Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Low-Valent Cobalt-Catalyzed C–H Allylation

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Table of Contents

1. Materials and Methods

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still.[1] NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution (HR MS) mass spectra were recorded by ESI-TOF.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., and other commercial suppliers and used as received. $Co(acac)_3$ (>98.0%), $Co(acac)_2$ (>99.0%), $CoCl_2$ (99.9%), and $CoBr_2$ (99.0%) were purchased from Aldrich Inc. and Tokyo Chemical Industry Co., and used as received. $Co(OAc)_2$ (>98.0%) were purchased from Alfa Aesar and used as received. Solvents were dried over sodium (for THF, Et_2O) by refluxing for overnight and freshly distilled prior to use. 2-Phenylpyridines[2], aromatic imines[3] and allyl carbonate[4] was prepared according to the corresponding literatures. Grignard reagents were purchased or were prepared from the corresponding halides and magnesium turnings in anhydrous THF, and titrated prior to use.

2. Investigation of the Key Reaction Parameters

The reactions were carried out according to the general procedure for cobalt catalyzed *ortho*-C–H allylation by the related parameter optimization shown in Tables S1, S2, and S3.

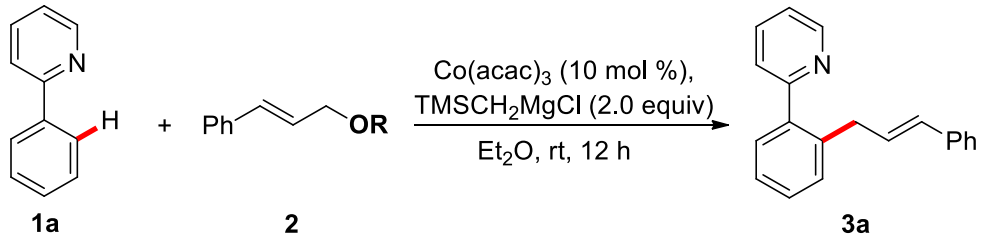


Table S1. *Investigation of the effect of allylic oxygen electrophiles (**2**) for the synthesis of (E)-2-(2-cinnamylphenyl)pyridine (**3a**)*[a]

Entry	OR	Cobalt salt	RMgX	Solvent	**3a** (%)
1	-OH	$Co(acac)_3$	$TMSCH_2MgCl$	Et_2O	n.d.
2	-OAc	$Co(acac)_3$	$TMSCH_2MgCl$	Et_2O	67
3	-OMe	$Co(acac)_3$	$TMSCH_2MgCl$	Et_2O	23
4	**-OBoc**	**$Co(acac)_3$**	**$TMSCH_2MgCl$**	**Et_2O**	**70**
5	-P(O)(OEt)2	$Co(acac)_3$	$TMSCH_2MgCl$	Et_2O	30

[a] Reactions conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $Co(acac)_3$ (10 mol %), $TMSCH_2MgCl$ (0.4 mmol), 25 ℃, 12 h, isolated yield. n.d. = Not detected by GC-MS and TLC analyses.

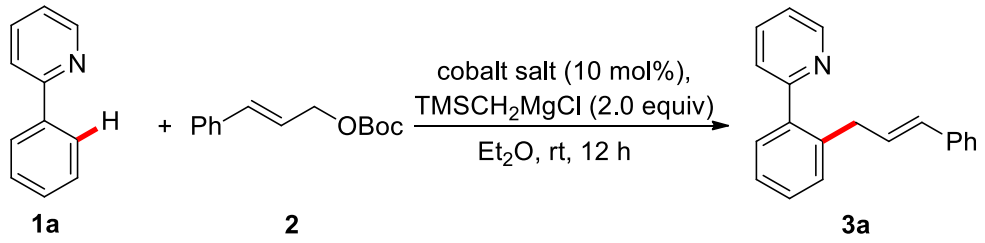


Table S2. *Investigation of the effect of Cobalt catalysts for the synthesis of (E)-2-(2-cinnamylphenyl)pyridine (**3a**)*[a]

Entry	OR	Cobalt salt	RMgX	Solvent	**3a** (%)
1	**-OBoc**	**$Co(acac)_3$**	**$TMSCH_2MgCl$**	**Et_2O**	**70**
2	-OBoc	$CoCl_2$	$TMSCH_2MgCl$	Et_2O	56
3	-OBoc	$CoBr_2$	$TMSCH_2MgCl$	Et_2O	50
4	-OBoc	$Co(acac)_2$	$TMSCH_2MgCl$	Et_2O	62
5	-OBoc	$Co(OAc)_2$	$TMSCH_2MgCl$	Et_2O	9

[a] Reactions conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Co] (10 mol %), $TMSCH_2MgCl$ (0.4 mmol), 25 ℃, 12 h, isolated yield.

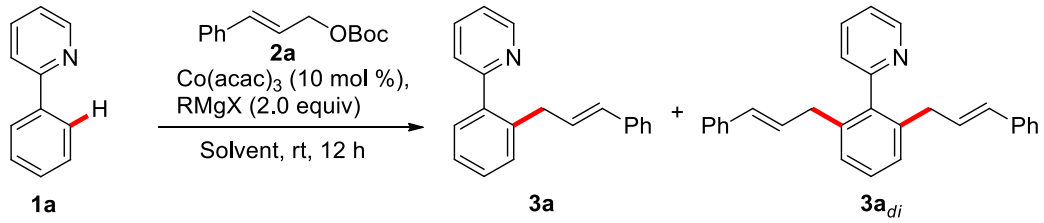


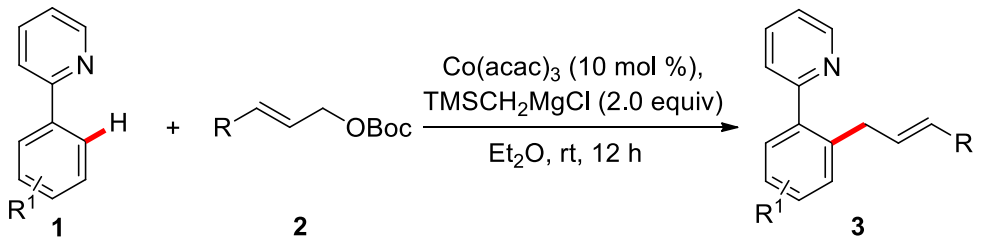
Table S3. *Investigation of the effect of* RMgX *for the synthesis of (E)-2-(2-cinnamylphenyl)pyridine (**3a**)*[a]

Entry	OR	Cobalt salt	RMgX	Solvent	**3a** (%)
1	-OBoc	$Co(acac)_3$	$TMSCH_2MgCl$	Et_2O	70
2[b]	**-OBoc**	**$Co(acac)_3$**	**$TMSCH_2MgCl$**	**Et_2O**	**95 (3a/3a$_{di}$ = 10/1)**[c]
3	-OBoc	$Co(acac)_3$	PhMgBr	THF	<10
4	-OBoc	$Co(acac)_3$	CH_3MgCl	THF	<10
5	-OBoc	$Co(acac)_3$	*i*-PrMgCl	THF	n.d.
6	-OBoc	$Co(acac)_3$	*n*-BuMgBr	THF	n.d.
7	-OBoc	$Co(acac)_3$	CyMgBr	THF	trace
8	-OBoc	$Co(acac)_3$	*t*-BuMgBr	THF	trace

[a] Reactions conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Co(acac)_3$ (10 mol %), $TMSCH_2MgCl$ (0.4 mmol), 25 ℃, 12 h, isolated yield. [b] **2a** (0.4 mmol) was used. [c] The ratio was detected by ^1H NMR spectroscopy. n.d. = Not detected by GC-MS and TLC analyses.

3. General Procedure for Cobalt-Catalyzed *ortho*-C–H Allylation

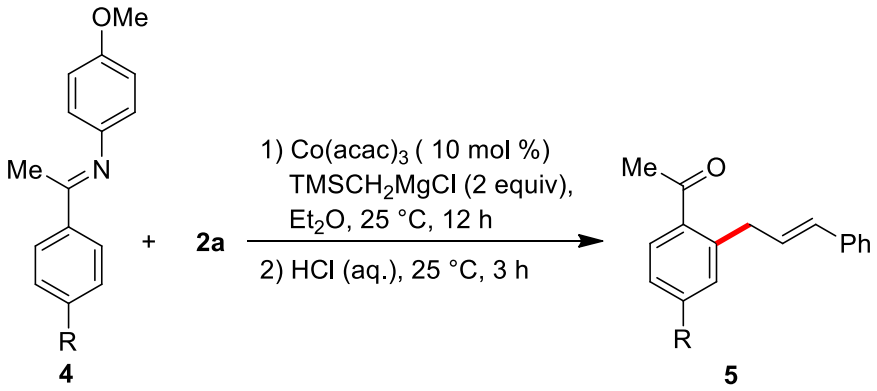
General Procedure A



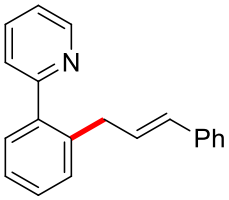
In a 10 mL Schlenk tube were placed 2-arylpyridine **1** (0.20 mmol), allyl carbonates **2** (0.40

mmol), $Co(acac)_3$ (7 mg, 0.02 mmol), and Et_2O (0.2 mL). To the mixture was added a solution of $TMSCH_2MgCl$ (1.0 M, 0.40 mL, 0.40 mmol) in Et_2O dropwise at 0 °C under N_2. The reaction mixture was stirred at 25 °C for 12 h, and then quenched by the addition of saturated NH_4Cl aqueous solution (2.0 mL). The resulting mixture was stirred at room temperature for 10 min, and then extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to provide the product **3**.

General Procedure B



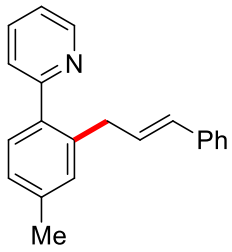
In a 10 mL Schlenk tube were placed aromatic imines **4** (0.20 mmol), allyl carbonate **2a** (0.40 mmol), $Co(acac)_3$ (7 mg, 0.02 mmol), and Et_2O (0.2 mL). To the mixture was added a solution of $TMSCH_2MgCl$ (1.0 M, 0.40 mL, 0.40 mmol) in Et_2O dropwise at 0 °C under N_2. The reaction mixture was stirred at 25 °C for 12 h, and then quenched by the addition of saturated 3 M HCl aqueous solution (2.0 mL). The resulting mixture was stirred at room temperature for 3 h, and then extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to provide the product **5**.



(*E*)-2-(2-Cinnamylphenyl)pyridine (Table 2, 3a)

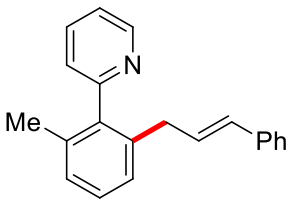
The general procedure A was applied to 2-phenylpyridine (31 mg, 0.2 mmol), (*E*)-*tert*-butyl

cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (46.5 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 4.4 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.37–7.32 (m, 3H), 7.26–7.24 (m, 5H), 7.17–7.16 (m, 1H), 6.29–6.18 (m, 2H), 3.65 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 149.1, 140.5, 137.9, 137.5, 136.2, 130.8, 130.2, 129.9, 129.5, 128.5, 128.4, 127.0, 126.4, 126.1, 124.5, 121.9, 36.7. HRMS (ESI$^+$): calcd for $C_{20}H_{18}N$ $[M+H]^+$ 272.1439, found 272.1435.



(*E*)-2-(2-Cinnamyl-4-methylphenyl)pyridine (Table 2, 3b)

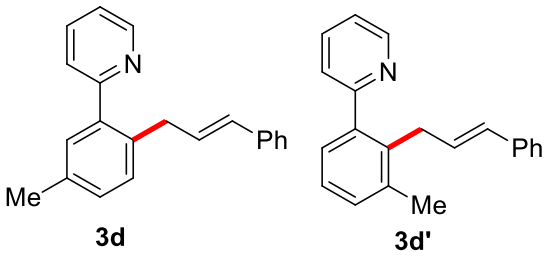
The general procedure A was applied to 2-(*p*-tolyl)pyridine (34 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (47 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 4.4 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.31–7.19 (m, 6H), 7.16–7.11 (m, 3H), 6.29–6.19 (m, 2H), 3.62 (d, *J* = 5.6 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 149.0, 138.2, 137.7, 137.6, 136.1, 130.8, 130.6, 129.8, 129.6, 128.4, 127.1, 126.9, 126.0, 124.2, 121.5, 36.6, 21.2. HRMS (ESI$^+$): calcd for $C_{21}H_{20}N$ $[M+H]^+$ 286.1596, found 286.1589.



(*E*)-2-(2-Cinnamyl-6-methylphenyl)pyridine (Table 2, 3c)

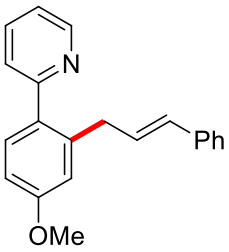
The general procedure A was applied to 2-(*o*-tolyl)pyridine (34 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15)

to afford the title compound (44.5 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 3.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.18–7.07 (m, 10H), 6.12–6.05 (m, 1H), 5.99 (d, J = 16.0 Hz, 1H), 3.20 (d, J = 5.2 Hz, 2H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 149.5, 140.2, 137.9, 137.5, 136.2, 136.1, 130.5, 129.2, 128.4, 128.2, 128.1, 127.0, 126.9, 126.0, 124.9, 121.8, 36.8, 20.3. HRMS (ESI^+): calcd for $C_{21}H_{20}N$ $[M+H]^+$ 286.1596, found 286.1590.



(*E*)-2-(2-Cinnamyl-5-methylphenyl)pyridine (Table 2, 3d) and (E)-2-(2-cinnamyl-3-methylphenyl)pyridine (Table 2, 3d')

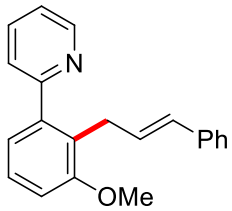
The general procedure A was applied to 2-(*m*-tolyl)pyridine (34 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title mixed compounds (49 mg, 86% yield). The ratio of **3d**/**3d'** (1/1.8) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (m, 1H), 7.71–7.65 (m, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.23–7.16 (m, 9H), 6.27–6.17 (m, 0.7H, **3d'**), 6.27–6.17 (m, 0.7H, **3d**), 6.06 (d, J = 16.0 Hz, 0.7H, **3d**), 3.59 (m, 2H), 2.40 (s, 2H, **3d'**), 2.37 (s, 1.1H, **3d**); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 159.9, 149.2, 149.1, 141.4, 140.3, 137.61, 137.59, 136.02, 135.97, 135.89, 135.5, 134.7, 130.54, 130.50, 130.13, 130.08, 129.7, 129.2, 128.7, 128.4, 127.8, 126.8, 126.2, 125.98, 125.94, 124.1, 121.7, 36.2, 33.2, 20.9, 20.0. HRMS (ESI^+): calcd for $C_{21}H_{20}N$ $[M+H]^+$ 286.1596, found 286.1591.



(*E*)-2-(2-Cinnamyl-4-methoxyphenyl)pyridine (Table 2, 3e)

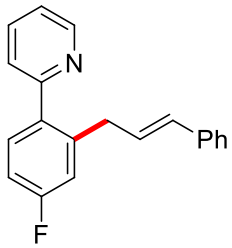
The general procedure A was applied to 2-(4-methoxyphenyl)pyridine (37 mg, 0.2 mmol),

(*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (47 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, J = 4.4 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.38–7.37 (m, 2H), 7.26–7.17 (m, 7H), 6.90 (s, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.32–6.08 (m, 2H), 3.83 (s, 3H), 3.65 (d, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 149.1, 139.5, 137.5, 136.1, 133.3, 131.2, 130.9, 129.3, 128.4, 126.9, 126.0, 124.2, 121.4, 115.6, 111.6, 55.3, 36.8. HRMS (ESI^+): calcd for $C_{21}H_{20}NO$ $[M+H]^+$ 302.1545, found 302.1538.



(*E*)-2-(2-Cinnamyl-3-methoxyphenyl)pyridine (Table 2, 3f)

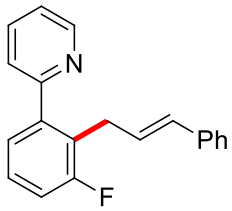
The general procedure A was applied to 2-(3-methoxyphenyl)pyridine (37 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (50.5 mg, 84% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, J = 4.0 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.31–7.23 (m, 6H), 7.15 (m, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.31–6.24 (m, 1H), 6.06 (d, J = 16.0 Hz, 1H), 3.88 (s, 3H), 3.58 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 157.9, 149.2, 142.1, 137.9, 135.9, 129.7, 129.4, 128.3, 127.1, 126.6, 126.4, 125.9, 124.3, 122.2, 121.8, 110.6, 55.7, 30.2. HRMS (ESI^+): calcd for $C_{21}H_{20}NO$ $[M+H]^+$ 302.1545, found 302.1536.



(*E*)-2-(2-Cinnamyl-4-fluorophenyl)pyridine (Table 2, 3g)

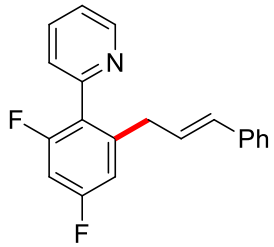
The general procedure A was applied to 2-(4-fluorophenyl)pyridine (35 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25

℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (42 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, J = 4.4 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.40–7.36 (m, 2H), 7.27–7.19 (m, 6H), 7.06 (d, J = 10.0 Hz, 1H), 6.98 (t, J = 8.4 Hz, 1H), 6.28–6.13 (m, 2H), 3.63 (d, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5 (d, J = 246.0 Hz), 158.9, 149.2, 140.6 (d, J = 7.0 Hz), 137.2, 136.5, 136.3, 131.5 (d, J = 8.0 Hz), 131.4, 128.4, 127.1, 126.1, 124.2, 121.9, 116.5 (d, J = 21.0 Hz), 113.2 (d, J = 21.0 Hz), 36.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –113.85. HRMS (ESI^{+}): calcd for $C_{20}H_{17}FN$ $[M+H]^{+}$ 290.1345, found 290.1337.



(*E*)-2-(2-Cinnamyl-3-fluorophenyl)pyridine (Table 2, 3h)

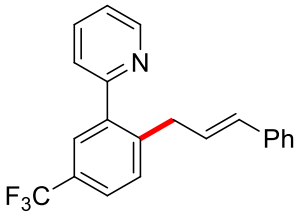
The general procedure A was applied to 2-(3-fluorophenyl)pyridine (35 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (48 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, J = 4.4 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.41–7.20 (m, 7H), 7.16–7.09 (m, 2H), 6.28–6.21 (m, 1H), 6.12 (d, J = 16.0 Hz, 1H), 3.64 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (d, J = 244.0 Hz), 158.6, 149.3, 142.7 (d, J = 4.0 Hz), 137.5, 136.3, 130.5, 128.3, 128.1, 127.5 (d, J = 9.0 Hz), 126.9, 126.0, 125.5 (d, J = 3.0 Hz), 125.3 (d, J = 16.0 Hz), 124.1, 122.2, 115.2 (d, J = 23.0 Hz), 29.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –116.83. HRMS (ESI^{+}): calcd for $C_{20}H_{17}FN$ $[M+H]^{+}$ 290.1345, found 290.1337.



(*E*)-2-(2-Cinnamyl-4,6-difluorophenyl)pyridine (Table 2, 3i)

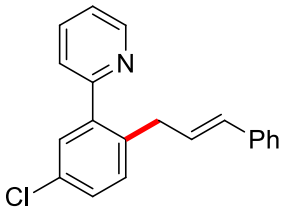
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol),

(*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (49 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, *J* = 4.0 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.31–7.21 (m, 6H), 6.90 (d, *J* = 9.2 Hz, 1H), 6.77 (t, *J* = 8.8 Hz, 1H), 6.19–6.07 (m, 2H), 3.46 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (dd, *J* = 248.0, 13.0 Hz), 159.1 (*J* = 248.0, 13.0 Hz), 153.1, 149.6, 142.9 (dd, *J* = 9.0, 4.0 Hz), 137.1, 136.2, 131.8, 128.5, 127.4, 127.3, 126.1, 126.0, 122.6, 112.2 (dd, *J* = 12.0, 4.0 Hz), 101.7 (t, *J* = 26.0 Hz), 36.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –110.05 (s, 1F), –112.27 (s, 1F). HRMS (ESI^+): calcd for $C_{20}H_{16}F_2N$ $[M+H]^+$ 308.1251, found 308.1243.



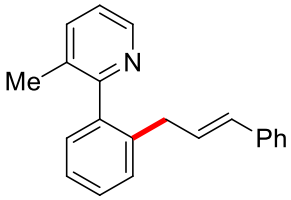
(*E*)-2-(2-Cinnamyl-5-(trifluoromethyl)phenyl)pyridine (Table 2, 3j)

The general procedure A was applied to 2-(3-(trifluoromethyl)phenyl)pyridine (45 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (44 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 4.8 Hz, 1H), 7.75 (td, *J* = 7.6, 1.6 Hz, 1H), 7.68 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33–7.29 (m, 1H), 7.27–7.26 (m, 4H), 7.22–7.17 (m, 1H), 6.27–6.17 (m, 2H), 3.66 (d, *J* = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 149.4, 142.2, 141.0, 137.2, 136.5, 131.6, 130.6, 128.5, 128.2, 127.2, 126.8 (q, *J* = 3.0 Hz), 126.1, 125.5 (q, *J* = 270.0 Hz), 125.1 (q, *J* = 4.0 Hz), 124.2, 122.2, 36.5; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –63.01. HRMS (ESI^+): calcd for $C_{21}H_{17}F_3N$ $[M+H]^+$ 340.1313, found 340.1313.



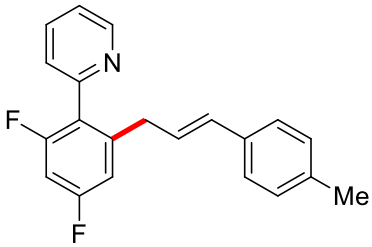
(*E*)-2-(5-Chloro-2-cinnamylphenyl)pyridine (Table 2, 3k)

The general procedure A was applied to 2-(3-chlorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (45 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 3.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.30–7.23 (m, 7H), 7.17–7.16 (m, 1H), 6.26–6.19 (m, 1H), 6.05 (d, *J* = 16.0 Hz, 1H), 3.73 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 149.3, 142.9, 137.6, 136.2, 135.5, 135.4, 130.8, 129.6, 128.6, 128.4, 127.5, 127.4, 126.9, 126.0, 124.2, 122.3, 33.7. HRMS (ESI$^+$): calcd for $C_{20}H_{17}Cl$ $[M+H]^+$ 306.1050, found 306.1043.



(*E*)-2-(2-Cinnamylphenyl)-3-methylpyridine (Table 2, 3l)

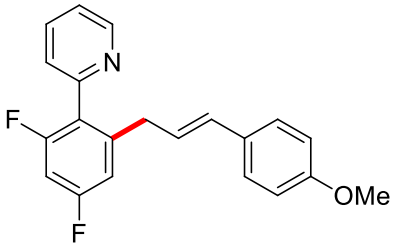
The general procedure A was applied to 3-methyl-2-phenylpyridine (34 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (43 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 4.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.27–7.24 (m, 7H), 7.19–7.14 (m, 3H), 6.20–6.13 (m, 1H), 6.06 (d, *J* = 16.0 Hz, 1H), 3.27 (d, *J* = 5.6 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 149.6, 140.3, 137.9, 137.6, 136.1, 136.0, 130.5, 129.2, 128.4, 128.1, 127.0, 126.9, 126.0, 124.9, 121.8, 37.1, 20.3. HRMS (ESI$^+$): calcd for $C_{21}H_{20}N$ $[M+H]^+$ 286.1596, found 286.1591.



(*E*)-2-(2,4-Difluoro-6-(3-(*p*-tolyl)allyl)phenyl)pyridine (Table 3, 3m)

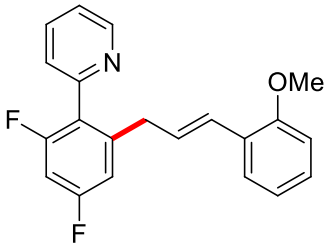
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol),

(*E*)-tert-butyl (3-(*p*-tolyl)allyl) carbonate (99 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (51 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 4.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.27 (t, *J* = 6.0 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 1H), 6.76 (t, *J* = 9.2 Hz, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 6.08–6.01 (m, 1H), 3.44 (d, *J* = 6.4 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0 (dd, *J* = 248.0, 13.0 Hz), 159.1 (dd, *J* = 246.0, 13.0 Hz), 153.2, 149.6, 143.1 (dd, *J* = 9.0, 4.0 Hz), 137.0, 136.2, 134.3, 131.6, 129.2, 126.3, 126.0, 124.4 (dd, *J* = 15.0, 4.0 Hz), 122.6, 112.2 (dd, *J* = 21.0, 3.0 Hz), 101.6 (t, *J* = 26.0 Hz), 36.4, 21.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –110.09– –110.13 (m, 1F), –112.34– –112.38 (m, 1F). HRMS (ESI^+): calcd for $C_{21}H_{18}F_2N$ $[M+H]^+$ 322.1407, found 322.1411.



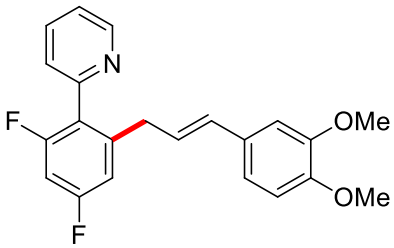
(*E*)-2-(2,4-Difluoro-6-(3-(4-methoxyphenyl)allyl)phenyl)pyridine (Table 3, 3n)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl (3-(4-methoxyphenyl)allyl) carbonate (106 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound (58 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 4.8 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 6.0 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 10.6 Hz, 1H), 6.82–6.76 (m, 3H), 6.09 (d, *J* = 15.6 Hz, 1H), 6.00–5.93 (m, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (dd, *J* = 247.0, 13.0 Hz), 159.0 (dd, *J* = 246.0, 13.0 Hz), 158.9, 149.6, 143.2 (dd, *J* = 9.0, 3.0 Hz), 136.2, 131.2, 129.9, 127.2, 125.9, 125.1, 124.4 (dd, *J* = 15.0, 3.0 Hz), 122.5, 113.9, 112.2 (dd, *J* = 21.0, 3.0 Hz), 101.6 (t, *J* = 26.0 Hz), 55.2, 36.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ =–110.13 (d, *J* = 7.5 Hz, 1F), –112.38 (d, *J* = 7.5 Hz, 1F). HRMS (ESI^+): calcd for $C_{21}H_{18}F_2NO$ $[M+H]^+$ 338.1356, found 338.1358.



(*E*)-2-(2,4-Difluoro-6-(3-(4-methoxyphenyl)allyl)phenyl)pyridine (Table 3, 3o)

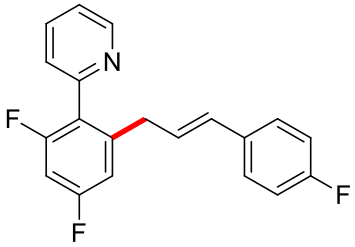
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl (3-(2-methoxyphenyl)allyl) carbonate (106 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound (61 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 4.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.31–7.25 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 9.2 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 9.2 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.16–6.08 (m, 1H), 3.81 (s, 3H), 3.46 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (dd, *J* = 248.0, 13.0 Hz), 159.0 (dd, *J* = 247.0, 13.0 Hz), 156.4, 153.2, 143.3 (dd, *J* = 9.0, 4.0 Hz), 136.2, 128.3, 128.0, 126.7, 126.6, 126.1, 126.0, 125.9, 124.3 (dd, *J* = 16.0, 4.0 Hz), 122.5, 120.5, 112.1 (dd, *J* = 22.0, 3.0 Hz), 110.7, 101.5 (t, *J* = 27.0 Hz), 55.3, 36.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ =–110.20 (d, *J* = 7.9 Hz, 1F), –112.46 (d, *J* = 7.2 Hz, 1F). HRMS (ESI^+): calcd for $C_{21}H_{18}F_2NO$ $[M+H]^+$ 338.1356, found 338.1357.



(*E*)-2-(2,4-Difluoro-6-(3-(4-methoxyphenyl)allyl)phenyl)pyridine (Table 3, 3p)

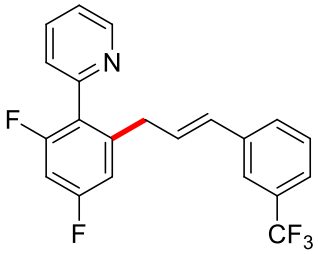
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl (3-(3,4-dimethoxyphenyl)allyl) carbonate (118 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/7) to afford the title compound (36 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, *J* = 2.8 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 6.4 Hz, 1H), 7.26 (s, 1H), 6.90 (d, *J* = 9.2 Hz, 1H), 6.81–6.78 (m, 4H), 6.09 (d, *J* = 16.0 Hz, 1H), 6.02–5.94 (m, 1H), 3.86 (m, 6H), 3.44 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 161.1 (dd, J = 248.0, 14.0 Hz), 159.1 (dd, J = 246.0, 12.0 Hz), 153.2, 149.7, 149.0, 148.6, 143.1 (dd, J = 9.0, 4.0 Hz), 136.2, 131.4, 130.2, 126.0, 125.5, 122.6, 119.2, 112.2 (dd, J = 21.0, 3.0 Hz), 111.1, 108.6, 101.6 (t, J = 26.0 Hz), 55.9, 55.8, 36.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ =–110.09 (d, J = 7.5 Hz, 1F), –112.29 (d, J = 7.5 Hz, 1F). HRMS (ESI^+): calcd for $C_{22}H_{20}F_2NO_2$ $[M+H]^+$ 368.1462, found 368.1464.



(*E*)-2-(2,4-Difluoro-6-(3-(4-fluorophenyl)allyl)phenyl)pyridine (Table 3, 3q)

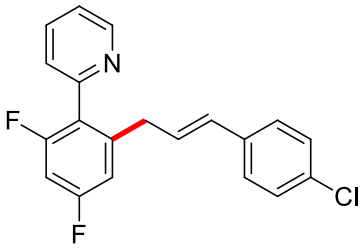
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl (3-(4-fluorophenyl)allyl) carbonate (101 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (59 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, J = 4.4 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 6.0 Hz, 1H), 7.21–7.18 (m, 2H), 6.97–6.88 (m, 3H), 6.77 (t, J = 9.2 Hz, 1H), 6.10 (d, J = 16.0 Hz, 1H), 6.05–5.98 (m, 1H), 3.45 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (dd, J = 248.0, 13.0 Hz), 160.9 (d, J = 245.0 Hz), 159.1 (dd, J = 246.0, 12.0 Hz), 152.9, 149.5, 142.8 (dd, J = 9.0, 3.0 Hz), 136.4, 133.2 (d, J = 4.0 Hz), 130.6, 127.5 (d, J = 8.0 Hz), 127.1 (d, J = 2.0 Hz), 126.0, 124.1 (dd, J = 15.0, 3.0 Hz), 122.7, 115.2 (d, J = 22.0 Hz), 112.2 (dd, J = 21.0, 3.0 Hz), 101.7 (t, J = 27.0 Hz), 36.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ =–109.84 (t, J = 7.5 Hz, 1F), –112.14 (t, J = 7.9 Hz, 1F), –114.93 (d, J = 7.5 Hz, 1F). HRMS (ESI^+): calcd for $C_{20}H_{15}F_3N$ $[M+H]^+$ 326.1157, found 326.1150.



(*E*)-2-(2,4-Difluoro-6-(3-(3-(trifluoromethyl)phenyl)allyl)phenyl)pyridine (Table 3, 3r)

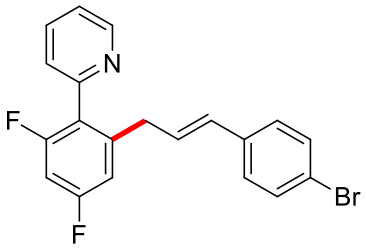
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl (3-(3-(trifluoromethyl)phenyl)allyl) carbonate (121 mg, 0.4 mmol) and

$Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (64 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, J = 4.4 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.46–7.29 (m, 6H), 6.89 (d, J = 9.2 Hz, 1H), 6.78 (t, J = 9.2 Hz, 1H), 6.22–6.14 (m, 2H), 3.50 (d, J = 3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (dd, J = 248.0, 13.0 Hz), 159.1 (dd, J = 247.0, 13.0 Hz), 153.0, 149.6, 142.4 (dd, J = 8.0, 3.0 Hz), 137.8, 136.3, 131.3, 131.0, 130.7, 130.3, 129.5, 129.2, 128.9, 126.0, 125.4 (q, J = 270.0 Hz), 124.4 (dd, J = 16.0, 4.0 Hz), 123.7 (q, J = 4.0 Hz), 122.8 (q, J = 4.0 Hz), 122.7, 112.3 (dd, J = 22.0, 3.0 Hz), 101.9 (t, J = 27.0 Hz), 36.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ = –62.77 (s, 3F), –109.79 (d, J = 7.5 Hz, 1F), –112.01 (d, J = 7.5 Hz, 1F). HRMS (ESI^+): calcd for $C_{21}H_{15}F_5N$ $[M+H]^+$ 376.1125, found 376.1124.



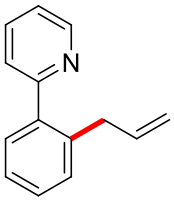
(*E*)-2-(2-(3-(4-Chlorophenyl)allyl)-4,6-difluorophenyl)pyridine (Table 3, 3s)

The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl (3-(4-chlorophenyl)allyl) carbonate (107 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (48 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 2.8 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 6.0 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 9.2 Hz, 1H), 6.77 (t, J = 9.2 Hz, 1H), 6.18–6.04 (m, 2H), 3.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (dd, J = 248.0, 13.0 Hz), 159.1 (dd, J = 247.0, 13.0 Hz), 153.1, 149.7, 142.6 (dd, J = 9.0, 4.0 Hz), 136.2, 135.6, 132.9, 130.5, 128.6, 128.2, 127.3, 125.9, 124.4 (dd, J = 16.0, 4.0 Hz), 122.6, 112.3 (dd, J = 21.0, 3.0 Hz), 101.8 (t, J = 25.0 Hz), 36.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ =–109.95 (d, J = 6.8 Hz, 1F), –112.16 (d, J = 7.5 Hz, 1F). HRMS (ESI^+): calcd for $C_{20}H_{15}ClF_2N$ $[M+H]^+$ 342.0861, found 342.0856.



(*E*)-2-(2-(3-(4-Bromophenyl)allyl)-4,6-difluorophenyl)pyridine (Table 3, 3t)

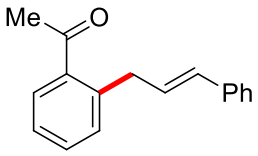
The general procedure A was applied to 2-(2,4-difluorophenyl)pyridine (38 mg, 0.2 mmol), (*E*)-*tert*-butyl (3-(4-bromophenyl)allyl) carbonate (125 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (60 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 3.2 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.38–7.29 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 9.2 Hz, 1H), 6.77 (t, *J* = 9.2 Hz, 1H), 6.15–6.05 (m, 2H), 3.46 (d, *J* = 3.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (dd, *J* = 247.0, 13.0 Hz), 159.1 (dd, *J* = 247.0, 12.0 Hz), 153.1, 149.7, 142.5 (dd, *J* = 9.0, 4.0 Hz), 136.2, 136.0, 131.5, 130.5, 128.3, 127.6, 125.9, 124.4 (dd, *J* = 16.0, 4.0 Hz), 122.6, 121.0, 112.2 (dd, *J* = 21.0, 4.0 Hz), 101.8 (t, *J* = 27.0 Hz), 36.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ =–109.90 (d, *J* = 7.9 Hz, 1F), –112.12 (d, *J* = 7.9 Hz, 1F). HRMS (ESI^+): calcd for $C_{20}H_{15}BrF_2N$ $[M+H]^+$ 386.0356 and 388.0335, found 386.0364 and 388.0343.



(*E*)-2-(2-Allylphenyl)pyridine (Table 3, 3u)[5]

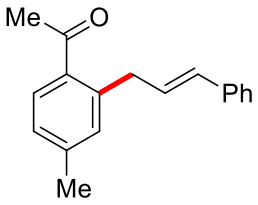
The general procedure A was applied to 2-phenylpyridine (31 mg, 0.2 mmol), (*E*)-*tert*-butyl allyl carbonate (63 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/15) to afford the title compound (16 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 4.8 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.40–7.28 (m, 5H), 7.26–7.23 (m, 1H), 5.93–5.83 (m, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 3.48 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 149.2, 140.5, 137.8, 137.7, 136.3, 130.1, 130.0, 128.6, 126.4, 124.3, 121.8, 115.7, 37.5, 27.3. HRMS (ESI^+): calcd for $C_{14}H_{14}N$ $[M+H]^+$ 196.1126, found

196.1129.



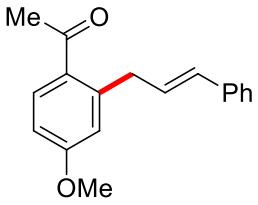
(*E*)-1-(2-Cinnamylphenyl)ethanone (Scheme 2, 5a)

The general procedure B was applied to (*E*)-4-methoxy-*N*-(1-phenylethylidene)aniline (45 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (28.5 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.26–7.24 (m, 3H), 7.20–7.14 (m, 3H), 7.07 (t, J = 7.2 Hz, 1H), 6.38–6.24 (m, 2H), 3.71 (d, J = 5.2 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 140.0, 137.9, 137.5, 131.5, 131.2, 131.0, 129.2, 129.1, 128.4, 127.0, 126.2, 126.1, 37.2, 29.8. HRMS (ESI^+): calcd for $C_{17}H_{17}O$ $[M+H]^+$ 237.1279, found 237.1276.



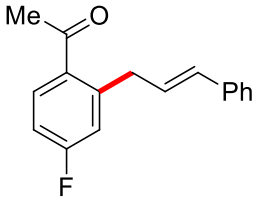
(*E*)-1-(2-Cinnamyl-4-methylphenyl)ethanone (Scheme 2, 5b)

The general procedure B was applied to (*E*)-4-methoxy-*N*-(1-(p-tolyl)ethylidene)aniline (48 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (29 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.14 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.48–6.34 (m, 2H), 3.80 (d, J = 4.8 Hz, 2H), 2.56 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.3, 142.2, 140.6, 137.6, 134.8, 132.1, 130.8, 129.8, 129.5, 128.4, 126.9, 126.8, 126.1, 37.4, 29.6, 21.4. HRMS (ESI^+): calcd for $C_{18}H_{19}O$ $[M+H]^+$ 251.1436, found 251.1444.



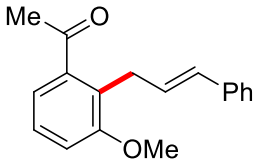
(*E*)-1-(2-Cinnamyl-4-methoxyphenyl)ethanone (Scheme 2, 5c)

The general procedure B was applied to (*E*)-4-methoxy-*N*-(1-(4-methoxyphenyl)ethylidene)-aniline (51 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound (37 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H), 7.29–7.26 (m, 2H), 7.16 (t, J = 7.2 Hz, 1H), 6.85 (s, 1H), 6.78 (d, J = 8.8 Hz, 1H), 6.46–6.35 (m, 2H), 3.86 (d, J = 4.8 Hz, 2H), 3.84 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 162.1, 143.9, 137.6, 132.5, 131.0, 129.9, 129.2, 128.4, 127.0, 126.2, 116.9, 110.8, 55.3, 37.9, 29.3. HRMS (ESI^+): calcd for $C_{18}H_{19}O_2$ $[M+H]^+$ 267.1385, found 267.1380.



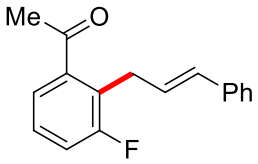
(*E*)-1-(2-Cinnamyl-4-fluorophenyl)ethanone (Scheme 2, 5d)

The general procedure B was applied to (*E*)-*N*-(1-(4-fluorophenyl)ethylidene)-4-methoxy-aniline (49 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (32.5 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.72 (m, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.30–7.26 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 10.0 Hz, 1H), 6.98 (t, J = 8.4 Hz, 1H), 6.45–6.30 (m, 2H), 3.82 (d, J = 6.4 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 163.0 (d, J = 252.0 Hz), 144.3 (d, J = 8.0 Hz), 137.3, 133.8 (d, J = 3.0 Hz), 131.9 (d, J = 9.0 Hz), 131.7, 128.5, 128.2, 127.2, 126.1, 118.0 (d, J = 21.0 Hz), 112.9 (d, J = 21.0 Hz), 37.3, 29.7; ^{19}F NMR (377 MHz, $CDCl_3$): δ =–107.20. HRMS (ESI^+): calcd for $C_{17}H_{16}FO$ $[M+H]^+$ 255.1185, found 255.1180.



(*E*)-1-(2-cinnamyl-3-methoxyphenyl)ethanone (Scheme 2, 5e)

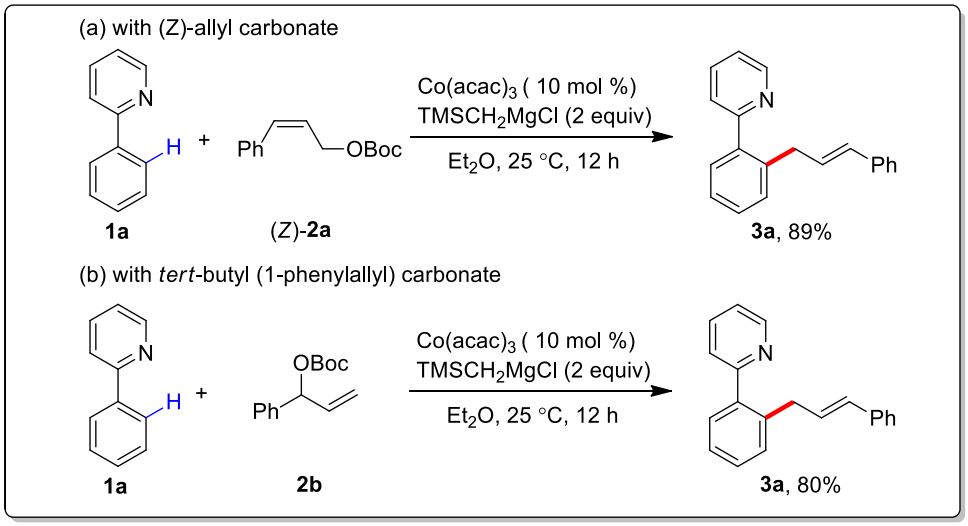
The general procedure B was applied to (*E*)-3-methoxy-*N*-(1-(4-methoxyphenyl)ethylidene)-aniline (51 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/30) to afford the title compound (33 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.22 (m, 5H), 7.17–7.13 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.41–6.29 (m, 2H), 3.86 (s, 3H), 3.74 (d, J = 5.2 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.2, 158.2, 140.7, 138.0, 130.4, 129.2, 128.5, 127.6, 127.1, 126.9, 126.2, 120.3, 113.3, 56.0, 30.7, 29.4. GC-MS (EI): calcd for $C_{18}H_{19}O_2$ [M] 266.13, found 266.15.



(*E*)-1-(2-Cinnamyl-3-fluorophenyl)ethanone (Scheme 2, 5f)

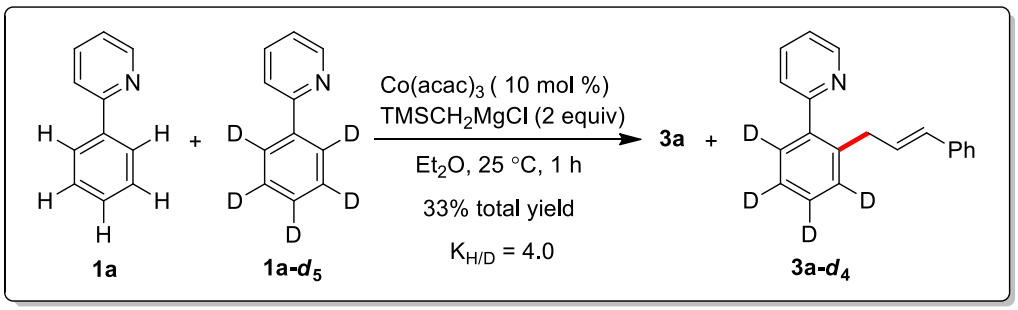
The general procedure B was applied to (*E*)-*N*-(1-(3-fluorophenyl)ethylidene)-4-methoxy-aniline (49 mg, 0.2 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (94 mg, 0.4 mmol) and $Co(acac)_3$ (7 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/40) to afford the title compound (33 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.6 Hz, 1H), 7.30–7.15 (m, 7H), 6.45–6.30 (m, 2H), 3.78 (d, J = 5.2 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 160.6 (d, J = 245.0 Hz), 140.4 (d, J = 4.0 Hz), 137.6, 131.2, 128.6, 127.9, 127.5 (d, J = 8.0 Hz), 127.2, 127.0 (d, J = 16.0 Hz), 126.3, 124.6 (d, J = 4.0 Hz), 118.5 (d, J = 24.0 Hz), 30.2, 28.8 (d, J = 5.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ = –115.64. GC-MS (EI): calcd for $C_{17}H_{16}FO$ [M] 254.11, found 254.11.

4. Cobalt-Catalyzed *ortho*-C–H Allylation of 2-Phenylpyridine with Allyl Carbonate (*Z*)-2a and 2b



The general procedure A was applied to 2-arylpyridine **1a** (31.0 mg, 0.20 mmol), allyl carbonate **2b** or **(*Z*)-2a** (93.6 mg, 0.40 mmol), and $Co(acac)_3$ (7.1 mg, 0.02 mmol) at 25 ℃ for 12 h. The crude product was purified by column chromatography on silica gel (EtOAc/PE =1/15) to provide the product **3a**. (**(*Z*)-2a:** 89% yield; **2b:** 80% yield**)**

5. Intermolecular Kinetic Isotopic Effect Experiment



The general procedure A was applied to 2-arylpyridine **1a** (31.0 mg, 0.20 mmol), **1a-*d*$_5$** (32.0 mg, 0.20 mmol), (*E*)-*tert*-butyl cinnamyl carbonate (93.6 mg, 0.4 mmol), and $Co(acac)_3$ (7.1 mg, 0.02 mmol) at 25 ℃ for 1 h. The crude residue was analyzed by ^{1}H NMR and then purified by column chromatography on silica gel (EtOAc/PE =1/15) to provide the mixed compounds **3a** and **3a-*d*$_4$**. The ^{1}H NMR data of the mixture suggest that the related KIE value is 4.0 (Figure S1). The KIE measurements were performed three runs giving the same result.

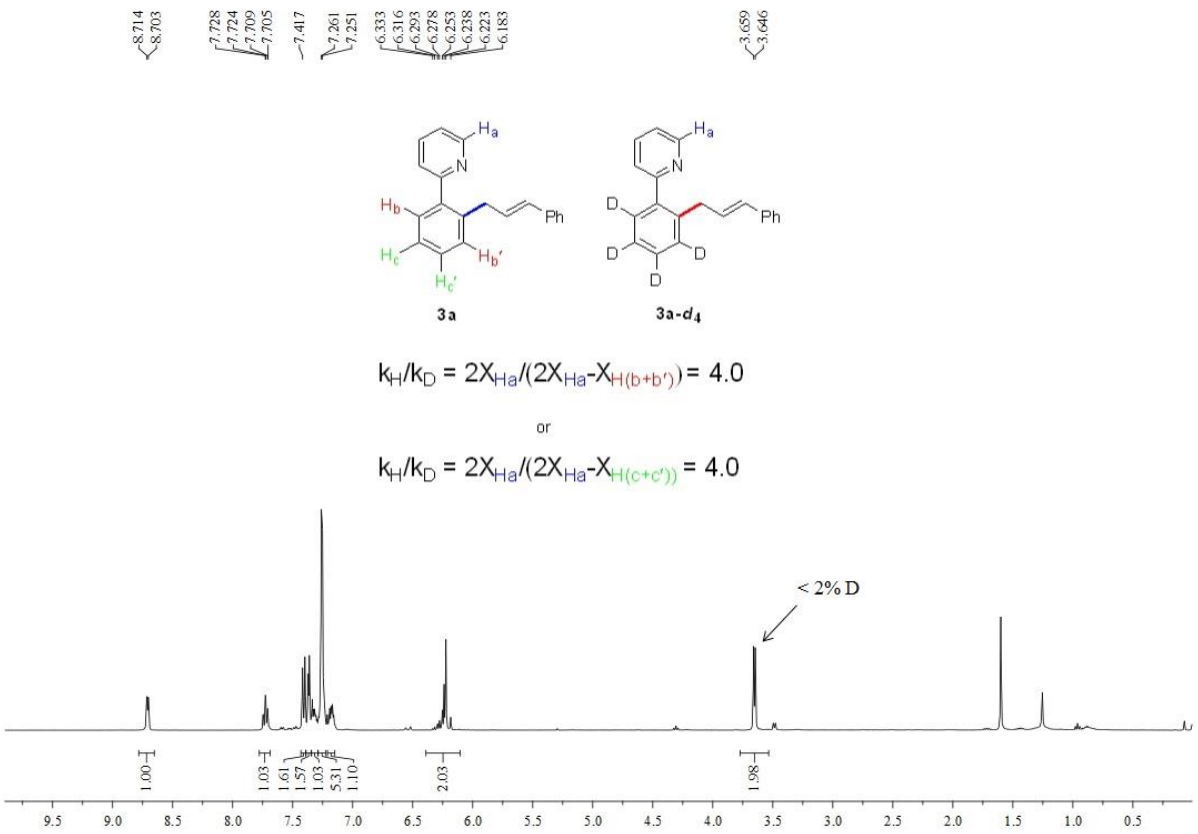


Figure S1. ^{1}H NMR spectrum of the mixed **3a** and **3a-*d*$_4$** measured in $CDCl_3$.

References

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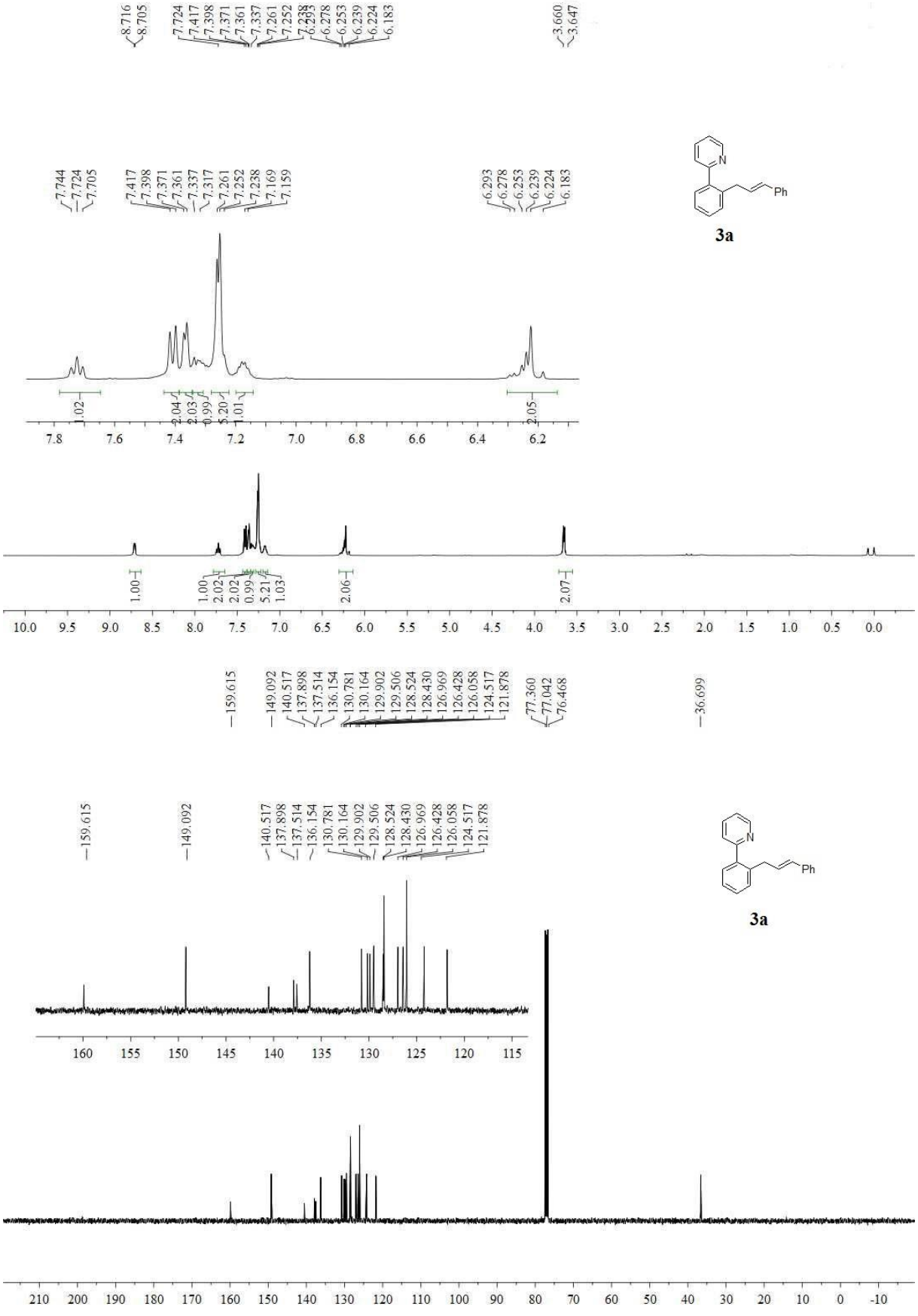
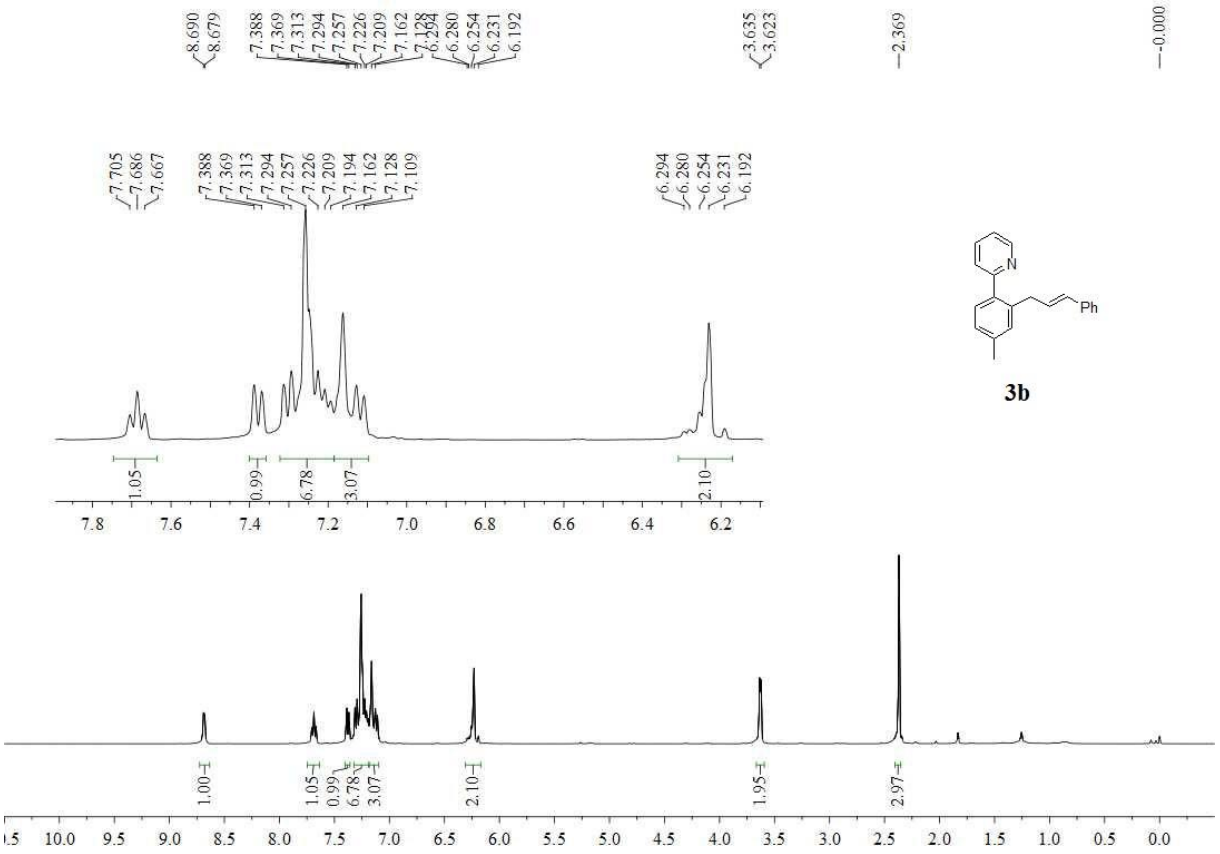
6. ^{1}H, ^{13}C and ^{19}F NMR Spectra

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6.231
6.192
3.635
3.623
2.369
0.000
7.705
7.686
7.667
7.388
7.369
7.313
7.294
7.257
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7.209
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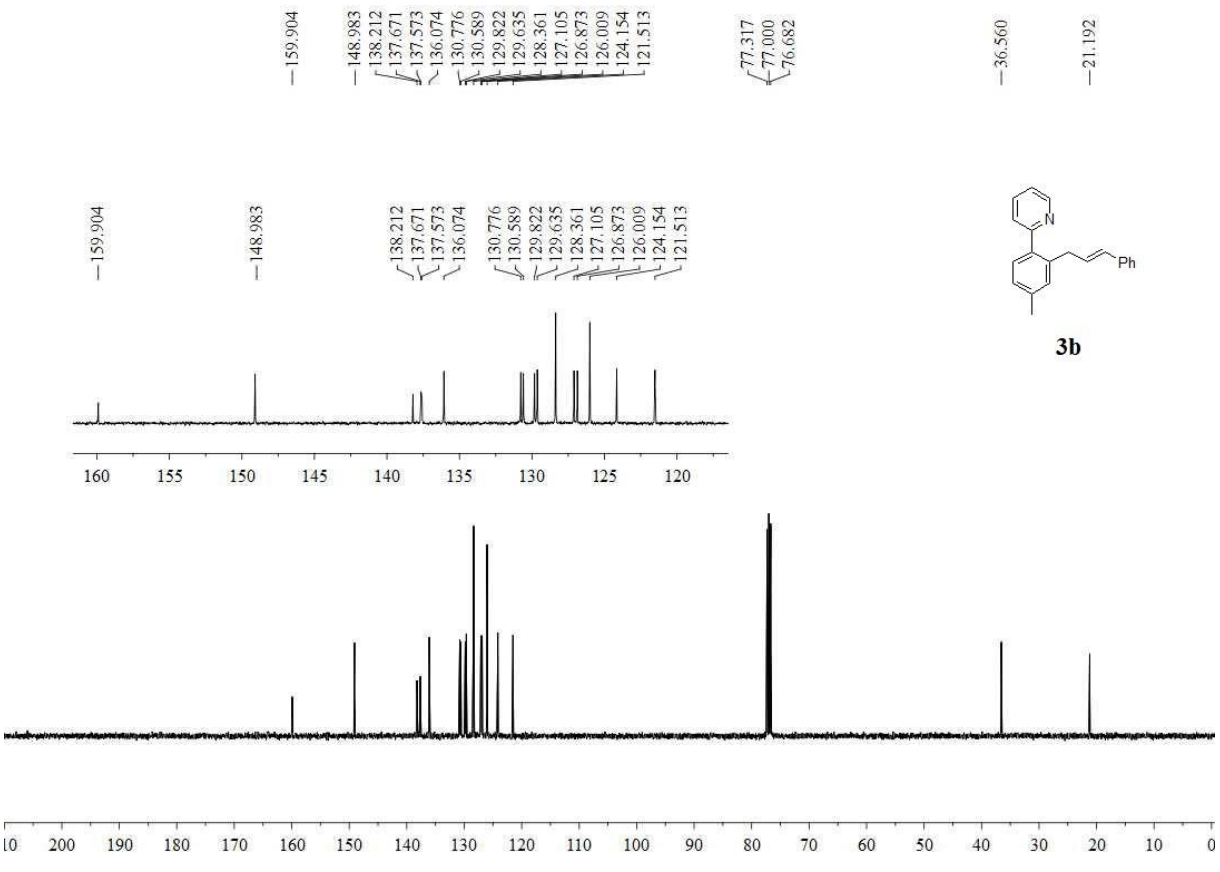
2.97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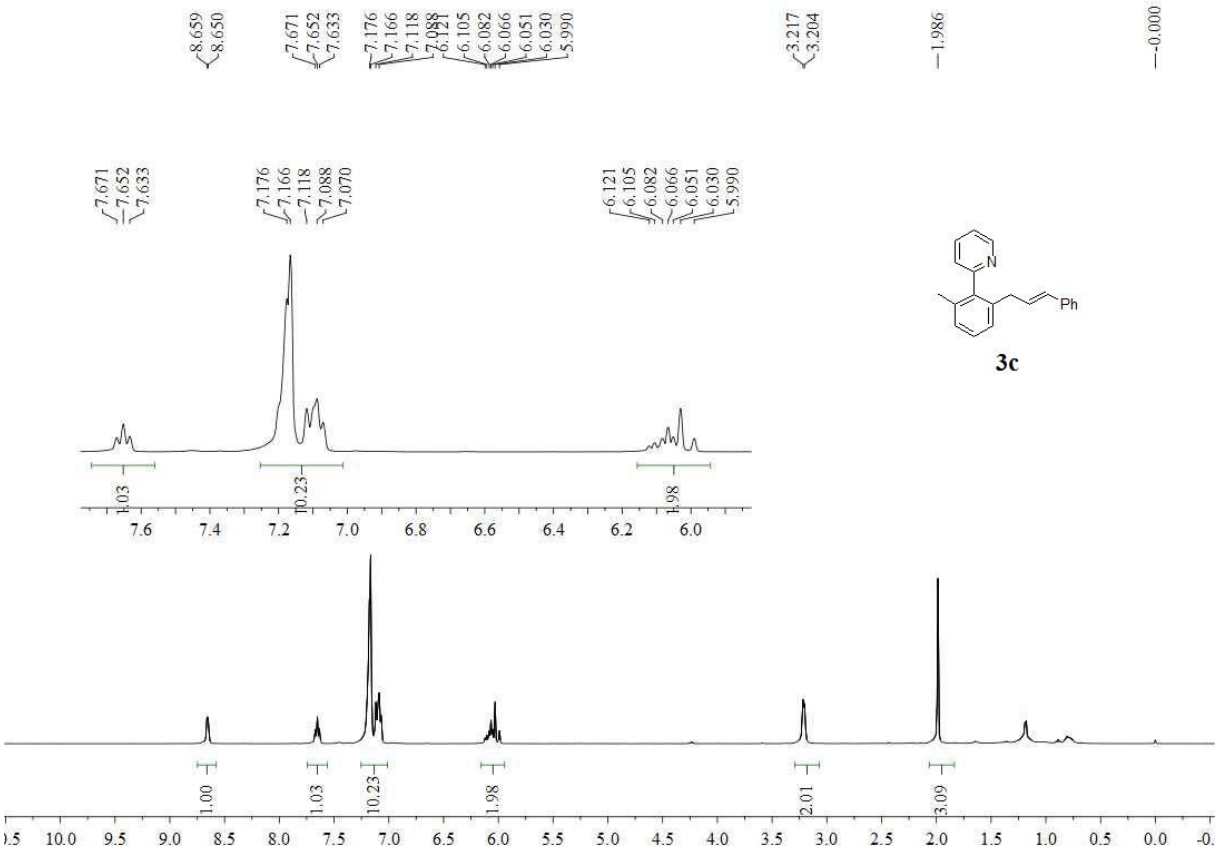
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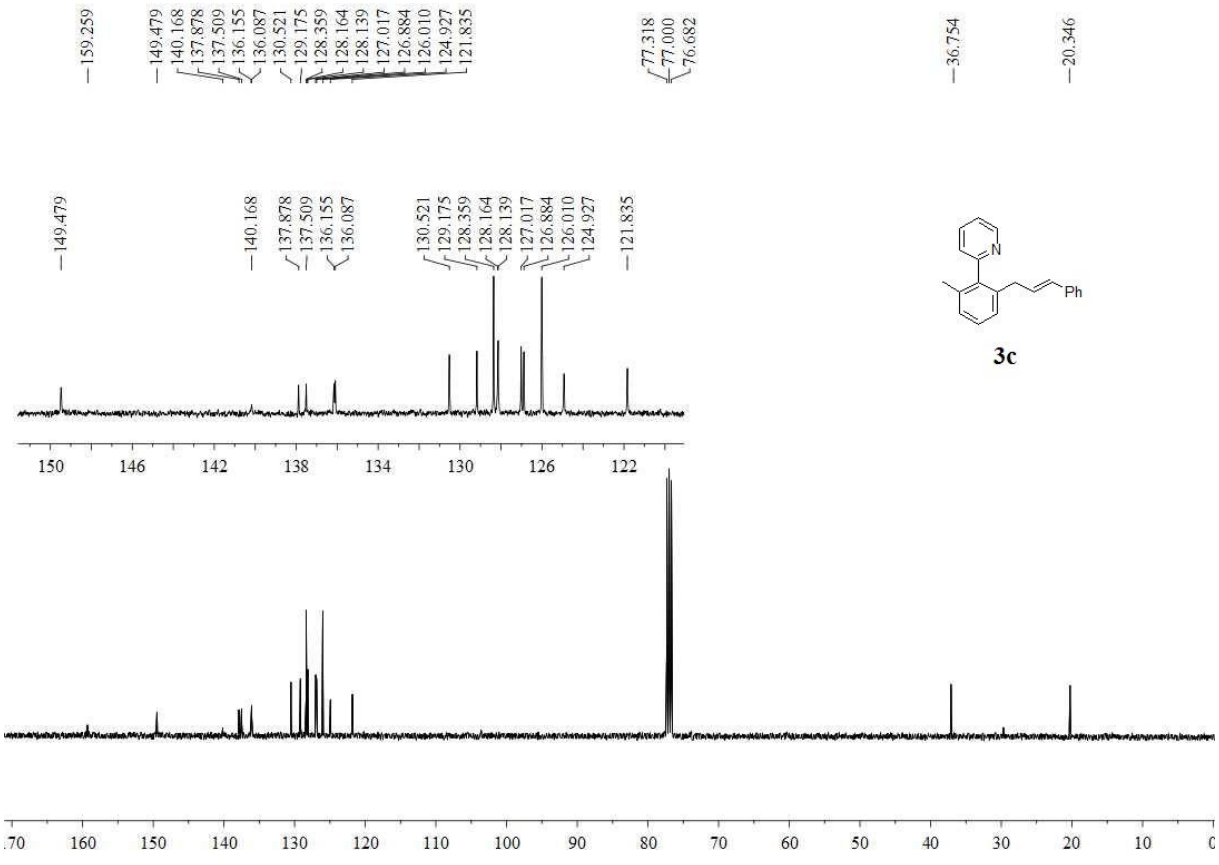
3c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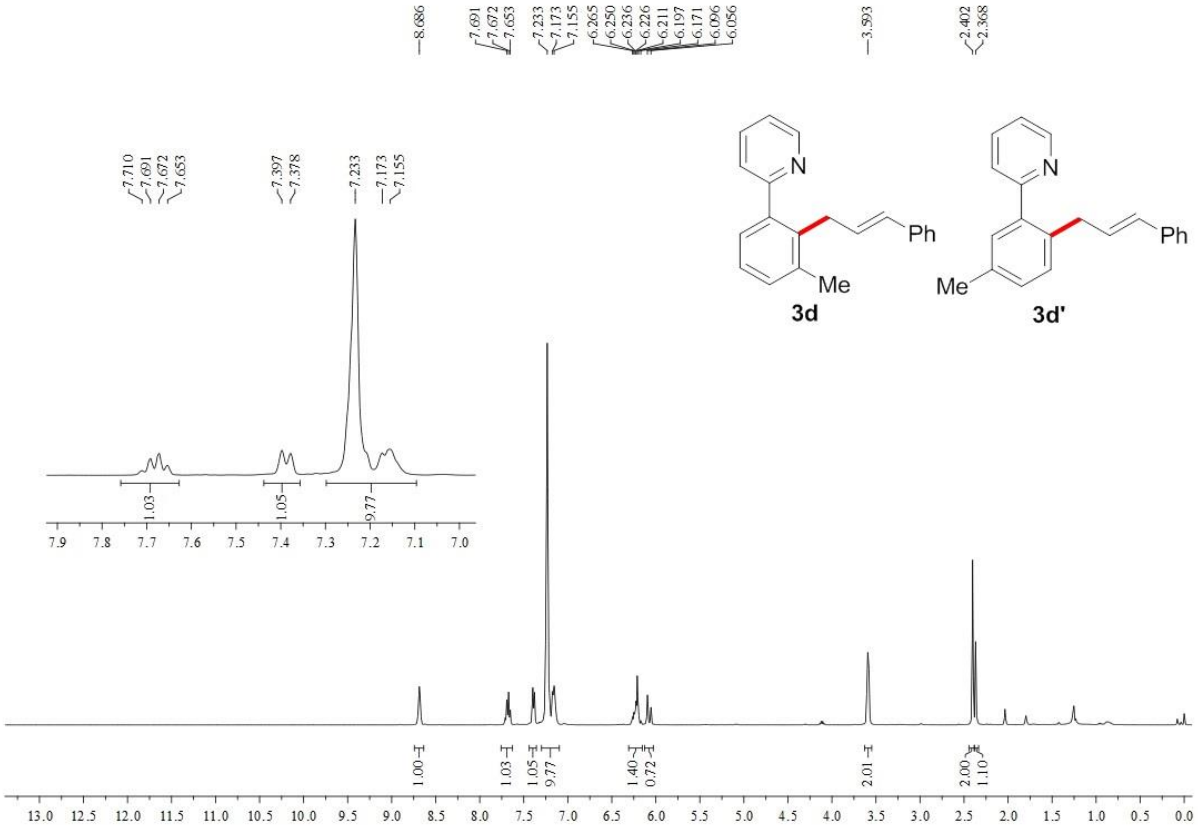
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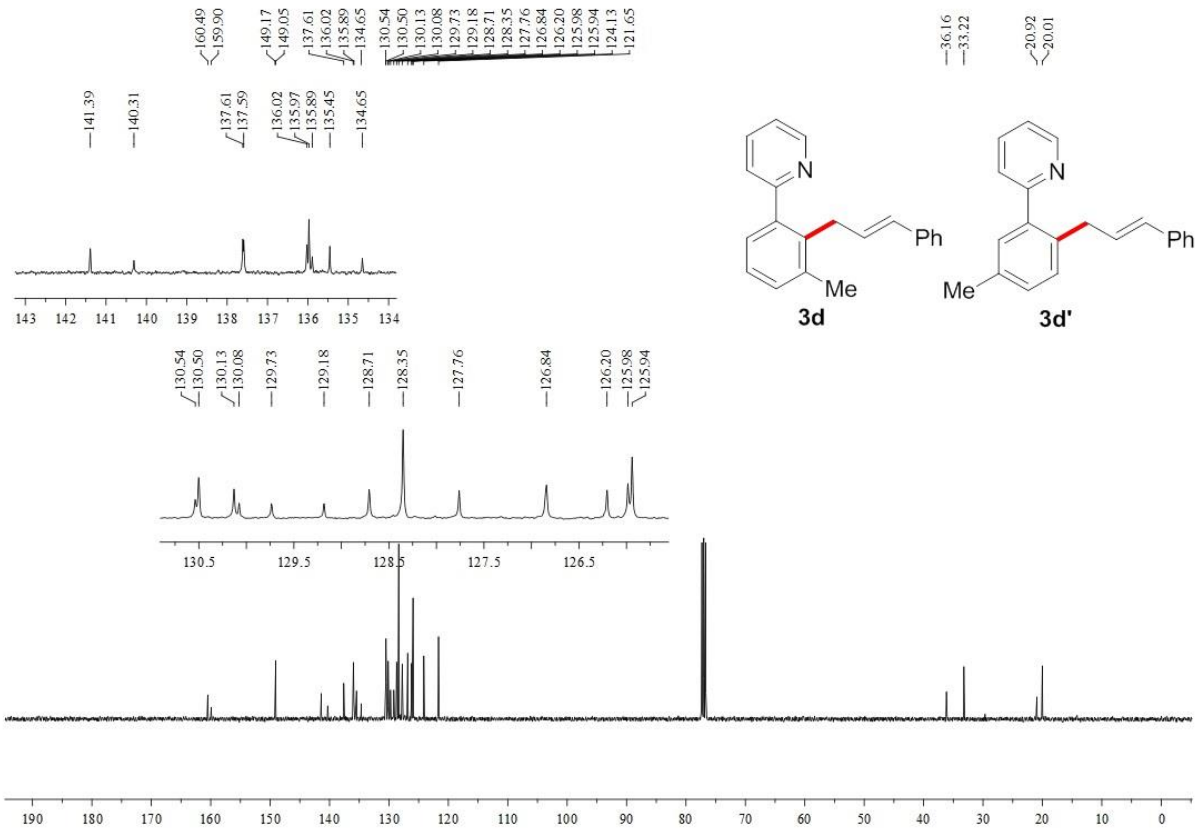
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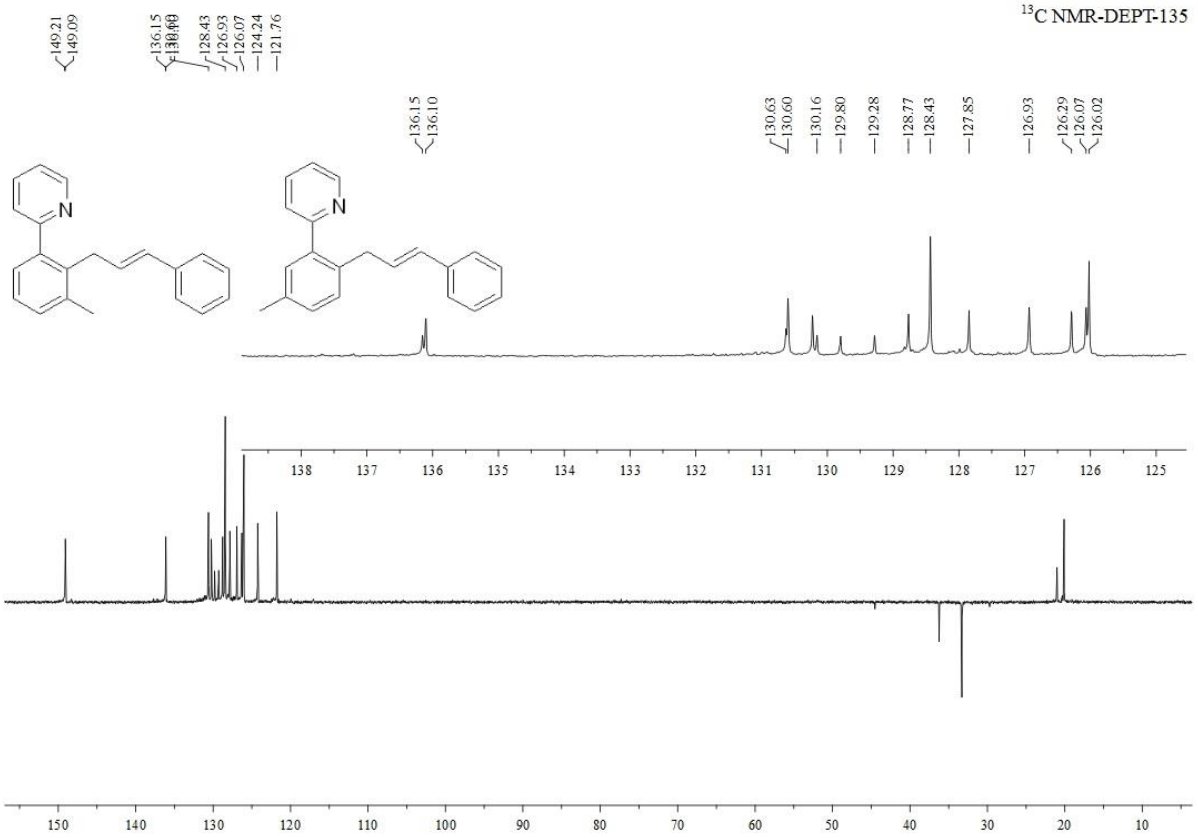
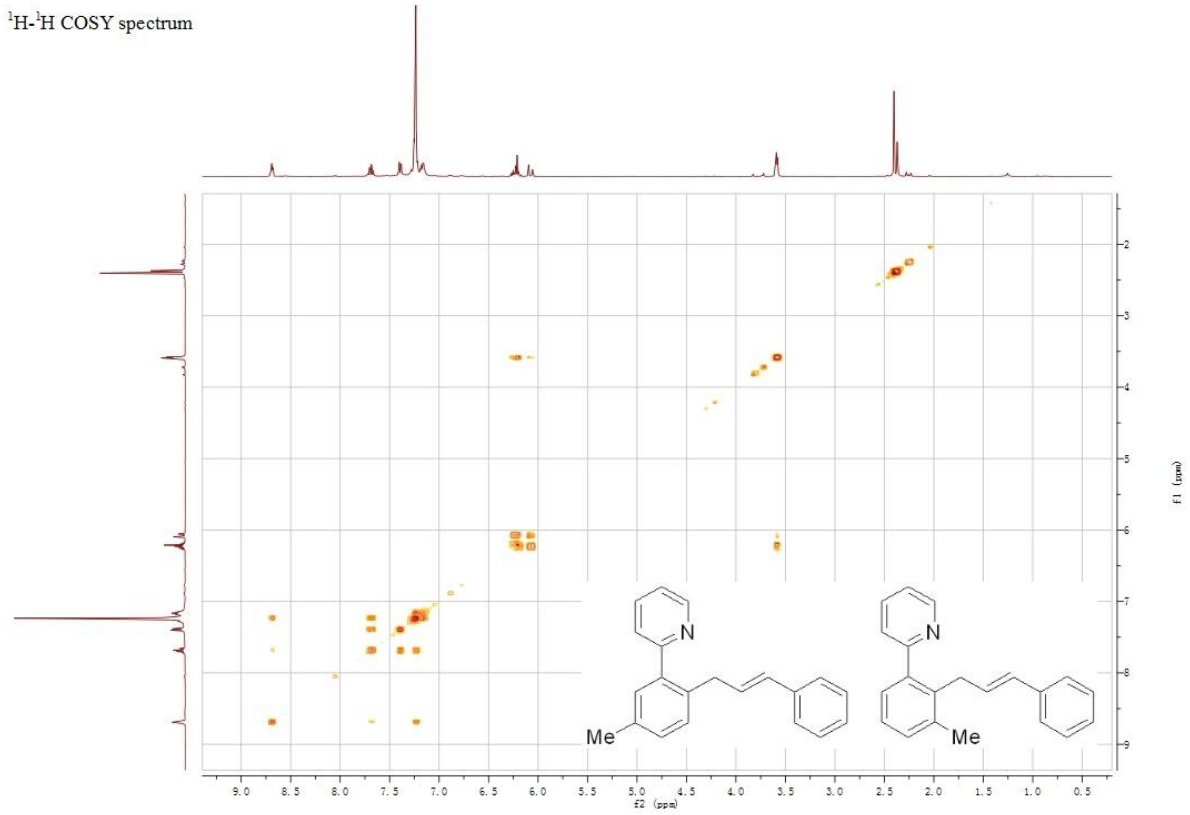
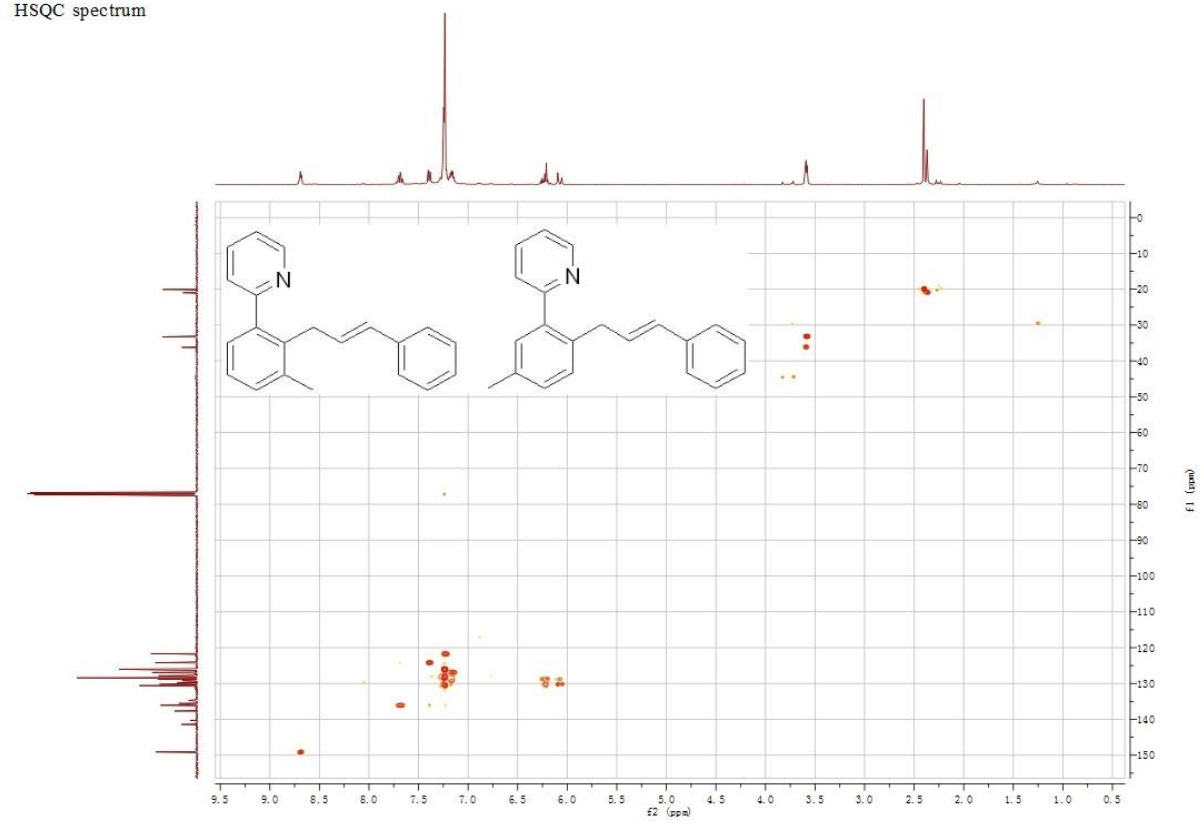
^{13}C NMR-DEPT-135



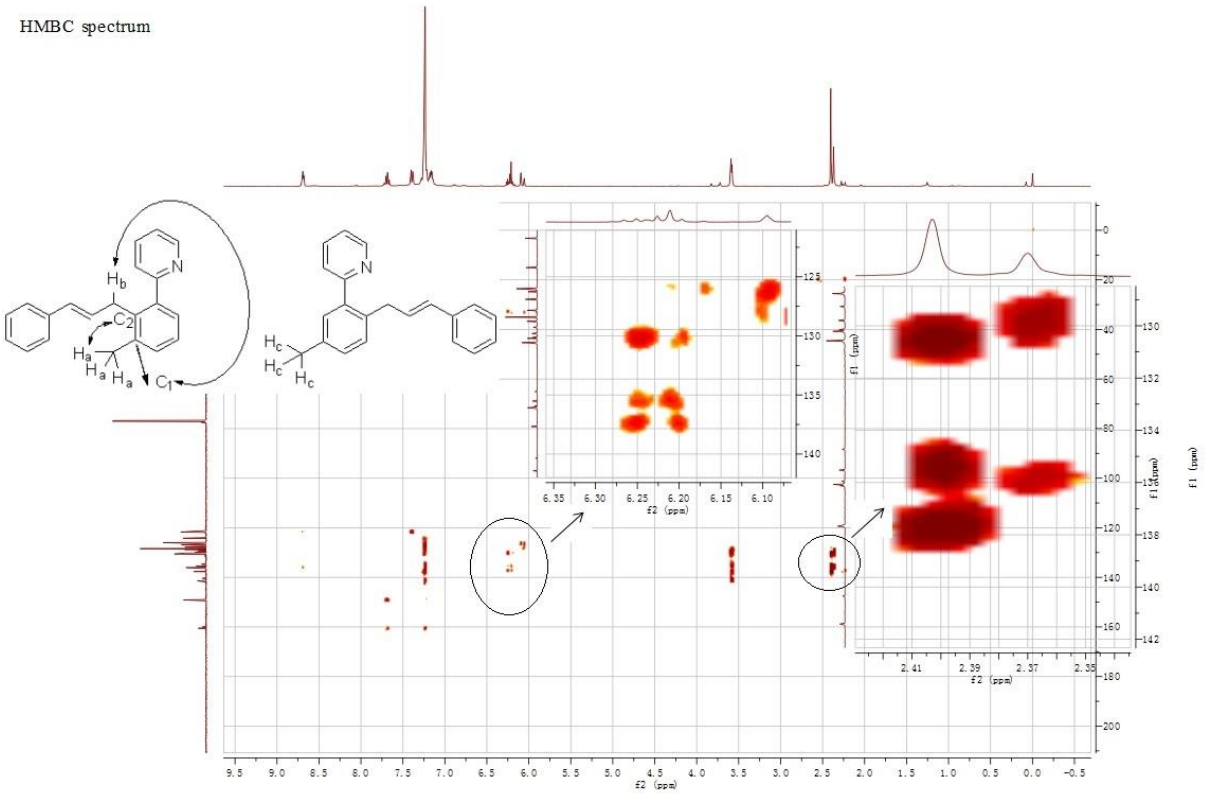
^{1}H-^{1}H COSY spectrum

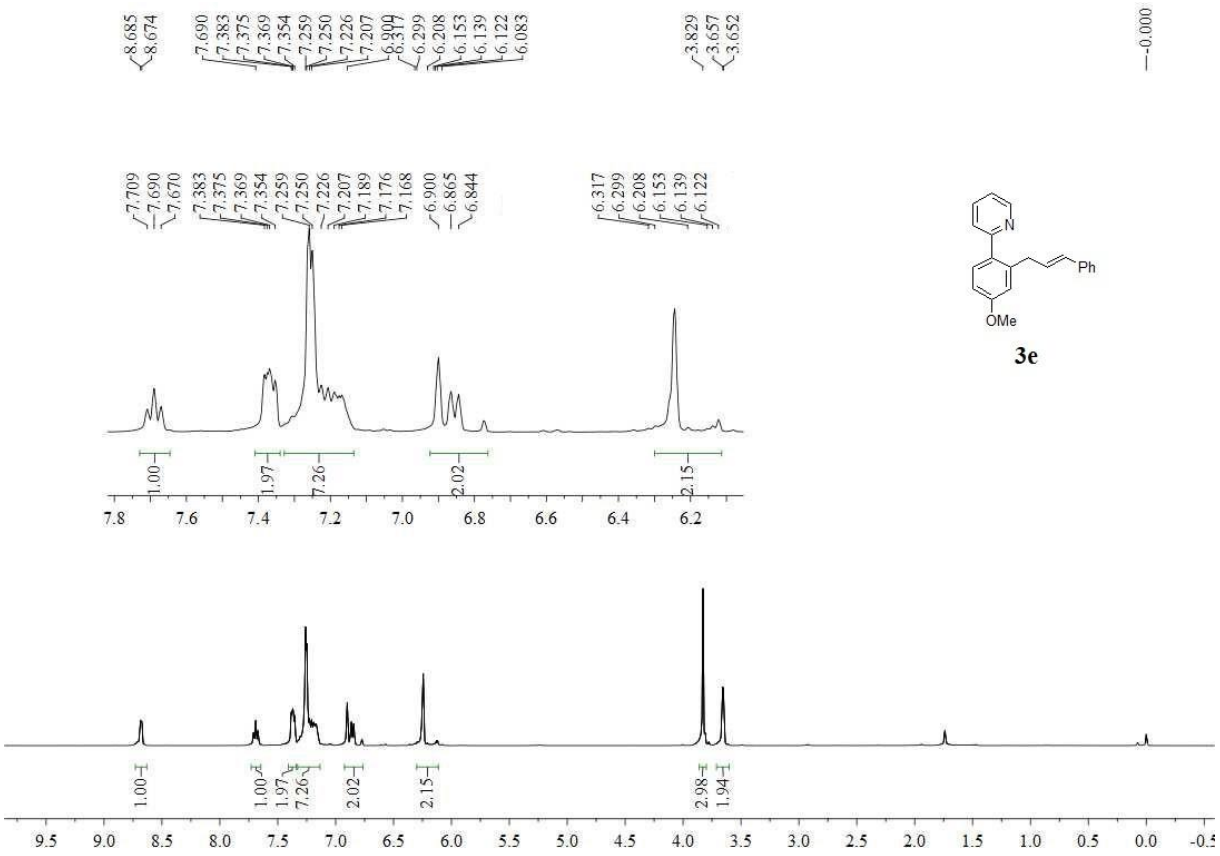


HSQC spectrum



HMBC spectrum

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6.299
6.208
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6.139
6.122
6.083
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3.652
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7.250
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7.207
7.189
7.176
7.168
6.900
6.865
6.844
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6.299
6.208
6.153
6.139
6.122
1.00
1.97
7.26
2.02
2.15
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
N
Ph
OMe
3e
1.00
1.00
1.97
7.26
2.02
2.15
2.98
1.94
9.5
9.0
8.5
8.0
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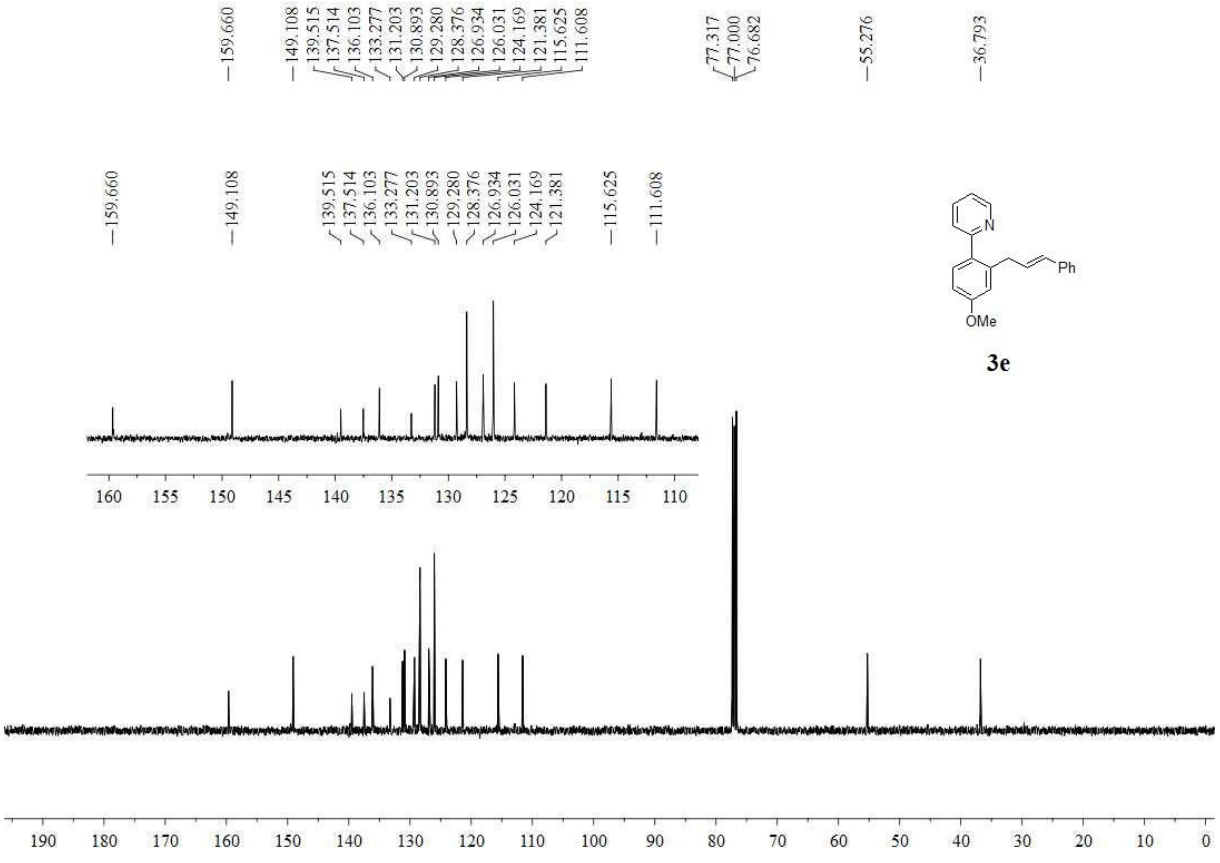
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139.515
137.514
136.103
133.277
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130.893
129.280
128.376
126.934
126.031
124.169
121.381
115.625
111.608
77.317
77.000
76.682
55.276
36.793
159.660
149.108
139.515
137.514
136.103
133.277
131.203
130.893
129.280
128.376
126.934
126.031
124.169
121.381
115.625
111.608
160
155
150
145
140
135
130
125
120
115
110
N
Ph
OMe
3e
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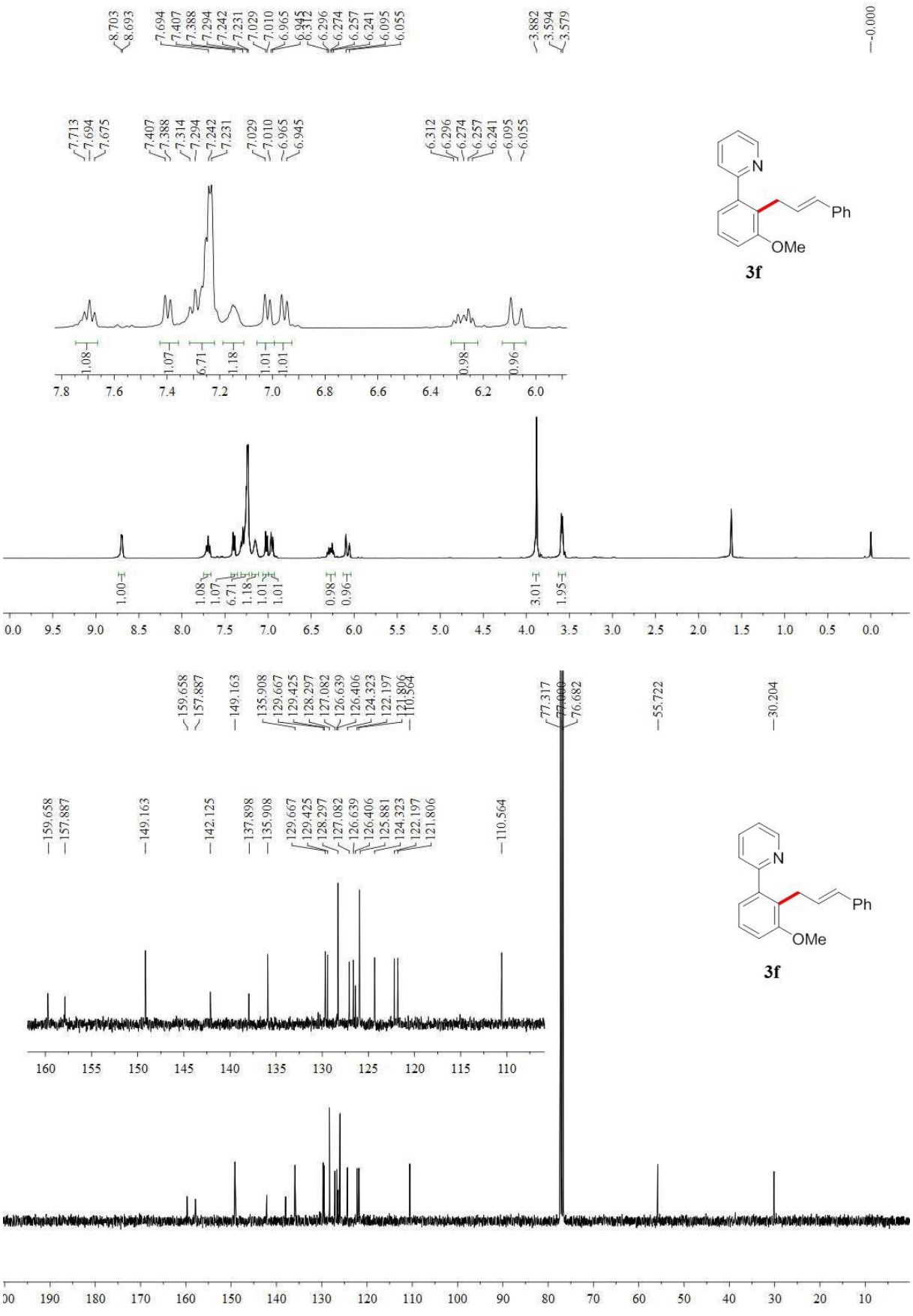
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7.242
7.231
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7.010
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6.312
6.296
6.274
6.257
6.241
6.095
6.055
3.882
3.594
3.579
-0.000
N
Ph
OMe
3f
1.00
1.08
1.07
6.71
1.18
1.01
1.01
0.98
0.96
3.01
1.95
159.658
157.887
149.163
135.908
129.667
129.425
128.297
127.082
126.639
126.406
124.323
122.197
121.806
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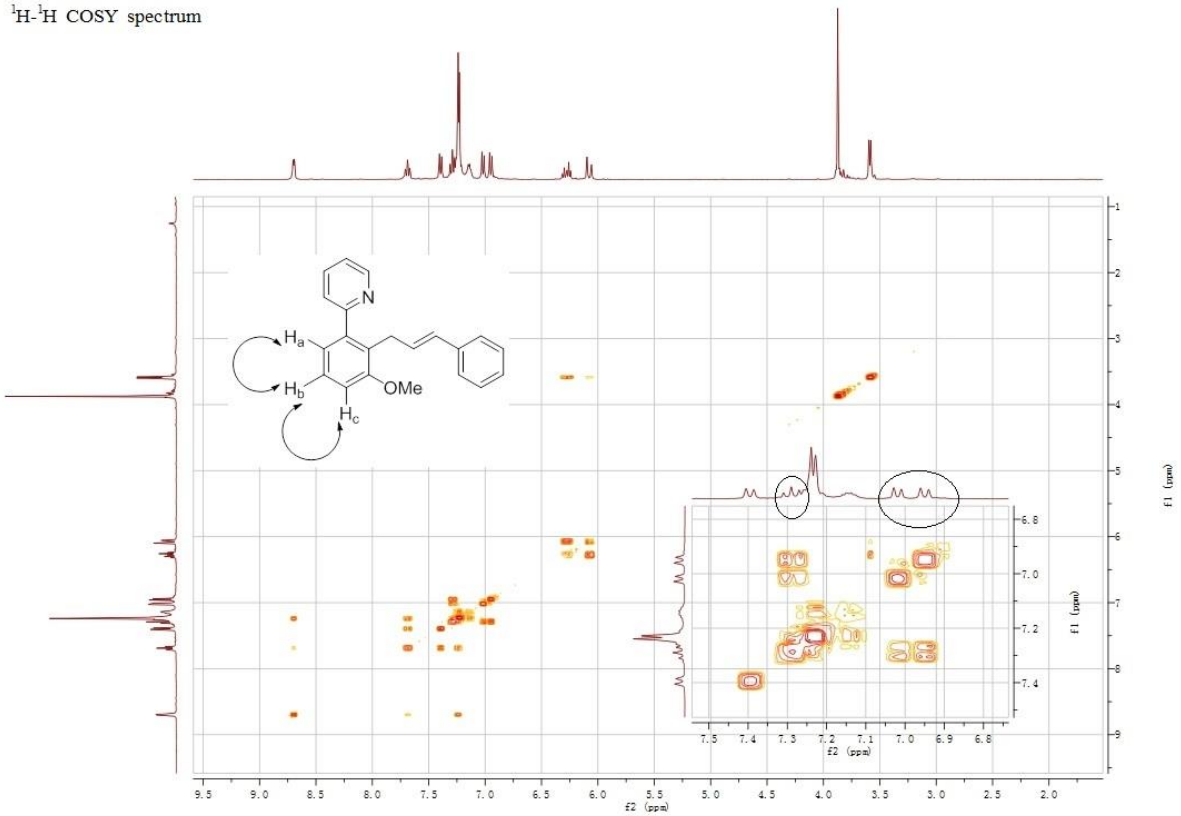
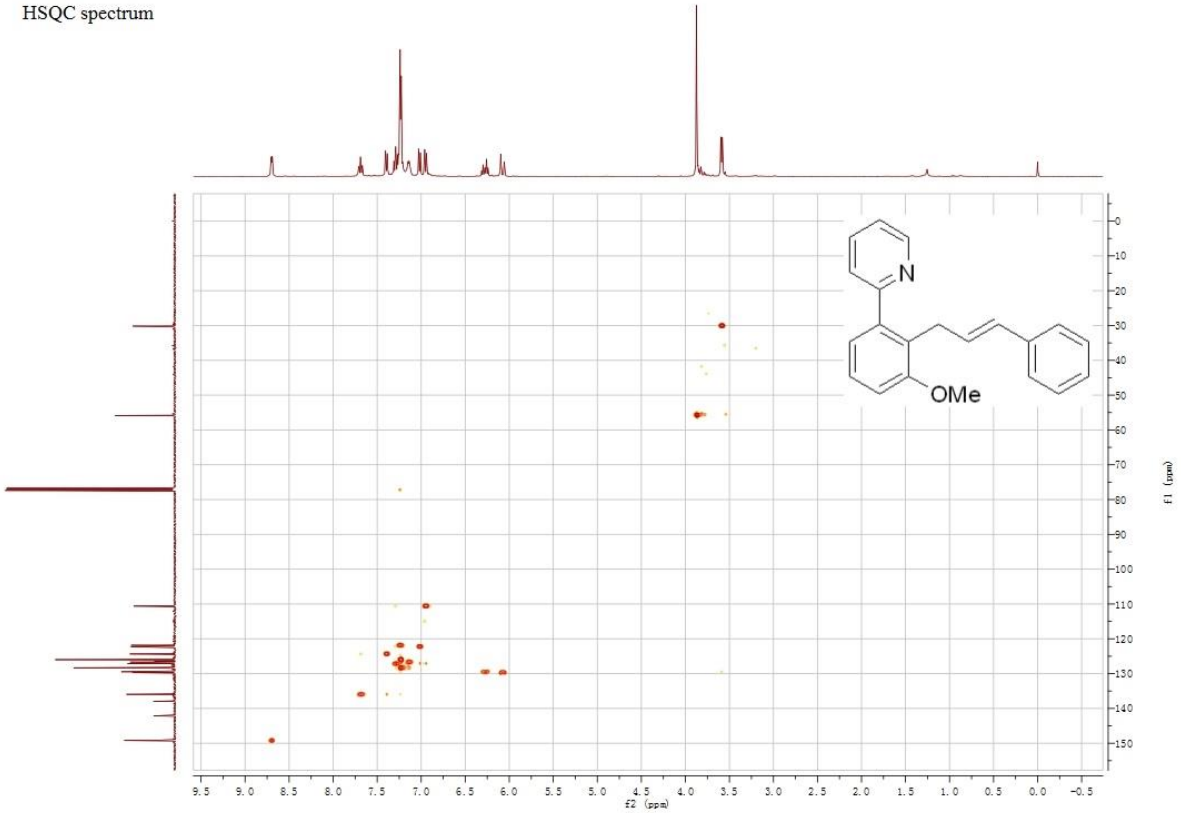
30.204
142.125
137.898
125.881
3f

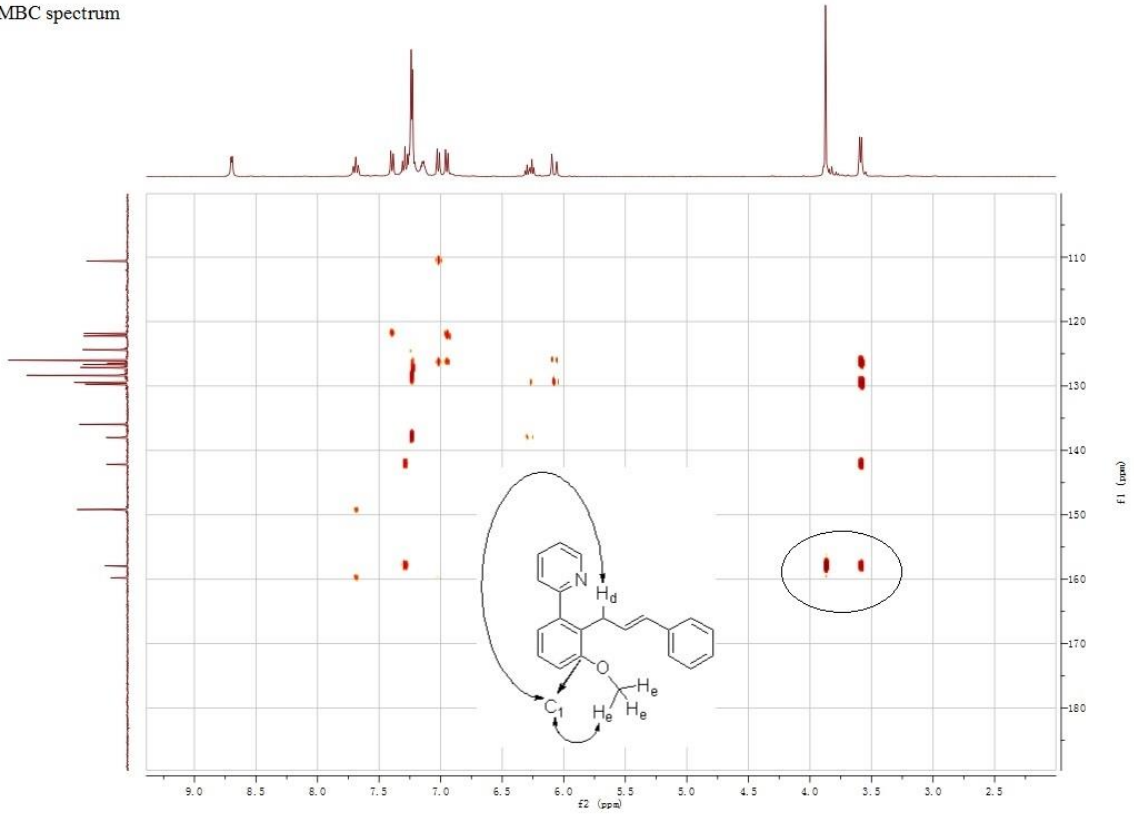
^{1}H-^{1}H COSY spectrum

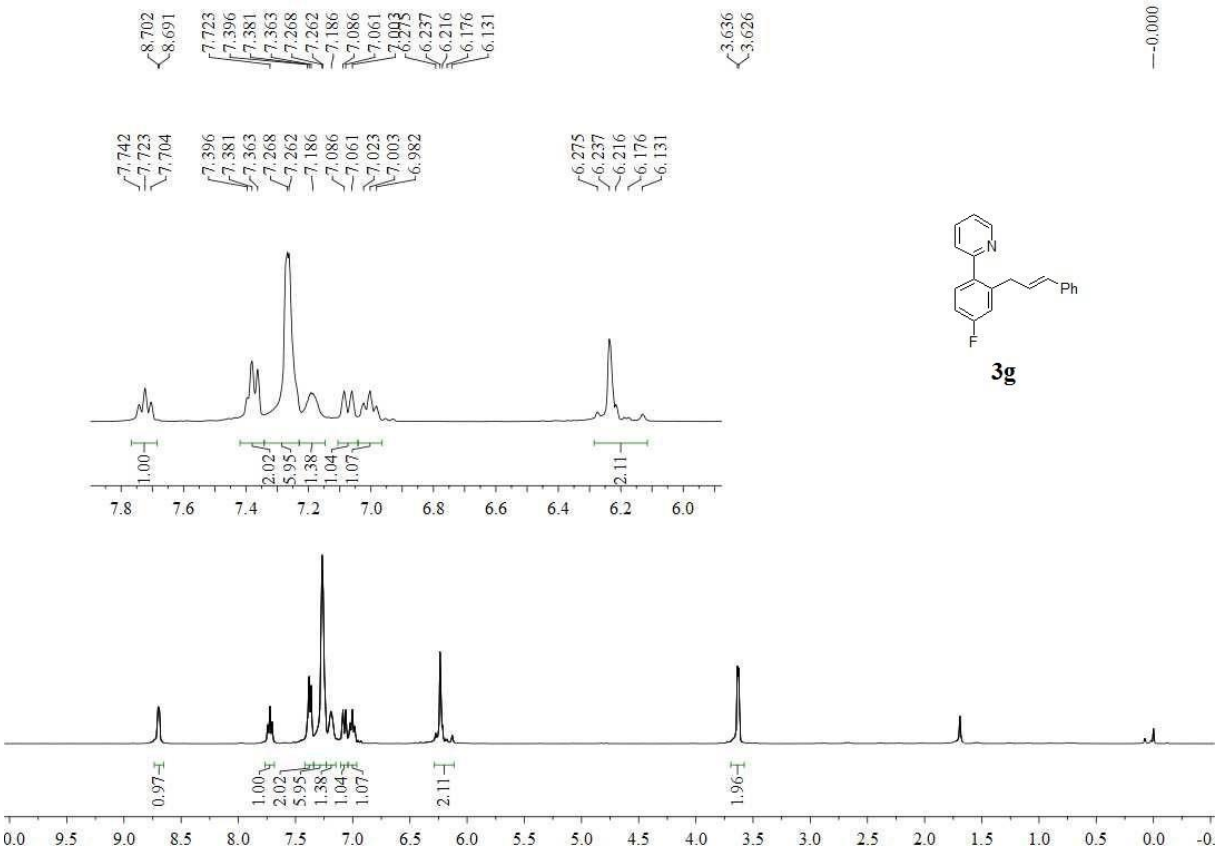


HSQC spectrum



HMBC spectrum

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7.003
6.982
6.275
6.237
6.216
6.176
6.131
3.636
3.626
-0.000
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3g
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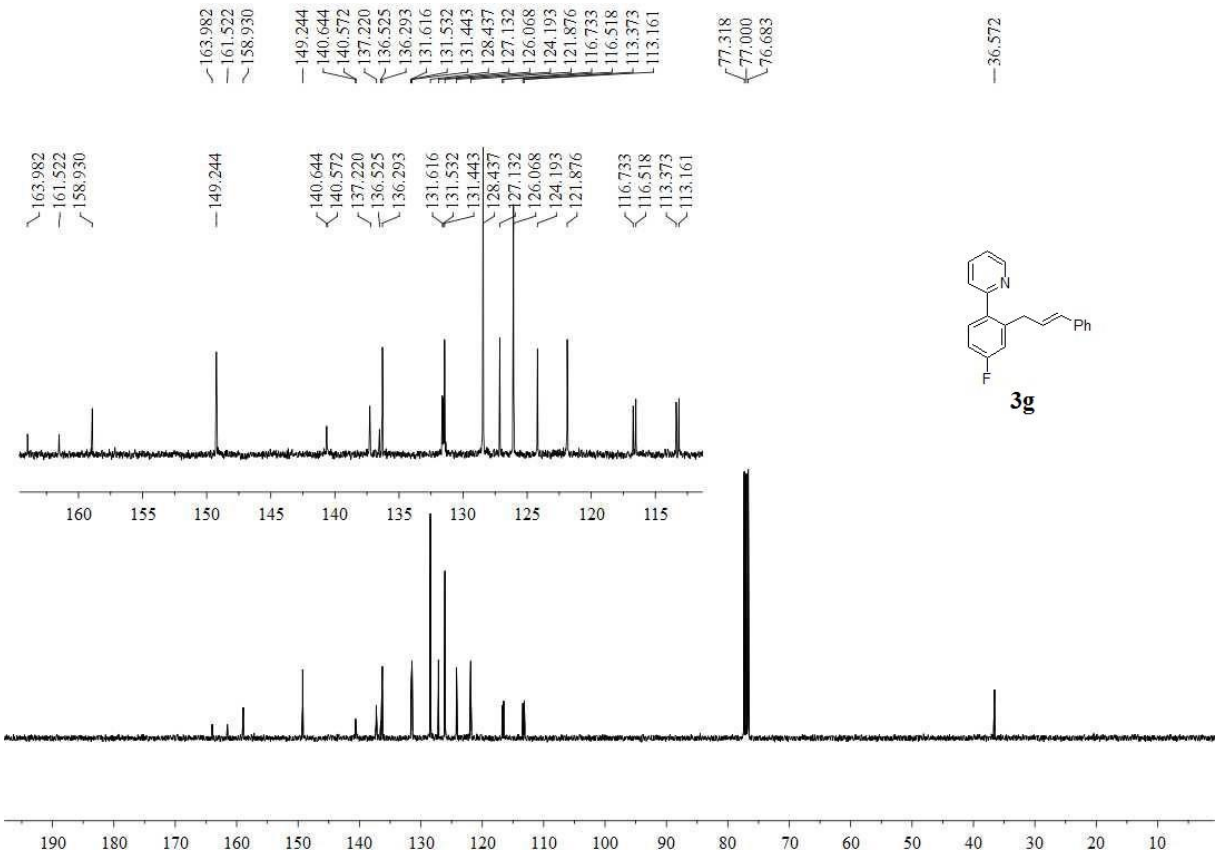
1.96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126.068
124.193
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113.161
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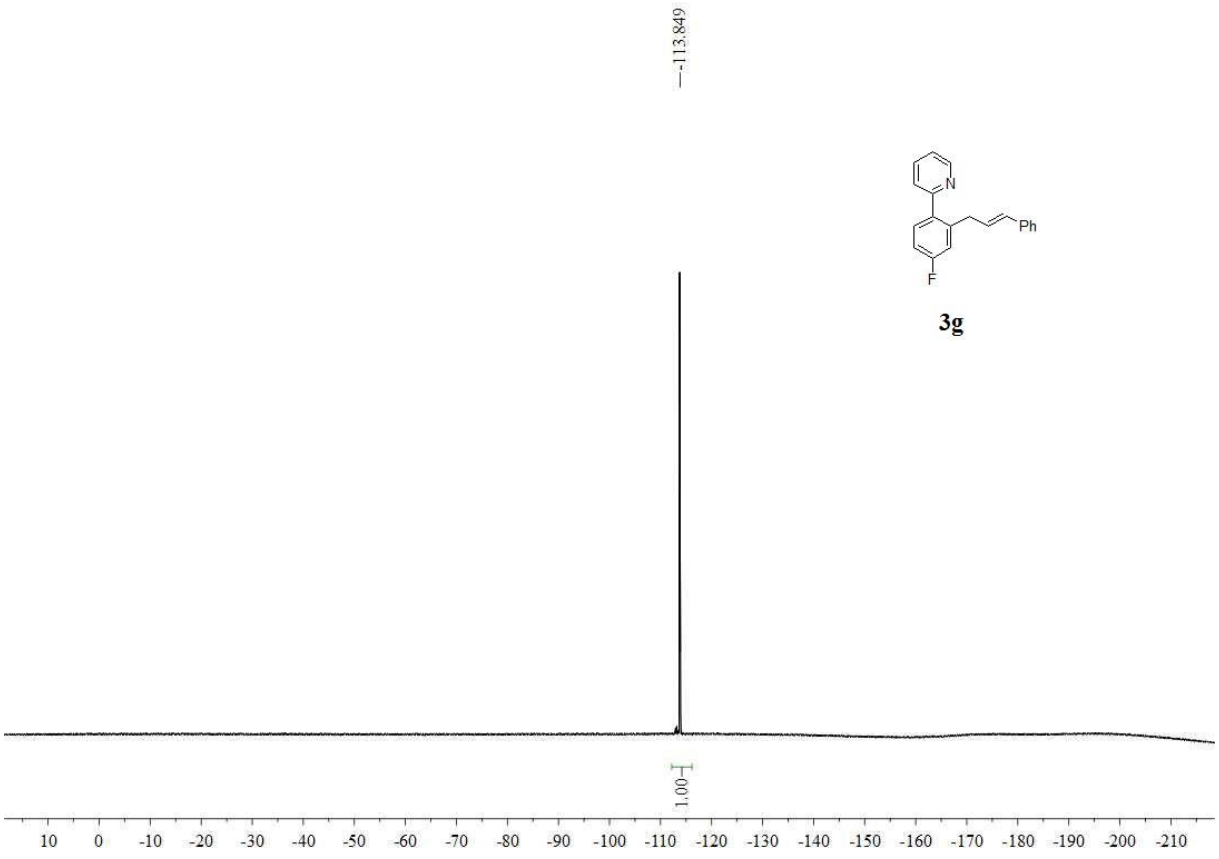
76.683
36.572
N
Ph
F
3g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F
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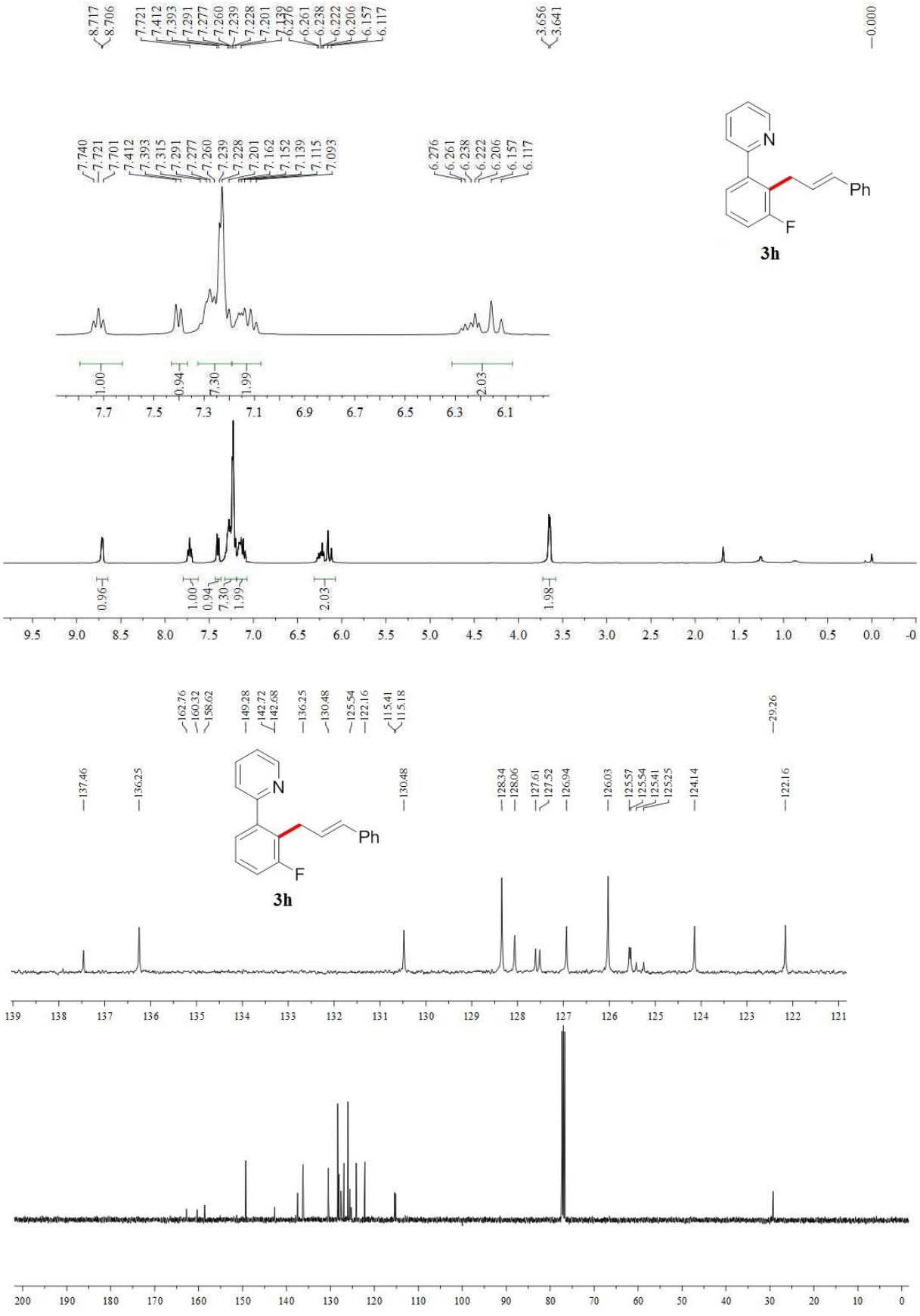
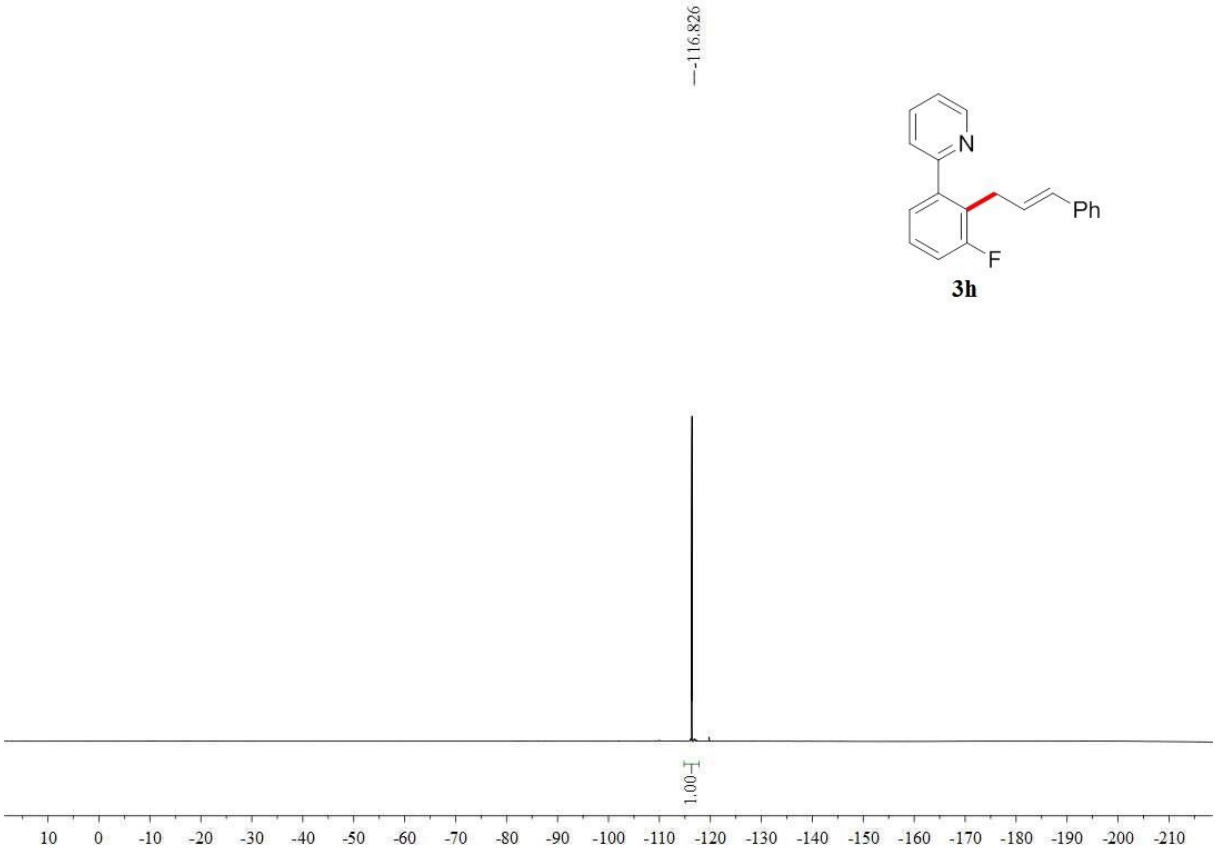
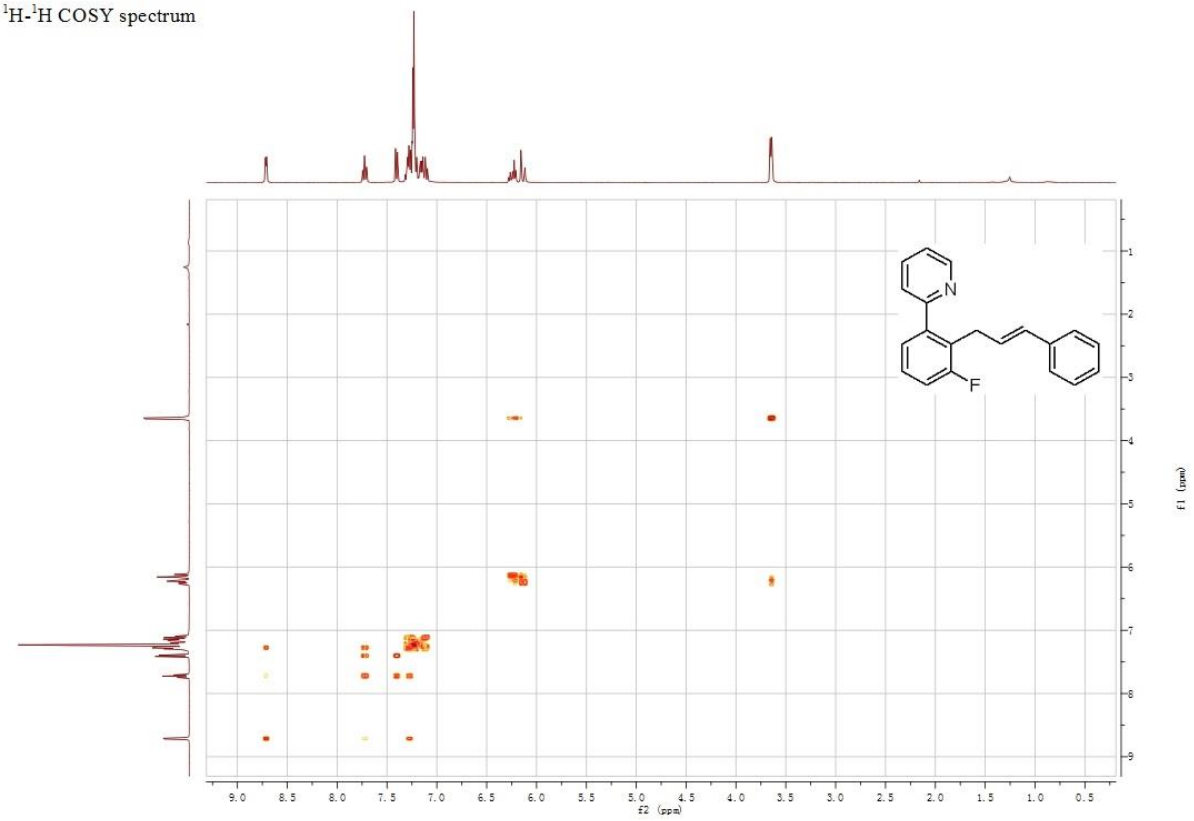
3g


3h
3h

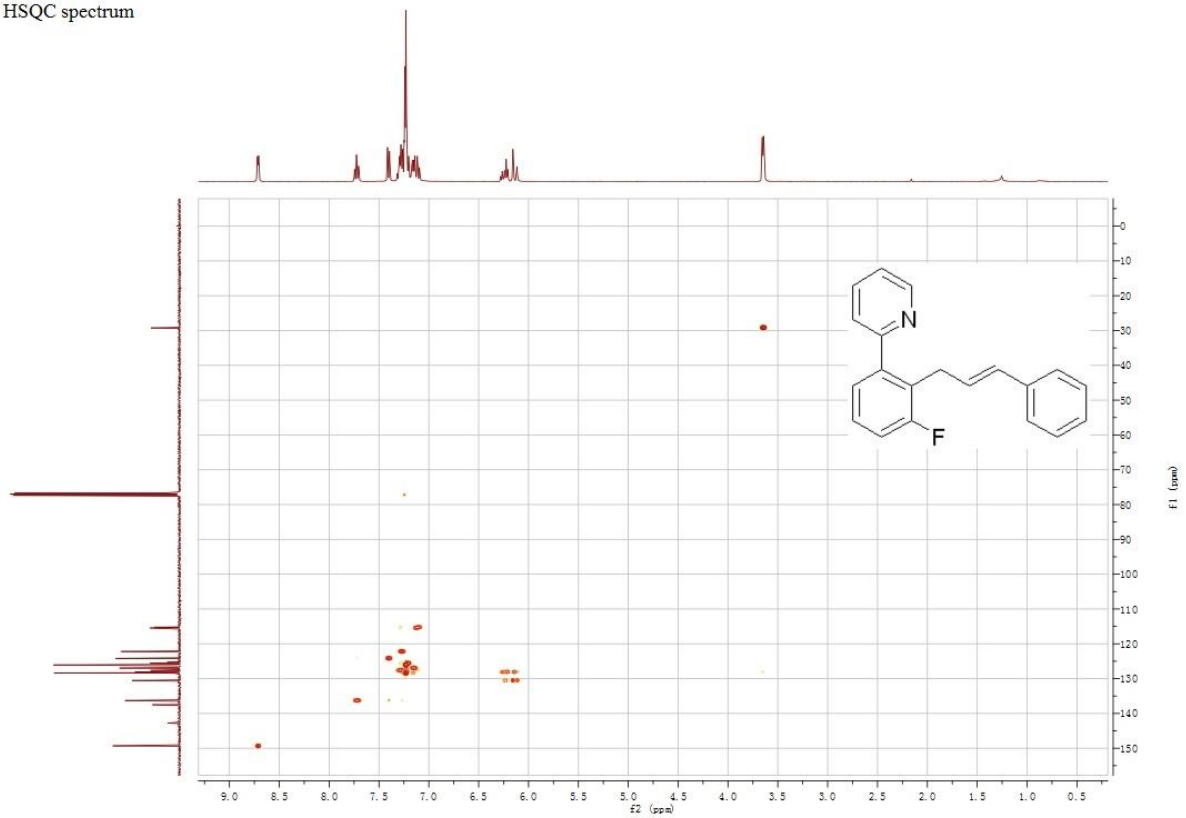


3h

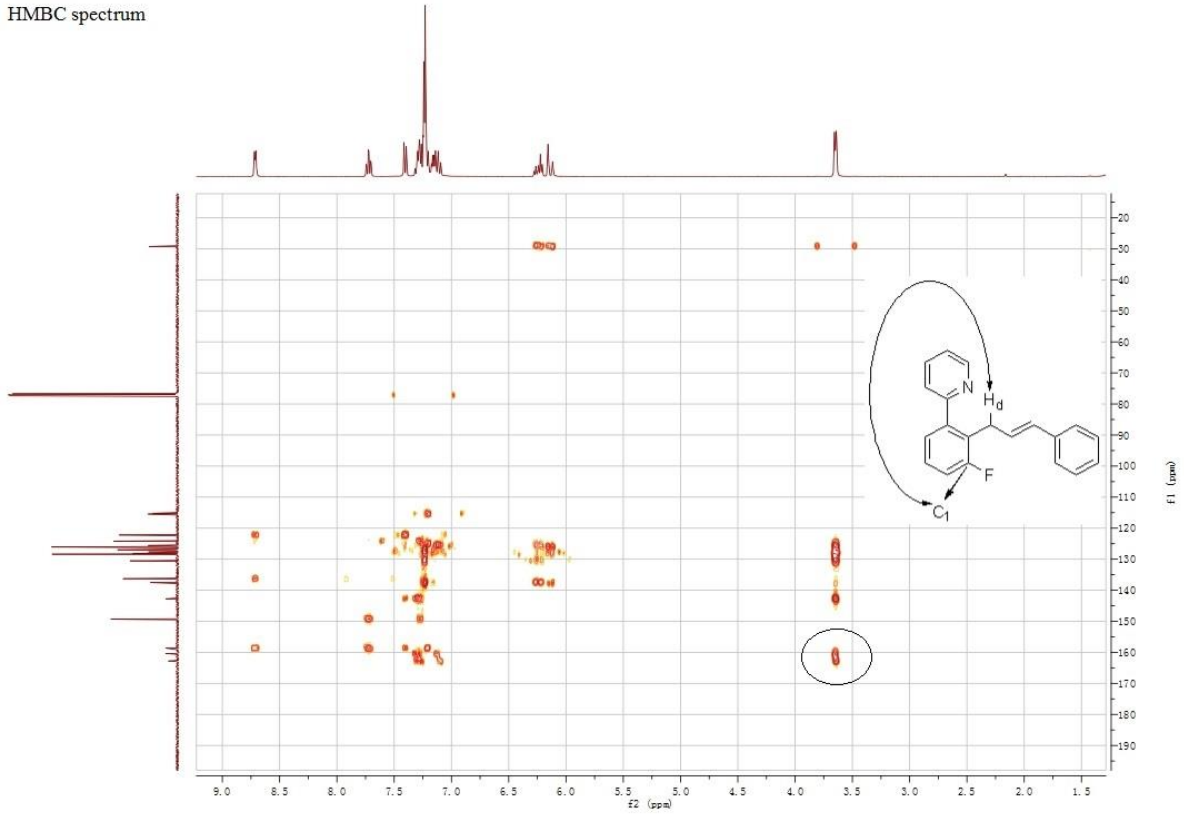
^{1}H-^{1}H COSY spectrum

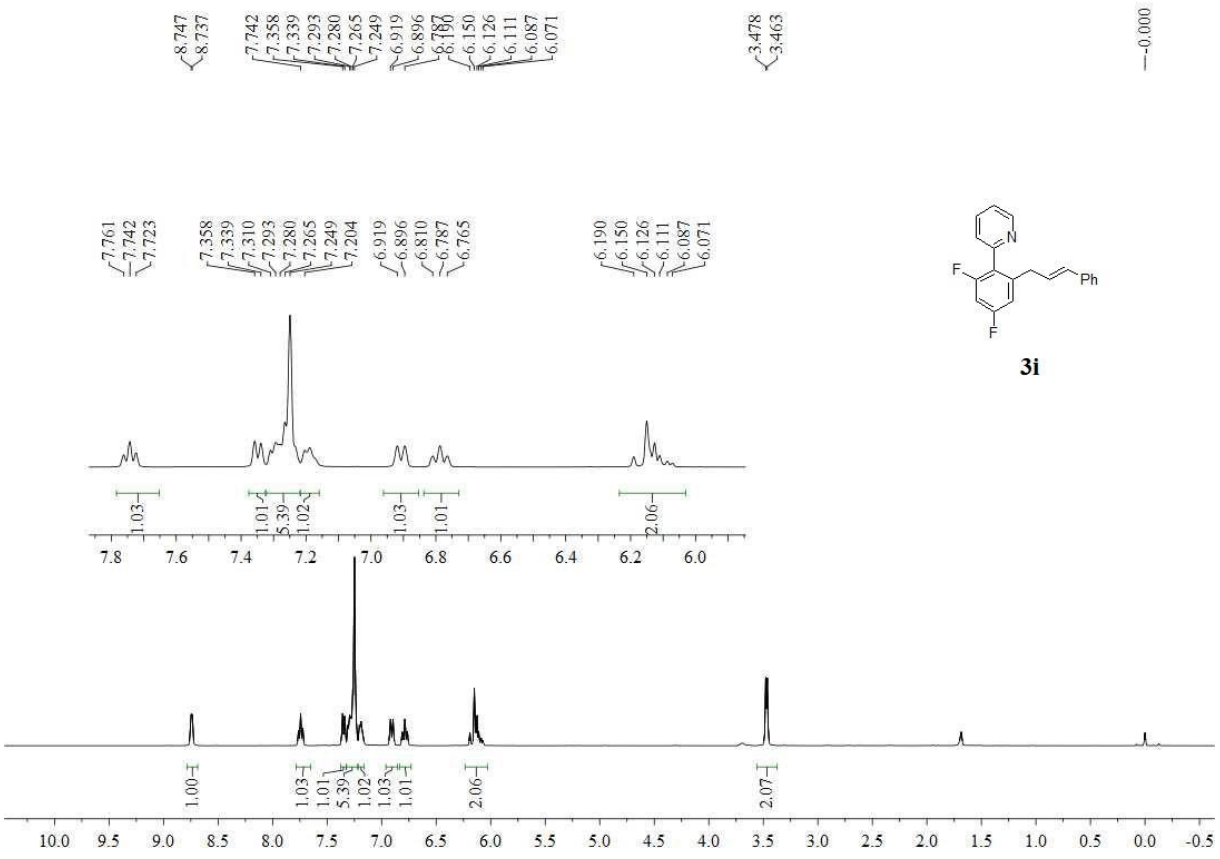


HSQC spectrum



HMBC spectrum

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6.126
6.111
6.087
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7.310
7.293
7.280
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7.249
7.204
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6.896
6.810
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6.150
6.126
6.111
6.087
6.071
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1.01
2.06
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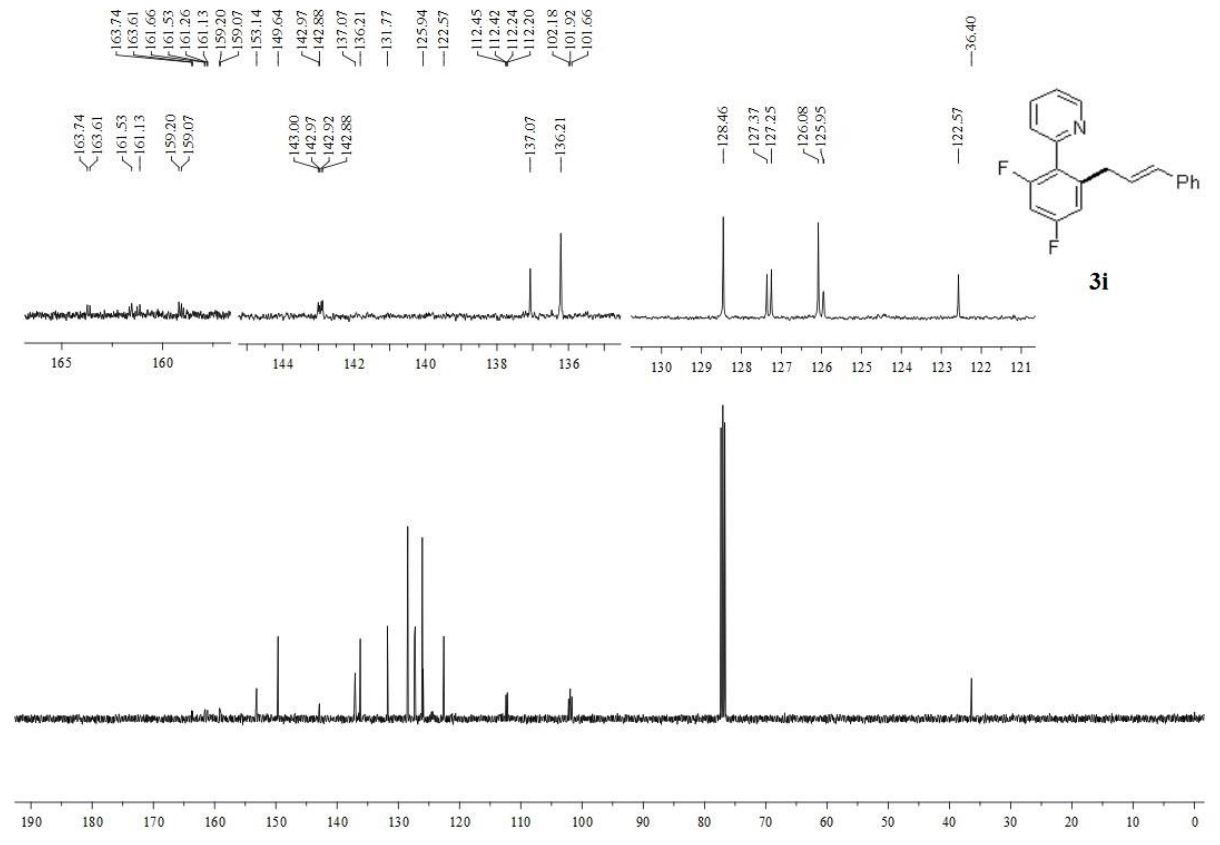
Ph
F
3i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122.57
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112.42
112.24
112.20
102.18
101.92
101.66
36.40
163.74
163.61
161.53
161.13
159.20
159.07
143.00
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142.92
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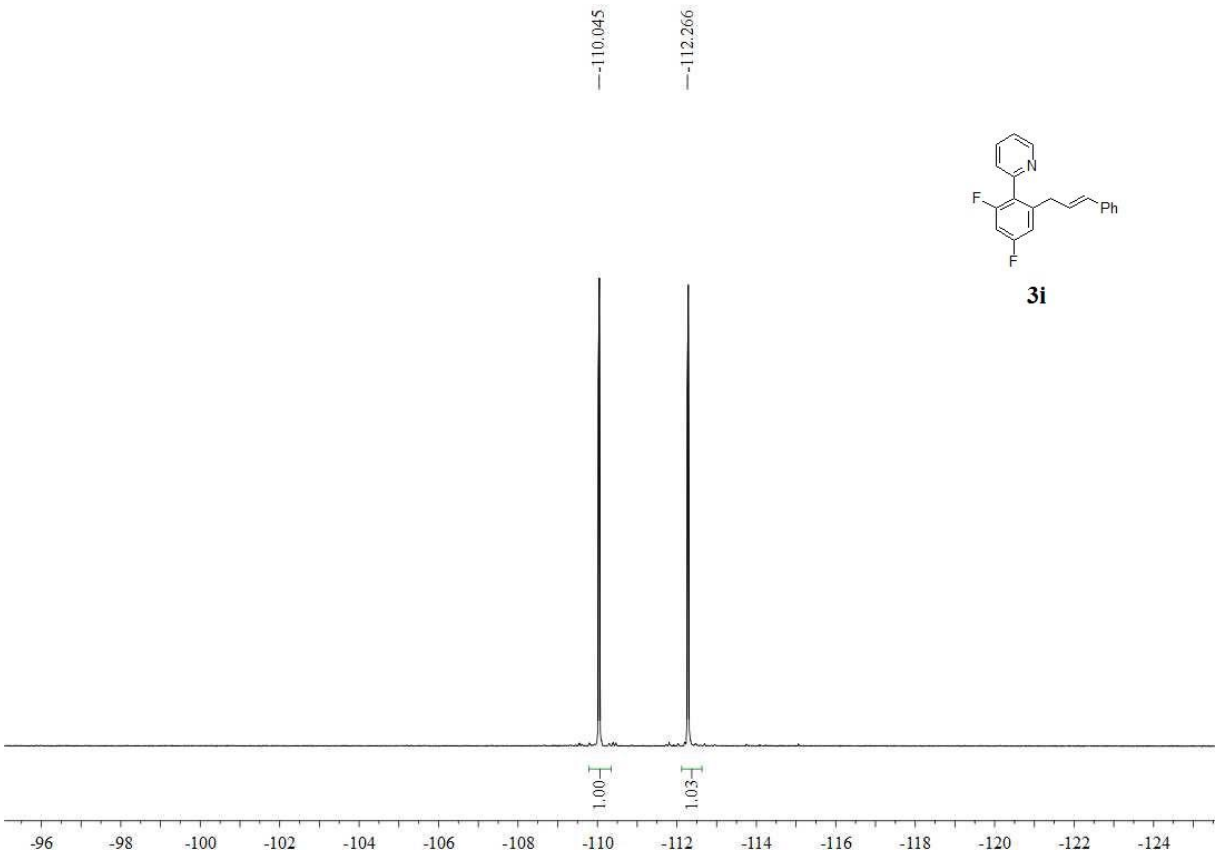
Ph
F
3i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-112.266
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F
F
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1.03
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-110
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-116
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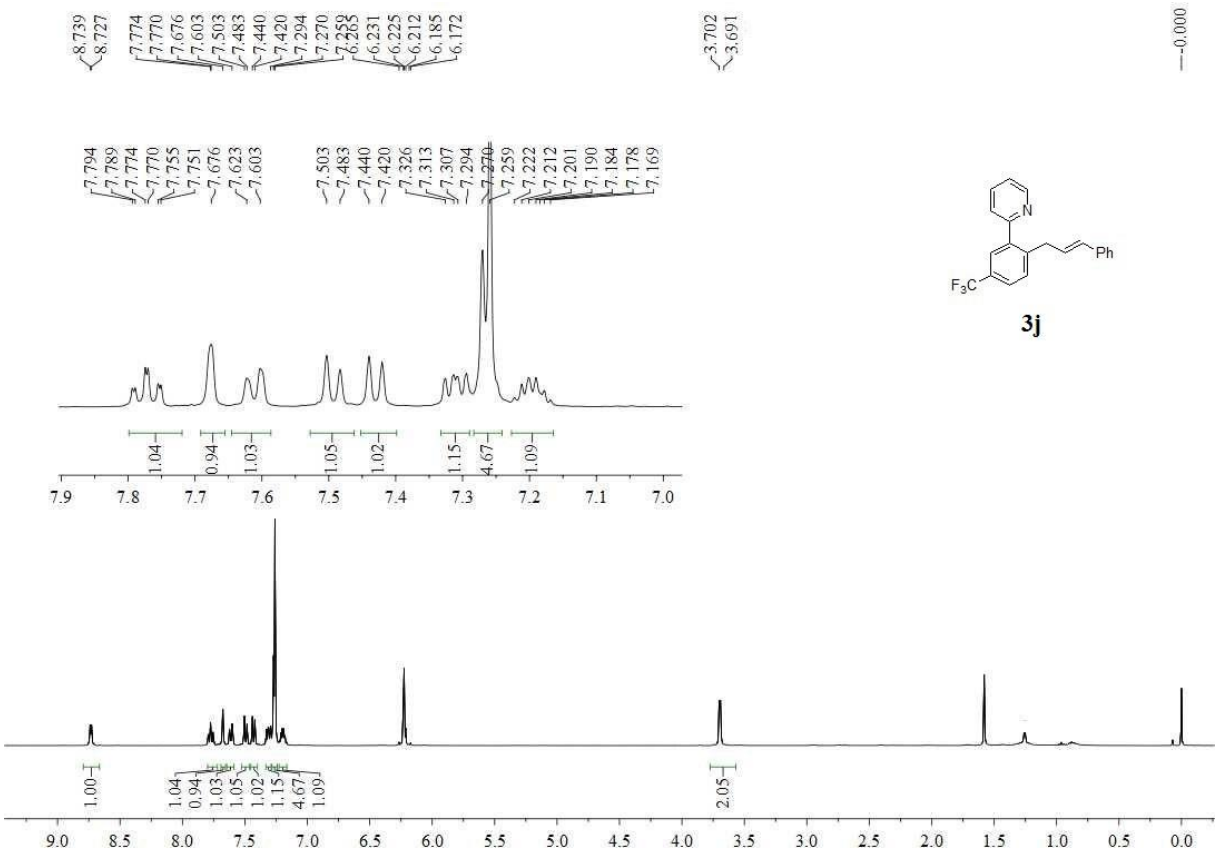
-124

3i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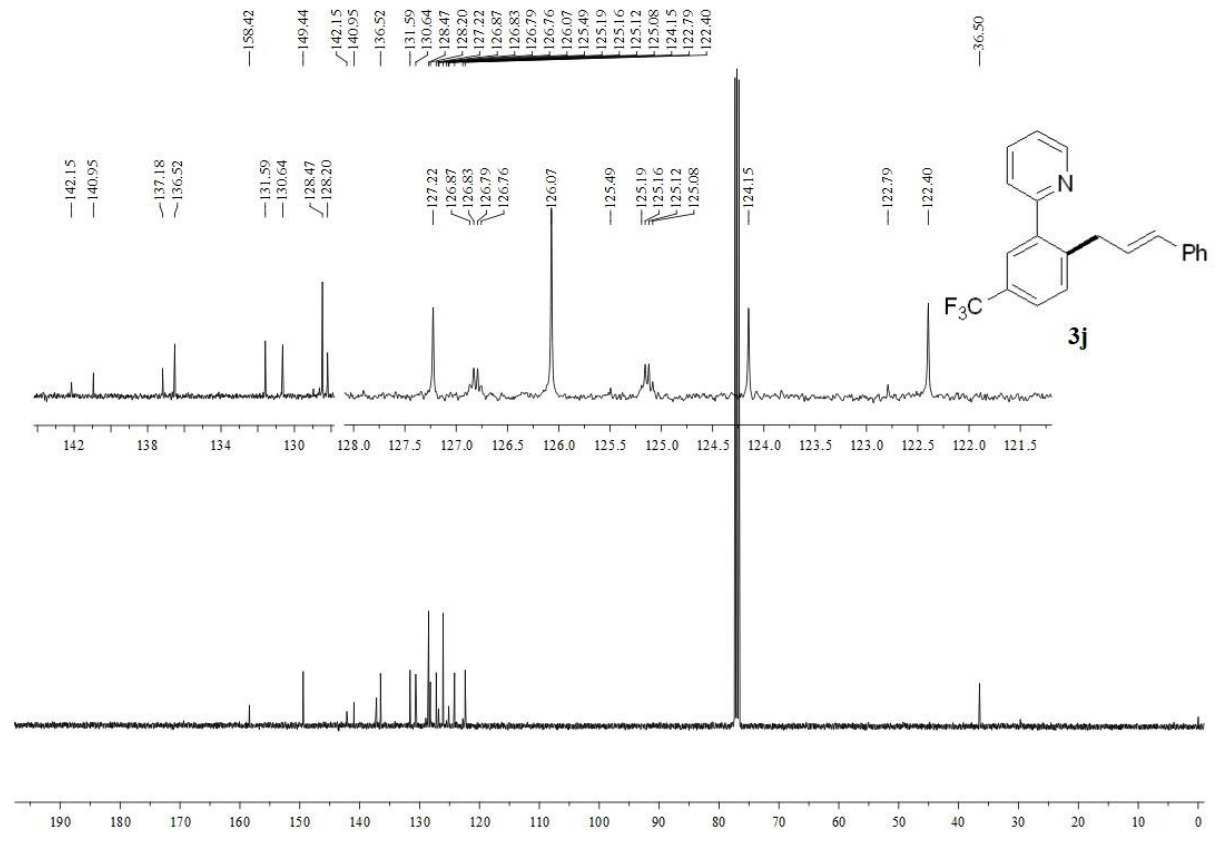
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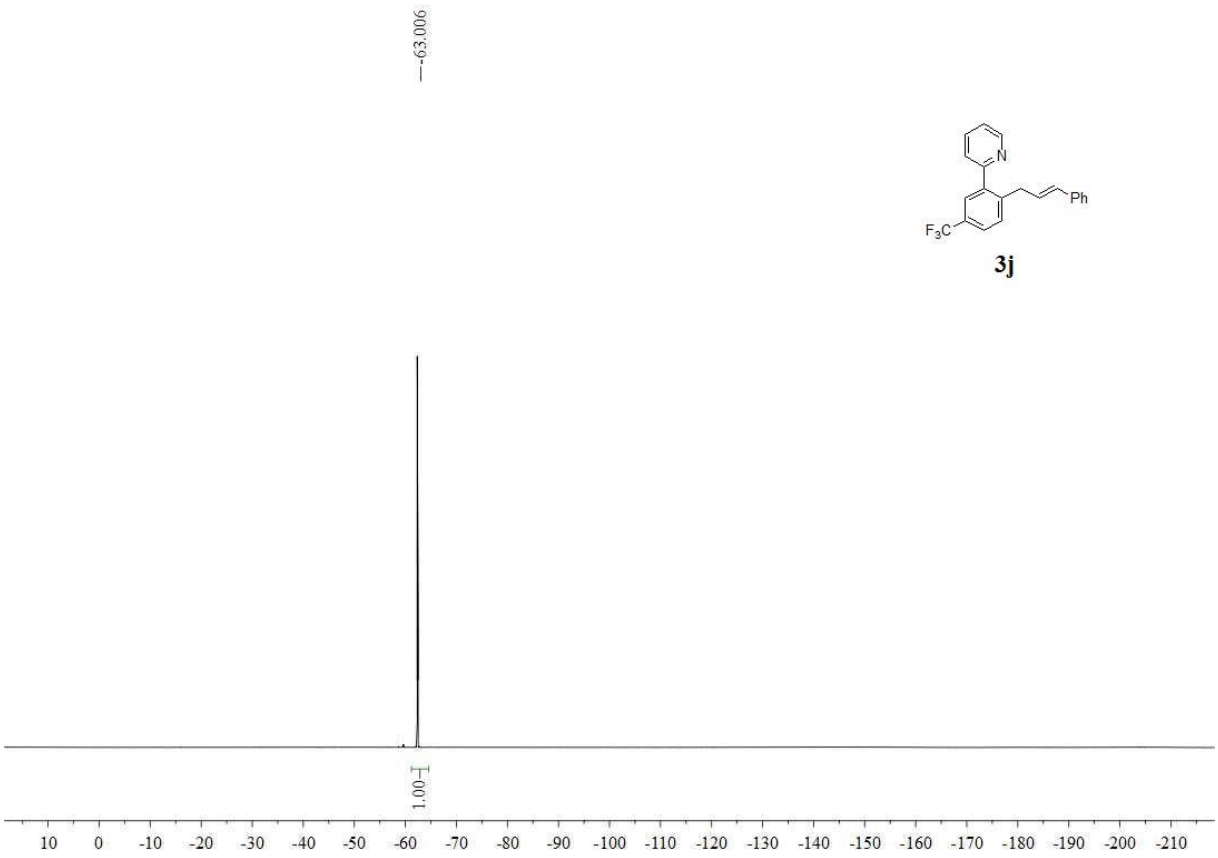
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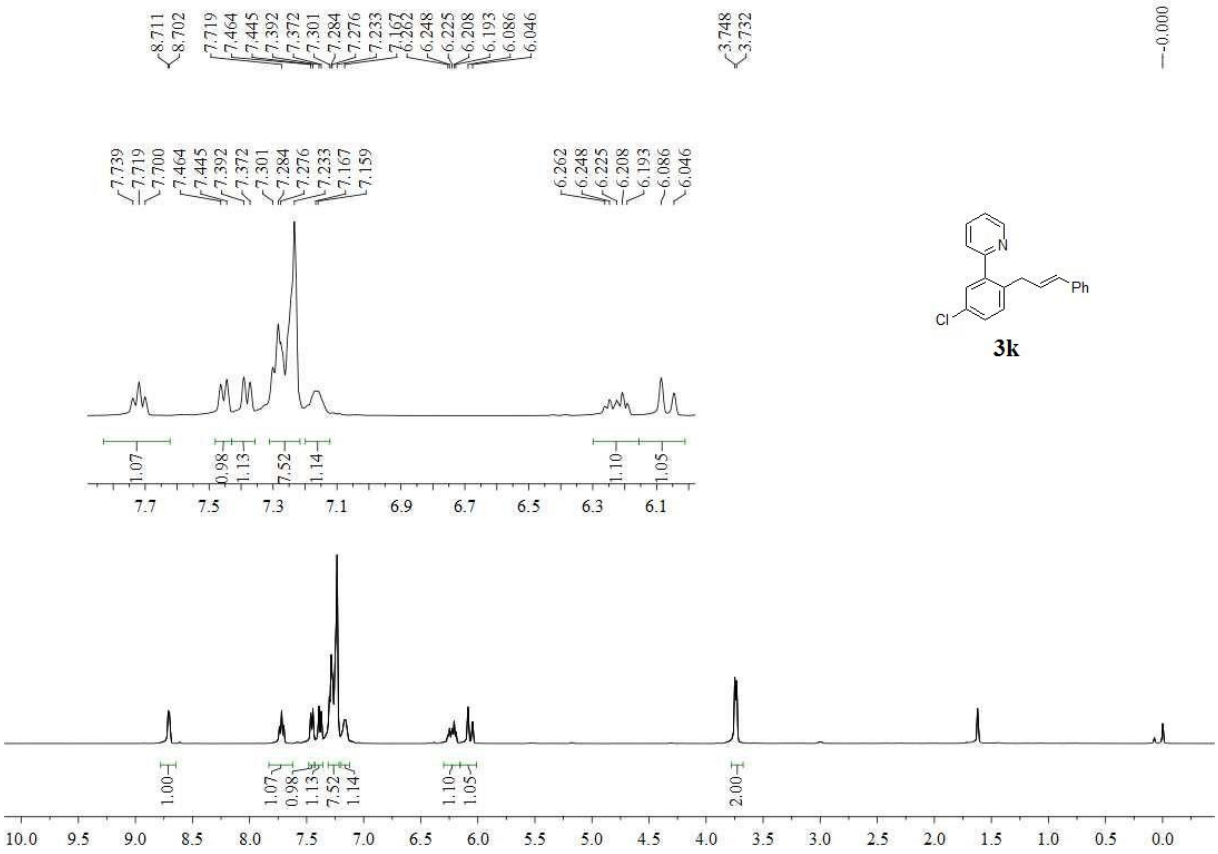
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6.193
6.086
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7.719
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7.372
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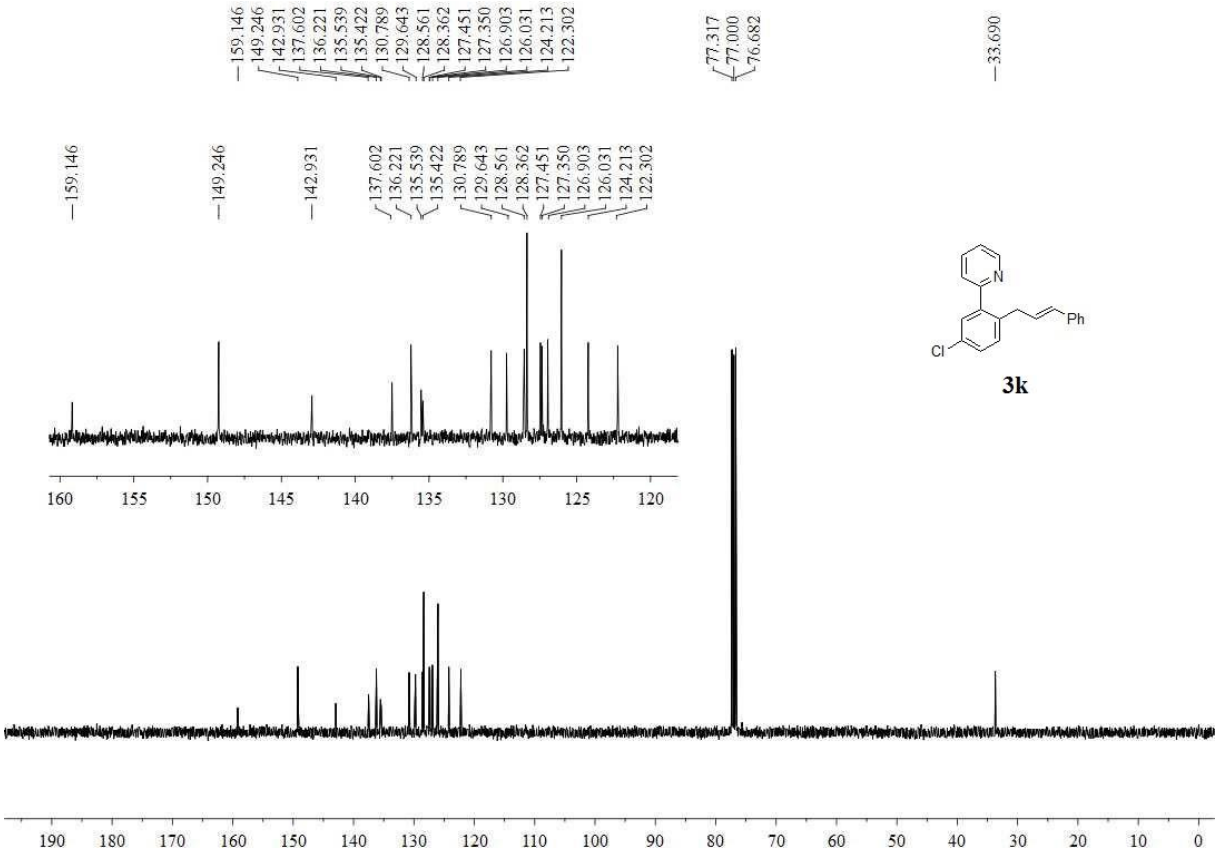
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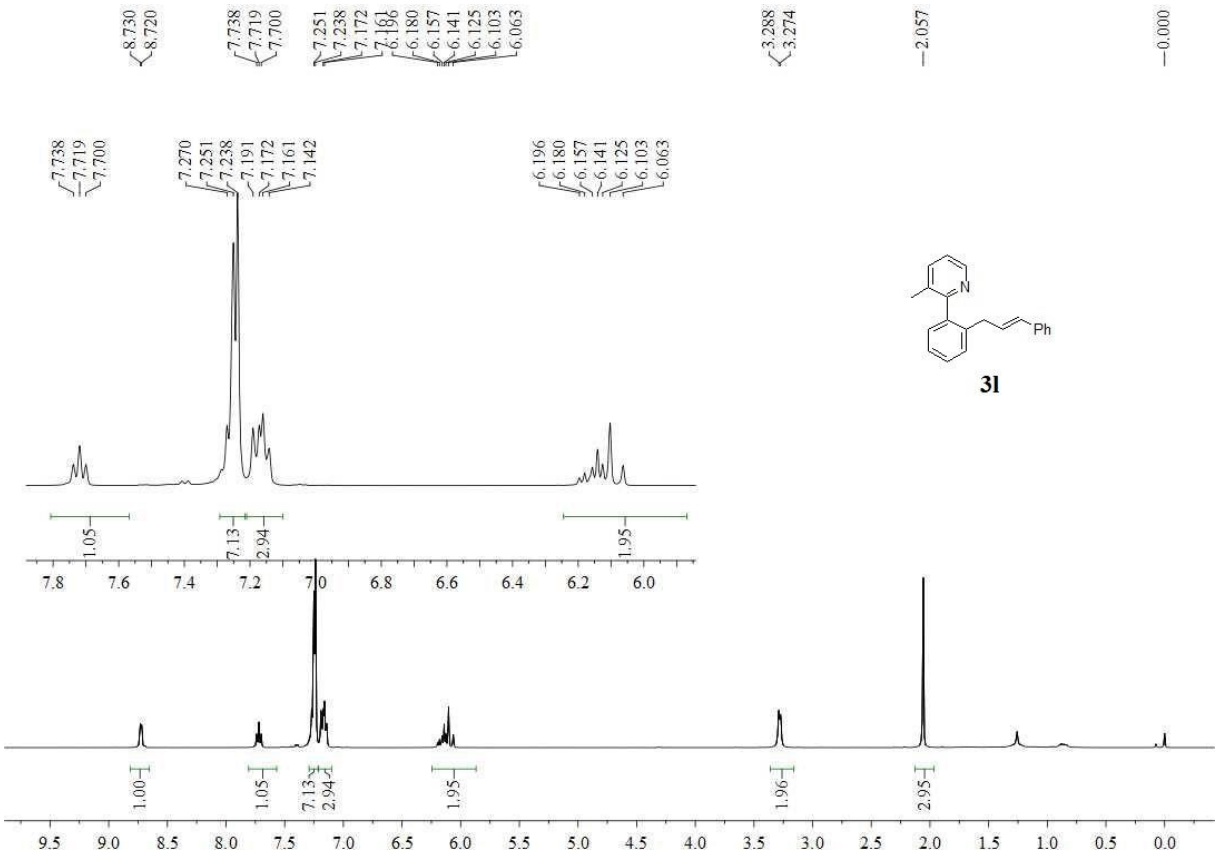
Cl
3k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6.063
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3.274
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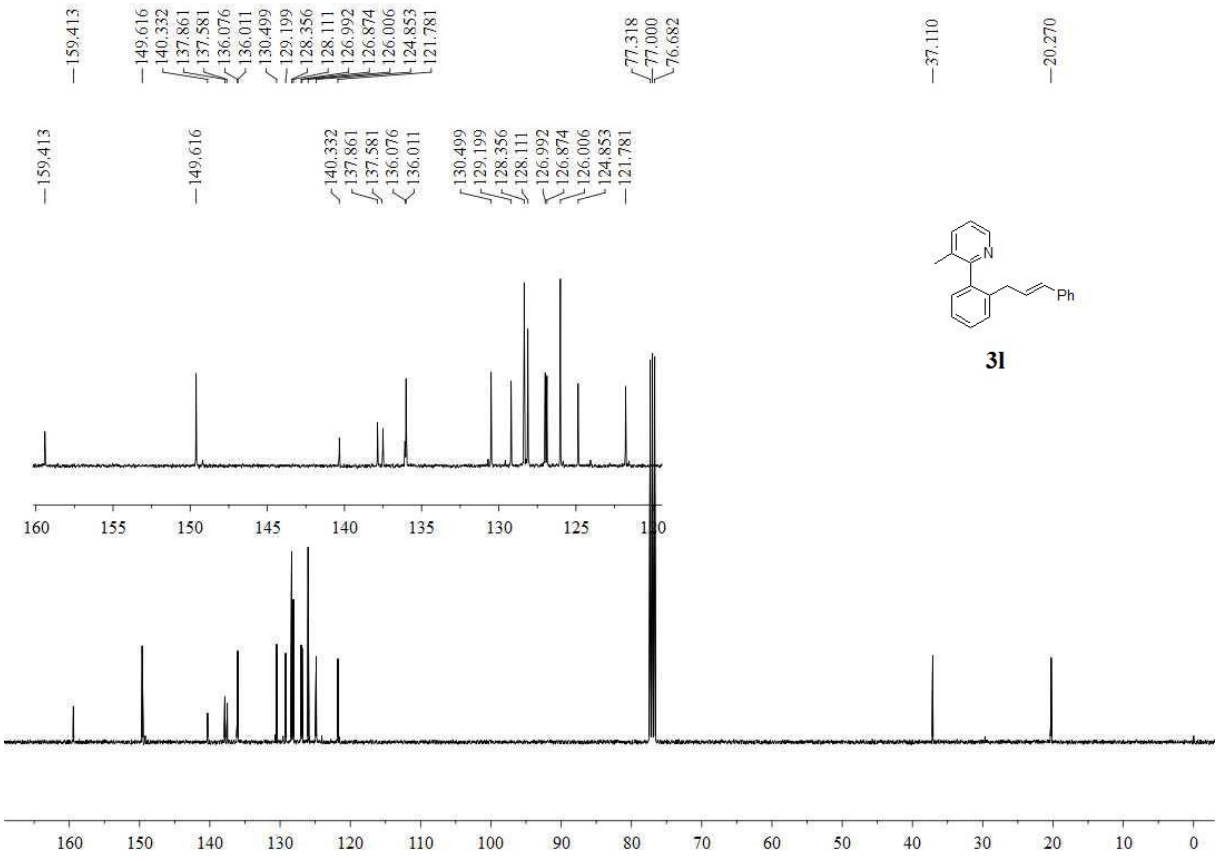
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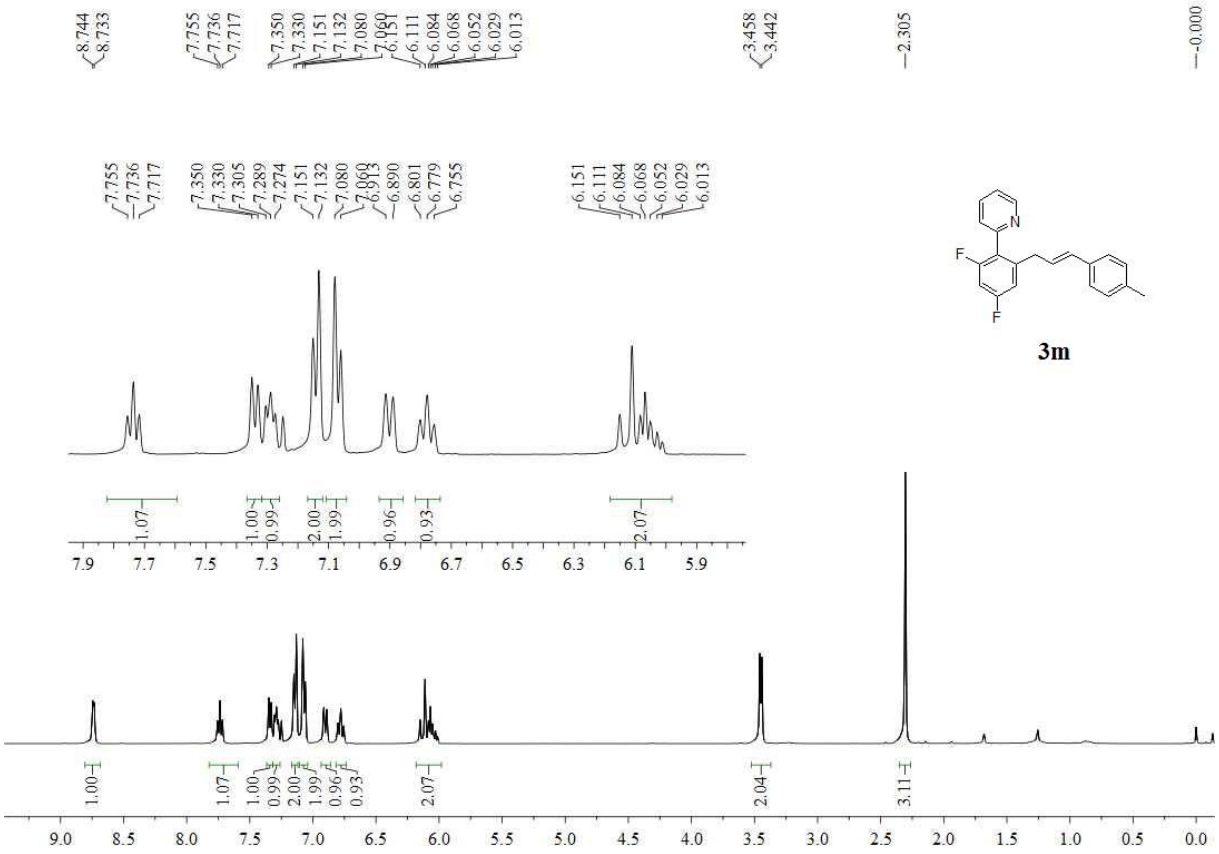
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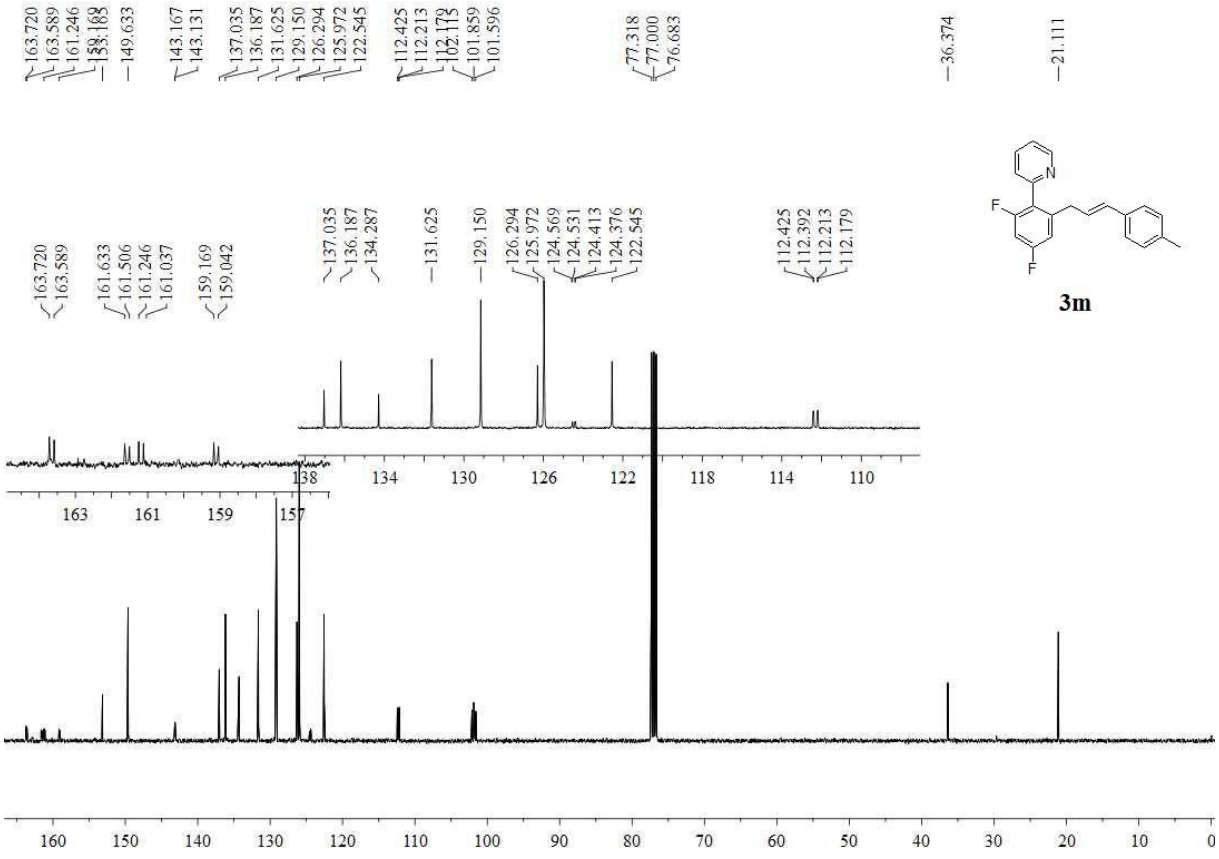
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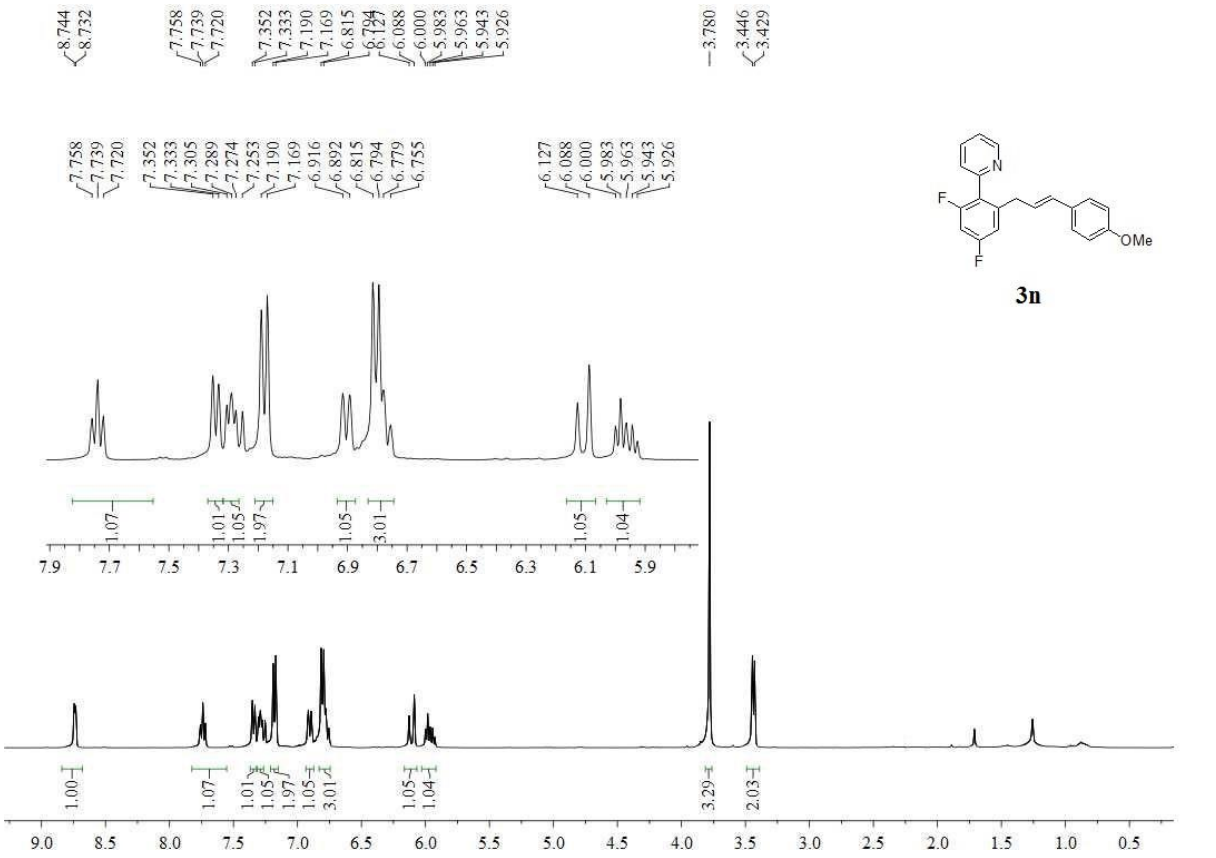
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5.943
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3.780
3.446
3.429
F
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OMe
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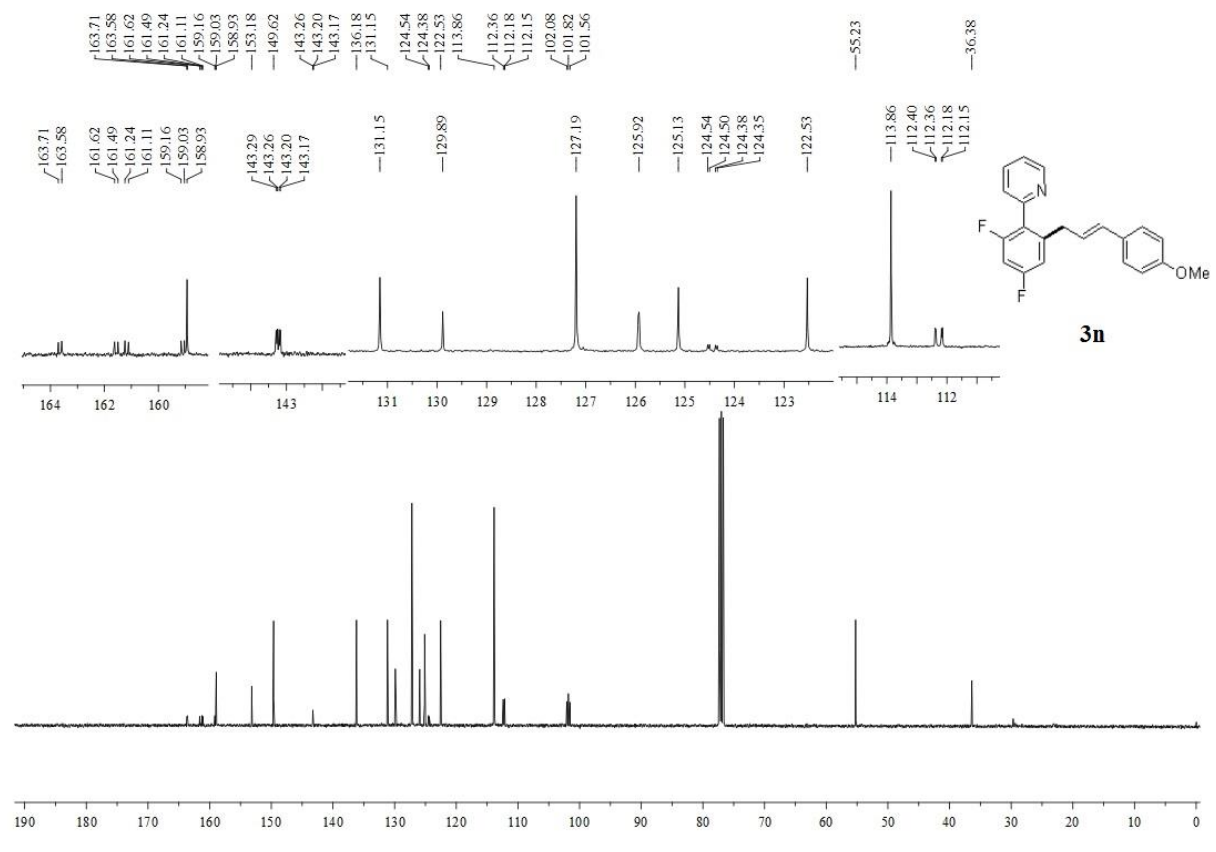
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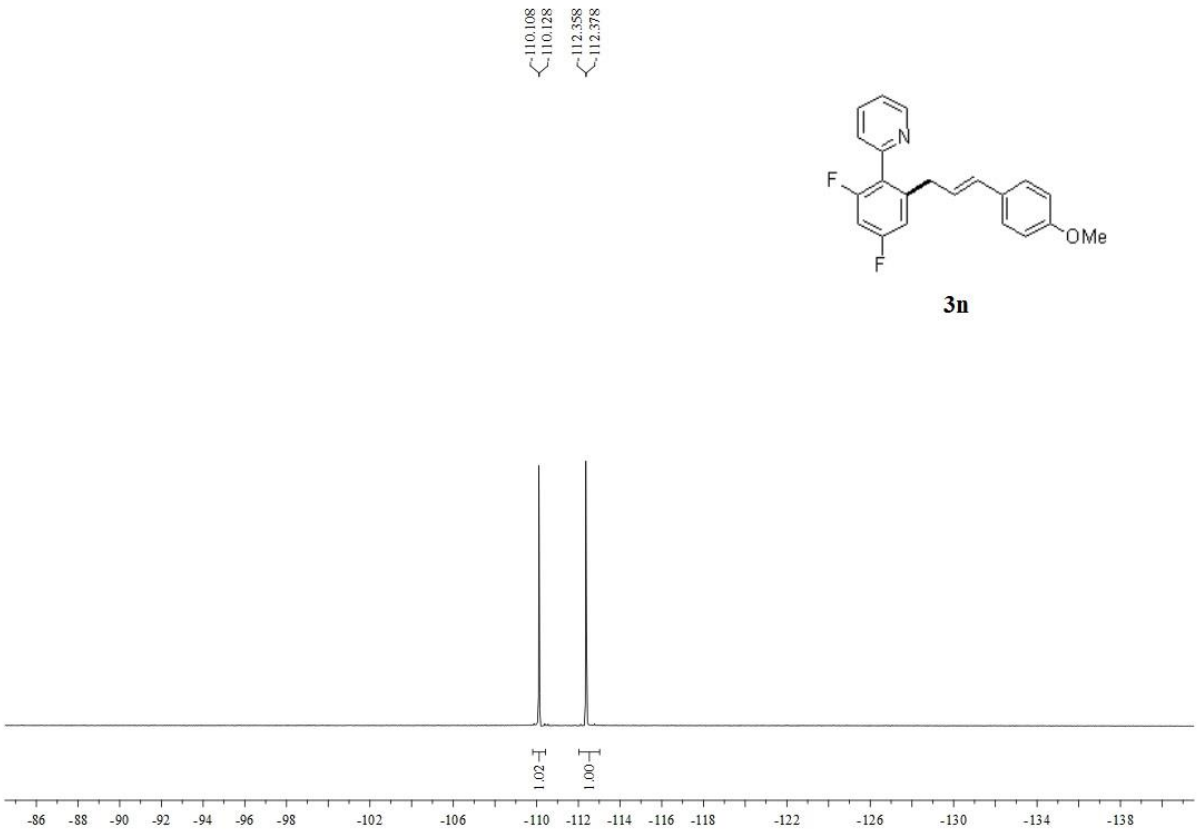
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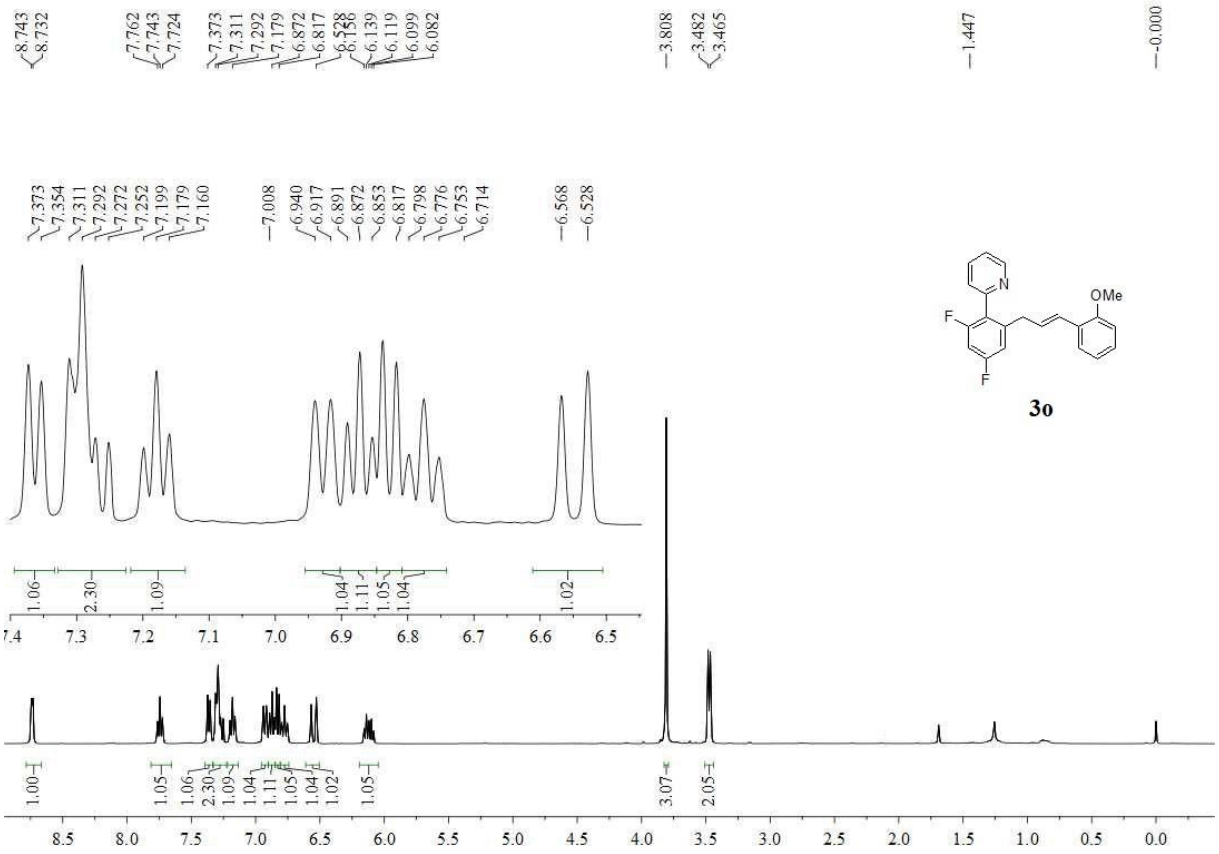
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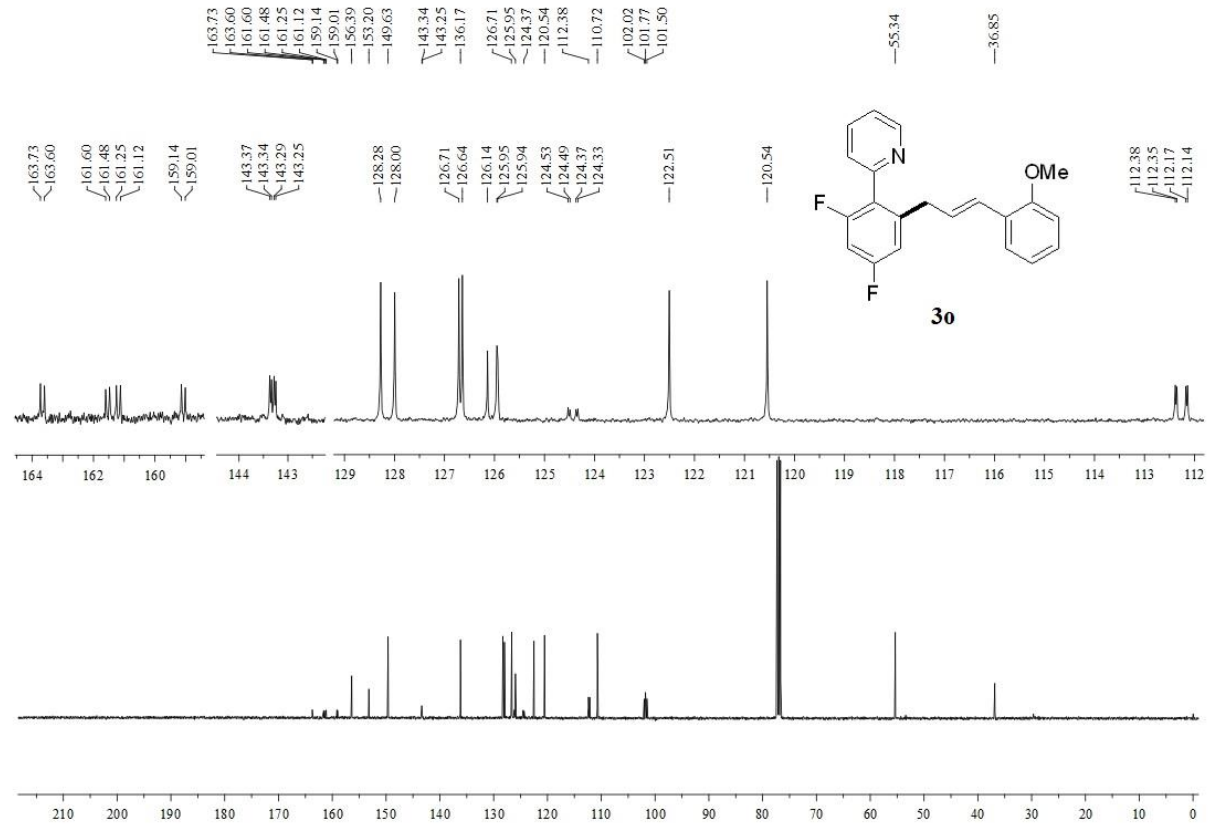
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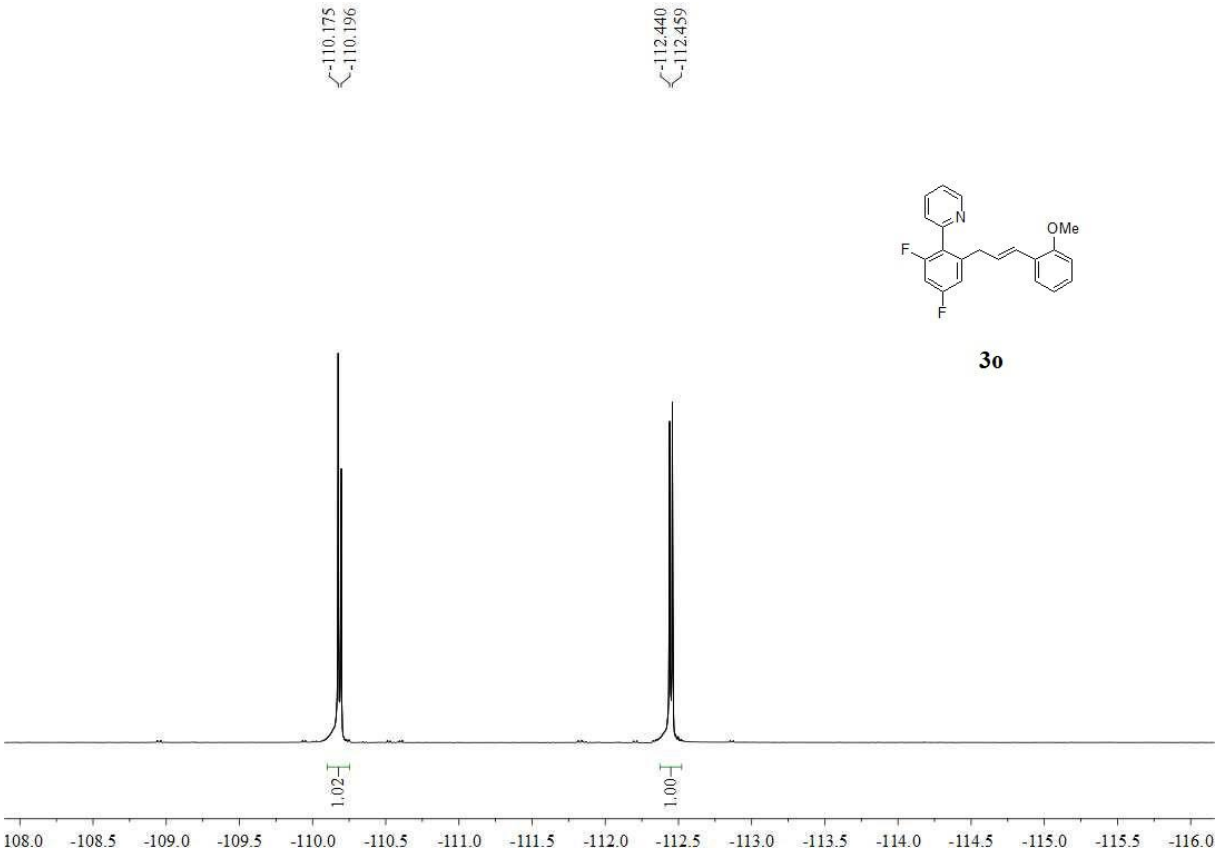
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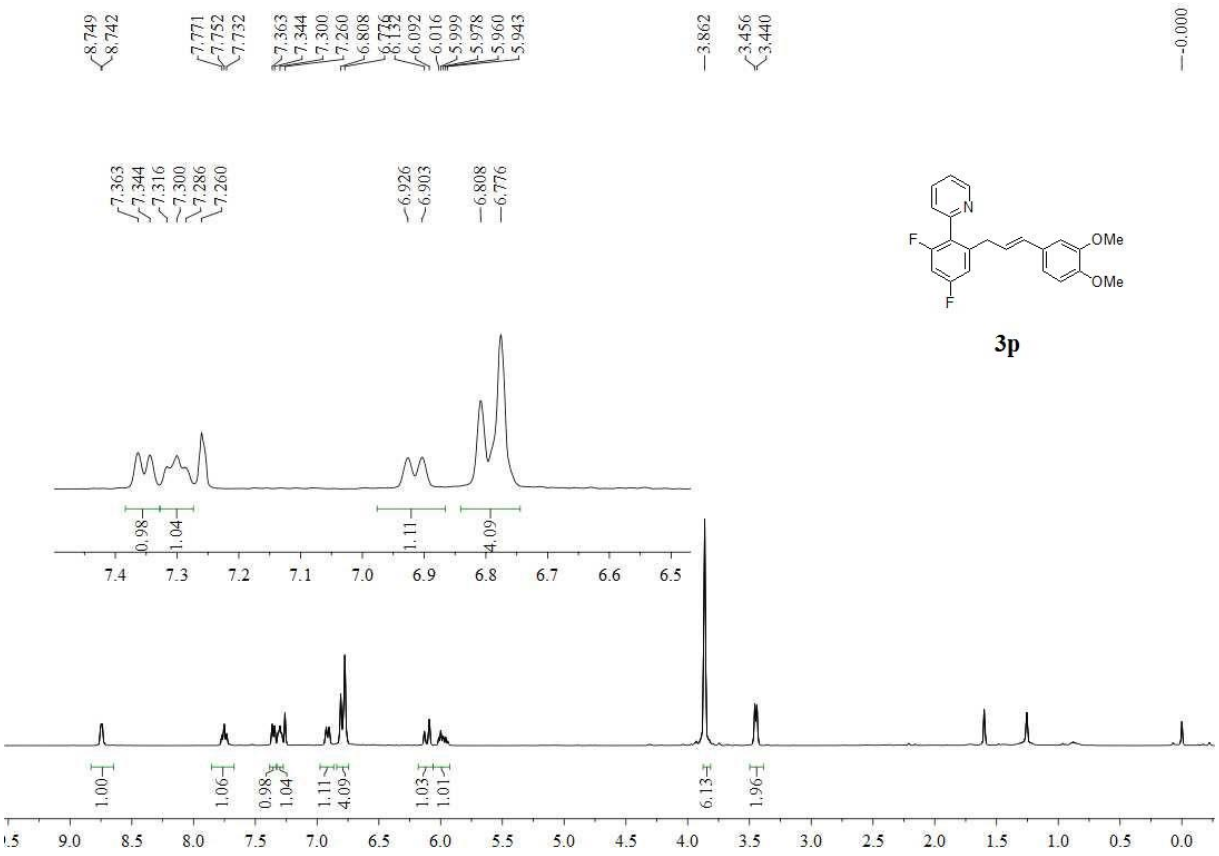
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OMe
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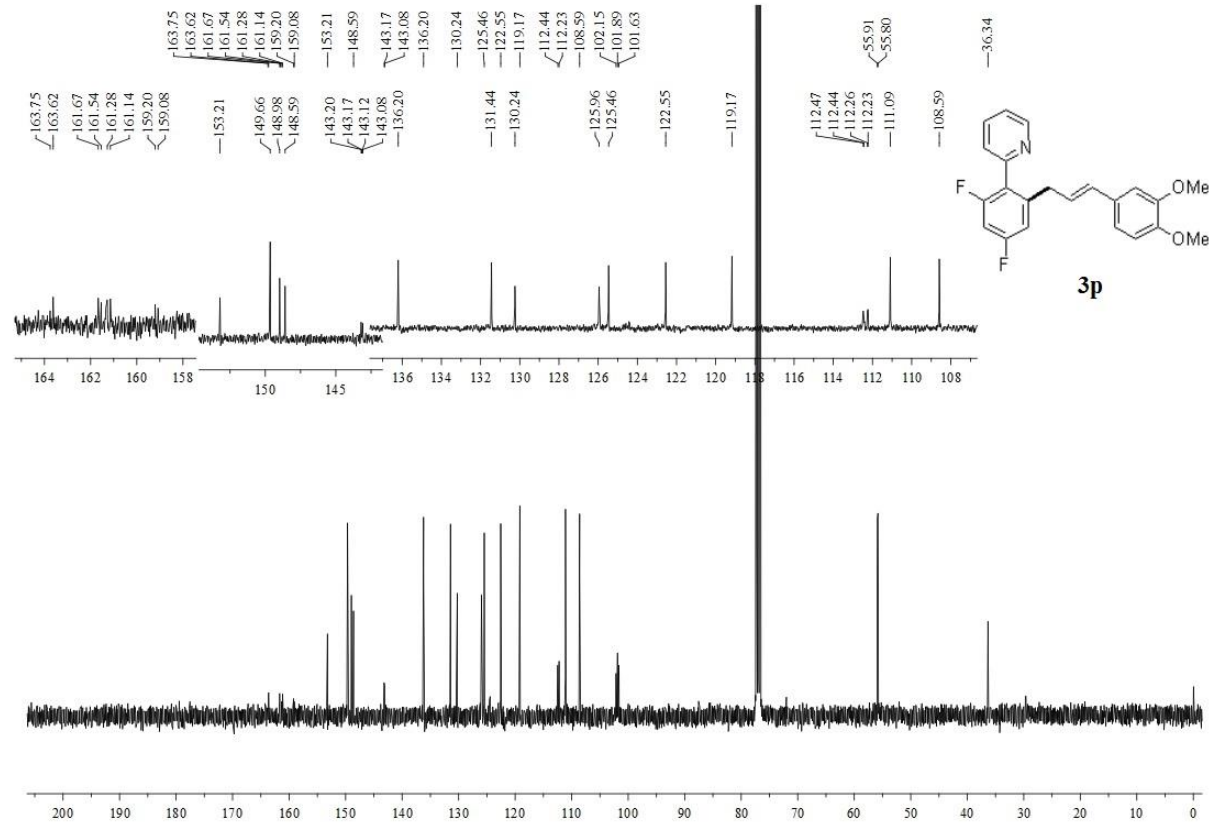
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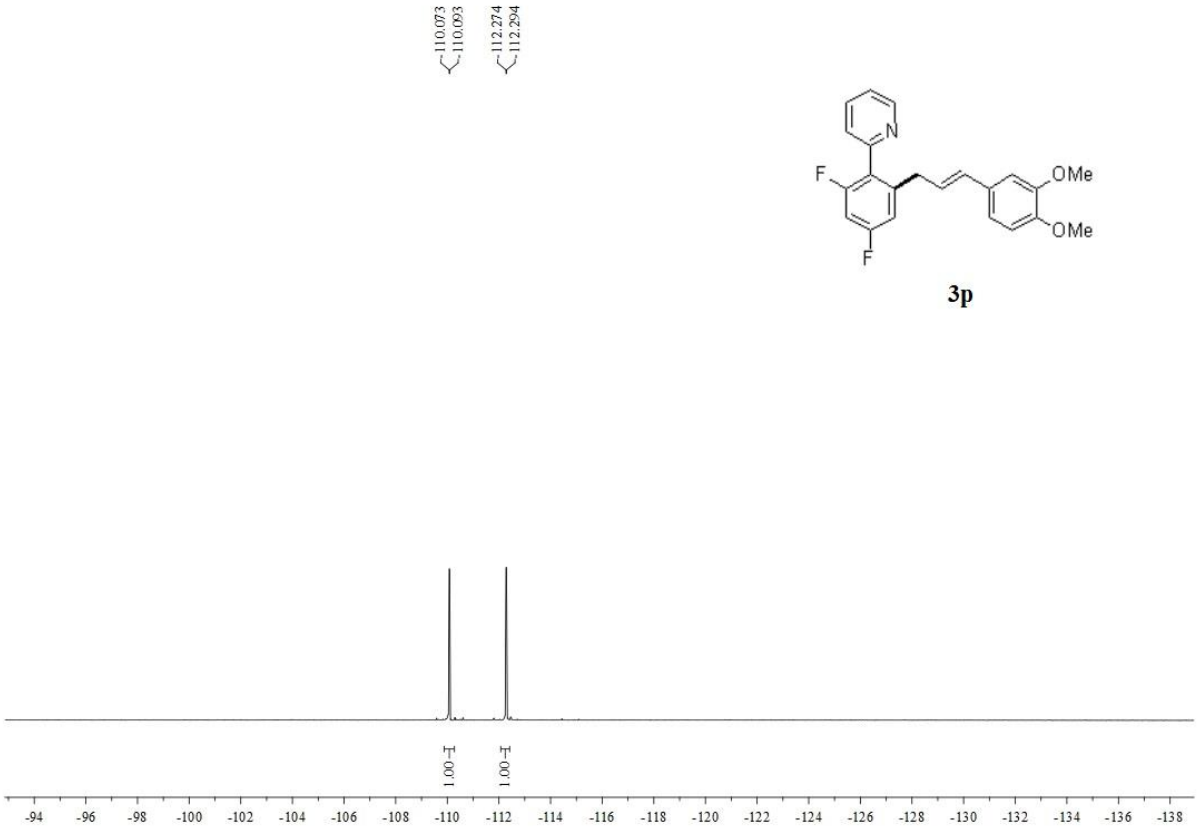
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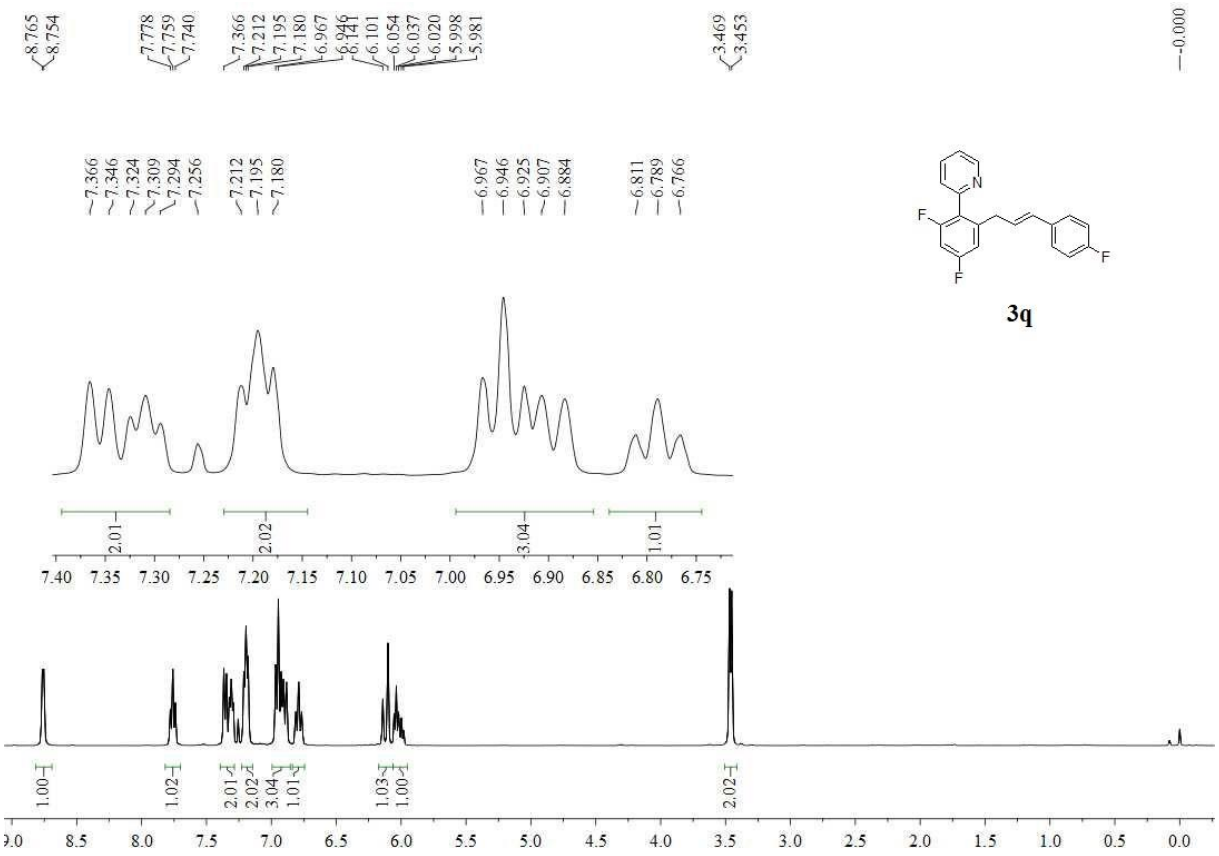
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2.02
3.04
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1.02
2.01
2.02
3.04
1.01
1.03
1.00
2.02
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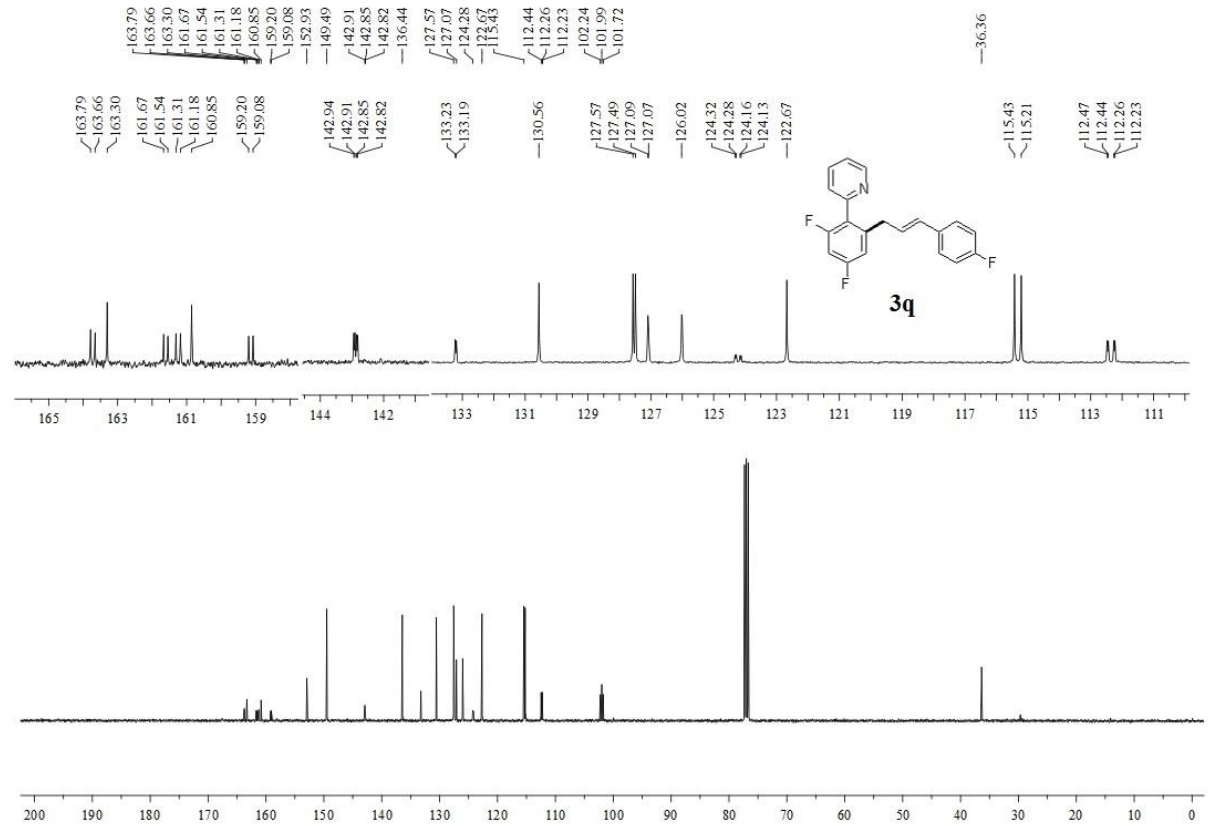
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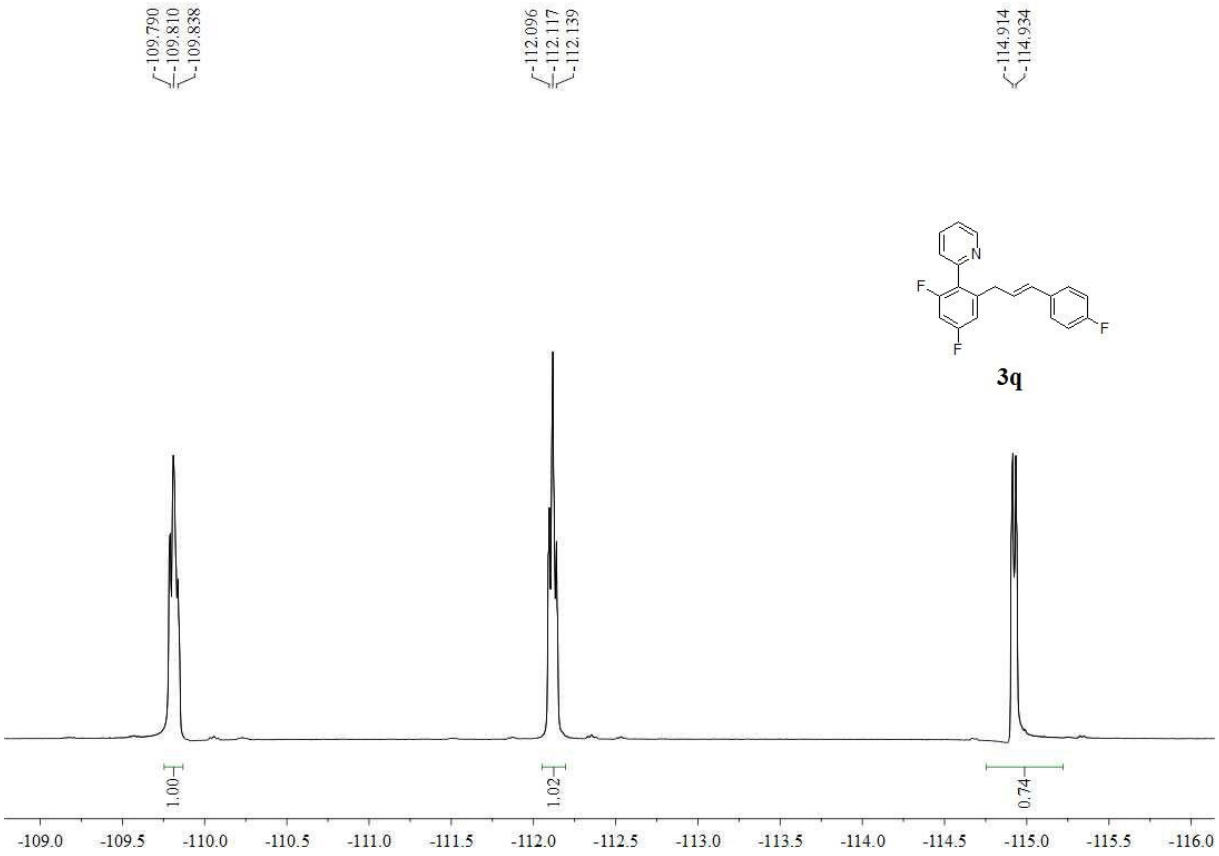
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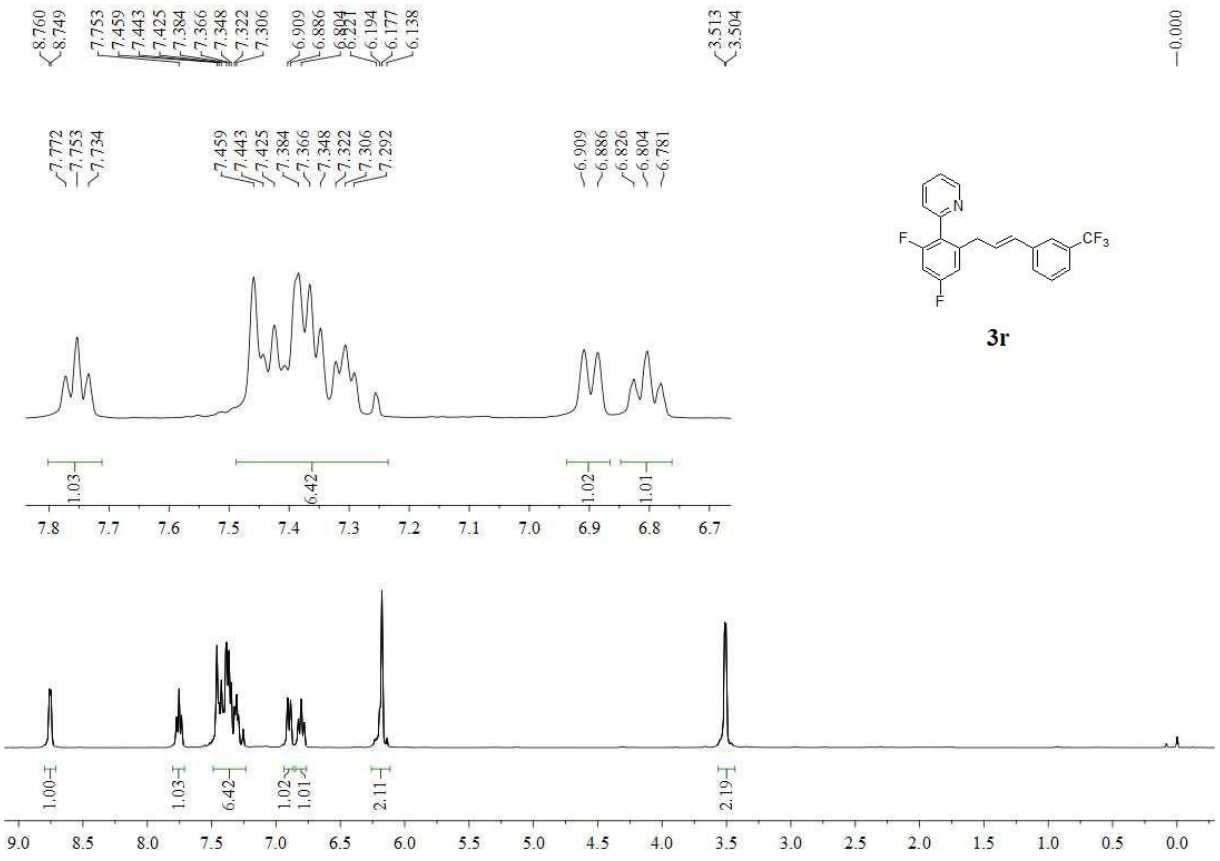
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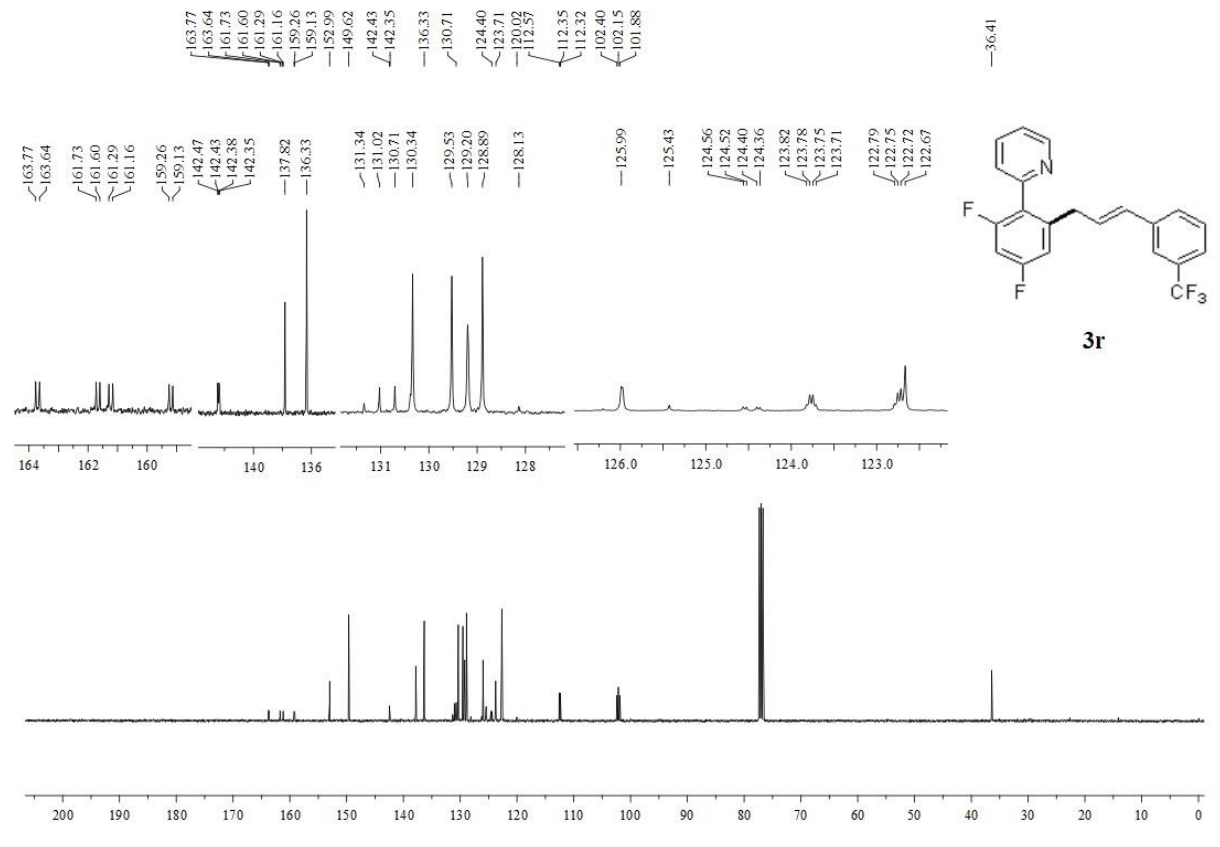
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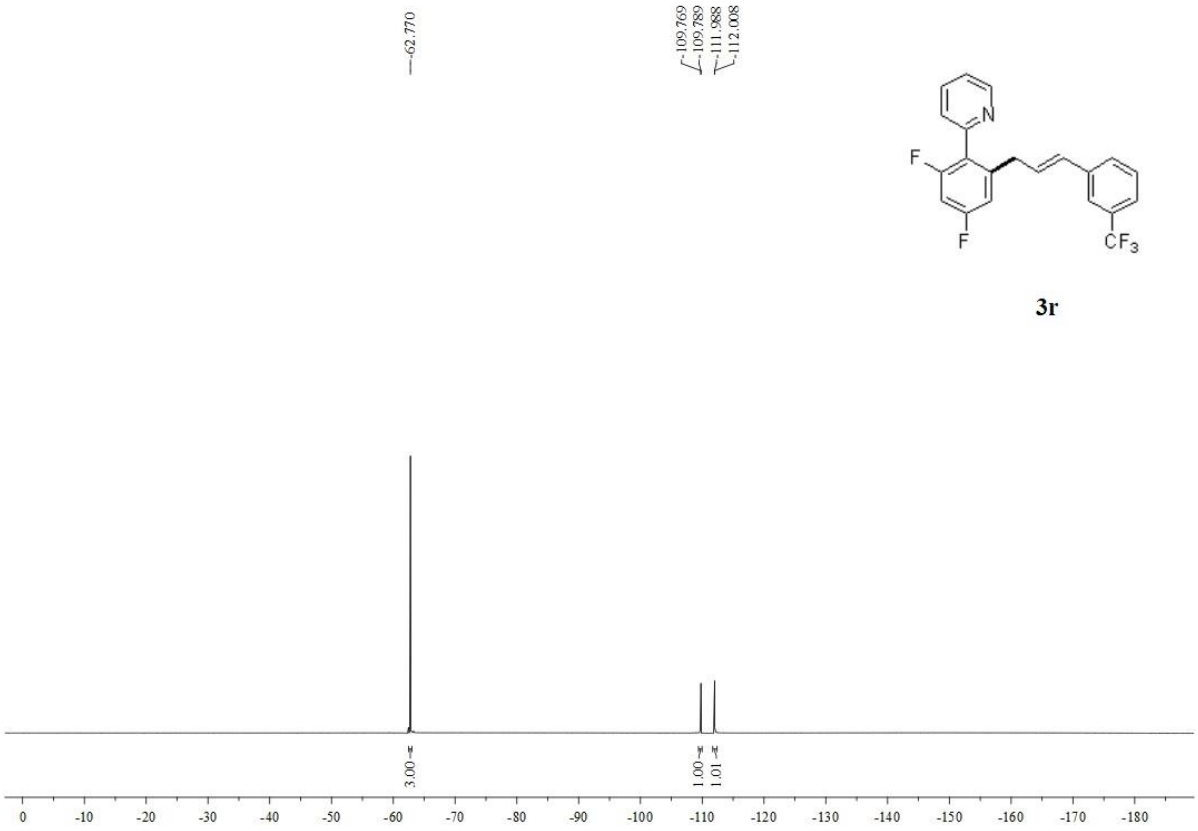
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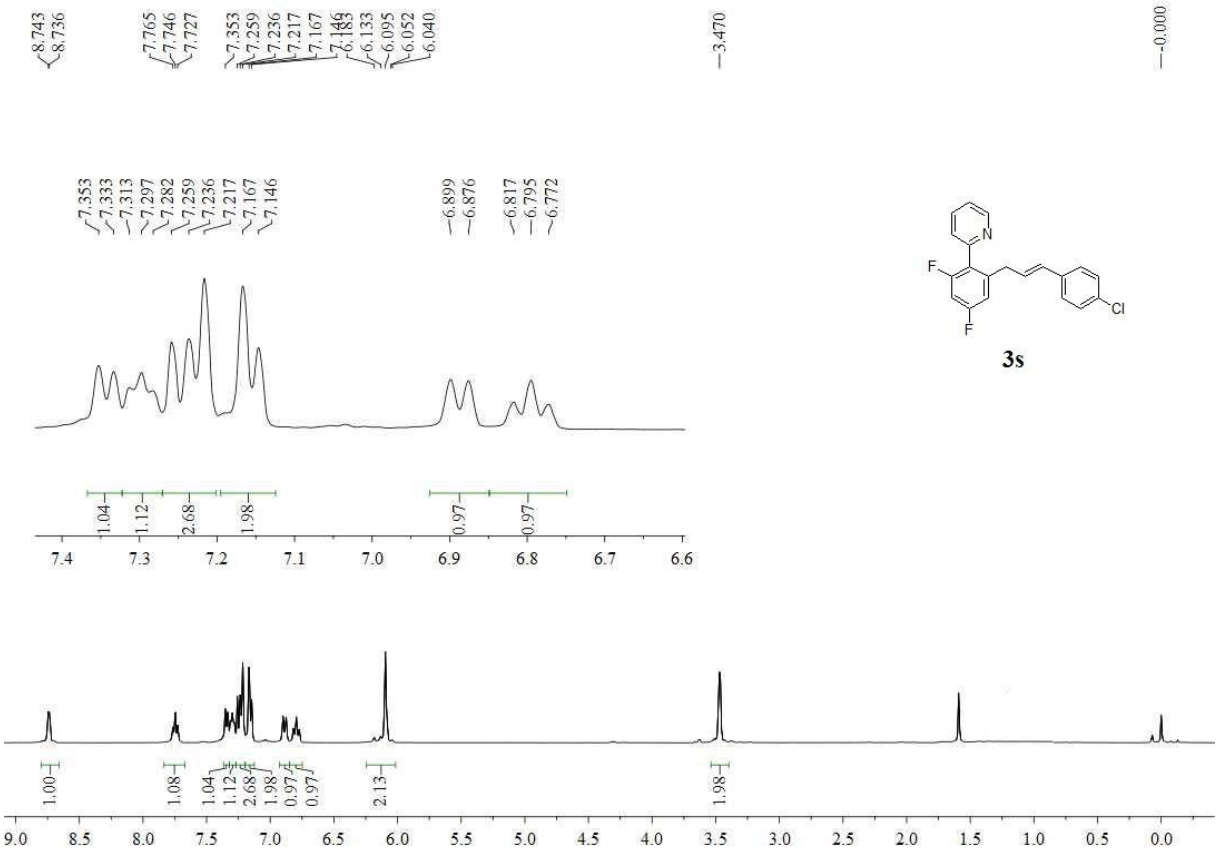
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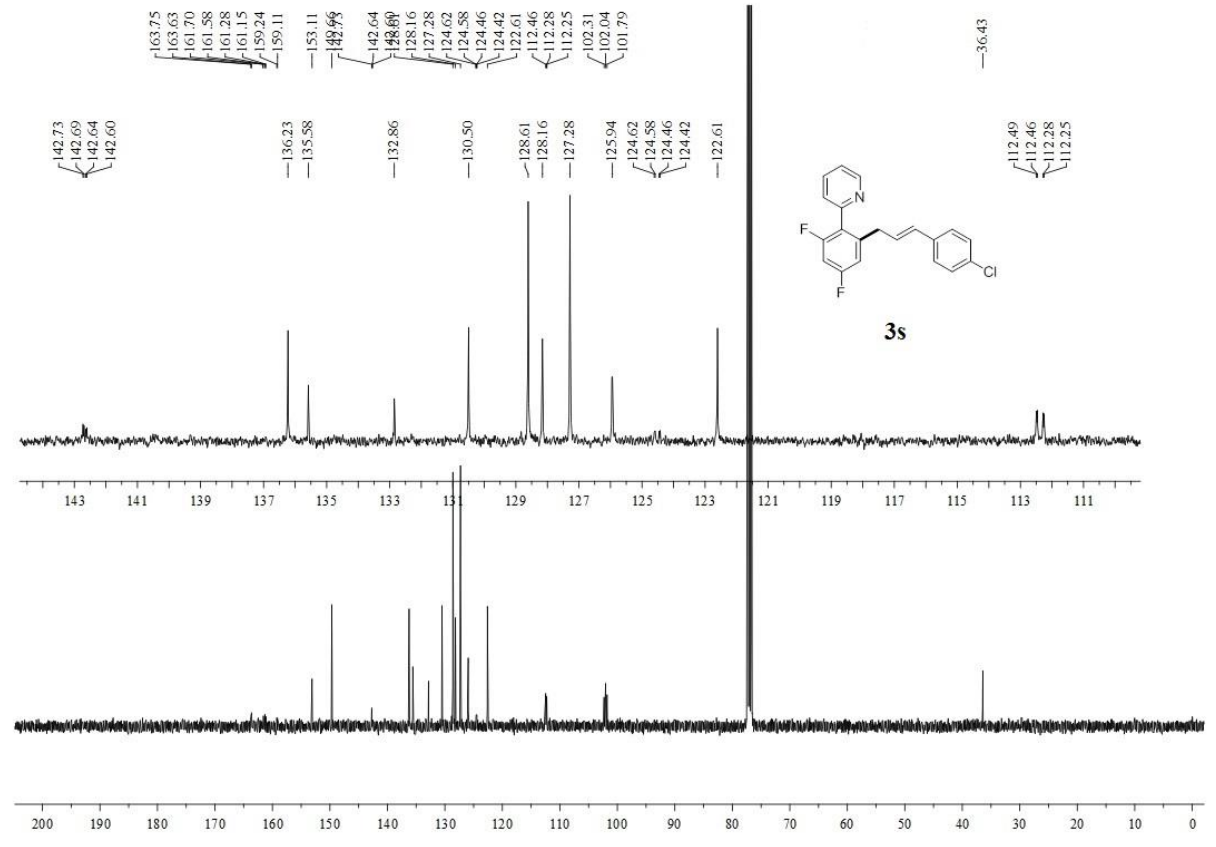
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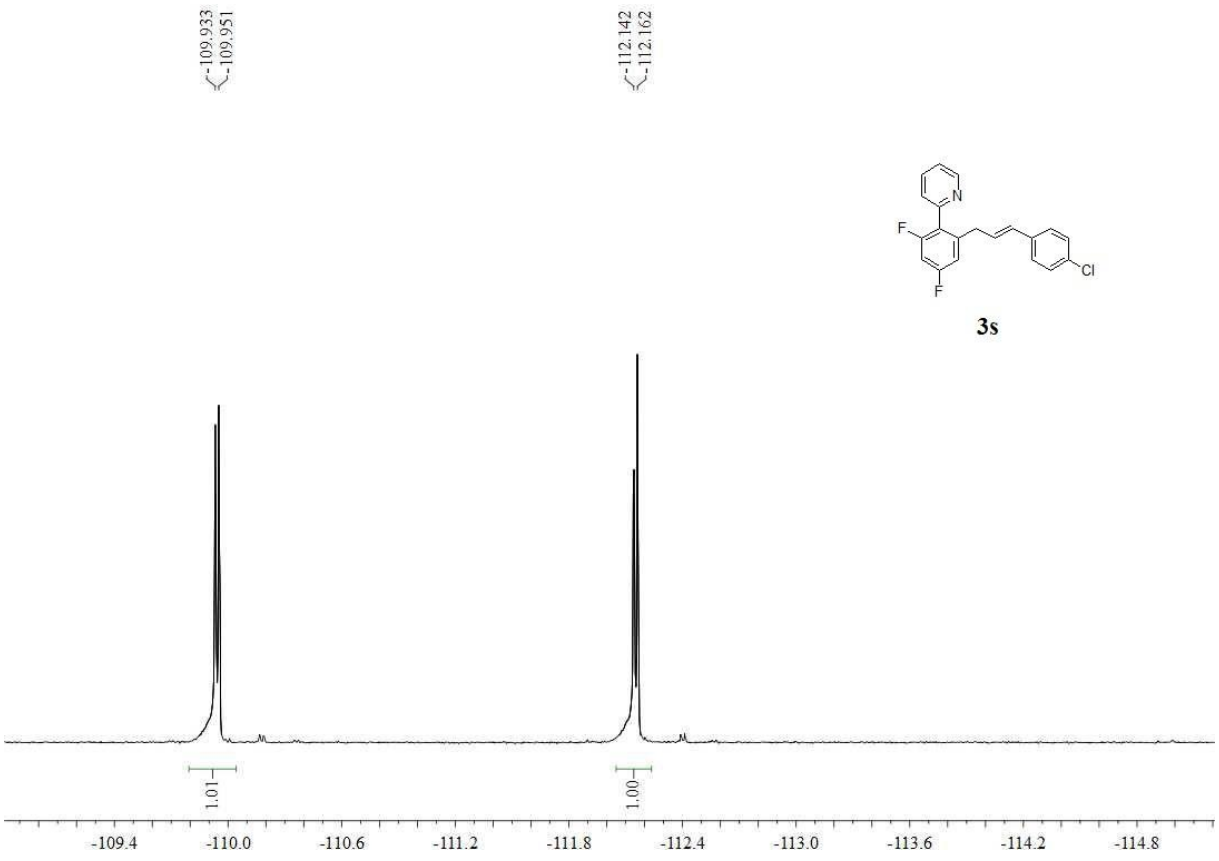
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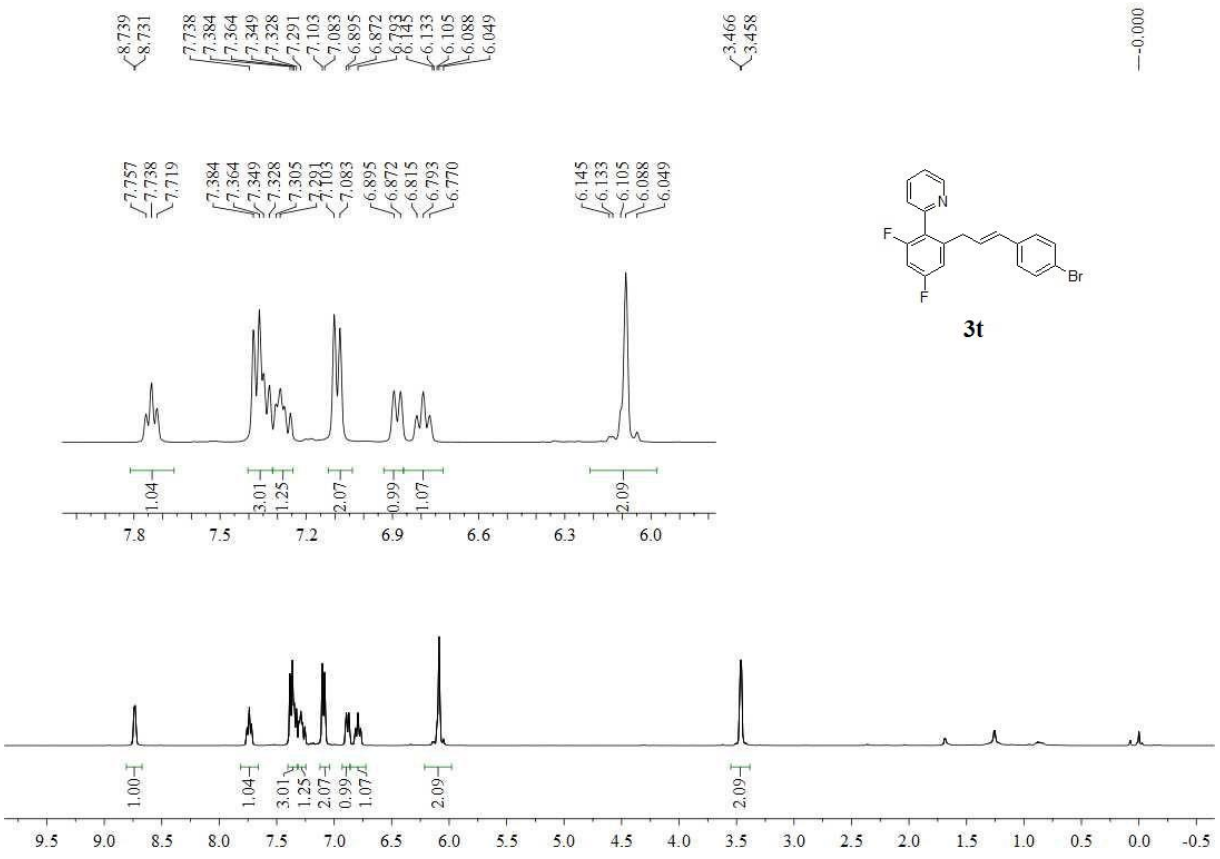
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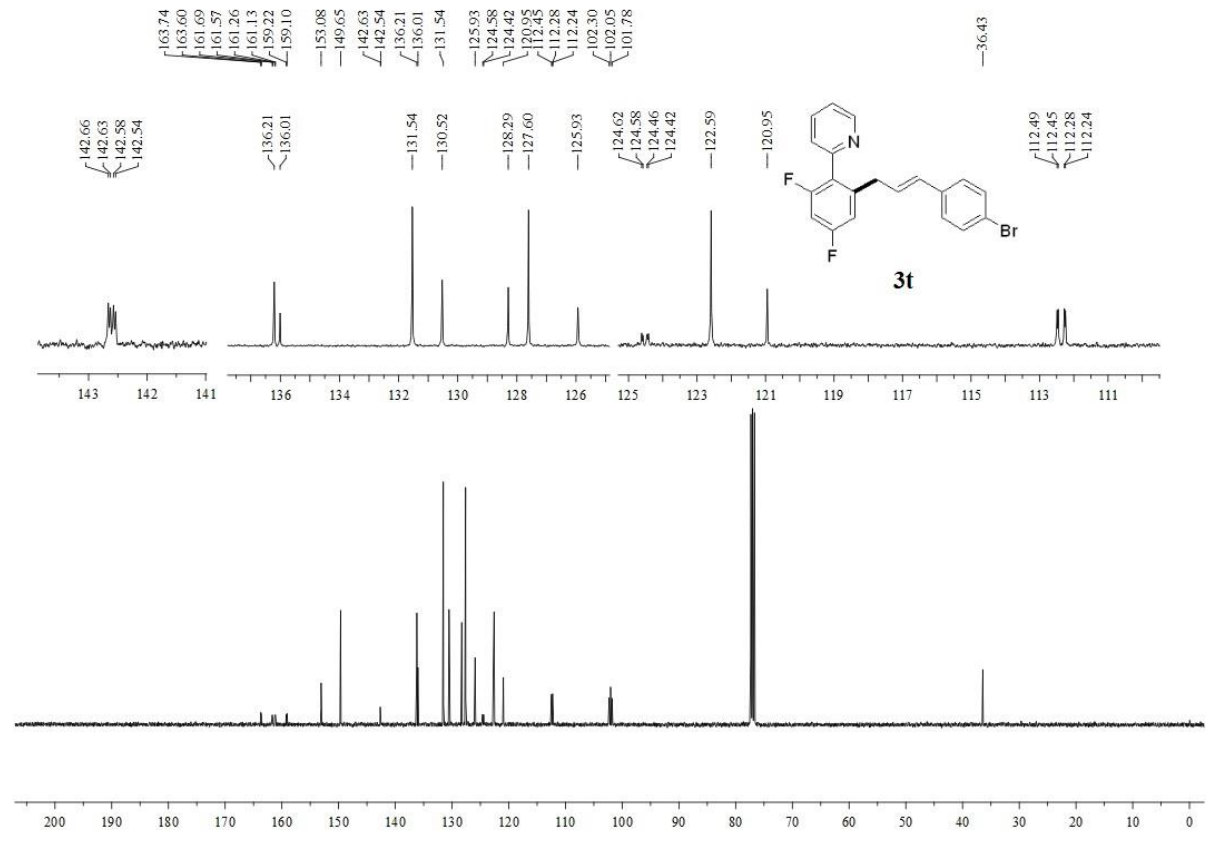
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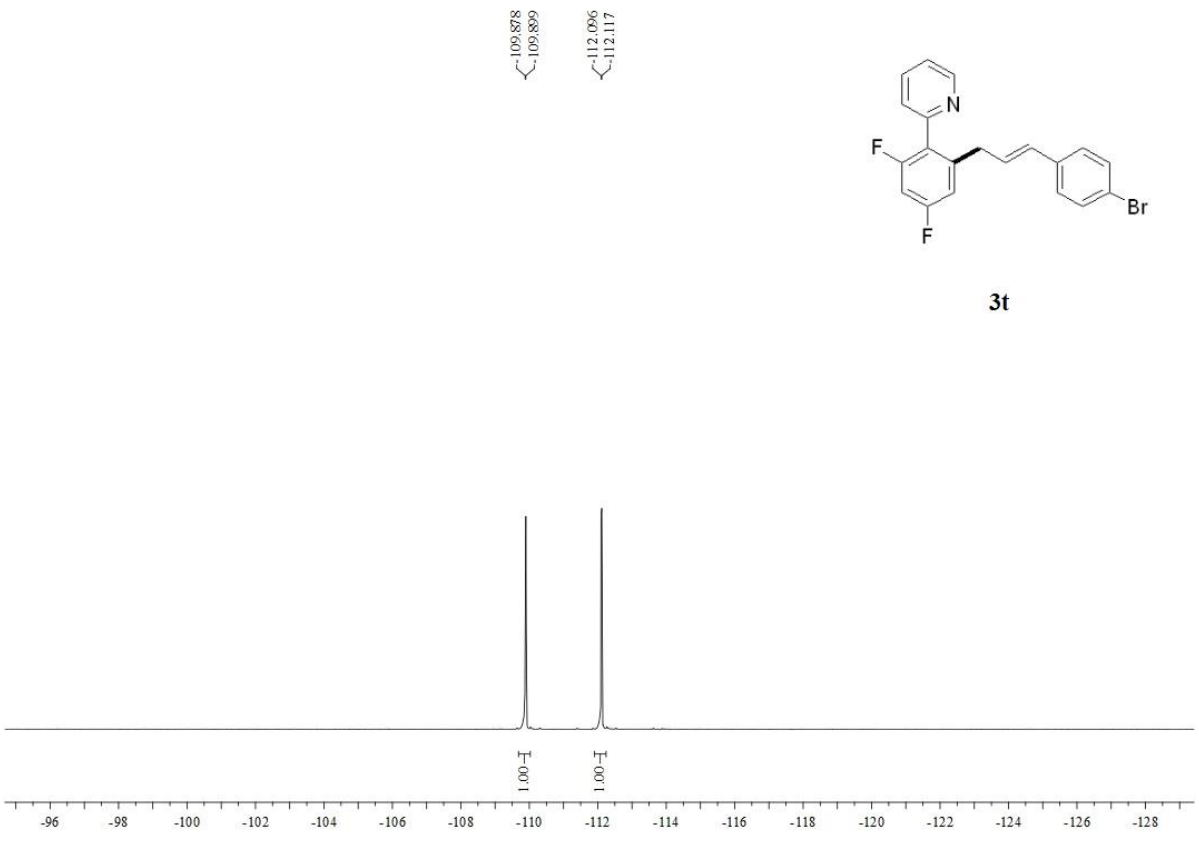
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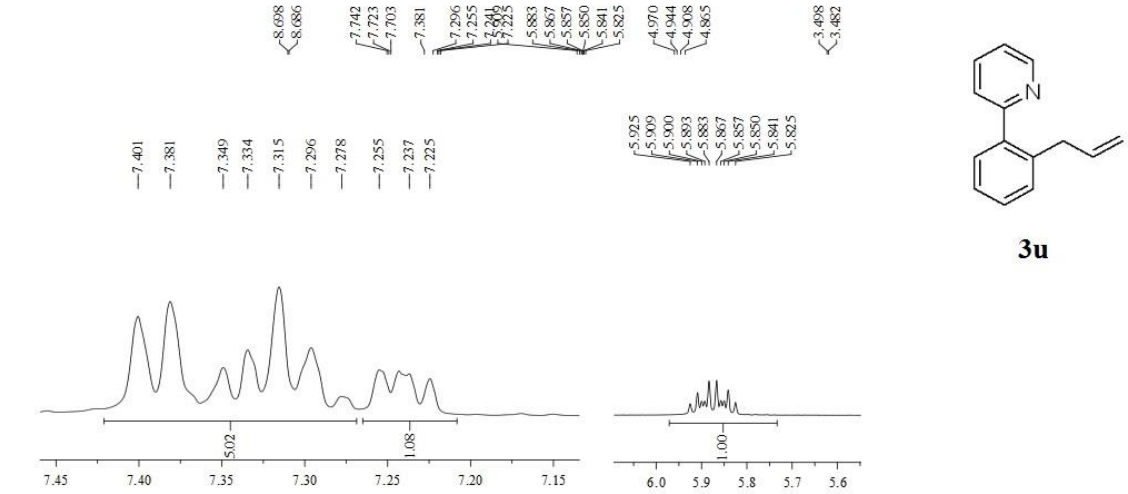
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3u

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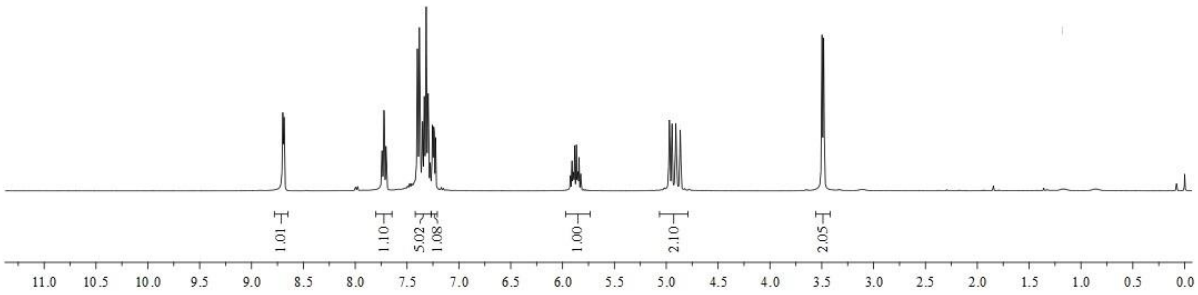
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2.5
2.0
1.5
1.0
0.5
0.0


159.94
149.22
140.48
137.77
137.68
136.26
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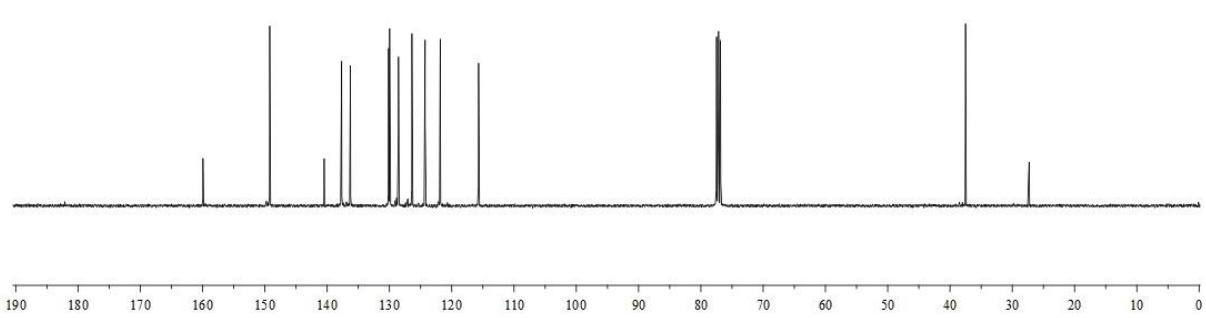
129.97
128.55
126.39
124.28
121.84
115.68
37.50
27.29
N

3u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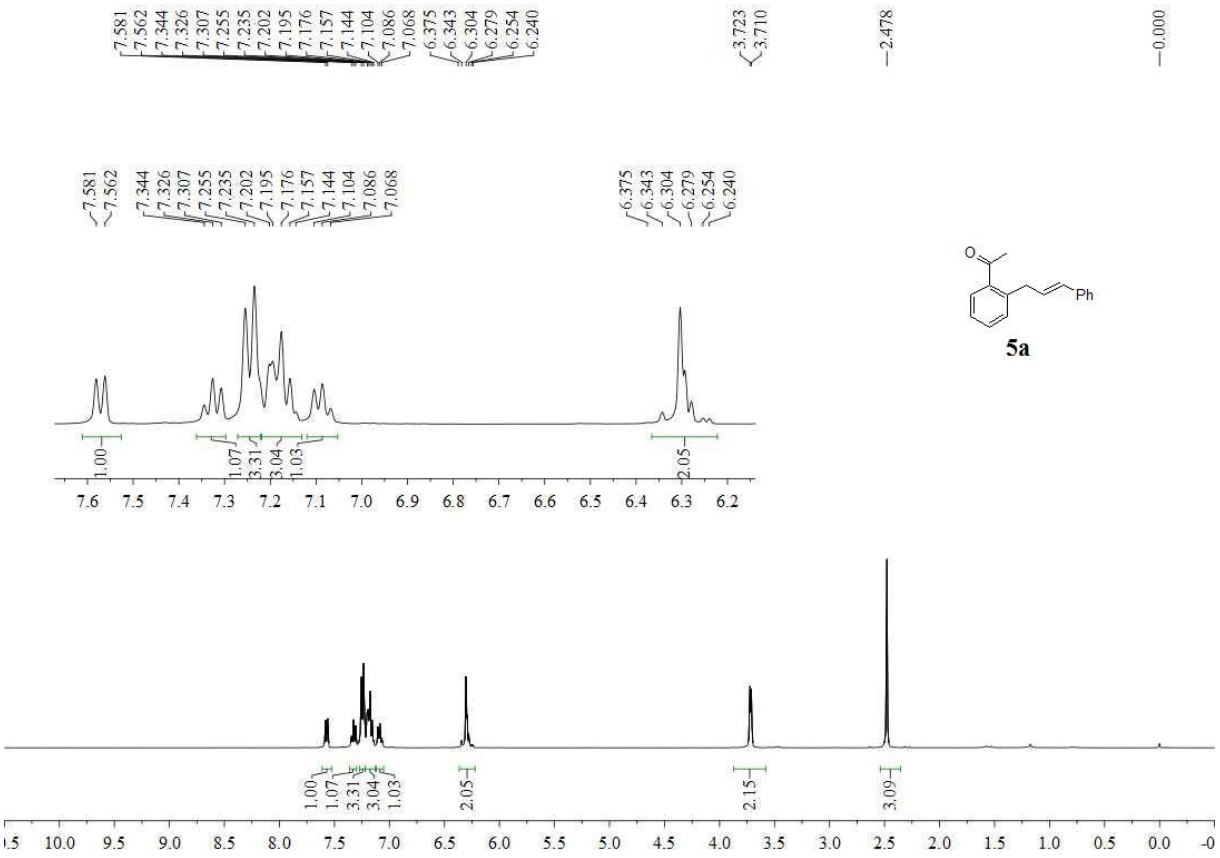
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7.326
7.307
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7.235
7.202
7.195
7.176
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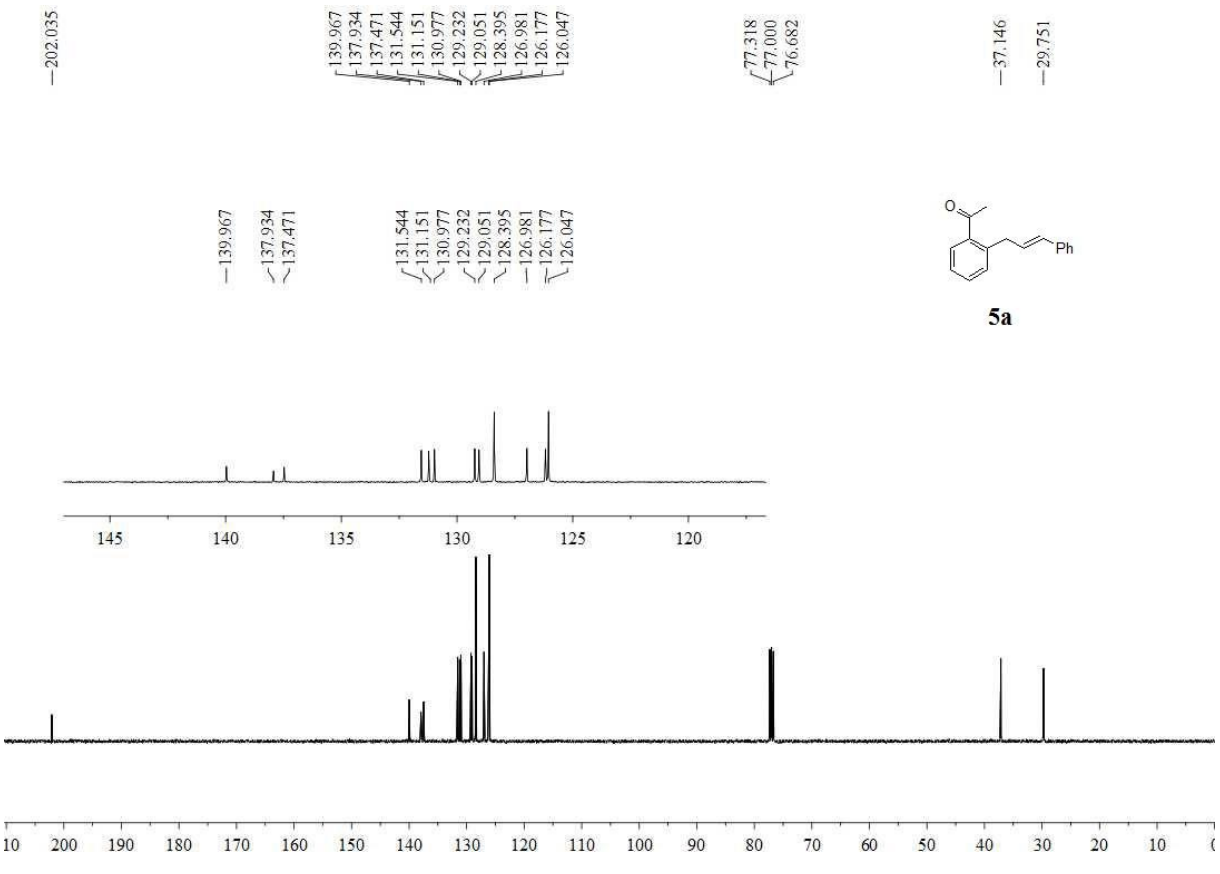
7.144
7.104
7.086
7.068
6.375
6.343
6.304
6.279
6.254
6.240
3.723
3.710
2.478
0.000
O
Ph
1.00
1.07
3.31
3.04
1.03
2.05
2.15
3.09

5a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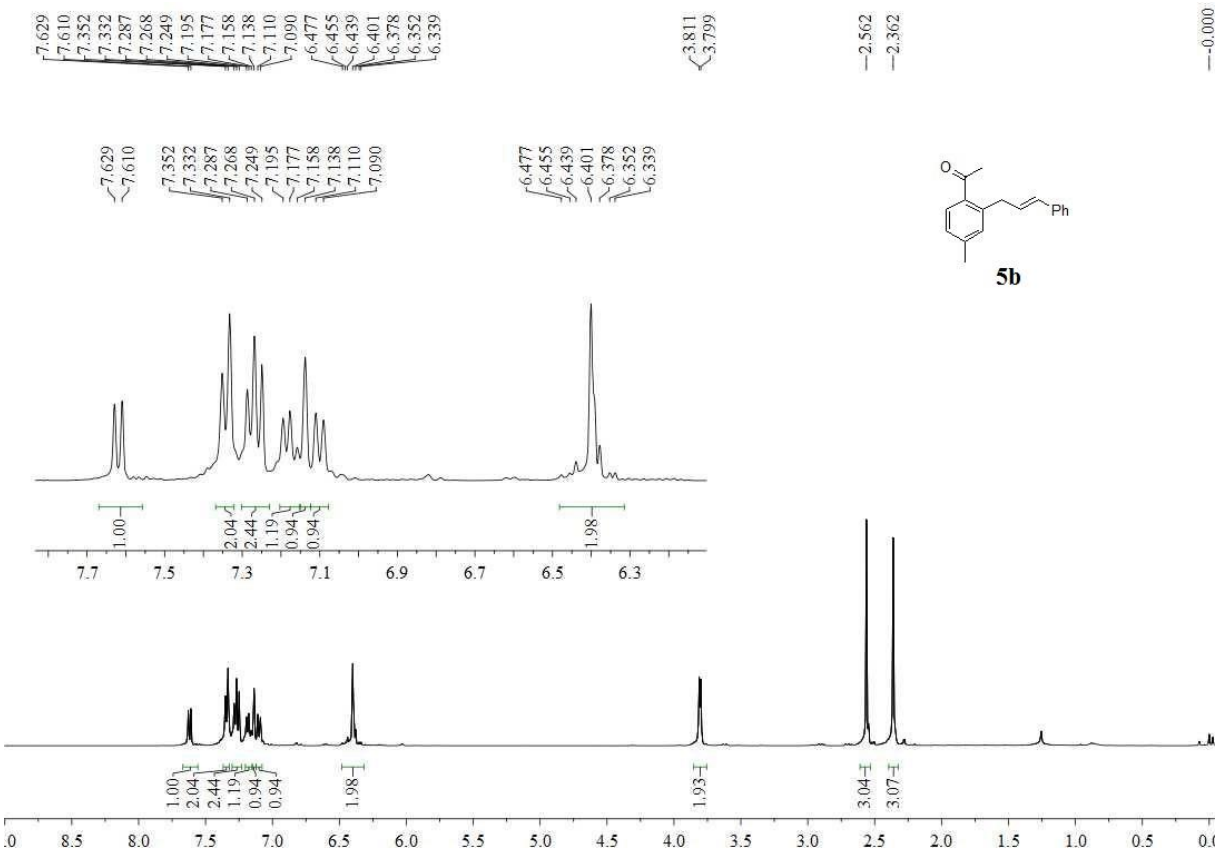
139.967
137.934
137.471
131.544
131.151
130.977
129.232
129.051
128.395
126.981
126.177
126.047
77.318
77.000
76.682
37.146
29.751
O
Ph

5a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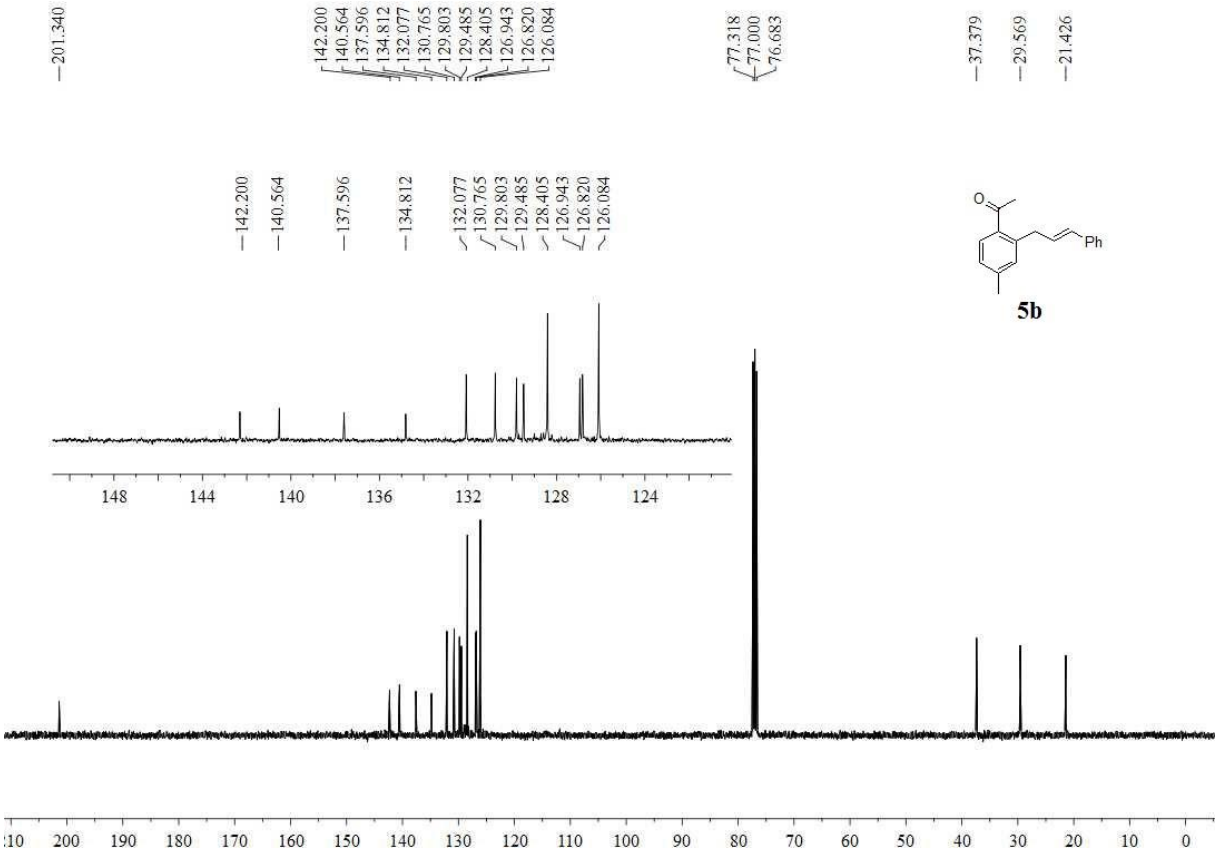
7.610
7.352
7.332
7.287
7.268
7.249
7.195
7.177
7.158
7.138
7.110
7.090
6.477
6.455
6.439
6.401
6.378
6.352
6.339
3.811
3.799
2.562
2.362
0.000
O
Ph
5b
1.00
2.04
2.44
1.19
0.94
0.94
1.98
1.93
3.04
3.07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142.200
140.564
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134.812
132.077
130.765
129.803
129.485
128.405
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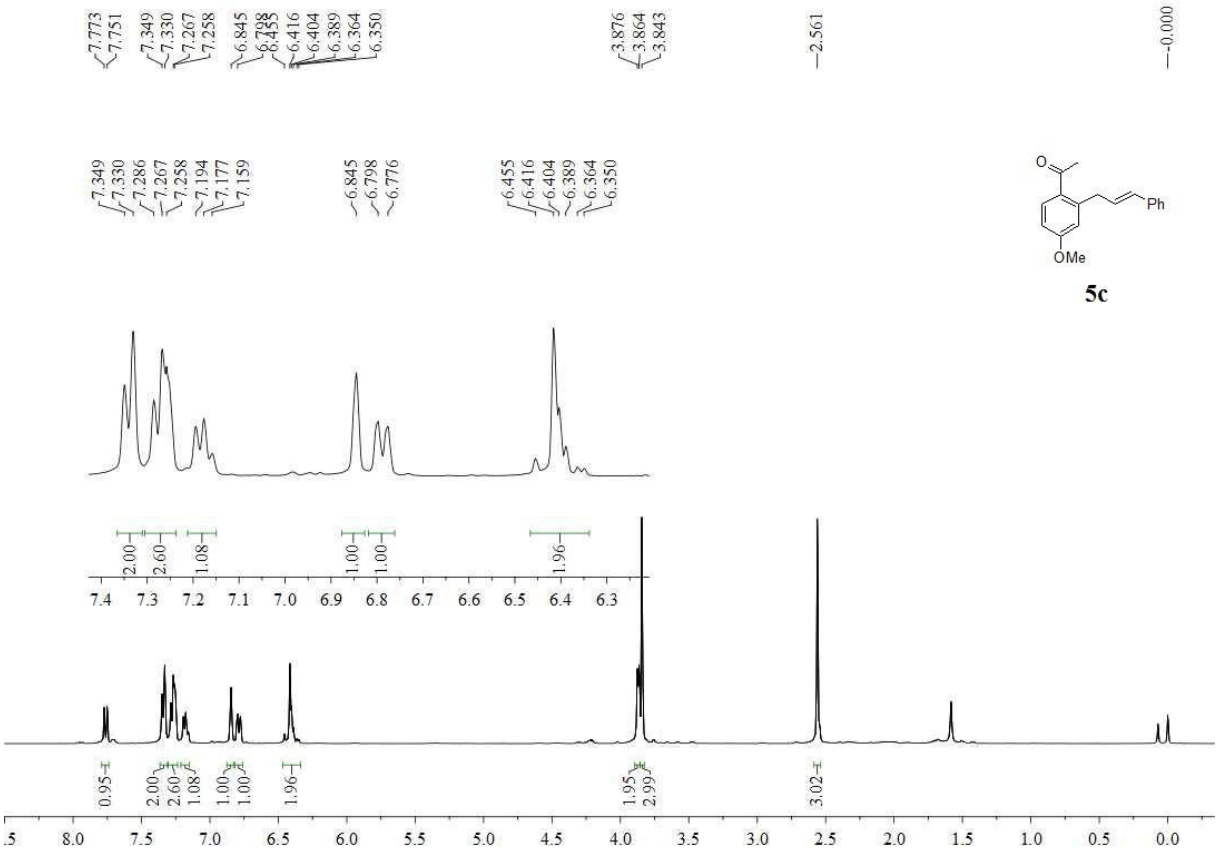
126.820
126.084
77.318
77.000
76.683
37.379
29.569
21.426
O
Ph
5b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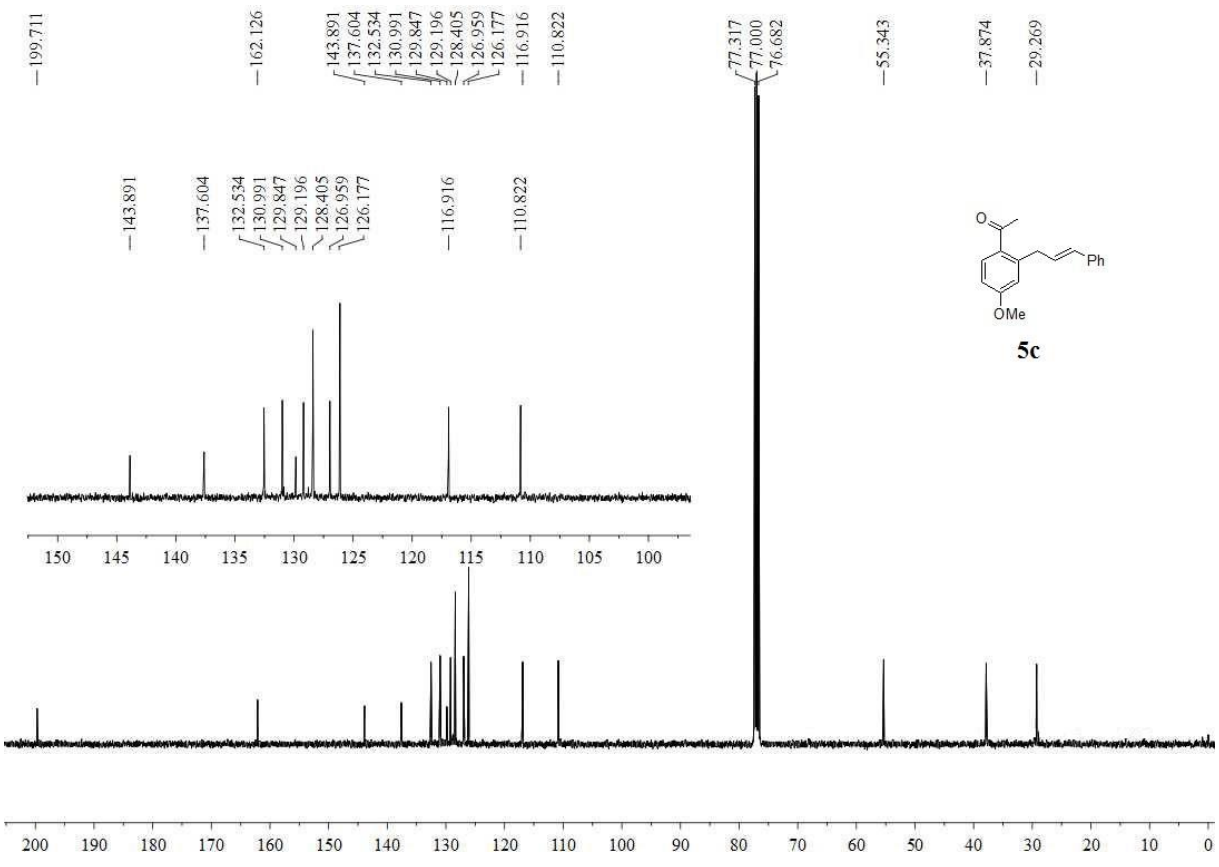
7.751
7.349
7.330
7.267
7.258
6.845
6.798
6.455
6.416
6.404
6.389
6.364
6.350
3.876
3.864
3.843
2.561
0.000
O
Ph
OMe

5c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137.604
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130.991
129.847
129.196
128.405
126.959
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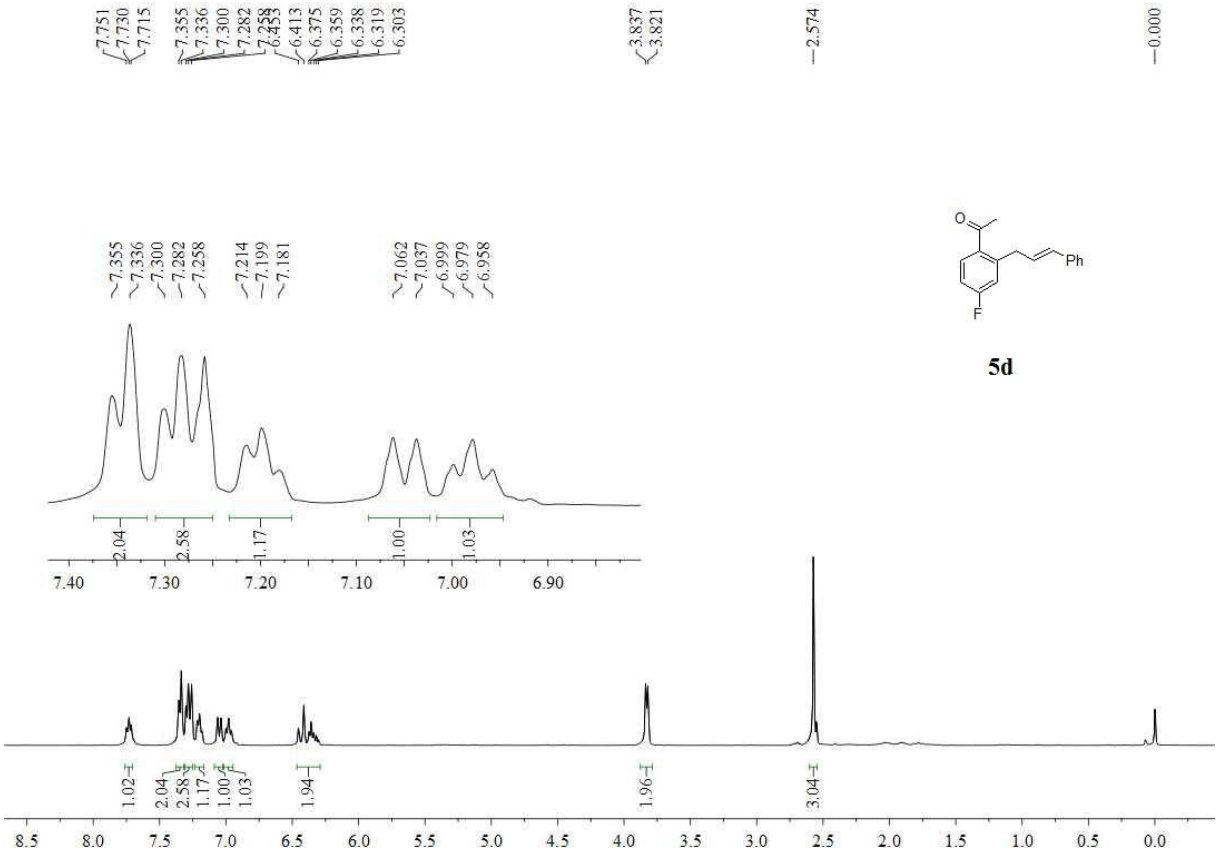
116.916
110.822
77.317
77.000
76.682
55.343
37.874
29.269
O
Ph
OMe

5c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7.715
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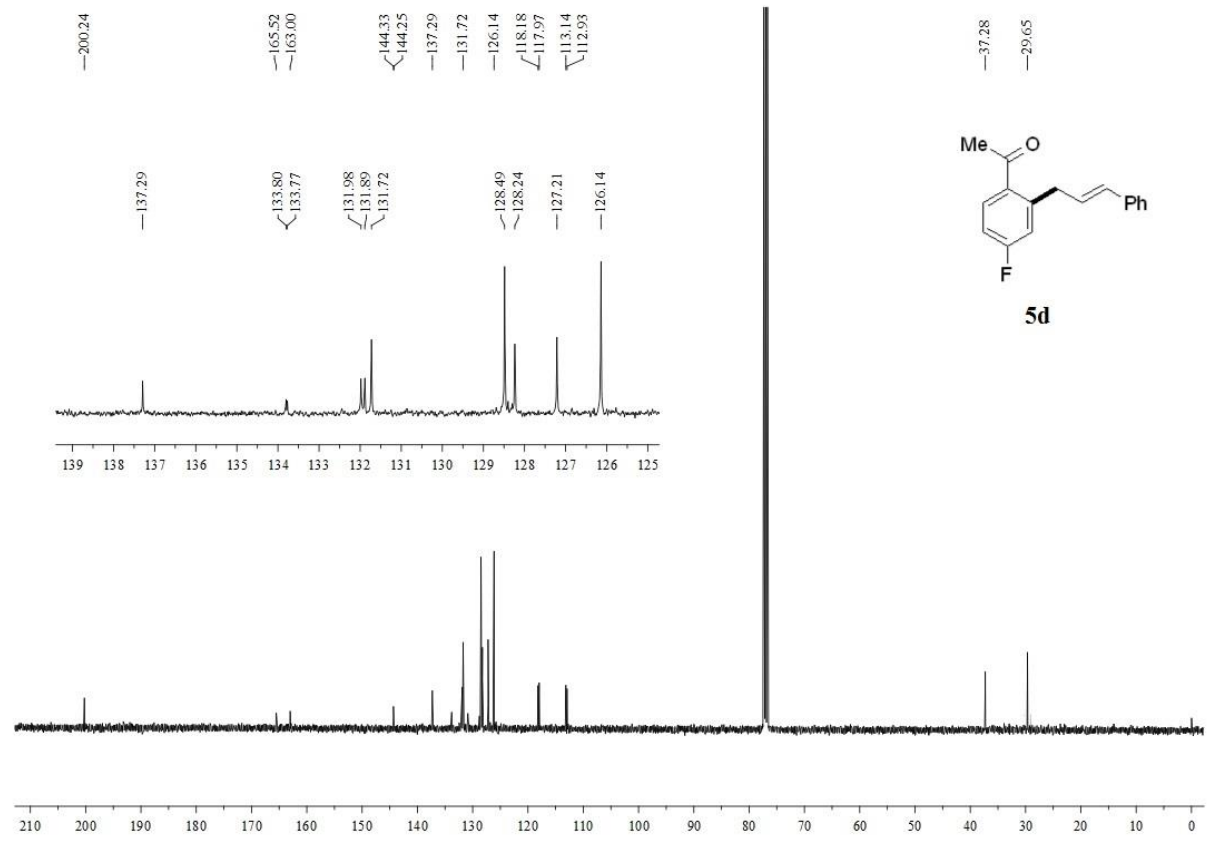
7.300
7.282
7.258
6.413
6.375
6.359
6.338
6.319
6.303
3.837
3.821
2.574
0.000
7.355
7.336
7.300
7.282
7.258
7.214
7.199
7.181
7.062
7.037
6.999
6.979
6.958
2.04
2.58
1.17
1.00
1.03
7.40
7.30
7.20
7.10
7.00
6.90
1.02
2.04
2.58
1.17
1.00
1.03
1.94
1.96
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
O
Ph
F
5d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144.25
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126.14
118.18
117.97
113.14
112.93
37.28
29.65
137.29
133.80
133.77
131.98
131.89
131.72
128.49
128.24
127.21
126.14
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
Me
O
Ph
F
5d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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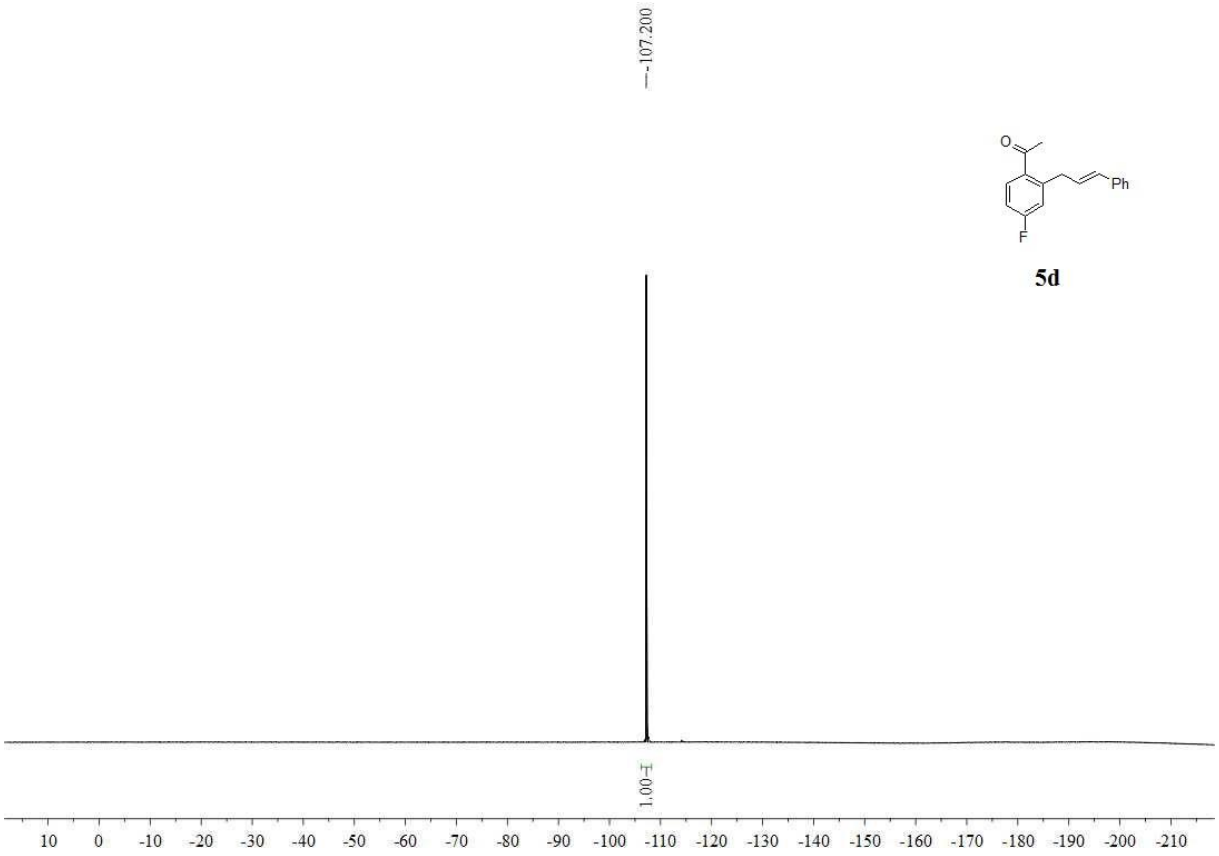
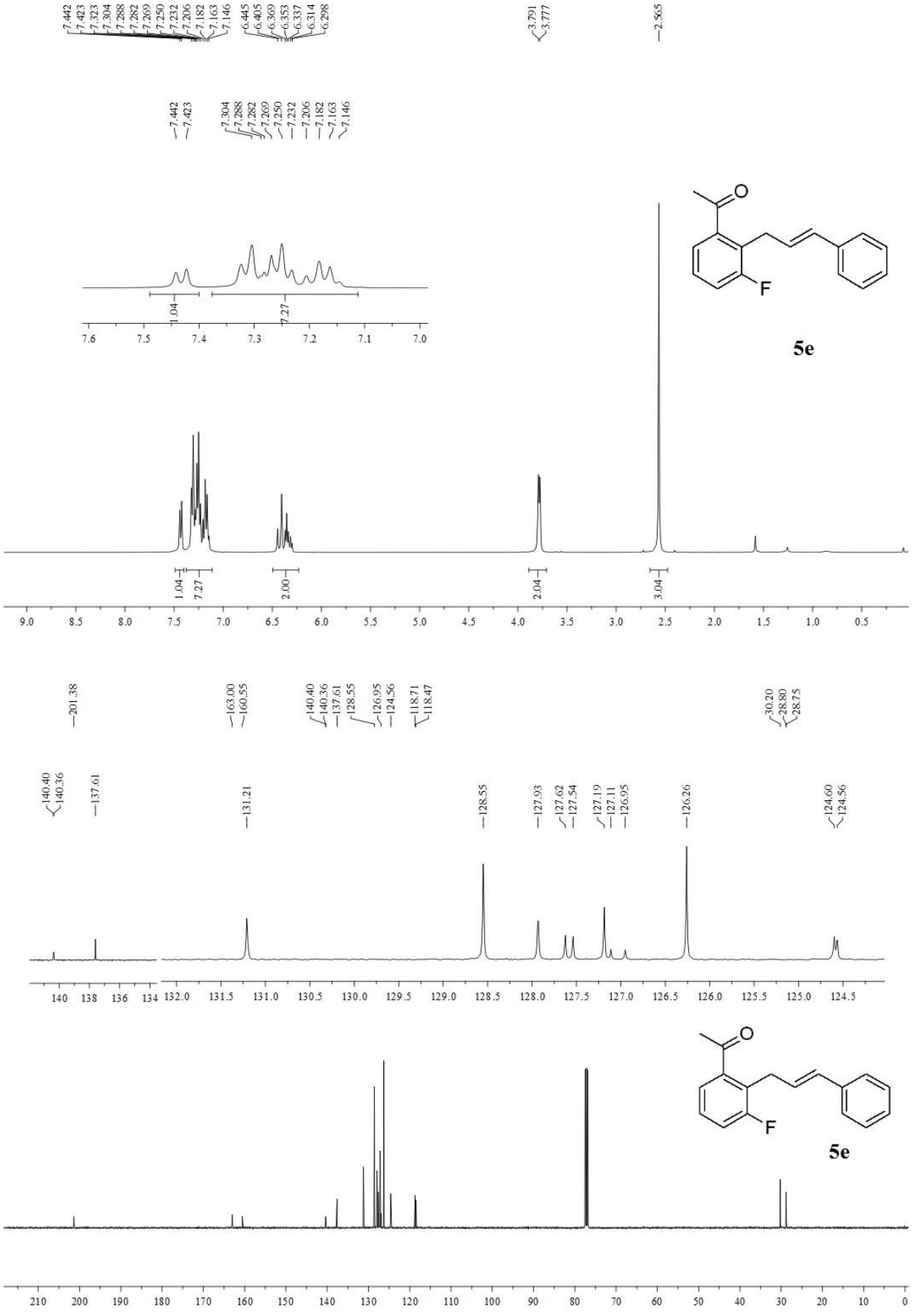
40
30
20
10
0


-107.200
O
Ph
F
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

5d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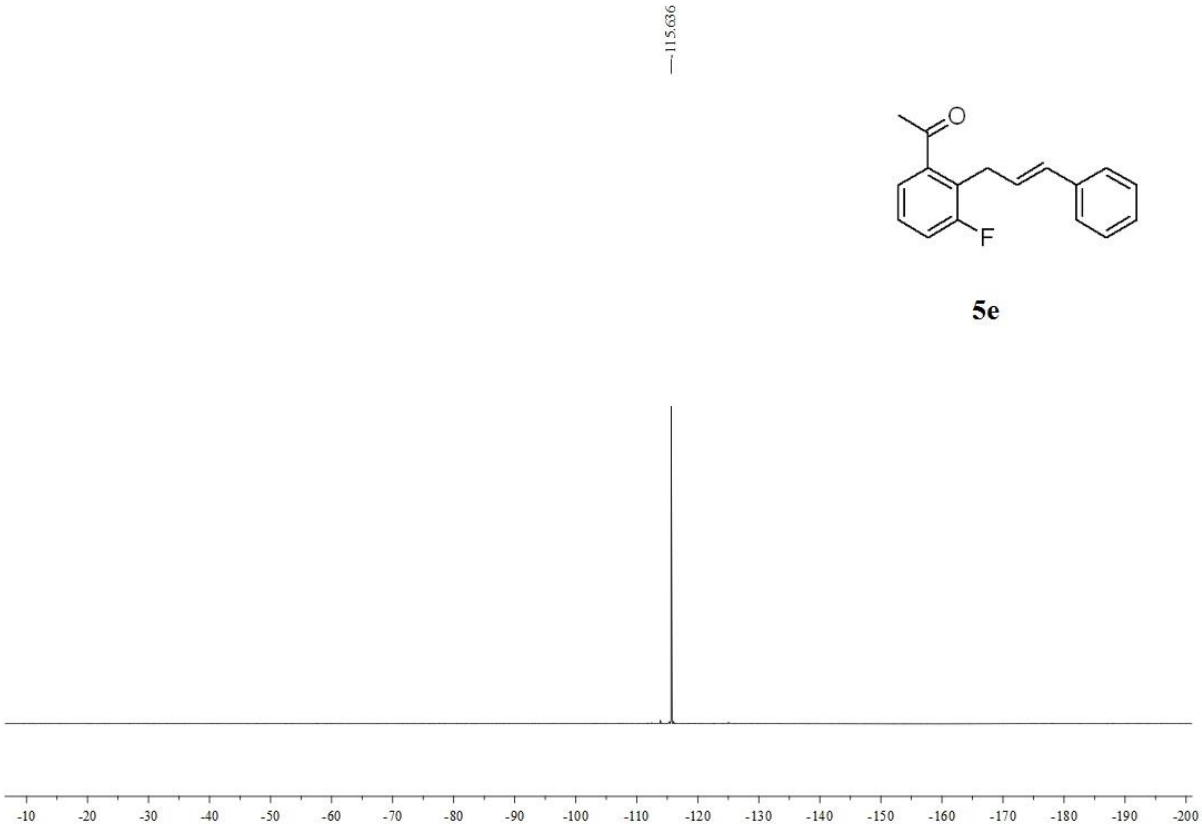
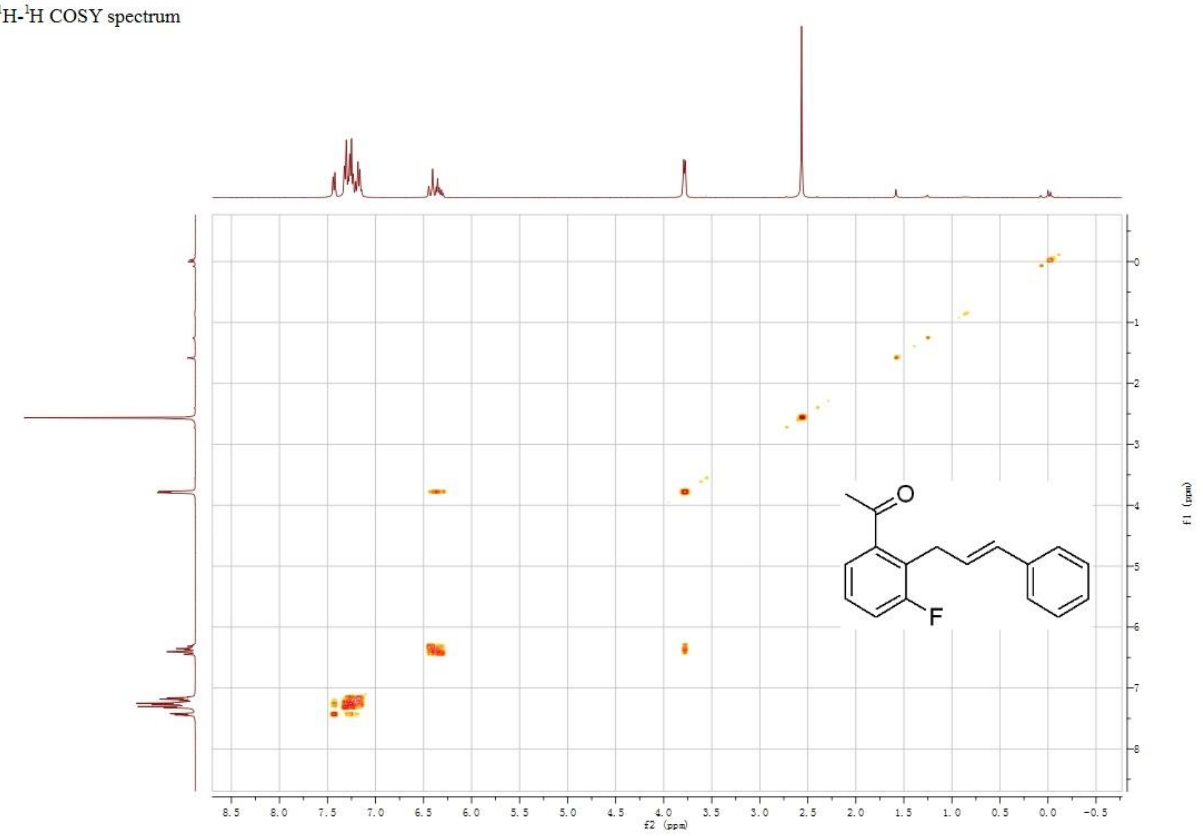
7.304
7.288
7.282
7.269
7.250
7.232
7.206
7.182
7.163
7.146
6.445
6.405
6.369
6.353
6.337
6.314
6.298
3.791
3.777
2.565
1.04
7.27
2.00
2.04
3.04
O
F
5e
201.38
163.00
160.55
140.40
140.36
137.61
128.55
126.95
124.56
118.71
118.47
30.20
28.80
28.75
131.21
128.55
127.93
127.62
127.54
127.19
127.11
126.95
126.26
124.60
124.56
5e

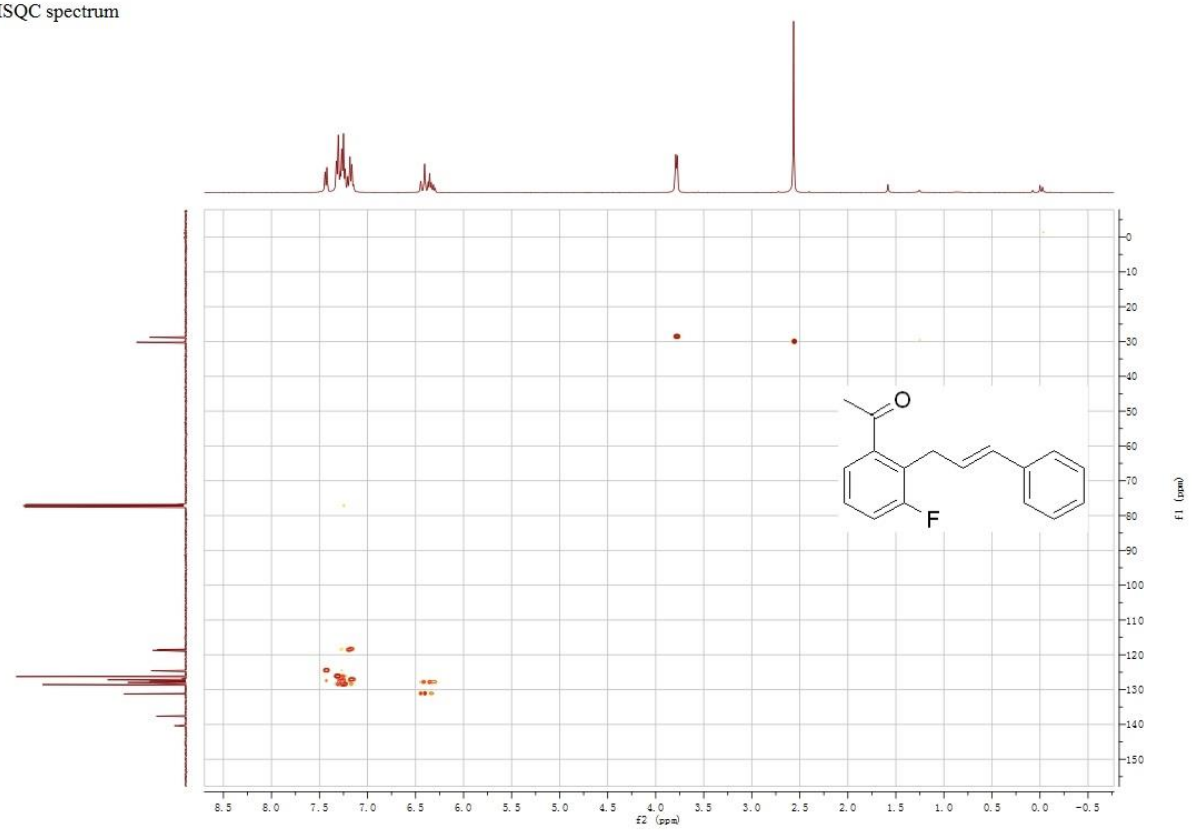


5e

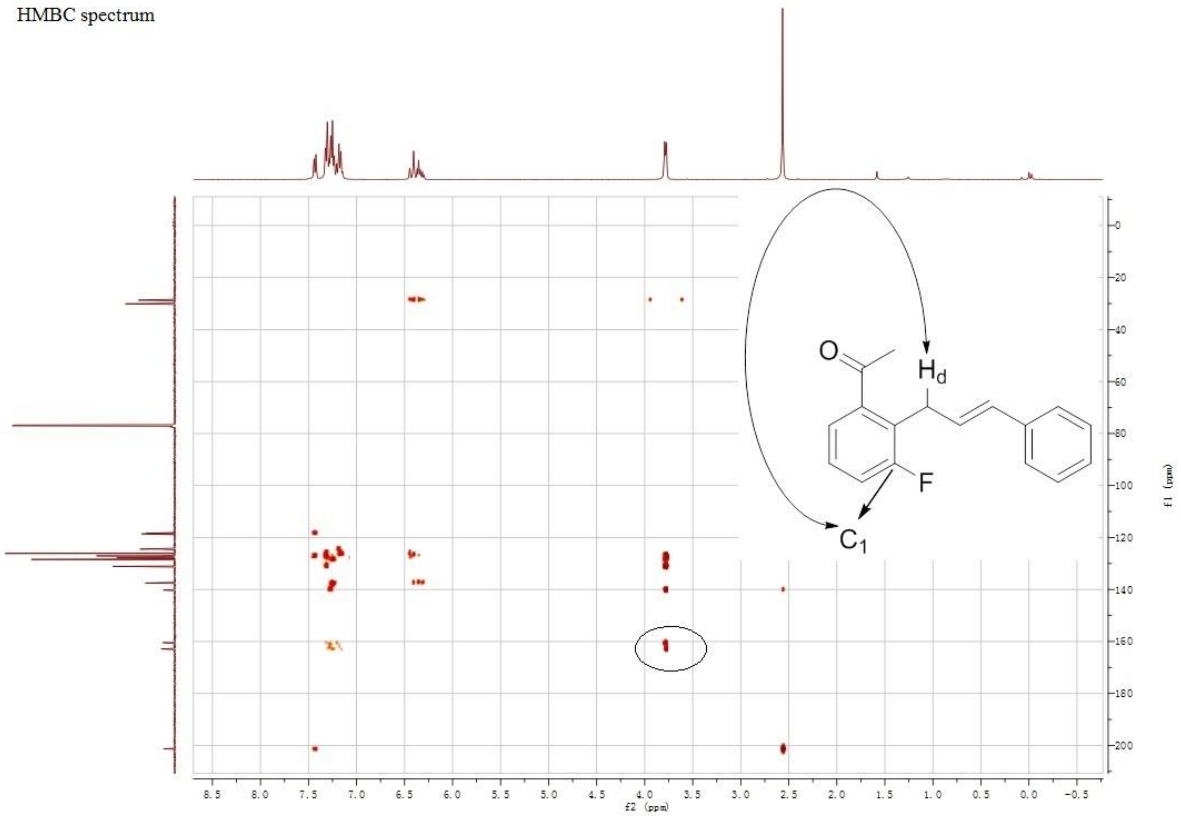
^{1}H-^{1}H COSY spectrum

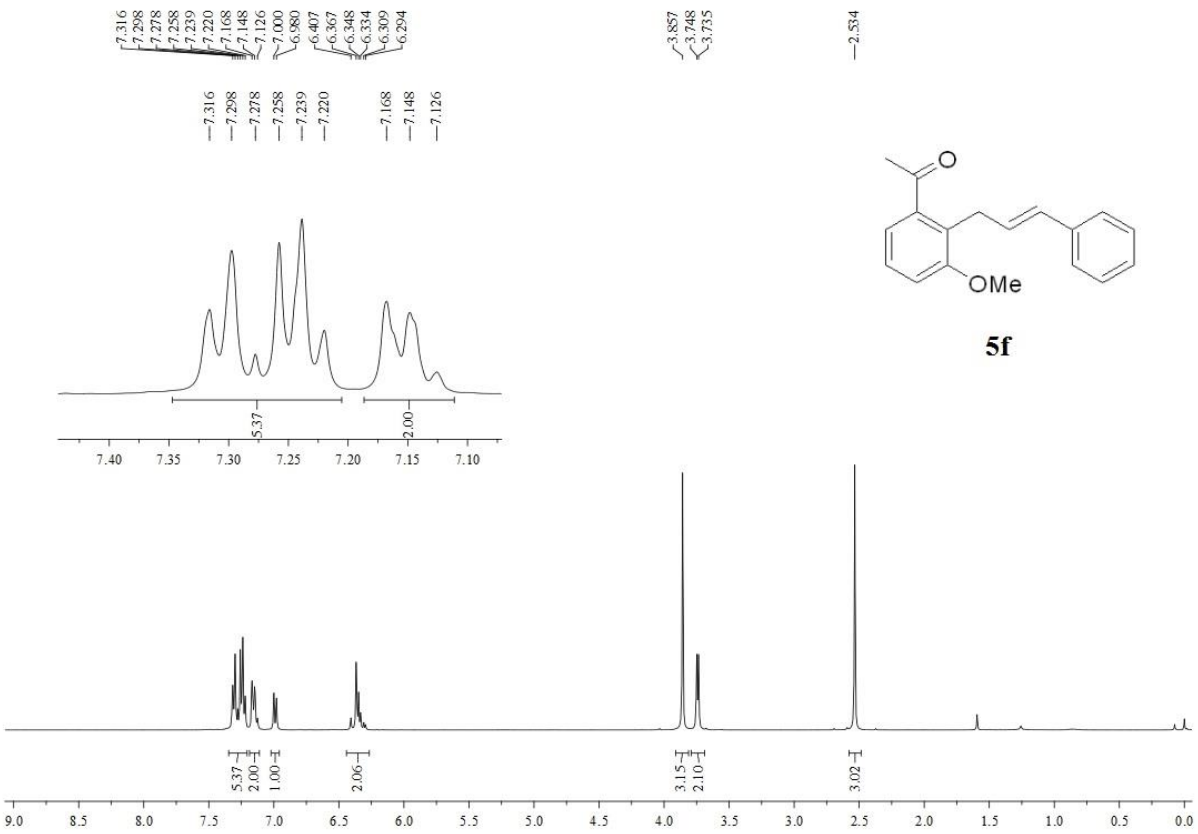


HSQC spectrum



HMBC spectrum

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7.000
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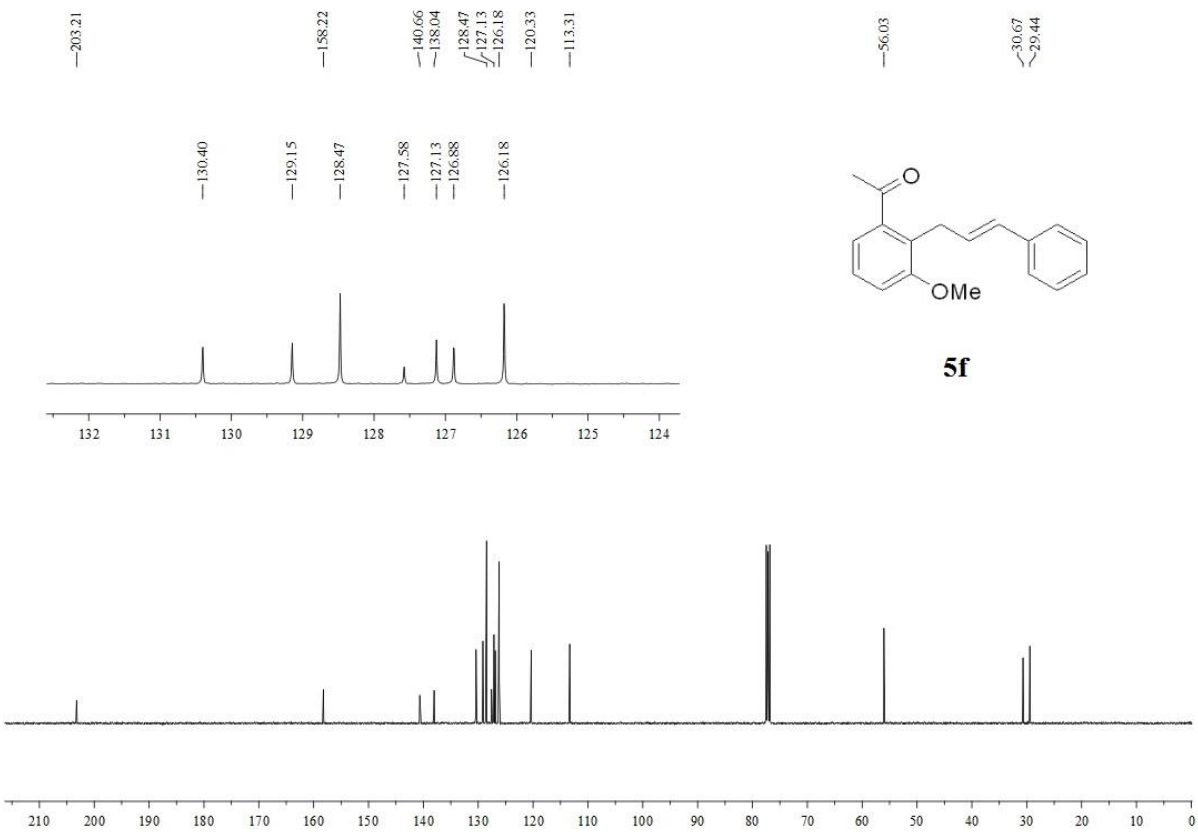
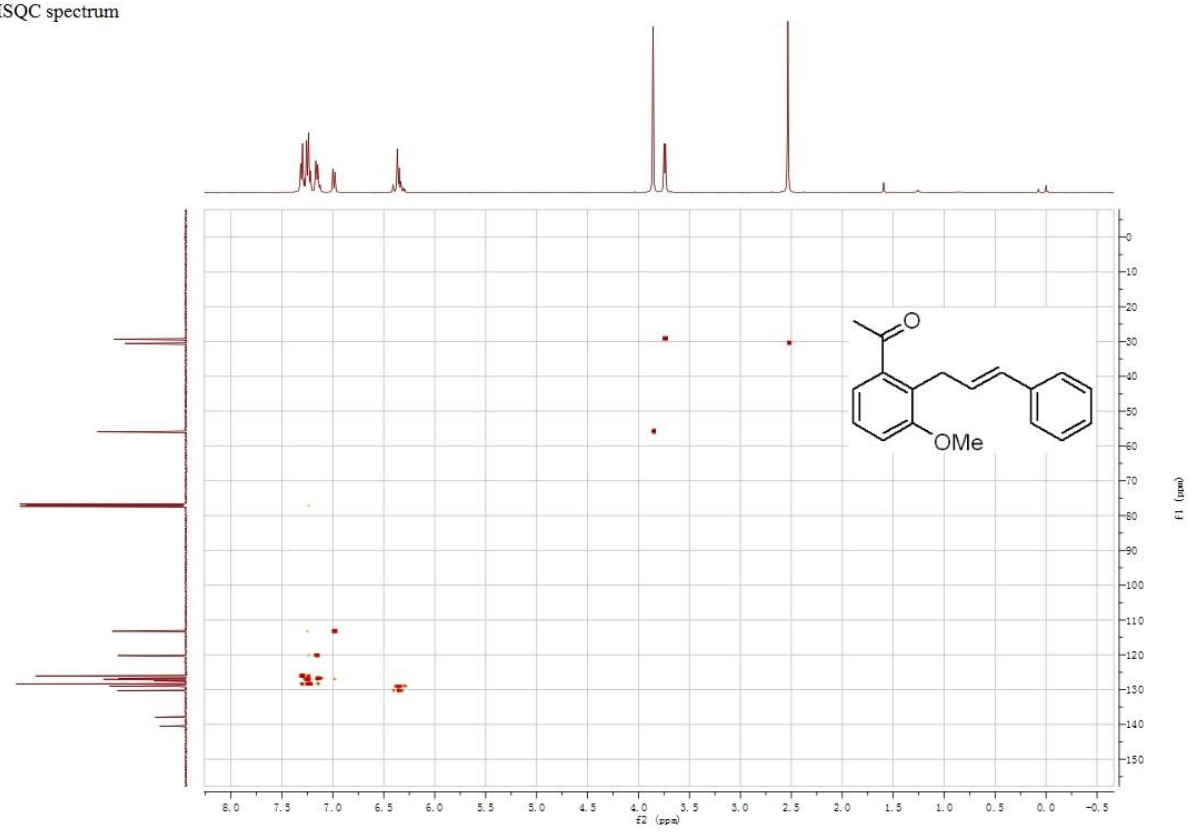
6.367
6.348
6.334
6.309
6.294
3.857
3.748
3.735
2.534
5.37
2.00
1.00
2.06
3.15
2.10
3.02
OMe

5f


203.21
158.22
140.66
138.04
128.47
127.13
126.18
120.33
113.31
56.03
30.67
29.44
130.40
129.15
128.47
127.58
127.13
126.88
126.18
OMe

5f

HSQC spectrum



HMBC spectrum