Supporting Information

Ru(II)-catalyzed, Cu(II)-mediated Carbene Migratory Insertion in the Synthesis of Trisubstituted Pyrroles from Isoxazoles

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Experimental:

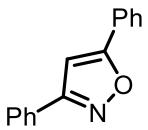
(1) General Methods:

All commercially available compounds were used without purification. Unless otherwise noted, all reactions were performed in oven-dried glassware. All reactions were run under argon or nitrogen atmosphere. All solvents used in the reactions were distilled before use. Dry tetrahydrofuran and toluene were distilled from sodium and benzophenone; whereas dry dichloromethane, dichloroethane and xylene were distilled from CaH_2.[1] Petroleum ether with a boiling range of 40-60 °C was used. Melting points are uncorrected. ^{1}H, ^{13}C and ^{19}F NMR: Recorded on Bruker Avance III 400 MHz NMR Spectrometer, Bruker Avance III 500 MHz NMR Spectrometer; spectra were recorded at 295 K in $CDCl_3$; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (1H δ 7.26; 13C δ 77.0). HRMS: Bruker Daltonics MicroTOFQ-II with electron spray ionization (ESI) and Atmospheric Pressure Chemical Ionization (APCI). GC-HRMS: Performed on Agilent 7200 GC-QToF (with Electron Impact (EI), 70eV) with 7890A GC using DB-5 column. GC-LRMS: Performed on Agilent 7890A GC with Agilent 5975C MS (EI 70 eV) using DB-5 column. IR: Perkin Elmer Spectrum BX FTIR, Shimadzu IRAffinity-1 FTIR and were recorded as thin films between KBr plates. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at low temperature.

(2) General procedures:

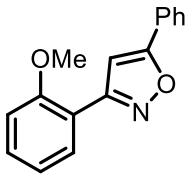
(2.1) Preparation of 3, 5-diaryl isoxazoles:[2]

3, 5-diphenylisoxazole (1a):[2]



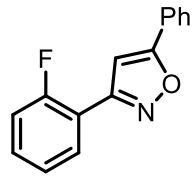
Prepared according to the general procedure and the title compound was isolated in 71% (550 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-(2-methoxyphenyl)-5-phenylisoxazole (1b):[2]



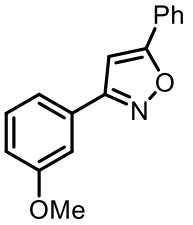
Prepared according to the general procedure and the title compound was isolated in 62% (545 mg) yield;

3-(2-fluorophenyl)-5-phenylisoxazole (1c):[2]



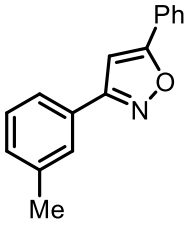
Prepared according to the general procedure and the title compound was isolated in 48% (402 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-(3-methoxyphenyl)-5-phenylisoxazole (1d):[2]



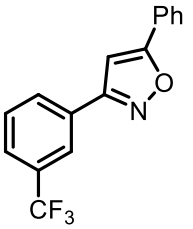
Prepared according to the general procedure and the title compound was isolated in 52% (457 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

5-phenyl-3-(*m*-tolyl)isoxazole (1e):[2]



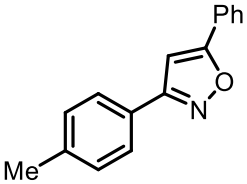
Prepared according to the general procedure and the title compound was isolated in 56% (461 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

5-phenyl-3-(3-(trifluoromethyl)phenyl)isoxazole (1f):[3]



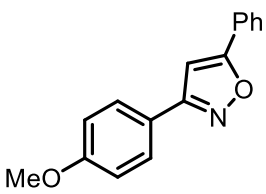
Prepared according to the general procedure and the title compound was isolated in 46% (465 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

5-phenyl-3-(p-tolyl)isoxazole (1g):[2]



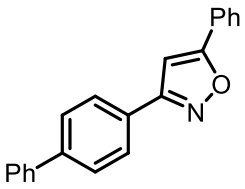
Prepared according to the general procedure and the title compound was isolated in 72% (592 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-(4-methoxyphenyl)-5-phenylisoxazole (1h):[2]



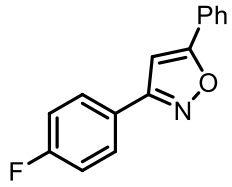
Prepared according to the general procedure and the title compound was isolated in 75% (659 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-([1,1'-biphenyl]-4-yl)-5-phenylisoxazole (1i):[3]



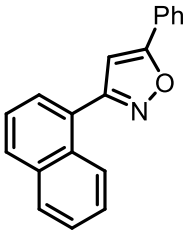
Prepared according to the general procedure and the title compound was isolated in 50% (520 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-(4-fluorophenyl)-5-phenylisoxazole (1j):[2]



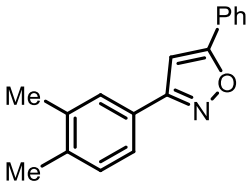
Prepared according to the general procedure and the title compound was isolated in 49% (410 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-(naphthalen-1-yl)-5-phenylisoxazole (1k):[4]



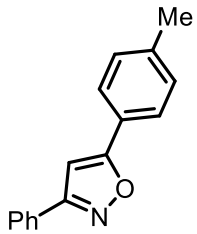
Prepared according to the general procedure and the title compound was isolated in 52% (494 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-(3,4-dimethylphenyl)-5-phenylisoxazole (1l):[3]



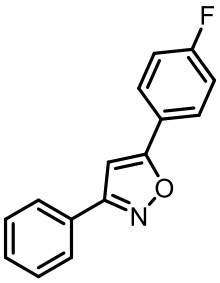
Prepared according to the general procedure and the title compound was isolated in 72% (628 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-phenyl-5-(*p*-tolyl)isoxazole (1m):[3]



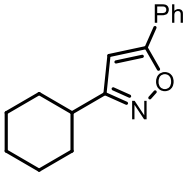
Prepared according to the general procedure and the title compound was isolated in 62% (510 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

5-(4-fluorophenyl)-3-phenylisoxazole (1n):[3]



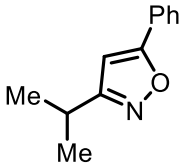
Prepared according to the general procedure and the title compound was isolated in 47% (393 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-cyclohexyl-5-phenylisoxazole (1o):[3]



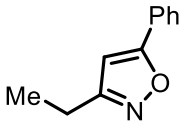
Prepared according to the general procedure and the title compound was isolated in 44% (350 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-isopropyl-5-phenylisoxazole (1p):[5]



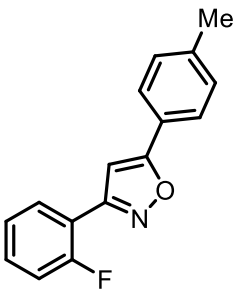
Prepared according to the general procedure and the title compound was isolated in 42% (275 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

3-ethyl-5-phenylisoxazole (1q):[4]



Prepared according to the general procedure and the title compound was isolated in 41% (244 mg) yield. Spectral data obtained were in good agreement with those reported in the literature.

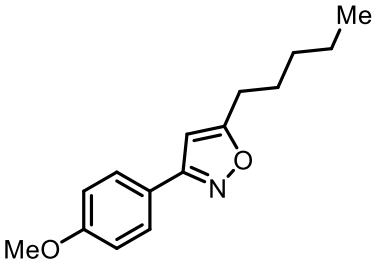
3-(2-fluorophenyl)-5-(*p*-tolyl)isoxazole (1r):



Prepared according to the general procedure and the title compound was isolated in 52% (461 mg) yield; Physical appearance: Colorless solid; M.p. 48-50 ^{o}C; TLC R_f 0.3 (19:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 – 7.81 (m, 2H), 7.57 (d, J = 7.9 Hz, 1H), 7.43 – 7.29 (m, 3H), 7.21 (t, J = 8.6 Hz, 2H), 6.67 (s, 1H), 2.55 (s, 3H); **^{13}C**

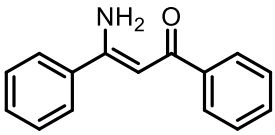
NMR (125 MHz, $CDCl_3$): δ 168.58, 163.76 (d, J_{C-F} = 251.1 Hz), 163.72, 164.76, 162.76, 136.92, 131.10, 129.57, 129.43, 128.73, 127.92 (d, J_{C-F} = 8.6 Hz),126.04, 123.88 (d, J_{C-F} = 3.4 Hz), 116.25 (d, J_{C-F}= 22.2 Hz), 99.98, 21.12; **ESI-HRMS**: Calculated for $C_{16}H_{13}FNO^+$ $[M+H]^+$ 254.0976, found 254.0948.

3-(4-methoxyphenyl)-5-pentylisoxazole (1s):[2,6]



Prepared according to the general procedure and the title compound was isolated in 48% (412 mg) yield. Physical appearance: Yellow gel; TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.24 (s, 1H), 3.87 (s, 3H), 2.79 (t, J = 7.6 Hz, 2H), 1.81 – 1.68 (m, 2H), 1.45 – 1.34 (m, 4H), 1.01 – 0.88 (m, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$): δ 174.04, 161.92, 160.80, 128.11, 121.98, 114.22, 98.53, 55.34, 31.26, 27.25, 26.77, 22.33, 13.94; **ESI-HRMS**: Calculated for $C_{15}H_{20}N_2O^+$ $[M+H]^+$ 246.1489, found 246.1459.

(Z)-3-amino-1,3-diphenylprop-2-en-1-one (1a'):[2]



Prepared according to the reported literature procedure and the title compound was isolated in 73% yield. Spectral data obtained were in good agreement with those reported in the literature.

2.2 General procedure for the preparation of tosylhydrazone derivatives:

Tosylhydrazide (1.0 equiv, 10.75 mmol) was dissolved in methanol (20 mL). To this rapidly stirring solution was added the acetophenone (1.0 equiv, 10.75 mmol) dropwise. (Solid reagents were added portion wise). A mildly exothermic reaction ensued and the tosylhydrazide dissolved. A reflux condenser was fitted on the flask and the reaction mixture was heated to 70 ^oC. After 3h the reaction was found to be complete and the solvent was removed under reduced pressure. The concentrated mixture was then poured into a separatory funnel. The organic phase was diluted with EtOAc and washed with brine. It was then dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to get almost pure tosylhydrazone which was used as such without any purification.[14]

2.3 General procedure for the synthesis of pyrroles

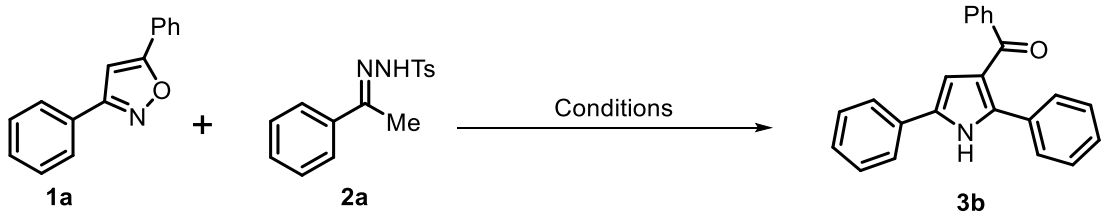
In a pressure tube equipped with a stir bar, isoxazole (1.0 equiv, 0.15 mmol) was dissolved in dry dichloroethane (2.0 mL) and tosylhydrazone (1.2 equiv, 0.18 mmol) was added. The reaction mixture was stirred for 10 min followed by the addition of the $[RuCl_2(p\text{-cym})]_2$ (0.05 equiv, 0.0075 mmol), $AgSbF_6$ (0.20 equiv, 0.03 mmol) and $Cu(OAc)_2.H_2O$ (1.5 equiv, 0.225 mmol). The tube was fitted with a Teflon screw cap under an argon flow and the reaction mixture was heated to 120 ^oC and allowed to stir for 16-26 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with saturated solution of $NaHCO_3$ and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash column chromatography to result in the desired product.

(2.3) Mechanistic Studies

(a) Radical trap experiments:

Procedure: In a pressure tube equipped with a stir bar, 3, 5-diaryisoxazole (1.0 equiv, 0.15 mmol) was dissolved in dry dichloroethane (2.0 mL) and tosylhydrazone (1.2 equiv, 0.18 mmol) was added. The reaction mixture was stirred for 10–15 min followed by the addition of $[RuCl_2(p\text{-cym})]_2$ (0.05 equiv, 0.0075 mmol), $AgSbF_6$ (0.20 equiv, 0.03 mmol), $Cu(OAc)_2.H_2O$ (1.5 equiv, 0.225 mmol) and radical trap agent (2.0 equiv). The tube was fitted with a Teflon screw cap under an argon flow, and the reaction mixture was heated to 120 ^oC and allowed to stir for 24h. Upon cooling to room temperature, the reaction mixture was diluted with ethylacetate and filtered through a pad of Celite. The filtrate was washed with saturated solution of $NaHCO_3$ and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by a silica gel flash column chromatography to yield the desired product.

Optimization studies for one pot synthesis of polysubstituted pyrroles:



1a 2a 3b

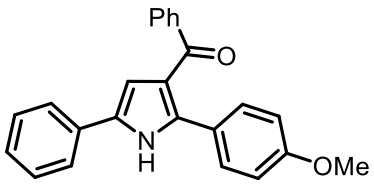
Table-S1

Entry	Conditions	Yield (%)[a]
1	$Cu(OAc)_2$ (10 mol%), DCE, 120 °C, 24 h	0
2	$Cu(OAc)_2.H_2O$ (2 equiv.), DCE, 120 °C, 24 h	trace
3	$Cu(OTf)_2$ (2 equiv.), DCE, 120 °C, 24 h	0
4	$Cu(OAc)_2.H_2O$ (1.5 equiv.), Ag_2CO_3 (1 equiv.), DCE, 120 °C, 24 h	30
5	$Cu(OAc)_2.H_2O$ (1.5 equiv.), Ag_2CO_3 (1 equiv.), THF, 120 °C, 24 h	0
6	$Cu(OAc)_2.H_2O$ (1.5 equiv.), Ag_2CO_3 (1 equiv.), Toluene, 120 °C, 24 h	0
7	$Co(OAc)_2.H_2O$ (1.5 equiv.), Ag_2CO_3 (1 equiv.), DCE, 120 °C, 24 h	0
8	$Cu(OAc)_2.H_2O$ (5 mol%), Ag_2CO_3 (1 equiv.), DCE, 120 °C, 24 h	0
9	$Sc(OTf)_3$ (10 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), Ag_2CO_3 (1equiv.), DCE, 120 °C, 24 h	trace
10	$RuCl_3$ (10 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), Ag_2CO_3 (1 equiv.), DCE, 120 °C, 24 h	35
11	$Ph_3PAuNTf_2$ (20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), Ag_2CO_3 (1 equiv.), DCE, 120 °C, 24 h	trace
12	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%) $Cu(OAc)_2.H_2O$ (1.5 equiv.), DCE, 120 °C, 24 h	47
13	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), THF, 120 °C, 24 h	trace
14	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%),$Cu(OAc)_2.H_2O$ (1.5 equiv.), Toluene, 120 °C, 24 h	40
15	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), Dioxane, 120 °C, 24 h	0
16	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), Methanol, 80 °C, 24 h	0
17	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), DCE:Toluene (1:1), 120 °C, 24 h	42
18	**$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), DCE, 120 °C, 24 h**	**65**
19	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$(20 mol%), DCE, 120 °C, 24 h	trace
20	$AgSbF_6$(20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.) DCE, 120 °C, 24 h	trace
21	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), CuI (1 equiv.), DCE, 120 °C, 24 h	0
22	$[RuCl_2(p\text{-cym})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2.H_2O$ (1.5 equiv.), DCE, r.t , 24 h	0

[a]Isolated yield.

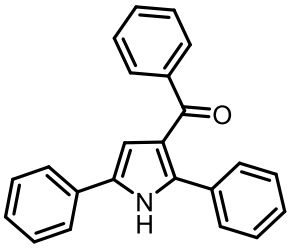
(A) Analytical Data:

(2-(4-methoxyphenyl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3a):



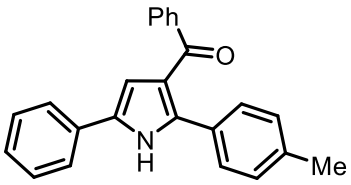
Yield: 72 % (38 mg); Physical appearance: Yellow solid; M.p. 130–132 ^{o}C; TLC R_f 0.2 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.57 – 7.29 (m, 10H), 6.91 –6.80 (m, 3H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.27, 159.63, 139.61, 138.03, 131.61, 131.50, 131.32, 129.83, 129.64, 129.06, 127.92, 127.04, 124.32, 124.02, 121.38, 113.90, 110.46, 55.32; **ESI-HRMS**: Calculated for $C_{24}H_{20}NO_2^+$ $[M+H]^+$ 354.1489, found 354.1507.

(2,5-diphenyl-1H-pyrrol-3-yl)(phenyl)methanone (3b):[7]



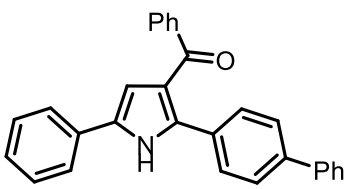
Yield: 70 % (34 mg); Physical appearance: Pale yellow solid; M.p. 140–142 ^{o}C; TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.87 – 7.80 (m, 2H), 7.59 – 7.54 (m, 2H), 7.51 – 7.39 (m, 5H), 7.38 – 7.26 (m, 6H), 6.88 (d, J = 2.8 Hz, 1H)., **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.35, 139.40, 137.77, 131.84, 131.79, 131.72, 131.41, 129.68, 129.09, 128.53, 128.45, 128.18, 127.91, 127.19, 124.11, 122.01, 110.50; **ESI-HRMS**: Calculated for $C_{23}H_{18}NO^+$ $[M+H]^+$ 324.1383, found 324.1361.

Phenyl(5-phenyl-2-(p-tolyl)-1H-pyrrol-3-yl)methanone (3c):



Yield: 65% (33 mg); Physical appearance: Yellow solid; M.p. 115–117 ^{o}C; TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.80 (d, J = 7.7 Hz, 2H), 7.50 (d, J = 7.7 Hz, 2H), 7.44 – 7.29 (m, 7H), 7.27 – 7.23 (m, 1H), 7.09 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 2.8 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.25, 139.53, 138.22, 138.00, 136.60, 131.64, 131.47, 129.66, 129.17, 129.08, 128.91, 128.29, 127.92, 127.11, 124.04, 121.68, 110.51, 21.28; **ESI-HRMS**: Calculated for $C_{24}H_{20}NO^+$ $[M+H]^+$ 338.1539, found 338.1521.

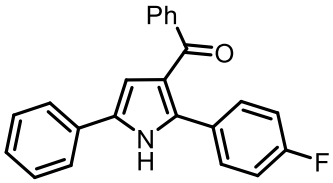
(2-([1,1'-biphenyl]-4-yl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3d):



Yield: 52% (31 mg); Physical appearance: Yellow solid; M.p. 192–194 ^{o}C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H**

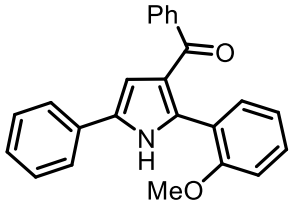
NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.65 – 7.54 (m, 8H), 7.52 – 7.36 (m, 8H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 2.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.44, 140.78, 140.41, 139.46, 137.50, 131.93, 131.78, 131.39, 130.62, 129.73, 129.07, 128.80, 128.76, 127.98, 127.49, 127.18, 127.05, 126.99, 124.15, 122.03, 110.72; **ESI-HRMS**: Calculated for $C_{29}H_{12}NO^+$ $[M+H]^+$ 400.1696, found 400.1697.

(2-(4-fluorophenyl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3e):



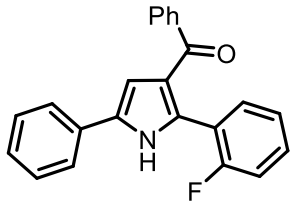
Yield: 48% (25 mg); Physical appearance: White solid; M.p. 156–158 °C; TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.47 – 7.30 (m, 7H), 7.27 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 2.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.32, 162.57 (d, *J* = 248.6 Hz), 139.36, 136.87, 131.88, 131.83, 131.30, 130.35 (d, *J* = 8.2 Hz), 129.63, 129.08, 127.99, 127.93 (d, *J* = 3.5 Hz), 127.25, 124.15, 121.91, 115.42 (d, *J* = 21.8 Hz), 110.48; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -112.91; **ESI-HRMS**: Calculated for $C_{23}H_{16}FNNaO^+$ $[M+Na]^+$ 364.1108, found 364.1114.

(2-(2-methoxyphenyl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3f):



Yield: 53% (28 mg); Physical appearance: Yellow solid; M.p. 120–122 °C; TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz $CDCl_3$): δ 9.38 (s, 1H), 7.88 – 7.81 (m, 2H), 7.58 – 7.53 (m, 2H), 7.46 – 7.41 (m, 4H), 7.36 – 7.28 (m, 3H), 7.26 – 7.21 (m, 1H), 6.92 – 6.84 (m, 3H), 3.83 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.76, 155.93, 139.40, 133.47, 131.73, 131.60, 131.28, 129.60, 129.39, 129.34, 129.03, 127.74, 126.93, 124.00, 123.05, 120.80, 120.17, 111.07, 109.77, 55.60; **ESI-HRMS**: Calculated for $C_{24}H_{19}NNaO_2^+$ $[M+Na]^+$ 376.1308, found 376.1314.

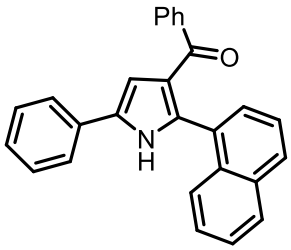
(2-(2-fluorophenyl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3g):



Yield: 46% (24 mg); Physical appearance: Yellow solid; M.p. 142–144 °C TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.08 (s, 1H), 7.89 – 7.83 (m, 2H), 7.60 – 7.54 (m, 2H), 7.52 – 7.35 (m, 6H), 7.34 – 7.22 (m, 2H), 7.13 – 7.02 (m, 2H), 6.89 (d, *J* = 2.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.35, 159.32 (d, *J* = 247.3 Hz), 139.20, 132.30, 131.86, 131.36, 131.32 (d, *J* = 3.2 Hz), 130.61, 129.85 (d, *J* = 8.3 Hz),

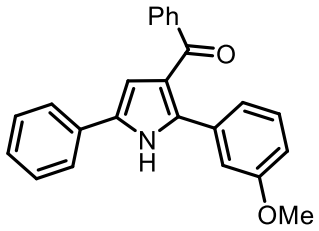
129.64, 129.09, 127.95, 127.31, 124.20, 124.15 (d, J = 3.5 Hz), 123.56, 119.47 (d, J = 12.8 Hz), 115.82 (d, J = 22.4 Hz), 110.04; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -115.31; **ESI-HRMS**: Calculated for $C_{23}H_{17}FNO^+$ $[M+H]^+$ 342.1289, found 342.1271.

(2-(naphthalen-1-yl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3h):



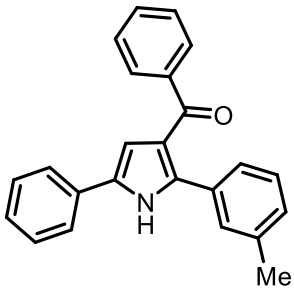
Yield: 56% (31 mg); Physical appearance: Yellow solid; M.p. 146–148 ^{o}C TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 7.96 – 7.89 (m, 1H), 7.88 – 7.75 (m, 2H), 7.70 – 7.62 (m, 2H), 7.61 – 7.55 (m, 2H), 7.54 – 7.36 (m, 6H), 7.35 – 7.27 (m, 2H), 7.17 – 7.05 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.10, 139.40, 136.28, 133.47, 132.13, 132.11, 131.45, 131.21, 129.95, 129.11, 129.02, 128.99, 128.64, 128.33, 127.43, 127.17, 126.72, 125.98, 125.28, 124.96, 124.19, 124.09, 109.22; **ESI-HRMS**: Calculated for $C_{27}H_{19}NNaO^+$ $[M+Na]^+$ 396.1359, found 396.1334.

(2-(3-methoxyphenyl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3i):



Yield: 57% (30 mg); Physical appearance: Red solid; M.p. 110–112 ^{o}C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 7.85 – 7.81 (m, 2H), 7.59 – 7.54 (m, 2H), 7.49 – 7.40 (m, 3H), 7.38 – 7.29 (m, 3H), 7.22 (t, J = 7.9 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 7.02 (s, 1H), 6.89 (d, J = 2.9 Hz, 1H), 6.82 (dd, J = 8.2, 1.7 Hz, 1H), 3.74 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.43, 159.44, 139.41, 137.44, 133.04, 131.89, 131.76, 131.38, 129.67, 129.49, 129.08, 127.91, 127.20, 124.13, 122.16, 120.59, 114.22, 114.00, 110.49, 55.29; **ESI-HRMS**: Calculated for $C_{24}H_{20}NO_2^+$ $[M+H]^+$ 354.1489, found 354.1463.

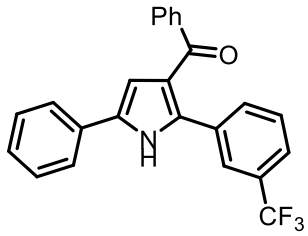
Phenyl(5-phenyl-2-(m-tolyl)-1H-pyrrol-3-yl)methanone (3j):



Yield: 55% (28 mg); Physical appearance: Yellow gell; TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.83 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.39 – 7.29 (m, 5H), 7.22 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 6.90 (d, J = 2.9 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.39, 139.52, 138.10, 138.00, 131.70, 131.66, 131.63, 131.45, 129.60, 129.21, 129.08, 128.97, 128.36, 127.86, 127.15, 125.47,

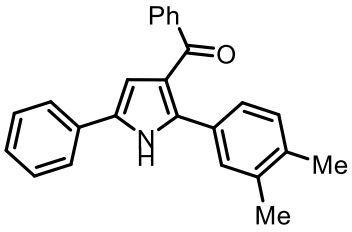
124.07, 121.99, 110.44, 21.31; **ESI-HRMS**: Calculated for $C_{24}H_{20}NO^+$ $[M+H]^+$ 338.1539, found 338.1542.

Phenyl(5-phenyl-2-(3-(trifluoromethyl)phenyl)-1H-pyrrol-3-yl)methanone (3k):



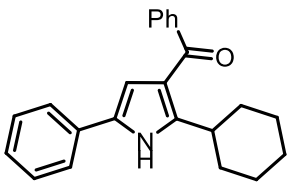
Yield: 49% (29 mg); Physical appearance: Yellow solid; M.p. 175–177 °C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 7.86 – 7.79 (m, 2H), 7.76 – 7.70 (m, 2H), 7.62 – 7.56 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.30 (m, 7H), 6.90 (d, J = 2.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.22, 139.17, 135.83, 132.61, 132.51, 131.99, 131.95, 131.09, 130.97, 130.71, 129.60, 129.13, 128.88, 128.03, 127.50, 125.00 (q, J = 3.5 Hz), 124.71 (q, J = 3.4 Hz), 124.29, 122.71, 110.72; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.67; **ESI-HRMS**: Calculated for $C_{24}H_{16}F_3NNaO^+$ $[M+Na]^+$ 414.1076, found 414.1090.

(2-(3,4-dimethylphenyl)-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3l):



Yield: 58% (31 mg); Physical appearance: Yellow solid; M.p. 183–185 °C TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 7.84 (d, J = 7.9 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.51 – 7.34 (m, 5H), 7.33 – 7.21 (m, 3H), 7.11 – 7.03 (m, 1H), 6.89 – 6.83 (m, 1H), 2.24 (s, 3H) 2.21 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.36, 139.68, 138.34, 136.83, 136.61, 131.53, 131.40, 129.68, 129.61, 129.24, 129.03, 127.87, 127.00, 125.81, 124.03, 121.57, 110.44, 19.67, 19.56; **ESI-HRMS**: Calculated for $C_{25}H_{22}NO^+$ $[M+H]^+$ 352.0696, found 352.1697.

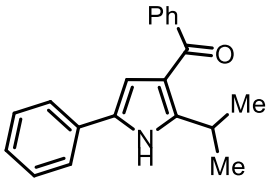
(2-cyclohexyl-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3m):



Yield: 50% (25 mg); Physical appearance: Pale Yellow solid; M.p. 174–176 °C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.87 (d, J = 7.2 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.45 (m, 4H), 7.43 –7.37 (m, 2H), 7.28 –7.23 (m, 1H), 6.66 (d, J = 2.7 Hz, 1H), 3.61 – 3.48 (m, 1H), 2.21 – 2.10 (m, 2H), 1.93 – 1.77 (m, 3H), 1.55 – 1.38 (m, 4H), 1.37 – 1.26 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.32, 146.71, 140.73, 131.81, 131.20, 129.30, 129.10, 129.00, 128.04, 126.73, 123.82, 119.87,

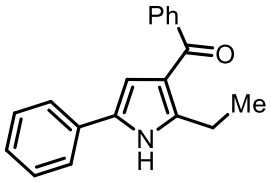
109.54, 36.18, 32.71, 26.49, 26.15; **ESI-HRMS**: Calculated for $C_{23}H_{23}NNaO^+$ $[M+Na]^+$ 352.1672, found 352.1670.

(2-isopropyl-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3n):



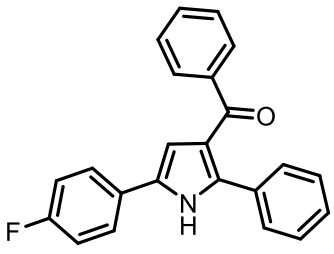
Yield: 52% (22 mg); Physical appearance: Light yellow solid; M.p. 152–154 °C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 7.89 – 7.84 (m, 2H), 7.58 – 7.53 (m, 1H)), 7.52 – 7.46 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.23 (m, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 3.91 (sept, *J* = 7.0 Hz, 1H), 1.41 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.26, 147.21, 140.73, 131.79, 131.20, 129.31, 129.09, 129.01, 128.05, 126.77, 123.85, 119.82, 109.67, 26.38, 22.05; **ESI-HRMS**: Calculated for $C_{20}H_{20}NO^+$ $[M+H]^+$ 290.1539, found 290.1552.

(2-ethyl-5-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3o):



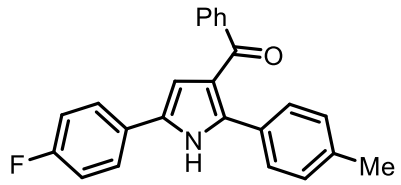
Yield: 49% (20 mg); Physical appearance: Brown solid; M.p. 137–139 °C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 7.91 – 7.83 (m, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.46 (m, 4H), 7.43 –7.37 (m, 2H), 7.28 – 7.23 (m, 1H), 6.69 (d, *J* = 2.8 Hz, 1H), 3.12 (q, *J* = 7.6 Hz, 2H), 1.38 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.25, 143.30, 140.58, 131.74, 131.22, 129.57, 129.06, 129.00, 128.08, 126.74, 123.81, 120.44, 109.46, 21.13, 13.45; **ESI-HRMS**: Calculated for $C_{19}H_{18}NO^+$ $[M+H]^+$ 276.1383, found 276.1403.

(5-(4-fluorophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3p):



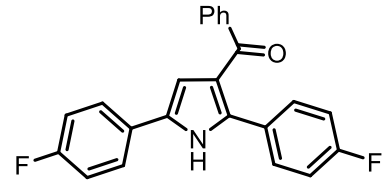
Yield: 58% (30 mg); Physical appearance: Pale yellow solid; M.p. 167–169 °C; TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.84 – 7.79 (m,2H), 7.56 – 7.43 (m, 5H)), 7.38 – 7.25 (m, 5H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 2.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.40, 162.02 (d, *J* = 246.9 Hz), 139.30, 137.84, 131.77, 131.67, 131.08, 129.67, 128.44, 128.42, 128.19, 127.92, 127.81 (d, *J* = 3.2 Hz), 125.91 (d, *J* = 8.0 Hz), 121.99, 116.08 (d, *J* = 21.8 Hz), 110.32; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -114.59; **ESI-HRMS**: Calculated for $C_{23}H_{17}FNO^+$ $[M+H]^+$ 342.1289, found 342.1273.

(5-(4-fluorophenyl)-2-(p-tolyl)-1H-pyrrol-3-yl)(phenyl)methanone (3q):



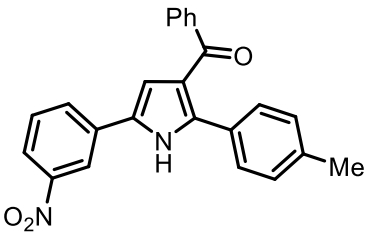
Yield: 60% (32 mg); Physical appearance: Orange solid; M.p. 140–142 ^{o}C; TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 7.86 – 7.80 (m, 2H), 7.54 – 7.44 (m, 3H), 7.40 – 7.33 (m, 4H), 7.14 – 7.07 (m, 4H), 6.77 (d, *J* = 2.9 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.36, 161.94 (d, *J* = 246.9 Hz), 139.44, 138.16, 131.69, 130.74, 129.66, 129.10, 128.77, 128.29, 127.92, 127.90, 127.89 (d, *J* = 3.3 Hz), 125.84 (d, *J* = 7.9 Hz), 121.61, 116.02 (d, *J* = 21.8 Hz), 110.31, 21.26; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -114.78; **ESI-HRMS**: Calculated for $C_{24}H_{19}FNO^{+}$ $[M+H]^{+}$ 356.1445, found 356.1446.

(2,5-bis(4-fluorophenyl)-1H-pyrrol-3-yl)(phenyl)methanone (3r):



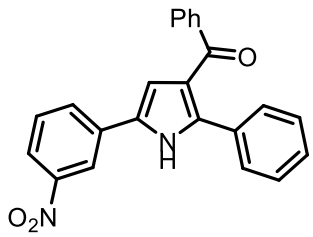
Yield: 50% (27 mg); Physical appearance: Yellow solid; M.p. 150–152 ^{o}C; TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.42 (m, 5H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 2.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.32, 163.27 (d, *J* = 51.6 Hz), 161.07 (d, *J* = 51.6 Hz), 139.28, 136.91, 131.89, 131.10, 130.33 (d, *J* = 8.2 Hz), 129.60, 128.01, 127.82 (d, *J* = 3.4 Hz), 127.69 (d, *J* = 3.2 Hz), 125.96 (d, *J* = 8.0 Hz), 121.90, 116.07 (d, *J* = 21.8 Hz), 115.41 (d, *J* = 21.9 Hz), 110.30; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -112.84, -114.46; **ESI-HRMS**: Calculated for $C_{23}H_{15}F_2NNaO^{+}$ $[M+Na]^{+}$ 382.1014, found 382.1019.

(5-(3-nitrophenyl)-2-(p-tolyl)-1H-pyrrol-3-yl)(phenyl)methanone (3s):



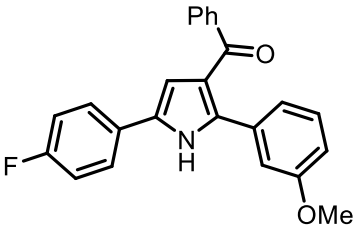
Yield: 56% (27 mg); Physical appearance: Yellow solid; M.p. 186–188 ^{o}C TLC R_f 0.3 (7:3, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.37 (s, 1H), 8.10 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.90 – 7.80 (m, 3H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 2.8 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.31, 148.82, 139.46, 139.12, 138.50, 133.20, 131.98, 129.97, 129.70, 129.68, 129.12, 129.10, 128.32, 128.25, 128.05, 121.89, 121.23, 118.36, 112.20, 21.26; **ESI-HRMS**: Calculated for $C_{24}H_{19}N2O3^{+}$ $[M+H]^{+}$ 383.1390, found 383.1403.

(5-(3-nitrophenyl)-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3t):



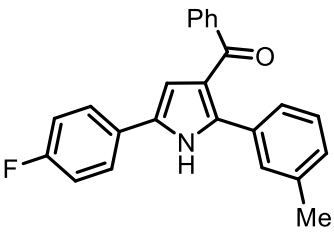
Yield: 40% (22 mg); Physical appearance: Yellow solid; M.p. 180–182 °C TLC R_f 0.3 (7:3, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.38 (s, 1H), 8.11 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 3H), 6.98 (d, *J* = 2.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.29, 148.85, 139.12, 138.99, 133.13, 132.05, 131.17, 130.04, 129.79, 129.67, 129.42, 128.50, 128.46, 128.05, 122.29, 121.39, 118.42, 112.19; **ESI-HRMS**: Calculated for $C_{23}H_{17}N2O3^+$ $[M+H]^+$ 369.1234, found 369.1236.

(5-(4-fluorophenyl)-2-(3-methoxyphenyl)-1H-pyrrol-3-yl)(phenyl)methanone (3u):



Yield: 56% (31 mg); Physical appearance: yellow solid; M.p. 145–147 °C; TLC R_f 0.2 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.00 (s, 1H), 6.80 (d, *J* = 2.6 Hz, 2H), 3.73 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.38, 162.04 (d, *J* = 247.1 Hz), 159.45, 139.32, 137.44, 132.94, 131.80, 131.09, 129.65, 129.50, 127.92, 127.76 (d, *J* = 3.3 Hz), 125.92 (d, *J* = 7.9 Hz), 122.18, 120.55, 116.09 (d, *J* = 21.9 Hz), 114.21, 114.01, 110.33, 55.28; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -114.52; **ESI-HRMS**: Calculated for $C_{24}H_{18}FNNaO_2^+$ $[M+Na]^+$ 394.1214, found 394.1221.

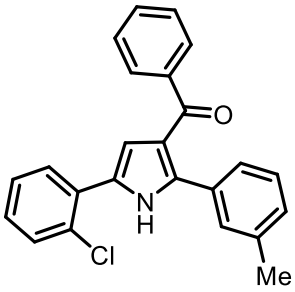
(5-(4-fluorophenyl)-2-(m-tolyl)-1H-pyrrol-3-yl)(phenyl)methanone (3v):



Yield: 52% (28 mg); Physical appearance: yellowish brown solid; M.p. 144–146 °C; TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.83 – 7.78 (m, 2H), 7.55 – 7.49 (m, 2H), 7.48 – 7.43 (m, 1H), 7.37 – 7.31 (m, 2H), 7.28 – 7.22 (m, 2H), 7.19 – 7.04 (m, 4H), 6.80 (d, *J* = 2.9 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.47, 161.98 (d, *J* = 246.9 Hz), 139.42, 138.13, 138.05, 131.68, 131.52, 130.95, 129.60, 129.21, 128.94, 128.31, 127.87, 127.85 (d, *J* = 3.6 Hz), 125.88 (d, *J* = 7.8 Hz), 125.48, 121.93, 116.04 (d, *J* = 21.9 Hz).,

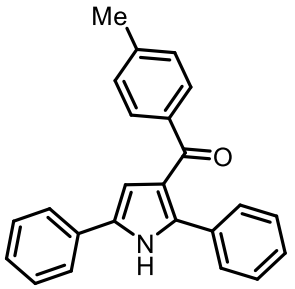
110.25, 21.28; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -114.70; **ESI-HRMS**: Calculated for $C_{24}H_{19}FNO^+$ $[M+H]^+$ 356.1445, found 356.1429.

(5-(2-chlorophenyl)-2-(m-tolyl)-1H-pyrrol-3-yl)(phenyl)methanone (3w):



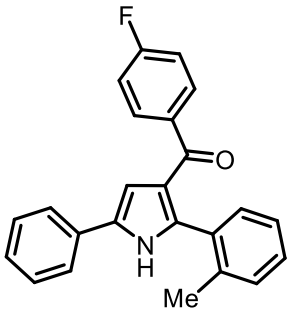
Yield: 46% (26 mg); Physical appearance: Pale yellow solid; M.p. 147–149 °C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 7.87 – 7.81 (m, 2H), 7.63 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.39 – 7.30 (m, 5H), 7.28 – 7.22 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 2.9 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.24, 139.51, 138.17, 137.77, 131.67, 131.57, 130.86, 130.13, 129.83, 129.63, 129.49, 129.21, 129.06, 128.85, 128.42, 128.28, 127.89, 127.43, 125.41, 121.14, 114.02, 21.34; **ESI-HRMS**: Calculated for $C_{24}H_{18}ClNNaO^+$ $[M+Na]^+$ 394.0969, found 394.0993.

(2,5-diphenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (3x):



Yield: 75% (38 mg); Physical appearance: Brown solid; M.p. 162–164 °C TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.50 (m, 4H), 7.46 – 7.40 (m, 2H), 7.37 – 7.29 (m, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 2.9 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.18, 142.40, 137.44, 136.70, 131.84, 131.72, 131.50, 129.93, 129.05, 128.64, 128.42, 128.35, 128.03, 127.08, 124.10, 122.11, 110.53, 21.58; **ESI-HRMS**: Calculated for $C_{24}H_{20}NO^+$ $[M+H]^+$ 338.1539, found 338.1533.

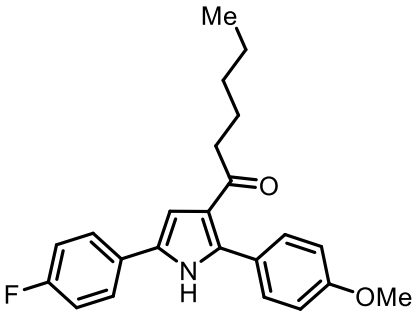
(4-fluorophenyl)(5-phenyl-2-(o-tolyl)-1H-pyrrol-3-yl)methanone (3y):



Yield: 55% (29 mg); Physical appearance: Yellow solid; M.p. 175–177 °C TLC R_f 0.3 (3:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 7.82– 7.74 (m, 2H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.23 (m, 3H), 7.21–7.15 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 2.8 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 190.44, 164.72 (d, *J* = 252.2 Hz), 137.47, 137.22, 135.56 (d, *J* = 3.1 Hz), 131.92, 131.73 (d, *J* = 9.0 Hz), 131.65, 131.39, 130.27, 129.12, 128.80, 127.19, 125.67, 124.00, 123.02, 114.77 (d, *J* = 21.6 Hz), 108.88,

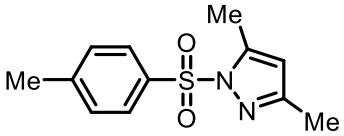
20.07; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -114.91 **ESI-HRMS**: Calculated for $C_{24}H_{18}FNNaO^+$ $[M+H]^+$ 378.1265, found 378.1291.

1-(5-(4-fluorophenyl)-2-(4-methoxyphenyl)-1H-pyrrol-3-yl)hexan-1-one (3z):



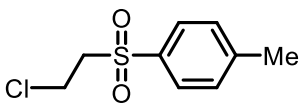
Yield: 46% (25 mg); Physical appearance: Pale yellow solid; M.p. 68–70 °C TLC R_f 0.3 (4:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.15 – 7.08 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 2.9 Hz, 1H), 3.87 (s, 3H), 2.71 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.35– 1.25 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.23, 161.94 (d, *J* = 247.0 Hz), 159.96, 137.01, 130.49, 130.43, 127.92 (d, *J* = 3.3 Hz), 125.75 (d, *J* = 8.1 Hz), 124.61, 122.47, 116.05 (d, *J* = 22.0 Hz), 113.82, 108.07, 55.37, 40.81, 31.60, 24.40, 22.55, 13.98;^{19}F NMR (376 MHz, $CDCl_3$) δ -114.81; **ESI-HRMS**: Calculated for $C_{23}H_{25}FNO_2^+$ $[M+H]^+$ 366.1864, found 366.1862.

3,5-dimethyl-1-tosyl-1H-pyrazole (3ad):



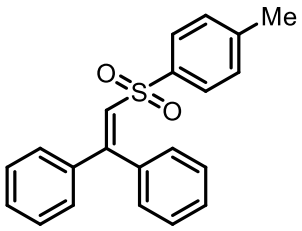
Yield: 28% (36 mg); Physical appearance: Pale yellow solid; M.p. 71–73 °C TLC R_f 0.3 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.91 (s, 1H), 2.51 (s, 3H), 2.43 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.37, 145.10, 144.07, 135.44, 129.87, 127.59, 110.70, 21.65, 13.84, 13.11; **ESI-HRMS**: Calculated for $C_{12}H_{14}N_2NaO_2S^+$ $[M+Na]^+$ 273.0668, found 273.0692.

1-((2-chloroethyl)sulfonyl)-4-methylbenzene (3ae):



Yield: 26% (28 mg); Physical appearance: Pale yellow gel; TLC R_f 0.5 (9:1, Petroleum ether: EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.27 (t, *J* = 6.0 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.49 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.23, 132.64, 129.96, 127.98, 68.91, 40.74, 21.66; **ESI-HRMS**: Calculated for $C_9H_{11}ClNaO_2S^+$ $[M+Na]^+$ 241.0060, found 241.0041.

(2-tosylethene-1,1-diyl)dibenzene (4a):[8]



Yield: 30% (18 mg); Physical appearance: White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 4H), 7.24 – 7.21 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.10 (m, 2H), 7.01 (s, 1H), 2.40 (s, 3H).

References:

(1) Armarego, W. L. F. *Purification of Laboratory Chemicals*; 8th Edition; Butterworth- Heinemann, **2017**.
(2) P. Kumar and M. Kapur, *Org. Lett*., **2019**, *21*, 2134.
(3) P. Kumar and M. Kapur, *Org. Lett*., **2020**, *22*, 5855.
(4) X. Lei, L. Li, Y.-P. He and Y. Tang, *Org. Lett.*, **2015**, *17*, 5224.
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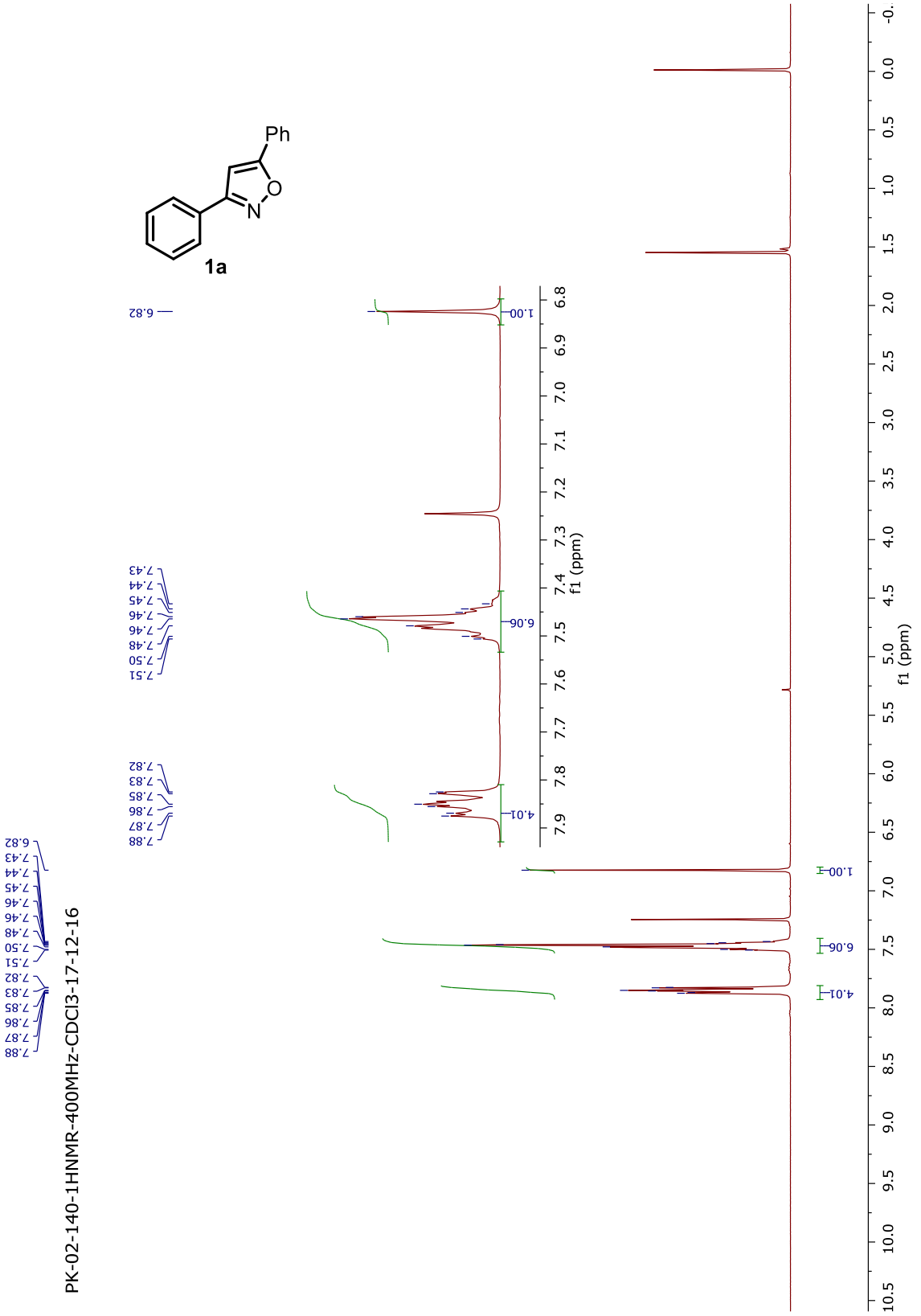
(6) P. Kumar and M. Kapur, *Asian J. Org., Chem.*, **2020**, *9*, 1065.
(7) G. C. Senadi, W.-P. Hu, A. M. Garkhedkar, S. S. K. Boominathana and J.-J. Wang, *Chem. Commun.*, **2015**, *51*, 13795.
(8) S. Mao, Y.-R. Gao, X.-Q. Zhu, D.-D. Guo and Y.-Q. Wang, *Org. Lett.*, **2015**, *17*, 1692.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O
N
1a
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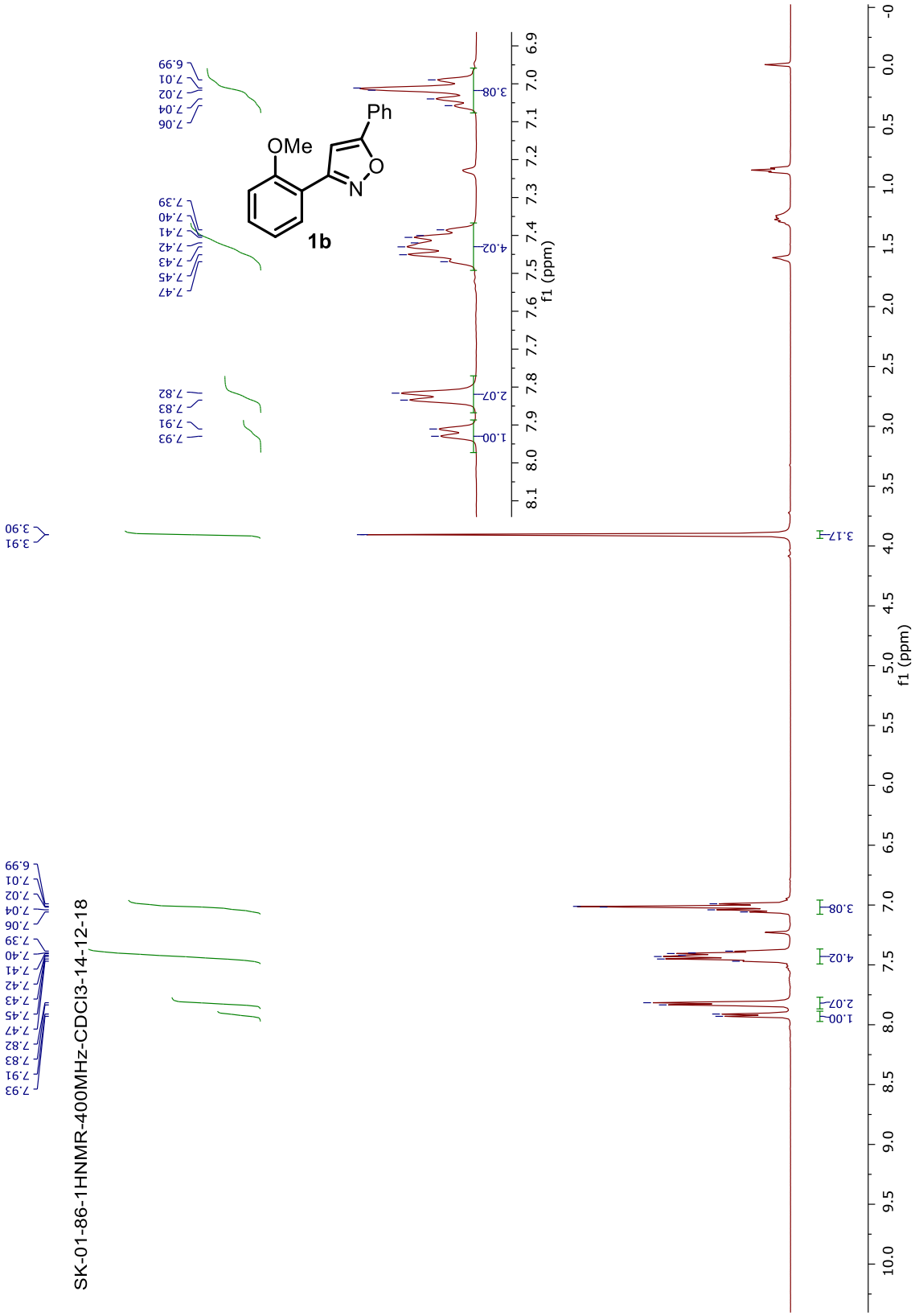
f1 (ppm)
1.00
6.06
4.01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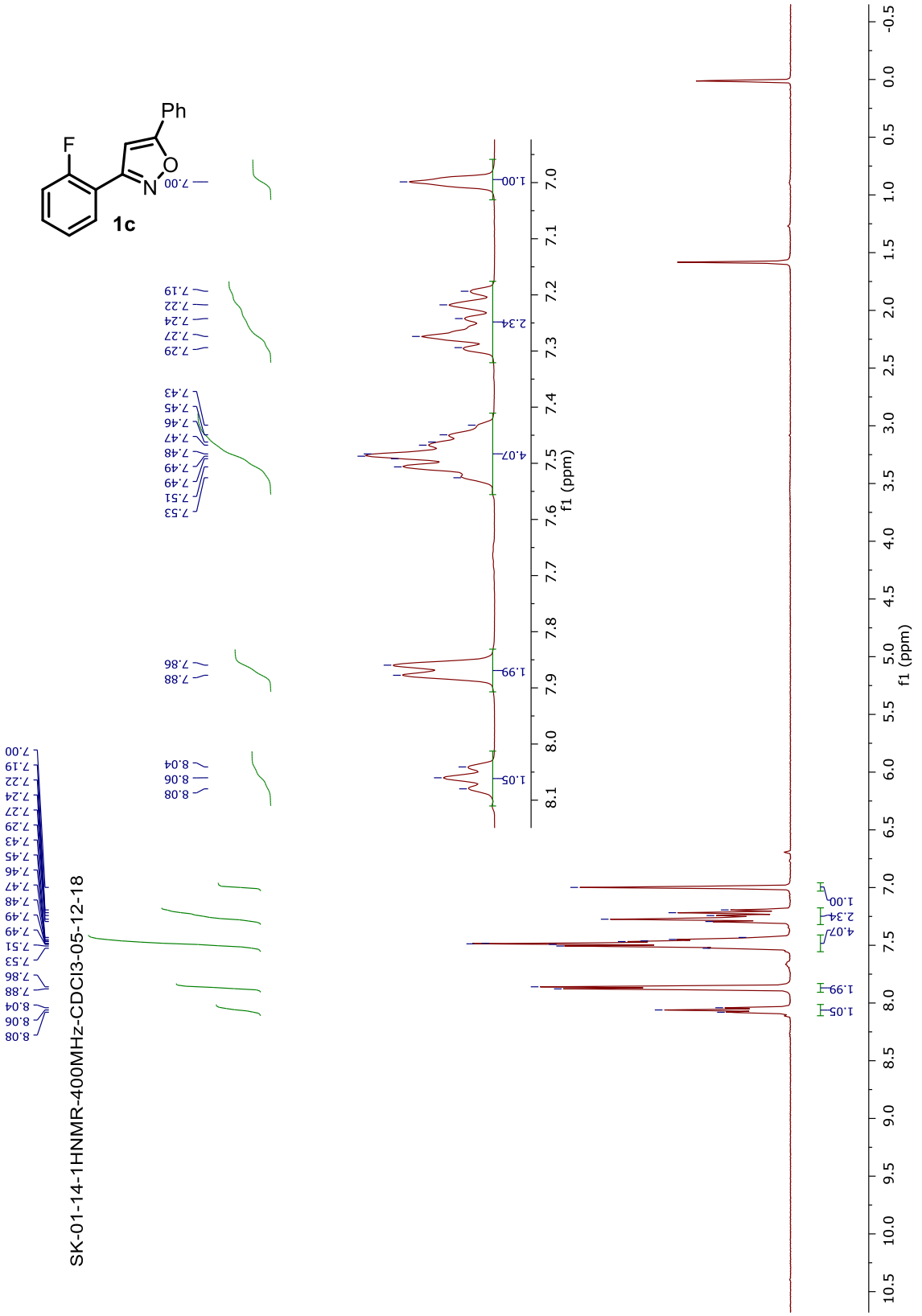
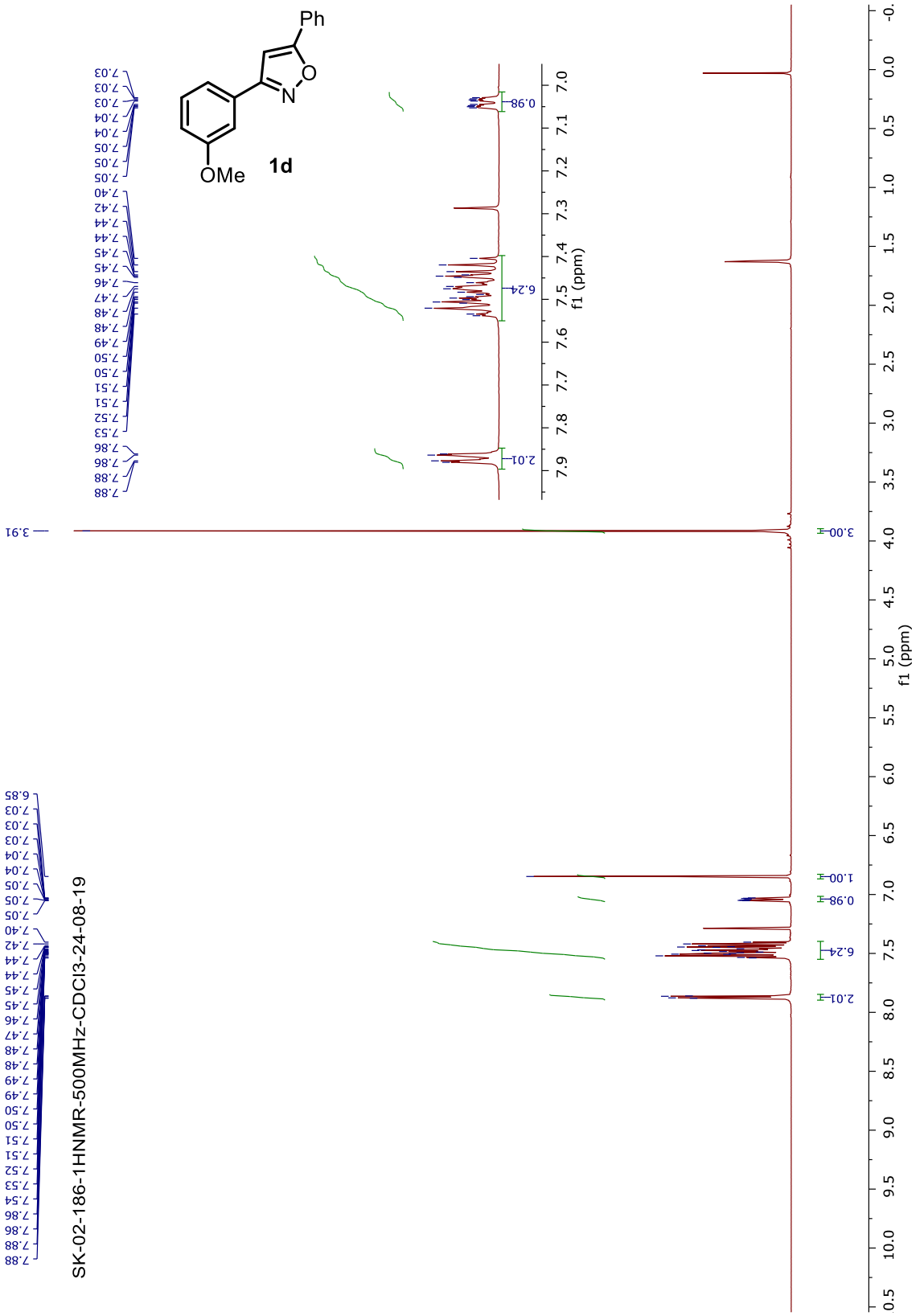
OMe
Ph
O
N
1b
f1 (ppm)


Ph
F
O
N
1c
SK-01-14-1HNMR-400MHz-CDCl3-05-12-18
f1 (ppm)
f1 (ppm)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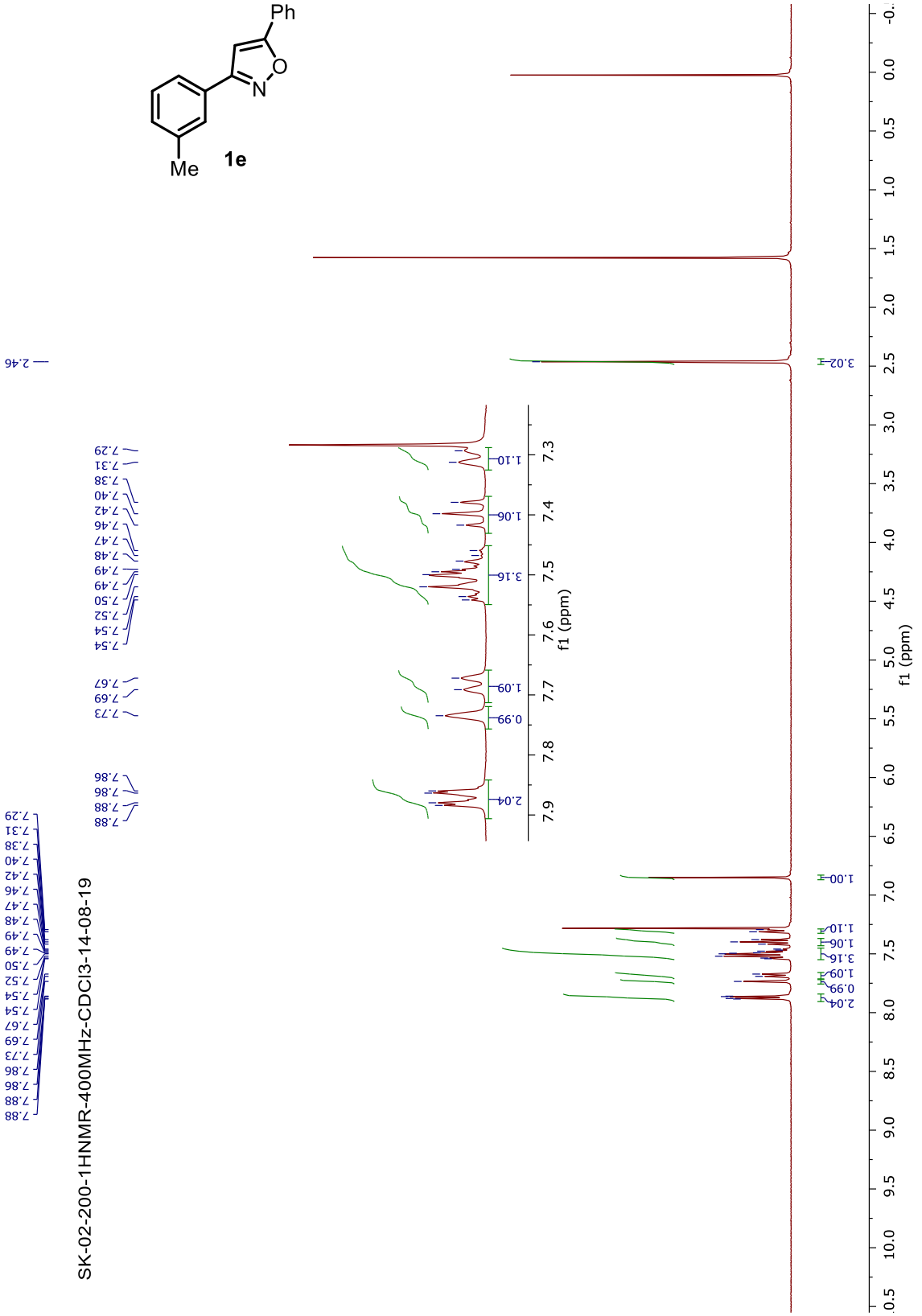
f1 (ppm)


Ph
O
N
Me
1e
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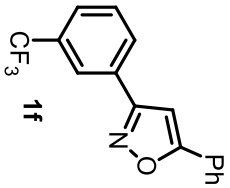
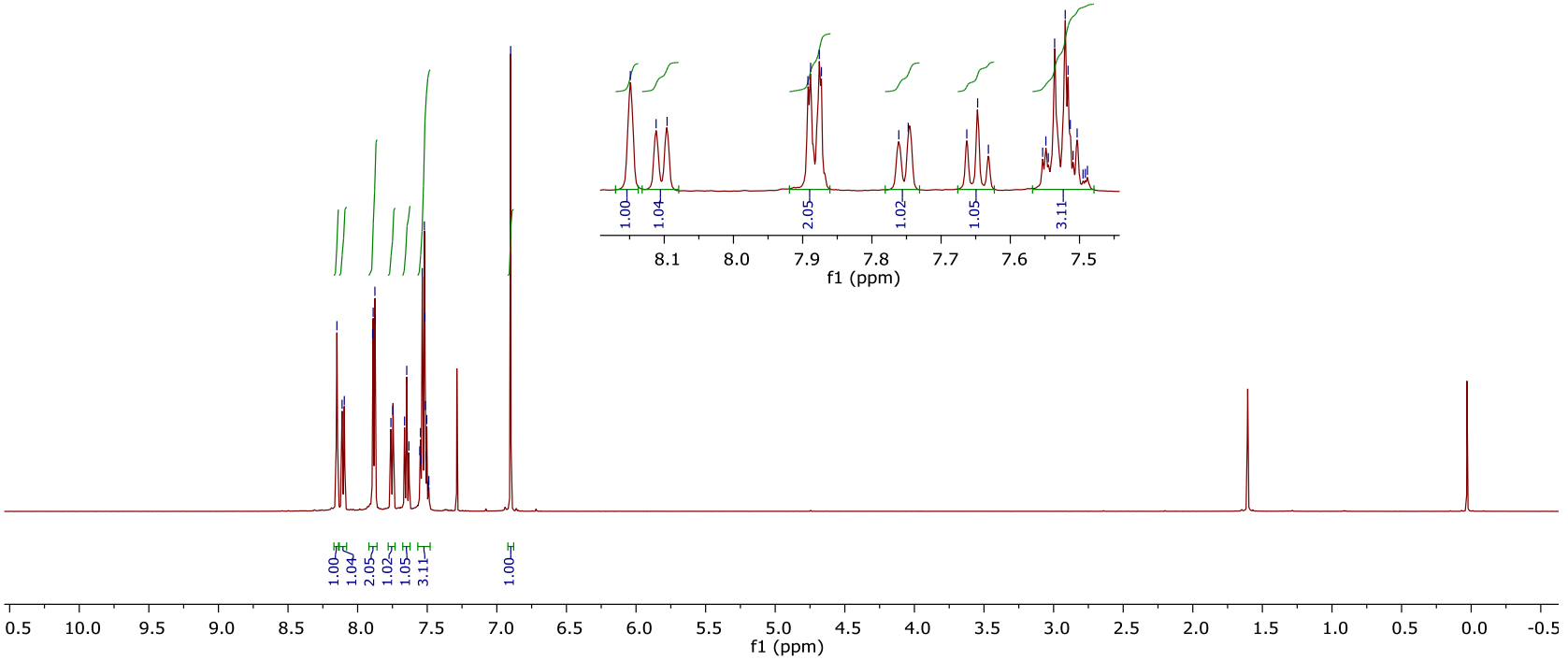
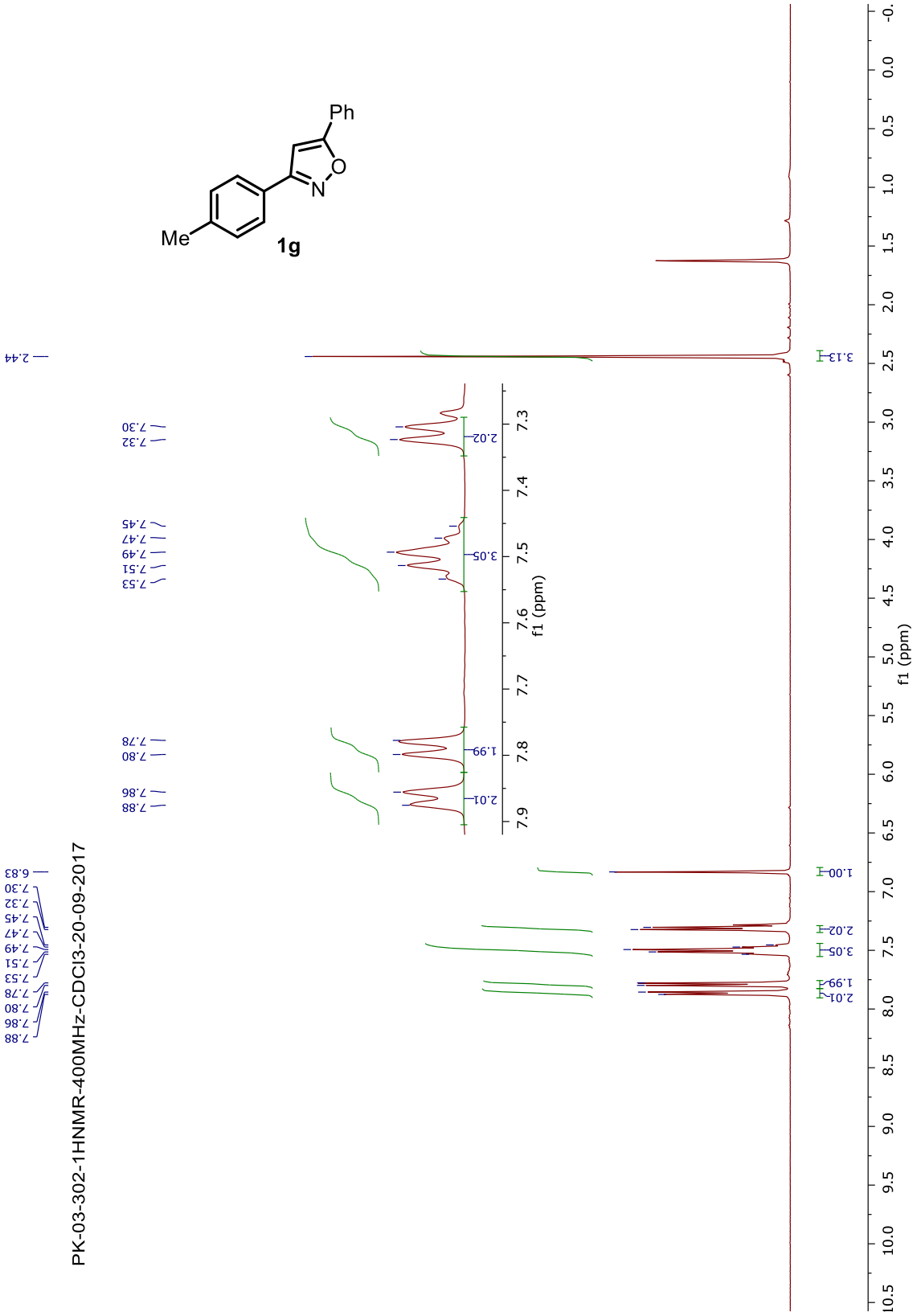
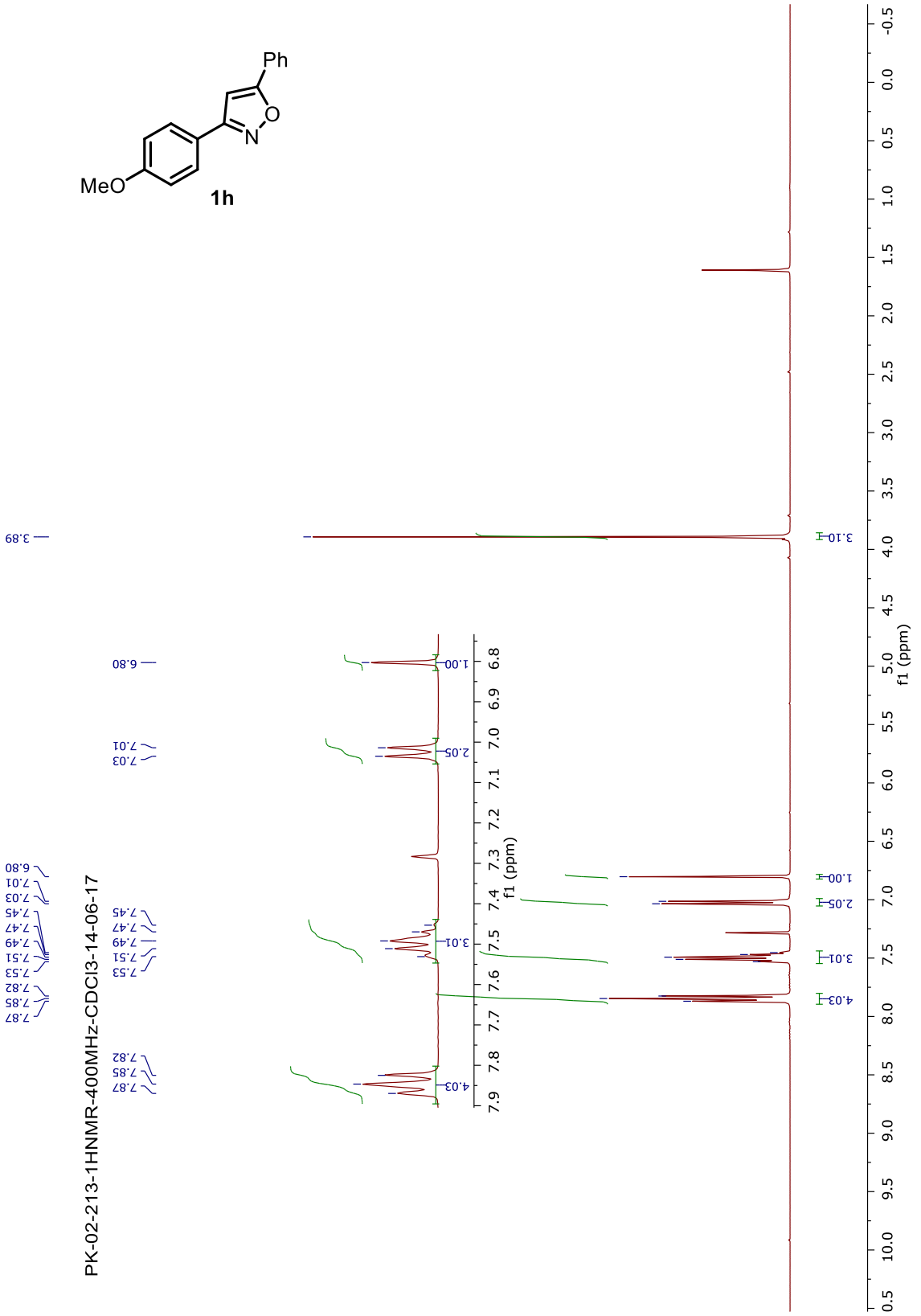
f1 (ppm)

SK-02-297-1HNMR-400MHz-CDCl3-08-06-19






Ph
O
N
Me
1g
PK-03-302-1HNMR-400MHz-CDCl3-20-09-2017
f1 (ppm)


Ph
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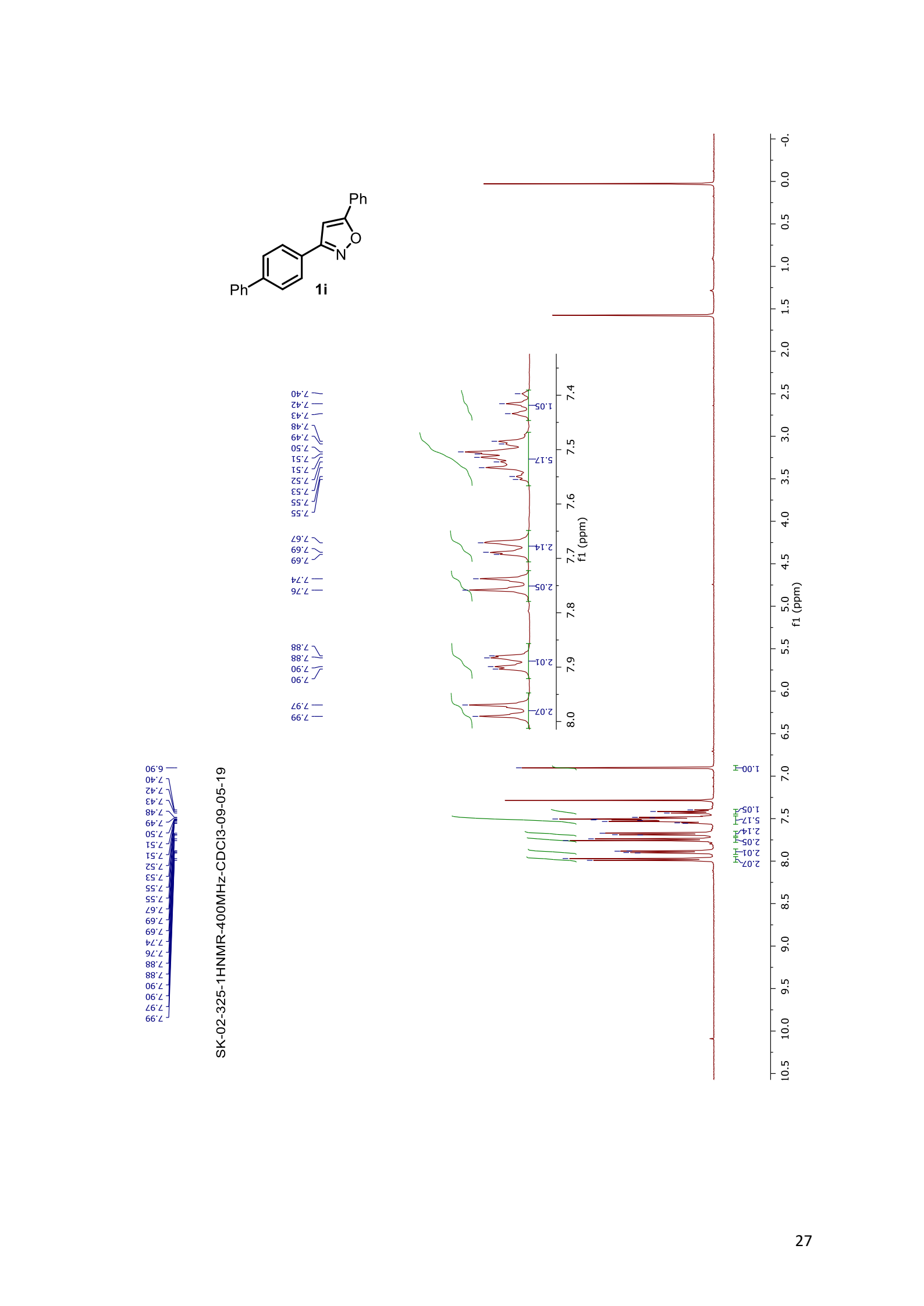
N
MeO
1h
PK-02-213-1HNMR-400MHz-CDCl3-14-06-17
f1 (ppm)


Ph
O
N
Ph
1i
SK-02-325-1HNMR-400MHz-CDCl3-09-05-19
f1 (ppm)
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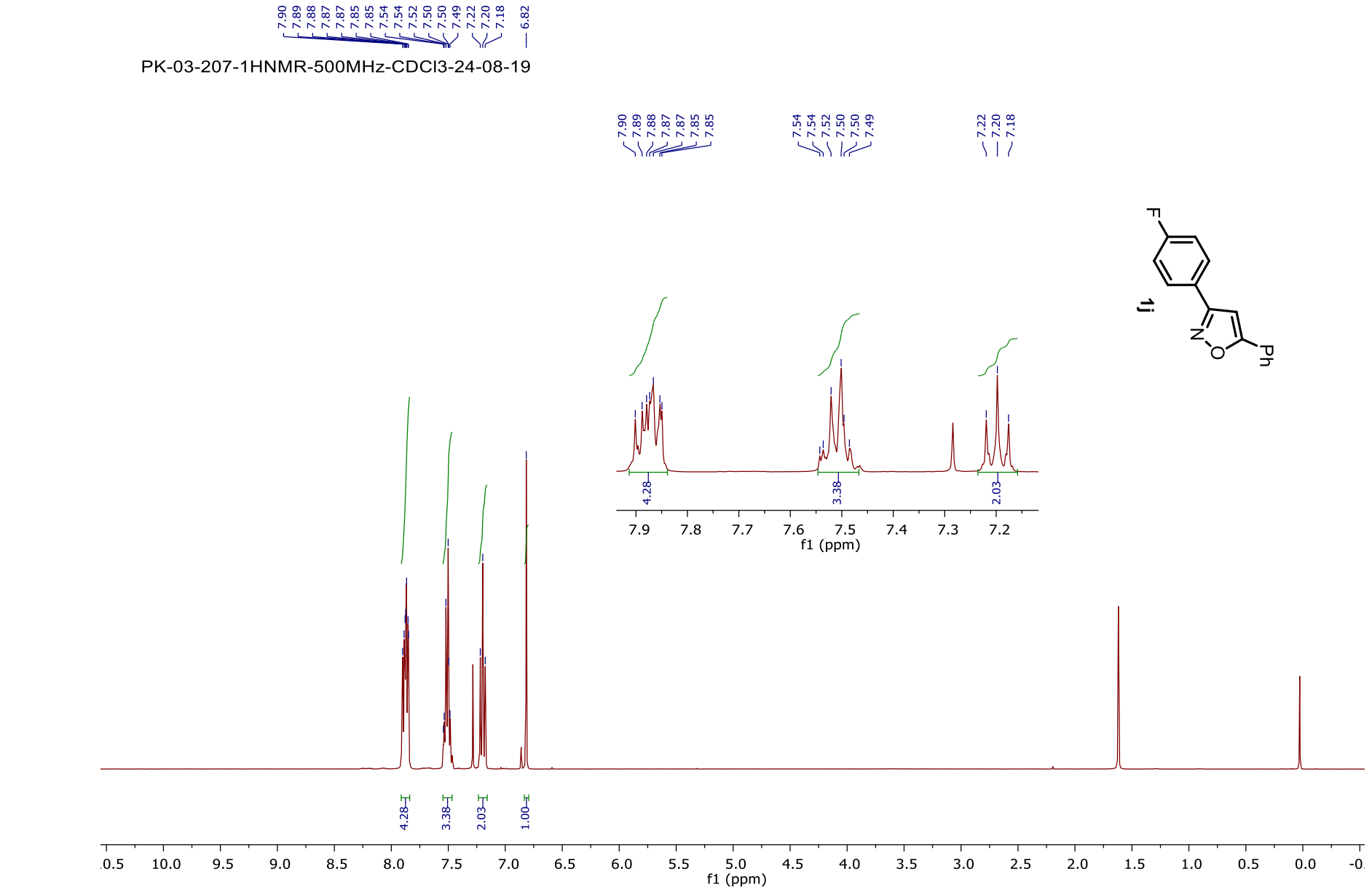
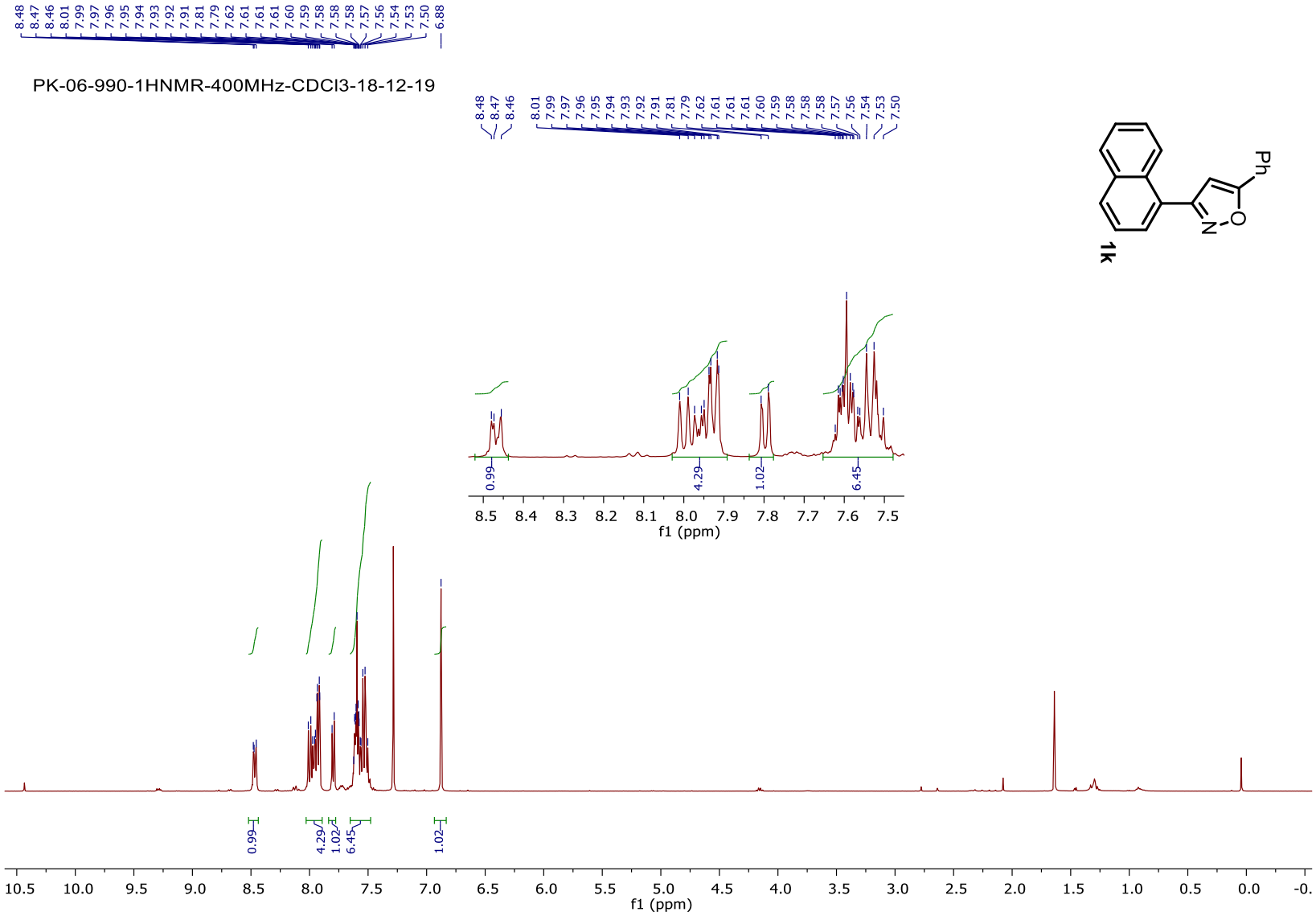
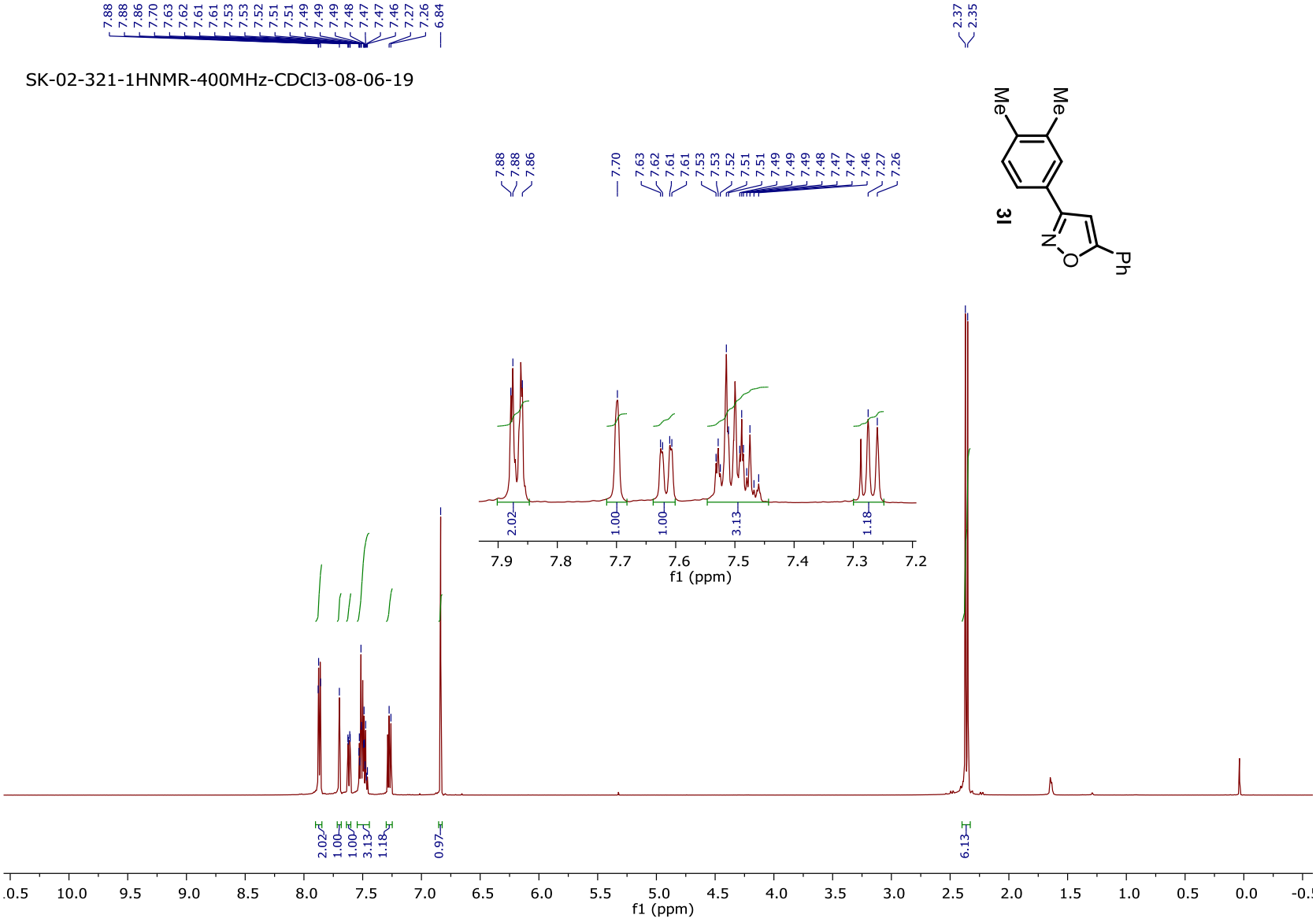
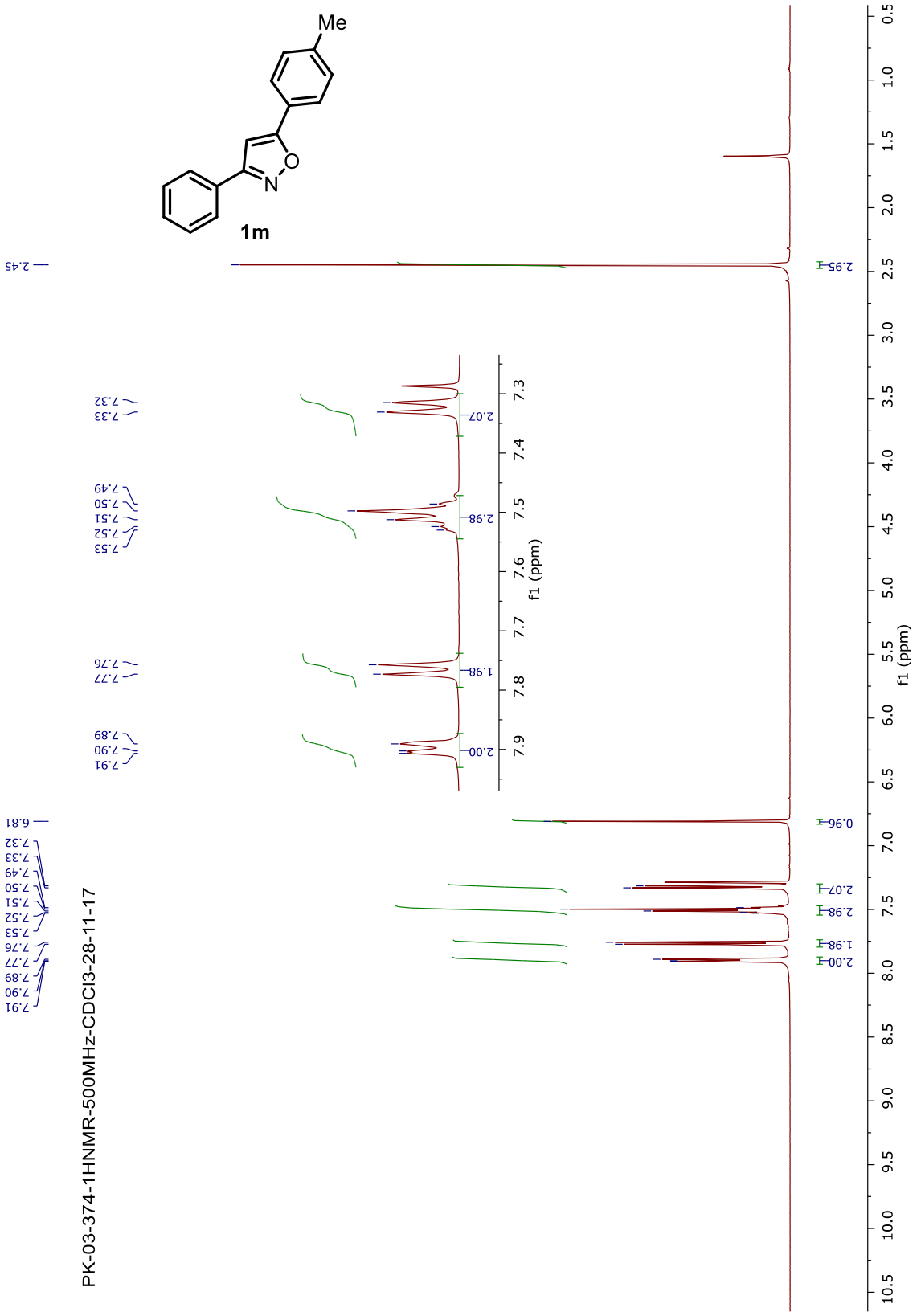
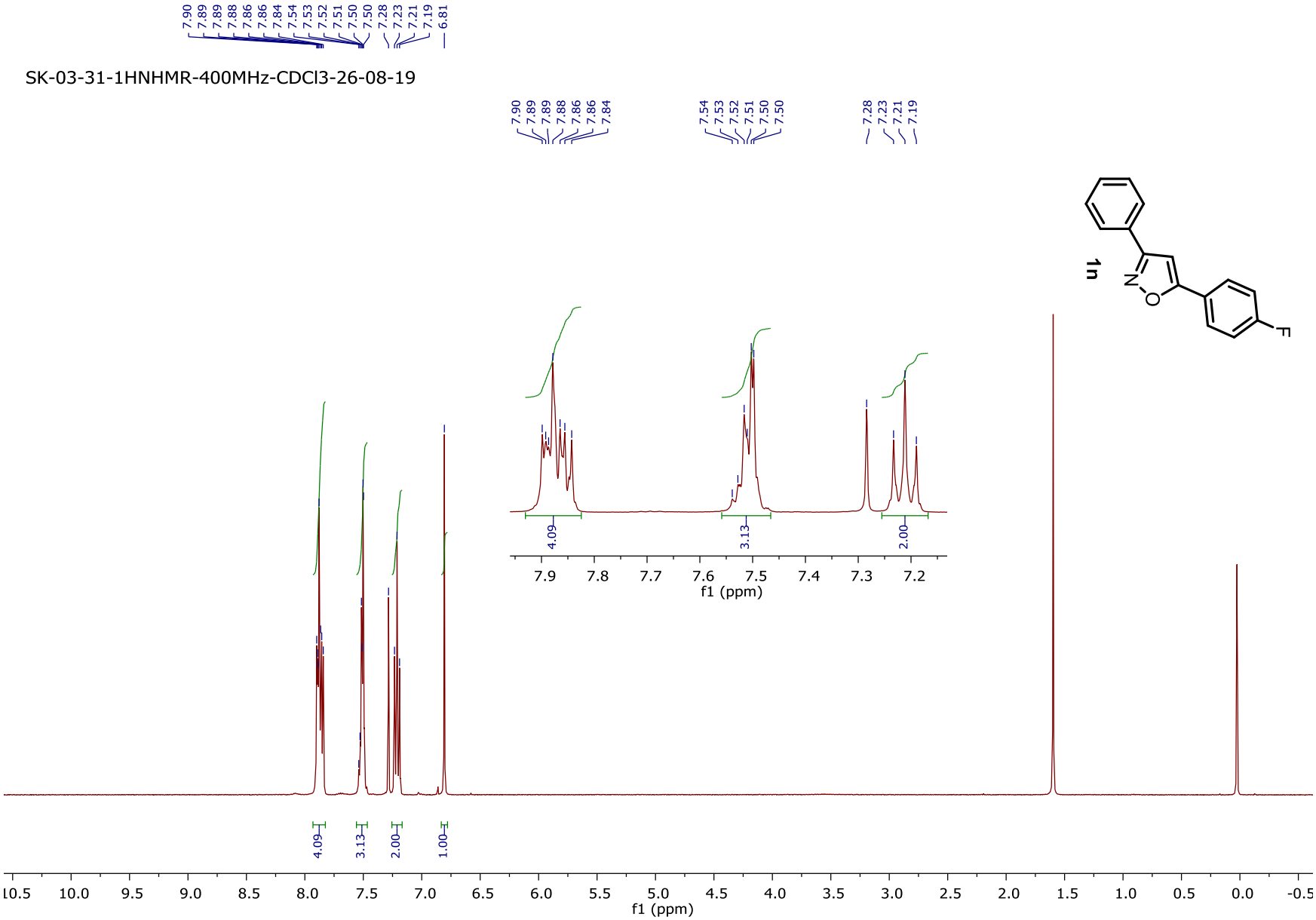
2.07
2.01
2.05
2.14
5.17
1.05

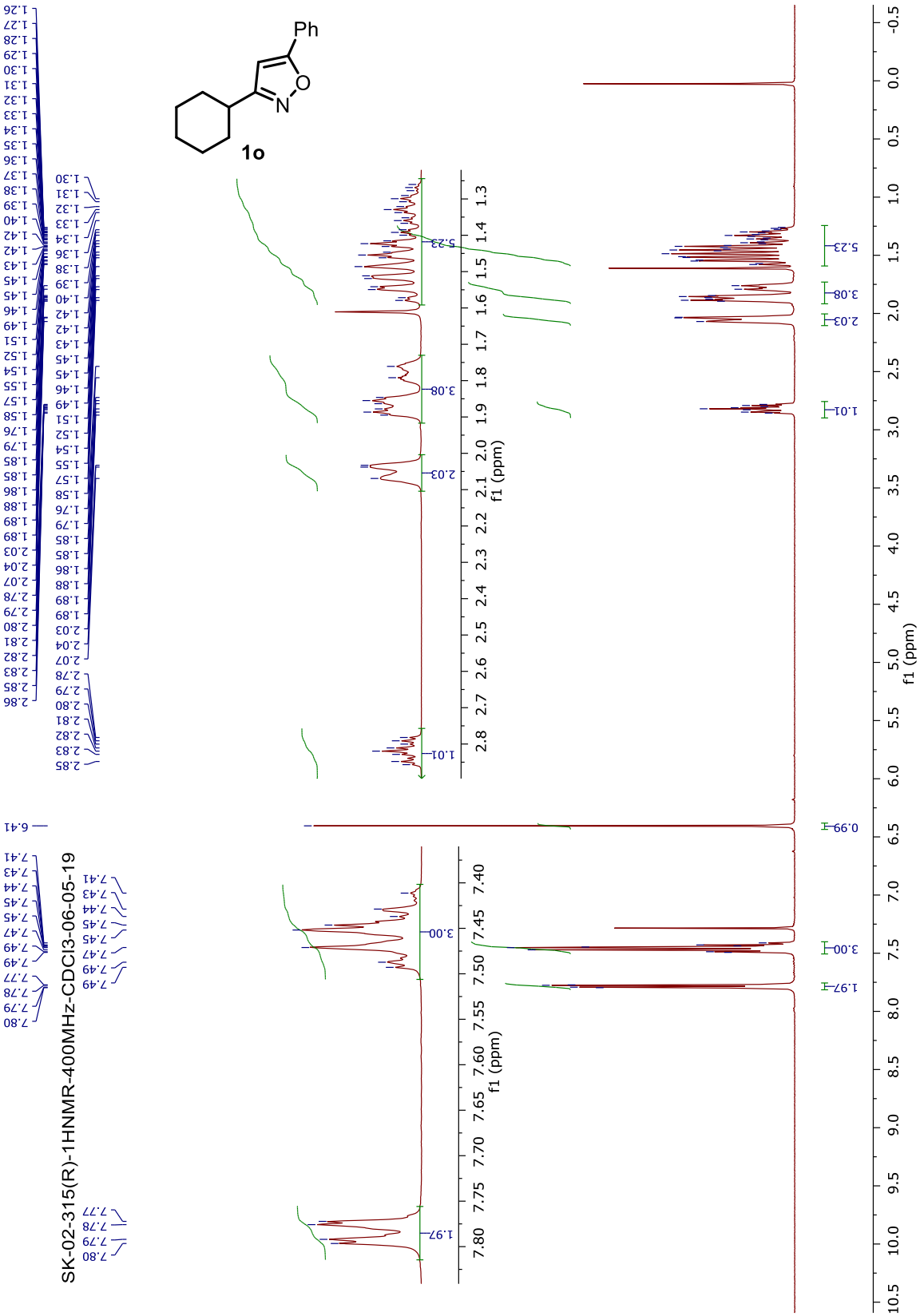

7.90
7.89
7.88
7.87
7.87
7.85
7.85
7.54
7.54
7.52
7.50
7.50
7.49
7.22
7.20
7.18
6.82
PK-03-207-1HNMR-500MHz-CDCl3-24-08-19
F
1j
N
O
Ph
4.28
3.38
2.03
1.00
f1 (ppm)

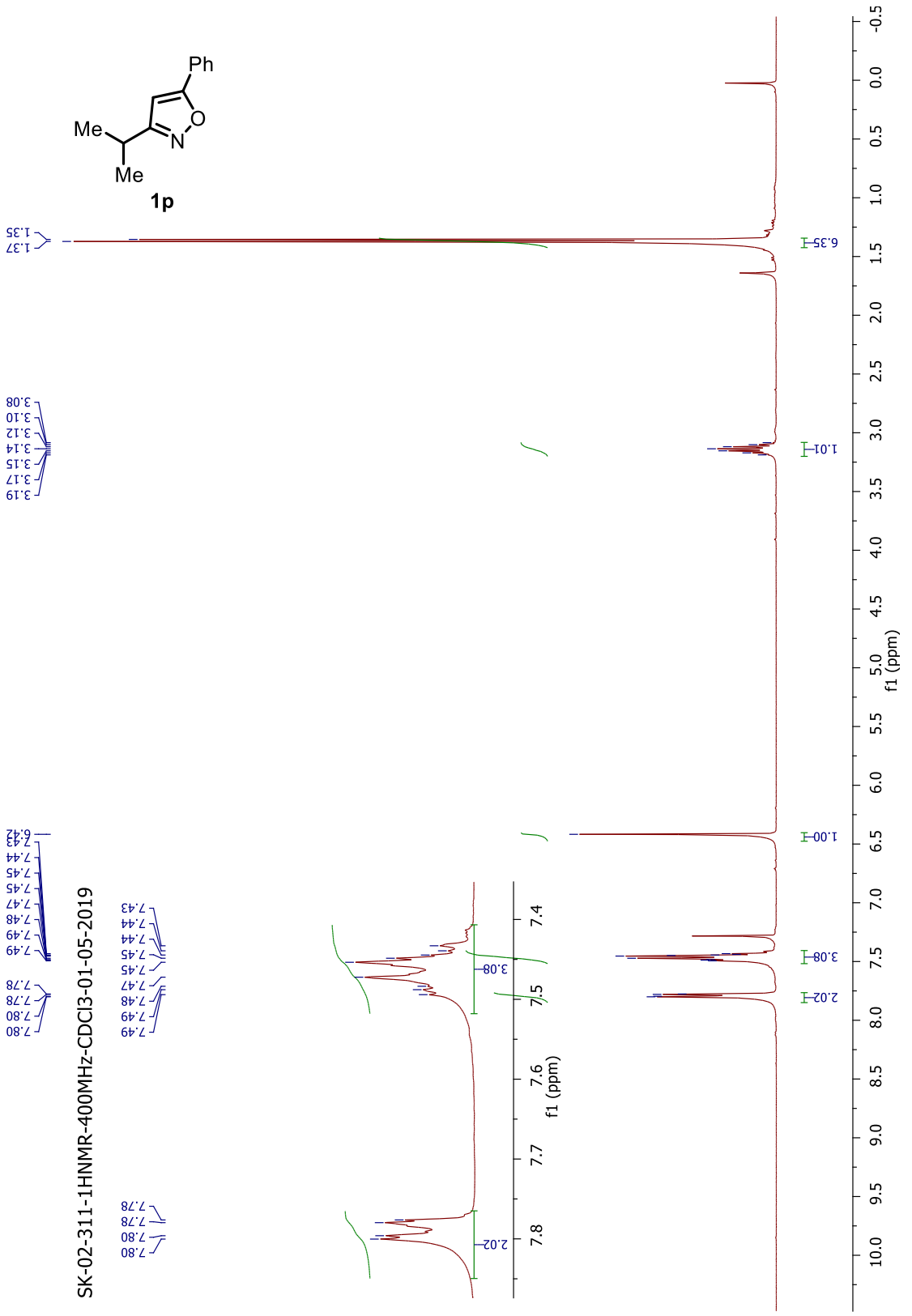

8.48 8.47 8.46 8.01 7.99 7.97 7.96 7.95 7.94 7.93 7.92 7.91 7.81 7.79 7.62 7.61 7.61 7.61 7.60 7.59 7.58 7.58 7.58 7.57 7.56 7.54 7.53 7.50 6.88
PK-06-990-1HNMR-400MHz-CDCl3-18-12-19
Ph
O
N
1k
0.99
4.29
1.02
6.45
1.02
f1 (ppm)

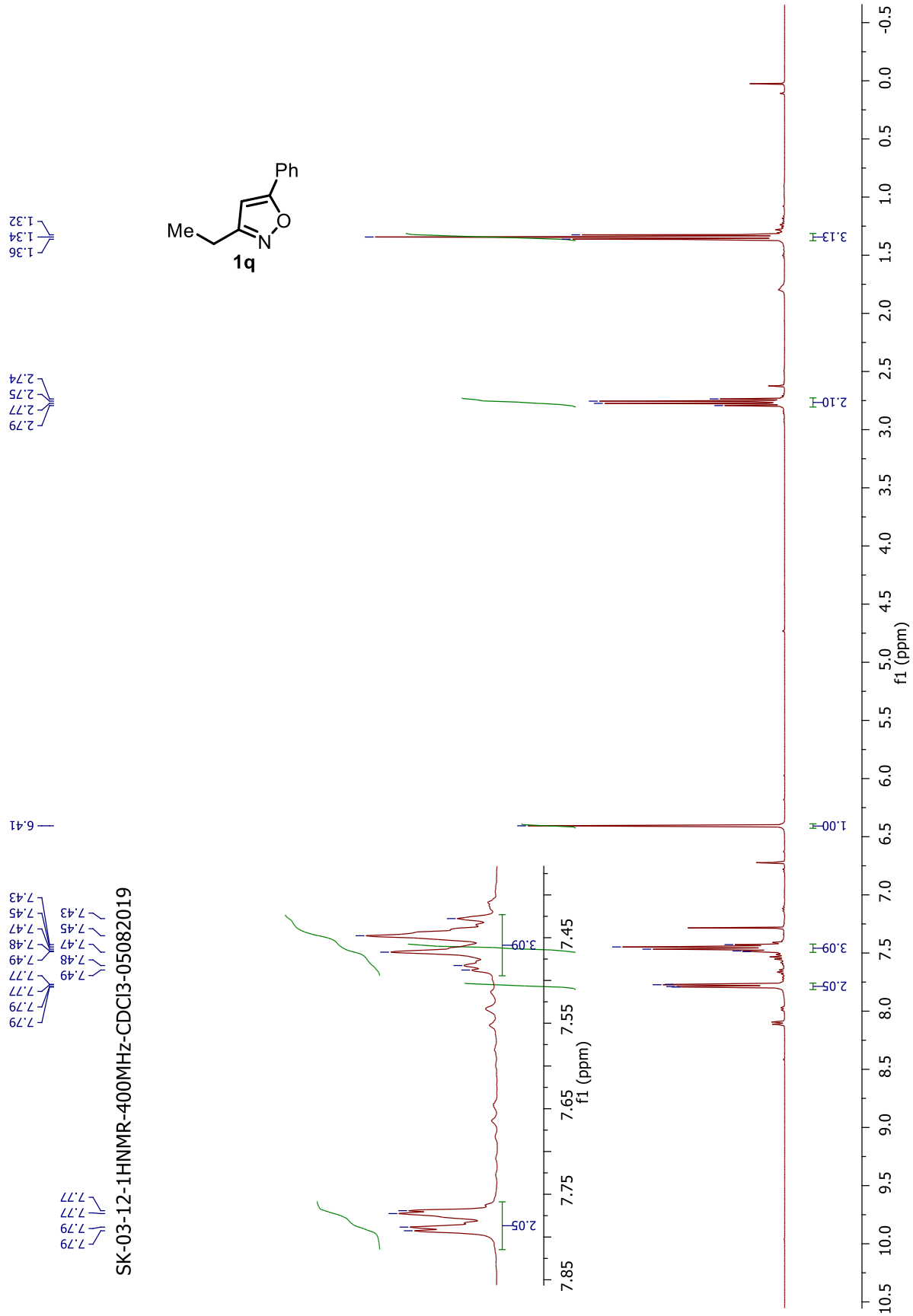

7.88
7.88
7.86
7.70
7.63
7.62
7.61
7.61
7.53
7.53
7.52
7.51
7.51
7.49
7.49
7.48
7.47
7.47
7.46
7.27
7.26
6.84
2.37
2.35
SK-02-321-1HNMR-400MHz-CDCl3-08-06-19
Me
Me
3l
N
O
Ph
2.02
1.00
1.00
3.13
1.18
0.97
6.13
f1 (ppm)


Me
O
N
1m
PK-03-374-1HNMR-500MHz-CDCl3-28-11-17
f1 (ppm)


7.90
7.89
7.89
7.88
7.86
7.86
7.84
7.54
7.53
7.52
7.51
7.50
7.50
7.28
7.23
7.21
7.19
6.81
SK-03-31-1HNHMR-400MHz-CDCl3-26-08-19
1n
F
4.09
3.13
2.00
1.00
f1 (ppm)


Ph
O
N
1o
SK-02-315(R)-1HNMR-400MHz-CDCl3-06-05-19
f1 (ppm)


Ph
Me
Me
O
N
1p
SK-02-311-1HNMR-400MHz-CDCl3-01-05-2019
f1 (ppm)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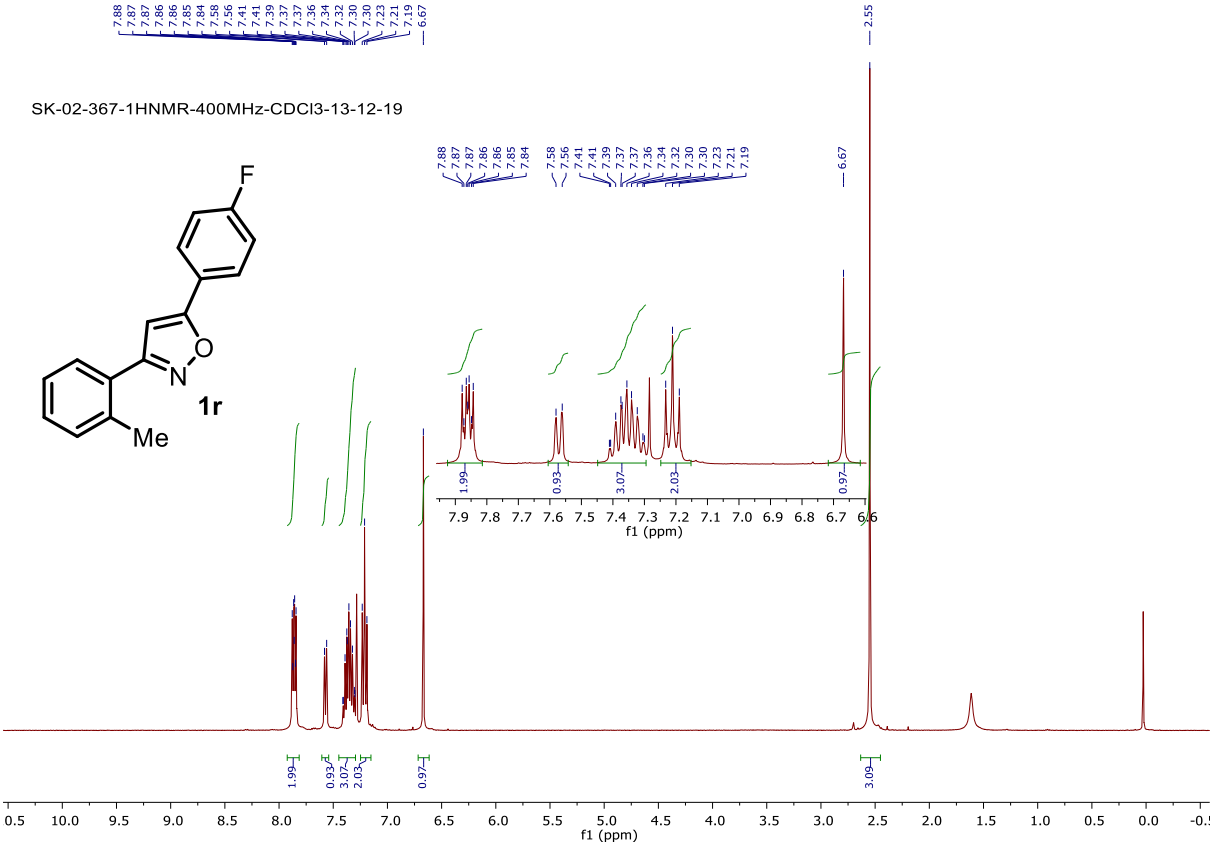
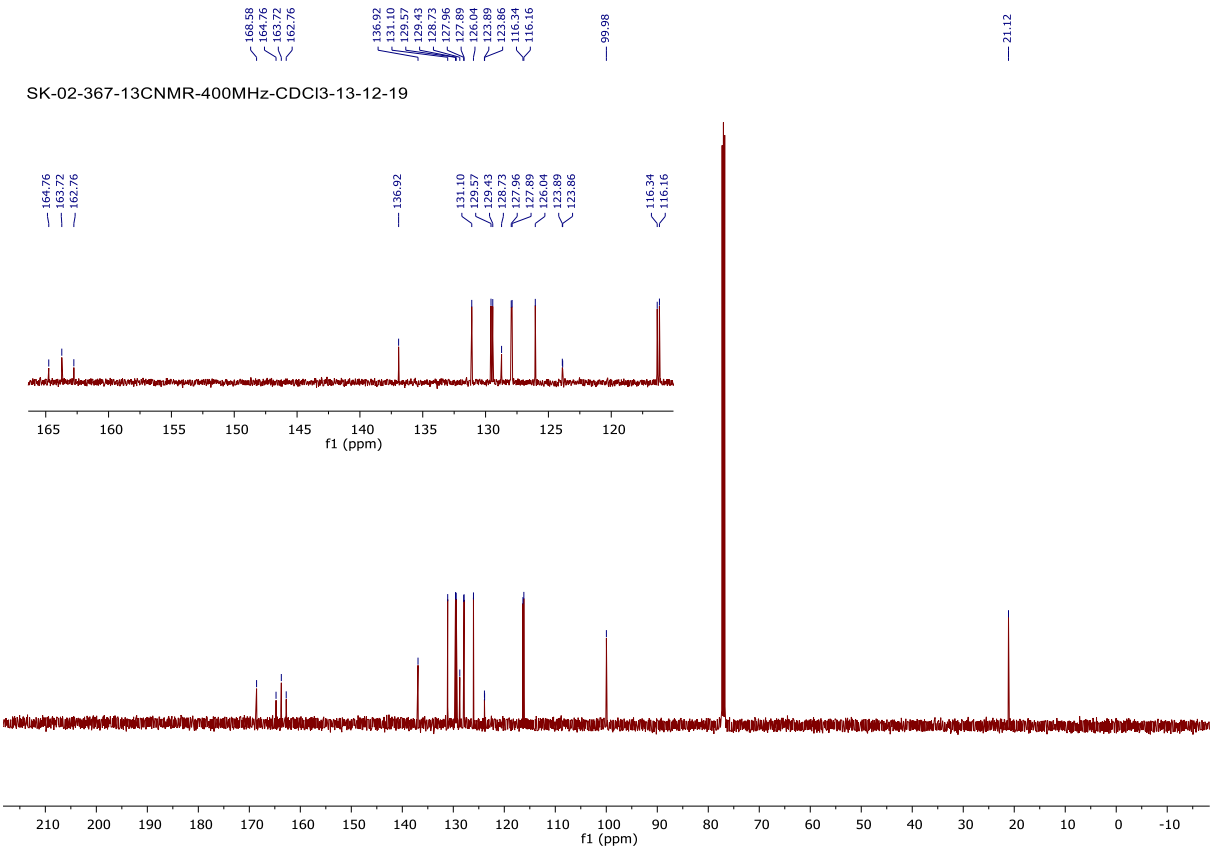
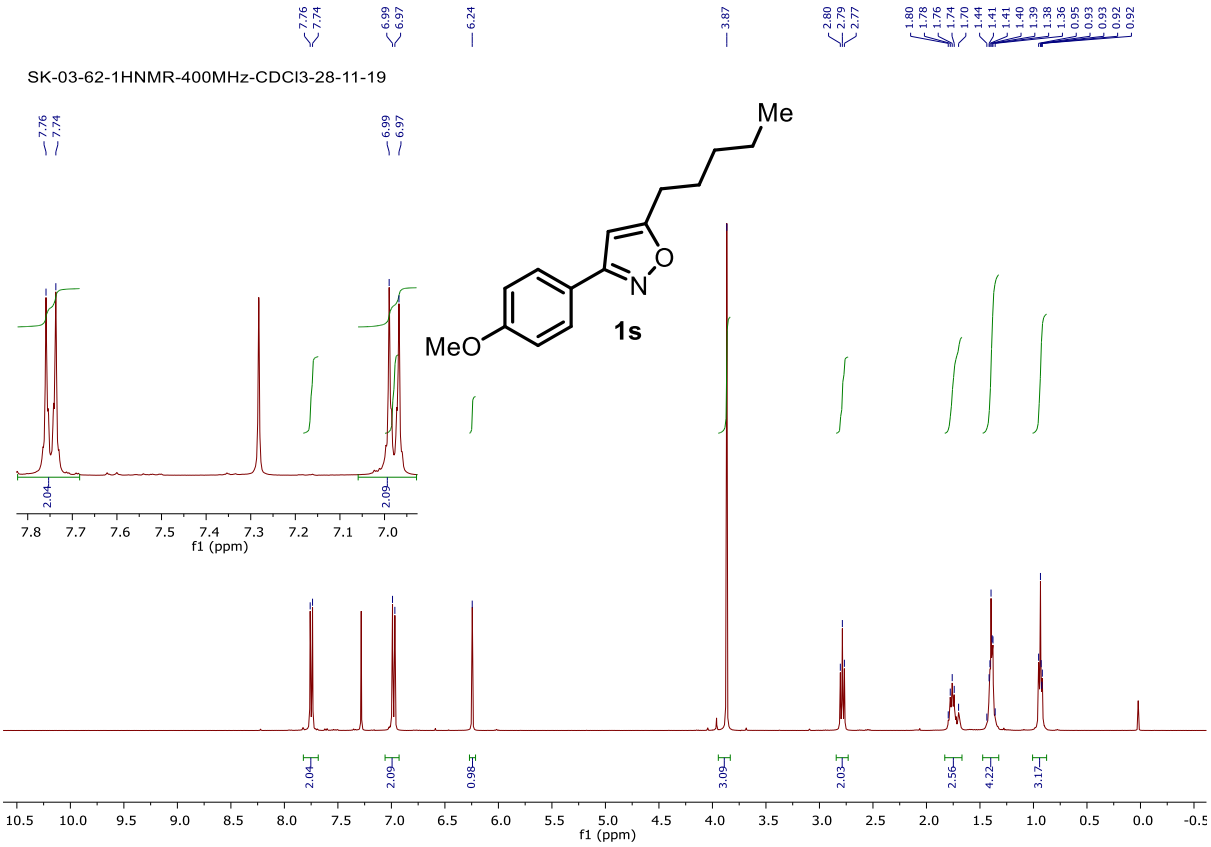
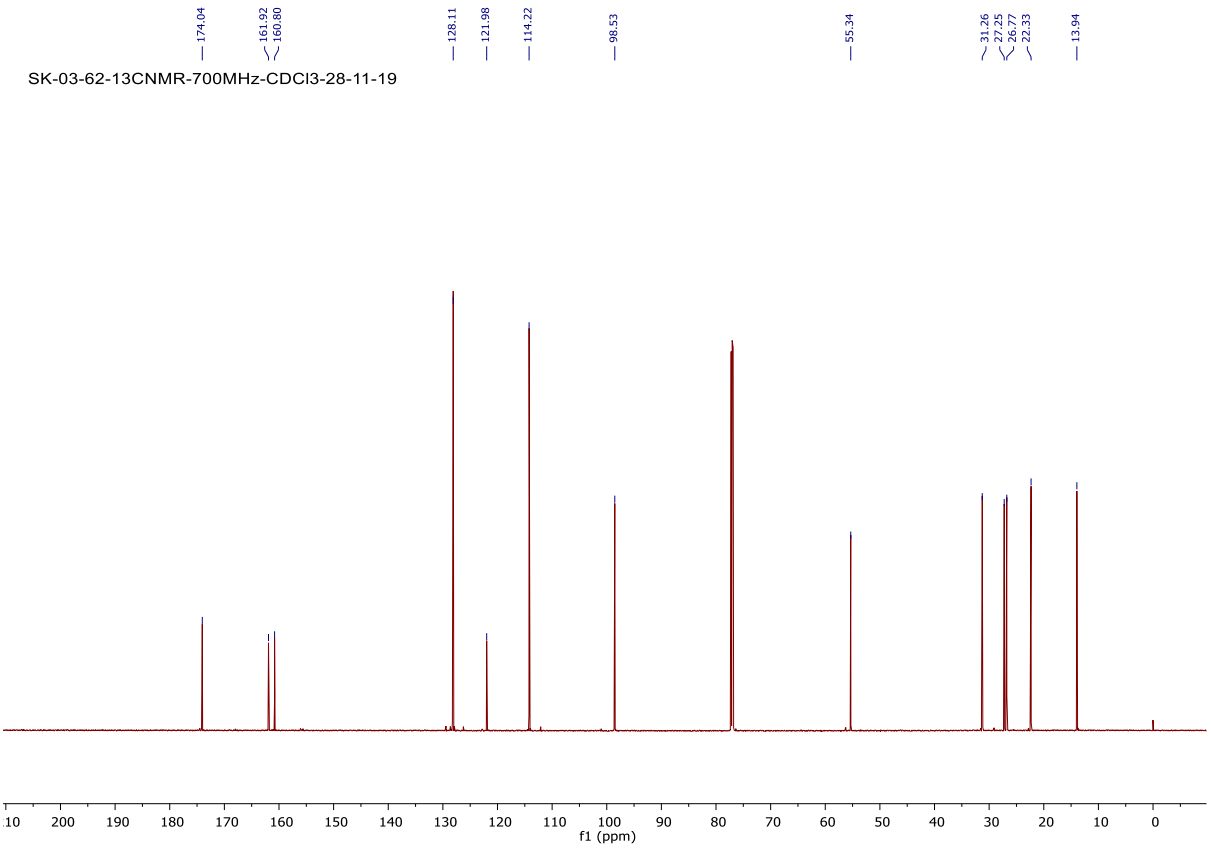
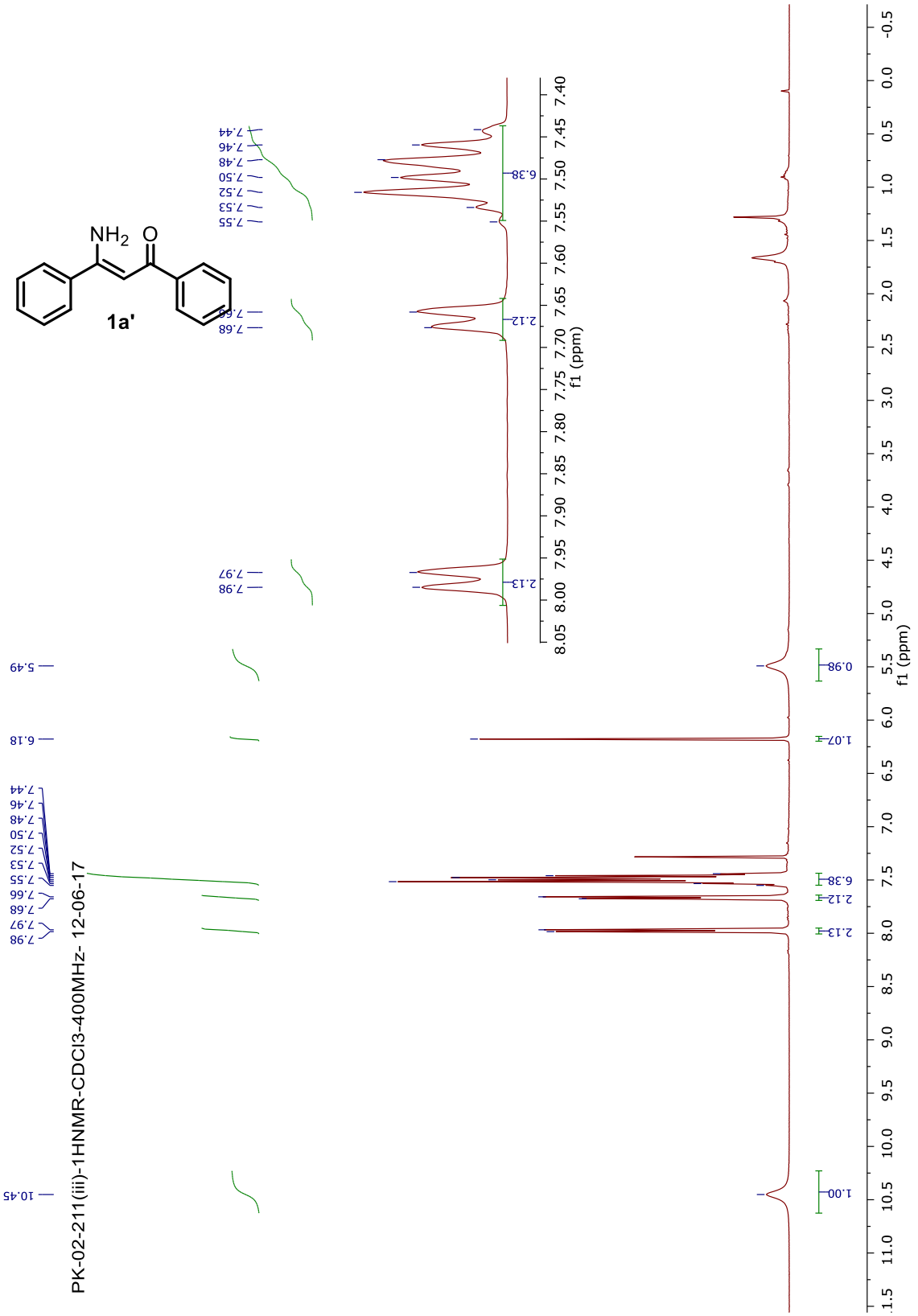
Ph
Me
O
N
1q
f1 (ppm)

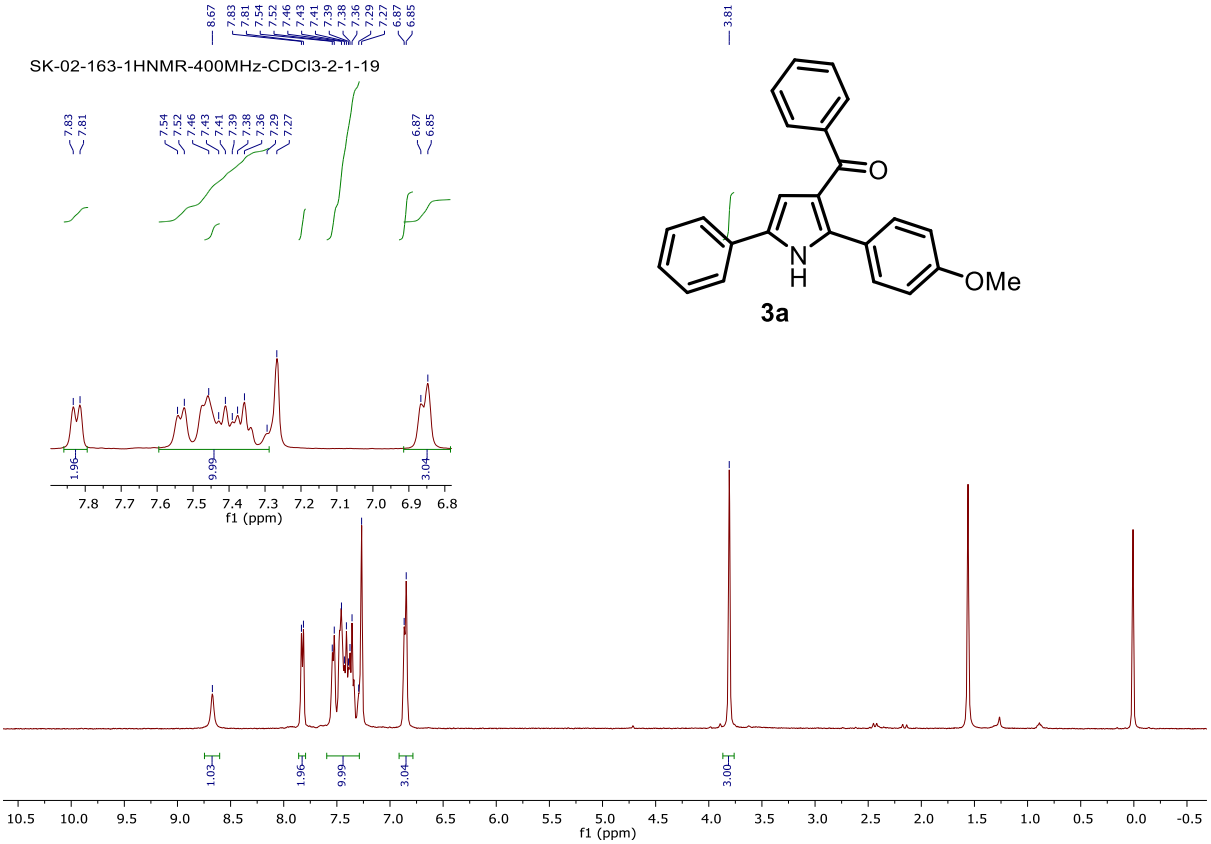

SK-02-367-1HNMR-400MHz-CDCl3-13-12-19
F
O
N
Me
1r
f1 (ppm)

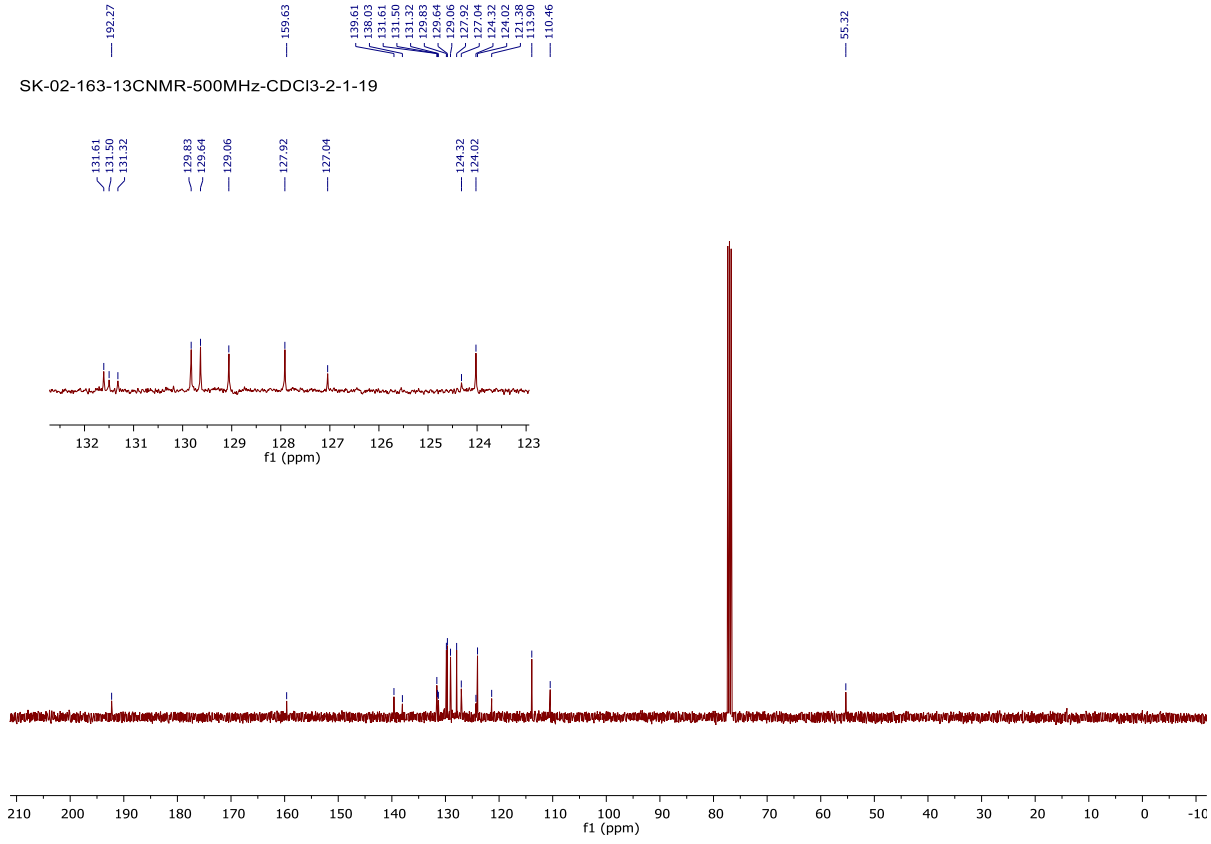

SK-02-367-13CNMR-400MHz-CDCl3-13-12-19
f1 (ppm)

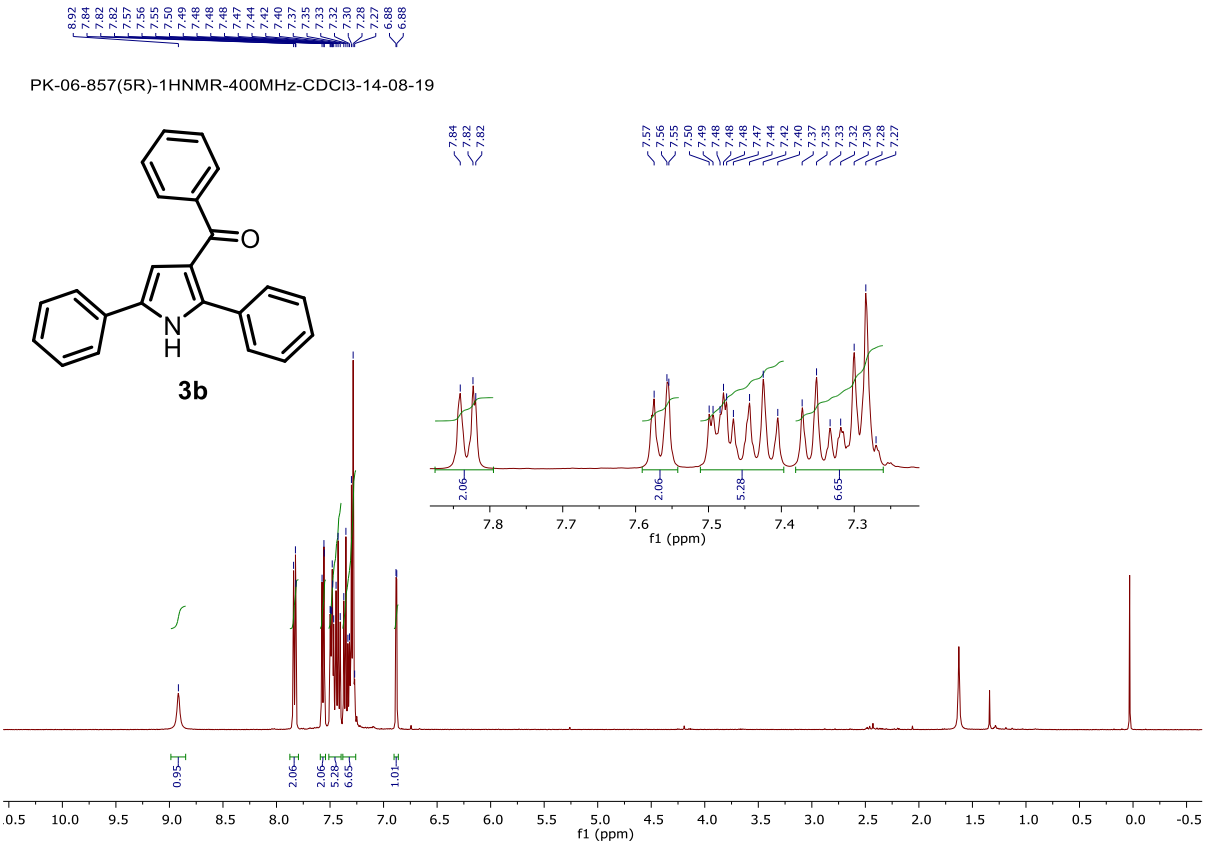

7.76
7.74
6.99
6.97
6.24
3.87
2.80
2.79
2.77
1.80
1.78
1.76
1.74
1.70
1.44
1.41
1.41
1.40
1.39
1.38
1.36
0.95
0.93
0.93
0.92
0.92
SK-03-62-1HNMR-400MHz-CDCl3-28-11-19
Me
O
N
MeO
1s
2.04
2.09
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.04
2.09
0.98
3.09
2.03
2.56
4.22
3.17
10.5 10.0 9.5 9.0 8.5 8.0 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 -0.5
f1 (ppm)

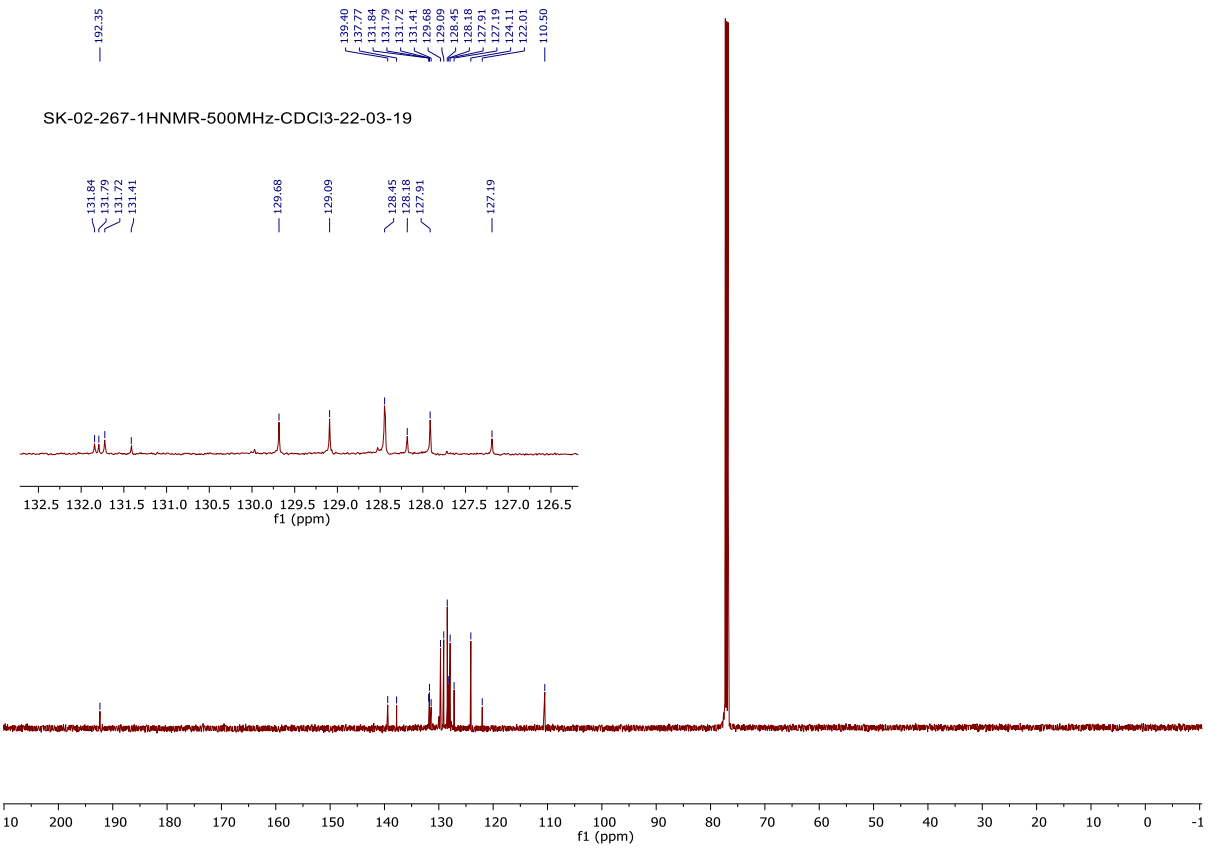

174.04
161.92
160.80
128.11
121.98
114.22
98.53
55.34
31.26
27.25
26.77
22.33
13.94
SK-03-62-13CNMR-700MHz-CDCl3-28-11-19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

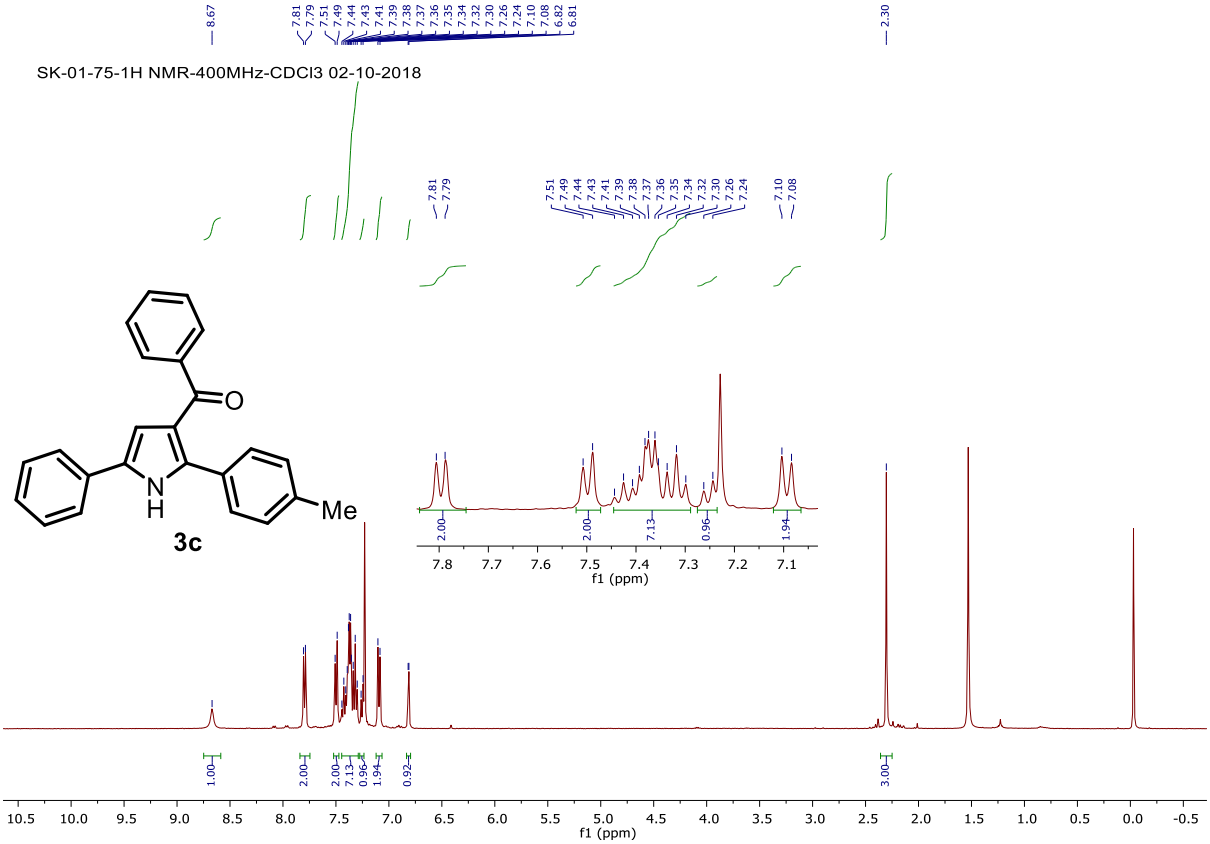

NH2
O
1a'
PK-02-211(iii)-1HNMR-CDCl3-400MHz- 12-06-17
f1 (ppm)

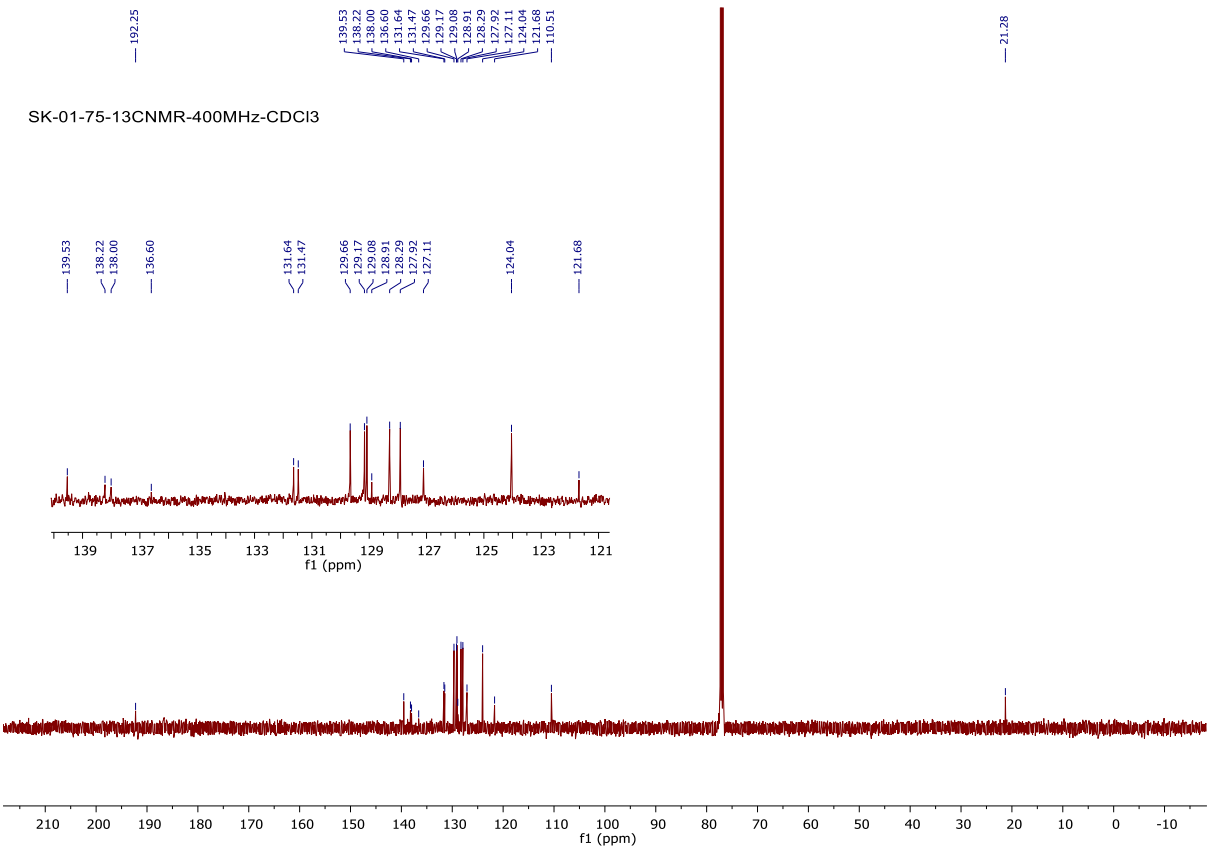

SK-02-163-1HNMR-400MHz-CDCl3-2-1-19
8.67
7.83
7.81
7.54
7.52
7.46
7.43
7.41
7.39
7.38
7.36
7.29
7.27
6.87
6.85
3.81
O
N
H
OMe
3a
1.03
1.96
9.99
3.04
3.00
f1 (ppm)

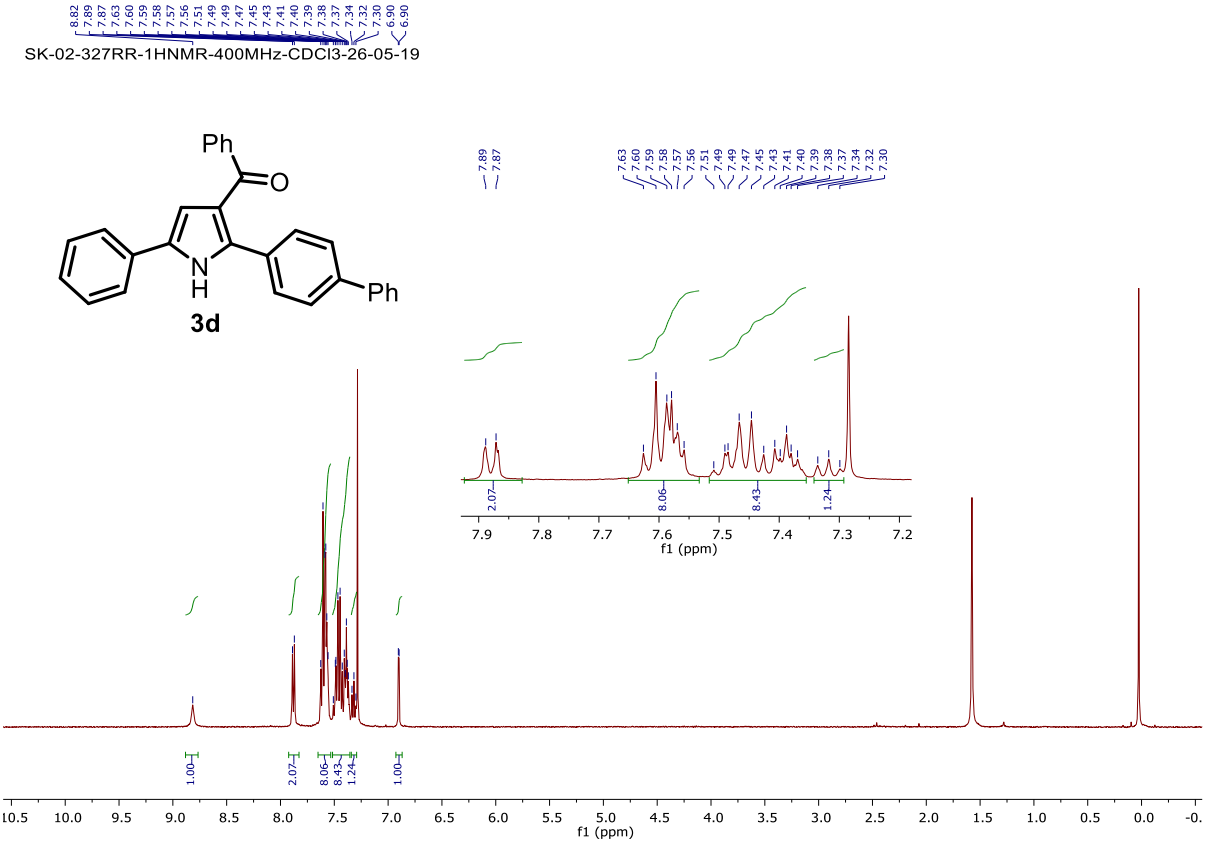

SK-02-163-13CNMR-500MHz-CDCl3-2-1-19
192.27
159.63
139.61
138.03
131.61
131.50
131.32
129.83
129.64
129.06
127.92
127.04
124.32
124.02
121.38
113.90
110.46
55.32
f1 (ppm)

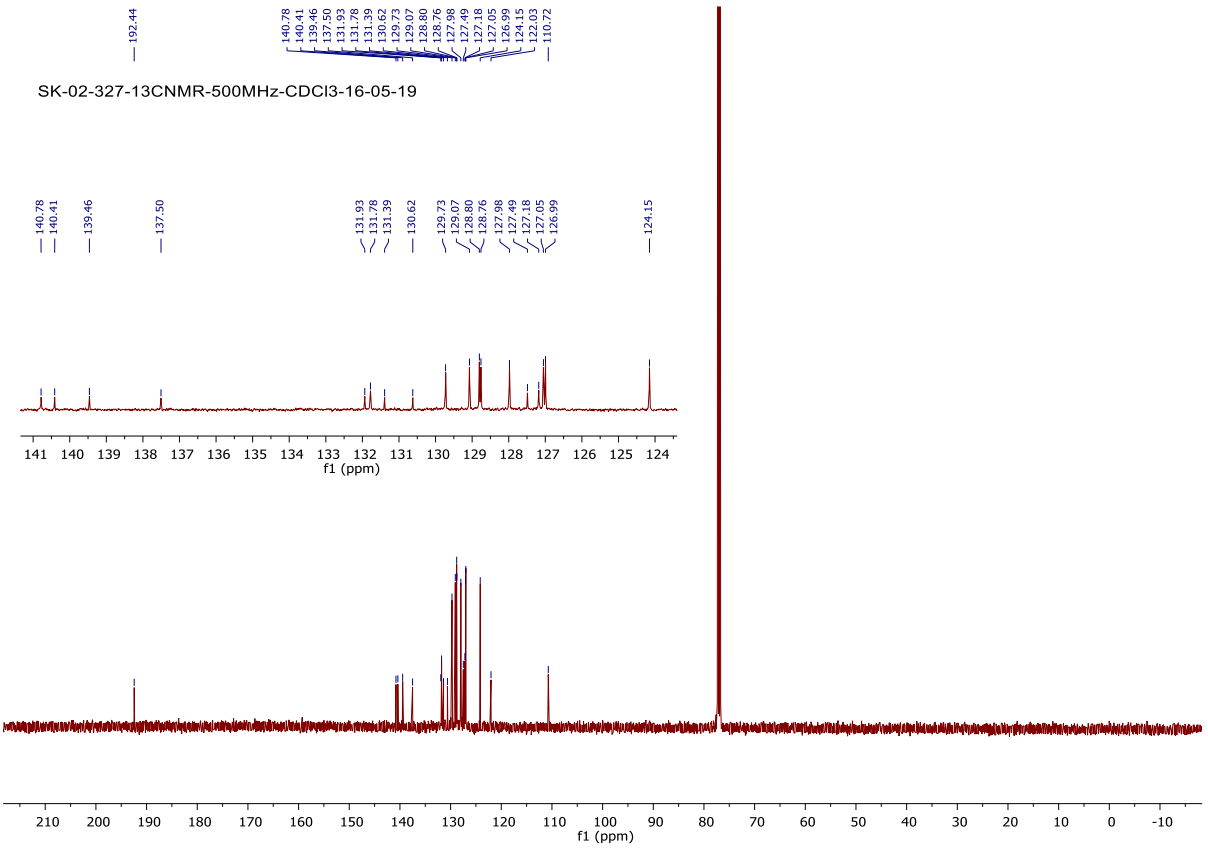

PK-06-857(5R)-1HNMR-400MHz-CDCl3-14-08-19
3b
f1 (ppm)

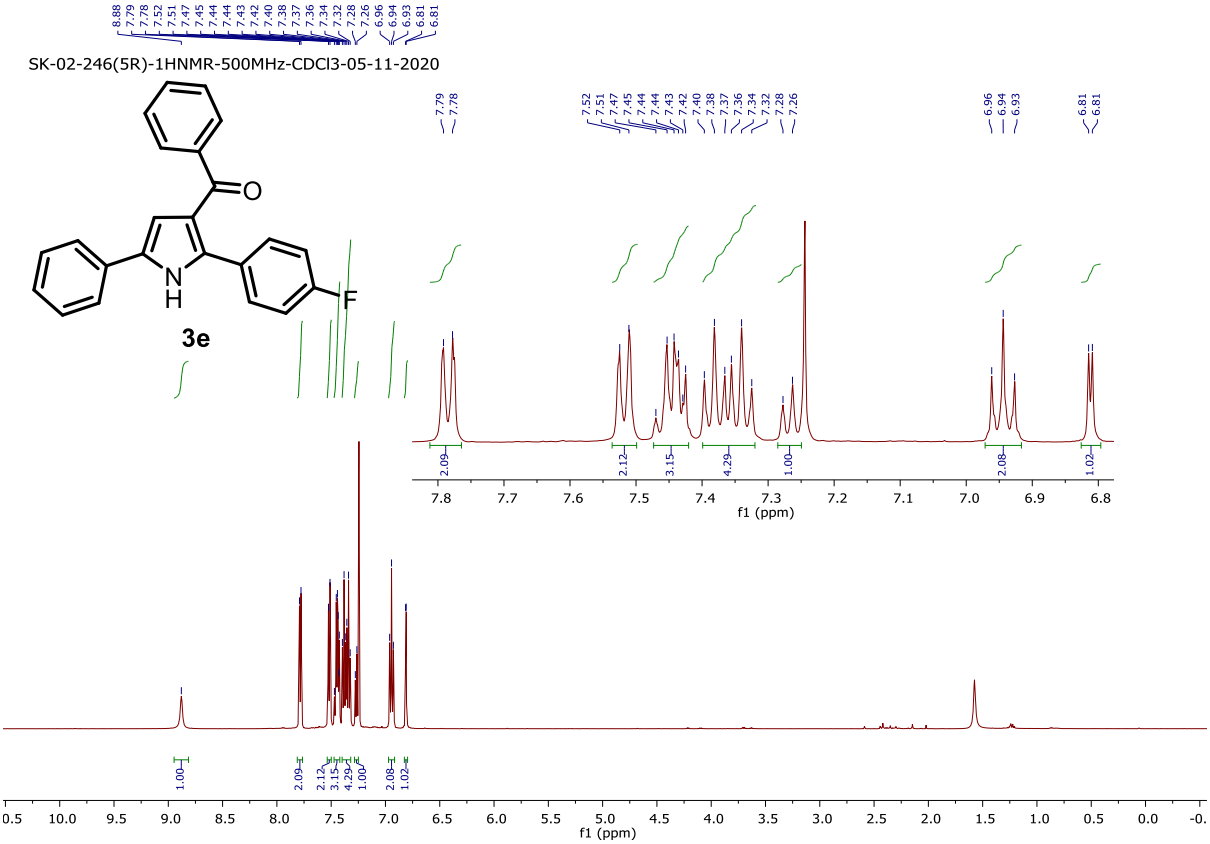

SK-02-267-1HNMR-500MHz-CDCl3-22-03-19
f1 (ppm)

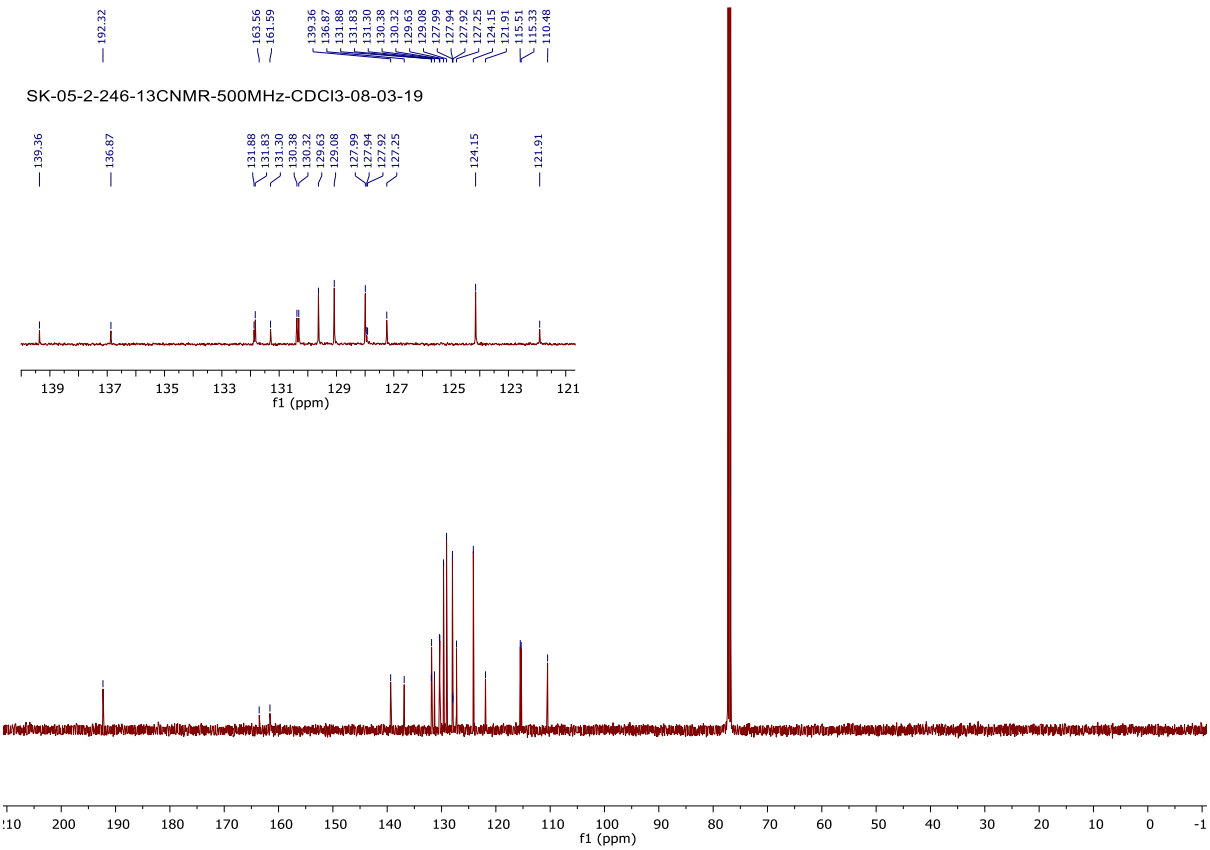

SK-01-75-1H NMR-400MHz-CDCl3 02-10-2018
8.67
7.81
7.79
7.51
7.49
7.44
7.43
7.41
7.39
7.38
7.37
7.36
7.35
7.34
7.32
7.30
7.26
7.24
7.10
7.08
6.82
6.81
2.30
O
N
H
Me
3c
f1 (ppm)

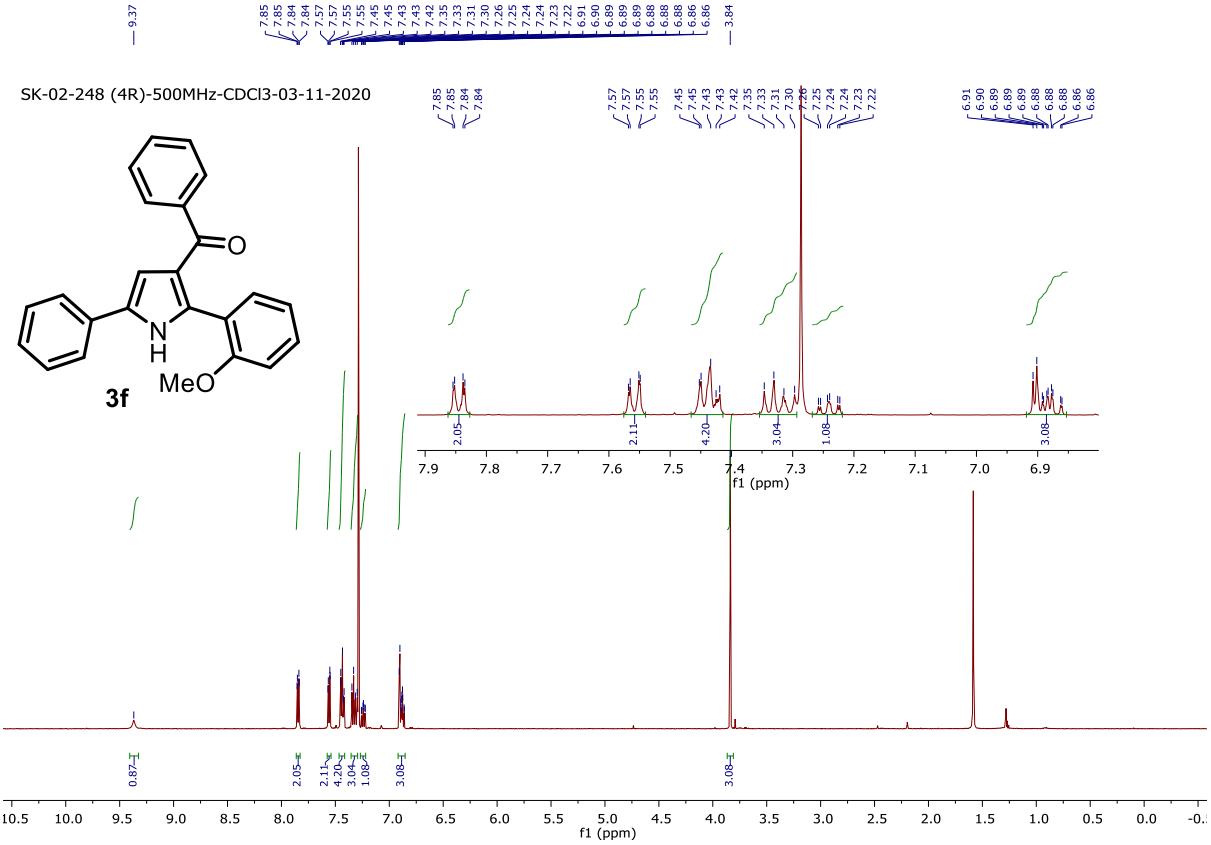

SK-01-75-13CNMR-400MHz-CDCl3
192.25
139.53
138.22
138.00
136.60
131.64
131.47
129.66
129.17
129.08
128.91
128.29
127.92
127.11
124.04
121.68
110.51
21.28
f1 (ppm)

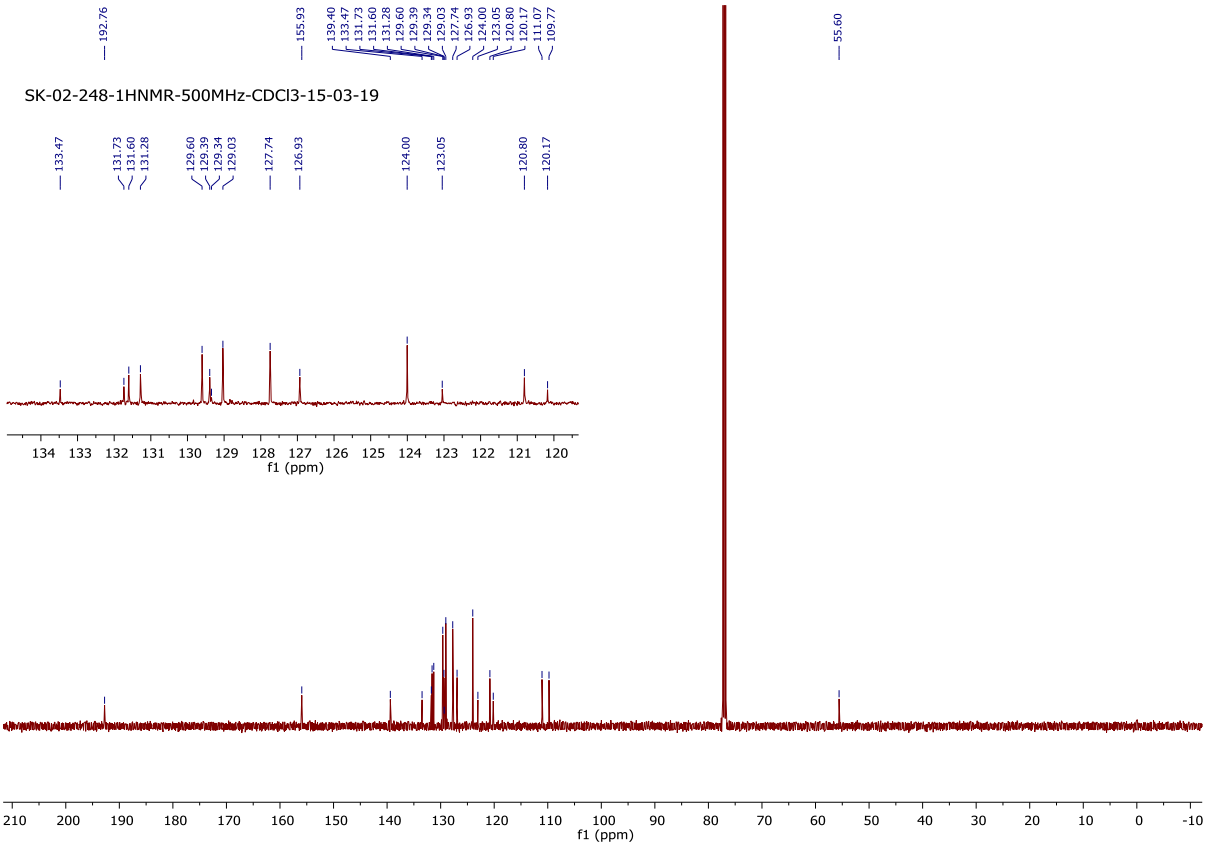

SK-02-327RR-1HNMR-400MHz-CDCl3-26-05-19
Ph
O
N
H
Ph
3d
f1 (ppm)

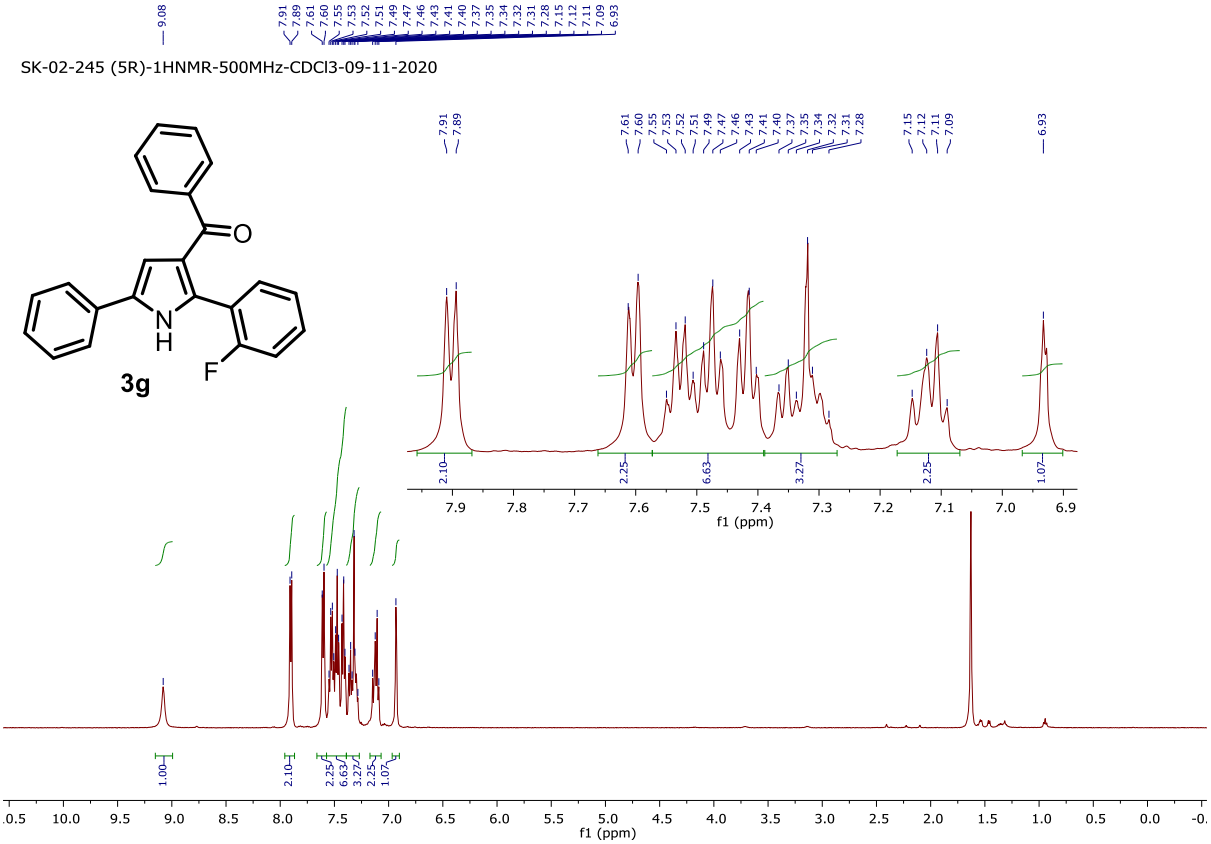

SK-02-327-13CNMR-500MHz-CDCl3-16-05-19
f1 (ppm)


SK-02-246(5R)-1HNMR-500MHz-CDCl3-05-11-2020
3e
f1 (ppm)


SK-05-2-246-13CNMR-500MHz-CDCl3-08-03-19
f1 (ppm)


SK-02-248 (4R)-500MHz-CDCl3-03-11-2020
3f
MeO
f1 (ppm)


SK-02-248-1HNMR-500MHz-CDCl3-15-03-19
f1 (ppm)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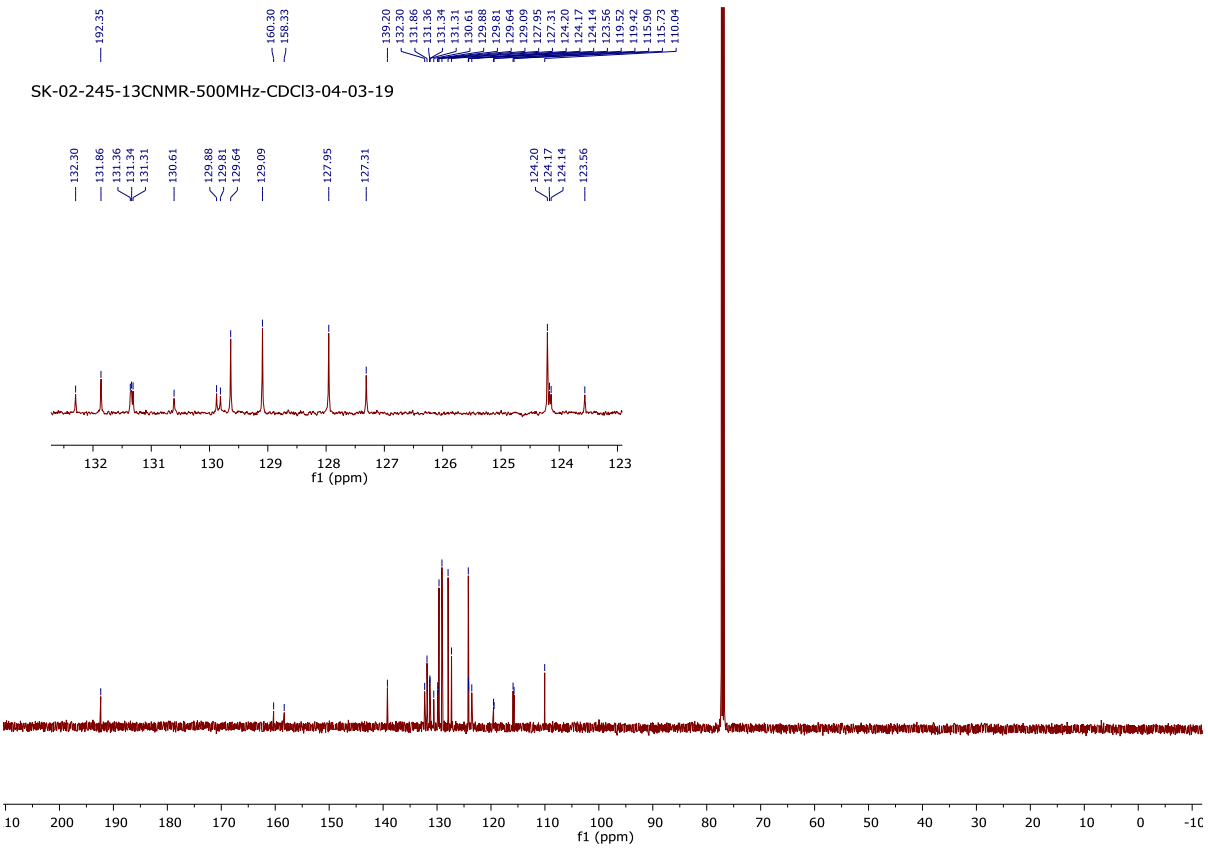
3g
f1 (ppm)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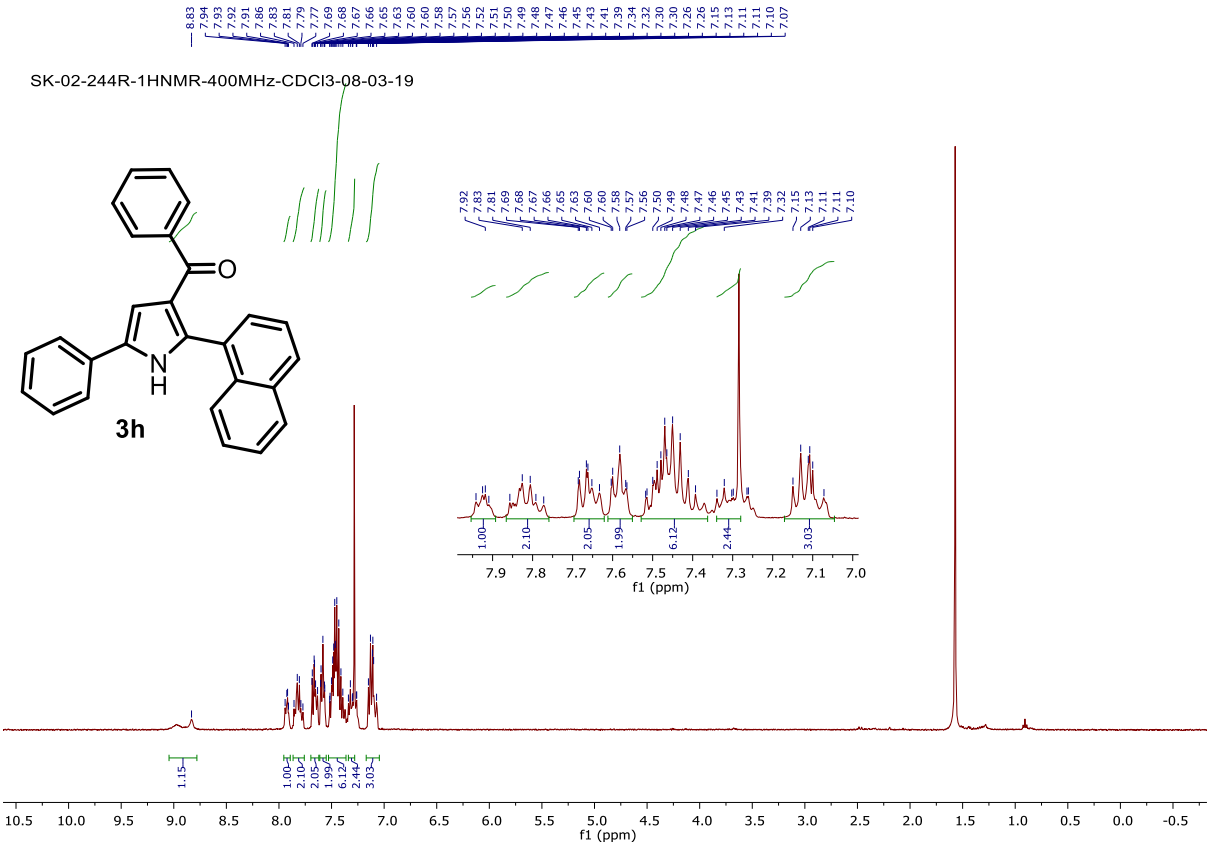
f1 (ppm)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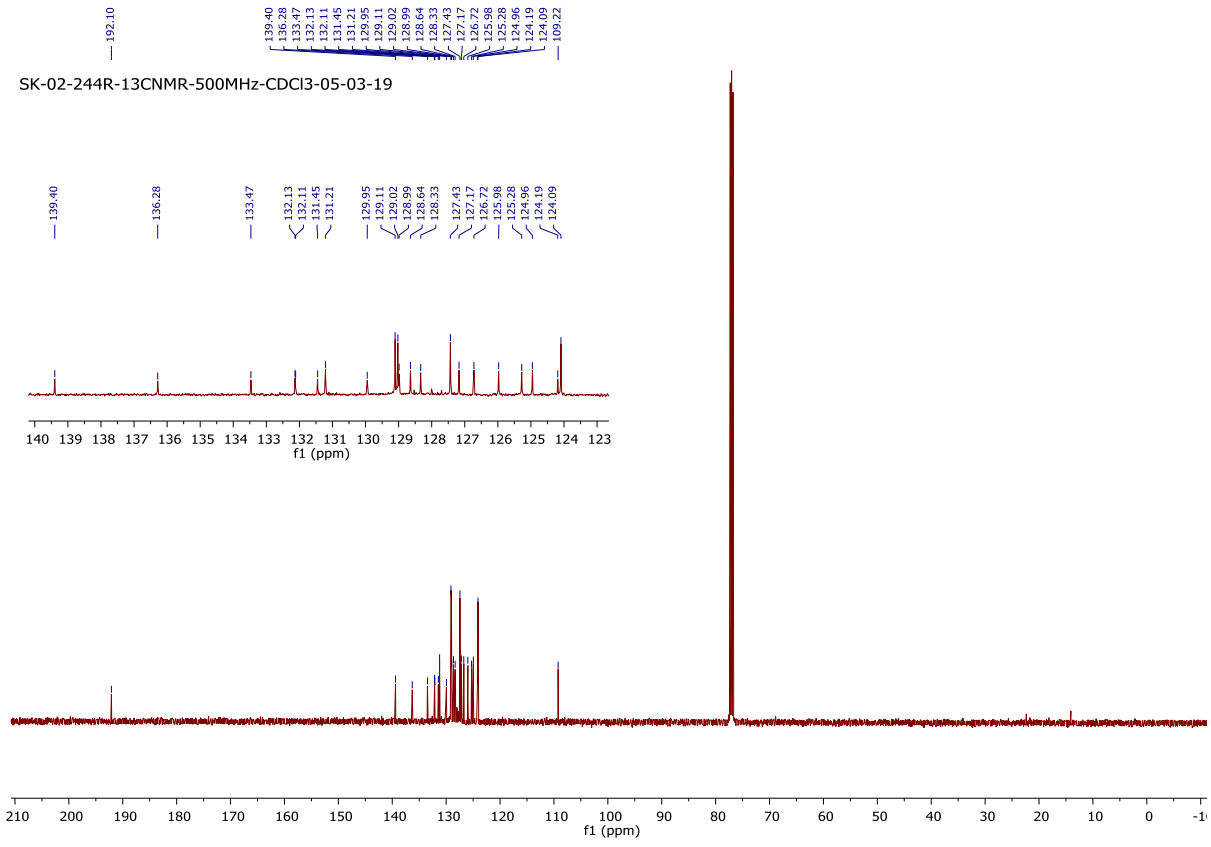
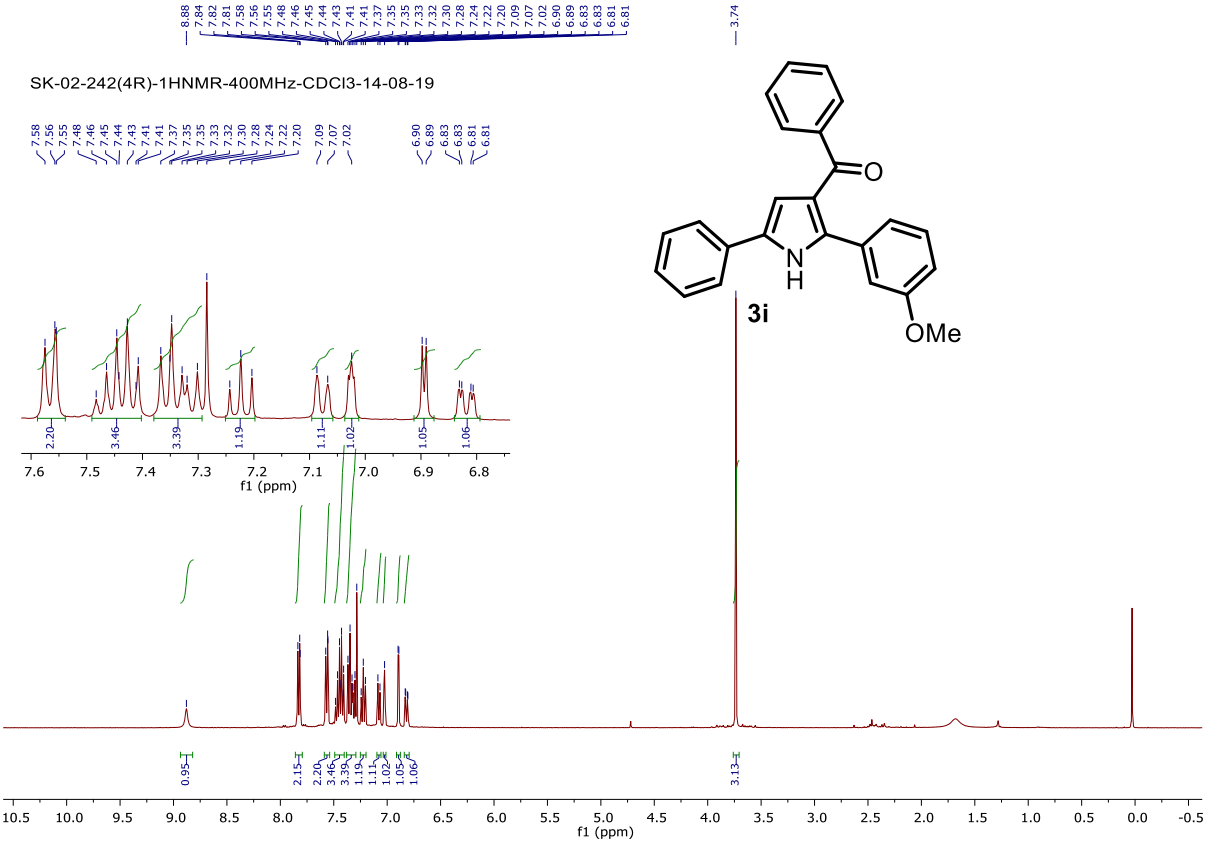
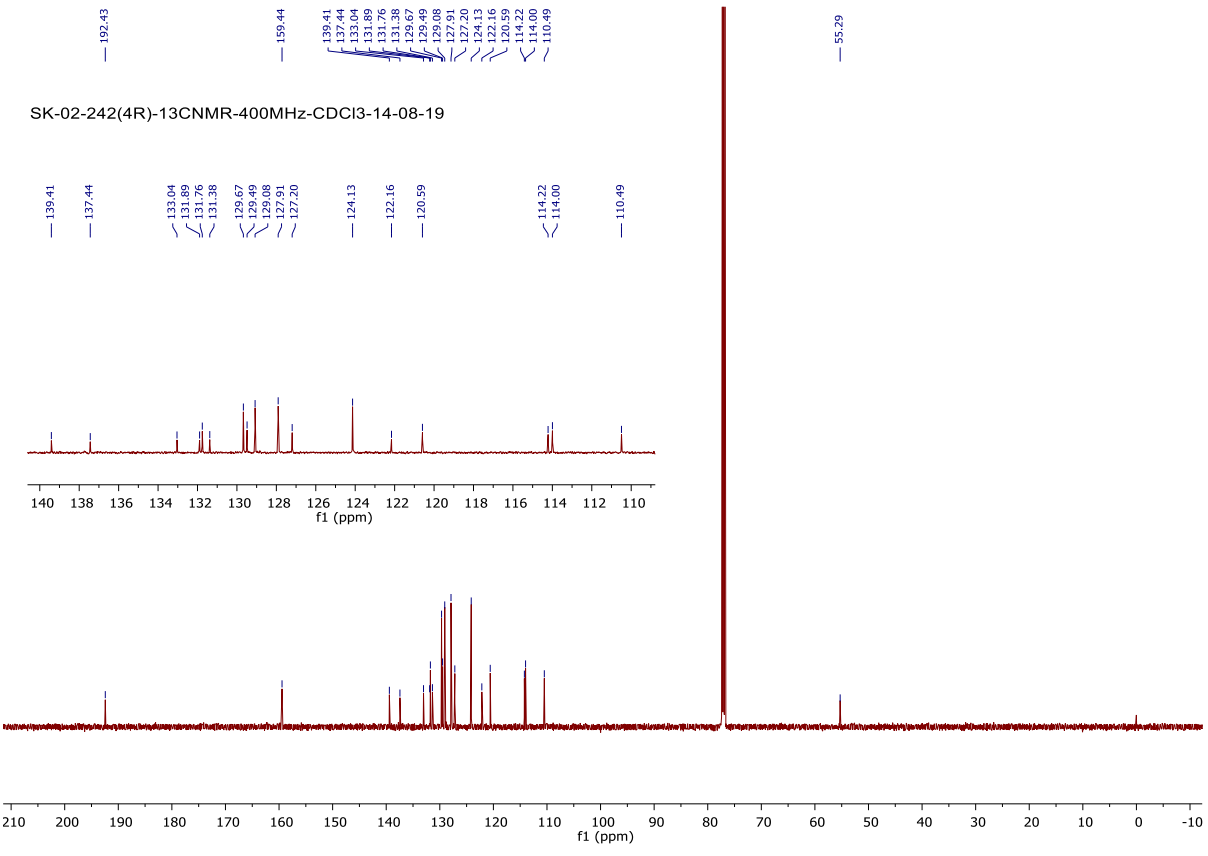
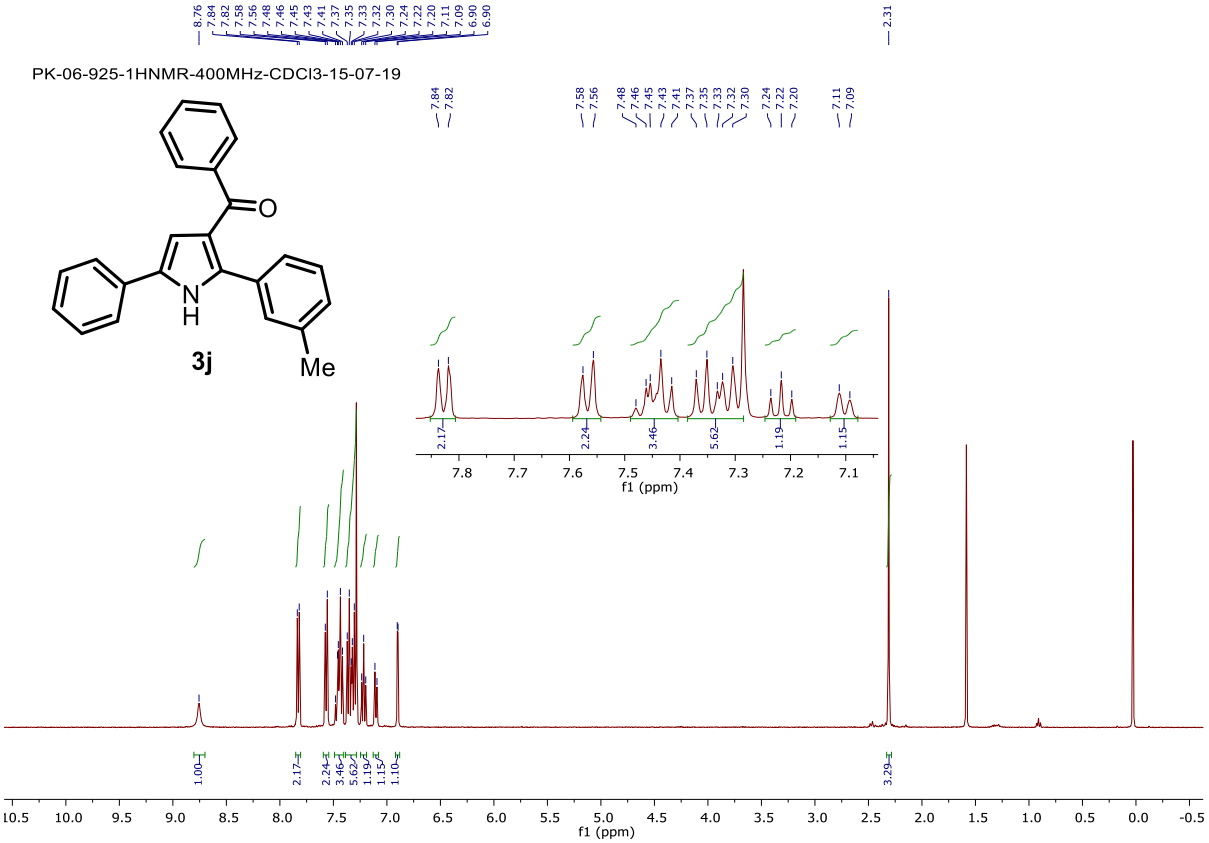
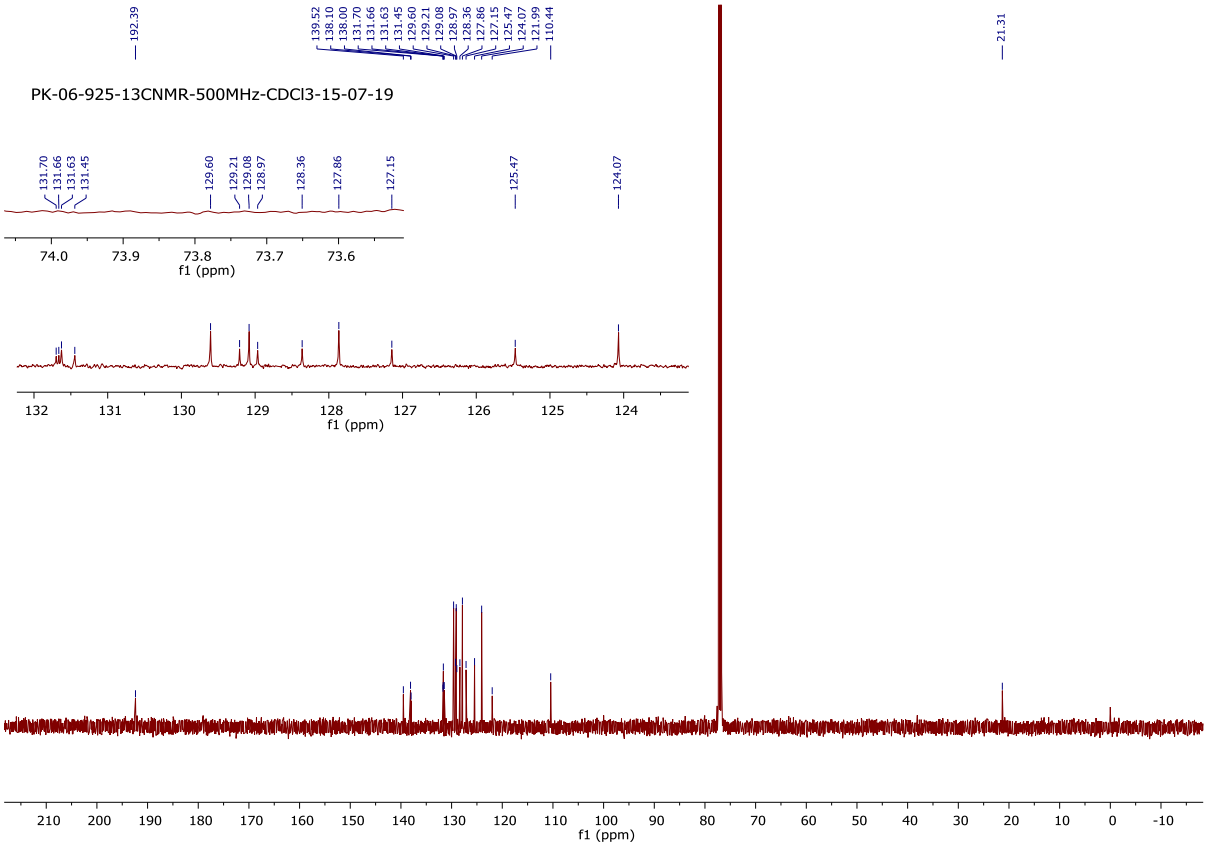
3h
f1 (ppm)

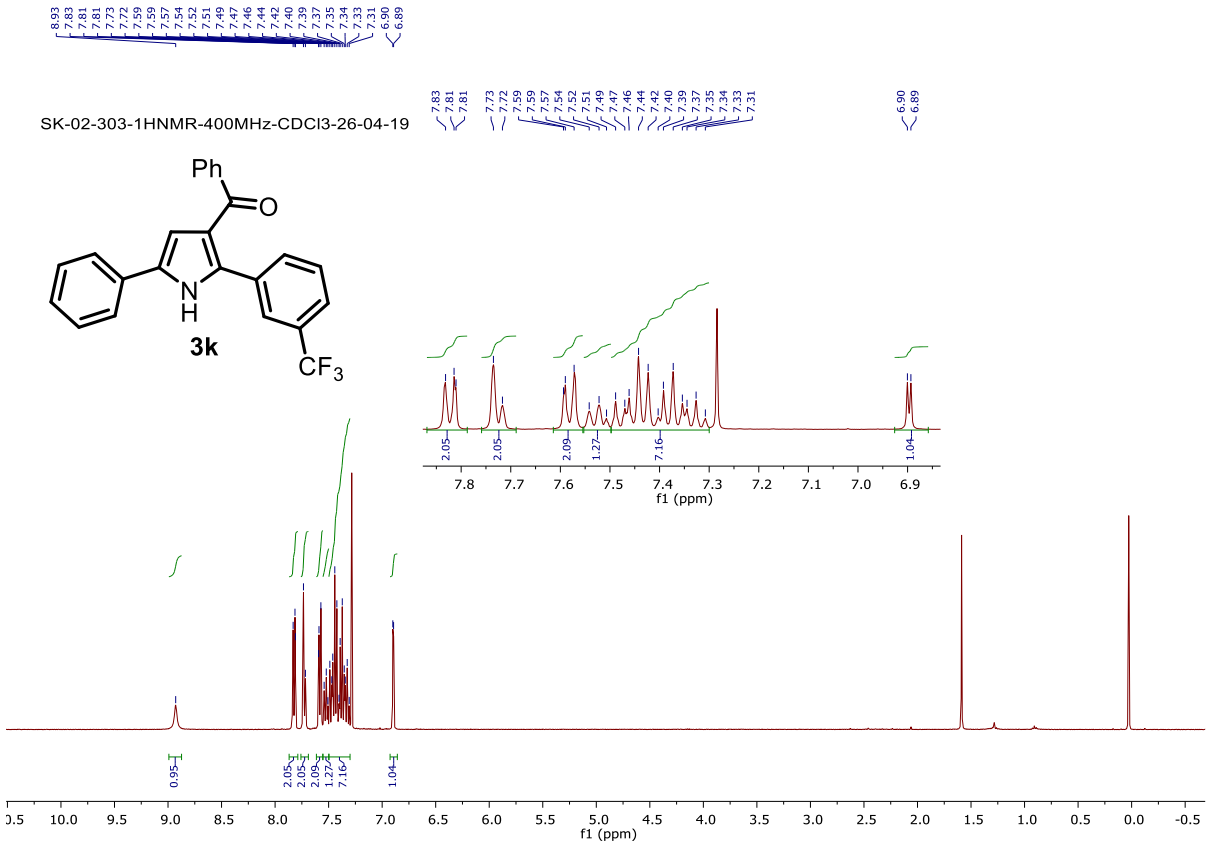

SK-02-244R-13CNMR-500MHz-CDCl3-05-03-19
f1 (ppm)

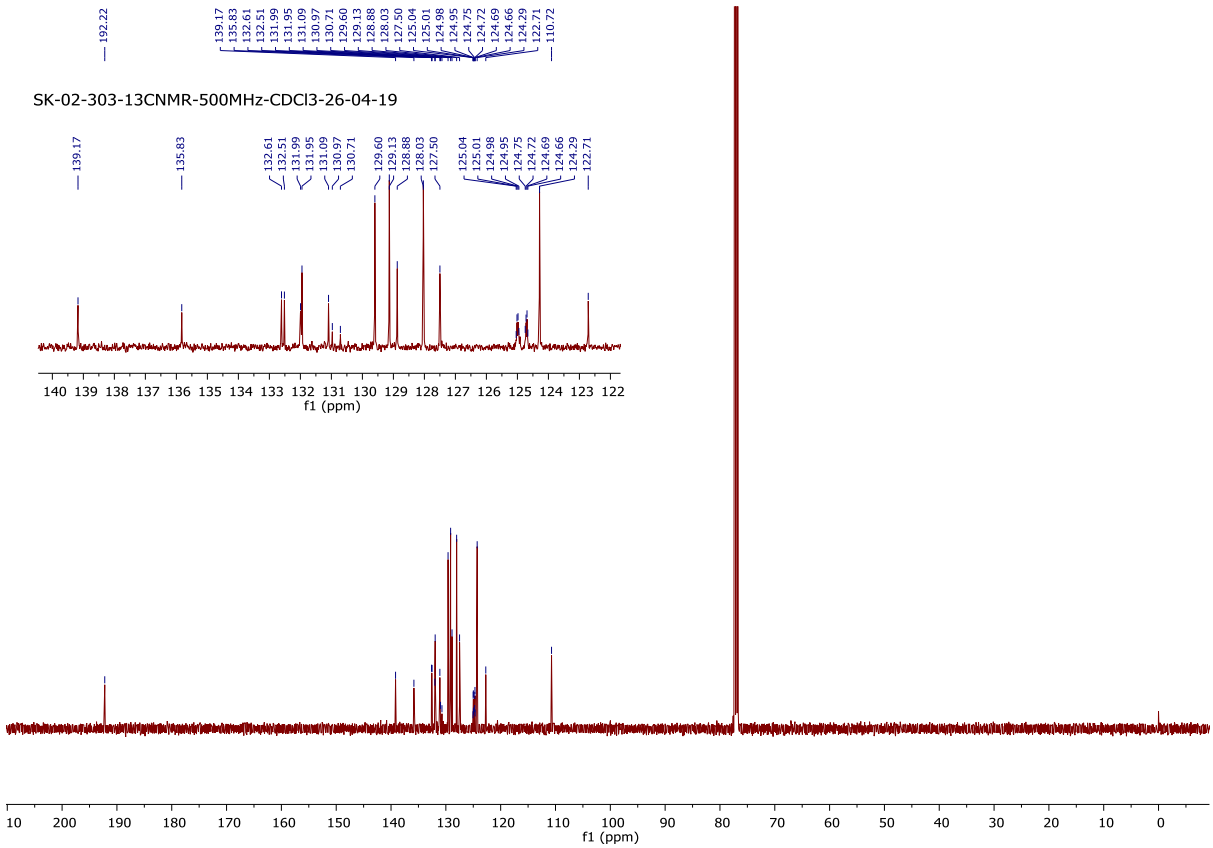

SK-02-242(4R)-1HNMR-400MHz-CDCl3-14-08-19
3i
OMe
f1 (ppm)

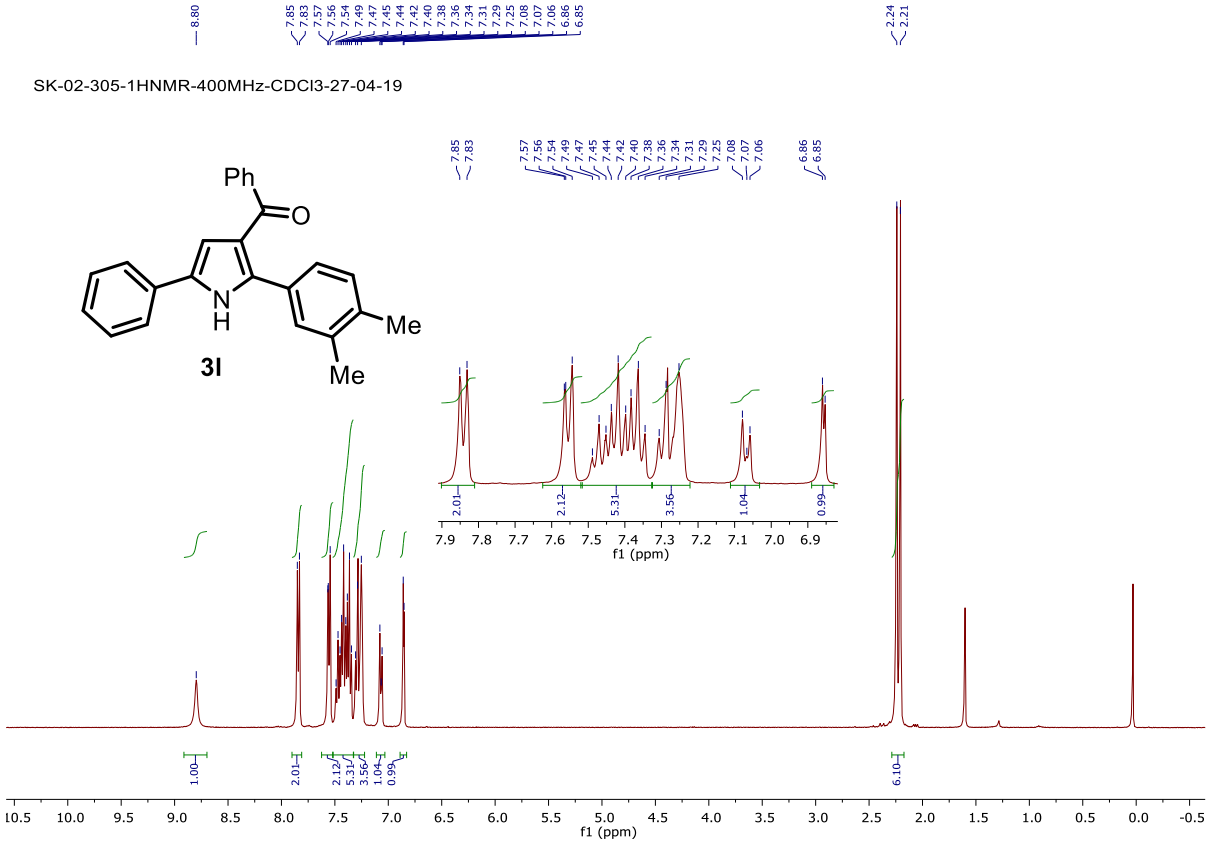

SK-02-242(4R)-13CNMR-400MHz-CDCl3-14-08-19
f1 (ppm)

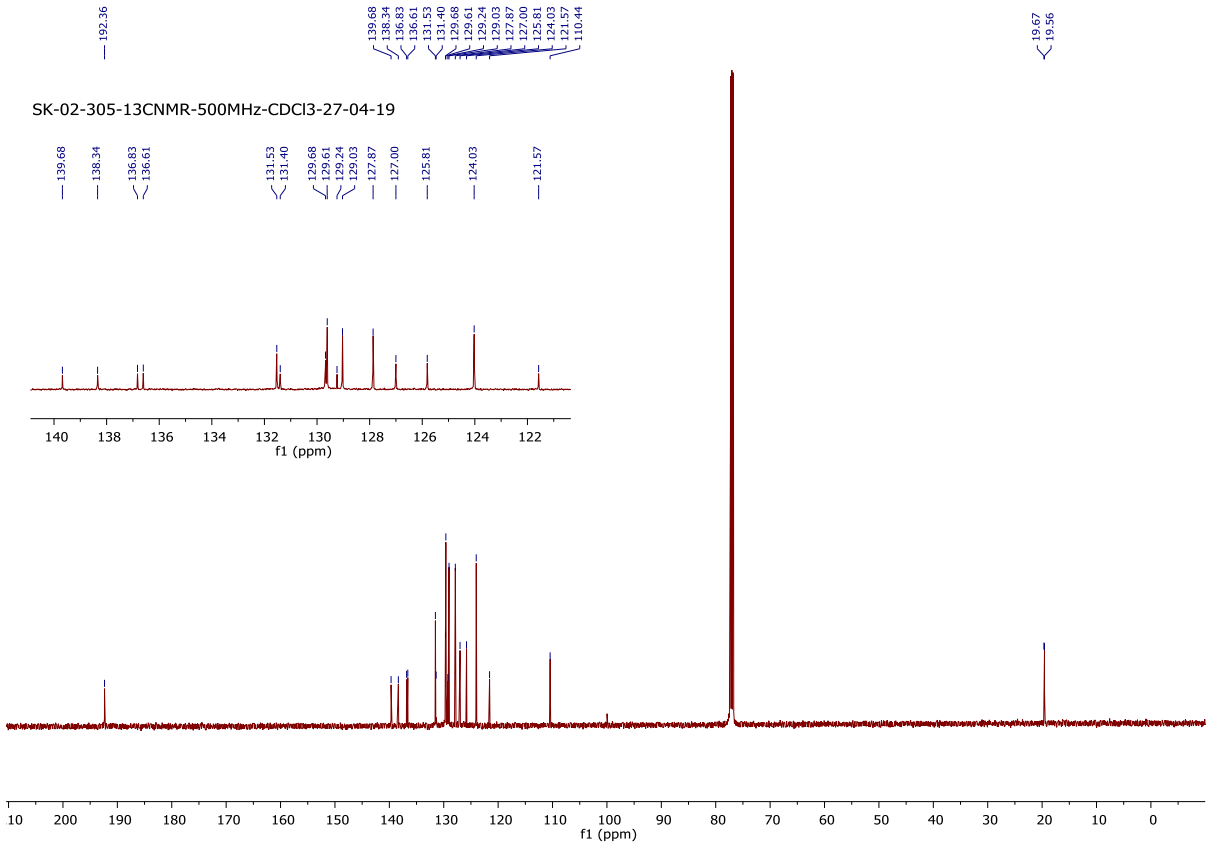

PK-06-925-1HNMR-400MHz-CDCl3-15-07-19
3j
Me
f1 (ppm)


PK-06-925-13CNMR-500MHz-CDCl3-15-07-19
f1 (ppm)

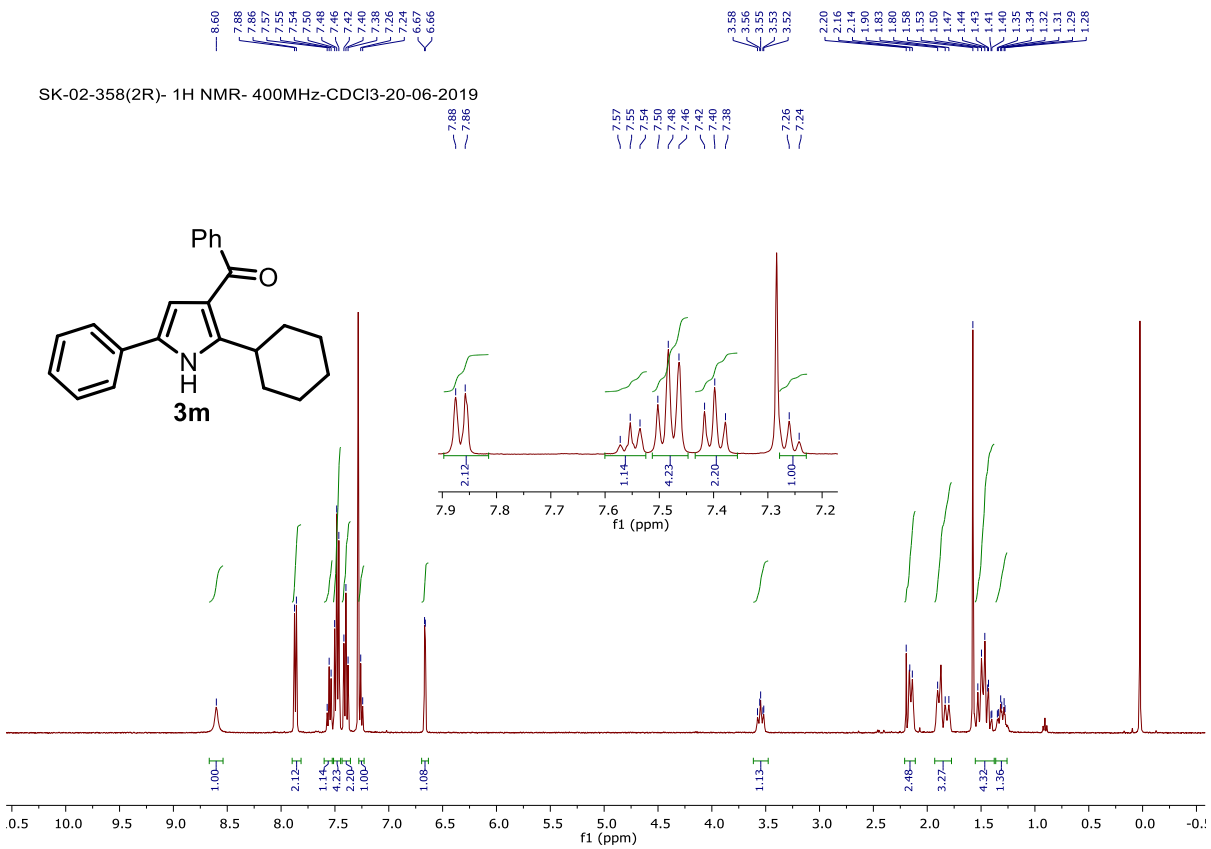

SK-02-303-1HNMR-400MHz-CDCl3-26-04-19
Ph
O
N
H
3k
CF3
f1 (ppm)


SK-02-303-13CNMR-500MHz-CDCl3-26-04-19
f1 (ppm)

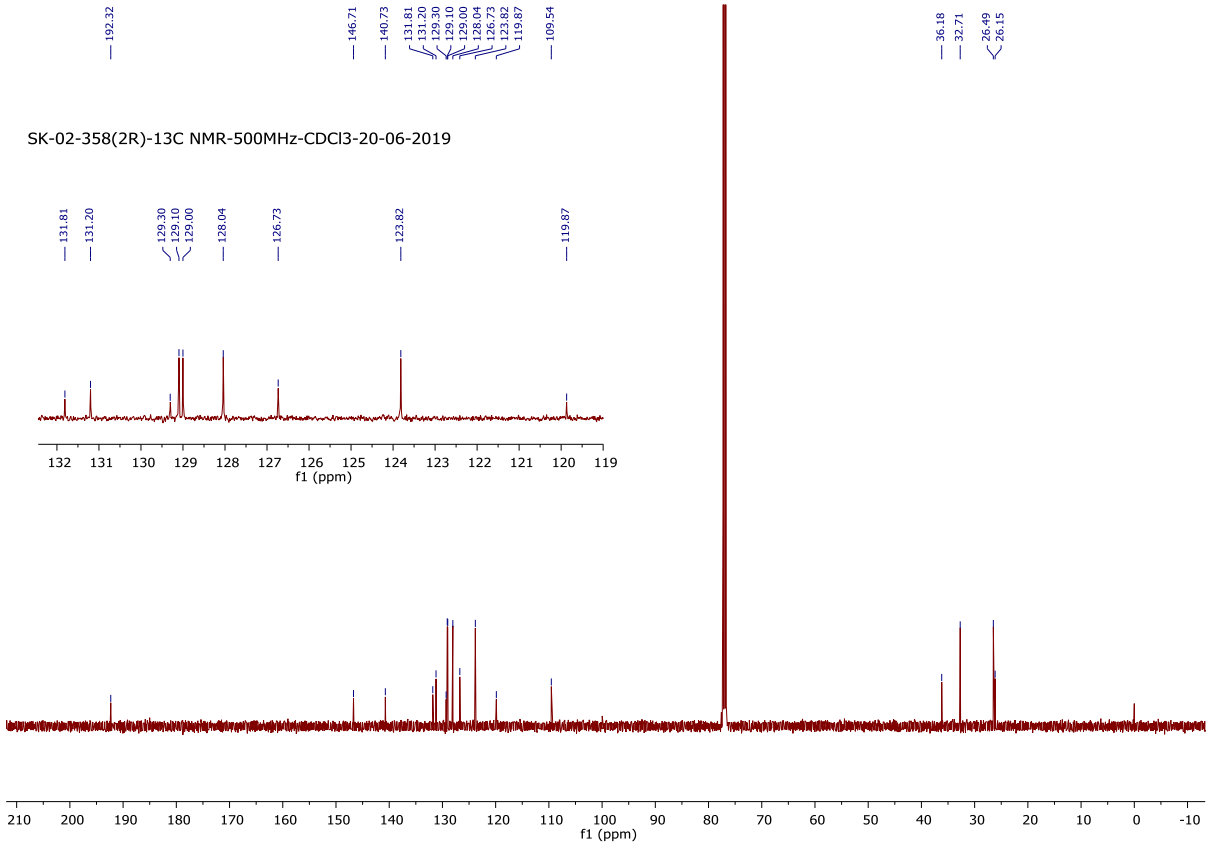

SK-02-305-1HNMR-400MHz-CDCl3-27-04-19
Ph
O
N
H
Me
Me
3l
f1 (ppm)

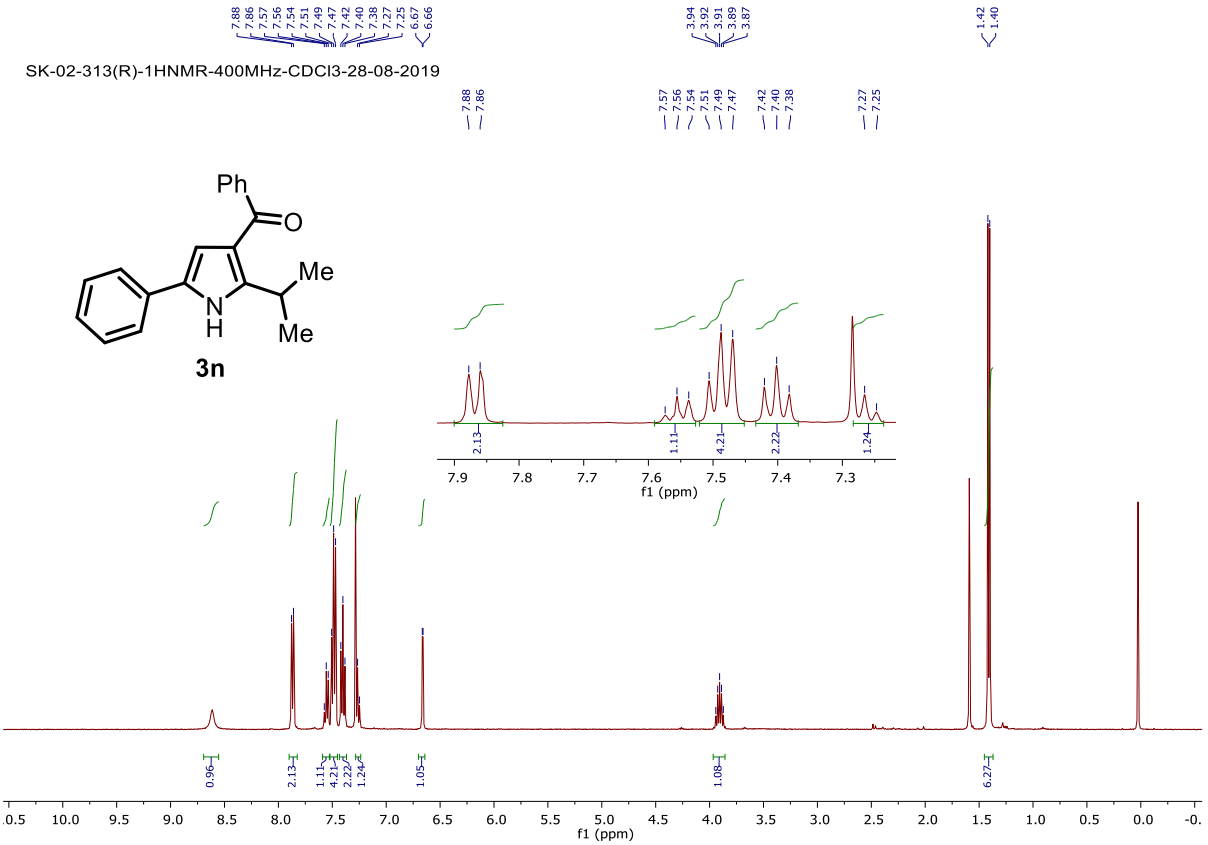

SK-02-305-13CNMR-500MHz-CDCl3-27-04-19
f1 (ppm)

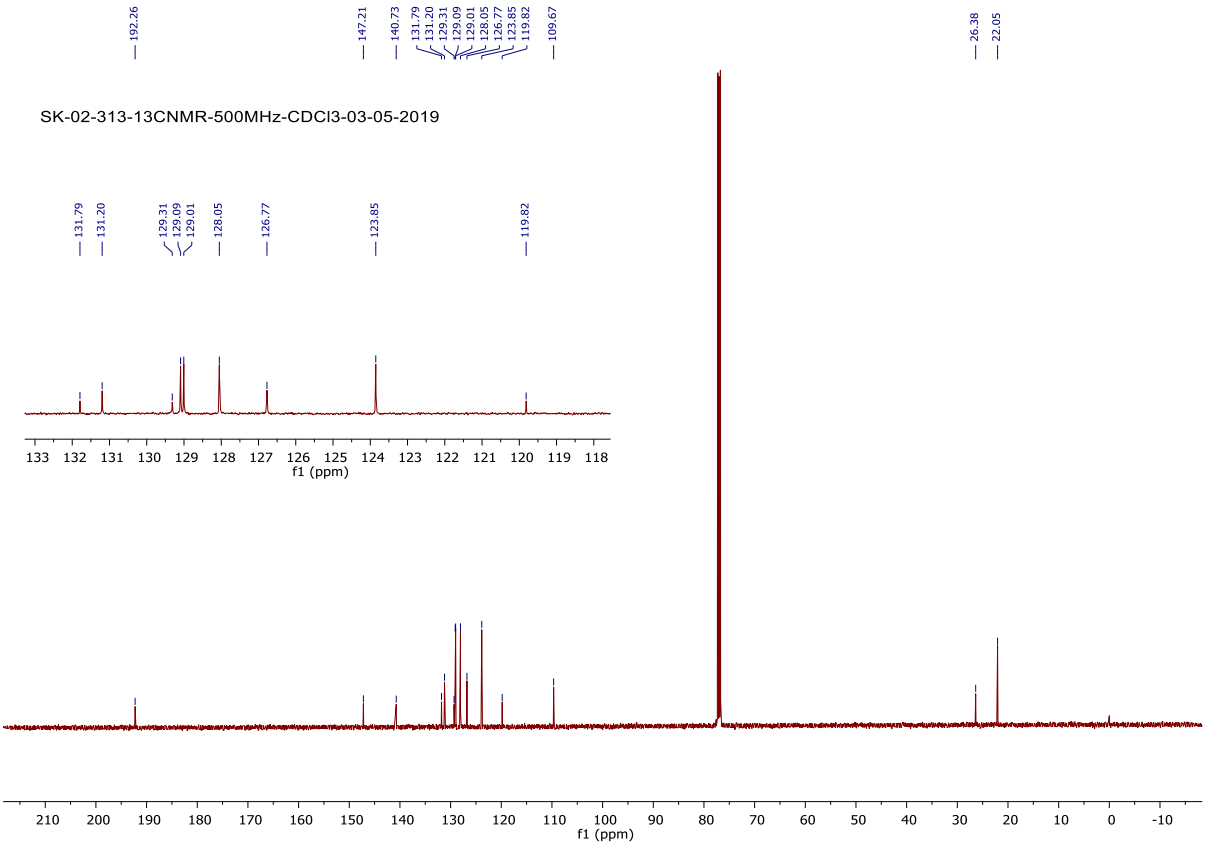
SK-02-358(2R)- 1H NMR- 400MHz-CDCl3-20-06-2019

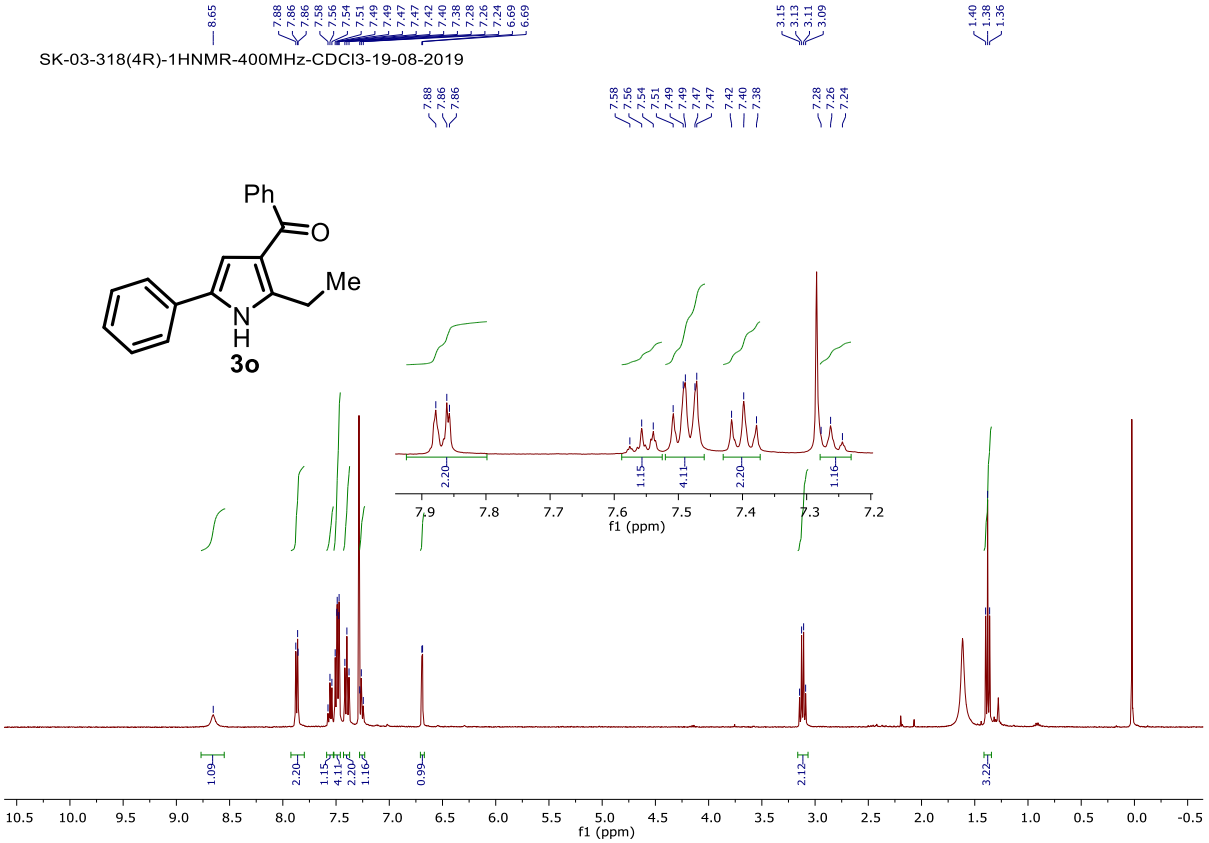


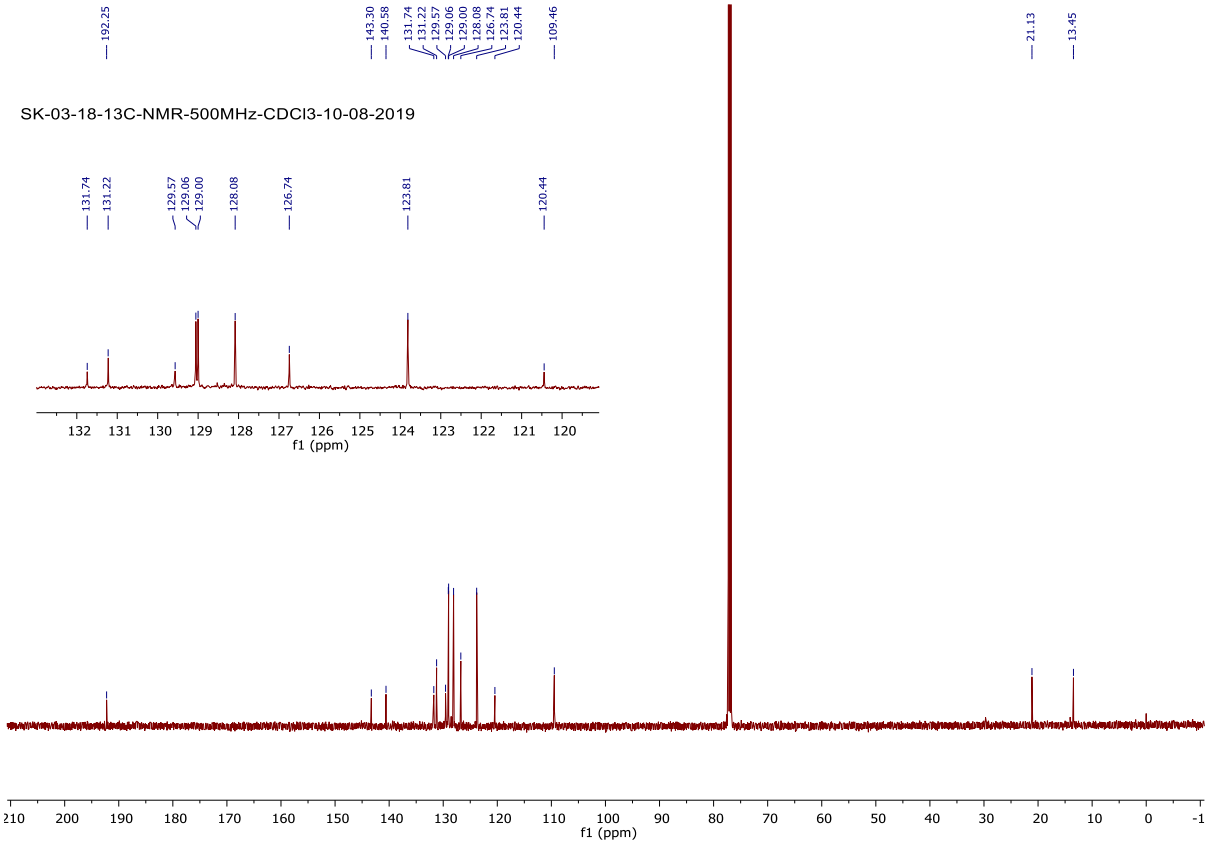
SK-02-358(2R)-13C NMR-500MHz-CDCl3-20-06-2019

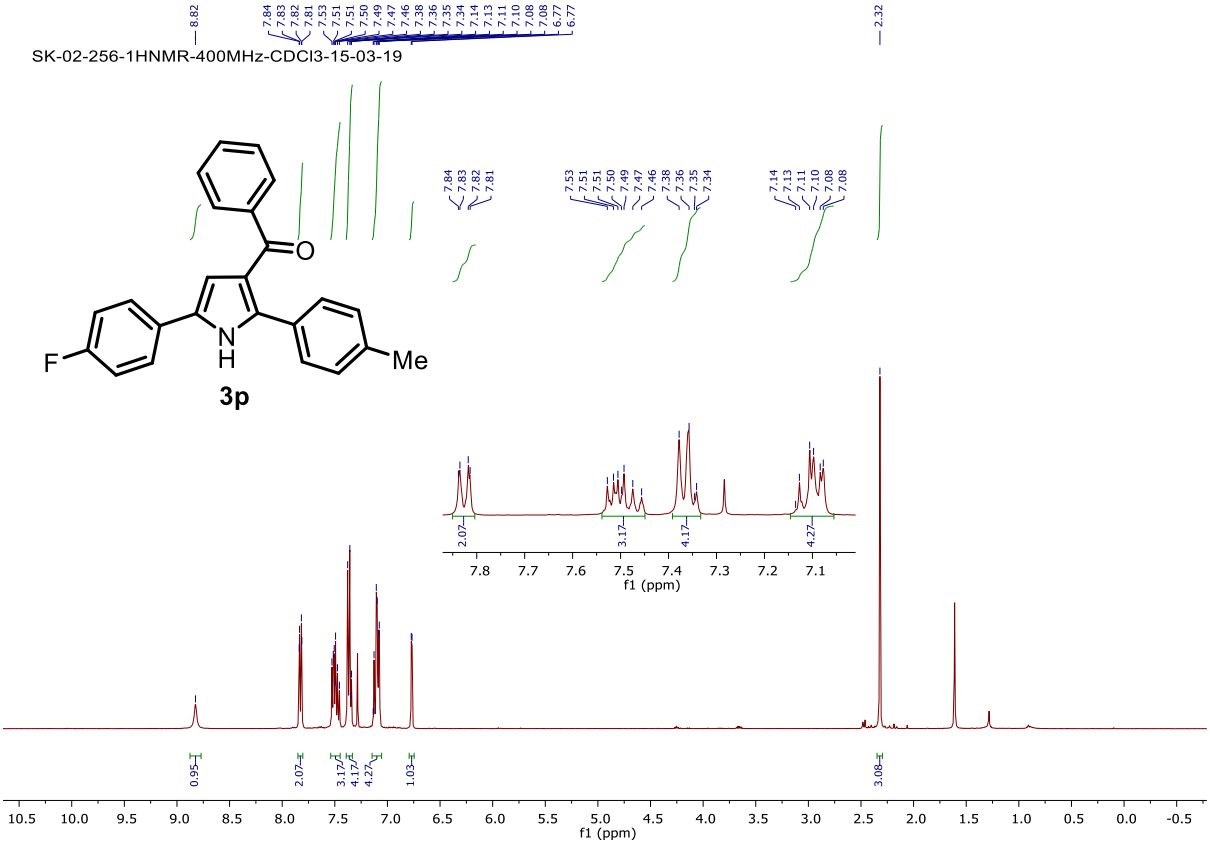


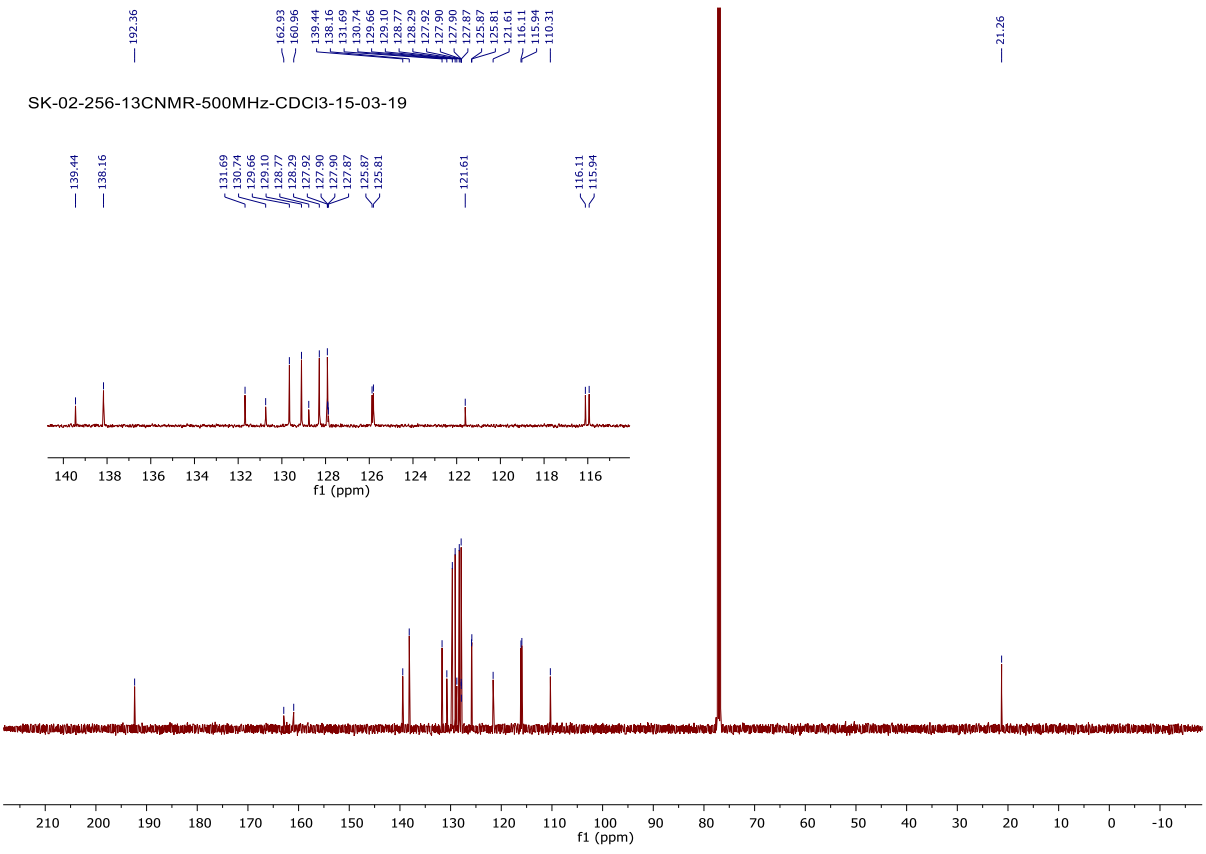

SK-02-313(R)-1HNMR-400MHz-CDCl3-28-08-2019
Ph
O
Me
N
H
Me
3n
f1 (ppm)

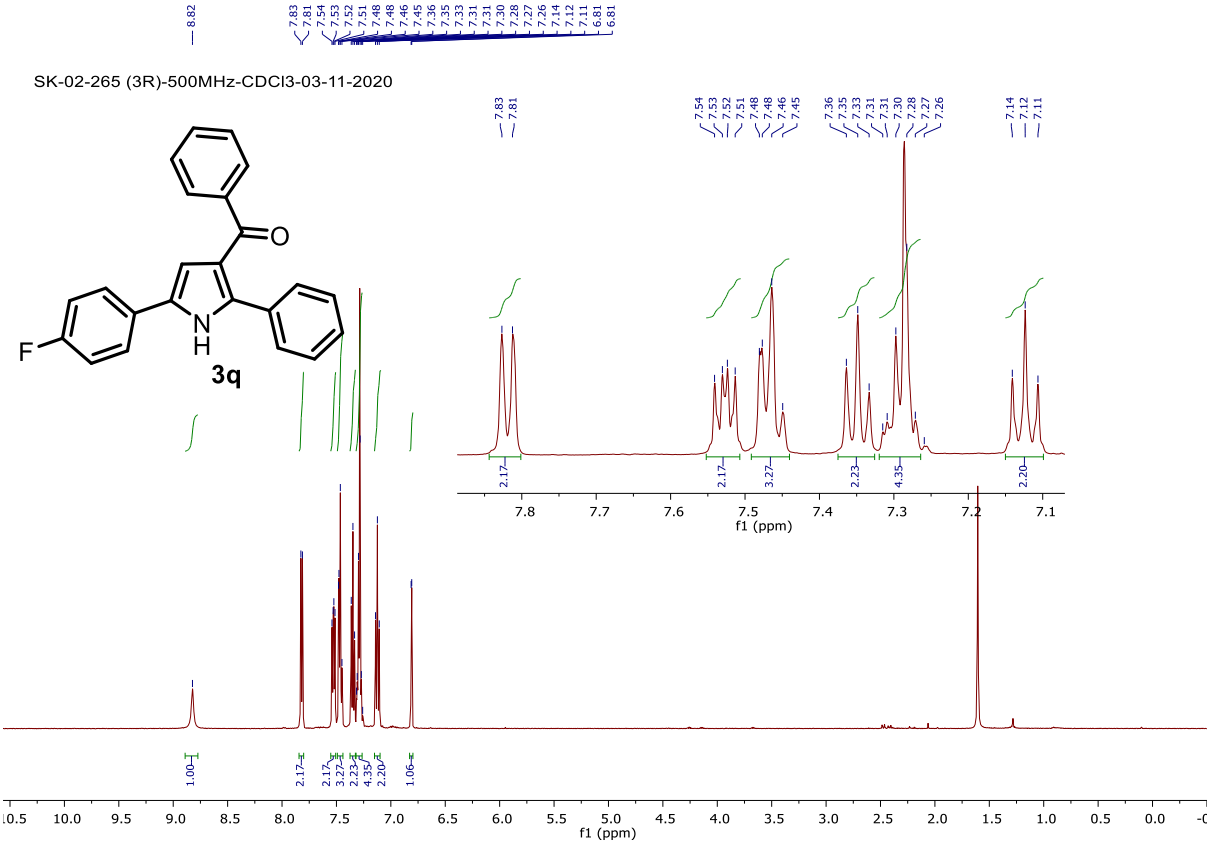

SK-02-313-13CNMR-500MHz-CDCl3-03-05-2019
f1 (ppm)

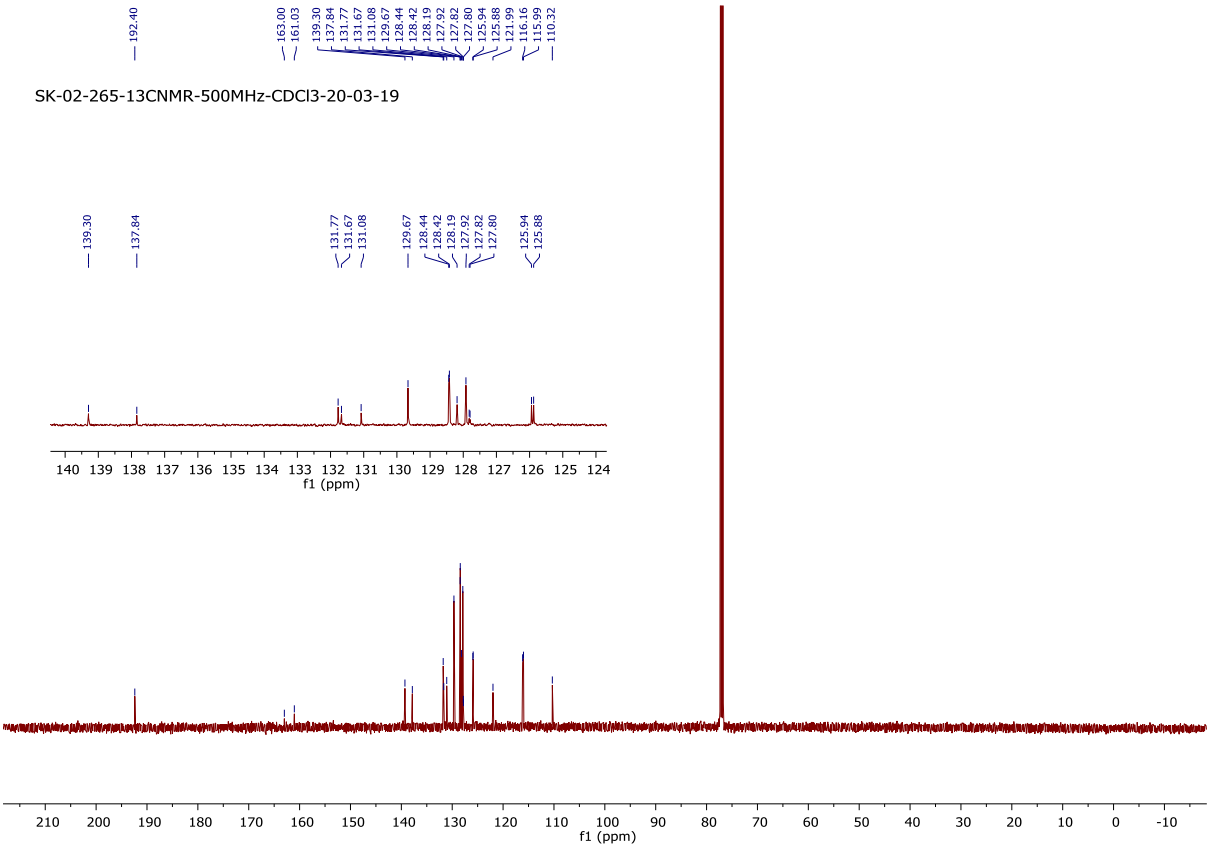

SK-03-318(4R)-1HNMR-400MHz-CDCl3-19-08-2019
Ph
O
Me
N
H
3o
f1 (ppm)

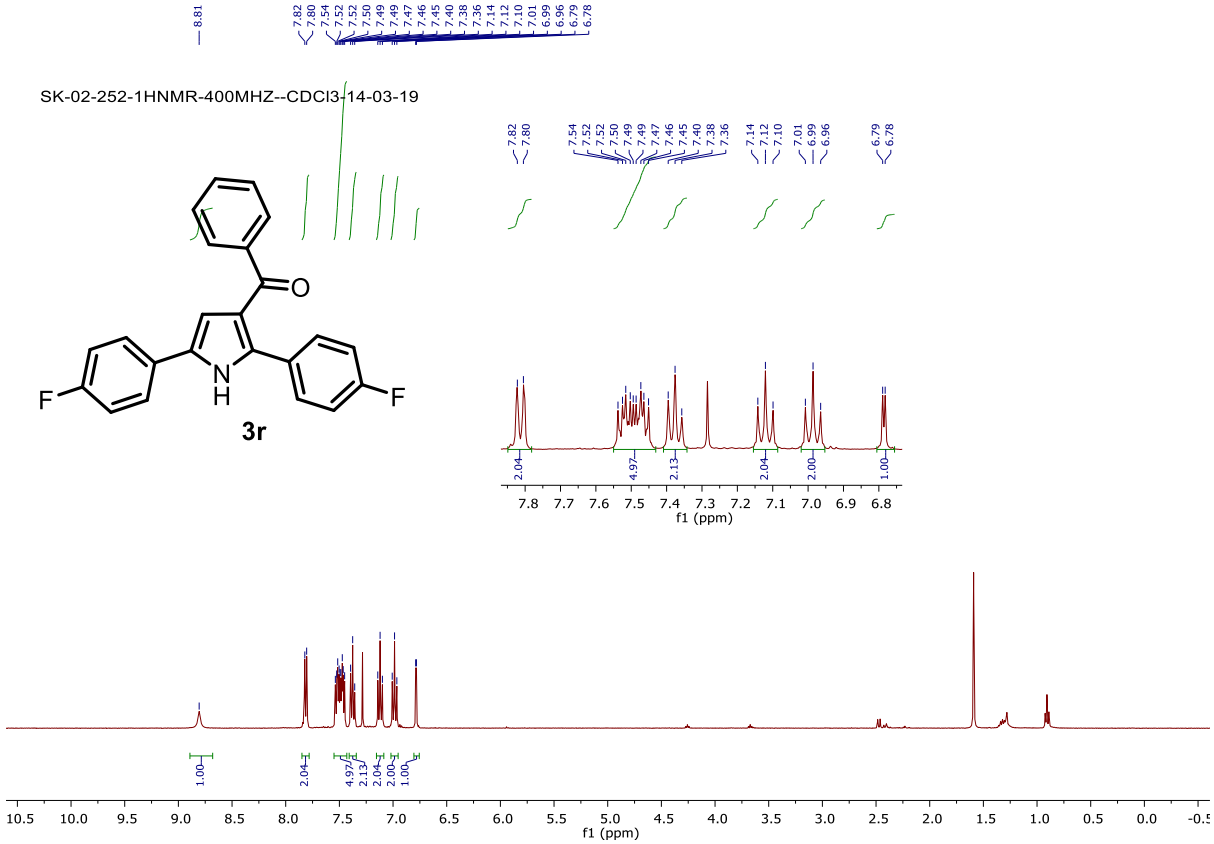

SK-03-18-13C-NMR-500MHz-CDCl3-10-08-2019
f1 (ppm)

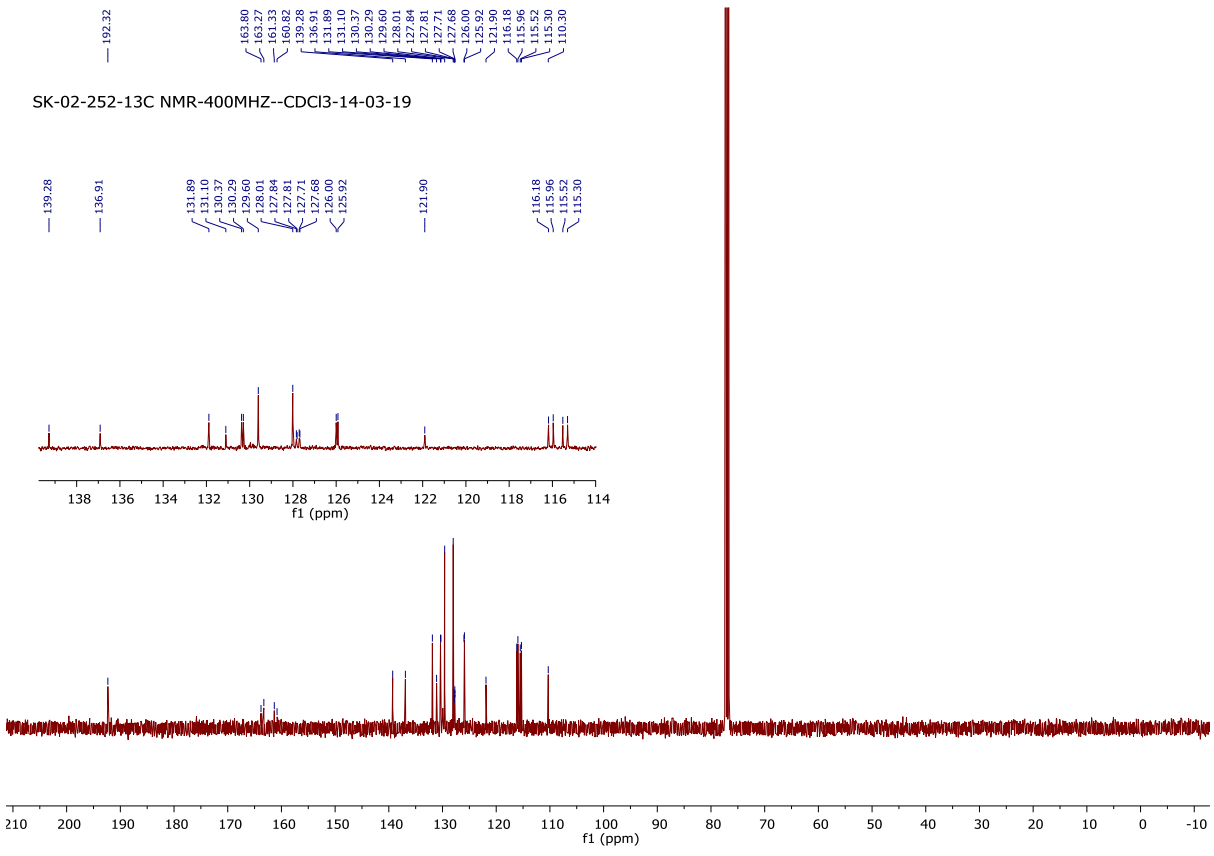

SK-02-256-1HNMR-400MHz-CDCl3-15-03-19
3p
f1 (ppm)

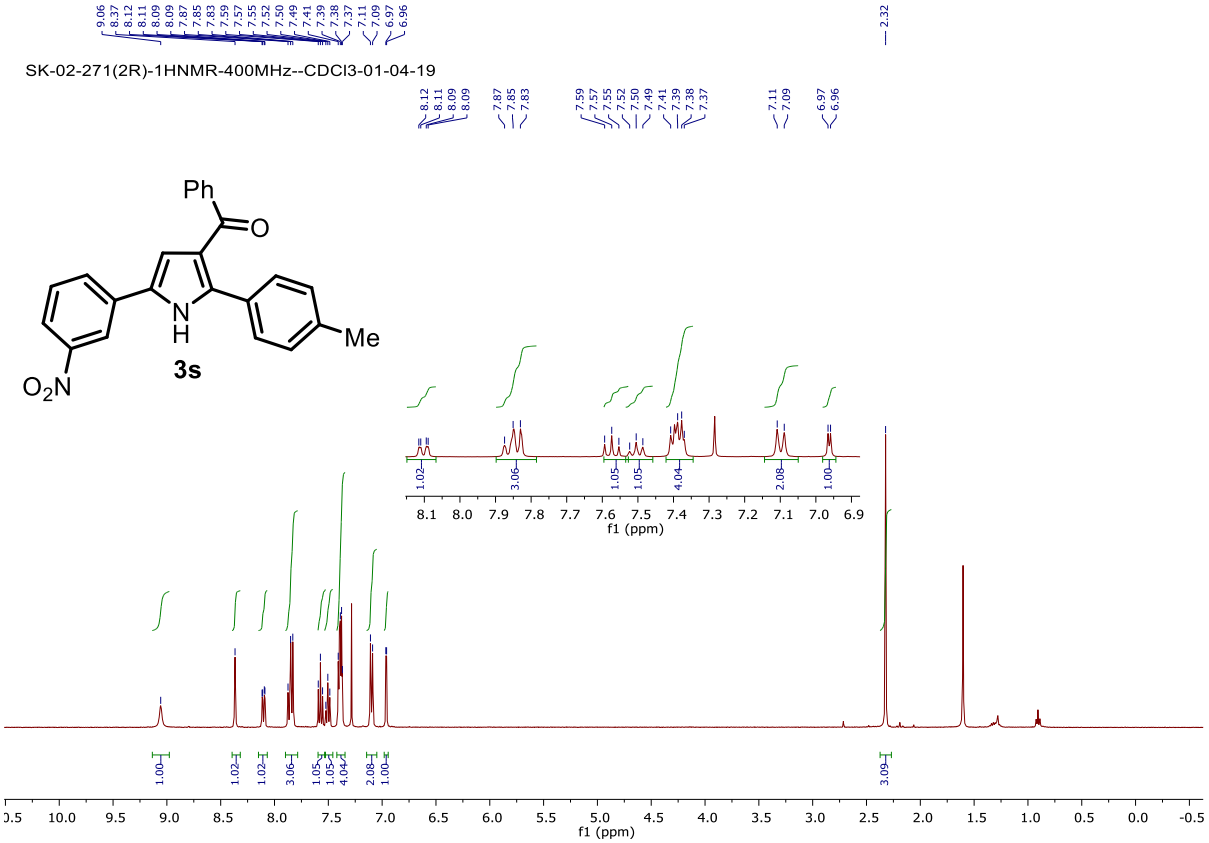

SK-02-256-13CNMR-500MHz-CDCl3-15-03-19
f1 (ppm)

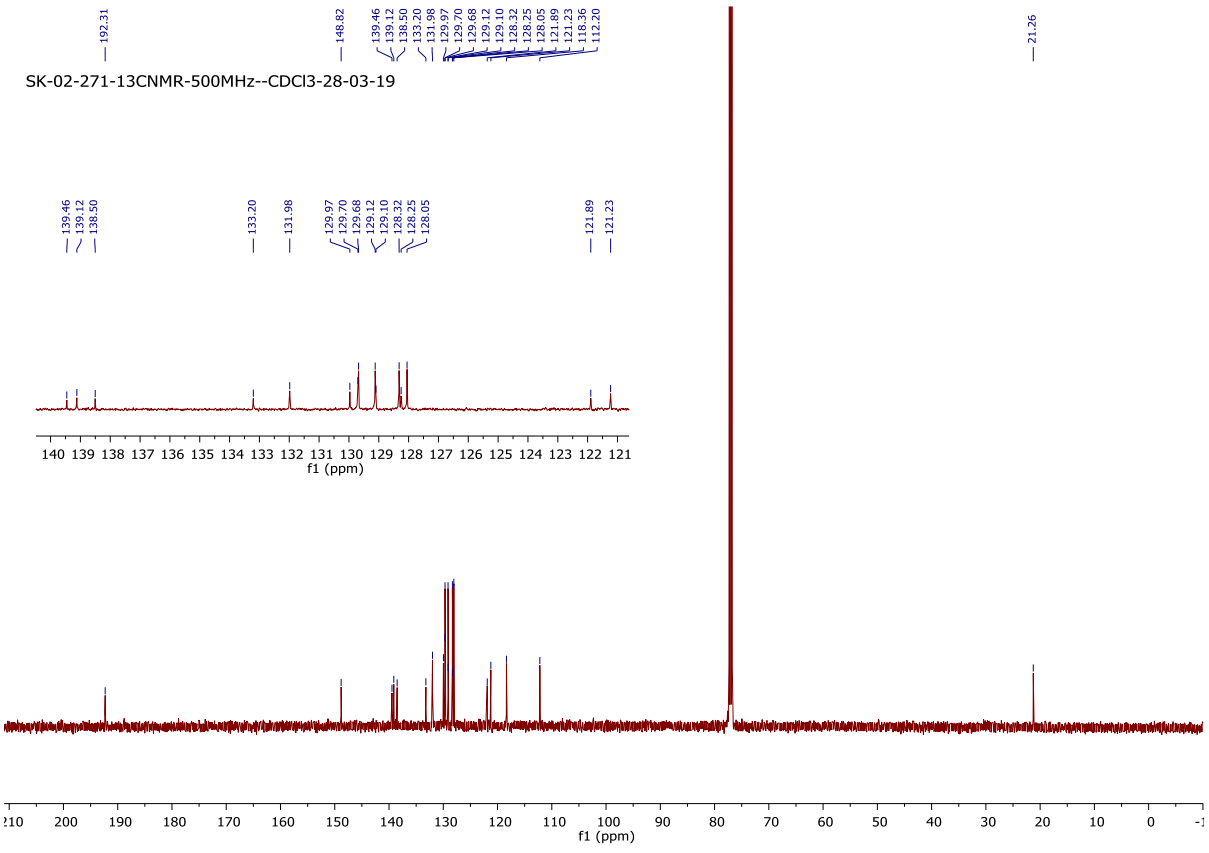

SK-02-265 (3R)-500MHz-CDCl3-03-11-2020
3q
f1 (ppm)

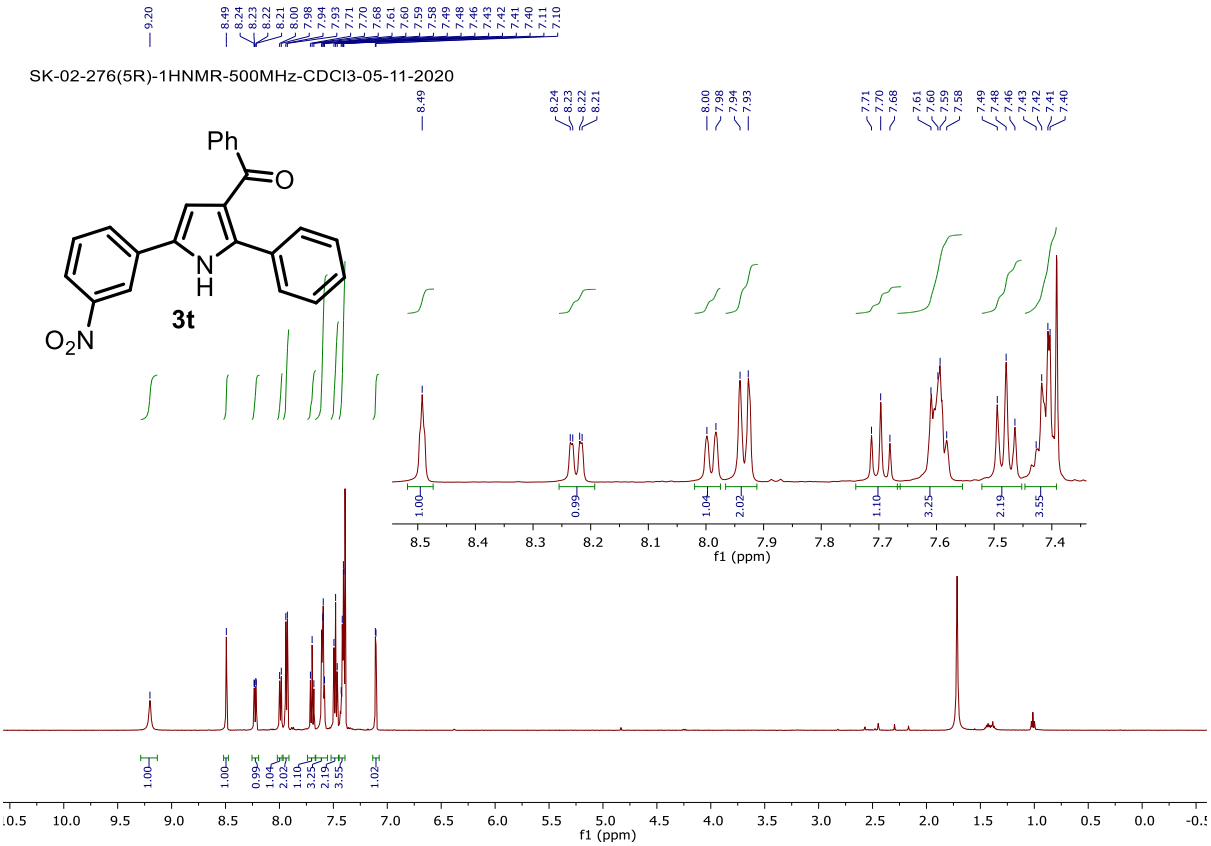

SK-02-265-13CNMR-500MHz-CDCl3-20-03-19
f1 (ppm)

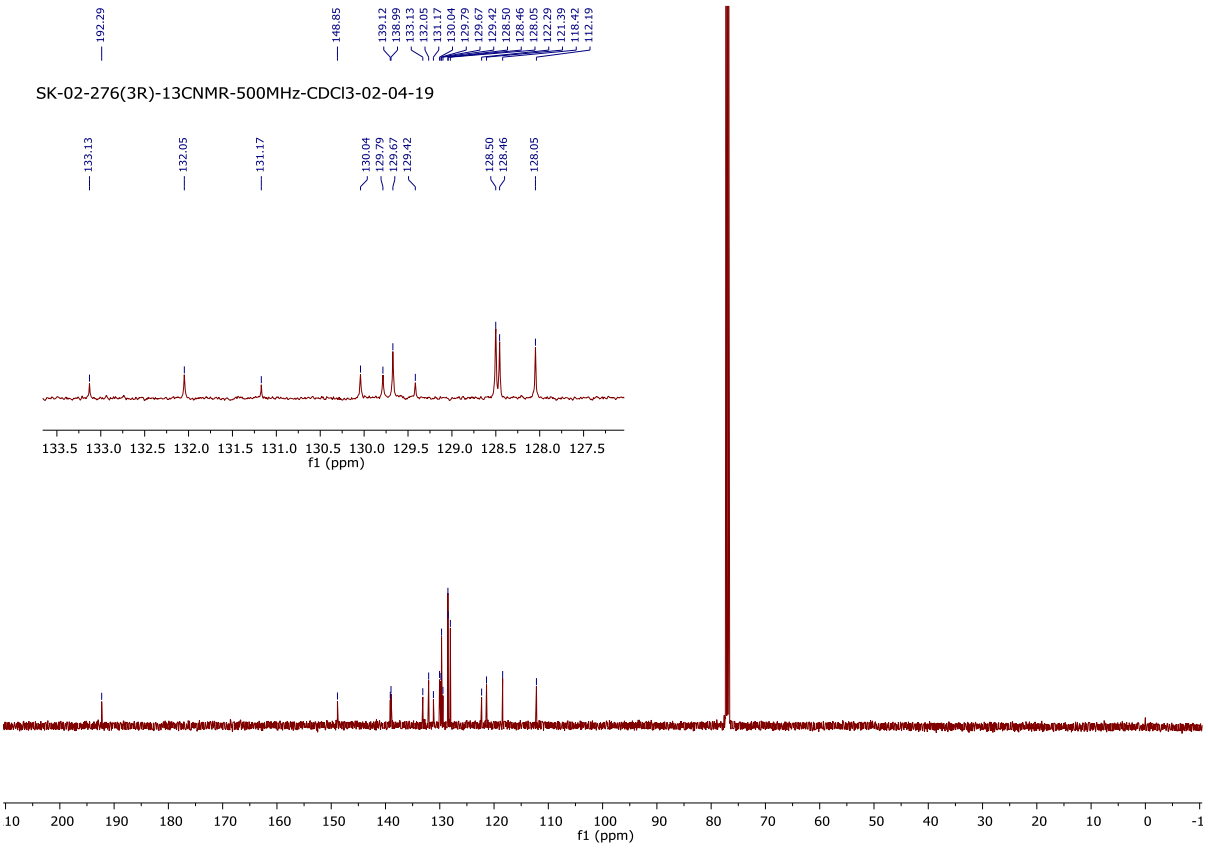

SK-02-252-1HNMR-400MHZ--CDCl3-14-03-19
3r
f1 (ppm)

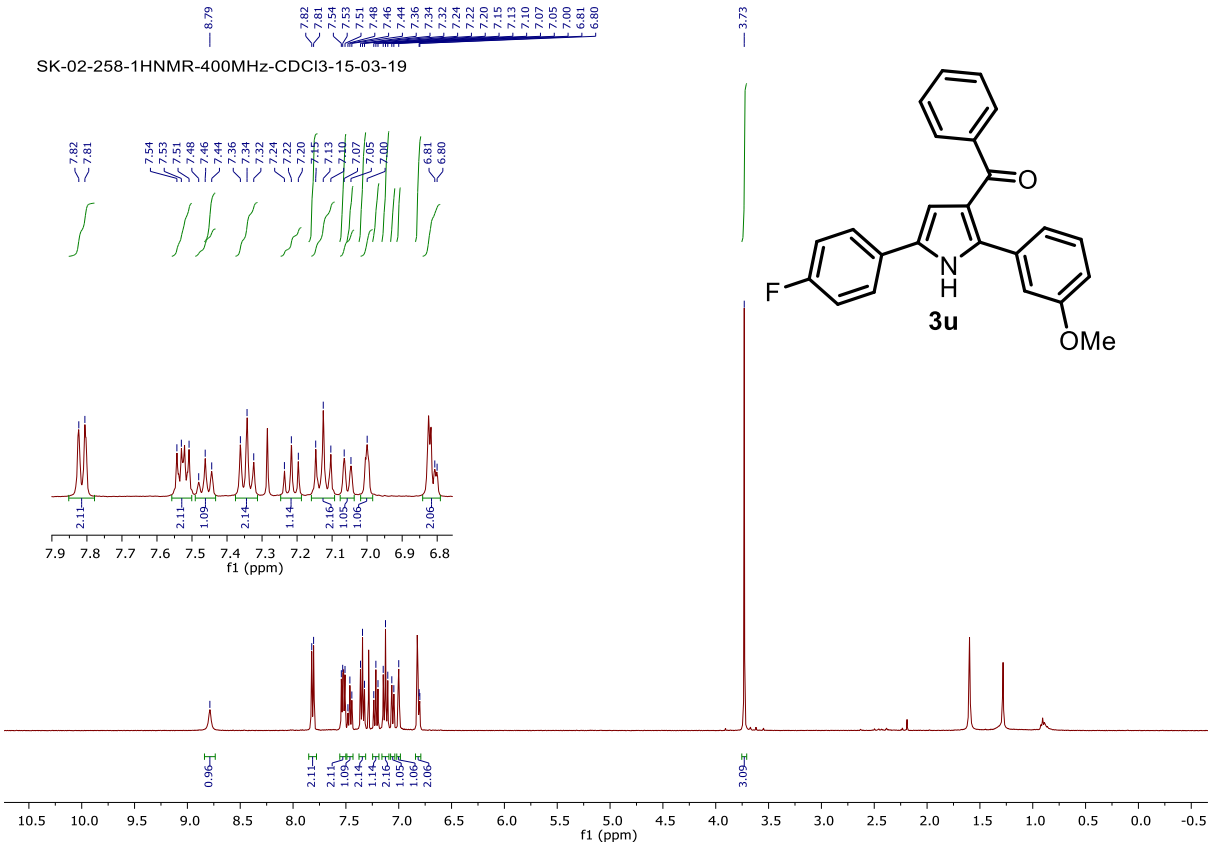

SK-02-252-13C NMR-400MHZ--CDCl3-14-03-19
f1 (ppm)

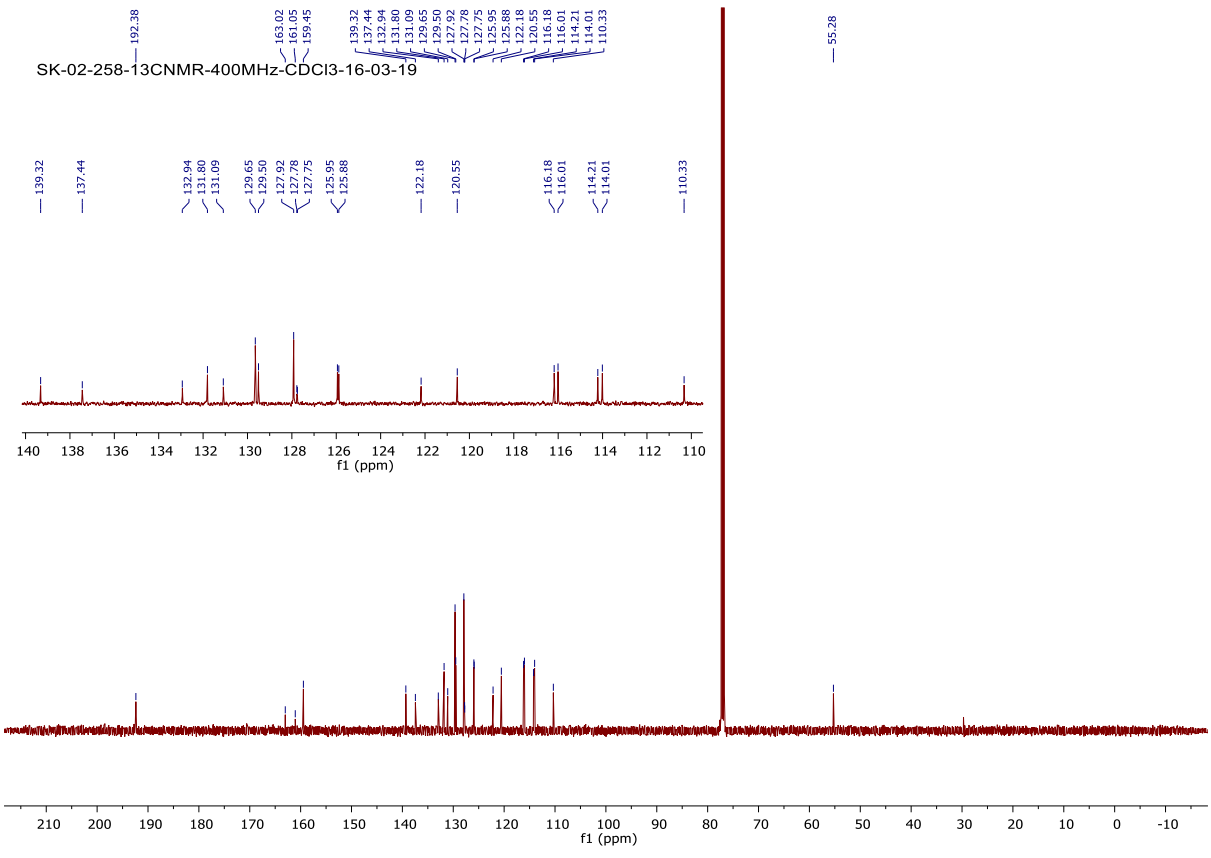

SK-02-271(2R)-1HNMR-400MHz--CDCl3-01-04-19
Ph
O
N
H
Me
O2N
3s
f1 (ppm)

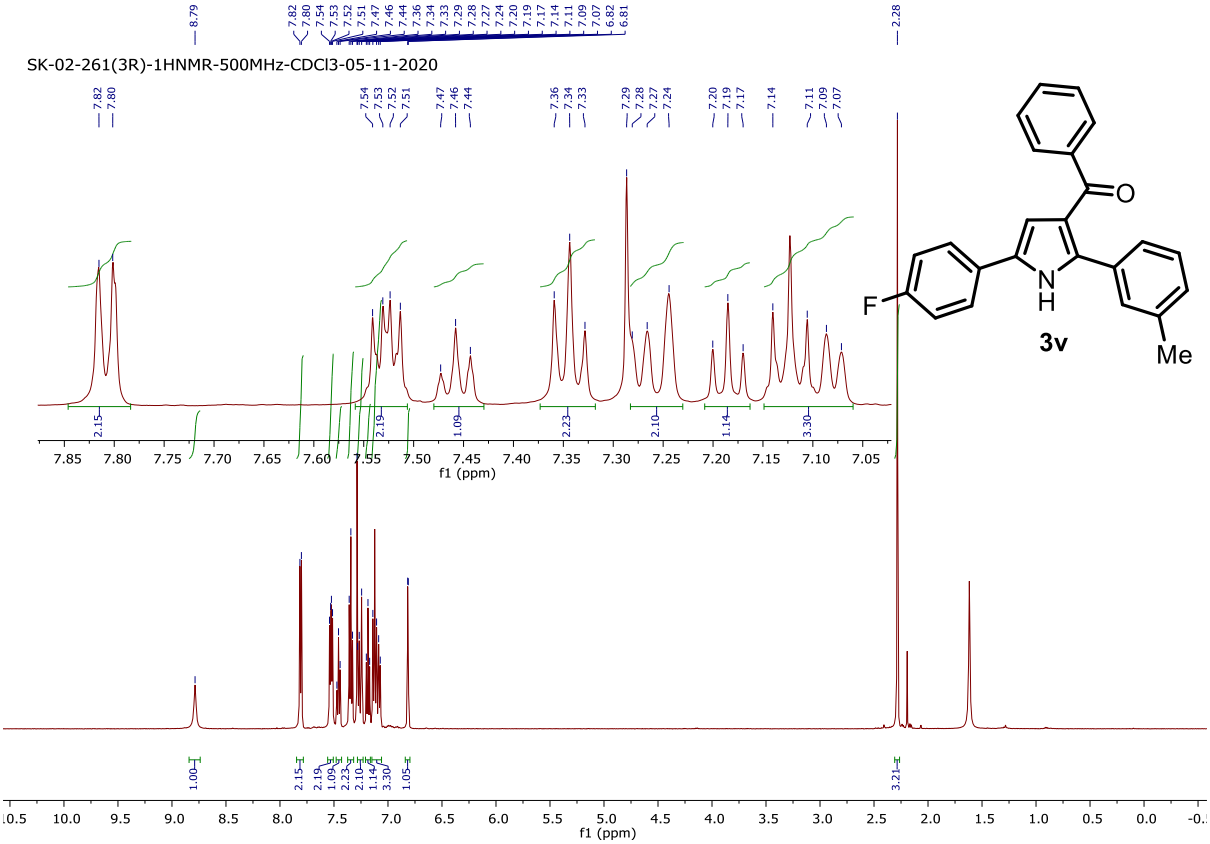

SK-02-271-13CNMR-500MHz--CDCl3-28-03-19
f1 (ppm)

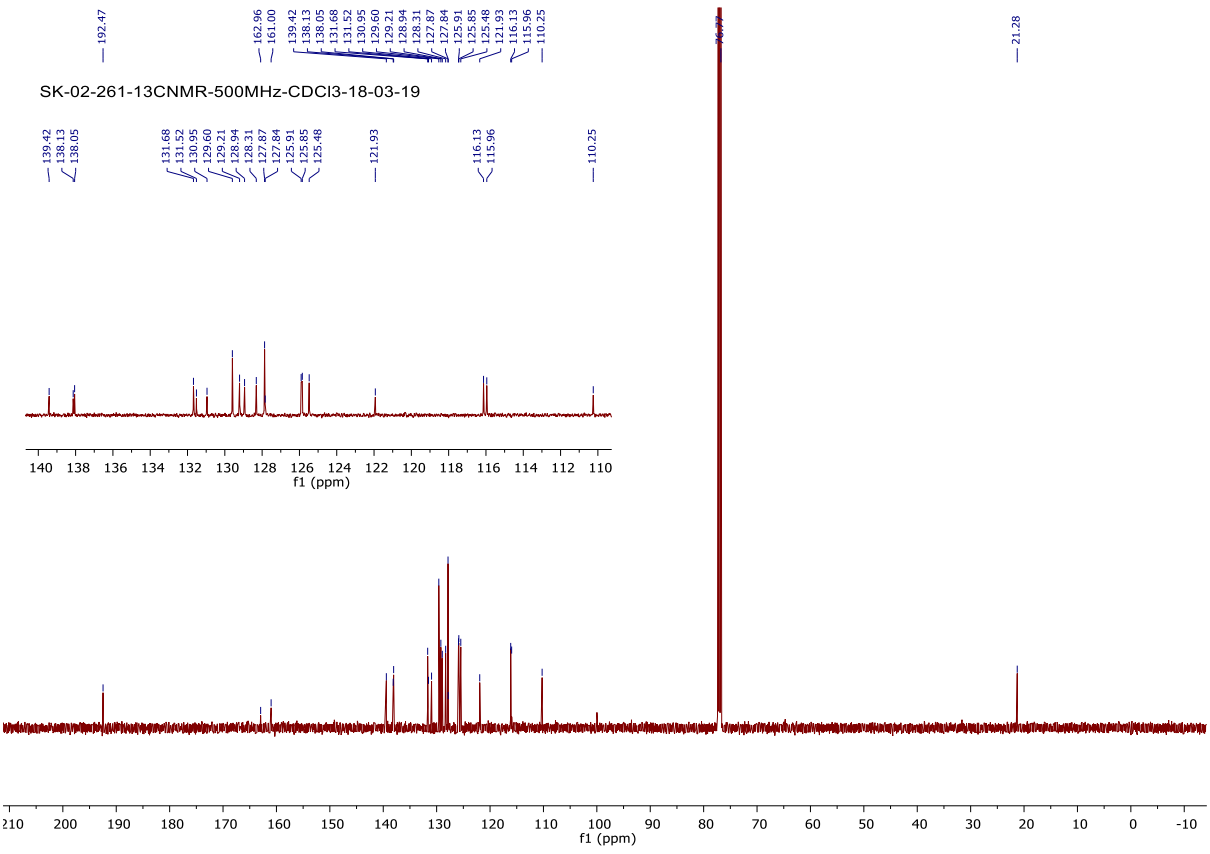

SK-02-276(5R)-1HNMR-500MHz-CDCl3-05-11-2020
Ph
O
N
H
O_2N
3t
f1 (ppm)

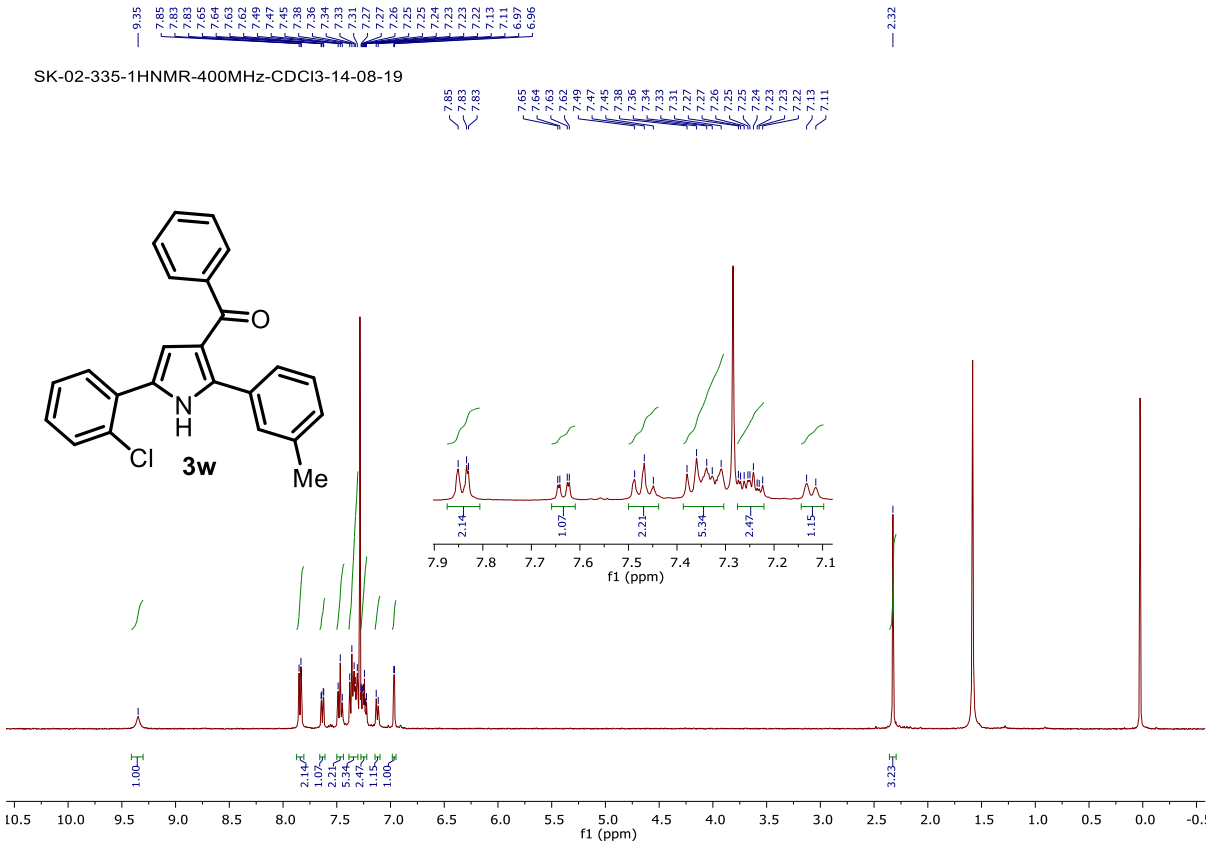

SK-02-276(3R)-13CNMR-500MHz-CDCl3-02-04-19
f1 (ppm)

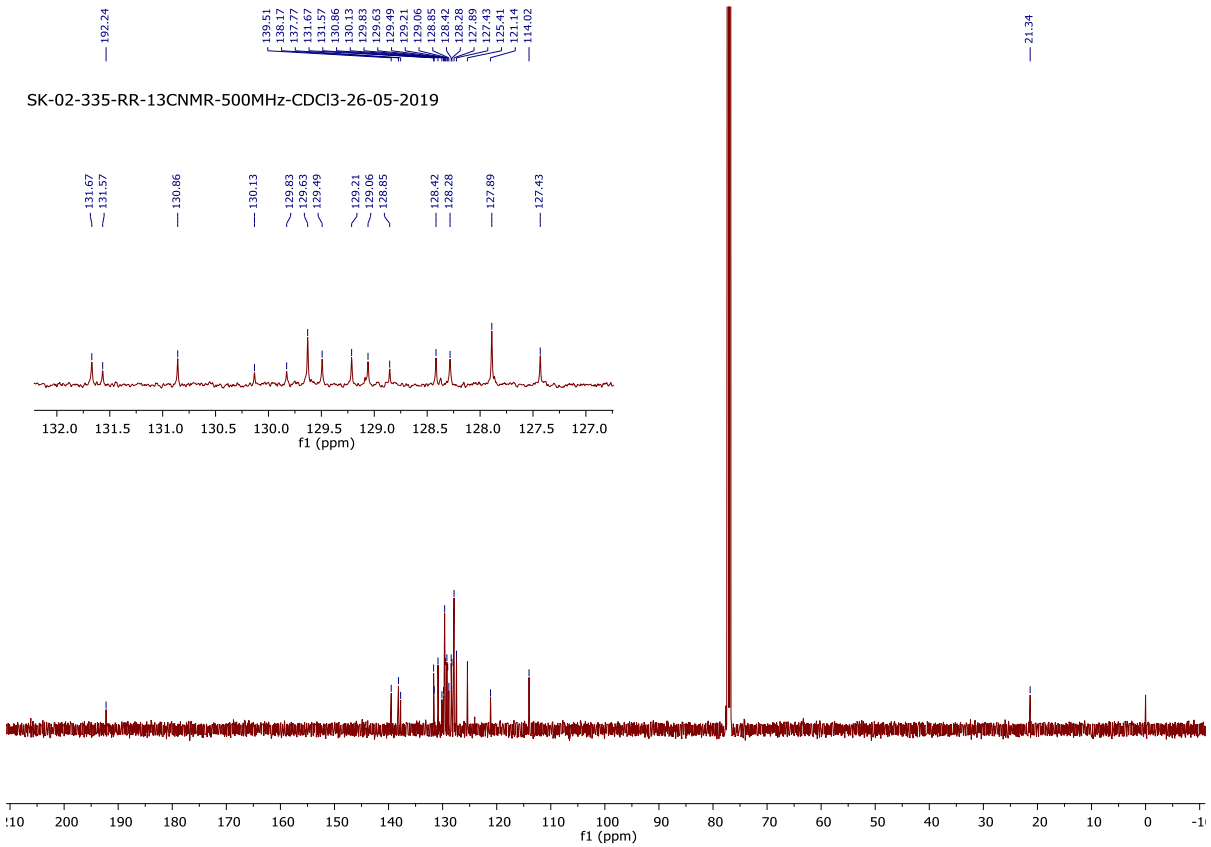

SK-02-258-1HNMR-400MHz-CDCl3-15-03-19
8.79
7.82
7.81
7.54
7.53
7.51
7.48
7.46
7.44
7.36
7.34
7.32
7.24
7.22
7.20
7.15
7.13
7.10
7.07
7.05
7.00
6.81
6.80
3.73
O
N
H
F
OMe
3u
f1 (ppm)

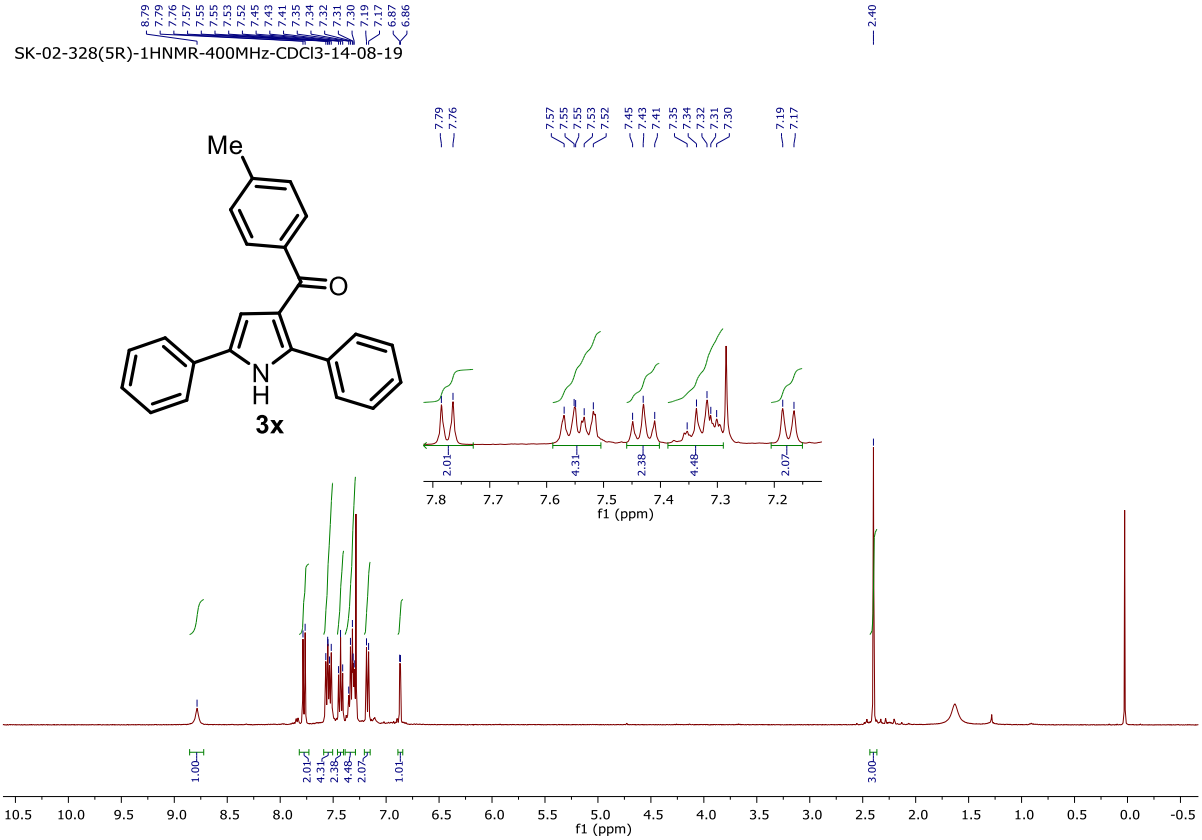

SK-02-258-13CNMR-400MHz-CDCl3-16-03-19
192.38
163.02
161.05
159.45
139.32
137.44
132.94
131.80
131.09
129.65
129.50
127.92
127.78
127.75
125.95
125.88
122.18
120.55
116.18
116.01
114.21
114.01
110.33
55.28
f1 (ppm)

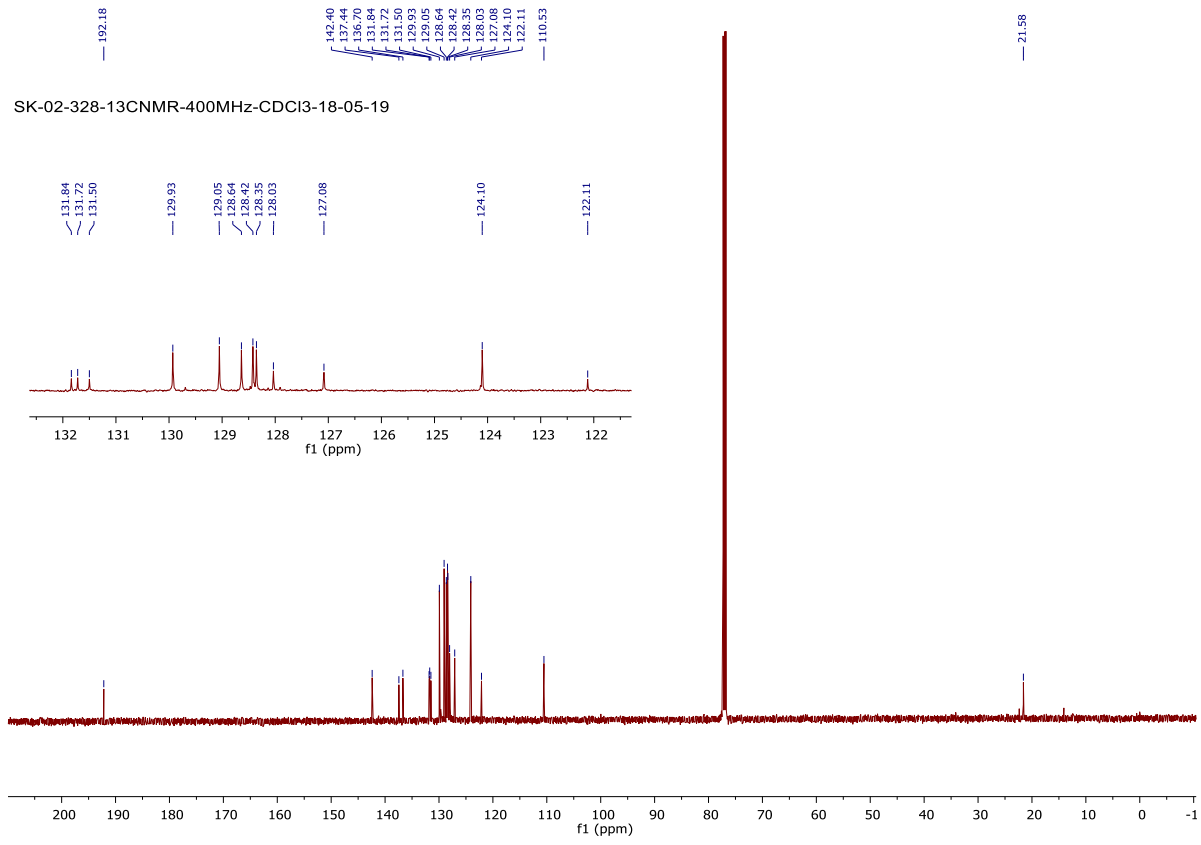

SK-02-261(3R)-1HNMR-500MHz-CDCl3-05-11-2020
f1 (ppm)
O
N
H
F
Me
3v

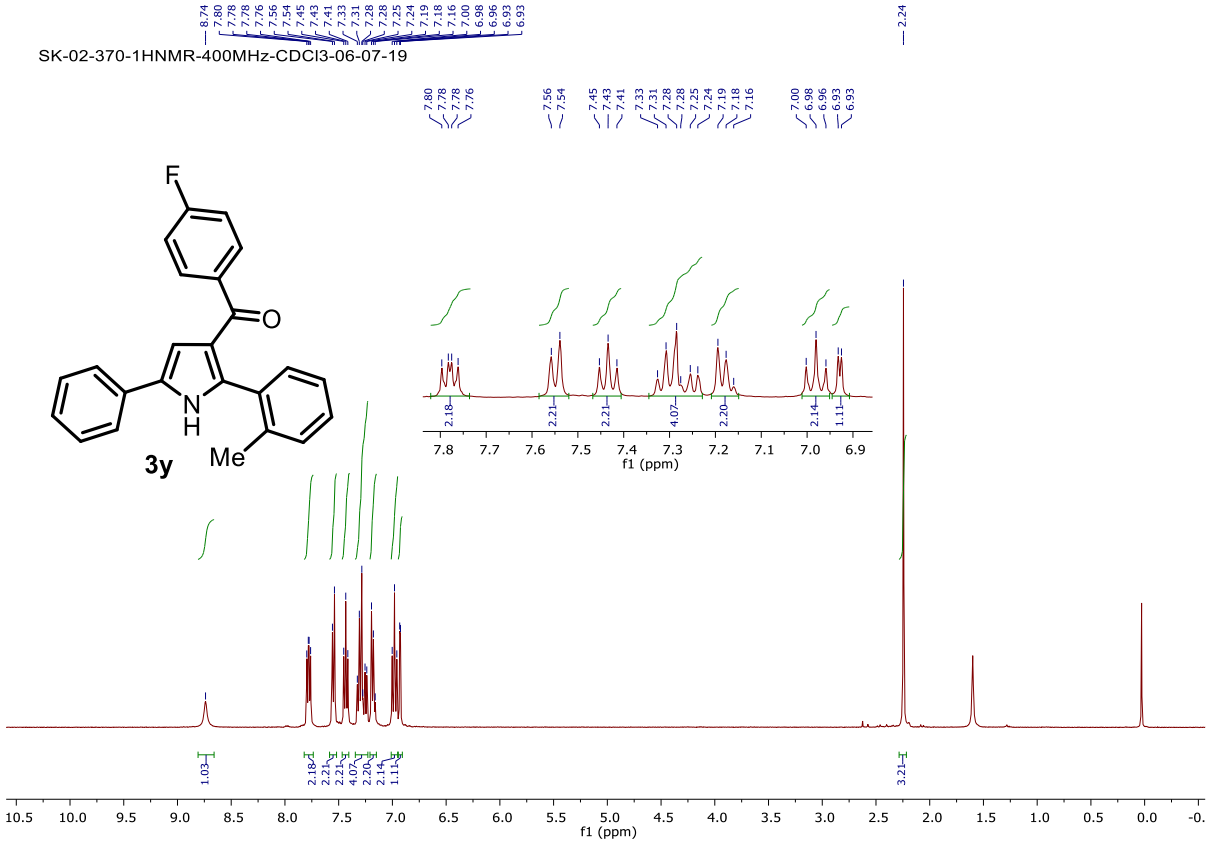

SK-02-261-13CNMR-500MHz-CDCl3-18-03-19
f1 (ppm)

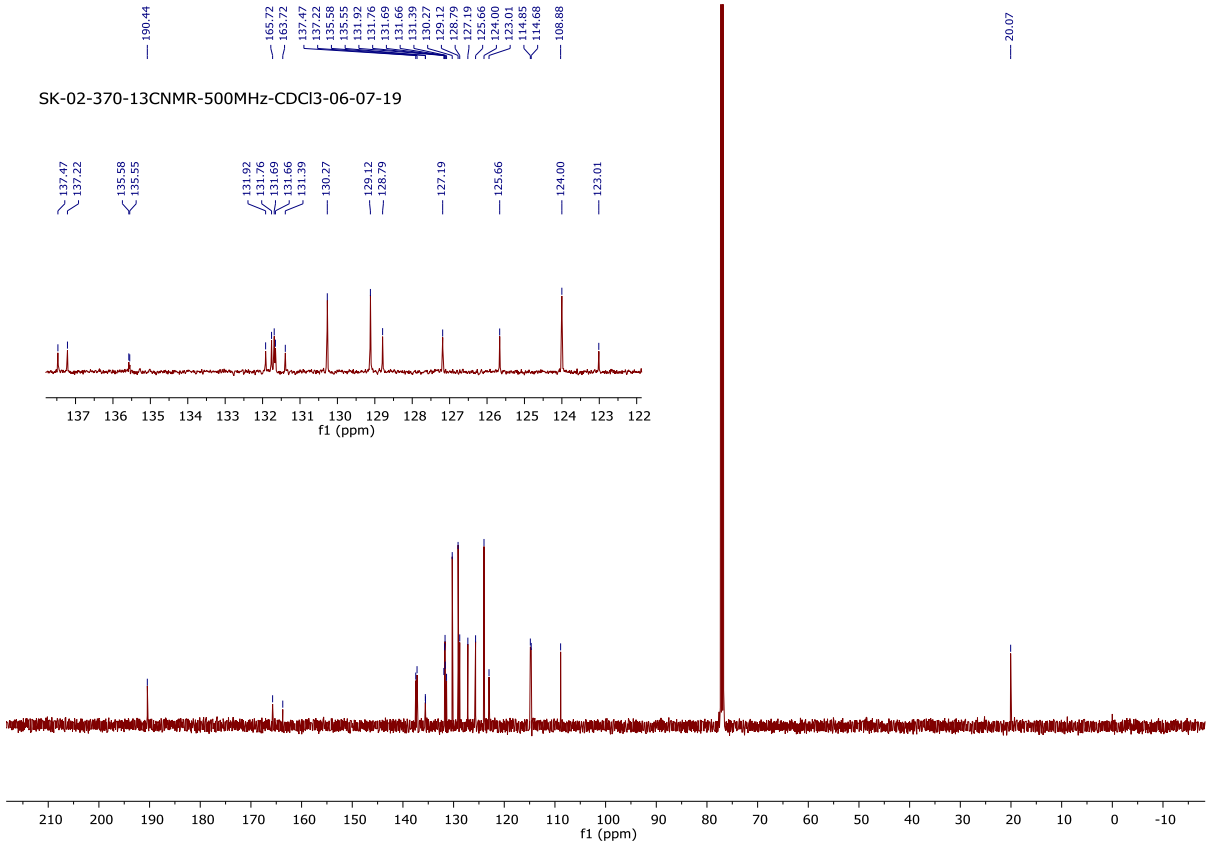

SK-02-335-1HNMR-400MHz-CDCl3-14-08-19
3w
Cl
Me
f1 (ppm)

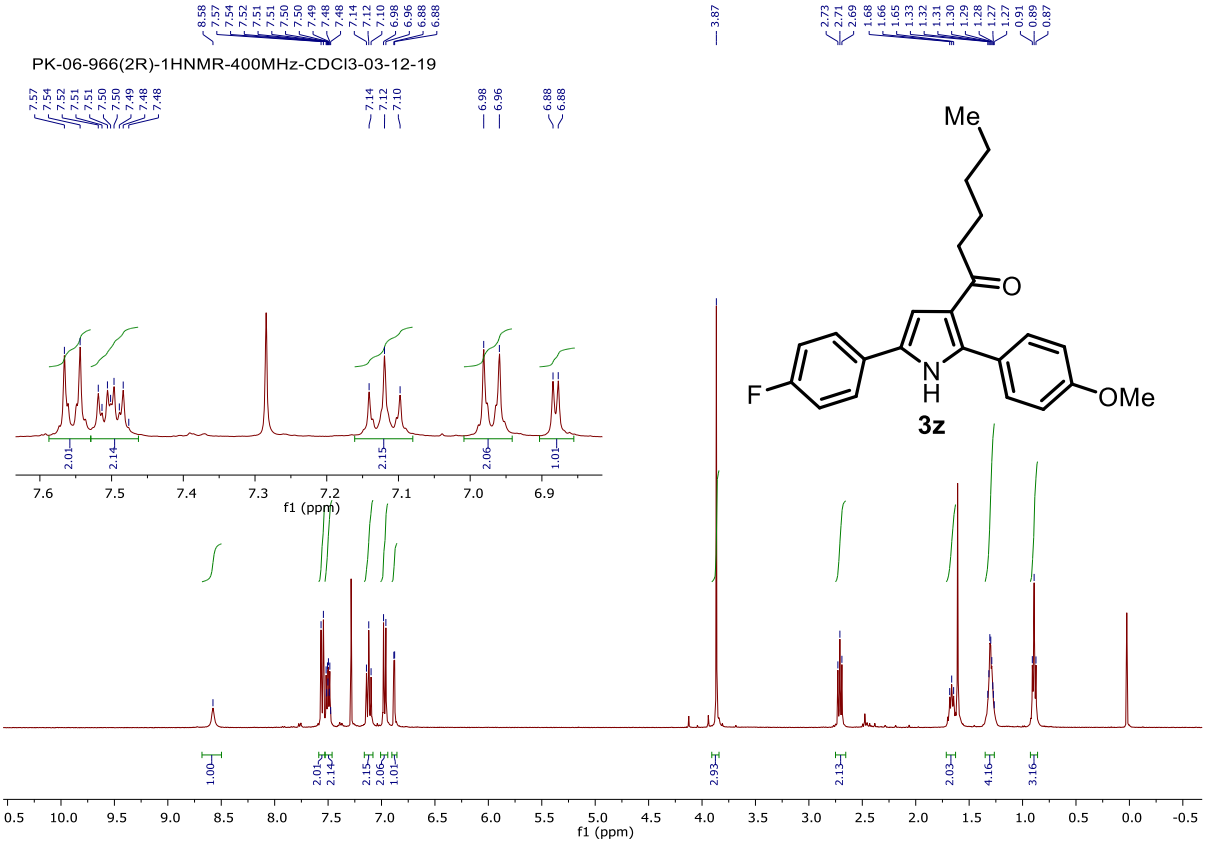

SK-02-335-RR-13CNMR-500MHz-CDCl3-26-05-2019
f1 (ppm)

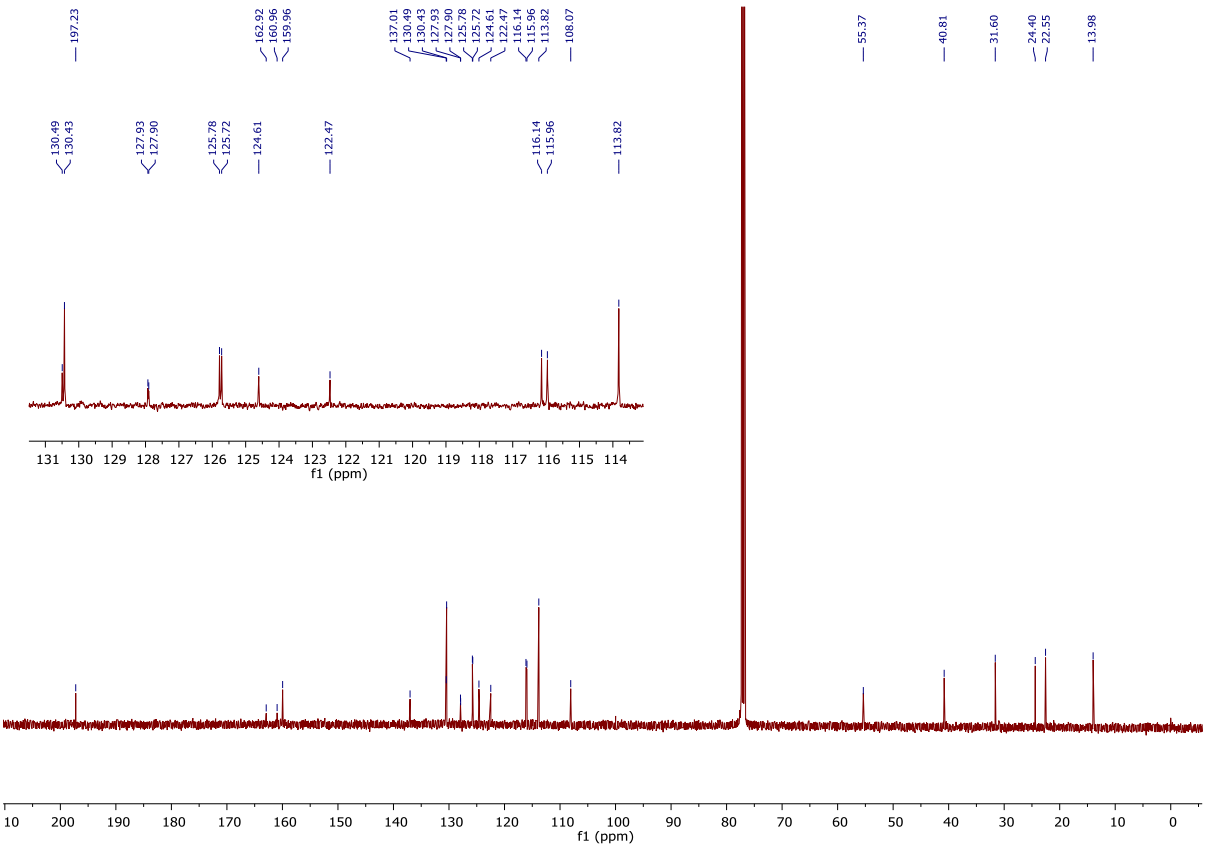

SK-02-328(5R)-1HNMR-400MHz-CDCl3-14-08-19
Me
O
N
H
3x
f1 (ppm)

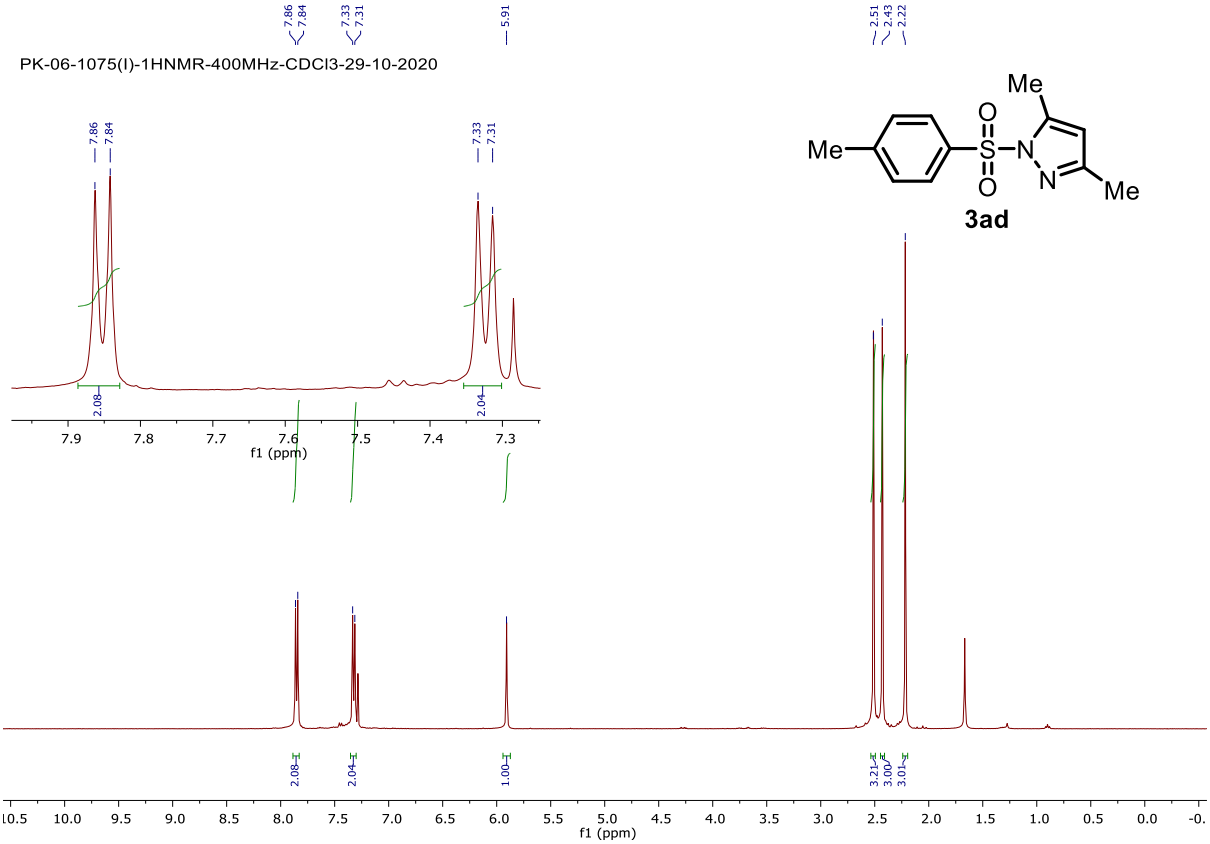

SK-02-328-13CNMR-400MHz-CDCl3-18-05-19
f1 (ppm)

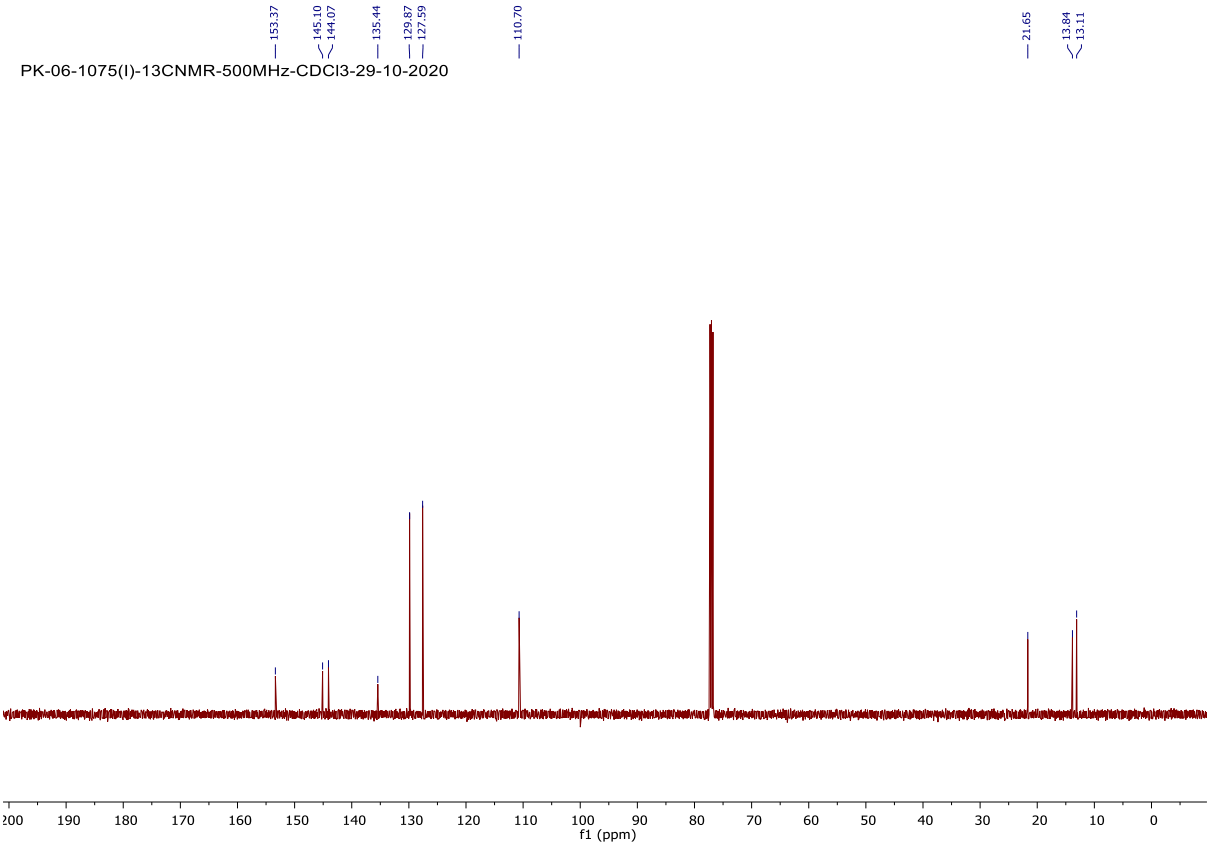

SK-02-370-1HNMR-400MHz-CDCl3-06-07-19
F
O
N
H
Me
3y
f1 (ppm)


SK-02-370-13CNMR-500MHz-CDCl3-06-07-19
f1 (ppm)

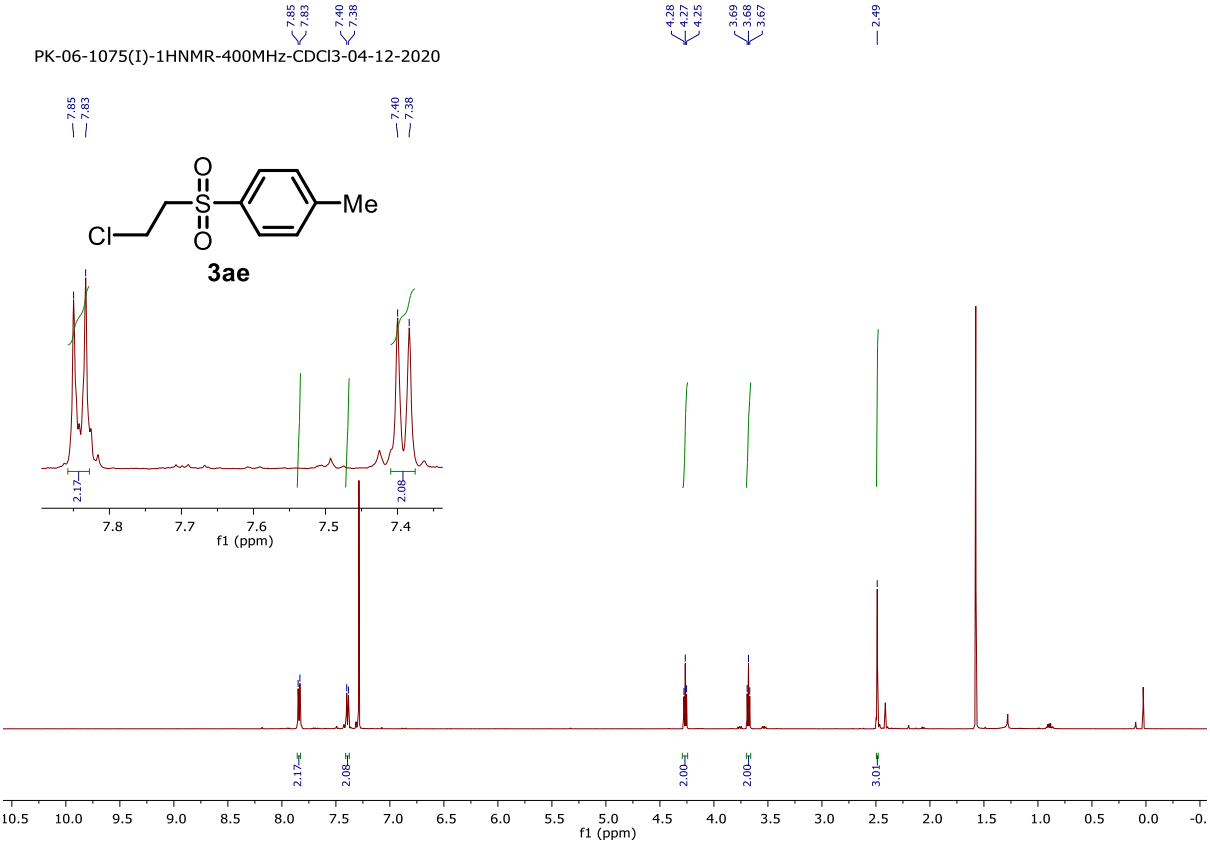

PK-06-966(2R)-1HNMR-400MHz-CDCl3-03-12-19
Me
O
N
H
F
OMe
3z
f1 (ppm)


f1 (ppm)

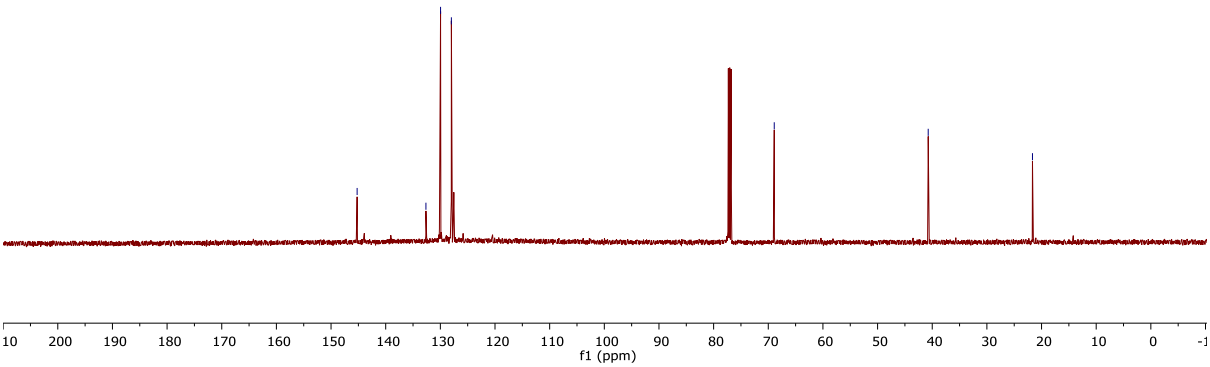

PK-06-1075(I)-1HNMR-400MHz-CDCl3-29-10-2020
7.86
7.84
7.33
7.31
5.91
2.51
2.43
2.22
Me
Me
Me
O
S
N
N
O
3ad
2.08
2.04
f1 (ppm)
1.00
3.21
3.00
3.01

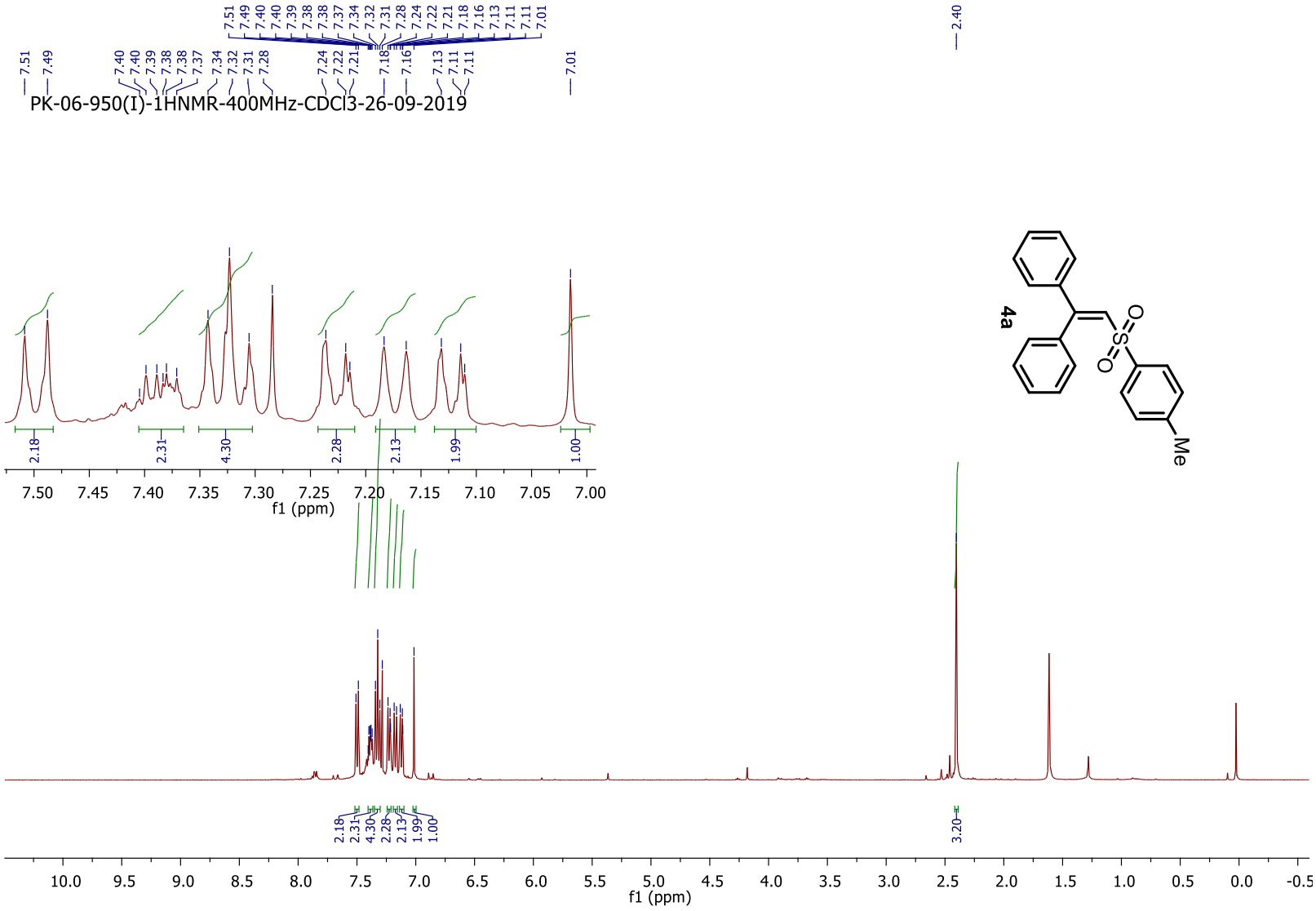

PK-06-1075(I)-13CNMR-500MHz-CDCl3-29-10-2020
153.37
145.10
144.07
135.44
129.87
127.59
110.70
21.65
13.84
13.11
f1 (ppm)

PK-06-1075(I)-1HNMR-400MHz-CDCl3-04-12-2020



PK-06-1075(I)-1HNMR-500MHz-CDCl3-29-10-2020



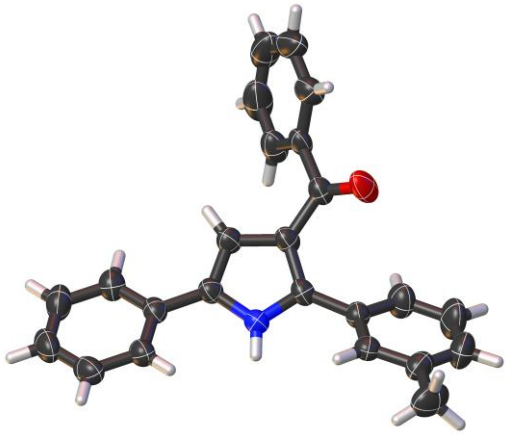

PK-06-950(I)-1HNMR-400MHz-CDCl3-26-09-2019
7.51
7.49
7.40
7.40
7.39
7.38
7.38
7.37
7.34
7.32
7.31
7.28
7.24
7.22
7.21
7.18
7.16
7.13
7.11
7.11
7.01
2.40
2.18
2.31
4.30
2.28
2.13
1.99
1.00
3.20
f1 (ppm)
4a
O
S
O
Me

X-ray diffraction structural analysis data of 3j:

Table 1 Crystal data and structure refinement for F1_a.

CCDC:1997416

Identification code	F1_a
Empirical formula	$C_{24}H_{19}NO$
Formula weight	337.40
Temperature/K	287.55
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.2820(13)
b/Å	13.5704(9)
c/Å	10.3175(9)
α/°	90
β/°	110.860(2)
γ/°	90
Volume/Å^3	1868.6(3)
Z	4
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	0.073
F(000)	712.0
Crystal size/mm^3	0.57 × 0.45 × 0.34
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.182 to 55.956
Index ranges	$-18 \leq h \leq 18$, $-14 \leq k \leq 17$, $-13 \leq l \leq 13$
Reflections collected	18733
Independent reflections	4495 [R_{int} = 0.1084, R_{sigma} = 0.1107]
Data/restraints/parameters	4495/0/236
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0701, wR_2 = 0.1276
Final R indexes [all data]	R_1 = 0.1752, wR_2 = 0.1598
Largest diff. peak/hole / e Å^{-3}	0.15/-0.18



Thermal ellipsoids shown at 50% probability level.

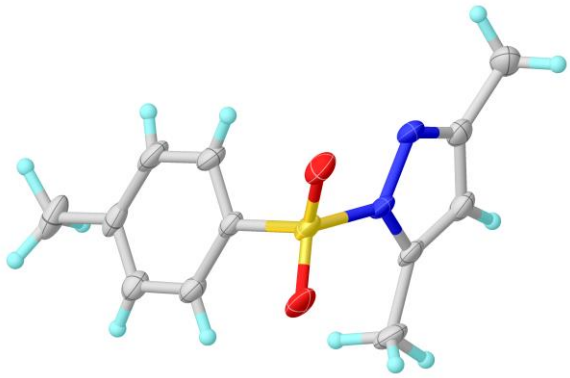
Figure S1. X-ray structure of (**3j**)

X-ray diffraction structural analysis data of 3ad:

Table 2 Crystal data and structure refinement for 3ad.

CCDC: 2060949

Identification code	Final
Empirical formula	$C_{12}H_{14}N_2O_2S$
Formula weight	250.31
Temperature/K	140(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.912(3)
b/Å	15.262(4)
c/Å	8.115(2)
α/°	90
β/°	98.518(10)
γ/°	90
Volume/Å^3	1214.1(5)
Z	4
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	0.258
F(000)	528.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.628 to 49.918
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -9 ≤ l ≤ 9
Reflections collected	25098
Independent reflections	2086 [R_{int} = 0.0450, R_{sigma} = 0.0194]
Data/restraints/parameters	2086/0/157
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0312, wR_2 = 0.0905
Final R indexes [all data]	R_1 = 0.0349, wR_2 = 0.0946
Largest diff. peak/hole / e Å^{-3}	0.31/-0.30



Thermal ellipsoids shown at 50% probability level.

Figure S2. X-ray structure of (**3ad**)

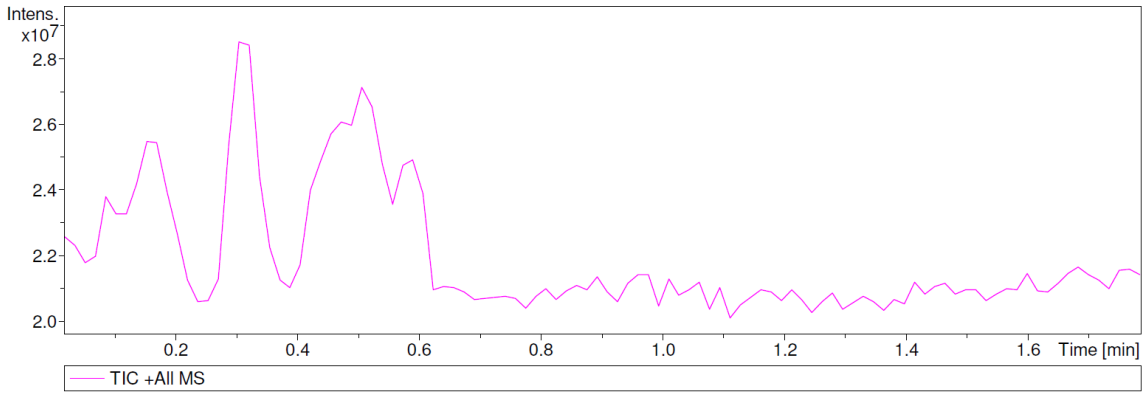
Display Report

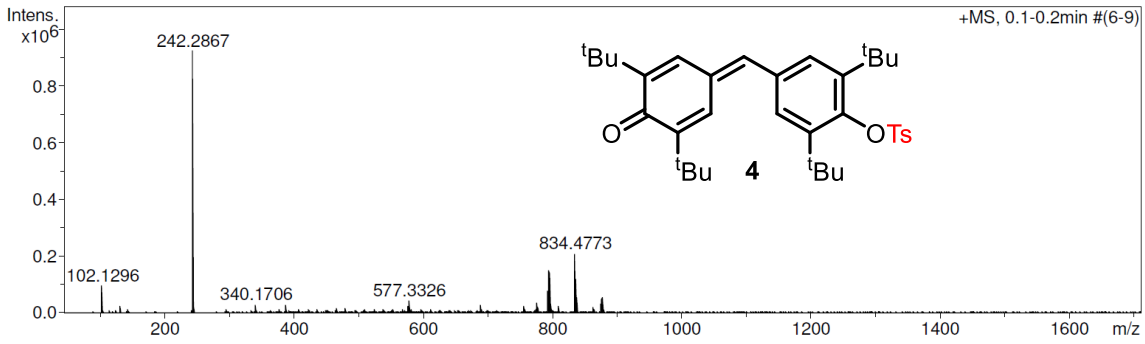
Analysis Info

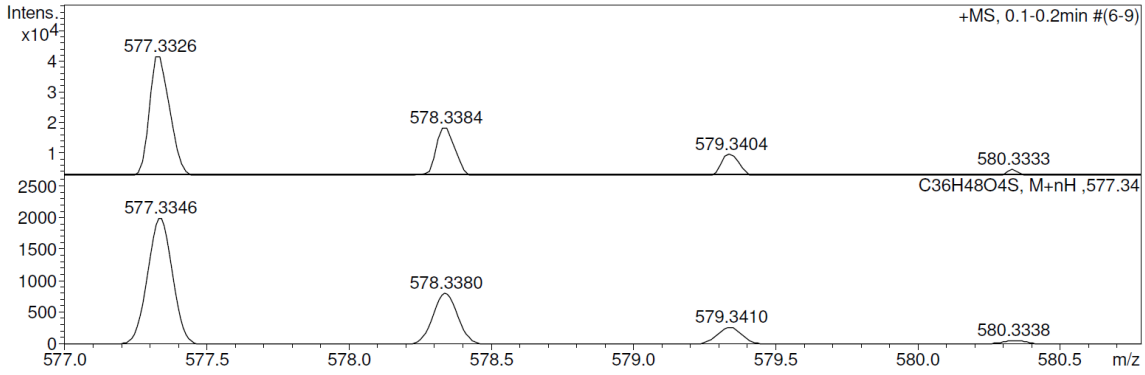
Analysis Name	D:\Data\new user data 2021\March-2021\01-Mar\Dr.M.Kapur-SK-05-37-DS-II.d	Acquisition Date	3/1/2021 4:24:33 PM
Method	tune mix_low.New.021117.m	Operator	RUCHI
Sample Name	SK-05-37-DS-II	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste







Display Report

Analysis Info

Analysis Name	D:\Data\NEW USER DATA 2017\2019\SEP\27 sep\Dr.M.Kapur-PK-06-950.d	Acquisition Date	9/27/2019 10:03:51 AM
Method	tune_low.m	Operator	RUCHI
Sample Name	PK-06-950	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste