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1,2,3-Triazole based ligands with phosphine and pyridine functionalities: Synthesis, Pd^{II}, Pt^{II} chemistry and catalytic studies

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NMR spectral data of α−alkylated acetophenones.

1,3-diphenylpropan-1-one (*Chart 2,* ***a***)[1] Prepared from acetophenone (0.5 mmol) and benzyl alcohol (0.6 mmol) . Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 85 % (89.36 mg) yield as a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 10.7, 4.4 Hz, 2H), 7.35 – 7.25 (m, 4H), 7.25 – 7.19 (m, 1H), 3.32 (t, *J* = 7.7 Hz, 2H), 3.12 – 3.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.33 (s), 141.41 (s), 136.98 (s), 133.17 (s), 128.82 – 128.44 (m), 128.15 (s), 126.25 (s), 40.55 (s), 30.24 (s).

3-phenyl-1-(p-tolyl)propan-1-one (Chart 2, ***b****)*[2] Prepared from 1-(*p*-tolyl)ethan-1-one (0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 87 % (97.57 mg) yield as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.32 (d, *J* = 7.1 Hz, 2H), 7.30 – 7.25 (m, 4H), 7.25 – 7.20 (m, 1H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.12 – 3.05 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.03 (s), 143.96 (s), 141.52 (s), 134.49 (s), 129.40 (s), 128.63 (s), 128.54 (s), 128.28 (s), 126.21 (s), 40.46 (s), 30.33 (s), 21.75 (s).

1-(3-bromophenyl)-3-phenylpropan-1-one (Chart 2, ***c****)*[3] Prepared from 1-(3-bromophenyl)ethan-1-one(0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 79 % (114.22 mg) yield as white crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.23 (d, *J* = 12.5 Hz, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.92 (s), 141.09 (s), 138.71 (s), 136.04 (s), 131.28 (s), 130.34 (s), 128.71 (s), 128.54 (s), 126.66 (s), 126.38 (s), 123.12 (s), 40.66 (s), 30.09 (s).

1-(4-bromophenyl)-3-phenylpropan-1-one (Chart 2, ***d****)*[3] Prepared from 1-(4-bromophenyl)ethan-1-one (0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 77 % (111.33 mg) yield as colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (dd, *J* = 13.3, 5.6 Hz, 3H), 3.27 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.32 (s), 141.16 (s), 135.67 (s), 132.05 (s), 129.70 (s), 128.70 (s), 128.54 (s), 128.37 (s), 126.36 (s), 40.54 (s), 30.15 (s).

3-(2-bromophenyl)-1-(p-tolyl)propan-1-one (Chart 2, ***e****)*[4] Prepared from 1-(*p*-tolyl)ethan-1-one (0.5 mmol) and (2-bromophenyl)methanol (0.6 mmol). Purified by column

chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 80 % (121.28 mg) yield as colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.55 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.27 – 7.21 (m, 4H), 7.08 (td, *J* = 7.8, 1.6 Hz, 1H), 3.30 – 3.26 (m, 2H), 3.21 – 3.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.76 (s), 144.05 (s), 140.82 (s), 134.44 (s), 133.01 (s), 130.93 (s), 129.43 (s), 128.35 (s), 128.08 (s), 127.76 (s), 124.51 (s), 38.65 (s), 31.02 (s), 21.78 (s).

3-(2-bromophenyl)-1-(4-bromophenyl)propan-1-one (Chart 2, ***f****)*[4] Prepared from 1-(4-bromophenyl)ethan-1-one (0.5 mmol) and (2-bromophenyl)methanol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 75 % (138.02 mg) yield as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.55 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.09 (td, *J* = 7.7, 1.8 Hz, 1H), 3.31 – 3.24 (m, 2H), 3.21 – 3.13 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.08 (s), 140.44 (s), 135.57 (s), 133.07 (s), 132.07 (s), 131.59 (s), 130.96 (s), 130.93 (s), 129.75 (s), 128.23 (s), 127.82 (s), 38.72 (s), 30.88 (s).

1-(4-iodophenyl)-3-phenylpropan-1-one (Chart 2, ***g****)*[5] Prepared from 1-(4-iodophenyl)ethan-1-one (0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 79 % (132.78 mg) yield as white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 3.26 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.50 (s), 141.05 (s), 137.94 (s), 129.46 (s), 128.58 (s), 128.42 (s), 128.06 (s), 126.24 (s), 101.03 (s), 40.37 (s), 30.02 (s).

1-(4-fluorophenyl)-3-phenylpropan-1-one (Chart 2, ***h****)*[3] Prepared from 1-(4-flourophenyl)ethan-1-one (0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 71 % (81.03 mg) yield as yellow liquid.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 14.7, 7.5 Hz, 3H), 7.12 (t, *J* = 8.6 Hz, 2H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.76 (s), 166.88 (s), 141.27 (s), 133.43 (s), 130.83 (s), 128.70 (s), 128.63 (s), 126.34 (s), 115.92 (s), 40.52 (s), 30.23 (s).

1-(4-chlorophenyl)-3-phenylpropan-1-one (Chart 2, ***i****)*[6] Prepared from 1-(4-chlorophenyl)ethan-1-one (0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 75 % (91.77 mg) yield as yellow solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 2.3, 1.7 Hz, 1H), 7.52 –

7.49 (m, 1H), 7.31 (dd, *J* = 15.6, 7.6 Hz, 3H), 7.22 (dt, *J* = 9.2, 4.3 Hz, 3H), 7.10 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 3.29 (t, *J* = 7.7 Hz, 2H), 3.09 – 3.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.34 (s), 156.52 (s), 141.15 (s), 138.22 (s), 130.07 (s), 128.68 (s), 128.52 (s), 126.32 (s), 120.82 (d, *J* = 8.3 Hz), 114.71 (s), 40.71 (s), 30.29 (s).

3-(4-methoxyphenyl)-1-phenylpropan-1-one (Chart 3, ***j)***[3] Prepared from acetophenone (0.5 mmol) and (4-methoxyphenyl)methanol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 65 % (78 mg) yield as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.99 – 7.91 (m, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.41 (m, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.27 (t, *J* = 8.4, 6.9 Hz, 2H), 3.02 (t, *J* = 8.4, 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.43, 158.02, 136.93, 133.33, 133.03, 129.36, 128.60, 128.05, 113.96, 55.29, 40.72, 29.31.

1-phenyl-3-(p-tolyl)propan-1-one (Chart 3, ***k)***[6] Prepared from acetophenone (0.5 mmol) and *p*-tolylmethanol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 68 % (76.26 mg) yield as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.42 – 7.51 (m, 1H), 7.60 – 7.51 (m, 2H), 7.50 – 7.40 (m, 4H), 3.33 – 3.24 (m, 2H), 3.04 (dd, *J* = 8.5, 6.9 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.39, 138.20, 136.92, 135.64, 133.03, 129.22, 128.60, 128.30, 128.06, 40.62, 29.74, 21.01.

1-(4-methoxyphenyl)-3-phenylpropan-1-one (Chart 3, ***l)***[3] Prepared from 1-(4-methoxyphenyl)ethan-1-one (0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 62 % (74.49 mg) yield as crystalline white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.41 – 7.16 (m, 5H), 7.00 – 6.91 (m, 2H), 3.89 (s, 3H), 3.28 (dd, *J* = 8.8, 6.9 Hz, 2H), 3.08 (dd, *J* = 8.6, 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.87, 163.47, 141.48, 130.33, 129.98, 128.48 (d, *J* = 8.1 Hz), 126.10, 113.75, 55.48, 40.14, 30.35.

1-(3-chlorophenyl)-3-phenylpropan-1-one (Chart 3, ***m)***[6] Prepared from 1-(3-chlorophenyl)ethan-1-one (0.5 mmol) and benzyl alcohol (0.6 mmol). Purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents, 72 % (88.09 mg) yield as colourless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 1.9 Hz, 1H), 7.85 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.37 – 7.19 (m, 5H), 3.30 (dd, *J* = 8.4, 6.9 Hz, 2H), 3.18 – 3.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.92, 140.98, 138.39, 134.98, 133.01, 129.96, 128.59, 128.42, 127.32, 126.26, 126.11, 39.51 (d, *J* = 213.7 Hz), 29.98.

Selected bond distances (Å) and angels (°) for compounds 2-14

Table S1 Selected bond distances (Å) for compounds **2-4**

Bond lengths (Å)	**2**	**3**	**4**
P1-C6	1.8451(18)	-	-
P1-C7	-	1.826(4)	1.8309(18)
P1-C14	1.838(2)	1.831(4)	1.8211(19)
P1-C20	1.8337(19)	1.817(4)	1.8309(19)
N1-N2	1.357(2)	1.351(5)	1.350(2)
N2-N3	1.312(2)	1.294(5)	1.314(2)
C6-Br1	-	1.891(4)	-

Table S2 Selected bond angels (°) for compounds **2-4**

Bond angels (°)	**2**	**3**	**4**
C6-P1-C14	102.53(8)	-	-
C7-P1-C14	-	101.01(19)	103.92(8)
C6-P1-C20	101.88(8)	-	-
C7-P1-C20	-	104.6(2)	99.40(8)
C14-P1-C20	101.43(9)	105.2(2)	103.32(8)
N1-N2-N3	106.78(15)	107.4(2)	107.27(13)

Table S3 Selected bond distances (Å) and angels (°) for compounds **5** and **6**

Bond lengths (Å)	**5**	**6**	Bond angels (°)	**5**	**6**
P1-C2	1.8497(14)	1.844(7)	C2-P1-C14	103.76(6)	100.9(3)
P2-C(triazole)	1.8275(14)	1.823(6)	C2-P1-C20	100.45(6)	99.7(3)
P1-C14	1.8288(14)	1.829(7)	C14-P1-C20	102.93(6)	101.4(3)

P2-C26	1.8261(15)	1.843(7)	C7-P2-C26	102.30(6)	-
P1···P2	3.995	5.202	C7-P2-C32	102.36(6)	-
N1-N2	1.3544(16)	1.364(7)	C6-P2-C26	-	103.3(3)
N2-N3	1.3114(17)	1.303(7)	C6-P2-C32	-	102.3(3)
			C26-P2-C32	103.82(6)	106.2(3)
			N1-N2-N2	106.68(11)	107.0(5)

Table S4 Selected bond distances (Å) for compounds **7** and **8**

Bond lengths (Å)	**7 (**M = Pd)	**8 (**M = Pt)	Bond angles (°)	**7 (**M = Pd)	**8 (**M = Pt)
M-P1	2.2136(8)	2.198(2)	P1-M-N4	167.63(7)	168.9(2)
M-N4	2.149(3)	2.144(6)	C7-M-Cl1	174.18(9)	172.4(3)
M-C7	1.933(3)	1.915(9)	P1-M-Cl1	97.25(3)	96.85(8)
M-Cl1	2.3480(7)	2.355(2)	P1-M-C7	88.50(9)	90.8(3)
N1-N2	1.395(4)	1.403(10)	N4-M-C7	79.66(11)	78.6(3)
N2-N3	1.306(4)	1.313(10)	N4-M-Cl1	94.55(7)	93.7(2)
C9-N4	1.367(4)	1.362(11)	N1-N2-N3	107.2(2)	106.3(2)
C13-N4	1.341(4)	1.337(10)	-	-	-

Table S5 Selected bond distances (Å) for compounds **9** and **10**

Bond lengths (Å)	**9 (**M = Pd)	**10 (**M = Pt)	Bond angles (°)	**9 (**M = Pd)	**10 (**M = Pt)
M-P1	2.2226(6)	2.2085(6)	P1-M-N4	93.78(6)	94.37(6)
M-N4	2.089(2)	2.0696(19)	Cl1-M-Cl2	90.08(2)	88.47(2)
M-Cl1	2.2701(6)	2.2801(6)	P1-M-Cl1	87.33(3)	88.92(2)
M-Cl2	2.3734(7)	2.3694(6)	P1-M-Cl2	169.88(2)	170.41(2)
N1-N2	1.352(3)	1.350(3)	N4-M-Cl1	167.39(6)	168.97(6)

N2-N3	1.304(3)	1.306(3)	N4-M-Cl2	90.89(6)	89.91(6)
C9-N4	1.350(3)	1.357(3)	N1-N2-N3	108.3(2)	107.90(19)
P11-C7	1.801(3)	1.794(2)			

Table S6 Selected bond distances (Å) for compounds **11-14**

Bond lengths (Å)	**11**	**12**	**13**	**14**
P1-M	2.2697(9)	2.2493(14)	2.2573(10)	2.2408(8)
P2-M	2.2406(9)	2.2473(15)	2.2453(10)	2.2279(8)
P1-C(Ph)	1.839(3)	1.843(5)	1.838(4)	1.841(3)
P2-C(triazole)	1.818(4)	1.822(5)	1814(4)	1.822(3)
M-Cl1	2.3407(9)	2.3511(13)	2.3304(10)	2.3379(8)
M-Cl2	2.3300(10)	2.3569(13)	2.3322(10)	2.3404(8)

Table S7 Selected bond angels (°) for compounds **11-14**

Bond Angels (°)	**11**	**12**	**13**	**14**
P1-M-P2	93.34(3)	95.66(5)	93.13(4)	93.60(3)
P1-M-Cl1	87.43(3)	92.48(5)	171.56(4)	171.81(3)
P1-M-Cl2	171.12(4)	171.47(5)	87.63(4)	88.42(3)
P2-M-Cl1	167.15(4)	169.48(5)	90.79(4)	91.57(3)
P2-M-Cl2	90.30(4)	86.64(5)	166.76(4)	168.97(3)
Cl1-M-Cl2	90.82(4)	86.27(5)	90.26(4)	87.72(3)

Crystallographic data for 2-14

Table S8 Crystallographic data for **2-6**

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{25}H_{19}N_4P$	$C_{25}H_{18}BrN_4P$	$C_{25}H_{19}N_4P$	$C_{37}H_{28}N_4P_2$	$C_{37}H_{28}N_4P_2$
Formula weight	406.41	485.31	406.41	590.57	590.57
Temperature/K	150	100	150	100	150
Crystal system	monoclinic	orthorhombic	Triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	P-1	$P2_1/n$	Pc
a/Å	11.3662(6)	9.5772(3)	8.7355(4)	14.8422(3)	10.2657(6)
b/Å	14.8698(11)	10.3094(4)	9.3623(4)	12.0763(2)	9.5652(5)
c/Å	12.1278(7)	21.5985(8)	12.7655(5)	18.5323(5)	16.3406(11)
α/°	90	90	83.817(3)	90	90
β/°	91.647(5)	90	74.007(4)	113.472(3)	104.332(7)
γ/°	90	90	81.161(4)	90	90
Volume/$Å^3$	2048.9(2)	2132.53(13)	989.34(8)	3046.86(13)	1554.60(17)
Z	4	4	2	4	2
$\rho_{calc}g/cm^3$	1.318	1.512	1.364	1.287	1.262
μ/mm^{-1}	0.154	2.023	0.159	0.176	0.173
F(000)	848	984	424	1232	616
Crystal size/mm^3	0.184 × 0.128 × 0.094	0.24 × 0.175 × 0.046	0.135 × 0.072 × 0.056	0.213 × 0.078 × 0.054	0.212 × 0.152 × 0.122
2Θ range	4.336 to 62.154	4.378 to 62.478	4.414 to 62.298	4.508 to 62.226	4.976 to 50
Reflections collected	12756	16217	21132	38937	5420
Independent reflections	5750	6271	5833	8601	5420
S	1.032	1.031	1.050	1.023	1.036
R_1	0.0591	0.0489	0.0573	0.0463	0.0583
wR_2	0.1651	0.1204	0.1327	0.1158	0.1441

Table S9 Crystallographic data for **7-11**

	7	**8**	**9**	**10**	**11**
Empirical formula	$C_{26}H_{19}Cl_4N_4PPd$	$C_{26}H_{19}Cl_4N_4PPt$	$C_{26}H_{21}Cl_4N_4PPd$	$C_{26}H_{21}Cl_4N_4PPt$	$C_{38}H_{29}Cl_5N_4P_2Pd$
Formula weight	666.62	755.31	668.64	757.33	887.24
Temperature/K	150	150	150	150	150
Crystal system	monoclinic	monoclinic	Monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	16.1762(6)	16.166(2)	10.8739(4)	10.8732(3)	11.0885(5)
b/Å	8.8589(2)	8.8783(12)	8.6646(3)	8.7056(2)	19.5981(10)
c/Å	18.7920(5)	18.6934(13)	28.1870(8)	28.1056(6)	17.1297(8)
α/°	90	90	90	90	90
β/°	103.650(3)	103.613(10)	94.066(3)	94.164(2)	100.185(4)
γ/°	90	90	90	90	90
Volume/$Å^3$	2616.90(14)	2607.7(5)	2649.04(15)	2653.39(11)	3663.9(3)
Z	4	4	4	4	4
$\rho_{calc}g/cm^3$	1.692	1.924	1.677	1.896	1.608
μ/mm^{-1}	1.203	5.877	1.189	5.776	0.994
F(000)	1328	1456	1336	1464	1784
Crystal size/mm^3	0.117 × 0.109 × 0.103	0.116 × 0.064 × 0.052	0.187 × 0.142 × 0.086	0.195 × 0.153 × 0.124	0.177 × 0.088 × 0.075
2Θ range	4.462 to 62.412	5.106 to 62.328	4.904 to 62.176	4.9 to 62.126	3.732 to 62.248
Reflections collected	41087	10677	23060	21258	17053
Independent reflections	7948	10677	7708	7678	10159
S	1.048	1.036	1.047	1.016	1.030
R_1	0.0475	0.0552	0.0387	0.0222	0.0543
wR_2	0.1084	0.1383	0.0833	0.0494	0.13

Table S10 Crystallographic data for **12-14**

	12	**13**	**14**
Empirical formula	$C_{39}H_{32}Cl_6N_4P_2Pt$	$C_{38}H_{30}Cl_4N_4P_2Pd$	$C_{38}H_{30}Cl_4N_4P_2Pt$
Formula weight	1026.41	852.8	941.49
Temperature/K	150	100	150
Crystal system	monoclinic	monoclinic	monoclinic
Space group	I2/a	$P2_1/c$	$P2_1/c$
a/Å	21.8778(9)	10.9552(3)	10.9893(2)
b/Å	12.5511(5)	19.8167(5)	19.7815(4)
c/Å	30.0950(12)	17.0756(6)	17.1355(4)
α/°	90	90	90
β/°	110.548(5)	100.667(3)	100.659(2)
γ/°	90	90	90
Volume/Å^3	7738.0(6)	3643.0(2)	3660.71(14)
Z	8	4	4
ρ_{calc}g/cm^3	1.762	1.555	1.708
μ/mm^{-1}	4.16	0.925	4.247
F(000)	4032	1720	1848
Crystal size/mm^3	0.21 × 0.124 × 0.087	0.21 × 0.112 × 0.089	0.242 × 0.161 × 0.123
2Θ range	5.416 to 62.416	4.306 to 62.484	4.298 to 62.314
Reflections collected	42720	33975	27118
Independent reflections	11051	10695	10604
S	1.038	1.06	1.052
R_1	0.0542	0.0614	0.033
wR_2	0.1174	0.1724	0.0845

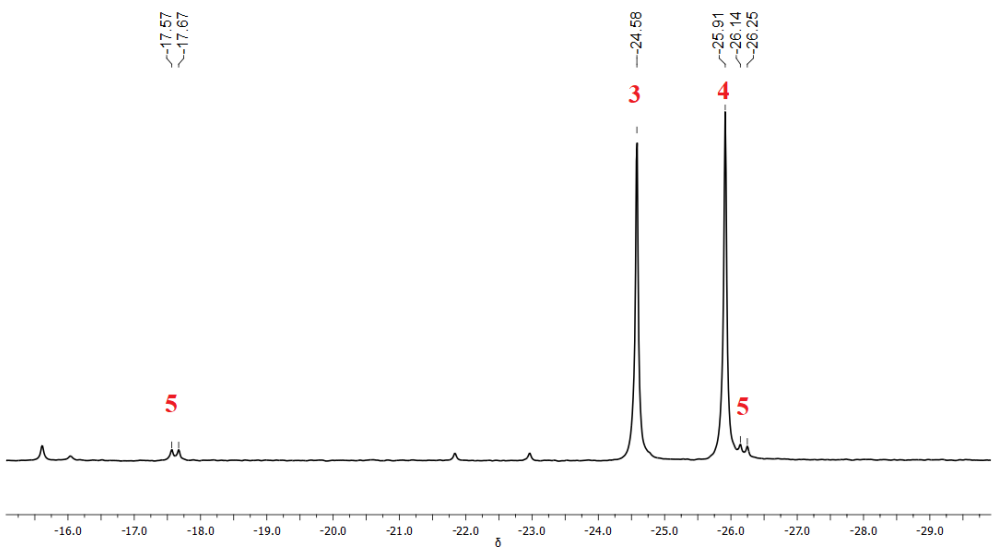


Fig. S1 $^{31}P\{^{1}H\}$ NMR spectrum of a crude mixture of **3**, **4** and **5**

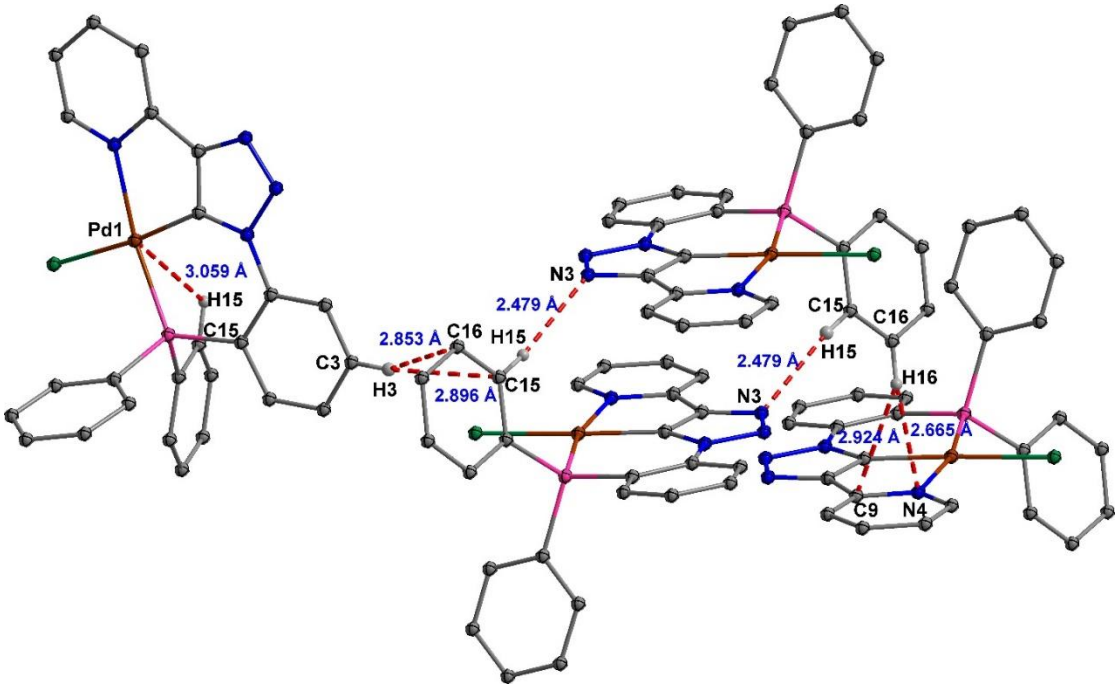


Fig. S2 Perspective view of the packing of **7** in crystalline phase.

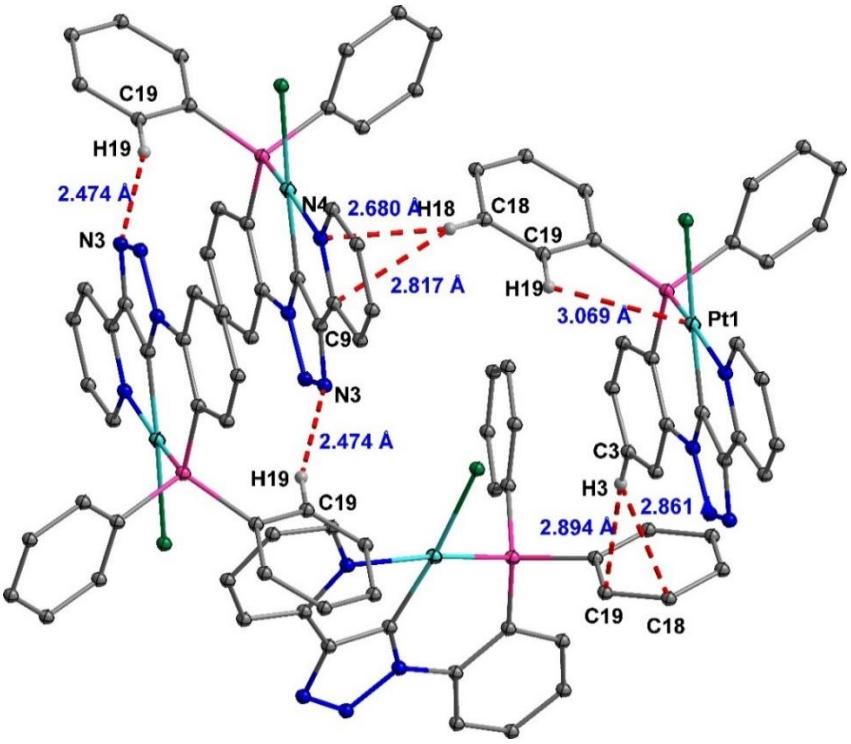


Fig. S3 Perspective view of the packing of **8** in the crystalline phase.

NMR and mass spectra of 2-14

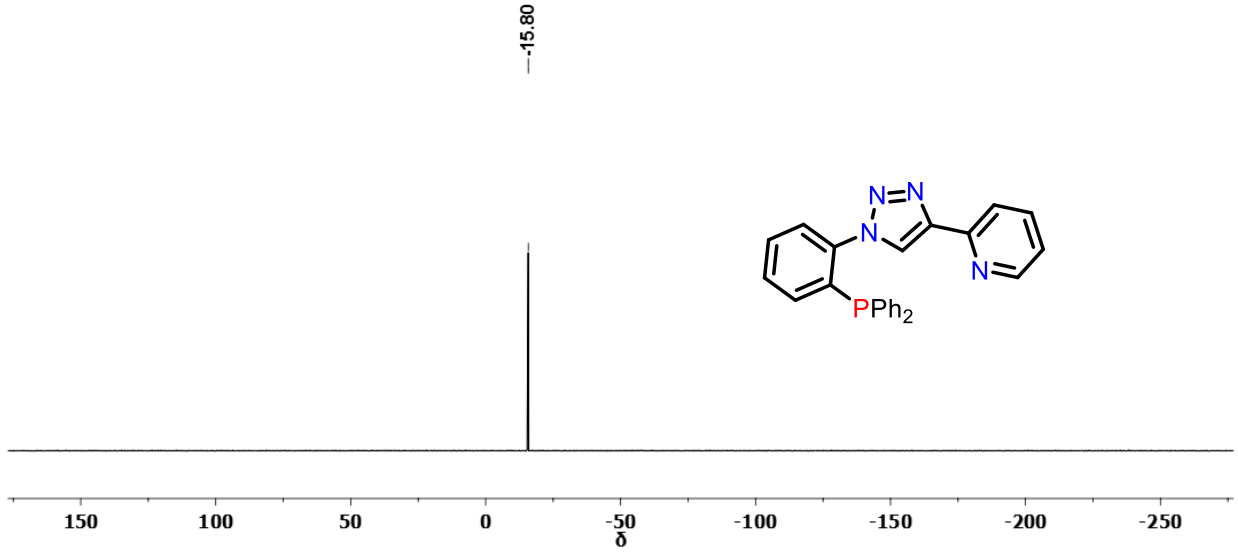


Fig. S4 $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ (162 MHz)

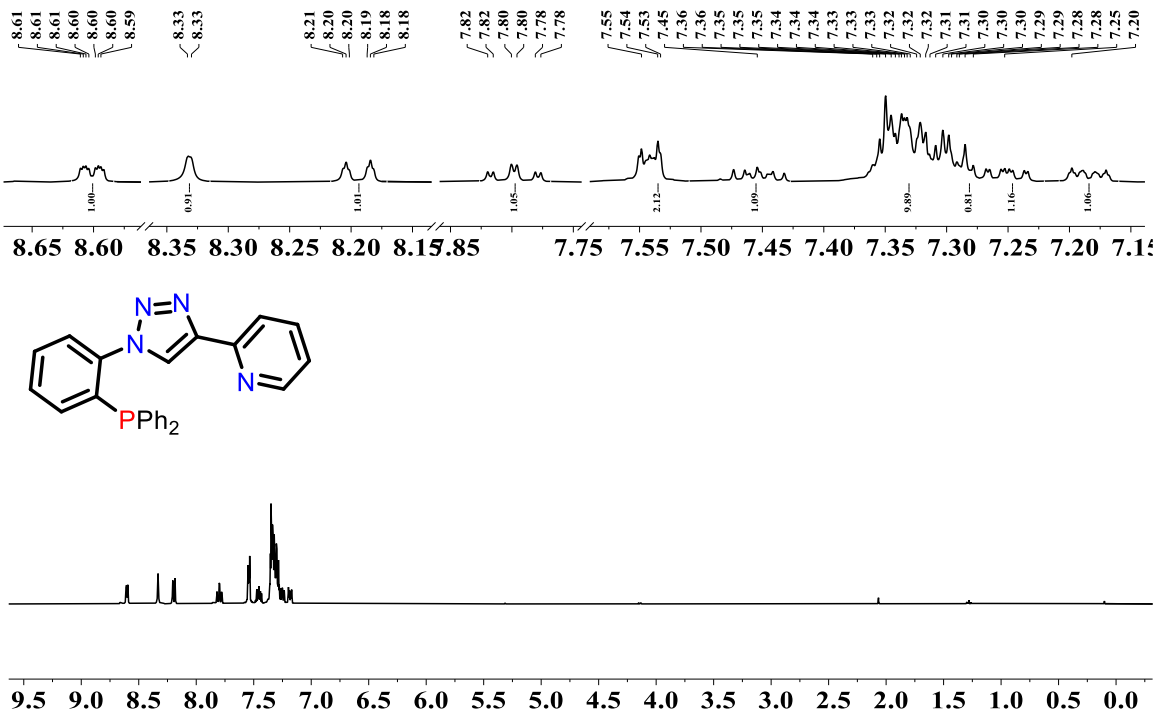


Fig. S5 ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz)

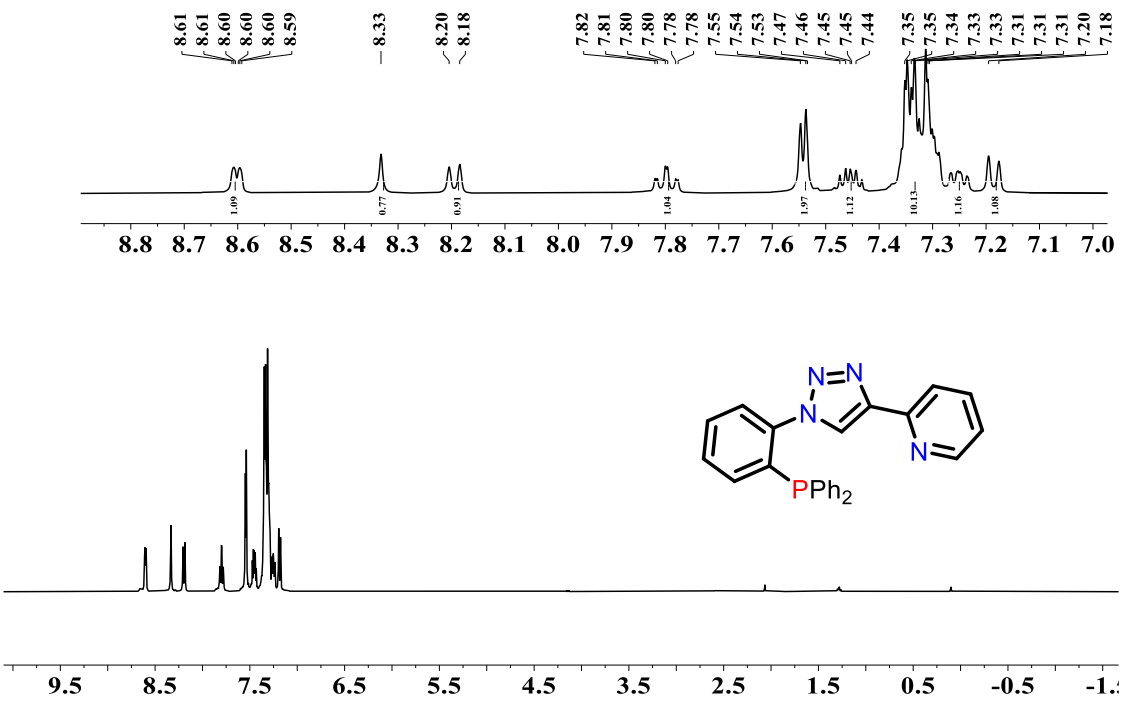


Fig. S6 $^{1}H\{^{31}P\}$ NMR spectrum of **2** in $CDCl_3$ (400 MHz)

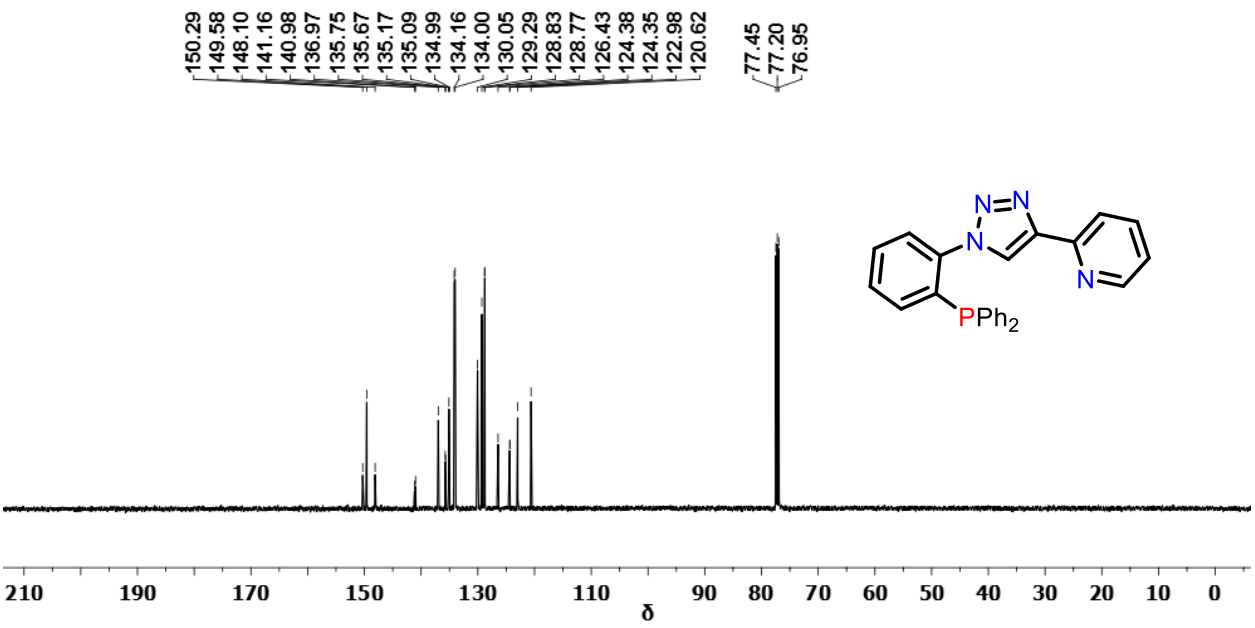
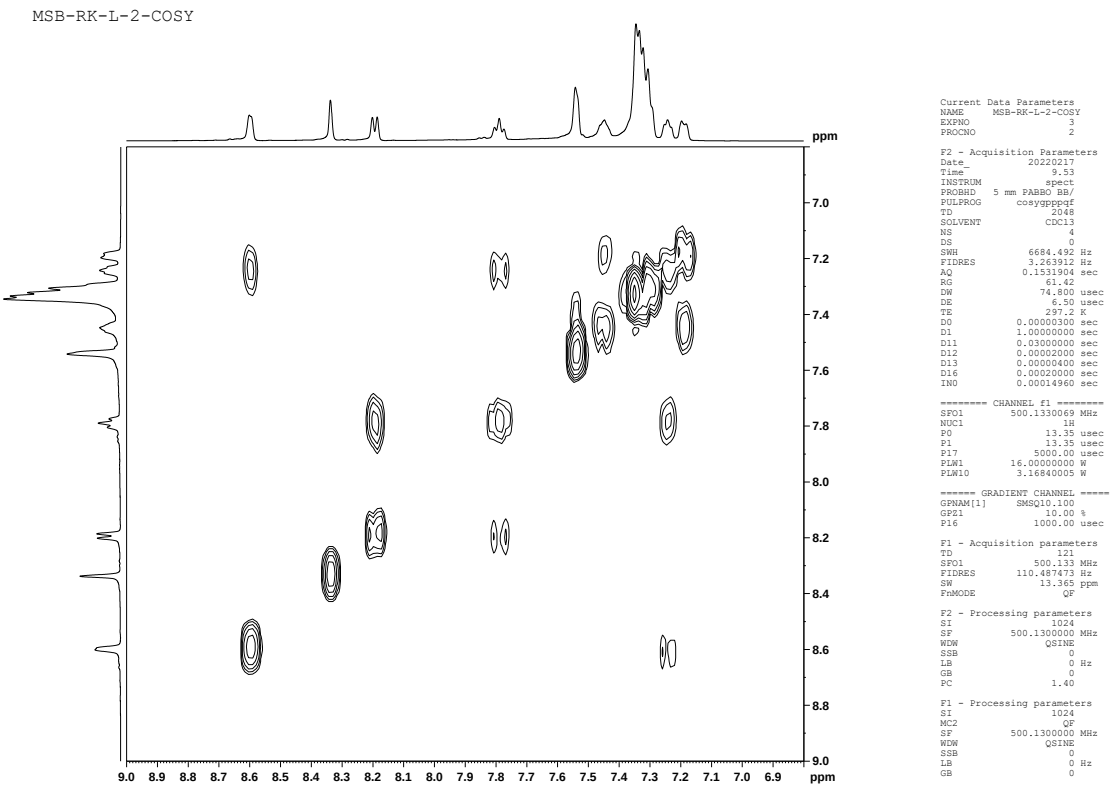


Fig. S7 ^{13}C NMR spectrum of **2** in $CDCl_3$ (126 MHz)

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PROCNO                  2

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SOLVENT            CDC13
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TE                297.2 K
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NUC1               1H
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P17             5000.00 usec
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LB                     0 Hz
GB                     0
PC                  1.40

F1 - Processing parameters
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MC2                  QF
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LB                     0 Hz
GB                     0
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Fig. S8 ^{1}H-^{1}H COSY spectrum of compound **2**

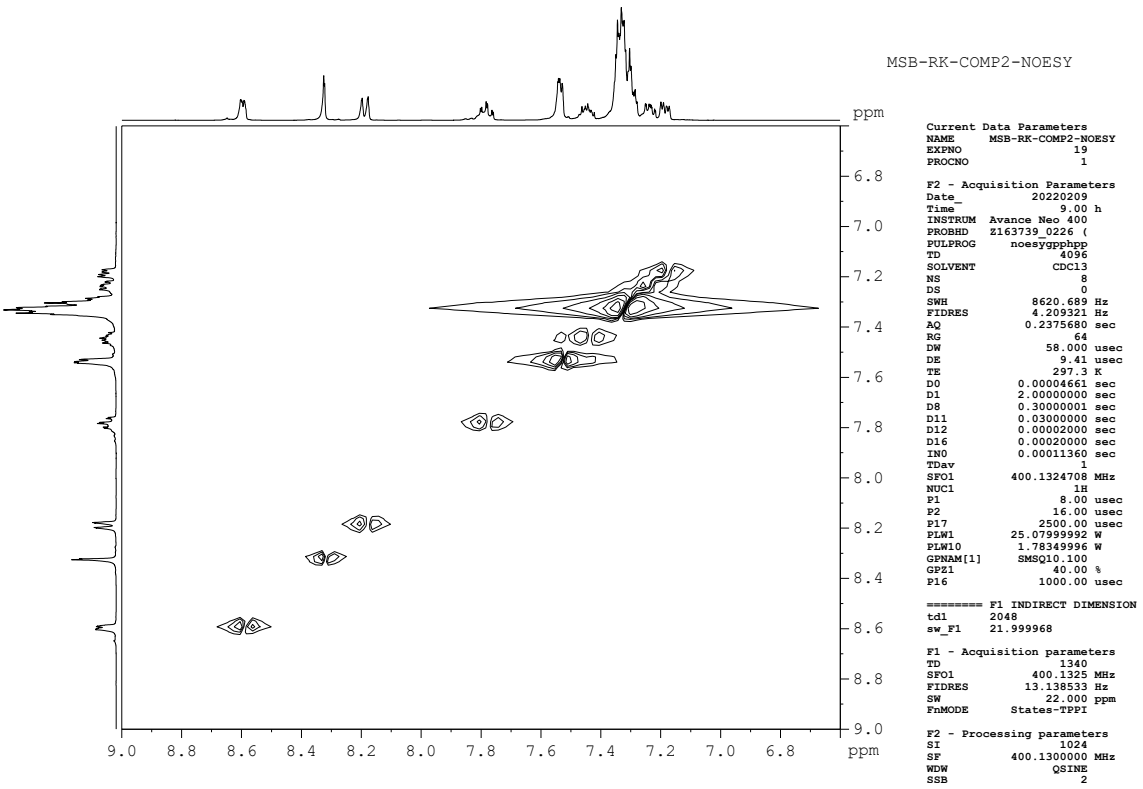


Fig. S9 ^{1}H-^{1}H NOSEY spectrum of compound **2**

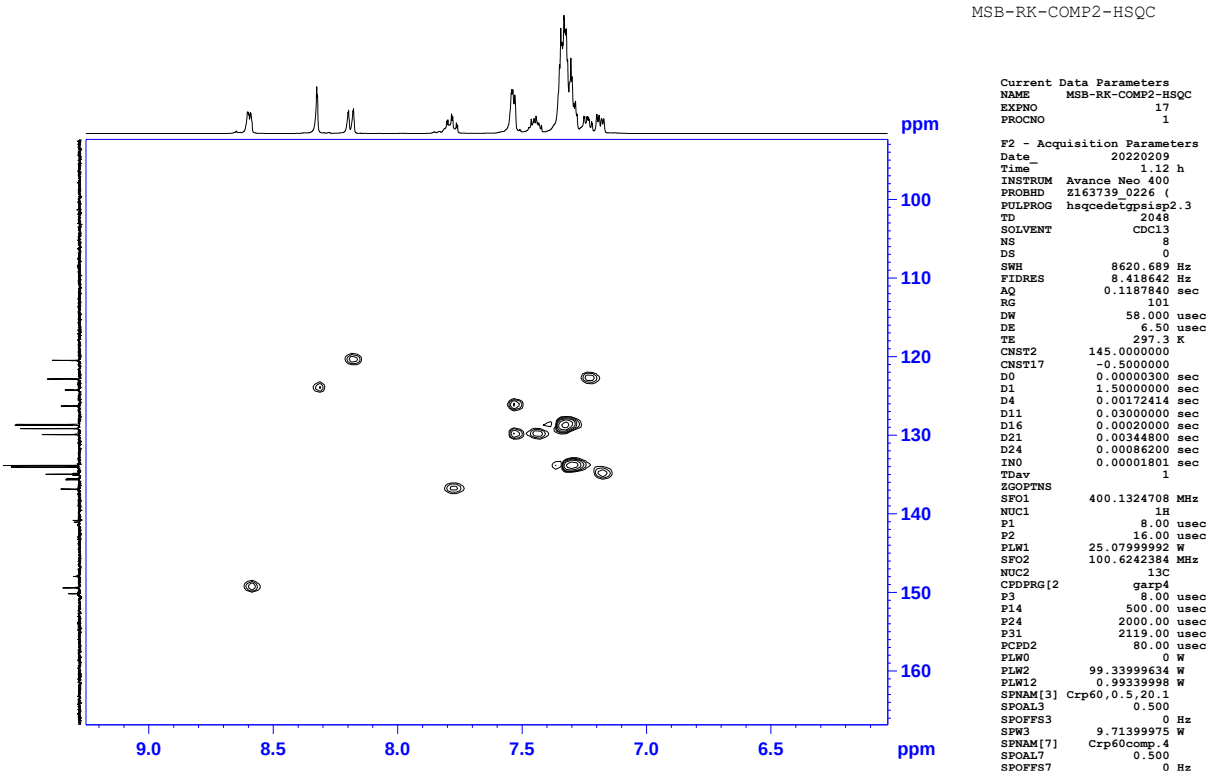
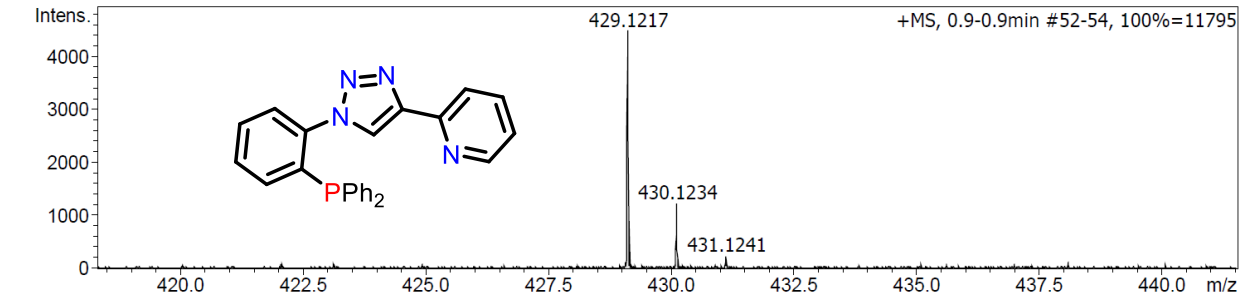


Fig. S10 1H-^{13}C HSQC spectrum of compound **2**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
429.1217	1	C25H19N4NaP	429.1240	-5.4	9.1	1	100.00	18.5	even	ok

Fig. S11 EI mass spectrum of **2**

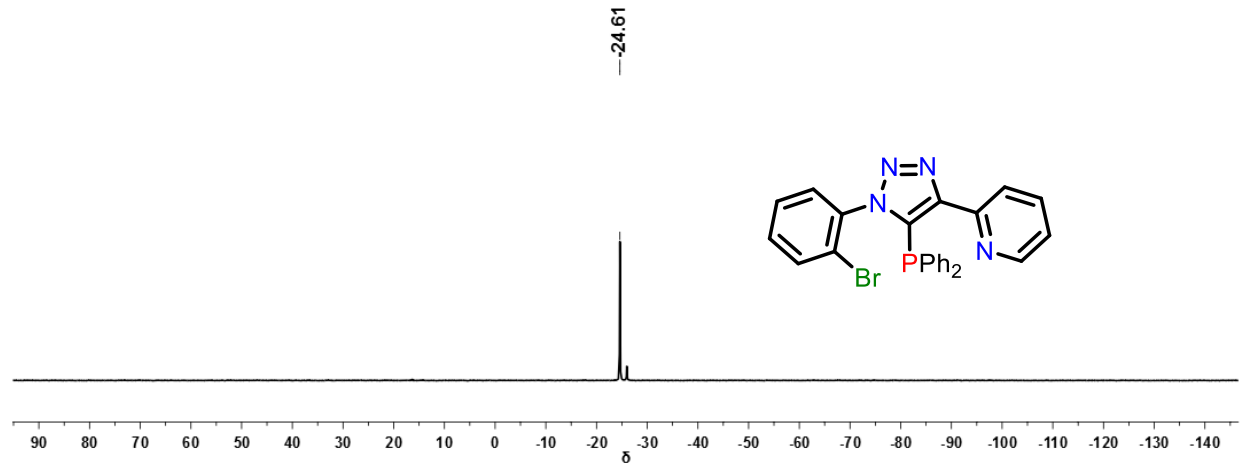


Fig. S12 $^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ (162 MHz)

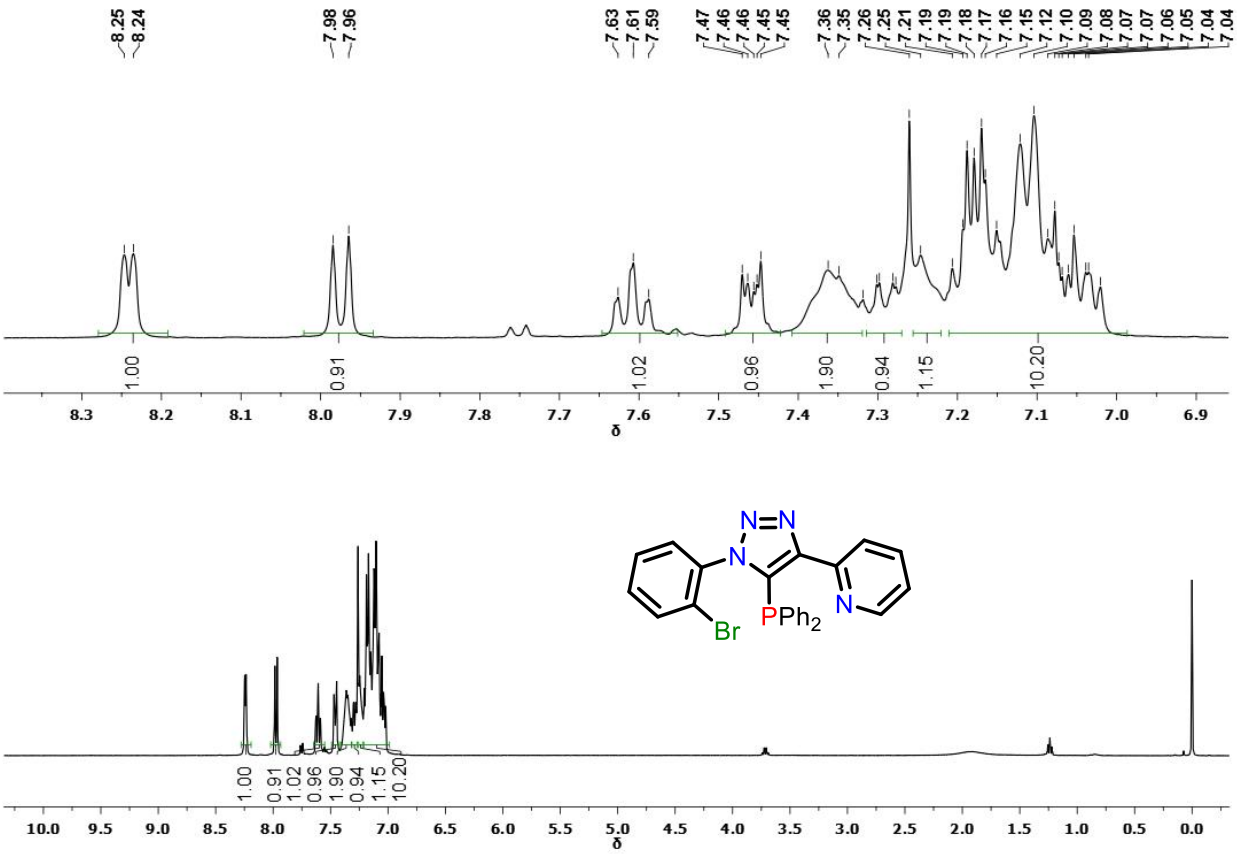


Fig. S13 ^{1}H NMR spectrum of **3** in $CDCl_3$ (400 MHz)

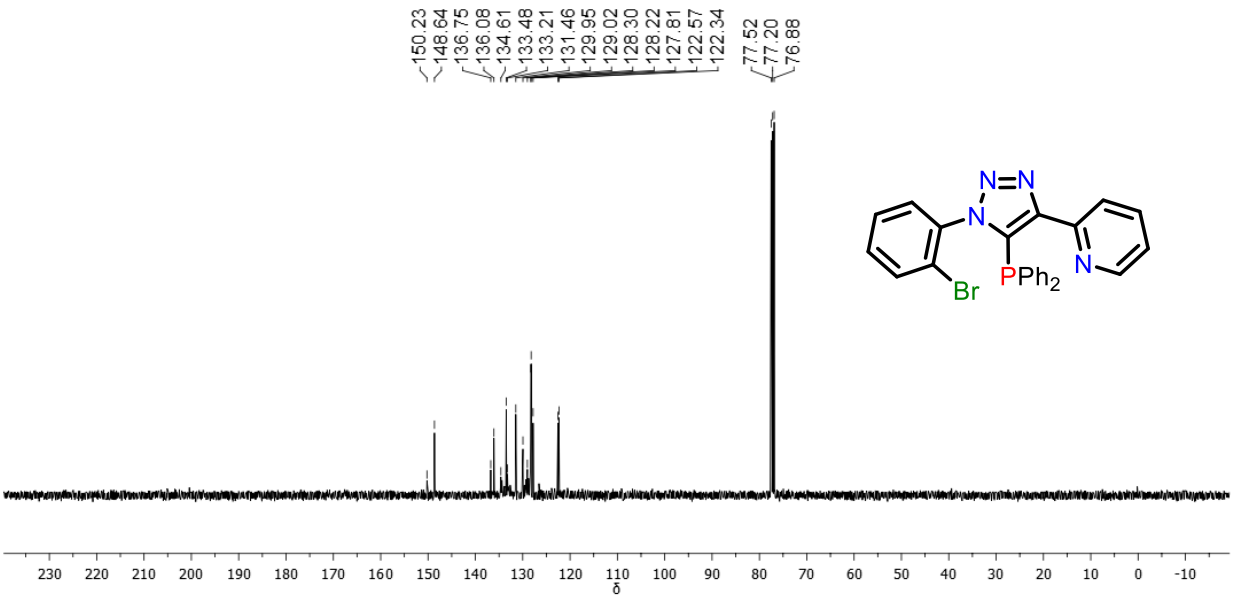
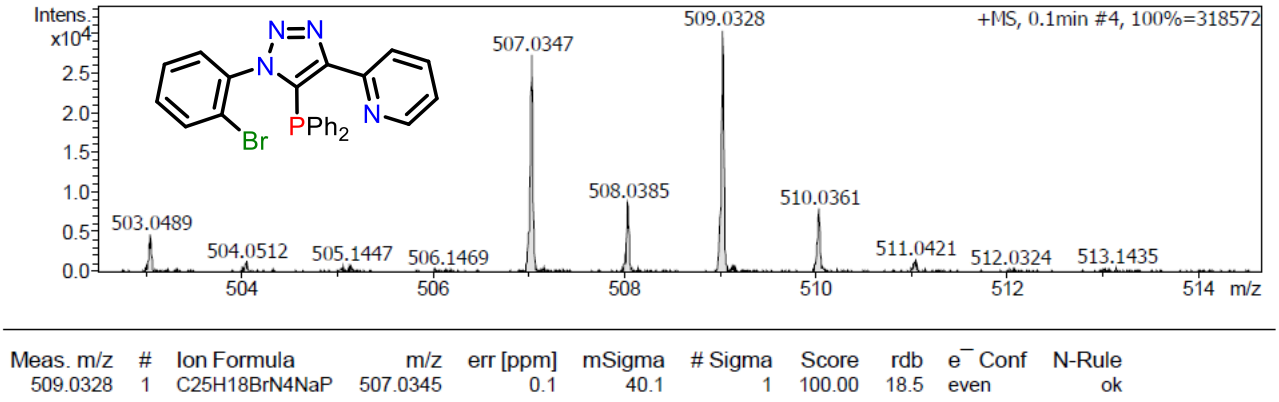


Fig. S14 ^{13}C NMR spectrum of **3** in $CDCl_3$ (101 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
509.0328	1	C25H18BrN4NaP	507.0345	0.1	40.1	1	100.00	18.5	even	ok

Fig. S15 EI mass spectrum of **3**

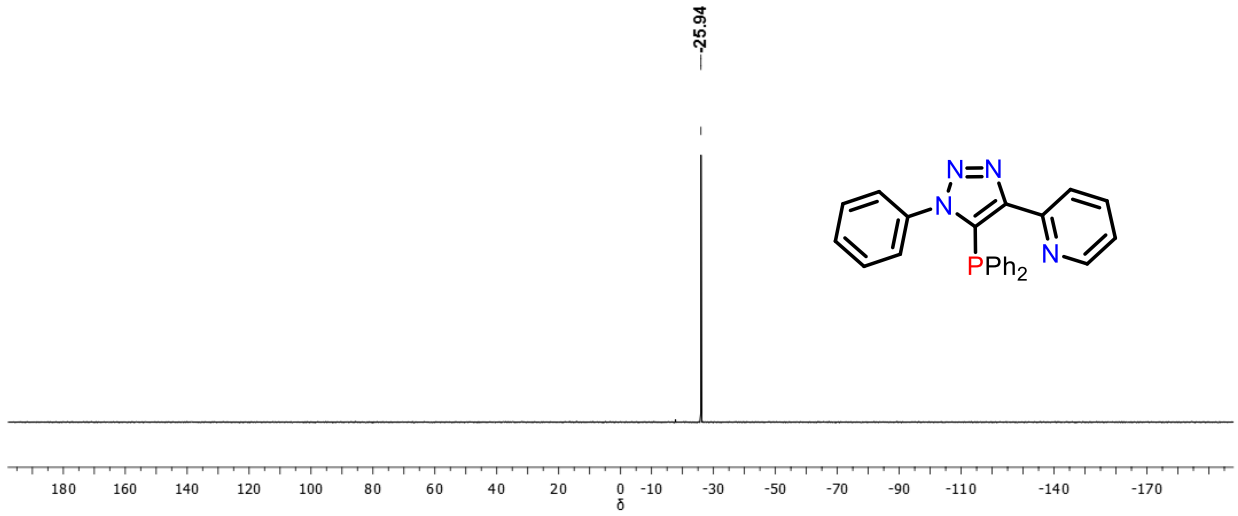


Fig. S16 $^{31}P\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ (162 MHz)

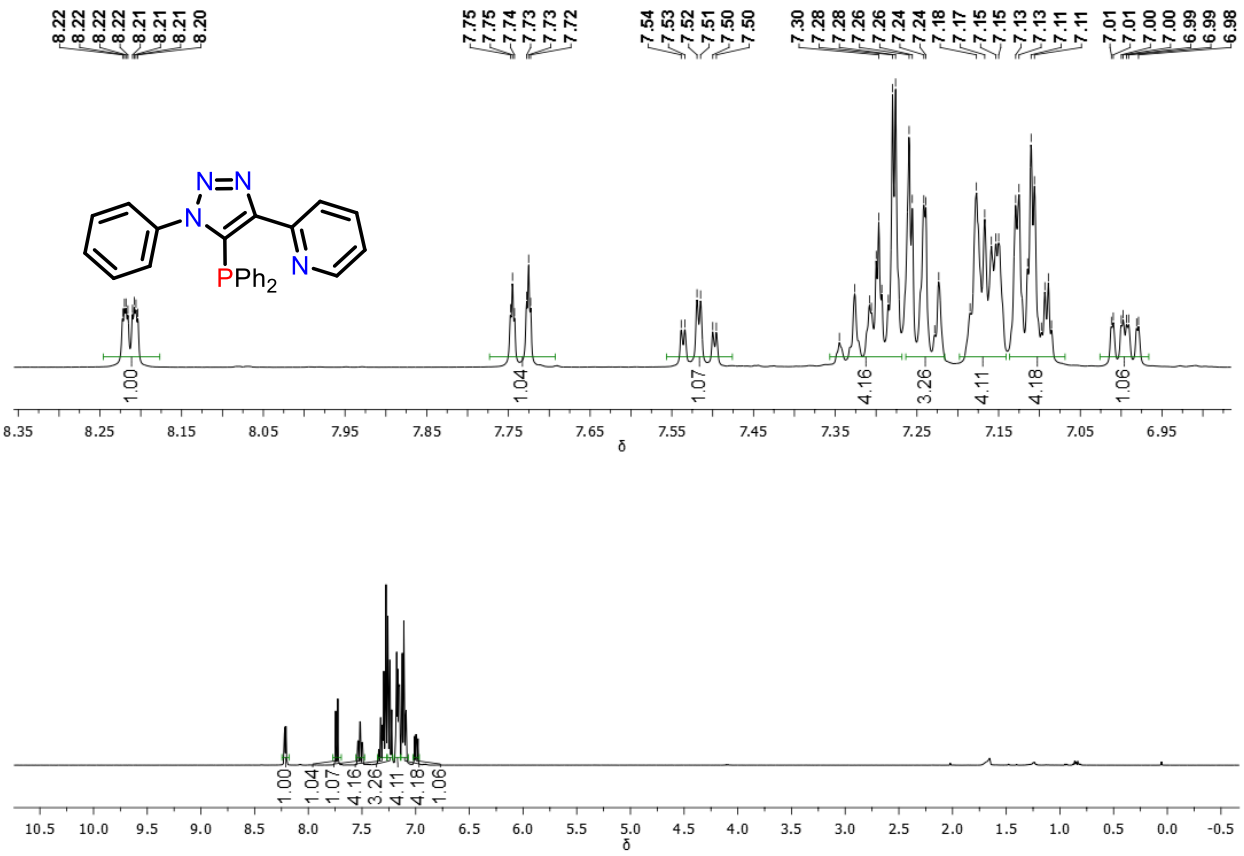


Fig. S17 ^{1}H NMR spectrum of **4** in $CDCl_3$ (400 MHz)

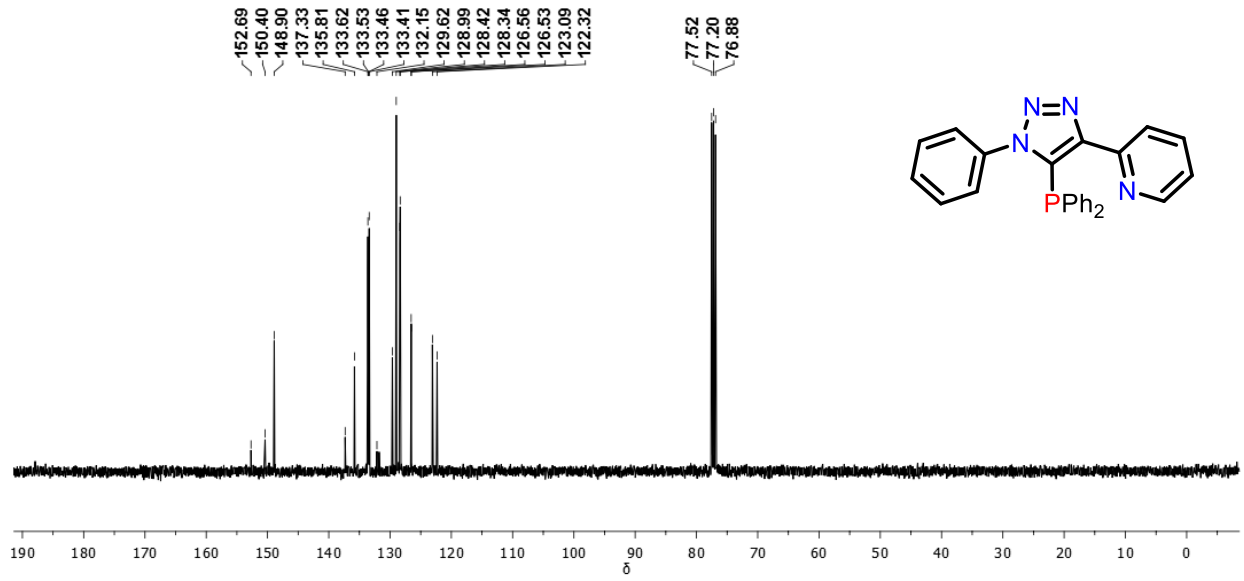
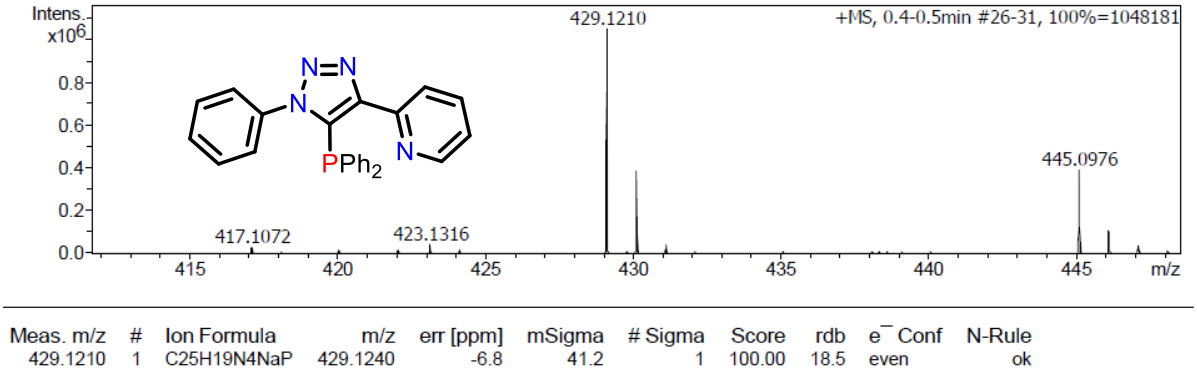


Fig. S18 ^{13}C NMR spectrum of **4** in $CDCl_3$ (101 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
429.1210	1	C25H19N4NaP	429.1240	-6.8	41.2	1	100.00	18.5	even	ok

Fig. S19 EI mass spectrum of **4**

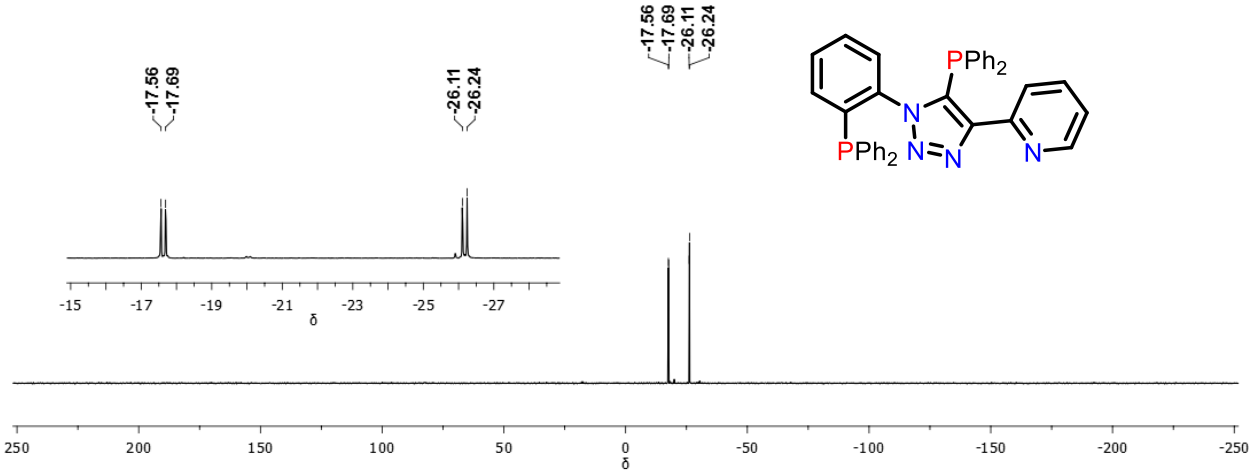


Fig. S20 $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$ (162 MHz)

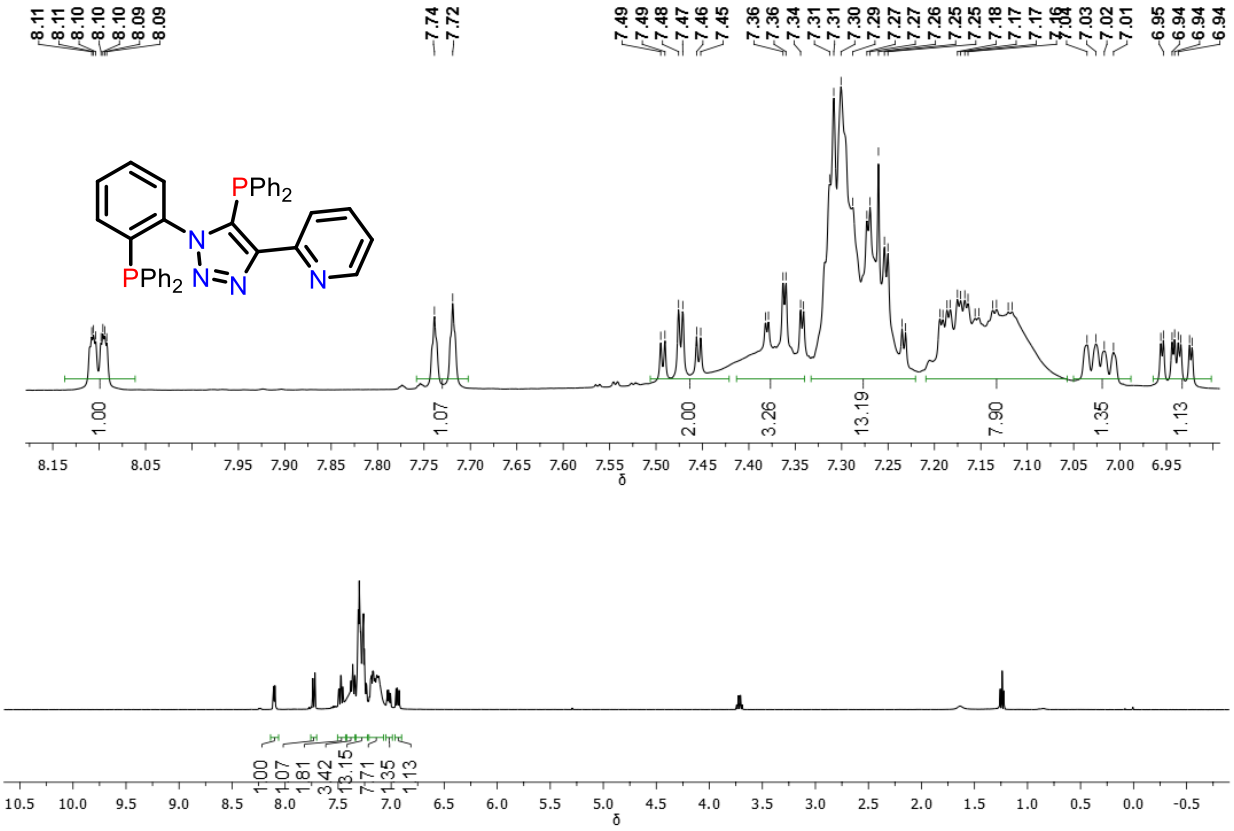


Fig. S21 ^{1}H NMR spectrum of **5** in $CDCl_3$ (400 MHz)

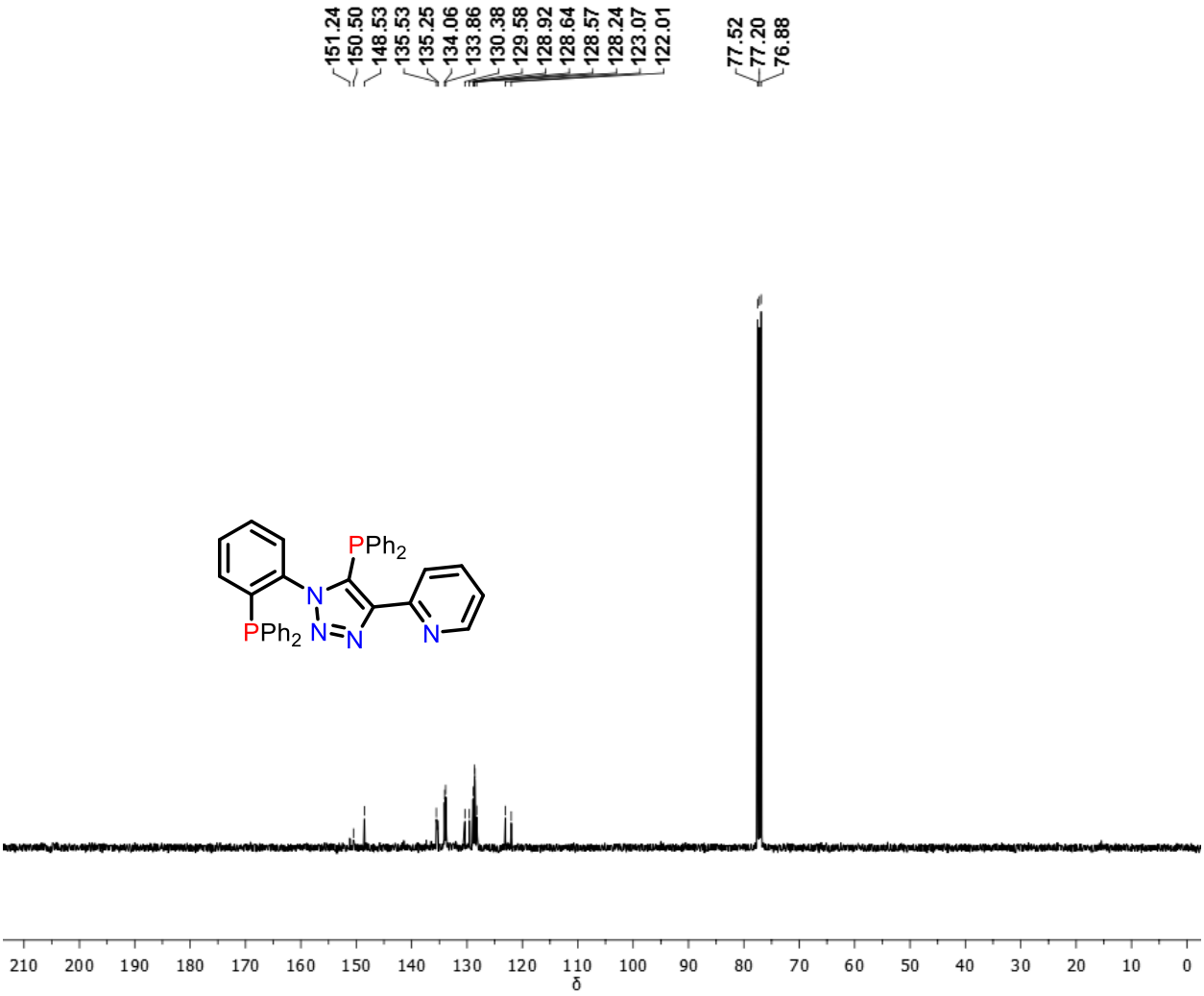
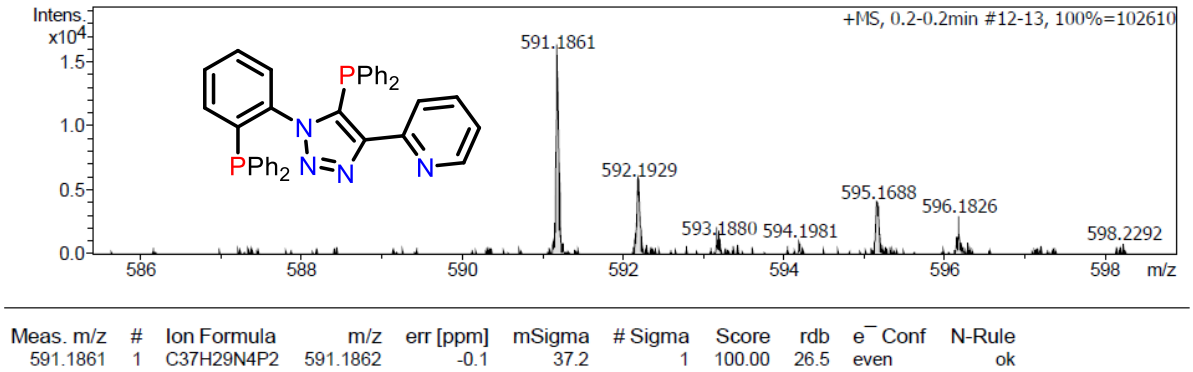


Fig. S22 ^{13}C NMR spectrum of **5** in $CDCl_3$ (101 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
591.1861	1	C37H29N4P2	591.1862	-0.1	37.2	1	100.00	26.5	even	ok

Fig. S23 EI mass spectrum of **5**

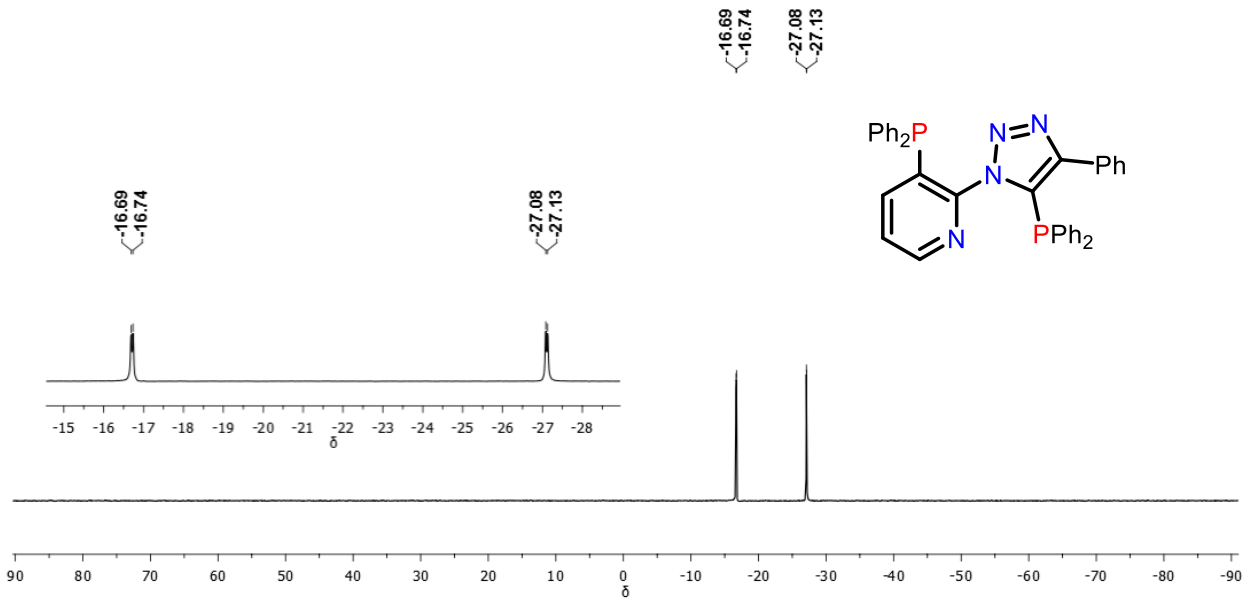


Fig. S24 $^{31}P\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$ (162 MHz)

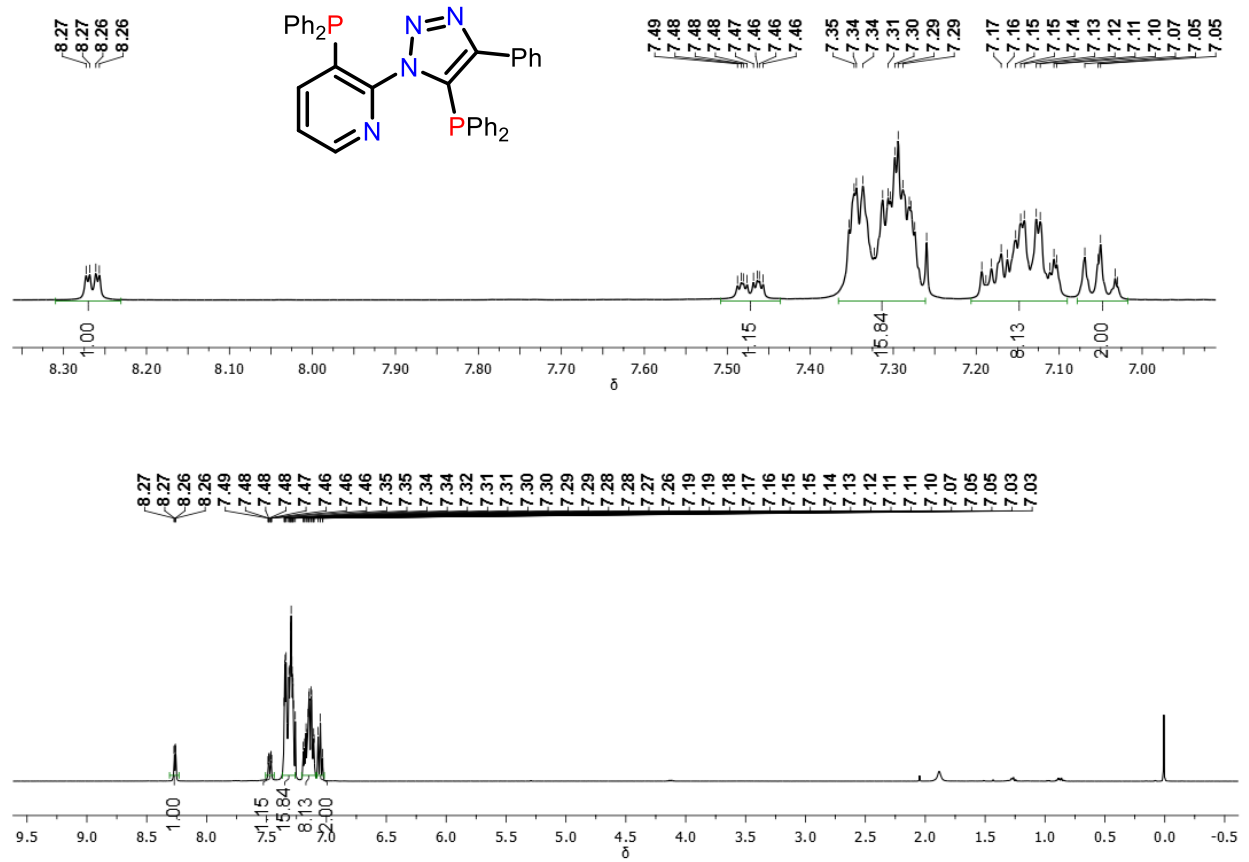


Fig. S25 ^{1}H NMR spectrum of **6** in $CDCl_3$ (400 MHz)

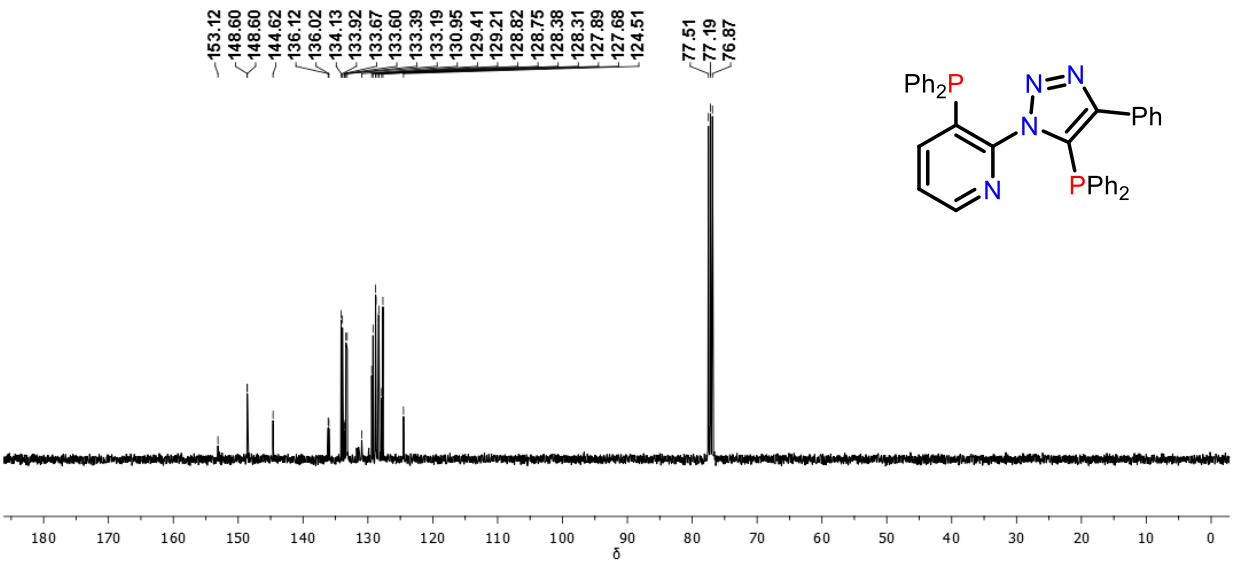
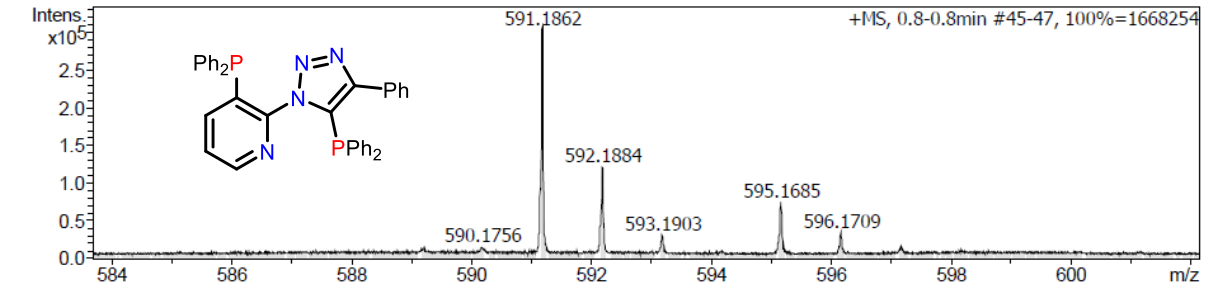


Fig. S26 ^{13}C NMR spectrum of **6** in $CDCl_3$ (101 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
591.1862	1	C37H29N4P2	591.1862	0.1	20.3	1	100.00	26.5	even	ok

Fig. S27 EI mass spectrum of **6**

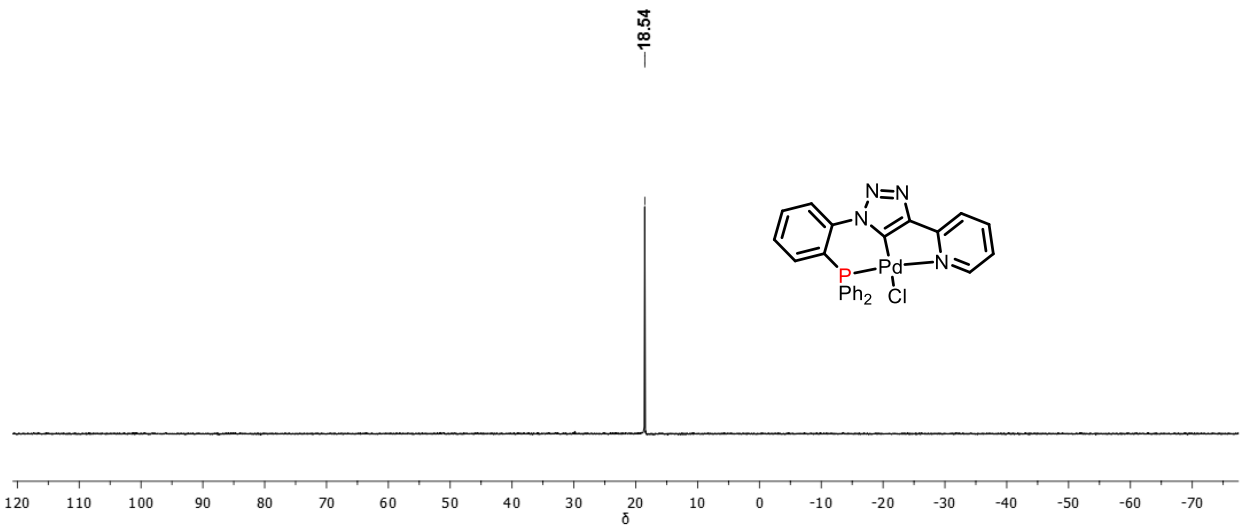


Fig. S28 $^{31}P\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$ (202 MHz)

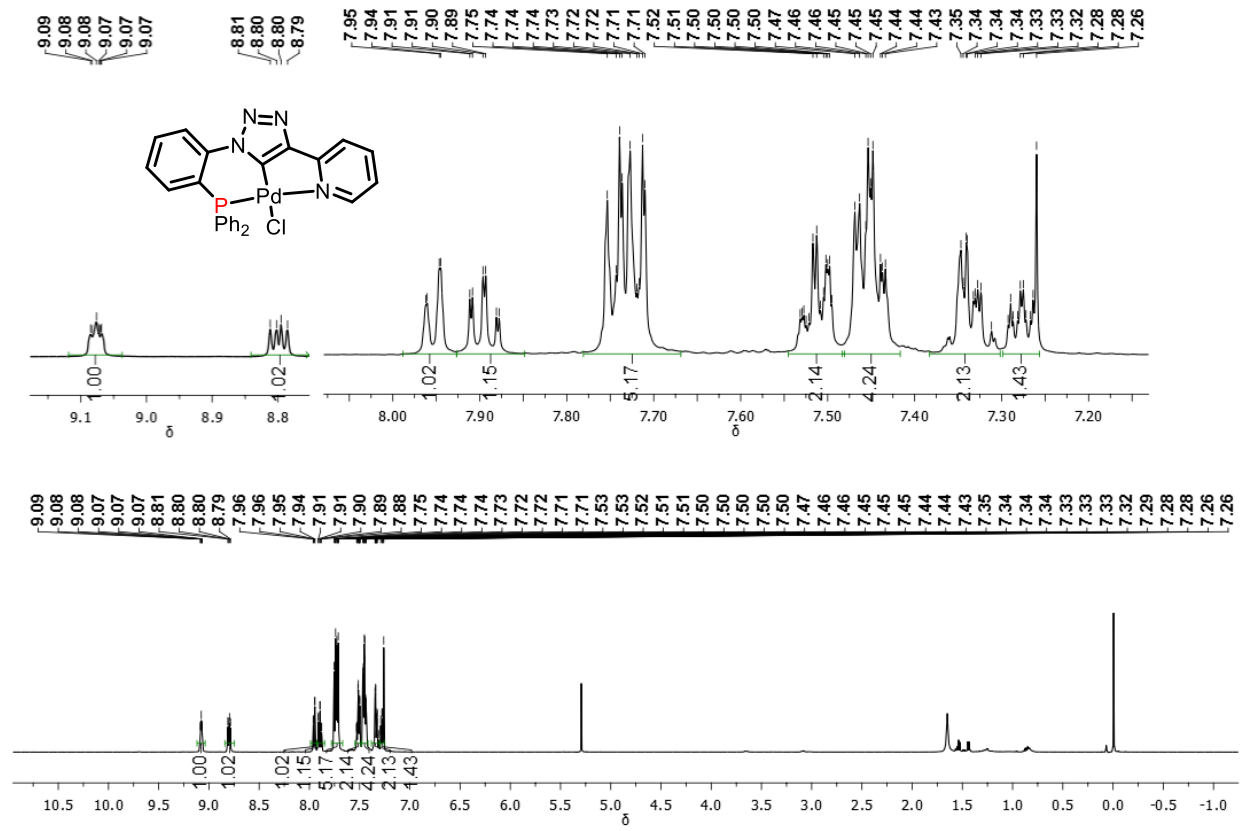


Fig. S29 ^{1}H NMR spectrum of **7** in $CDCl_3$ (400 MHz)

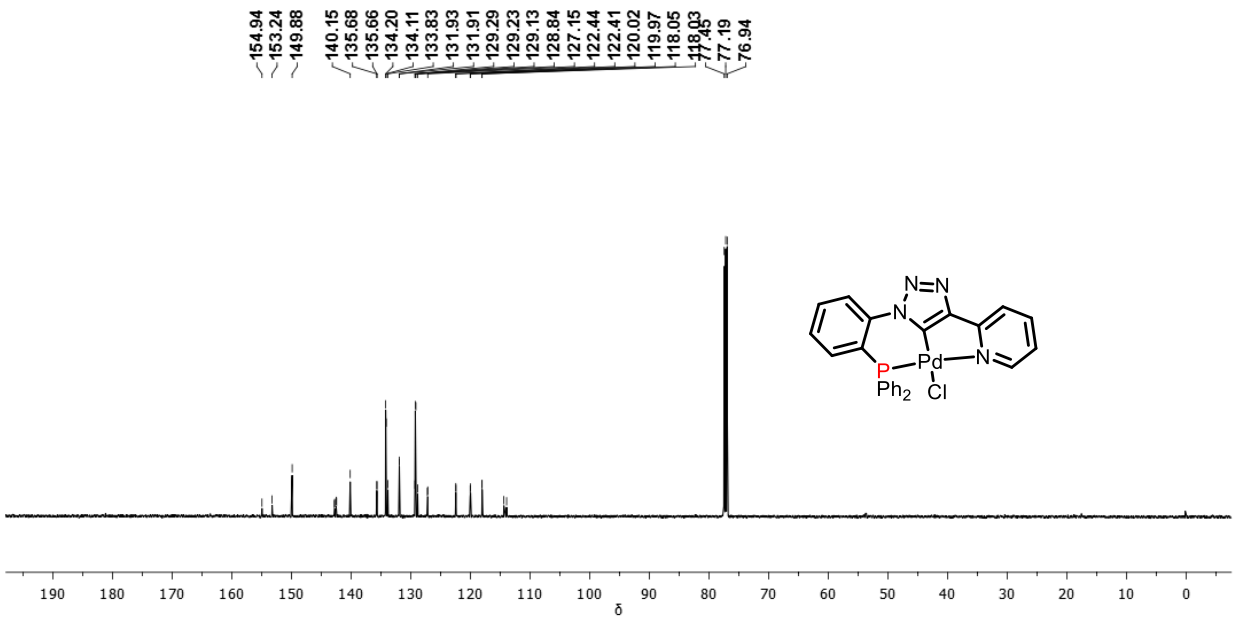
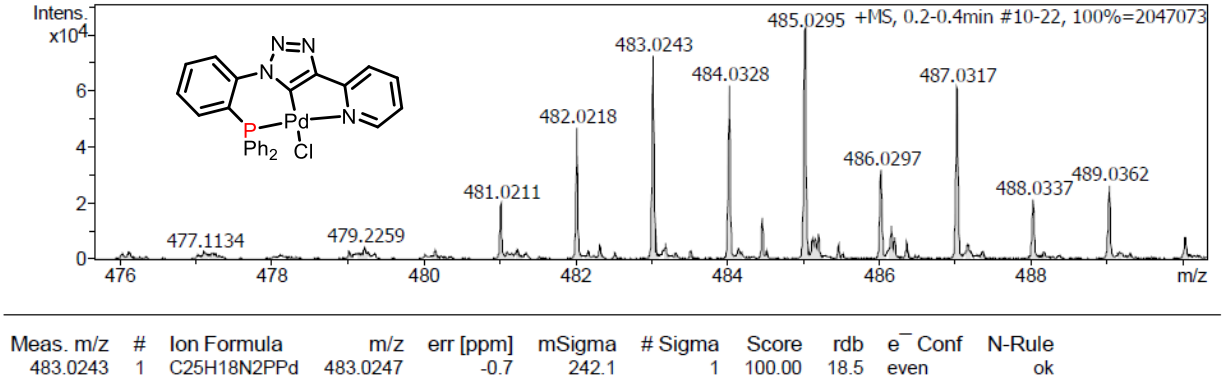


Fig. S30 ^{13}C NMR spectrum of **7** in $CDCl_3$ (101 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
483.0243	1	C25H18N2PPd	483.0247	-0.7	242.1	1	100.00	18.5	even	ok

Fig. S31 EI mass spectrum of **7**

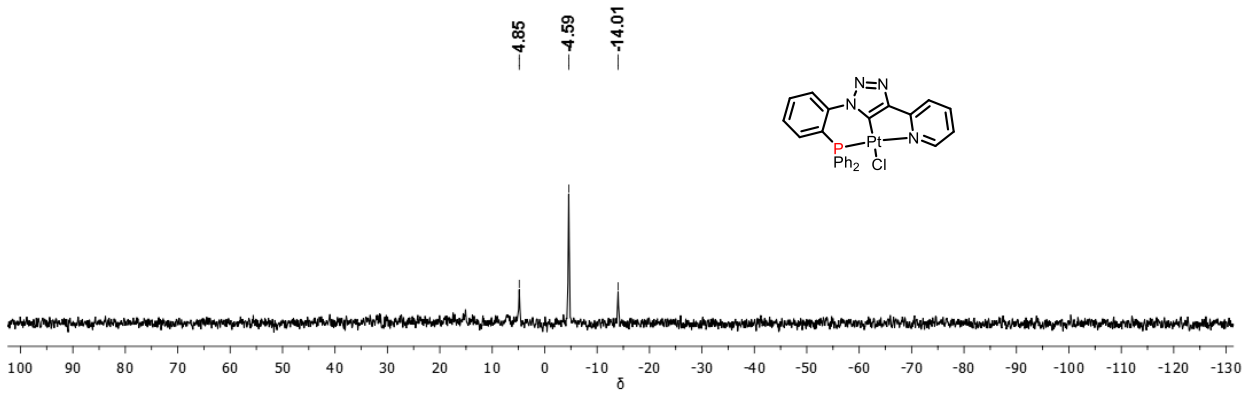


Fig. S32 $^{31}P\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$ (202 MHz)

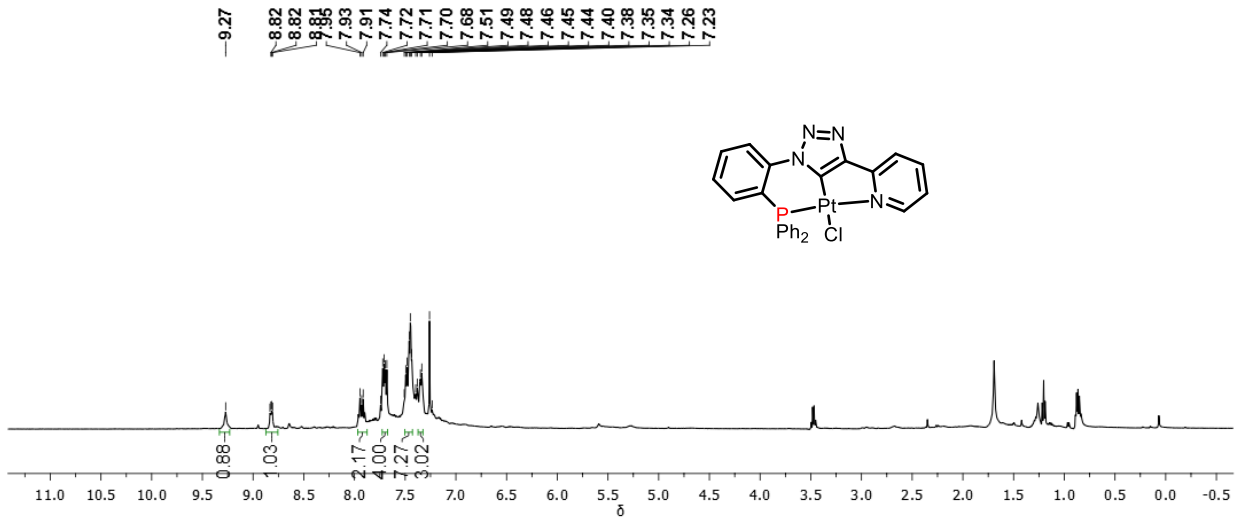
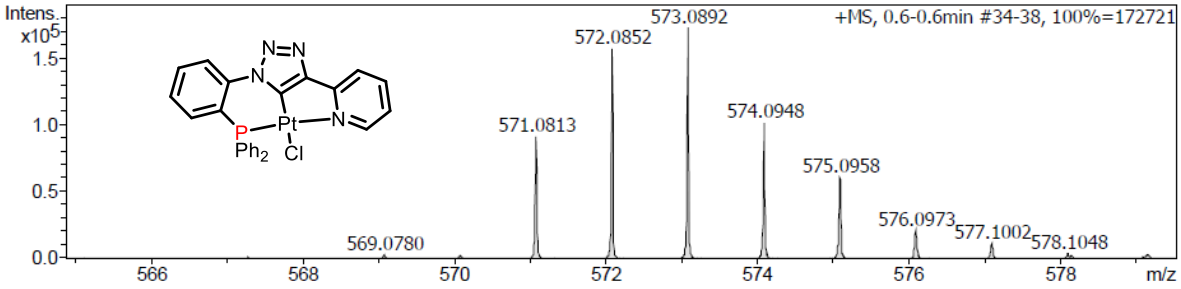


Fig. S33 ^{1}H NMR spectrum of **8** in $CDCl_3$ (400 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
572.0852	1	C25H18N2PPt	572.0852	-0.0	176.4	1	100.00	18.5	even	-

Fig. S34 EI mass spectrum of **8**

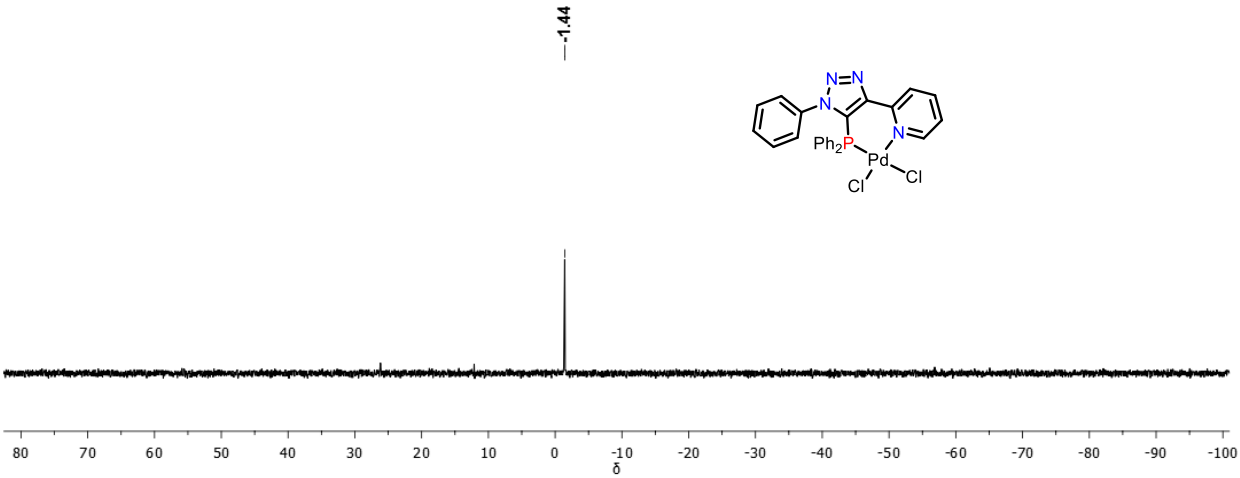


Fig. S35 $^{31}P\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$ (162 MHz)

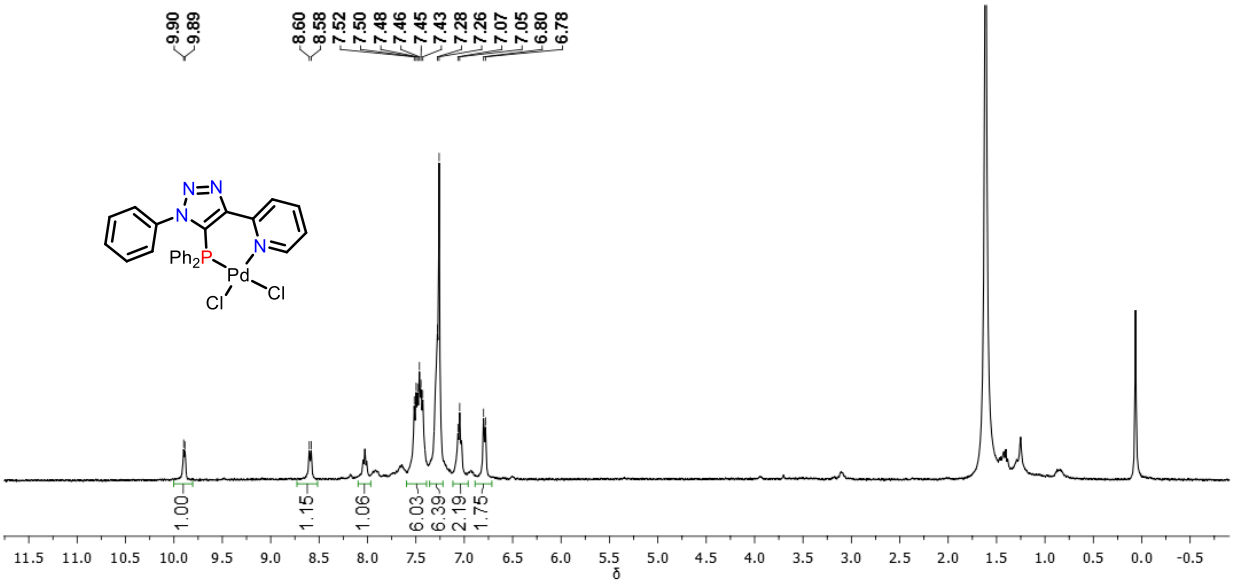
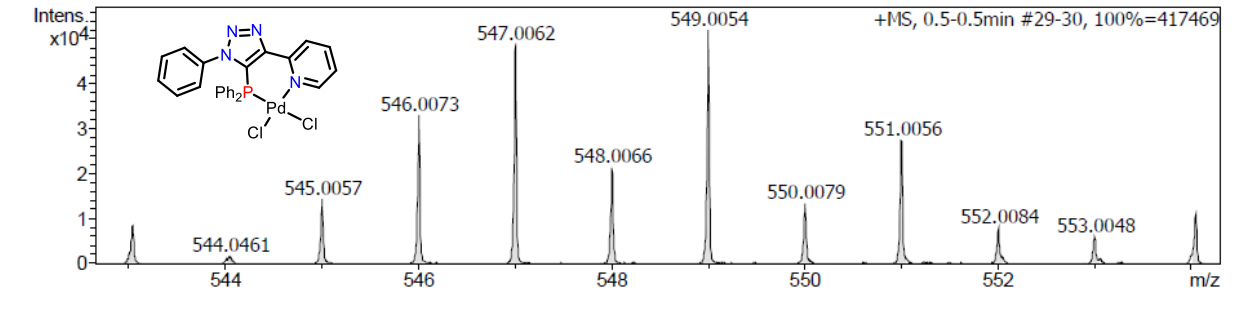


Fig. S36 ^{1}H NMR spectrum of **9** in $CDCl_3$ (400 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
549.0054	1	C25H19ClN4PPd	547.0072	-1.8	23.2	1	100.00	18.5	even	ok

Fig. S37 EI mass spectrum of **9**

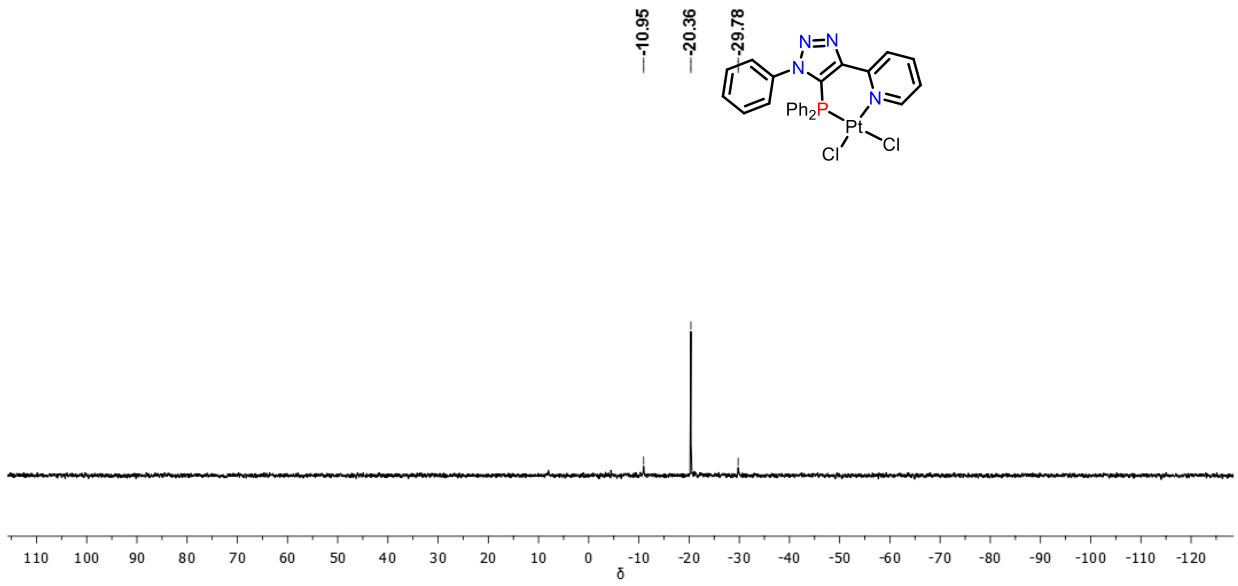


Fig. S38 $^{31}P\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$ (202 MHz)

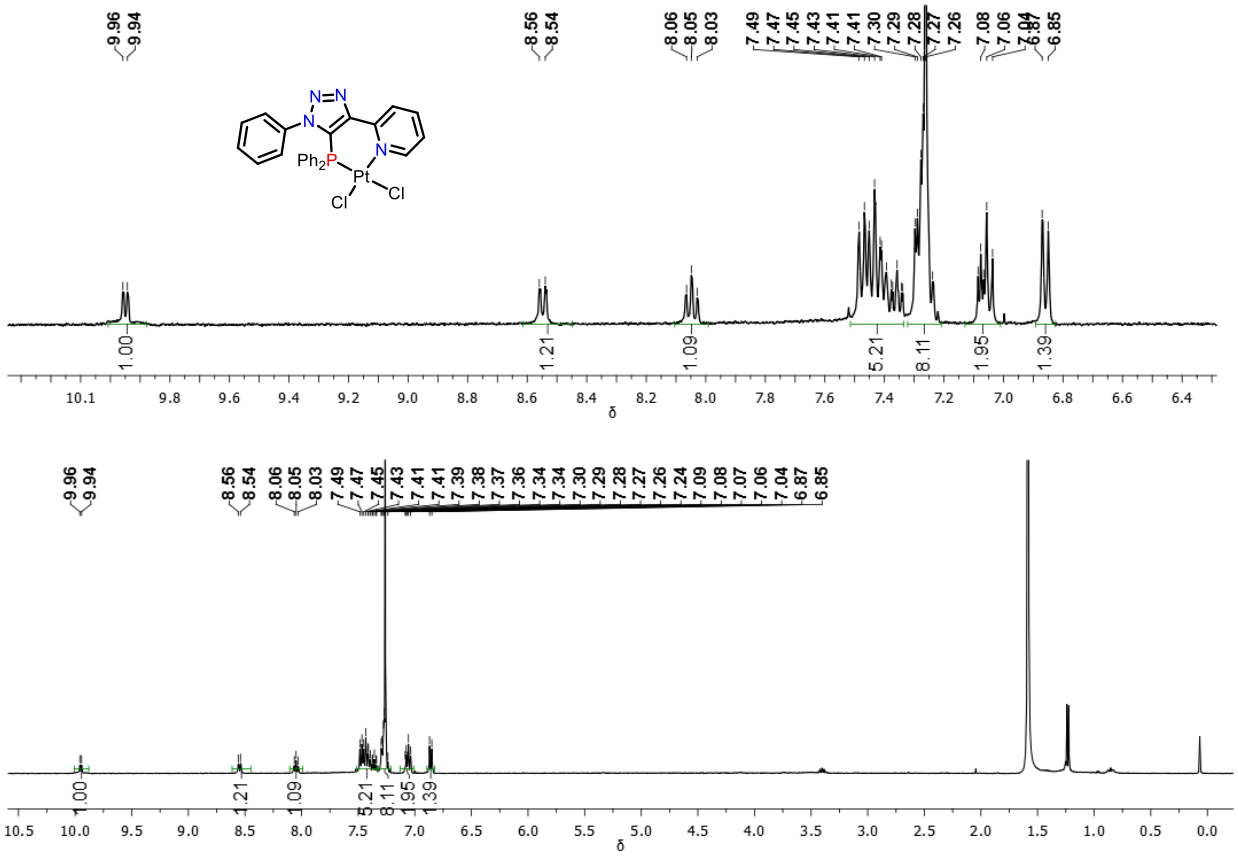
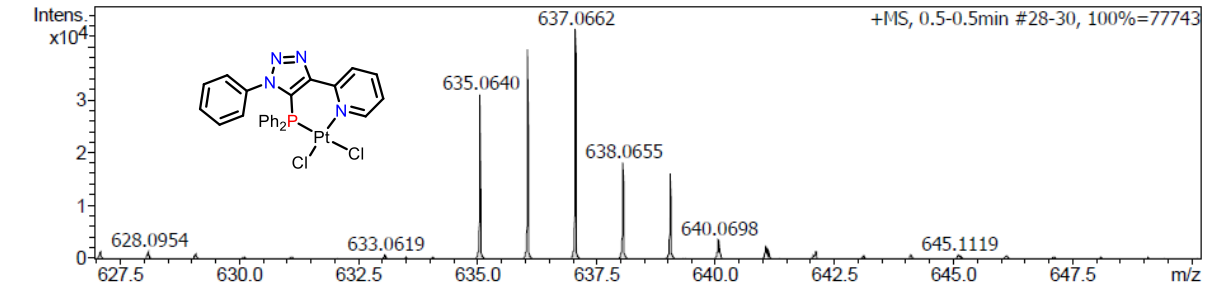


Fig. S39 ^{1}H NMR spectrum of **10** in $CDCl_3$ (400 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
637.0662	1	C25H19ClN4PPt	636.0680	-2.1	28.1	1	100.00	18.5	even	-

Fig. S40 EI mass spectrum of **10**

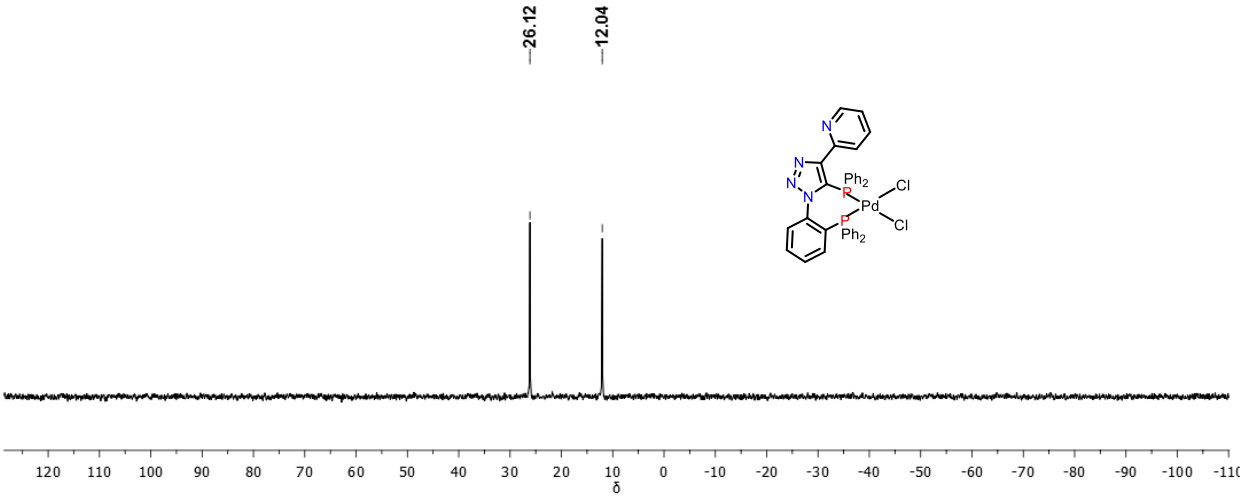


Fig. S41 $^{31}P\{^{1}H\}$ NMR spectrum of **11** in $CDCl_3$ (162 MHz)

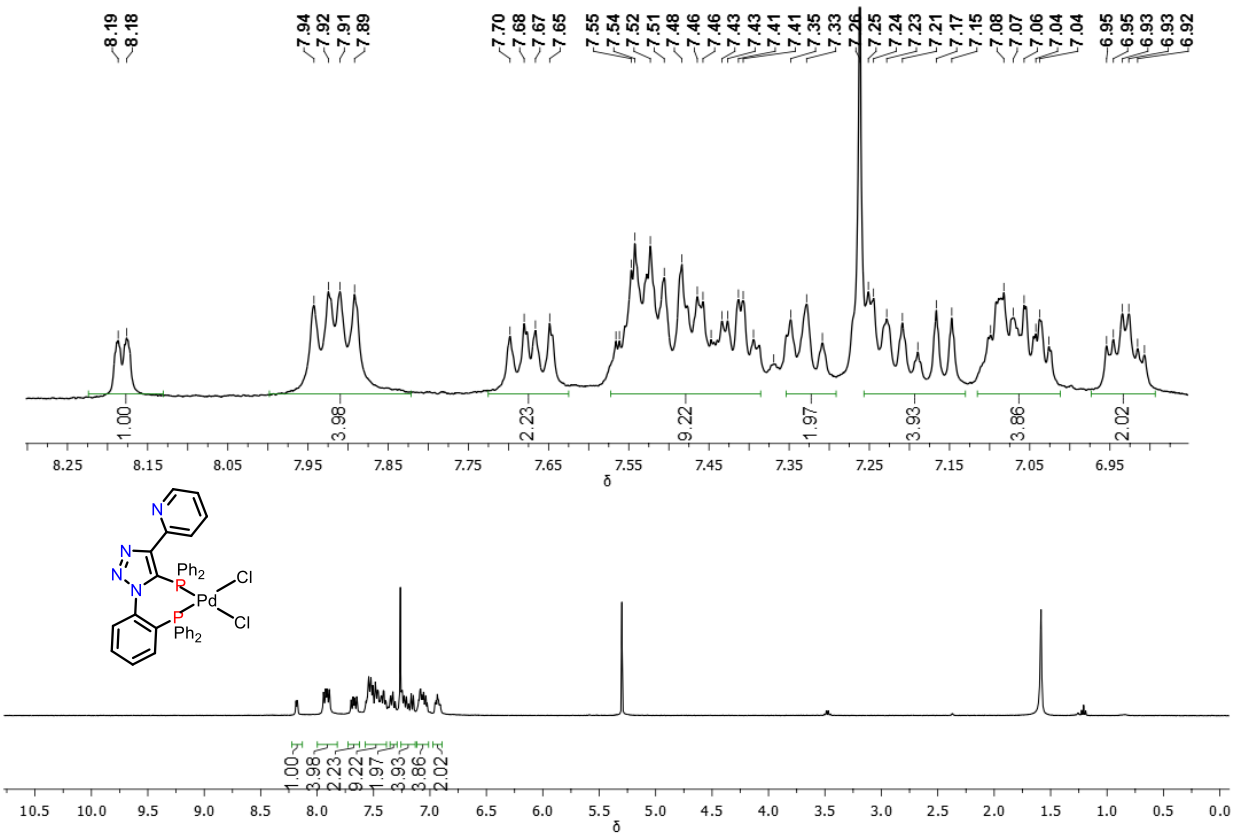


Fig. S42 ^{1}H NMR spectrum of **11** in $CDCl_3$ (400 MHz)

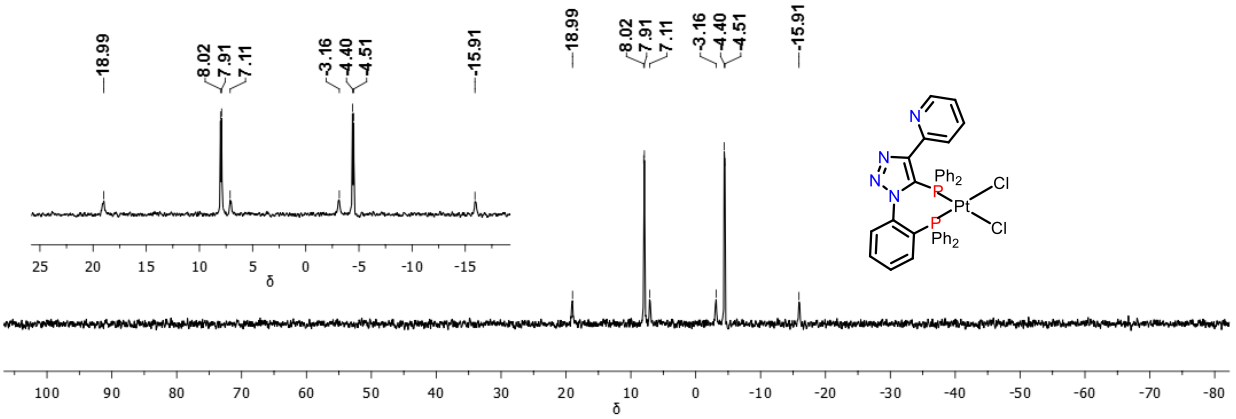


Fig. S43 $^{31}P\{^{1}H\}$ NMR spectrum of **12** in $CDCl_3$ (162 MHz)

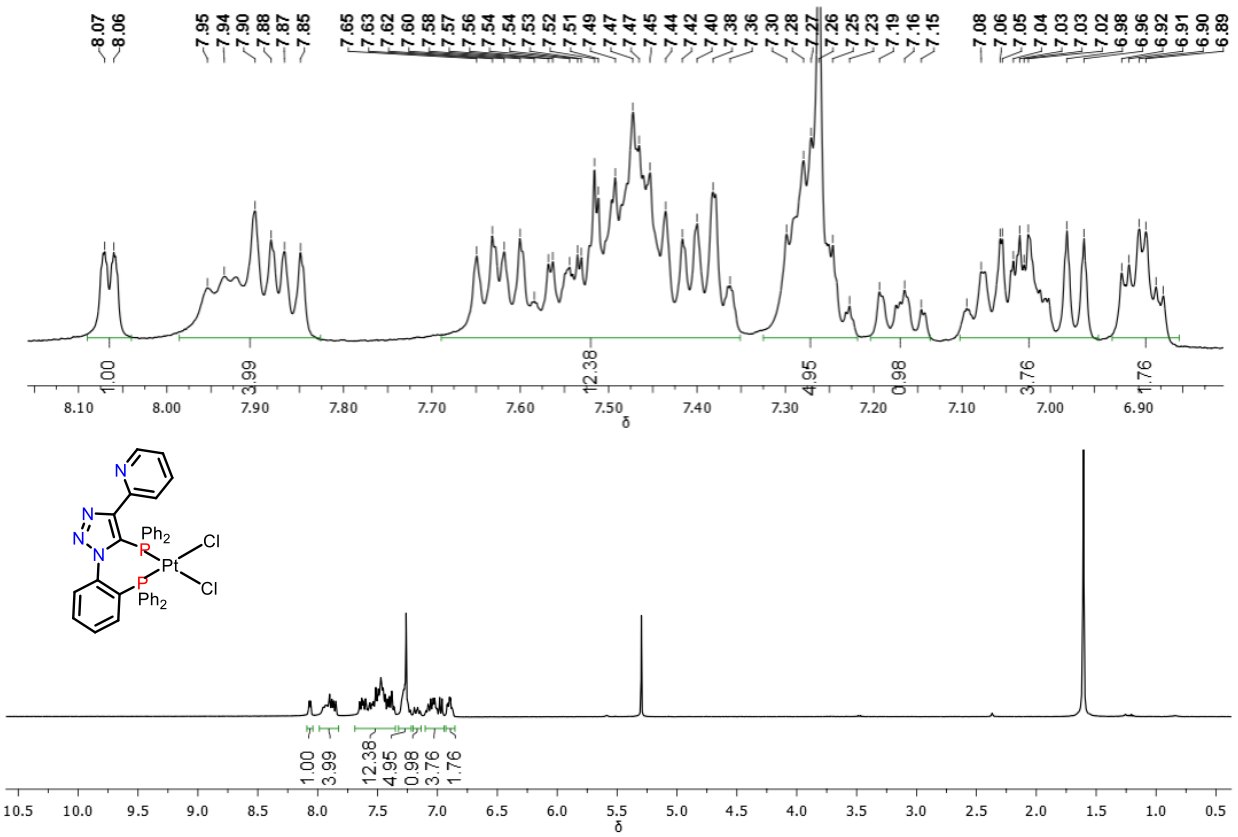
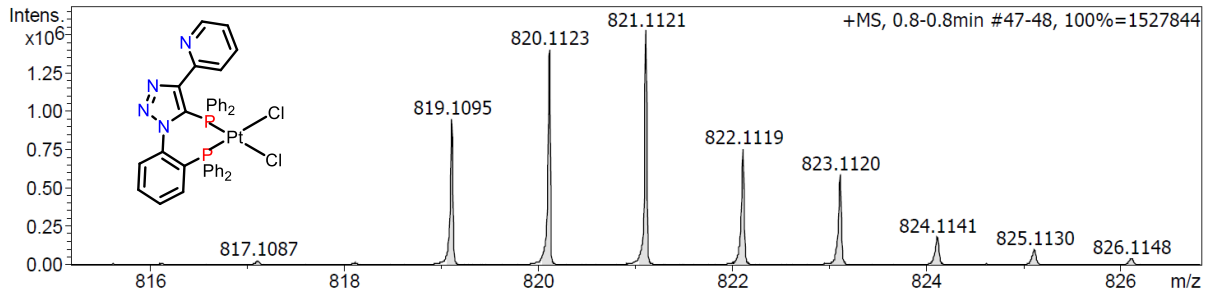


Fig. S44 ^{1}H NMR spectrum of **12** in $CDCl_3$ (400 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
821.1121	1	C37H28ClN4P2Pt	820.1123	-0.0	25.9	1	100.00	26.5	even	-

Fig. S45 EI mass spectrum of **12**

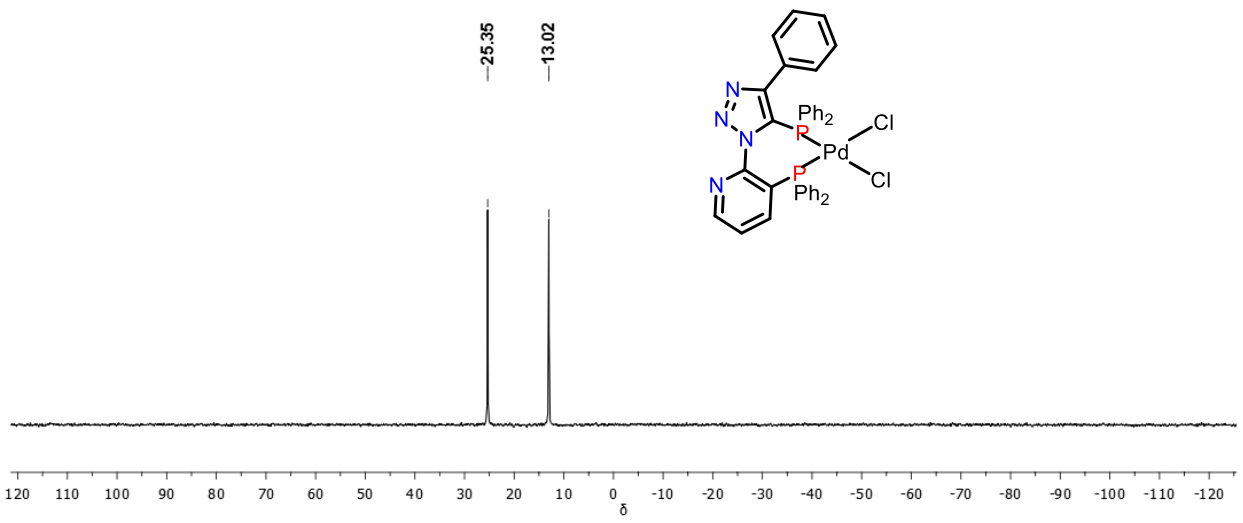


Fig. S46 $^{31}P\{^{1}H\}$ NMR spectrum of **13** in $CDCl_3$ (202 MHz)

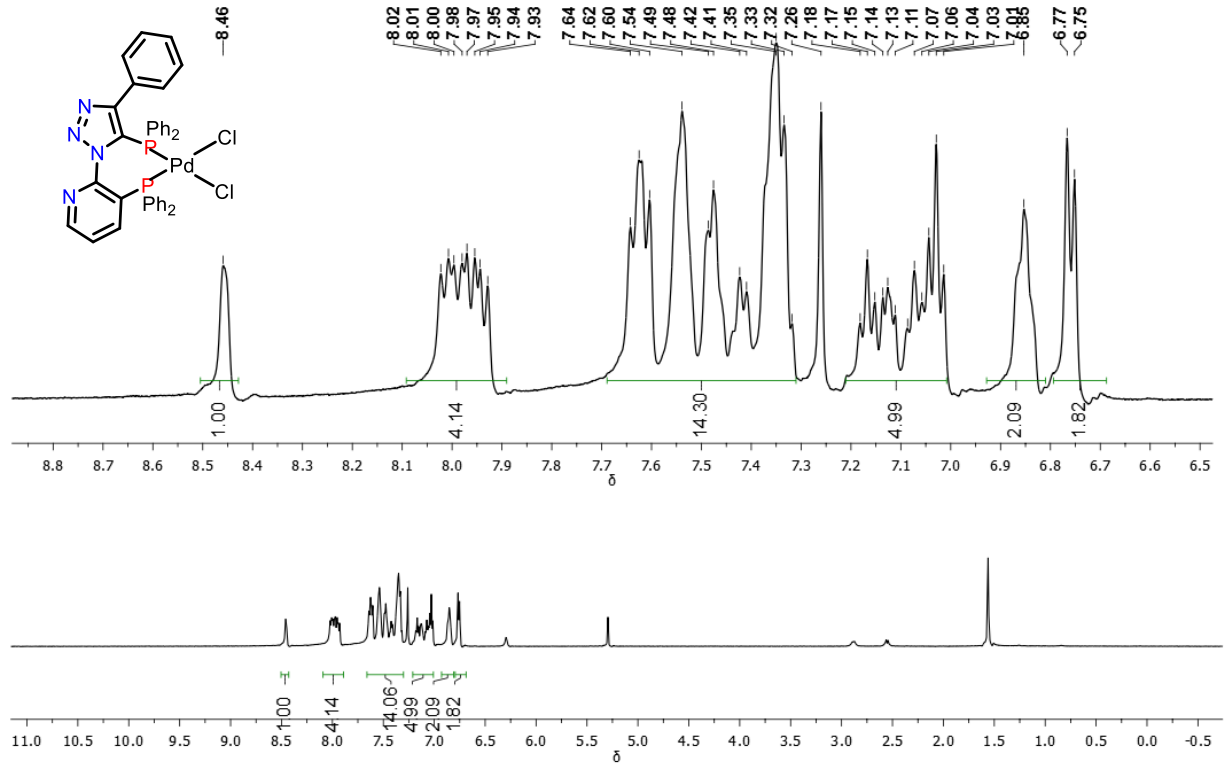


Fig. S47 ^{1}H NMR spectrum of **13** in $CDCl_3$ (500 MHz)

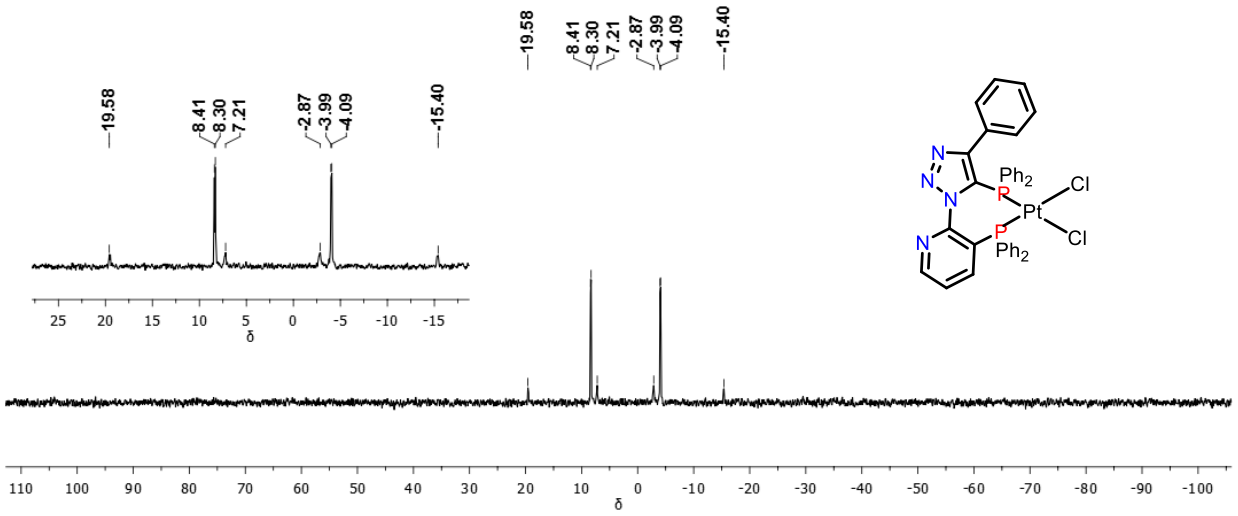


Fig. S48 $^{31}P\{^{1}H\}$ NMR spectrum of **14** in $CDCl_3$ (162 MHz)

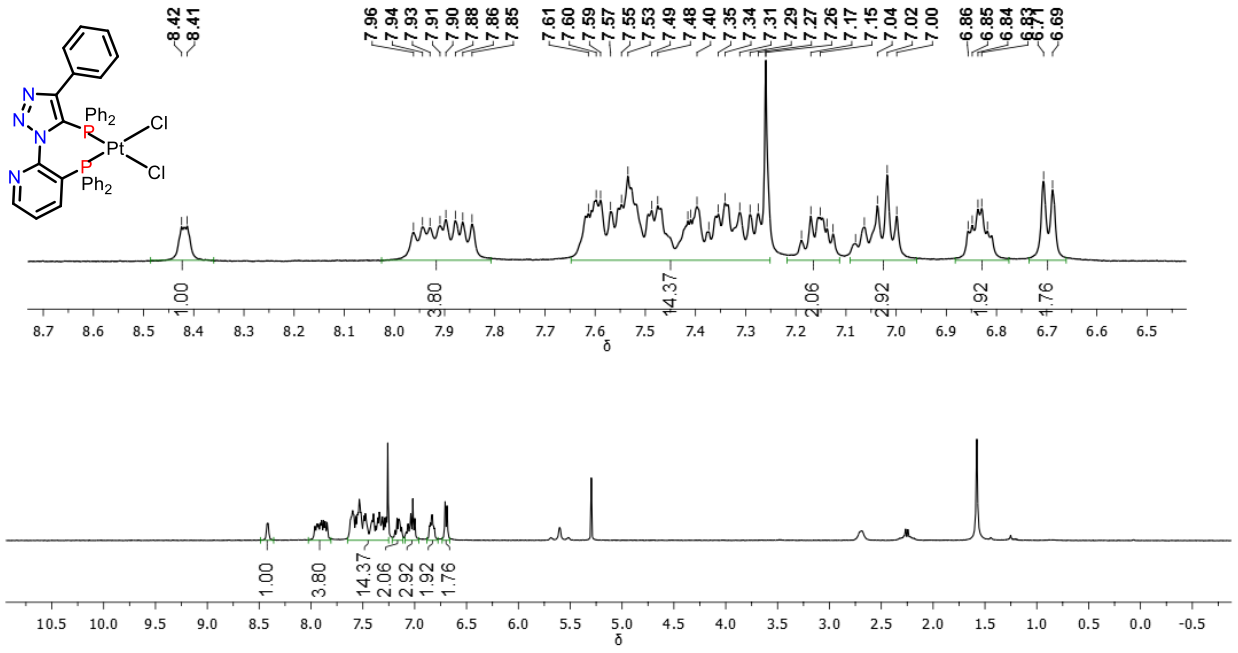
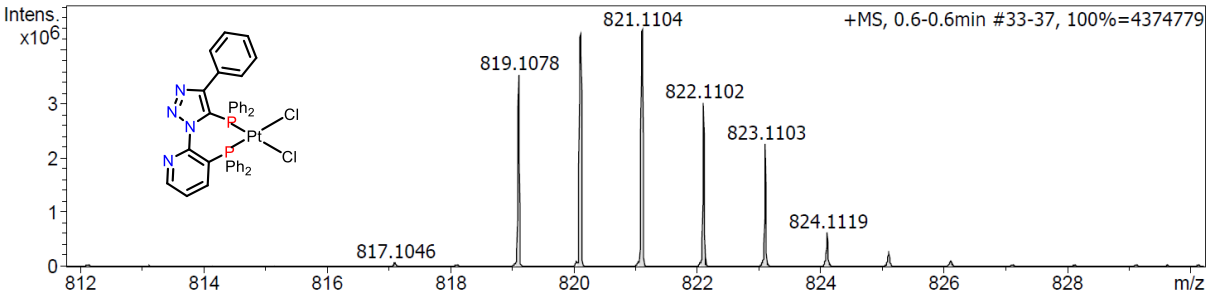


Fig. S49 ^{1}H NMR spectrum of **14** in $CDCl_3$ (400 MHz)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
821.1104	1	C37H28ClN4P2Pt	820.1123	-2.2	75.7	1	100.00	26.5	even	-

Fig. S50 EI mass spectrum of **14**

NMR spectra of a-m

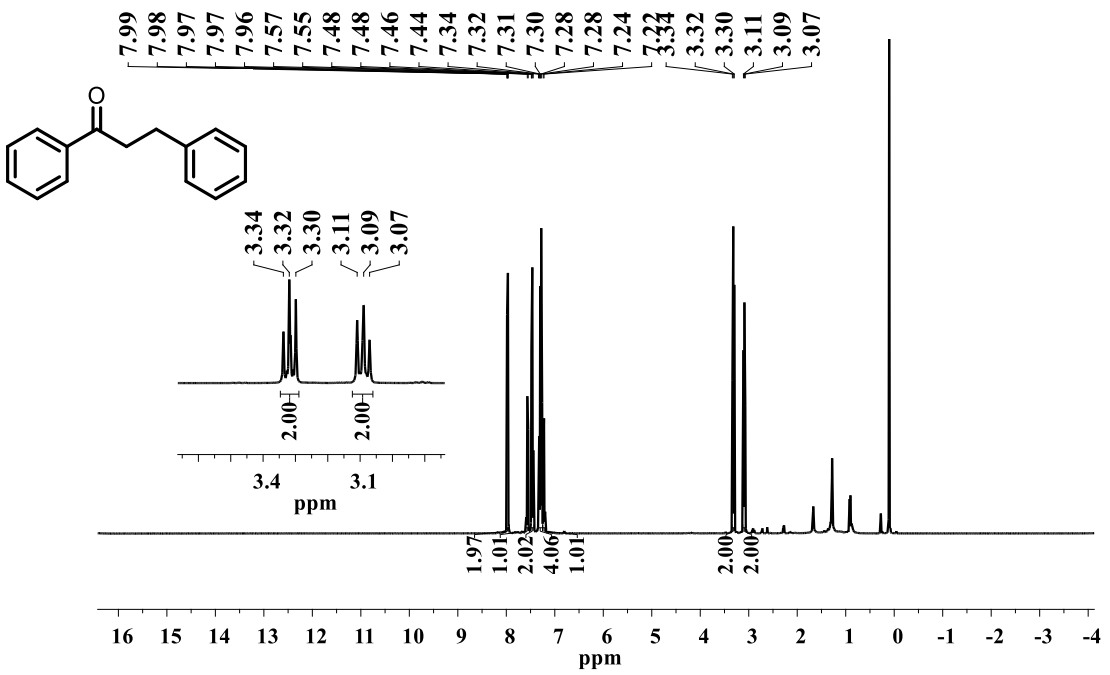


Fig. S51 ^{1}H NMR spectrum of **a** in $CDCl_3$ (400 MHz)

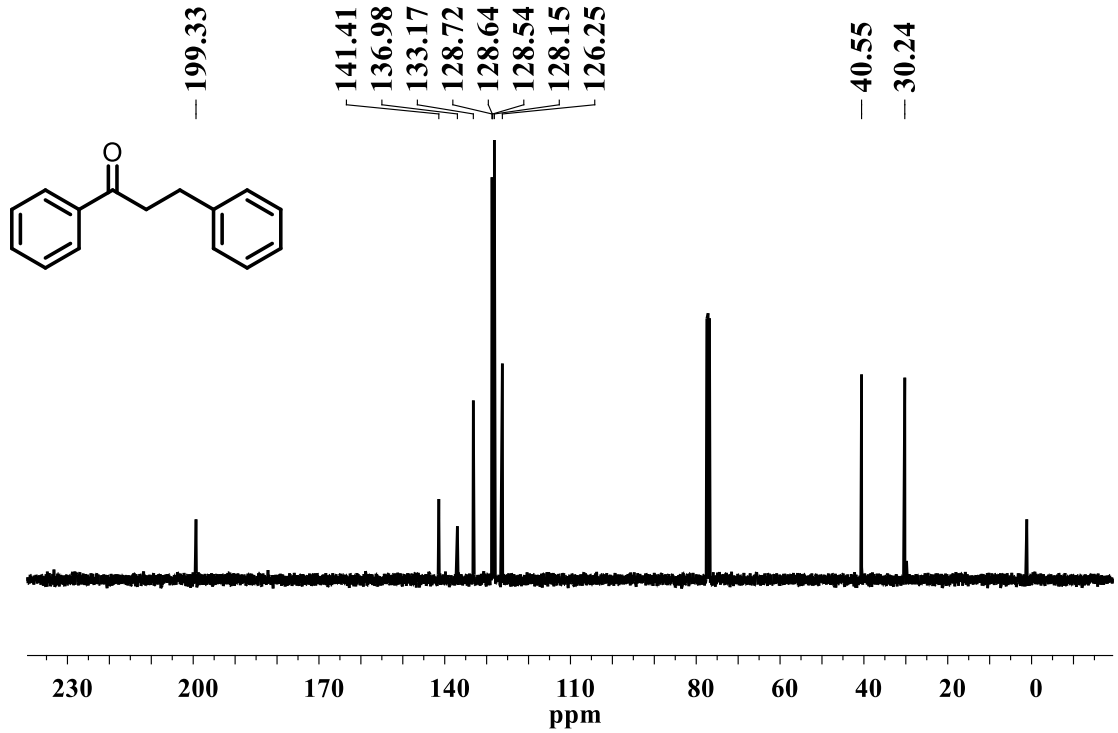


Fig. S52 ^{13}C NMR spectrum of **a** in $CDCl_3$ (101 MHz)

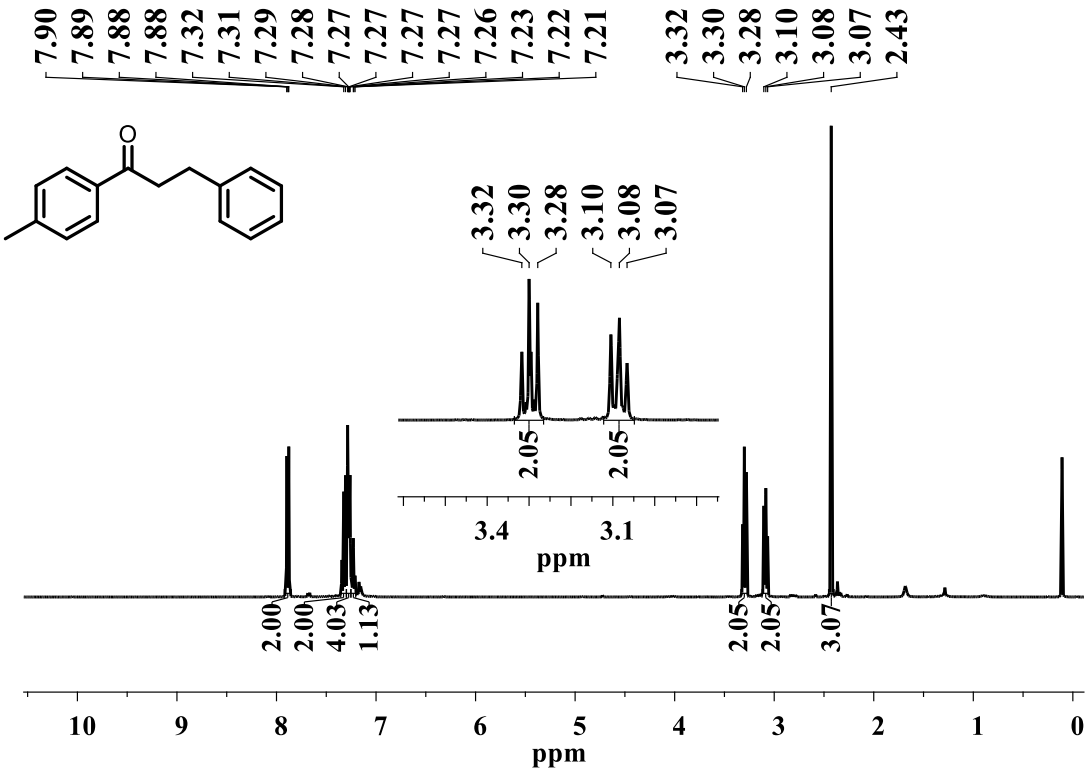


Fig. S53 ^{1}H NMR spectrum of **b** in $CDCl_3$ (400 MHz)

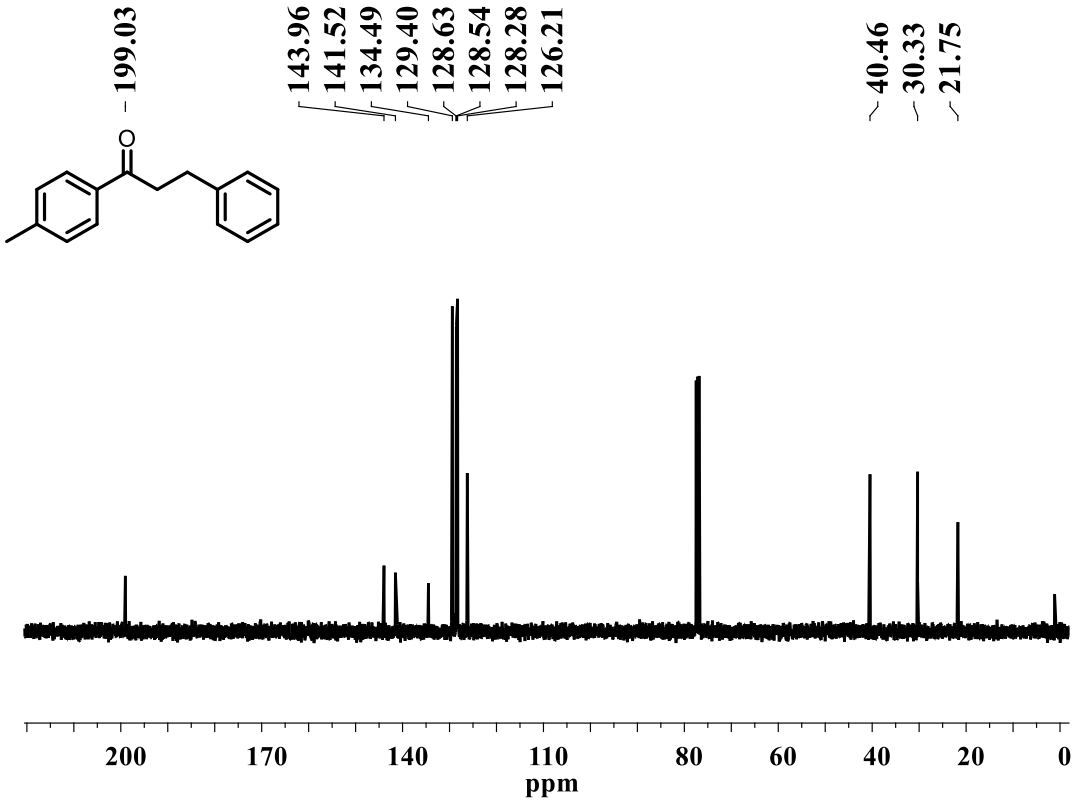


Fig. S54 ^{13}C NMR spectrum of **b** in $CDCl_3$ (101 MHz)

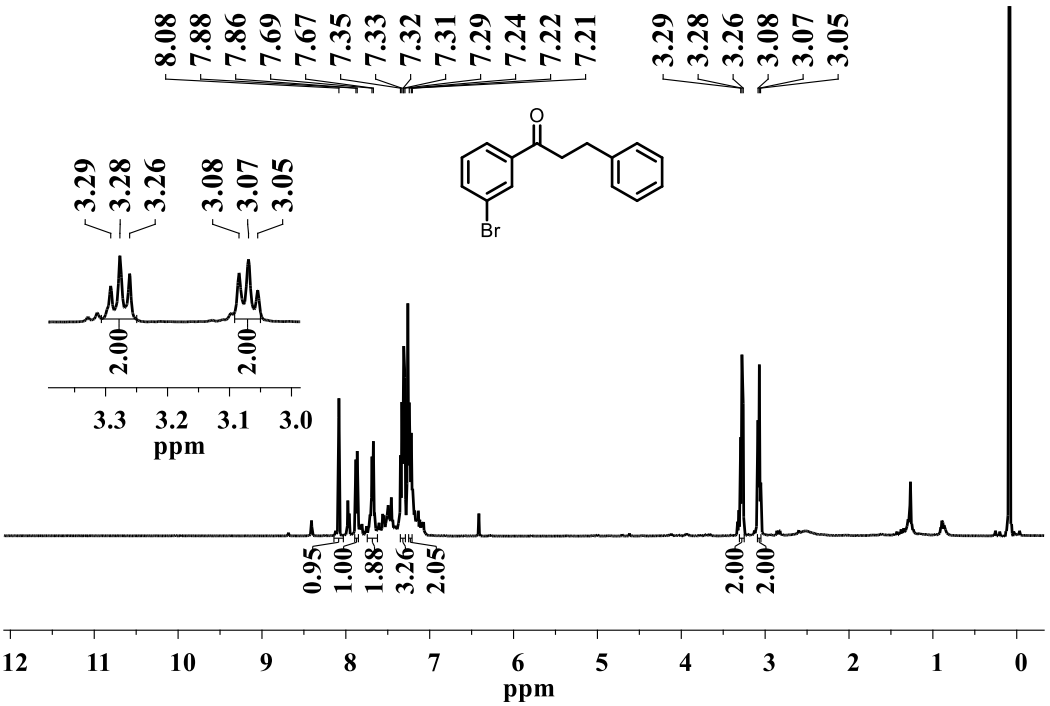


Fig. S55 ^{1}H NMR spectrum of **c** in $CDCl_3$ (500 MHz)

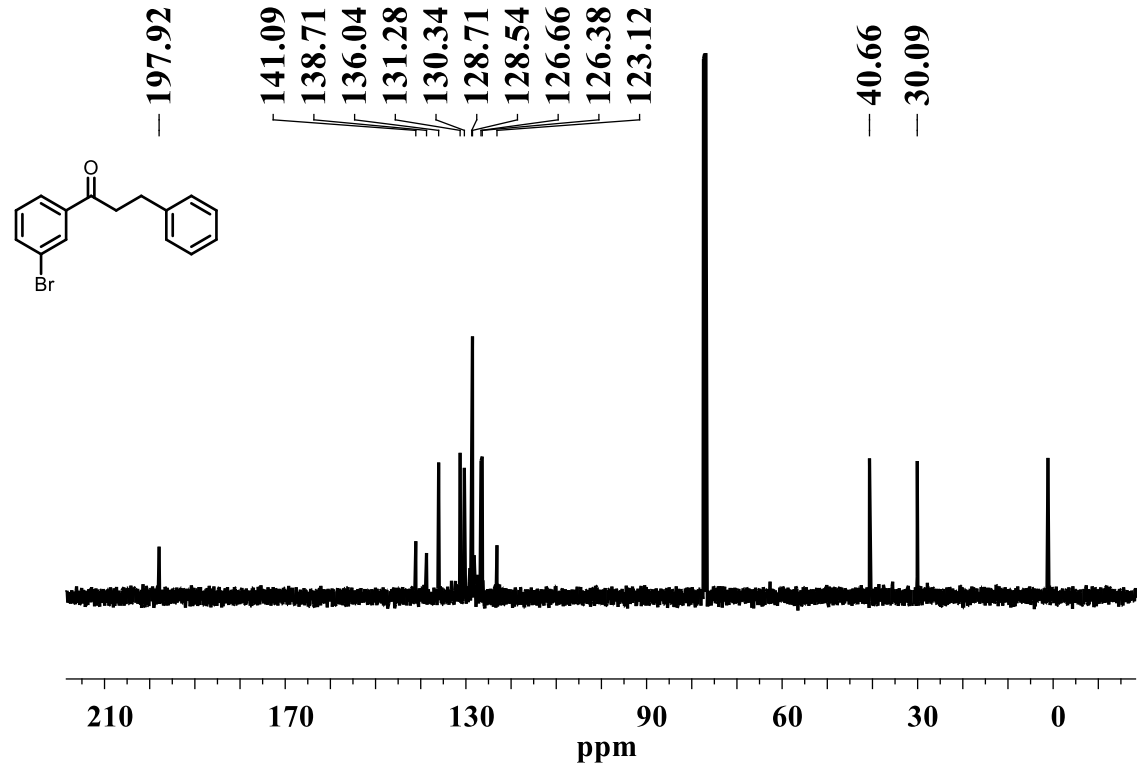


Fig. S56 ^{13}C NMR spectrum of **c** in $CDCl_3$ (126 MHz)

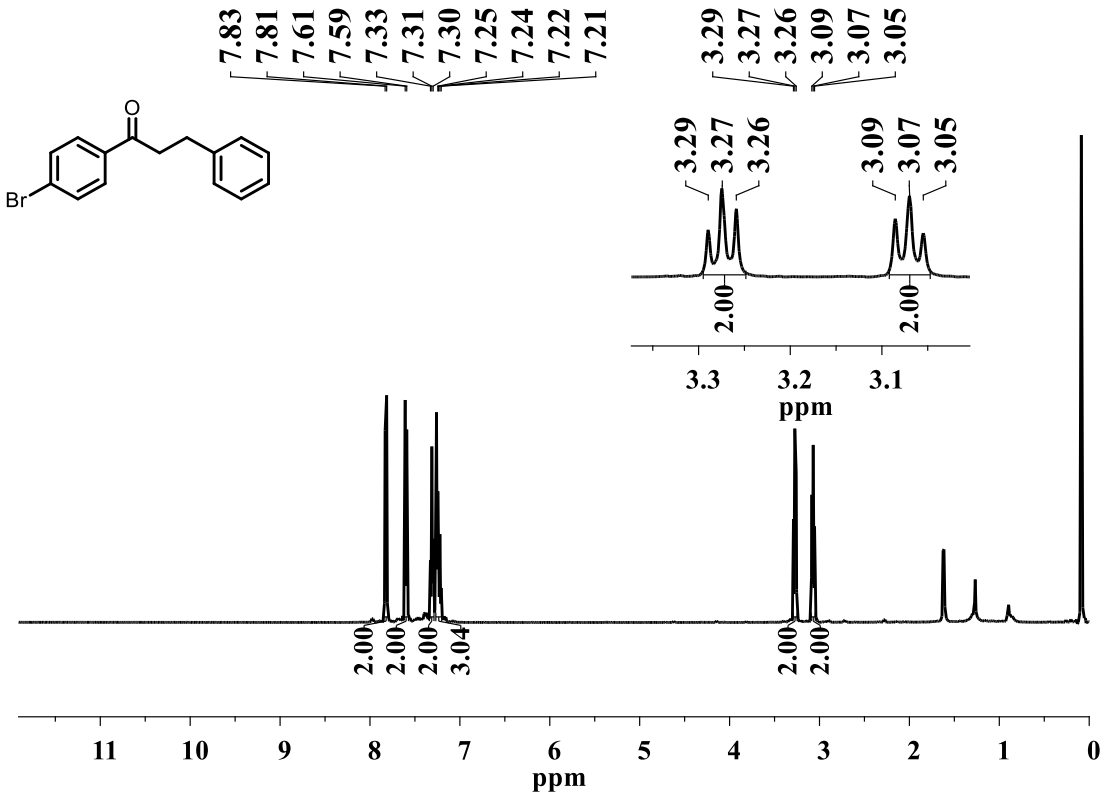


Fig. S57 ^{1}H NMR spectrum of **d** in $CDCl_3$ (500 MHz)

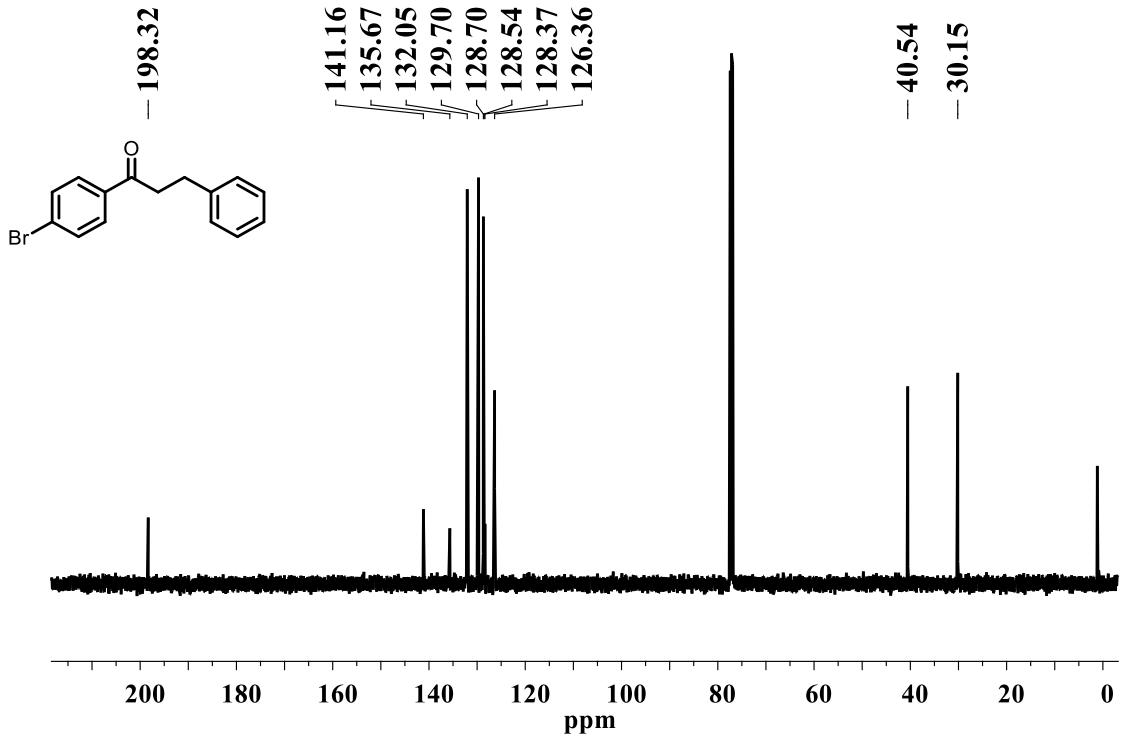


Fig. S58 ^{13}C NMR spectrum of **d** in $CDCl_3$ (126 MHz)

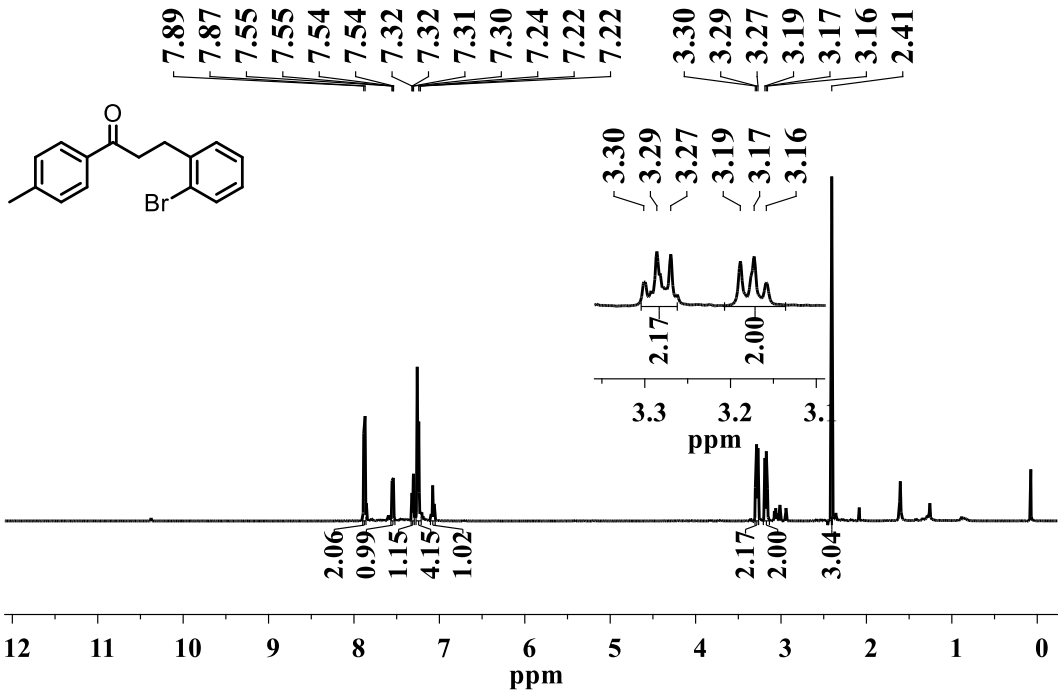


Fig. S59 ^{1}H NMR spectrum of **e** in $CDCl_3$ (500 MHz)

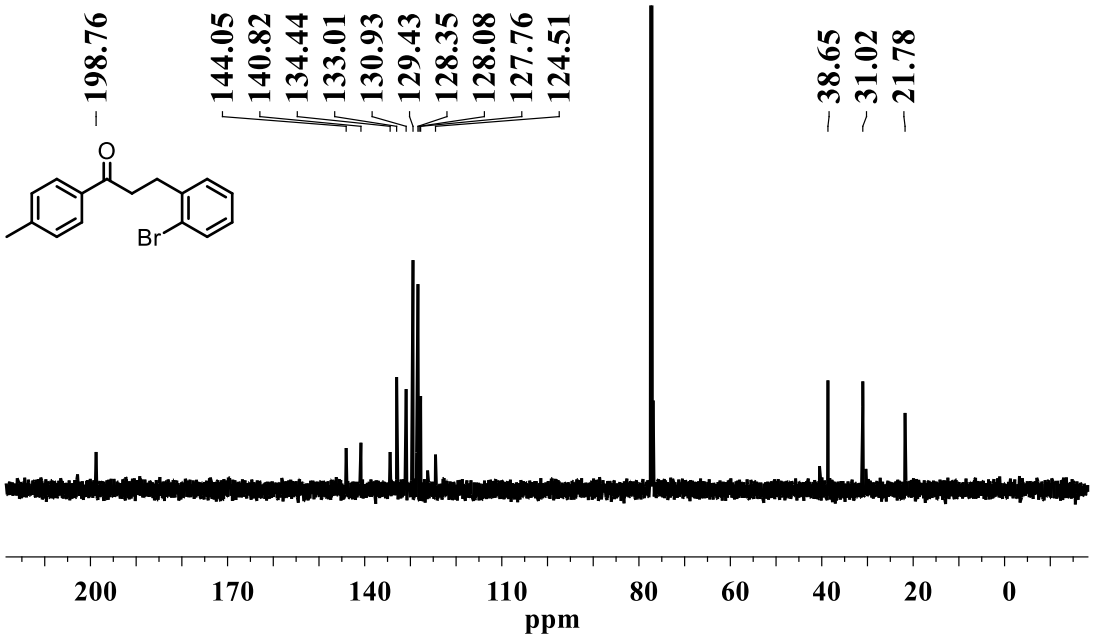


Fig. S60 ^{13}C NMR spectrum of **e** in $CDCl_3$ (126 MHz)

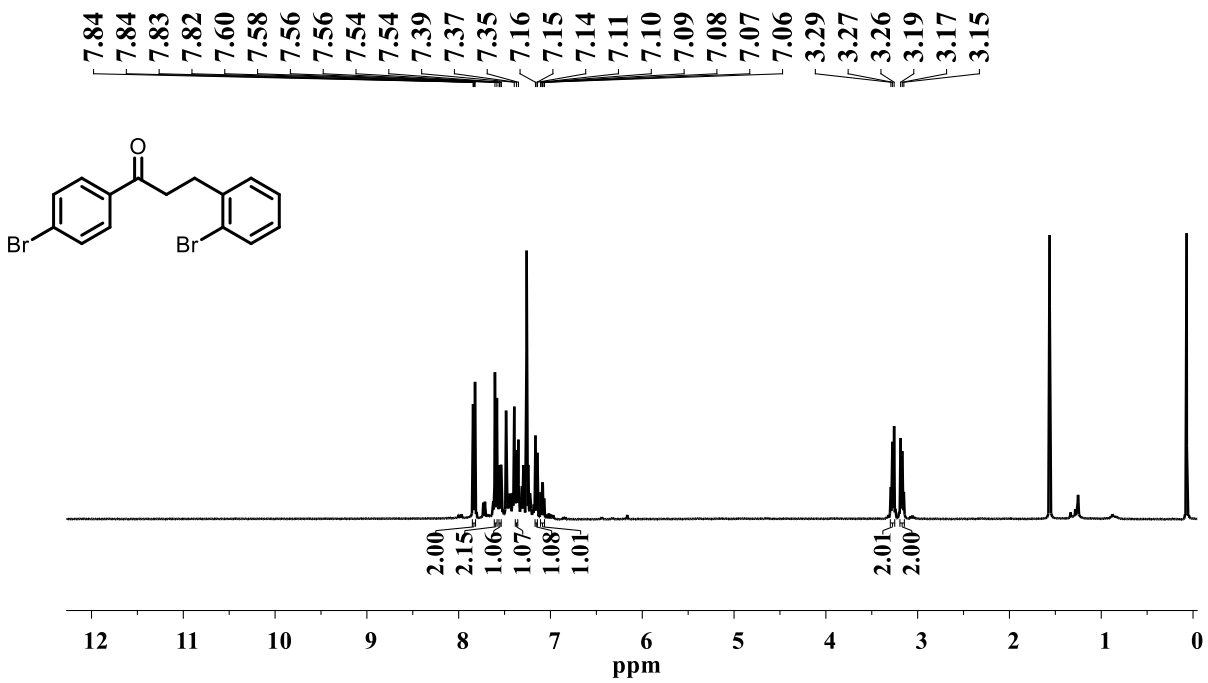


Fig. S61 ^{1}H NMR spectrum of **f** in $CDCl_3$ (400 MHz)

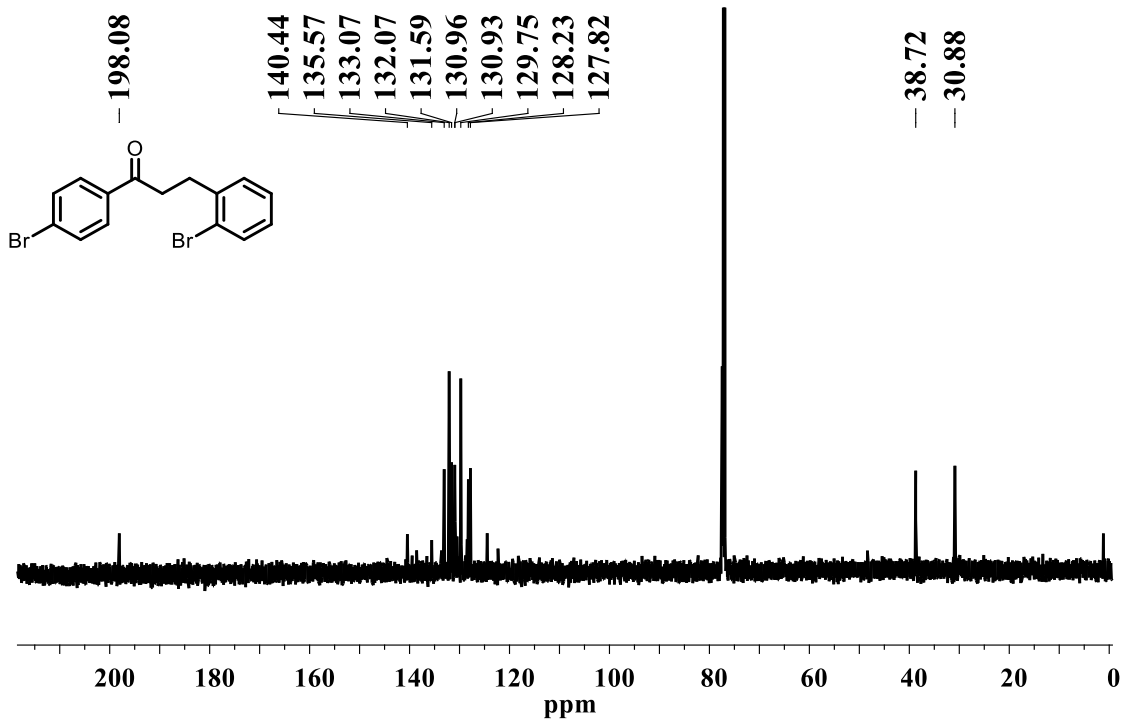


Fig. S62 ^{13}C NMR spectrum of **f** in $CDCl_3$ (126 MHz)

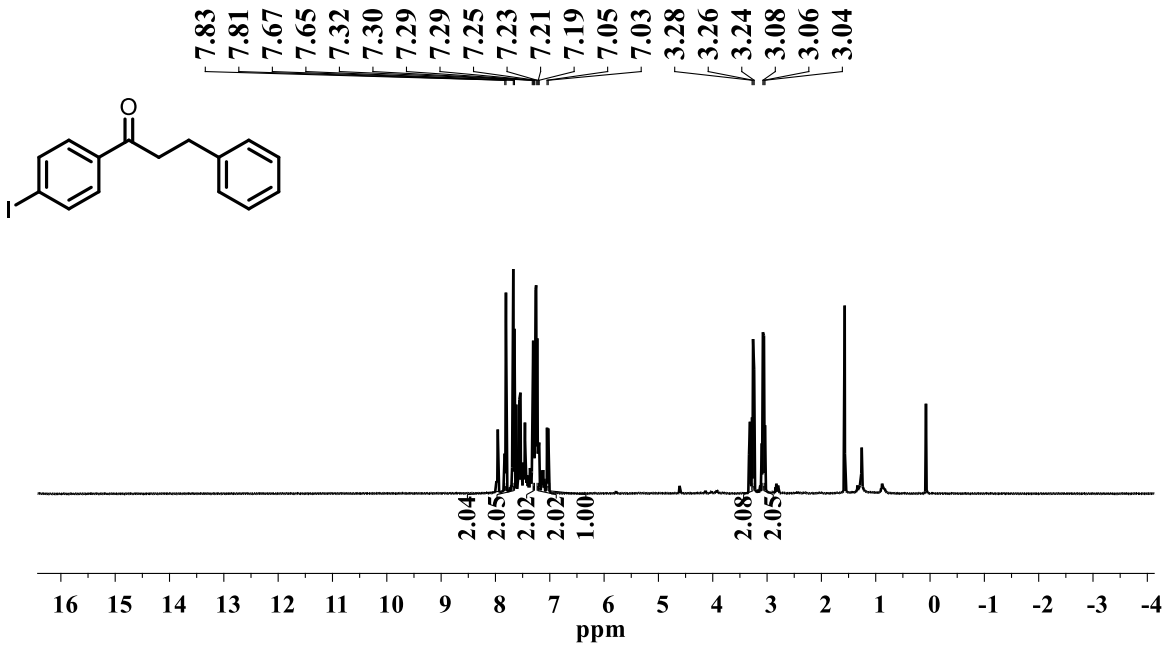


Fig. S63 ^{1}H NMR spectrum of **g** in $CDCl_3$ (400 MHz)

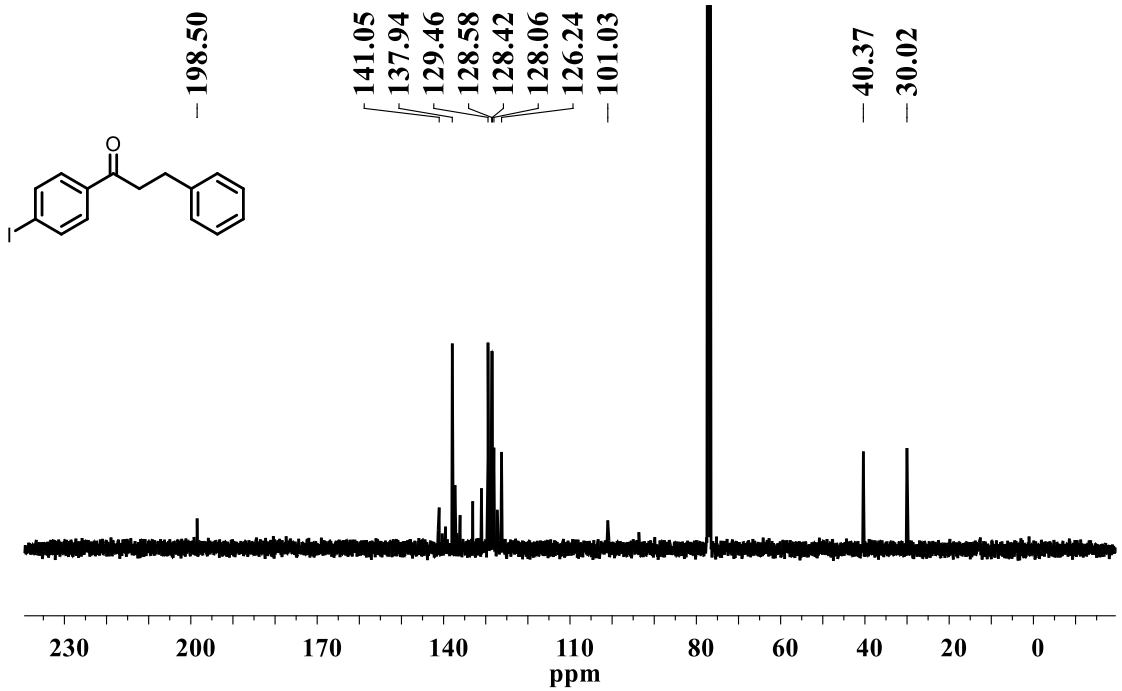


Fig. S64 ^{13}C NMR spectrum of **g** in $CDCl_3$ (101 MHz)

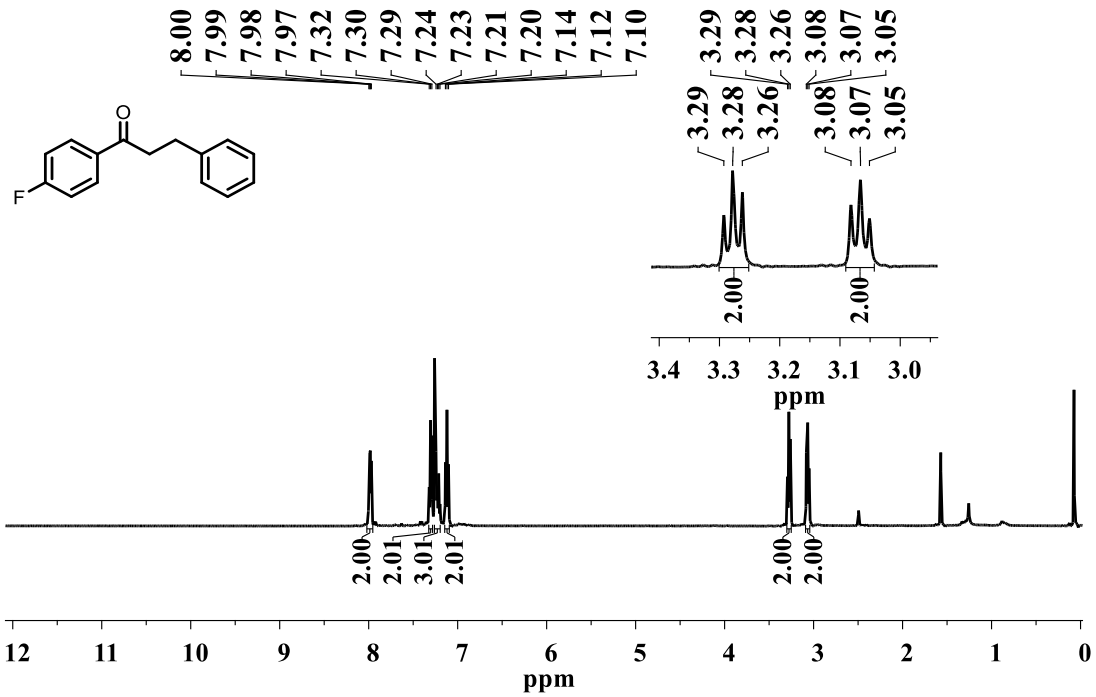


Fig. S65 ^{1}H NMR spectrum of **h** in $CDCl_3$ (500 MHz)

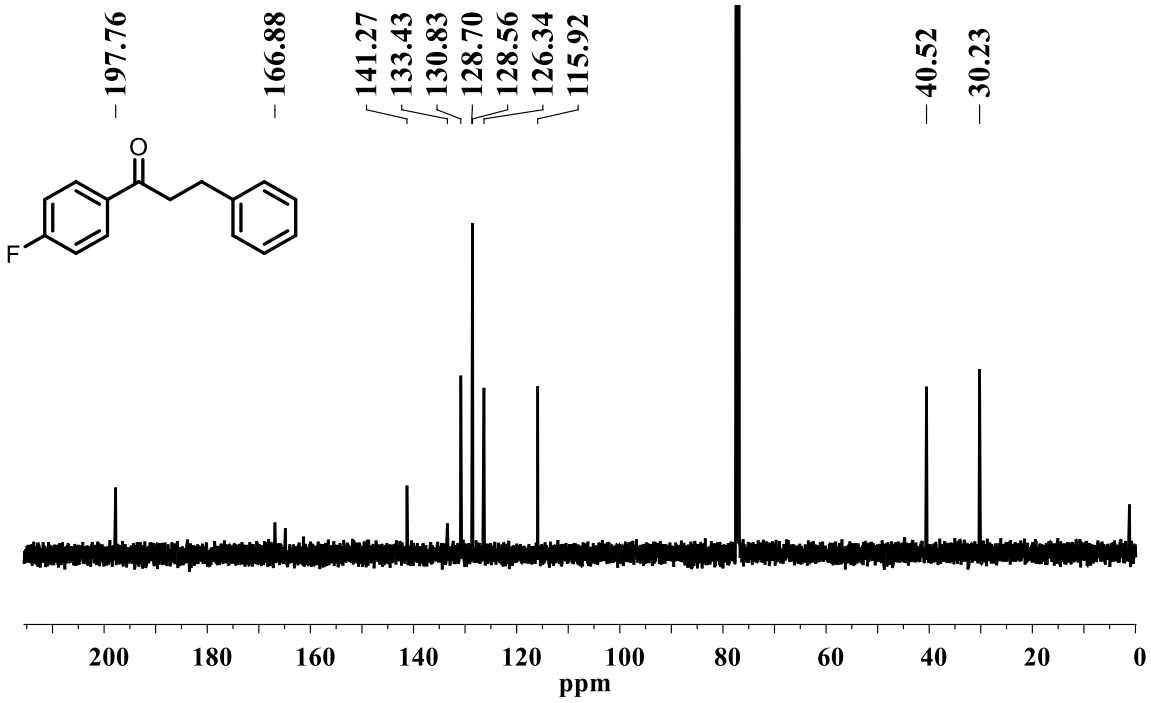


Fig. S66 ^{13}C NMR spectrum of **h** in $CDCl_3$ (126 MHz)

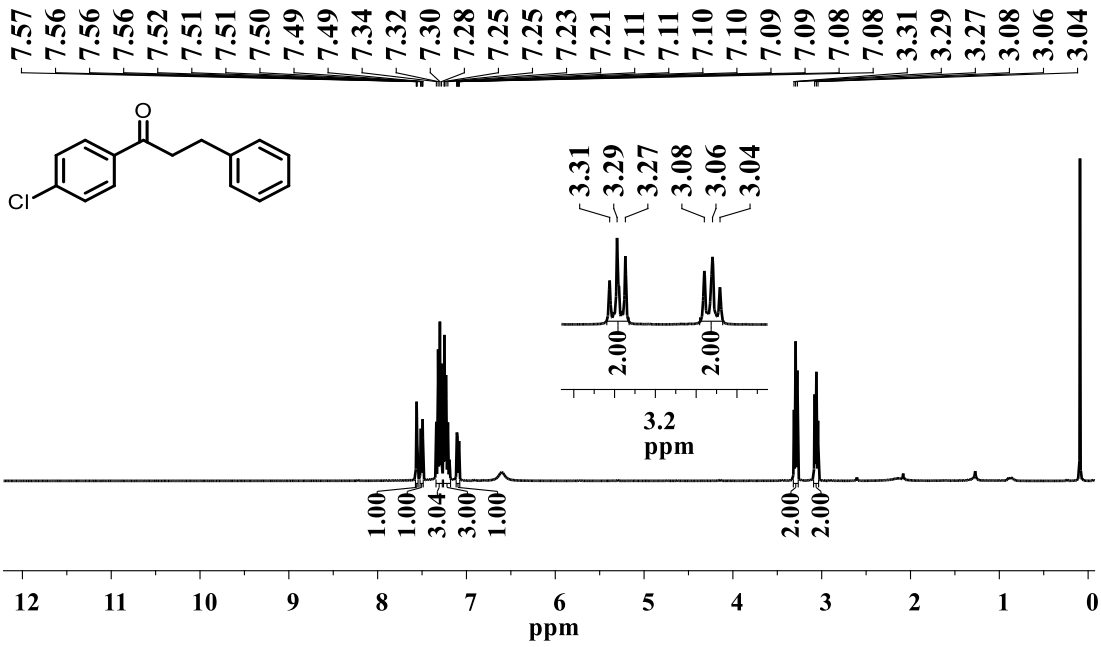


Fig. S67 ^{1}H NMR spectrum of **i** in $CDCl_3$ (400 MHz)

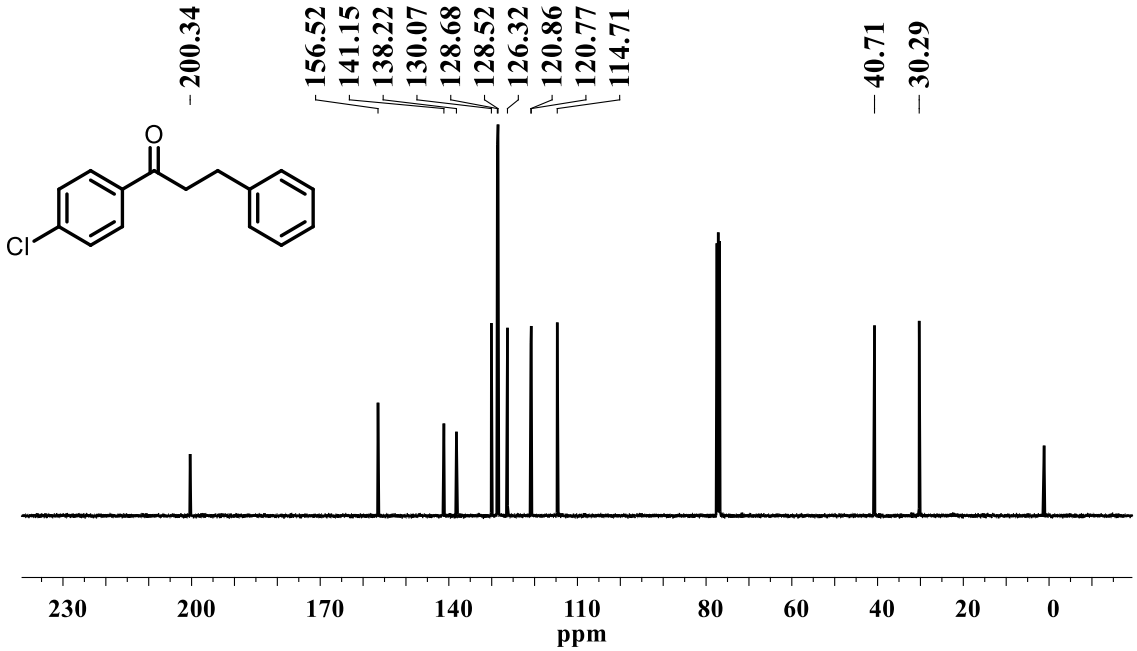


Fig. S68 ^{13}C NMR spectrum of **i** in $CDCl_3$ (101 MHz)

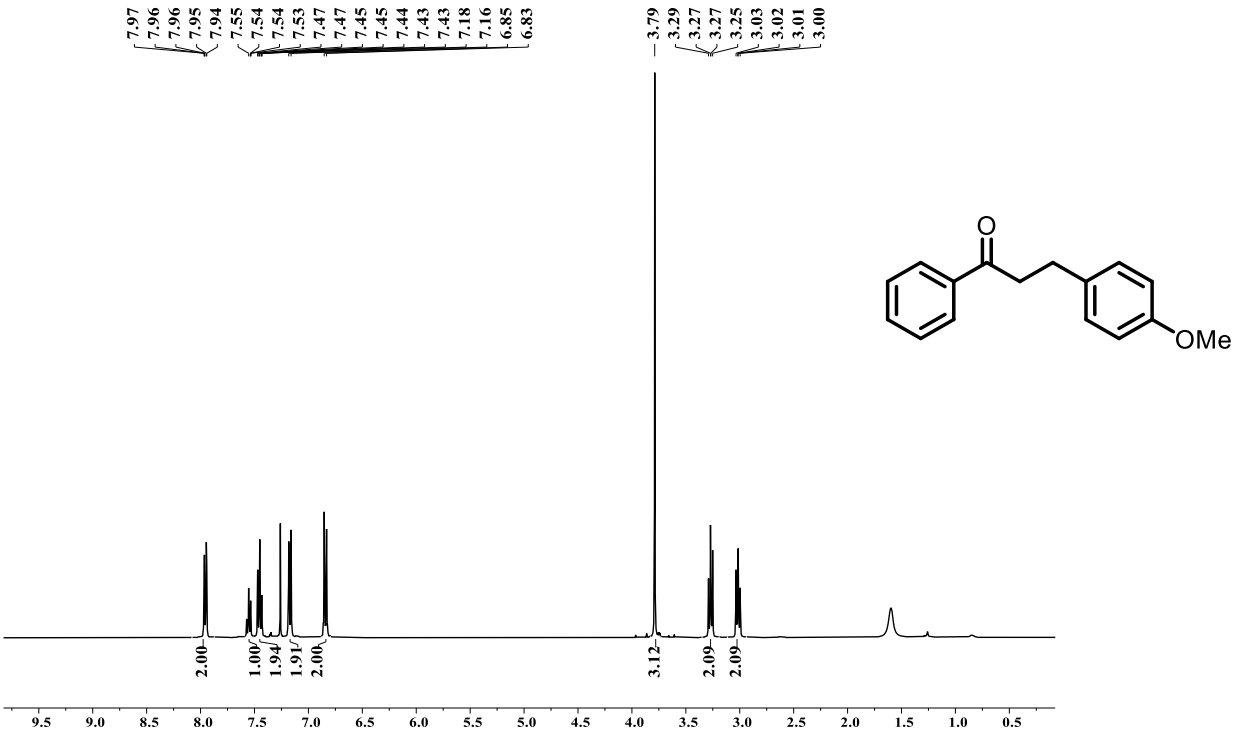


Fig. S69 ^{1}H NMR spectrum of **j** in $CDCl_3$ (400 MHz)

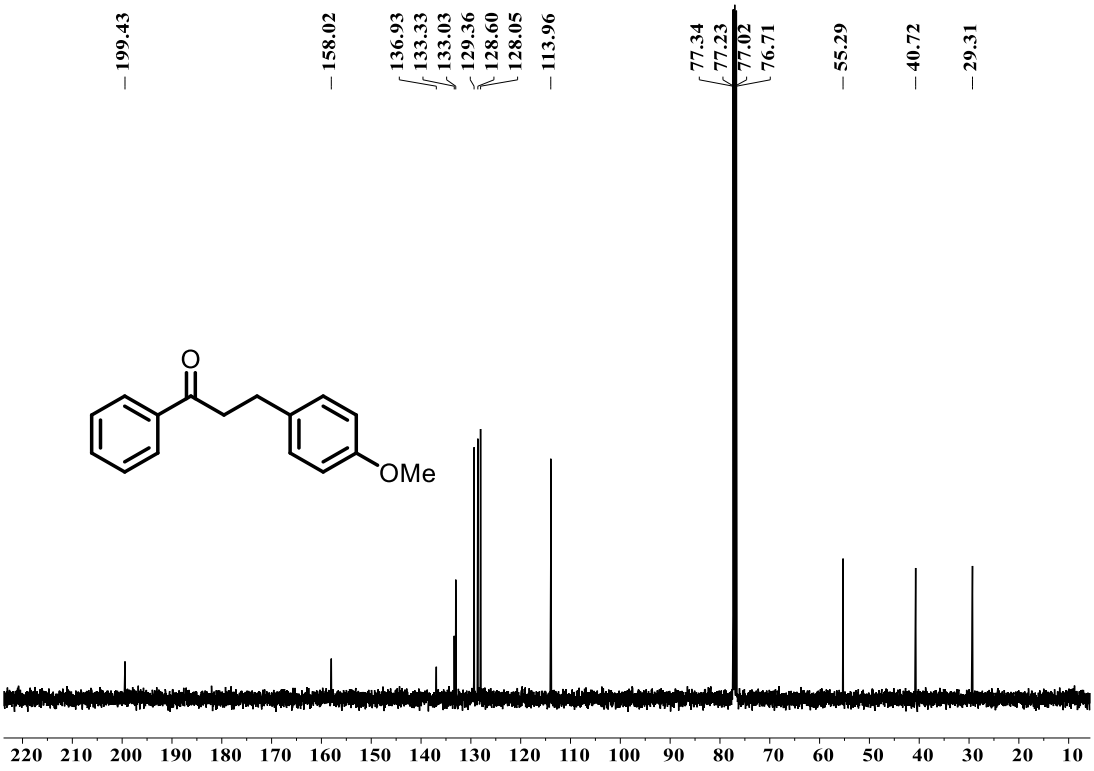


Fig. S70 ^{13}C NMR spectrum of **j** in $CDCl_3$ ((101 MHz)

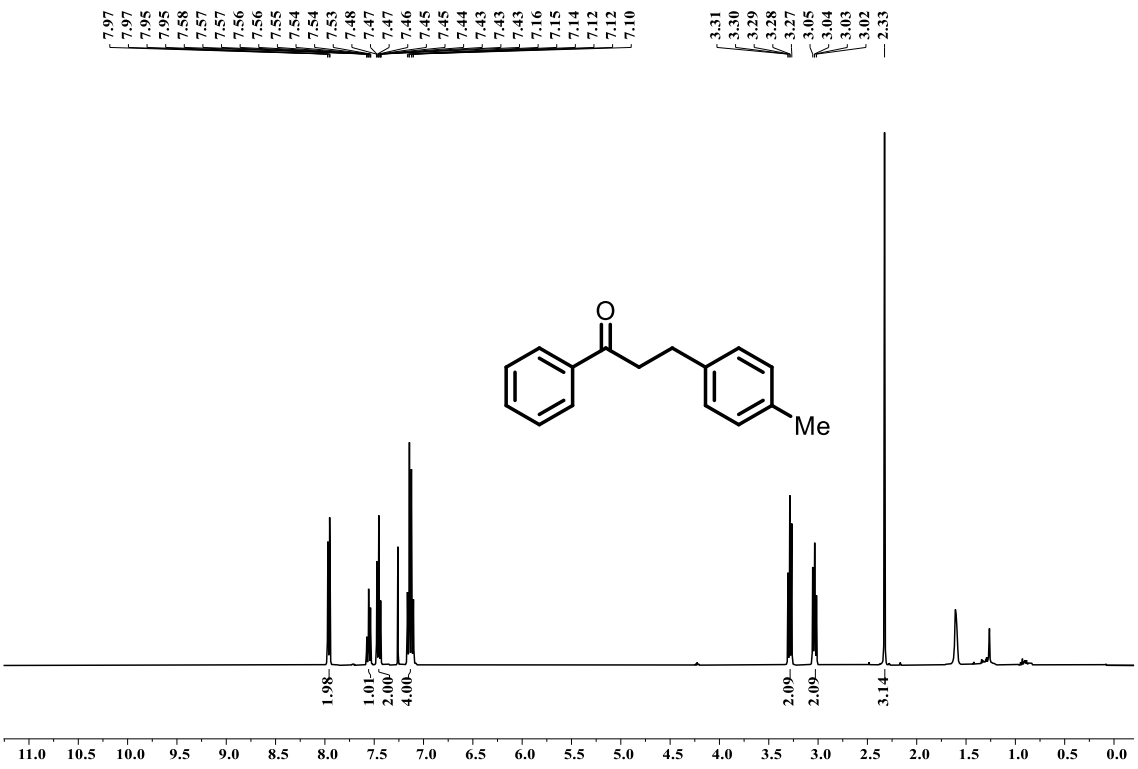


Fig. S71 ^{1}H NMR spectrum of **k** in $CDCl_3$ (400 MHz)

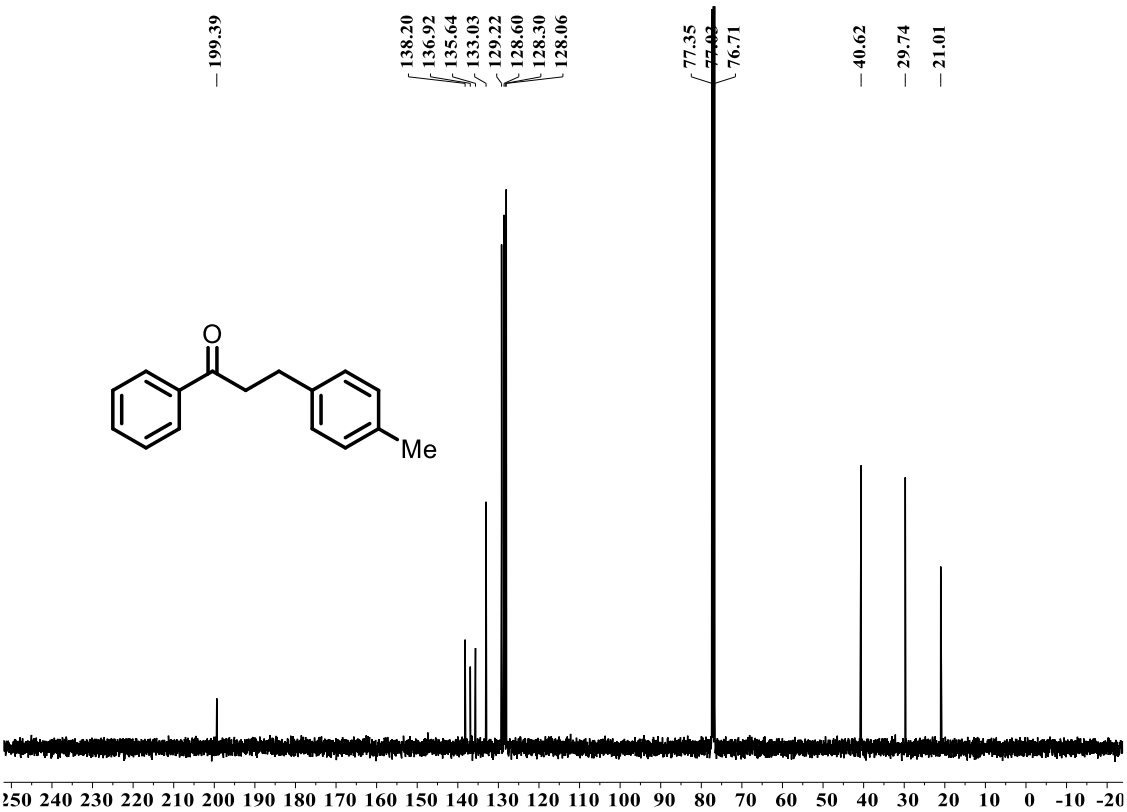


Fig. S72 ^{13}C NMR spectrum of **k** in $CDCl_3$ (101 MHz)

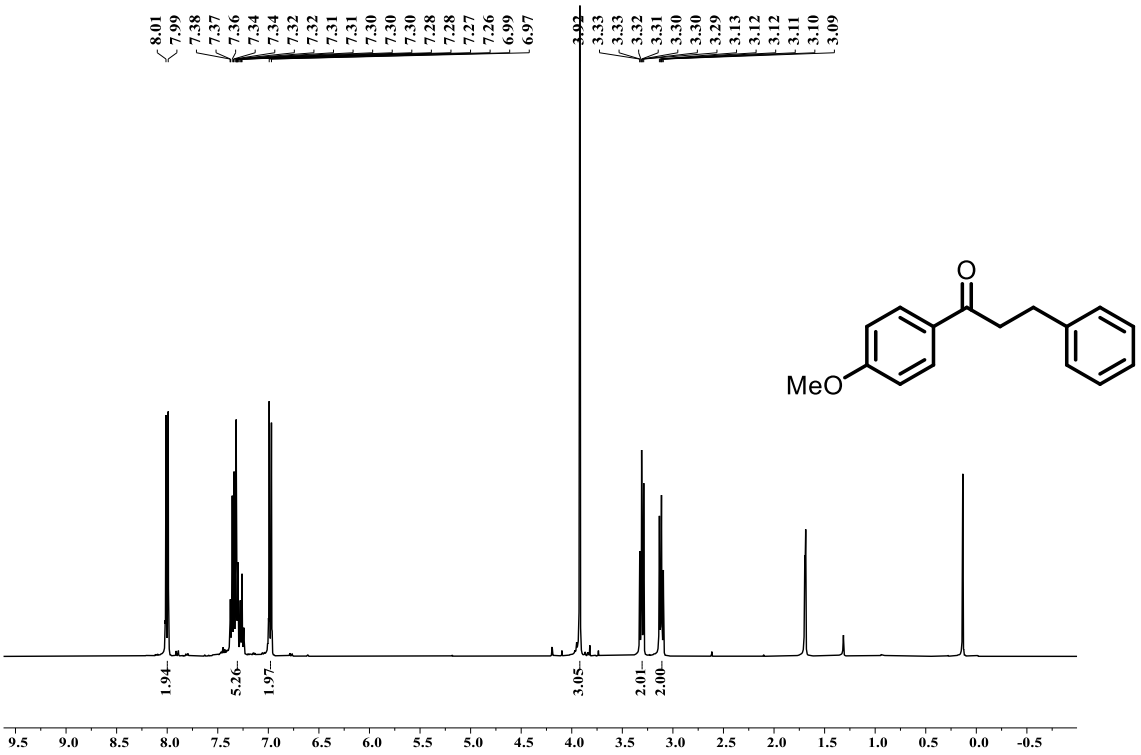


Fig. S73 ^{1}H NMR spectrum of **l** in $CDCl_3$ (400 MHz)

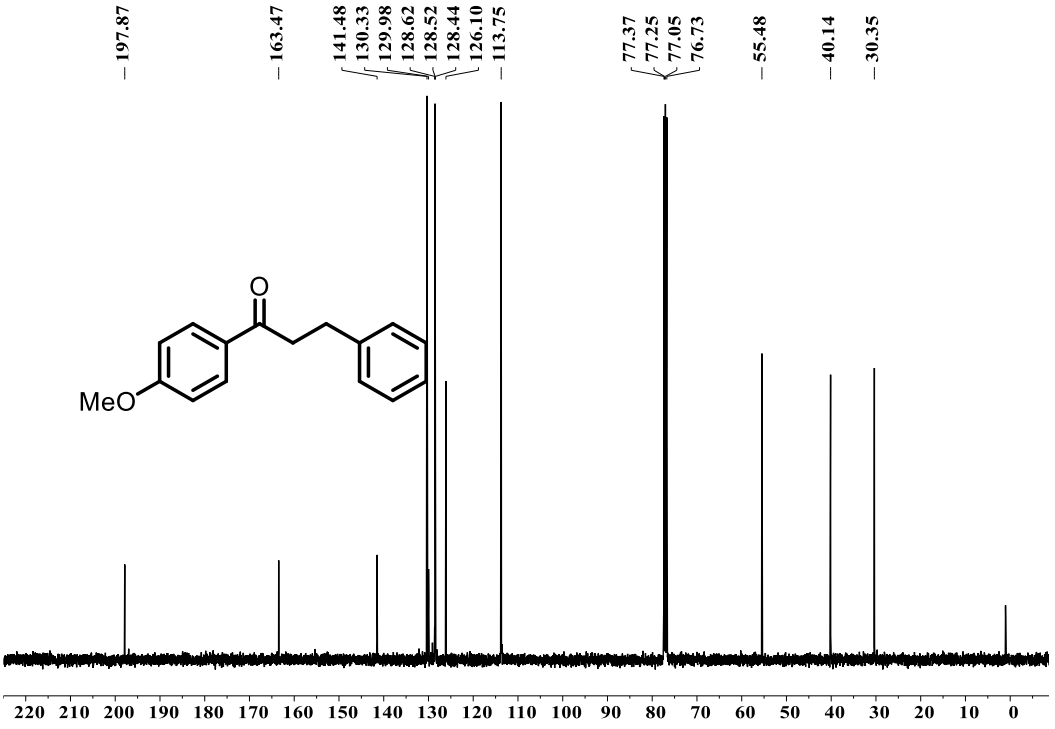


Fig. S74 ^{13}C NMR spectrum of **l** in $CDCl_3$ (101 MHz)

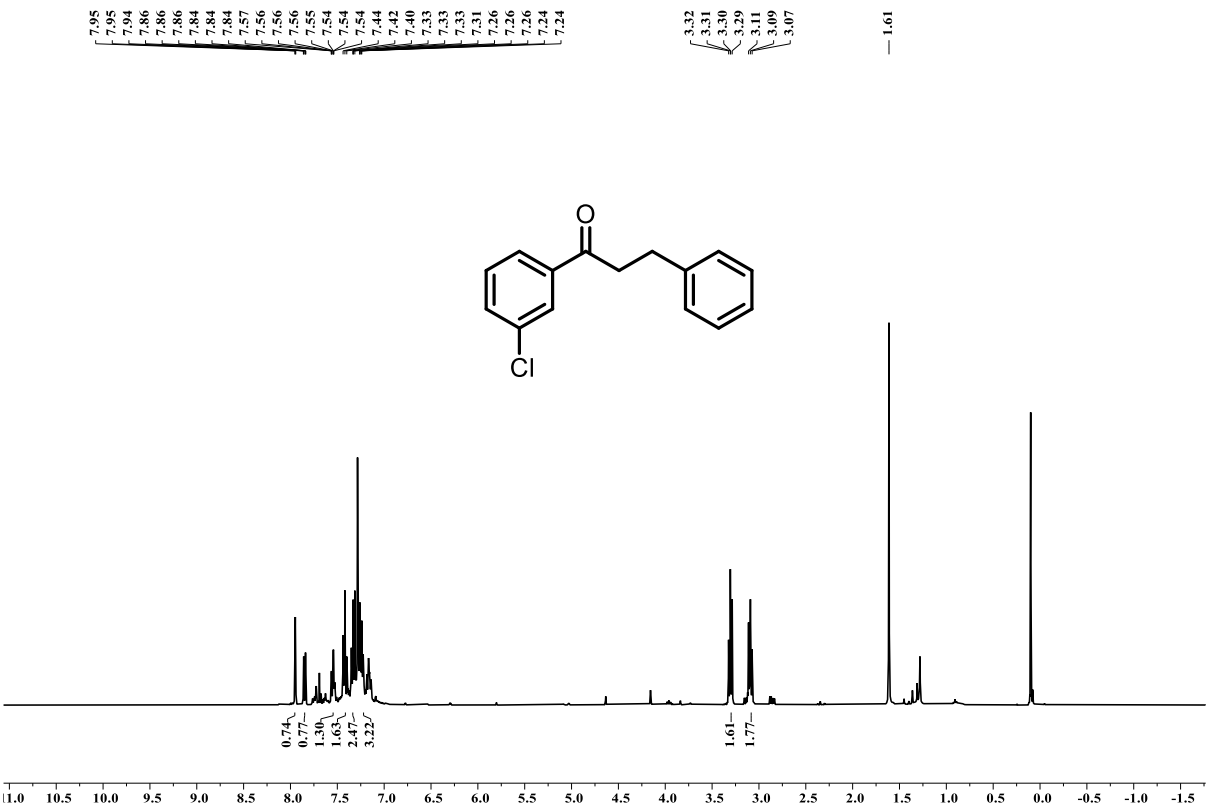


Fig. S75 ^{1}H NMR spectrum of **m** in $CDCl_3$ (400 MHz)

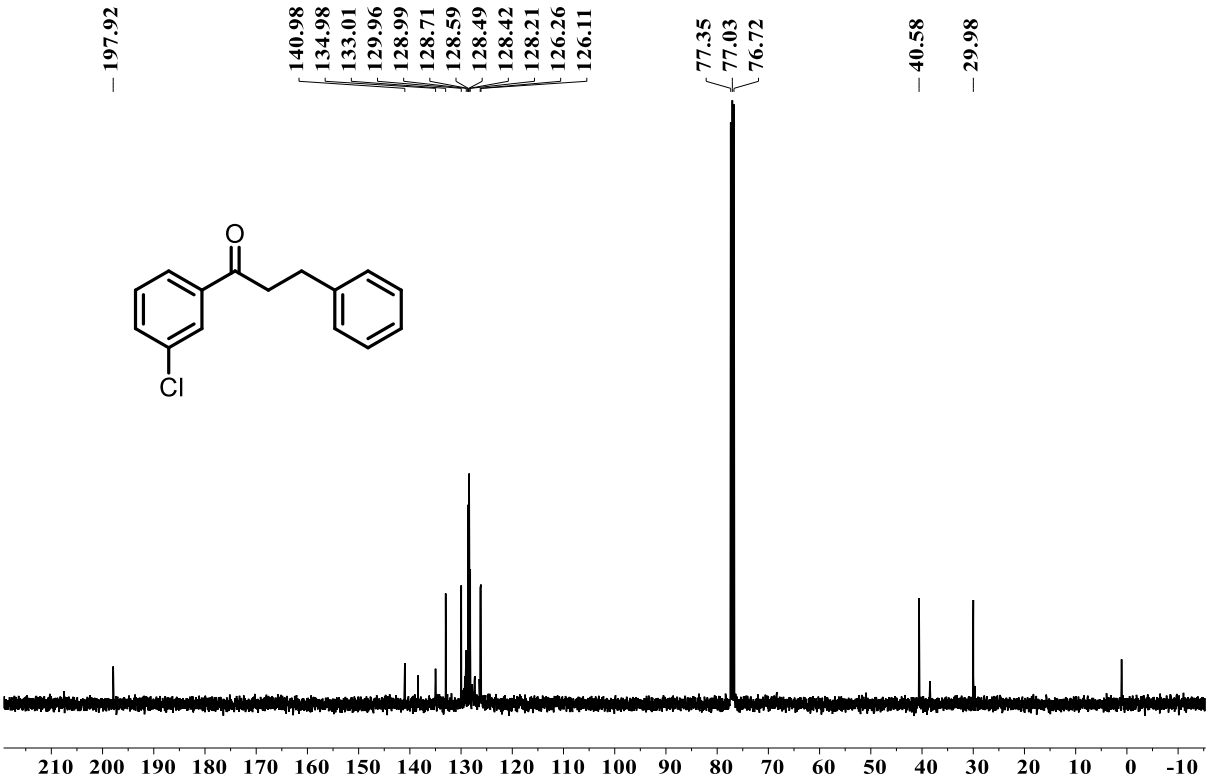


Fig. S76 ^{13}C NMR spectrum of **m** in $CDCl_3$ (101 MHz)

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