Tandem Electrophilic Thiocyanation/Cyclization of *α*-Alkynyl Oximes for Synthesis of 4-Thiocyanatoisoxazoles

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Supporting Information

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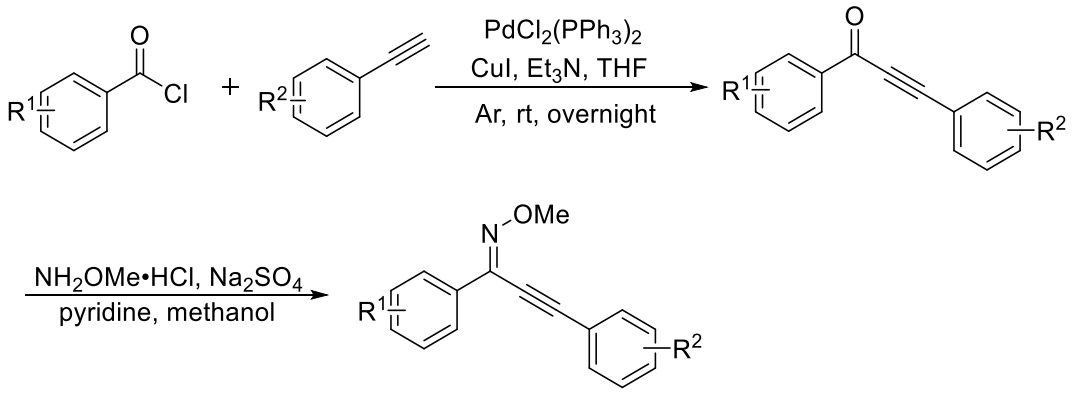
1. General Information

All chemicals were bought from commercial companies and used directly unless noted. All reactions monitored by thin-layer chromatography (TLC). TLC was performed on silica gel F_{254} TLC glass plates and visualized with UV light. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 500 M NMR spectrometers ($CDCl_3$, DMSO-d_6 as solvent). ^{19}F NMR were recorded with Brucker Avance (471 MHz) ^{19}F NMR chemical shifts are reported in ppm from trichlorofluoromethane. ^{1}H NMR spectra were recorded with Brucker Avance (500 MHz) spectrometer, ^{1}H NMR chemical shifts are reported in ppm from tetramethylsilane, ^{13}C $\{^{1}H\}$ NMR spectra were recorded with Brucker Avance (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, = δ 77.0). s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, PE = petroleum ether, EA = ethyl acetate. The high resolution mass spectrum (HRMS) were recorded on an Agilent (Q-TOF6520) unit with an ESI source. IR spectra were measured on a Shimadzu IRAffinnity-1s spectrometer. Melting points were measured on a binocular microscope XT4A melting point apparatus (uncorrected).

2. Preparation of *O*-Methyl oxime

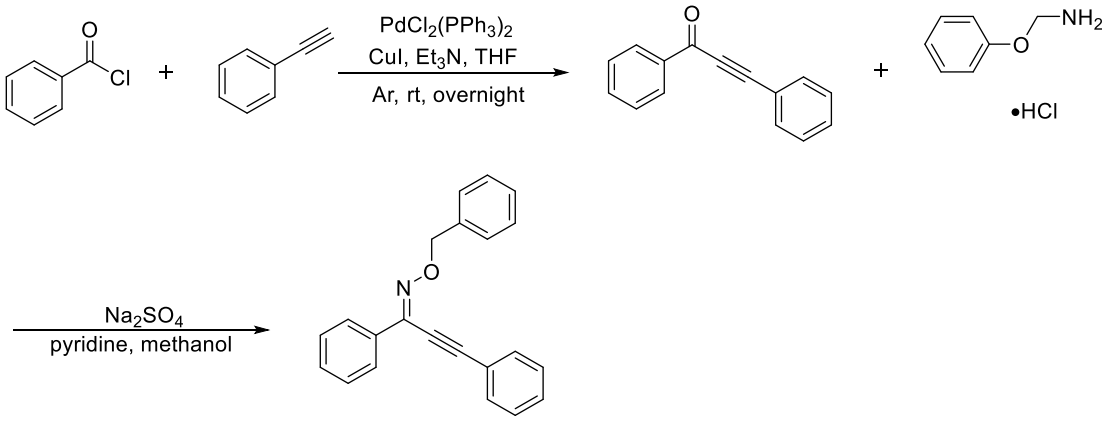
Substrates **1a**-**1v** were prepared according to literature procedures.[1-9]



Procedure for the Synthesis of 1a-1v. Under an argon atmosphere, a mixture of acyl chloride (12 mmol), $PdCl_2(PPh_3)_2$ (2 mol%), and Et_3N (12 mmol) in anhydrous

THF (30 mL) was stirred at room temperature in a 100 mL round-bottom flask for 10 min. CuI (4 mol%) was added, and stirring was continued for an additional 10 min. Subsequently, the terminal alkyne (10 mmol) was introduced, and the resulting mixture was stirred at room temperature overnight (reaction progress monitored by TLC). After complete consumption of the starting material, water (50 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Purification by silica gel column chromatography (eluent: PE/EA) afforded the desired product.

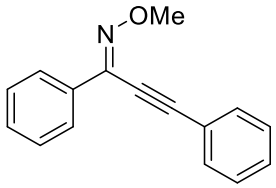
In a 50 mL round-bottom flask, a mixture of ynone (4 mmol), methoxyamine hydrochloride (8 mmol), anhydrous Na_2SO_4 (8 mmol), pyridine (1.2 mL), and methanol (15 mL) was stirred at room temperature overnight (reaction monitored by TLC). When the reaction was completed, the reaction was quenched with water (40 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. After concentration under reduced pressure, the residue was purified by silica gel column chromatography (eluent: PE/EA) to afford the desired products **1a-1v** in 35-76% yields.



Procedure for the Synthesis of 1a'. Under an argon atmosphere, a mixture of benzoyl chloride (12 mmol), $PdCl_2(PPh_3)_2$ (2 mol%), and Et_3N (12 mmol) in anhydrous THF (30 mL) was stirred at room temperature in a 100 mL round-bottom flask for 10 min. CuI (4 mol%) was added, and stirring was continued for an additional 10 min. Subsequently, the phenylacetylene (10 mmol) was introduced, and the resulting

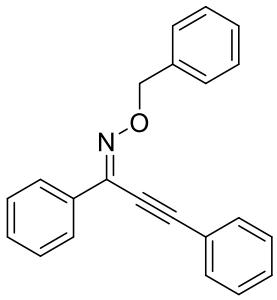
mixture was stirred at room temperature overnight (reaction progress monitored by TLC). After complete consumption of the starting material, water (50 mL) was added. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Purification by silica gel column chromatography (eluent: PE/EA) afforded the desired product.

In a 50 mL round-bottom flask, a mixture of 1,3-diphenyl-2-propyn-1-one (4 mmol), *O*-Benzylhydroxylamine hydrochloride (8 mmol), anhydrous Na_2SO_4 (8 mmol), pyridine (1.2 mL), and methanol (15 mL) was stirred at room temperature overnight (reaction monitored by TLC). When the reaction was completed, the reaction was quenched with water (40 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. After concentration under reduced pressure, the residue was purified by silica gel column chromatography (eluent: PE/EA) to afford the desired products **1a'** in 65% yields.



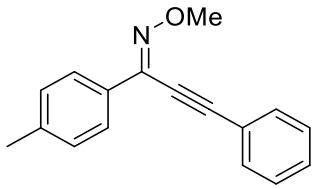
1,3-Diphenyl-2-propyn-1-one *O*-methyloxime (1a)[3]

Yellow solid, (602 mg, 64%), mp: 42-44 ºC. Purified by column chromatography (PE/EA = 100/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2H), 7.63-7.61 (m, 2H), 7.41-7.38 (m, 6H), 4.14 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 133.6, 132.2, 129.7, 129.6, 128.5, 128.4, 126.5, 121.8, 101.2, 79.5, 63.2 ppm; HRMS (ESI) m/z: calcd. for $C_{16}H_{14}NO$ $[M + H]^+$ 236.1070, found 236.1080.



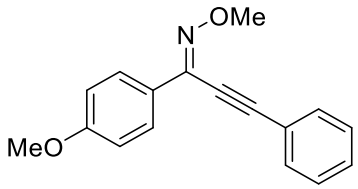
1,3-Diphenyl-2-propyn-1-one *O*- benzyloxime (1a')[4]

Colorless oil, (810 mg, 65%). Purified by column chromatography (PE/EA = 50/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91-7.90 (m, 2H), 7.60-7.58 (m, 2H), 7.48-7.46 (m, 2H), 7.41-7.31 (m, 9H), 5.38 (s, 3H) ppm.



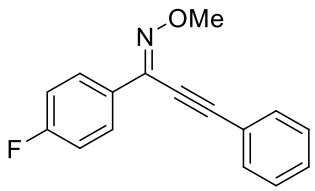
1-(4-Methylphenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1b)[3]

Yellow oil, (648 mg, 65%). Purified by column chromatography (PE/EA = 70/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.62-7.60 (m, 2H), 7.40-7.36 (m, 3H), 7.20 (d, J = 7.5 Hz, 2H), 4.12 (s, 3H) , 2.38 (s, 3H) ppm.



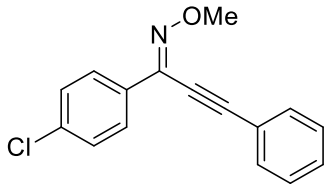
1-(4-Methoxyphenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1c)[2]

White solid, (626 mg, 59%), mp: 57-59 ^{o}C. Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.62-7.60 (m, 2H), 7.40-7.38 (m, 3H), 6.93-6.91 (m, 2H), 4.11 (s, 3H) , 3.84 (s, 3H) ppm.



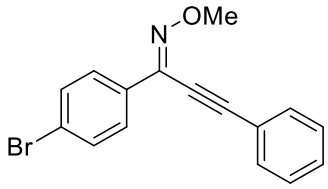
1-(4-Fluorophenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1d)[3]

Yellow oil, (587 mg, 58%). Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.62-7.60 (m, 2H), 7.41-7.36 (m, 3H), 7.10-7.07 (m, 2H), 4.13 (s, 3H) ppm.



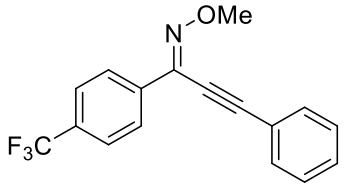
1-(4-Chlorophenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1e)[3]

Colourless oil, (453 mg, 42%). Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.61-7.60 (m, 2H), 7.40-7.36 (m, 5H), 4.13 (s, 3H) ppm.



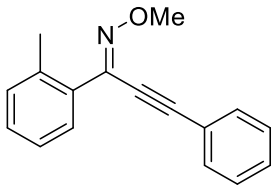
1-(4-Bromophenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1f)[6]

Yellow solid, (665 mg, 53%), mp: 54-56 ºC. Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.61-7.60 (m, 2H), 7.54-7.51 (m, 2H), 7.43-7.36 (m, 3H), 4.13 (s, 3H) ppm.



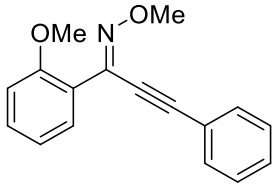
3-Phenyl-1-[4-(trifluoromethyl)phenyl]-2-propyn-1-one *O*-methyloxime (1g)[3]

Pale yellow solid, (424 mg, 35%), mp: 58-60 ºC. Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.63-7.61 (m, 2H), 7.43-7.38 (m, 3H), 4.17 (s, 3H) ppm.



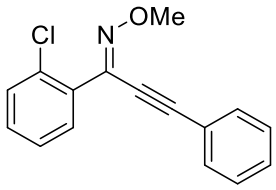
1-(2-Methylphenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1h)[6]

Yellow oil, (648 mg, 65%). Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.53 (m, 3H), 7.35-7.33 (m, 3H), 7.29-7.27 (m, 1H), 7.25-7.22 (m, 2H), 4.12 (s, 3H), 2.54 (s, 3H) ppm.



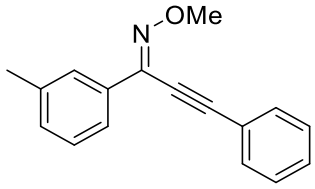
1-(2-Methoxyphenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1i)[3]

Yellow oil, (795 mg, 75%). Purified by column chromatography (PE/EA = 10/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.50-7.48 (m, 1H), 7.37-7.32 (m, 4H), 7.01-6.95 (m, 2H), 4.12 (s, 3H), 3.88 (s, 3H) ppm.



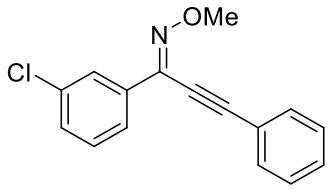
1-(2-Chlorophenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1j)[1]

Pale yellow oil, (485 mg, 45%). Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.52 (m, 3H), 7.45-7.44 (m, 1H), 7.37-7.31 (m, 5H), 4.14 (s, 3H) ppm.



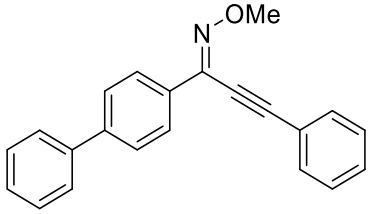
1-(3-Methylphenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1k)[6]

Yellow oil, (618 mg, 62%). Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.63-7.61 (m, 2H), 7.40-7.36 (m, 3H), 7.31-7.28 (m, 1H), 7.22-7.20 (m, 1H), 4.14 (s, 3H), 2.40 (s, 3H) ppm.



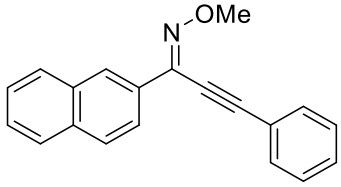
1-(3-Chlorophenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1l)[6]

Yellow oil, (539 mg, 50%). Purified by column chromatography (PE/EA = 40/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91-7.90 (m, 1H), 7.80-7.78 (m, 1H), 7.62-7.60 (m, 2H), 7.39-7.31 (m, 5H), 4.14 (s, 3H) ppm.



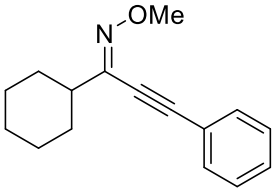
1-[1,1′-Biphenyl]-4-yl-3-phenyl-2-propyn-1-one *O*-methyloxime (1m)[1]

White solid, (497 mg, 40%), mp: 111-113 ºC. Purified by column chromatography (PE/EA = 80/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.64-7.61 (m, 6H), 7.46-7.43 (m, 2H), 7.40-7.36 (m, 4H), 4.16 (s, 3H) ppm.



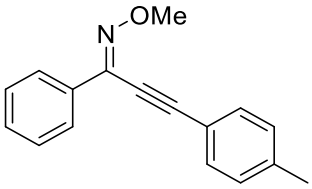
1-(2-Naphthalenyl)-3-phenyl-2-propyn-1-one *O*-methyloxime (1n)[6]

Pale yellow solid, (536 mg, 47%), mp: 107-109 ºC. Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.08-8.06 (m, 1H), 7.91-7.89 (m, 1H), 7.84-7.82 (m, 2H), 7.68-7.66 (m, 2H), 7.51-7.47 (m, 2H), 7.42-7.37 (m, 3H), 4.18 (s, 3H) ppm.



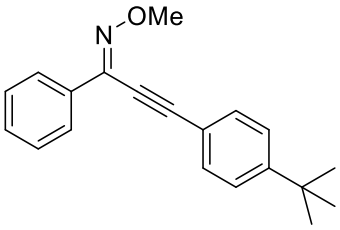
1-Cyclohexyl-3-phenyl-2-propyn-1-one *O*-methyloxime (1o)[1]

Yellow oil, (512 mg, 53%). Purified by column chromatography (PE/EA = 50/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.36-7.34 (m, 3H), 3.96 (s, 3H), 2.44-2.38 (m, 1H), 1.90-1.78 (m, 4H), 1.72-1.68 (m, 1H), 1.53-1.47 (m, 2H), 1.37-1.29 (m, 2H), 1.25-1.20 (m, 1H) ppm.



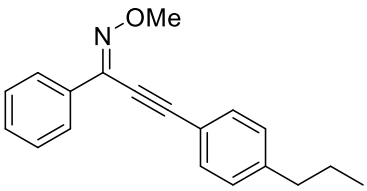
3-(4-Methylphenyl)-1-phenyl-2-propyn-1-one *O*-methyloxime (1p)[3]

Yellow oil, (688 mg, 69%). Purified by column chromatography (PE/EA = 60/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.52-7.50 (m, 2H), 7.40-7.39 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 4.14 (s, 3H), 2.38 (s, 3H) ppm.



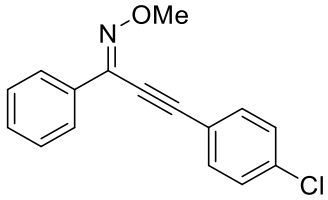
3-[4-(1,1-Dimethylethyl)phenyl]-1-phenyl-2-propyn-1-one *O*-methyloxime (1q)[6]

Pale yellow oil, (816 mg, 70%). Purified by column chromatography (PE/EA = 50/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2H), 7.56-7.53 (m, 2H), 7.40-7.38 (m, 5H), 4.13 (s, 3H), 1.32 (s, 9H) ppm.



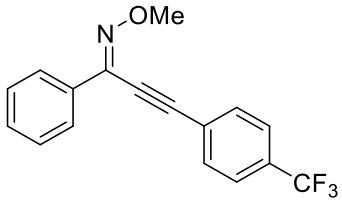
3-(4-Propylphenyl)-1-phenyl-2-propyn-1-one *O*-methyloxime (1r)[7]

Yellow oil, (843 mg, 76%). Purified by column chromatography (PE/EA = 50/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2H), 7.53-7.51 (m, 2H), 7.40-7.36 (m, 3H), 7.17 (d, J = 8.5 Hz, 2H), 4.13 (s, 3H), 2.59 (t, J = 7.5 Hz, 2H), 1.67-1.59 (m, 2H) , 0.92 (t, J = 7.5 Hz, 3H) ppm.



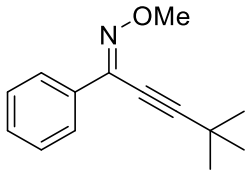
3-(4-Chlorophenyl)-1-phenyl-2-propyn-1-one *O*-methyloxime (1s)[6]

Pale yellow solid, (615 mg, 57%), mp: 40-42 °C. Purified by column chromatography (PE/EA = 40/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.53-7.51 (m, 2H), 7.40-7.38 (m, 3H), 7.35-7.32 (m, 2H), 4.13 (s, 3H) ppm.



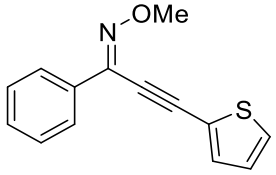
1-Phenyl-3-[4-(trifluoromethyl)phenyl]-2-propyn-1-one *O*-methyloxime (1t)[6]

Yellow oil, (630 mg, 52%). Purified by column chromatography (PE/EA = 40/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.41-7.39 (m, 3H), 4.14 (s, 3H) ppm.



4,4-Dimethyl-1-phenyl-2-pentyn-1-one *O*-methyloxime (1u)[8]

Colourless oil, (629 mg, 73%). Purified by column chromatography (PE/EA = 20/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.35-7.34 (m, 3H), 4.06 (s, 3H), 1.37 (s, 9H) ppm.

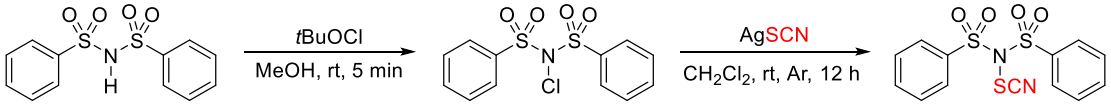


1-Phenyl-3-(2-thienyl)-2-propyn-1-one *O*-methyloxime (1v)[9]

Brown oil, (579 mg, 60%). Purified by column chromatography (PE/EA = 50/1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.43-7.42 (m, 1H), 7.40-7.39 (m, 4H), 7.05-7.03 (m, 1H), 4.13 (s, 3H) ppm.

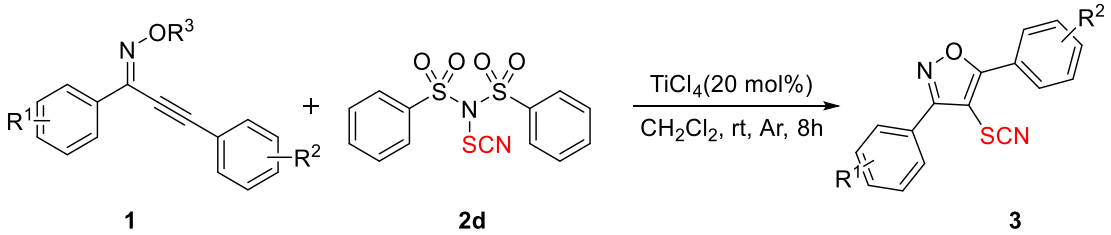
3. Preparation of *N*-thiocyanato-dibenzenesulfonimide

Reagents **2d** were prepared according to the literatures.[10]



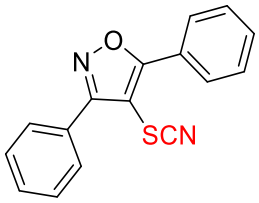
N-(Phenylsulfonyl)benzenesulfonamide (9.0 g, 30.30 mmol) and tert-butyl hypochlorite (33.33 mmol, 1.1 equiv) were stirred in methanol (50 mL) for 5 min at room temperature. Then the suspension was filtered giving the *N*-chloro-*N*-(phenylsulfonyl)-benzenesulfonamide as a white powder. *N*-chloro-*N*-(phenylsulfonyl)-benzenesulfonamide (2.6 g, 7.9 mmol) was treated with AgSCN (2 g, 11.9 mmol, 1.5 equiv) in CH_2Cl_2 (25.0 mL) for 12 h at room temperature.. Then the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to afford the product.

4. General Procedure for the Synthesis of 3



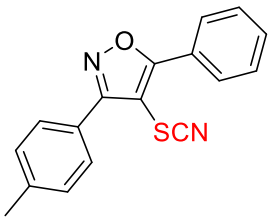
A 25 mL reaction tube was charged with substrate **1a-1v** (0.10 mmol, 1.0 equiv) and $TiCl_4$ (0.02 mmol, 0.2 equiv) under an argon atmosphere. The mixture was

dissolved in anhydrous DCM (0.5 mL). *N*-Thiocyanato-dibenzenesulfonimide (1.50 mmol, 1.5 equiv) was added to the reaction mixture. The resulting solution was stirred at room temperature until the reaction was complete, as monitored by TLC. Upon completion, the crude mixture was purified by column chromatography on silica gel using PE/ $^{i}Pr_2O$ as the eluent to afford products **3a-3v**.



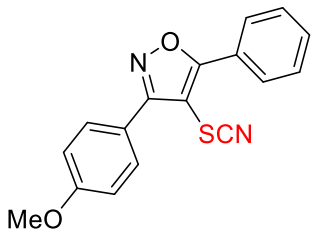
3,5-Diphenyl-4-thiocyanatoisoxazole (3a)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 30/1, v/v), TLC R_f = 0.3, white solid (23.4 mg, 84%), mp: 169-171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.86-7.84 (m, 2H), 7.61-7.57 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 164.1, 132.1, 130.8, 129.3, 129.1, 128.8, 128.0, 126.8, 125.6,109.5, 93.4 ppm; IR (KBr) 2922, 2160 (SCN), 912 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{11}N_2OS$ $[M + H]^+$ 279.0587, found 279.0594.



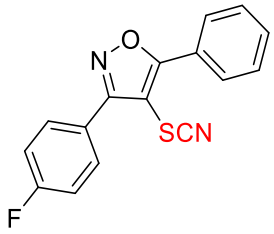
3-(4-Methylcyclohexa-1,5-dien-1-yl)-5-phenyl-4-thiocyanatoisoxazole (3b)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 10/1, v/v), TLC R_f = 0.5, white solid (28.2 mg, 96%), mp: 127-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.61-7.59 (m, 3H), 7.38 (d, J = 7.5 Hz, 2H), 2.46 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 164.1, 141.1, 132.0, 129.8, 129.3, 128.6, 128.0, 125.7, 123.9, 109.6, 93.3, 21.5 ppm; IR (KBr) 2924, 2158 (SCN), 1660, 1581, 1377, 812, 736 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{13}N_2OS$ $[M + H]^+$ 293.0744, found 293.0757.



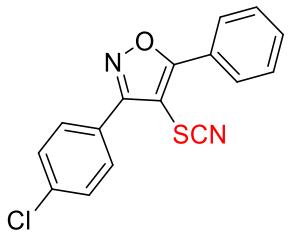
3-(4-Methoxyphenyl)-5-phenyl-4-thiocyanatoisoxazole (3c)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 8/1, v/v), TLC R_f = 0.5, white solid (27.1 mg, 88%), mp: 161-163°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.61-7.60 (m, 3H), 7.08 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 163.7, 161.6, 132.0, 130.2, 129.3, 128.1, 125.7, 119.0, 114.6, 109.7, 93.2, 55.5 ppm; IR (KBr) 2924, 2351, 2158 (SCN), 1606, 1382, 1255 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{13}N_2O_2S$ $[M + H]^+$ 309.0693, found 309.0694.



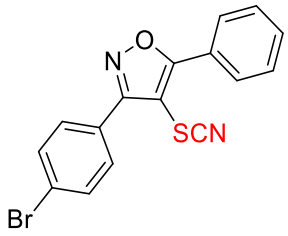
3-(4-Fluorophenyl)-5-phenyl-4-thiocyanatoisoxazole (3d)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 6/1, v/v), TLC R_f = 0.5, White solid (23.4 mg, 79%), mp: 130-132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 7.88-7.86 (m, 2H), 7.63-7.60 (m, 3H), 7.27-7.25 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 164.3 (d, J = 253.3 Hz), 163.3, 132.2, 130.8 (d, J = 8.8 Hz), 129.3, 128.0, 125.5, 122.9 (d, J = 3.8 Hz), 116.4 (d, J = 22.7 Hz), 109.4, 93.3 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.8 ppm; IR (KBr) 2920, 2351, 2160 (SCN), 1556, 1417, 1236, 840 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{10}FN_2OS$ $[M + H]^+$ 297.0493, found 297.0492.



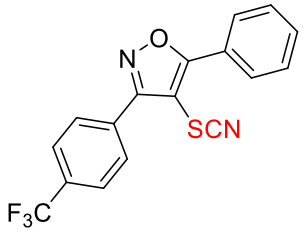
3-(4-Chlorophenyl)-5-phenyl-4-thiocyanatoisoxazole (3e)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 6/1, v/v), TLC R_f = 0.4, white solid (25.0 mg, 80%), mp: 102-104 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 7.83-7.80 (m, 2H), 7.65-7.58 (m, 3H), 7.57-7.54 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 163.2, 137.3, 132.3, 130.0, 129.5, 129.3, 128.1, 125.5, 125.3, 109.3, 93.3 ppm; IR (KBr) 2829, 2351, 2158 (SCN), 1598, 1352, 1091, 831 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{10}ClN_2OS$ $[M + H]^+$ 313.0197, found 313.0206.



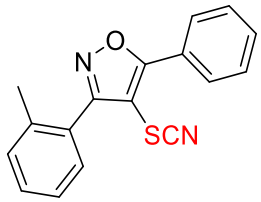
3-(4-Bromophenyl)-5-phenyl-4-thiocyanatoisoxazole (3f)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 6/1, v/v), TLC R_f = 0.4, white solid (26.8 mg, 75%), mp: 117-119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 7.76-7.70 (m, 4H), 7.65-7.59 (m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 163.2, 132.4, 132.3, 130.2, 129.3, 128.0, 125.7, 125.6, 125.4, 109.3, 93.2 ppm; IR (KBr) 2829, 2351, 2160 (SCN), 1593, 1352, 1105 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{10}BrN_2OS$ $[M + H]^+$ 356.9692, found 356.9691.



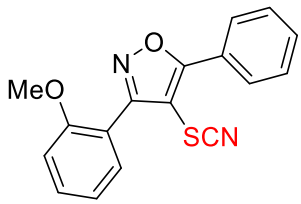
5-Phenyl-4-thiocyanato-3-(4-(trifluoromethyl)phenyl)isoxazole (3g)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 6/1, v/v), TLC R_f = 0.4, white solid (29.4 mg, 85%), mp: 83-85 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.65-7.61 (m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 163.1, 132.8 (q, J = 32.8 Hz), 132.4, 130.4, 129.4, 129.2, 128.1, 126.1 (q, J = 3.8 Hz), 125.3, 123.7 (q, J = 273.4 Hz), 109.2, 93.4 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.0 ppm; IR (KBr) 2929, 2351, 2160 (SCN), 1589, 1325, 1126, 1068, 844 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{10}F_3N_2OS$ $[M + H]^+$ 347.0461, found 347.0460.



5-Phenyl-4-thiocyanato-3-(*o*-tolyl)isoxazole (3h)

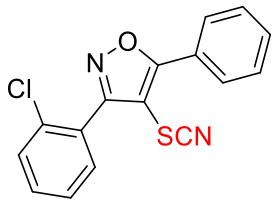
Purified by column chromatography (PE/ $^{i}Pr_2O$ = 6/1, v/v), TLC R_f = 0.5, pale yellow solid (24.0 mg, 82%), mp: 166-168 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.62-7.60 (m, 3H), 7.47-7.45 (m, 1H), 7.40-7.37 (m, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 165.4, 137.6, 132.1, 130.9, 130.5, 130.1, 129.3, 127.9, 126.1, 126.0, 125.7, 109.0, 94.8, 20.0 ppm; IR (KBr) 2814, 2351, 2318, 2158 (SCN), 1593, 1377, 1350, 1111, 734 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{13}N_2OS$ $[M + H]^+$ 293.0744, found 293.0750.



3-(2-Methoxyphenyl)-5-phenyl-4-thiocyanatoisoxazole (3i)

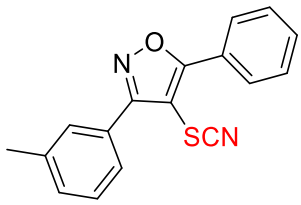
Purified by column chromatography (PE/ $^{i}Pr_2O$ = 4/1, v/v), TLC R_f = 0.5, white solid (24.1 mg, 78%), mp: 153-155 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.61-7.59 (m, 3H), 7.57-7.50 (m, 2H), 7.14-7.07 (m, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 163.7, 157.2, 132.5, 131.9, 131.2, 129.2, 127.9, 125.9, 121.1, 115.7, 111.1, 109.9, 95.8, 55.6 ppm; IR (KBr) 2937, 2308, 2158 (SCN), 1604,

1384, 1249, 1112, 750, 617 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{13}N_2O_2S$ $[M + H]^+$ 309.0693 found 309.0699.



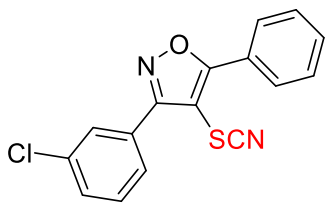
3-(2-Chlorophenyl)-5-phenyl-4-thiocyanatoisoxazole (3j)

Purified by column chromatography (PE/ $^iPr_2O$ = 6/1, v/v), TLC R_f = 0.4, white solid (22.8 mg, 73%), mp: 98-100 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.61-7.57 (m, 4H), 7.55-7.51 (m, 2H), 7.47-7.44 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 164.0, 133.8, 132.2, 132.1, 131.8, 130.1, 129.3, 127.8, 127.3, 126.0, 125.5, 109.0, 95.4 ppm; IR (KBr) 2816, 2351, 2310, 2160 (SCN), 1585, 1384, 1130, 1064, 759 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{10}ClN_2OS$ $[M + H]^+$ 313.0197, found 313.0203.



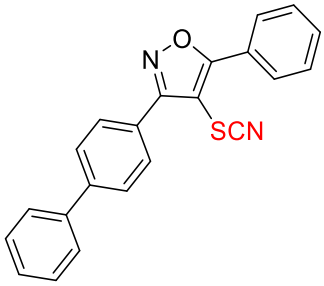
5-Phenyl-4-thiocyanato-3-(*m*-tolyl)isoxazole (3k)

Purified by column chromatography (PE/ $^iPr_2O$ = 9/1, v/v), TLC R_f = 0.4, pale yellow solid (26.0 mg, 89%), mp: 144-146 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.66-7.64 (m, 2H), 7.62-7.59 (m, 3H), 7.48-7.44 (m, 1H), 7.38 (d, J = 7.5 Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 164.3, 139.0, 132.1, 131.6, 129.4, 129.3, 129.0, 128.1, 126.7, 125.9, 125.7, 109.6, 93.4, 21.5 ppm; IR (KBr) 2920, 2351, 2308, 2158 (SCN), 1583, 1556, 1384, 1136, 727, 688 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{13}N_2OS$ $[M + H]^+$ 293.0744, found 293.0749.



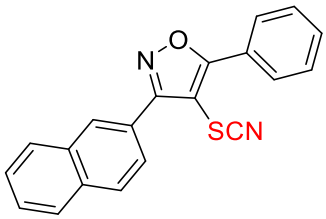
3-(3-Chlorophenyl)-5-phenyl-4-thiocyanatoisoxazole (3l)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 6/1, v/v), TLC R_f = 0.5, pale yellow solid (23.8 mg, 76%), mp: 79-81 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07-8.06 (m, 2H), 7.86-7.85 (m, 1H), 7.78-7.76 (m, 1H), 7.63-7.60 (m, 3H), 7.57-7.50 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 163.0, 135.2, 132.3, 131.0, 130.4, 129.4, 128.8, 128.5, 128.1, 126.9, 125.4, 109.2, 93.4 ppm; IR (KBr) 3082, 2362, 2160 (SCN), 1575, 1386, 1350, 1097, 769, 727, 686, 619 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{10}ClN_2OS$ $[M + H]^+$ 313.0197, found 313.0204.



3-([1,1'-Biphenyl]-4-yl)-5-phenyl-4-thiocyanatoisoxazole (3m)

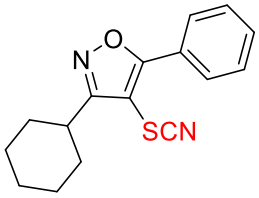
Purified by column chromatography (PE/ $^{i}Pr_2O$ = 9/1, v/v), TLC R_f = 0.4, white solid (28.0 mg, 79%), mp: 187-190 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 7.0 Hz, 2H), 7.63-7.62 (m, 3H), 7.51-7.48 (m, 2H), 7.43-7.40 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 163.8, 143.7, 140.0, 132.1, 129.3, 129.1, 129.0, 128.1, 128.0, 127.8, 127.3, 125.6, 125.5, 109.6, 93.4 ppm; IR (KBr) 2848, 2351, 2154 (SCN), 1593, 1377, 736 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{22}H_{15}N_2OS$ $[M + H]^+$ 355.0900, found 355.0904.



3-(Naphthalen-2-yl)-5-phenyl-4-thiocyanatoisoxazole (3n)

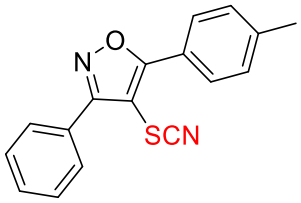
Purified by column chromatography (PE/ $^{i}Pr_2O$ = 9/1, v/v), TLC R_f = 0.4, white solid (23.0 mg, 70%), mp: 163-165 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.12-

8.10 (m, 2H), 8.04-7.99 (m, 2H), 7.95-7.92 (m, 2H), 7.64-7.59 (m, 5H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 164.1, 134.2, 133.0, 132.2, 129.3, 129.1, 129.0, 128.8, 128.1, 127.9, 127.7, 127.0, 125.6, 125.2, 124.1, 109.6, 93.5 ppm; IR (KBr) 3057, 2918, 2358, 2341, 2158 (SCN), 1647, 1558, 1394, 750 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{13}N_2OS$ $[M + H]^+$ 329.0744, found 329.0746.



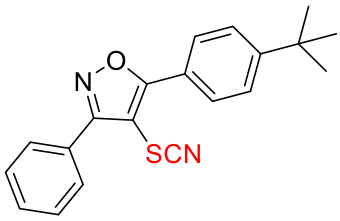
3-Cyclohexyl-5-phenyl-4-thiocyanatoisoxazole (3o)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 15/1, v/v), TLC R_f = 0.4, colourless oil (23.8 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.58-7.56 (m, 3H), 2.98-2.92 (m, 1H), 2.11-2.08 (m, 2H), 1.94-1.90 (m, 2H), 1.82-1.78 (m, 1H), 1.74-1.66 (m, 2H), 1.51-1.42 (m, 2H), 1.39-1.33 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 169.1, 131.8, 129.2, 127.9, 125.8, 109.5, 92.9, 35.8, 31.2, 26.15, 25.8 ppm; IR (KBr) 2929, 2852, 2351, 2158 (SCN), 1564, 1446, 688 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{17}N_2OS$ $[M + H]^+$ 285.1057, found 285.1068.



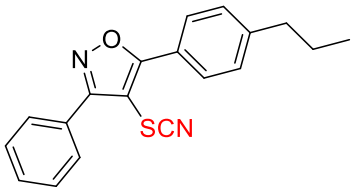
3-Phenyl-4-thiocyanato-5-(*p*-tolyl)isoxazole (3p)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 9/1, v/v), TLC R_f = 0.5, white solid (27.2 mg, 93%), mp: 137-139 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.5 Hz, 2H), 7.85-7.84 (m, 2H), 7.58-7.56 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 164.1, 142.9, 130.7, 130.0, 129.1, 128.8, 127.9, 126.9, 122.8, 109.7, 92.6, 21.7 ppm; IR (KBr) 2954, 2924, 2848, 2362, 2322, 2158 (SCN), 1635, 1608, 1386, 1109 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{13}N_2OS$ $[M + H]^+$ 293.0744, found 293.0753.



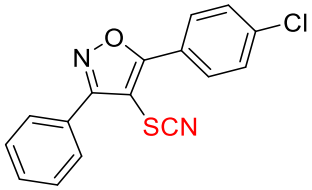
5-(4-(tert-Butyl)phenyl)-3-phenyl-4-thiocyanatoisoxazole (3q)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 10/1, v/v), TLC R_f = 0.4, white solid (30.1 mg, 90%), mp: 133-135 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.86-7.85 (m, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.58-7.56 (m, 3H), 1.39 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 164.1, 155.8, 130.7, 129.0, 128.8, 127.8, 126.9, 126.3, 122.8, 109.7, 92.6, 35.2, 31.1 ppm; IR (KBr) 2964, 2808, 2351, 2158 (SCN), 1608, 1573, 1381, 1269, 839, 721, 694 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{19}N_2OS$ $[M + H]^+$ 335.1213, found 335.1216.



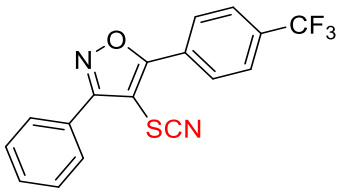
3-Phenyl-5-(4-propylphenyl)-4-thiocyanatoisoxazole (3r)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 10/1, v/v), TLC R_f = 0.4, white solid (29.5mg, 92%), mp: 140-142 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.86-7.84 (m, 2H), 7.58-7.55 (m, 3H), 7.40 (d, J = 8.0 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 1.75-1.68 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 164.1, 147.5, 130.7, 129.4, 129.1, 128.8, 127.9, 126.9, 123.0, 109.7, 92.6, 38.0, 24.2, 13.8 ppm; IR (KBr) 2960, 2935, 2349, 2158 (SCN), 1608, 1384, 1350, 1118, 694 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{17}N_2OS$ $[M + H]^+$ 321.1057, found 321.1070.



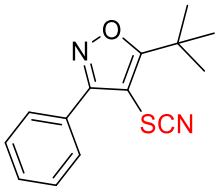
5-(4-Chlorophenyl)-3-phenyl-4-thiocyanatoisoxazole (3s)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 9/1, v/v), TLC R_f = 0.5, white solid (25.0 mg, 80%), mp: 167-169 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.05-8.02 (m, 2H), 7.85-7.83 (m, 2H), 7.60-7.56 (m, 5H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 164.2, 138.6, 130.9, 129.7, 129.2, 129.1, 128.7, 126.6, 124.0, 109.2, 93.8 ppm; IR (KBr) 2926, 2814, 2351, 2320, 2160 (SCN), 1597, 1487, 1381, 1093, 1014, 833, 732 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{10}ClN_2OS$ $[M + H]^+$ 313.0197, found 313.0204.



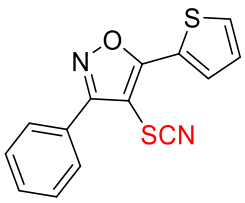
3-Phenyl-4-thiocyanato-5-(4-(trifluoromethyl)phenyl)isoxazole (3t)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 10/1, v/v), TLC R_f = 0.3, colourless oil (21.8 mg, 63%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 2H), 7.89-7.84 (m, 4H), 7.59-7.58 (m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 164.3, 133.7 (q, J = 32.8 Hz), 131.1, 129.2, 128.8, 128.4, 126.3 (q, J = 3.8 Hz), 123.5 (q, J = 173.4 Hz), 108.9, 95.1 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.2 ppm; IR (KBr) 2937, 2818, 2160 (SCN), 1587, 1382, 1323, 1170, 1128, 1068, 1016, 846 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{17}H_{10}F_3N_2OS$ $[M + H]^+$ 347.0461, found 347.0466.



5-(tert-Butyl)-3-phenyl-4-thiocyanatoisoxazole (3u)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 10/1, v/v), TLC R_f = 0.5, colourless oil (22.5 mg, 87%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.54-7.53 (m, 3H), 1.60 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.8, 164.2, 130.6, 129.0, 128.8, 127.0, 110.2, 92.8, 35.2, 28.4 ppm; IR (KBr) 2974, 2351, 2320, 2158 (SCN), 1589, 1541, 1384, 1276, 696 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{14}H_{15}N_2OS$ $[M + H]^+$ 259.0900, found 259.0907.

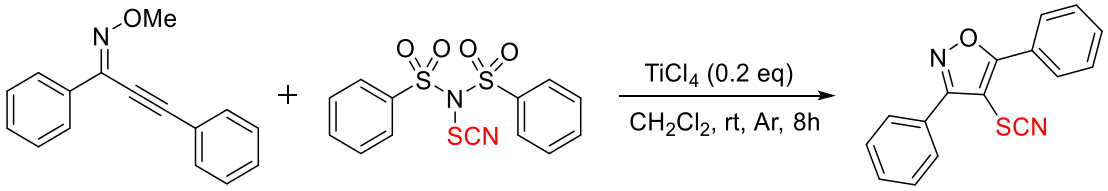


3-Phenyl-4-thiocyanato-5-(thiophen-2-yl)isoxazole (3v)

Purified by column chromatography (PE/ $^{i}Pr_2O$ = 5/1, v/v), TLC R_f = 0.5, white solid (19.6 mg, 69%), mp: 80-82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 3.5 Hz, 1H), 7.85-7.83 (m, 2H), 7.72 (d, J = 5.0 Hz, 1H), 7.57-7.54 (m, 3H), 7.28-7.26 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 163.7, 131.8, 130.9, 130.8, 129.1, 128.6, 128.3, 126.5, 126.4, 108.9, 91.3 ppm; IR (KBr) 3082, 2362, 2160 (SCN), 1575, 1413, 1386, 1109, 769, 729, 696, 524 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{14}H_9N_2OS_2$ $[M + H]^+$ 285.0151, found 285.0162.

5. Gram Scale Reaction and Derivatization of Products

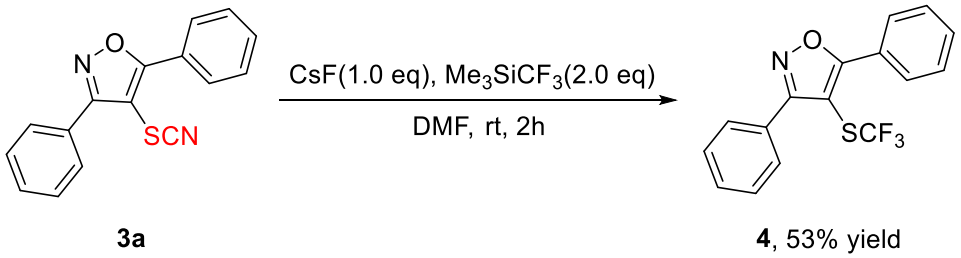
Gram Scale Reaction



1a, 4.50 mmol, 1.06g **2d**, 6.75mmol, 2.39g **3a**, 977mg, 78% yield

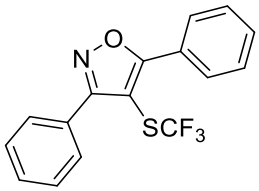
Under an argon atmosphere, a solution of **1a** (1.06 g, 4.50 mmol) in anhydrous DCM (45 mL) was charged into an oven-dried 100 mL round-bottom flask. $TiCl_4$ (89.91 μL, 0.90 mmol, 0.2 equiv) was added dropwise at ambient temperature, followed by the addition of reagent **2d** (2.39 g, 6.75 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 8 h (reaction progress monitored by TLC). When the reaction was completed, the solvent was removed under reduced pressure. Purification of the crude material by flash column chromatography on silica gel (eluent: PE/$^{i}Pr_2O$) afforded product **3a** (977 mg, 78% yield).

Derivatization of Products



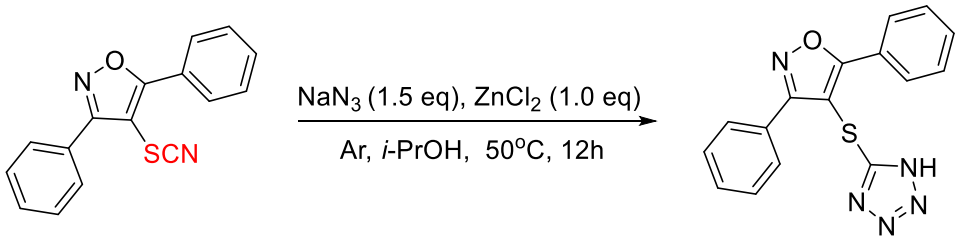
3a **4**, 53% yield

Under an argon atmosphere, substrate **3a** (55.6 mg, 0.2 mmol, 1.0 equiv) was dissolved in anhydrous DMF (2.0 mL) in a 25 mL reaction tube. To this solution, CsF (30.4 mg, 0.2 mmol, 1.0 equiv) and Me_3SiCF_3 (56.8 mg, 0.4 mmol, 2.0 equiv) were added successively. The reaction mixture was stirred at room temperature for 2 h (reaction progress monitored by TLC). When the reaction was completed, the mixture was extracted with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by silica gel column chromatography (eluent: PE) afforded product **4** (34 mg, 53% yield).



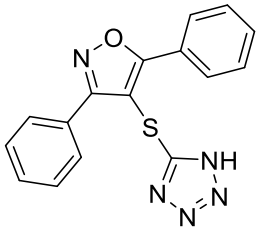
3,5-diphenyl-4-((trifluoromethyl)thio)isoxazole (4)

Purified by column chromatography (PE), TLC R_f = 0.3, white solid (34 mg, 53%), mp: 112-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.15 (m, 2H), 7.86-7.84 (m, 2H), 7.56-7.52 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 165.2, 131.7, 130.3, 129.0, 128.8, 128.7, 128.6 (q, J = 312.5 Hz), 127.9, 127.6, 126.3, 95.2 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.0 ppm; IR (KBr) 2922, 2814, 2355, 2322, 1583, 1446, 1382, 1350, 1112, 765, 731cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{11}F_3NOS$ $[M + H]^+$ 322.0508, found 322.0520.



3a **5**, 68% yield

Under an argon atmosphere, compound **3a** (55.6 mg, 0.2 mmol) was dissolved in anhydrous *i*-PrOH (6.0 mL) in an oven-dried 25 mL round-bottom flask. $ZnCl_2$ (27.3 mg, 0.2 mmol) and NaN_3 (19.5 mg, 0.3 mmol) were added sequentially at room temperature. The reaction mixture was gradually heated to 50°C and stirred for 12 h (progress monitored by TLC). When the reaction was completed, the reaction was quenched with H_2O (6.0 mL) and extracted with EA (3 × 6 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica gel (gradient elution: CH_2Cl_2/MeOH = 3/1, v/v) afforded the desired product **5** (44 mg, 68% yield).



4-((1*H*-Tetrazol-5-yl)thio)-3,5-diphenylisoxazole (5)

Purified by column chromatography (CH_2Cl_2/MeOH = 3/1, v/v), TLC R_f = 0.4, white solid (44 mg, 68%). ^{1}H NMR (500 MHz, C_2D_6SO) δ 8.07-8.05 (m, 2H), 7.82-7.80 (m, 2H), 7.60-7.54 (m, 3H), 7.51-7.47 (m, 3H) ppm; ^{13}C NMR (126 MHz, C_2D_6SO) δ 172.3, 164.9, 155.7, 131.9, 130.7, 129.5, 129.2, 128.9, 128.1, 128.0, 126.7, 101.2 ppm; IR (KBr) 2814, 2351, 2310, 1651, 1575, 1456, 1338 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{12}N_5OS$ $[M + H]^+$ 322.0758, found 322.0769.

6. Single Crystal X-Ray Data for Compound 3j (CCDC 2486964)

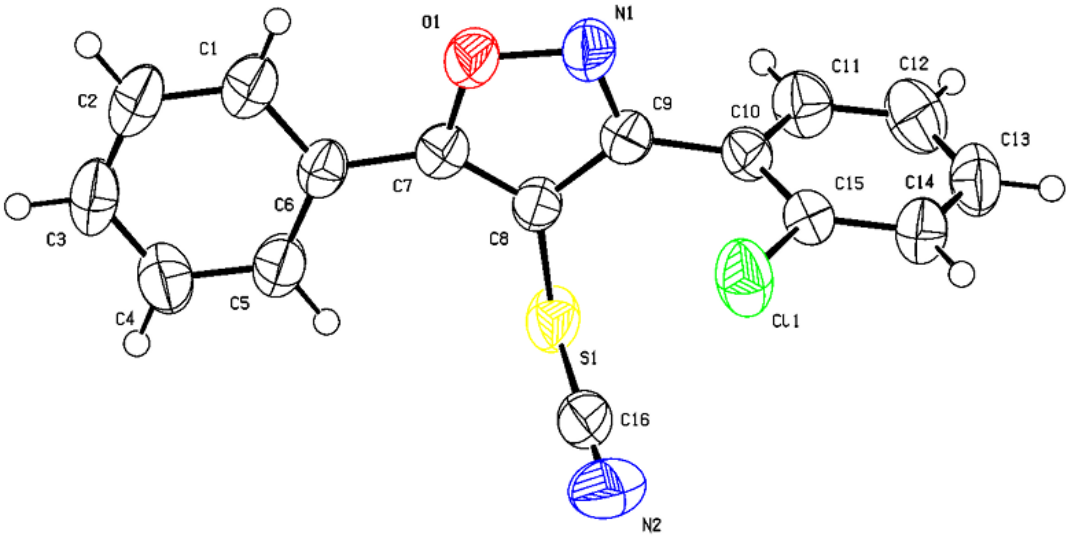


Table S1 Single Crystal Data of 3j

Compound	**3j**
Empirical formula	$C_{16}H_9ClN_2OS$
Formula weight	312.76
Temperature/K	293.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.794(3)
b/Å	11.032(2)
c/Å	7.8875(17)
α/°	90
β/°	101.768(7)
γ/°	90
Volume/Å^3	1430.7(5)
Z	4
ρ_{calc}g/cm^3	1.452
μ/mm^{-1}	0.411
F(000)	640.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.956 to 50.77
Index ranges	$-20 \le h \le 20$, $-12 \le k \le 13$, $-8 \le l \le 9$
Reflections collected	9917

Independent reflections	2619 [R_{int} = 0.0401, R_{sigma} = 0.0362]
Data/restraints/parameters	2619/0/190
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1330
Final R indexes [all data]	R_1 = 0.0600, wR_2 = 0.1494
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.31
CCDC	2486964

7. References

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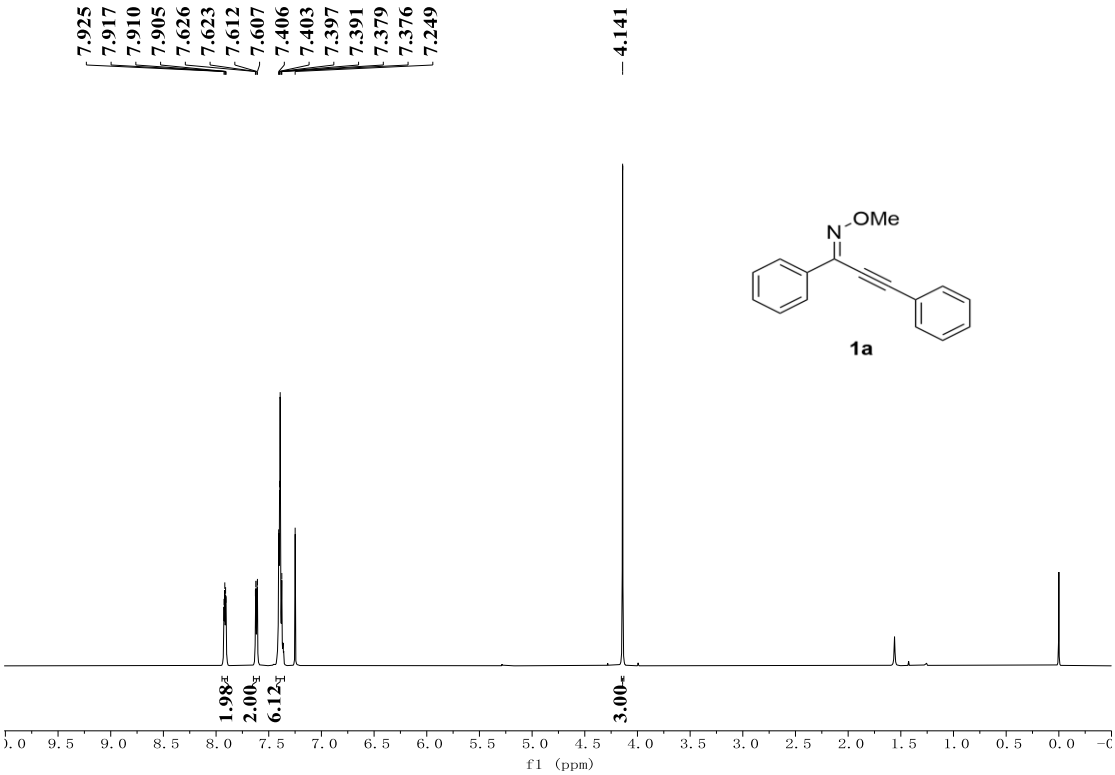
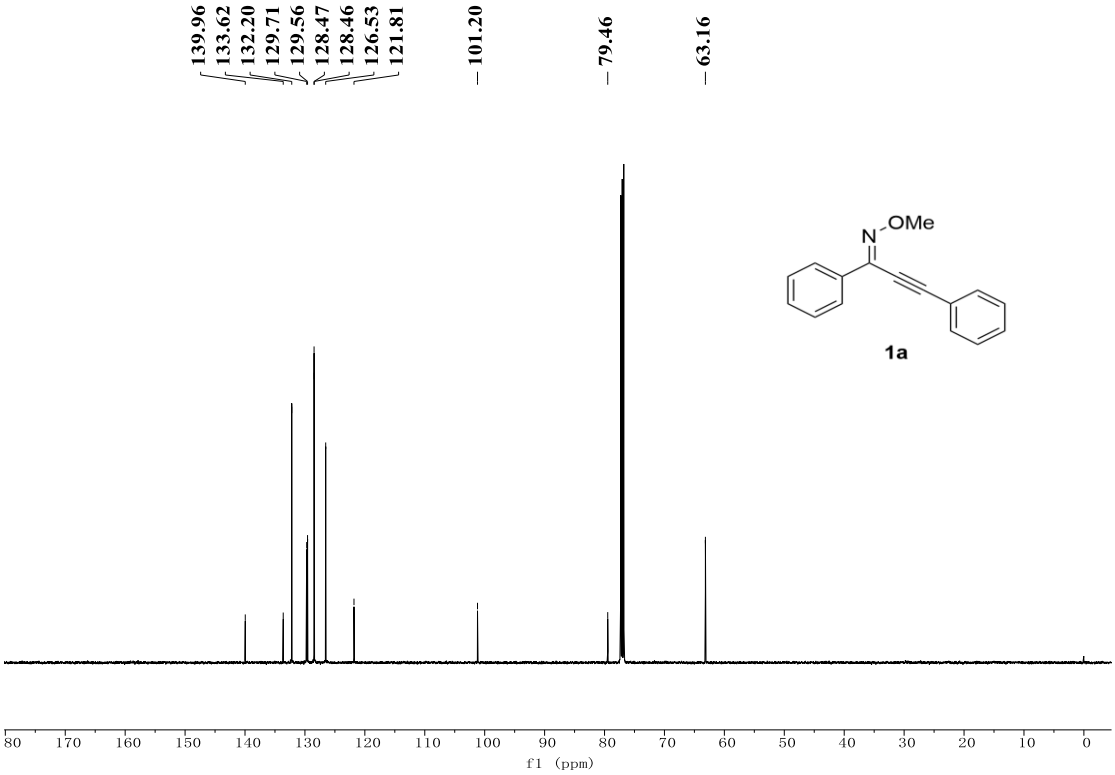
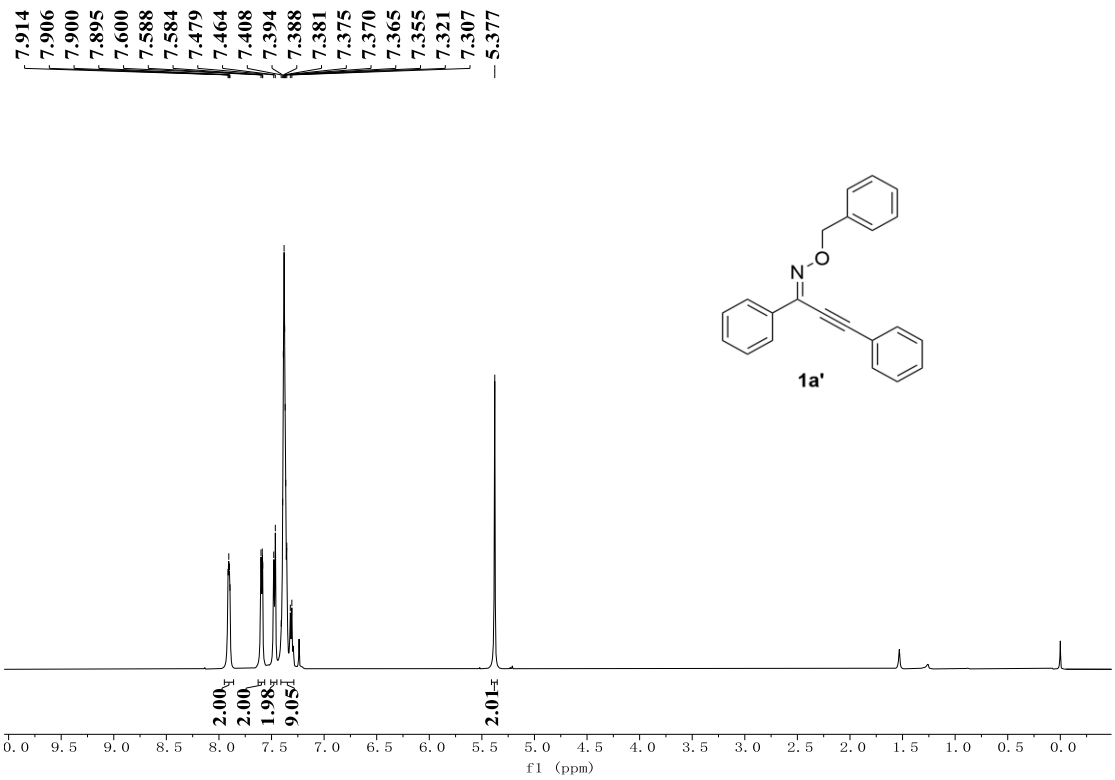
8. Copies of ^{1}H ,^{13}C and ^{19}F NMR Spectra



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O
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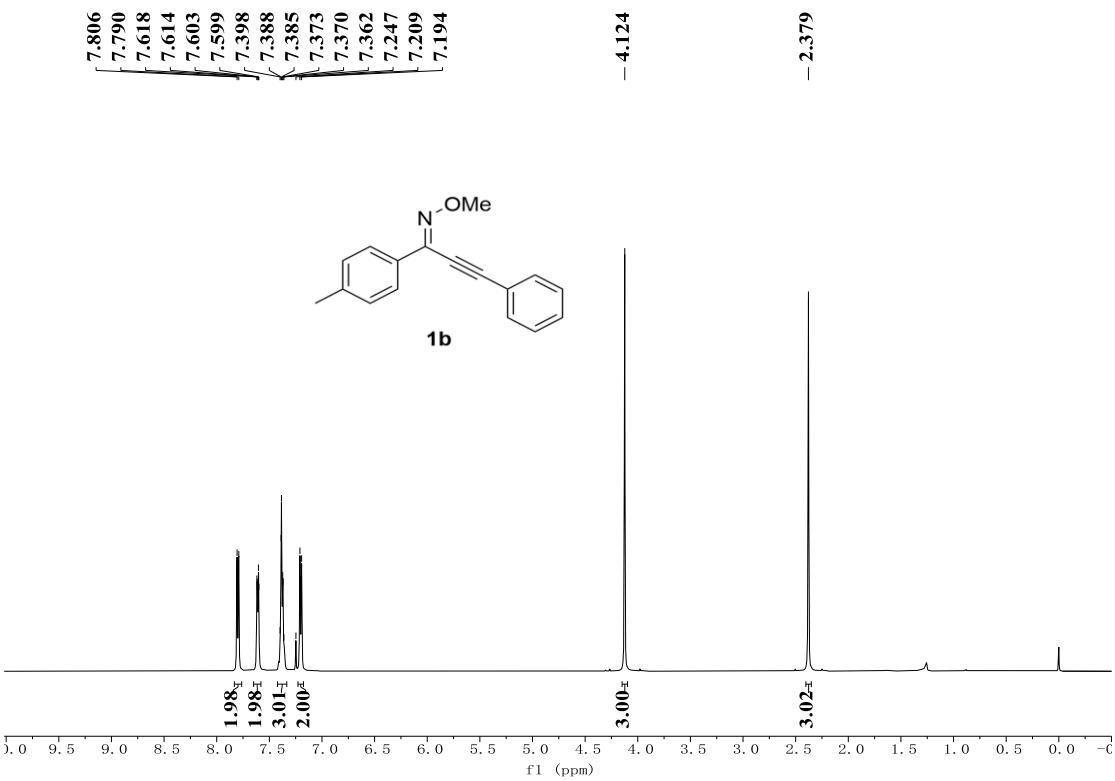
1.98
9.05
2.01
f1 (ppm)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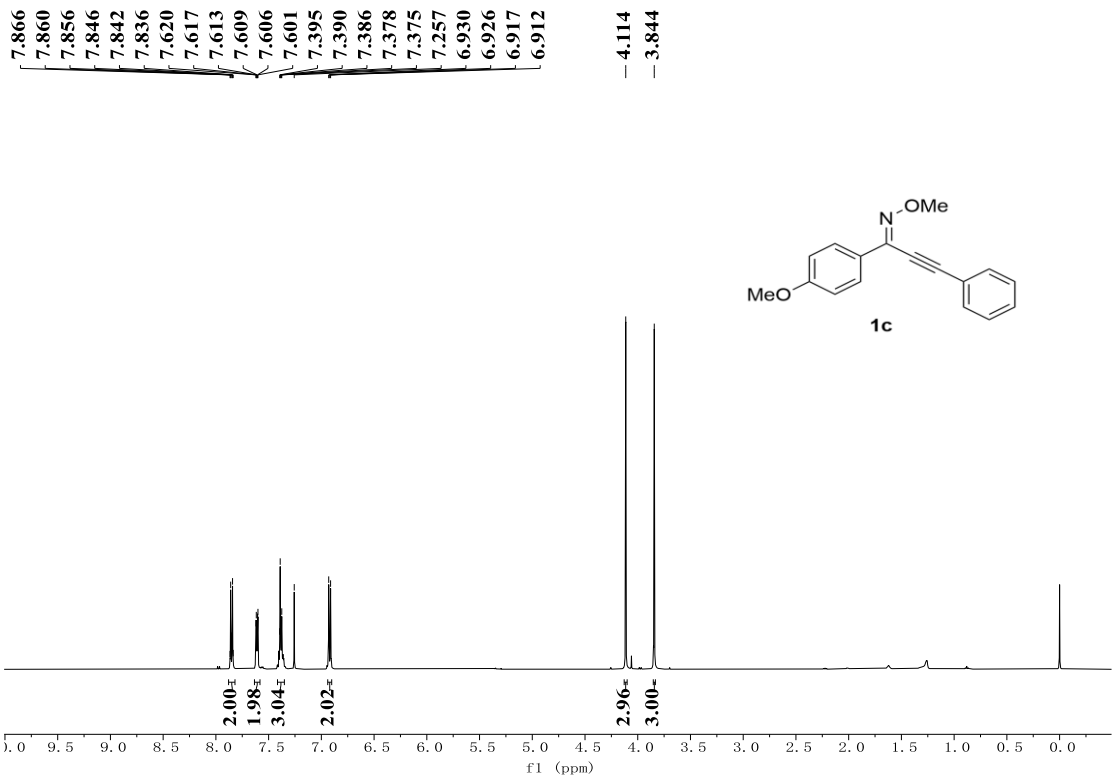
f1 (ppm)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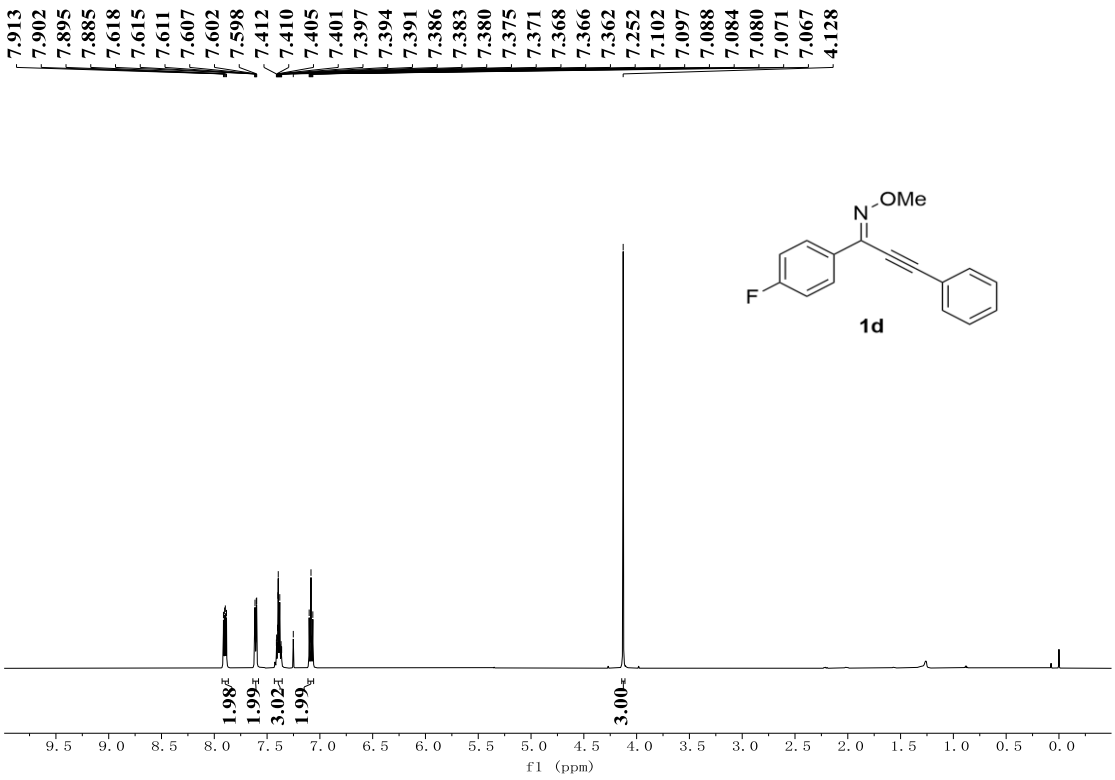
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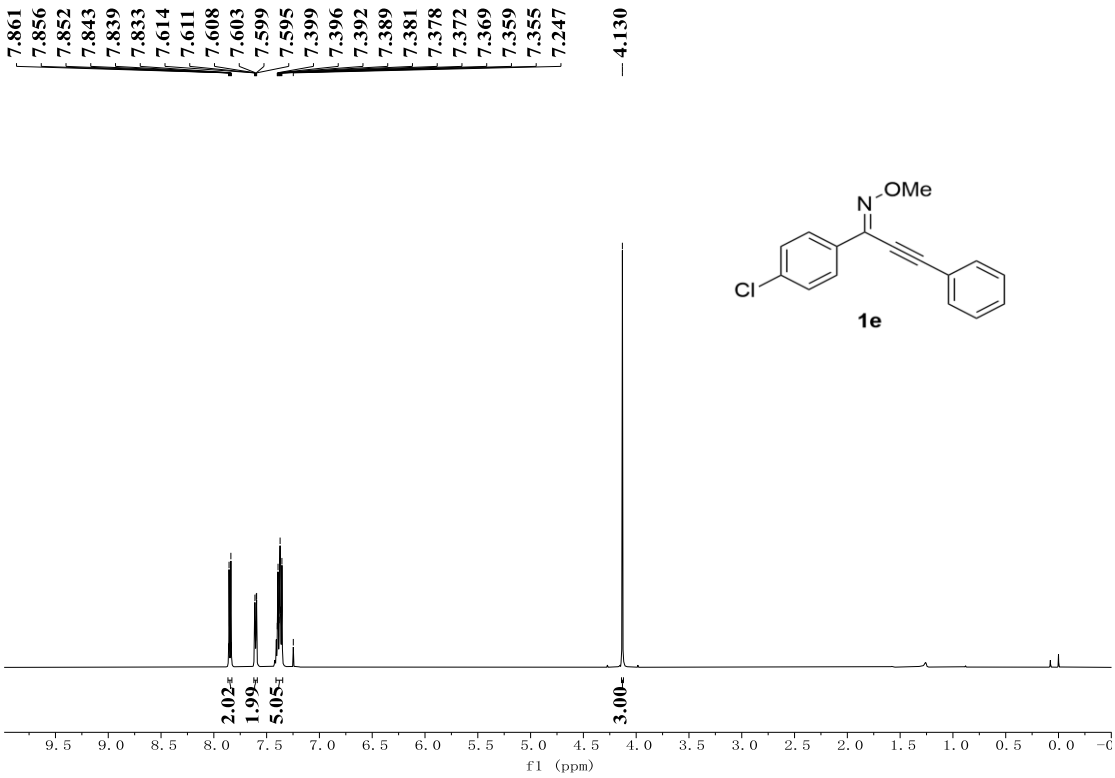
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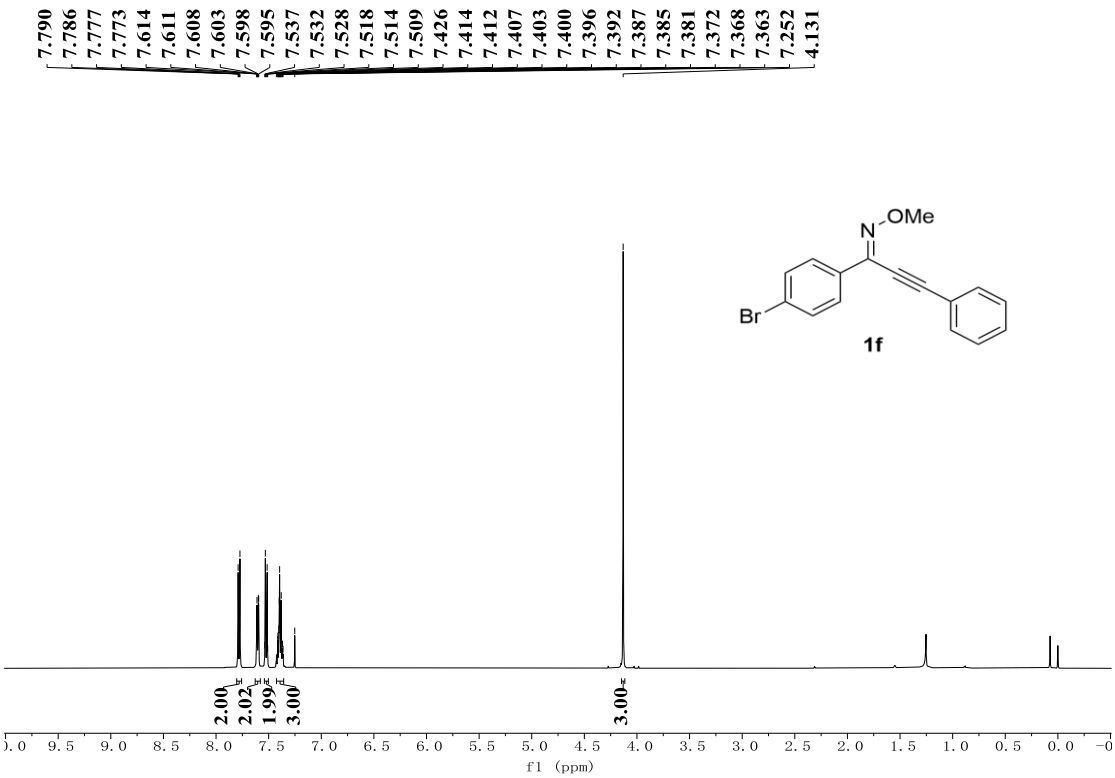
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7.400
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7.392
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7.368
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Br
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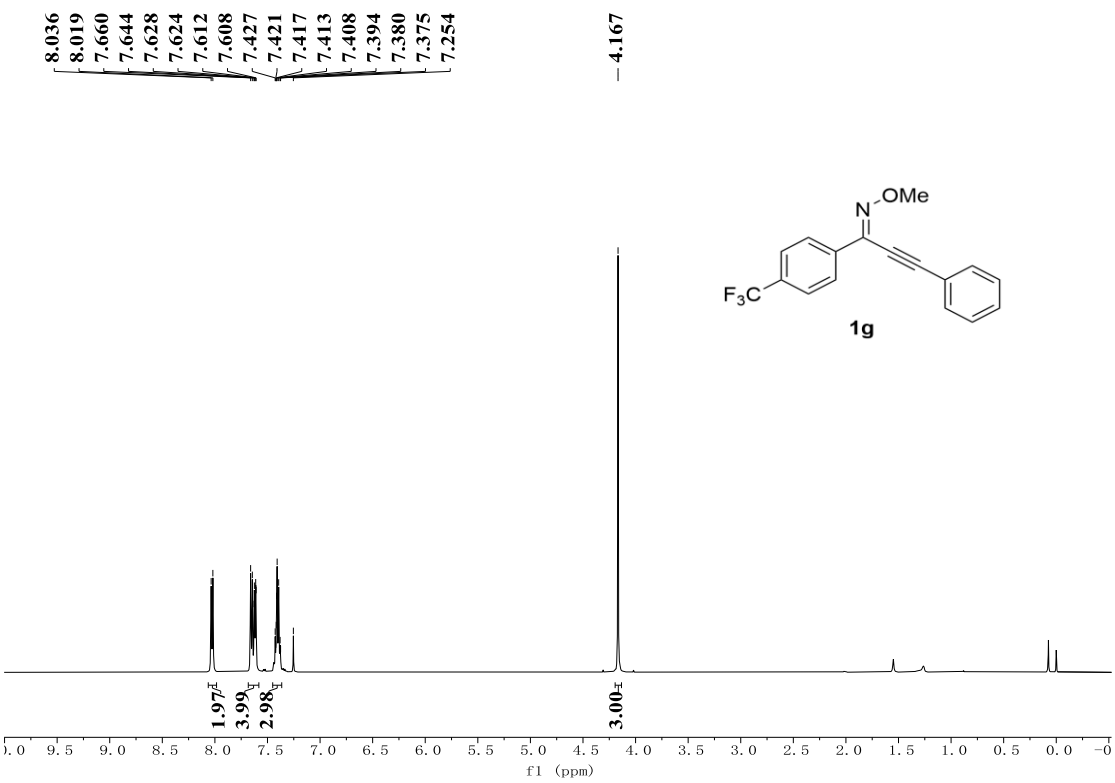
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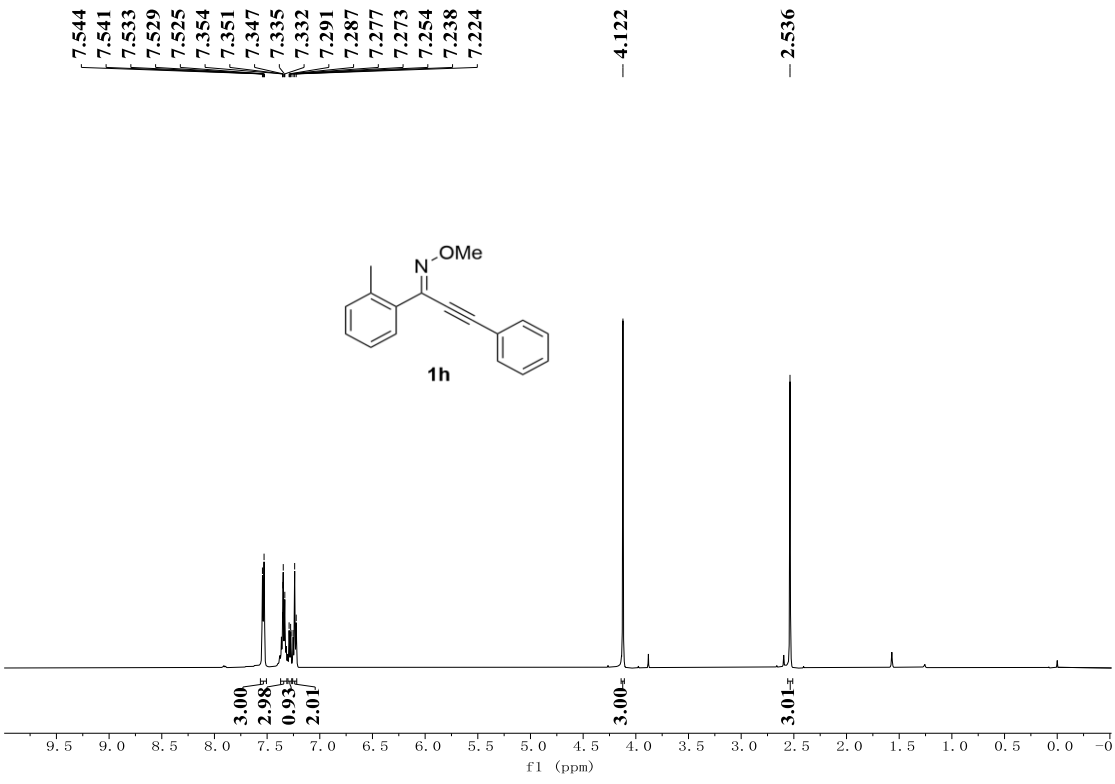
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7.277
7.273
7.254
7.238
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OMe
1h
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3.00
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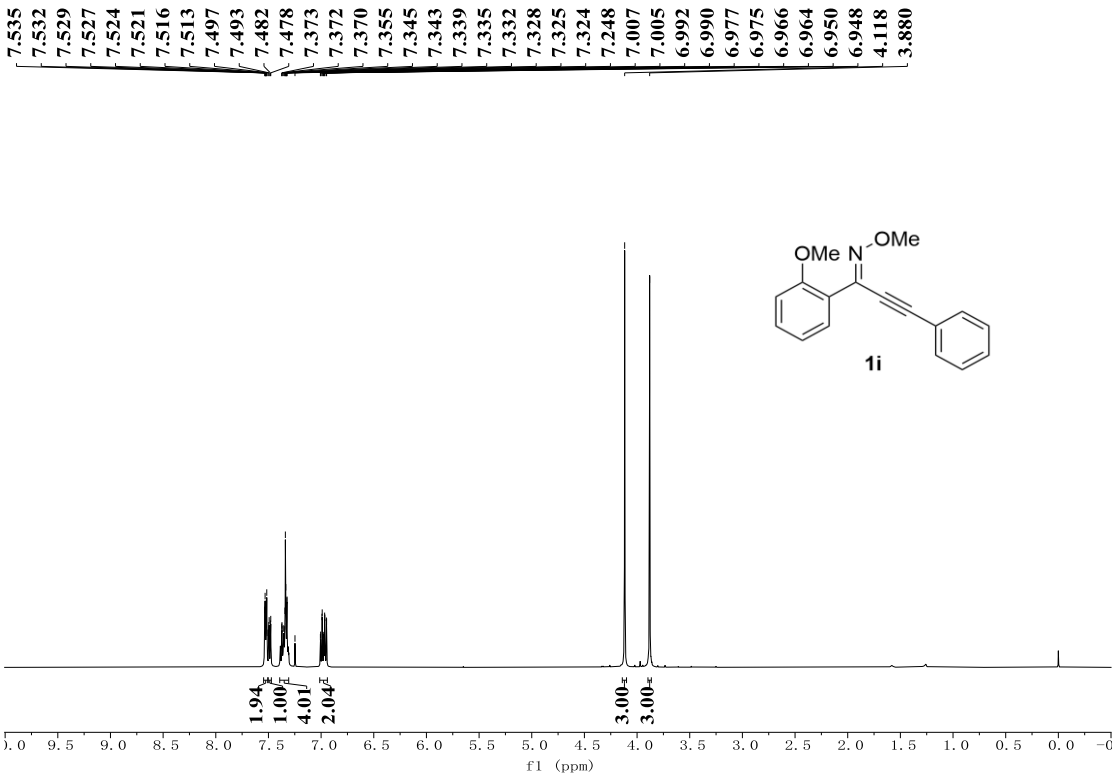
f1 (ppm)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7.372
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7.335
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7.325
7.324
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7.005
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6.990
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6.966
6.964
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6.948
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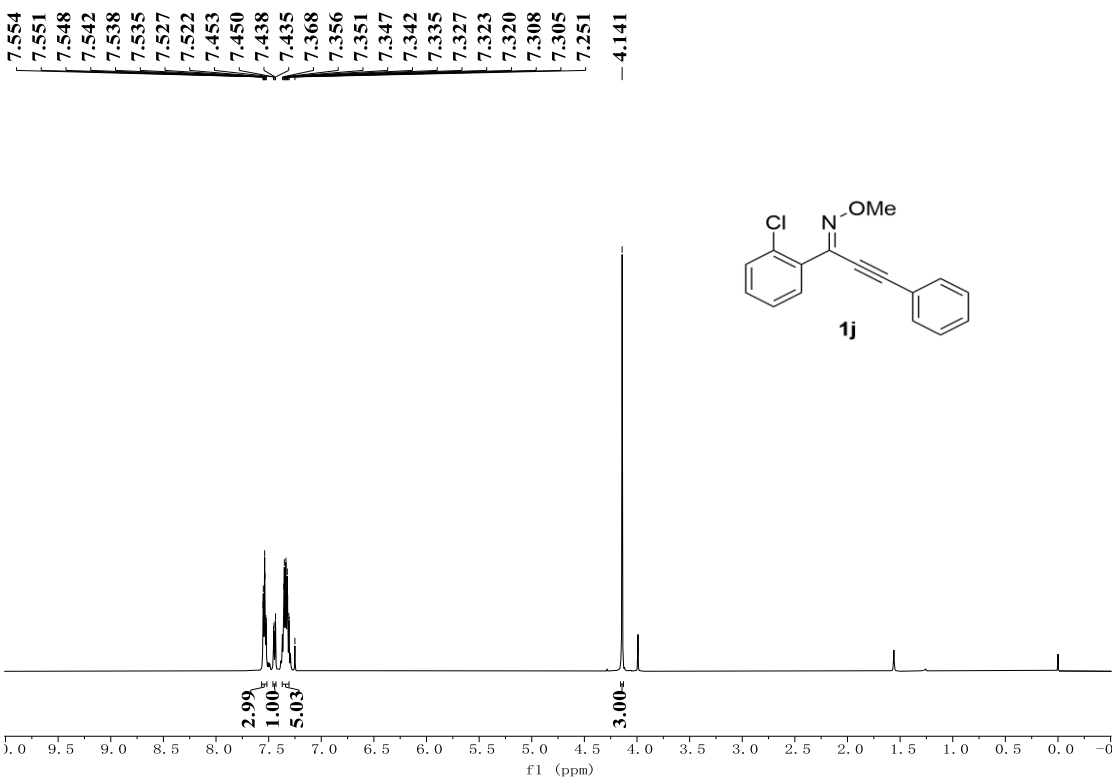
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7.356
7.351
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7.342
7.335
7.327
7.323
7.320
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Cl
N
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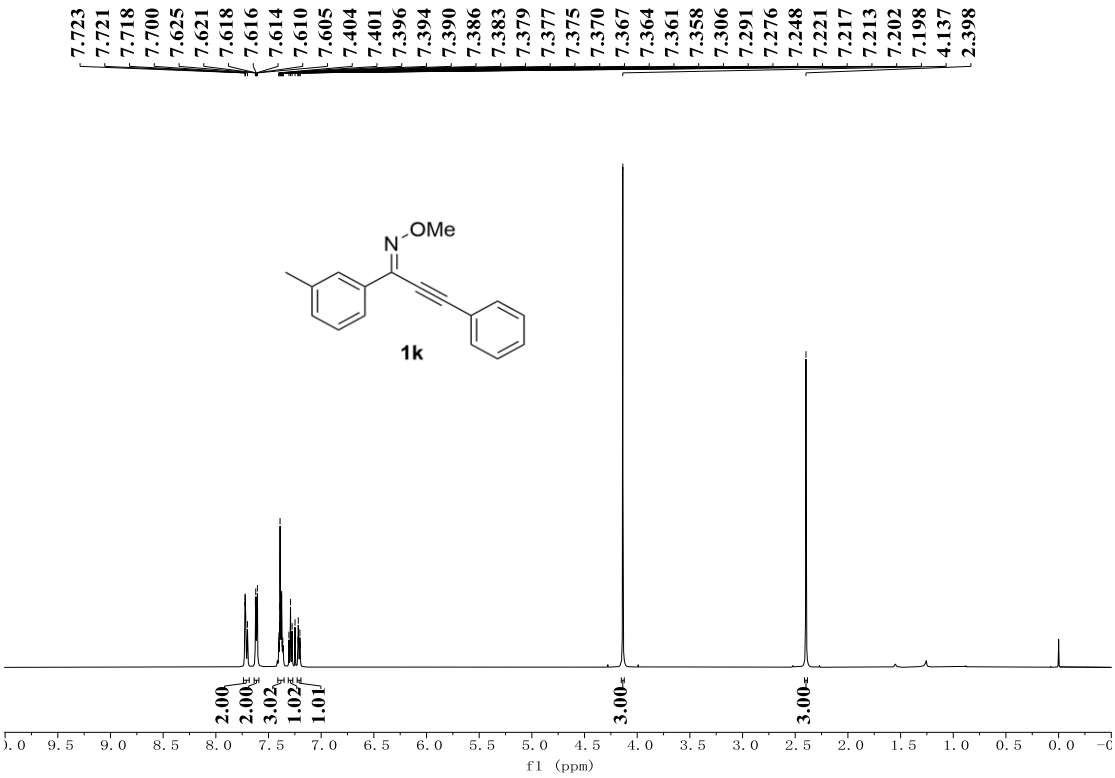
f1 (ppm)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7.610
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7.401
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7.394
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7.386
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7.361
7.358
7.306
7.291
7.276
7.248
7.221
7.217
7.213
7.202
7.198
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1.01
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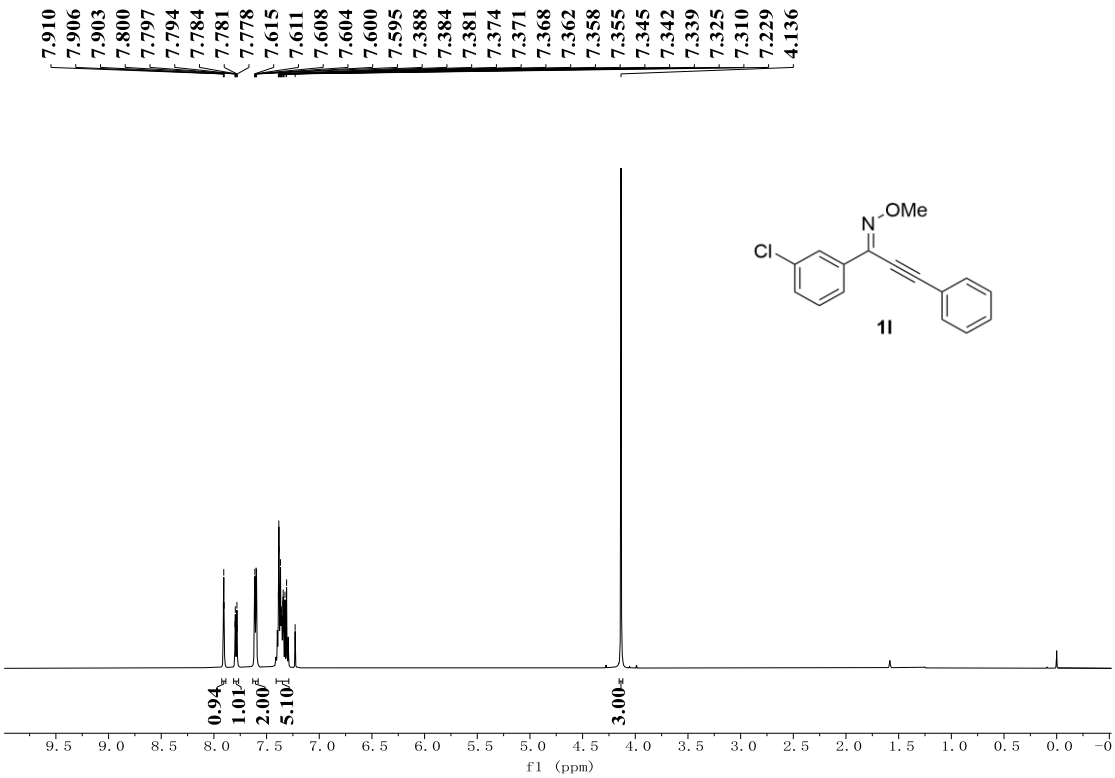
3.00
f1 (ppm)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7.611
7.608
7.604
7.600
7.595
7.388
7.384
7.381
7.374
7.371
7.368
7.362
7.358
7.355
7.345
7.342
7.339
7.325
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N
OMe
Cl
1l
0.94
1.01
2.00
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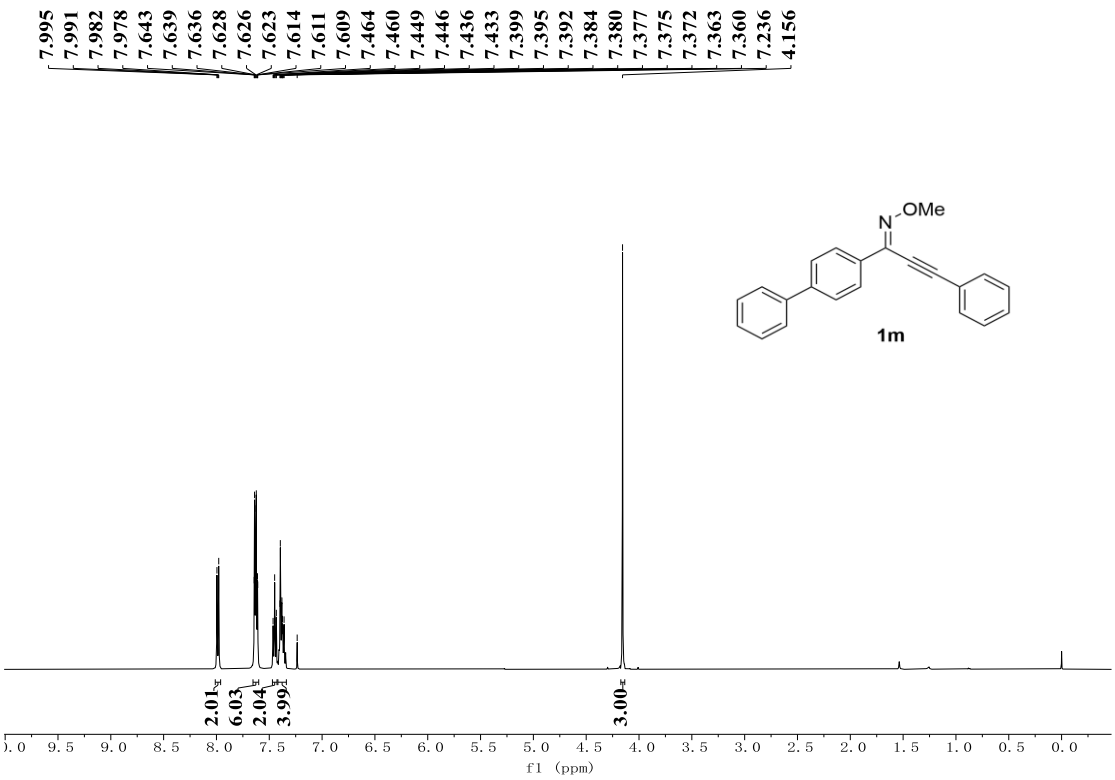
3.00
f1 (ppm)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7.614
7.611
7.609
7.464
7.460
7.449
7.446
7.436
7.433
7.399
7.395
7.392
7.384
7.380
7.377
7.375
7.372
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OMe
1m
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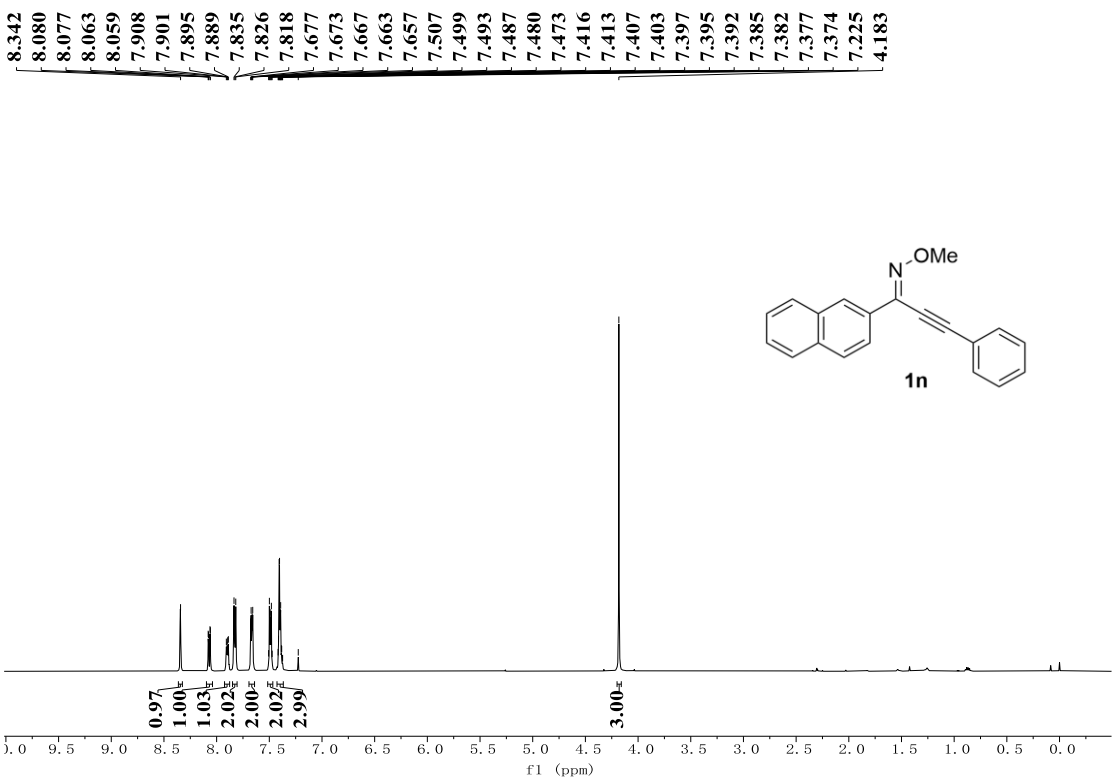
6.03
2.04
3.99
3.00
f1 (ppm)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7.818
7.677
7.673
7.667
7.663
7.657
7.507
7.499
7.493
7.487
7.480
7.473
7.416
7.413
7.407
7.403
7.397
7.395
7.392
7.385
7.382
7.377
7.374
7.225
4.183
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0.97
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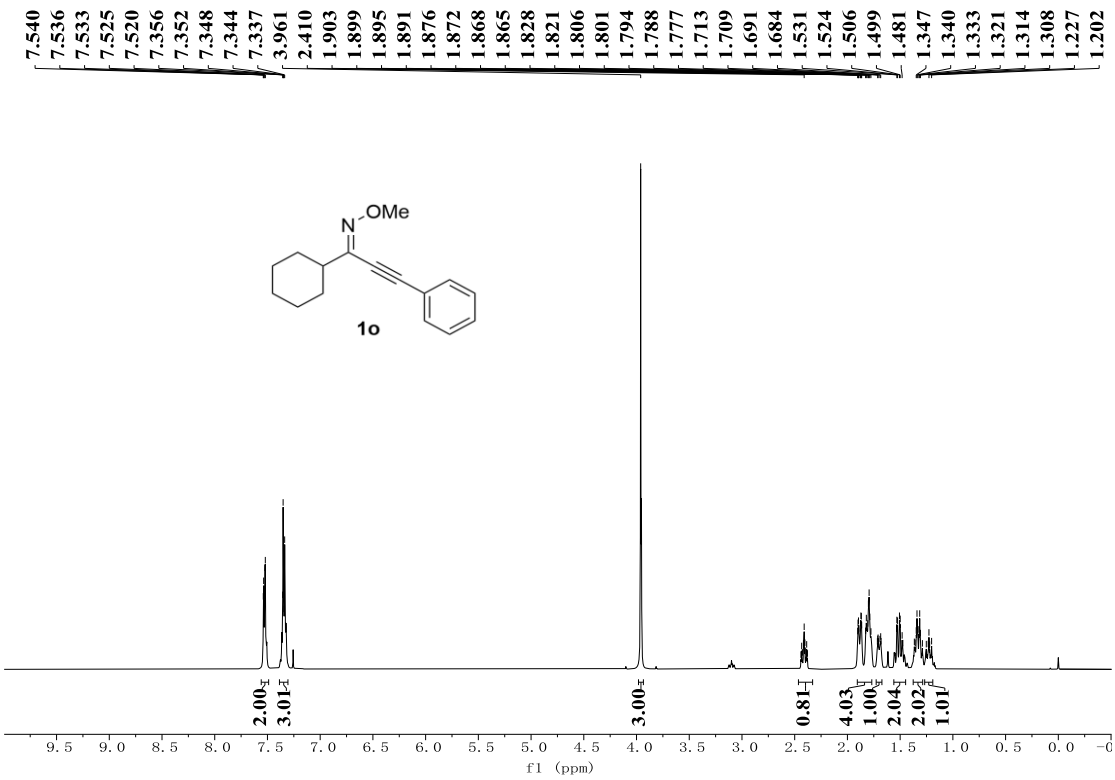
1.03
2.02
2.00
2.02
2.99
3.00
f1 (ppm)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7.344
7.337
3.961
2.410
1.903
1.899
1.895
1.891
1.876
1.872
1.868
1.865
1.828
1.821
1.806
1.801
1.794
1.788
1.777
1.713
1.709
1.691
1.684
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1.524
1.506
1.499
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1.347
1.340
1.333
1.321
1.314
1.308
1.227
1.202
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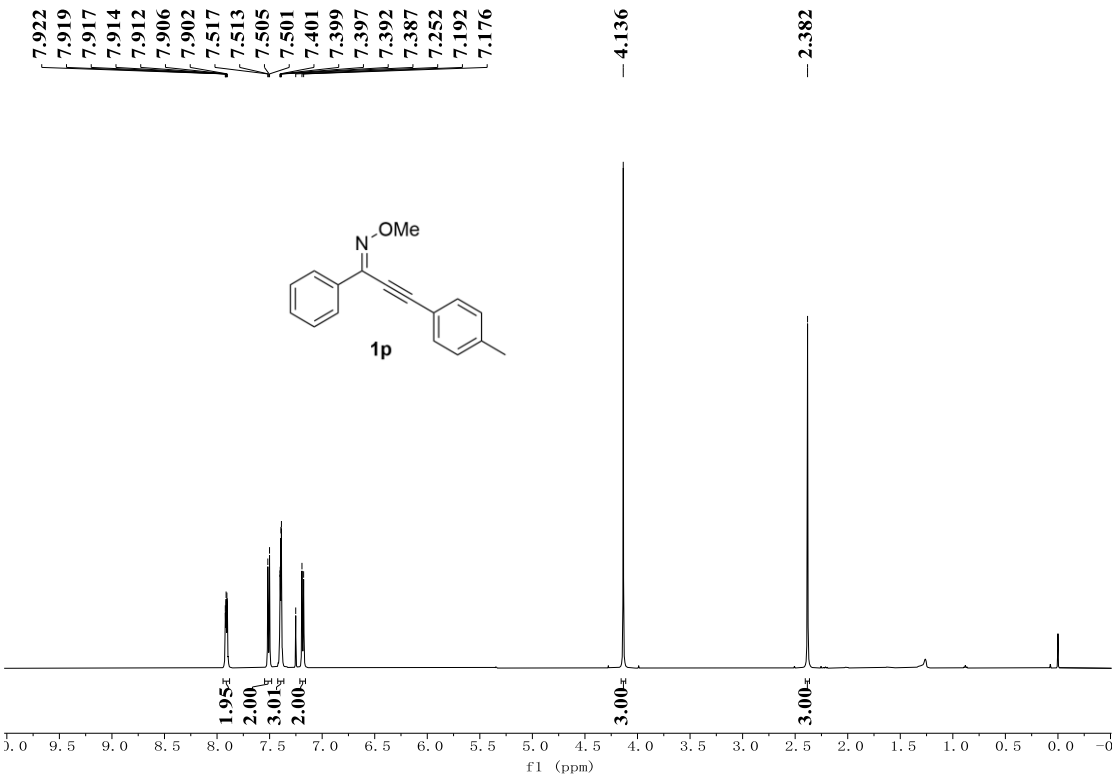
2.04
2.02
1.01
f1 (ppm)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7.513
7.505
7.501
7.401
7.399
7.397
7.392
7.387
7.252
7.192
7.176
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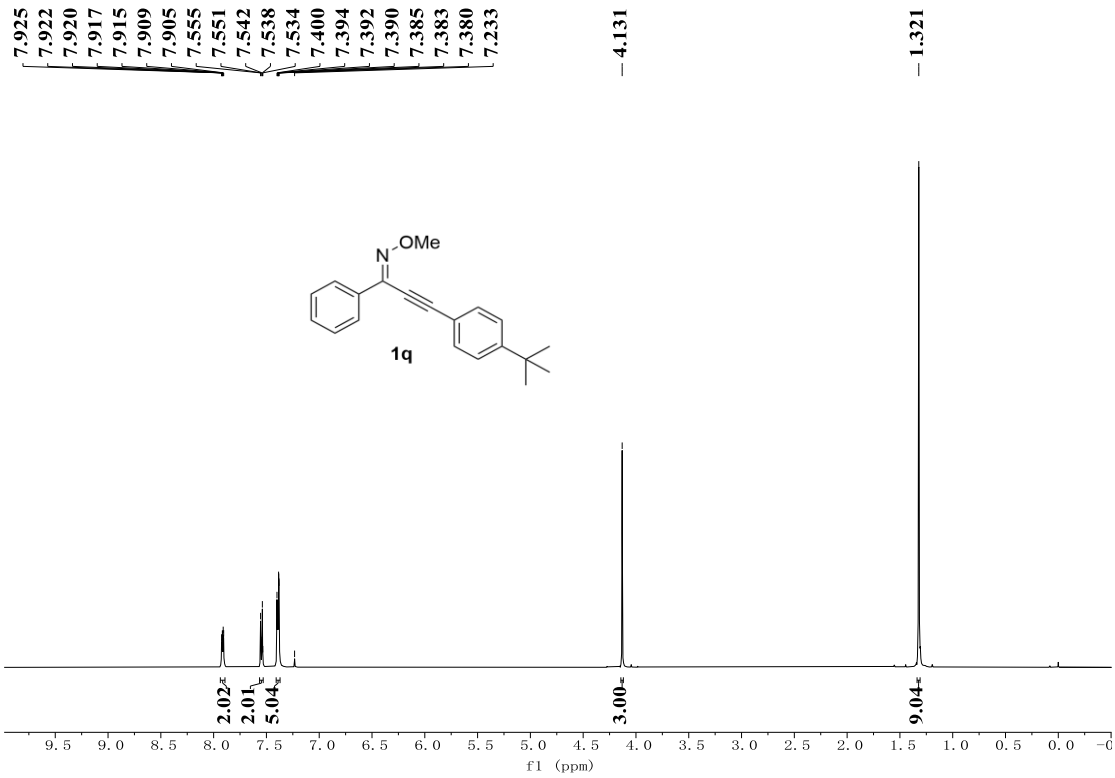
N
OMe
1p
1.95
2.00
3.01
2.00
3.00
3.00
f1 (ppm)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7.551
7.542
7.538
7.534
7.400
7.394
7.392
7.390
7.385
7.383
7.380
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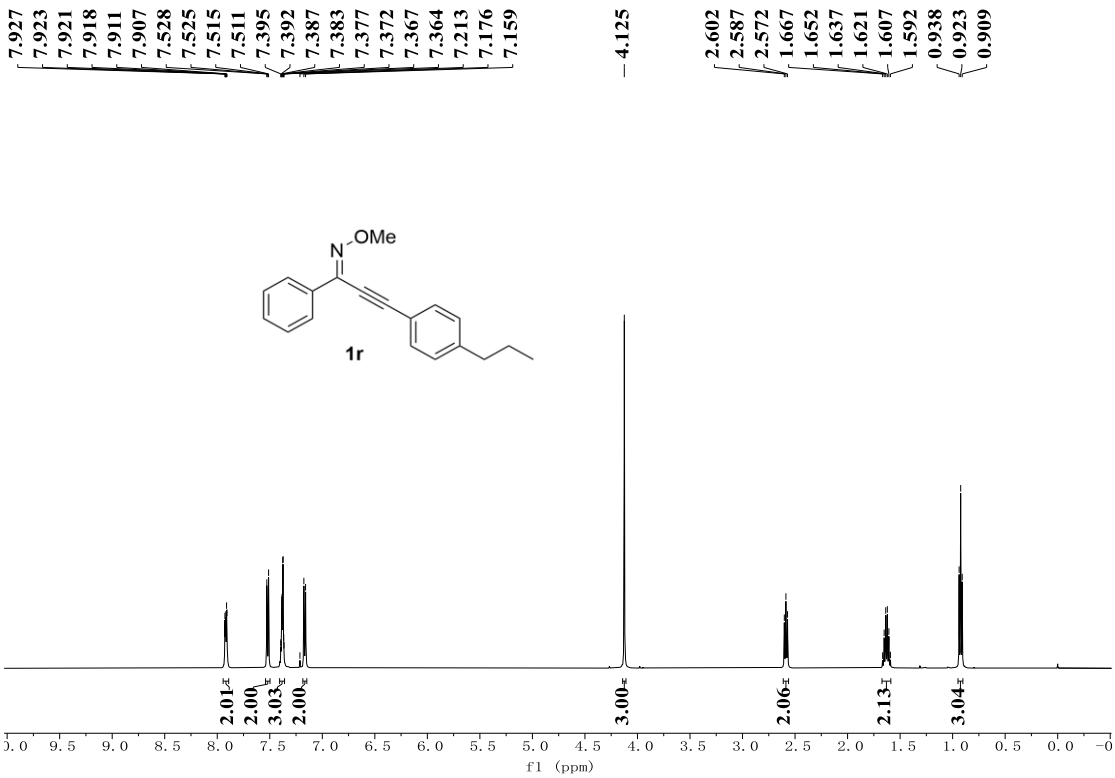
1.321
N
OMe
1q
2.02
2.01
5.04
3.00
9.04
f1 (ppm)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7.511
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7.392
7.387
7.383
7.377
7.372
7.367
7.364
7.213
7.176
7.159
4.125
2.602
2.587
2.572
1.667
1.652
1.637
1.621
1.607
1.592
0.938
0.923
0.909
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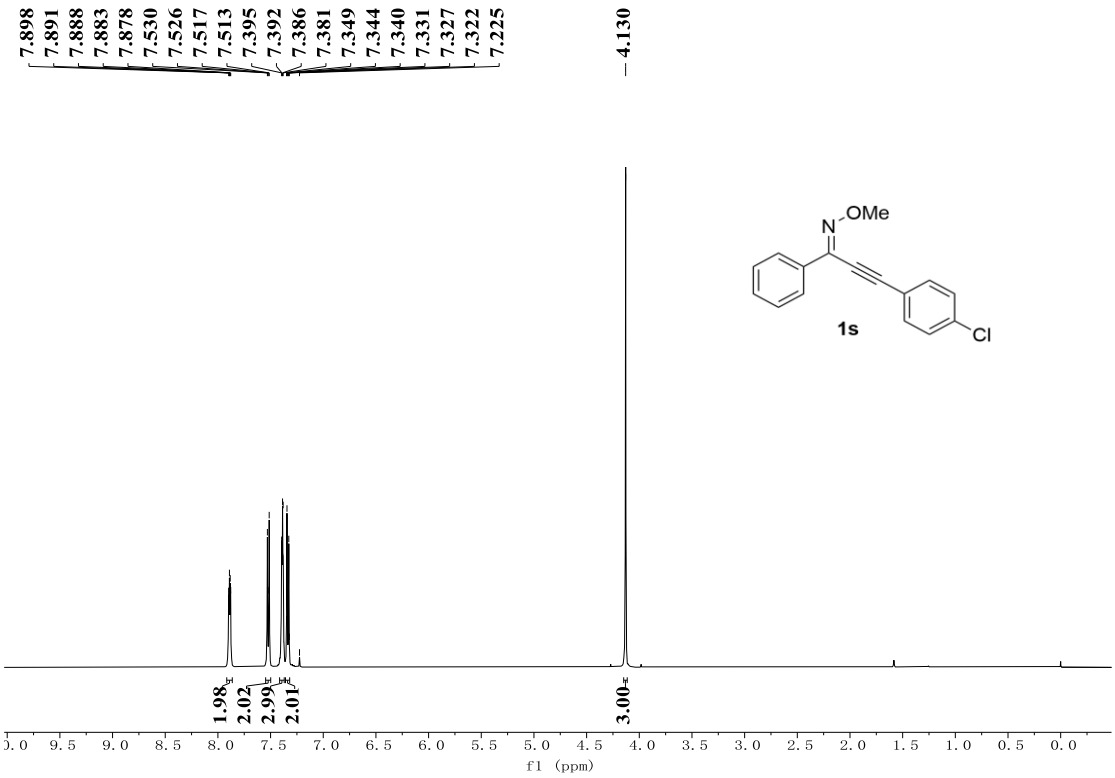
2.00
3.03
2.00
3.00
2.06
2.13
3.04
f1 (ppm)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7.517
7.513
7.395
7.392
7.386
7.381
7.349
7.344
7.340
7.331
7.327
7.322
7.225
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OMe
N
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Cl
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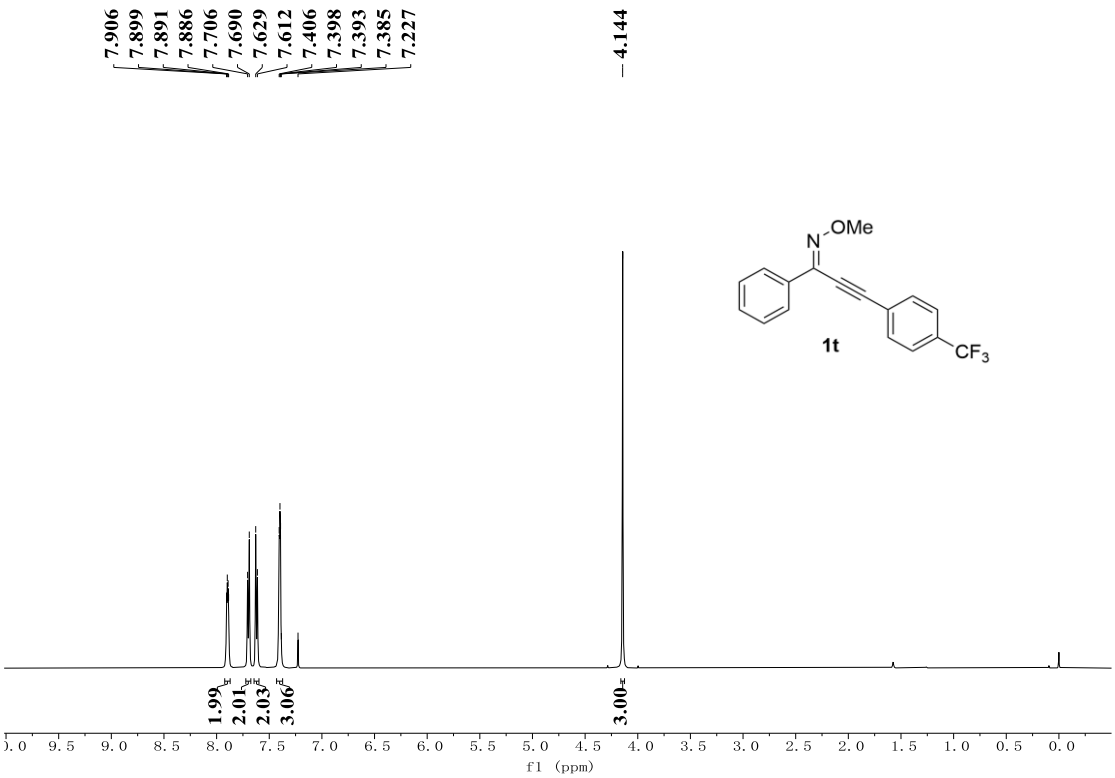
2.99
2.01
3.00
f1 (ppm)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7.690
7.629
7.612
7.406
7.398
7.393
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CF3
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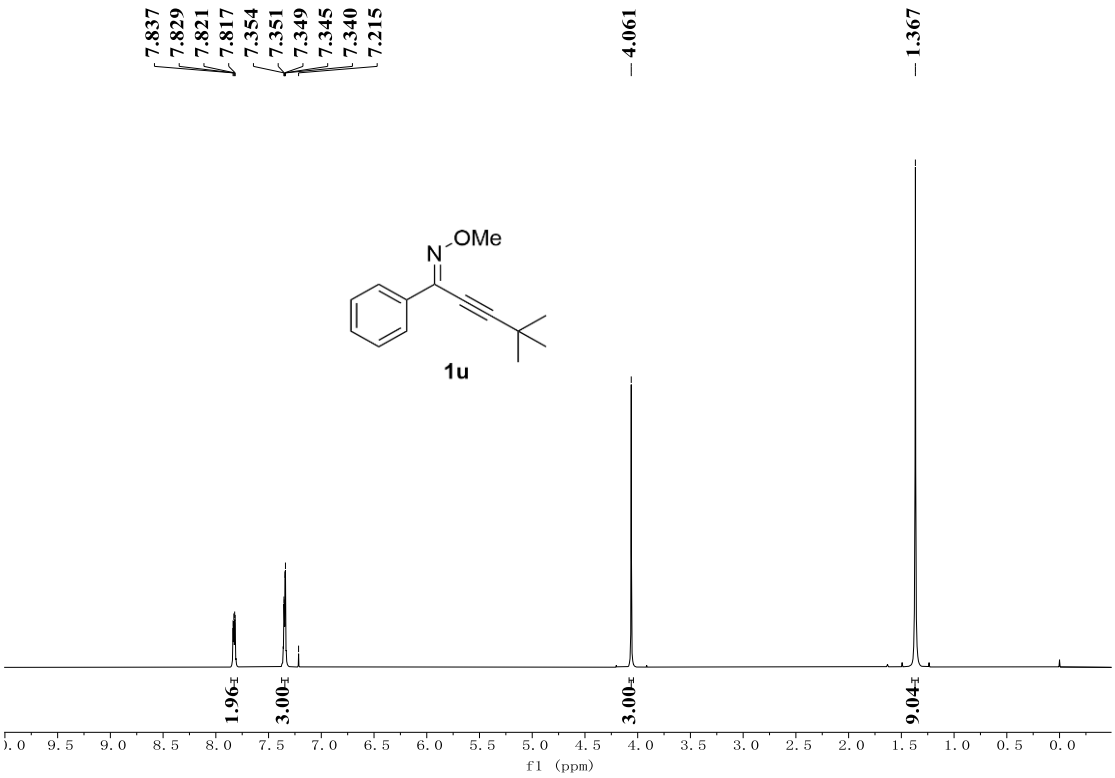
2.01
2.03
3.06
3.00
f1 (ppm)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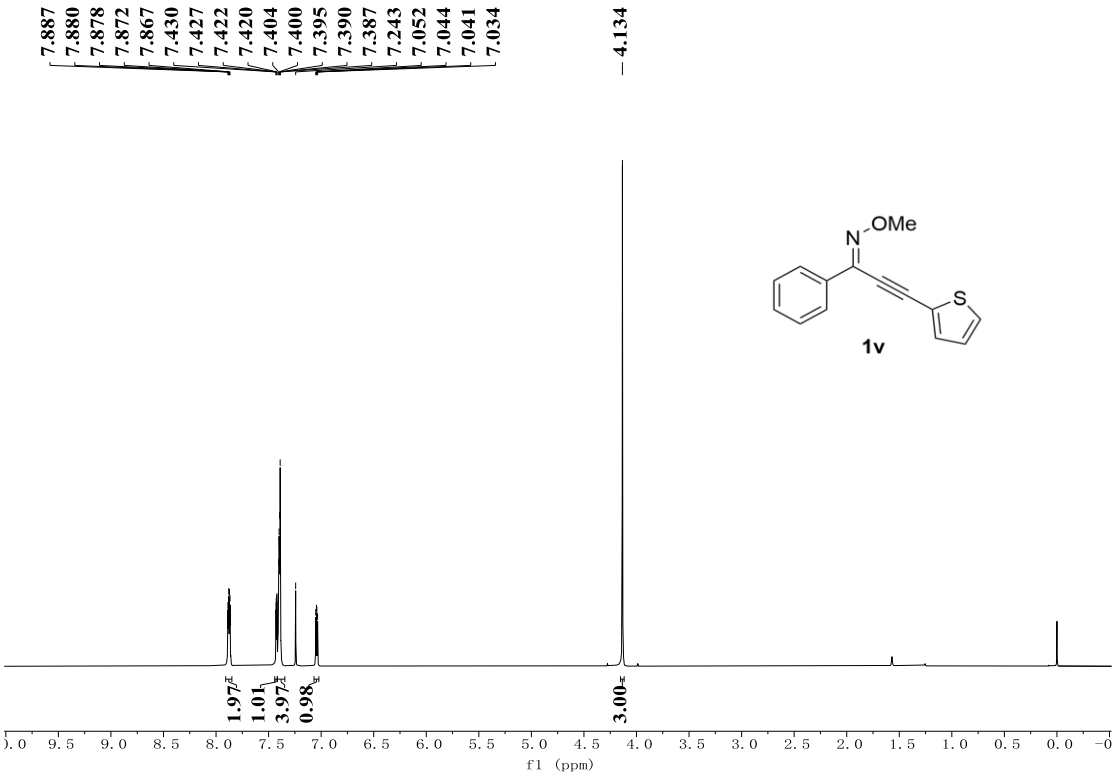
f1 (ppm)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7.400
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7.390
7.387
7.243
7.052
7.044
7.041
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OMe
N
S
1v
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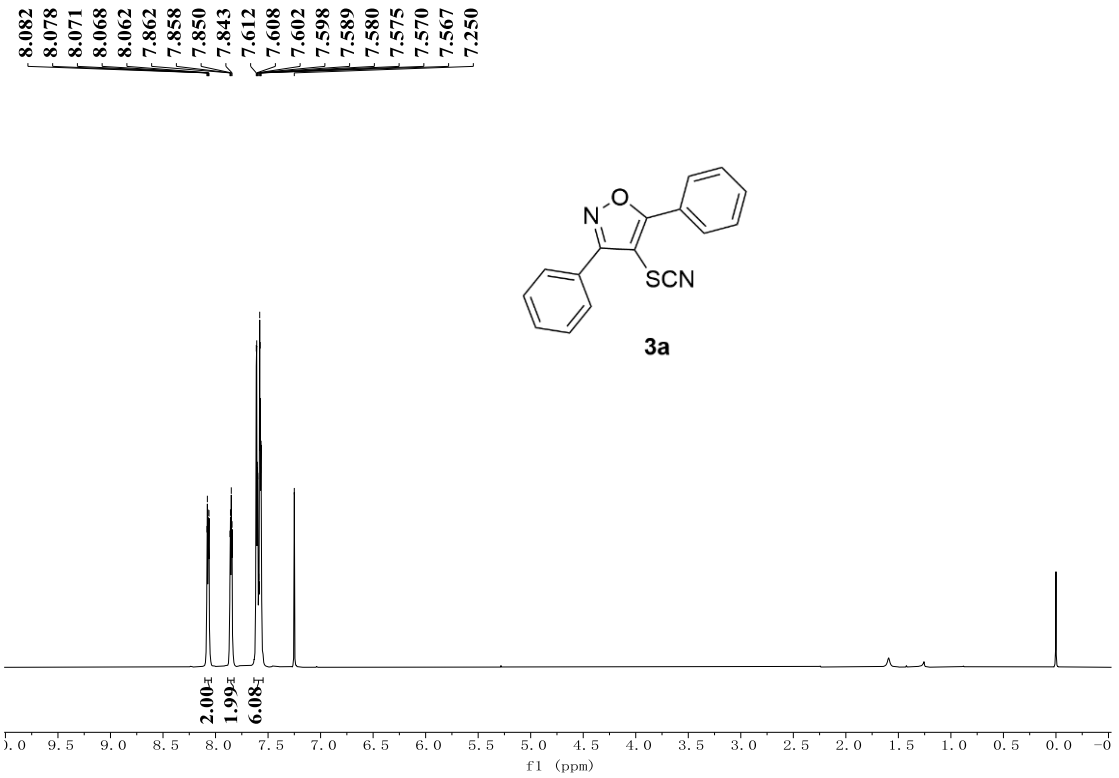
1.01
3.97
0.98
3.00
f1 (ppm)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7.850
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7.612
7.608
7.602
7.598
7.589
7.580
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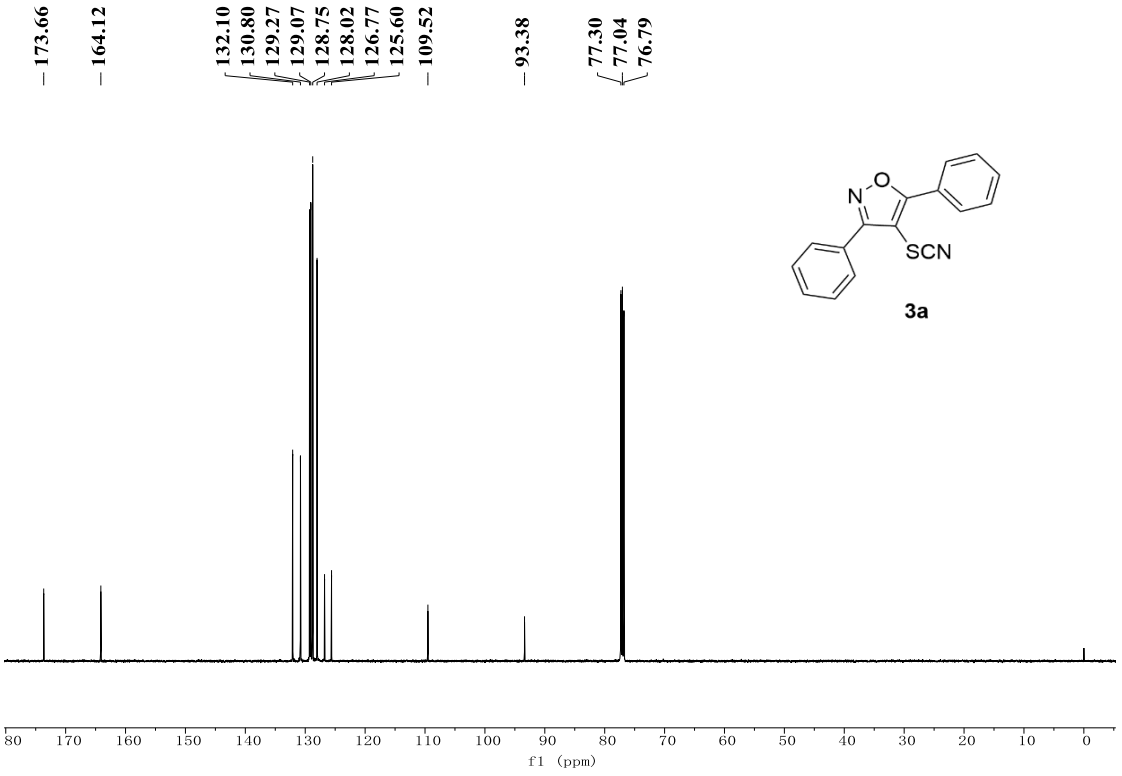
7.567
7.250
N
O
SCN
3a
2.00
1.99
6.08
f1 (ppm)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132.10
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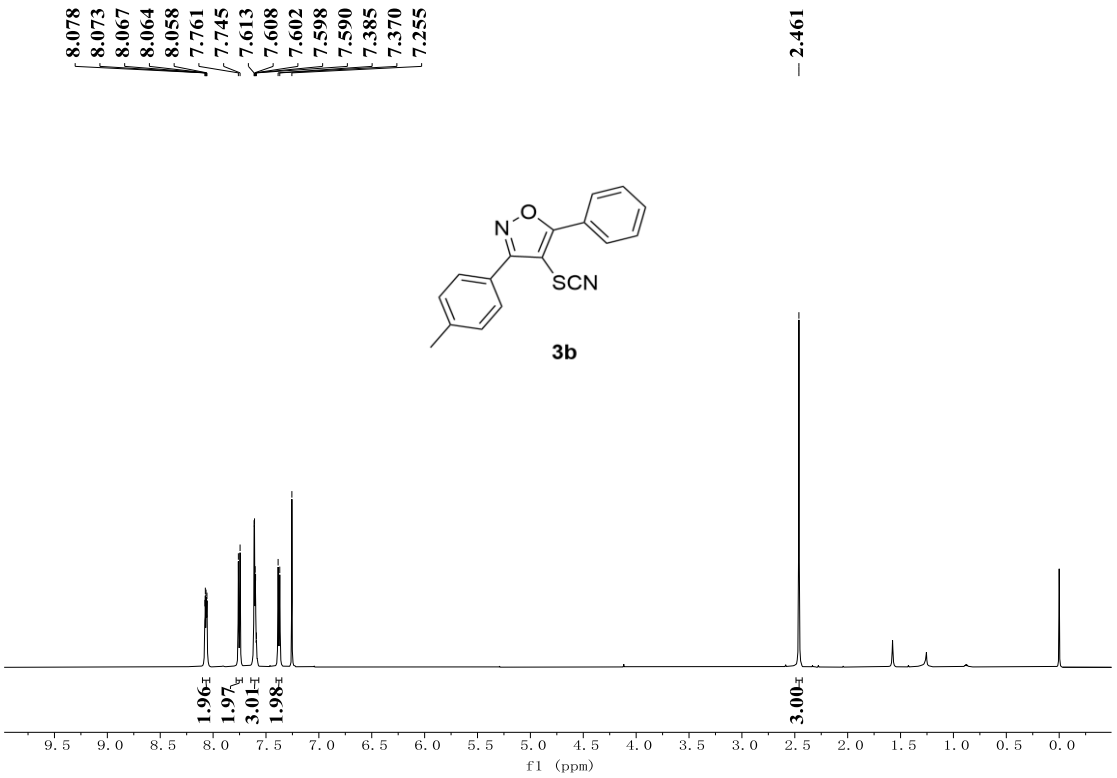
129.27
129.07
128.75
128.02
126.77
125.60
109.52
93.38
77.30
77.04
76.79
N
O
SCN
3a
f1 (ppm)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7.598
7.590
7.385
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N
O
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3b
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1.97
3.01
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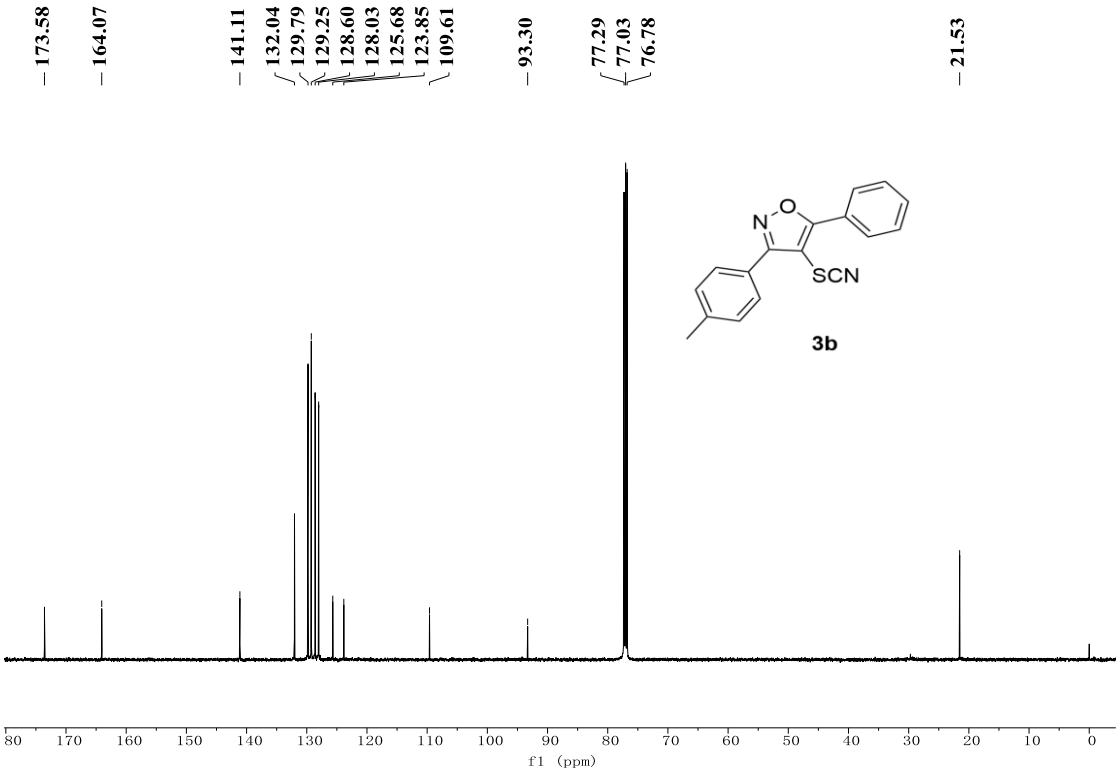
3.00
f1 (ppm)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129.79
129.25
128.60
128.03
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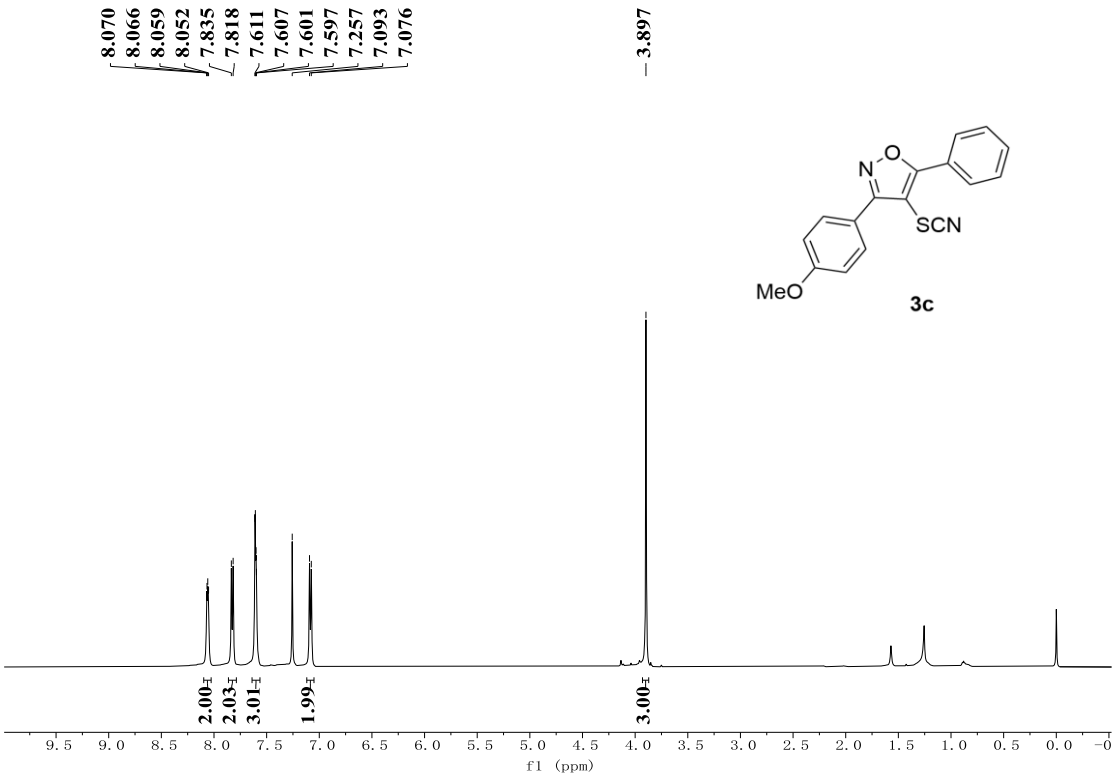
77.03
76.78
21.53
N
O
SCN
3b
f1 (ppm)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7.818
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7.607
7.601
7.597
7.257
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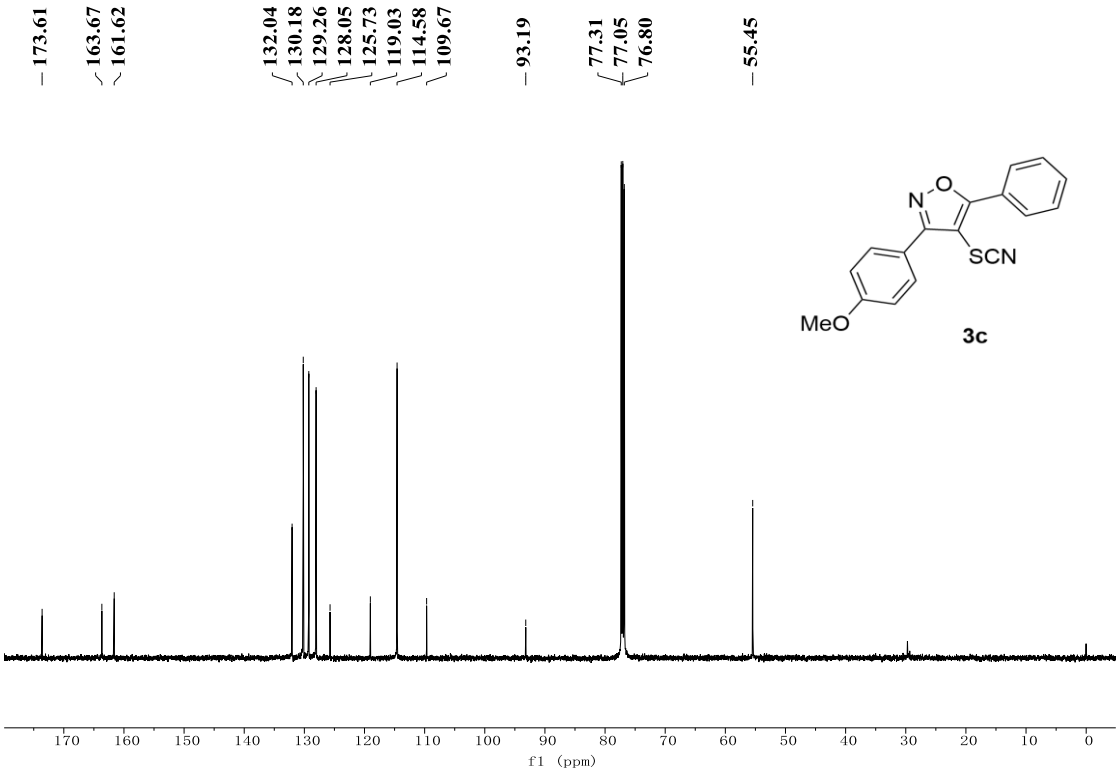
7.076
3.897
SCN
MeO
3c
2.00
2.03
3.01
1.99
3.00
f1 (ppm)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129.26
128.05
125.73
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93.19
77.31
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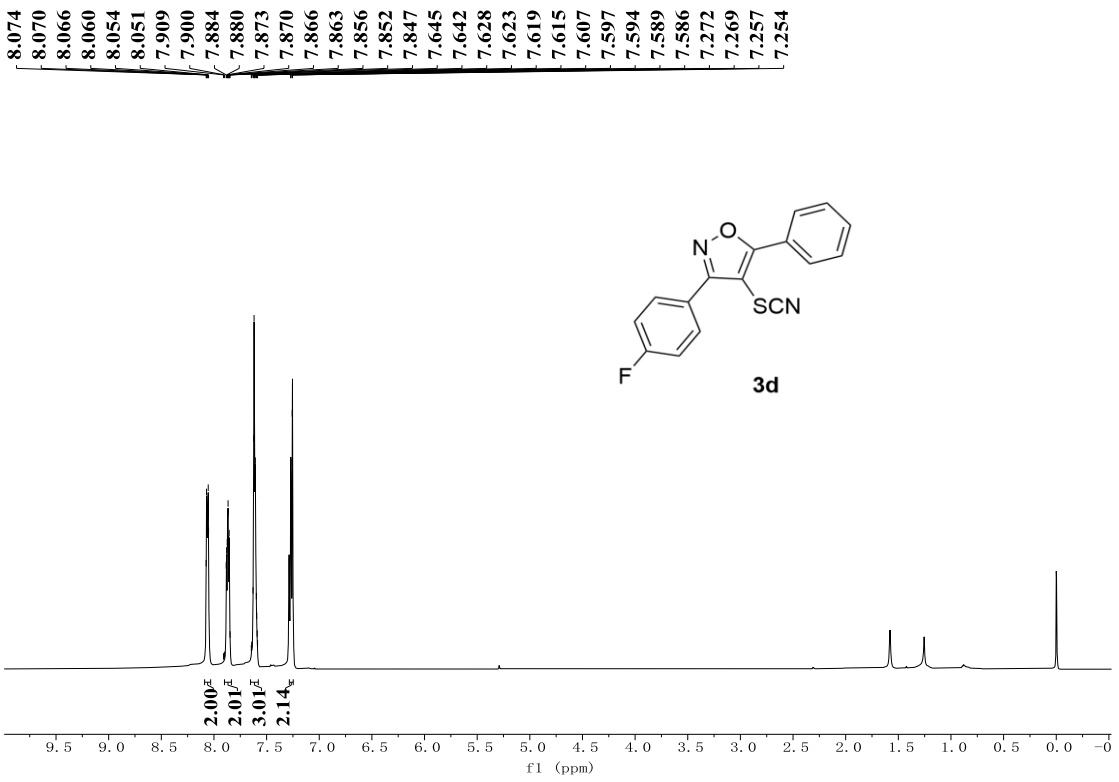
55.45
SCN
MeO
3c
f1 (ppm)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7.852
7.847
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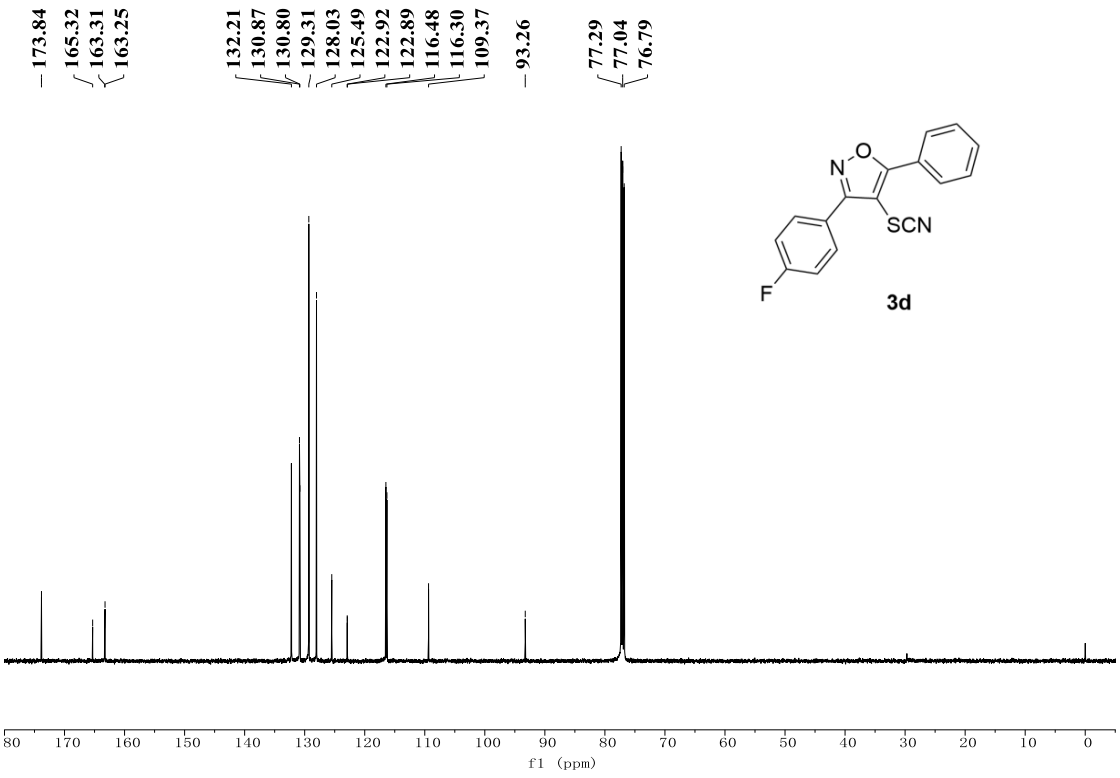
7.628
7.623
7.619
7.615
7.607
7.597
7.594
7.589
7.586
7.272
7.269
7.257
7.254
N
O
SCN
F
3d
2.00
2.01
3.01
2.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.87
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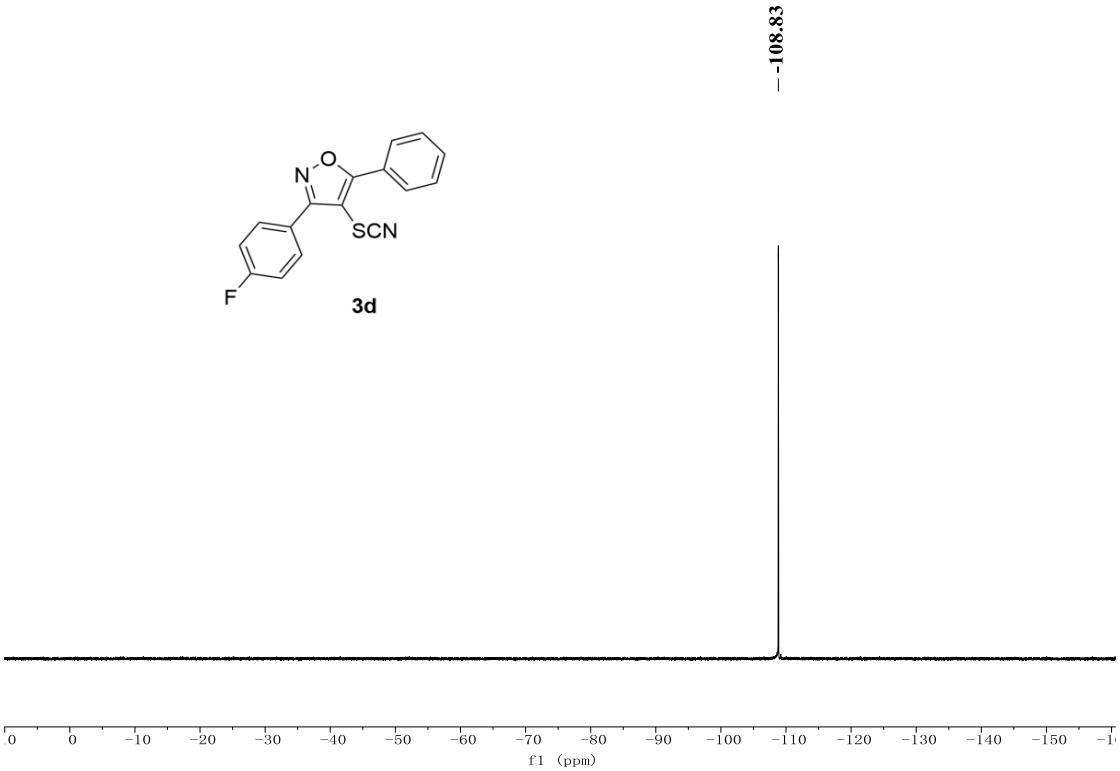
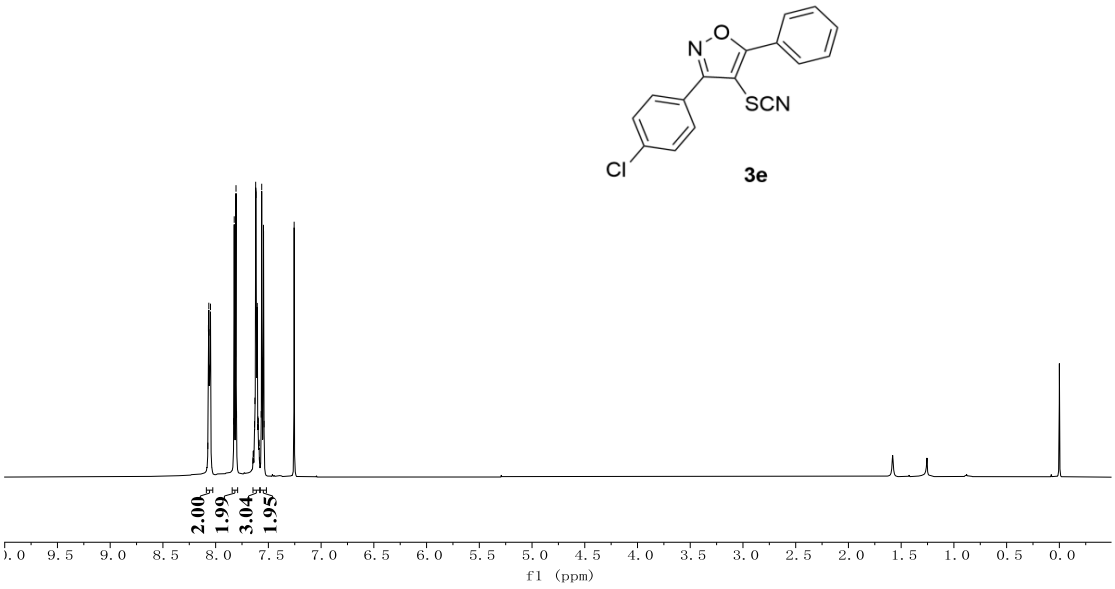
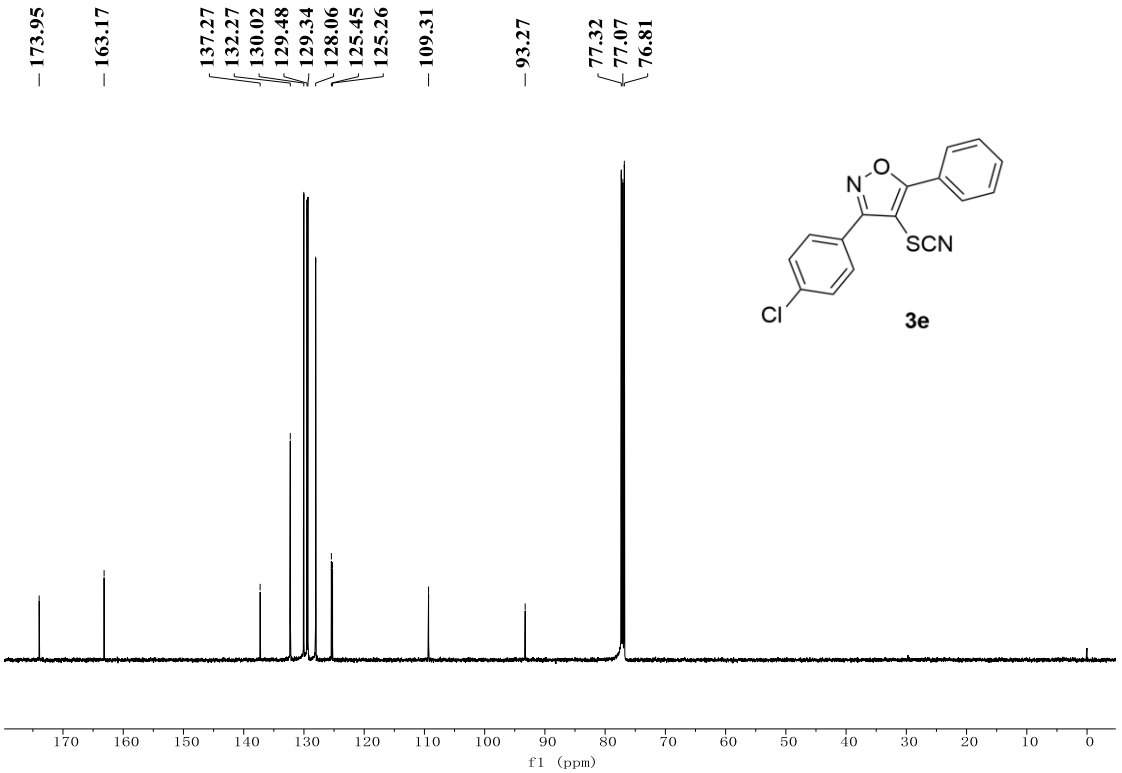
129.31
128.03
125.49
122.92
122.89
116.48
116.30
109.37
93.26
77.29
77.04
76.79
N
O
SCN
F
3d
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



8.074 8.068 8.065 8.061 8.059 8.054 8.049 7.829 7.824 7.820 7.811 7.807 7.802 7.647 7.644 7.641 7.631 7.628 7.620 7.618 7.613 7.608 7.605 7.599 7.595 7.591 7.588 7.584 7.568 7.563 7.559 7.550 7.546 7.541 7.256

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128.06
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125.26
109.31
93.27
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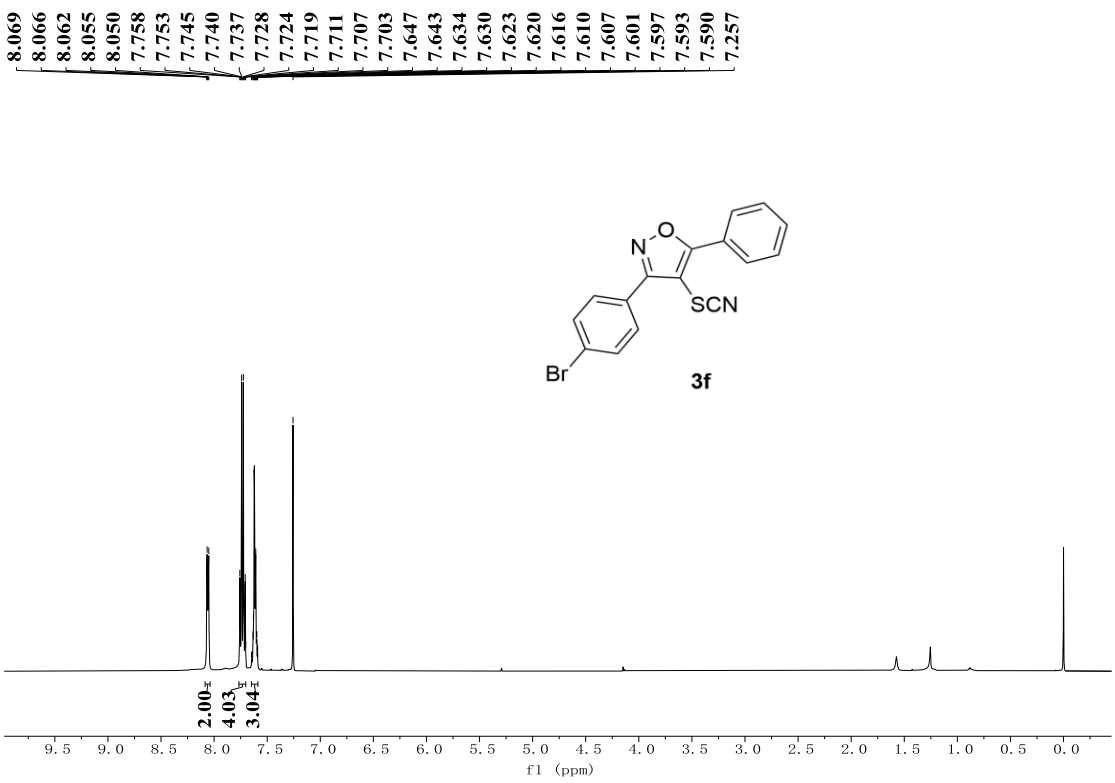
76.81
N
O
SCN
Cl
3e
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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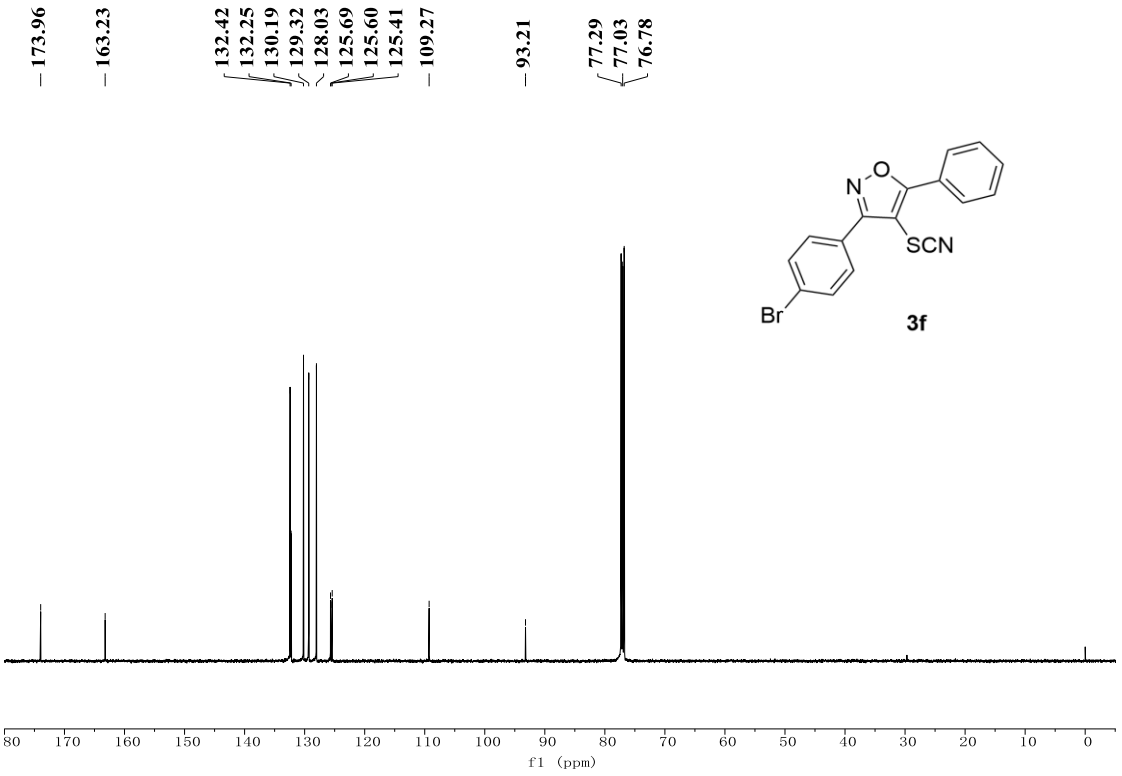
7.593
7.590
7.257
N
O
SCN
Br
3f
2.00
4.03
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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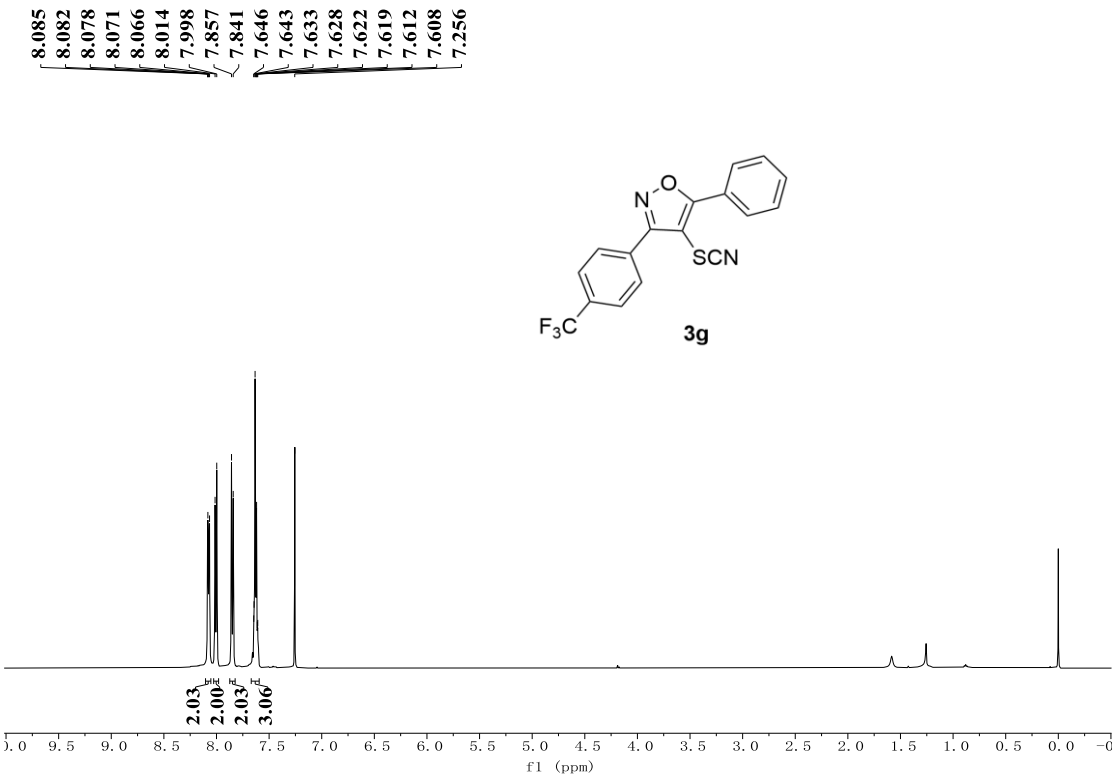
163.23
132.42
132.25
130.19
129.32
128.03
125.69
125.60
125.41
109.27
93.21
77.29
77.03
76.78
N
O
SCN
Br
3f
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.071
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8.014
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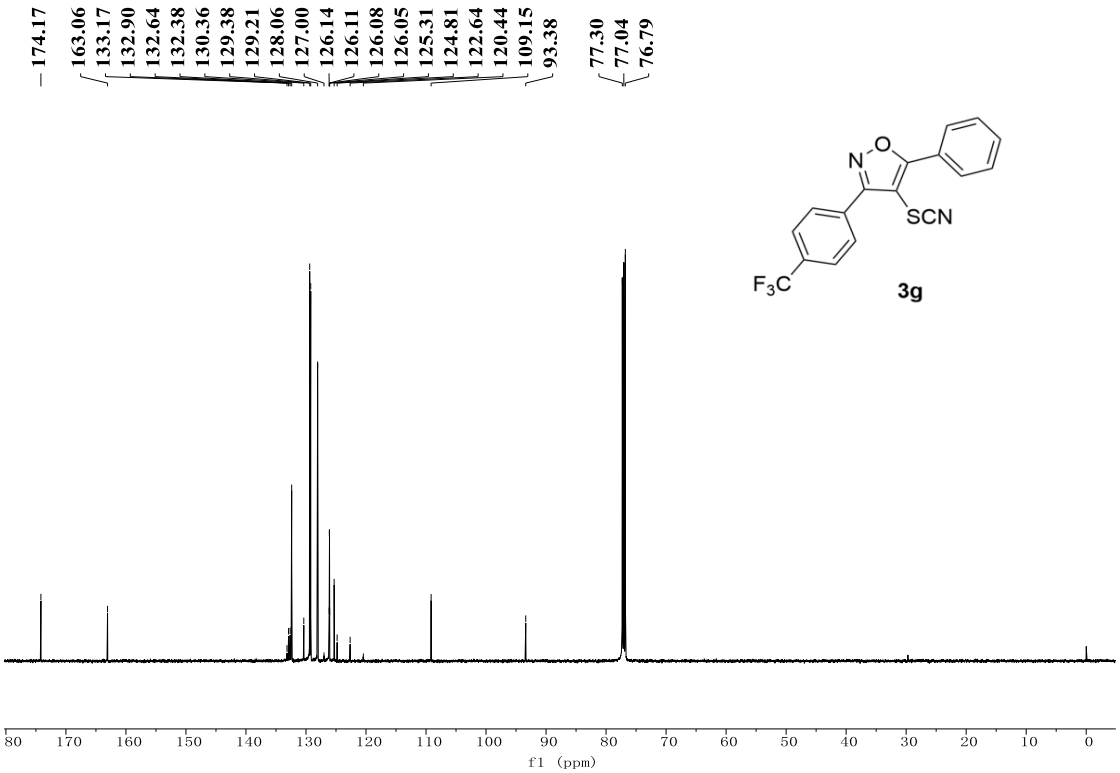
7.857
7.841
7.646
7.643
7.633
7.628
7.622
7.619
7.612
7.608
7.256
N
O
SCN
F3C
3g
2.03
2.00
2.03
3.06
f1 (ppm)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129.38
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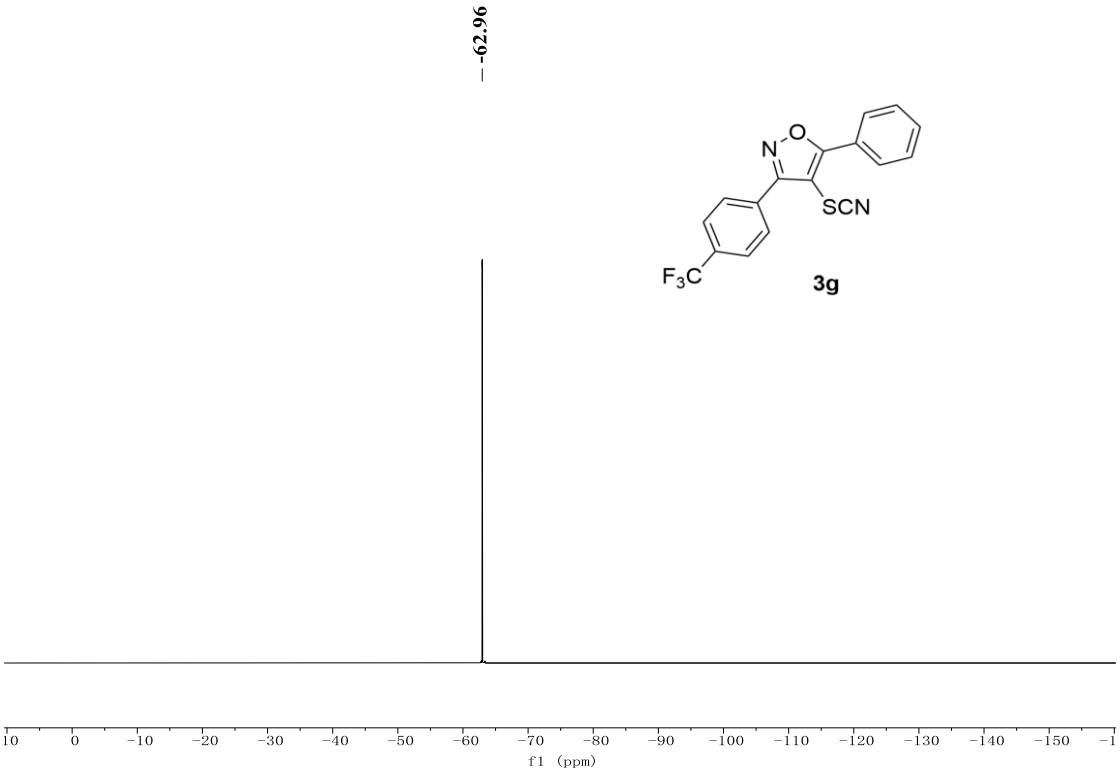
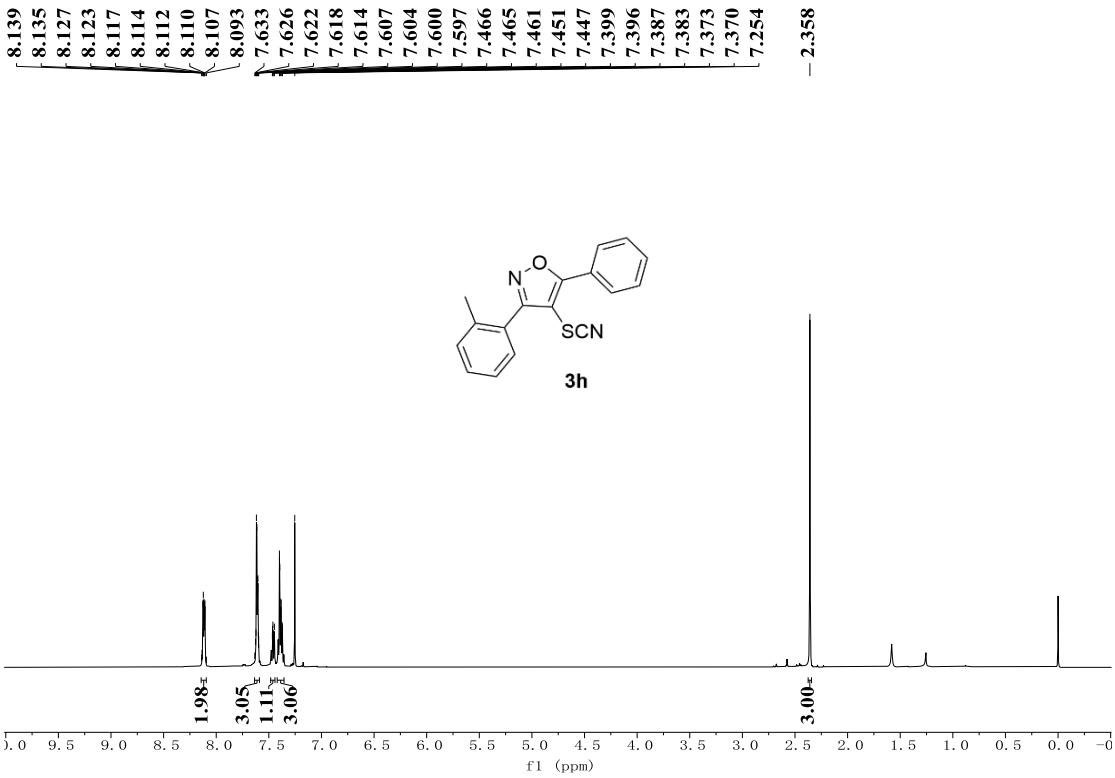
126.14
126.11
126.08
126.05
125.31
124.81
122.64
120.44
109.15
93.38
77.30
77.04
76.79
N
O
SCN
F3C
3g
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.96
N
O
SCN
F3C
3g
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −1
f1 (ppm)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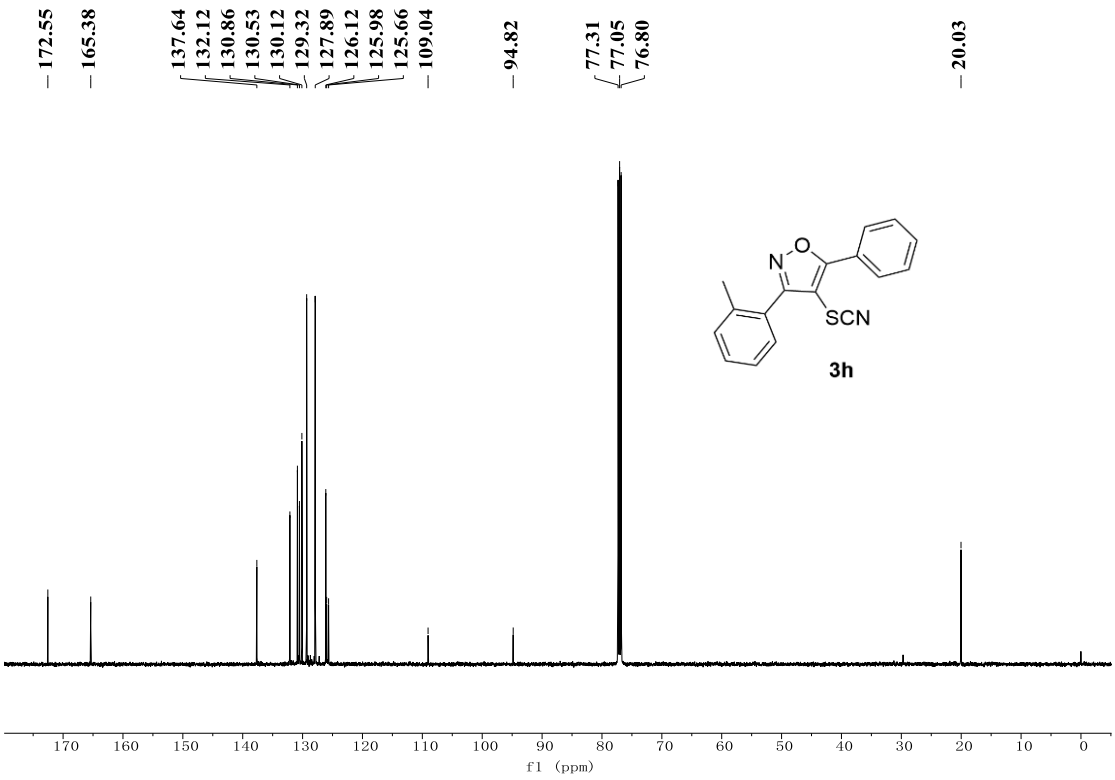
8.135
8.127
8.123
8.117
8.114
8.112
8.110
8.107
8.093
7.633
7.626
7.622
7.618
7.614
7.607
7.604
7.600
7.597
7.466
7.465
7.461
7.451
7.447
7.399
7.396
7.387
7.383
7.373
7.370
7.254
2.358
N
O
SCN
3h
1.98
3.05
1.11
3.06
3.00
f1 (ppm)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165.38
137.64
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130.53
130.12
129.32
127.89
126.12
125.98
125.66
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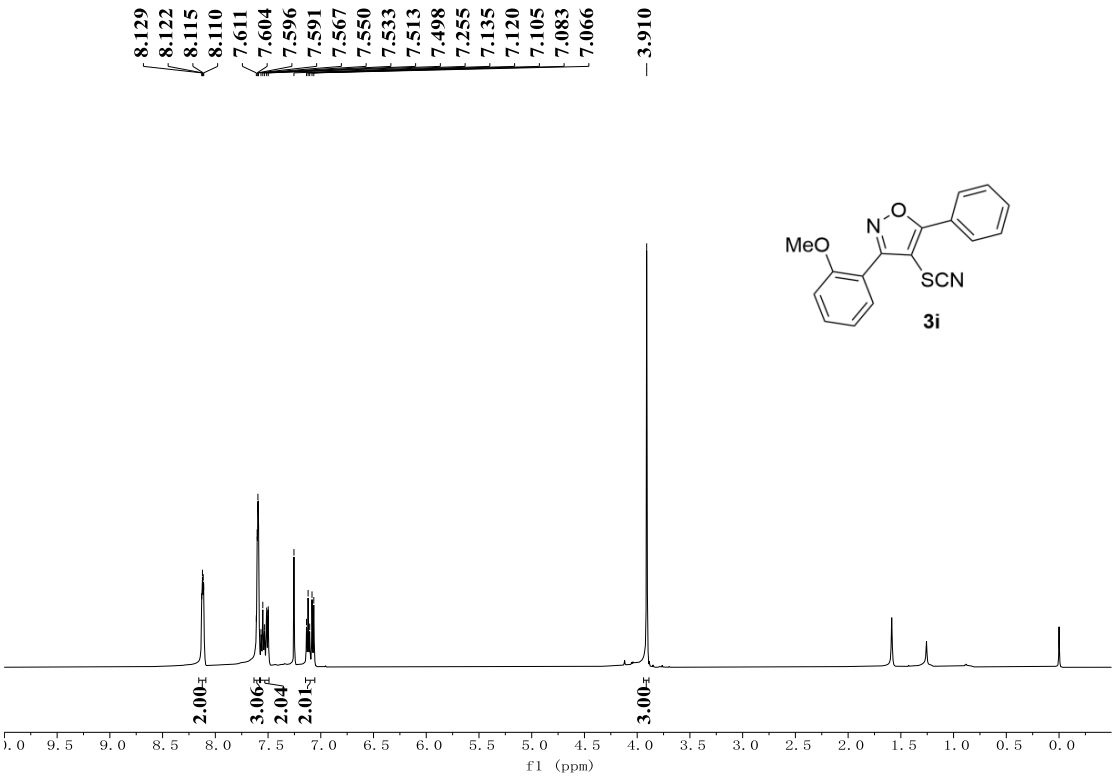
94.82
77.31
77.05
76.80
20.03
N
O
SCN
3h
f1 (ppm)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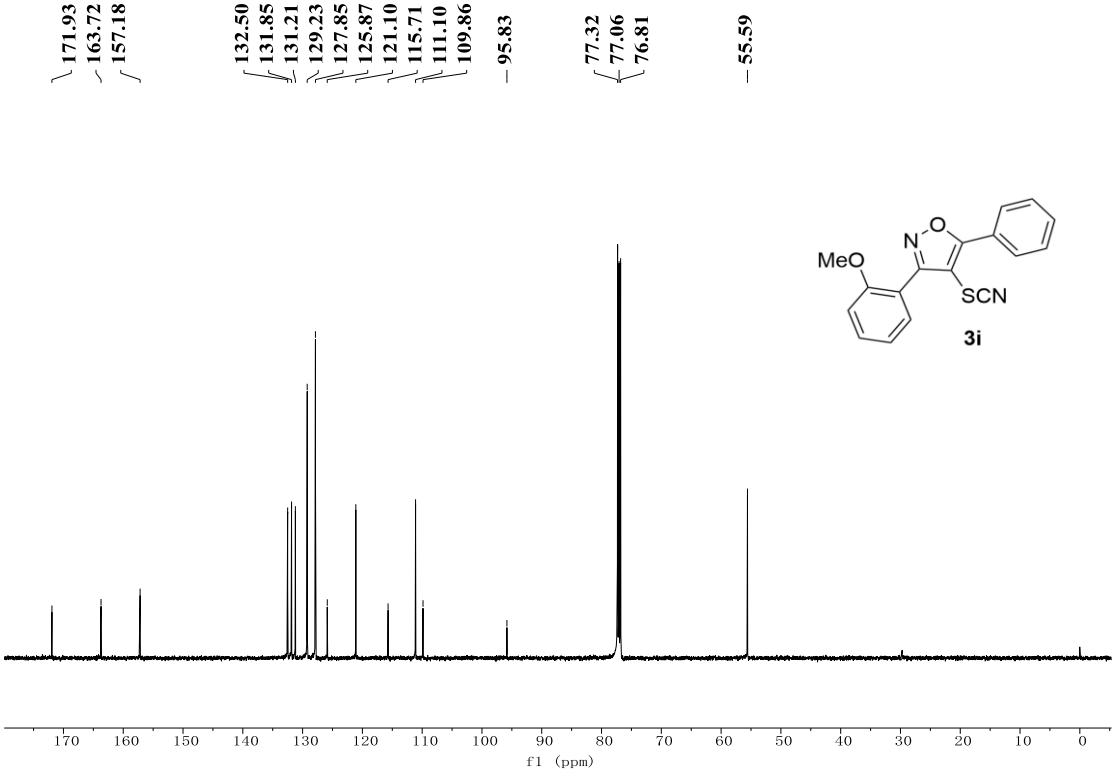
8.122
8.115
8.110
7.611
7.604
7.596
7.591
7.567
7.550
7.533
7.513
7.498
7.255
7.135
7.120
7.105
7.083
7.066
3.910
MeO
N
O
SCN
3i
2.00
3.06
2.04
2.01
3.00
f1 (ppm)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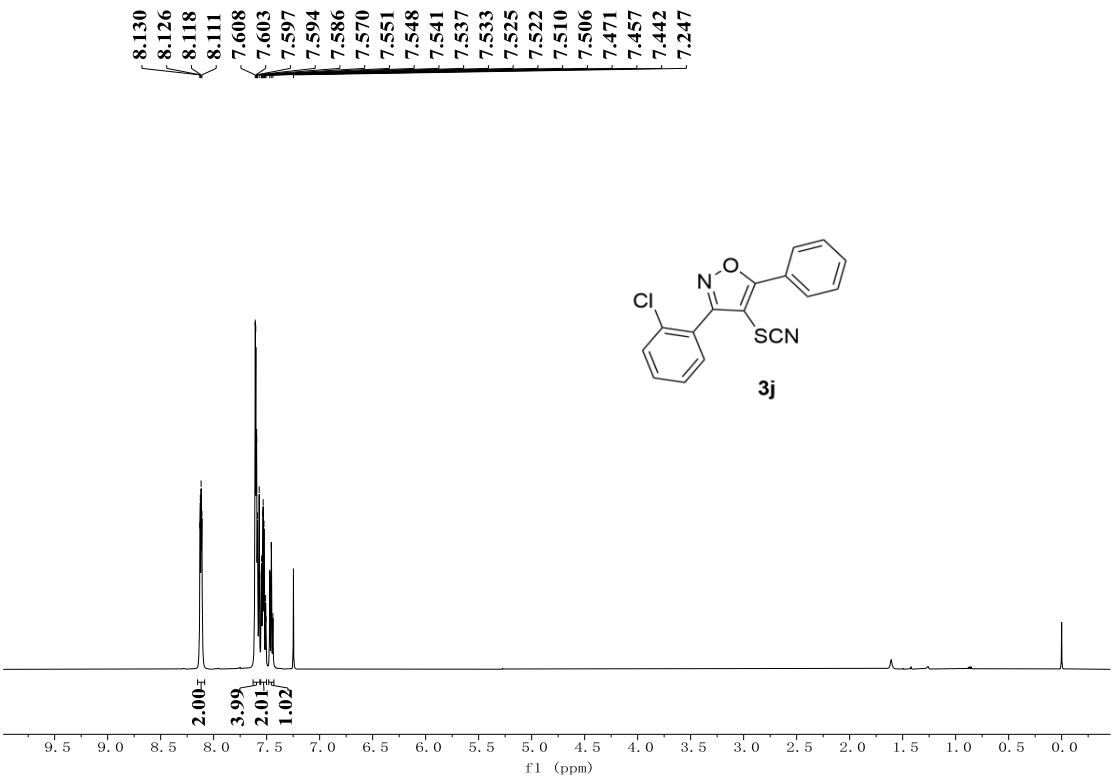
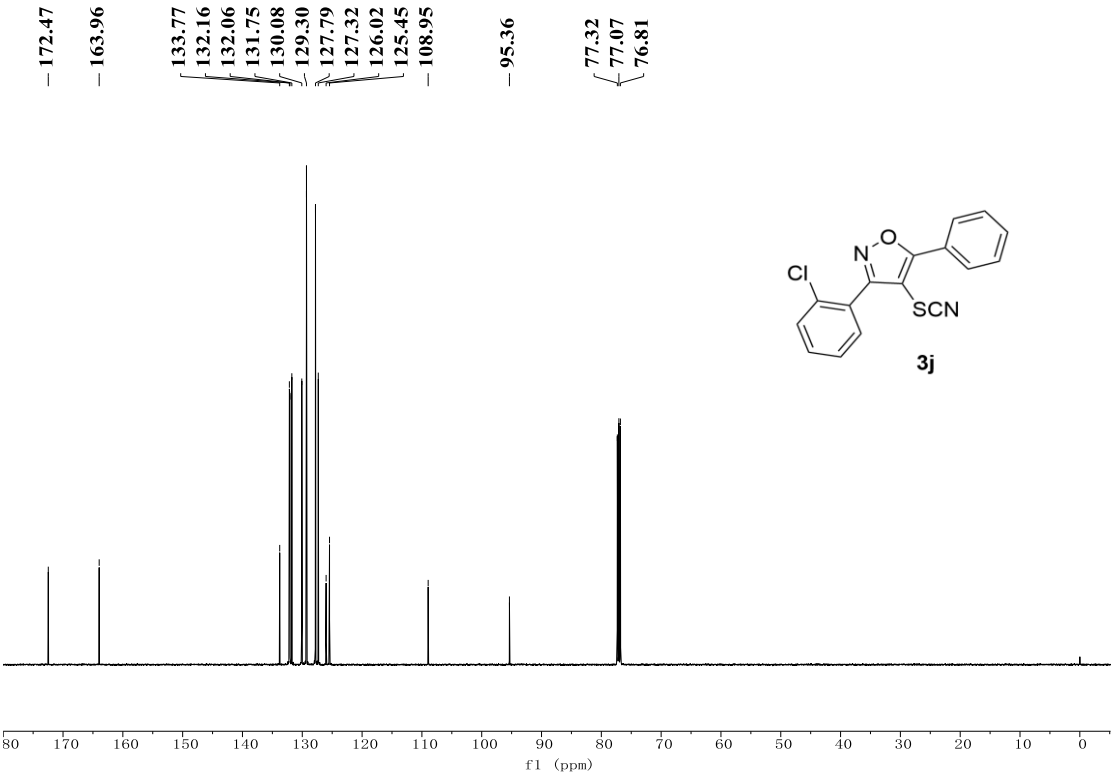
163.72
157.18
132.50
131.85
131.21
129.23
127.85
125.87
121.10
115.71
111.10
109.86
95.83
77.32
77.06
76.81
55.59
MeO
N
O
SCN
3i
f1 (ppm)


8.130
8.126
8.118
8.111
7.608
7.603
7.597
7.594
7.586
7.570
7.551
7.548
7.541
7.537
7.533
7.525
7.522
7.510
7.506
7.471
7.457
7.442
7.247
Cl
N
O
SCN
3j
2.00
3.99
2.01
1.02
f1 (ppm)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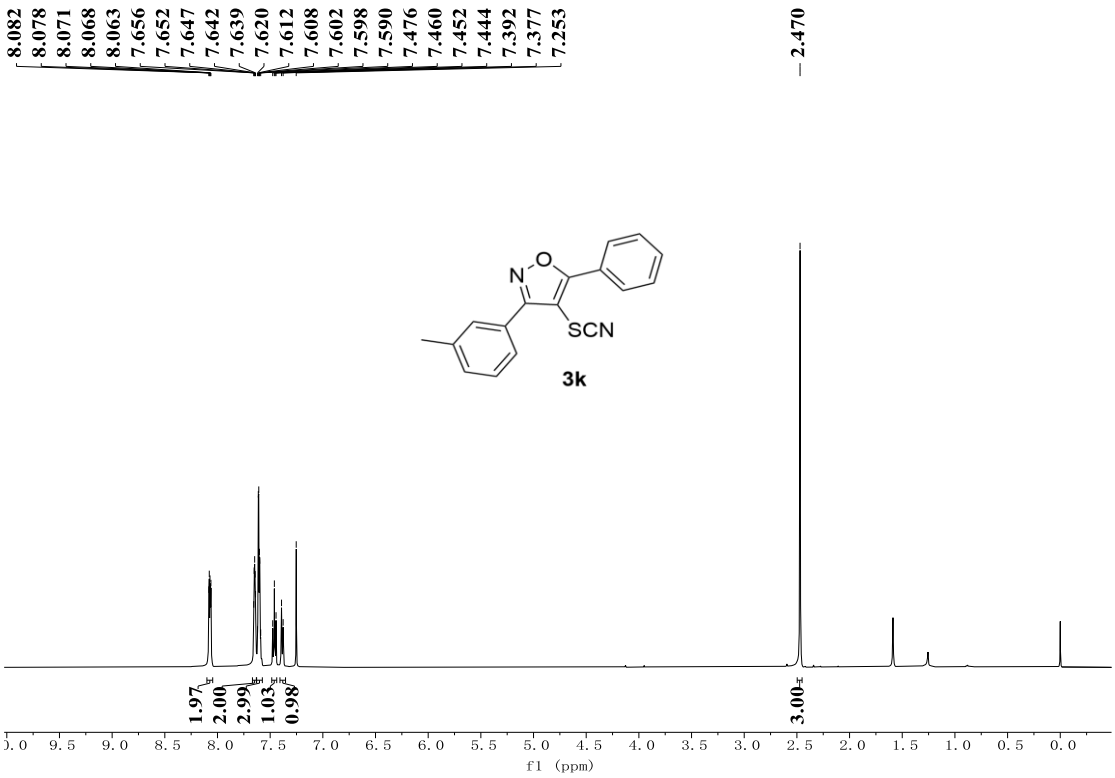
163.96
133.77
132.16
132.06
131.75
130.08
129.30
127.79
127.32
126.02
125.45
108.95
95.36
77.32
77.07
76.81
Cl
N
O
SCN
3j
f1 (ppm)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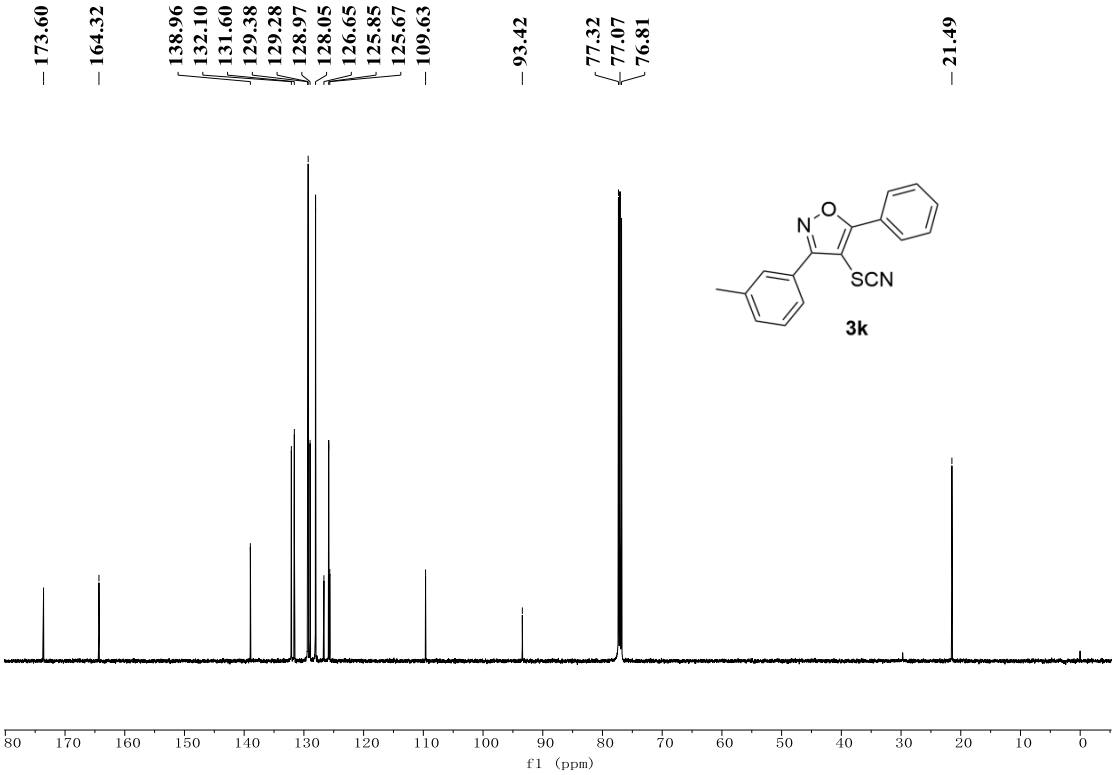
8.078
8.071
8.068
8.063
7.656
7.652
7.647
7.642
7.639
7.620
7.612
7.608
7.602
7.598
7.590
7.476
7.460
7.452
7.444
7.392
7.377
7.253
2.470
N
O
SCN
3k
1.97
2.00
2.99
1.03
0.98
3.00
f1 (ppm)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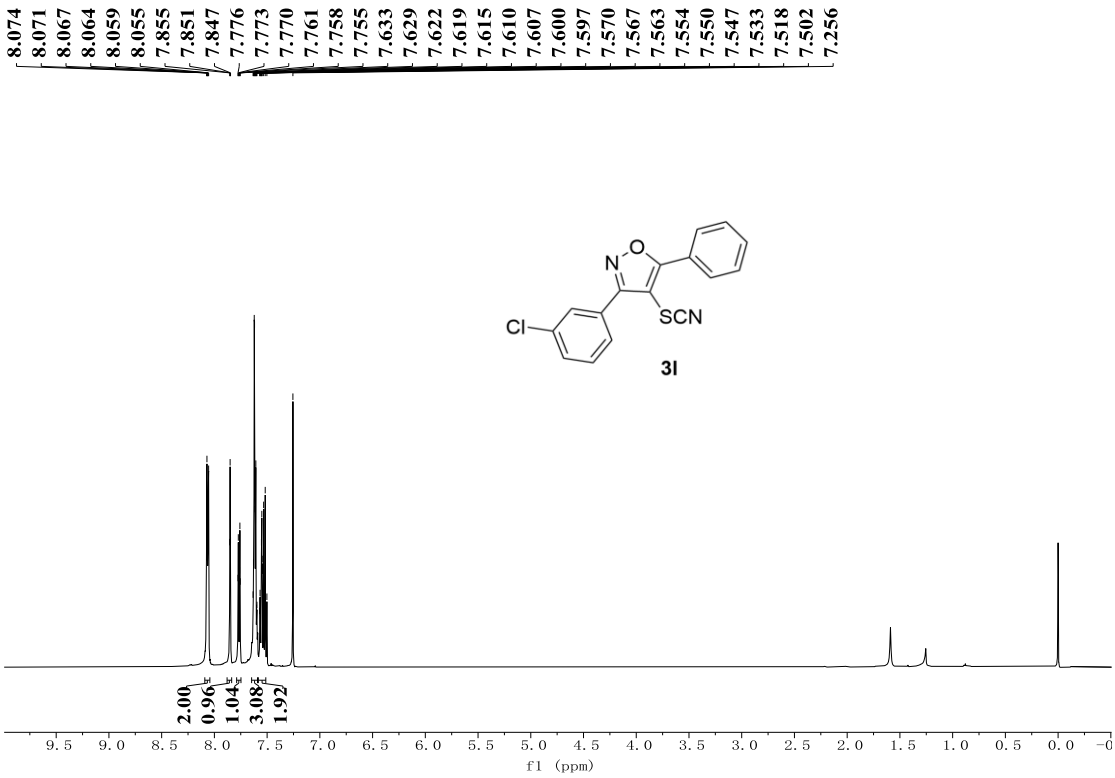
164.32
138.96
132.10
131.60
129.38
129.28
128.97
128.05
126.65
125.85
125.67
109.63
93.42
77.32
77.07
76.81
21.49
N
O
SCN
3k
f1 (ppm)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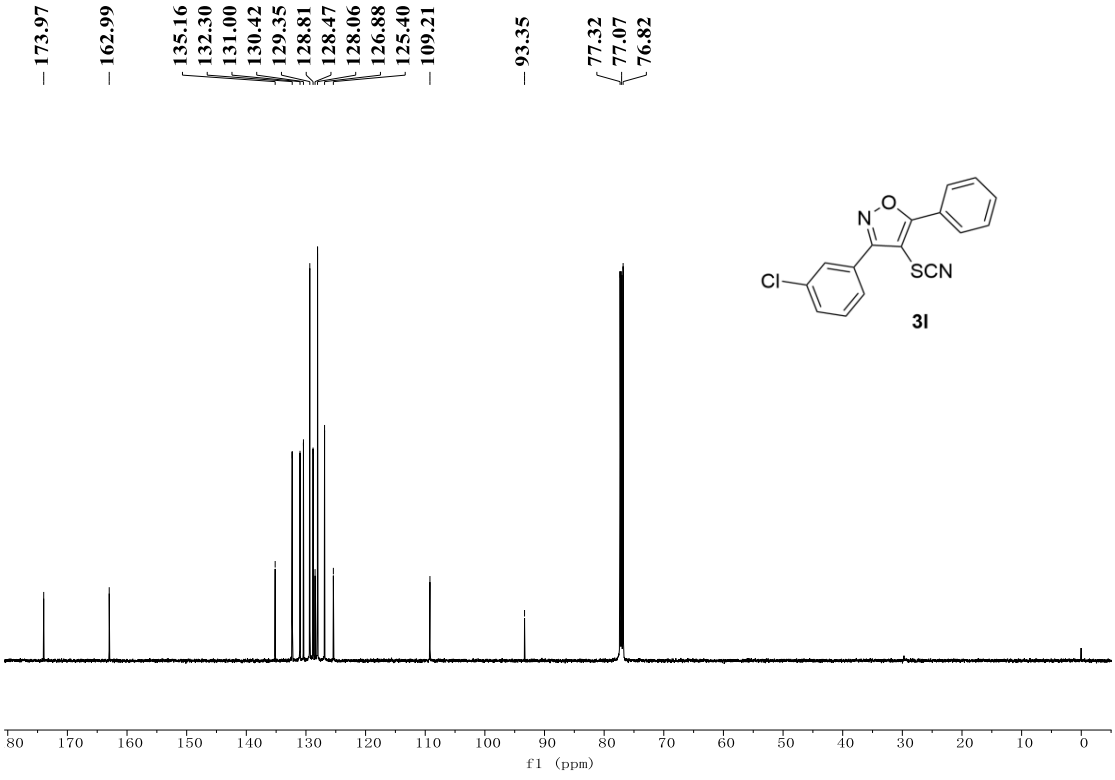
8.067
8.064
8.059
8.055
7.855
7.851
7.847
7.776
7.773
7.770
7.761
7.758
7.755
7.633
7.629
7.622
7.619
7.615
7.610
7.607
7.600
7.597
7.570
7.567
7.563
7.554
7.550
7.547
7.533
7.518
7.502
7.256
Cl
N
O
SCN
3l
2.00
0.96
1.04
3.08
1.92
f1 (ppm)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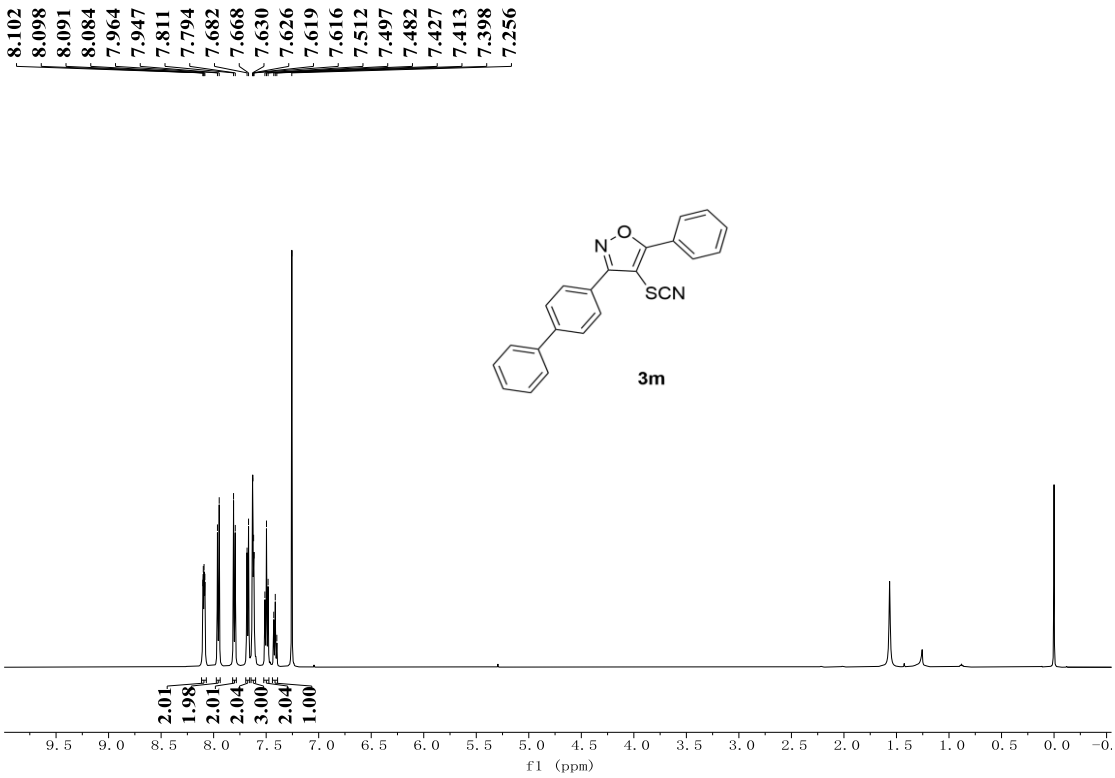
131.00
130.42
129.35
128.81
128.47
128.06
126.88
125.40
109.21
93.35
77.32
77.07
76.82
Cl
N
O
SCN
3l
f1 (ppm)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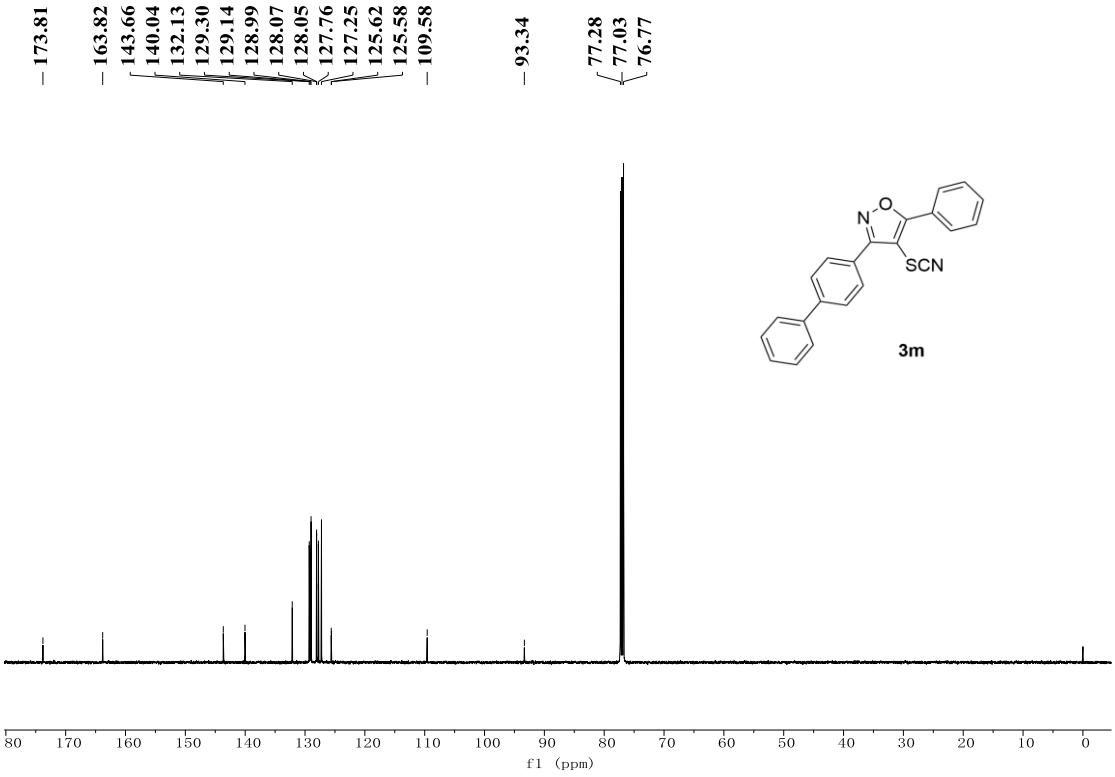
8.098
8.091
8.084
7.964
7.947
7.811
7.794
7.682
7.668
7.630
7.626
7.619
7.616
7.512
7.497
7.482
7.427
7.413
7.398
7.256
N
O
SCN
3m
2.01
1.98
2.01
2.04
3.00
2.04
1.00
f1 (ppm)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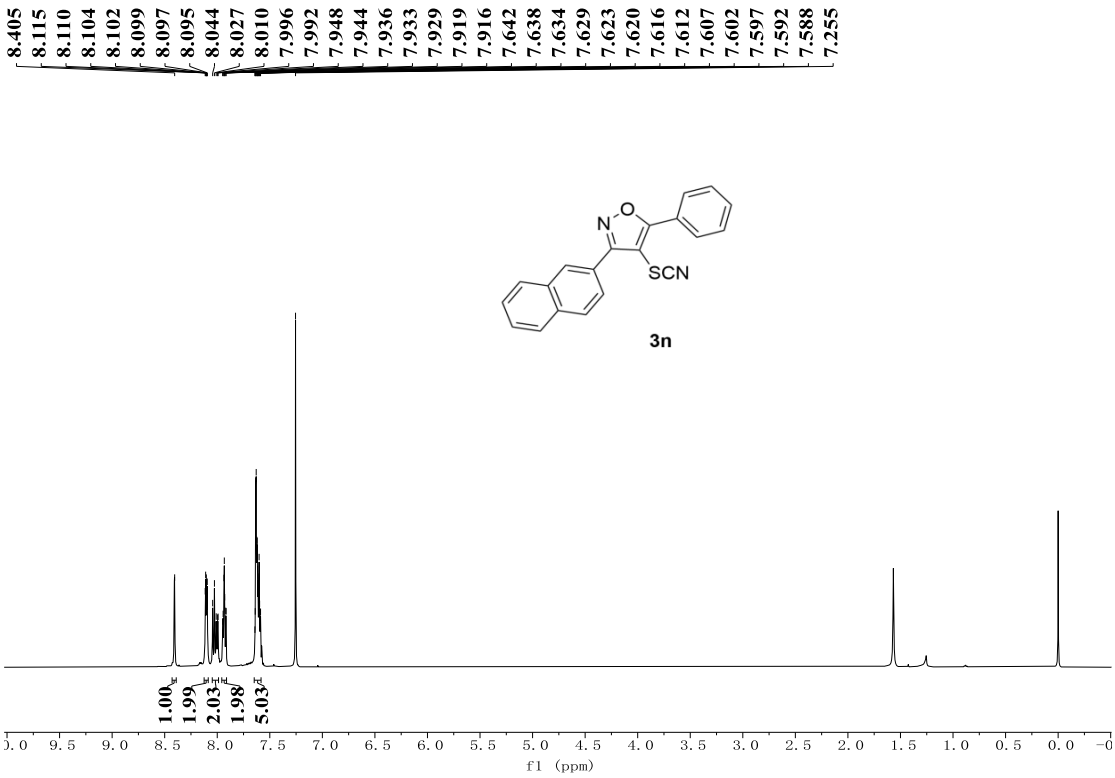
163.82
143.66
140.04
132.13
129.30
129.14
128.99
128.07
128.05
127.76
127.25
125.62
125.58
109.58
93.34
77.28
77.03
76.77
N
O
SCN
3m
f1 (ppm)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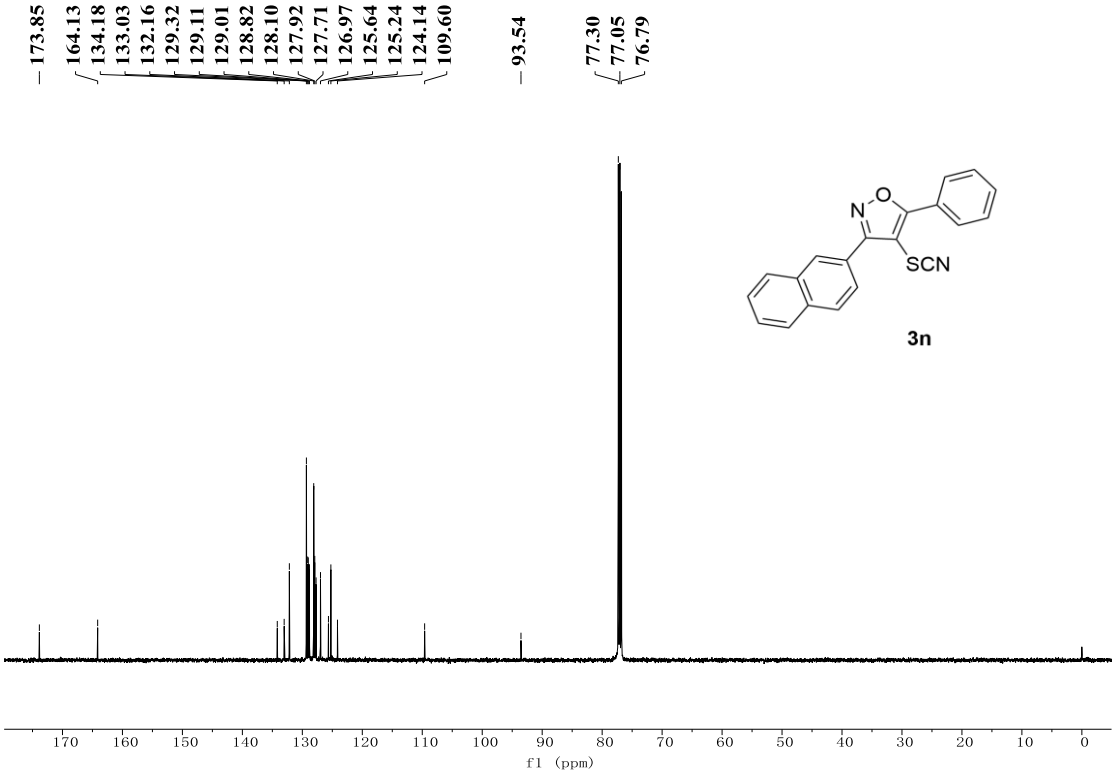
8.102
8.099
8.097
8.095
8.044
8.027
8.010
7.996
7.992
7.948
7.944
7.936
7.933
7.929
7.919
7.916
7.642
7.638
7.634
7.629
7.623
7.620
7.616
7.612
7.607
7.602
7.597
7.592
7.588
7.255
N
O
SCN
3n
1.00
1.99
2.03
1.98
5.03
f1 (ppm)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134.18
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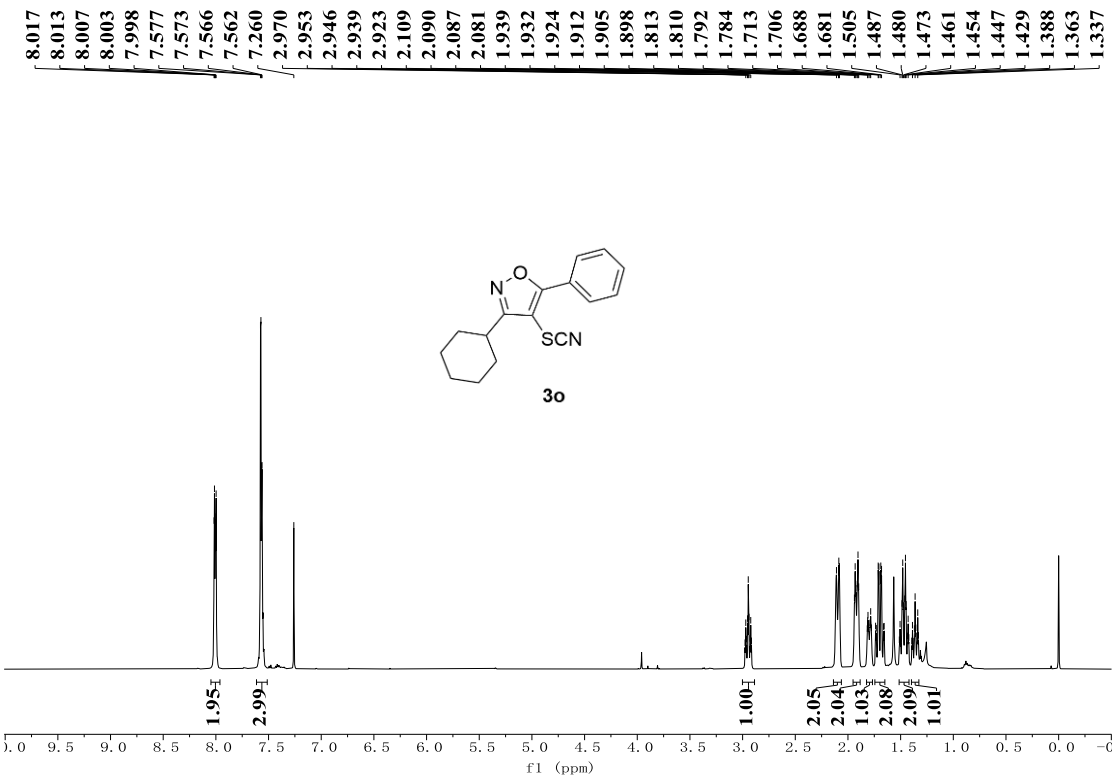
132.16
129.32
129.11
129.01
128.82
128.10
127.92
127.71
126.97
125.64
125.24
124.14
109.60
93.54
77.30
77.05
76.79
N
O
SCN
3n
f1 (ppm)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7.577
7.573
7.566
7.562
7.260
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2.953
2.946
2.939
2.923
2.109
2.090
2.087
2.081
1.939
1.932
1.924
1.912
1.905
1.898
1.813
1.810
1.792
1.784
1.713
1.706
1.688
1.681
1.505
1.487
1.480
1.473
1.461
1.454
1.447
1.429
1.388
1.363
1.337
N
O
SCN
3o
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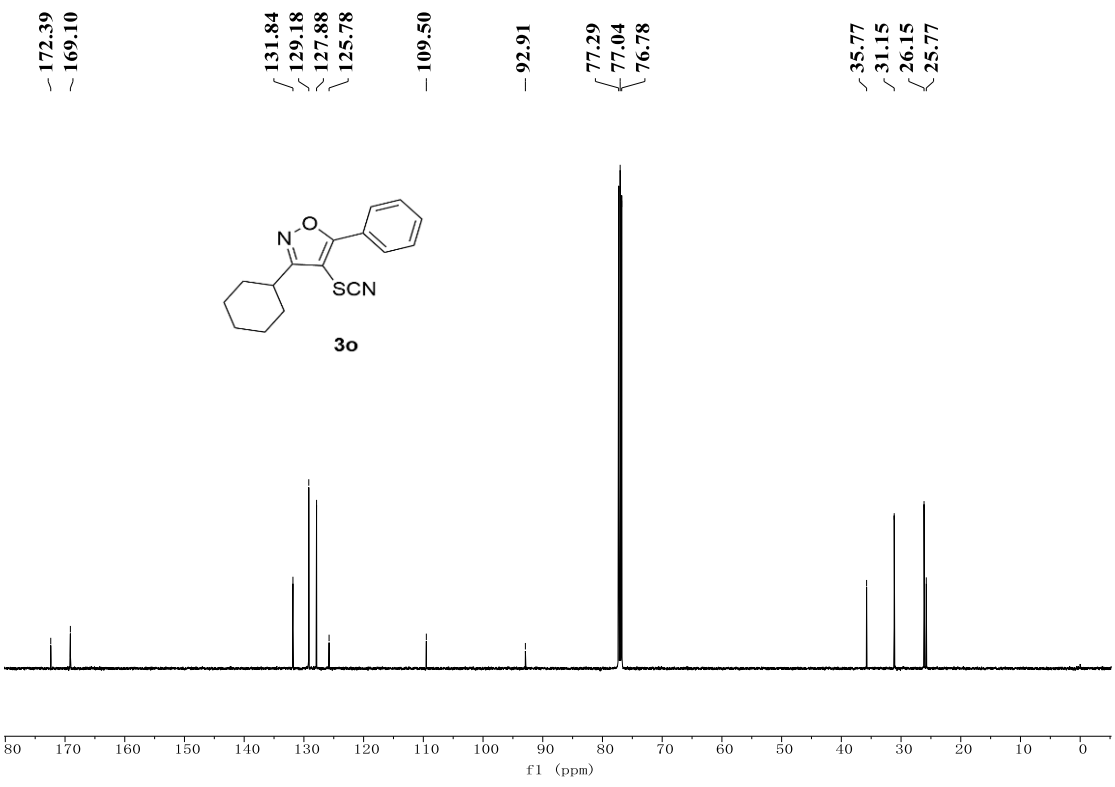
2.99
1.00
2.05
2.04
1.03
2.08
2.09
1.01
f1 (ppm)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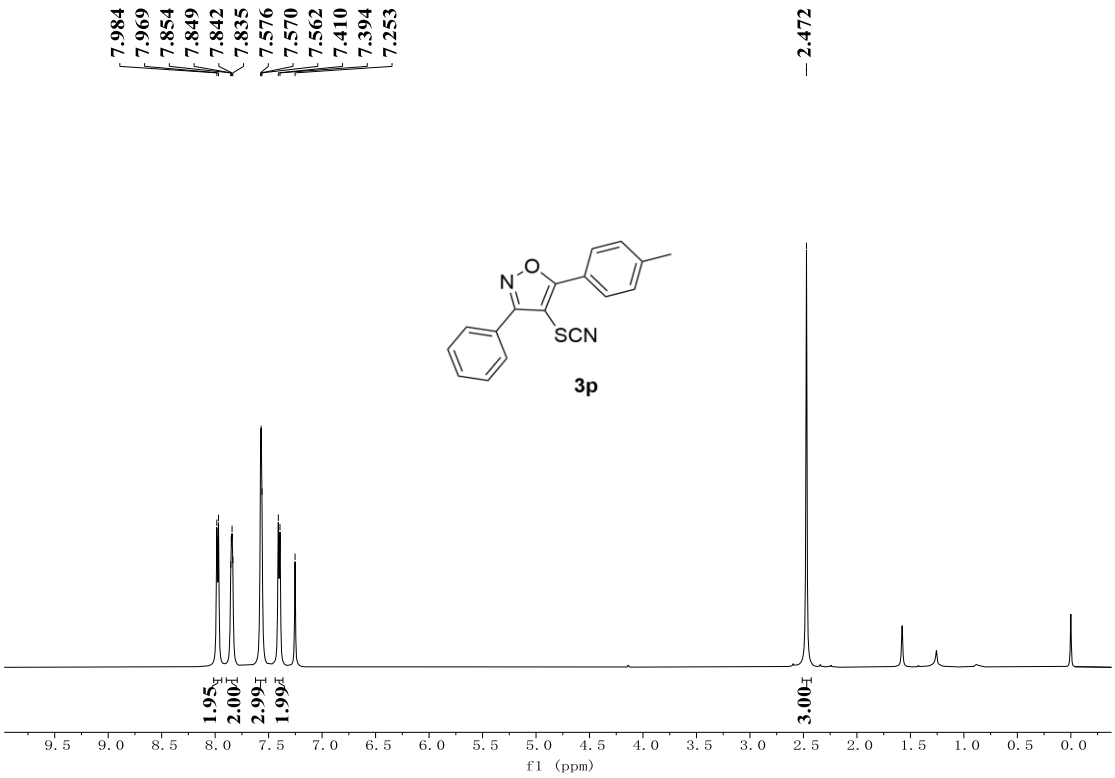
127.88
125.78
109.50
92.91
77.29
77.04
76.78
35.77
31.15
26.15
25.77
N
O
SCN
3o
f1 (ppm)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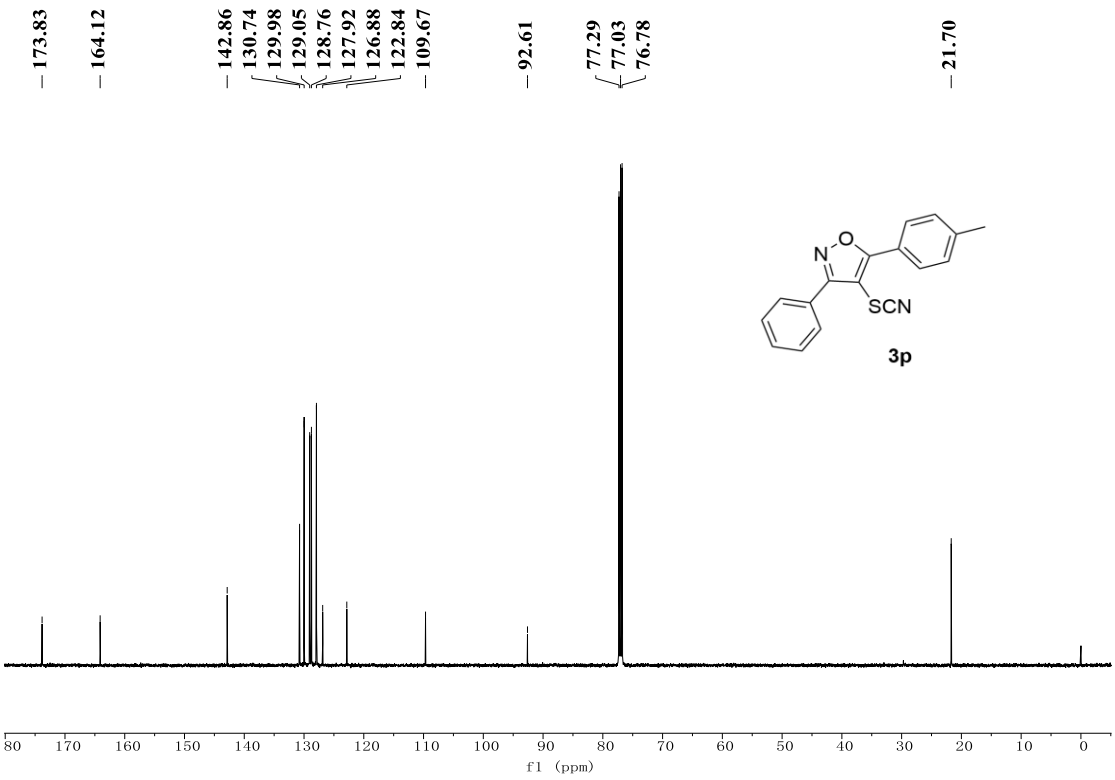
7.842
7.835
7.576
7.570
7.562
7.410
7.394
7.253
2.472
SCN
3p
1.95
2.00
2.99
1.99
3.00
f1 (ppm)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129.98
129.05
128.76
127.92
126.88
122.84
109.67
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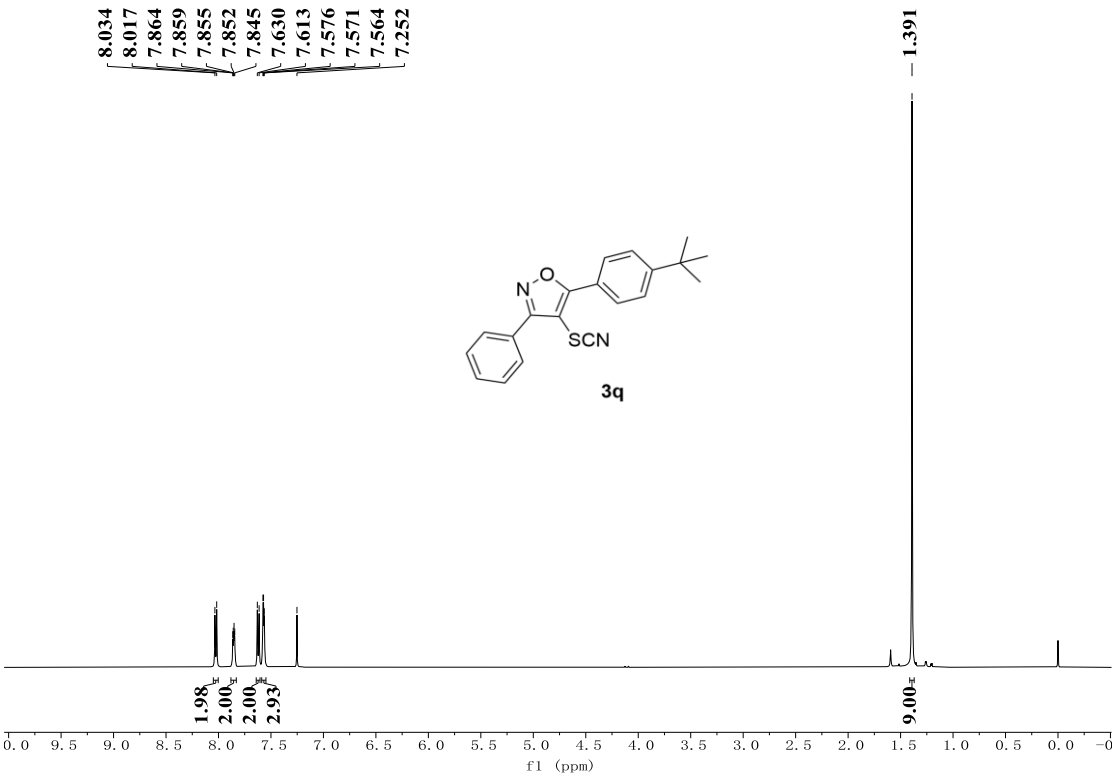
77.03
76.78
21.70
SCN
3p
f1 (ppm)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7.855
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7.845
7.630
7.613
7.576
7.571
7.564
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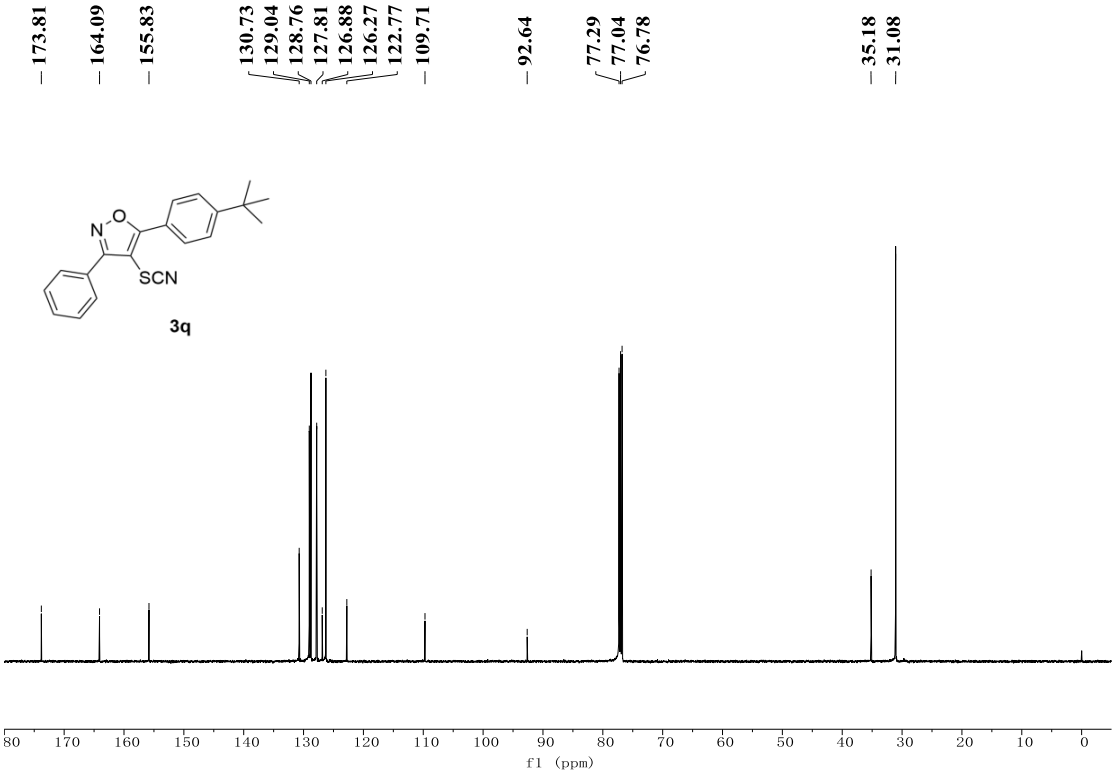
N
O
SCN
3q
1.98
2.00
2.00
2.93
9.00
f1 (ppm)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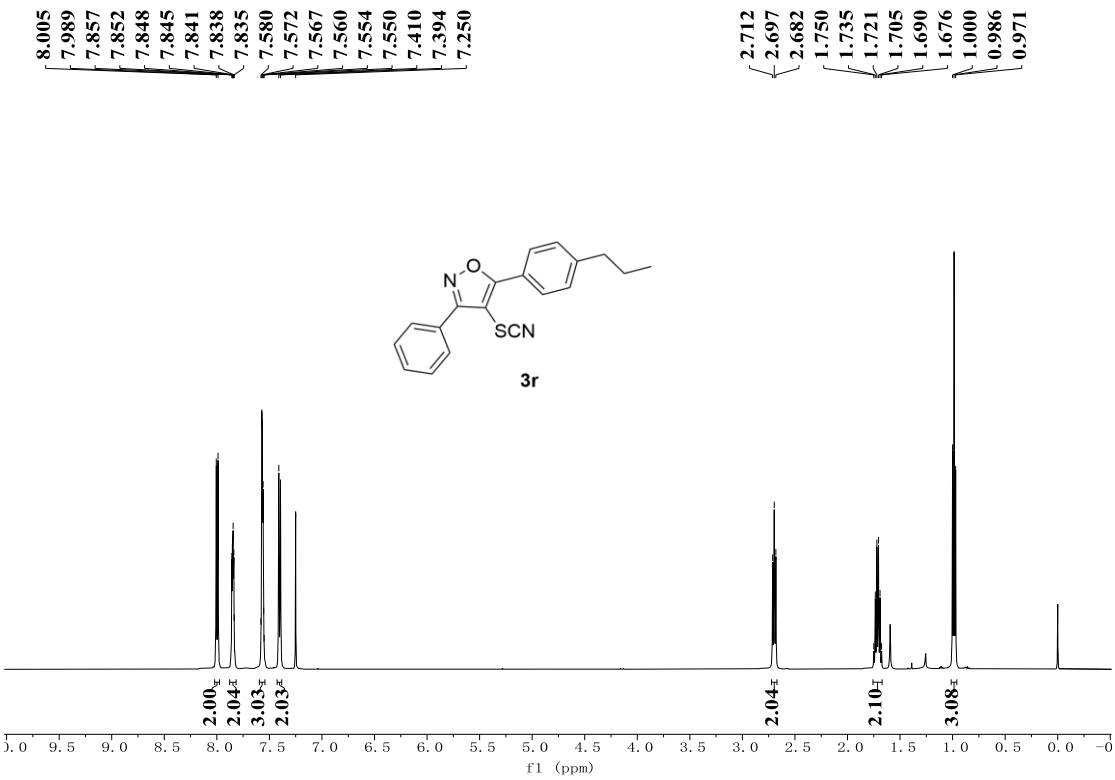
155.83
130.73
129.04
128.76
127.81
126.88
126.27
122.77
109.71
92.64
77.29
77.04
76.78
35.18
31.08
N
O
SCN
3q
f1 (ppm)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7.845
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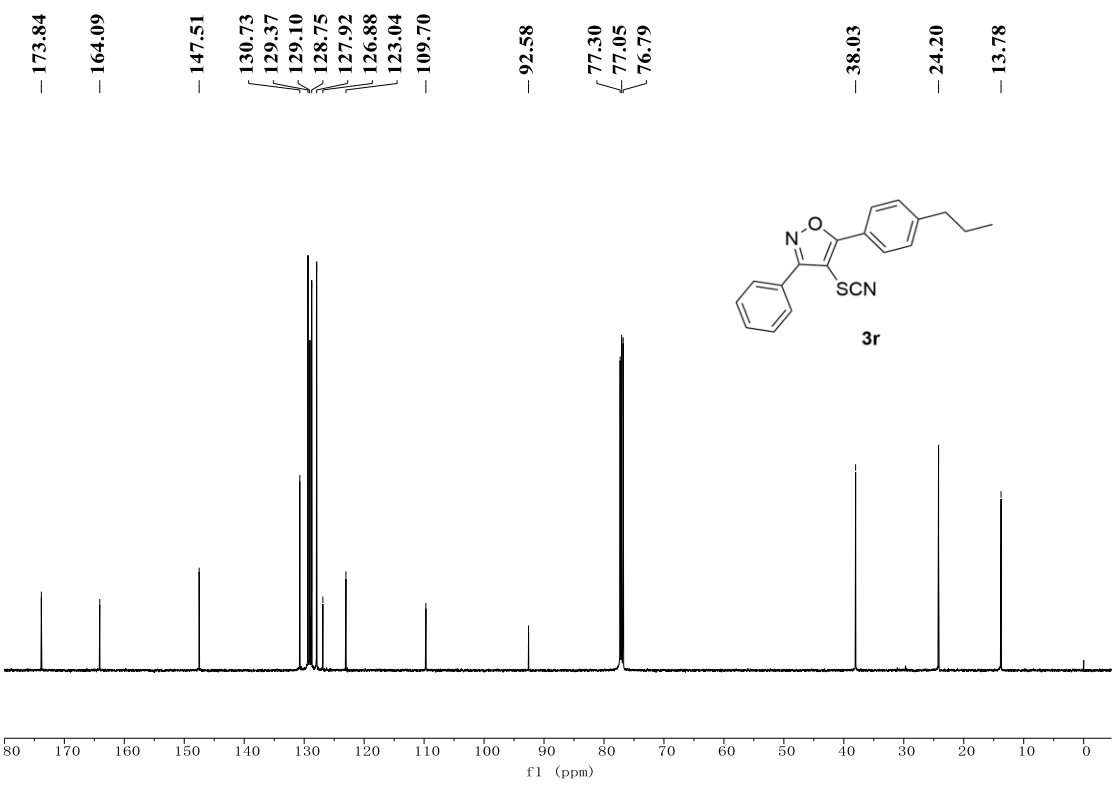
7.838
7.835
7.580
7.572
7.567
7.560
7.554
7.550
7.410
7.394
7.250
2.712
2.697
2.682
1.750
1.735
1.721
1.705
1.690
1.676
1.000
0.986
0.971
SCN
3r
2.00
2.04
3.03
2.03
2.04
2.10
3.08
f1 (ppm)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164.09
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129.37
129.10
128.75
127.92
126.88
123.04
109.70
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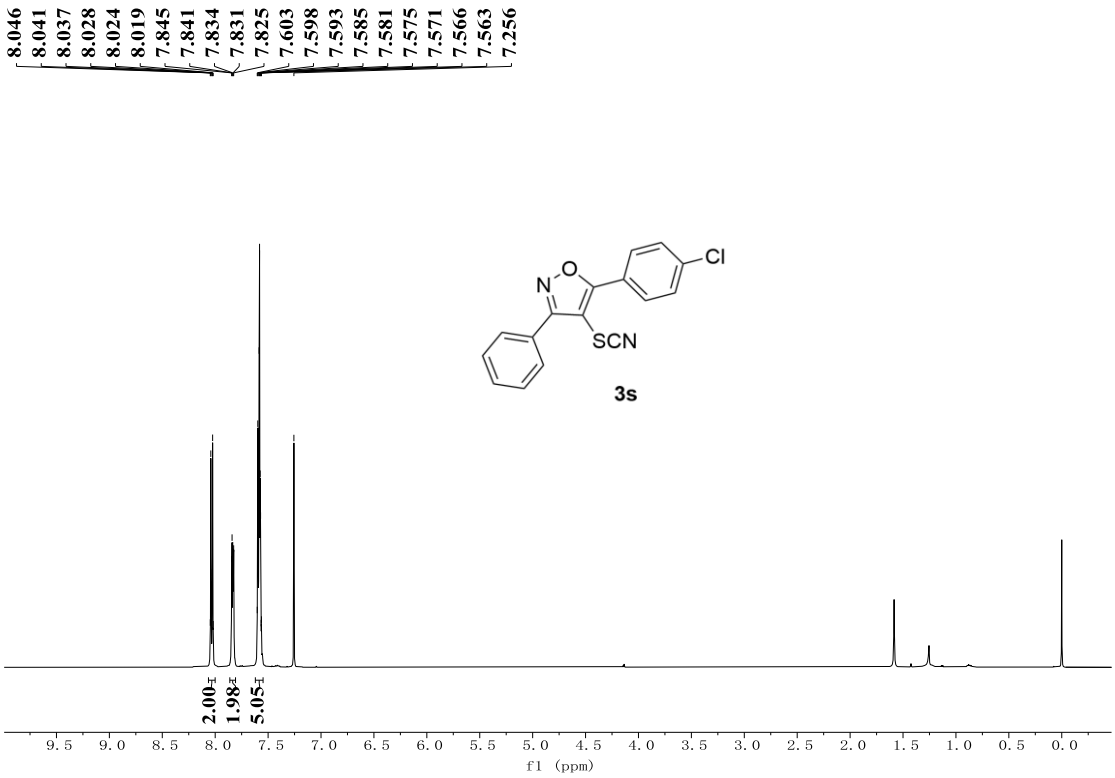
77.30
77.05
76.79
38.03
24.20
13.78
SCN
3r
f1 (ppm)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7.845
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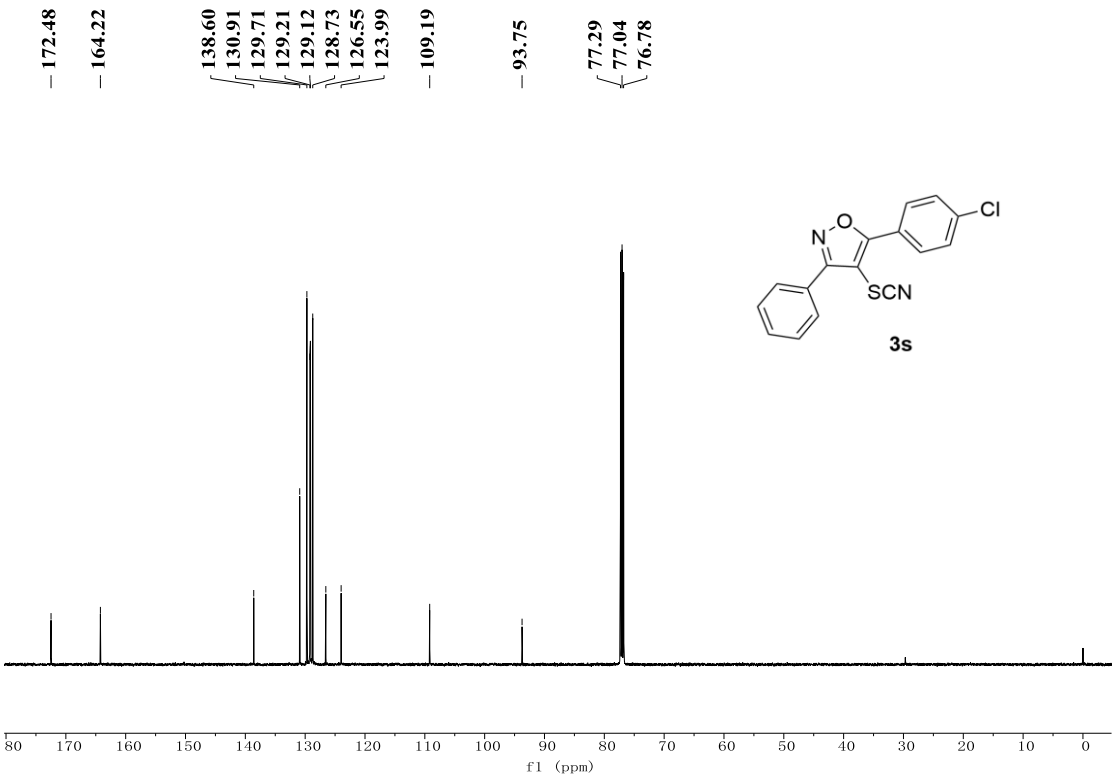
7.834
7.831
7.825
7.603
7.598
7.593
7.585
7.581
7.575
7.571
7.566
7.563
7.256
Cl
N
O
SCN
3s
2.00
1.98
5.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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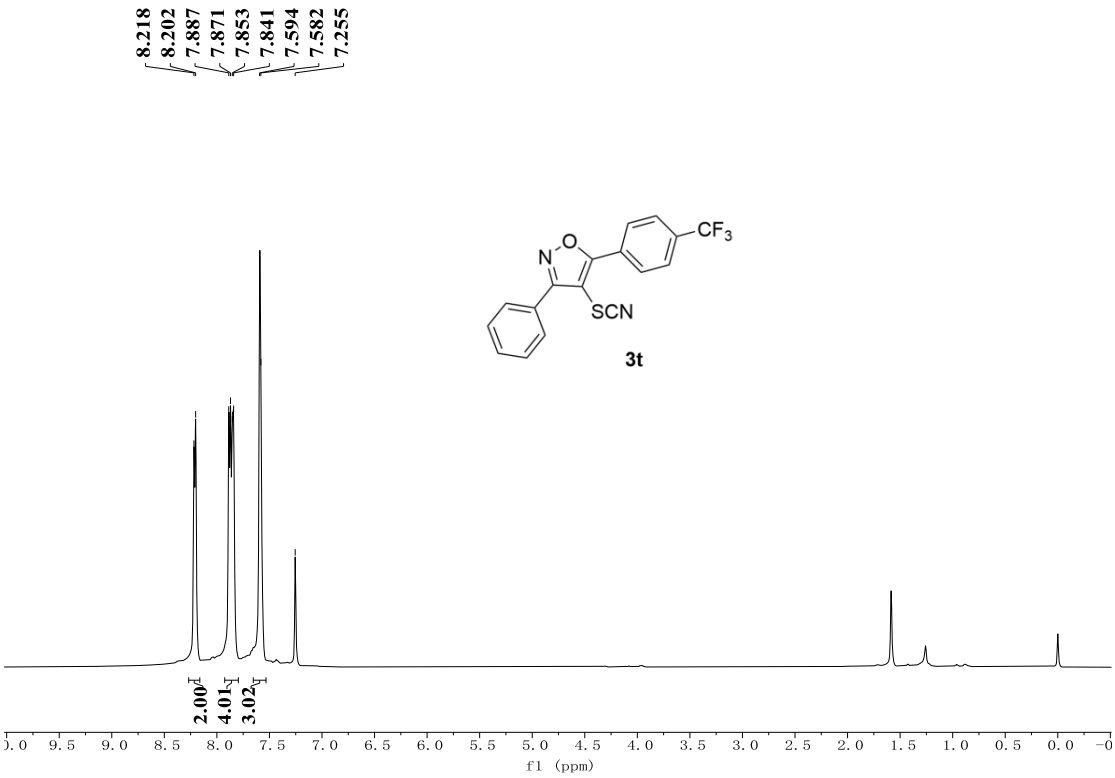
130.91
129.71
129.21
129.12
128.73
126.55
123.99
109.19
93.75
77.29
77.04
76.78
Cl
N
O
SCN
3s
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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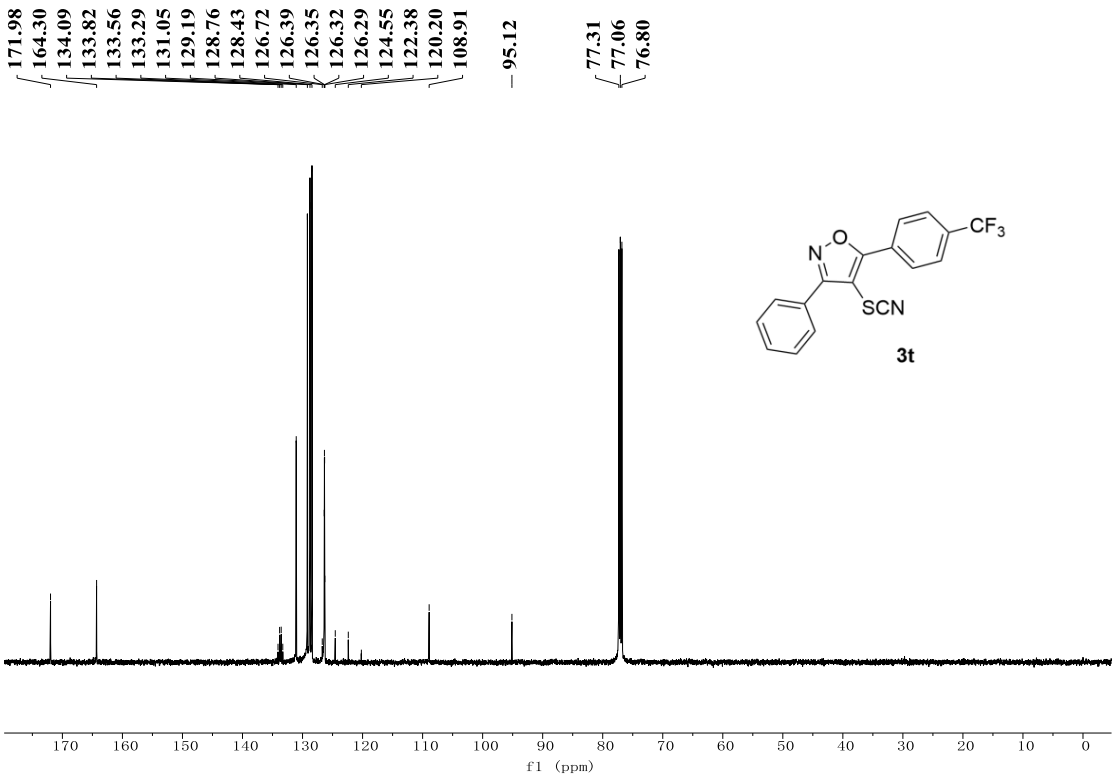
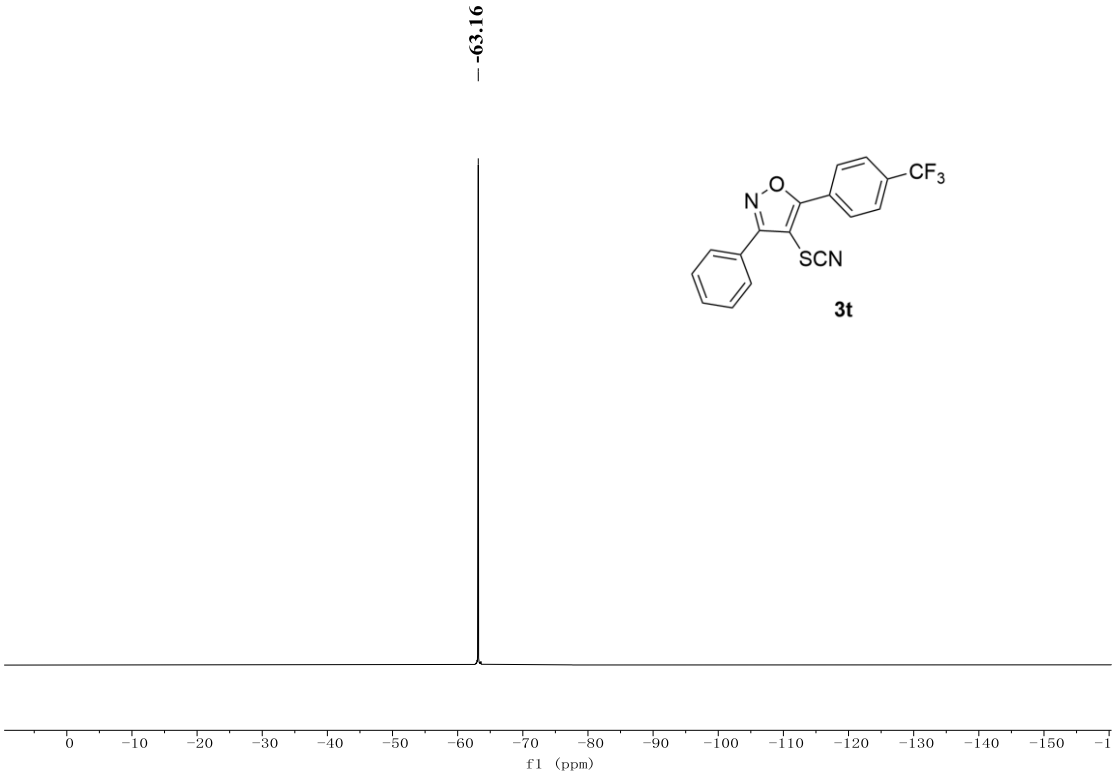
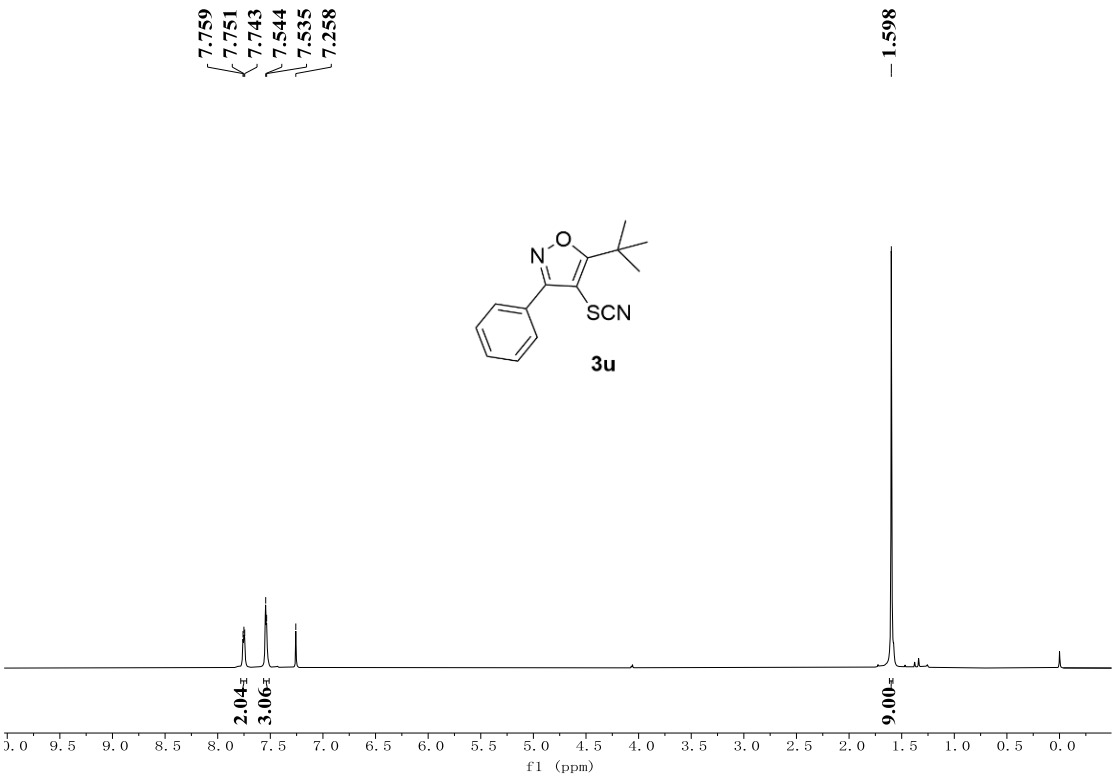
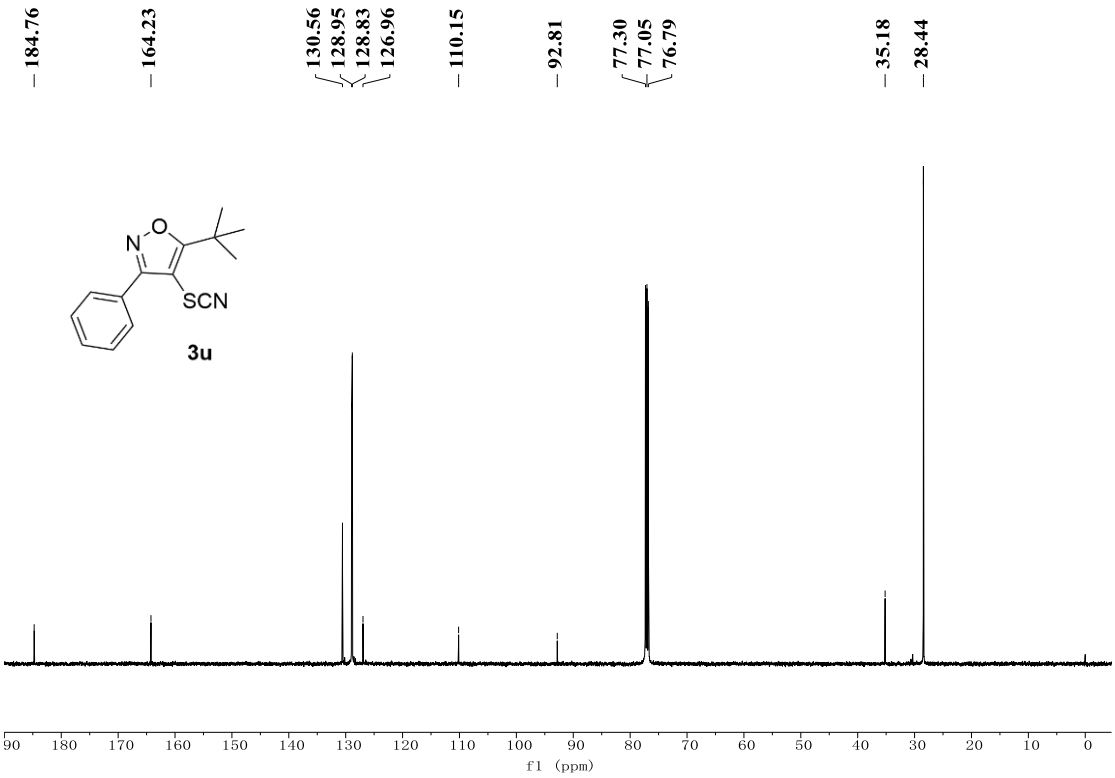
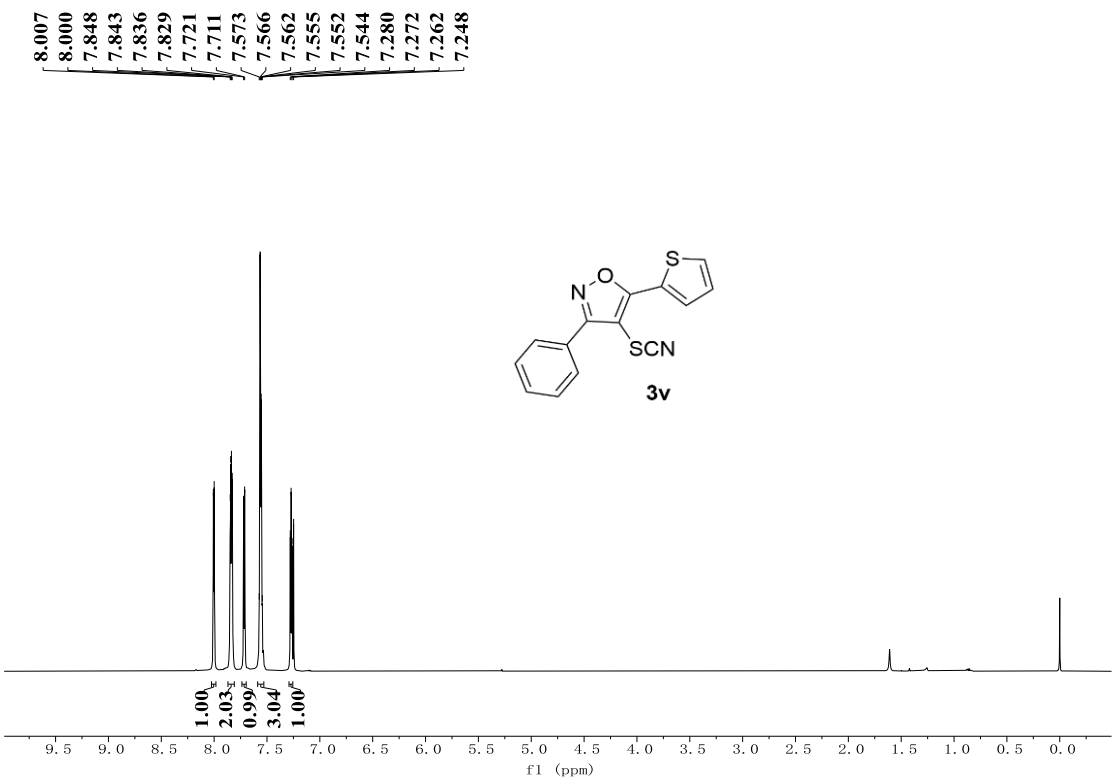
7.871
7.853
7.841
7.594
7.582
7.255
CF3
N
O
SCN
3t
2.00
4.01
3.02
f1 (ppm)

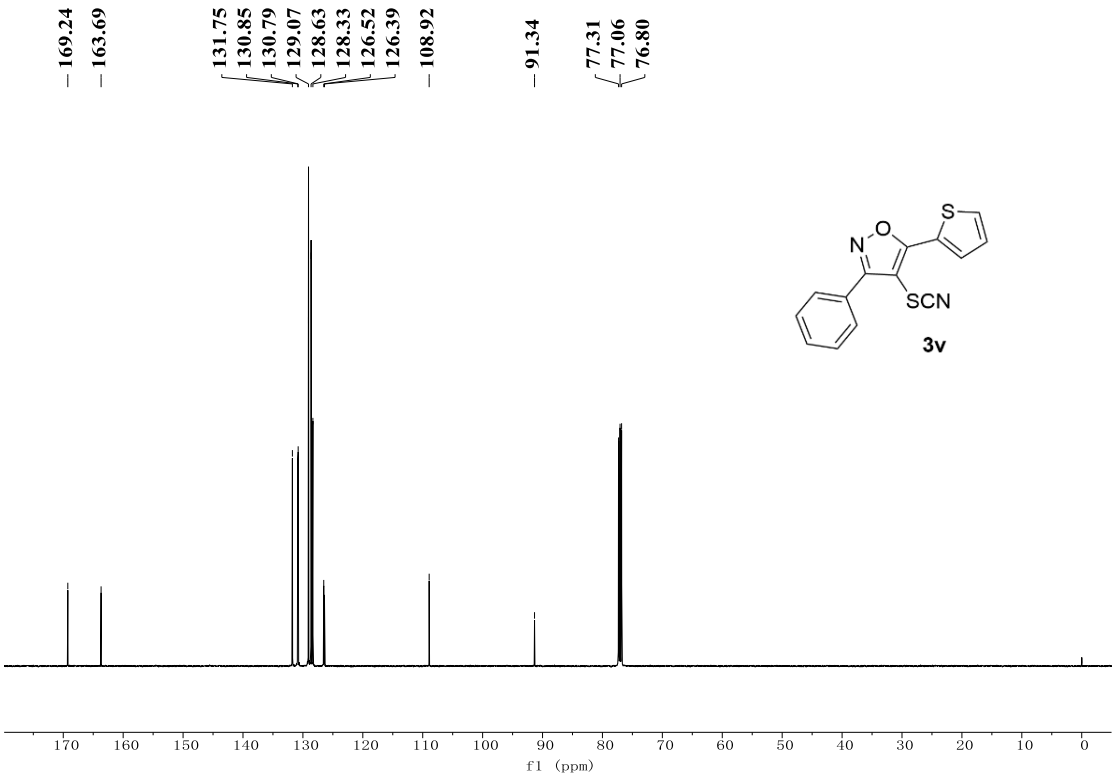

171.98
164.30
134.09
133.82
133.56
133.29
131.05
129.19
128.76
128.43
126.72
126.39
126.35
126.32
126.29
124.55
122.38
120.20
108.91
95.12
77.31
77.06
76.80
CF3
N
O
SCN
3t
f1 (ppm)

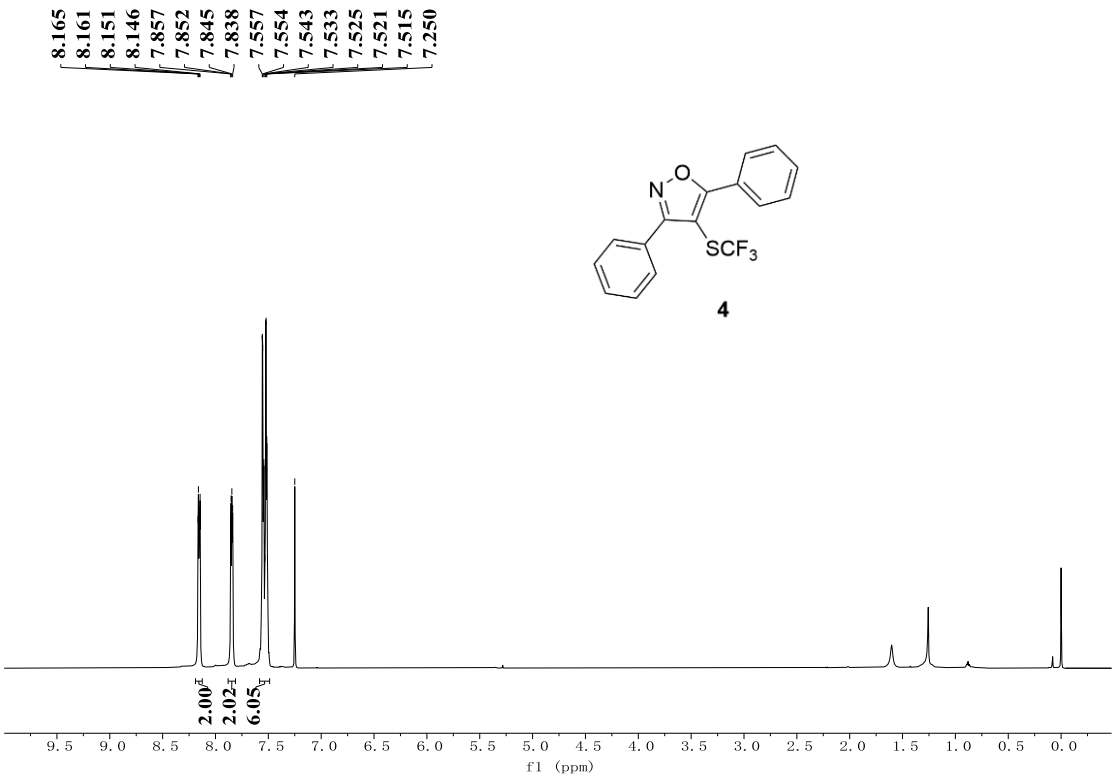

-63.16
CF3
N
O
SCN
3t
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

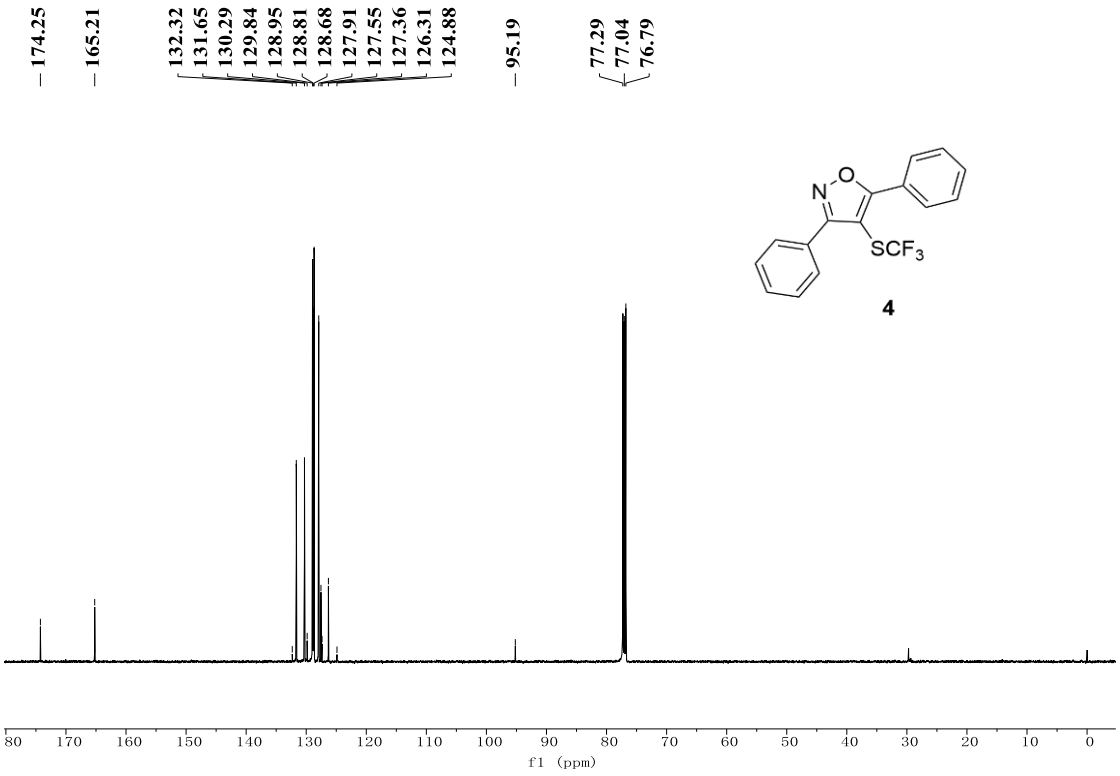

7.759
7.751
7.743
7.544
7.535
7.258
1.598
N
O
SCN
3u
2.04
3.06
9.00
f1 (ppm)

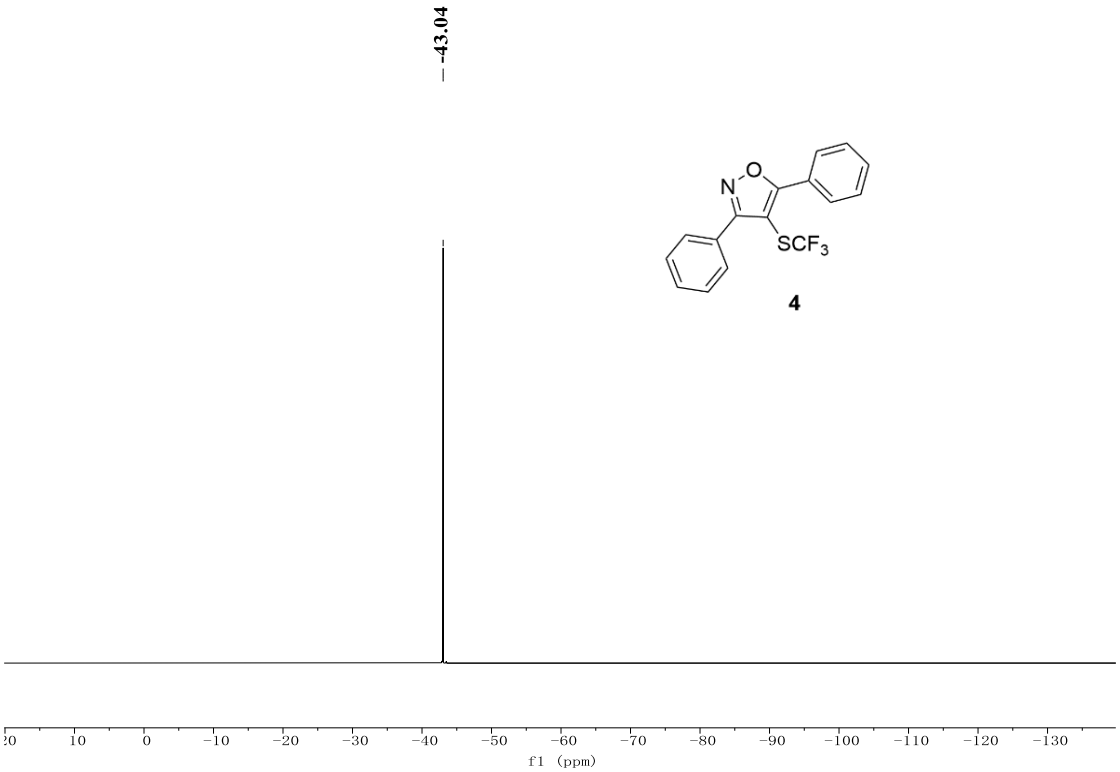

184.76
164.23
130.56
128.95
128.83
126.96
110.15
92.81
77.30
77.05
76.79
35.18
28.44
SCN
3u
f1 (ppm)

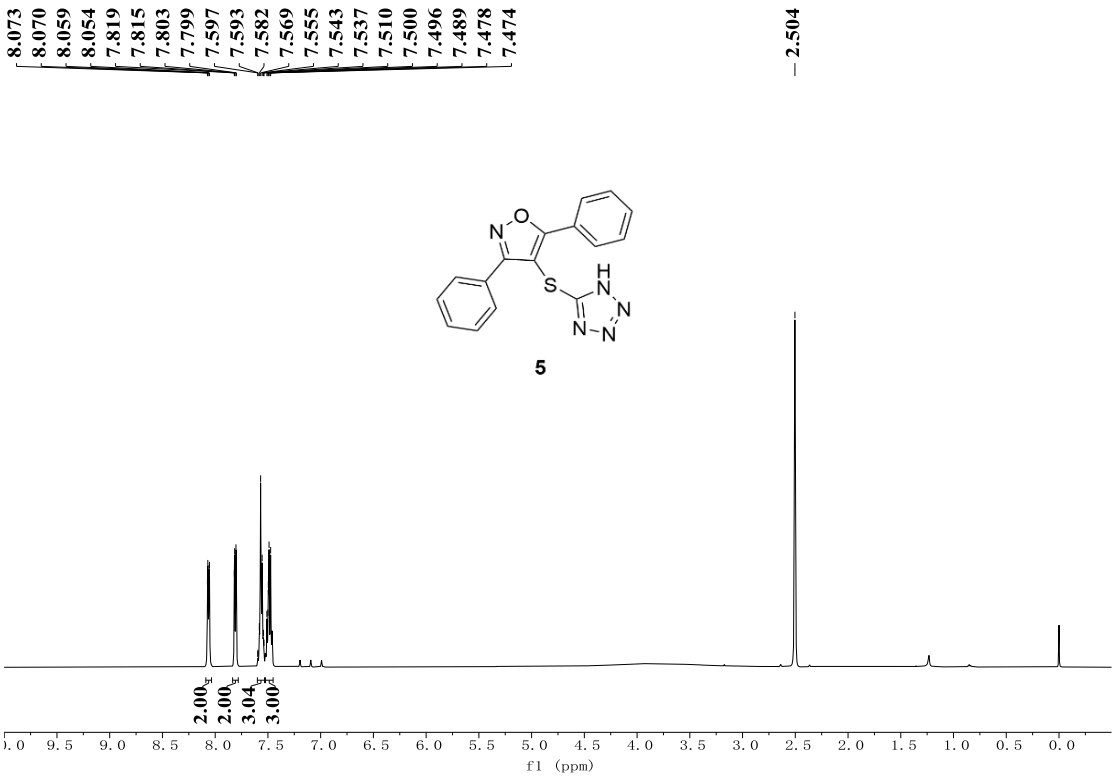

8.007
8.000
7.848
7.843
7.836
7.829
7.721
7.711
7.573
7.566
7.562
7.555
7.552
7.544
7.280
7.272
7.262
7.248
S
SCN
3v
1.00
2.03
0.99
3.04
1.00
f1 (ppm)

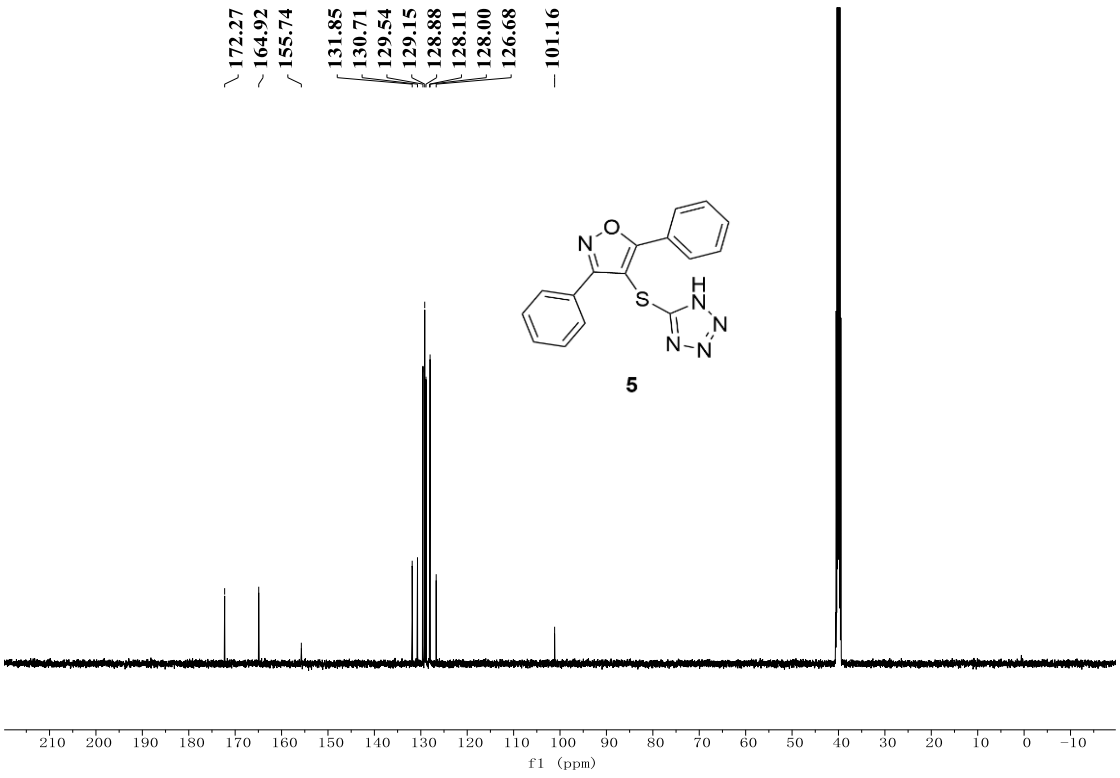

169.24
163.69
131.75
130.85
130.79
129.07
128.63
128.33
126.52
126.39
108.92
91.34
77.31
77.06
76.80
S
N
O
SCN
3v
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

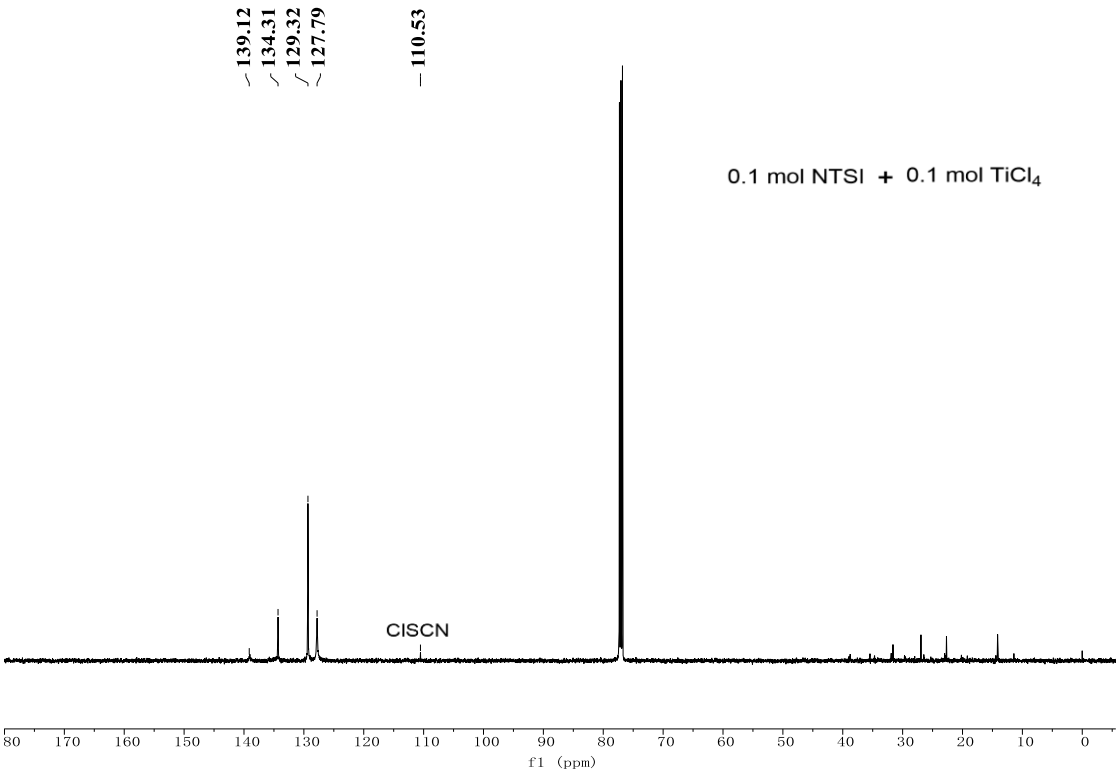

8.165
8.161
8.151
8.146
7.857
7.852
7.845
7.838
7.557
7.554
7.543
7.533
7.525
7.521
7.515
7.250
N
O
SCF3
4
2.00
2.02
6.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.25
165.21
132.32
131.65
130.29
129.84
128.95
128.81
128.68
127.91
127.55
127.36
126.31
124.88
95.19
77.29
77.04
76.79
N
O
SCF3
4
f1 (ppm)


-43.04
N
O
SCF3
4
f1 (ppm)


8.073
8.070
8.059
8.054
7.819
7.815
7.803
7.799
7.597
7.593
7.582
7.569
7.555
7.543
7.537
7.510
7.500
7.496
7.489
7.478
7.474
2.504
5
2.00
2.00
3.04
3.00
f1 (ppm)


172.27
164.92
155.74
131.85
130.71
129.54
129.15
128.88
128.11
128.00
126.68
101.16
5
f1 (ppm)


139.12
134.31
129.32
127.79
110.53
0.1 mol NTSI + 0.1 mol TiCl4
ClSCN
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)