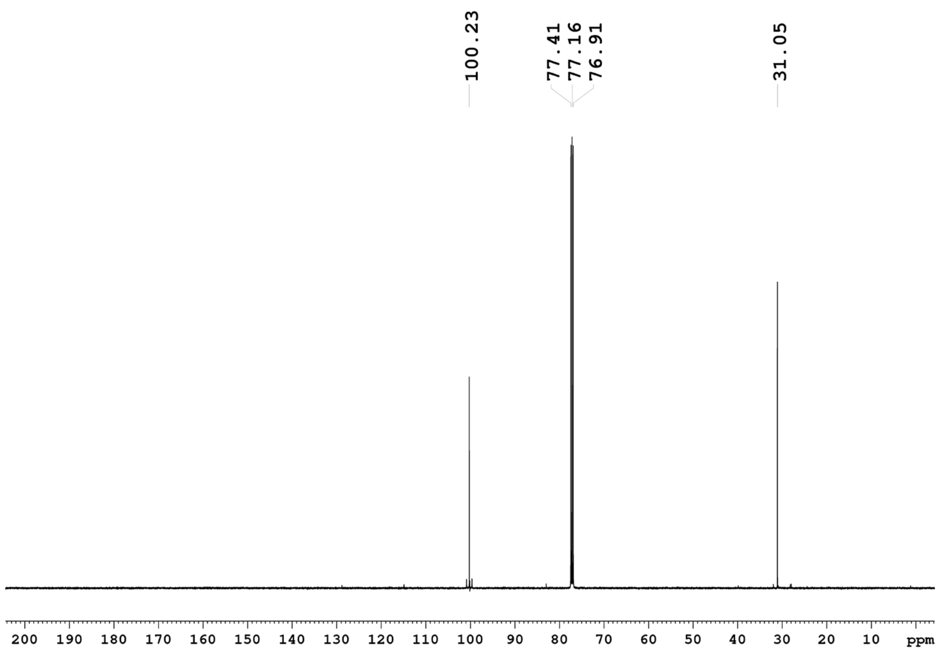
1523,62
1510,06
1492,08
1452,60
1417,56
1348,17
1309,53
1247,31
1081,91
1001,77
914,86
867,03
822,22
786,26
768,47

1.4 Synthesis of [PtCl$_2$(cod)] (9)



A solution of potassium tetrachloroplatinate (0.5 g, 1.2 mmol) in water (30 mL) was heated to 65 °C with stirring for 15 min. Then, a solution of 1,5-cyclooctadiene (0.5 mL, 440 mg, 4.0 mmol) in ethanol (40 mL) was added to the clear light red solution. Stirring at 65 °C was continued until the colour of the solution turned from red to pale yellow, during which a white precipitate formed (about 30 min). The mixture was then cooled in ice and the white precipitate collected, washed with water (4×10 mL) and diethyl ether (4×10mL), and dried under vacuum for 3 d to obtain a white microcrystalline material. Yield: 80% (0.36 g, 0.96 mmol). **IR** (ATR): $\tilde{\nu}$ = 3009, 2963, 2896, 2031, 1972, 1476, 1451, 1425, 1339, 1311, 1179, 1088, 1009, 911, 872, 832, 812, 781, 778 cm^{-1}; **^{1}H NMR** (400.40 MHz, CDCl$_3$): δ = 5.68–5.54 (m, 4H, C*H*), 2.75–2.68 (m, 4H, C*H*$_2$), 2.32–2.21 (m, 4H, C*H*$_2$) ppm; **^{13}C NMR** (125.76 MHz, CDCl$_3$): **δ** = 100.23 (d, $^{1}J_{C\text{-}Pt}$ = 152.2 Hz, *C*H), 31.05 (*C*H$_2$) ppm; **^{195}Pt NMR** (107.51 MHz, CDCl$_3$): δ = -3332 ppm; **Elemental analysis** (%) calcd. for $C_8H_{12}Cl_2Pt$ (374.16 g mol^{-1}): C 25.68, H 3.23; found (%): C 25.85, H 3.25.


7.26
5.68
5.61
5.61
5.61
5.54
2.75
2.74
2.73
2.72
2.72
2.72
2.71
2.71
2.71
2.70
2.70
2.70
2.69
2.68
2.67
2.32
2.31
2.30
2.29
2.29
2.29
2.27
2.25
2.24
2.24
2.23
2.21
2.17
1.57
11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
3.92
4.02
4.00


100.23
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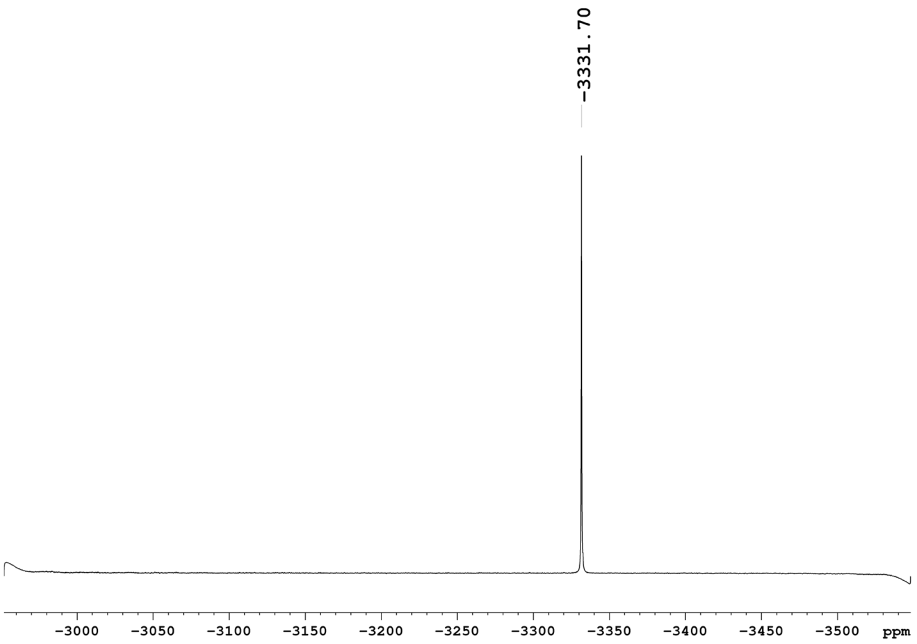
76.91
31.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



-3331.70
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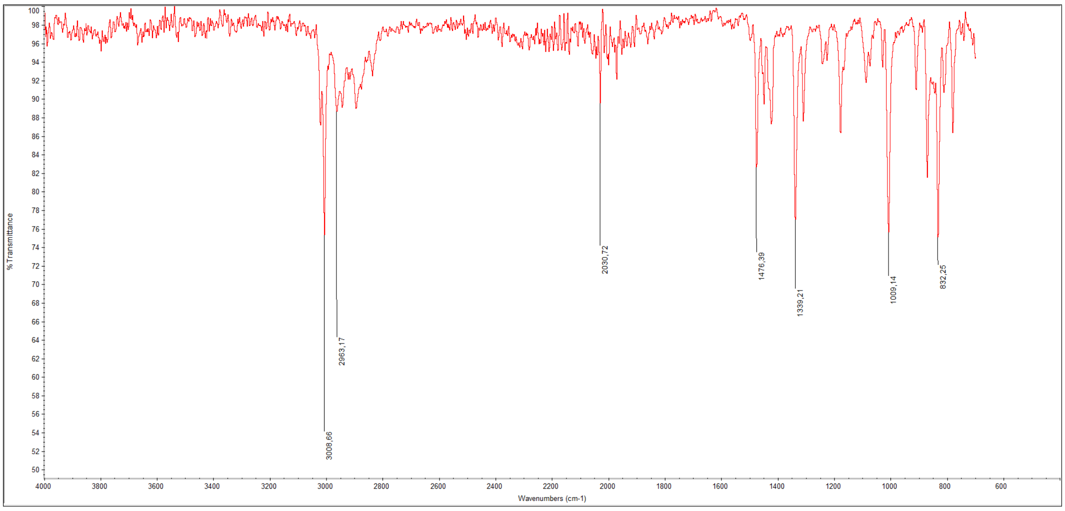
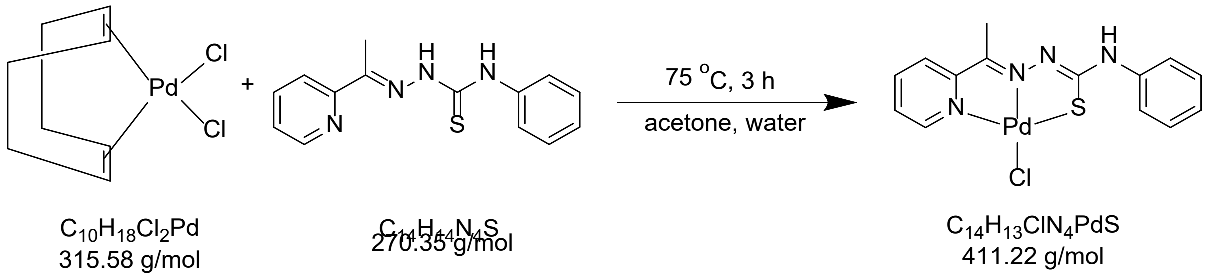
-3050
-3100
-3150
-3200
-3250
-3300
-3350
-3400
-3450
-3500
ppm

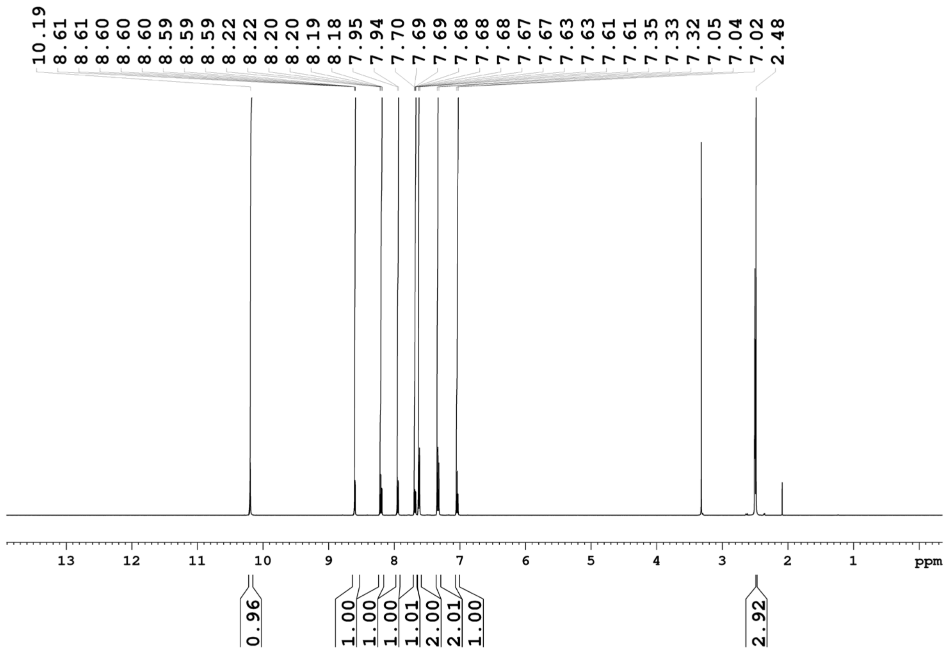


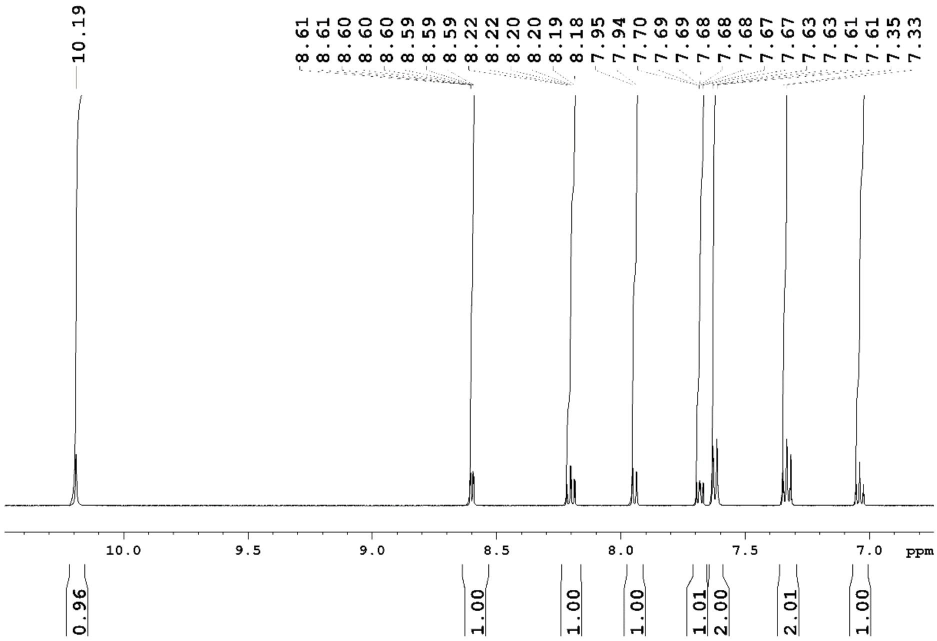
3008,66
2963,17
2030,72
1476,39
1339,21
1009,14
832,25
% Transmittance
Wavenumbers (cm-1)

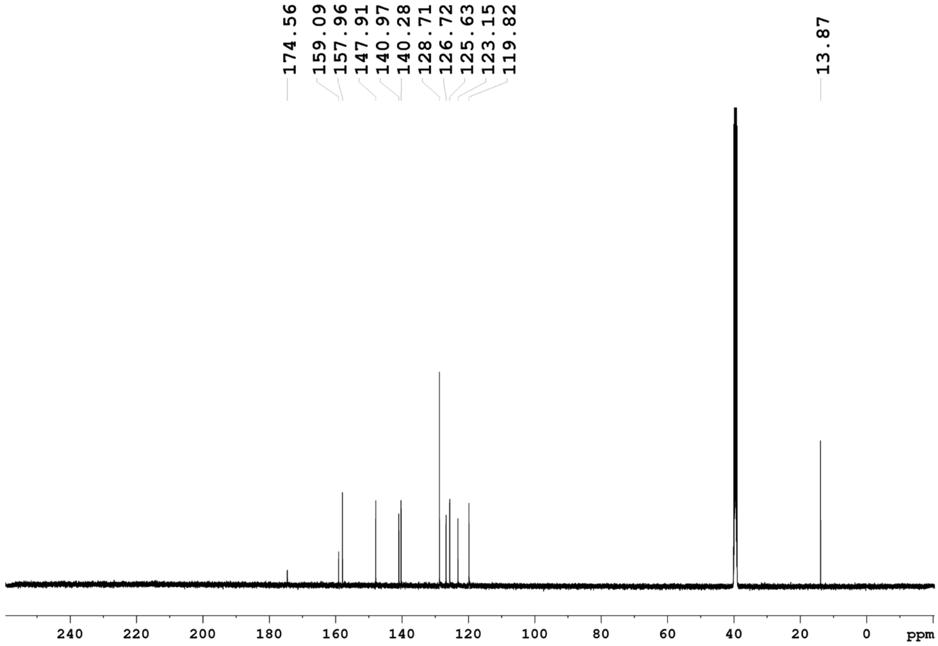
1.6 Synthesis of [PdCl(L)] (10)

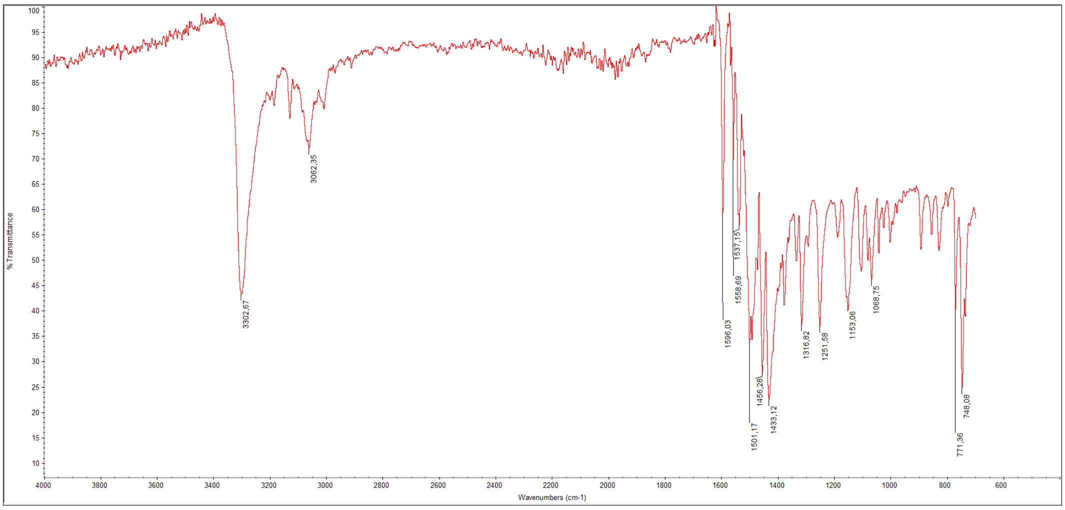


A mixture of [PdCl$_2$(cod)] (85 mg, 0.27 mmol) suspended in water (15 mL) and *N*-phenyl-2-[1-(2-pyridinyl)ethylidene]hydrazine carbothioamide (82.6 mg, 0.31 mmol) dissolved in acetone (10 mL) was stirred with heating at 75 °C. Stirring and heating were continued for 3 h. Then the solution was cooled to room temperature, the resulting yellow precipitate filtered off, washed with acetone (3×2 mL) and water (3×5 mL), and dried under vacuum for 1 d. Yield: 100% (109 mg, 0.27 mmol). IR (ATR): $\tilde{\nu}$ = 3303, 3062, 1596, 1559, 1537, 1501, 1456, 1433, 1317, 1252, 1153, 1069, 771, 748 cm^{-1}; **^{1}H NMR** (500.13 MHz, DMSO-d_6): δ = 10.19 (s, 1H, N*H*-phenyl), 8.60 (ddd, 1H, $^{3}J_{H6,H5}$ = 5.3 Hz, $^{4}J_{H6,H4}$ = 1.6 Hz, $^{5}J_{H6,H3}$ = 0.6 Hz, py-H6), 8.20 (dt, 1H, $^{3}J_{H4,H3/H5}$ = 7.9 Hz, $^{4}J_{H4,H6}$ = 1.6 Hz, py-H4), 7.94 (d, 1H, $^{3}J_{H3,H4}$ = 7.6 Hz, py-H3), 7.68 (ddd, 1H, $^{3}J_{H5,H4}$ = 7.7 Hz, $^{3}J_{H5,H6}$ = 5.3 Hz, $^{4}J_{H5,H3}$ = 1.3 Hz, py-H5), 7.62 (d, 2H, $^{3}J_{H3'/H5',H2'/H6'}$ = 7.7 Hz, phenyl-H3'/H5'), 7.33 (t, $^{3}J_{H2'/H6',H3'/H5'}$ = 8.0 Hz, phenyl-H2'/H6'), 7.04 (t, $^{3}J_{H4',H3'/H5'}$ = 7.4 Hz, phenyl-H4'), 2.48 (s, 3H, C*H$_3$*) ppm; **^{13}C NMR** (125.76 MHz, DMSO-d_6): δ = 174.56 (*C*-S), 159.09 (*C*=N), 157.96 (py-C2), 147.91 (py-C6), 140.97 (phenyl-C1'), 140.28 (py-C4), 128.71 (phenyl-C3'/C5'), 126.72 (py-C5), 125.63 (py-C3), 123.15 (phenyl-C4'), 119.82 (phenyl-C2'/C6'), 13.87 (*C*H$_3$) ppm; **Elemental analysis** (%) calcd. for $C_{14}H_{13}ClN_4PdS$ (411.22 g mol^{-1}): C 40.89 H 3.19 N 13.62 S 7.80; found (%): C 40.97 H 3.19 N 13.56 S 7.71.

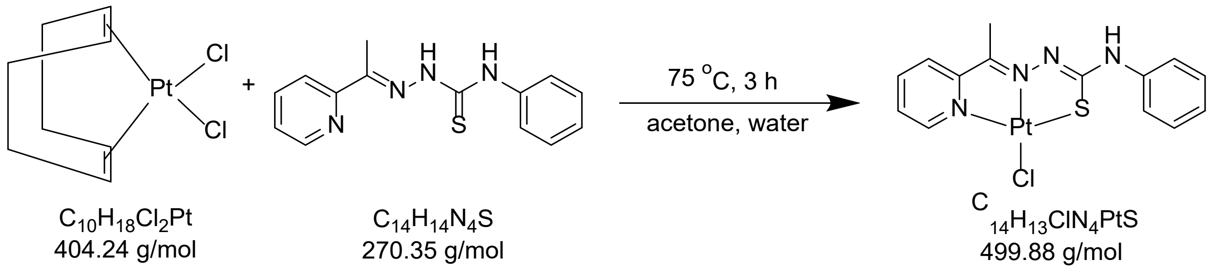

10.19
8.61
8.61
8.60
8.60
8.60
8.59
8.59
8.59
8.22
8.22
8.20
8.20
8.19
8.18
7.95
7.94
7.70
7.69
7.69
7.68
7.68
7.68
7.67
7.67
7.63
7.63
7.61
7.61
7.35
7.33
7.32
7.05
7.04
7.02
2.48
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.00
1.00
1.00
1.01
2.00
2.01
1.00
2.92


10.19
8.61
8.61
8.60
8.60
8.60
8.59
8.59
8.59
8.22
8.22
8.20
8.20
8.19
8.18
7.95
7.94
7.70
7.69
7.69
7.68
7.68
7.68
7.67
7.67
7.63
7.63
7.61
7.61
7.35
7.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
0.96
1.00
1.00
1.00
1.01
2.00
2.01
1.00

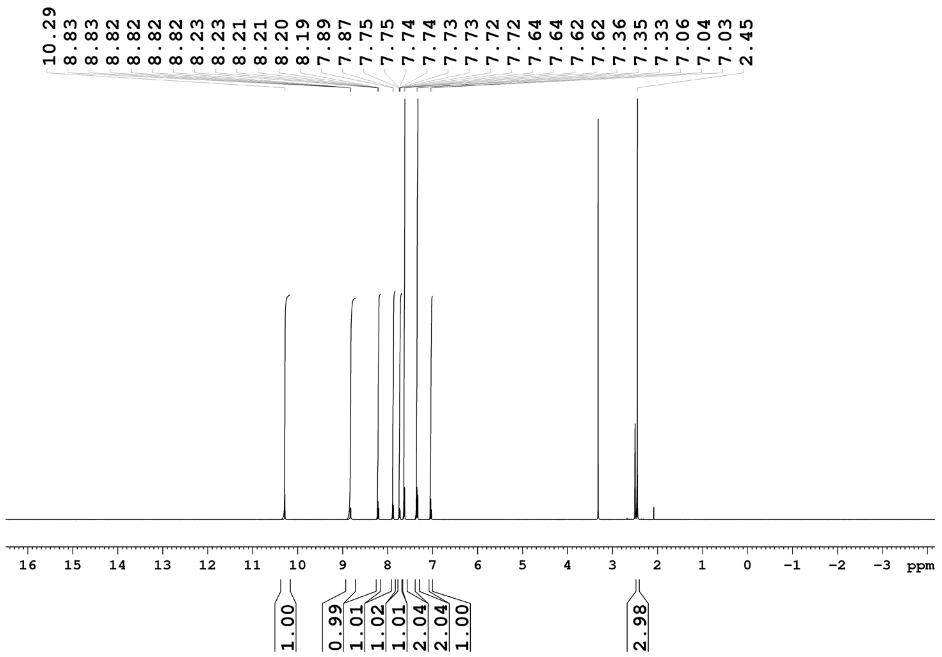

174.56
159.09
157.96
147.91
140.97
140.28
128.71
126.72
125.63
123.15
119.82
13.87
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

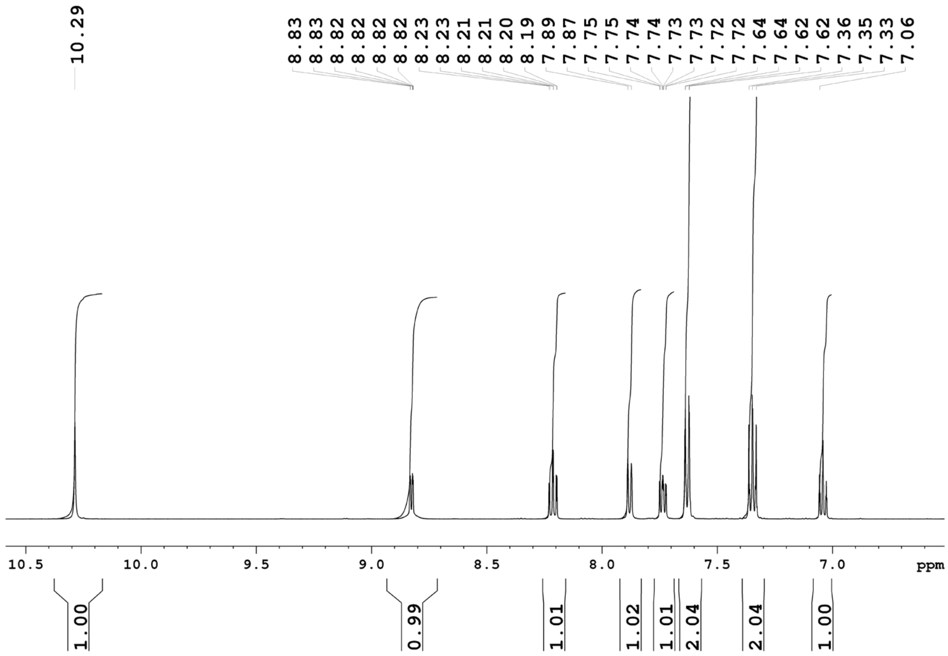

% Transmittance
Wavenumbers (cm-1)
3302,67
3062,35
1596,03
1558,69
1537,15
1501,17
1456,28
1433,12
1316,82
1251,58
1153,06
1068,75
771,36
748,08

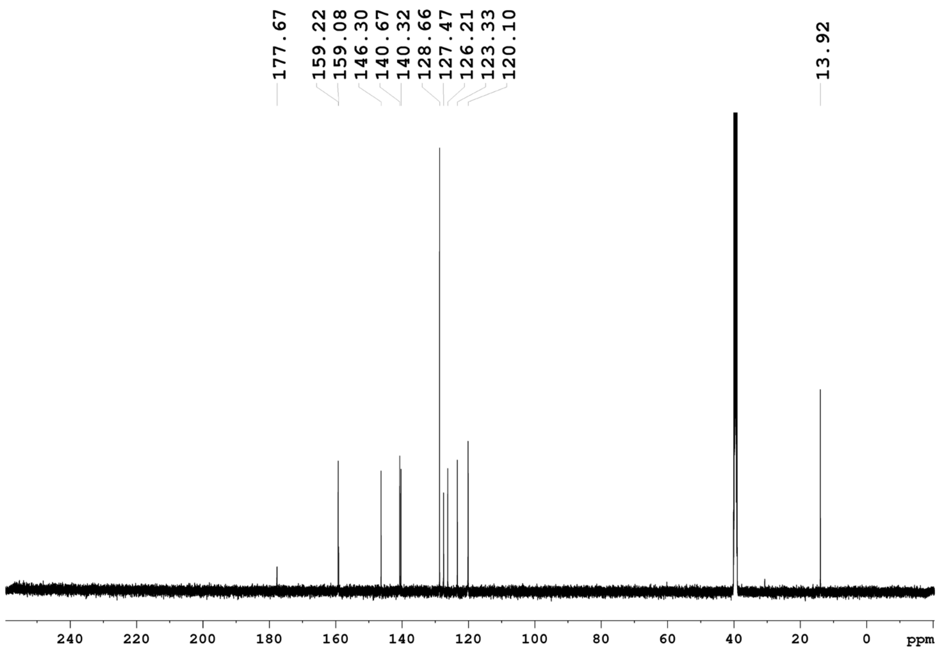
1.7 Synthesis of [PtCl(L)] (11)

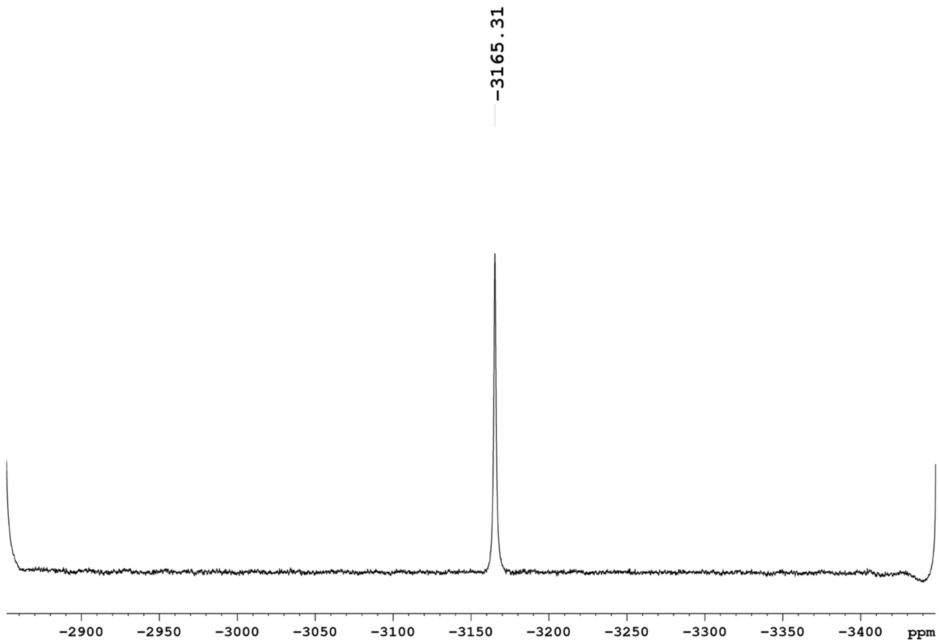


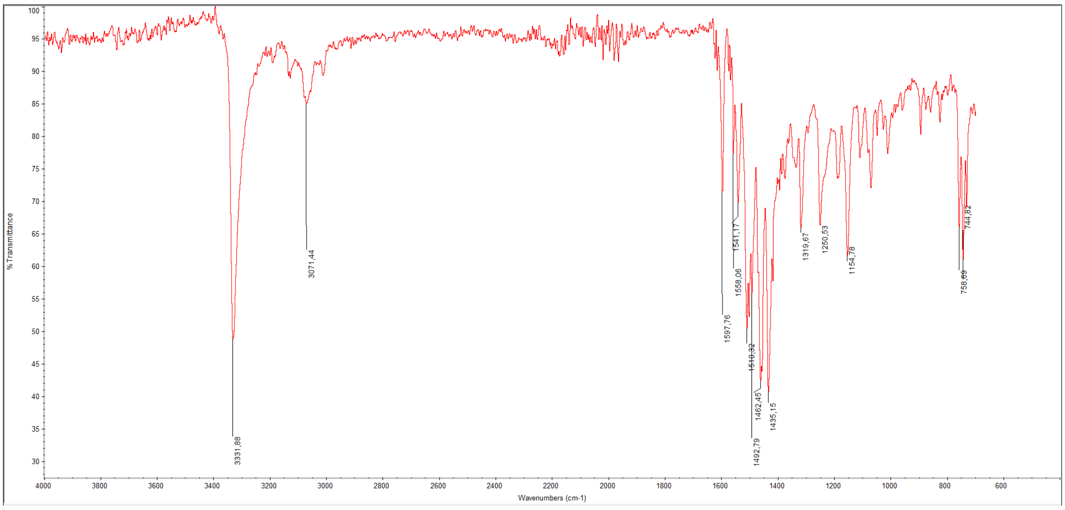
A mixture of [PtCl$_2$(cod)] (60 mg, 0.15 mmol) suspended in water (7 mL) and *N*-phenyl-2-[1-(2-pyridinyl)ethylidene]hydrazine carbothioamide (45 mg, 0.17 mmol) dissolved in acetone (7 mL) was stirred with heating at 75 °C. Stirring and heating were continued for 3 h. Then, the solution was cooled to room temperature, the resulting red precipitate filtered off, washed with acetone (3 x 2 mL) and water (3 x 5 mL), and dried under vacuum for 1 d. Yield: 97% (72.2 mg, 0.14 mmol). **IR** (ATR): $\tilde{\nu}$ = 3332, 3071, 1598, 1558, 1541, 1510, 1493, 1462, 1435, 1320, 1250, 1155, 759, 745 cm^{-1}; **^{1}H NMR** (500.13 MHz, DMSO-*d*$_6$): δ = 10.29 (s, 1H, N*H*-phenyl), 8.83 (ddd, 1H, $^3J_{H6,H5}$ = 5.5 Hz, $^4J_{H6,H4}$ = 1.5 Hz, $^5J_{H6,H3}$ = 0.6 Hz, py-H6), 8.21 (dt, 1H, $^3J_{H4,H3/H5}$ = 7.9 Hz, $^4J_{H4,H6}$ = 1.6 Hz, py-H4), 7.88 (d, 1H, $^3J_{H3,H4}$ = 7.6 Hz, py-H3), 7.74 (ddd, 1H, $^3J_{H5,H4}$ = 7.7 Hz, $^3J_{H5,H6}$ = 5.5 Hz, $^4J_{H5,H3}$ = 1.3 Hz, py-H5), 7.63 (d, 2H, $^3J_{H3'/H5',H2'/H6'}$ = 7.7 Hz, phenyl-H3'/H5'), 7.35 (t, 2H, $^3J_{H2'/H6',H3'/H5'}$ = 8.0 Hz, phenyl-H2'/H6'), 7.04 (t, 1H, $^3J_{H4',H3'/H5'}$ = 7.4 Hz, phenyl-H4'), 2.45 (s, 3H, C*H$_3$*) ppm; **^{13}C NMR** (125.76 MHz, DMSO-*d*$_6$): δ = 177.67 (*C*-S), 159.22 (py-C2), 159.08 (*C*=N), 146.30 (py-C6), 140.67 (phenyl-C1'), 140.32 (py-C4), 128.66 (phenyl-C3'/C5'), 127.47 (py-C5), 126.21 (py-C3), 123.33 (phenyl-C4'), 120.10 (phenyl-C2'/C6'), 13.87 (*C*H$_3$) ppm; **^{195}Pt NMR** (107.51 MHz, DMSO-*d*$_6$): δ = -3165 ppm; **Elemental analysis** (%) calcd. for $C_{14}H_{13}ClN_4PtS$ (499.88 g mol^{-1}): C 33.64 H 2.62 N 11.21 S 6.41; found (%): C 33.82 H 2.70 N 11.26 S 6.36.






177.67
159.22
159.08
146.30
140.67
140.32
128.66
127.47
126.21
123.33
120.10
13.92
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

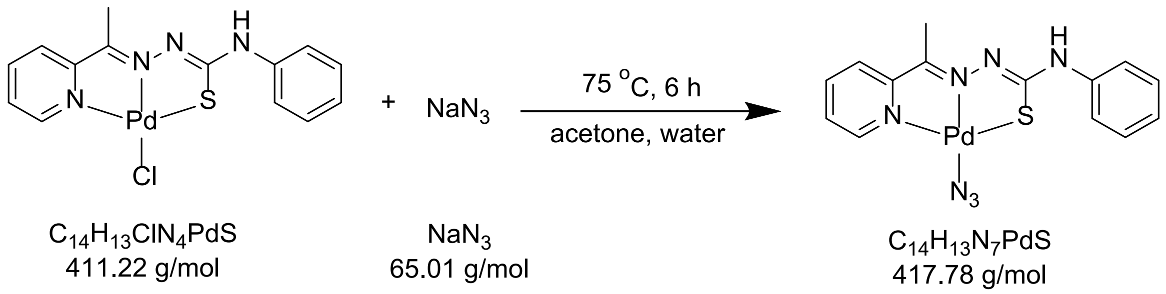

-3165.31
-2900
-2950
-3000
-3050
-3100
-3150
-3200
-3250
-3300
-3350
-3400
ppm

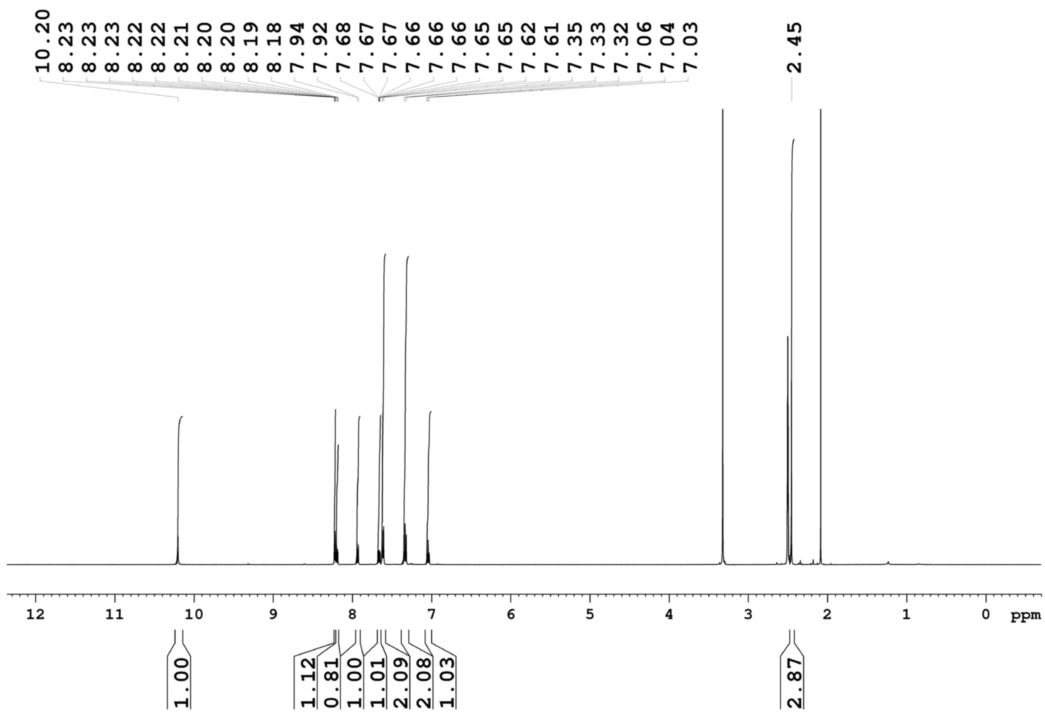


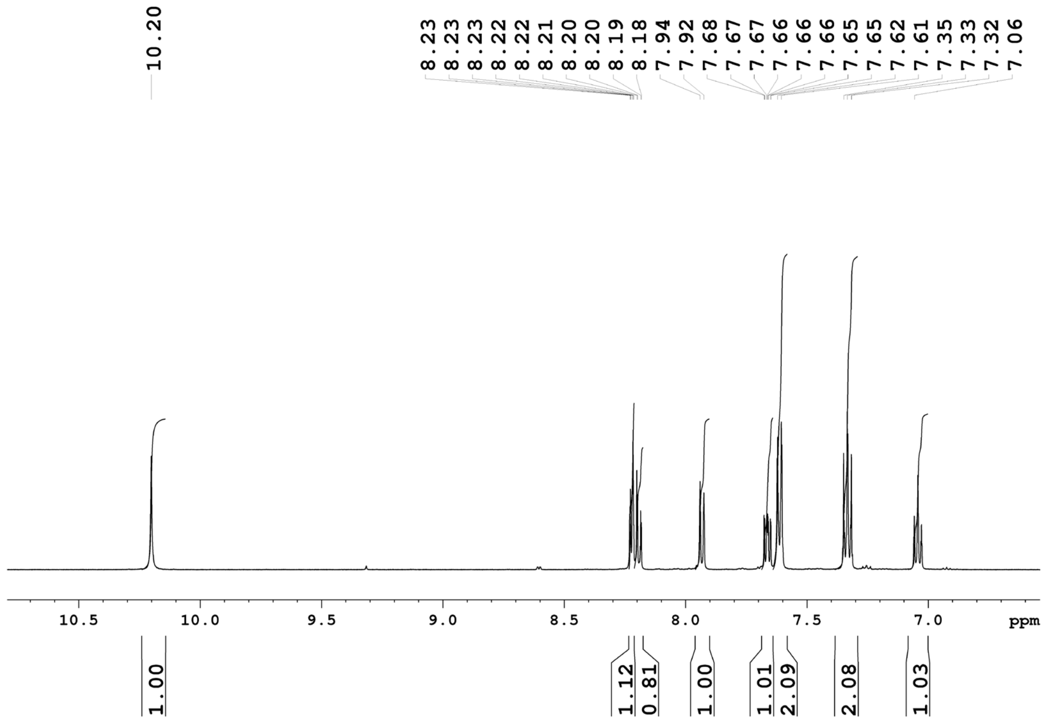
% Transmittance
Wavenumbers (cm-1)
3331,88
3071,44
1597,76
1558,06
1541,17
1510,32
1492,79
1462,45
1435,15
1319,67
1250,53
1154,78
758,69
744,82

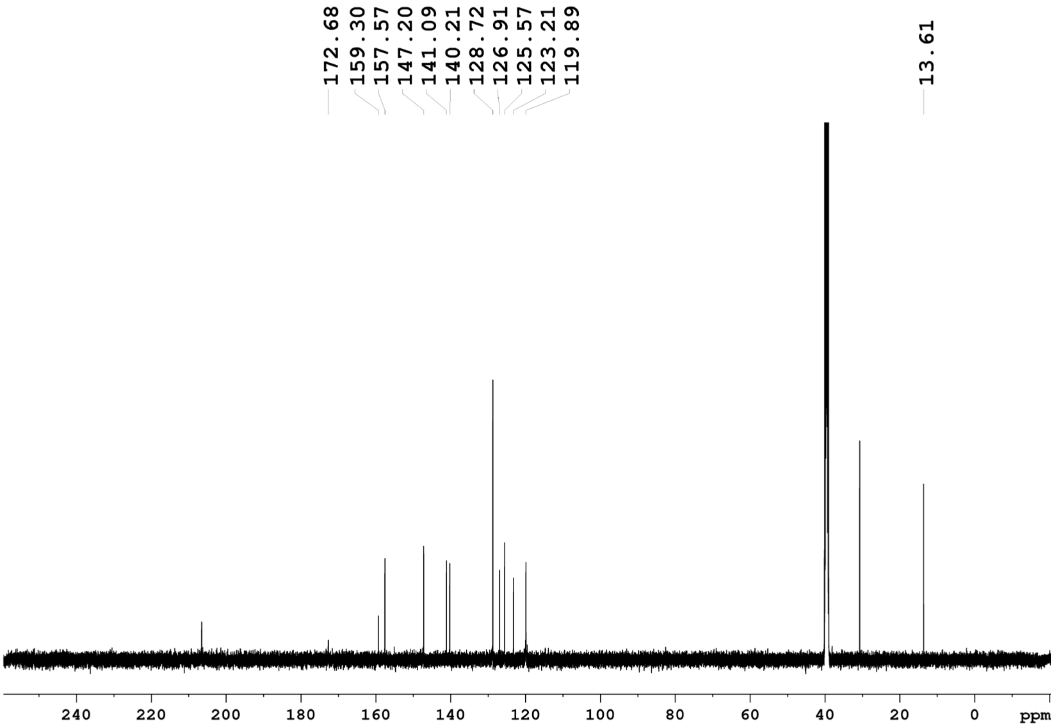
2. IR and NMR spectra of metal complexes

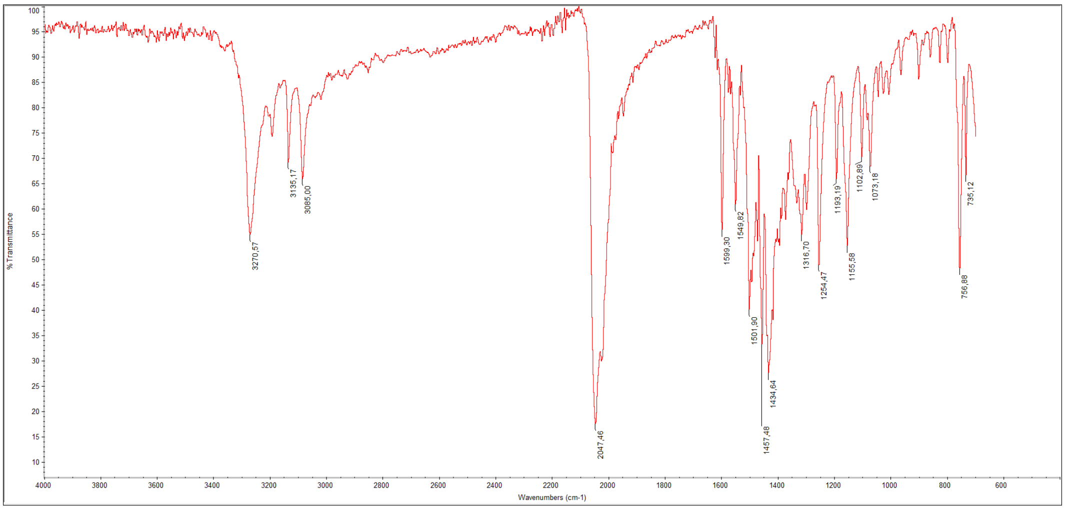
2.1 [Pd(N_3)(L)] (12)



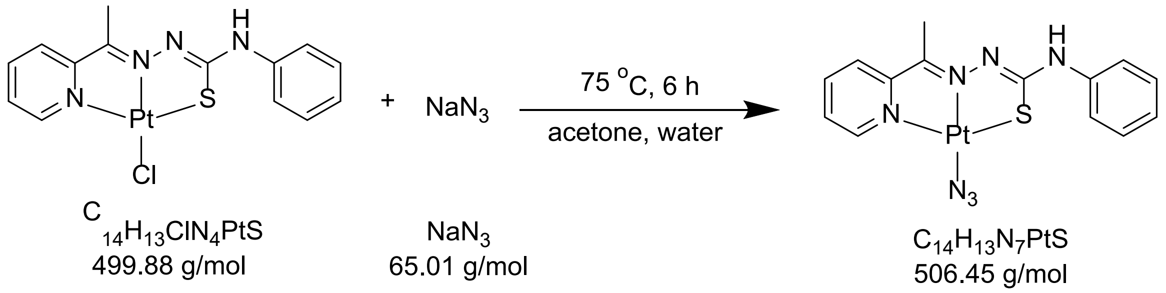



10.20
8.23 8.23 8.23 8.22 8.22 8.21 8.20 8.20 8.19 8.18 7.94 7.92 7.68 7.67 7.67 7.66 7.66 7.66 7.65 7.65 7.62 7.61 7.35 7.33 7.32 7.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 ppm
1.00 1.12 0.81 1.00 1.01 2.09 2.08 1.03

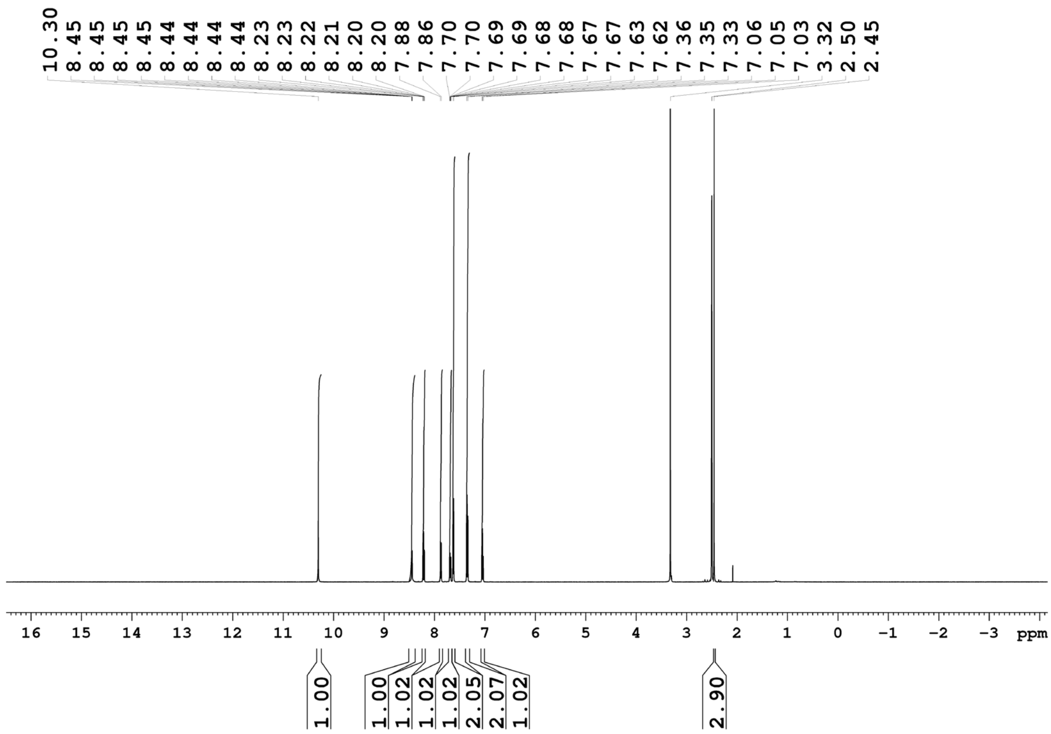

172.68 159.30 157.57 147.20 141.09 140.21 128.72 126.91 125.57 123.21 119.89
13.61
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm

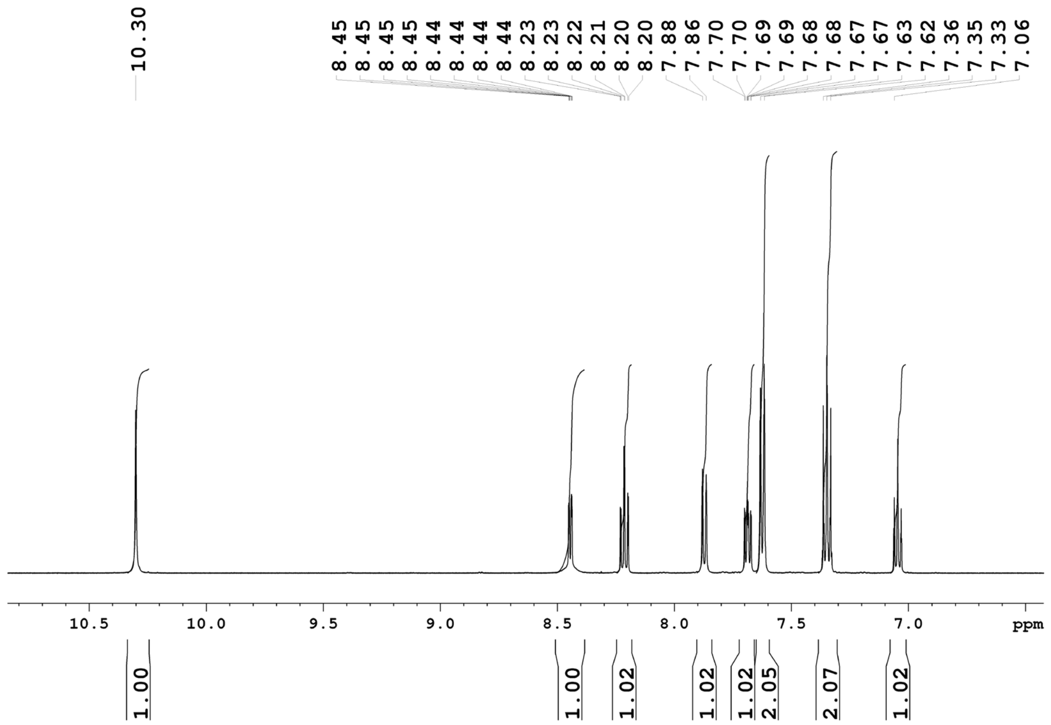

% Transmittance
Wavenumbers (cm-1)
3270,57
3135,17
3085,00
2047,46
1599,30
1549,82
1501,90
1457,48
1434,64
1316,70
1254,47
1193,19
1155,58
1102,89
1073,18
756,88
735,12

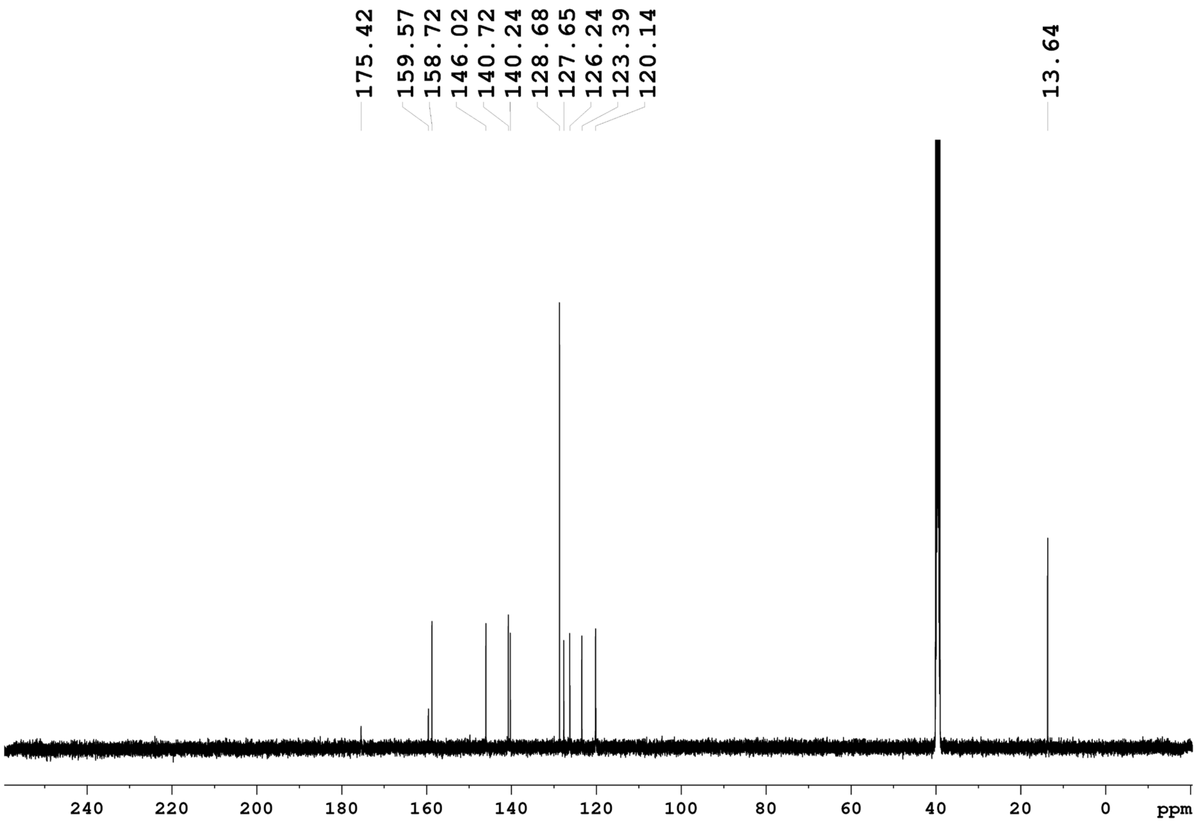
2.2 [Pt(N3)(L)] (13)

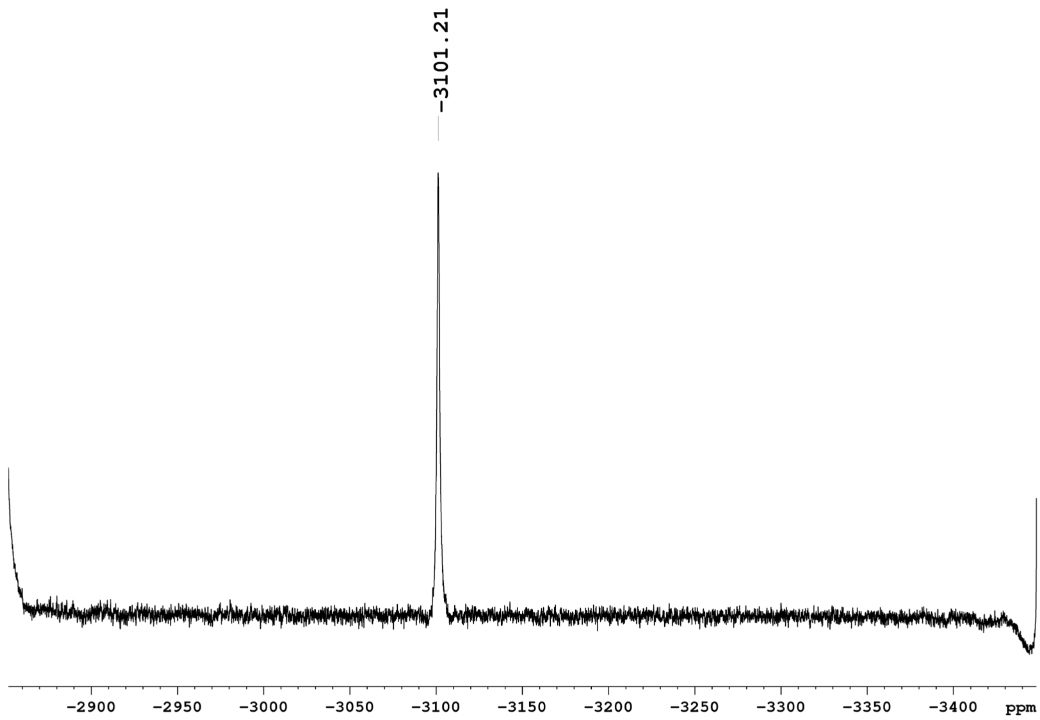


75 °C, 6 h
acetone, water
NaN3
C14H13ClN4PtS
499.88 g/mol
65.01 g/mol
C14H13N7PtS
506.45 g/mol



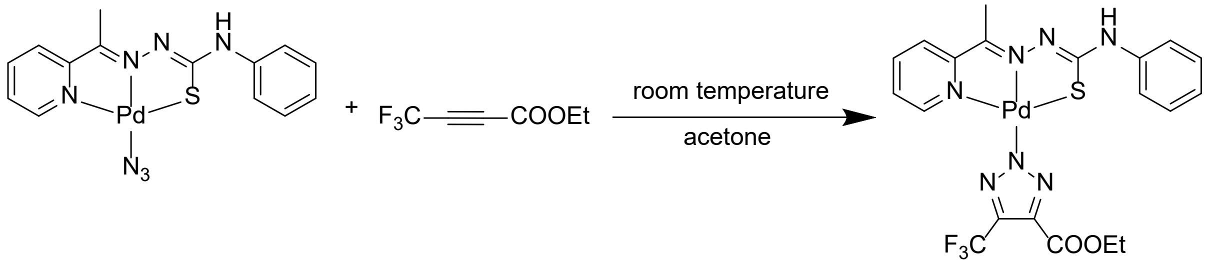

10.30
8.45
8.45
8.45
8.45
8.44
8.44
8.44
8.44
8.23
8.22
8.21
8.20
8.20
7.88
7.86
7.70
7.70
7.69
7.69
7.68
7.68
7.67
7.67
7.63
7.62
7.36
7.35
7.33
7.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
1.00
1.00
1.02
1.02
1.02
2.05
2.07
1.02


175.42
159.57
158.72
146.02
140.72
140.24
128.68
127.65
126.24
123.39
120.14
13.64
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


-3101.21
-2900
-2950
-3000
-3050
-3100
-3150
-3200
-3250
-3300
-3350
-3400
ppm


% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
3279,29
3136,50
3085,87
2060,49
1600,33
1550,05
1493,37
1457,70
1434,08
1251,63
1154,35
1072,64
754,90
734,86
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)

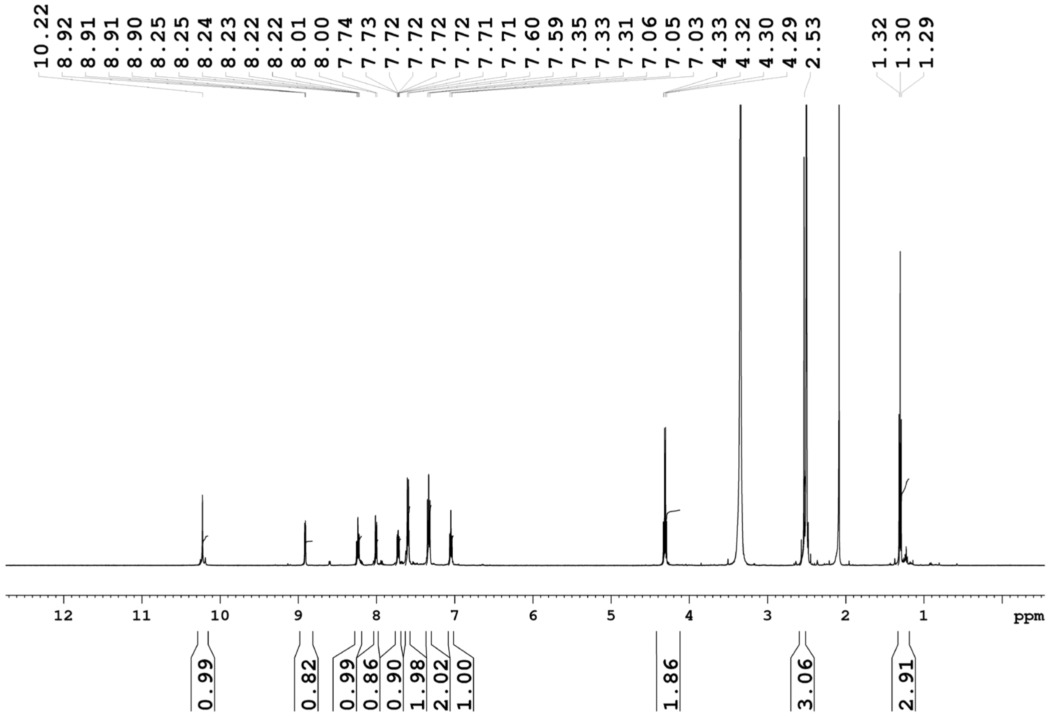
2.3 [Pd(triazolate^{CF3,COOEt}-N^2)(L)] (17)

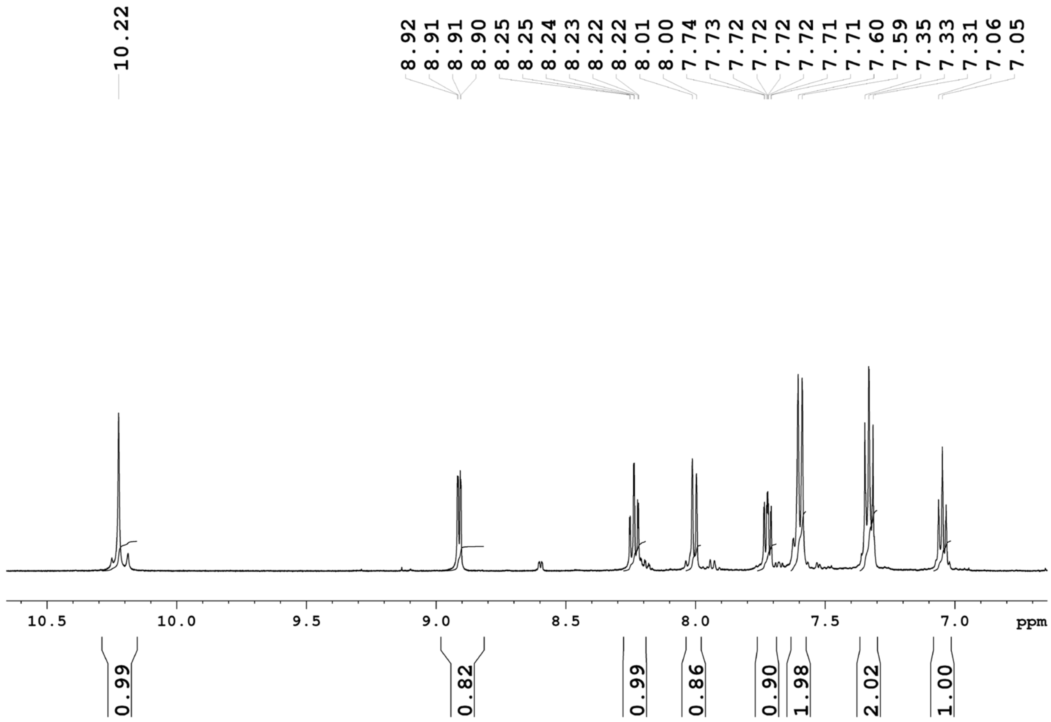


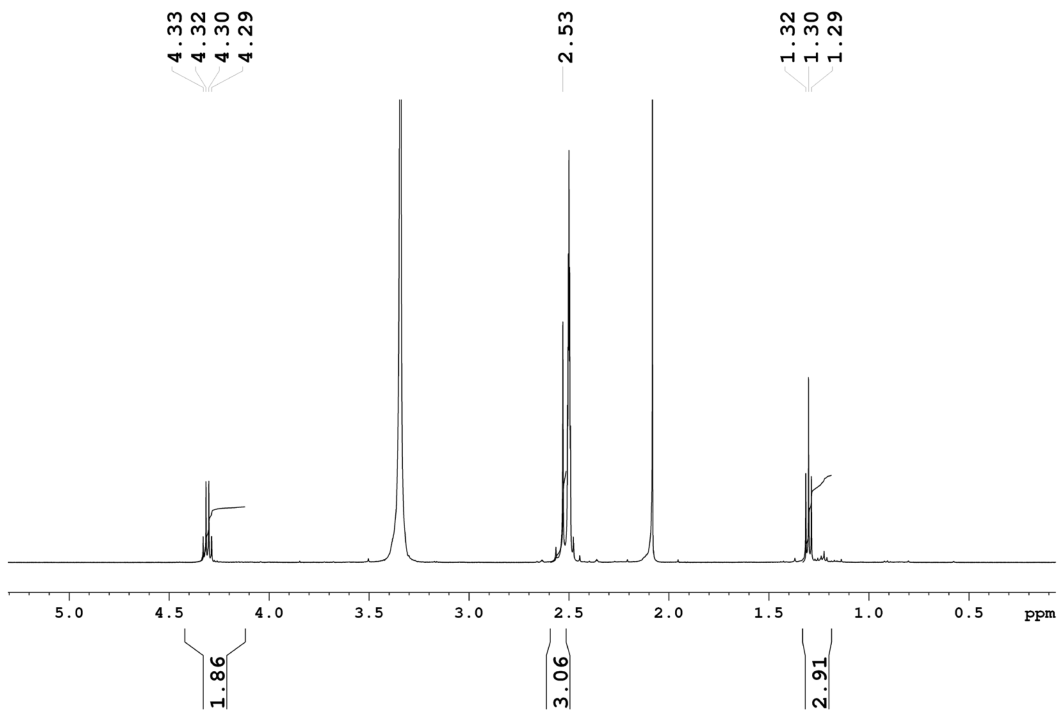
$C_{14}H_{13}N_7PdS$
417.79 g/mol

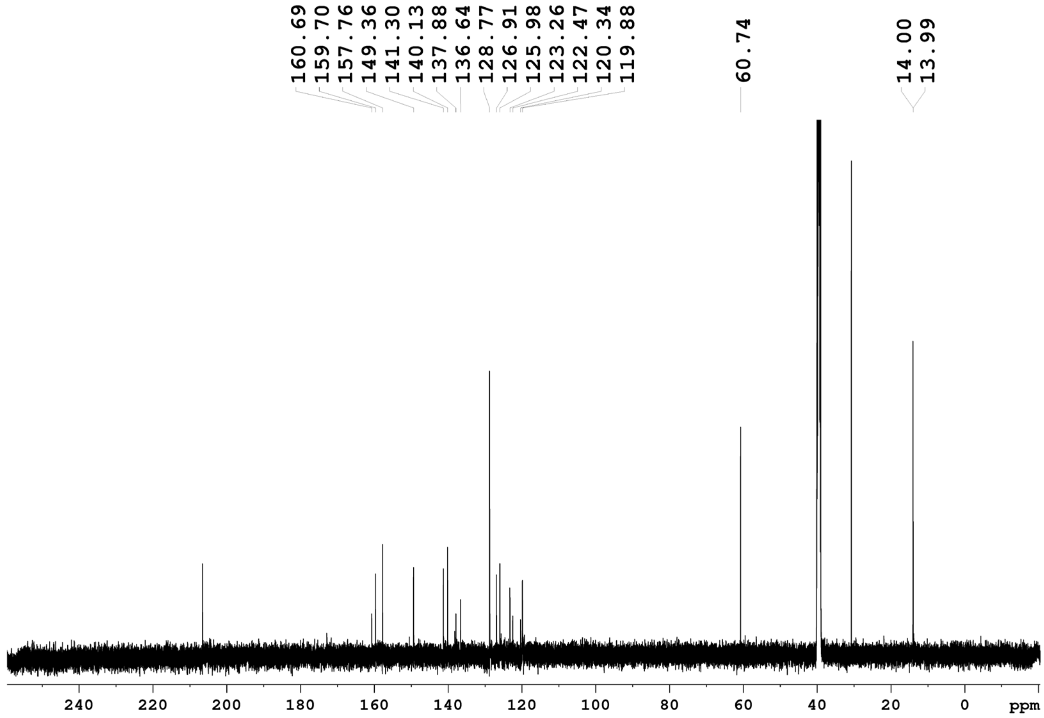
$C_6H_5F_3O_2$
166.10 g/mol

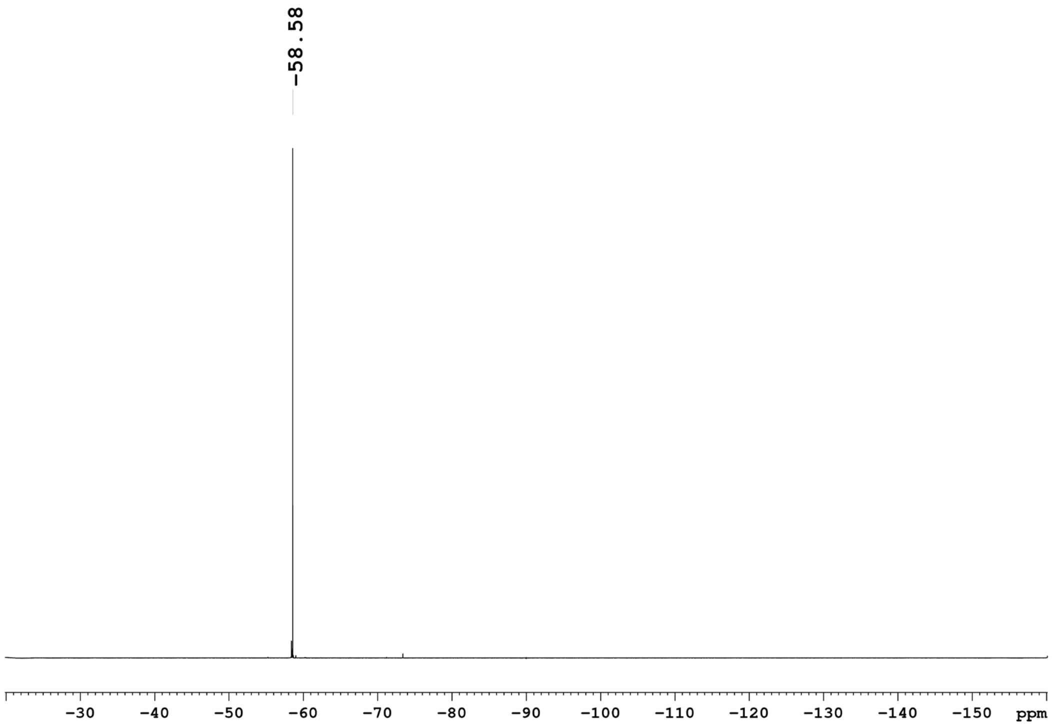
$C_{20}H_{18}F_3N_7O_2PdS$
583.89 g/mol

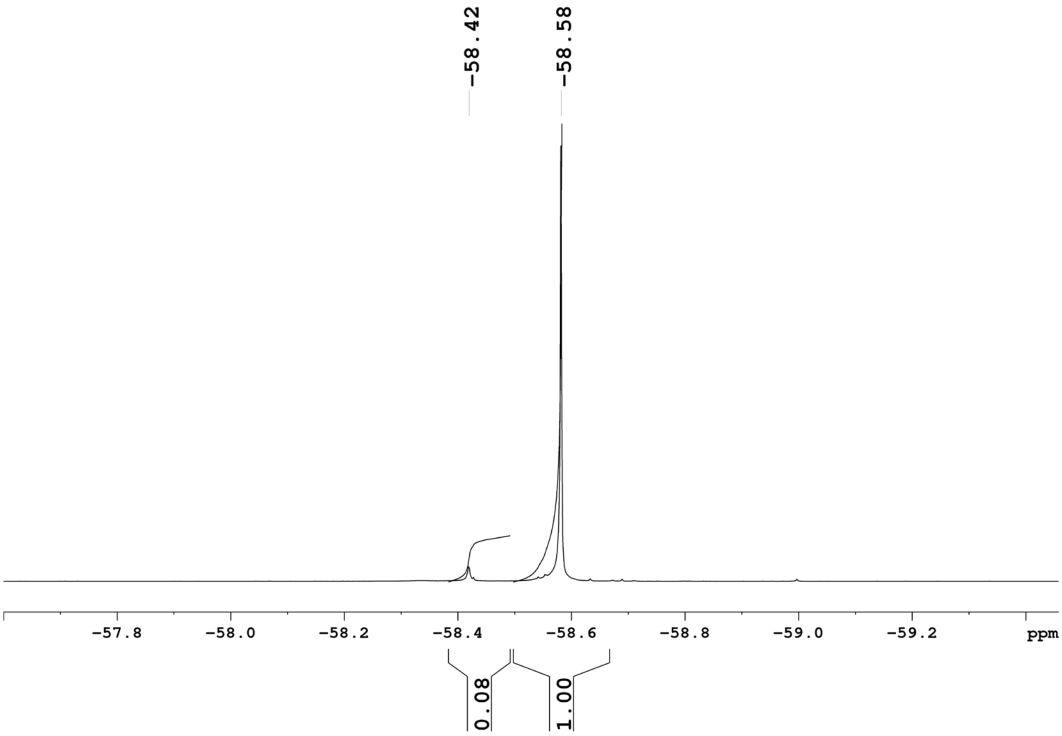



10.22
8.92 8.91 8.91 8.90 8.25 8.25 8.24 8.23 8.22 8.22 8.01 8.00 7.74 7.73 7.72 7.72 7.72 7.72 7.71 7.71 7.60 7.59 7.35 7.33 7.31 7.06 7.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 ppm
0.99 0.82 0.99 0.86 0.90 1.98 2.02 1.00

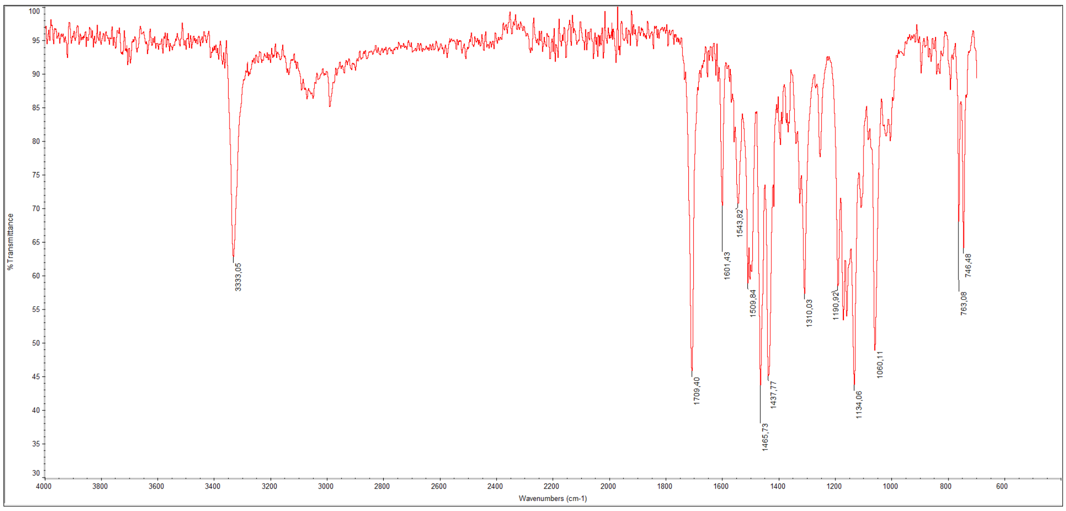

4.33 4.32 4.30 4.29
2.53
1.32 1.30 1.29
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.86 3.06 2.91


160.69
159.70
157.76
149.36
141.30
140.13
137.88
136.64
128.77
126.91
125.98
123.26
122.47
120.34
119.88
60.74
14.00
13.99
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm


-58.58
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 ppm

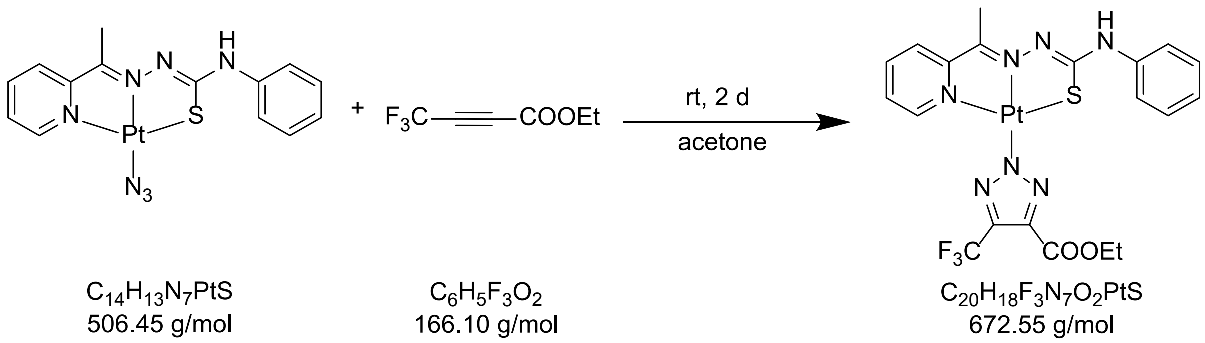


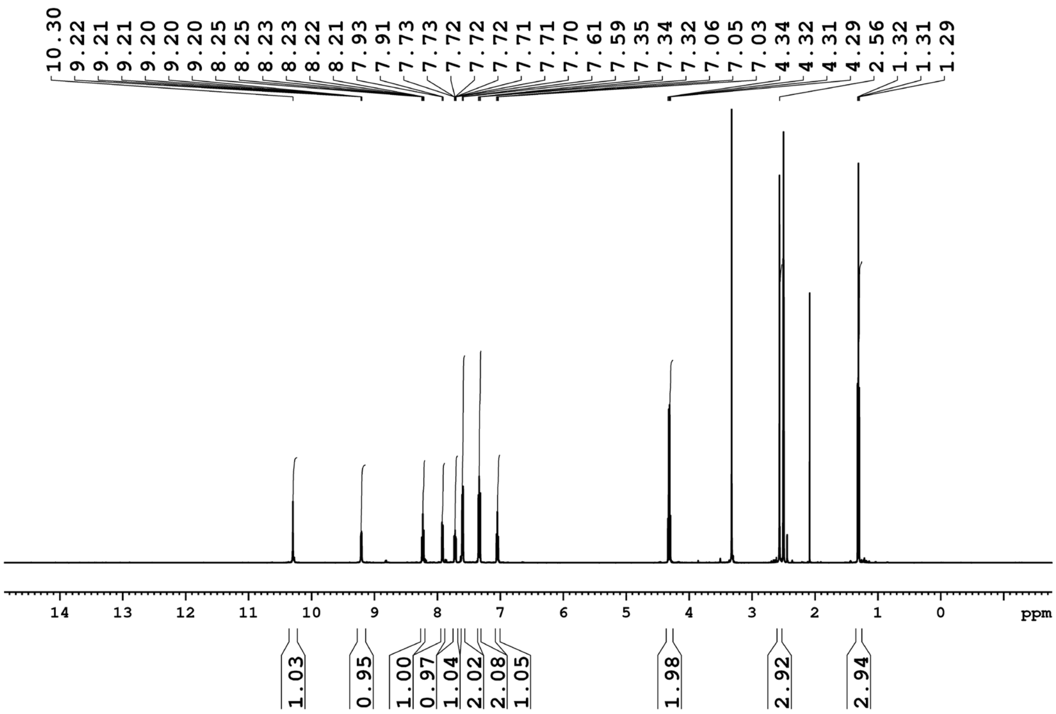
-58.42
-58.58
-57.8
-58.0
-58.2
-58.4
-58.6
-58.8
-59.0
-59.2
ppm
0.08
1.00

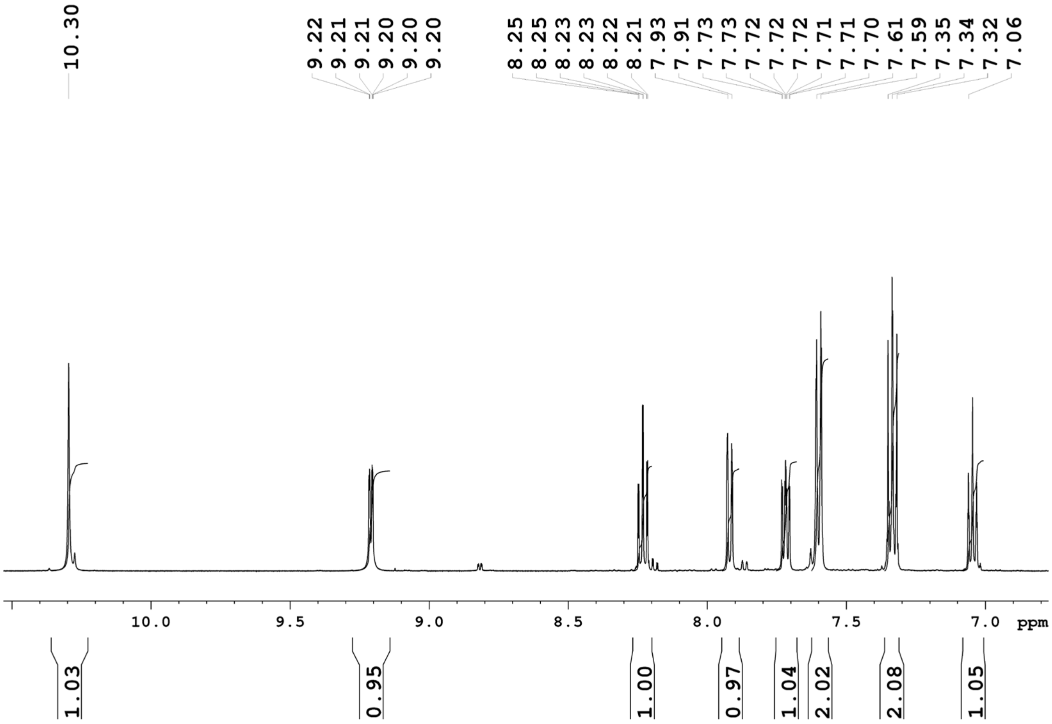


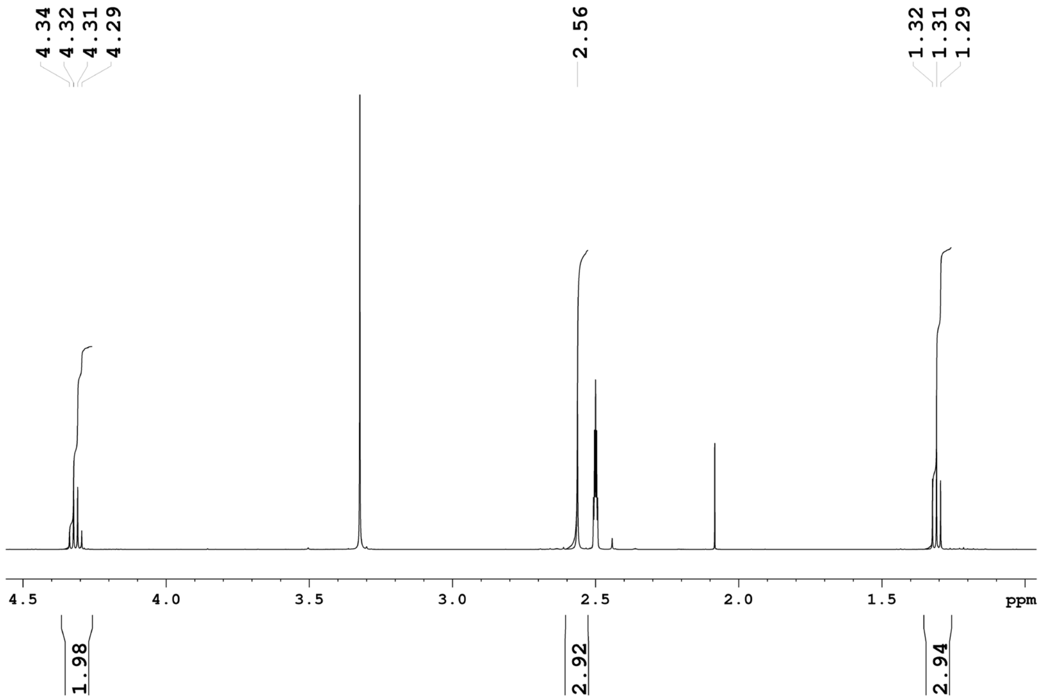
% Transmittance
Wavenumbers (cm-1)
3333,05
1709,40
1601,43
1543,82
1509,84
1465,73
1437,77
1310,03
1190,92
1134,06
1060,11
763,08
746,48

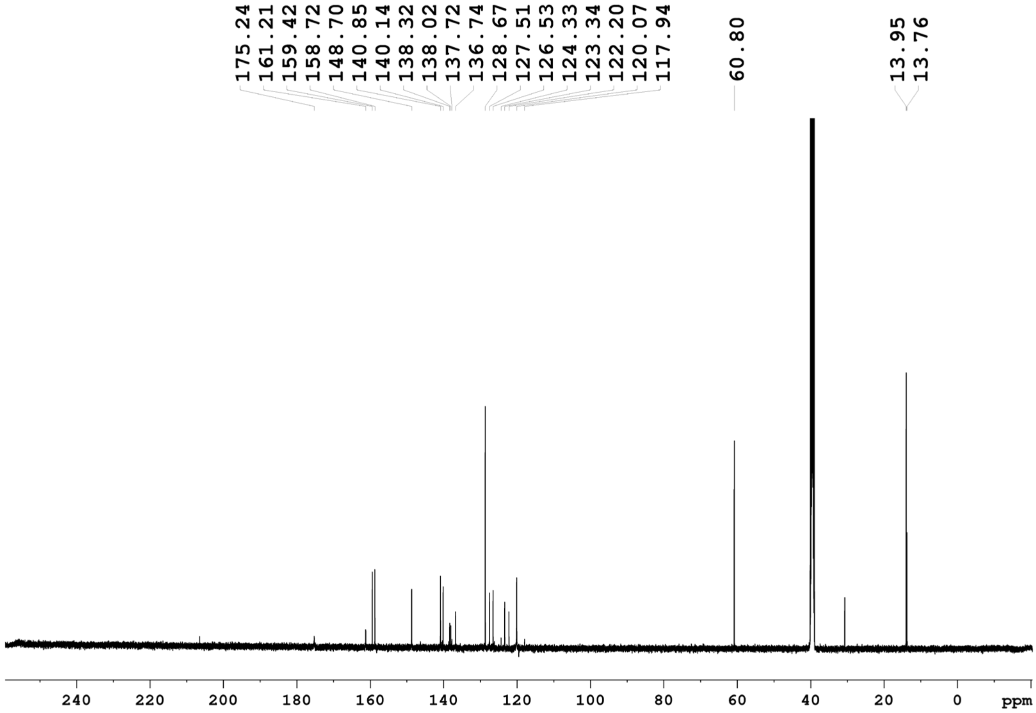
2.4 [Pt(triazolate^{CF3,COOEt}-N^2)(L)] (21)

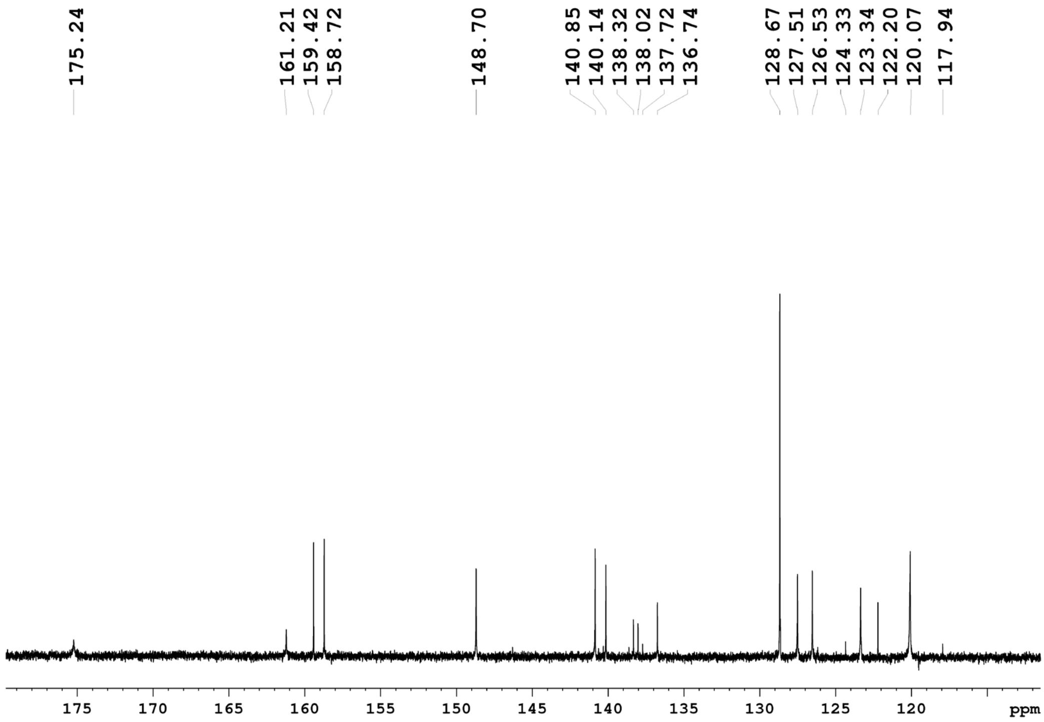


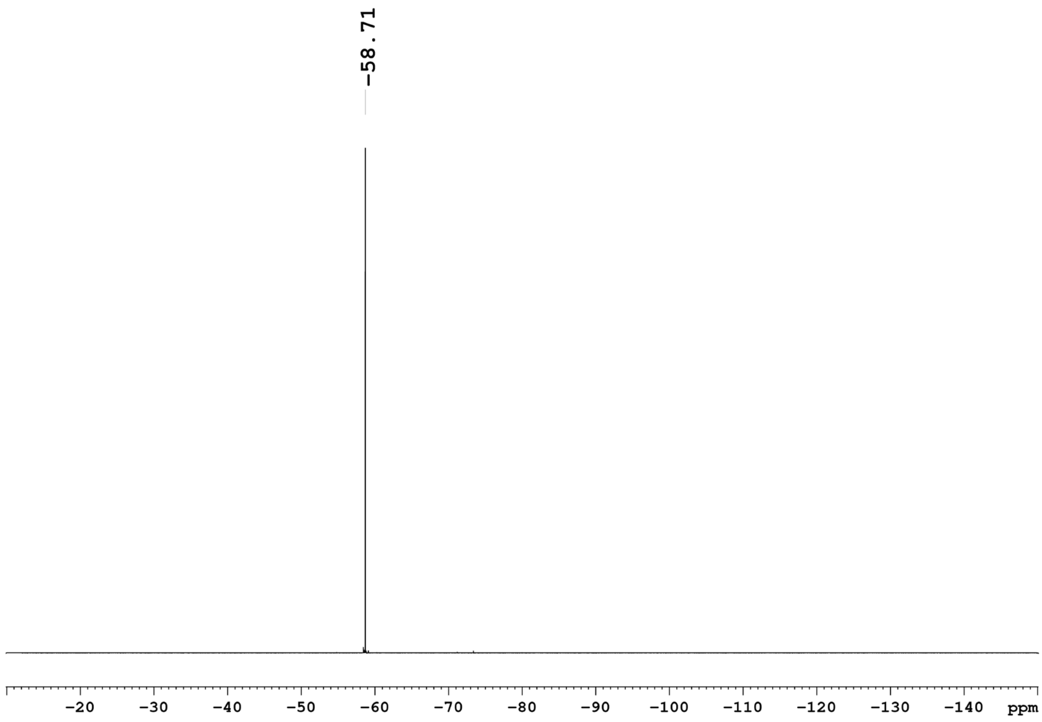



10.30
9.22 9.21 9.21 9.20 9.20 9.20
8.25 8.25 8.23 8.23 8.22 8.21 7.93 7.91 7.73 7.73 7.72 7.72 7.72 7.71 7.71 7.70 7.61 7.59 7.35 7.34 7.32 7.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 ppm
1.03 0.95 1.00 0.97 1.04 2.02 2.08 1.05

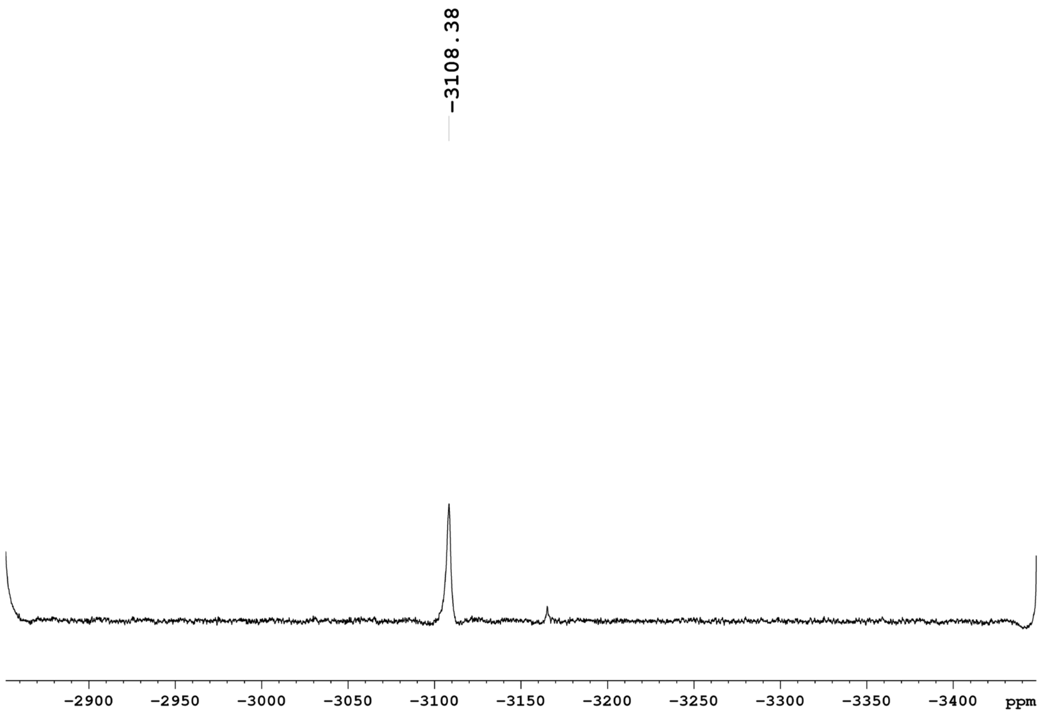

4.34 4.32 4.31 4.29
2.56
1.32 1.31 1.29
4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
1.98 2.92 2.94


175.24
161.21
159.42
158.72
148.70
140.85
140.14
138.32
138.02
137.72
136.74
128.67
127.51
126.53
124.33
123.34
122.20
120.07
117.94
60.80
13.95
13.76
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm

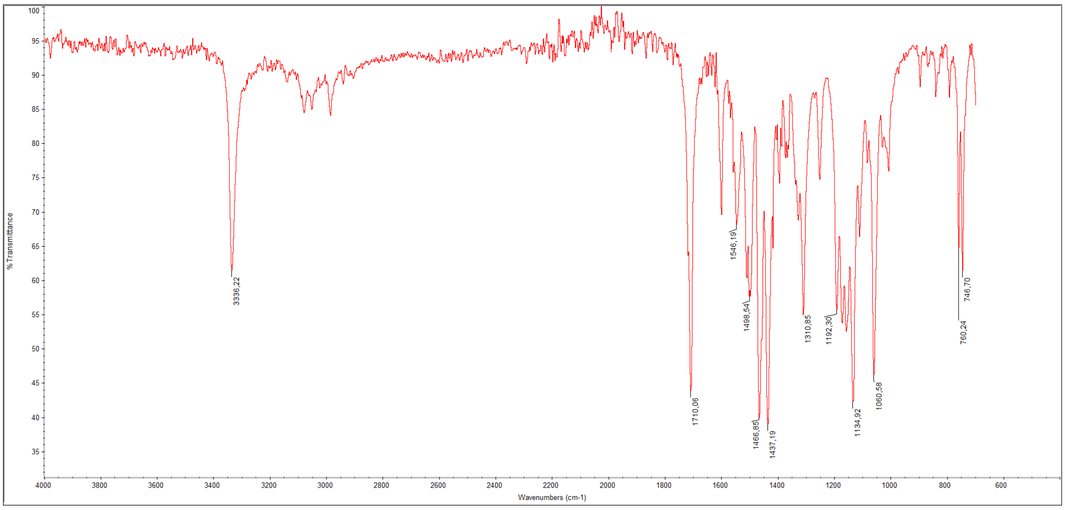

175.24
161.21
159.42
158.72
148.70
140.85
140.14
138.32
138.02
137.72
136.74
128.67
127.51
126.53
124.33
123.34
122.20
120.07
117.94
175 170 165 160 155 150 145 140 135 130 125 120 ppm



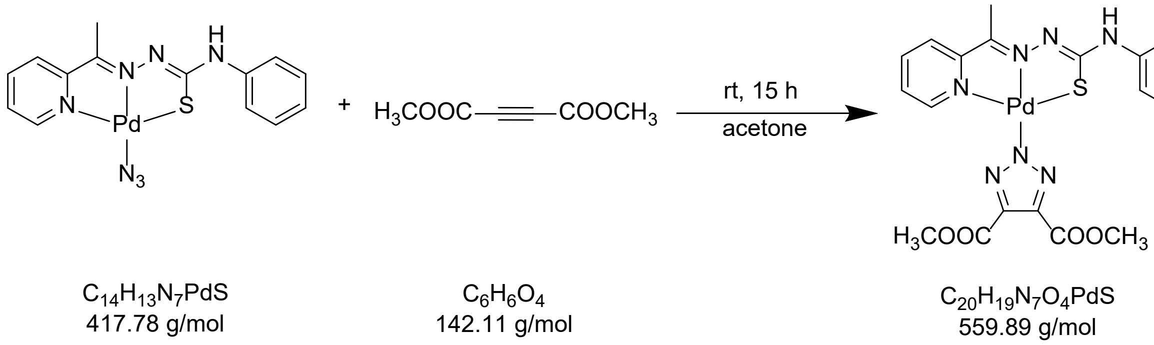
-58.71
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm

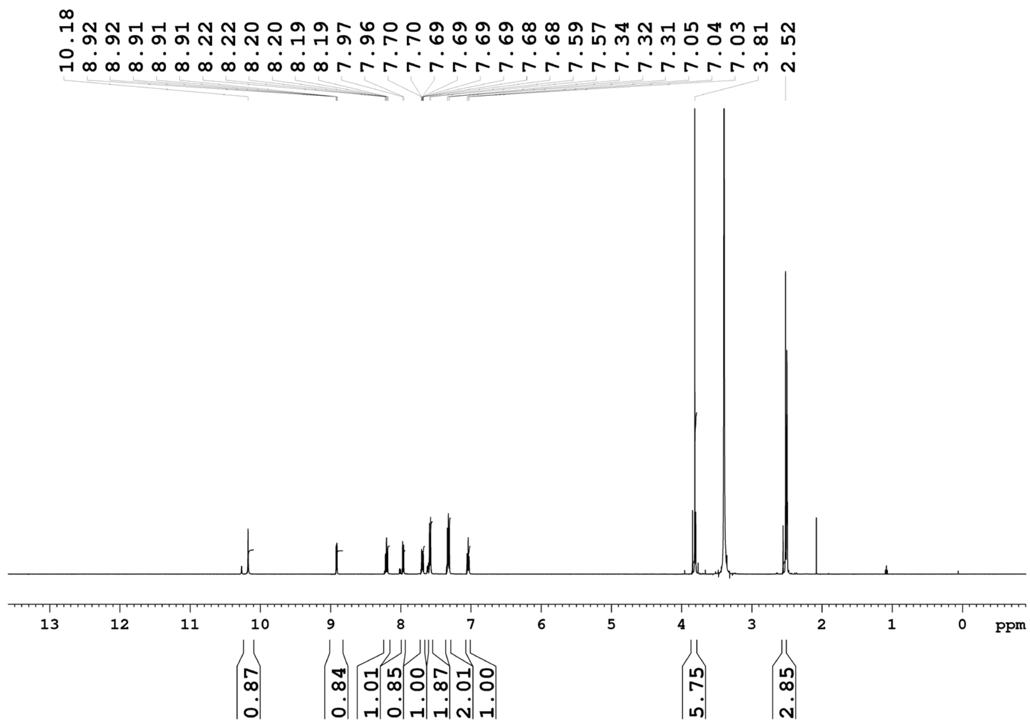


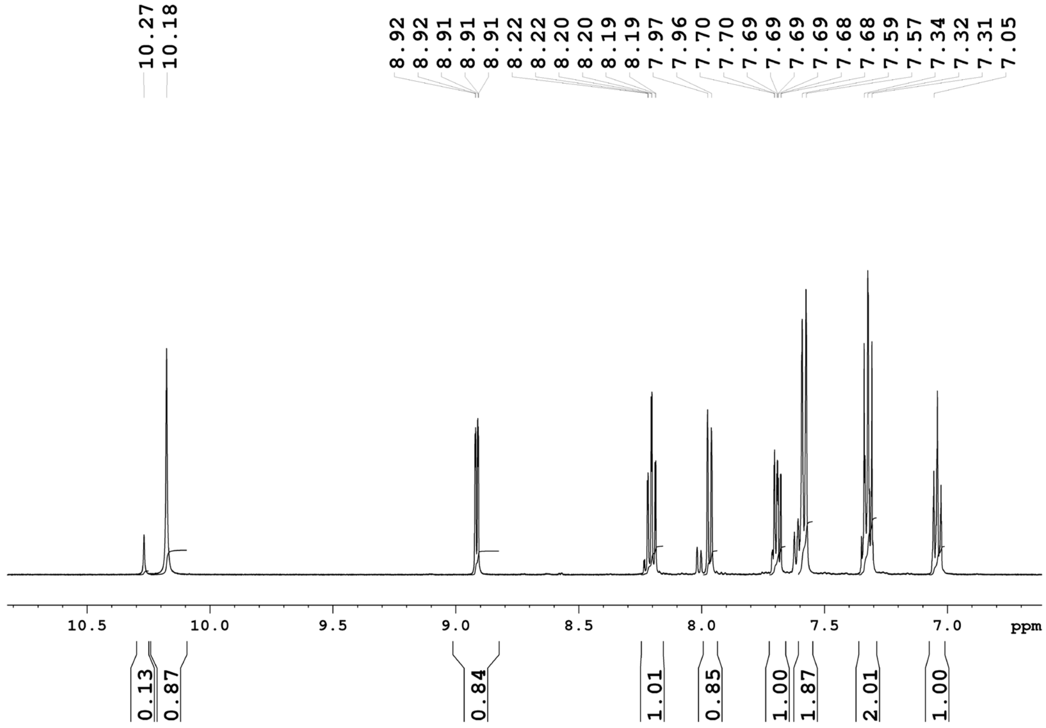
-3108.38
-2900
-2950
-3000
-3050
-3100
-3150
-3200
-3250
-3300
-3350
-3400
ppm


% Transmittance
Wavenumbers (cm-1)
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
3336,22
1710,06
1546,19
1498,54
1466,85
1437,19
1310,85
1192,30
1134,92
1060,58
760,24
746,70

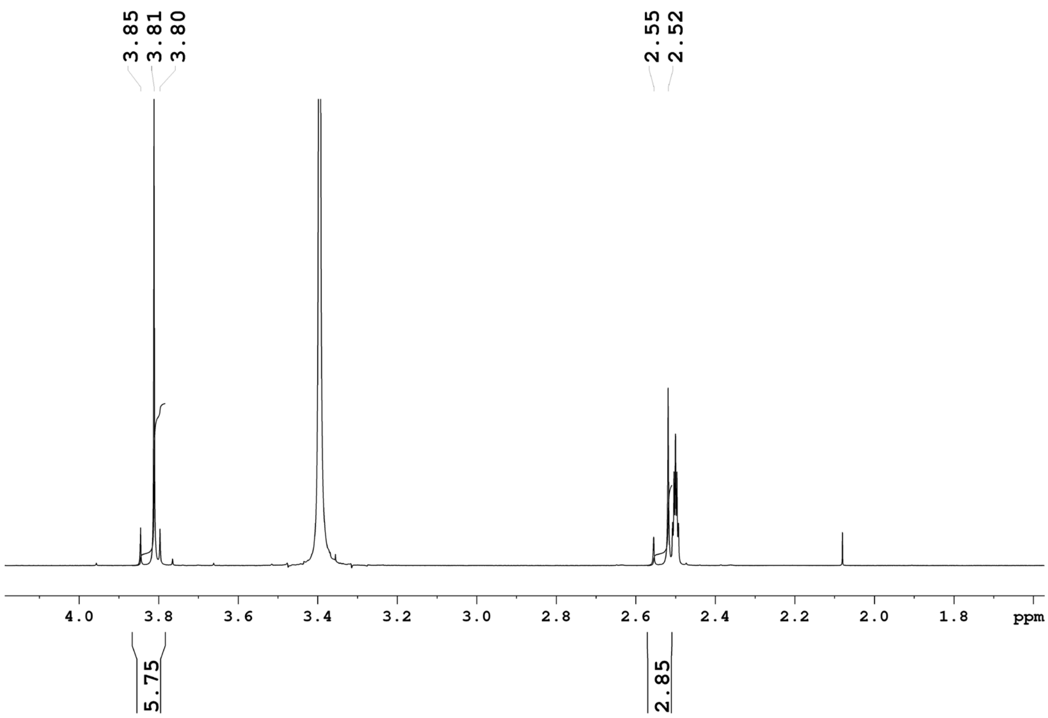
2.5 [Pd(triazolate^{COOCH3,COOCH3}-N^2)(L)] (18)



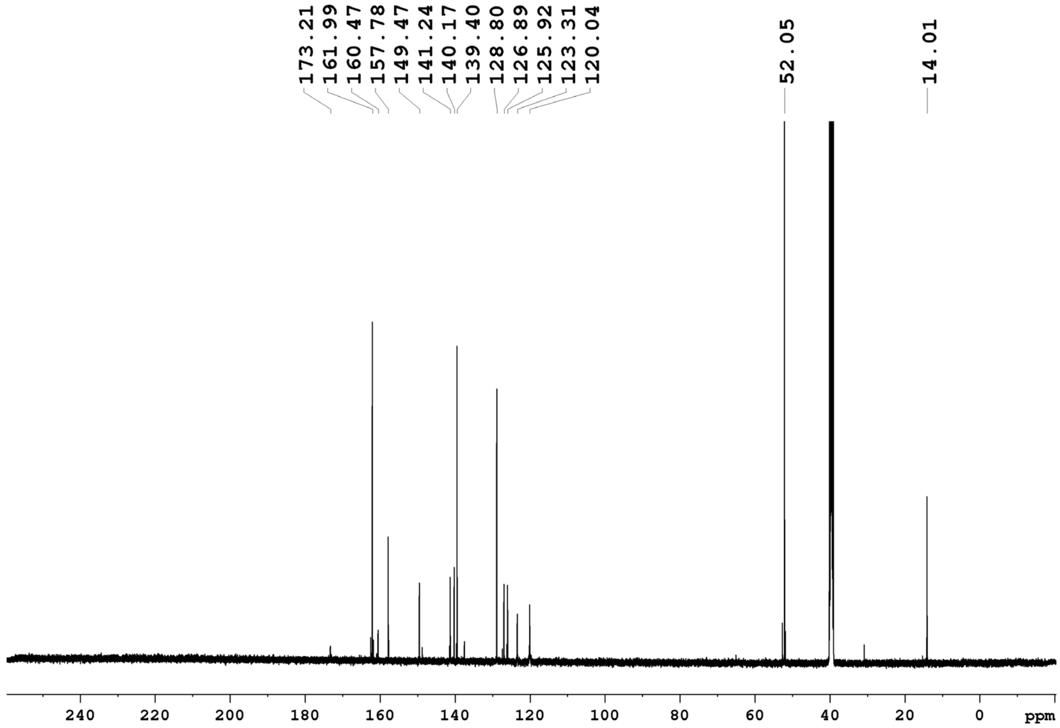


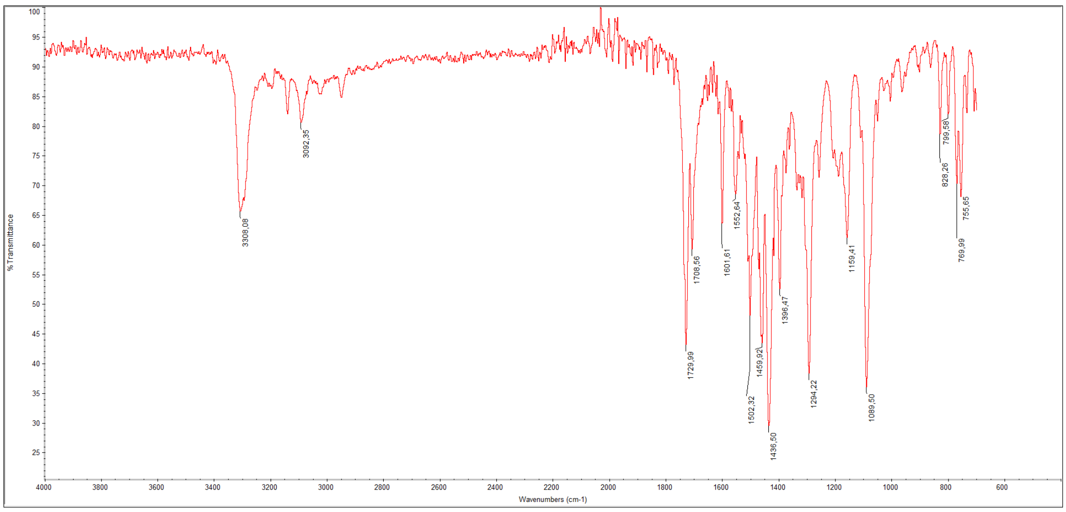


10.27
10.18
8.92
8.92
8.91
8.91
8.91
8.22
8.22
8.20
8.20
8.19
8.19
7.97
7.96
7.70
7.70
7.69
7.69
7.69
7.69
7.68
7.68
7.59
7.57
7.34
7.32
7.31
7.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
0.13
0.87
0.84
1.01
0.85
1.00
1.87
2.01
1.00

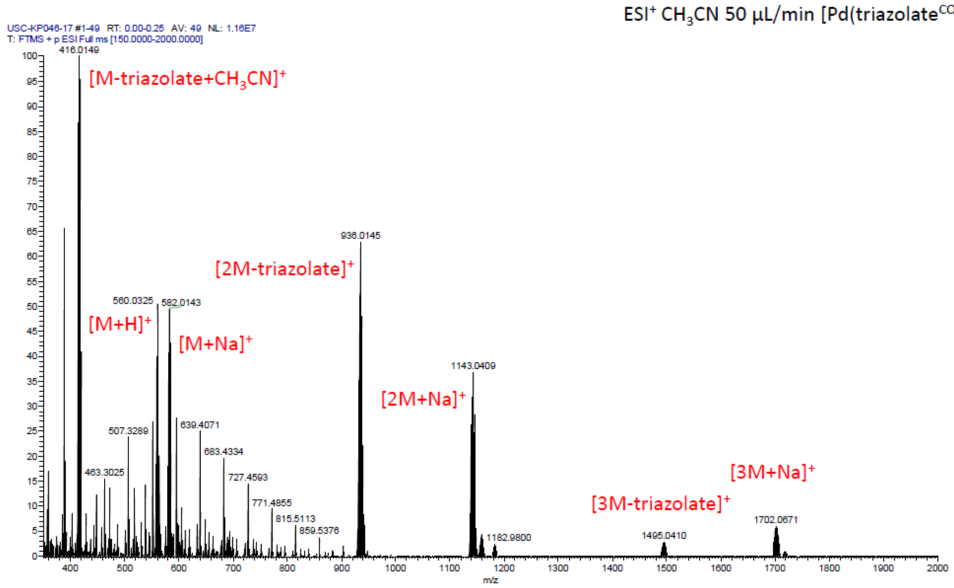


3.85
3.81
3.80
2.55
2.52
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
ppm
5.75
2.85

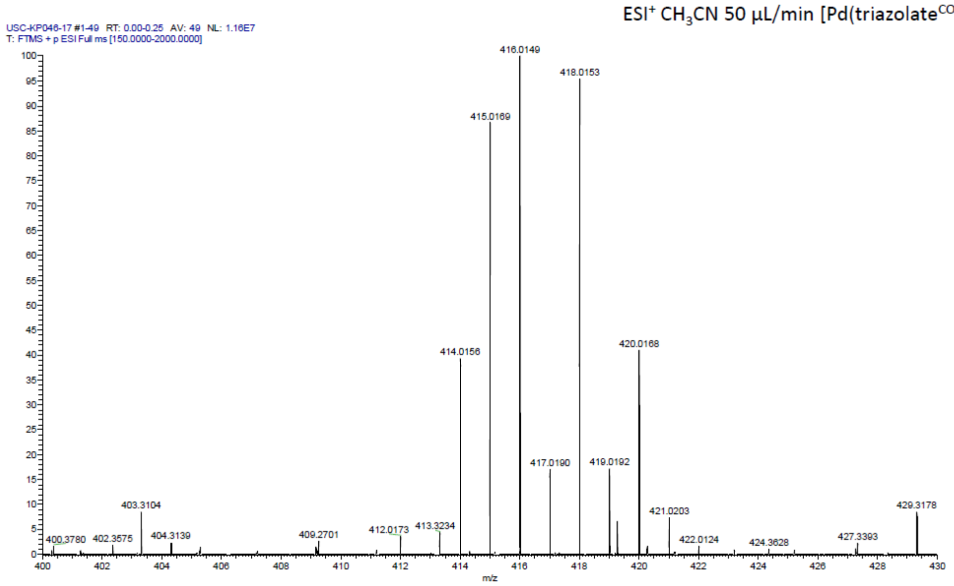

173.21
161.99
160.47
157.78
149.47
141.24
140.17
139.40
128.80
126.89
125.92
123.31
120.04
52.05
14.01
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

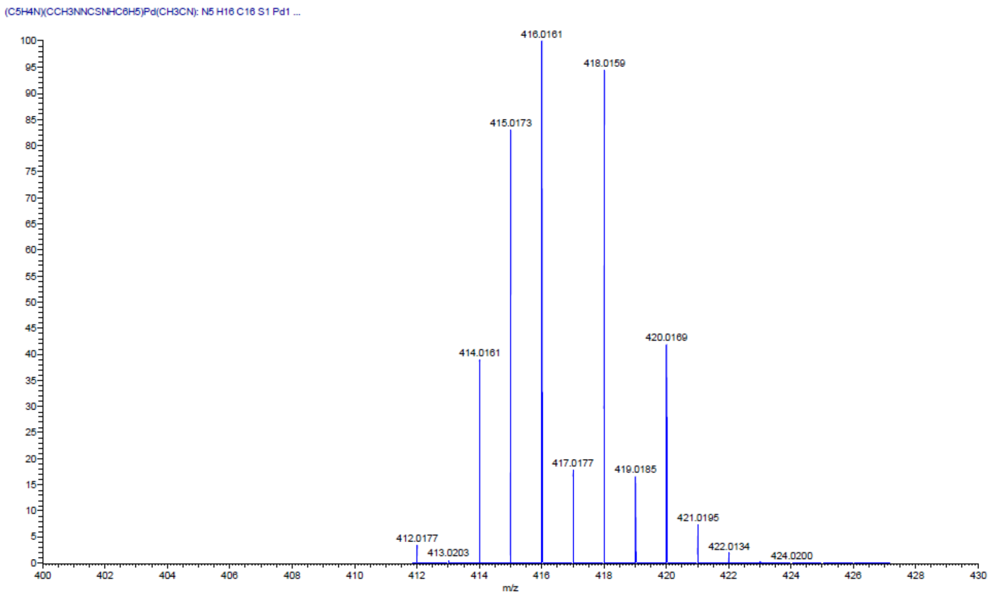

% Transmittance
Wavenumbers (cm-1)
3308,08
3092,35
1729,99
1708,56
1601,61
1552,64
1502,32
1459,92
1436,50
1396,47
1294,22
1159,41
1089,50
828,26
799,58
769,99
755,65

ESI+ CH_3CN 50 µL/min [Pd(triazolate^{COOCH3,COOCH3})(L)]

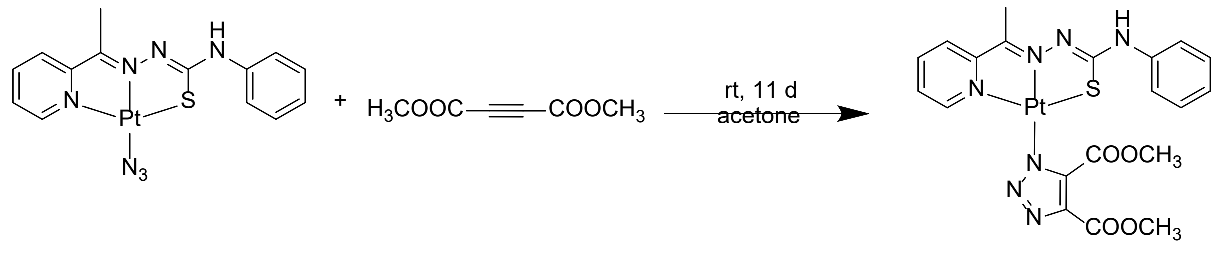


ESI+ CH_3CN 50 µL/min [Pd(triazolate^{COOCH3,COOCH3})(L)]

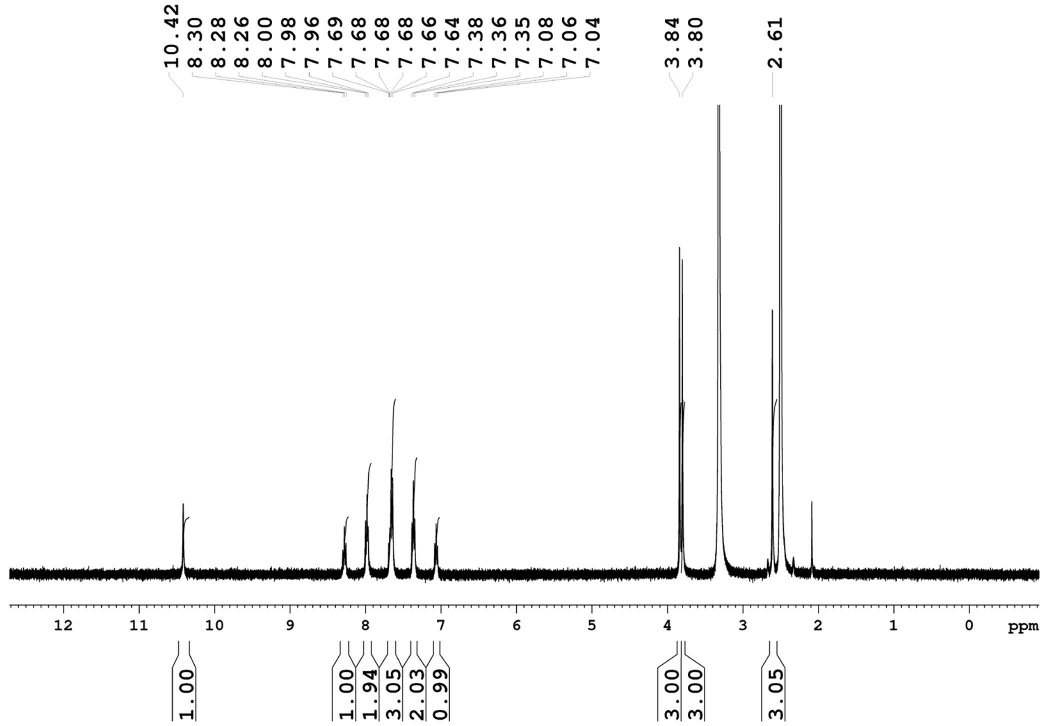


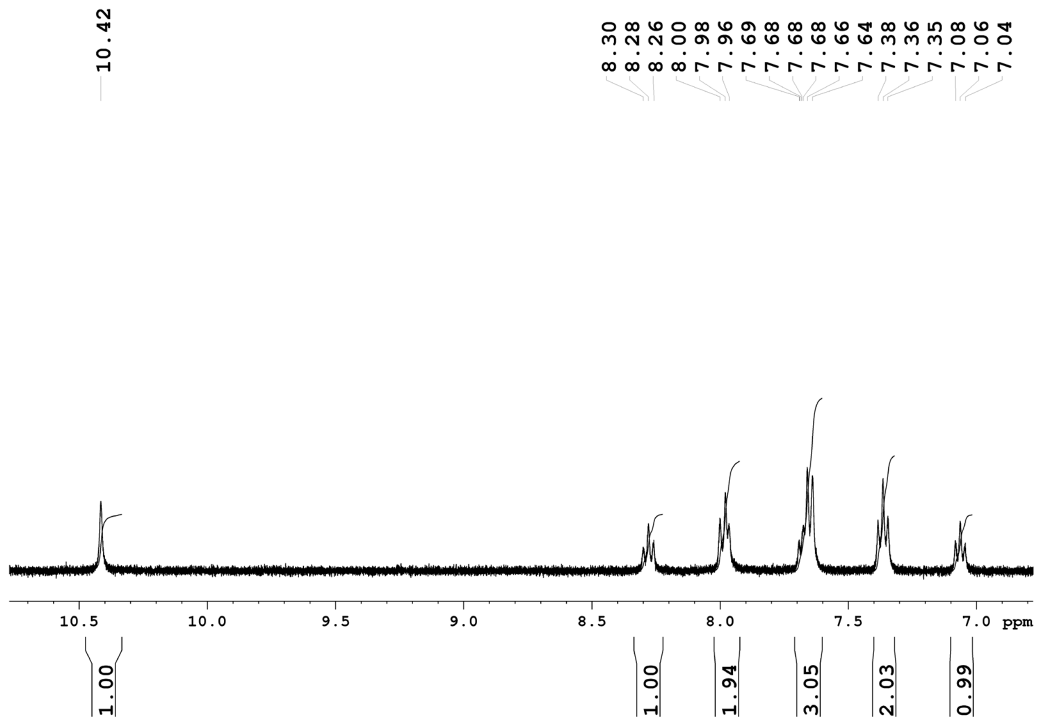


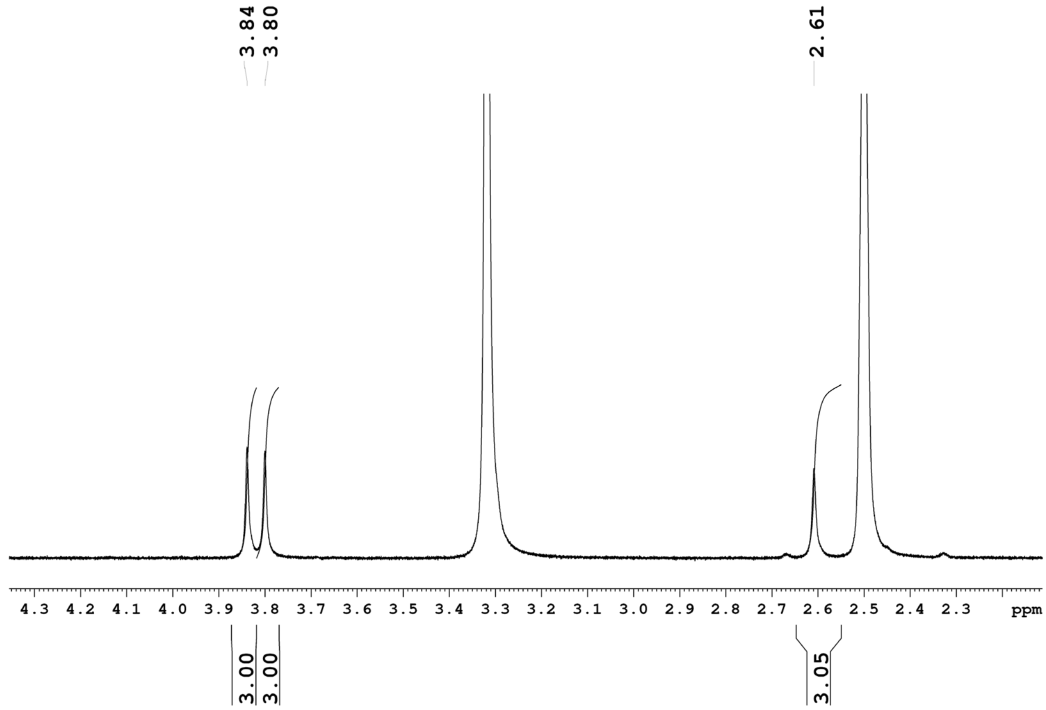
2.6 [Pt(triazolate^{COOCH3,COOCH3}-N^1)(L)] (22)

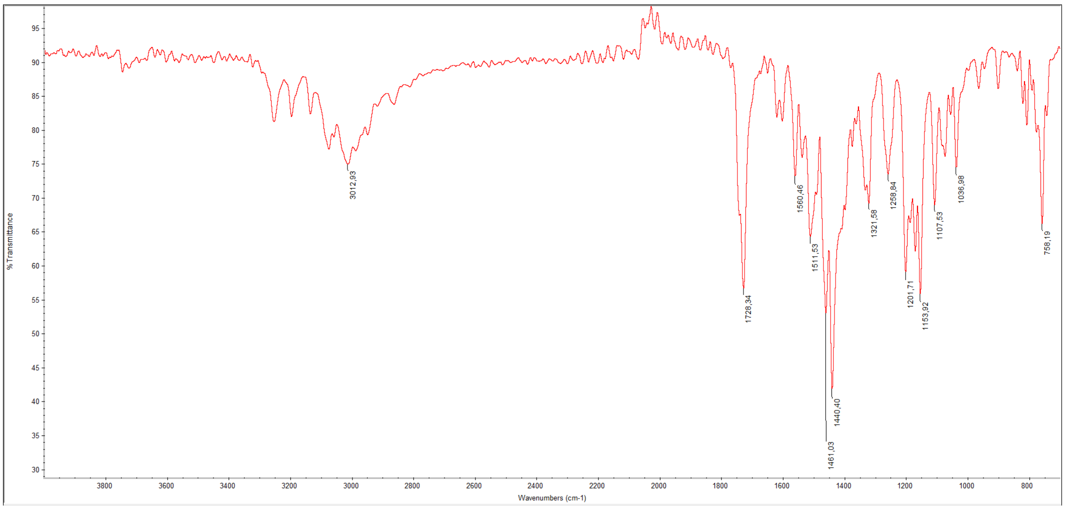


$C_{14}H_{13}N_7PtS$	$C_6H_6O_4$	$C_{20}H_{19}N_7O_4PtS$
506.45 g/mol	142.11 g/mol	648.56 mol/L



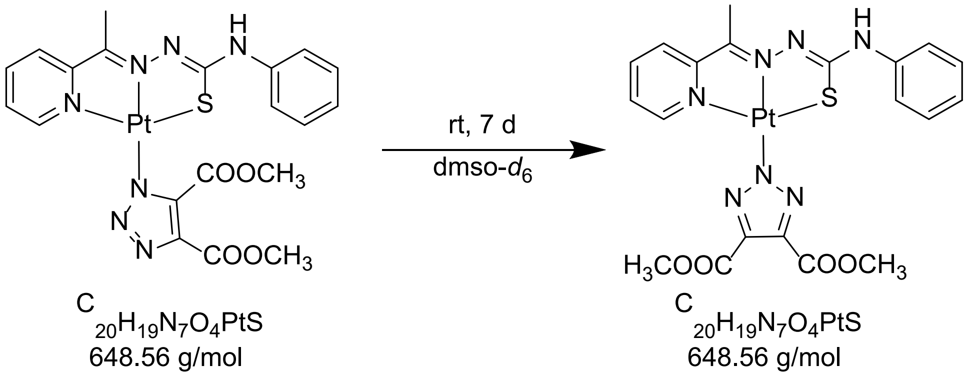

10.42
8.30 8.28 8.26 8.00 7.98 7.96 7.69 7.68 7.68 7.68 7.66 7.64 7.38 7.36 7.35 7.08 7.06 7.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 ppm
1.00 1.00 1.94 3.05 2.03 0.99

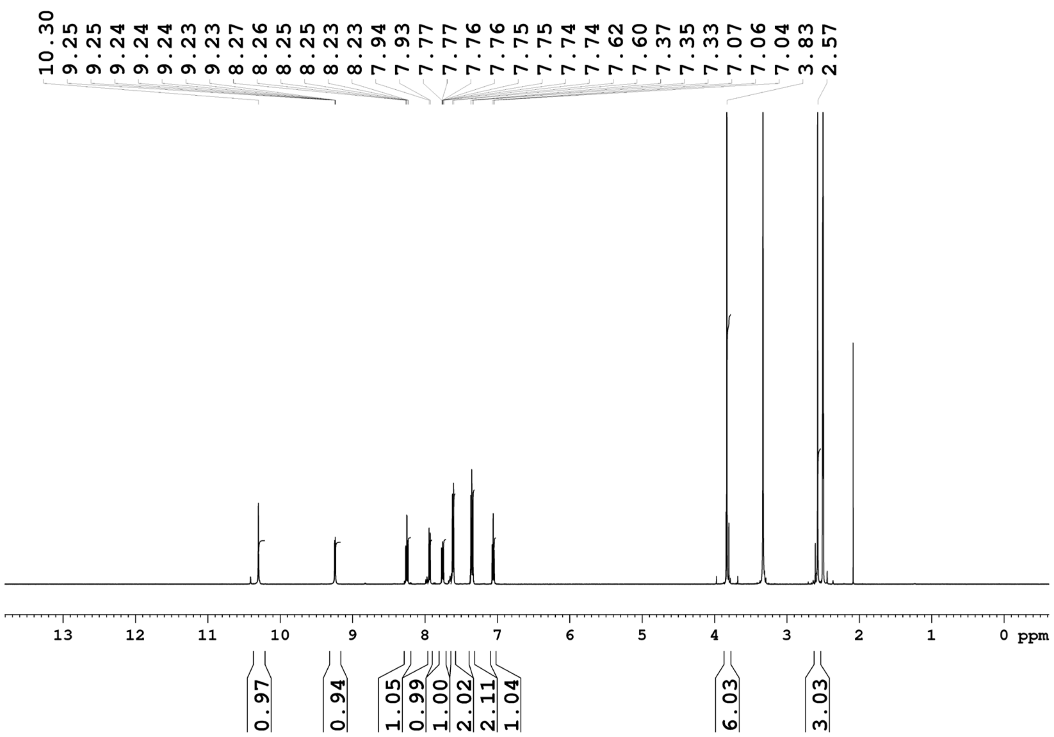

3.84 3.80 2.61
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 ppm
3.00 3.00 3.05

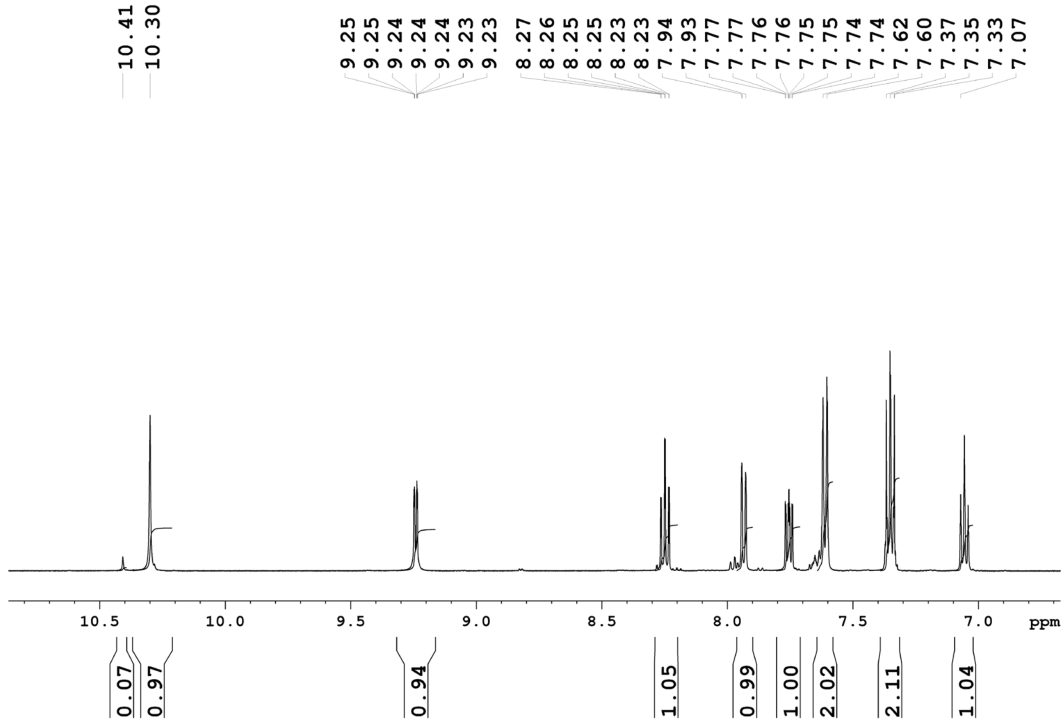


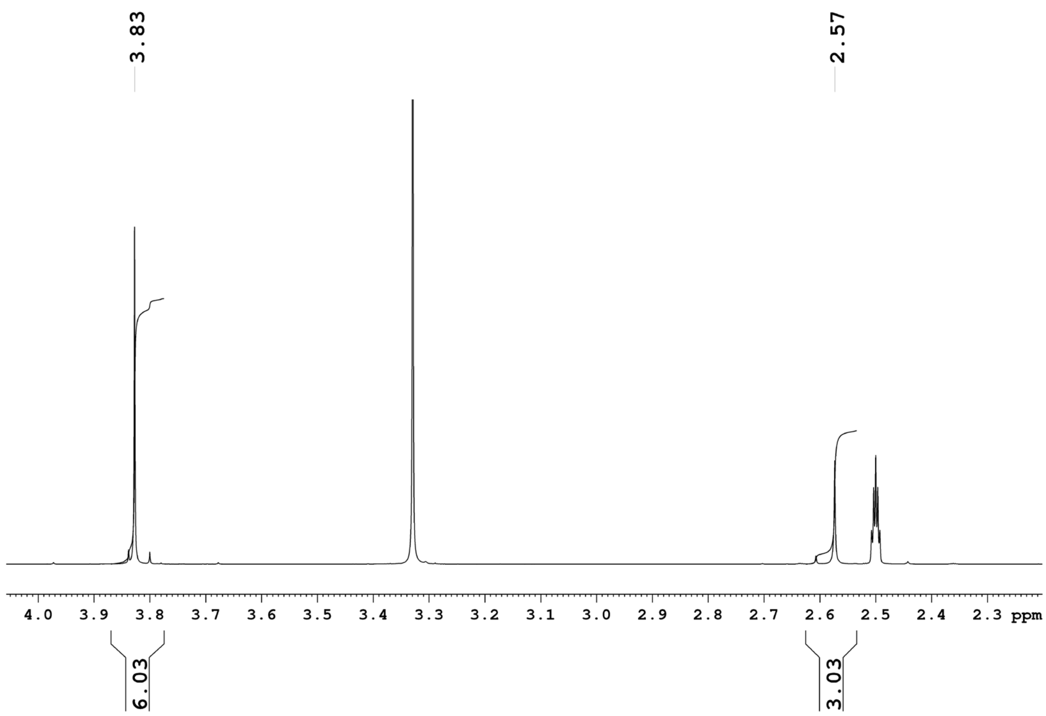
% Transmittance
Wavenumbers (cm-1)
3012,93
1728,34
1560,46
1511,53
1461,03
1440,40
1321,58
1258,84
1201,71
1153,92
1107,53
1036,98
758,19

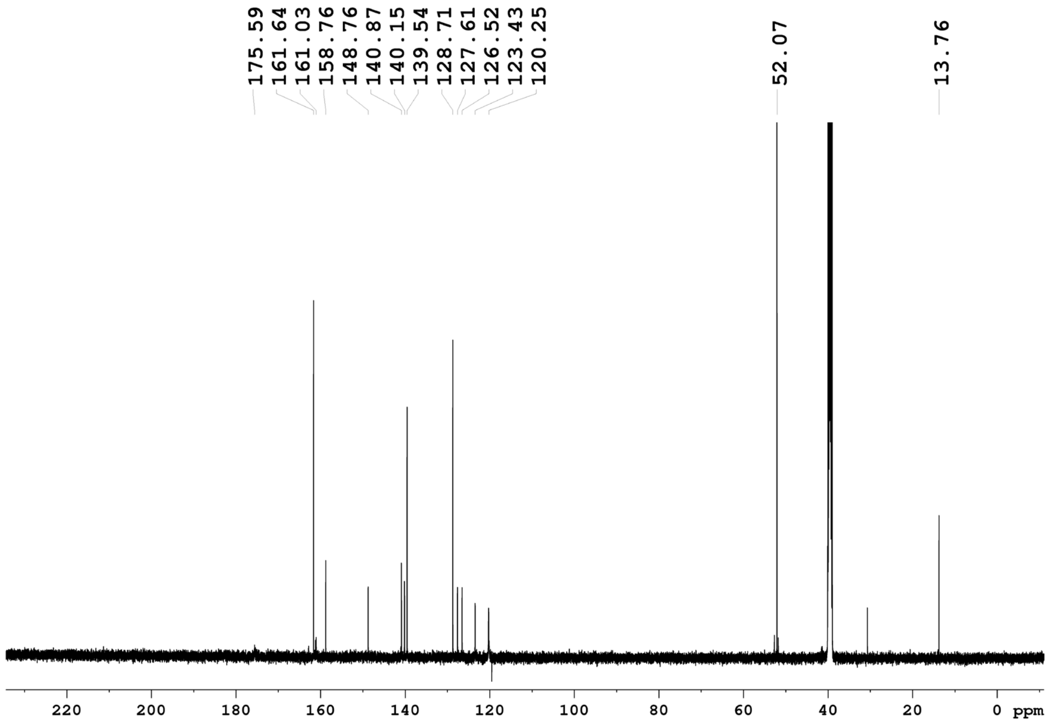
2.7 [Pt(triazolate^{COOCH3,COOCH3}-N^2)(L)] (25)

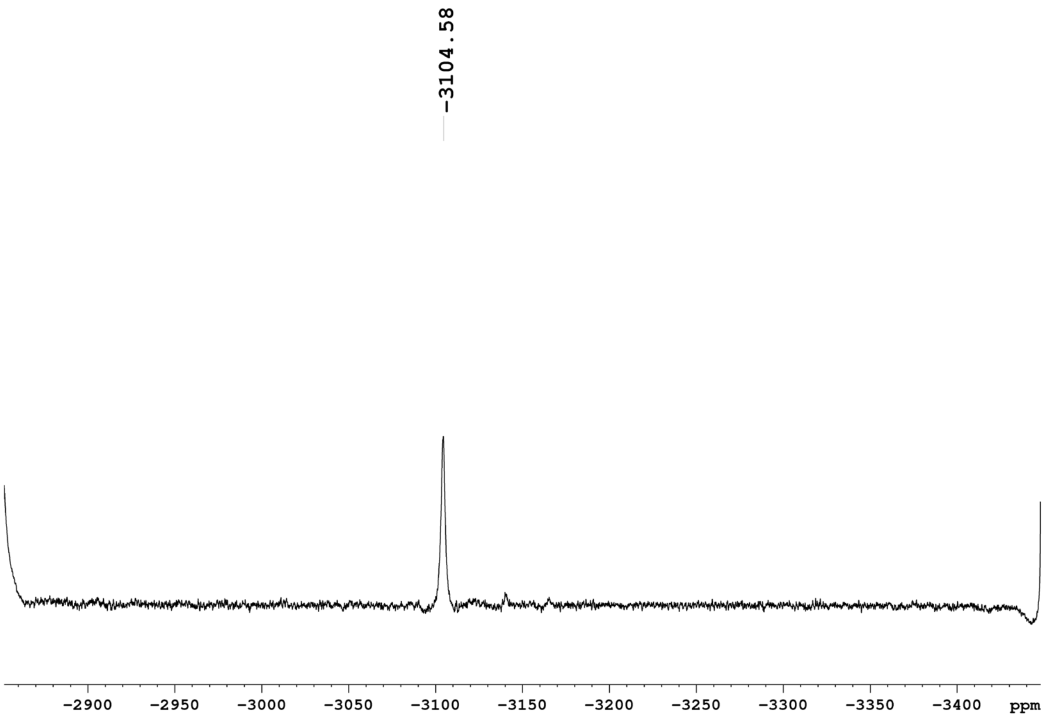




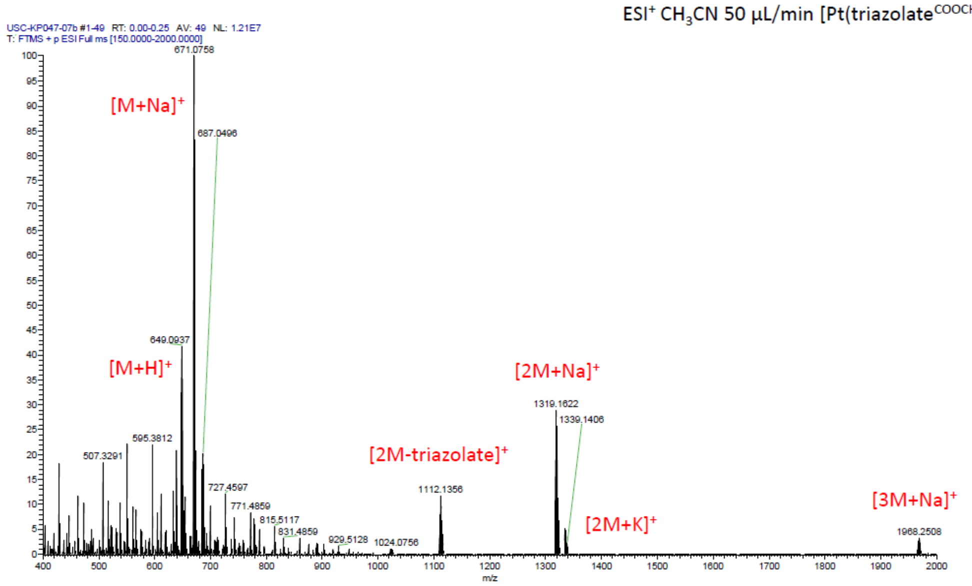

10.41
10.30
9.25
9.25
9.24
9.24
9.24
9.23
9.23
8.27
8.26
8.25
8.25
8.23
8.23
7.94
7.93
7.77
7.77
7.76
7.76
7.75
7.75
7.74
7.74
7.62
7.60
7.37
7.35
7.33
7.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 ppm
0.07
0.97
0.94
1.05
0.99
1.00
2.02
2.11
1.04


3.83
2.57
4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 ppm
6.03
3.03

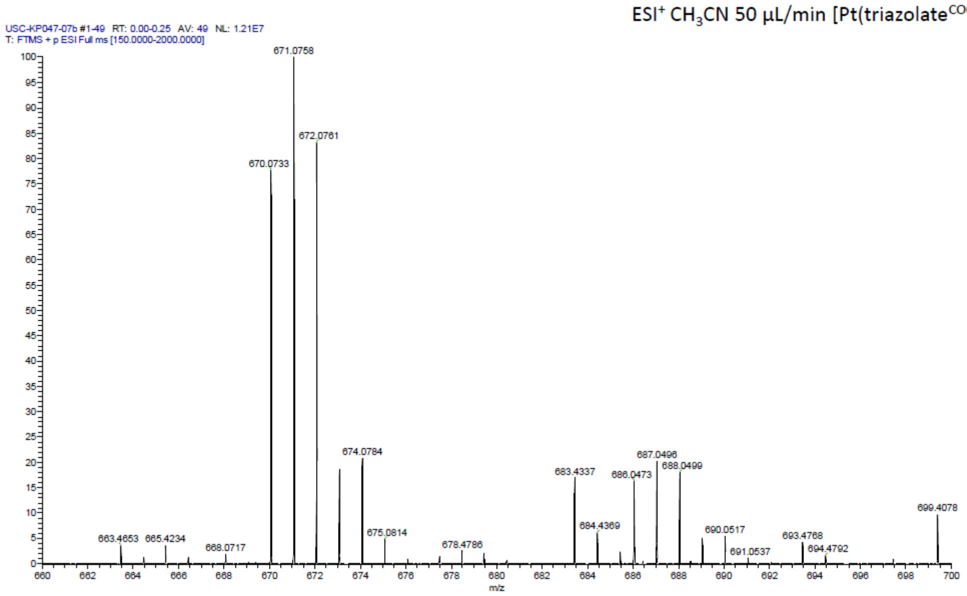

175.59
161.64
161.03
158.76
148.76
140.87
140.15
139.54
128.71
127.61
126.52
123.43
120.25
52.07
13.76
220
200
180
160
140
120
100
80
60
40
20
0
ppm

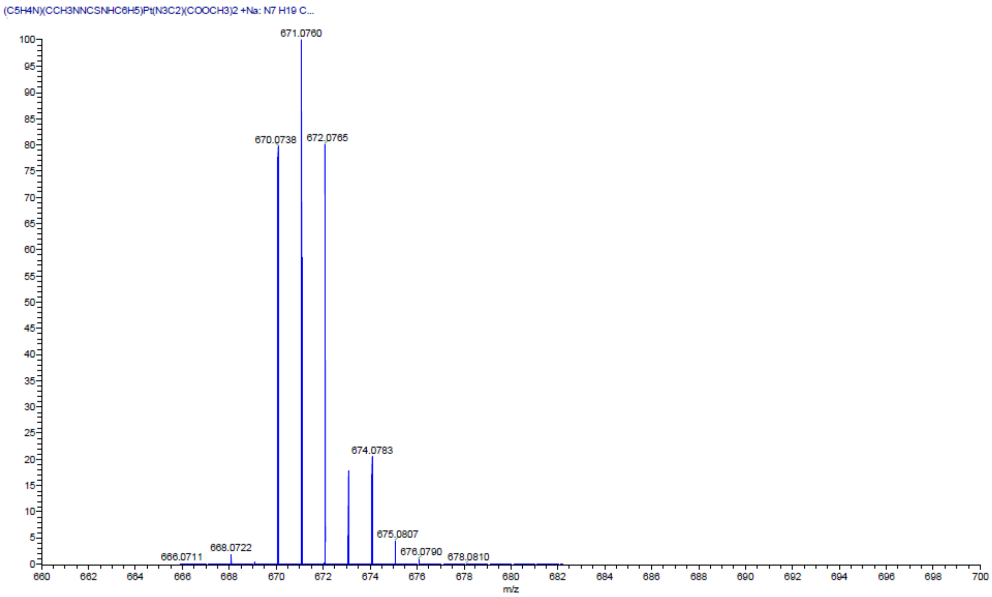

-3104.58
-2900
-2950
-3000
-3050
-3100
-3150
-3200
-3250
-3300
-3350
-3400
ppm

ESI$^+$ CH_3CN 50 μL/min [Pt(triazolate^{COOCH3,COOCH3})(L)]

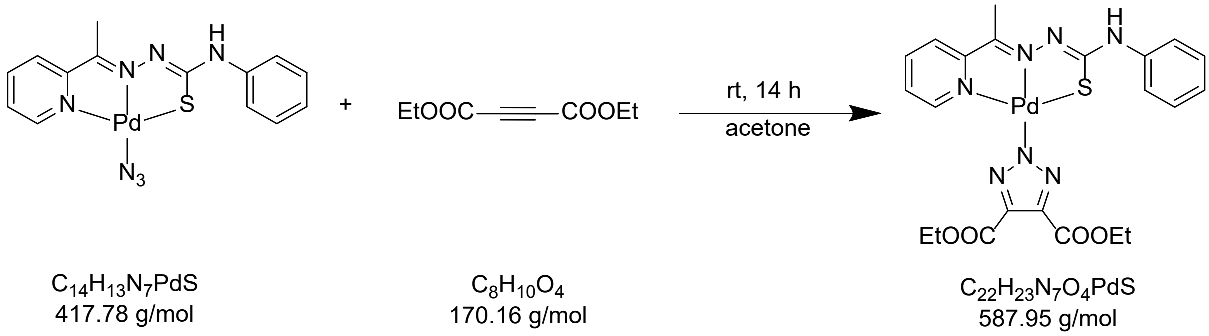


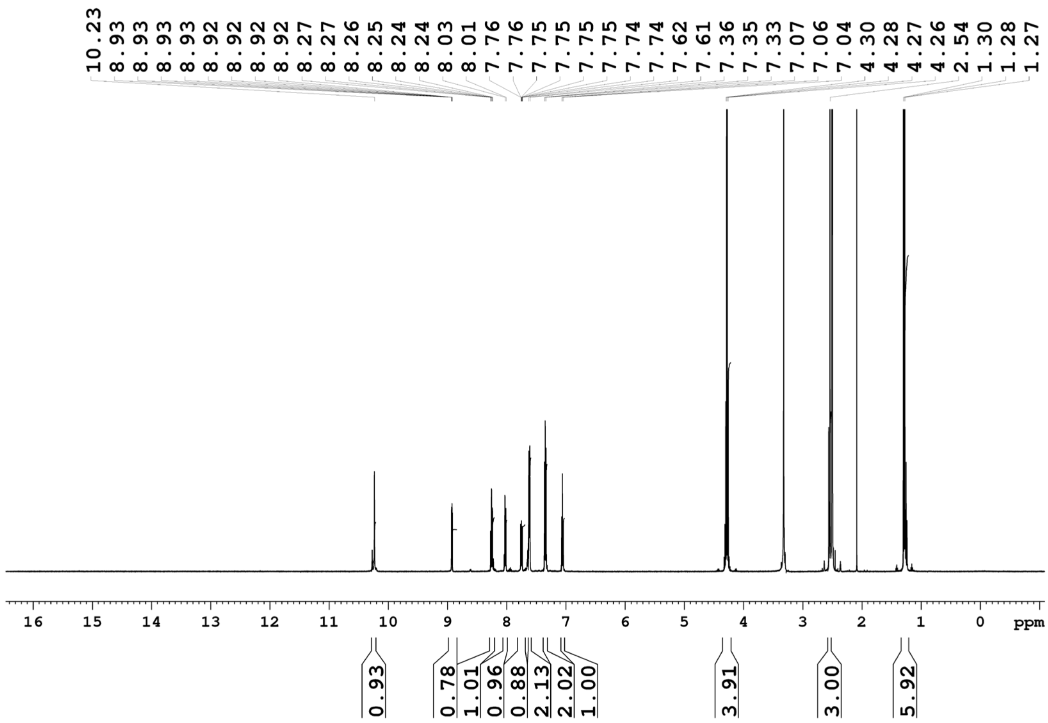
ESI$^+$ CH_3CN 50 μL/min [Pt(triazolate^{COOCH3,COOCH3})(L)]

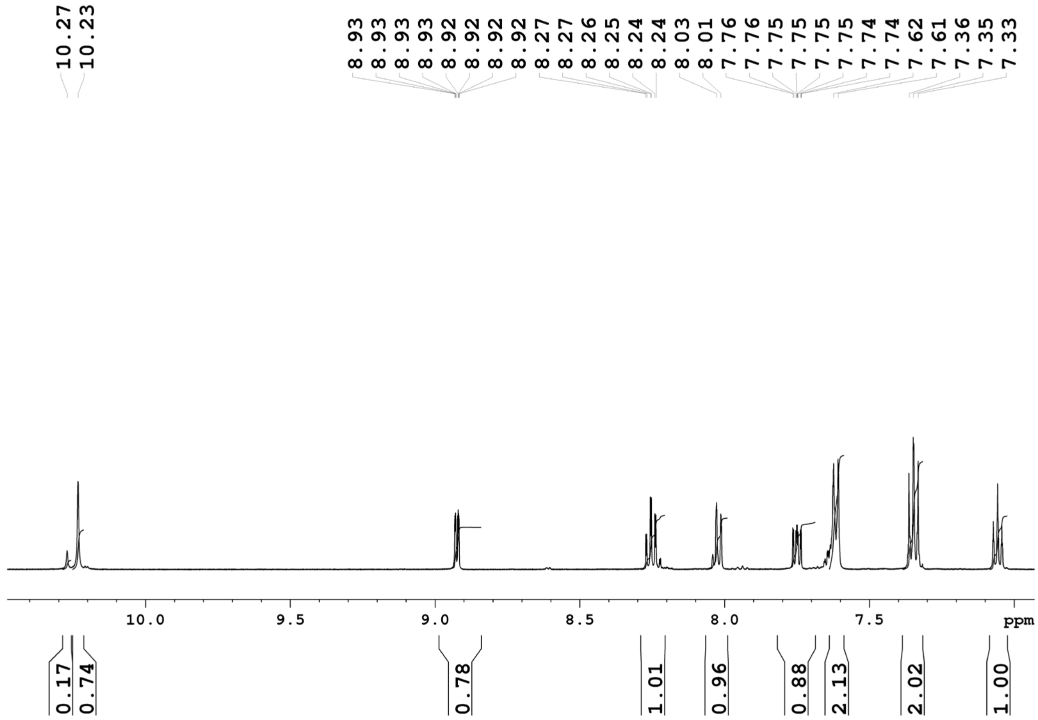


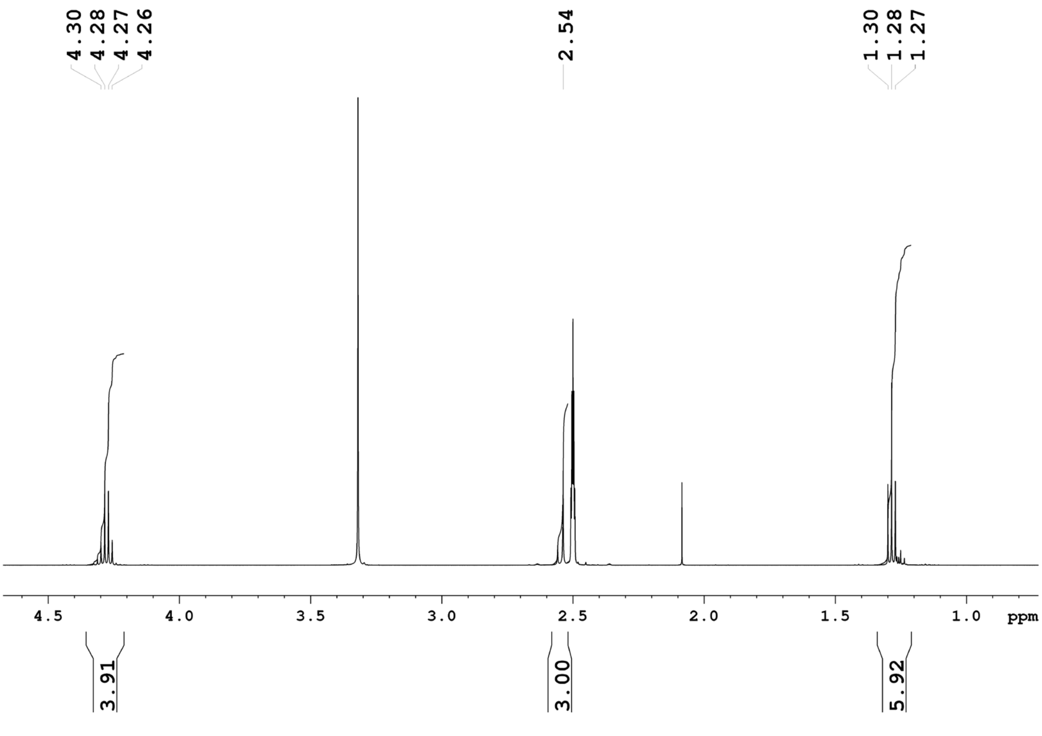


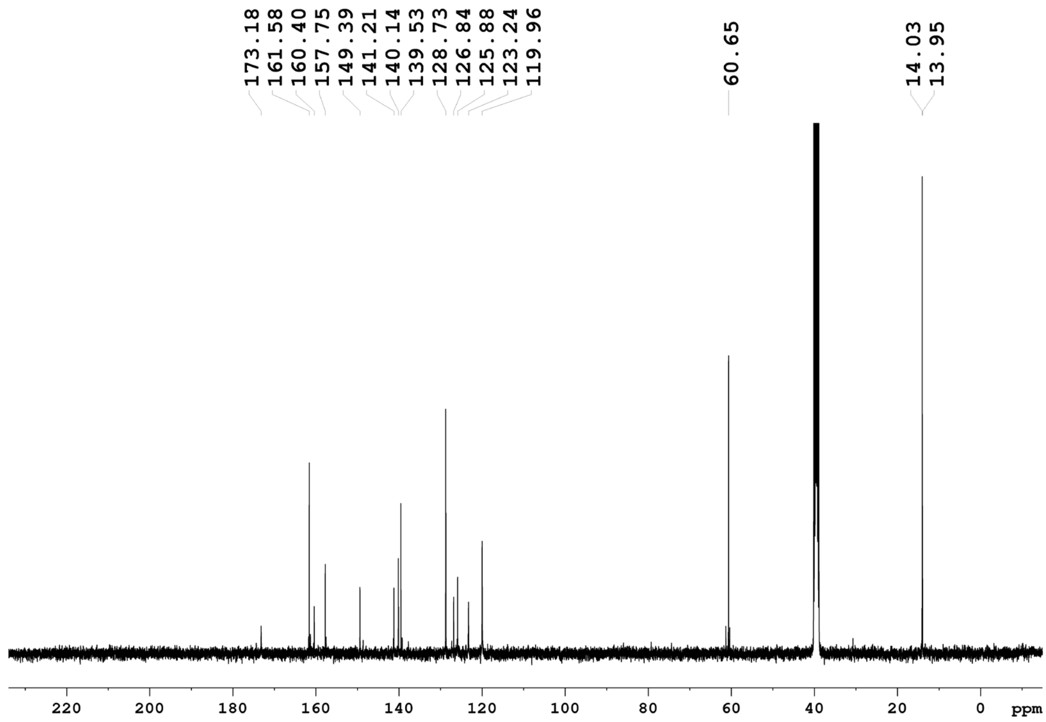
2.8 [Pd(triazolate^{COOEt,COOEt}-N^2)(L)] (19)

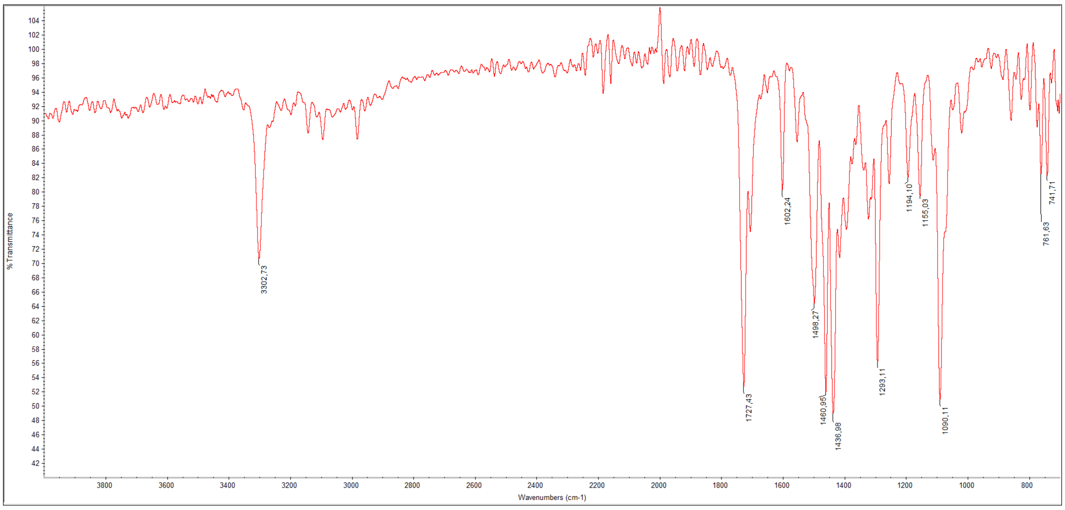




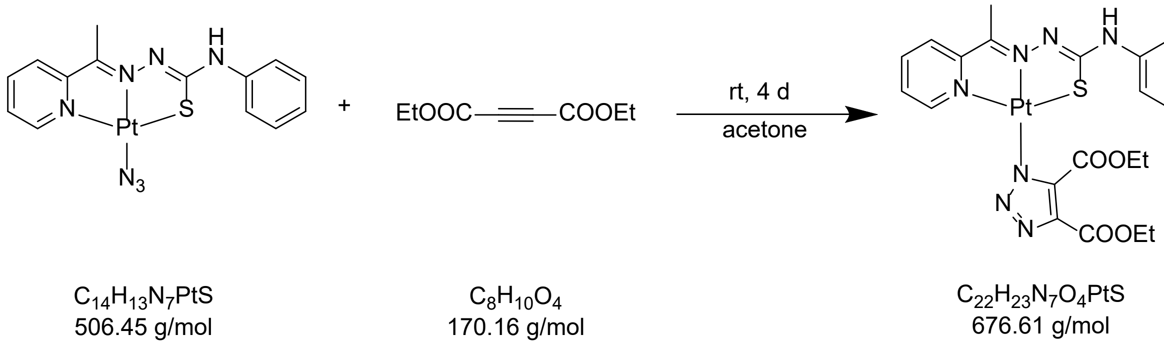

10.27
10.23
8.93
8.93
8.93
8.93
8.92
8.92
8.92
8.92
8.27
8.27
8.26
8.25
8.24
8.24
8.03
8.01
7.76
7.75
7.75
7.75
7.75
7.74
7.74
7.62
7.61
7.36
7.35
7.33
10.0
9.5
9.0
8.5
8.0
7.5
ppm
0.17
0.74
0.78
1.01
0.96
0.88
2.13
2.02
1.00

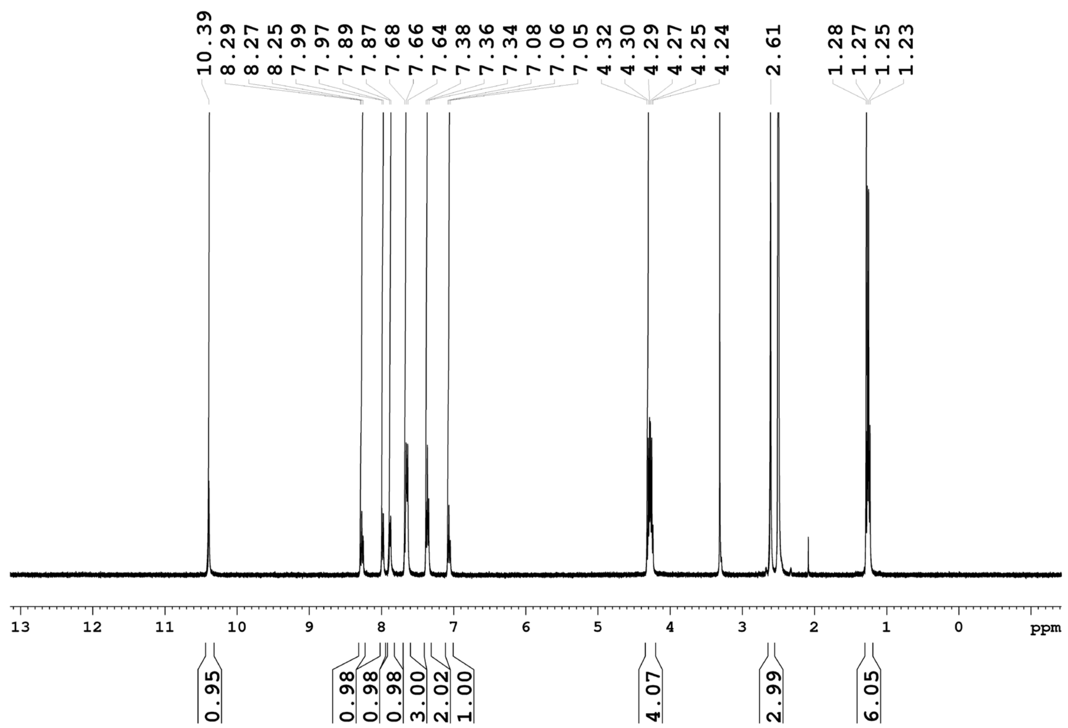

4.30
4.28
4.27
4.26
2.54
1.30
1.28
1.27
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.91
3.00
5.92

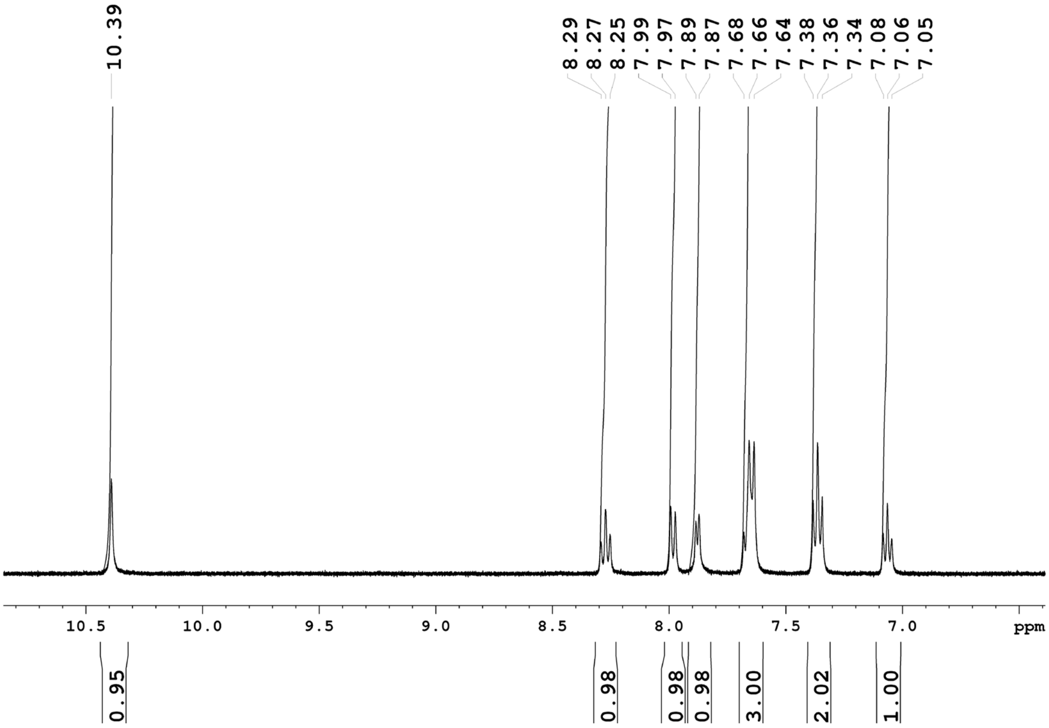

173.18
161.58
160.40
157.75
149.39
141.21
140.14
139.53
128.73
126.84
125.88
123.24
119.96
60.65
14.03
13.95
220
200
180
160
140
120
100
80
60
40
20
0
ppm

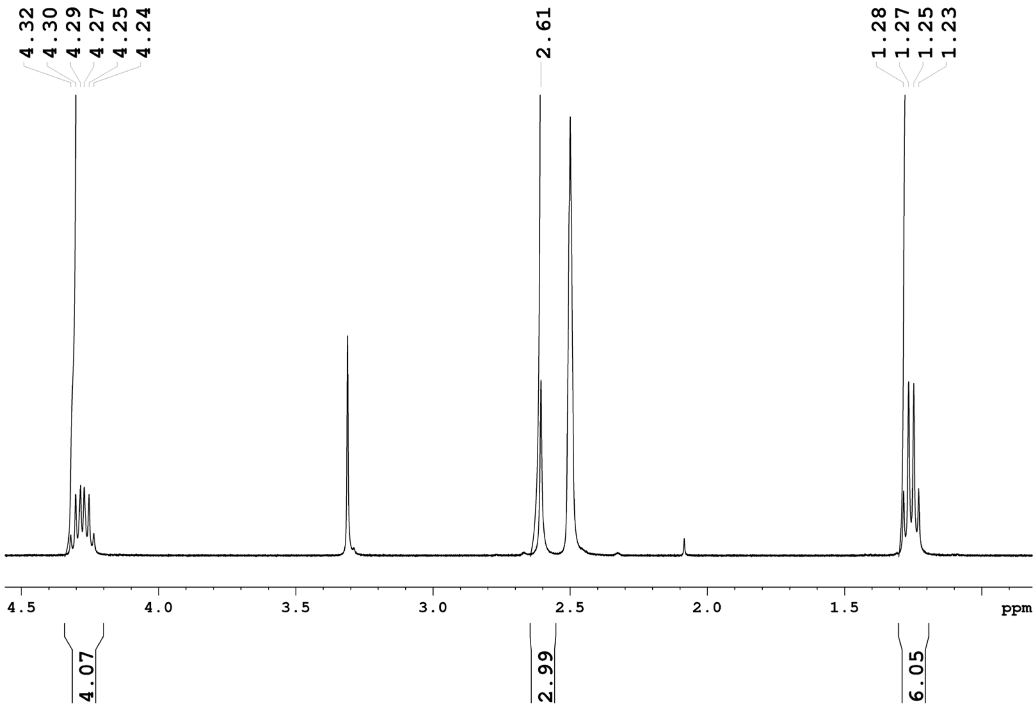

% Transmittance
Wavenumbers (cm-1)
3302,73
1727,43
1602,24
1498,27
1460,95
1436,98
1293,11
1194,10
1155,03
1090,11
761,63
741,71

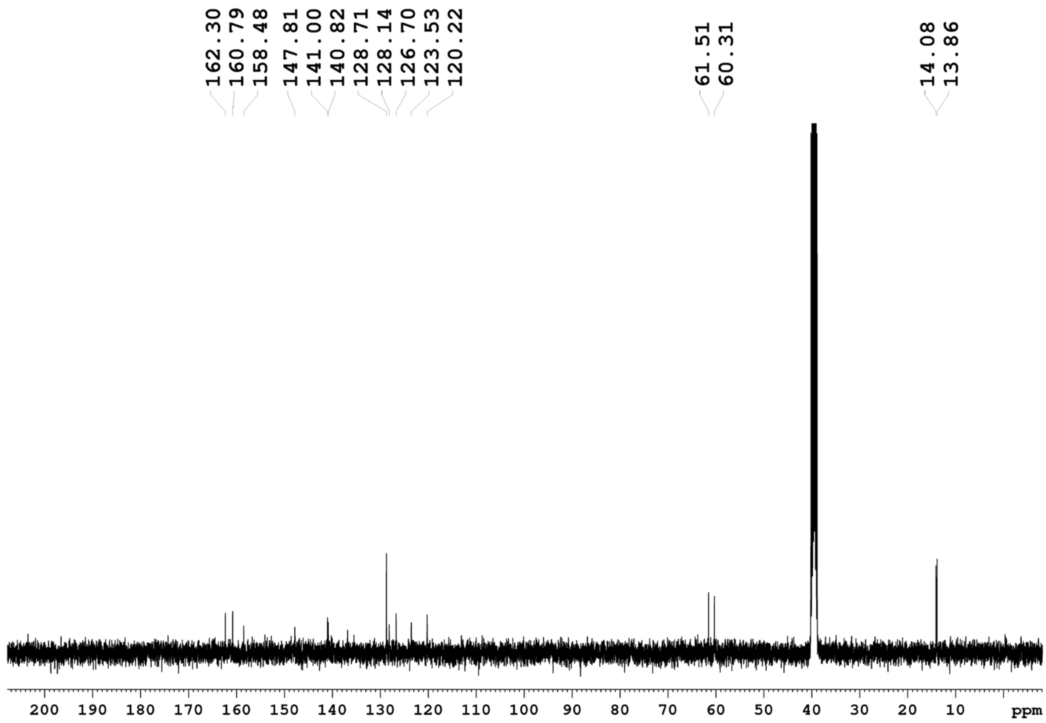
2.9 [Pt(triazolate^{COOEt,COOEt}-N^1)(L)] (23)

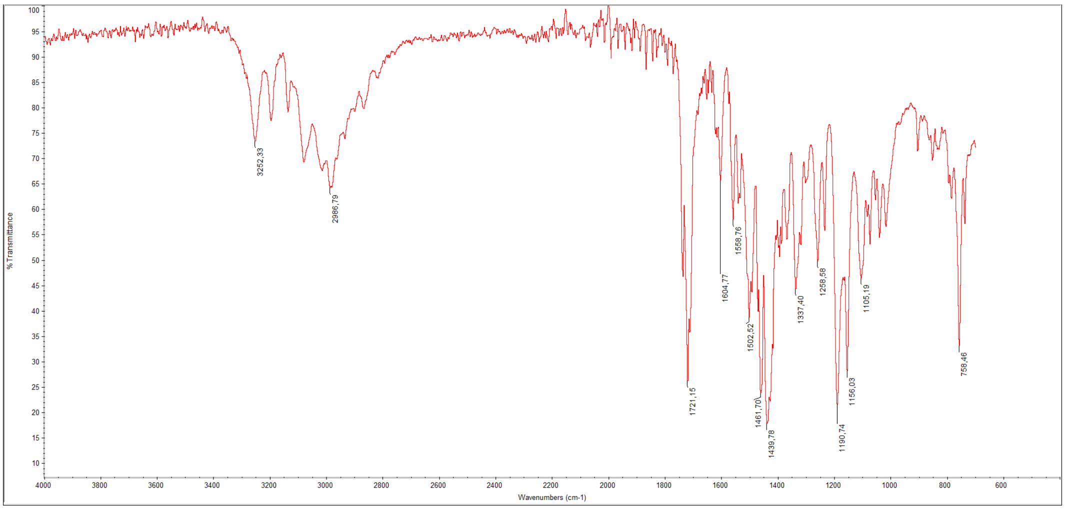




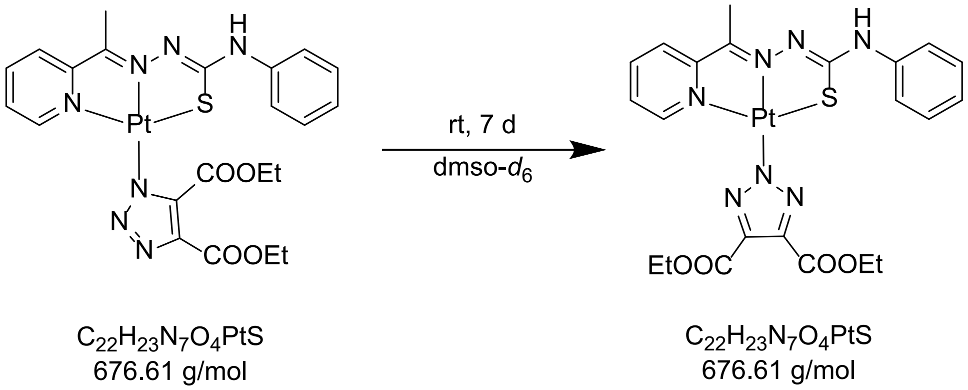

10.39
8.29
8.27
8.25
7.99
7.97
7.89
7.87
7.68
7.66
7.64
7.38
7.36
7.34
7.08
7.06
7.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
0.95
0.98
0.98
0.98
3.00
2.02
1.00

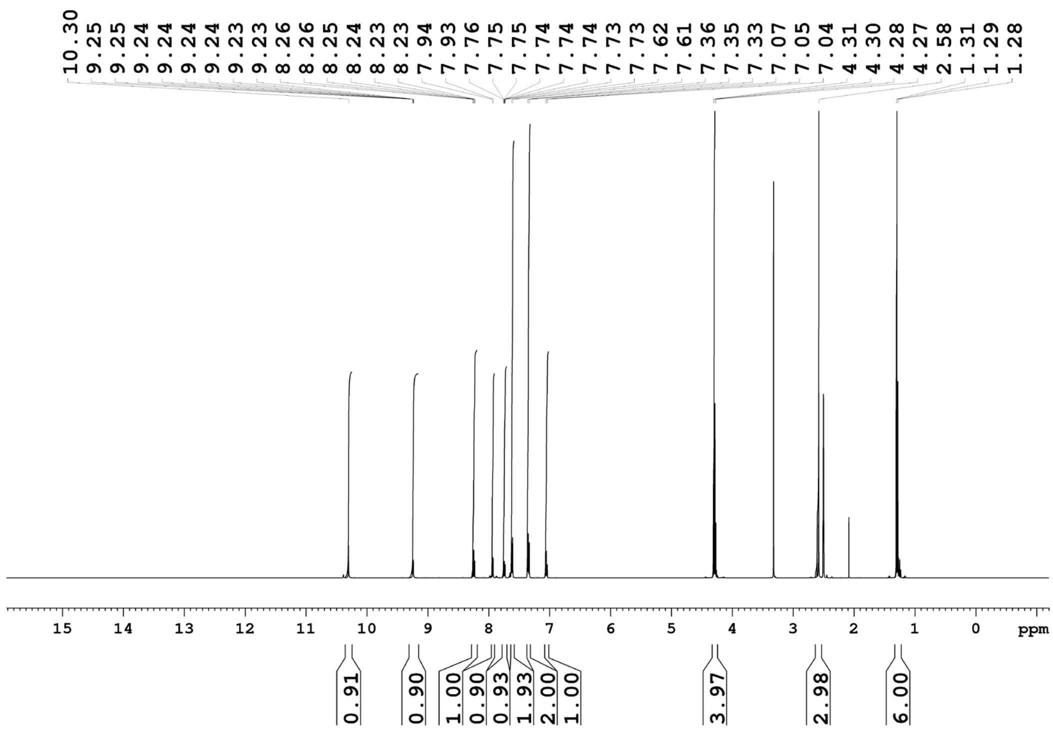

4.32
4.30
4.29
4.27
4.25
4.24
2.61
1.28
1.27
1.25
1.23
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
4.07
2.99
6.05

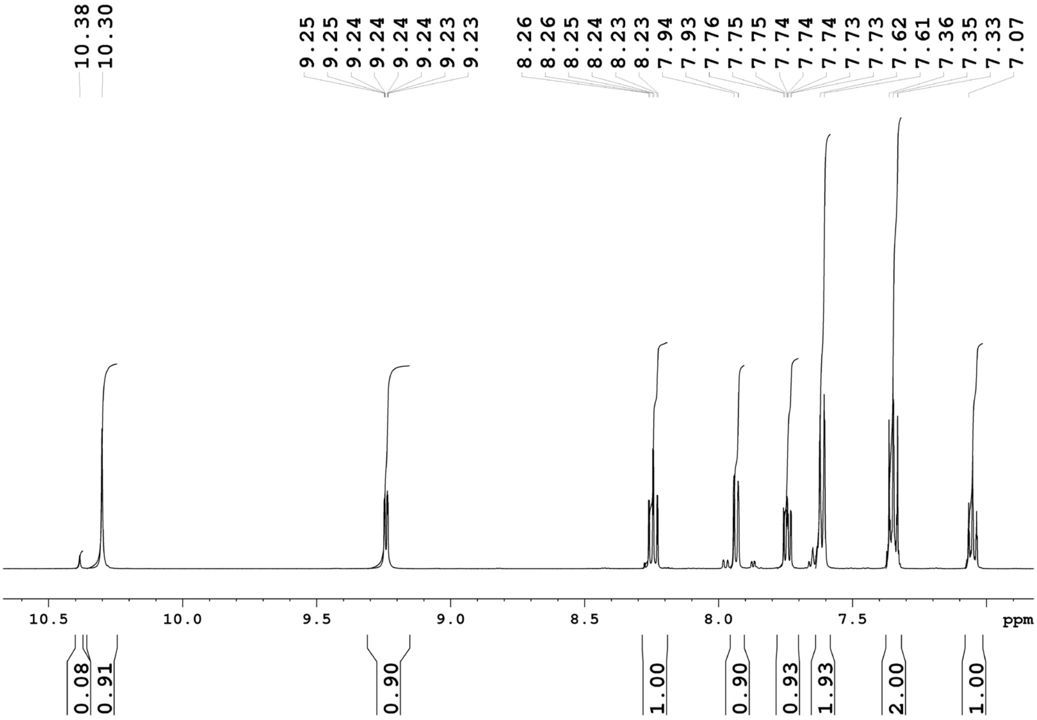

162.30
160.79
158.48
147.81
141.00
140.82
128.71
128.14
126.70
123.53
120.22
61.51
60.31
14.08
13.86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

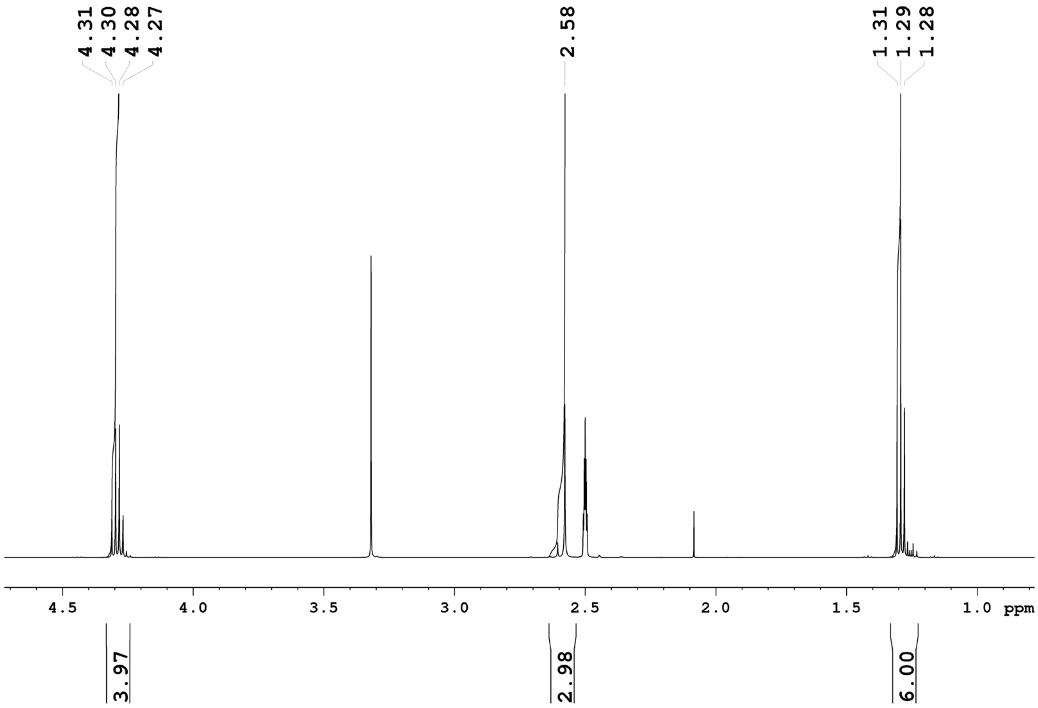

% Transmittance
Wavenumbers (cm-1)
3252,33
2986,79
1721,15
1604,77
1558,76
1502,52
1461,70
1439,78
1337,40
1258,58
1190,74
1156,03
1105,19
758,46

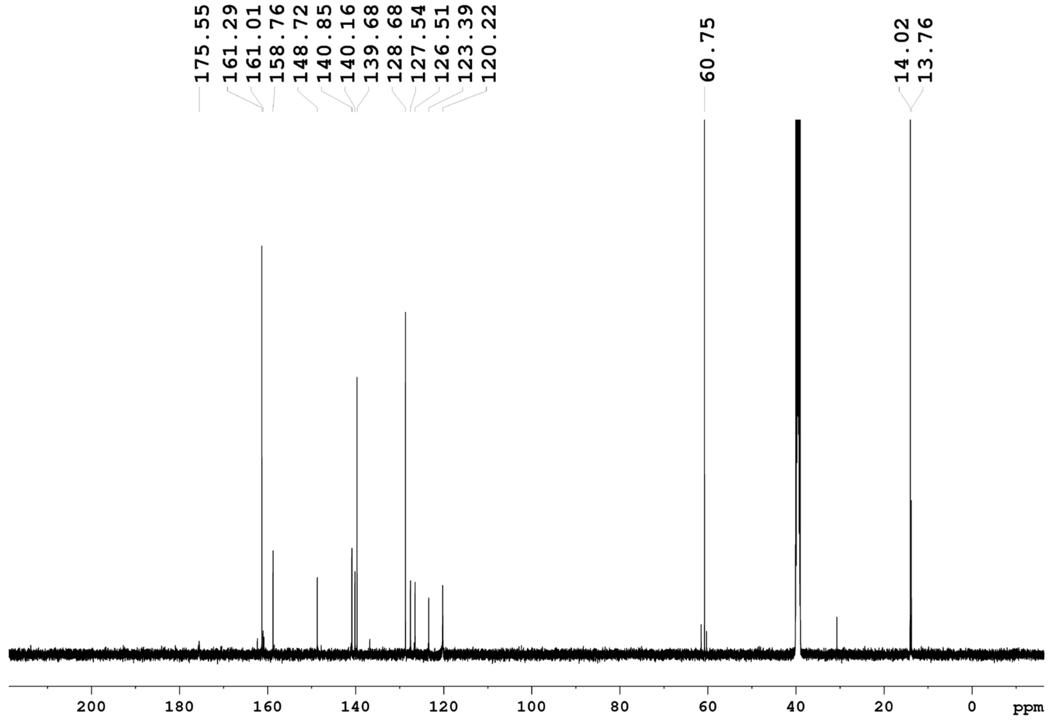
2.10 [Pt(triazolate^{COOEt,COOEt}-N^2)(L)] (26)

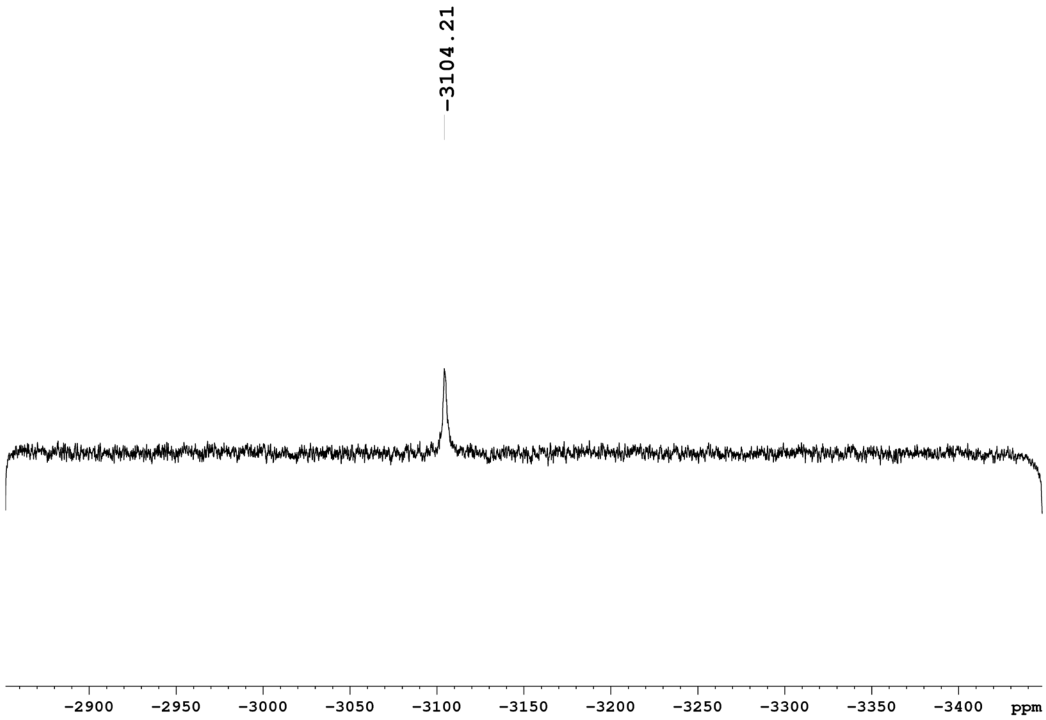




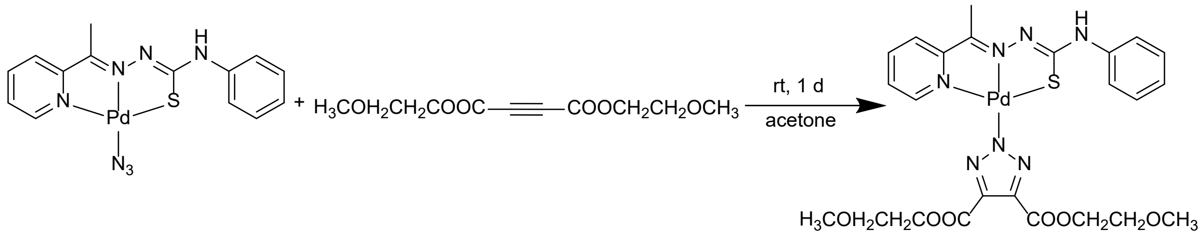

10.38
10.30
9.25
9.25
9.24
9.24
9.24
9.24
9.23
9.23
8.26
8.26
8.25
8.24
8.23
8.23
7.94
7.93
7.76
7.75
7.75
7.74
7.74
7.74
7.73
7.73
7.62
7.61
7.36
7.35
7.33
7.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
ppm
0.08
0.91
0.90
1.00
0.90
0.93
1.93
2.00
1.00


4.31
4.30
4.28
4.27
2.58
1.31
1.29
1.28
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 ppm
3.97
2.98
6.00


175.55
161.29
161.01
158.76
148.72
140.85
140.16
139.68
128.68
127.54
126.51
123.39
120.22
60.75
14.02
13.76
200
180
160
140
120
100
80
60
40
20
0
ppm


-3104.21
-2900
-2950
-3000
-3050
-3100
-3150
-3200
-3250
-3300
-3350
-3400
ppm

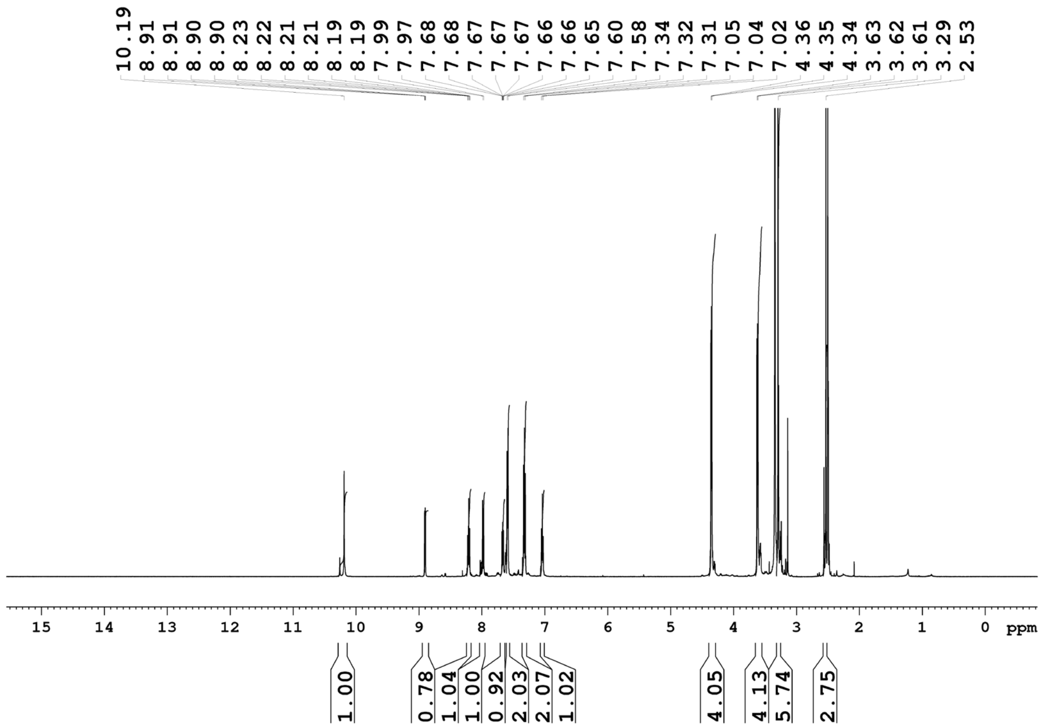
2.11 [Pd(triazolate^{COOCH2CH2OCH3,COOCH2CH2OCH3}-N^2)(L)] (20)

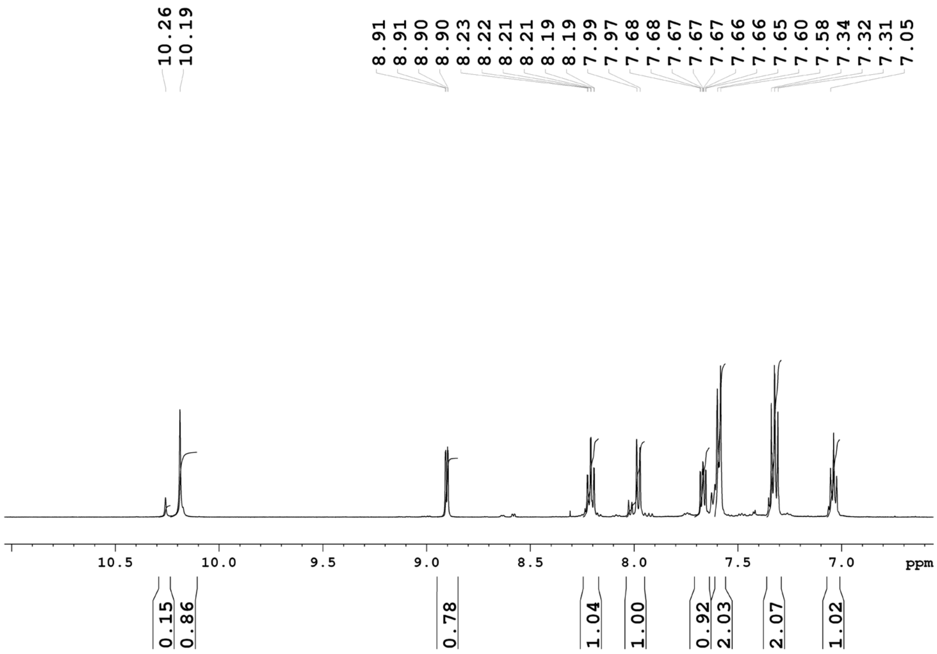


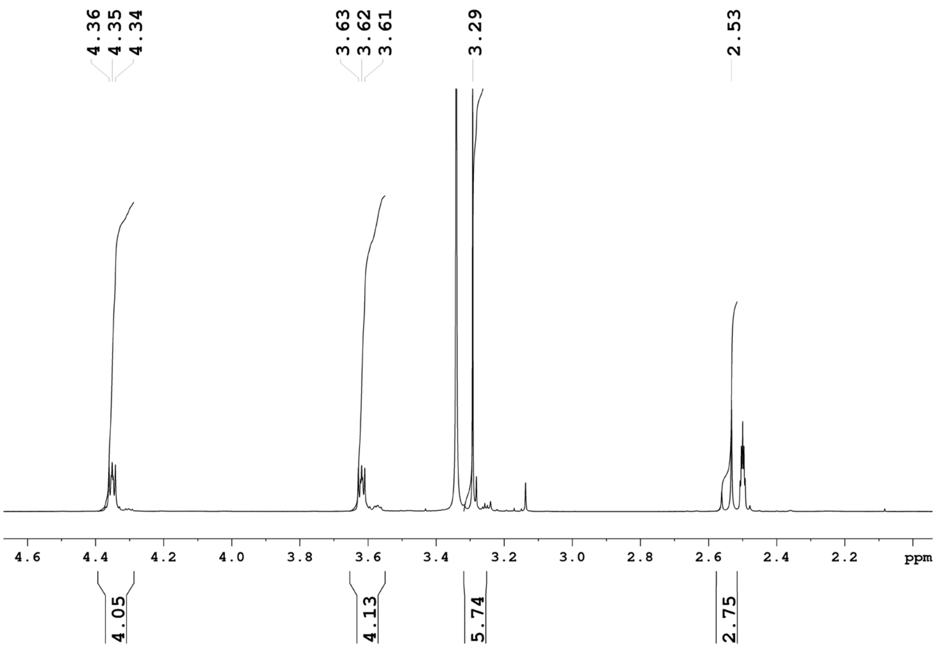
$C_{14}H_{12}N_7PdS$
416.78 g/mol

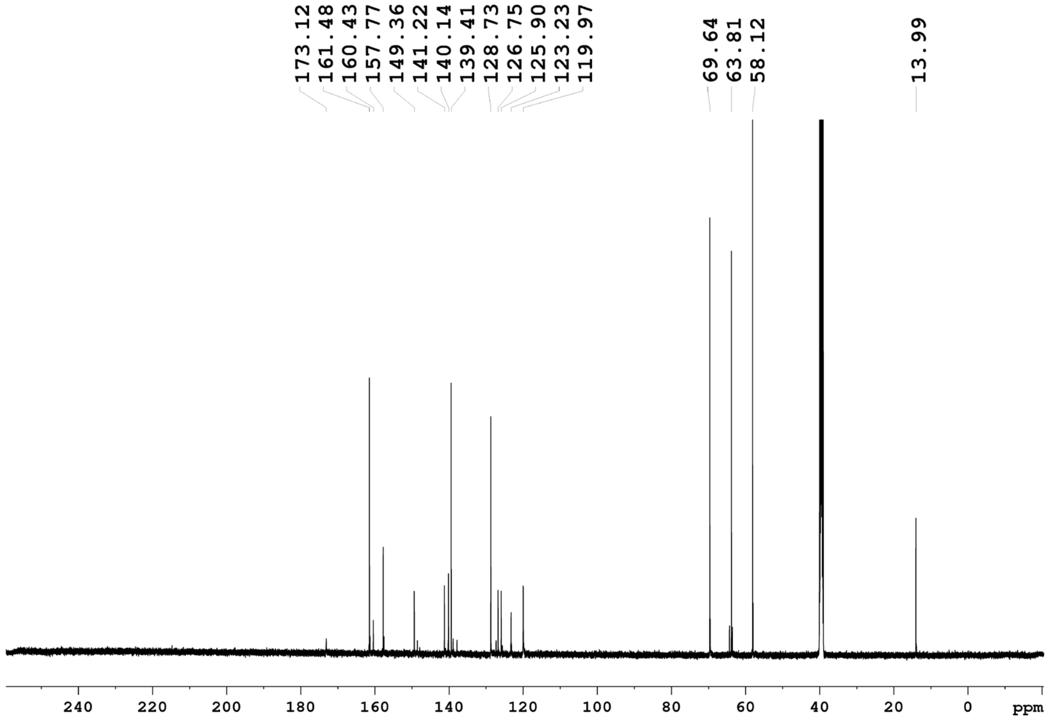
$C_{10}H_{14}O_6$
230.22 g/mol

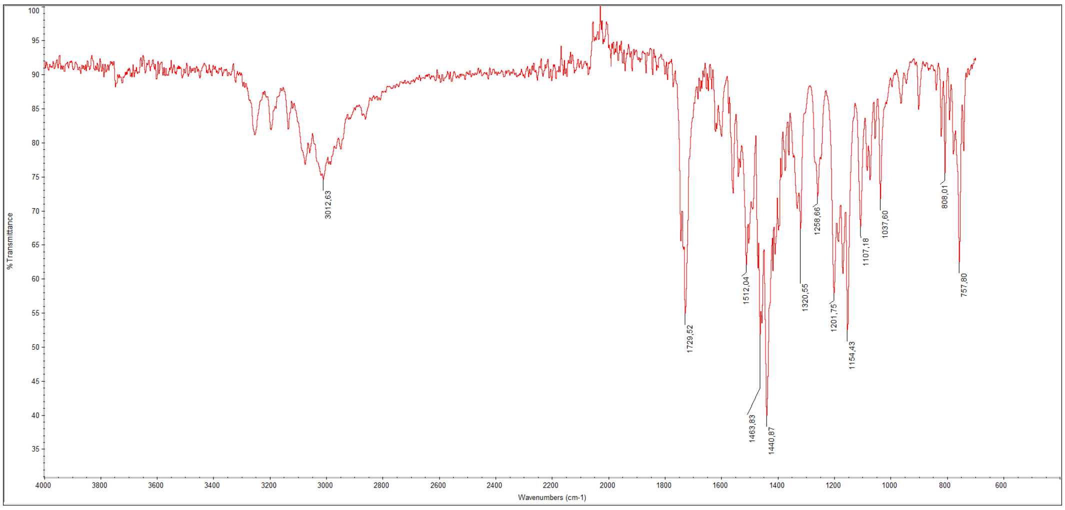
$C_{24}H_{27}N_7O_6PdS$
648.00 g/mol



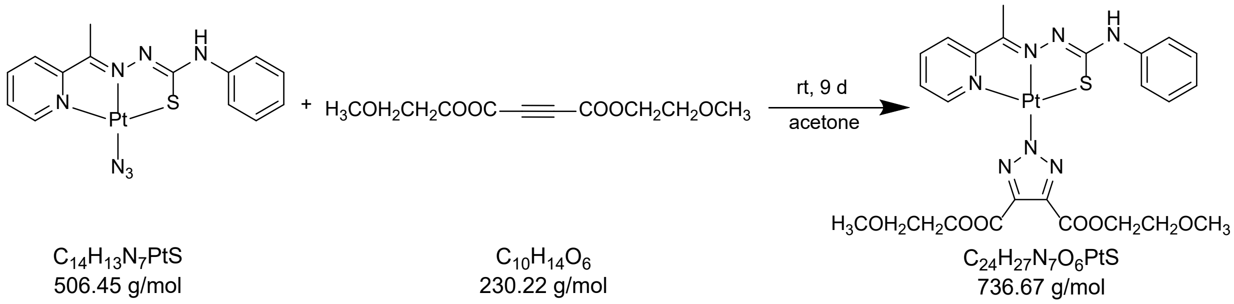

10.26
10.19
8.91
8.91
8.90
8.90
8.23
8.22
8.21
8.21
8.19
8.19
7.99
7.97
7.68
7.67
7.67
7.67
7.66
7.65
7.60
7.58
7.34
7.32
7.31
7.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
0.15
0.86
0.78
1.04
1.00
0.92
2.03
2.07
1.02

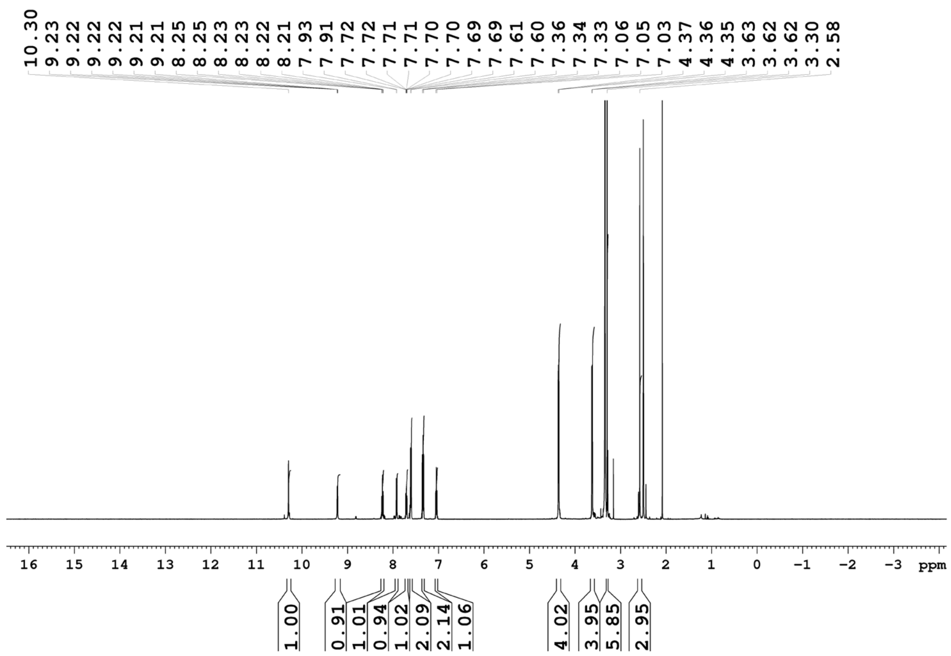

4.36
4.35
4.34
3.63
3.62
3.61
3.29
2.53
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
ppm
4.05
4.13
5.74
2.75

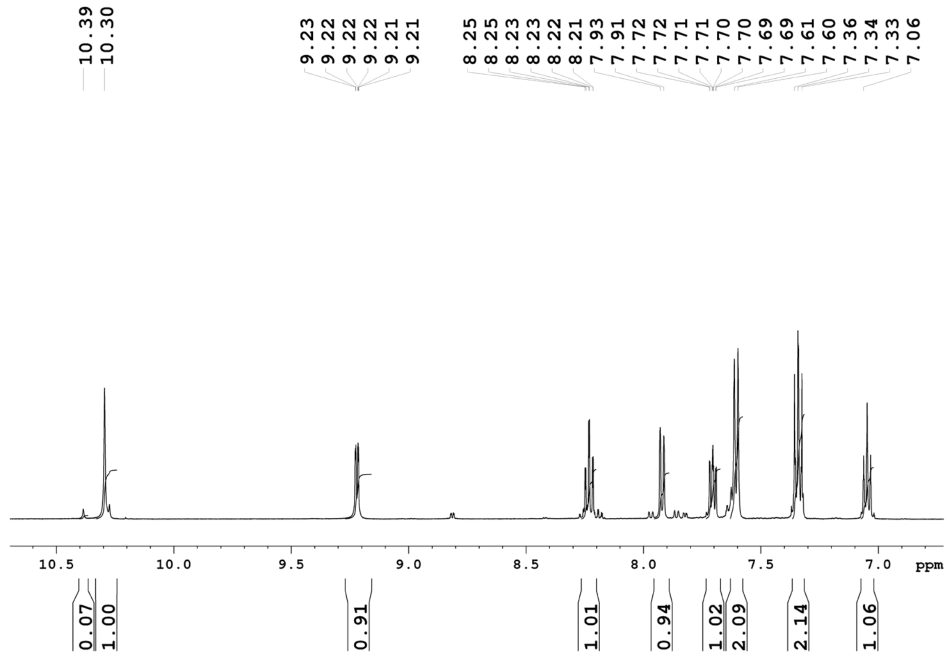

173.12
161.48
160.43
157.77
149.36
141.22
140.14
139.41
128.73
126.75
125.90
123.23
119.97
69.64
63.81
58.12
13.99
ppm

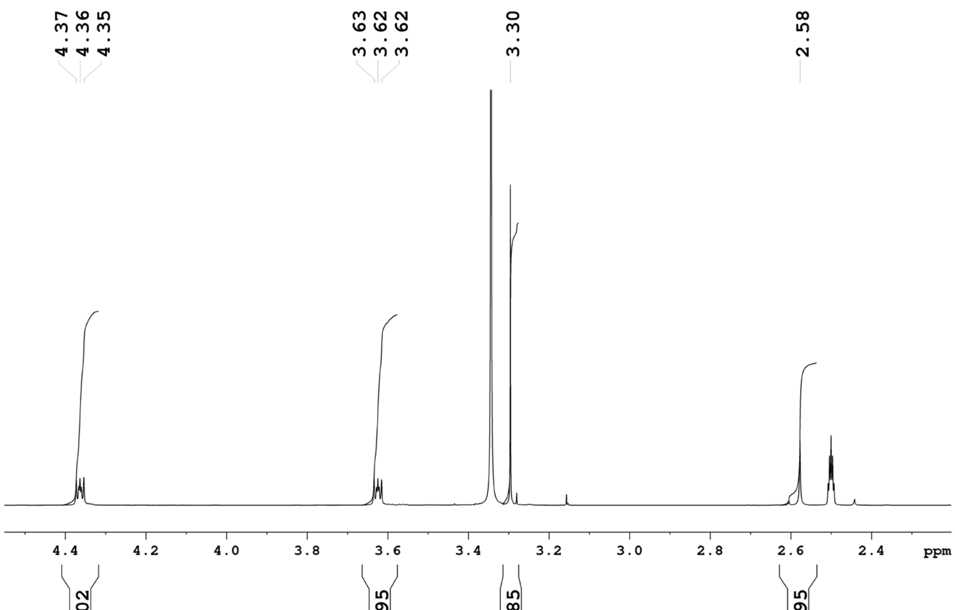

% Transmittance
Wavenumbers (cm-1)
3012,63
1729,52
1512,04
1463,83
1440,87
1320,55
1258,66
1201,75
1154,43
1107,18
1037,60
808,01
757,80

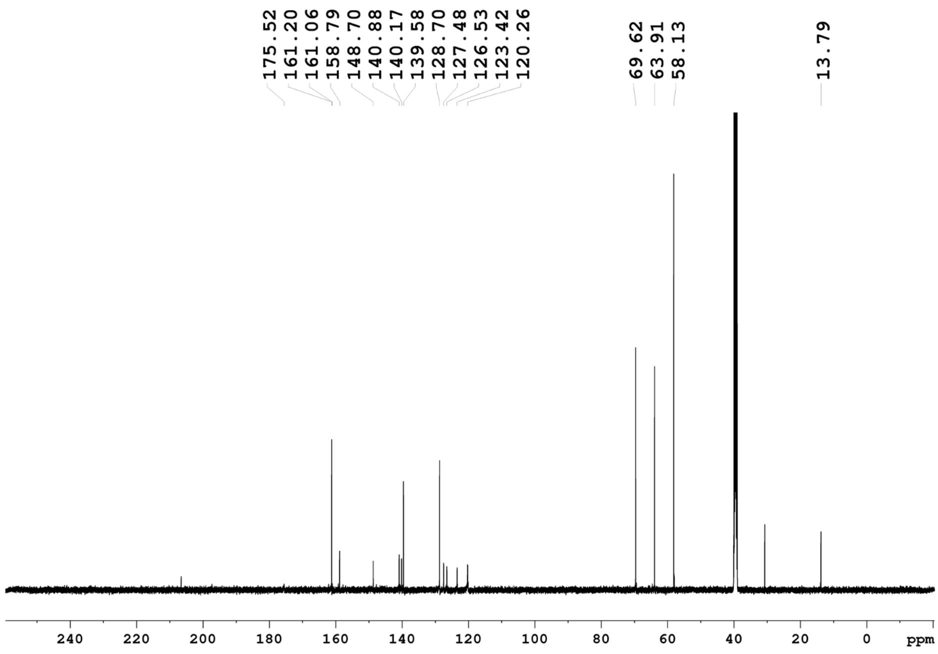
2.12 [Pt(triazolate^{COOCH2CH2OCH3,COOCH2CH2OCH3}-N^2)(L)] (24)

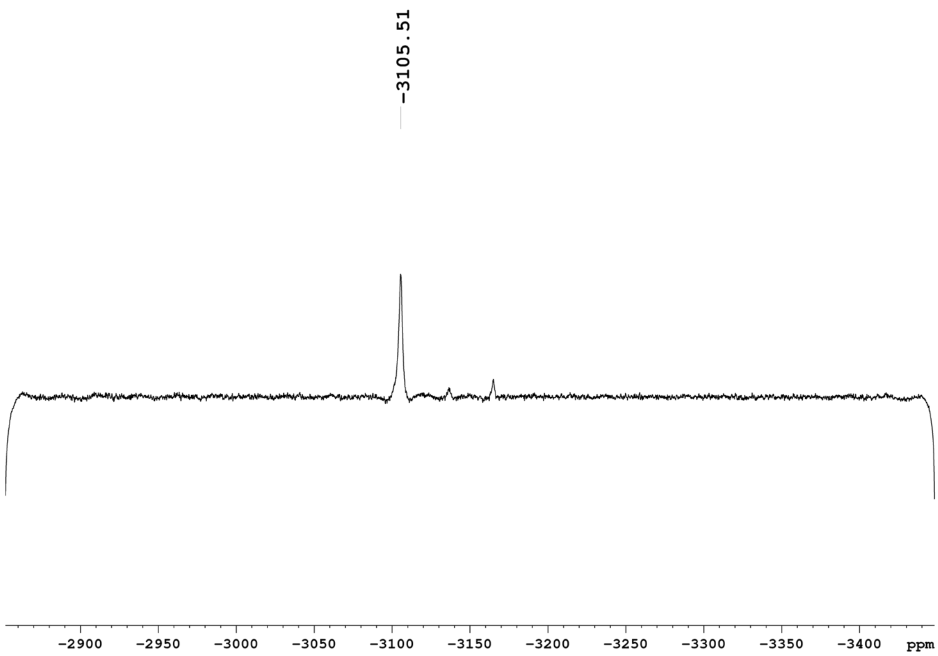





10.39
10.30
9.23
9.22
9.22
9.22
9.21
9.21
8.25
8.25
8.23
8.23
8.22
8.21
7.93
7.91
7.72
7.72
7.71
7.71
7.70
7.70
7.69
7.69
7.61
7.60
7.36
7.34
7.33
7.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
0.07
1.00
0.91
1.01
0.94
1.02
2.09
2.14
1.06


4.37
4.36
4.35
3.63
3.62
3.62
3.30
2.58
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
ppm
4.02
3.95
5.85
2.95


175.52
161.20
161.06
158.79
148.70
140.88
140.17
139.58
128.70
127.48
126.53
123.42
120.26
69.62
63.91
58.13
13.79
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm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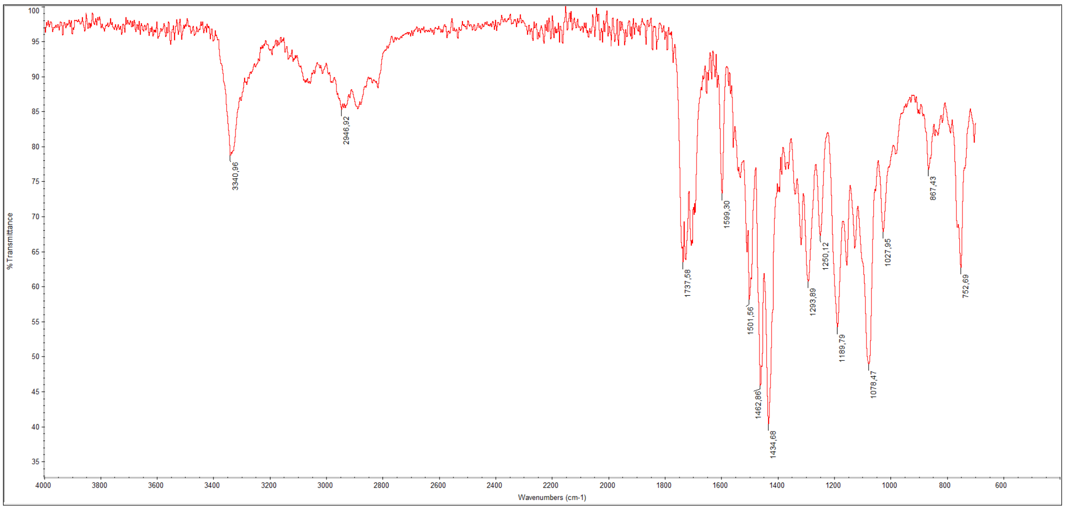
-3100
-3150
-3200
-3250
-3300
-3350
-3400
ppm



% Transmittance
Wavenumbers (cm-1)
3340,96
2946,92
1737,58
1599,30
1501,56
1462,86
1434,68
1293,89
1250,12
1189,79
1078,47
1027,95
867,43
752,69