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SUPPORTING INFORMATION

New *sp*^{3} diphosphine-based rhodium catalysts for the asymmetric conjugate addition of aryl boronic acids to 3-azaarylpropenones

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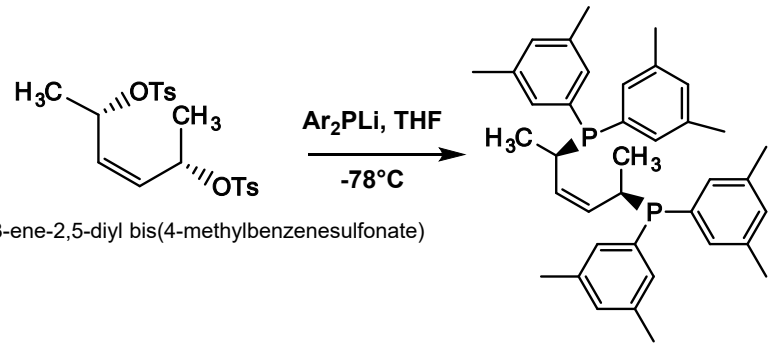
1. Synthesis of Ligand L7-L9

1.1 Preparation of (*R,R*)-Xylyl-ZEDPHOS, L7

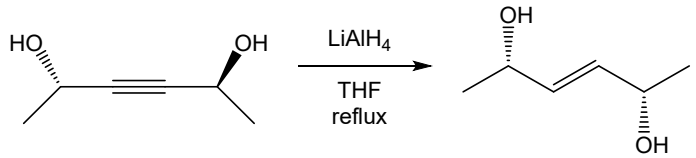


(2*S*,5*S*,*Z*)-hex-3-ene-2,5-diyl bis(4-methylbenzenesulfonate)

(*R,R*)-Xylyl-ZEDPHOS
(*R,R*)-L7

A solution of Ar_2PLi (7.6 ml; 0.26 M in THF; MW=214.13g/mol; 1.98 mmol) was slowly dropped into a solution of (2*S*,5*S*,*Z*)-hex-3-ene-2,5-diyl bis(4-methylbenzenesulfonate)[1] (0.40 g; 0.94 mmol; MW=424.53 g/mol) in 10 ml of dry THF at -78 °C, under argon. After the addition the temperature was allowed to rise to room temperature and stirred for an additional 30 min. The excess of Ar_2PLi was neutralized by $Na_2SO_4 \cdot 10H_2O$ and the mixture was filtered under argon. Evaporation of the solvent followed by trituration with dry methanol afforded the chiral diphosphine **L7**-(*R*,*R*)-Xylyl-ZEDPHOS enantiomerically and chemically pure. %Yield=95%; ^{31}P NMR (C_6D_6, 300 MHz) δ: -2.9 (s) ppm; ^1H NMR (C_3D_6O, 300 MHz) δ: 7.76-7.81 (m, 1H); 7.42–7.45 (m, 7H); 6.69 (d, *J* = 6.7 Hz, 4H); 5.48 (2H, m); 3.41 (2H, m); 2.28–2.32 (m, 24H); 0.46–0.53 (m, 6H) ppm; ^{13}C NMR (C_6D_6, 101 MHz) δ 138.11, 137.96, 137.90, 137.80, 137.74, 137.63, 137.61, 137.57, 137.26, 137.13, 137.09, 137.04, 132.91, 132.14, 132.05, 131.82, 131.73, 131.62, 130.57, 130.38, 129.18, 129.01, 128.93, 128.01, 32.24, 32.20, 32.15, 32.11, 20.98, 20.97, 20.91, 20.86, 20.82, 17.87, 17.77, 17.70, 17.67, 13.55. MS (ESI): *m/z* calcd for $[C_{38}H_{46}P_2]$: 564.31; found: *m/z* 565.47 $[M+H]^+$.

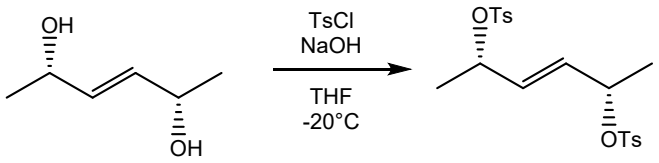
1.2 Synthesis of *trans*-(2S,5S,E)-hex-3-ene-2,5-diol



(2*S*,5*S*)-hex-3-yne-2,5-diol (2*S*,5*S*,*E*)-hex-3-ene-2,5-diol

To a solution of (2*S*,5*S*)-3-hex3-yne-2,5-diol (20 mmol) in THF dry (20 mL) was added dropwise to a suspension of $LiAlH_4$ in THF anhydrous (200 mL) at 0 ºC. After addition, the mixture was refluxed overnight. Then, EtOAc and $Na_2SO_4 \cdot 10H_2O$ were added cautiously. The reaction mixture was filtered nd the organic phase was dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by flash column chromatography affording (2*S*,5*S*,E)-hex-3-ene-2,5-diol as a Colorless oil. %Yield: 70%; ^1H NMR ($CDCl_3$, 300 MHz): δ 5.73-5.75 (m, 2H); 4.31-3.35 (m, 2H); 1.73 (s, 2H); 1.28-1.30 (d, 6H) ppm; $[\alpha]_D^{20}$= + 6.21 (c = 1.1 in $CHCl_3$); GC equipped with a capillary column with a chiral stationary phase MEGA DAcTButSilBETA (25 m, internal diameter 0.35 mm); analytical method: T_1= 120°C x 20', $Rt_{(E-(S,S)-7)}$ = 8.7 min.[2]

1.3 Synthesis of *trans*-(2S,5S,E)-hex-3-ene-2,5-diyl bis(4-methylbenzenesulfonate)

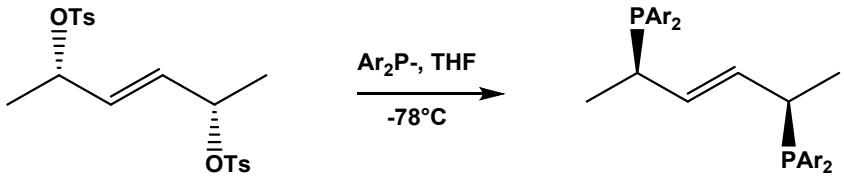


(2*S*,5*S*,*E*)-hex-3-ene-2,5-diol

(2*S*,5*S*,*E*)-hex-3-ene-2,5-diyl bis(4-methylbenzenesulfonate)

A 10% solution of 7.59 g (39.71 mmol) tosyl chloride in either THF or diethyl ether was added to a solution of 1.85 g (15.88 mmol) **(**2S,5S,E)-hex-3-ene-2,5-diol in THF, and the reaction mixture cooled to -20 °C. Thereafter a large excess of finely powdered sodium hydroxide was added in small portions to the vigorously stirred solution. The temperature was kept below -20 °C during the sodium hydroxide addition. To complete the reaction, the solution was stirred for another 3 h at -20 °C and then poured into ice water. The aqueous phase was extracted several times with dichloromethane. After the collected organic extracts were dried over anhydrous Na_2SO_4, the solvent was removed in vacuo and the crude product crystallized from diethyl ether. The colourless crystals had to be stored at -18 °C to prevent thermal decomposition. % Yield = 52%. ^{1}H NMR ($CDCl_3$; 300 MHz): δ 7.74-7.77(d, 4H); 7.33-7.36(d, 4H); 5.50-5.60(m, 2H); 4.92-4.49 (m, 2H); 2.46(s, 6H); 1.23 (d, 6H) ppm; $[\alpha]^{20}_D$= -40 (c = 0.63 in CH_2Cl_2); Elemental analysis for $C_{20}H_{24}O_6S_2$: calculated C, 56.59; H, 5,70; found C, 55.52; H, 5.61;

1.4 Synthesis of L8-(*R*,*R*)-EPHOS and L9-(*R*,*R*)-Xylyl-EPHOS



(2*S*,5*S*,*E*)-hex-3-ene-2,5-diyl bis(4-methylbenzenesulfonate)

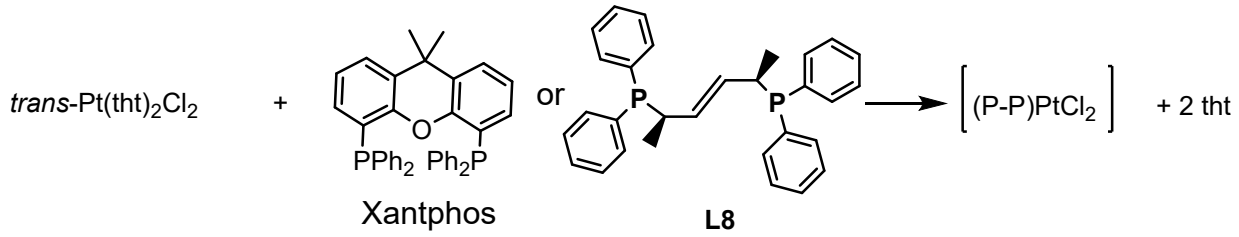
L8, Ar = Ph
L9, Ar = -C_7H_9

L8-(*R*,*R*)-EPHOS and **L9-(*R*,*R*)-Xylyl-EPHOS** were synthesized following the same synthetic methodology used for the preparation of **L7-(*R*,*R*)-Xylyl-ZEDPHOS**, starting from (2*S*,5*S*,E)-hex-3-ene-2,5-diyl bis(4-methylbenzenesulfonate).

L8-(*R*,*R*)-EPHOS: % yield= 65%; ^{31}P NMR (300 MHz; C_3D_6O): (ppm) δ -1.85 (s); ^{1}H NMR (C_3D_6O, 300 MHz): δ 7.32–7.49 (m, 20H); 5.37–5.38 (m, 2H); 3.05–3.08 (m, 2H); 1.02 (m, 6H) ppm; ^{13}C NMR (C_3D_6O, 300 MHz): δ 137.49, 137.39, 137.25, 137.07, 133.78, 133.58, 133.38, 131.84, 131.25, 130.94, 128.67, 128.52, 128.33, 128.04, 128.01, 34.36, 34.23, 16.88, 16.68 ppm; $[\alpha]^{20}_D$= +96.9 (c = 0.13 in CH_2Cl_2); MS (ESI): *m/z* calcd for $[C_{30}H_{30}P_2]$: 452.18; found: *m/z* 453.43 $[M+H]^+$.

L9-(*R*,*R*)-Xylyl-EPHOS: % yield= 65%; ^{31}P NMR (C_6D_6, 300 MHz): δ -1.62 (s) ppm; ^{1}H NMR (C_3D_6O, 300 MHz): δ 7.30 (d, *J* = 7.5 Hz, 8H); 6.72 (d, *J* = 8.5 Hz, 4H); 5.67–5.70 (m, 2H); 3.06–3.11 (m, 2H); 2.08 (d, *J* = 13.0 Hz, 24H); 1.00 (q, *J* = 6.86 Hz, 6H) ppm; ^{13}C NMR (C_6D_6, 101 MHz) δ 138.06, 138.04, 137.86, 137.84, 137.68, 137.66, 137.55, 137.50, 137.46, 137.43, 137.39, 137.09, 137.05, 137.02, 132.21, 132.11, 132.01, 131.74, 131.72, 131.67, 131.65, 131.62, 131.56, 131.53, 131.51, 131.46, 131.44, 130.39, 130.17, 34.77, 34.73, 34.67, 34.63, 21.00, 20.93, 17.36, 17.17 ppm; $[\alpha]^{20}_D$= +63 (c = 0.06 in CH_2Cl_2); MS (ESI): *m/z* calcd for $[C_{38}H_{46}P_2]$: 564.31; found: *m/z* 565.37 $[M+H]^+$.

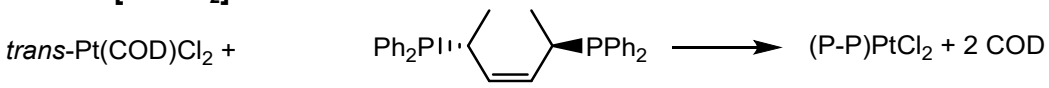
1.5 Synthesis of [L-$PtCl_2$] for Xantphos and L8



Xantphos **L8**

A mixture of ligand (1eq.) and *trans*-Pd(tht)$_2$Cl$_2$ (MW = 442.32 g/mol; 1eq.) in argon-degassed CH_2Cl_2 (5 ml) was stirred at rt for 30 min, under an argon atmosphere; the solvent was reduced in vacuo and the Pt complex was precipitated by addition of hexane. The solvent was removed by filtration to give the corresponding complex. For [**L8**PtCl$_2$]: Elemental analysis for $C_{30}H_{30}P_2PtCl_2$: calculated C, 50.20; H, 4.22; found C, 50.57; H, 4.20. ^{31}P NMR ($CDCl_3$, 300 MHz): 23.56 (s, J_{Pt-P} = 2554 Hz) ppm; FAB$^+$ ($C_{30}H_{30}P_2PtCl$)$^+$ 683 m/z, 100%. For [**Xantphos**PtCl$_2$]: Elemental analysis for $C_{39}H_{32}Cl_2OP_2Pt$: calculated C, 55.46; H, 3.82; found C, 54.51; H, 4.08; MS-FAB$^+$ ($C_{39}H_{32}ClOP_2Pt$)$^+$ 809 m/z, 100%, ($C_{39}H_{32}OP_2Pt$)$^+$, 773 m/z, 60%. ^{31}P NMR ($CDCl_3$, 300 MHz): 7.37 (s, J_{Pt-P} = 3692 Hz) ppm.

1.6 Synthesis of [L-PtCl$_2$] for L6



L6

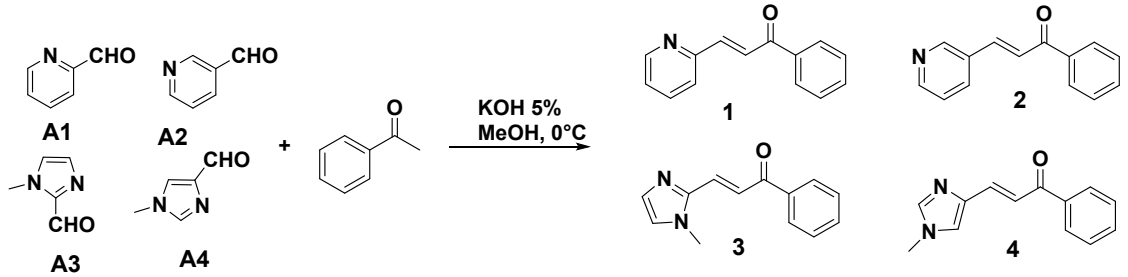
A mixture of **L6** (MW = 452.2 g/mol; 0.21 mmol) and Pt(COD)Cl$_2$ (MW = 373 g/mol; 0.21 mmol) in argon-degassed acetone (5 ml) was stirred at rt for 30 min, under an argon atmosphere; the solvent was reduced in vacuo and the Pt complex was precipitated by addition of hexane. The solvent was removed by filtration to give a [**L6PtCl$_2$]** complex as a white solid. Recrystallization of the product by slow diffusion of ether into a CH_2Cl_2-saturated solution afforded crystals suitable for X-ray structure analysis. Elemental analysis for $C_{30}H_{30}P_2PtCl_2$: calculated C, 50.20; H, 4.22; found C, 51.26; H, 4.66. ^{31}P NMR ($CDCl_3$, 300 MHz): 6.75 (s, J_{Pt-P} = 3610 Hz) ppm.

1.7 Synthesis of rhodium(I) complexes

Ligand **Xantphos, L6** or **L8** (2.2 eq) was dissolved in 1 mL of THF-*d8*. The dimer [Rh(coe)$_2$Cl]$_2$ (1 eq) was added, and the suspension was stirred for 30 minutes. The solution was analyzed by NMR spectroscopy without further purification.

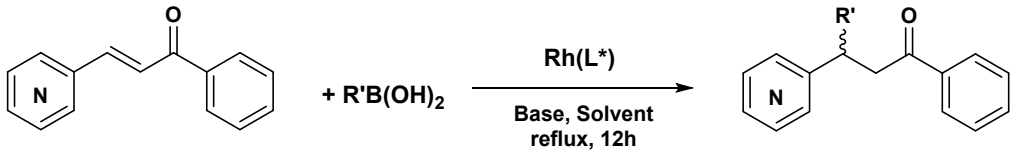
2. General Procedure for the synthesis of 3-azaarylpropenone substrates

The azaarene substrates, used in the asymmetric reaction addition,were synthetized by adding 30 mL of methanol and 5 mmol of acetophenone at 0 ° C in a round-bottom flask under magnetic stirring. Then, KOH 5% (25 mL) and 6 mmol of aldehyde (A1, A2, A3, A4) were slowly added and the reaction mixture was stirred at room temperature for 3 hours. The solvent was removed, and ethyl acetate was added. The organic layer was washed with water and brine, dried with anhydrous Na_2SO_4, filtered, concentrated and, eventually, purified. Generally, a light-yellow solid is obtained.

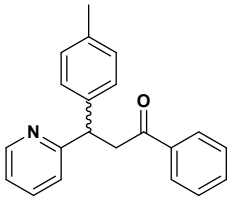


The analyses on products 1, 2, 3 and 4 resulted in accordance with those reported in literature.[3]

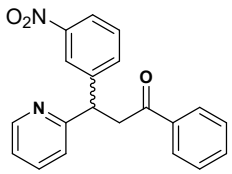
3. General procedure for the enantioselective rhodium catalysed addition of organoboronic acids to 3-azaarylpropenones



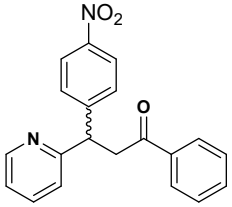
In a Schelnk tube, under nitrogen atmosphere, were added in the following order: 0.001 mmol of rhodium complex, 0.003 mmol of ligand (L*) and 0.6 mL of anhydrous solvent. The reaction mixture was stirred for 30 minutes, then the 3-azaarylpropenone substrate (0.1 mmol), the boronic acid (0.15 mmol), 0.05 mL of base and 0.4 ml of anhydrous solvent were added. The mixture was stirred at reflux for 12 hours. Afterwards, the mixture was quenched by dropping H_2O and ethyl acetate was added. The organic layer was concentrated under reduced pressure and the product was isolated by flash column chromatography.



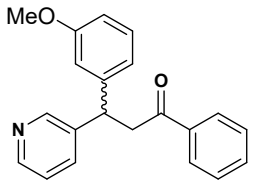
1g: 1-phenyl-3-(pyridin-2-yl)-3-(p-tolyl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.47 (s, 1H), 8.15 – 7.85 (m, 2H), 7.62 – 7.32 (m, 5H), 7.23 (d, J = 6.5 Hz, 2H), 7.07 (d, *J* = 22.0 Hz, 3H), 4.86 (s, 1H), 4.32 (s, 1H), 3.48 (s, 1H), 2.29 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 199.05, 162.61, 148.49, 140.25, 137.32, 136.28, 132.77, 129.28, 128.39, 128.08, 127.96, 123.76, 121.23, 47.15, 43.84, 21.31 ppm. MS (ESI): *m/z* calcd for [$C_{21}H_{19}NO$]: 301,15; found: *m/z* 302.34 [M+H]$^+$. HPLC analysis: 9.2 min (*maj*); 11.2 min (*min*); column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



1i: 3-(3-nitrophenyl)-1-phenyl-3-(pyridin-2-yl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 4.6 Hz, 1H), 8.29 (s, 1H), 8.13 – 7.91 (m, 3H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.69 – 7.36 (m, 6H), 7.28 (dd, *J* = 10.2, 4.2 Hz, 3H), 7.21 – 7.03 (m, 1H), 5.06 – 4.85 (m, 1H), 4.34 (dd, *J* = 17.8, 7.7 Hz, 1H), 3.66 (dd, *J* = 17.7, 5.8 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.86, 160.84, 160.36, 149.71, 148.85, 137.63, 137.19, 134.71, 133.51, 129.66, 128.54, 128.37, 124.49, 123.12, 122.59, 121.99, 47.64, 44.01, 30.18 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{16}N_2O_3$]: 332,12; found: *m/z* 333.39 [M+H]$^+$. HPLC analysis: 35.5 min (*min)*; 39.5 min (*maj)*; column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.

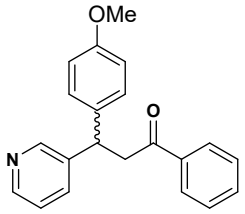


1l: **3-(4-nitrophenyl)-1-phenyl-3-(pyridin-2-yl)propan-1-one.** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.54 (d, J = 4.7 Hz, 1H), 8.13 (t, J = 8.2 Hz, 2H), 7.99 (d, J = 7.7 Hz, 2H), 7.71 – 7.37 (m, 7H), 7.16 (s, 1H), 5.02 (t, J = 6.9 Hz, 1H), 4.29 (dt, J = 63.8, 31.9 Hz, 1H), 3.78 – 3.57 (m, 2H), 3.49 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$)δ: 204.80, 169.44, 145.96, 139.97, 138.47, 133.04, 129.71, 129.05, 128.58, 128.10, 125.24, 123.86, 121.58, 116.25, 47.79, 43.54 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{16}N_2O_3$]: 332,12; found: *m/z* 333.27 [M+H]$^+$. HPLC analysis: 24.9 min (*maj*); 30.4 min (*min*); column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.

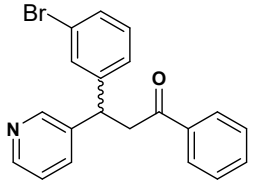


2b: 3-(3-methoxyphenyl)-1-phenyl-3-(pyridin-3-yl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 2.2 Hz, 1H), 8.46 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.17 – 7.84 (m, 3H), 7.79 – 7.38 (m, 6H), 7.30 – 7.08 (m, 3H), 6.95 – 6.53 (m, 4H), 4.83 (t, *J* = 7.3 Hz, 1H), 3.75 – 3.72 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.27, 159.59, 147.85, 146.84, 143.67, 139.42, 132.88, 129.64, 127.98, 123.66, 120.12, 114.06, 111.87, 54.80, 44.39, 44.07 ppm. MS (ESI): *m/z* calcd

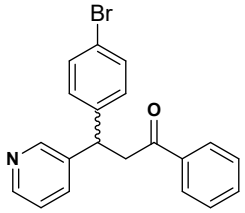
for [$C_{21}H_{19}NO_2$]:317,14; found: ***m/z*** 318.24 [M+H]$^+$. HPLC analysis: 11.9 min (*maj)*; 16.2 min (*min)*; column: Chiralpak AD, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



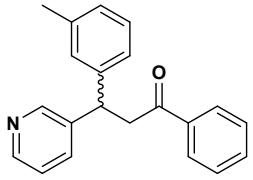
2c: 3-(4-methoxyphenyl)-1-phenyl-3-(pyridin-3-yl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ:8.62 (s, 1H), 8.48 (d, *J* = 3.4 Hz, 1H), 8.11 – 7.79 (m, 3H), 7.74 – 7.37 (m, 5H), 7.34 – 7.07 (m, 4H), 7.03 – 6.68 (m, 3H), 4.81 (t, *J* = 7.3 Hz, 1H), 3.76 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.45, 158.93, 148.41, 146.43, 136.95, 135.20, 134.74, 133.61, 128.70, 128.04, 123.75, 114.17, 113.23, 55.07, 44.80, 42.57 ppmn. MS (ESI): ***m/z*** calcd for [$C_{21}H_{19}NO_2$]: 317,14; found: ***m/z*** 318.32 [M+H]$^+$. HPLC analysis: 36.1 min (*maj)*; 40.9 min (*min)*; column: Chiralpak AD, eluent: 2-propanol/hexane=10/90, flow=1.0 mL/min, λ=240 nm.



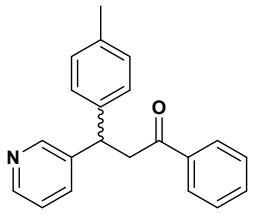
2d: 3-(3-bromophenyl)-1-phenyl-3-(pyridin-3-yl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ:8.52 (d, *J* = 25.4 Hz, 1H), 8.50 – 8.26 (m, 1H), 8.11 – 7.86 (m, 2H), 7.69 – 6.88 (m, 10H), 4.83 (t, *J* = 7.2 Hz, 1H), 3.85 – 3.52 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.92, 150.70, 149.56, 144.82, 137.97, 134.29, 133.26, 132.91, 130.33, 128.97, 127.99, 126.84, 126.01, 124.25, 122.88, 44.12 ppm. MS (ESI): ***m/z*** calcd for [$C_{20}H_{16}BrNO$]: 365,04; found: ***m/z*** 366.31 [M+H]$^+$. HPLC analysis: 16.0 min (*maj)*; 23.3 min (*min)*; column: Chiralpak AD, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



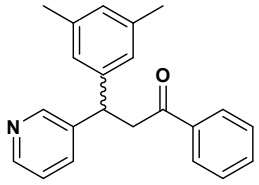
2e: 3-(4-bromophenyl)-1-phenyl-3-(pyridin-3-yl)propan-1-one. ^{1}H NMR (300 MHz, cdcl$_3$) δ: 8.55 (d, *J* = 2.3 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.99 – 7.80 (m, 2H), 7.70 – 7.35 (m, 7H), 7.24 – 6.90 (m, 4H), 4.81 (t, *J* = 7.3 Hz, 1H), 3.74 (t, *J* = 8.8 Hz, 2H) ppm. ^{13}C NMR (75 MHz, cdcl$_3$) δ 196.62, 149.30, 148.04, 141.85, 138.95, 136.67, 135.23, 133.37, 132.02, 129.49,128.69, 127.96, 123.63, 120.75, 44.05, 43.07 ppm. MS (ESI): ***m/z*** calcd for [$C_{20}H_{16}BrNO$]: 365,04; found: ***m/z*** 366.32 [M+H]$^+$. HPLC analysis: 32.2 (*maj)*; 39.1 min (*min)*; column: Chiralpak OJ-H, eluent: 2-propanol/hexane=10/90, flow=1.0 mL/min, λ=240 nm.



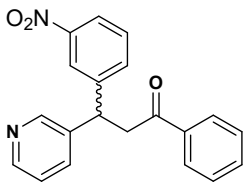
2f: 1-phenyl-3-(pyridin-3-yl)-3-(m-tolyl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ:8.56 (s, 1H), 8.51 – 8.36 (m, 1H), 8.00 – 7.88 (m, 2H), 7.67 – 7.53 (m, 2H), 7.49 – 7.10 (m, 9H), 4.83 (t, *J* = 7.2 Hz, 1H), 3.73 (t, *J* = 17.5 Hz, 2H), 2.31 (d, *J* = 9.0 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.18, 153.21, 149.91, 148.72, 145.65, 140.81, 140.29, 136.60, 133.98, 131.26, 129.17, 128.23, 127.35, 125.88, 124.93, 123.41, 44.11, 42.95 ppm. MS (ESI): ***m/z*** calcd for [$C_{21}H_{19}NO$]: 301,15; found: ***m/z*** 302.34 [M+H]$^+$. HPLC analysis: 15.6 min (*min*); 20.4 min (*maj*); column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



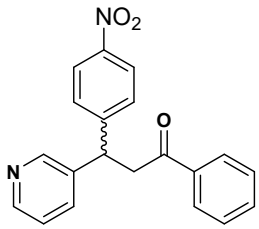
2g: 1-phenyl-3-(pyridin-3-yl)-3-(p-tolyl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ:8.57 (s, 1H), 8.43 (s, 1H), 7.65 – 7.49 (m, 3H), 7.45 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.18 – 6.96 (m, 5H), 4.82 (t, *J* = 7.3 Hz, 1H), 3.71 (t, *J* = 17.5 Hz, 2H), 2.28 (d, *J* = 9.0 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ :197.14, 148.68, 147.09, 139.39, 136.63, 136.02, 133.01, 132.77, 130.34, 129.41, 128.48, 127.87, 127.57, 123.96, 44.21, 43.49, 21.31 ppm. MS (ESI): ***m/z*** calcd for [$C_{21}H_{19}NO$]: 301,15; found: ***m/z*** 302.27 [M+H]$^+$. HPLC analysis: 13.6 min (*maj*); 14.8 min (*min*); column: Chiralpak OD-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



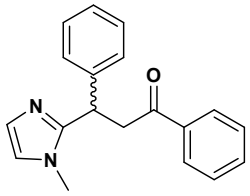
2h: 3-(3,5-dimethylphenyl)-1-phenyl-3-(pyridin-3-yl)propan-1-one. ^{1}H NMR (300 MHz, CDCl3) δ: 8.57 (d, J = 2.3 Hz, 1H), 8.42 (dd, J = 4.8, 1.6 Hz, 1H), 8.05 – 7.83 (m, 2H), 7.66 – 7.50 (m, 2H), 7.45 (ddd, J = 8.2, 2.3, 0.8 Hz, 2H), 7.20 (ddd, J = 7.9, 4.8, 0.7 Hz, 1H), 6.86 (d, J = 6.4 Hz, 3H), 4.76 (t, J = 7.3 Hz, 1H), 3.82 – 3.68 (m, 2H), 2.26 (t, J = 3.7 Hz, 7H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ :197.02, 149.58, 147.46, 142.66, 139.64, 137.85, 136.67, 135.53, 132.48, 128.61, 127.99, 125.22, 123.39, 44.15, 42.96, 21.29 ppm. MS (ESI): *m/z* calcd for [$C_{22}H_{21}NO$]: 315,16; found: *m/z* 316.35 [M+H]$^+$. HPLC analysis: 7.6 min (*min*); 10.8 min (*maj*); column: Chiralpak OJ-H, eluent: 2-propanol/hexane=10/90, flow=1.0 mL/min, λ=240 nm.



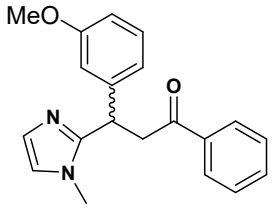
2i: 3-(3-nitrophenyl)-1-phenyl-3-(pyridin-3-yl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.52 – 8.40 (m, 1H), 8.00 – 7.83 (m, 2H), 7.71 – 7.51 (m, 2H), 7.52 – 7.31 (m, 4H), 7.30 – 7.10 (m, 3H), 4.98 (t, *J* = 7.2 Hz, 1H), 3.83 (d, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.70, 150.78, 149.90, 149.28, 140.82, 136.98, 136.06, 134.83, 134.31, 133.01, 128.86, 128.22, 127.90, 126.18, 125.56, 124.36, 43.84, 43.18 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{16}N_2O_3$]: 332,12; found: *m/z* 333.41 [M+H]$^+$. HPLC analysis: 27.9 min (*maj)*; 35.3 min (*min)*; column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



2l: 3-(4-nitrophenyl)-1-phenyl-3-(pyridin-3-yl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.3 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.05 – 7.84 (m, 2H), 7.66 – 7.34 (m, 7H), 7.23 – 7.06 (m, 3H) 4.98 (t, *J* = 7.2 Hz, 1H), 3.90 – 3.68 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.50, 144.51, 140.64, 137.84, 133.63, 132.97, 132.38, 129.54, 128.37, 127.94, 123.92, 123.08, 122.49, 118.47, 44.01, 43.01 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{16}N_2O_3$]: 332,12; found: *m/z* 333.35 [M+H]$^+$. HPLC analysis: 26.6 min (*maj)*; 33.8 min (*min)*; column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.

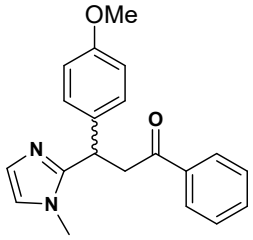


3a: 3-(1-methyl-1H-imidazol-2-yl)-1,3-diphenylpropan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.60 – 7.44 (m, 1H), 7.41 – 7.33 (m, 1H), 6.91 (t, *J* = 10.9 Hz, 1H), 6.76 (d, *J* = 1.2 Hz, 1H), 4.82 (dd, *J* = 8.3, 5.4 Hz, 1H), 4.34 (dd, *J* = 18.0, 8.3 Hz, 1H), 3.47 (s, 2H) ppm. ^{13}C NMR (75 MHz,$CDCl_3$) δ: 197.78, 149.19, 141.71, 136.39, 133.21, 128.78, 128.43, 128.17, 127.88, 126.88, 126.72, 120.90, 45.34, 37.99, 32.43 ppm. MS (ESI): *m/z* calcd for [$C_{19}H_{18}N_2O$]: 290,14; found: *m/z* 291.24 [M+H]$^+$. HPLC analysis: 13.8 min (*maj)*; 20.3 min (*min)*; column: Chiralpak AD, eluent: 2-propanol/hexane=10/90, flow=1.0 mL/min, λ=240 nm.

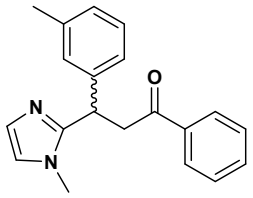


3b: 3-(3-methoxyphenyl)-3-(1-methyl-1H-imidazol-2-yl)-1-phenylpropan-1-one

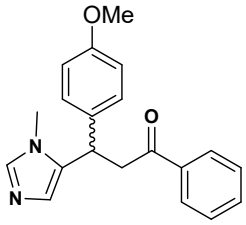
1H NMR (500 MHz,$CDCl_3$) δ: 7.85 – 7.57 (m, 1H), 7.50 – 7.17 (m, 2H), 6.92 (dd, J = 54.8, 4.1 Hz, 2H). 5.16 (s, 1H), 3.72 (s, J = 5.9 Hz, 3H), 3.67 (s, 3H), 3.55 (dd, J = 18.0, 6.6 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.36, 160.39, 158.92, 148.72, 136.66, 133.03, 130.39, 128.53, 126.19, 121.04, 119.58, 113.80, 112.62, 54.94, 43.84, 37.56, 32.72 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{20}N_2O_2$]: 320,15; found: *m/z* 321.28 [M+H]$^+$. HPLC analysis: 11.4 min (*min)*; 13.4 min (*maj)*; column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



3c: 3-(4-methoxyphenyl)-3-(1-methyl-1H-imidazol-2-yl)-1-phenylpropan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08 – 7.83 (m, 1H), 7.58 – 7.44 (m, 1H), 7.40 (dd, *J* = 10.3, 4.6 Hz, 1H), 7.19 (dd, *J* = 9.2, 6.3 Hz, 1H), 7.02 – 6.61 (m, 2H), 4.88 – 4.61 (m, 1H), 4.29 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.75 (s, 1H), 3.54 (dd, *J* = 17.5, 5.3 Hz, 1H), 3.53 – 3.37 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.72, 158.74, 149.29, 136.89, 132.63, 129.50, 129.01, 128.18, 127.42, 126.30, 121.16, 114.11, 113.30, 55.21, 44.56, 37.31, 32.84 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{20}N_2O_2$]: 320,15; found: *m/z* 321.35 [M+H]$^+$. HPLC analysis: 16.8 min (*maj)*; 29.2 min (*min)*; column: Chiralpak AD, eluent: 2-propanol/hexane=10/90, flow=1.0 mL/min, λ=240 nm.



3d: 3-(1-methyl-1H-imidazol-2-yl)-1-phenyl-3-(m-tolyl)propan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.11 – 7.89 (m, 1H), 7.61 – 7.46 (m, 1H), 7.42 (tt, *J* = 8.2, 1.2 Hz, 1H), 7.21 – 6.89 (m, 3H), 6.74 (t, *J* = 17.5 Hz, 1H), 4.82 (dd, *J* = 8.4, 5.3 Hz, 1H), 3.62 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ :198.51, 148.95, 139.34, 136.98, 133.02, 129.17, 128.86, 128.21, 127.94, 127.37, 124.67, 120.74, 44.15, 38.41, 32.41, 21.32 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{20}N_2O$]: 304,16; found: *m/z* 305.32 [M+H]$^+$. HPLC analysis: 6.2 min (*maj*); 7.1 min (*min)*; column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.



4c: 3-(4-methoxyphenyl)-3-(1-methyl-1H-imidazol-5-yl)-1-phenylpropan-1-one. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 3.7 Hz, 2H) 7.40– 7.46 (m, 2H), 7.28-7.33 (m, 3H), 4.67 (t, *J* = 4.8, 1H), 3.75 (s, 3H), 3.55 (s, 3H), 3.96 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.53 (dd, *J* = 6.7, 3.8 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.56, 143.62, 142.03, 139.28, 137.42, 136.53, 135.25, 133.66, 133.01, 129.09, 128.43, 127.53, 125.38, 121.32, 114.23, 113.01, 56.43, 46.56, 36.11, 31.46 ppm. MS (ESI): *m/z* calcd for [$C_{20}H_{20}N_2O$]: 304,16; found: *m/z* 305.32 [M+H]$^+$. HPLC analysis: 22.0 min (*min)*; 26.4 min (*maj)*; column: Chiralpak OJ-H, eluent: 2-propanol/hexane=20/80, flow=1.0 mL/min, λ=240 nm.

4. NMR Spectra of ligands L7-L9

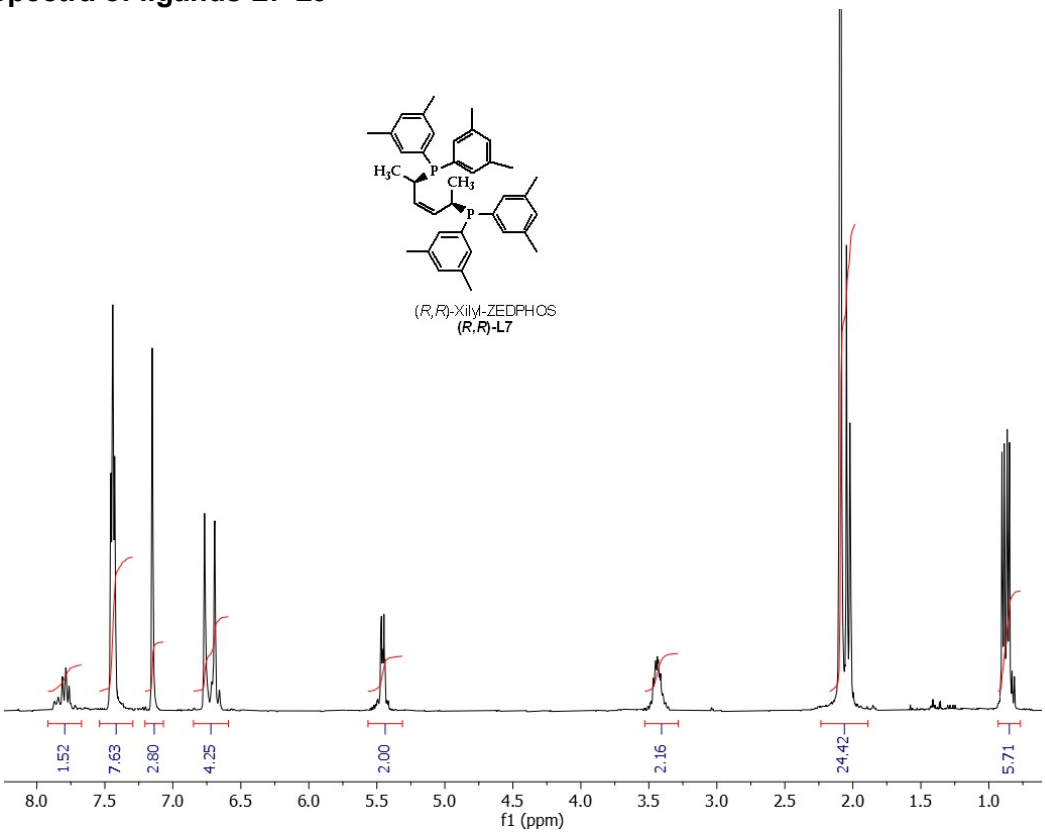


Figure S1. ^{1}H-NMR spectrum of ligand **L7**.

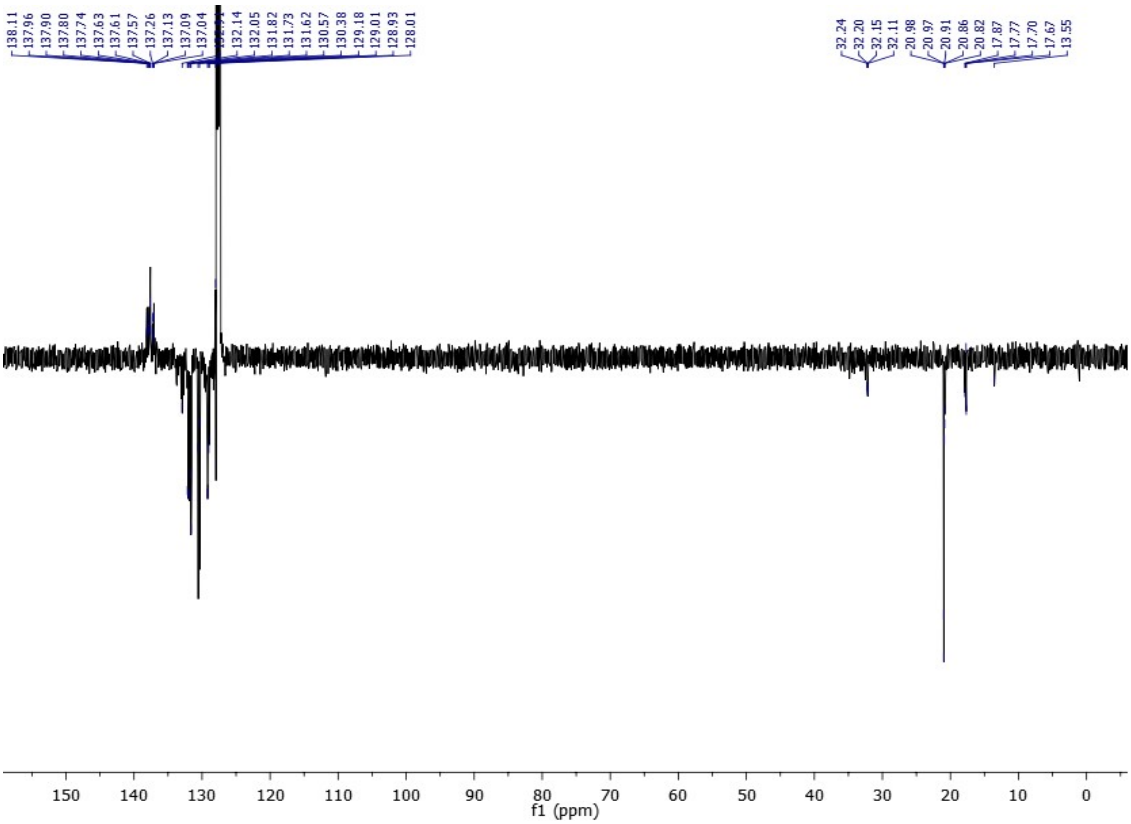


Figure S2. ^{13}C-NMR spectrum of ligand **L7**.

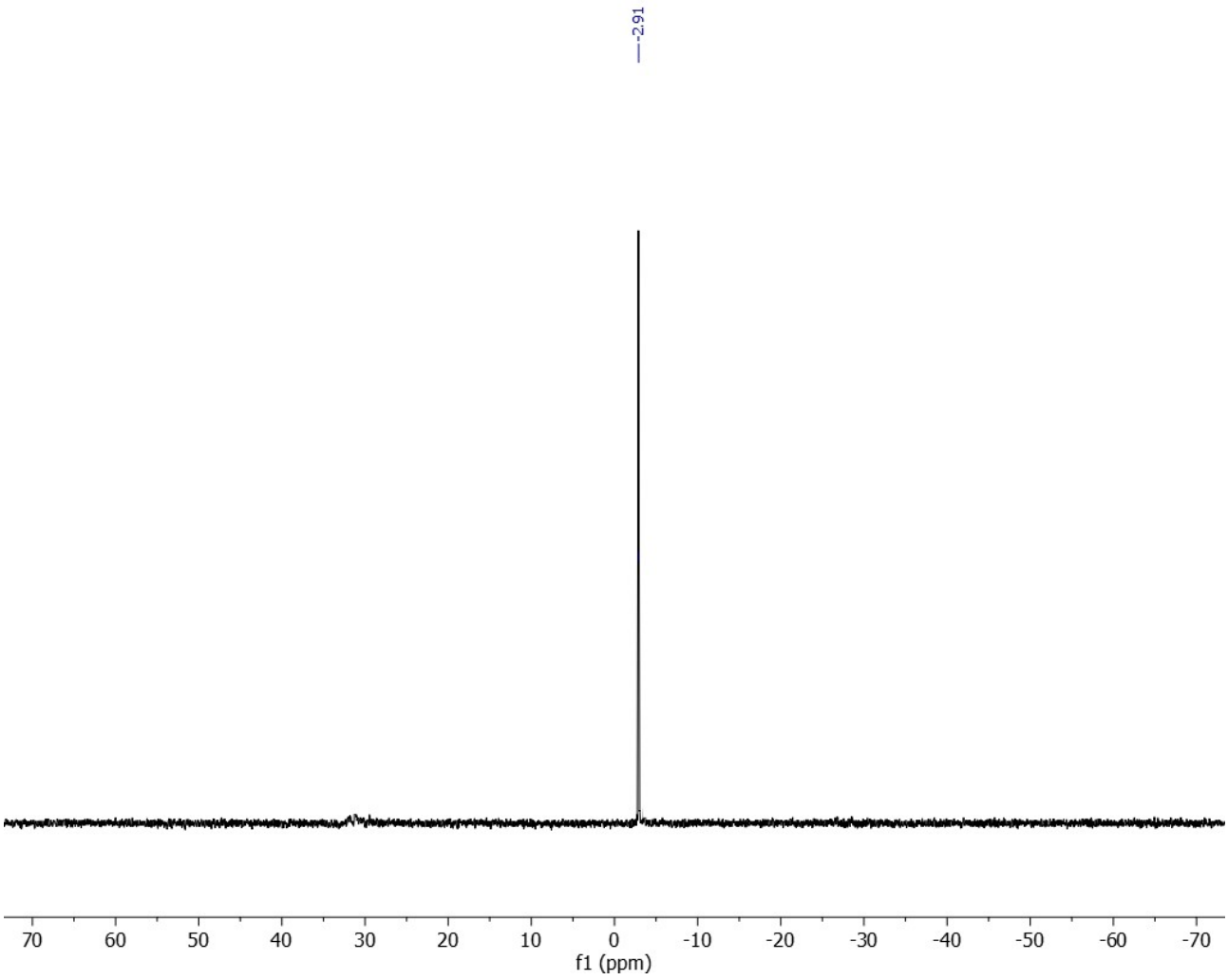


Figure S3. ^{31}P-NMR spectrum of ligand **L7.**

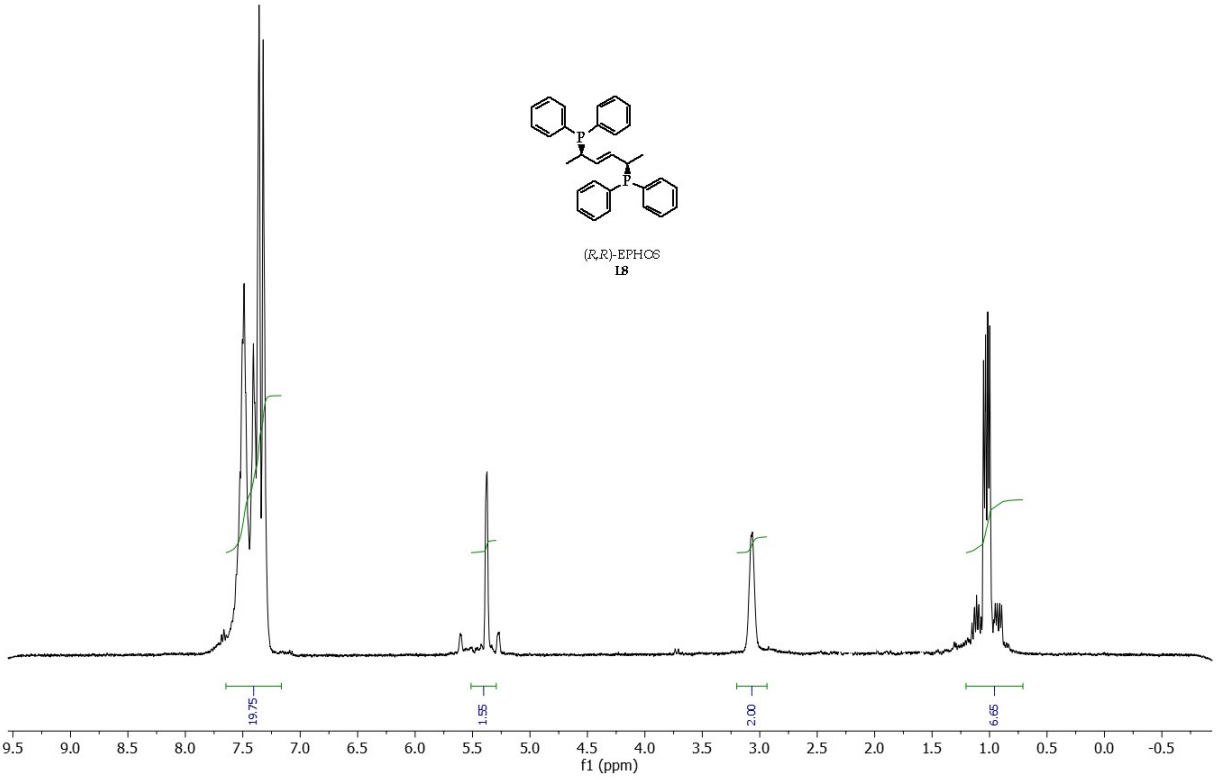


Figure S4. ^{1}H-NMR spectrum of ligand **L8**.

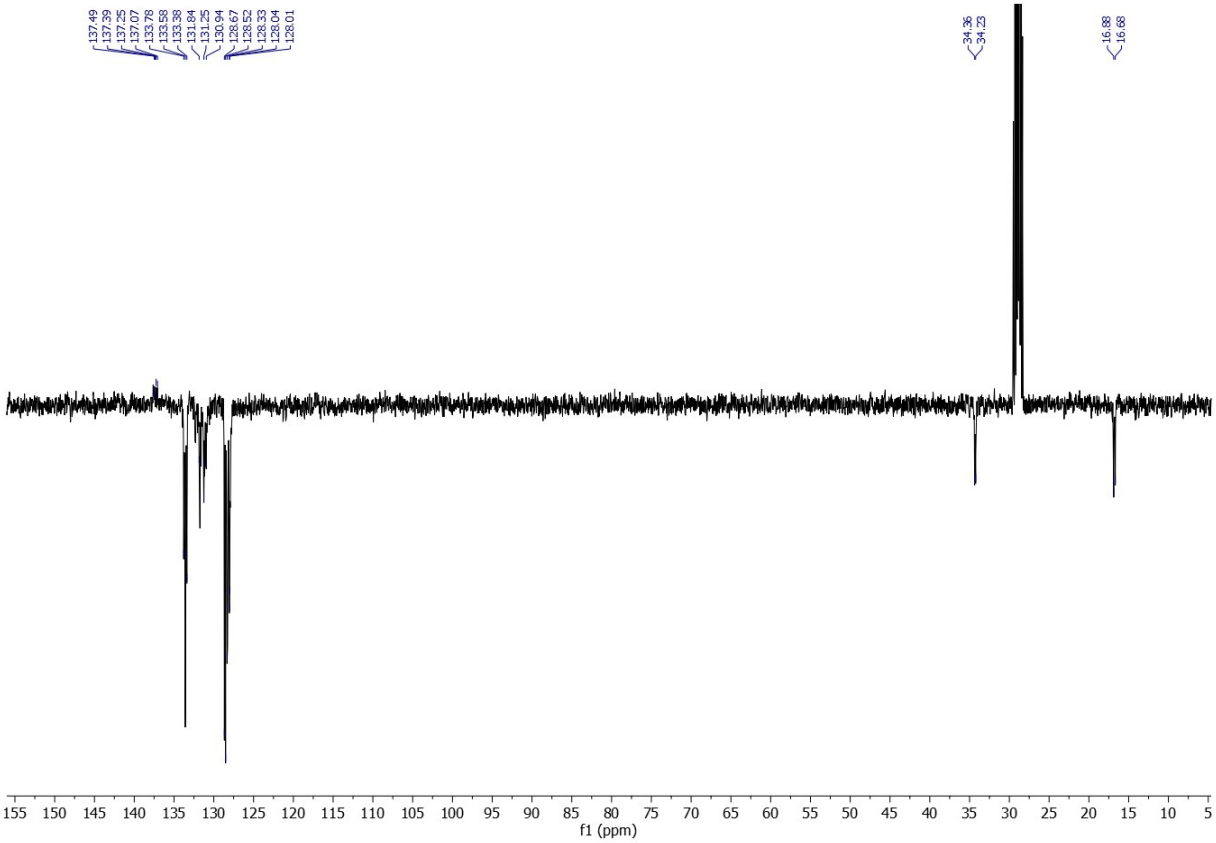


Figure S5. ^{13}C-NMR spectrum of ligand **L8**.

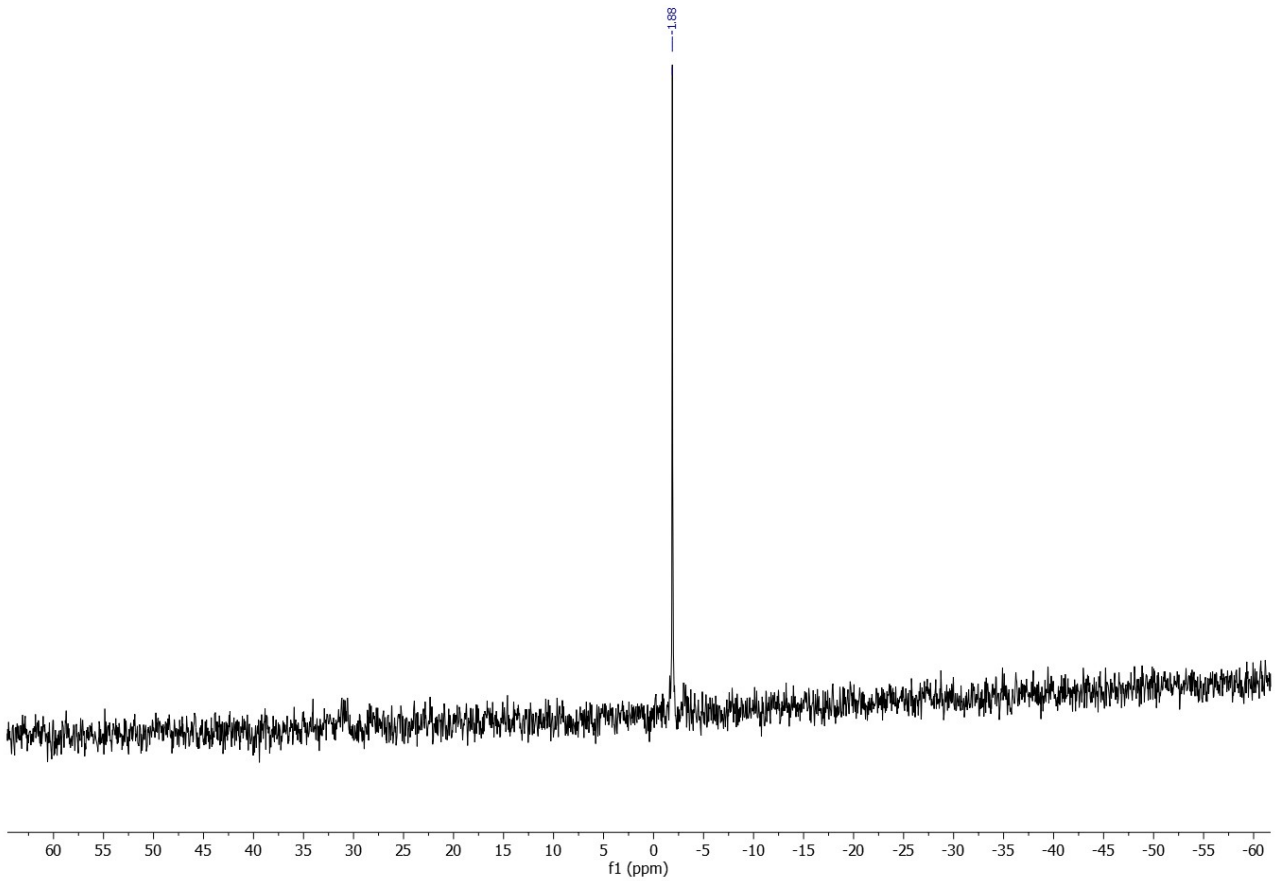


Figure S6. ^{31}P-NMR spectrum of ligand **L8.**

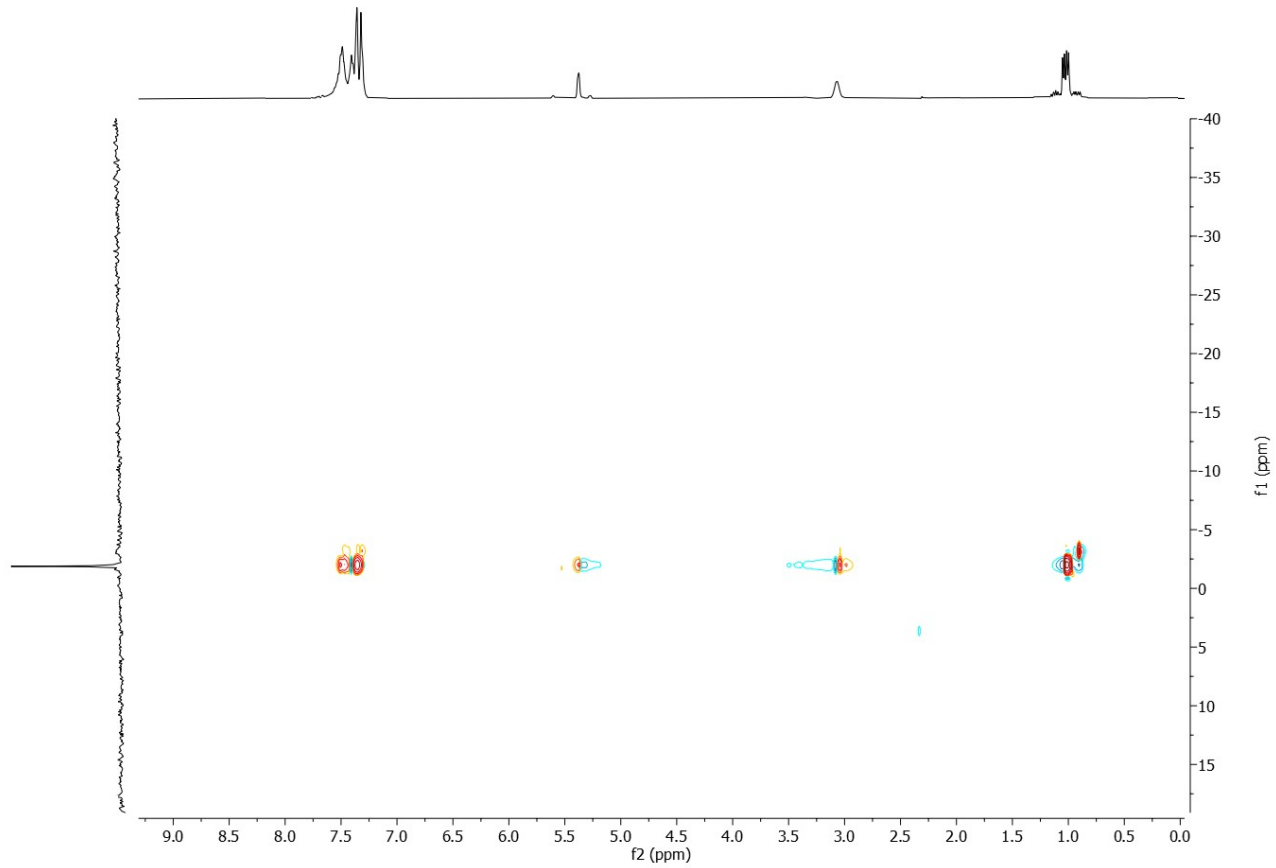


Figure S7. Inverse correlation ^{31}P-^{1}H NMR with gradient of ligand **L8.**

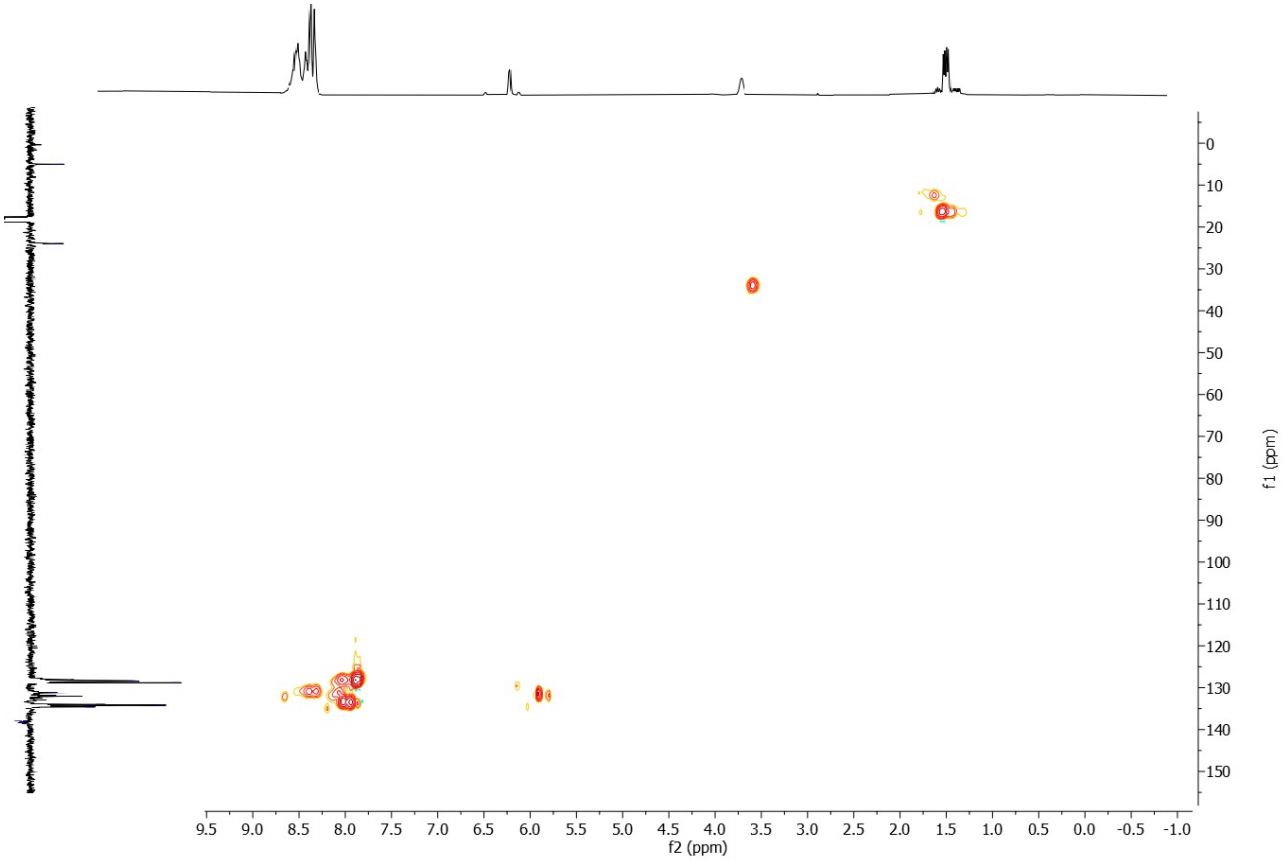


Figure S8: HSQC spectrum of ligand **L8.**

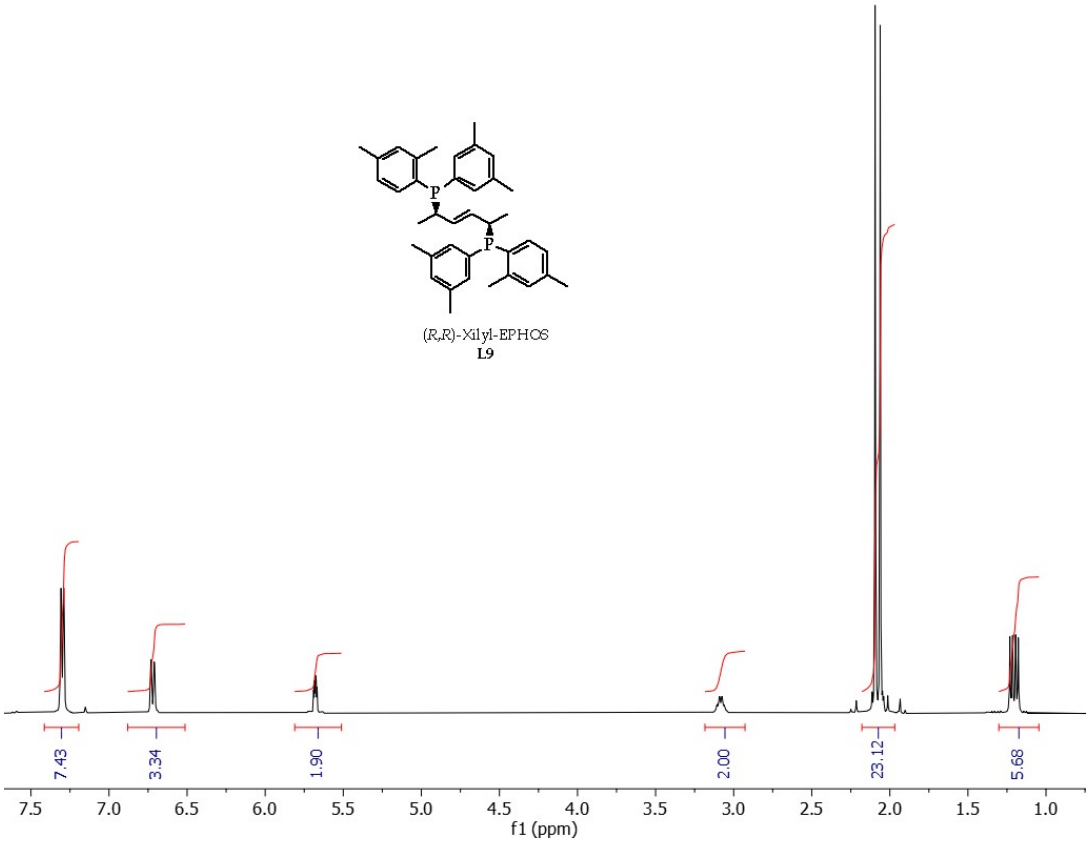


Figure S9. ^{1}H-NMR spectrum of ligand **L9**.

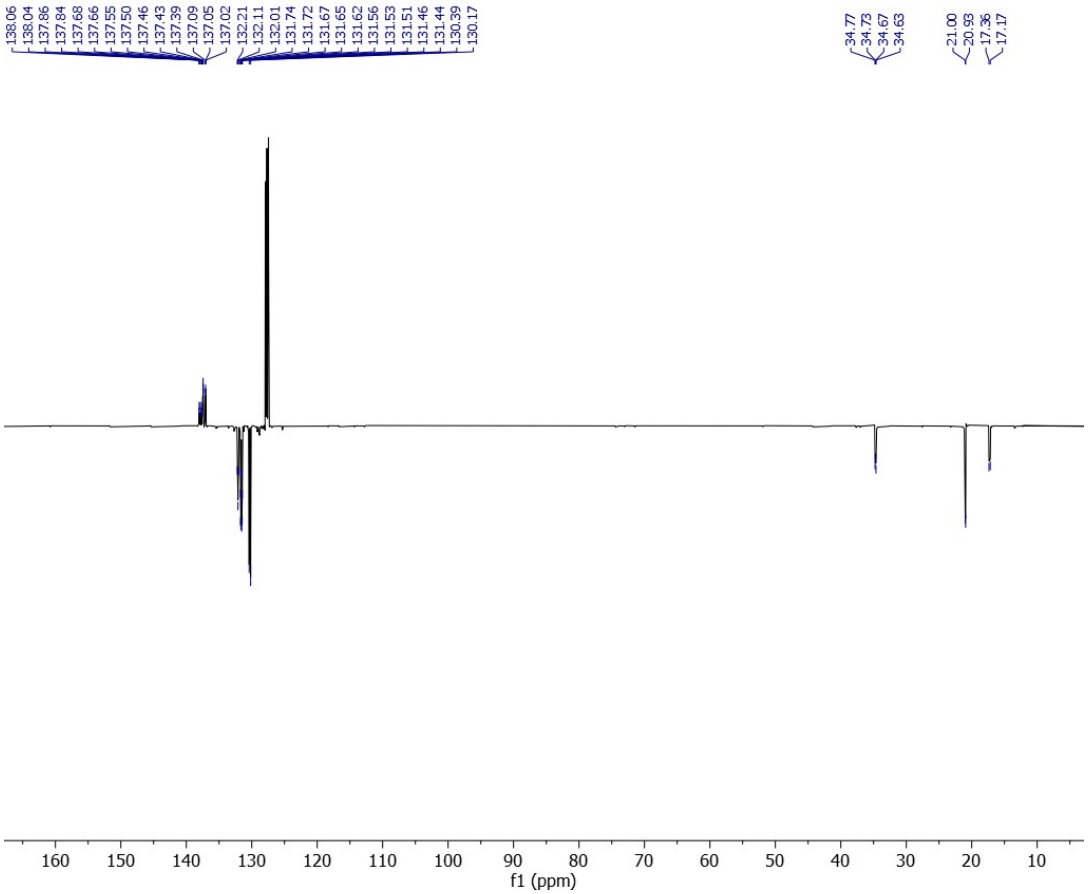


Figure S10. ^{13}C-NMR spectrum of ligand **L9**.

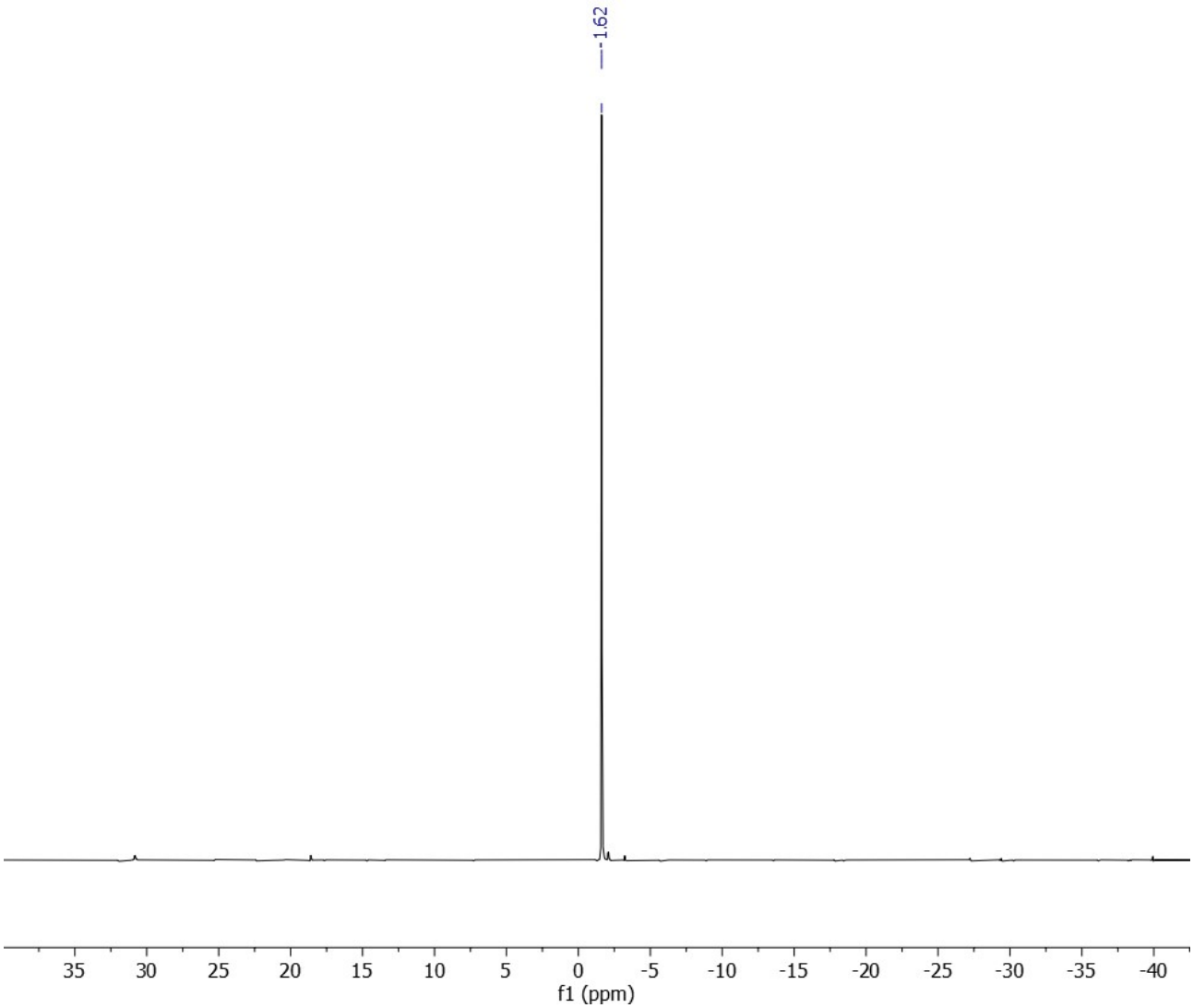


Figure S11. ^{31}P-NMR spectrum of ligand **L9.**

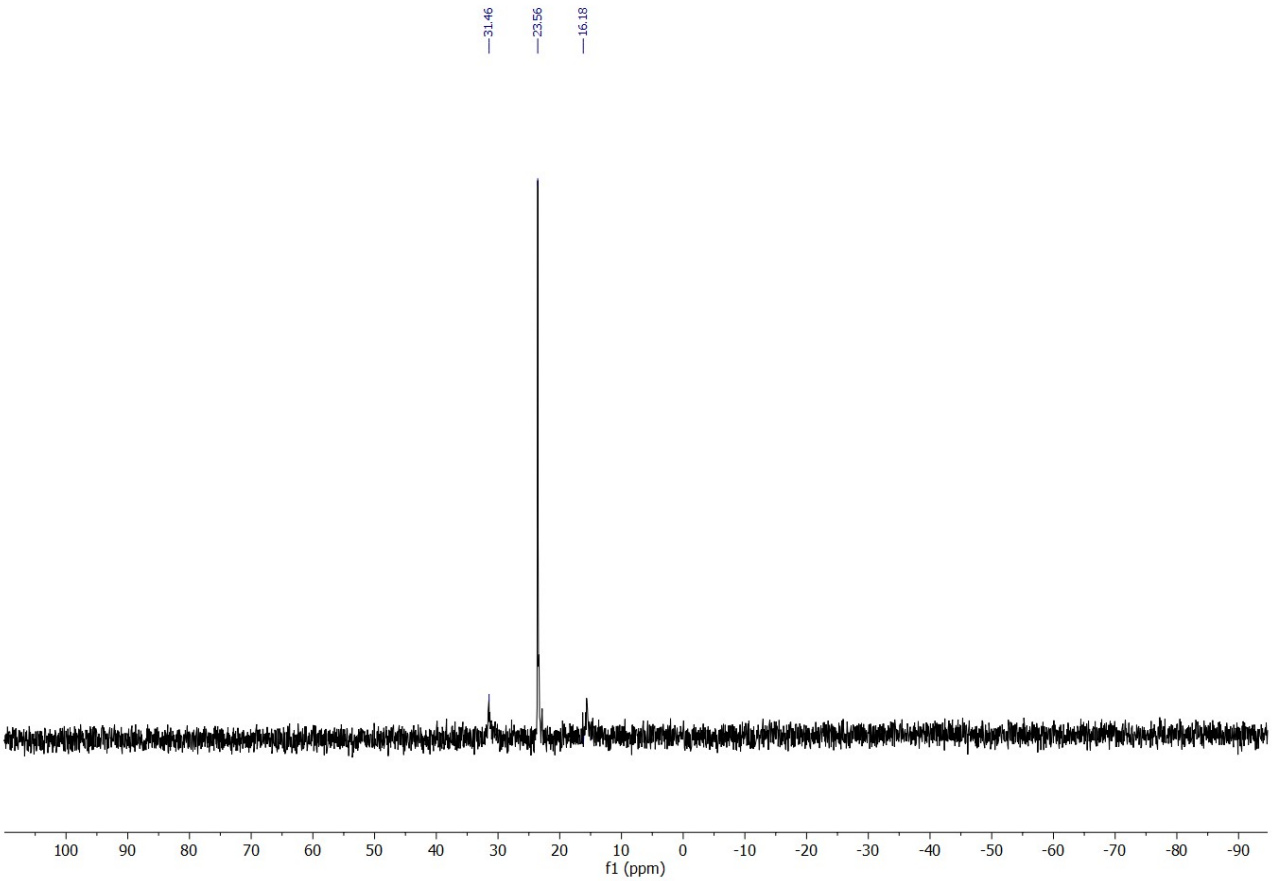


Figure S12. ^{31}P-NMR spectrum of [**L8**PtCl2]**.**

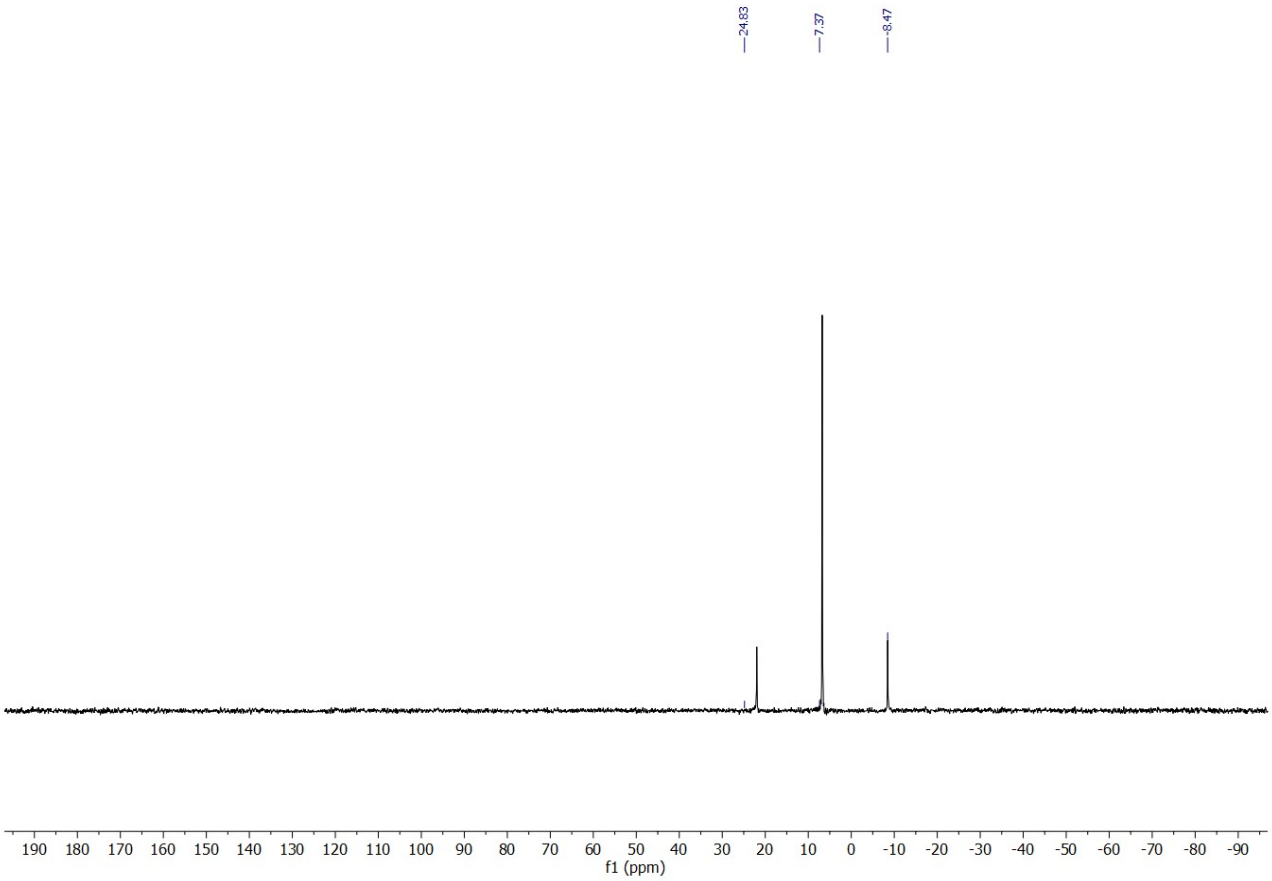


Figure S13. ^{31}P-NMR spectrum of [**Xantphos**$PtCl_2$]**.**

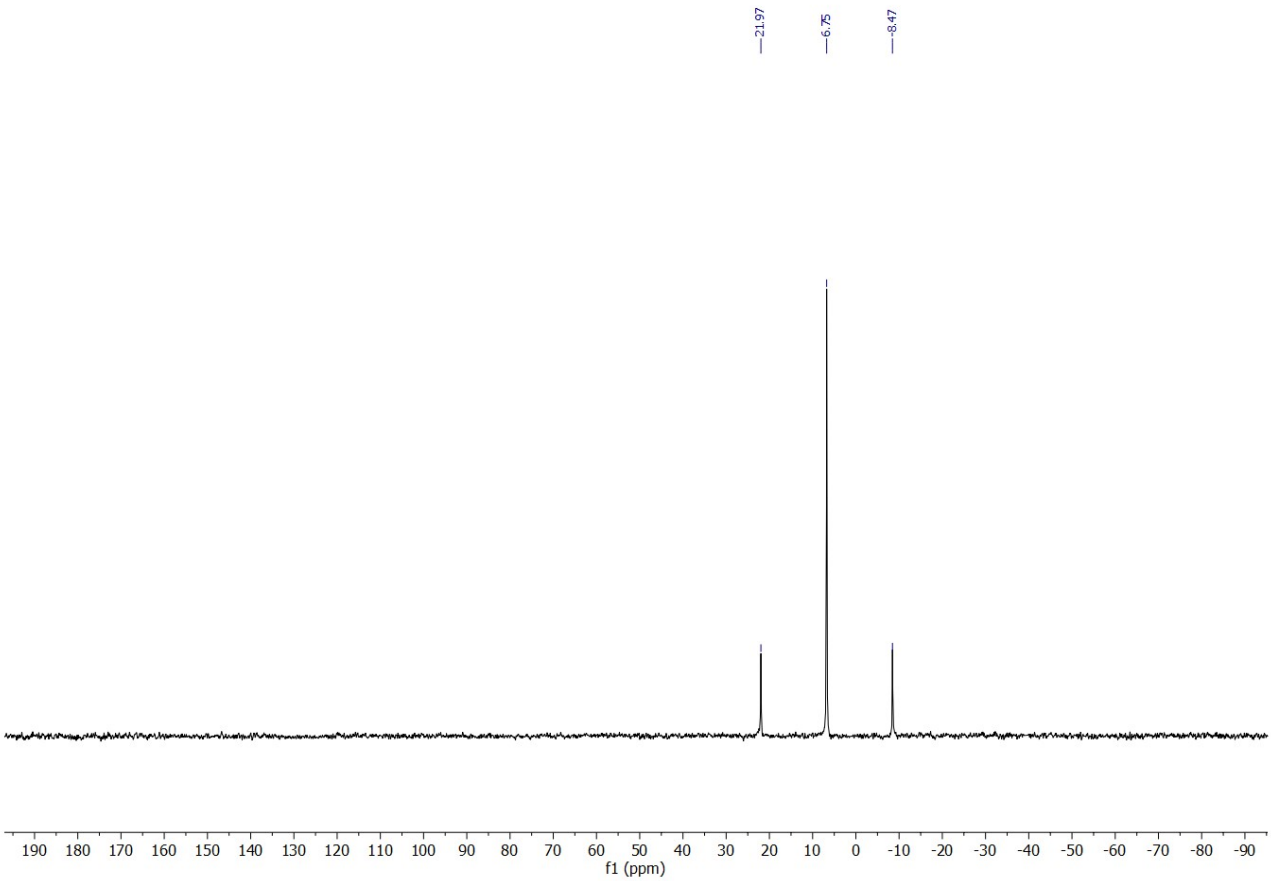


Figure S14. ^{31}P-NMR spectrum of [**L6**$PtCl_2$]**.**

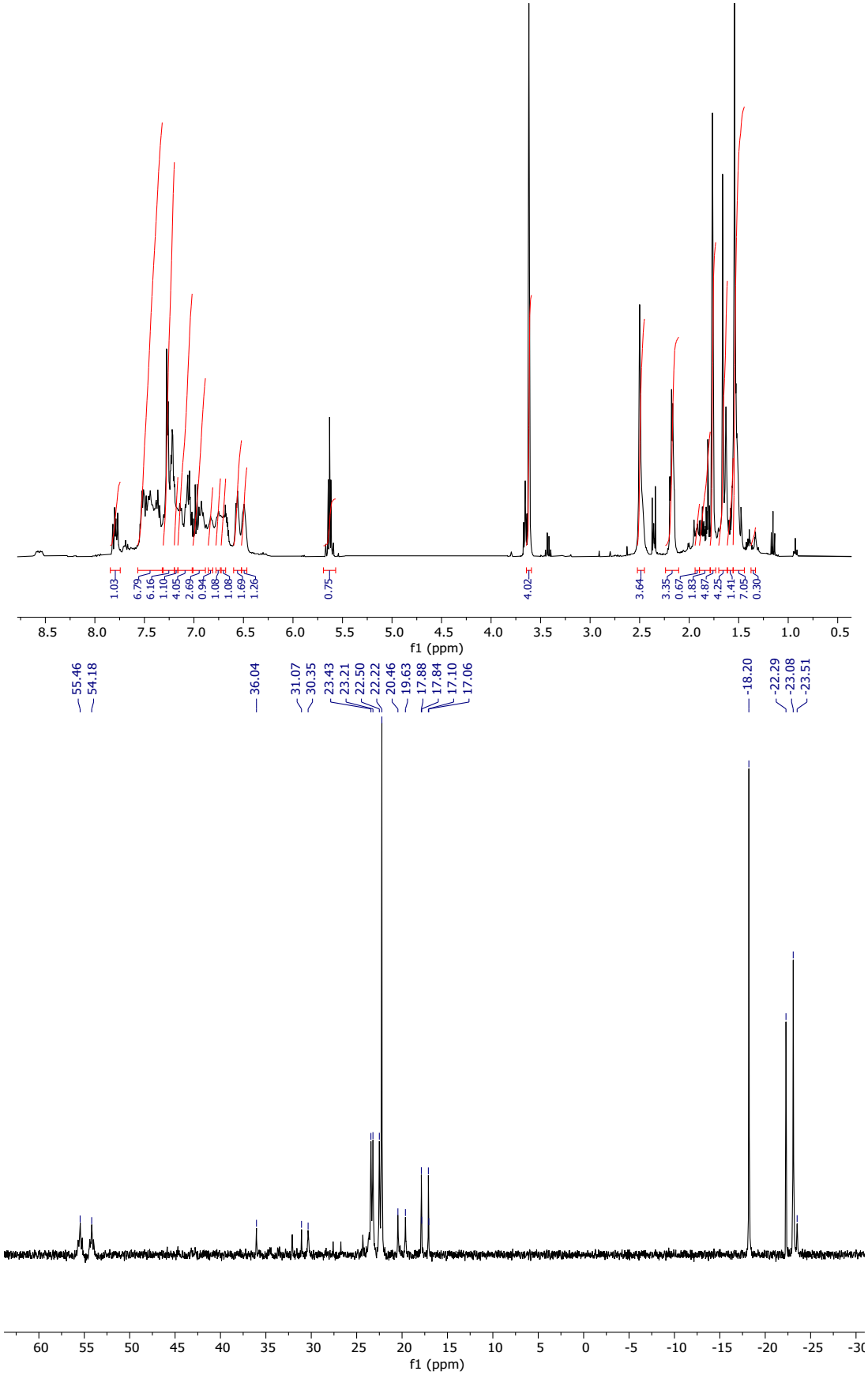


Figure S15. ^{1}H-NMR and ^{31}P-NMR spectrum of rhodium complex with **Xantphos.**

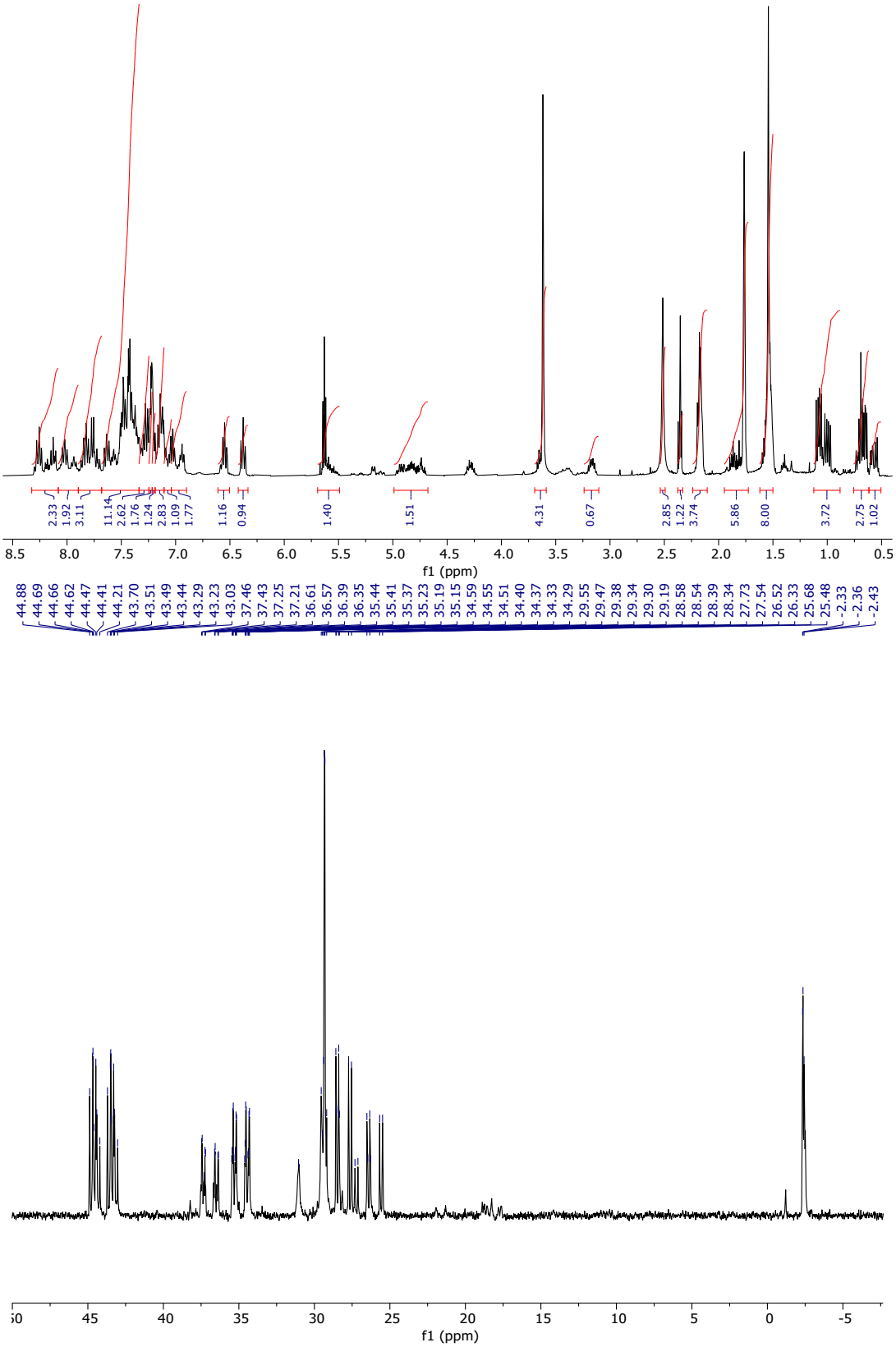


Figure S16. ^{1}H-NMR and ^{31}P-NMR spectrum of rhodium complex with **L6.**

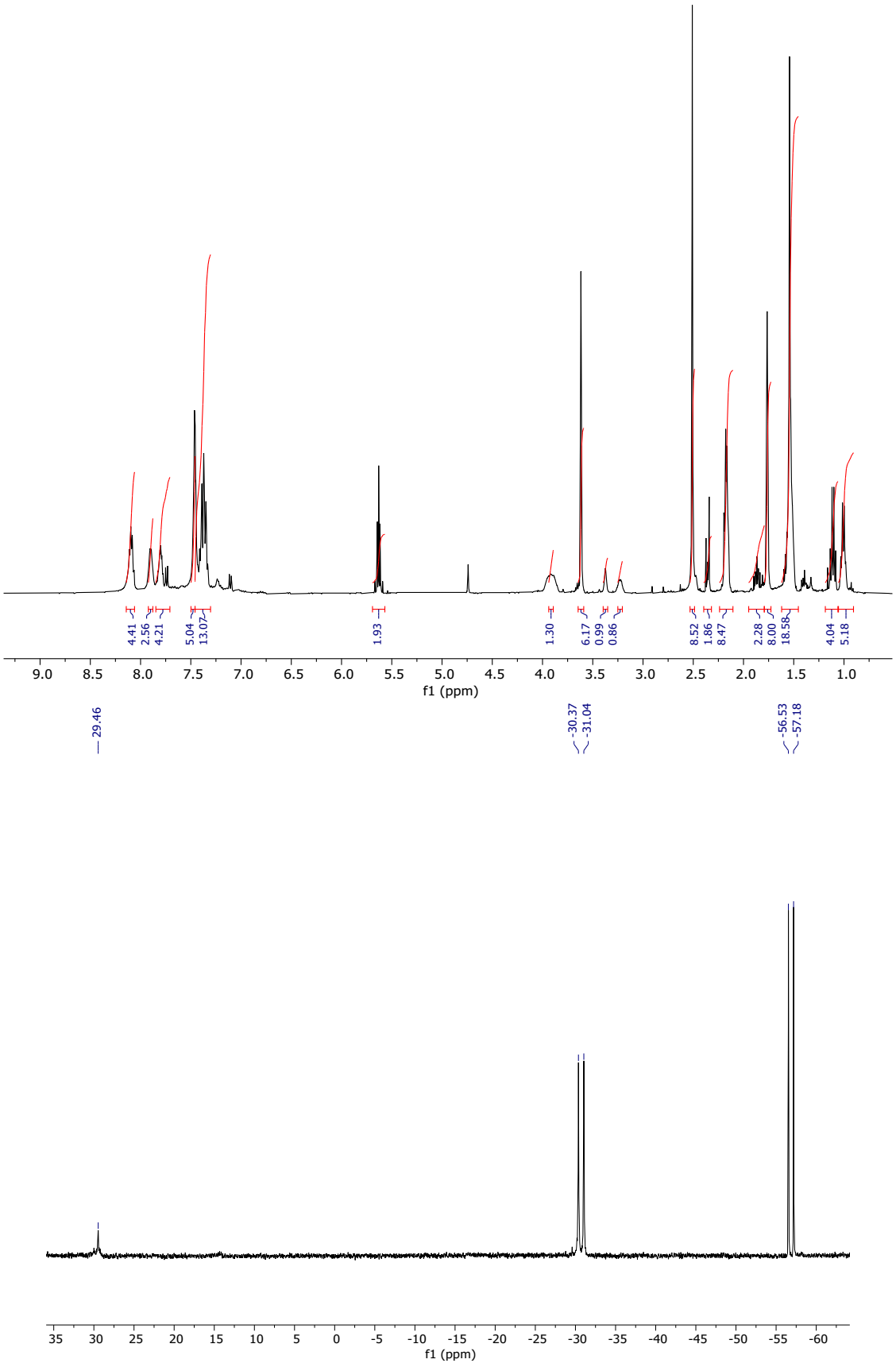


Figure S17. ^{1}H-NMR and ^{31}P-NMR spectrum of rhodium complex with **L8.**

5. NMR spectra of products not reported in literature

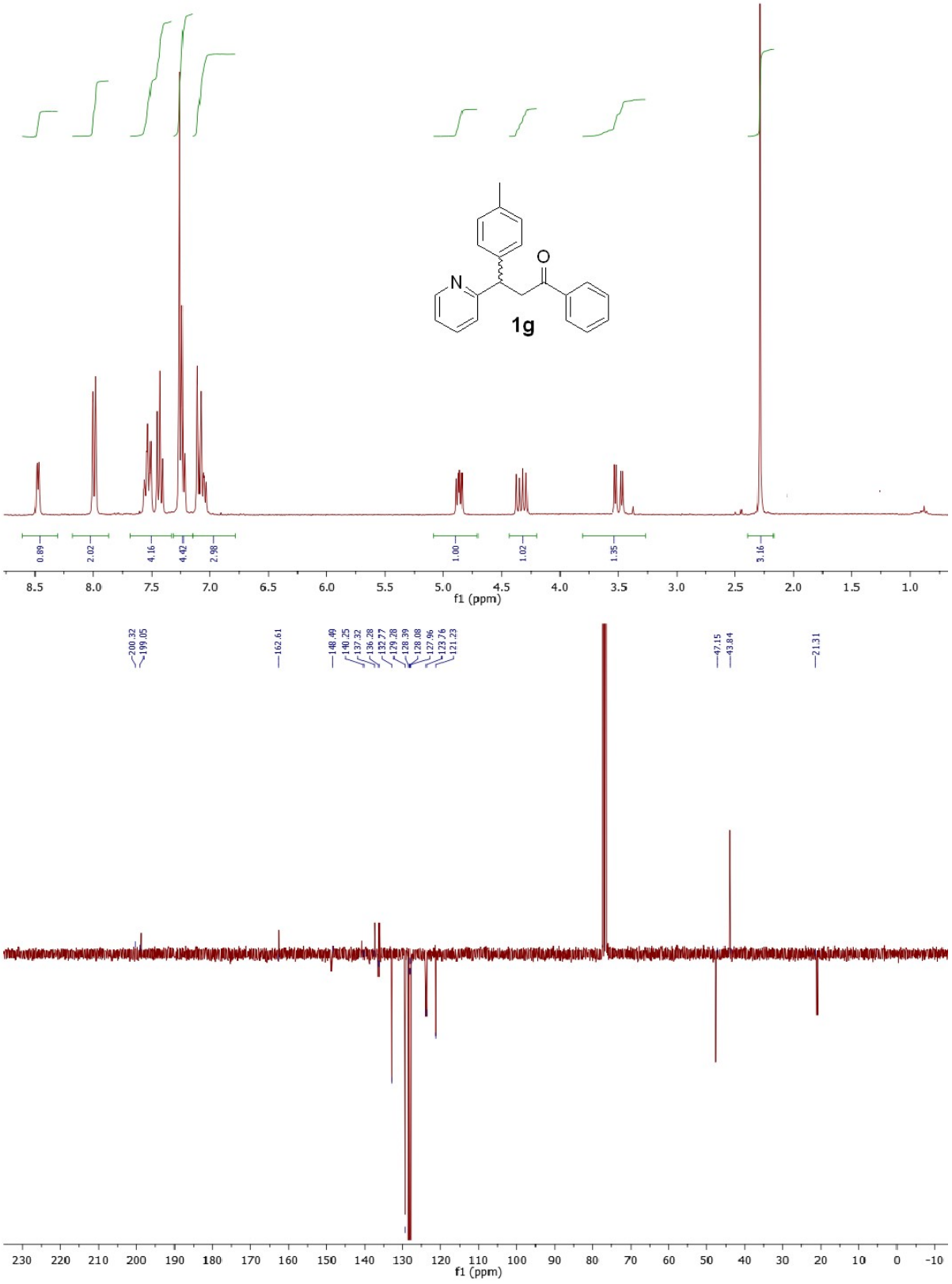


Figure S18: ^{1}H- and ^{13}C-NMR spectra of **1g.**

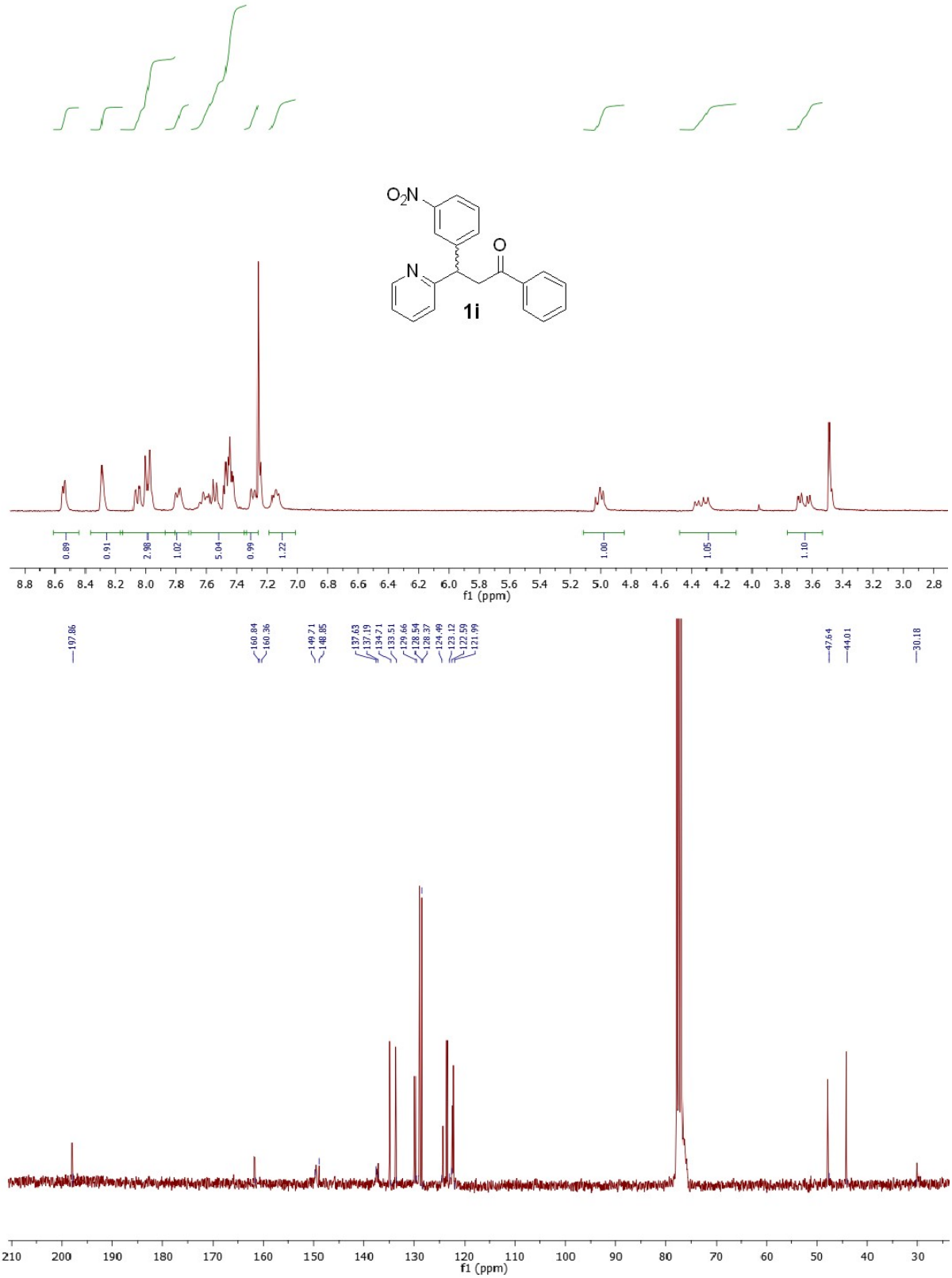


Figure S19: ^{1}H- and ^{13}C-NMR spectra of **1i.**

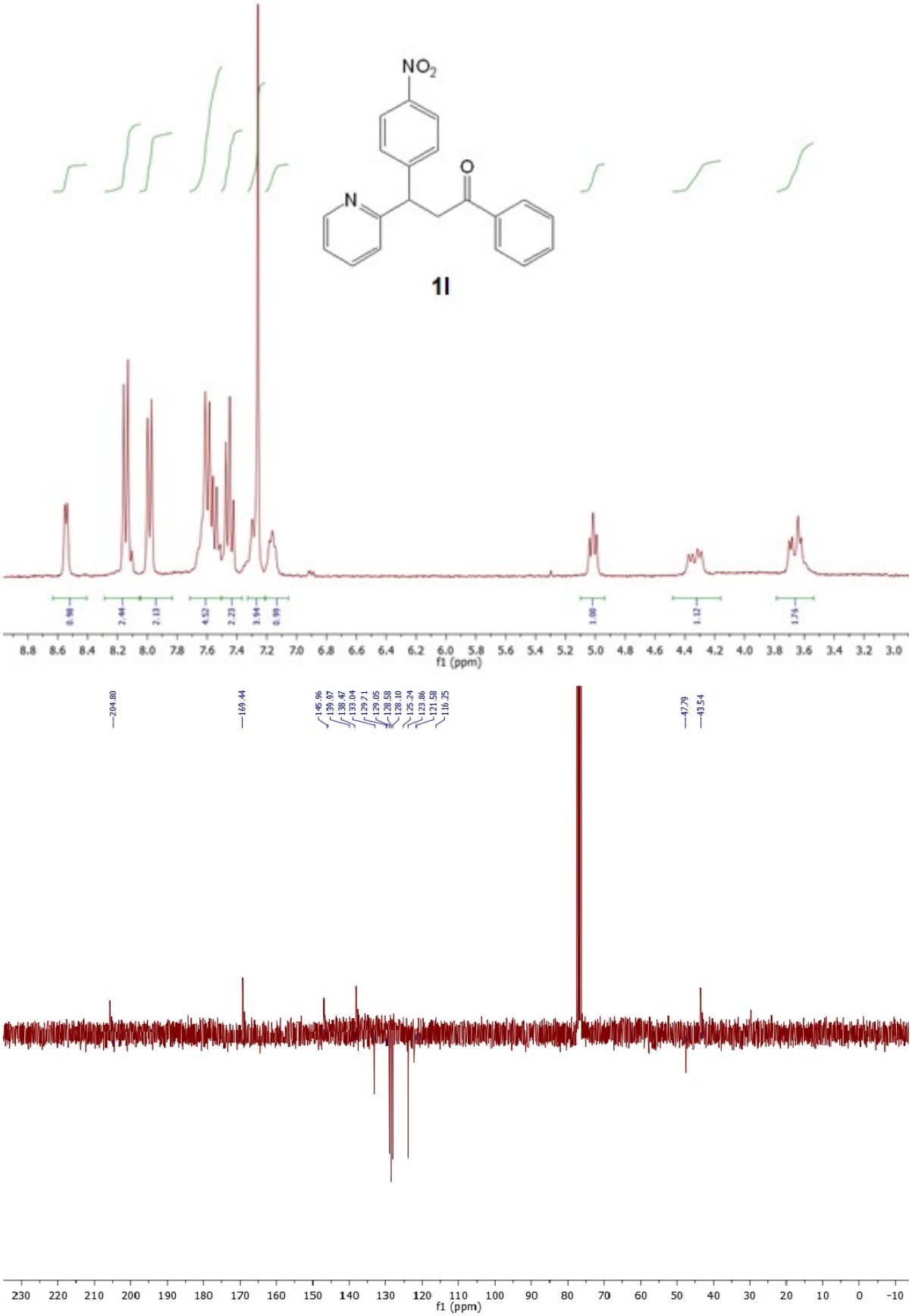


Figure S20: ^{1}H- and ^{13}C-NMR spectra of **1l.**

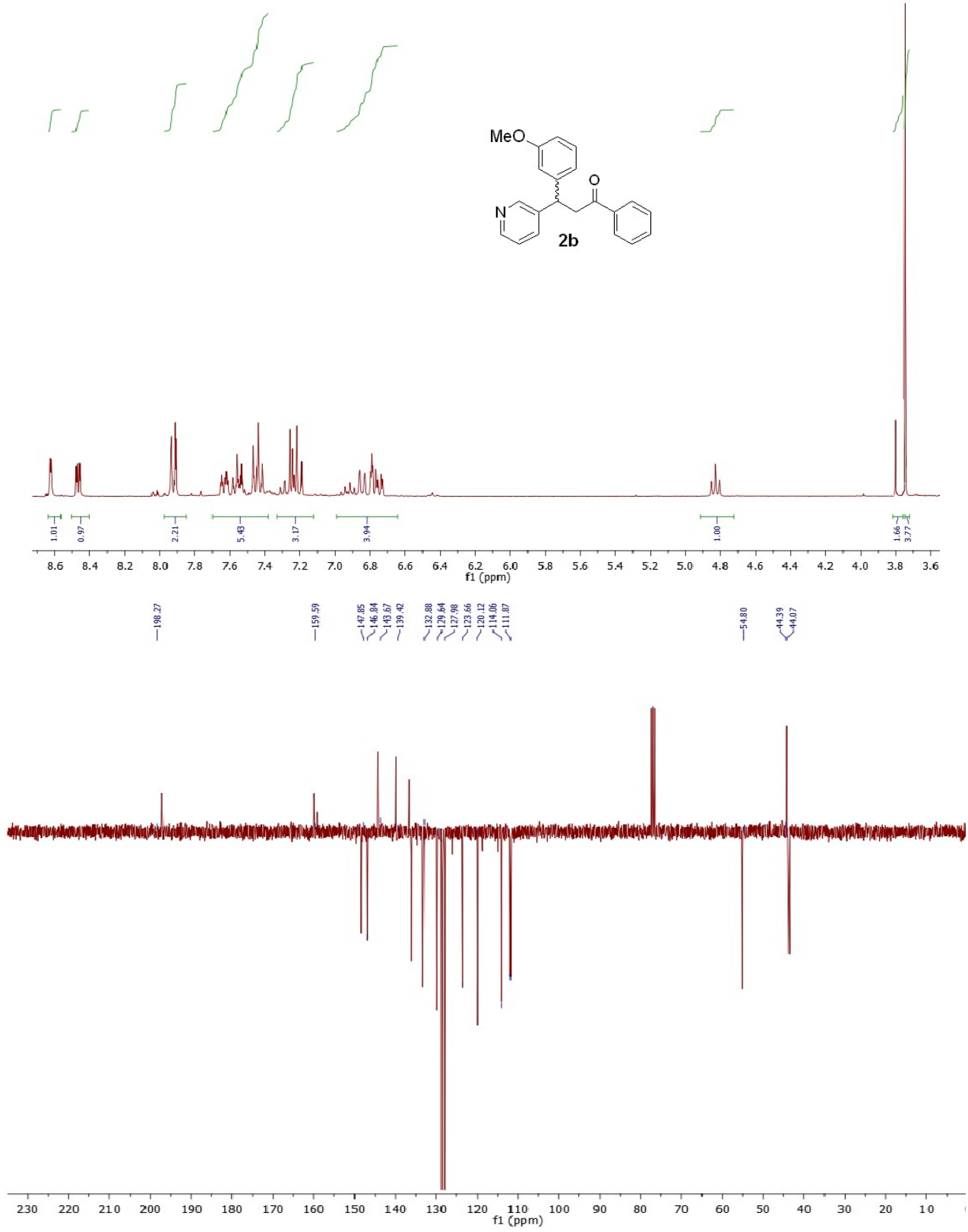


Figure S21: ^{1}H- and ^{13}C-NMR spectra of **2b.**

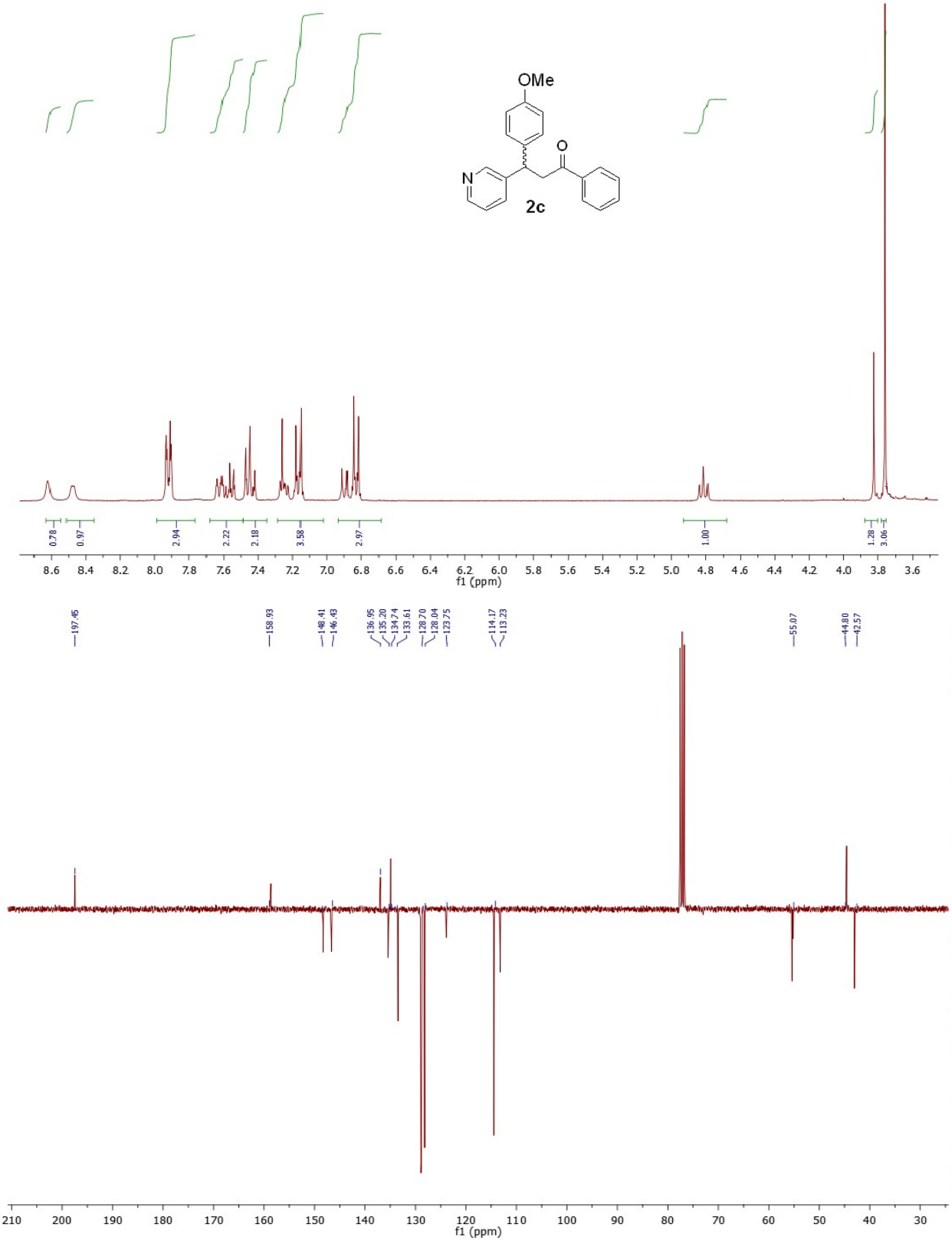


Figure S22: ^{1}H- and ^{13}C-NMR spectra of **2c.**

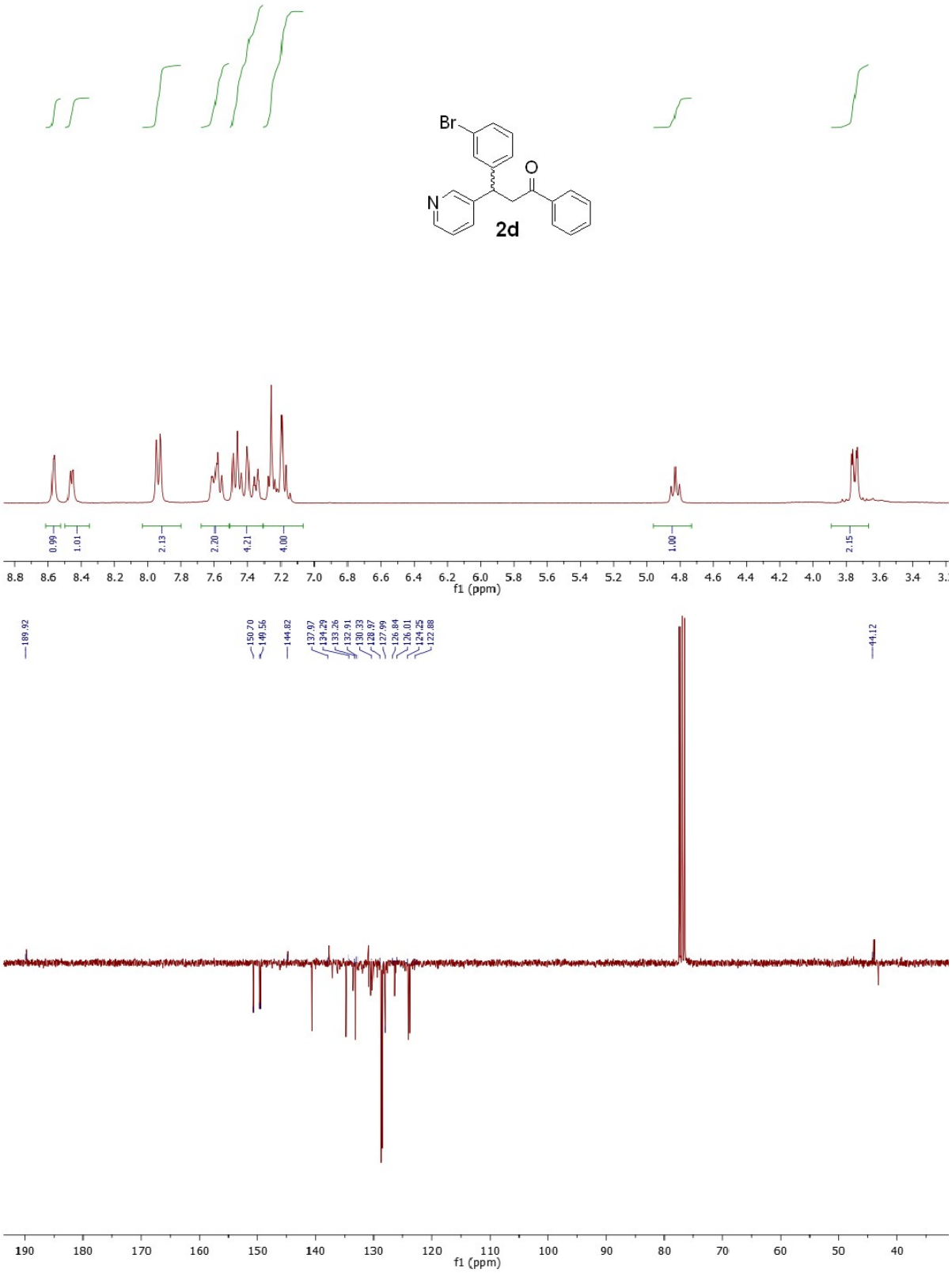


Figure S23: ^{1}H- and ^{13}C-NMR spectra of **2d.**

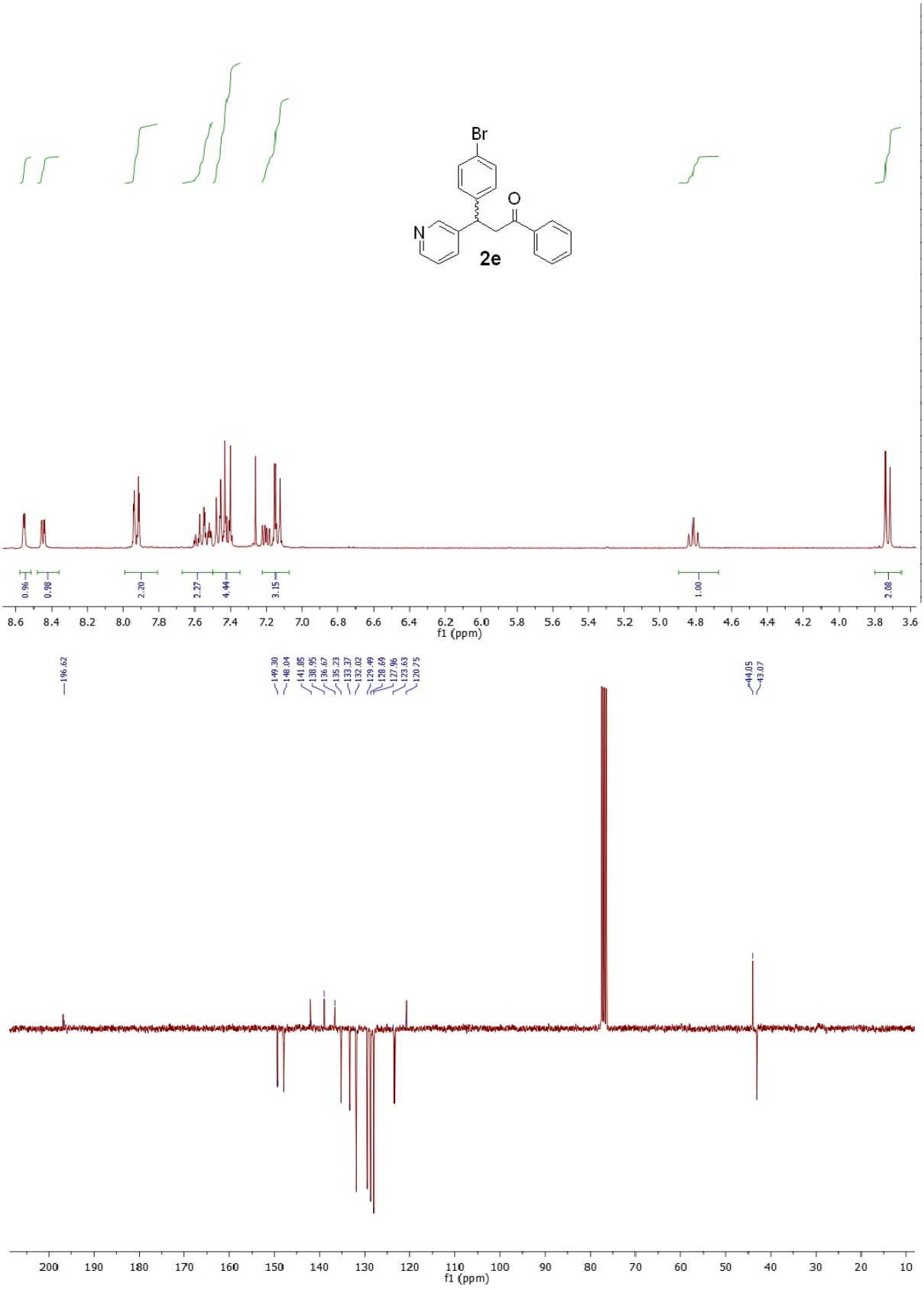


Figure S24: ^{1}H- and ^{13}C-NMR spectra of **2e.**

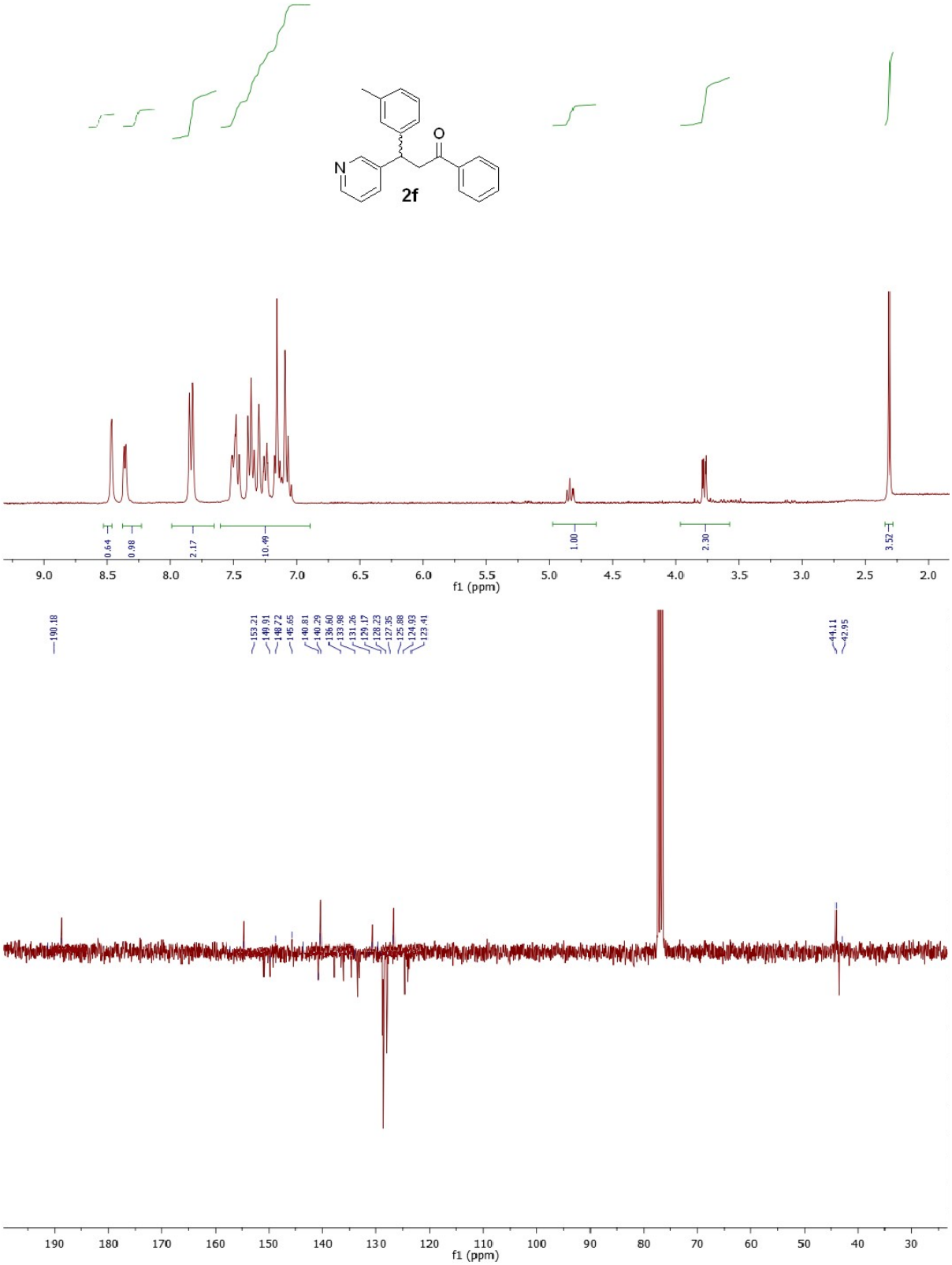


Figure S25: ^{1}H- and ^{13}C-NMR spectra of **2f.**

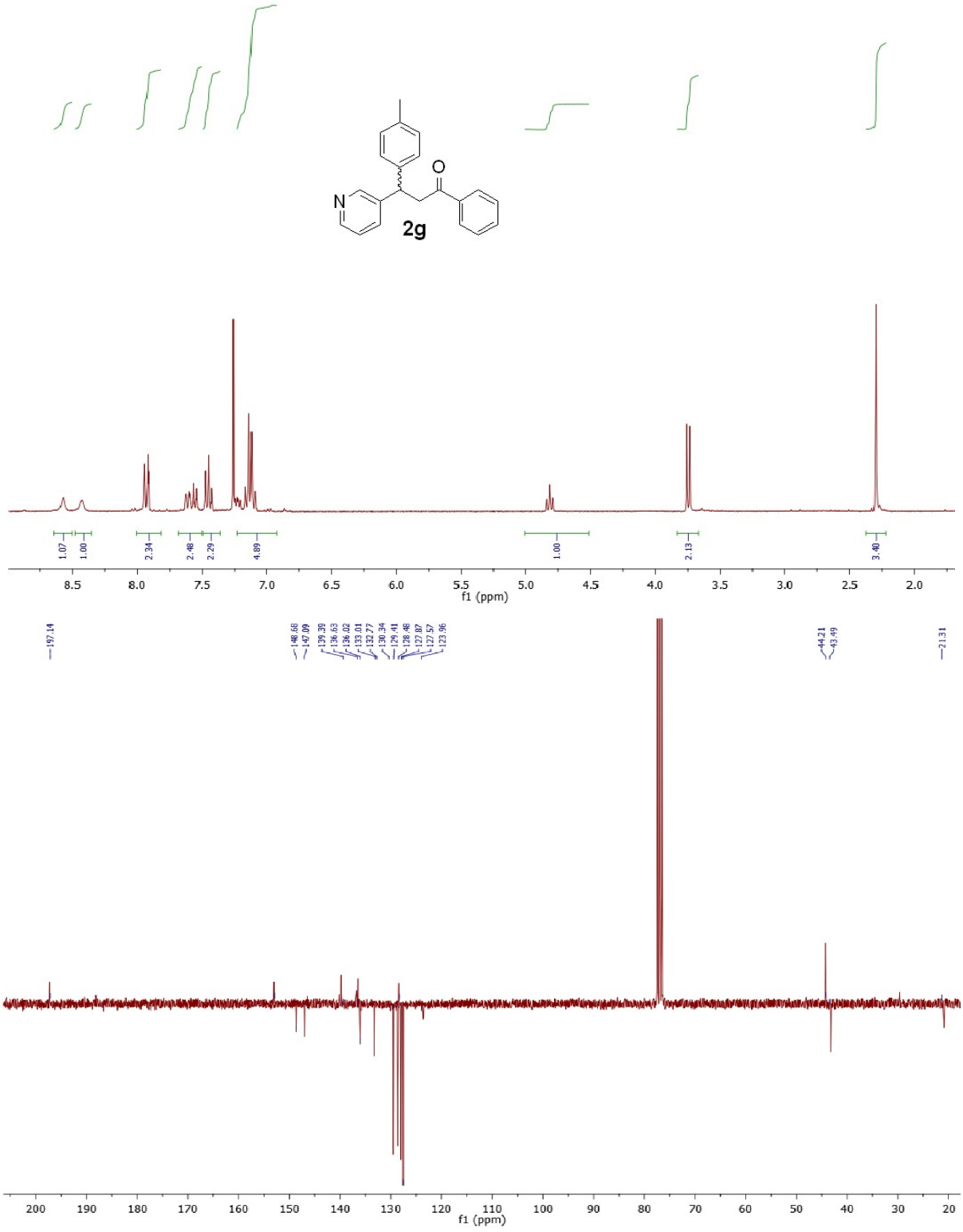


Figure S26: ^{1}H- and ^{13}C-NMR spectra of **2g.**

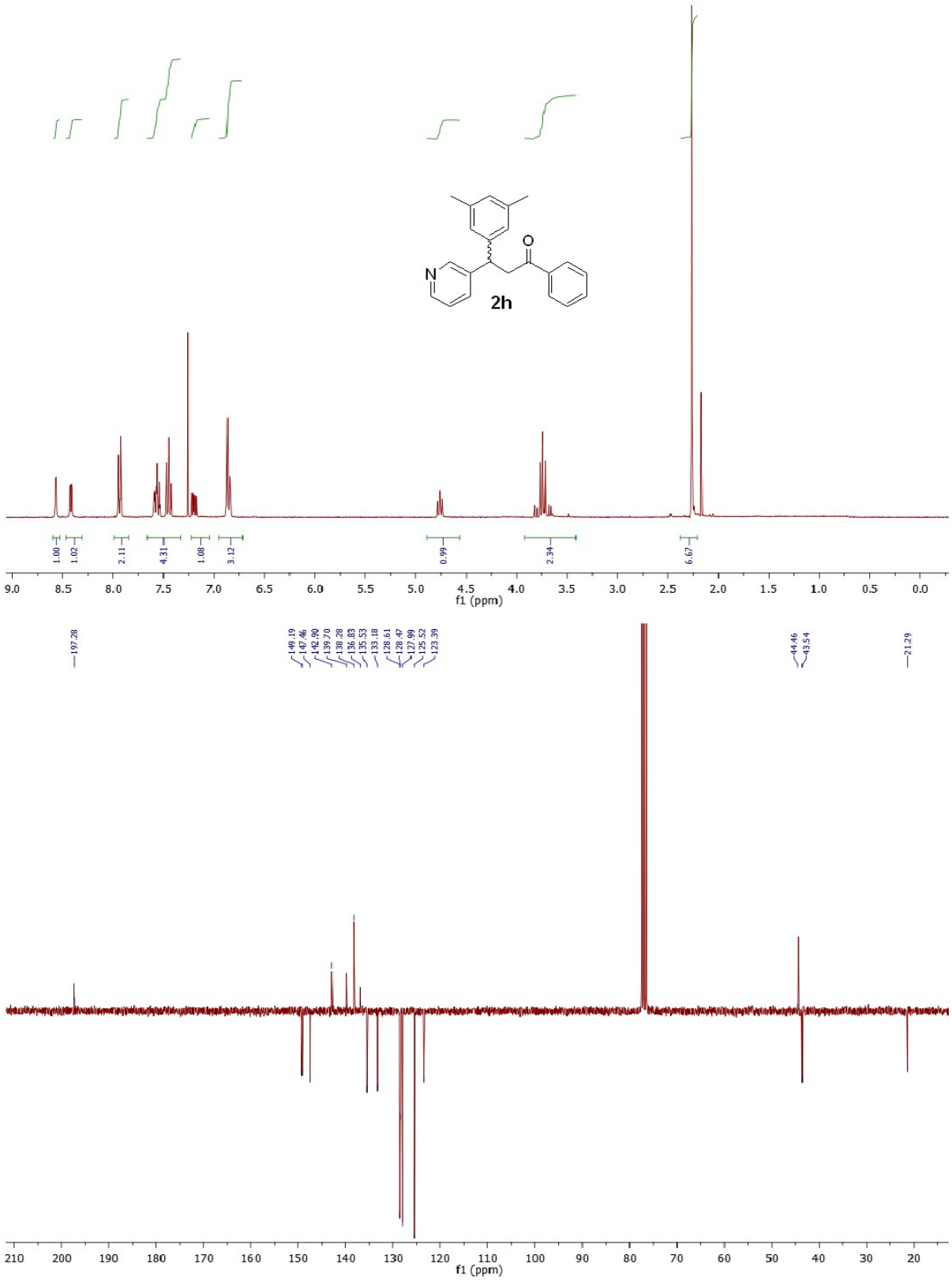


Figure S27: ^{1}H- and ^{13}C-NMR spectra of **2h.**

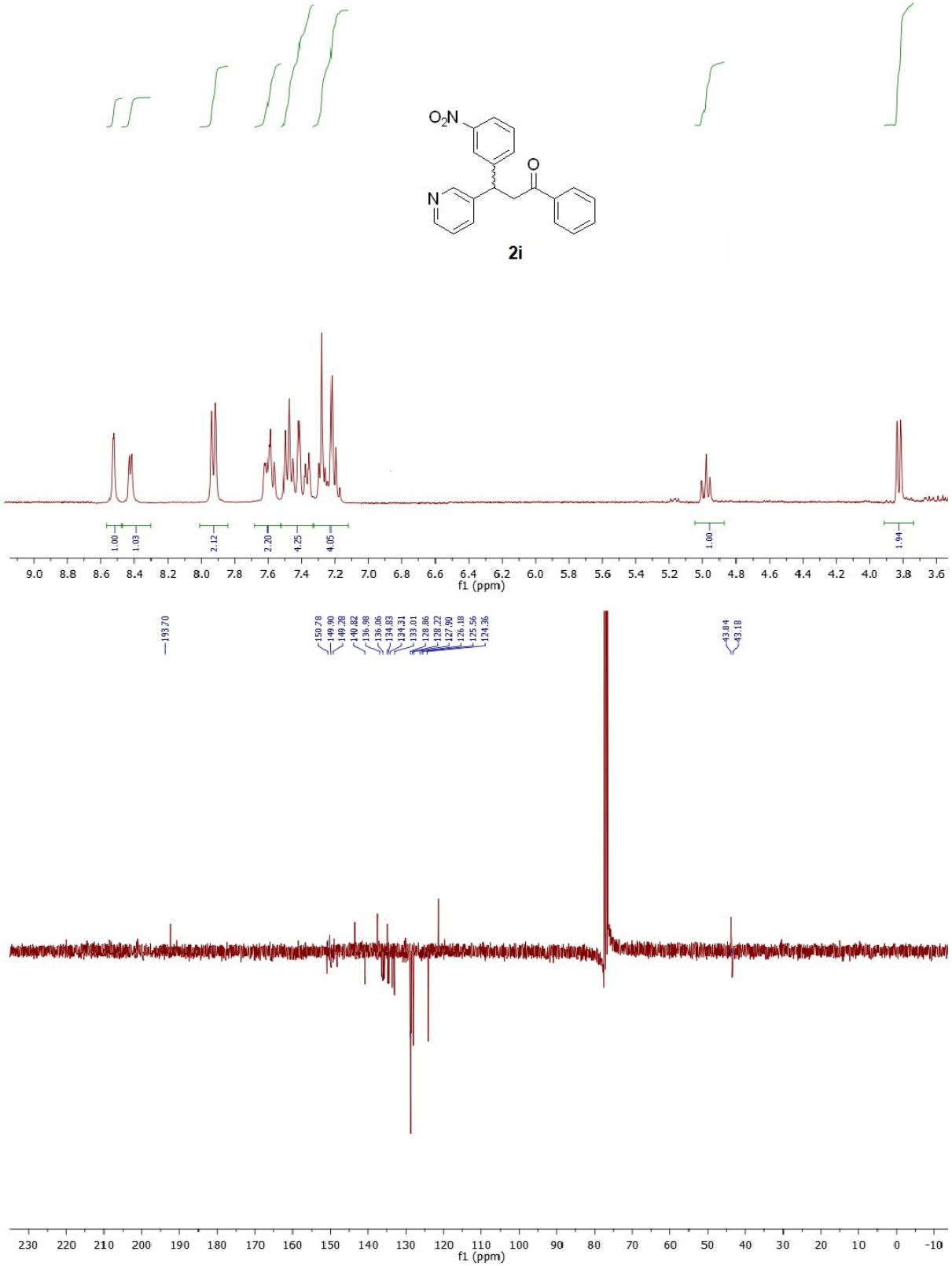


Figure S28: ^{1}H- and ^{13}C-NMR spectra of **2i.**

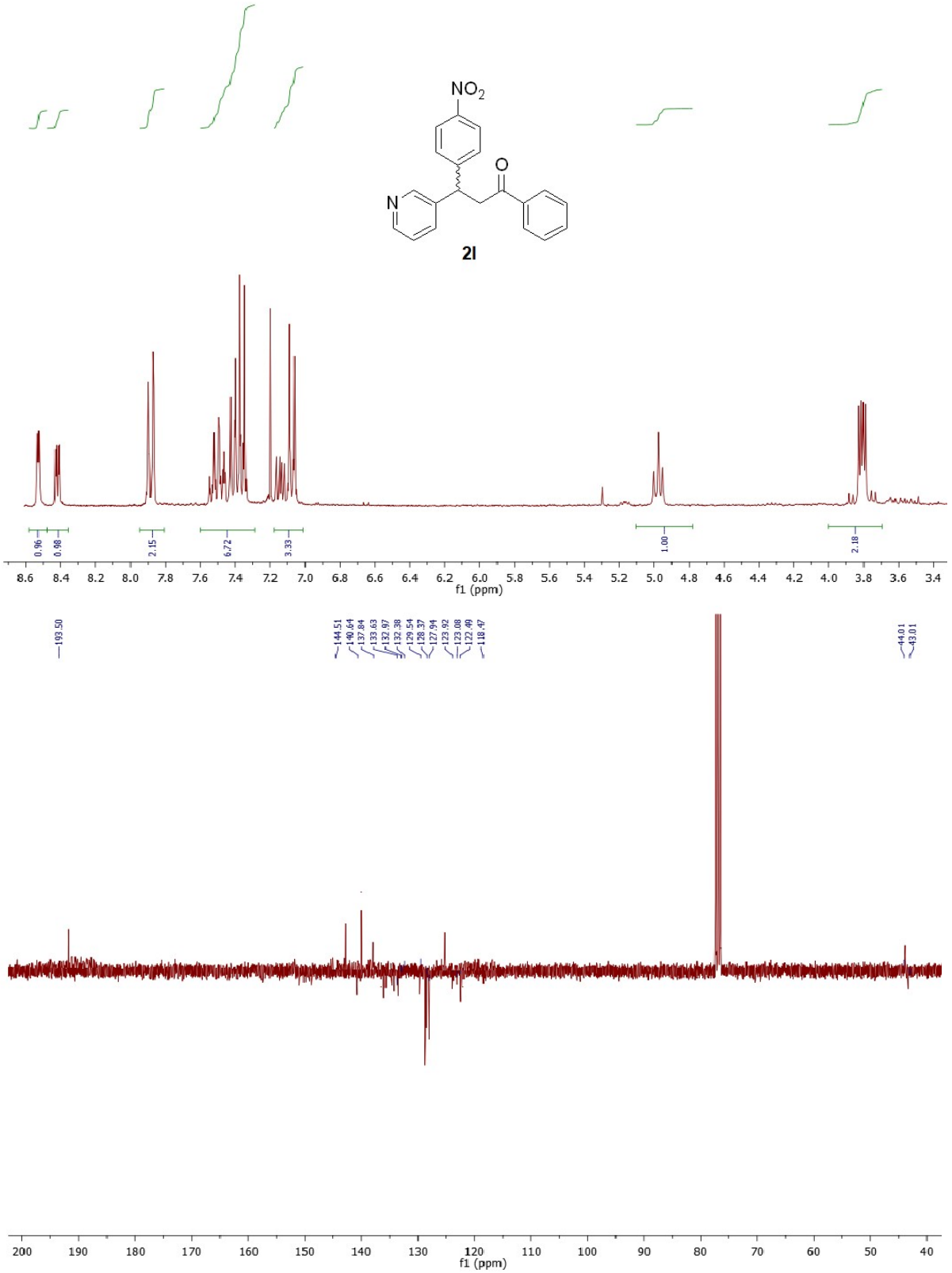


Figure S29: ^{1}H- and ^{13}C-NMR spectra of **2l.**

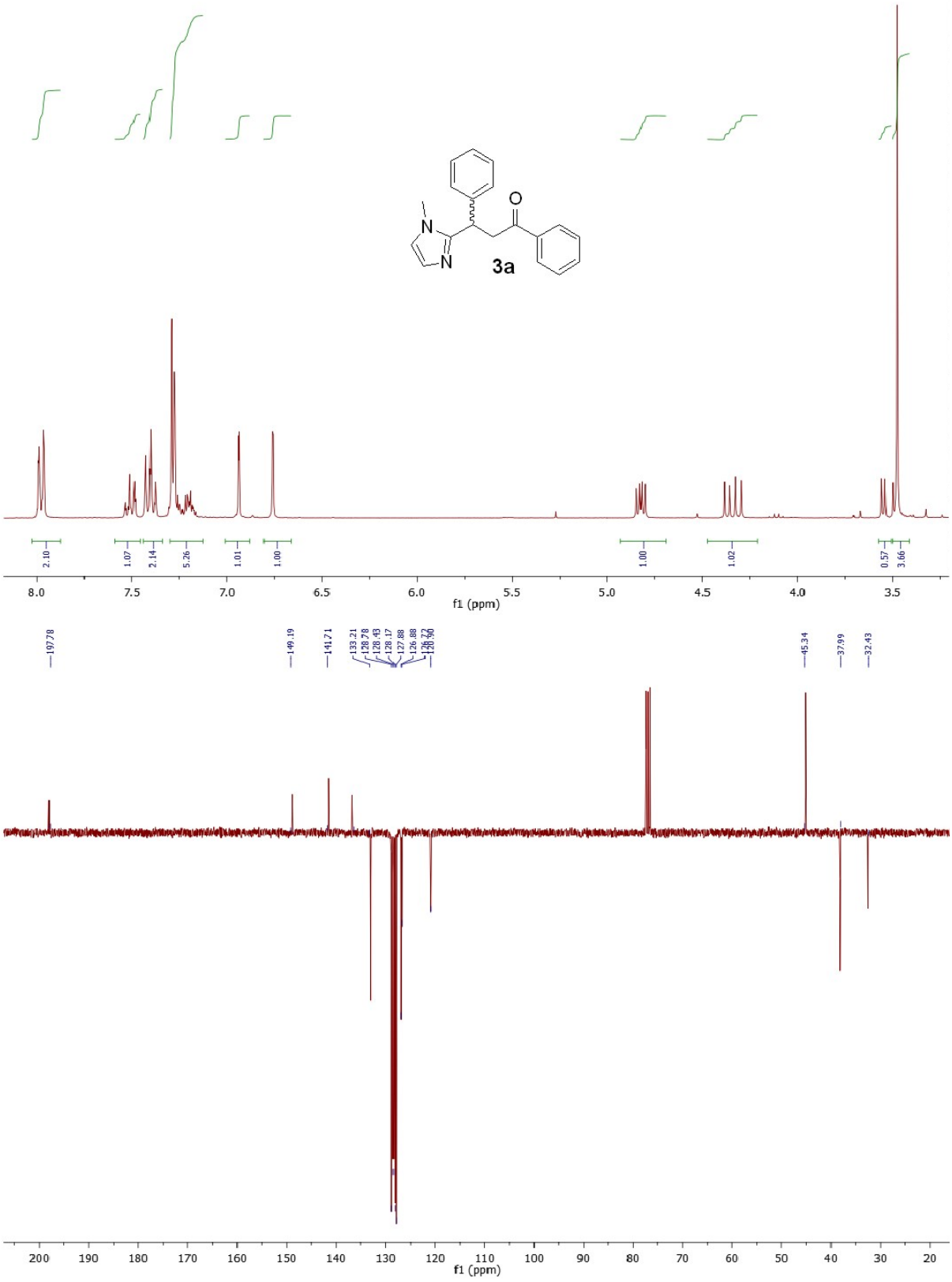


Figure S30: ^{1}H- and ^{13}C-NMR spectra of **3a.**

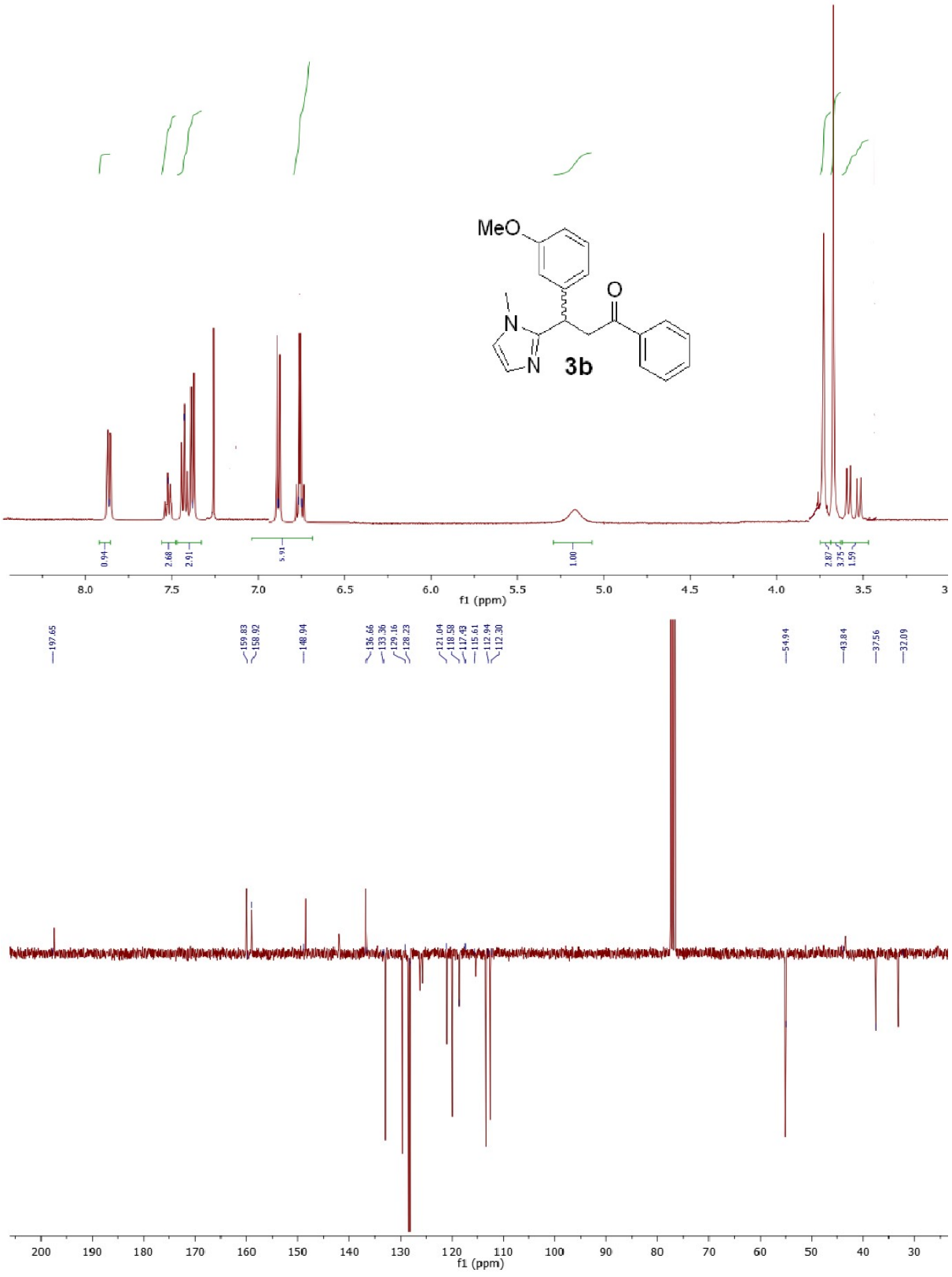


Figure S31: ^{1}H- and ^{13}C-NMR spectra of **3b.**

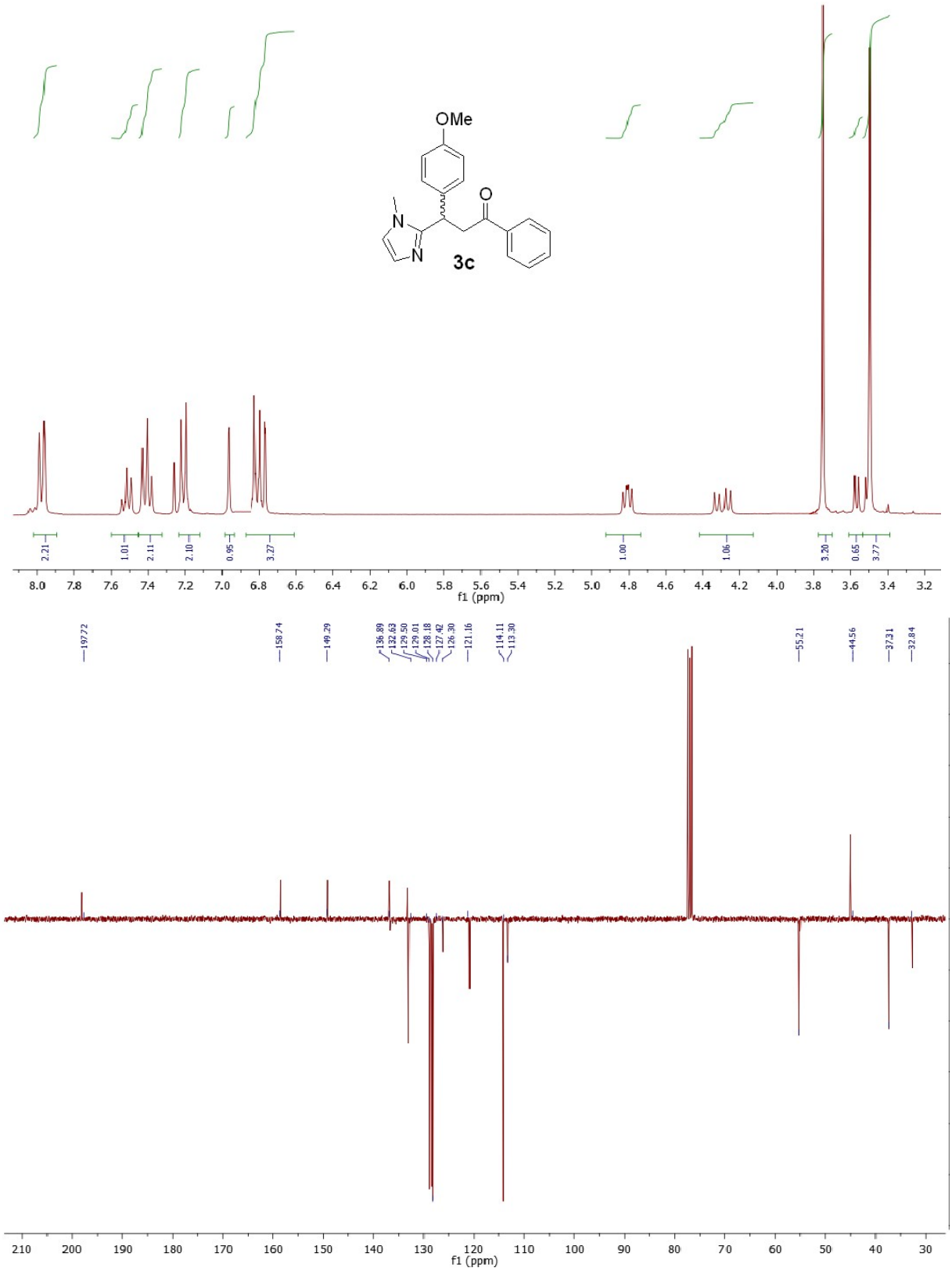


Figure S32: ^{1}H- and ^{13}C-NMR spectra of **3c.**

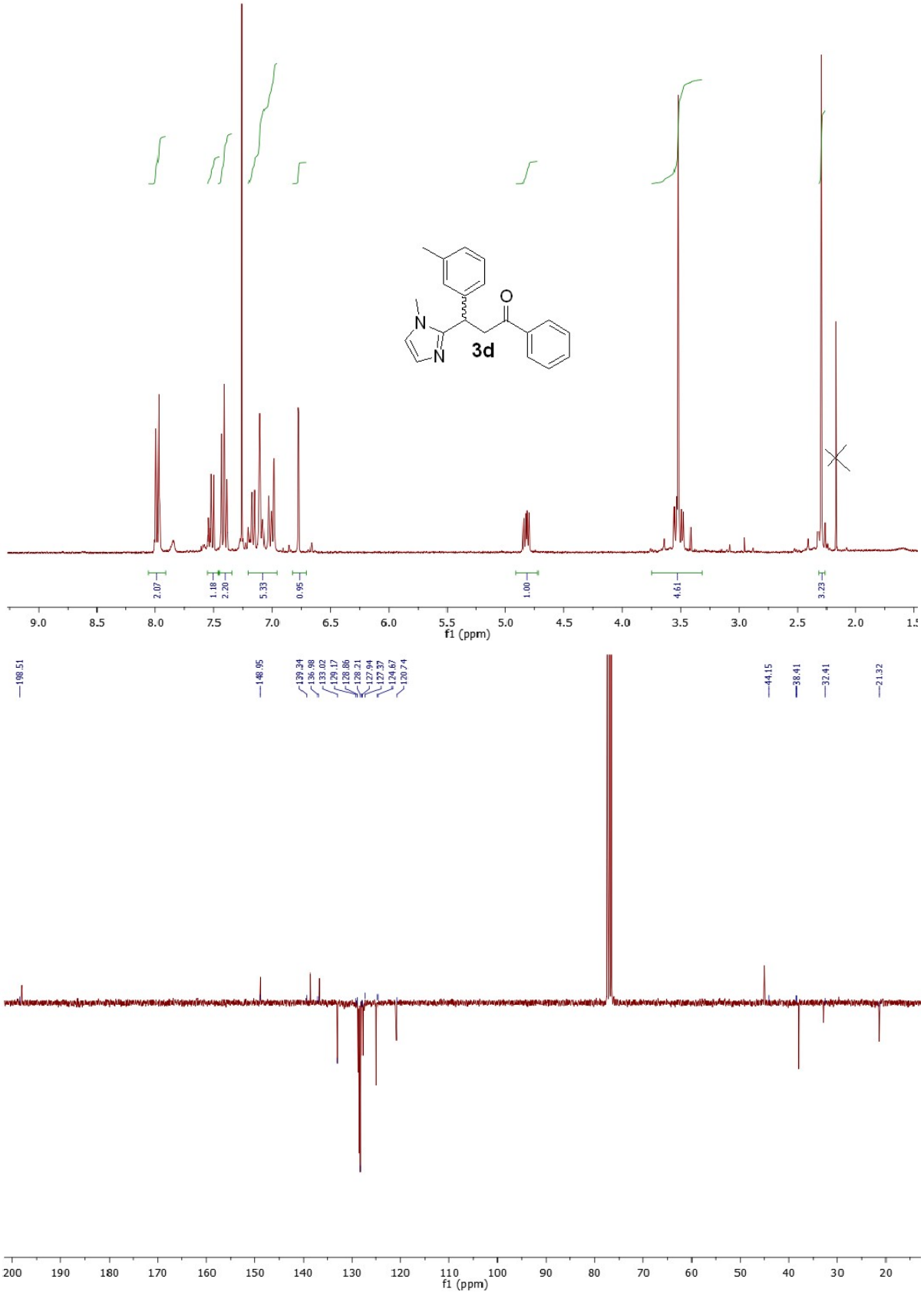


Figure S33: ^{1}H- and ^{13}C-NMR spectra of **3d.**

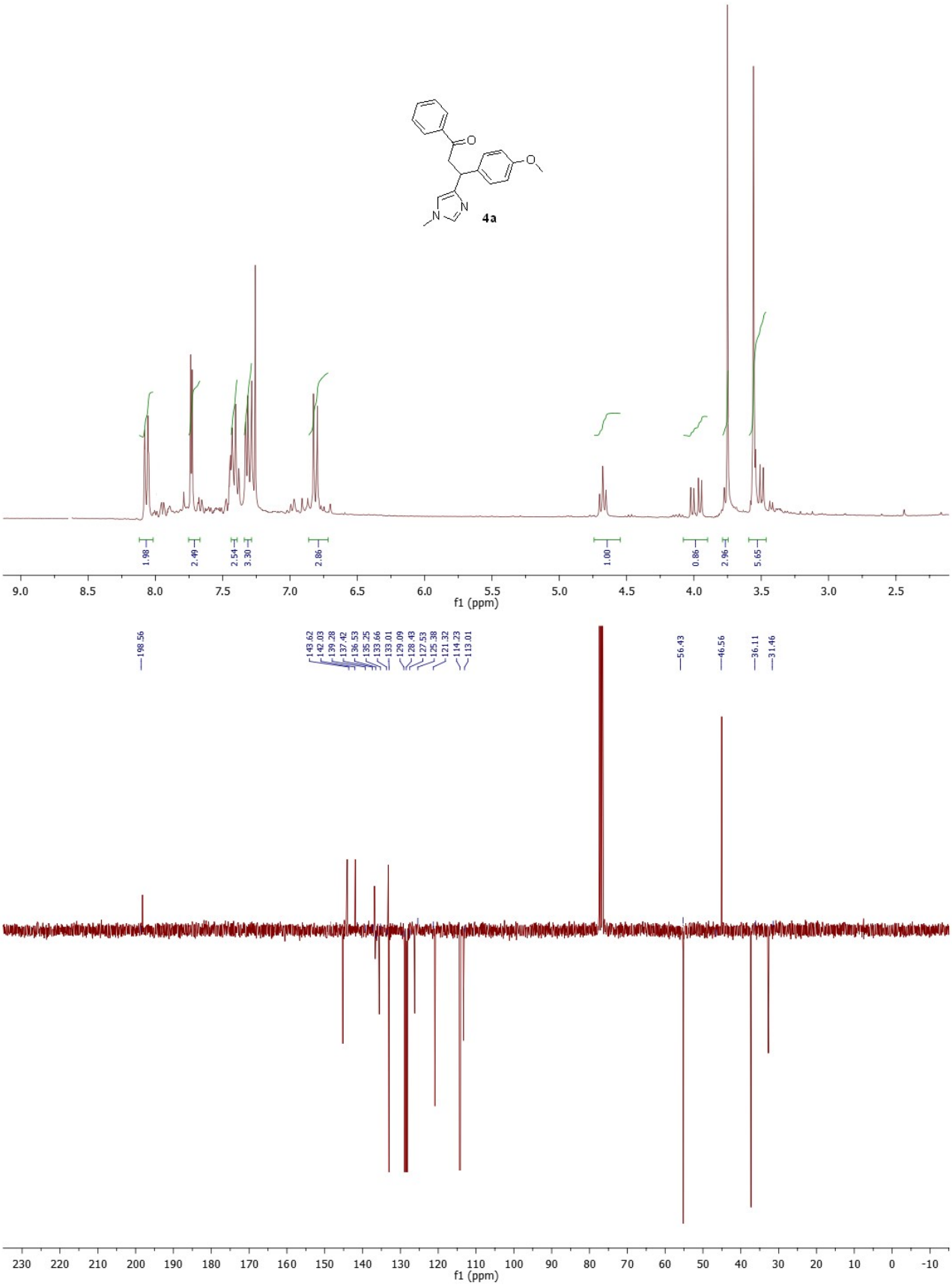
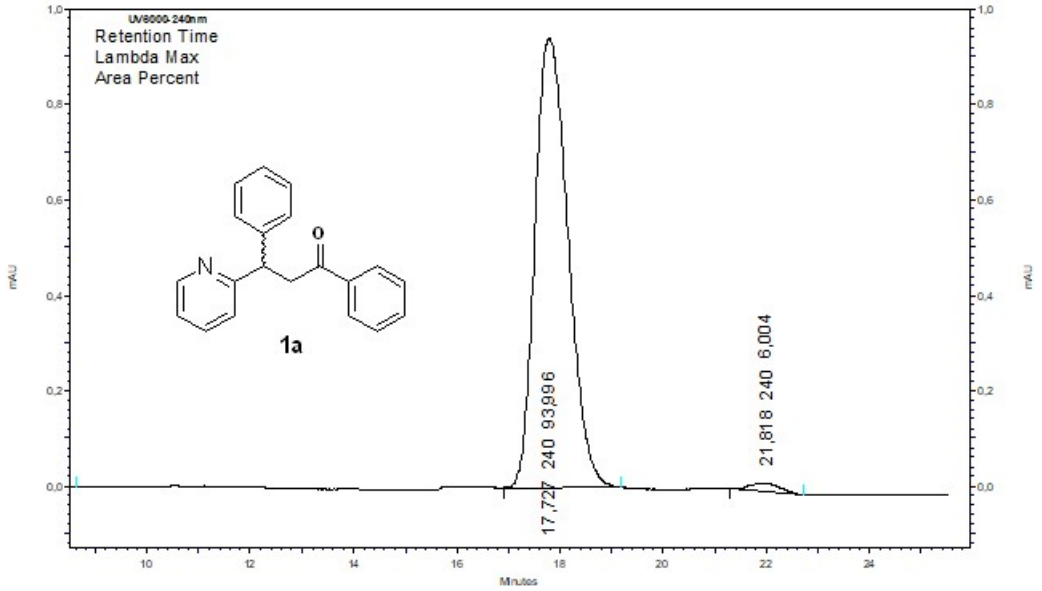
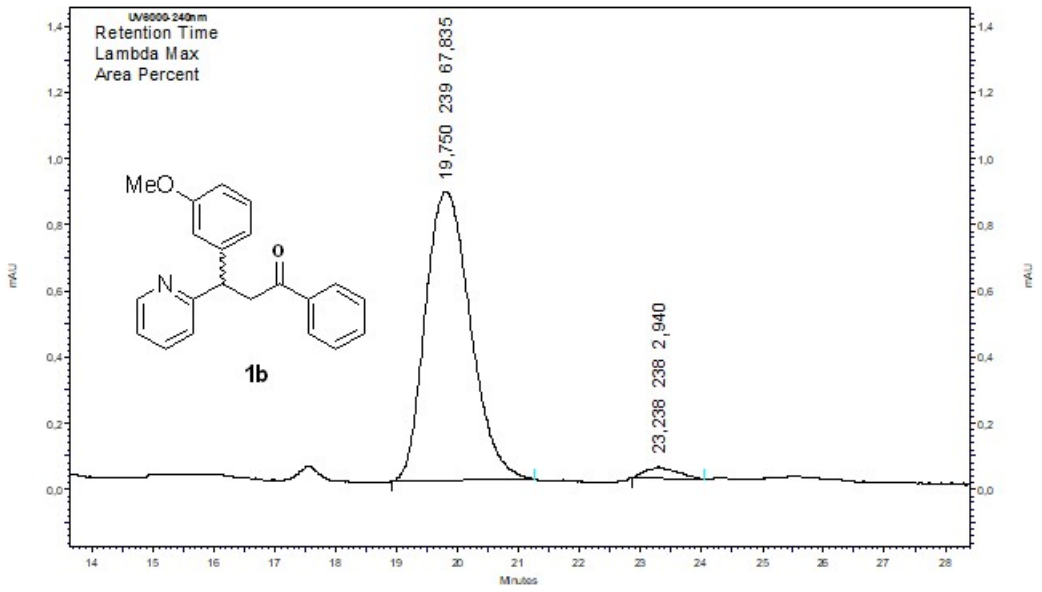
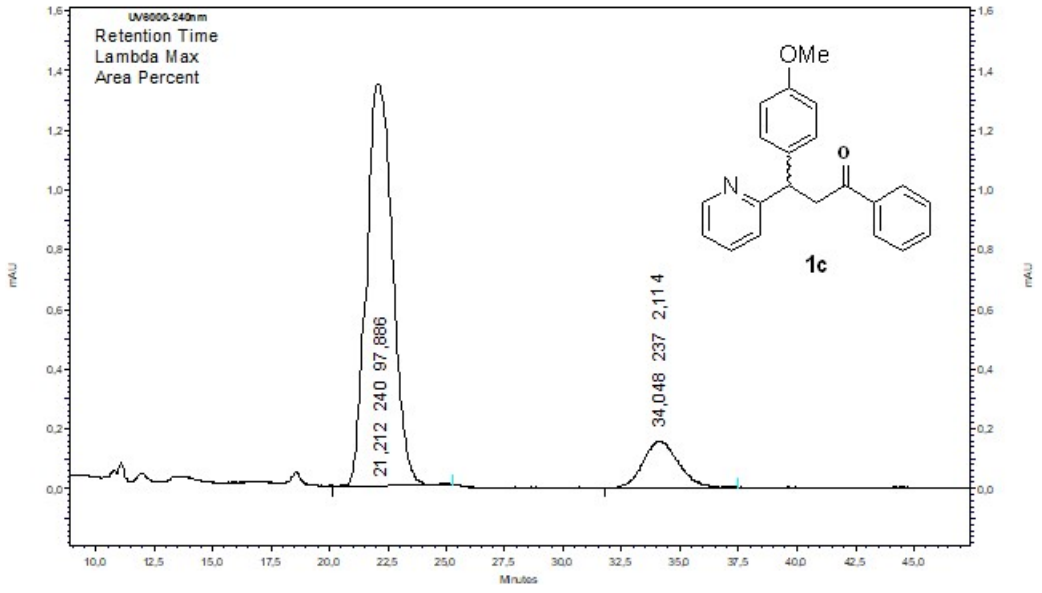


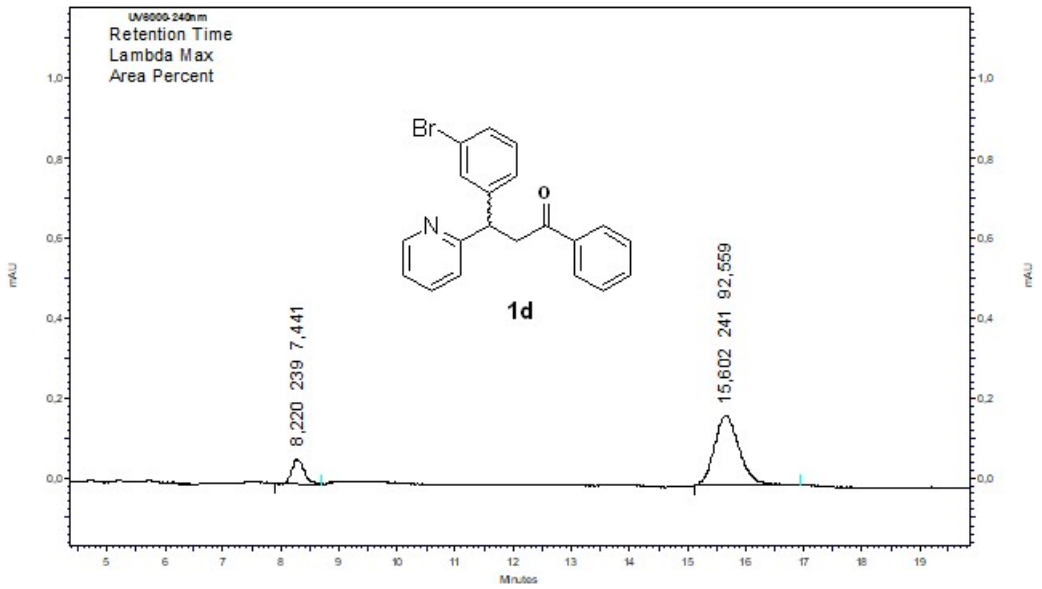
Figure S34: ^{1}H- and ^{13}C-NMR spectra of **4a.**

6. HPLC spectra of products





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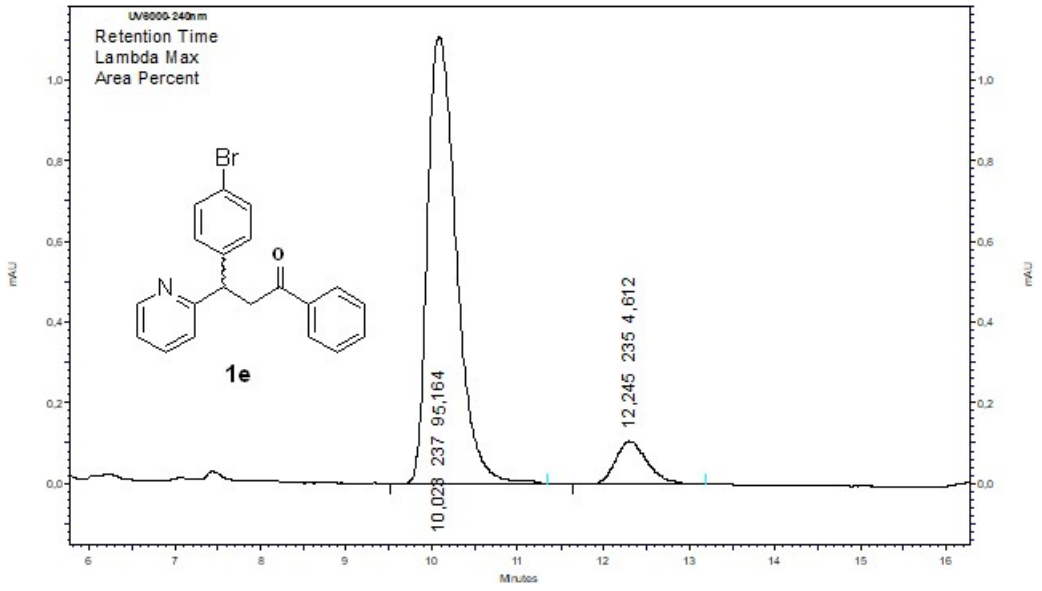
Minutes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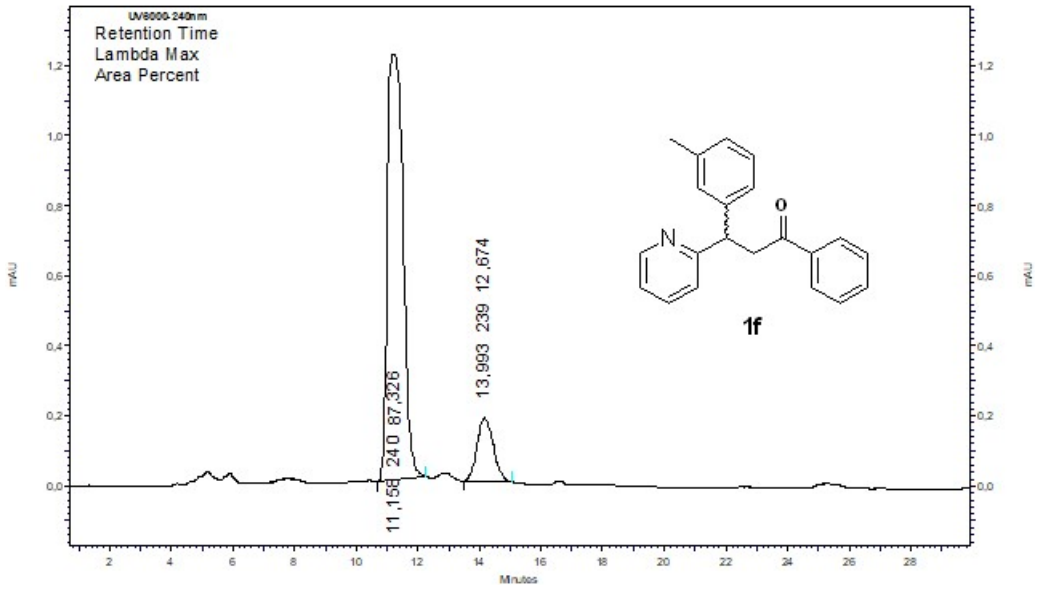
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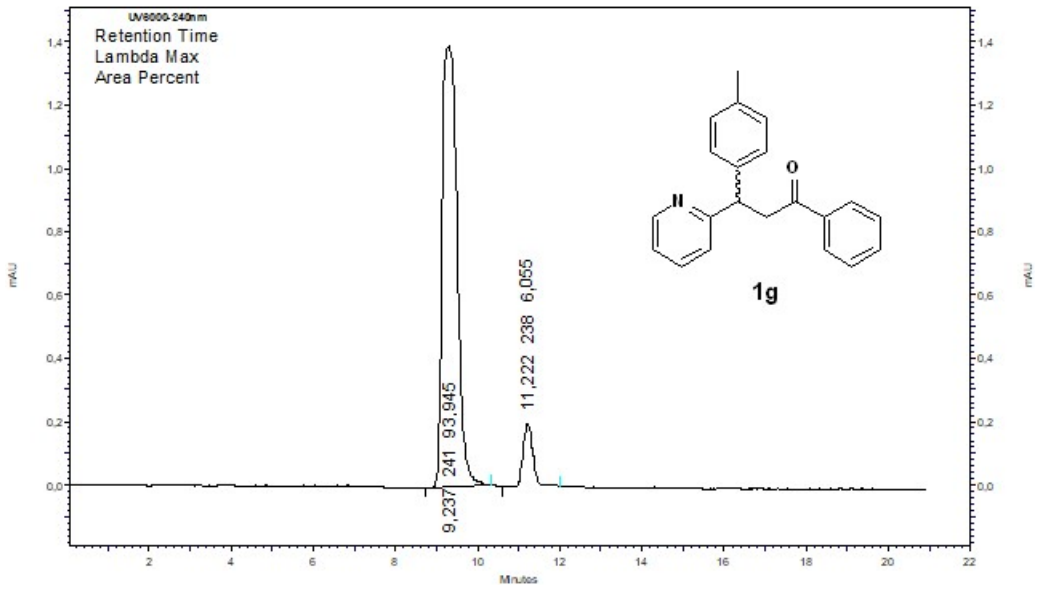
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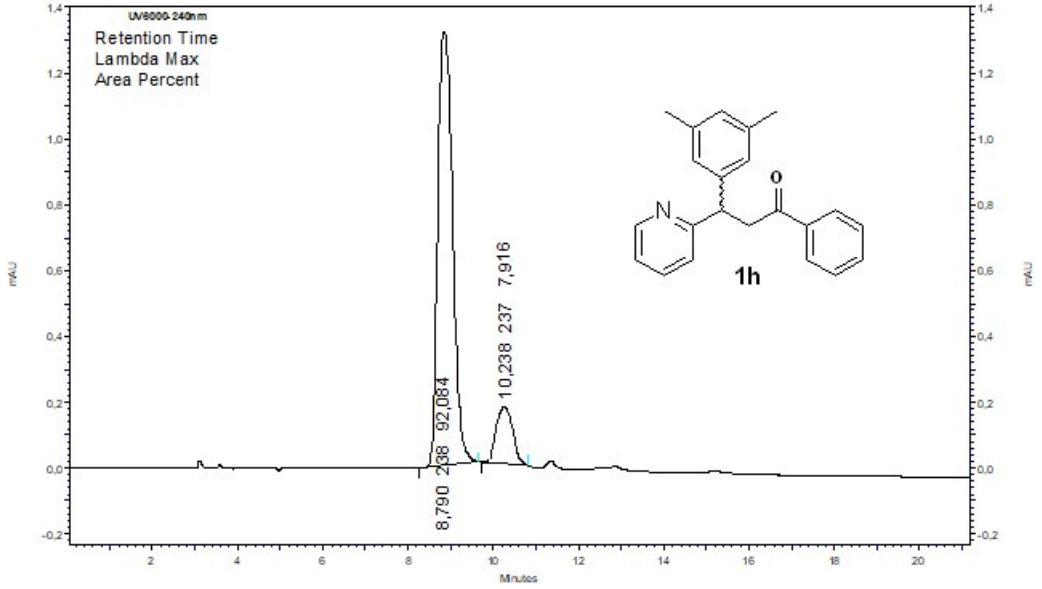
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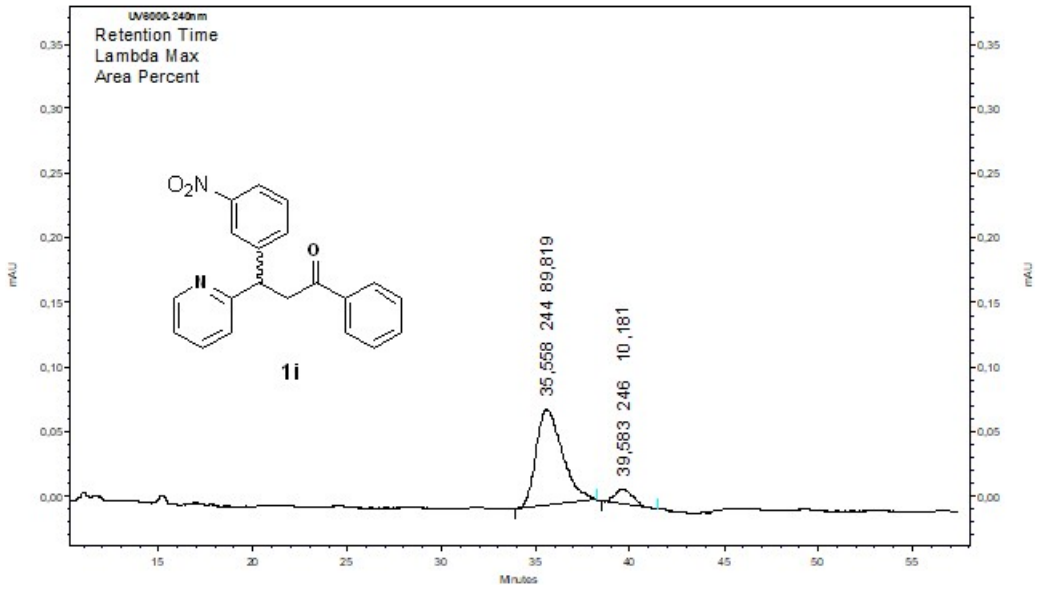
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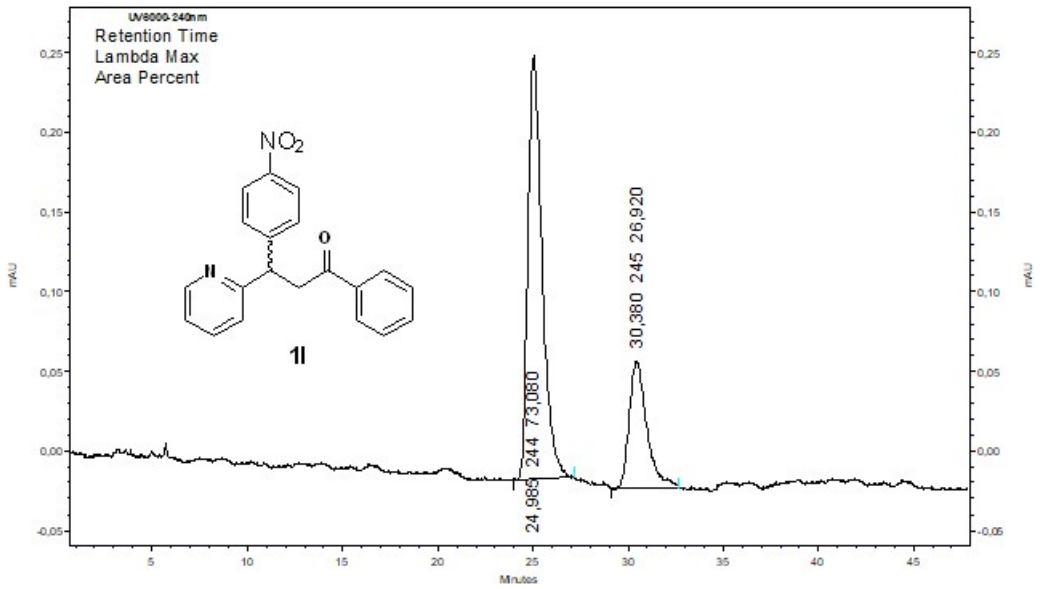
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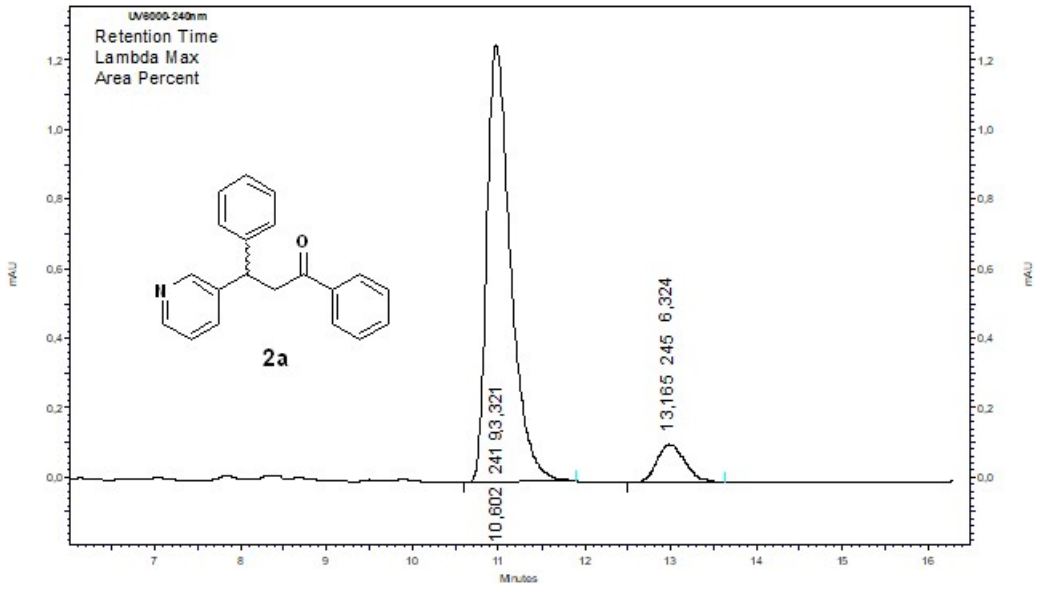
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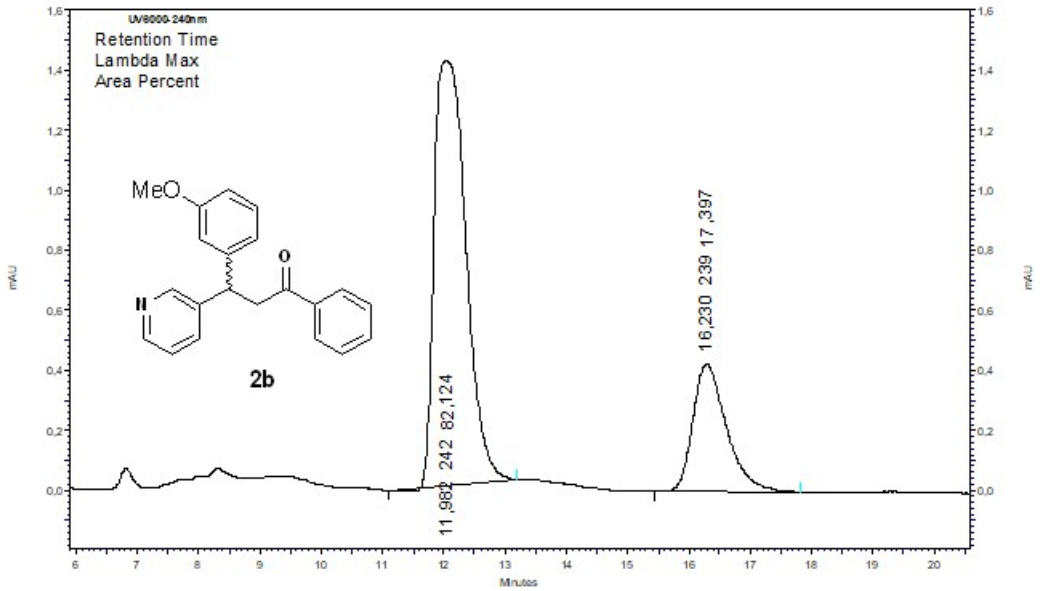
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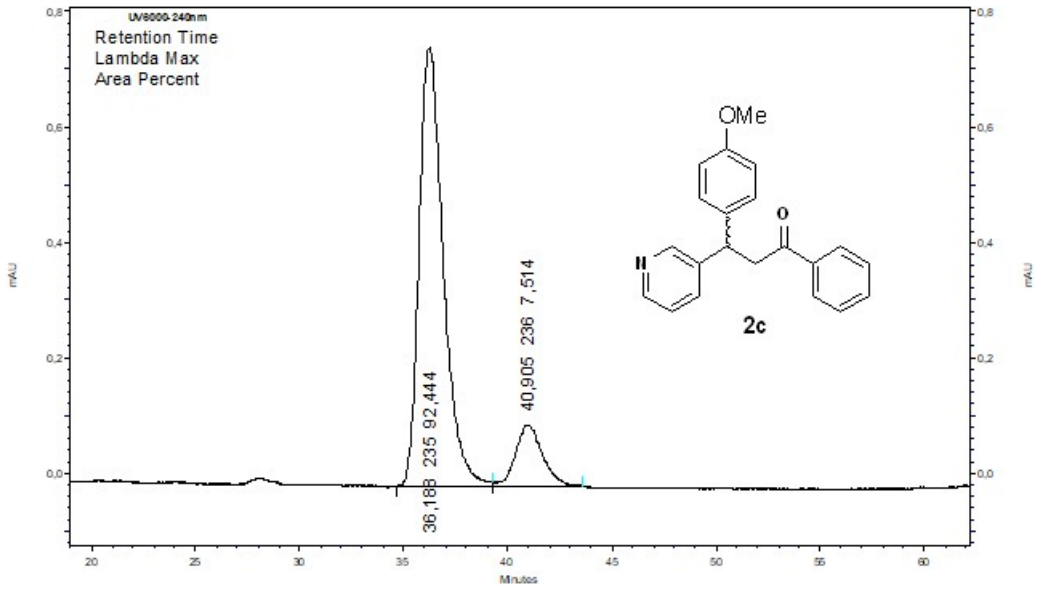
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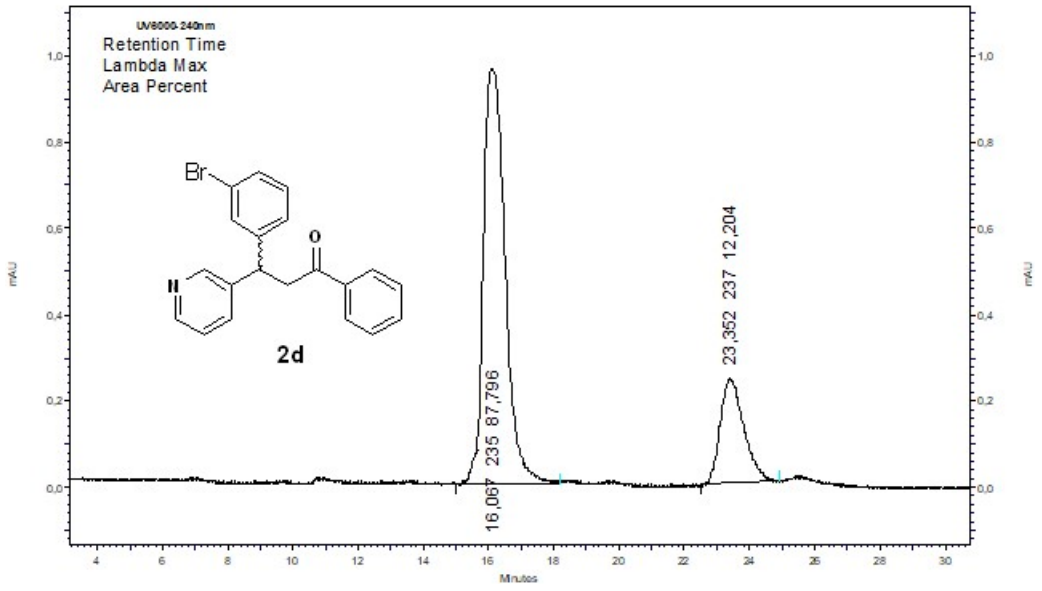
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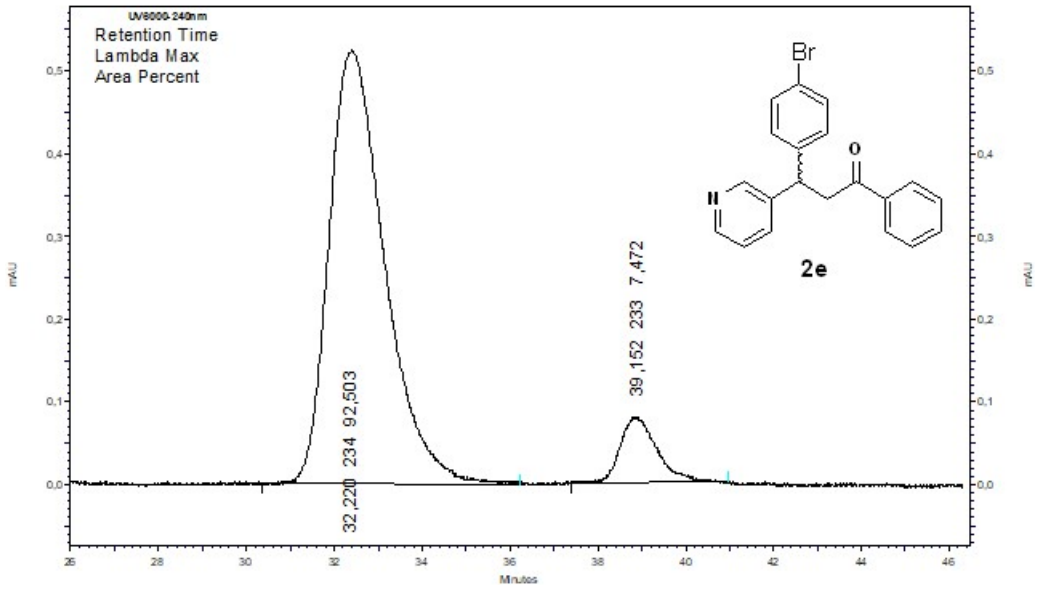
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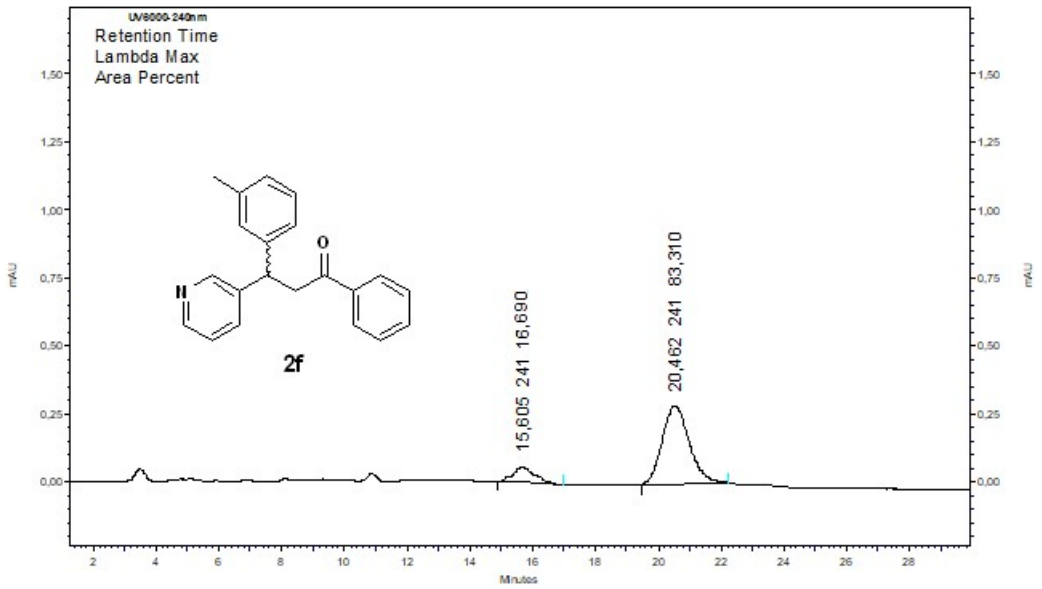
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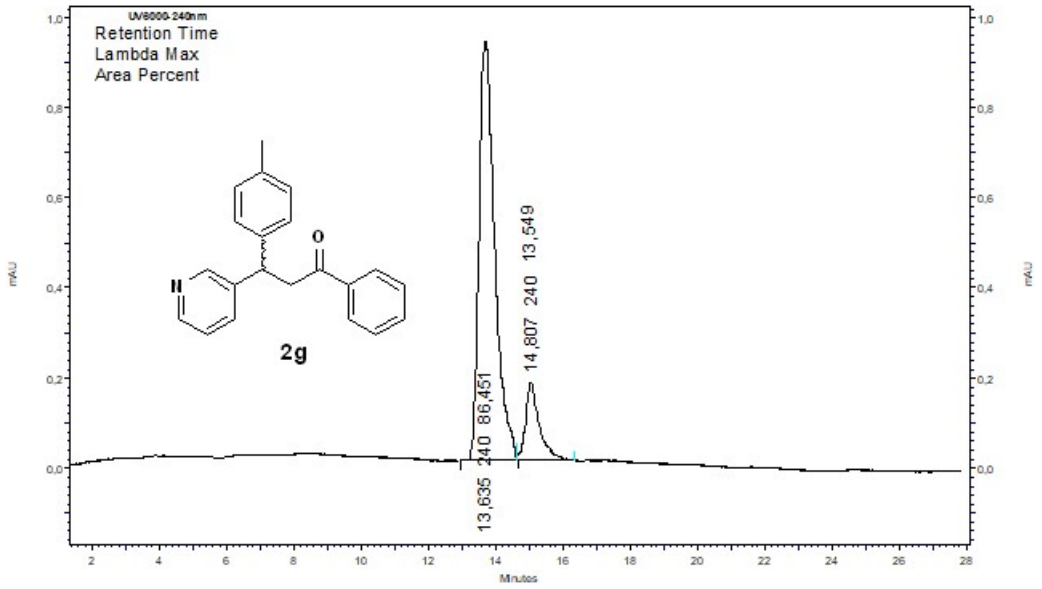
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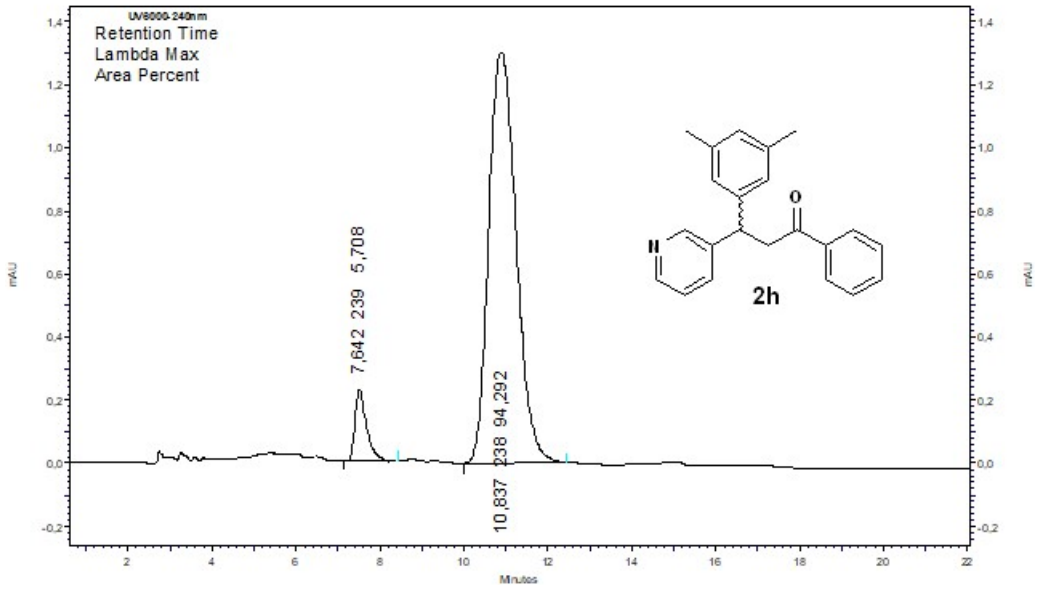
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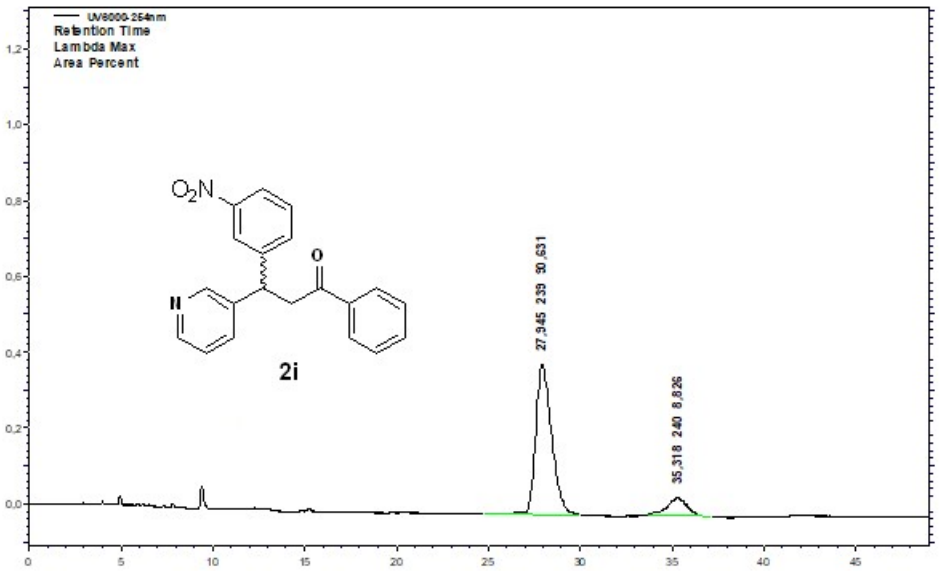
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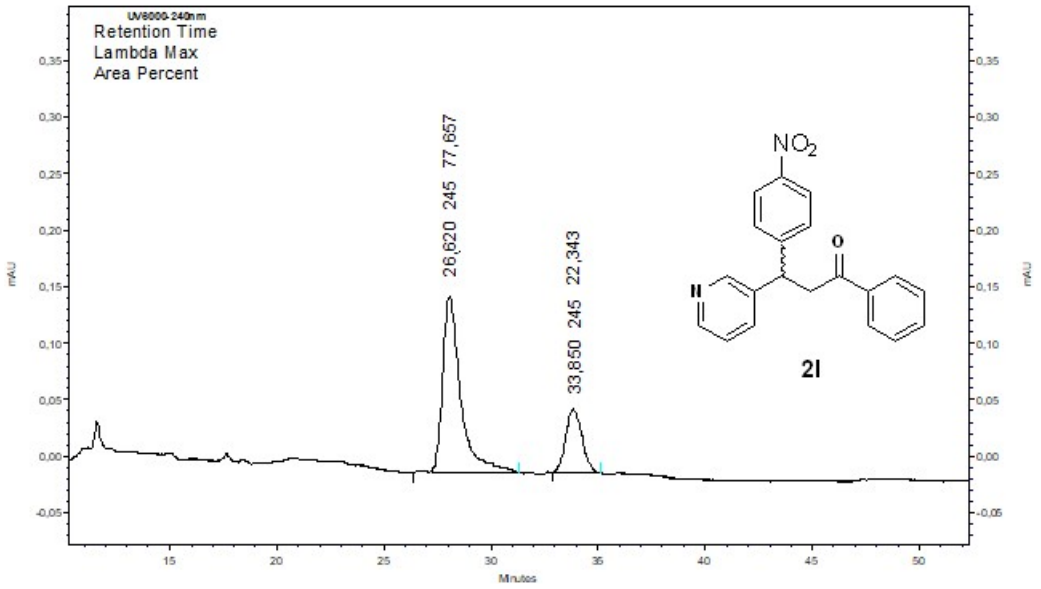
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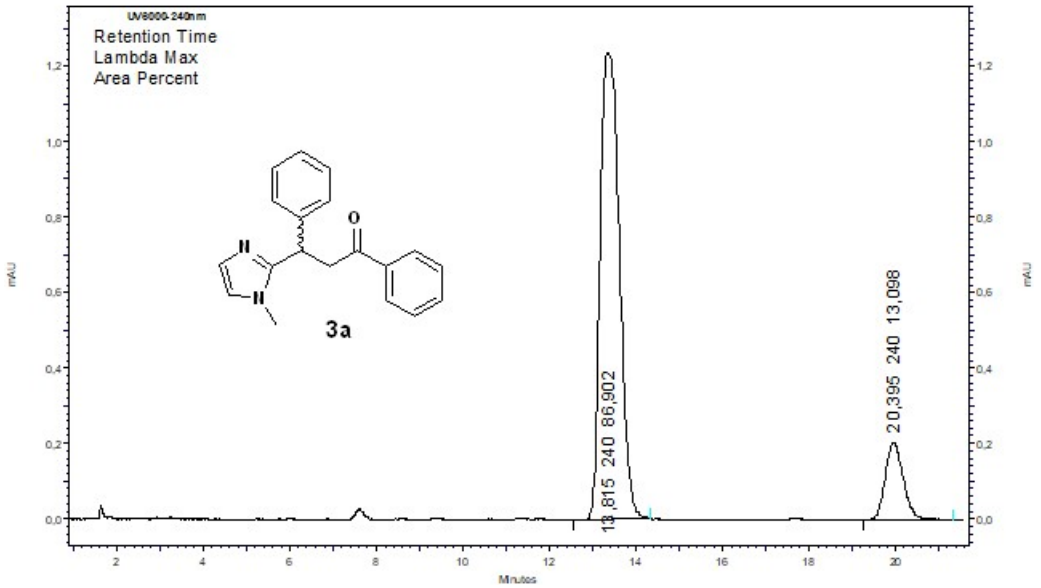
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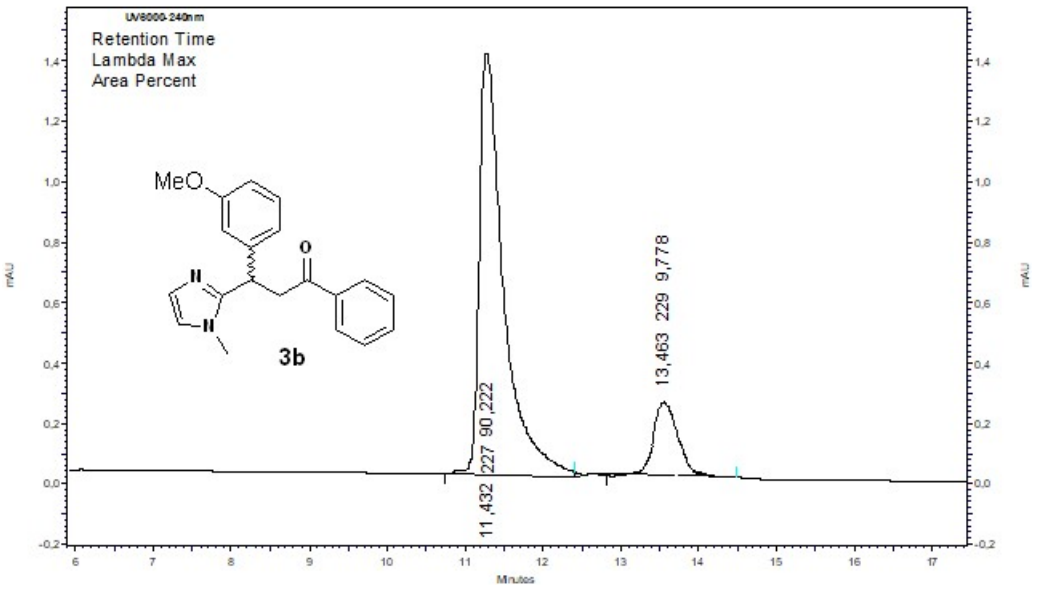
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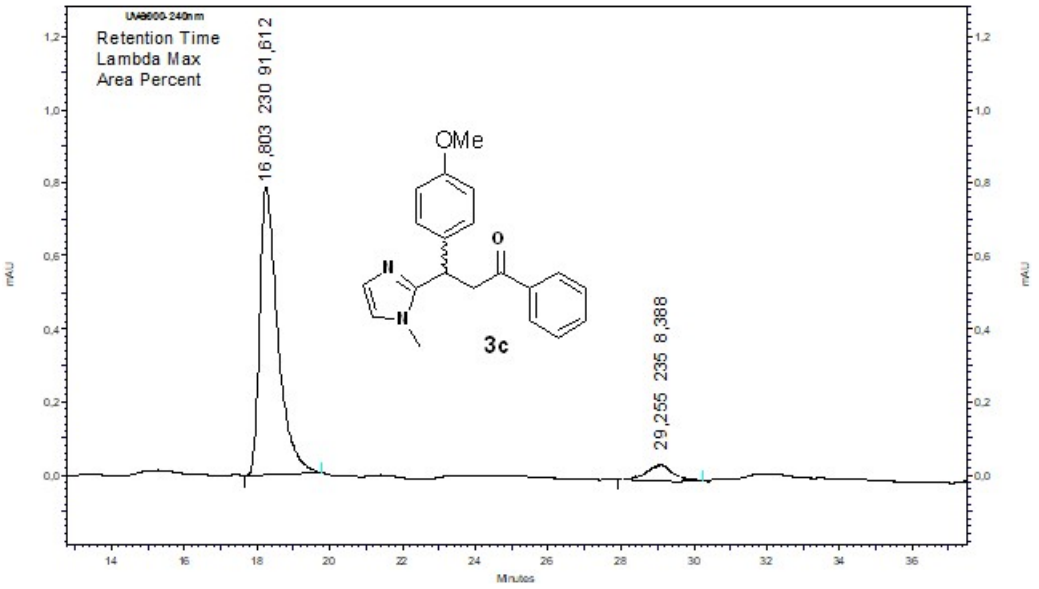
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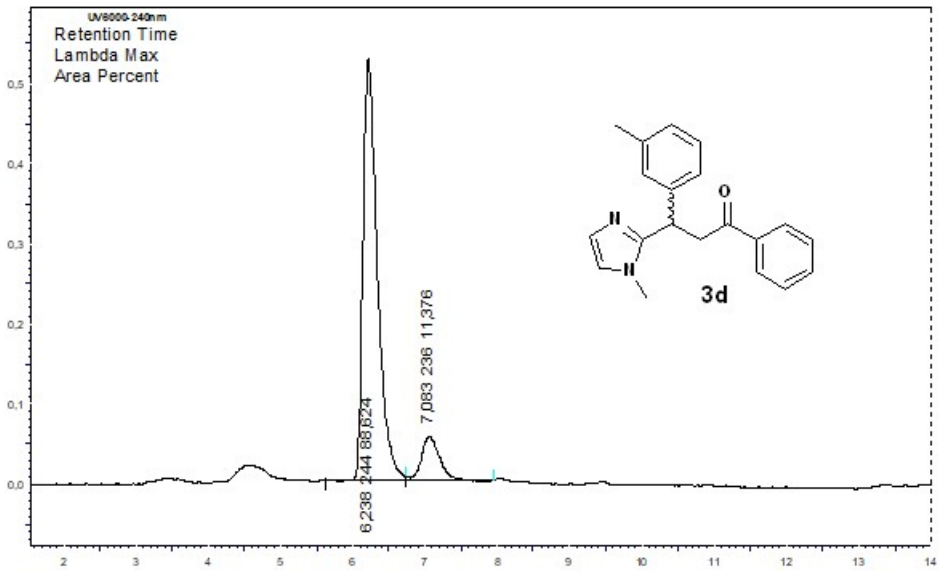
Minutes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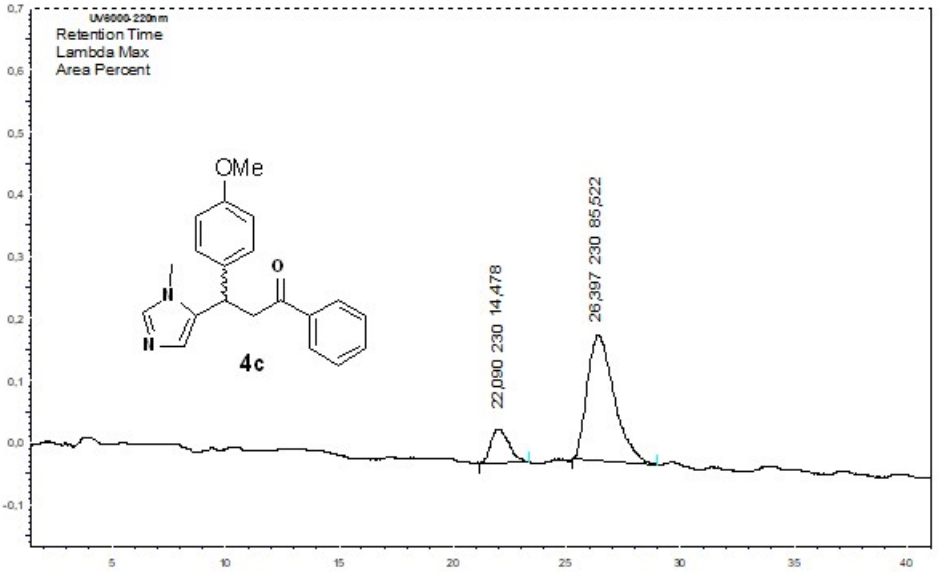
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Area Percent
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4c
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7. Computational Details

Molecular models were realized using the Jmol software[**Jmol: an open-source Java viewer for chemical structures in 3D.**[4] starting from the X-ray crystal structure reported in literature. The systems were then optimized employing the GFN2-xTB method[5] including implicit solvation model (GBSA) as implemented in the xTB standalone programs.[6]

The molecular systems were then reoptimized and the ^{31}P chemical shifts were computed at the B3LYP[7, 8] level of theory, also including empirical dispersion D3BJ,[9] in conjunction with 6-31G(d) basis set and LANL2DZ pseudo potential on Pt atoms. Bulk solvent effects were again accounted for using CPCM.[10] To compute the ^{31}P chemical shifts, PH_3 spectra was simulated at the same level of theory and then used as the reference (-266.1 ppm). DFT computations were performed using the G16.C01 version of the Gaussian suite of programs.[11]

Molecular representations and computing of hydrogen bonds were performed with the UCSF-Chimera package.[12]

Table 1. Experimental Simulated chemical shifts (δ in ppm) in CDCl3 of the [(PP)Pt(II)Cl2] complexes. The mean values of the two phosphorus atoms are reported.

Complex	Simulated	Experimental
cis-[(Xanthpos)$PtCl_2$]	5.9	7
trans-[(Xanthpos)$PtCl_2$]	-5.1	
cis-[(EPHOS)$PtCl_2$]	30	23
trans-[(EPHOS)$PtCl_2$]	6	
cis-[(ZEDPHOS)$PtCl_2$]	5.9	7

Cartesian coordinates in XYZ format

In the following the electronic energy in Hartree at B3LYP-D3(BJ) /6-31G(d) level of theory are reported in the comment line of xyz format (Angstrom).

cis-[(ZEDPHOS)$PtCl_2$]

65
Enegy: -2883.85030376

C	1.591692	-0.003555	2.386701
H	2.587979	0.204163	2.790028
C	0.710683	1.171732	2.731264
H	1.249362	2.089108	2.954255
C	-0.624043	1.234328	2.709114
H	-1.094262	2.191246	2.927258
C	-1.575793	0.116838	2.384485
H	-1.139680	-0.840520	2.664793
C	1.196323	-1.401914	2.895670
H	0.788559	-1.333780	3.908709
H	2.078291	-2.045760	2.921618
H	0.461918	-1.897614	2.254948
C	-2.905343	0.280534	3.134062
H	-2.711800	0.236893	4.211280
H	-3.614257	-0.511368	2.880610
H	-3.367108	1.247192	2.914899
C	2.576622	1.624690	0.198470
C	3.482277	2.211273	1.098767
H	3.780480	1.692289	2.003630
C	4.016169	3.473752	0.843675
H	4.715199	3.913099	1.548892
C	3.649603	4.169324	-0.310374
H	4.062492	5.154557	-0.505551
C	2.752306	3.593685	-1.210672
H	2.464587	4.126037	-2.112147
C	2.219360	2.328650	-0.961067
H	1.535745	1.879964	-1.671245
C	3.132337	-1.280088	0.328169

C	4.494086	-0.963496	0.389620
H	4.813432	0.068975	0.477622
C	5.450749	-1.977711	0.313468
H	6.505995	-1.723856	0.351628
C	5.053663	-3.308588	0.179512
H	5.799844	-4.095277	0.117883
C	3.694349	-3.627151	0.112262
H	3.380459	-4.659837	-0.006861
C	2.736965	-2.617948	0.179438
H	1.681985	-2.859712	0.094952
C	-2.550753	1.606064	0.101643
C	-1.730268	2.613320	-0.428213
H	-0.690752	2.395856	-0.646828
C	-2.247602	3.883763	-0.676397
H	-1.603185	4.654280	-1.088757
C	-3.588791	4.159758	-0.403220
H	-3.993323	5.147365	-0.604061
C	-4.410490	3.163163	0.127066
H	-5.454490	3.371923	0.340523
C	-3.895439	1.892622	0.385109
H	-4.543823	1.128656	0.797959
C	-3.010569	-1.330000	0.344930
C	-2.768412	-2.536716	1.019741
H	-1.886385	-2.653162	1.642450
C	-3.650577	-3.607915	0.888229
H	-3.451934	-4.536105	1.415514
C	-4.781242	-3.486331	0.077594
H	-5.468769	-4.320487	-0.025853
C	-5.018118	-2.294112	-0.608354
H	-5.886689	-2.198667	-1.252962
C	-4.135078	-1.221724	-0.483277
H	-4.309371	-0.313324	-1.045064
P	1.832298	-0.013485	0.533255
P	-1.782592	0.009184	0.525797
Pt	0.031699	-0.381486	-0.836018
Cl	1.714374	-0.758801	-2.559132
Cl	-1.661234	-0.587625	-2.583278

cis-[(EPHOS)$PtCl_2$]

65
Enegy: -2883.82861122

C	0.556542	-0.030017	2.755552
C	-0.640313	0.558378	2.802032
H	-0.705387	1.644843	2.742310
C	-1.889177	-0.189061	2.478222
H	-1.734589	-1.262885	2.635286
C	-3.147062	0.287400	3.204892
H	-3.063323	0.020728	4.264108
H	-4.055044	-0.171715	2.806328
H	-3.248585	1.374325	3.143748
C	-2.080210	1.797243	0.292145
C	-1.031809	2.510719	-0.302116
H	-0.153846	1.983271	-0.646138
C	-1.117056	3.892249	-0.475572
H	-0.290736	4.422619	-0.939528
C	-2.260220	4.576636	-0.062361
H	-2.332005	5.651880	-0.196796
C	-3.322094	3.871903	0.512137
H	-4.221738	4.396571	0.819565
C	-3.237482	2.491439	0.686971
H	-4.079907	1.955256	1.107751
C	-3.521998	-0.701712	0.099014
C	-3.963327	-1.887252	0.703512
H	-3.348776	-2.386385	1.446022
C	-5.189452	-2.444581	0.346051
H	-5.522840	-3.361545	0.822624
C	-5.981885	-1.828243	-0.624919
H	-6.936667	-2.263701	-0.904395
C	-5.540168	-0.655723	-1.240135
H	-6.146549	-0.177928	-2.003848
C	-4.314518	-0.094657	-0.883048
H	-3.973777	0.809538	-1.374690
P	-1.903912	-0.003429	0.580333
Pt	-0.044010	-0.845613	-0.583850

Cl	1.626977	-1.679886	-2.155843
Cl	-1.630163	-2.073395	-1.935792
C	1.762123	0.699733	2.267445
H	1.533299	1.769812	2.224589
C	3.048192	0.457661	3.063265
P	1.831348	0.140773	0.438544
H	2.930121	0.897740	4.059445
H	3.927209	0.903579	2.590160
H	3.244468	-0.611011	3.180785
C	2.424140	1.618230	-0.467188
C	3.212015	-1.052034	0.486310
C	3.110266	2.650360	0.192599
C	2.154407	1.745577	-1.839866
C	4.523517	-0.668130	0.191003
C	2.950693	-2.353526	0.937898
H	3.337911	2.578448	1.249491
C	3.513454	3.789146	-0.505335
C	2.555810	2.887827	-2.531286
H	1.632825	0.951163	-2.360285
H	4.730357	0.334594	-0.167815
C	5.568350	-1.580980	0.348532
C	3.997412	-3.257181	1.103996
H	1.927628	-2.661785	1.133133
H	4.042680	4.579364	0.018585
C	3.232488	3.913015	-1.866854
H	2.335776	2.975015	-3.590903
H	6.584089	-1.281148	0.107925
C	5.308734	-2.872243	0.808854
H	3.789222	-4.264894	1.450962
H	3.540106	4.803305	-2.407263
H	6.123071	-3.580283	0.930994
H	0.622179	-1.118436	2.782329

trans-[(EPHOS)$PtCl_2$]

65
Enegy: -2883.81032819

C	-0.585970	0.511067	2.390657
C	0.533017	-0.218420	2.492078
H	0.459276	-1.298399	2.591862
C	1.898805	0.327476	2.184247
H	1.854304	1.420546	2.226672
C	2.993833	-0.161903	3.133269
H	2.700808	0.071882	4.162792
H	3.948925	0.334097	2.938207
H	3.139365	-1.243571	3.060172
C	3.366666	-1.385768	0.039223
C	3.014057	-2.334245	-0.932164
H	2.065399	-2.241731	-1.446888
C	3.872683	-3.392673	-1.231324
H	3.585234	-4.119950	-1.984650
C	5.092189	-3.515276	-0.564831
H	5.758517	-4.341707	-0.794480
C	5.461645	-2.564143	0.389668
H	6.417851	-2.643043	0.898452
C	4.609698	-1.501364	0.684936
H	4.929576	-0.751157	1.396796
C	3.242571	1.485263	-0.166295
C	2.806461	2.773351	0.185106
H	1.882054	2.907171	0.735063
C	3.537117	3.896154	-0.197408
H	3.188135	4.884909	0.085380
C	4.703737	3.751854	-0.951747
H	5.271048	4.628110	-1.251518
C	5.130479	2.477636	-1.327188
H	6.031476	2.355760	-1.921315
C	4.405282	1.350043	-0.939482
H	4.749899	0.366561	-1.236619
P	2.237603	0.027570	0.302879
Pt	0.000923	-0.155896	-0.478736
C	-1.956771	-0.071429	2.161755
H	-1.934110	-1.143744	2.384786
C	-3.064744	0.629109	2.955703
P	-2.229398	-0.043701	0.260781
H	-2.912046	0.449497	4.025442

H	-4.063436	0.274011	2.686356
H	-3.045972	1.709255	2.785593
C	-3.322809	-1.439676	-0.153629
C	-3.230840	1.449134	-0.053480
C	-4.210561	-2.021788	0.760210
C	-3.268060	-1.924948	-1.468745
C	-4.529528	1.364537	-0.574402
C	-2.694199	2.710691	0.253203
H	-4.262020	-1.666717	1.783130
C	-5.038218	-3.071855	0.359661
C	-4.104056	-2.965721	-1.868629
H	-2.557974	-1.492456	-2.167855
H	-4.956493	0.397663	-0.815501
C	-5.280214	2.523286	-0.781262
C	-3.451447	3.862958	0.055281
H	-1.680987	2.792026	0.628164
H	-5.720156	-3.521531	1.075280
C	-4.989658	-3.541503	-0.954040
H	-4.055000	-3.335323	-2.888469
H	-6.284530	2.445818	-1.187410
C	-4.745717	3.772396	-0.464033
H	-3.027057	4.832776	0.297617
H	-5.635152	-4.358440	-1.262929
H	-5.332152	4.672539	-0.623448
H	-0.502527	1.589898	2.252010
Cl	0.027305	1.988772	-1.486988
Cl	-0.108481	-2.472206	0.190271

cis-[(Xantphos)$PtCl_2$]

77

Enegy: -3303.28708563

C	2.204525	1.416666	-0.698258
C	3.368831	1.821349	-1.368064
C	3.534334	3.158225	-1.732094
C	2.559526	4.113386	-1.430219
C	1.399187	3.747886	-0.744008
C	1.271843	2.402214	-0.399109
C	0.266088	4.683049	-0.309425
C	-1.036544	3.904177	-0.520220
C	-1.018037	2.541470	-0.212977
C	-2.089142	1.675274	-0.398022
C	-3.291775	2.242004	-0.853209
C	-3.360929	3.605056	-1.137182
C	-2.241225	4.428390	-0.990762
C	0.279262	6.005344	-1.083987
C	0.429202	4.977667	1.206151
C	-3.494296	-0.697091	-0.701377
C	-3.674249	-0.854683	-2.082893
C	-4.935760	-1.141650	-2.593512
C	-6.026589	-1.283550	-1.729926
C	-5.849228	-1.131204	-0.355873
C	-4.585686	-0.831480	0.160250
C	3.425740	-1.083624	-0.626172
C	3.639580	-1.425530	-1.969584
C	4.882056	-1.899150	-2.378715
C	5.916270	-2.049873	-1.449371
C	5.702668	-1.719532	-0.112481
C	4.460500	-1.230774	0.300432
C	-1.915161	-0.331353	1.719244
C	-2.056944	-1.634743	2.226487
C	-2.075224	-1.844748	3.602765
C	-1.923410	-0.768882	4.481465
C	-1.763169	0.521515	3.978740
C	-1.767645	0.743823	2.600898
C	1.872078	-0.206672	1.672501
C	2.335886	0.922058	2.359527
C	2.330746	0.943048	3.754227
C	1.872204	-0.164085	4.469118
C	1.422706	-1.295927	3.787024
C	1.415787	-1.319976	2.394266
O	0.142892	1.975430	0.266659
P	1.838519	-0.305784	-0.154617
P	-1.860551	-0.135464	-0.099864
H	4.133781	1.095856	-1.612493
H	4.434400	3.459217	-2.259300
H	2.711425	5.144293	-1.731166

H	-4.163159	1.619073	-1.002802
H	-4.295121	4.027744	-1.493959
H	-2.313753	5.479477	-1.248076
H	1.217105	6.541753	-0.911538
H	-0.528423	6.659691	-0.742673
H	0.164205	5.843715	-2.160616
H	0.434456	4.052535	1.789636
H	-0.396440	5.604825	1.559586
H	1.372377	5.504407	1.387856
H	-2.820475	-0.774984	-2.748160
H	-5.066430	-1.271717	-3.663735
H	-7.009292	-1.517381	-2.129527
H	-6.692095	-1.244247	0.320032
H	-4.454260	-0.705800	1.229221
H	2.826338	-1.339956	-2.682969
H	5.038982	-2.168941	-3.418896
H	6.882313	-2.430430	-1.768801
H	6.500142	-1.841541	0.614953
H	4.300088	-0.970860	1.340924
H	-2.146315	-2.471039	1.539177
H	-2.195466	-2.853104	3.988339
H	-1.923923	-0.938091	5.554636
H	-1.635390	1.360221	4.656893
H	-1.656525	1.752566	2.220892
H	2.699927	1.783405	1.809956
H	2.685502	1.824956	4.280351
H	1.863792	-0.144527	5.555319
H	1.059054	-2.157415	4.337556
H	1.056974	-2.194173	1.860863
Pt	-0.073594	-1.530456	-0.726257
Cl	-1.772608	-3.197532	-1.063802
Cl	1.416128	-3.400536	-0.886397

trans-[(Xantphos)$PtCl_2$]

77

Enegy: -3303.27870807

C	2.278419	1.359153	-0.342143
C	3.449973	1.961600	-0.823038
C	3.515120	3.335452	-1.035258
C	2.410109	4.139002	-0.755547
C	1.230140	3.581762	-0.259452
C	1.178945	2.194607	-0.073094
C	-0.000070	4.390103	0.155487
C	-1.230252	3.581729	-0.259442
C	-1.179022	2.194579	-0.073085
C	-2.278477	1.359096	-0.342128
C	-3.450047	1.961515	-0.823022
C	-3.515228	3.335368	-1.035237
C	-2.410238	4.138944	-0.755526
C	-0.000118	5.798959	-0.449852
C	-0.000072	4.513292	1.704418
C	-3.531550	-1.157401	-1.164054
C	-3.149212	-1.704124	-2.397481
C	-4.113081	-2.238548	-3.252570
C	-5.459118	-2.238311	-2.880580
C	-5.843556	-1.702947	-1.648749
C	-4.884933	-1.164892	-0.790654
C	3.531525	-1.157340	-1.164112
C	3.149148	-1.704166	-2.397481
C	4.112999	-2.238602	-3.252586
C	5.459054	-2.238278	-2.880665
C	5.843531	-1.702816	-1.648889
C	4.884928	-1.164750	-0.790779
C	-2.881801	-0.675786	1.609905
C	-3.317802	-1.945593	2.018254
C	-3.771222	-2.144314	3.319928
C	-3.776883	-1.083964	4.230533
C	-3.330059	0.176656	3.832786
C	-2.884335	0.382717	2.526168
C	2.881879	-0.675712	1.609857
C	2.884363	0.382782	2.526131
C	3.330151	0.176741	3.832730
C	3.777087	-1.083849	4.230447
C	3.771476	-2.144190	3.319830
C	3.317994	-1.945489	2.018174
O	-0.000030	1.641909	0.399855

P	2.236500	-0.462659	-0.081854
P	-2.236501	-0.462708	-0.081835
H	4.310333	1.343959	-1.052316
H	4.427433	3.780666	-1.419395
H	2.475085	5.207996	-0.921217
H	-4.310392	1.343853	-1.052297
H	-4.427553	3.780563	-1.419368
H	-2.475237	5.207940	-0.921189
H	0.877162	6.359692	-0.115627
H	-0.877476	6.359605	-0.115679
H	-0.000085	5.770441	-1.544180
H	-0.000039	3.528650	2.180290
H	-0.890157	5.057996	2.037214
H	0.889980	5.058053	2.037209
H	-2.102274	-1.699727	-2.681555
H	-3.810720	-2.660020	-4.206601
H	-6.207084	-2.659799	-3.545814
H	-6.888638	-1.707391	-1.353469
H	-5.185524	-0.761685	0.170825
H	2.102197	-1.699835	-2.681501
H	3.810607	-2.660151	-4.206573
H	6.207006	-2.659774	-3.545910
H	6.888629	-1.707196	-1.353662
H	5.185550	-0.761475	0.170661
H	-3.302773	-2.774574	1.318575
H	-4.112017	-3.128815	3.626324
H	-4.126332	-1.242053	5.246663
H	-3.331329	1.004018	4.536391
H	-2.545410	1.367225	2.222634
H	2.545350	1.367266	2.222619
H	3.331384	1.004095	4.536343
H	4.126583	-1.241924	5.246562
H	4.112359	-3.128667	3.626202
H	3.303013	-2.774462	1.318483
Cl	-0.000027	0.054817	-2.487562
Cl	0.000061	-2.492743	1.559148
Pt	0.000019	-1.066698	-0.348160

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