SUPPORTING INFORMATION

Thermally induced N-S bond insertion reaction of diazo compounds with *N*-sulfenyl imides: synthresis of sulfides and mechanism studies

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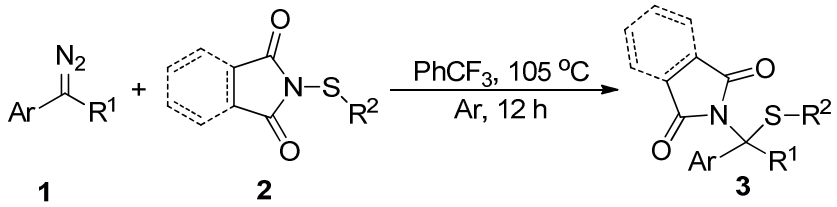
General Information

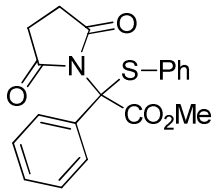
All reactions are carried out in oven-dried (140°C) glassware under an atmosphere of argon. Solvents are dried and degassed by the standard methods. Flash column chromatography is performed using silica gel (300-400 mesh). Analytical thin-layer chromatography is performed using glass plates pre-coated with 300-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra are recorded in $CDCl_3$ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet, comp = composite. High-resolution mass spectra (HRMS) are recorded on a commercial apparatus (ESI or CI Source). The diazo compounds[1] and *N*-sulfenylsuccinimides[2,3] were prepared according to the previously published procedures and had physical and spectral properties identical to those earlier reported.

General Procedure for N-S Bond Insertion Reaction.

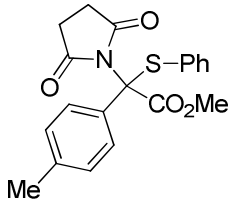


1 2 3

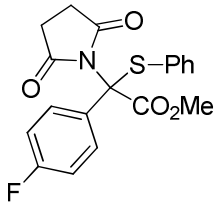
To a 10-mL oven-dried vial containing a magnetic stirring bar, and **2** (0.2 mmol) in $PhCF_3$ (0.5 mL), was added the solution of diazo compound **1** (0.4 mmol) in $PhCF_3$ (1.5 mL) via a syringe pump in 5 hours at 105 ^{o}C under argon atmosphere. The reaction mixture was stirred for additional 7 h under these conditions. After the reaction was completed, the reaction mixture was directly purified by column chromatography on silica gel without any additional treatment (eluent: Hexanes : EtOAc = 20:1 to 3:1) to give the pure products **3** in moderate to high yields.



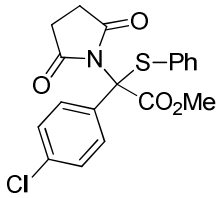
Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-phenyl-2-(phenylthio)acetate (3aa). White solid, mp: 148.8-149.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.91 – 7.72 (m, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.30 (comp, 4H), 7.29 – 7.20 (m, 2H), 3.63 (s, 3H), 2.55 – 2.38 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.7, 167.6, 137.8, 135.0, 130.4, 130.0, 128.8, 128.8, 128.2, 128.0, 76.4, 53.6, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{17}NaNO_4S[M+Na]^+$: 378.0776, found 378.0780.



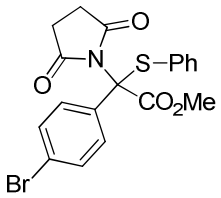
Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(phenylthio)-2-(*p*-tolyl)acetate (3ba). White solid, mp: 78.7-80.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.63 (s, 3H), 2.54 – 2.40 (comp, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.7, 138.7, 137.8, 132.0, 130.4, 130.1, 128.9, 128.8, 127.9, 76.4, 53.6, 28.0, 21.2; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}NNaO_4S[M+Na]^+$: 392.0932, found 392.0923.



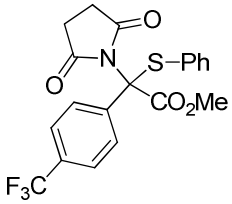
Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-fluorophenyl)-2-(phenylthio)acetate (3ca). White solid, mp: 104.4-105.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.87 – 7.81 (m, 2H), 7.49 – 7.44 (m, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.09 – 7.01 (m, 2H), 3.64 (s, 3H), 2.73 – 2.34 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.5, 162.9 (d, *J* = 249.1 Hz), 137.7, 130.9 (d, *J* = 3.4 Hz), 130.6, 130.2, 130.1, 128.9, 115.1 (d, *J* = 21.8 Hz), 75.8, 53.7, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}FNNaO_4S[M+Na]^+$: 396.0682, found 396.0672.



Methyl 2-(4-Chlorophenyl)-2-(2,5-dioxopyrrolidin-1-yl)-2-(phenylthio)acetate (3da). White solid, mp: 64.1-64.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.83 – 7.76 (m, 2H), 7.48 – 7.43 (m, 2H), 7.39 – 7.31 (m, 3H), 7.28 – 7.22 (m, 2H), 3.63 (s, 3H), 2.58 – 2.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.7, 167.3, 137.8, 134.9, 133.7, 130.6, 129.7, 129.6, 128.9, 128.3, 75.8, 53.7, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}ClNNaO_4S[M+Na]^+$: 412.0386, found 412.0389.

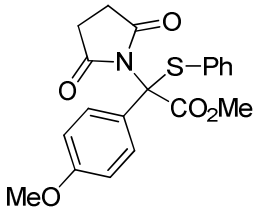


Methyl 2-(4-Bromophenyl)-2-(2,5-dioxopyrrolidin-1-yl)-2-(phenylthio)acetate (3ea). White solid, mp: 70.6-71.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.76 – 7.71 (m, 2H), 7.52 – 7.43 (comp, 4H), 7.40 – 7.35 (m, 1H), 7.28 – 7.22 (m, 2H), 3.63 (s, 3H), 2.57 – 2.39 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.7, 167.2, 137.8, 134.3, 131.3, 130.6, 129.9, 129.7, 128.9, 123.6, 75.9, 53.8, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}BrNNaO_4S$ $[M+Na]^+$: 415.9881, found 455.9880.

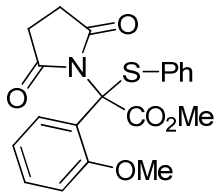


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(phenylthio)-2-(4-(trifluoromethyl)phenyl)acetate (3fa). White solid, mp: 125.4-126.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.98 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 3.65 (s, 3H), 2.58 – 2.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.7, 167.1, 139.2, 137.8, 130.84 (d, J = 32.6 Hz), 130.75, 129.5, 129.0, 128.6, 125.2 (q, J = 3.7 Hz), 124.0 (d, J =

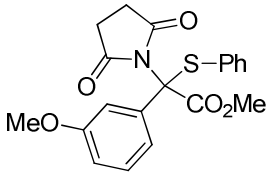
272.4 Hz), 75.9, 53.9, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{16}F_3NNaO_4S[M+Na]^+$: 446.0650, found 446.0641.



Methyl2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)-2-(phenylthio)acetate (3ga). White solid, mp: 133.8-134.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.79 – 7.73 (m, 2H), 7.51 – 7.45 (m, 2H), 7.39 – 7.33 (m, 1H), 7.23 (d, J = 7.5 Hz, 2H), 6.91 – 6.85 (m, 2H), 3.82 (s, 3H), 3.63 (s, 3H), 2.54 – 2.41 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.7, 159.9, 137.7, 130.4, 130.2, 129.5, 128.8, 126.9, 113.5, 76.1, 55.4, 53.6, 28.1; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}NNaO_5S[M+Na]^+$: 408.0882, found 408.0876.

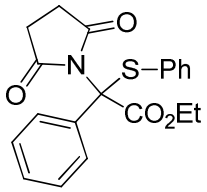


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(2-methoxyphenyl)-2-(phenylthio)acetate (3ha). White solid, mp: 74.0-76.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.88 – 7.50 (comp, 3H), 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 7.02 – 6.96 (m, 1H), 6.86 – 6.81 (m, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.40 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.5, 167.5, 157.2, 137.5, 131.0, 130.2, 129.9, 129.5, 128.5, 123.5, 120.6, 112.1, 75.3, 56.0, 53.7, 27.9; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}NaNO_5S[M+Na]^+$: 408.0882, found 408.0883.

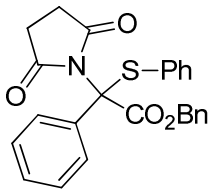


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(3-methoxyphenyl)-2-(phenylthio)acetate (3ia). White solid, mp: 99.8-101.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.87 (d, J = 8.0 Hz, 1H), 7.49 (d,

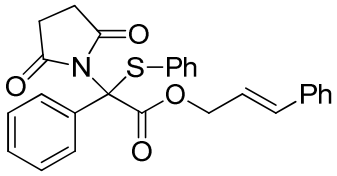
J = 7.3 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 2.39 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.5, 167.5, 157.2, 137.5, 130.9, 130.2, 129.9, 129.4, 128.4, 123.4, 120.5, 112.1, 75.2, 55.9, 53.6, 27.8; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}NaNO_5S[M+Na]^+$: 408.0882, found 408.0877.



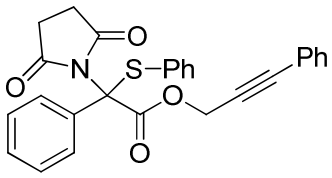
Ethyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-phenyl-2-(phenylthio)acetate (3ja). White solid, mp: 131.1-131.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.88 – 7.79 (m, 2H), 7.50 (d, *J* = 7.1 Hz, 2H), 7.40 – 7.30 (comp, 4H), 7.24 (t, *J* = 7.7 Hz, 2H), 4.33 – 3.95 (m, 2H), 2.46 (comp, 4H), 1.12 (t, *J* = 7.1 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 174.7, 167.0, 137.8, 135.0, 130.4, 130.1, 128.8, 128.7, 128.04, 128.03, 76.5, 63.0, 28.0, 13.8; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}NNaO_4S[M+Na]^+$: 392.0932, found 392.0923.



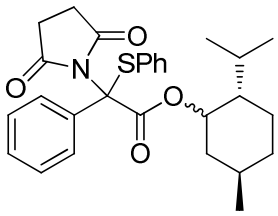
Benzyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-phenyl-2-(phenylthio)acetate (3ka). White solid, mp: 43.1-48.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.82 – 7.76 (m, 2H), 7.54 – 7.49 (m, 2H), 7.35 (comp, 4H), 7.25 (comp, 5H), 7.09 – 7.04 (m, 2H), 5.15 (d, *J* = 12.3 Hz, 1H), 4.96 (d, *J* = 12.3 Hz, 1H), 2.44 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 174.7, 166.9, 137.9, 135.0, 134.9, 130.4, 129.9, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0, 127.9, 76.5, 68.4, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{25}H_{22}NO_4S[M+H]^+$: 432.1270, found 432.1267.



Cinnamyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-phenyl-2-(phenylthio)acetate (3la). White solid, mp: 43.1-48.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.88 – 7.82 (m, 2H), 7.54 – 7.49 (m, 2H), 7.40 – 7.33 (m, 4H), 7.30 (comp, 4H), 7.27 – 7.21 (m, 4H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.10 – 6.00 (m, 1H), 4.79 – 4.59 (m, 1H), 2.53 – 2.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.7, 166.9, 137.9, 136.3, 135.0, 134.2, 130.4, 130.0, 128.84, 128.81, 128.7, 128.2, 128.1 126.7, 122.4, 76.6, 67.2, 28.1; HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{24}NO_4S[M+H]^+$: 458.1426, found 458.1417.

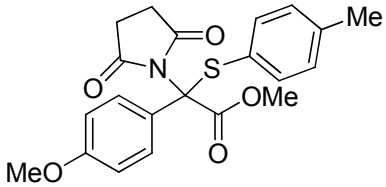


3-Phenylprop-2-yn-1-yl2-(2,5-dioxopyrrolidin-1-yl)-2-phenyl-2-(phenylthio)acetate (3ma). White solid, mp: 52.2-54.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.85 (d, *J* = 6.9 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.40 – 7.34 (comp, 6H), 7.31 (t, *J* = 7.4 Hz, 3H), 7.25 (m, 2H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 2.53 – 2.46 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.7, 166.4, 137.9, 134.7, 131.9, 130.5, 129.8, 128.9, 128.8, 128.4, 128.2, 128.1, 126.8, 122.2, 87.2, 82.1, 76.2, 55.1, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{21}NNaO_4S[M+Na]^+$: 478.1089, found 478.1089.

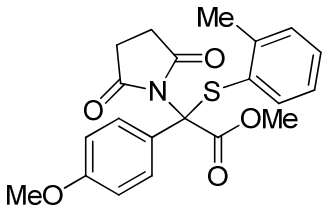


2-Isopropyl-5-methylcyclohexyl2-(2,5-dioxopyrrolidin-1-yl)-2-phenyl-2-(phenylthio)acetate (3na). White solid, mp: 61.7-62.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) one isomer: 7.71 – 7.69 (m, 2H), 7.56 – 7.54 (m, 2H), 7.38 – 7.19 (comp, 6H), 4.64 (td, *J* = 10.9, 4.2 Hz, 1H), 2.50 –

0.76 (comp, 13H), 0.84 (d, J = 6.5 Hz, 3H), 0.60 (d, J = 7.0 Hz, 3H), 0.43 (d, J = 7.0 Hz, 3H); the other isomer: 7.91 – 7.89 (m, 2H), 7.49 – 7.47 (m, 2H), 7.38 – 7.19 (comp, 6H), 4.55 (td, J = 10.9, 4.2 Hz, 1H), 2.50 – 0.76 (comp, 13H), 0.87 (d, J = 6.4 Hz, 3H), 0.71 (d, J = 6.8 Hz, 3H), 0.39 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) combination of the two isomers: 174.6, 174.4, 166.9, 166.8, 138.1, 137.7, 135.0, 134.6, 130.4, 130.3, 130.25, 130.0, 128.8, 128.6, 128.4, 128.3, 127.9, 127.8, 127.5, 77.8, 77.4, 77.2, 76.6, 47.4, 47.2, 39.9, 34.2, 31.5, 28.0, 25.6, 24.9, 23.2, 22.7, 22.1, 22.0, 21.0, 20.8, 15.7, 15.4; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{33}NNaO_4S$ $[M+Na]^+$:502.2028, found 502.2013.

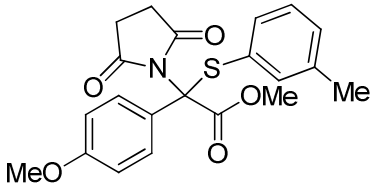


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)-2-(p-tolylthio)acetate (3gb). White solid, mp: 78.6-79.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.79 – 7.68 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H), 3.62 (s, 3H), 2.54 – 2.41 (m, 4H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.7, 159.8, 140.8, 137.6, 129.6, 129.4, 126.9, 126.6, 113.4, 75.9, 55.3, 53.5, 28.0, 21.4; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{21}NNaO_5S$ $[M+Na]^+$:422.1038, found 422.1024.

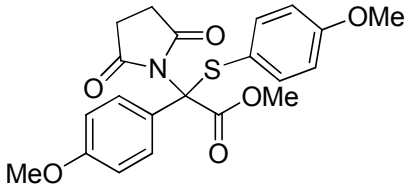


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)-2-(*o*-tolylthio)acetate (3gc). White solid, mp: 131.8-132.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.81 – 7.75 (m, 2H), 7.38 (dd, J = 7.7, 1.0 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 (d, J = 6.9 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.90 – 6.83 (m, 2H), 3.81 (s, 3H), 3.55 (s, 3H), 2.46 (comp, 4H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.9, 167.7, 159.8, 145.3, 138.8, 130.6, 130.3, 130.2, 129.7, 127.6, 125.9, 113.3, 75.6, 55.4,

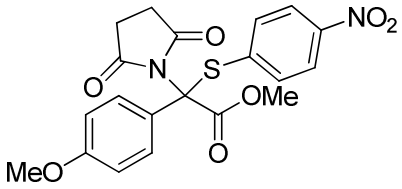
53.3, 28.1, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{21}NNaO_5S[M+Na]^+$: 422.1038, found 422.1024.



Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)-2-(*m*-tolylthio)acetate (3gd). White solid, mp: 146.8-147.1 ^oC. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.79 – 7.70 (m, 2H), 7.29 (d, J = 8.9 Hz, 2H), 7.14 (m, 2H), 6.91 – 6.85 (m, 2H), 3.82 (s, 3H), 3.63 (s, 3H), 2.46 (comp, 4H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.8, 159.8, 138.6, 138.2, 134.7, 131.1, 129.8, 129.5, 128.6, 126.9, 113.5, 76.1, 55.4, 53.5, 28.0, 21.3; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{21}NNaO_5S[M+Na]^+$: 422.1038, found 422.1033.

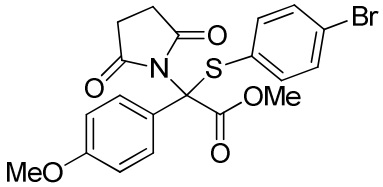


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)-2-[(4-methoxyphenyl)thio]acetate (3ge). White solid, mp: 109.4-109.8 ^oC. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 – 7.69 (m, 2H), 7.40 – 7.35 (m, 2H), 6.89 – 6.84 (m, 2H), 6.79 – 6.73 (m, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 3.63 (s, 3H), 2.48 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.9, 167.8, 161.5, 159.7, 139.3, 129.4, 126.9, 120.7, 114.3, 113.5, 76.0, 55.4, 55.3, 53.5, 28.0; HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{21}NNaO_6S[M+Na]^+$: 438.0987, found 438.0988.

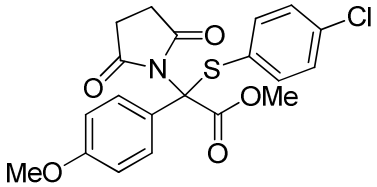


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)-2-[(4-nitrophenyl)thio]acetate (3gf). White solid, mp: 77.6-78.2 ^oC. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.04 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 3.63

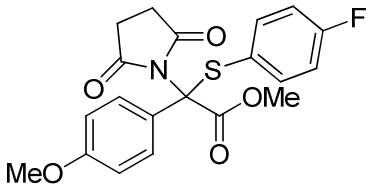
(s, 3H), 2.61 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.9, 167.0, 160.1, 148.4, 139.3, 136.7, 129.7, 126.0, 123.4, 113.7, 75.9, 55.4, 53.7, 28.1; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{18}N_2NaO_7S[M+Na]^+$: 453.0732, found 453.0725.



Methyl 2-[(4-Bromophenyl)thio]-2-(2,5-dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)acetate (3gg) White solid, mp: 96.9-97.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.76 – 7.66 (m, 2H), 7.40 – 7.29 (m, 4H), 6.91 – 6.84 (m, 2H), 3.81 (s, 3H), 3.63 (s, 3H), 2.55 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.4, 159.9, 138.9, 132.0, 129.5, 129.3, 126.7, 125.2, 113.6, 75.8, 55.4, 53.6, 28.1; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{18}BrNNaO_5S[M+Na]^+$: 485.9981, found 485.9972.

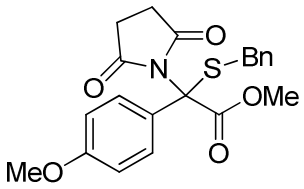


Methyl 2-[(4-Chlorophenyl)thio]-2-(2,5-dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)acetate (3gh) White solid, mp: 65.6-66.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.75 – 7.67 (m, 2H), 7.42 – 7.36 (m, 2H), 7.24 – 7.17 (m, 2H), 6.90 – 6.84 (m, 2H), 3.81 (s, 3H), 3.63 (s, 3H), 2.54 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.9, 167.4, 159.9, 138.7, 136.9, 129.4, 129.0, 128.7, 126.7, 113.6, 75.9, 55.4, 53.6, 28.1; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{18}ClNNaO_5S[M+Na]^+$: 442.0492, found 442.0481.

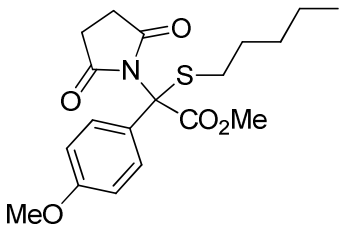


Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-[(4-fluorophenyl)thio]-2-(4-methoxyphenyl)acetate (3gi) White solid, mp: 45.3-46.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.76 – 7.67 (m, 2H),

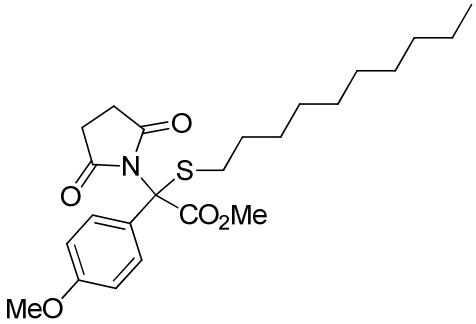
7.50 – 7.42 (m, 2H), 6.99 – 6.83 (comp, 4H), 3.81 (s, 3H), 3.63 (s, 3H), 2.62 – 2.45 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.6, 164.3 (d, J = 251.8 Hz), 159.9, 139.7 (d, J = 8.7 Hz), 129.4, 126.7, 125.6 (d, J = 3.4 Hz), 116.0 (d, J = 21.7 Hz), 113.6, 75.9, 55.4, 53.6, 28.1; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{18}FNNaO_5S[M+Na]^+$: 426.0787, found 426.0773.



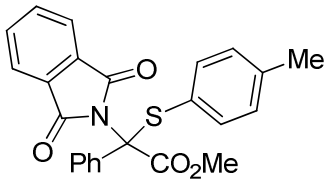
Methyl 2-(Benzylthio)-2-(2,5-dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)acetate (3gj). White solid, mp: 45.3-46.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 (d, J = 9.0 Hz, 2H), 7.29 (comp, 4H), 7.21 (t, J = 7.0 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 3.86 (q, J = 14.2 Hz, 2H), 3.81 (s, 3H), 3.71 (s, 3H), 2.34 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 175.6, 167.8, 159.8, 136.5, 131.5, 129.5, 129.1, 128.6, 127.3, 125.6, 114.0, 113.7, 73.3, 55.4, 53.7, 35.4, 28.2. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{21}NNaO_5S$ $[M+Na]^+$: 422.1038, found 422.1040.



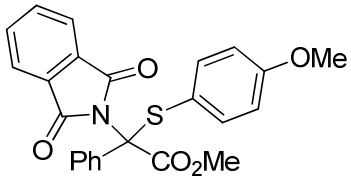
Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)-2-(pentylthio)acetate (3gk). Colorless oil**.** ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 – 7.55 (m, 2H), 6.89 – 6.83 (m, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 2.77 (s, 4H), 2.54 – 2.41 (m, 2H), 1.54 – 1.47 (m, 2H), 1.30 (comp, 4H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 175.7 167.7, 159.8, 129.7, 126.1, 113.6, 73.0, 55.4, 53.6, 31.5, 31.3, 28.4, 28.1, 22.4, 14.0; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{25}NNaO_5S[M+Na]^+$: 402.1351, found 402.1352.



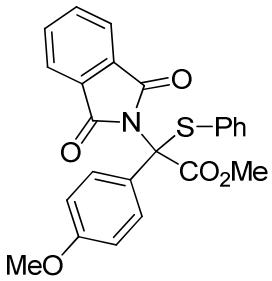
Methyl 2-(Decylthio)-2-(2,5-dioxopyrrolidin-1-yl)-2-(4-methoxyphenyl)acetate (3gl). White solid, mp: 42.2-44.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60 – 7.54 (m, 2H), 6.90 – 6.83 (m, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 2.77 (s, 4H), 2.54 – 2.38 (m, 2H), 1.56 – 1.44 (m, 2H), 1.35 – 1.22 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 175.7, 167.7, 159.8, 129.7, 126.1, 113.6, 73.0, 55.4, 53.6, 32.0, 31.6, 29.7, 29.6, 29.4, 29.4, 29.1, 28.4, 28.39, 22.8, 14.2; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{35}NNaO_5S[M+Na]^+$: 472.2134, found 472.2132.



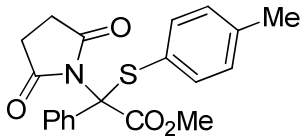
Methyl 2-(1,3-Dioxoisoindolin-2-yl)-2-phenyl-2-(*p*-tolylthio)acetate (3am).[3] ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.90 (d, *J* = 6.8 Hz, 2H), 7.69 (s, 4H), 7.41 – 7.33 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 3.69 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.0, 166.4, 140.5, 137.7, 135.4, 134.3, 131.4, 129.5, 128.7, 128.1, 128.1, 126.2, 123.3, 76.5, 53.6, 21.3.



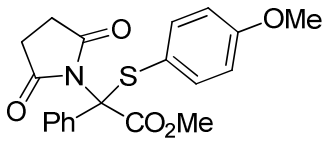
Methyl 2-(1,3-Dioxoisoindolin-2-yl)-2-((4-methoxyphenyl)thio)-2-phenylacetate (3an).[3] ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.89 (d, *J* = 7.0 Hz, 2H), 7.69 (s, 4H), 7.37 (comp, 5H), 6.51 (d, *J* = 8.6 Hz, 2H), 3.69 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.0, 166.4, 161.3, 139.4, 135.4, 134.3, 131.3, 128.6, 128.1, 128.0, 123.3, 120.4, 114.2, 76.5, 55.3, 53.6.



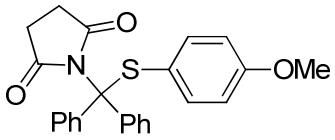
Methyl 2-(1,3-Dioxoisoindolin-2-yl)-2-(4-methoxyphenyl)-2-(phenylthio)acetate (3go).[3] ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.83 (d, *J* = 9.0 Hz, 2H), 7.68 (s, 4H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.69 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.1, 166.4, 159.9, 137.7, 134.3, 131.3, 130.0, 129.9, 129.6, 128.7, 127.0, 123.3, 113.5, 76.3, 55.4, 53.6.



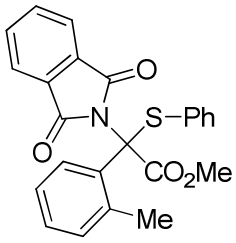
Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-phenyl-2-(p-tolylthio)acetate (3ab).[3] ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.84 – 7.77 (m, 2H), 7.35 (comp, 5H), 7.05 (d, *J* = 7.9 Hz, 2H), 3.63 (s, 3H), 2.48 (comp, 4H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.7, 140.9, 137.8, 135.1, 129.6, 128.7, 128.1, 128.0, 126.4, 76.3, 53.6, 28.1, 21.5; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}NNaO_4S[M+Na]^+$: 392.0932, found 392.0919.



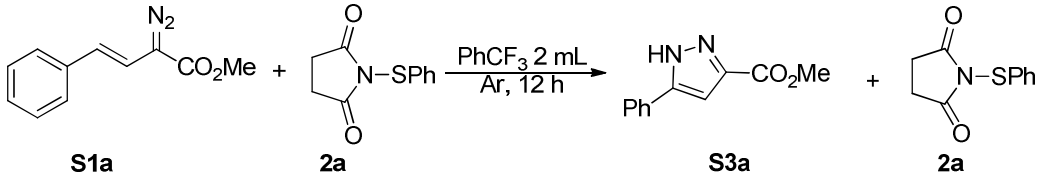
Methyl 2-(2,5-Dioxopyrrolidin-1-yl)-2-[(4-methoxyphenyl)thio]-2-phenylacetate (3ae). White solid, mp: 60.0-61.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.83 – 7.76 (m, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.32 (m, 3H), 6.79 – 6.74 (m, 2H), 3.76 (s, 3H), 3.64 (s, 3H), 2.52 – 2.48 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 167.7, 161.6, 139.4, 135.1, 128.7, 128.2, 127.9, 120.6, 114.3, 76.4, 55.5, 53.6, 28.1; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}NNaO_5S[M+Na]^+$: 408.0882, found 408.0872.



1-{[(4-Methoxyphenyl)thio]diphenylmethyl}pyrrolidine-2,5-dione (3oe). White solid, mp: 66.1-66.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.43 (d, *J* = 8.8 Hz, 2H), 7.30 (comp, 5H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.49 (s, 1H), 3.82 (s, 3H), 2.72 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 176.8 160.2, 138.8, 137.5, 136.0, 135.0, 129.5, 128.6, 128.5, 127.9, 127.6, 123.6, 115.2, 58.1, 55.5, 28.3; HRMS (TOF MS ESI^{+}) calculated for $C_{24}H_{22}NO_3S[M+H]^{+}$: 404.1320, found 404.1311.



Methyl 2-(1,3-Dioxoisoindolin-2-yl)-2-(phenylthio)-2-(*o*-tolyl)acetate (3qo).[3] ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.10 – 8.02 (m, 1H), 7.73 – 7.64 (m, 4H), 7.45 – 7.38 (m, 2H), 7.26 – 7.19 (m, 2H), 7.15 – 7.08 (m, 2H), 6.96 (t, *J* = 7.7 Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.9, 166.3, 137.7, 137.1, 134.4, 133.6, 132.9, 131.2, 130.2, 129.9, 129.0, 128.6, 128.4, 125.9, 123.4, 77.3, 53.8, 21.7.



To a 10-mL oven-dried vial containing a magnetic stirring bar, and **2a** (0.2 mmol, 41.5mg) in $PhCF_3$ (0.5 mL), was added the solution of diazo compound **S1a** (0.4 mmol, 80.9mg) in $PhCF_3$ (1.5 mL) *via* a syringe pump in 5 hours at 105 ^{o}C under argon atmosphere. The reaction mixture was stirred for additional 7 h under these conditions. After the reaction was completed, the solvent was removed under reduced pressure and the crude reaction mixture was subjected to proton NMR analysis

(Figure S1). Most of the material **2a** remains untouched and **S3a** is observed as the only product.

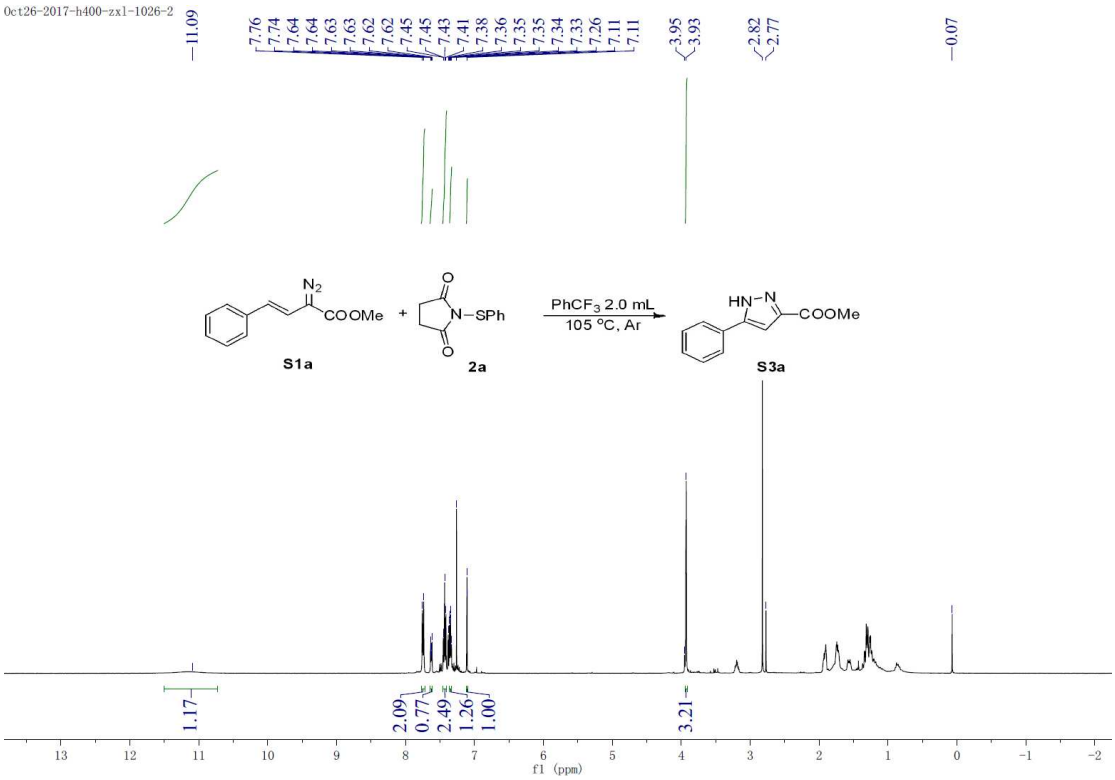
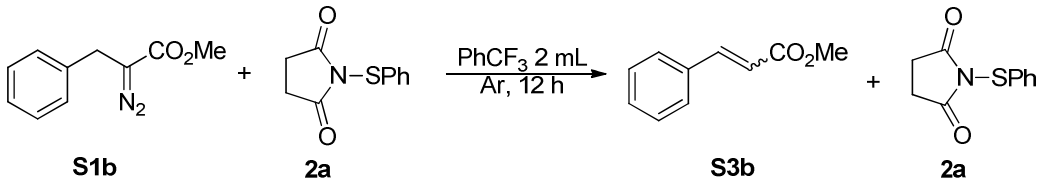


Fig. S1 Proton NMR of the crude reaction mixture of **S1a** with **2a**.



To a 10-mL oven-dried vial containing a magnetic stirring bar, and **2a** (0.2 mmol, 41.5 mg) in $PhCF_3$ (0.5 mL), was added the solution of diazo compound **S1b** (0.4 mmol, 76.1 mg) in $PhCF_3$ (1.5 mL) *via* a syringe pump in 5 hours at 105 ^oC under argon atmosphere. The reaction mixture was stirred for additional 7 h under these conditions. After the reaction was completed, the solvent was removed under reduced pressure and the crude reaction mixture was subjected to proton NMR analysis. Most of the material **2a** remains untouched and **S3b** is observed as two isomer (*Z*:*E* = 0.6:1).

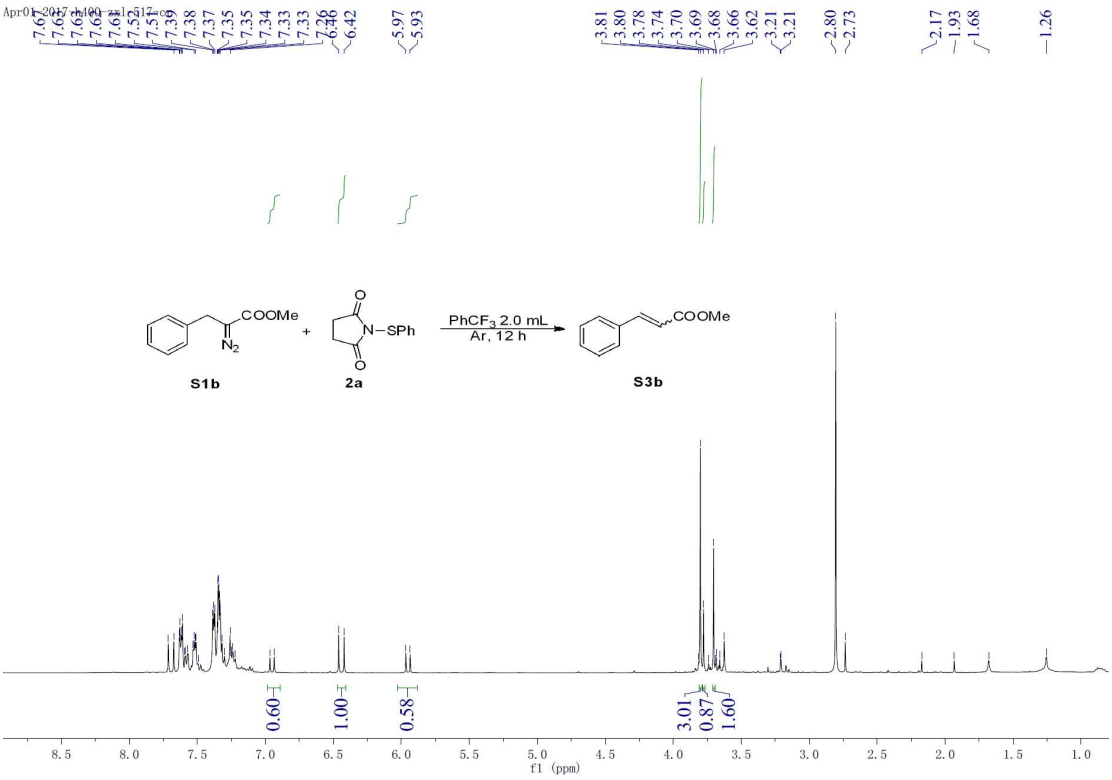
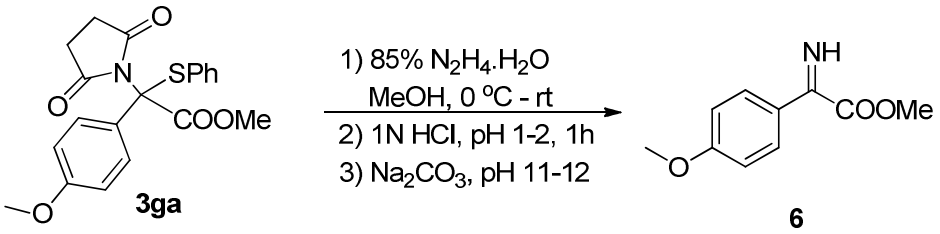


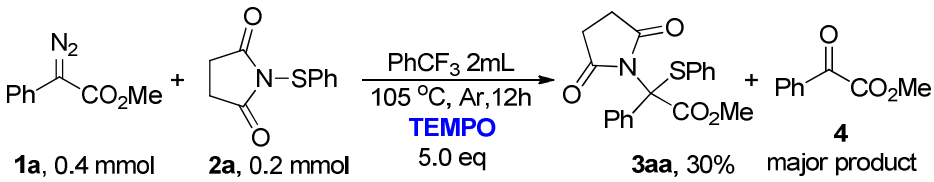
Fig. S2 Proton NMR of the crude reaction mixture of **S1a** with **2a**.

Derivatization: Synthesis of 6.



To a 10-mL oven-dried vial containing a magnetic stirring bar, **3ga** (77 mg, 0.2 mmol) in MeOH (2.0 mL), was added 85% hydrazine hydrate (64 uL, 1.0 mmol) dropwise over 2 min at 0 °C under stirring. The reaction mixture was stirred at 0 °C for additional 1 h, and then warmed up to room temperature and reacted overnight. After the reaction completed, the solvents were removed in vacuo and the residue was dissolved in water (8.0 mL), the pH of solution was then adjusted to 1-2 by adding 1N HCl at 0 °C. The mixture was stirred for 1h at room temperature, and then filtered. The filtrate was treated with solid Na_2CO_3 until the pH reached at 11-12. The mixture was extracted with CH_2Cl_2 (5.0 mL x 3). The combined extracts were dried over Na_2SO_4, concentrated and dried in vacuo after filtration to provide a yellow oil **6** in 73% yield (28.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) (δ ppm) 7.26 – 7.22 (m, 2H), 7.03 – 6.98 (m, 2H), 6.21 (s, 1H), 3.84 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm) 165.2, 160.4, 137.4, 130.4, 121.4, 114.8, 55.5, 52.5. HRMS (TOF MS CI^+) calculated for $C_{10}H_{12}NO_3[M+H]^+$: 194.0817, found 194.0818.

Control Experiments.



To a 10-mL oven-dried vial containing a magnetic stirring bar, **2a** (43.7 mg, 0.2 mmol), and TEMPO (156.2 mg, 1.0 mmol) in anhydrous $PhCF_3$ (0.5 mL), was added a solution of diazo compound **1a** (70.5 mg, 0.4 mmol) in anhydrous $PhCF_3$ (1.5 mL) *via* a syringe pump over 5 h at 105°C under argon atmosphere. And the mixture was stirred for additional 7 h under these conditions. When the reaction was completed, The reaction mixture was subjected to proton NMR (Figure 3) and HRMS analysis (Figure 4) after evaporation of the solvent in *vacuo*. And then the reaction mixture was purified by column chromatography on silica gel (eluent: Hexanes : EtOAc = 5:1 to 3:1) to give the product **3aa** in 30% yield. In this study, ketone **4** was also isolated as the major by product.

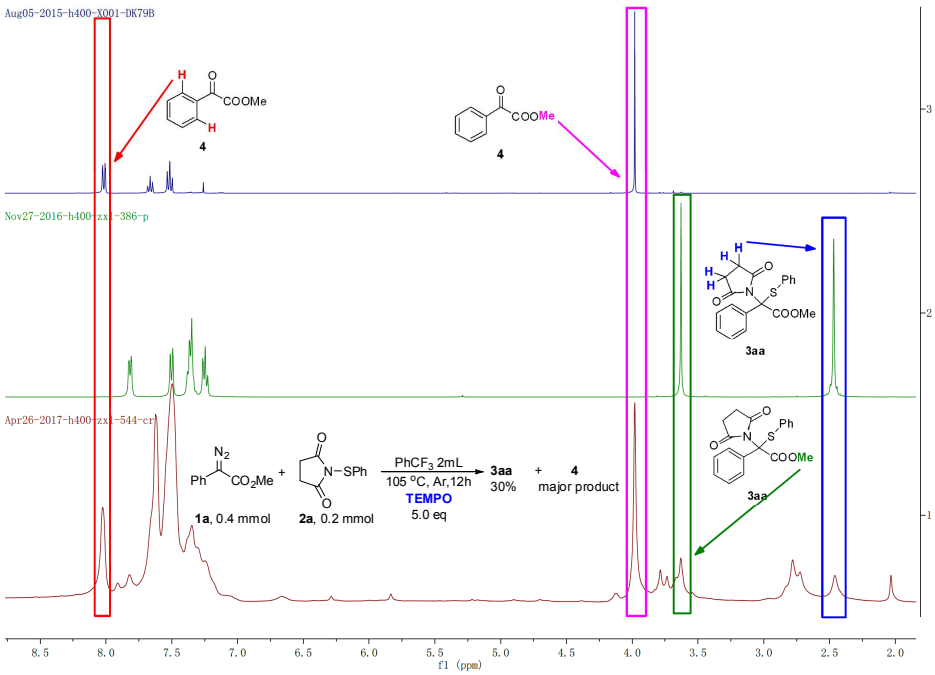


Figure S3. Proton NMR of the crude reaction mixture with TEMPO.

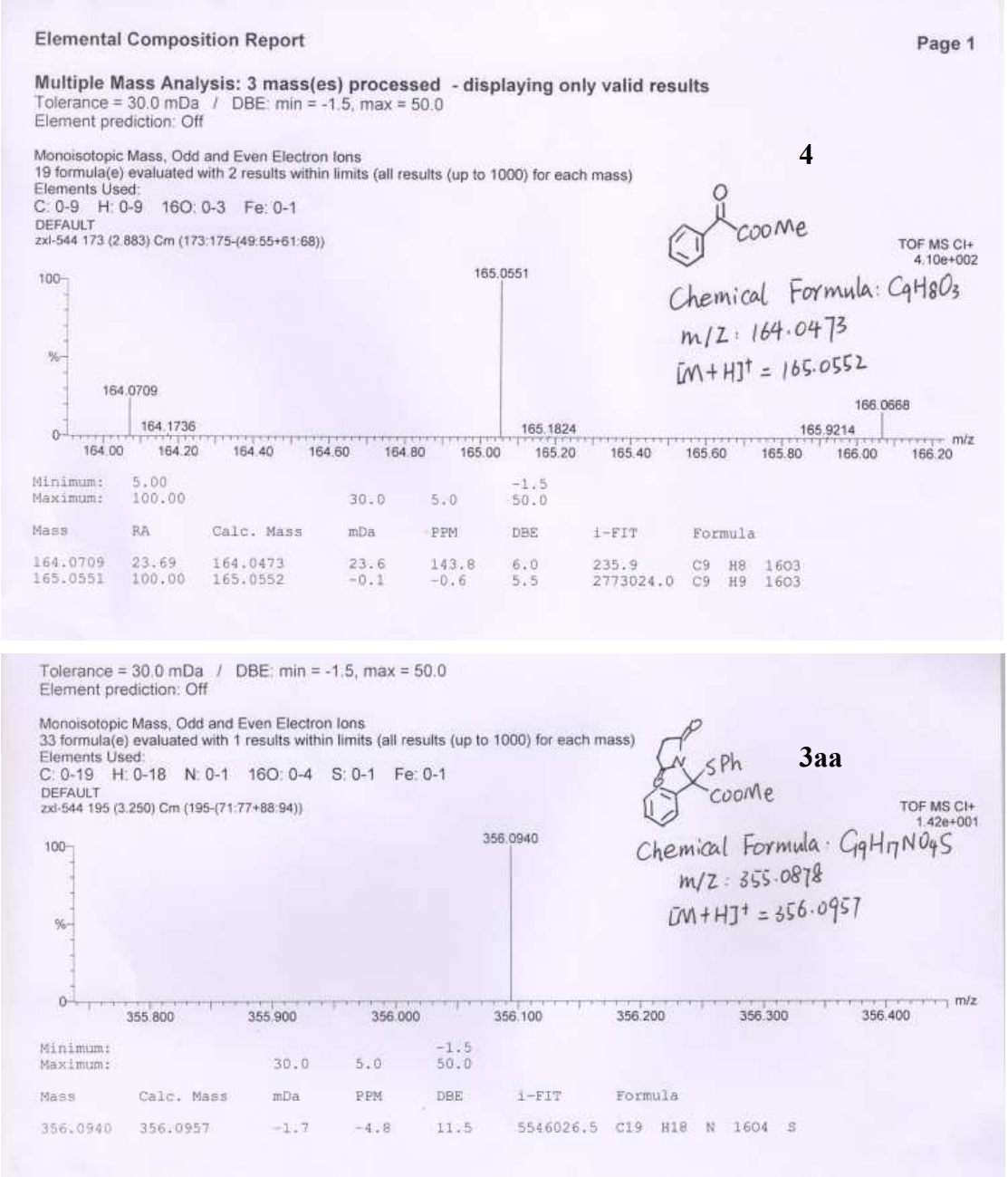
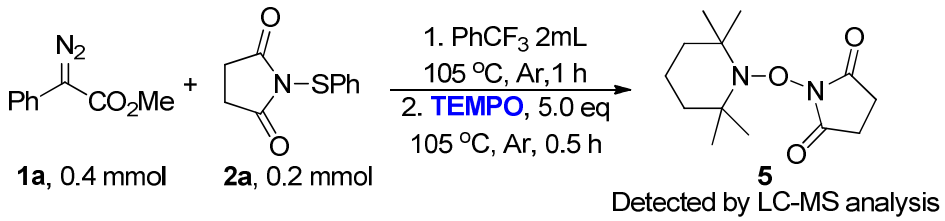


Figure S4. HRMS Analysis of the crude reaction mixturewith TEMPO.



To a 10-mL oven-dried vial containing a magnetic stirring bar, **2a** (43.7 mg, 0.2 mmol), diazo compound **1a** (70.5 mg, 0.4 mmol) and anhydrous $PhCF_3$ (1.5 mL) were

added in sequence, and the reaction mixture was stirred over 1 h at 105°C under argon atmosphere. Then TEMPO (156.2 mg, 1.0 mmol) in anhydrous $PhCF_3$ (0.5 mL) was added *via* a syringe pump, and the mixture was stirred for additional 0.5 h under these conditions. The crude reaction mixture was then subjected to LC-MS analysis and molecular weight of compound **5** was detected (See Fig. S3).

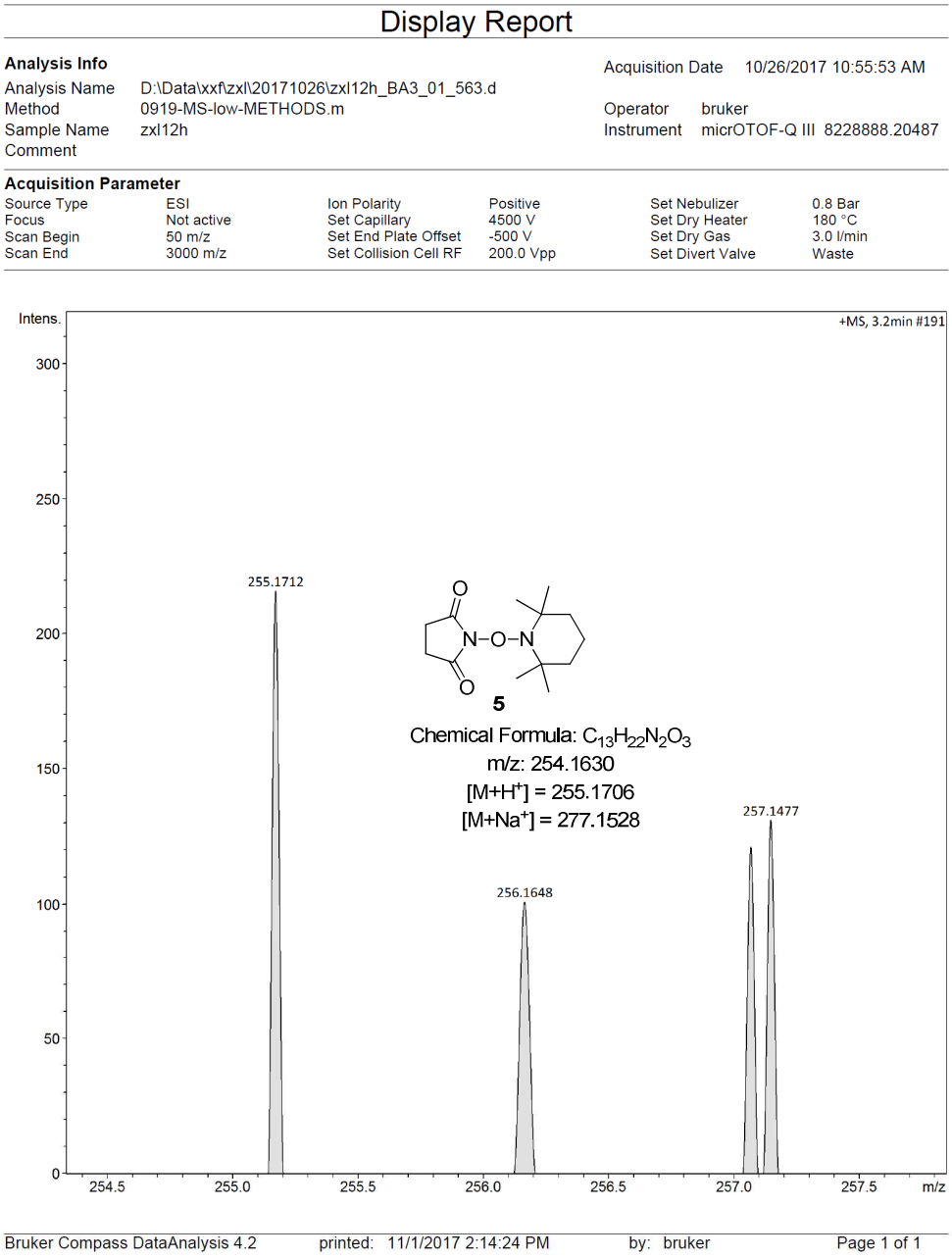
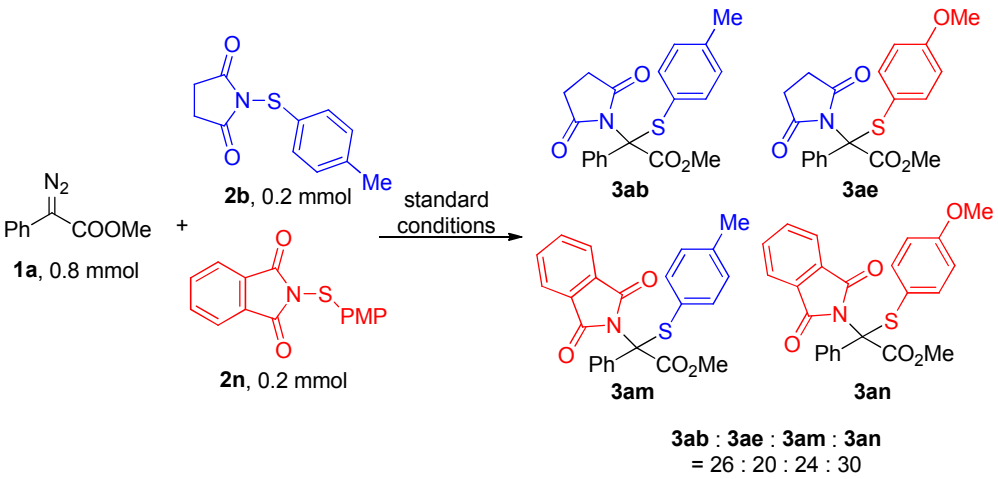


Fig. S5 LC-MS Analysis of compound **5**.

Cross-Coupling Experiment:



To a 10-mL oven-dried vial containing a magnetic stirring bar, **2b** (44.3 mg, 0.2 mmol), and **2n** (57.1 mg, 0.2 mmol) in anhydrous $PhCF_3$ (1.0 mL), was added diazo compound **1a** (141.0 mg, 0.8 mmol) in anhydrous $PhCF_3$ (3.0 mL) *via* a syringe pump over 5 h at 105°C under argon atmosphere. And the reaction mixture was stirred for additional 7h under these conditions. When the reaction was completed, the reaction mixture was subjected to proton NMR analysis after evaporation of the solvent in *vacuo* (Figure S6). In this study, four products **3ab**, **3ae**, **3am**, **3an** were obtained with a ratio of 26 : 20 : 24 : 30. And each was further confirmed by HPLC-HRMS analysis (Figure S7-S10).

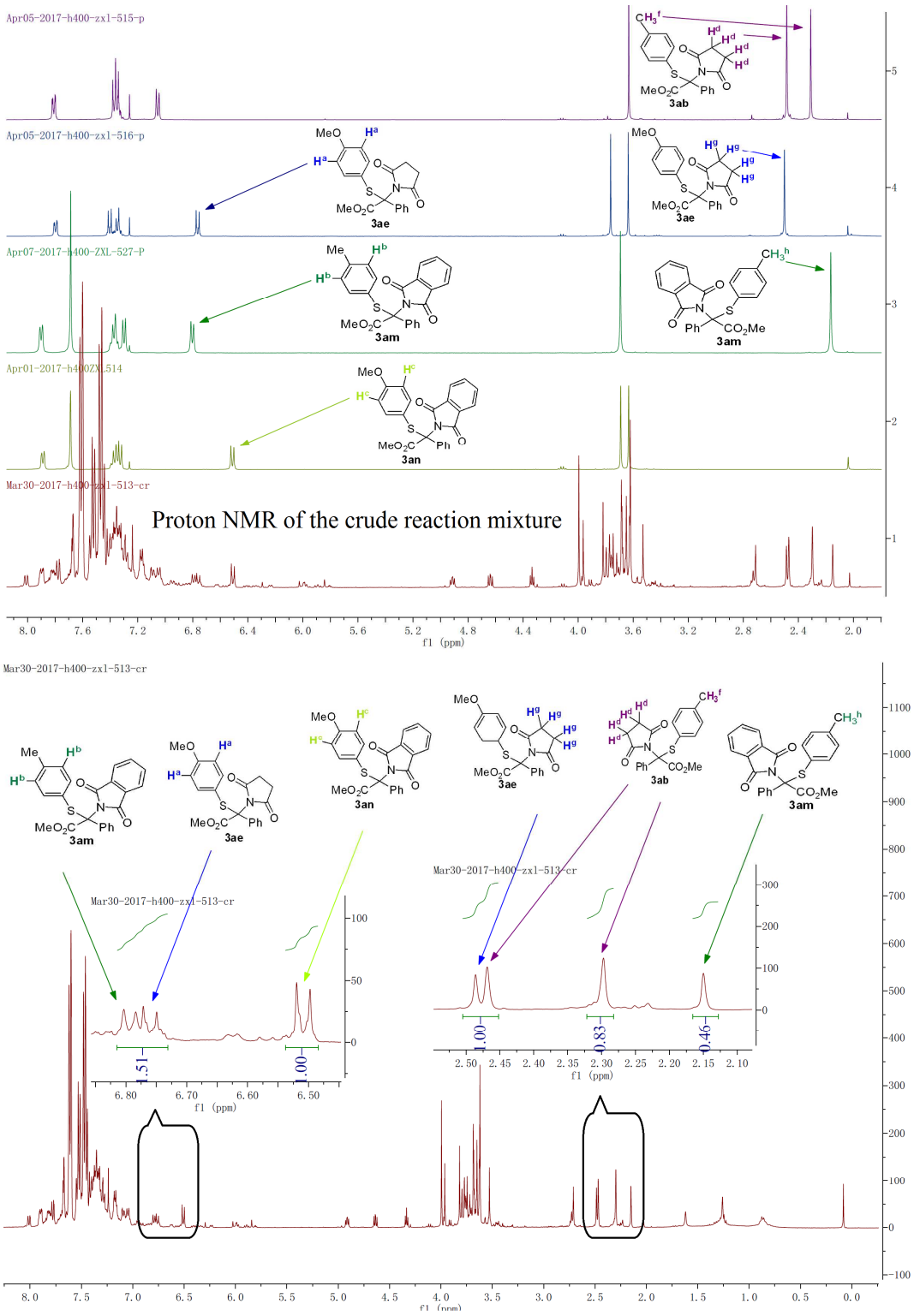


Figure S6. Proton NMR of the crude reaction mixture of the cross-coupling experiment.

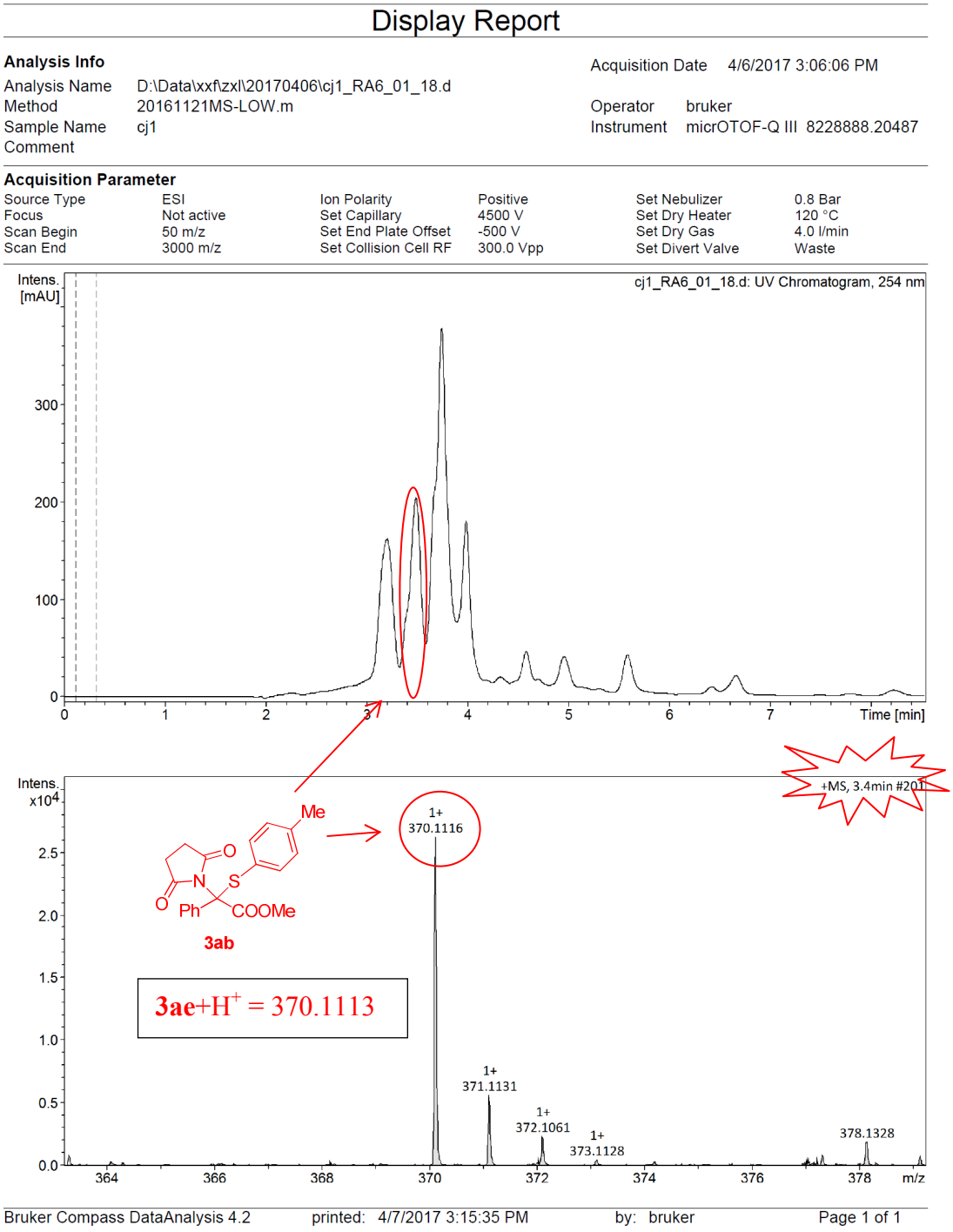


Figure S7. HPLC-HRMS Analysis of the crude reaction mixture of the cross-coupling experiment_1.

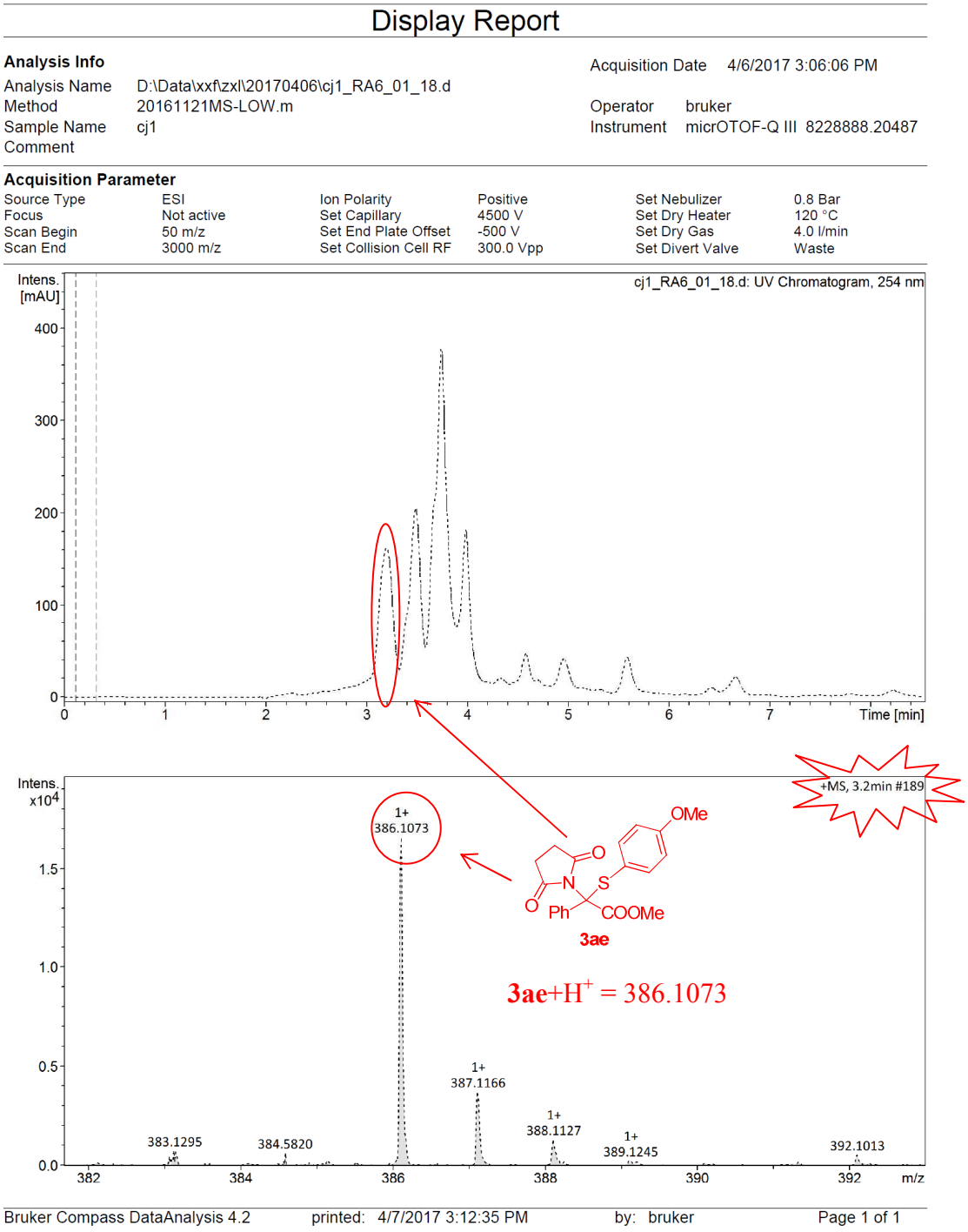


Figure S8. HPLC-HRMS Analysis of the crude reaction mixture of the cross-coupling experiment_2.

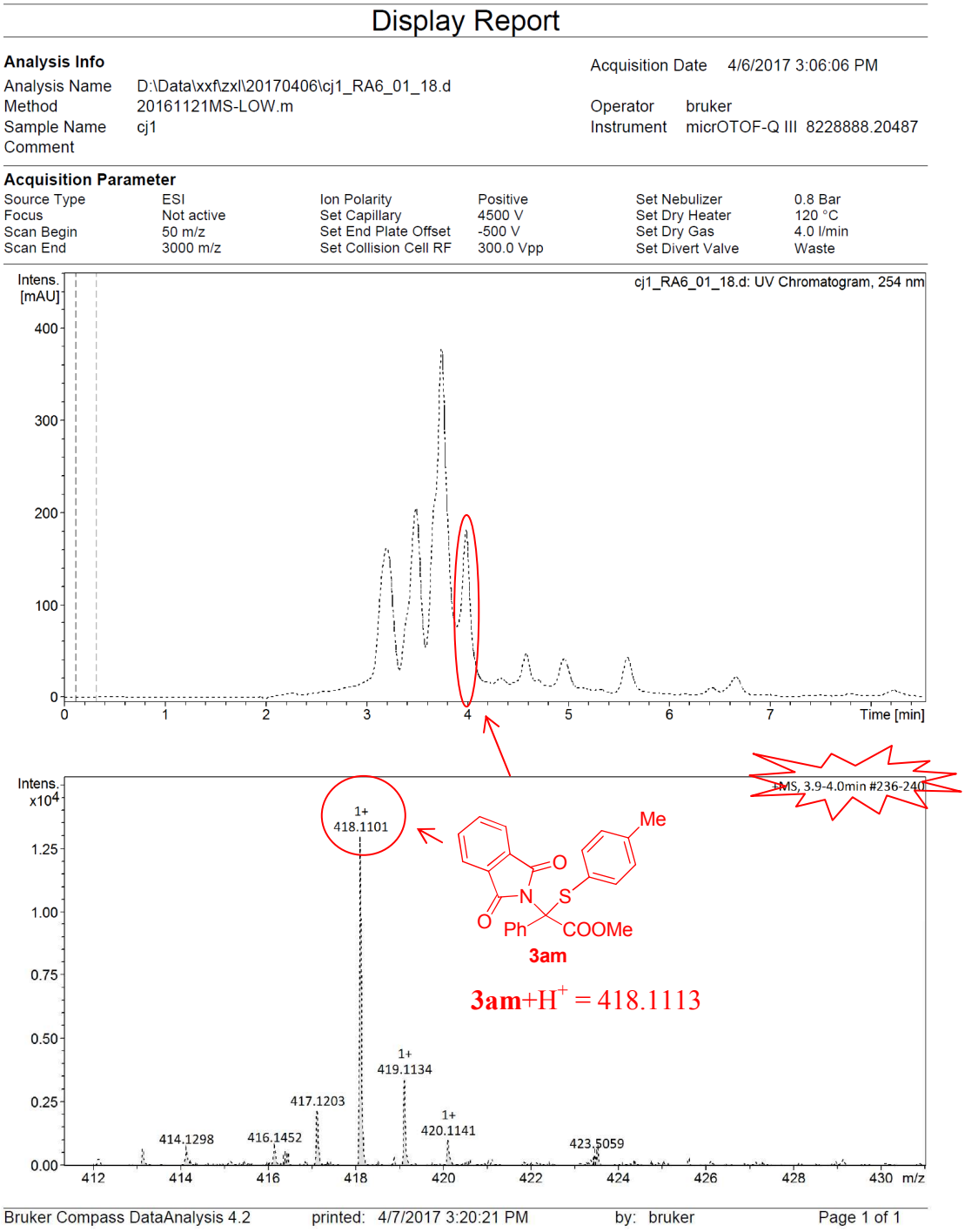


Figure S9. HPLC-HRMS Analysis of the crude reaction mixture of the cross-coupling experiment_3.

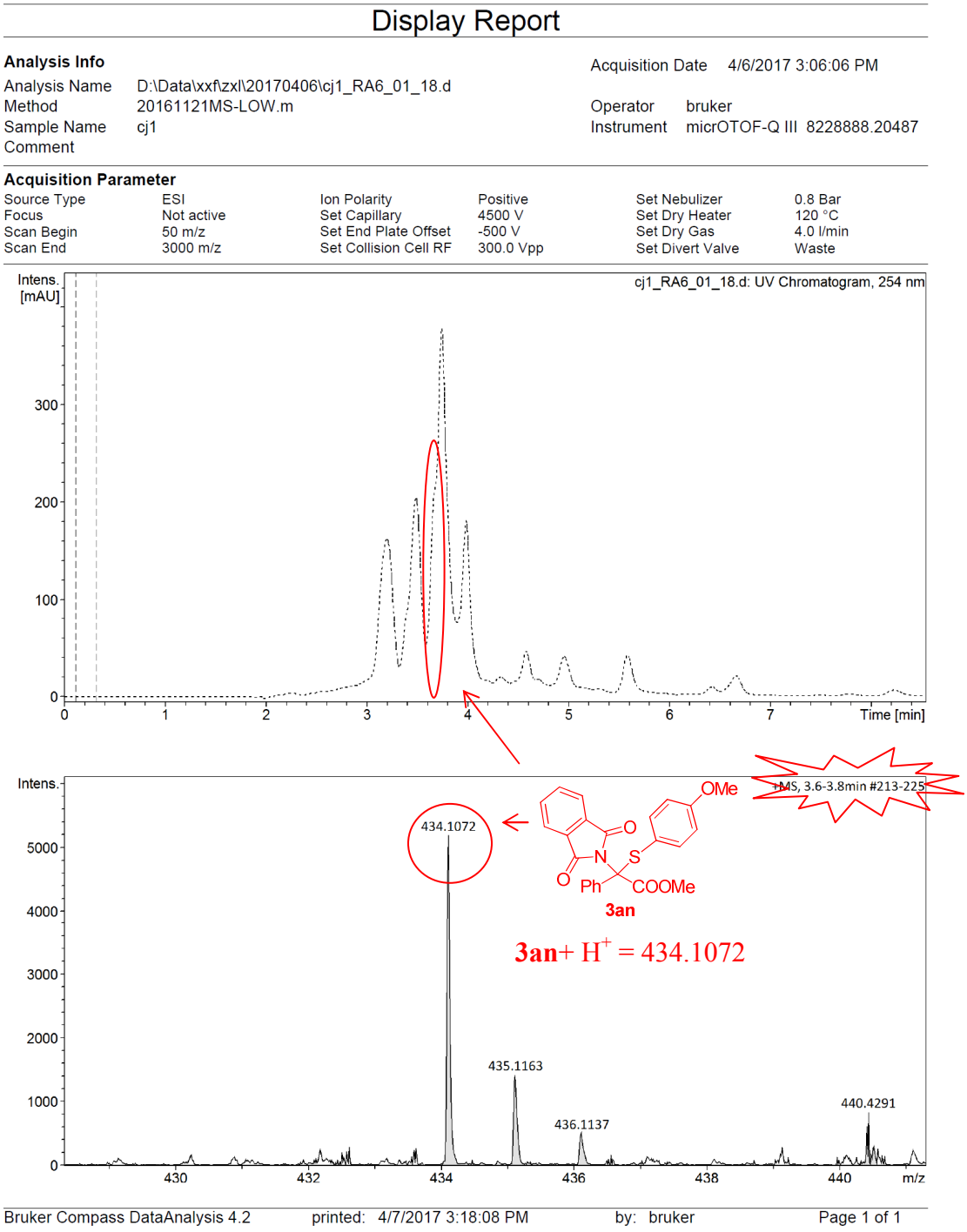
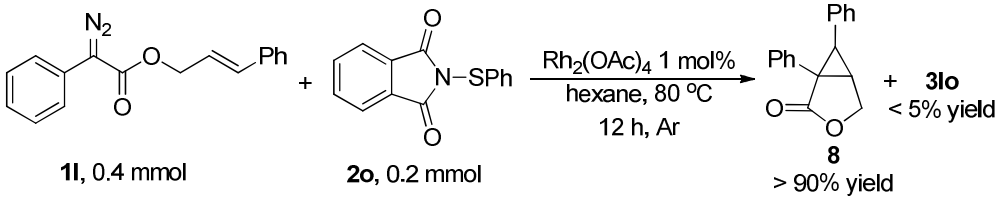


Figure S10. HPLC-HRMS Analysis of the crude reaction mixture of the cross-coupling experiment_4.

Comparative Experiment in the Presence of $Rh_2(OAc)_4$:



1l, 0.4 mmol **2o**, 0.2 mmol

To a 10-mL oven-dried vial containing a magnetic stirring bar, **1l** (51.6 mg, 0.4 mmol, 2.0 equiv.), and **2o** (111.3 mg, 0.2 mmol, 1.0 equiv.) in anhydrous hexane (4 mL), was added $Rh_2(OAc)_4$ (8.8 mg, 1.0 mol %). The reaction was stirred for 12 h at 80 °C under argon atmosphere. Then the solvent was evaporated in *vacuo* and the residue was directly subjected to proton NMR analysis (Figure S11). Then the reaction mixture was purified by column chromatography on silica gel (eluent: Hexanes : EtOAc = 5:1 to 3:1) to give the product **8** in >90% yield,[4] and unreacted **2o** was recovered.

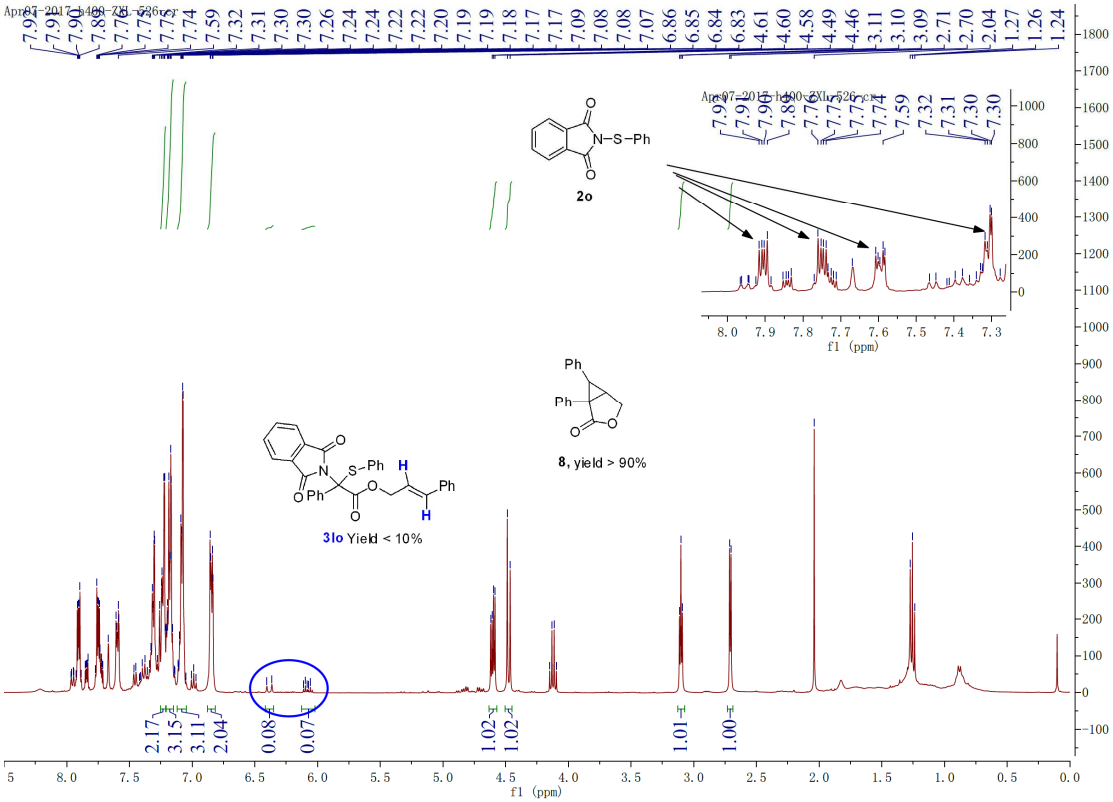


Figure S11. Proton NMR of the crude reaction in the presence of $Rh_2(OAc)_4$.

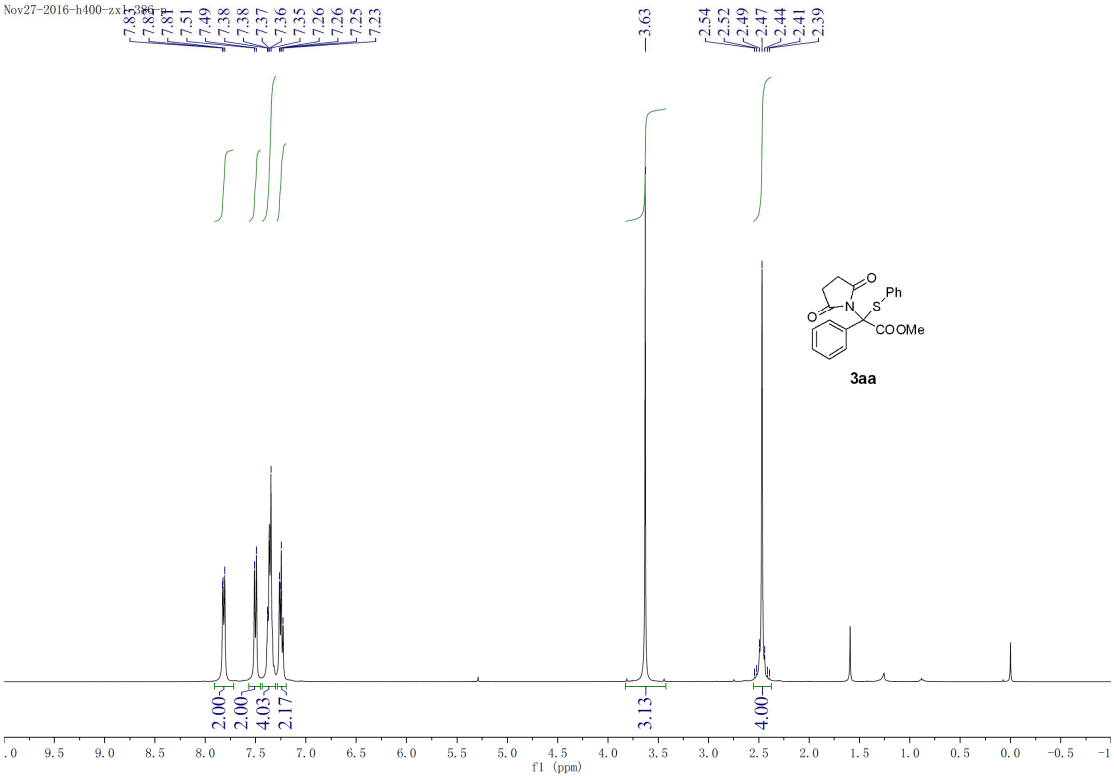
References:

(1) M. Hu, J. Rong, W. Miao, C. Ni, Y. Han and J. Hu, *Org. Lett.*, 2014, **16**, 2030.

(2) W.Gao, T. Liu, B. Zhang, X. Li, W. Wei, Q. Liu, J. Tian and H. Chang, *J. Org. Chem.,* 2016, **81**, 11297.

(3) Z. Song, Y. Wu, T. Xin, C. Jin, X. Wen, H. Sun and Q. Xu, *Chem. Commun.,* 2016, **52**, 6079.

(4) J. Shen, S. Zhu, Y. Cai, H. Xu, X. Xie and Q. Zhou, *Angew. Chem. Int. Ed.*, 2014, **53**, 13188.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7.25
7.23
3.63
2.54
2.52
2.49
2.47
2.44
2.41
2.39
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N
O
O
COOMe
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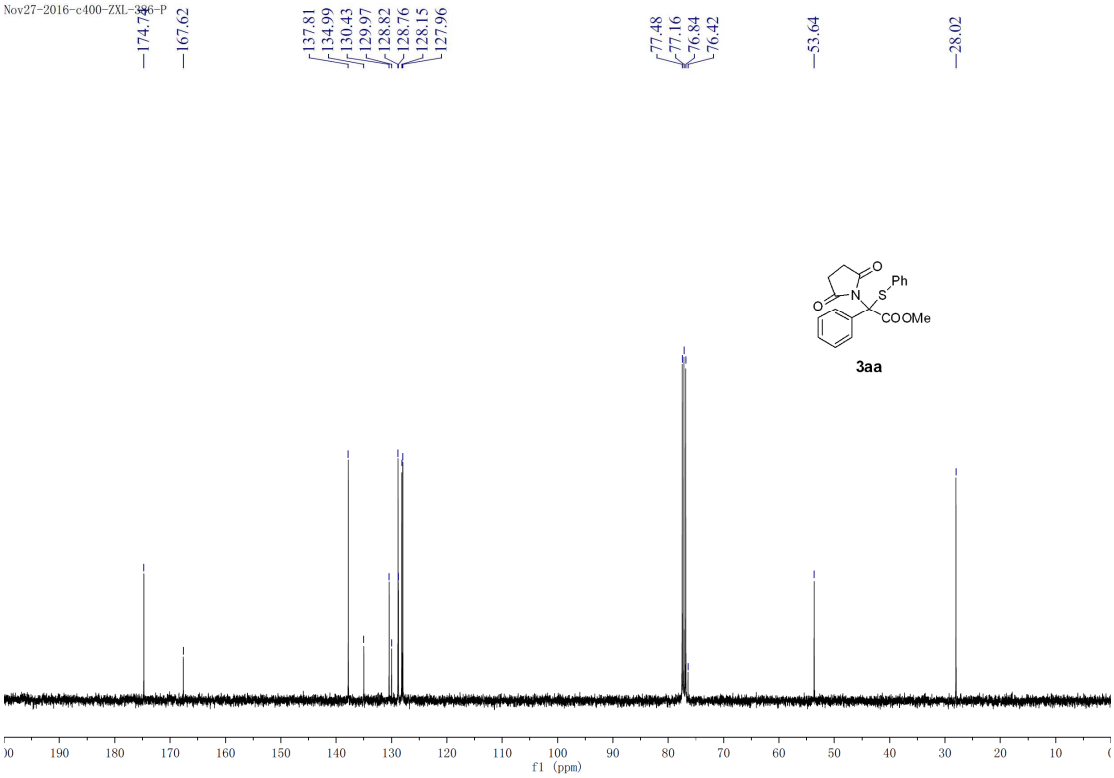
2.00
4.03
2.17
3.13
4.00
f1 (ppm)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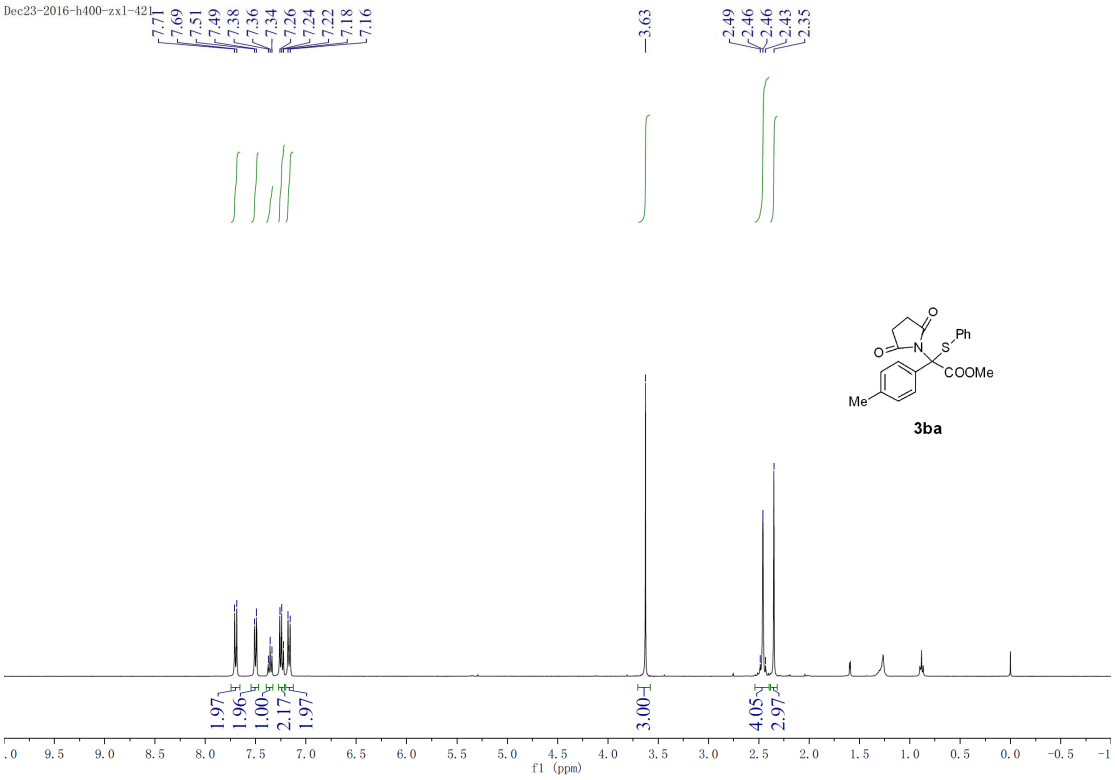
f1 (ppm)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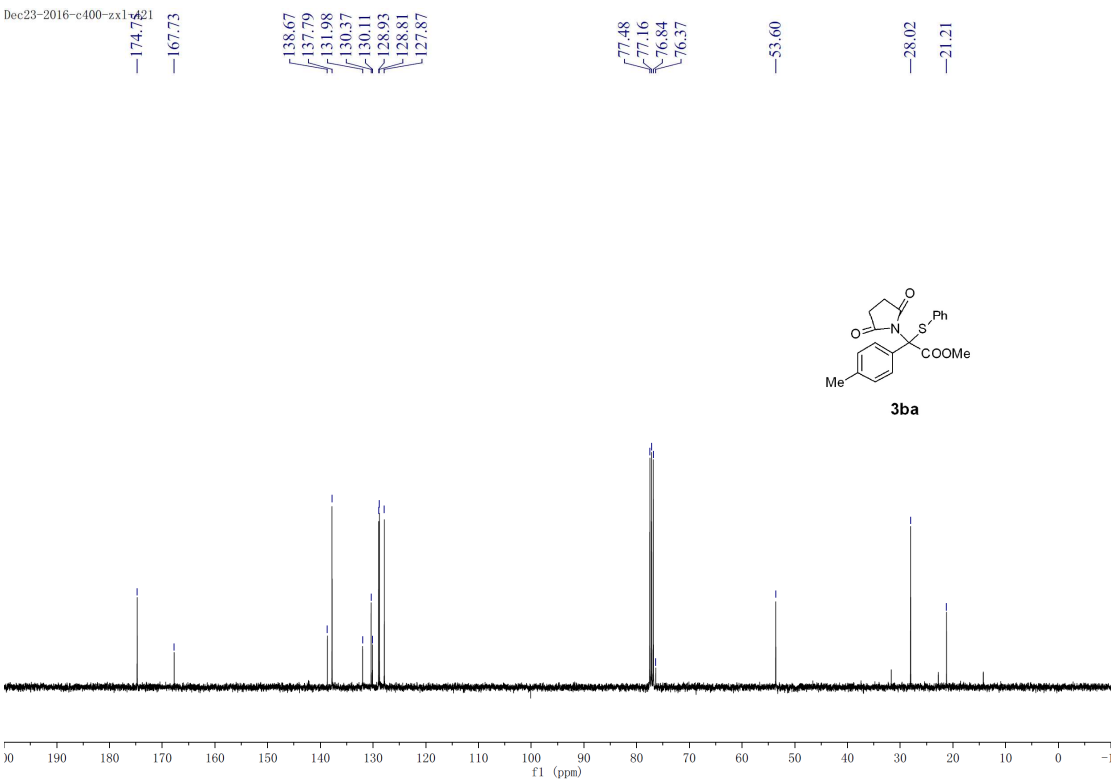
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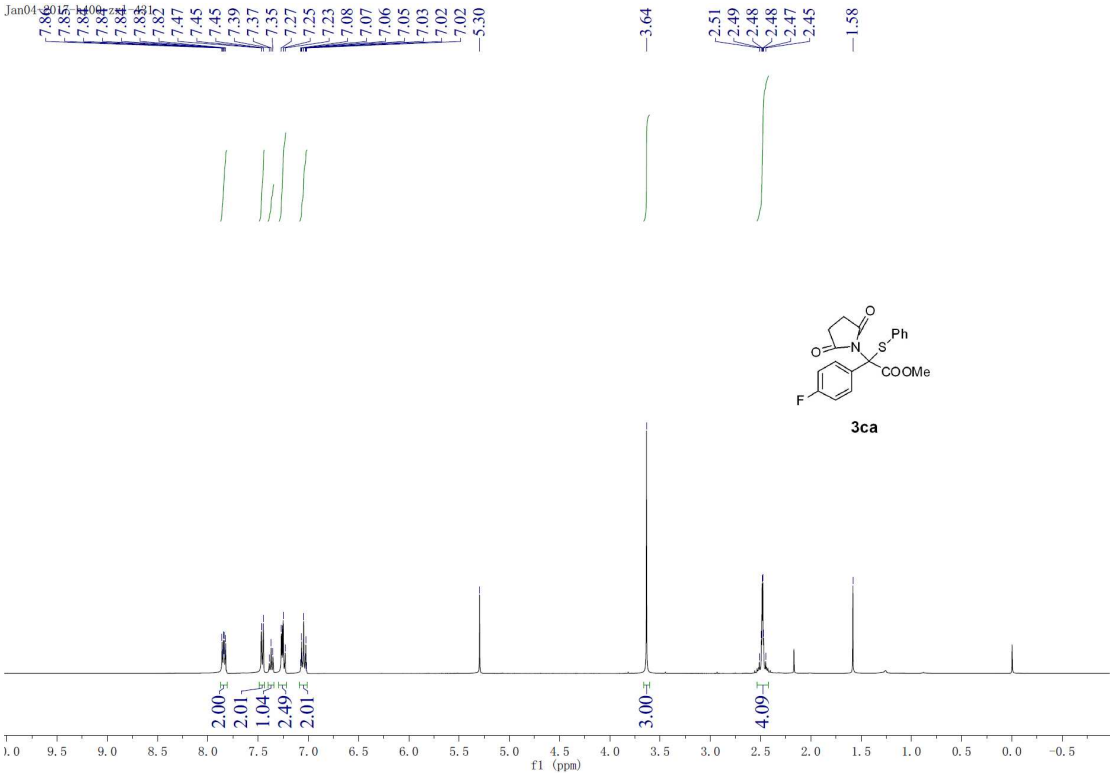
f1 (ppm)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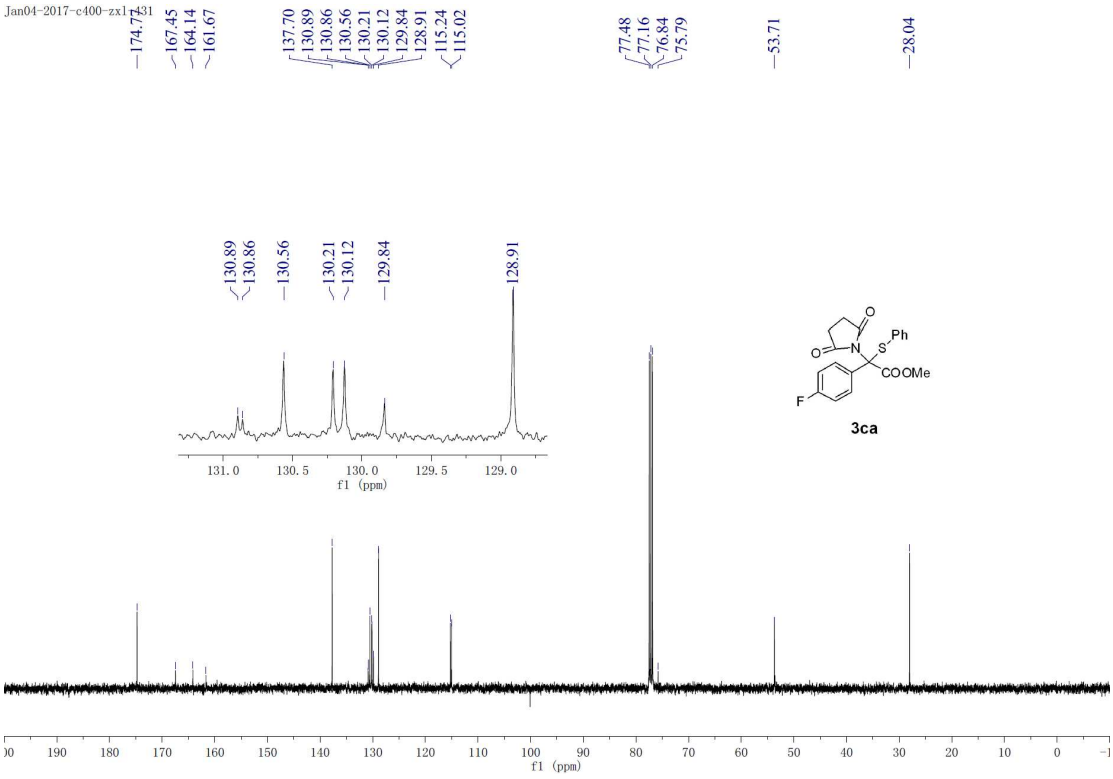
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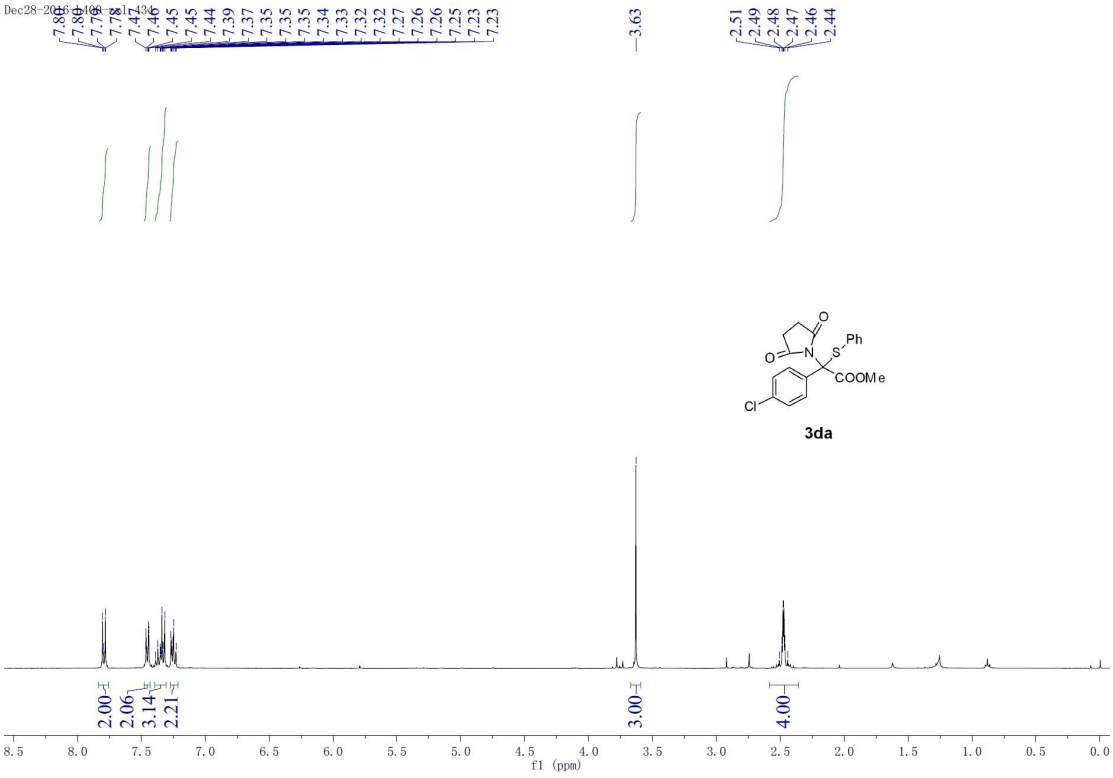
f1 (ppm)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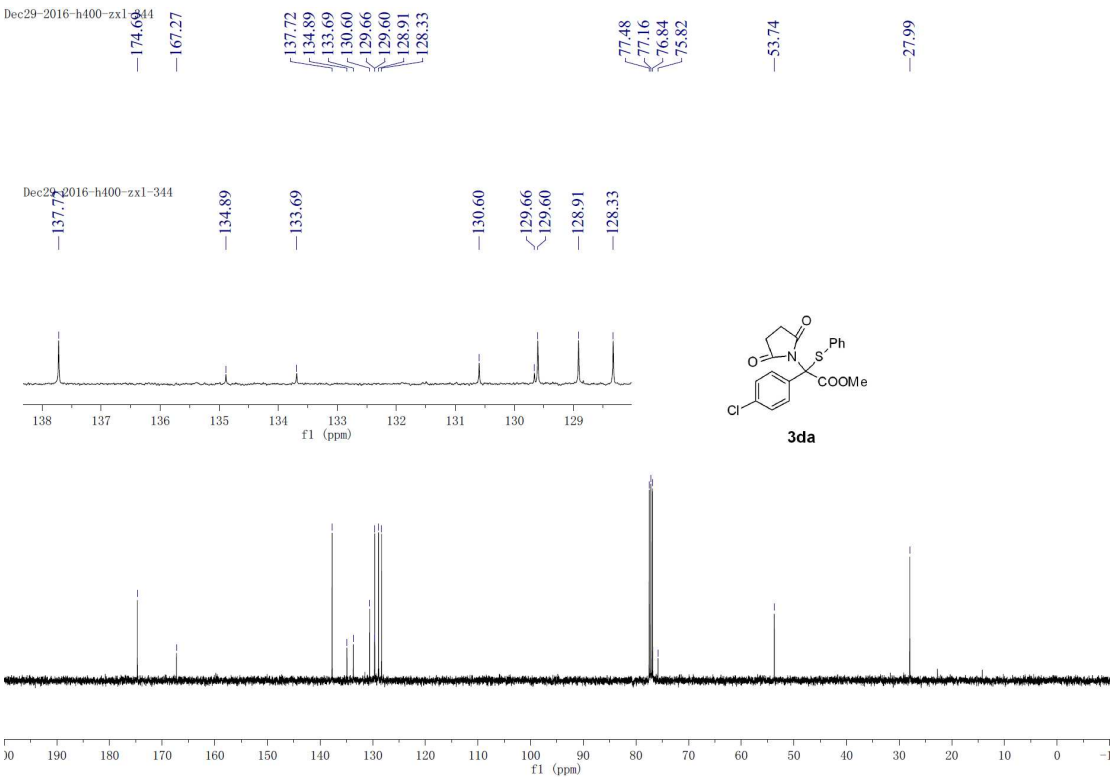
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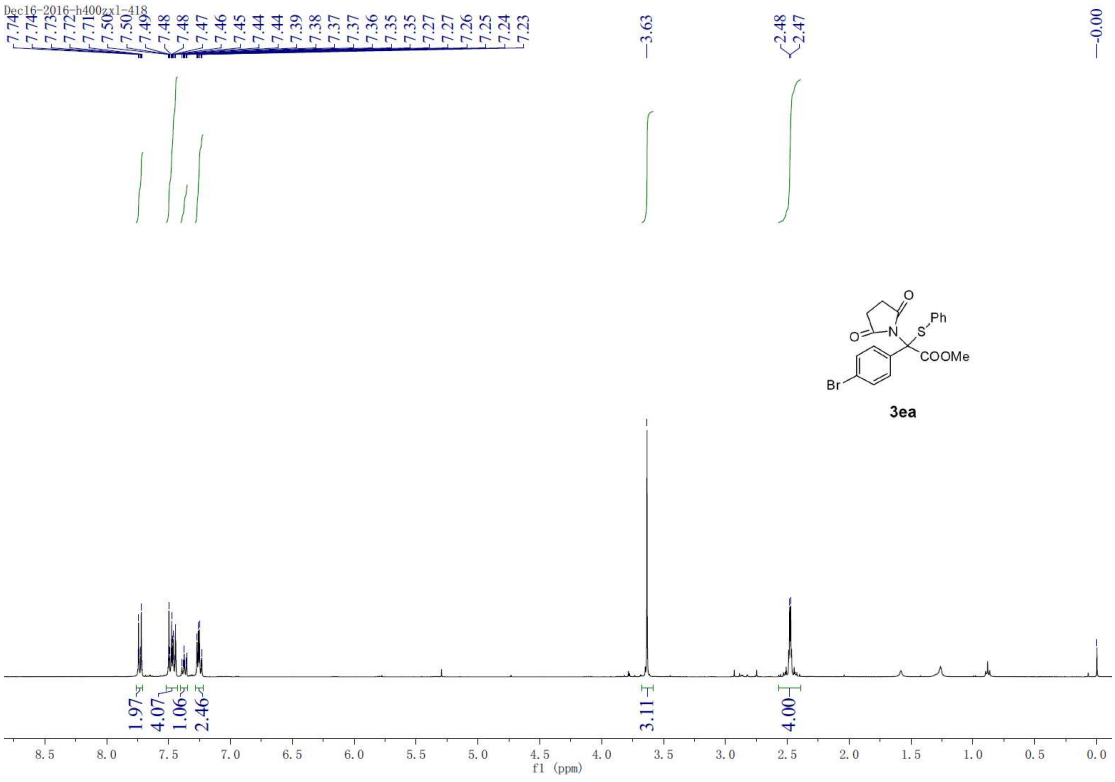
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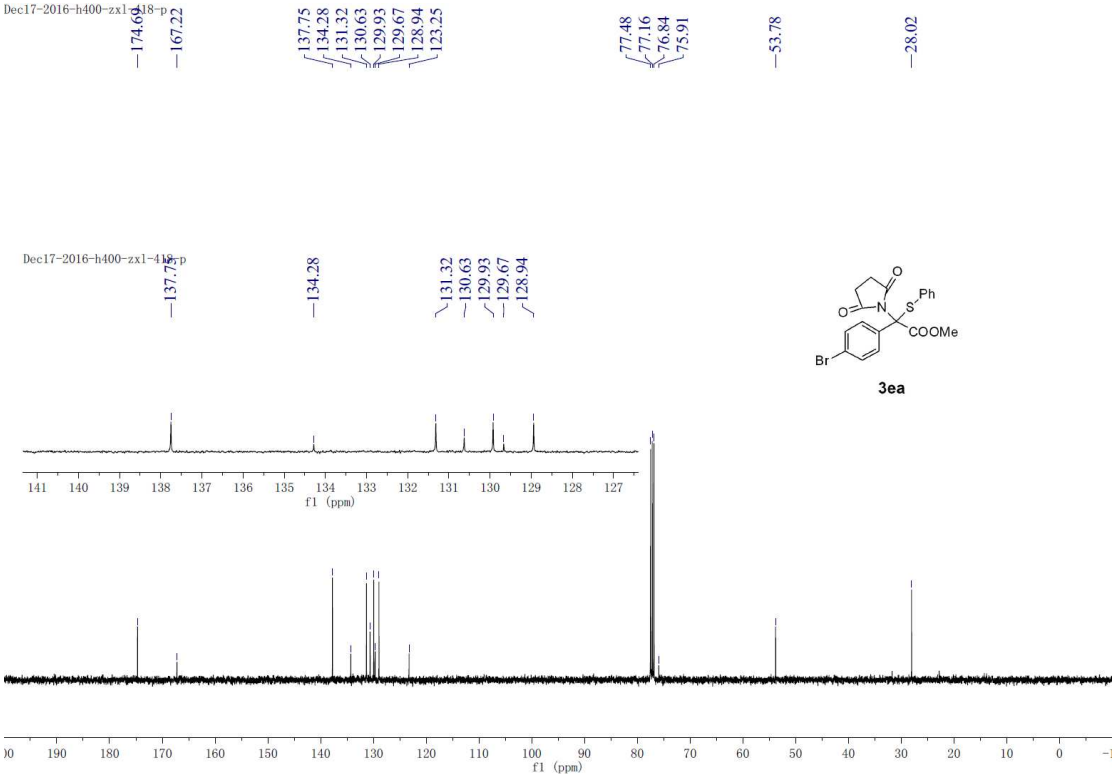
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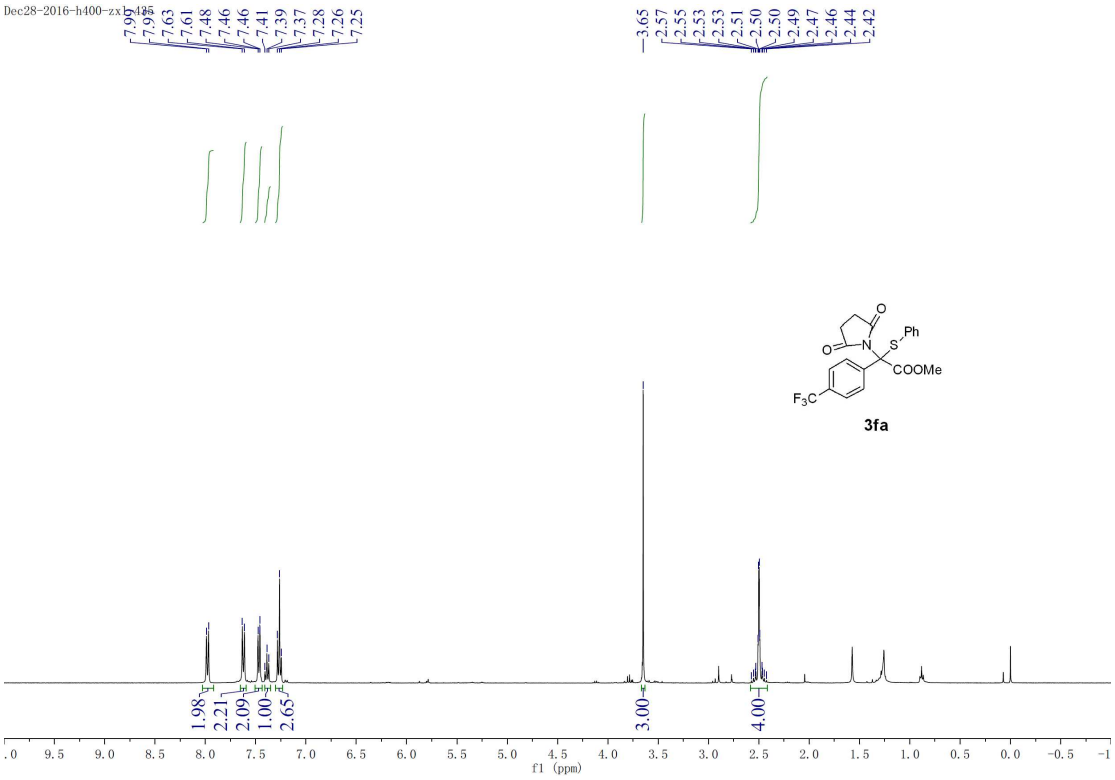
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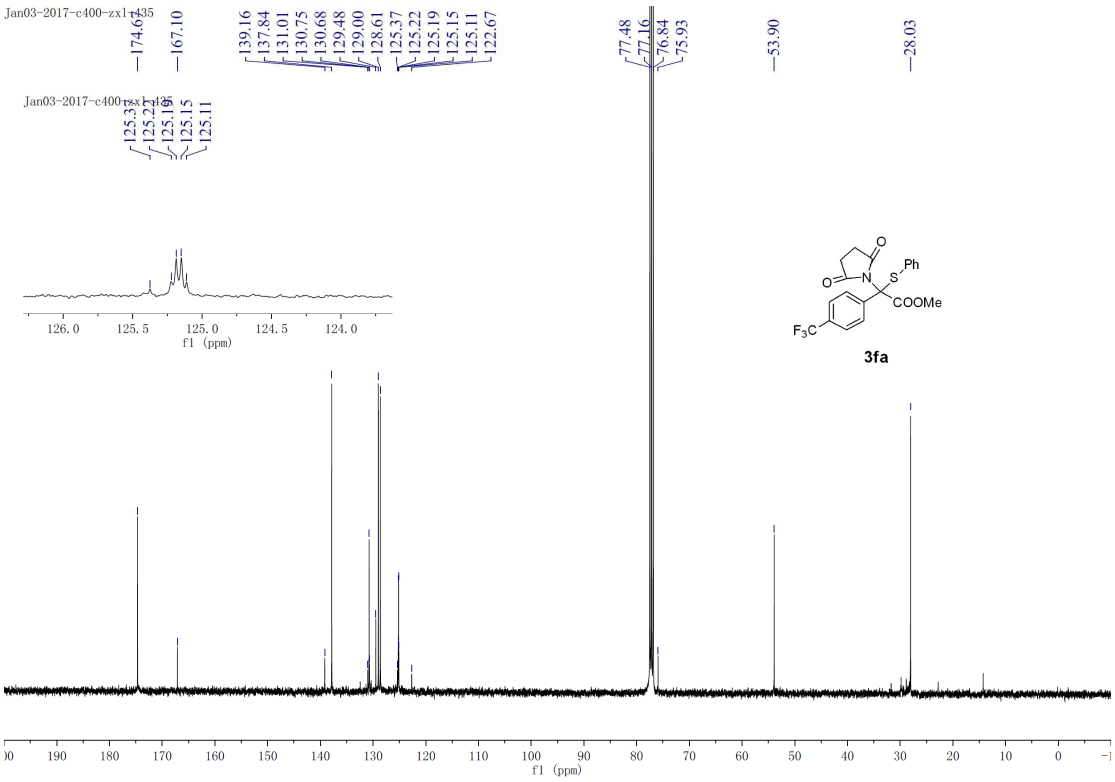
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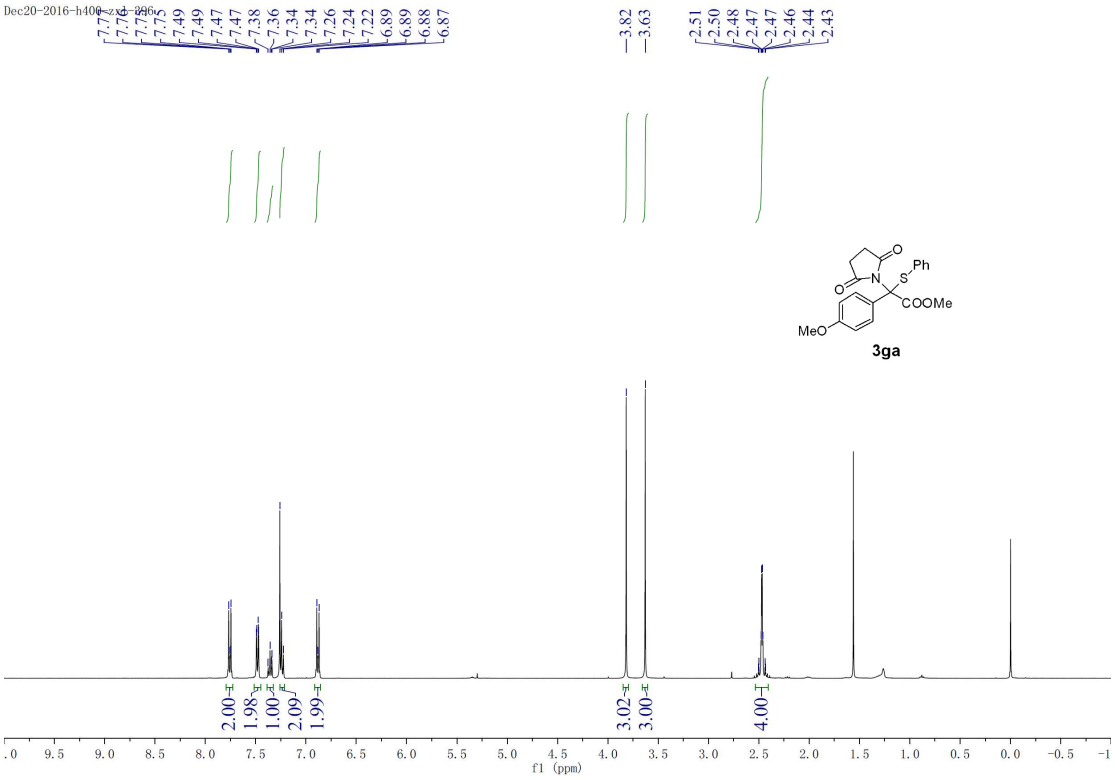
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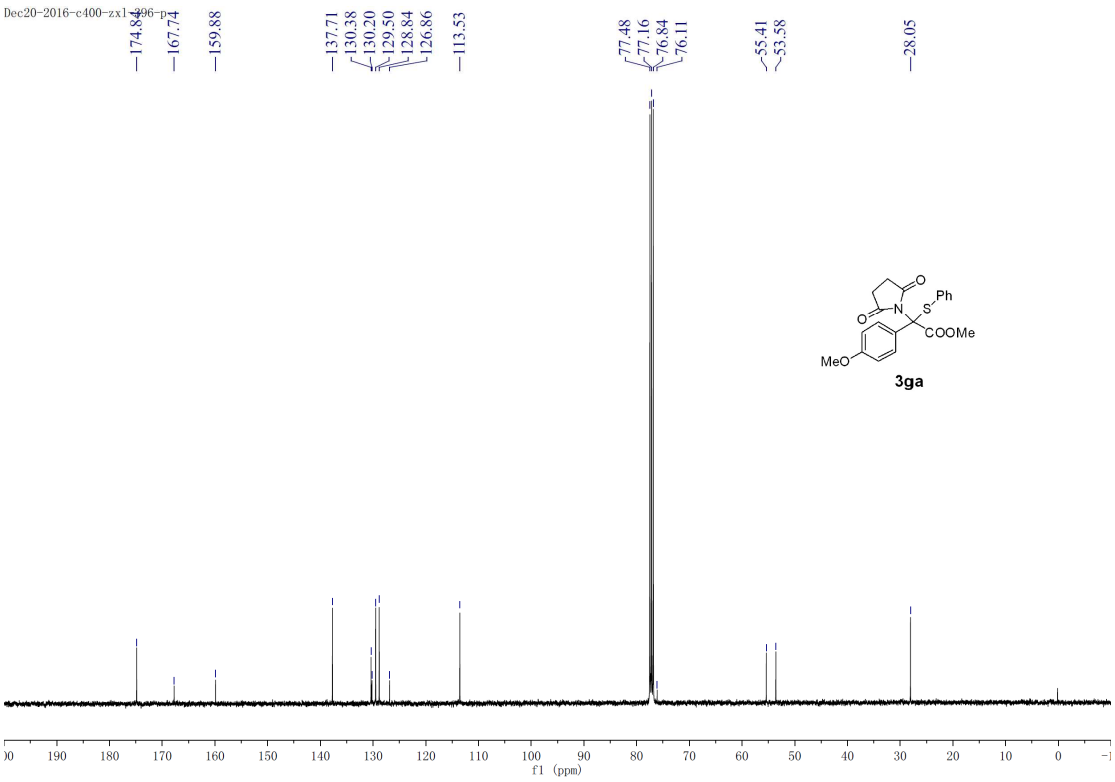
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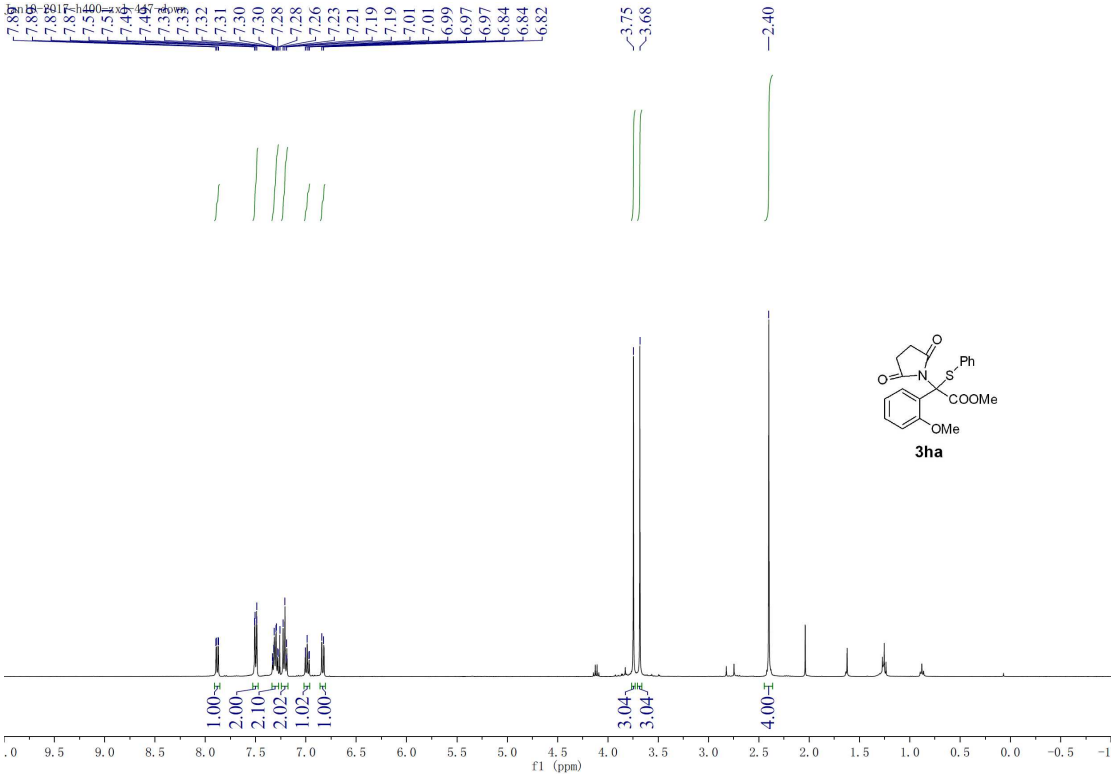
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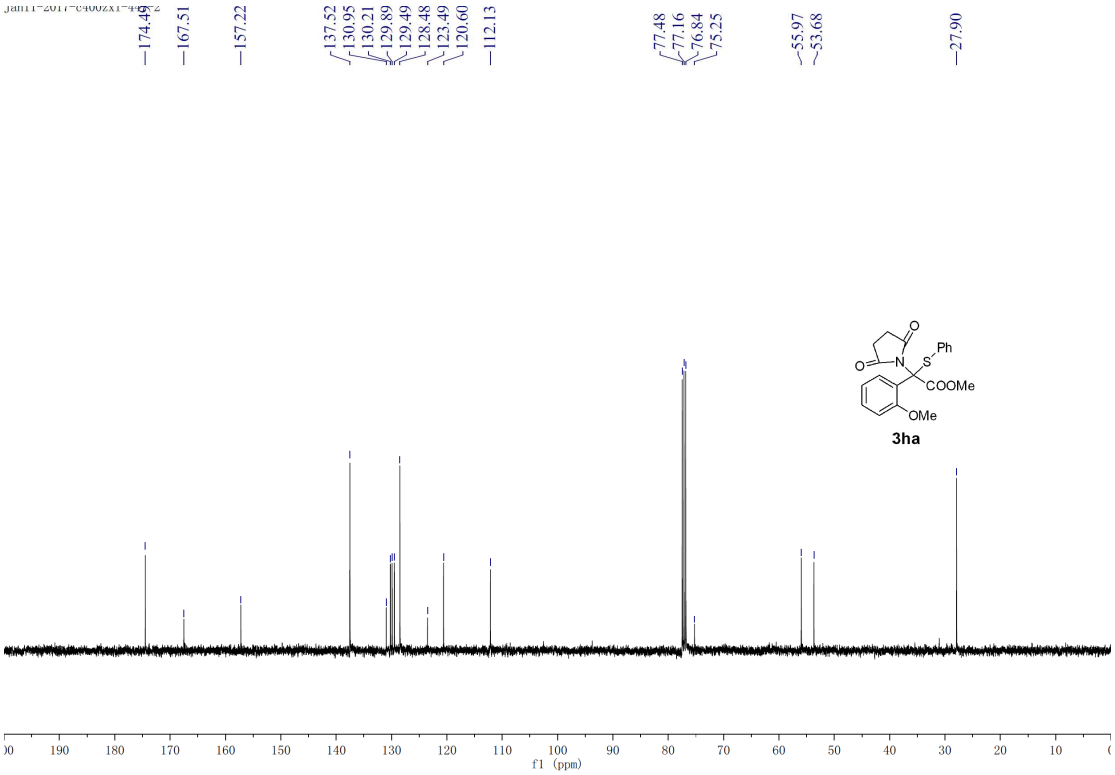
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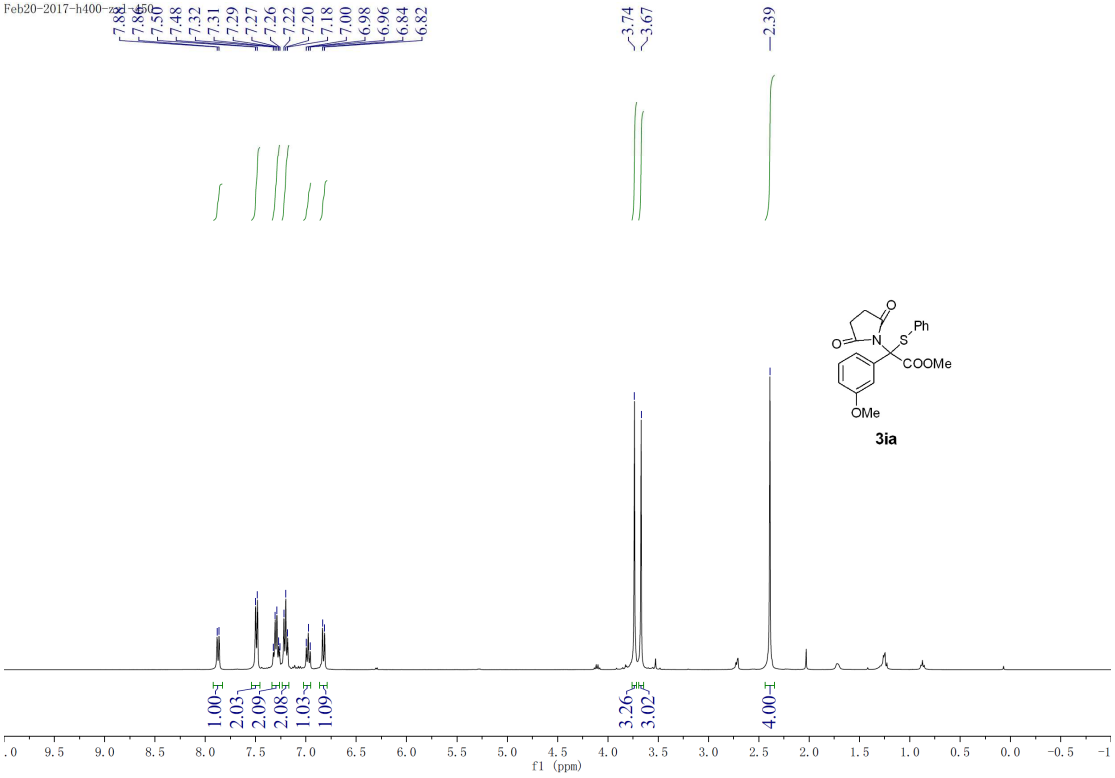
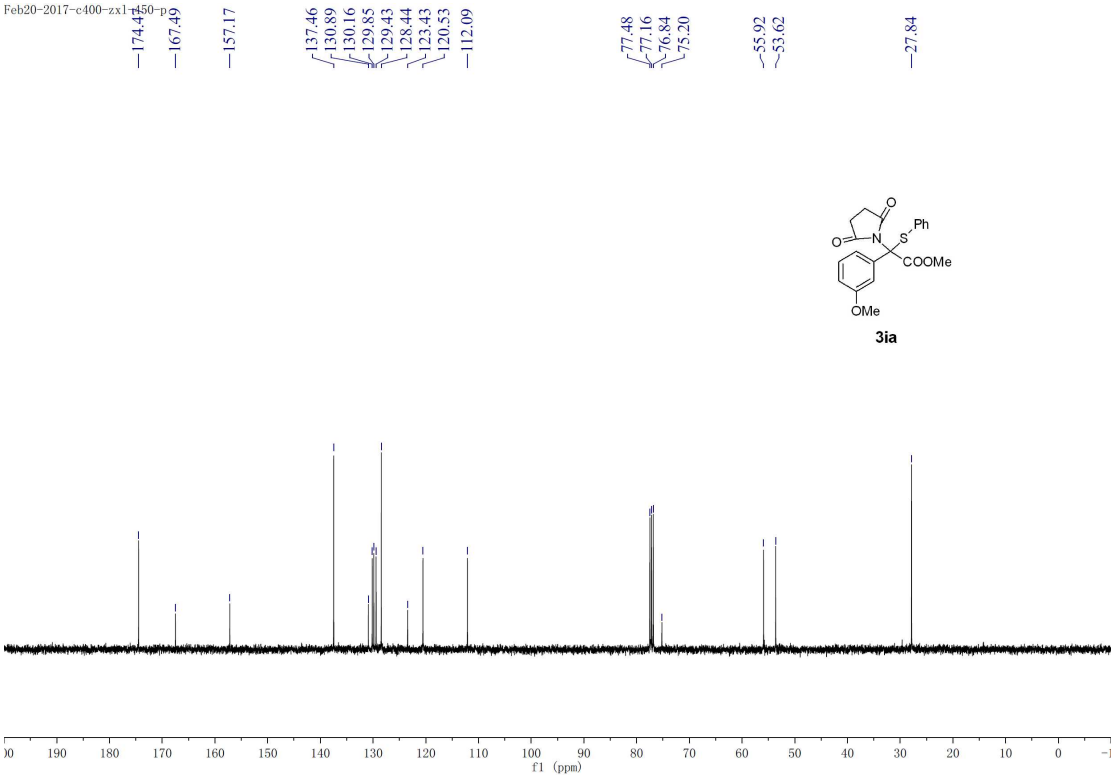
77.48
77.16
76.84
75.25
55.97
53.68
27.90
f1 (ppm)
Ph
S
N
O
O
COOMe
OMe
3ha


7.88
7.86
7.50
7.48
7.32
7.31
7.29
7.27
7.26
7.22
7.20
7.18
7.00
6.98
6.96
6.84
6.82
3.74
3.67
2.39
1.00
2.03
2.09
2.08
1.03
1.09
3.26
3.02
4.00
f1 (ppm)

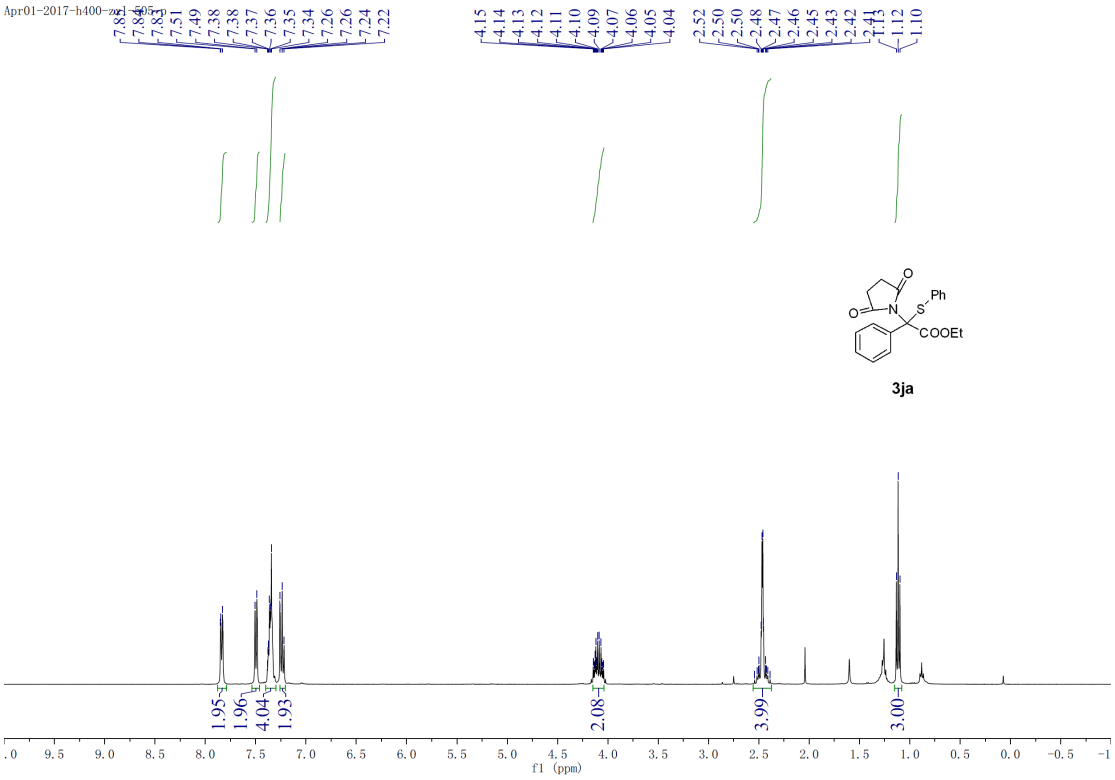
O
O
N
S
Ph
COOMe
OMe

3ia

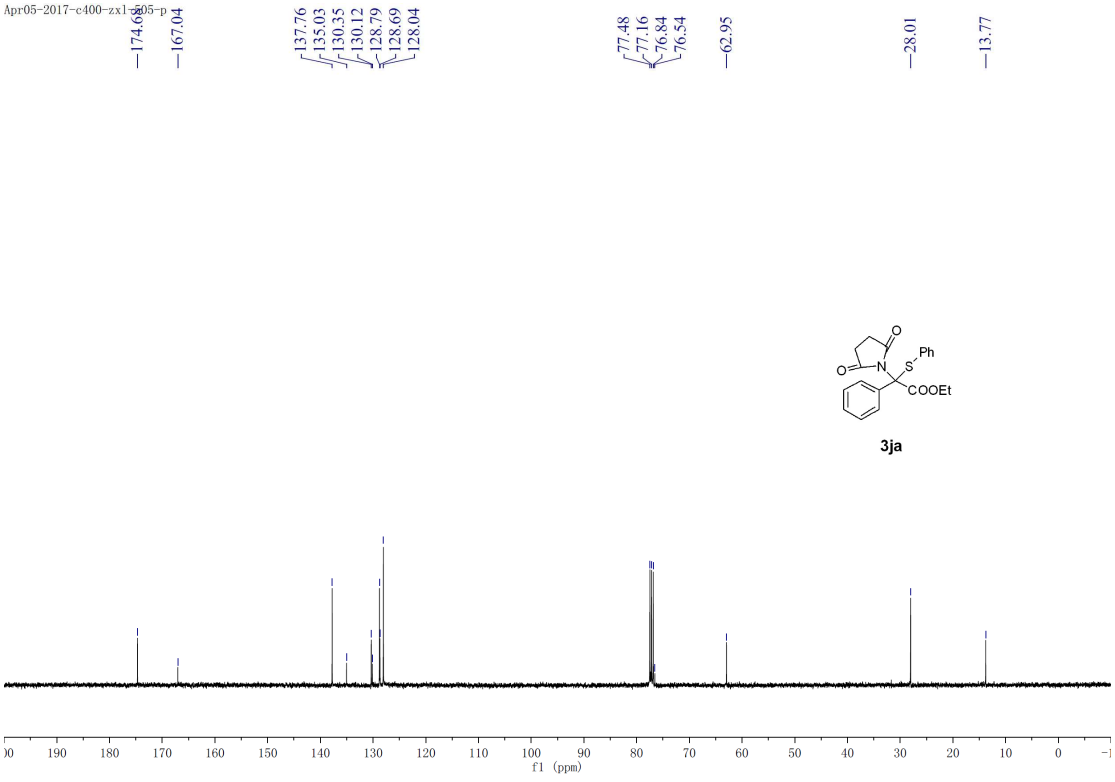

174.47
167.49
157.17
137.46
130.89
130.16
129.85
129.43
128.44
123.43
120.53
112.09
77.48
77.16
76.84
75.20
55.92
53.62
27.84
f1 (ppm)

O
O
N
S
Ph
COOMe
OMe

3ia


Apr01-2017-h400-zxl-505-p
7.88
7.84
7.83
7.51
7.49
7.38
7.38
7.37
7.36
7.35
7.34
7.26
7.26
7.24
7.22
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.07
4.06
4.05
4.04
2.52
2.50
2.50
2.48
2.47
2.46
2.45
2.43
2.42
2.41
1.13
1.12
1.10
Ph
S
N
O
O
COOEt
1.95
1.96
4.04
1.93
2.08
3.99
3.00
f1 (ppm)

3ja


Apr05-2017-c400-zxl-505-p
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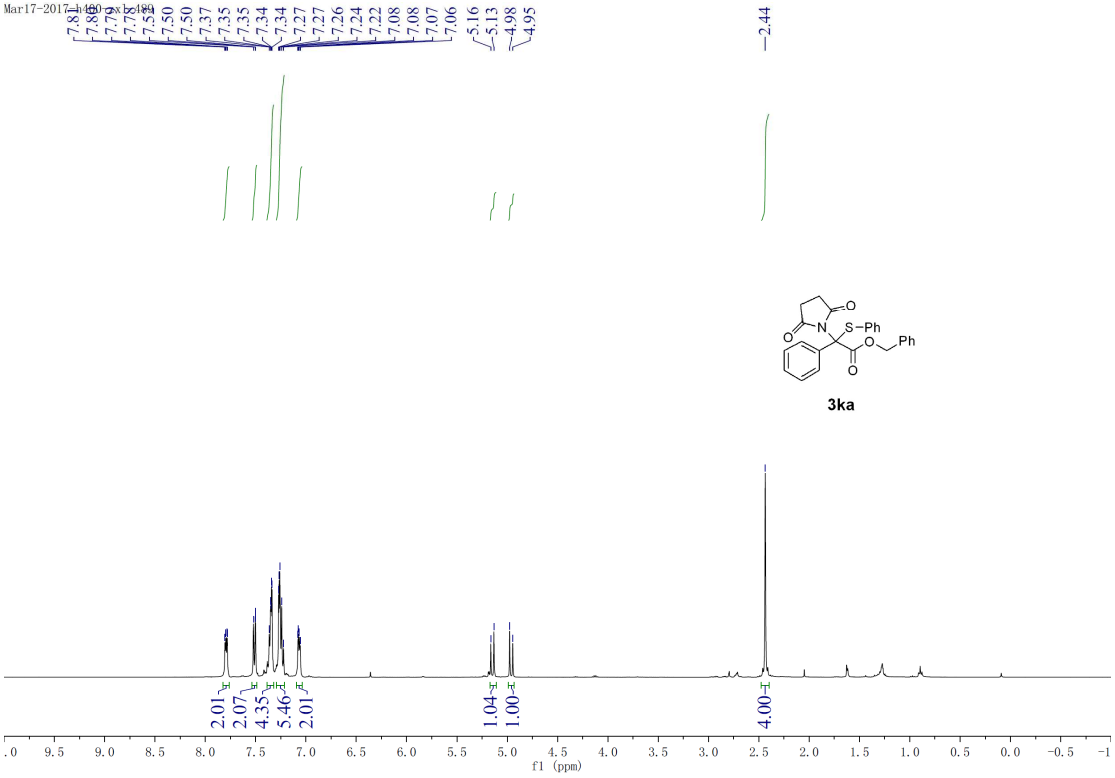
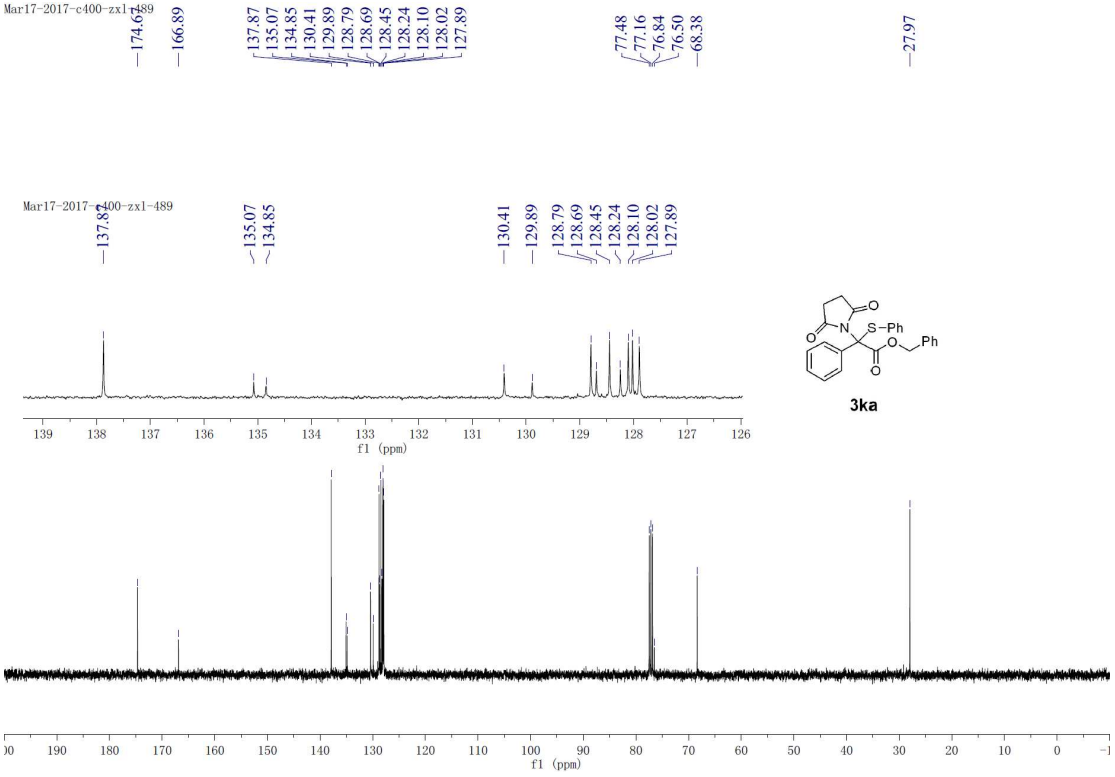
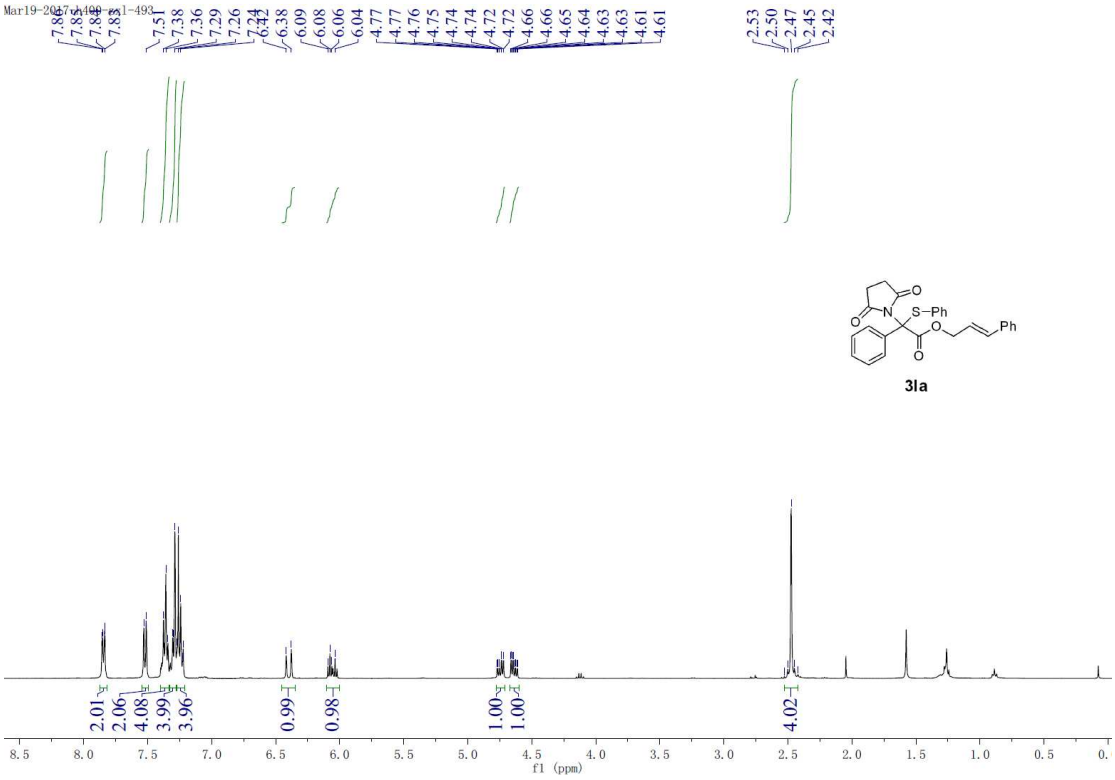
167.04
137.76
135.03
130.35
130.12
128.79
128.69
128.04
77.48
77.16
76.84
76.54
62.95
28.01
13.77
Ph
S
N
O
O
COOEt
f1 (ppm)

3ja


Mar17-2017-c400-zx1-489
7.85
7.86
7.79
7.78
7.53
7.50
7.50
7.37
7.35
7.35
7.34
7.34
7.27
7.27
7.26
7.24
7.22
7.08
7.08
7.07
7.06
5.16
5.13
4.98
4.95
2.44
S–Ph
O–Ph
3ka
2.01
2.07
4.35
5.46
2.01
1.04
1.00
4.00
f1 (ppm)


Mar17-2017-c400-zx1-489
174.67
166.89
137.87
135.07
134.85
130.41
129.89
128.79
128.69
128.45
128.24
128.10
128.02
127.89
77.48
77.16
76.84
76.50
68.38
27.97
Mar17-2017-c400-zx1-489
137.87
135.07
134.85
130.41
129.89
128.79
128.69
128.45
128.24
128.10
128.02
127.89
S–Ph
O–Ph
3ka
f1 (ppm)
f1 (ppm)


Mar19-2017-c400-zxl-493
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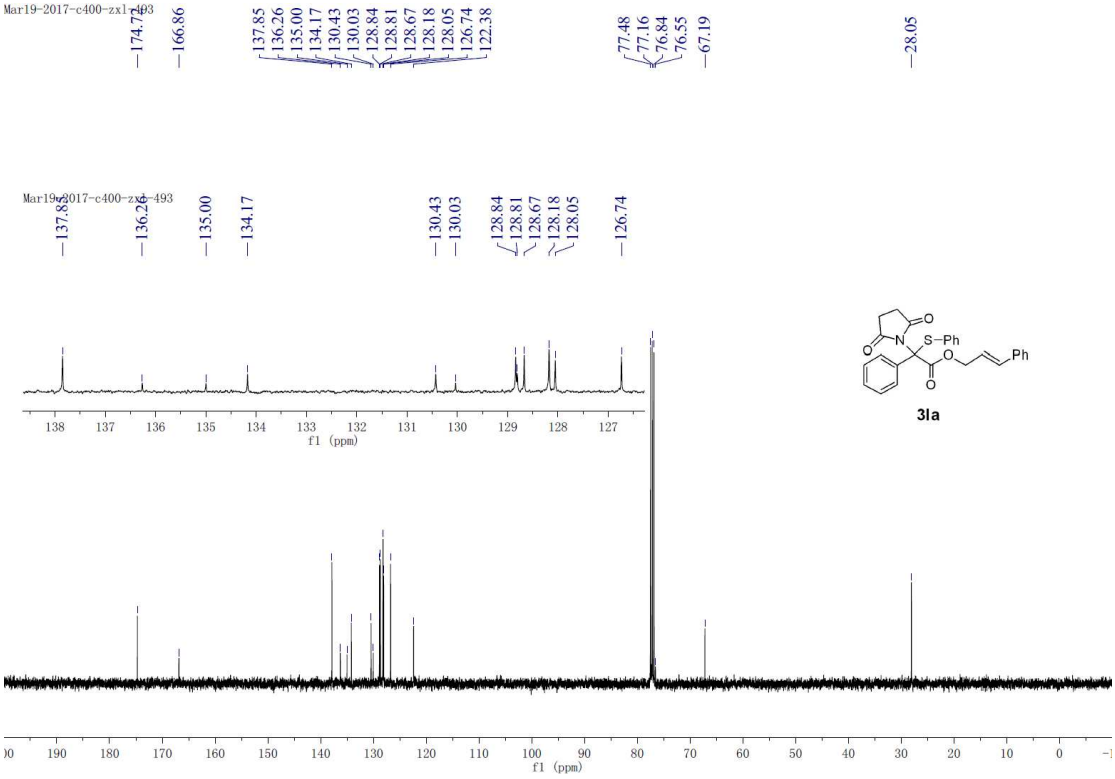
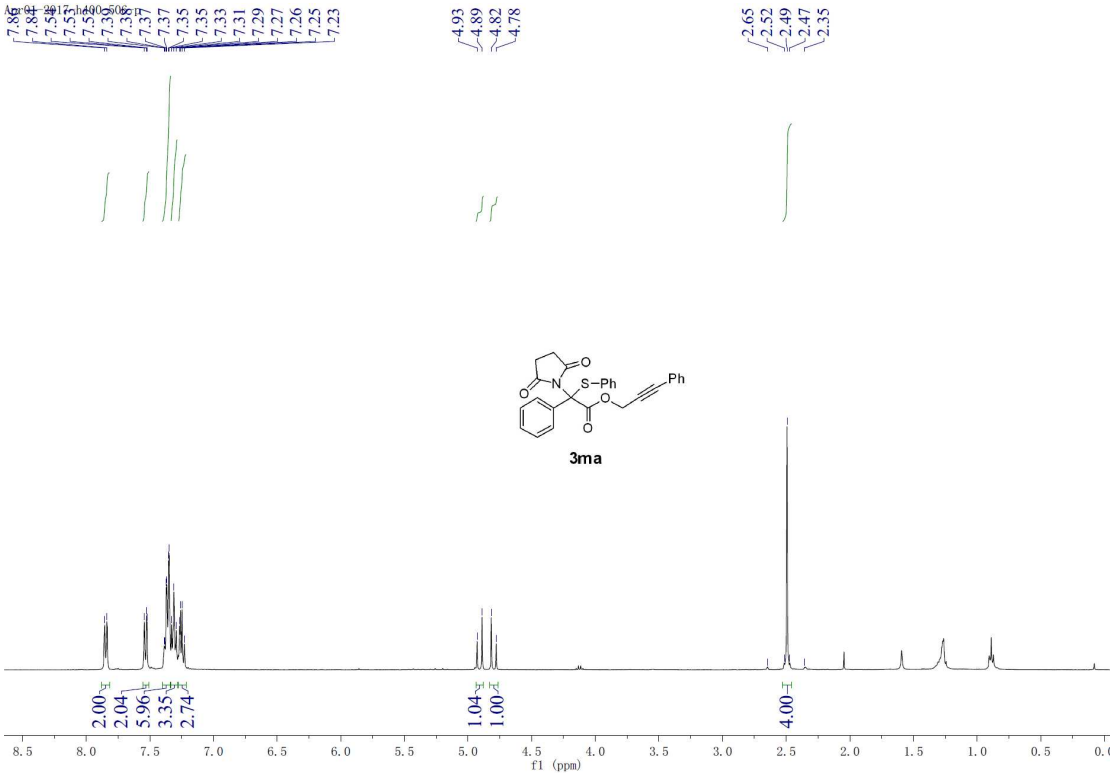
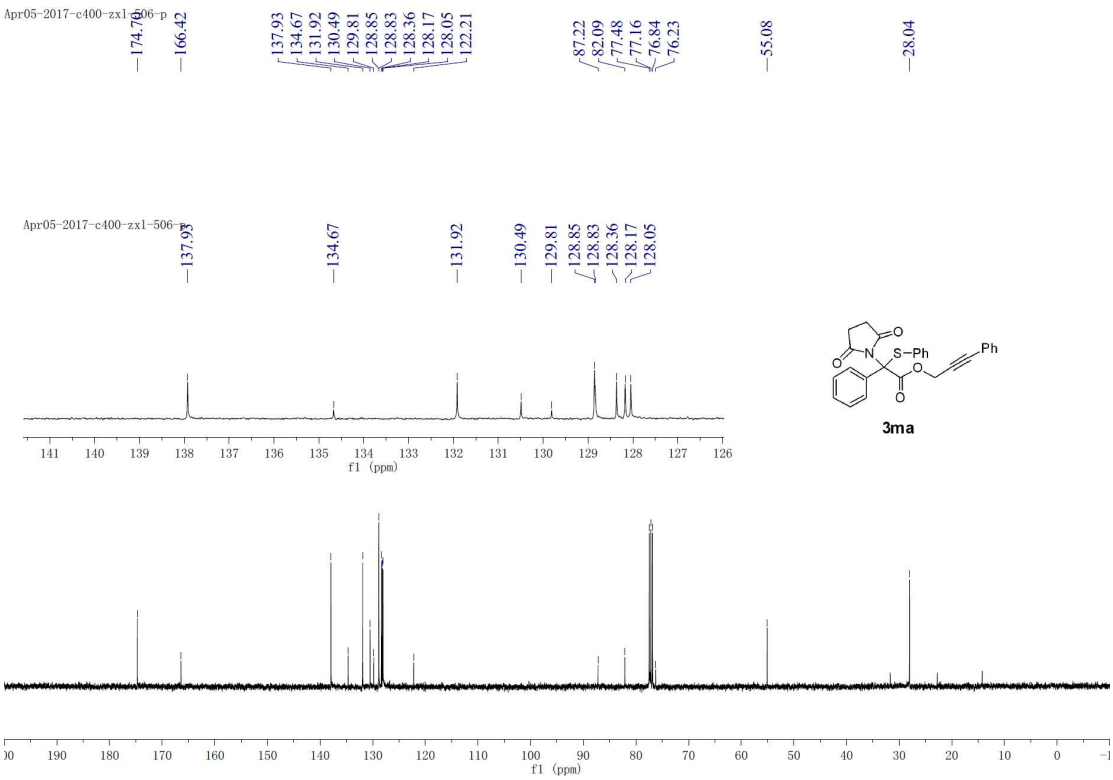
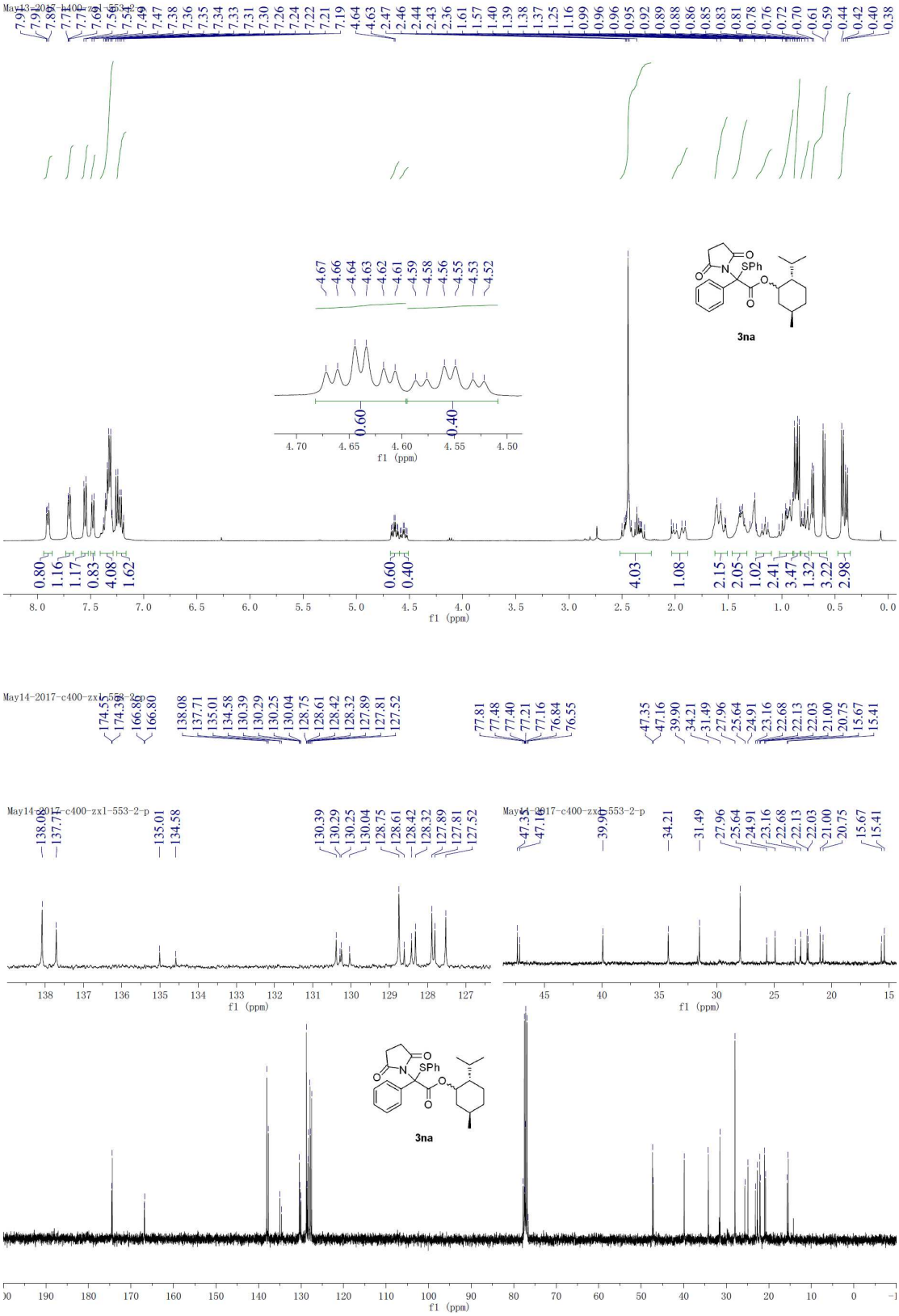
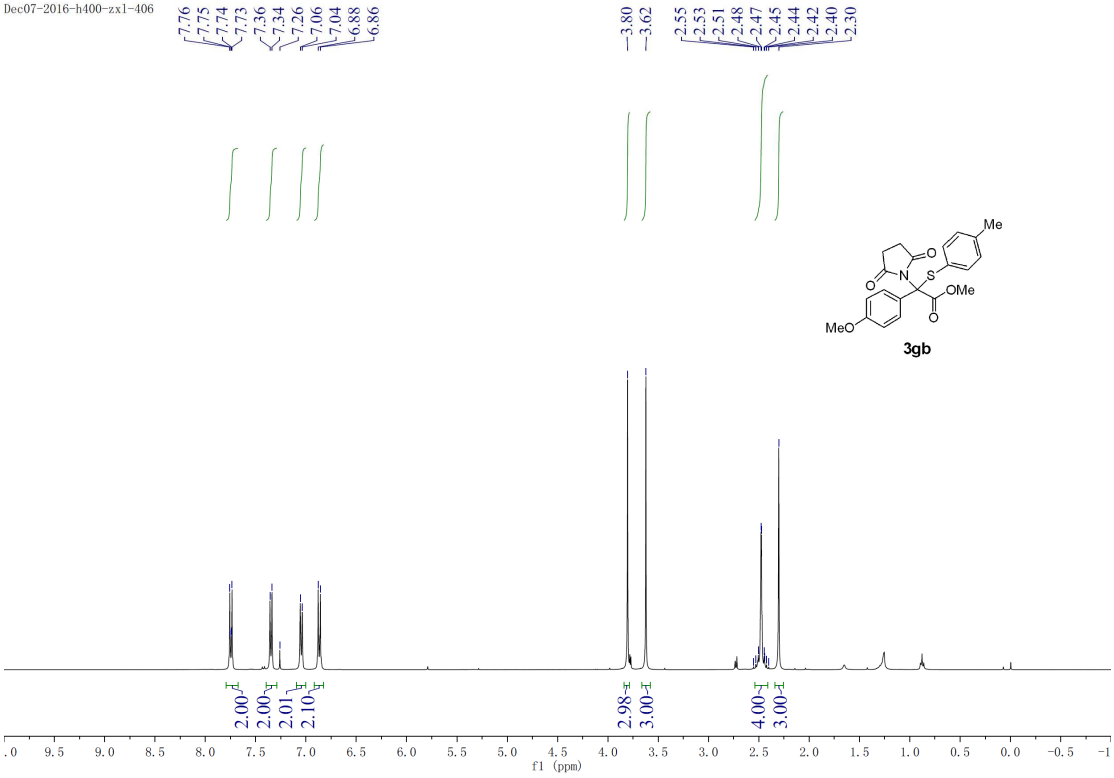
7.84
7.83
7.51
7.38
7.36
7.29
7.26
6.38
6.09
6.08
6.06
6.04
4.77
4.76
4.75
4.74
4.72
4.66
4.65
4.64
4.63
4.61
2.53
2.50
2.47
2.45
2.42
S—Ph
Ph
3la
2.01
2.06
4.08
3.99
3.96
0.99
0.98
1.00
1.00
4.02
f1 (ppm)

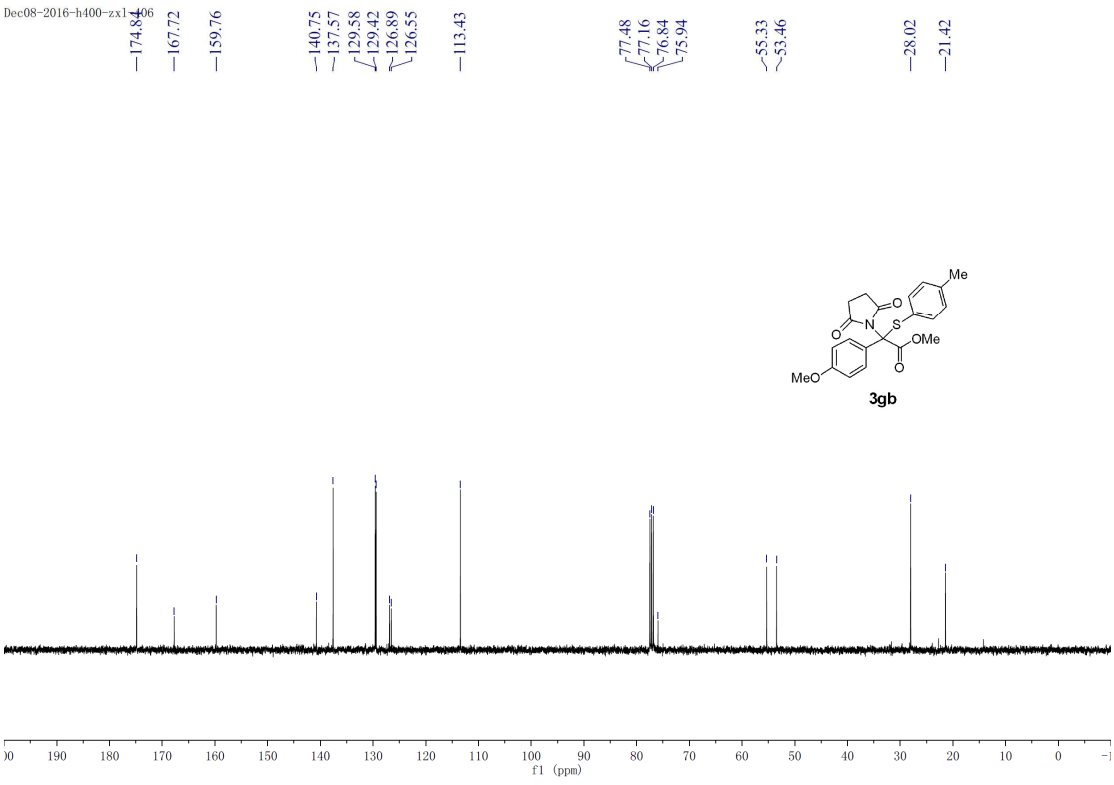

Mar19-2017-c400-zxl-493
174.72
166.86
137.85
136.26
135.00
134.17
130.43
130.03
128.84
128.81
128.67
128.18
128.05
126.74
122.38
77.48
77.16
76.84
76.55
67.19
28.05
S—Ph
Ph
3la
f1 (ppm)

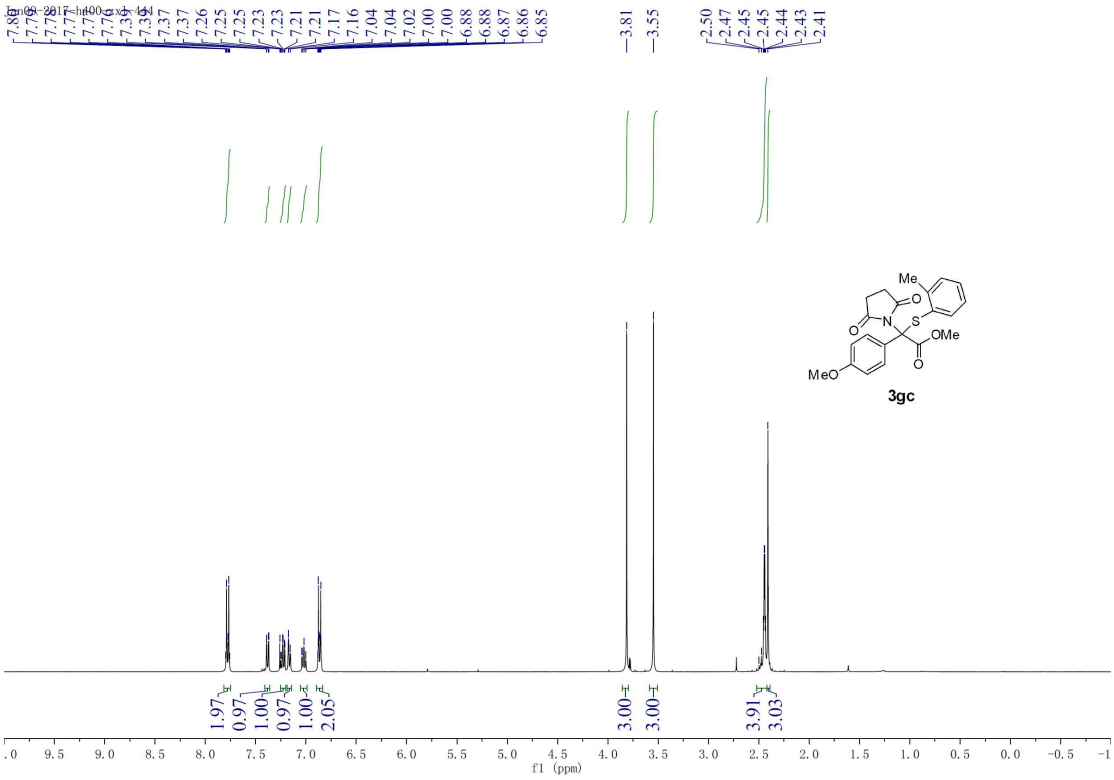

7.86
7.84
7.54
7.53
7.52
7.51
7.38
7.37
7.37
7.35
7.35
7.33
7.31
7.29
7.27
7.26
7.25
7.23
4.93
4.89
4.82
4.78
2.65
2.52
2.49
2.47
2.35
S–Ph
Ph
3ma
2.00
2.04
5.96
3.35
2.74
1.04
1.00
4.00
f1 (ppm)

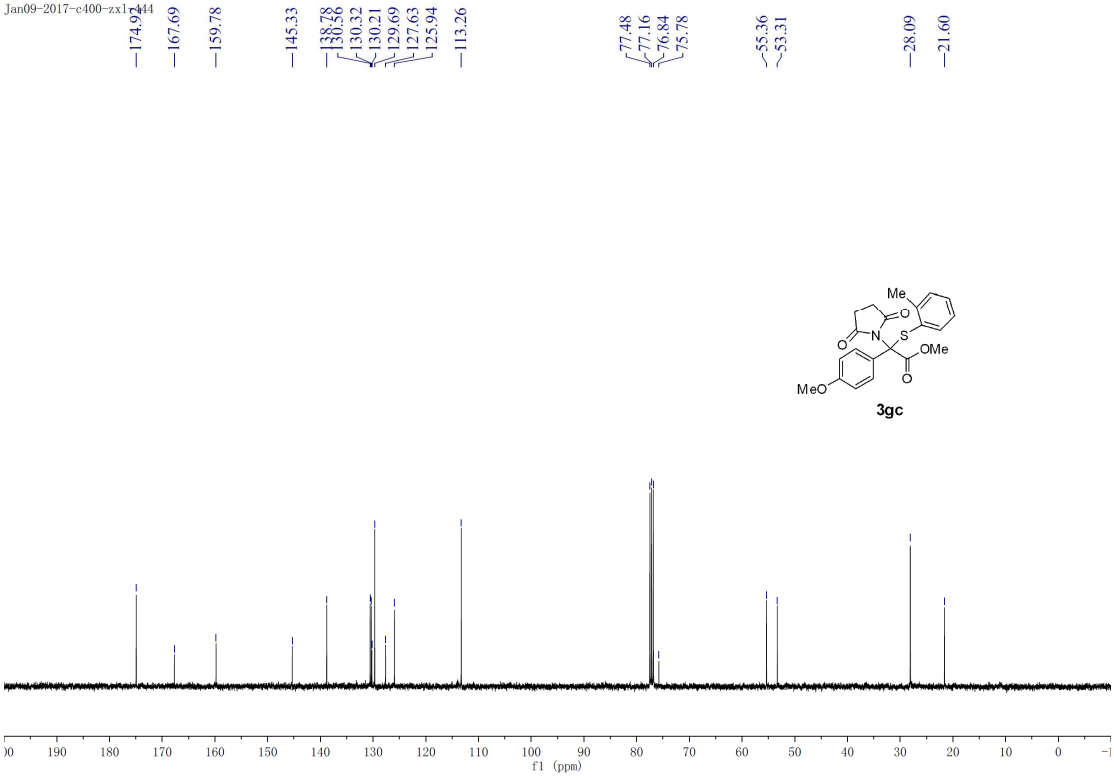

Apr05-2017-c400-zx1-506-p
174.70
166.42
137.93
134.67
131.92
130.49
129.81
128.85
128.83
128.36
128.17
128.05
122.21
87.22
82.09
77.48
77.16
76.84
76.23
55.08
28.04
S–Ph
Ph
3ma
f1 (ppm)

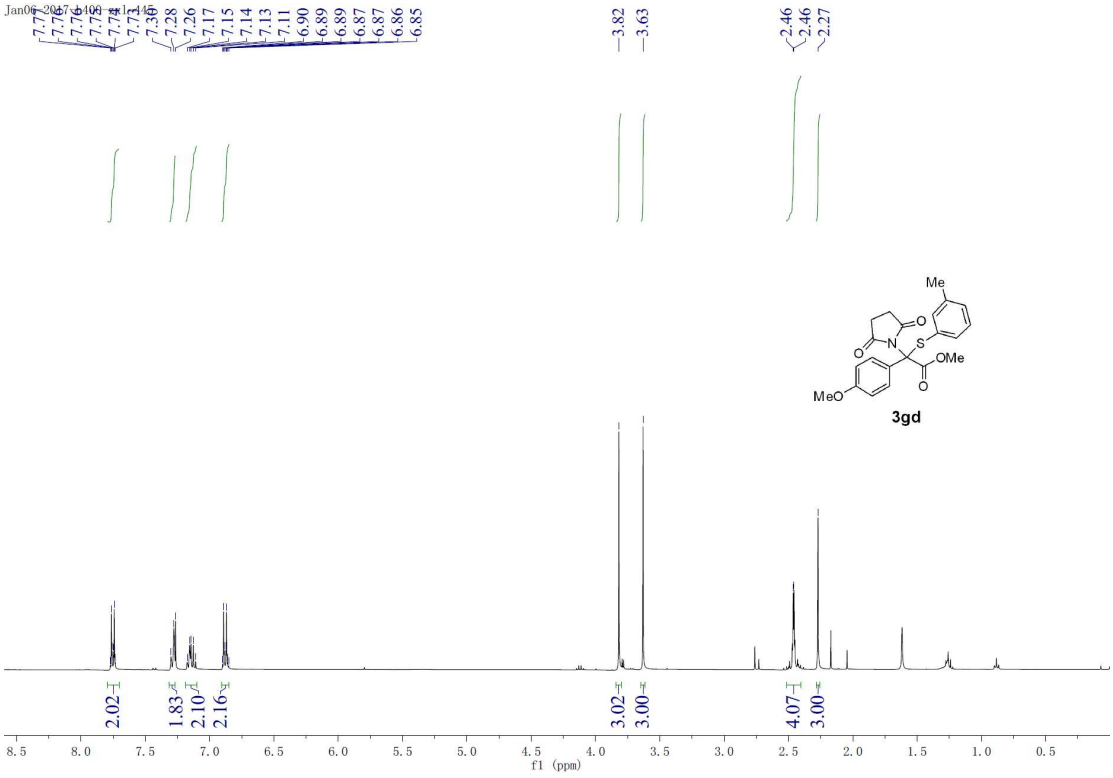

3na
f1 (ppm)

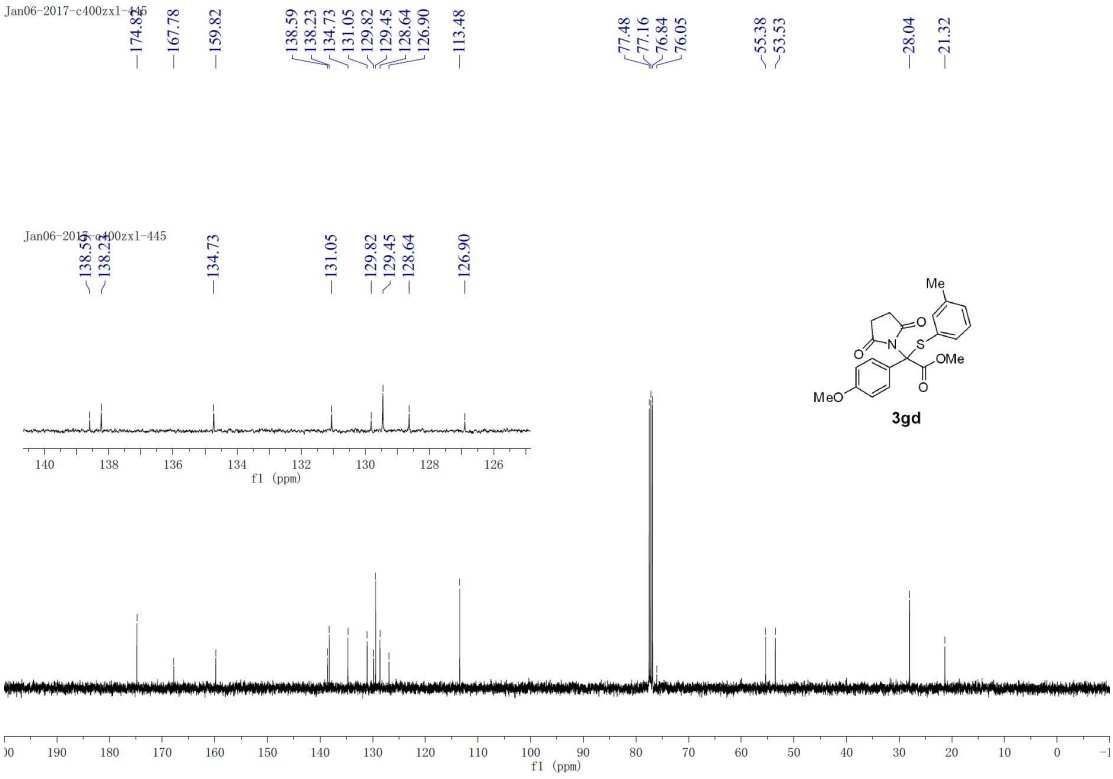

Dec07-2016-h400-zx1-406
7.76
7.75
7.74
7.73
7.36
7.34
7.26
7.06
7.04
6.88
6.86
3.80
3.62
2.55
2.53
2.51
2.48
2.47
2.45
2.44
2.42
2.40
2.30
Me
O
N
S
O
OMe
O
MeO
3gb
2.00
2.00
2.01
2.10
2.98
3.00
4.00
3.00
f1 (ppm)


Dec08-2016-h400-zx1-406
174.84
167.72
159.76
140.75
137.57
129.58
129.42
126.89
126.55
113.43
77.48
77.16
76.84
75.94
55.33
53.46
28.02
21.42
Me
O
N
S
O
OMe
O
MeO
3gb
f1 (ppm)


7.86
7.78
7.78
7.77
7.77
7.76
7.76
7.35
7.34
7.37
7.37
7.26
7.25
7.25
7.23
7.23
7.21
7.21
7.17
7.16
7.04
7.04
7.02
7.00
7.00
6.88
6.88
6.87
6.86
6.85
3.81
3.55
2.50
2.47
2.45
2.45
2.44
2.43
2.41
Me
O
O
N
S
OMe
O
MeO
3gc
1.97
0.97
1.00
0.97
1.00
2.05
3.00
3.00
3.91
3.03
f1 (ppm)


Jan09-2017-c400-zx1-c44
174.92
167.69
159.78
145.33
138.78
138.36
130.32
130.21
129.69
127.63
125.94
113.26
77.48
77.16
76.84
75.78
55.36
53.31
28.09
21.60
Me
O
O
N
S
OMe
O
MeO
3gc
f1 (ppm)


7.77
7.76
7.76
7.74
7.74
7.73
7.35
7.28
7.26
7.17
7.15
7.14
7.13
7.11
6.90
6.89
6.89
6.87
6.87
6.86
6.85
3.82
3.63
2.46
2.46
2.27
Me
O
N
S
OMe
O
O
MeO
3gd
2.02
1.83
2.10
2.16
3.02
3.00
4.07
3.00
f1 (ppm)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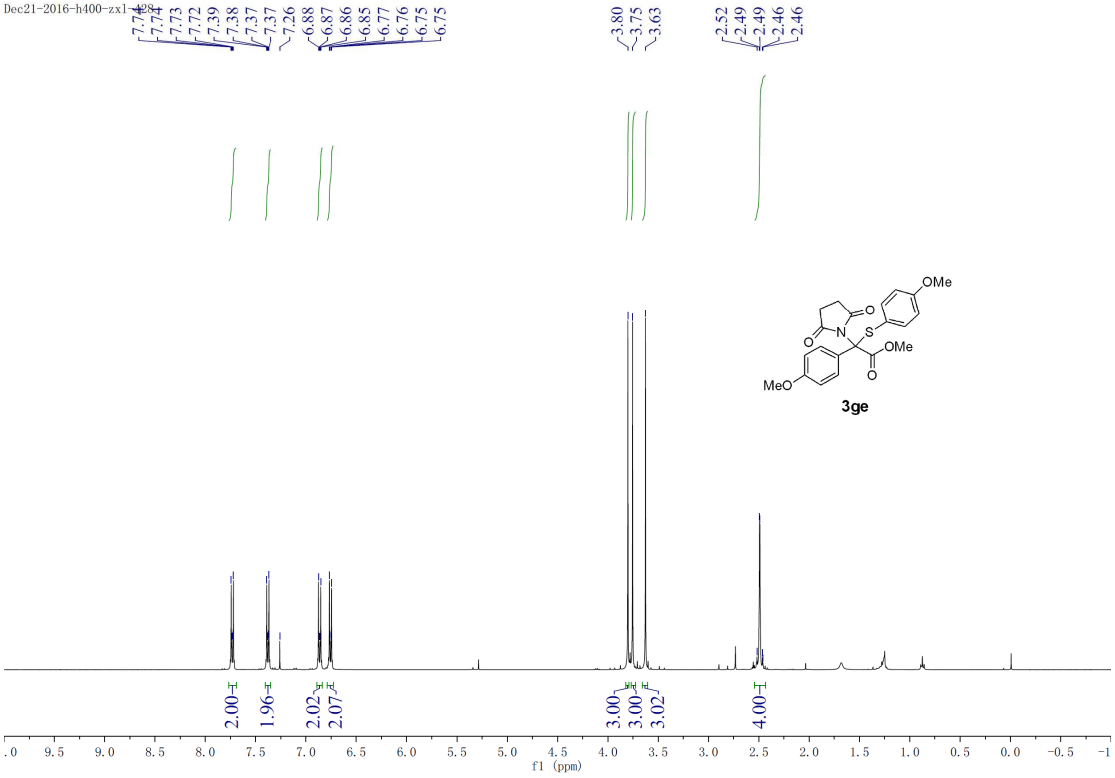
167.78
159.82
138.59
138.23
134.73
131.05
129.82
129.45
128.64
126.90
113.48
77.48
77.16
76.84
76.05
55.38
53.53
28.04
21.32
Me
O
N
S
OMe
O
O
MeO
3gd
f1 (ppm)


Dec21-2016-h400-zx1-428
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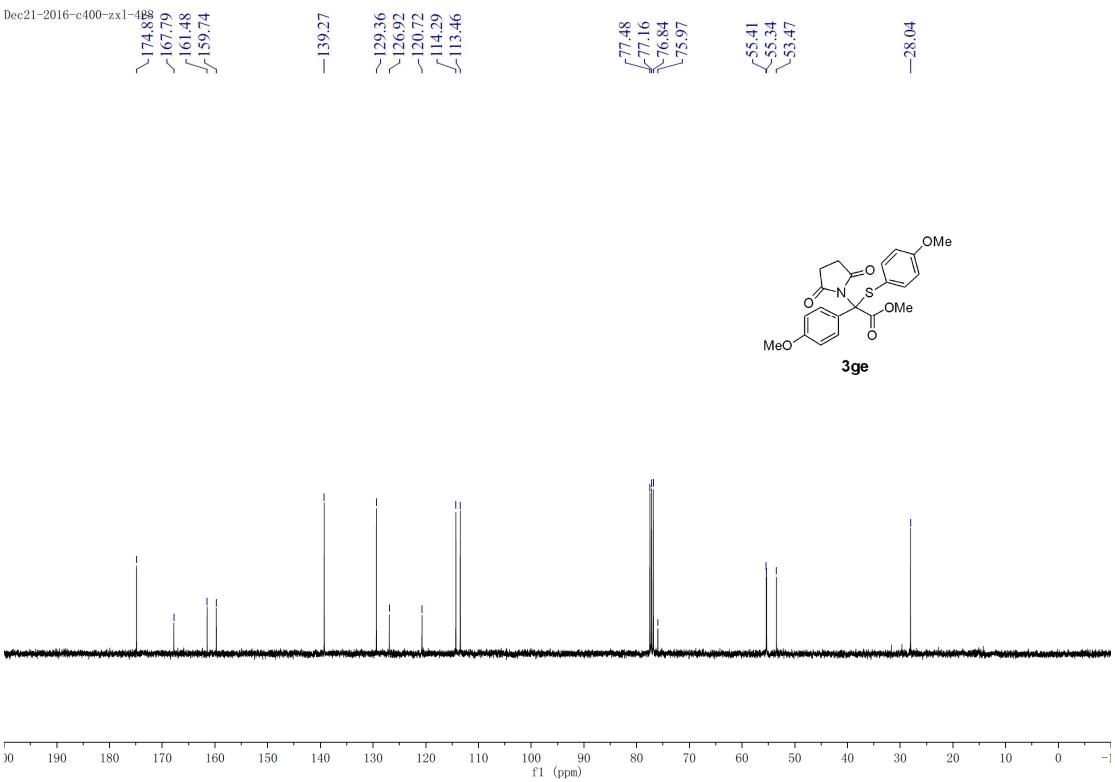
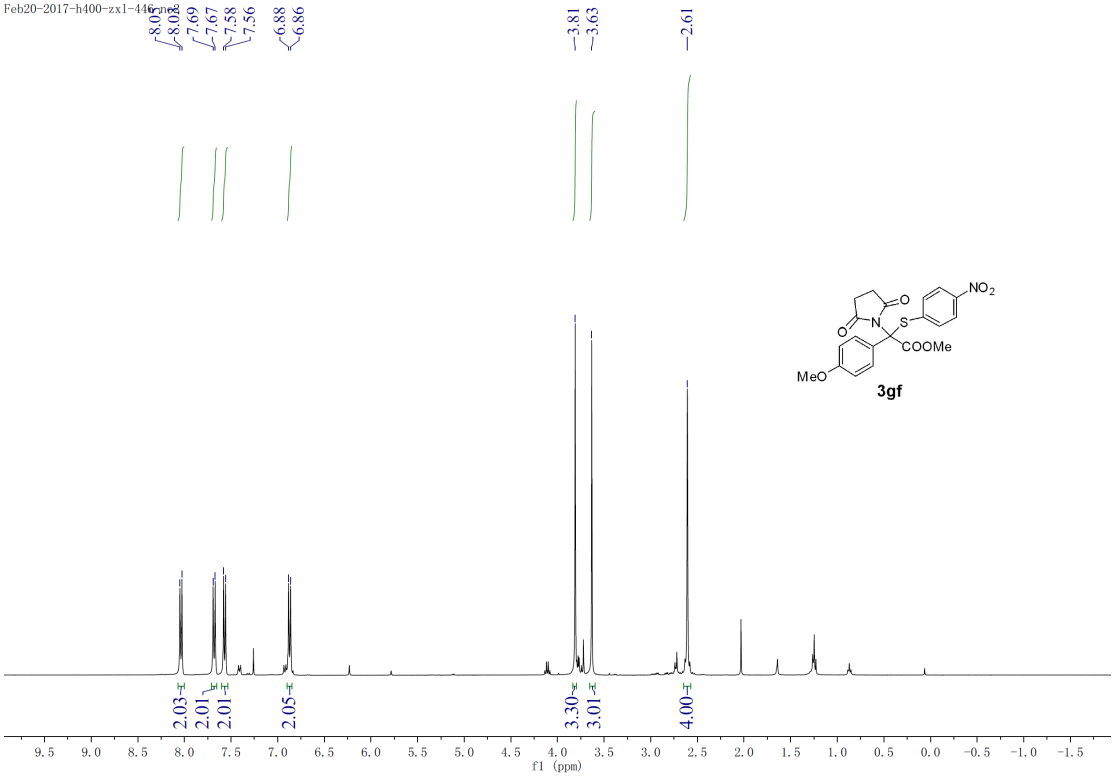
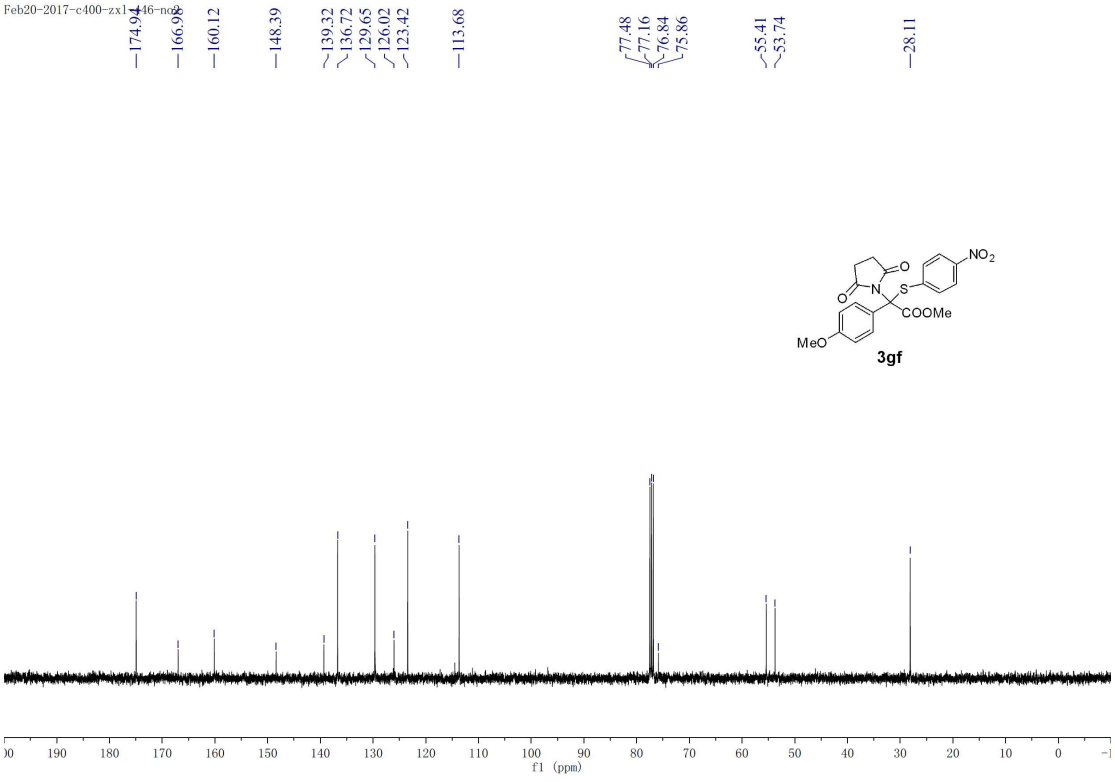
7.74
7.73
7.72
7.39
7.38
7.37
7.37
7.26
6.88
6.87
6.86
6.85
6.77
6.76
6.75
6.75
3.80
3.75
3.63
2.52
2.49
2.49
2.46
2.46
OMe
O
N
S
OMe
O
MeO
3ge
2.00
1.96
2.02
2.07
3.00
3.00
3.02
4.00
f1 (ppm)


Dec21-2016-c400-zx1-428
174.88
167.79
161.48
159.74
139.27
129.36
126.92
120.72
114.29
113.46
77.48
77.16
76.84
75.97
55.41
55.34
53.47
28.04
OMe
O
N
S
OMe
O
MeO
3ge
f1 (ppm)


Feb20-2017-h400-zx1-446-no2
8.05
8.03
7.69
7.67
7.58
7.56
6.88
6.86
3.81
3.63
2.61
2.03
2.01
2.01
2.05
3.30
3.01
4.00
f1 (ppm)

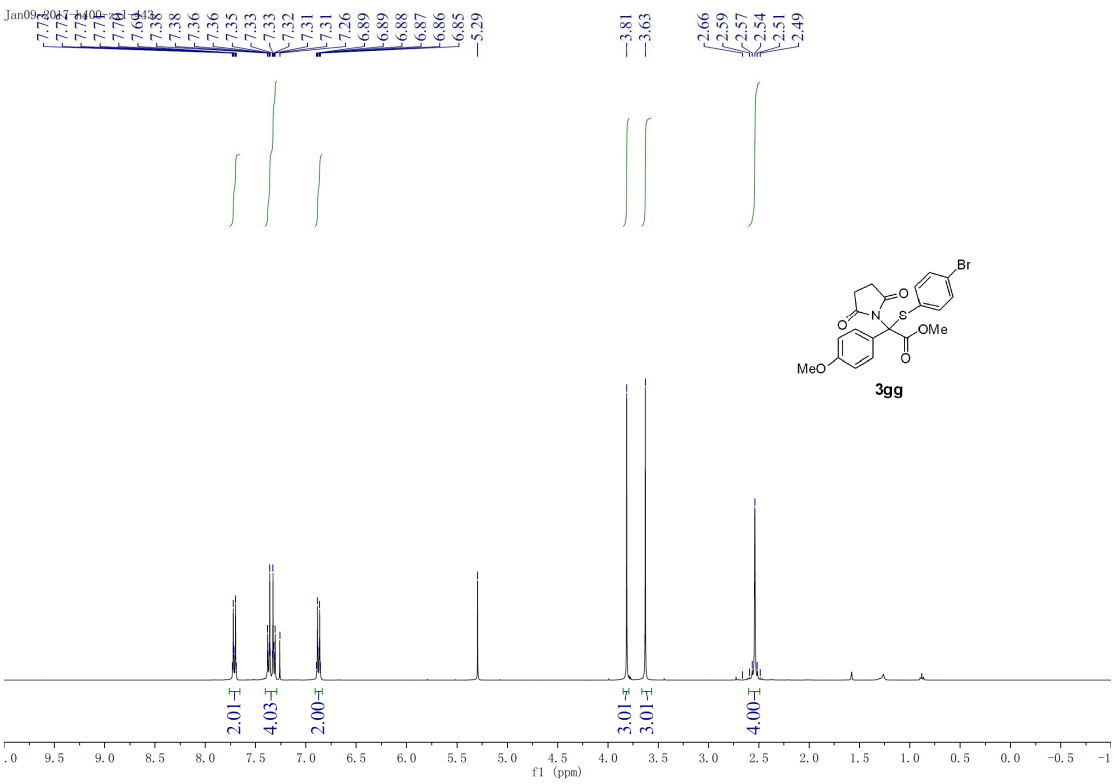
NO2
O
O
N
S
COOMe
MeO

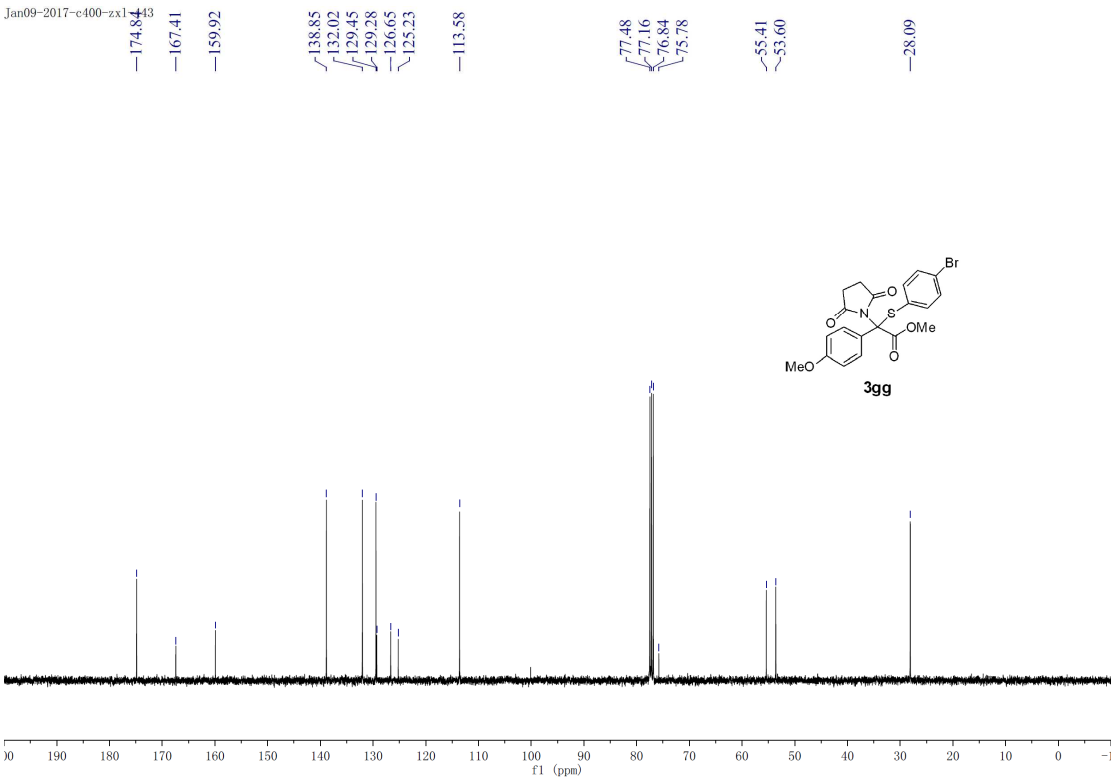
3gf

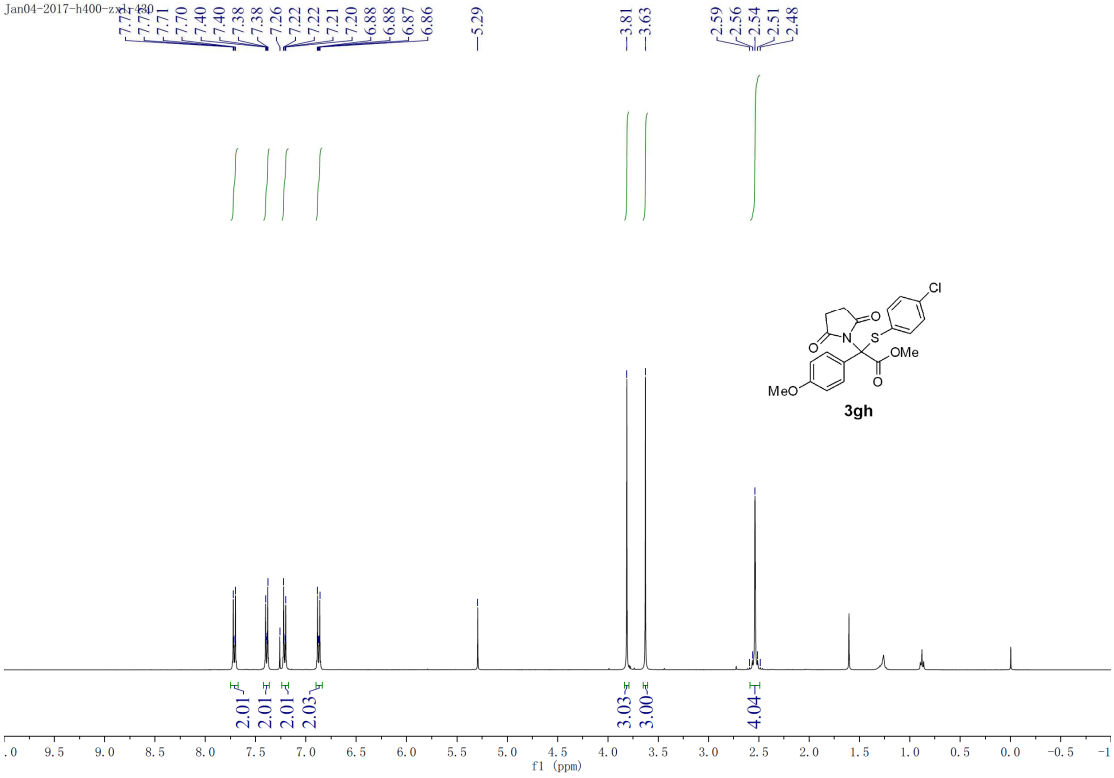

Feb20-2017-c400-zx1-446-no2
174.94
166.98
160.12
148.39
139.32
136.72
129.65
126.02
123.42
113.68
77.48
77.16
76.84
75.86
55.41
53.74
28.11
f1 (ppm)

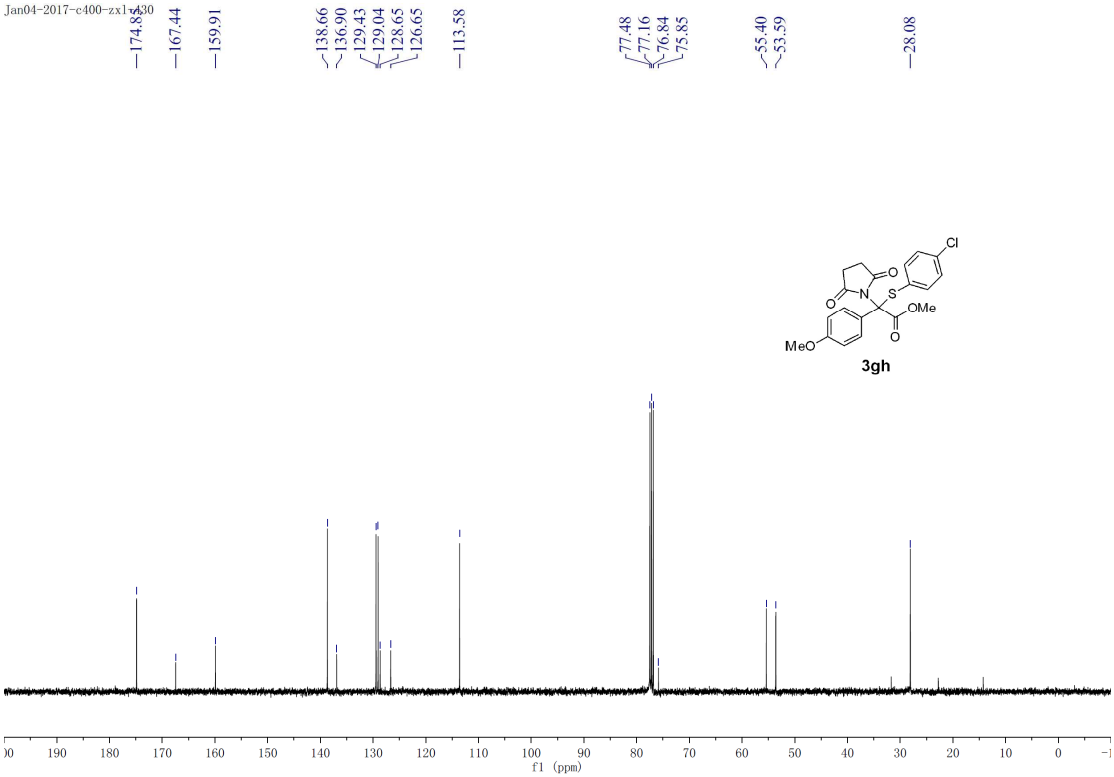
NO2
O
O
N
S
COOMe
MeO

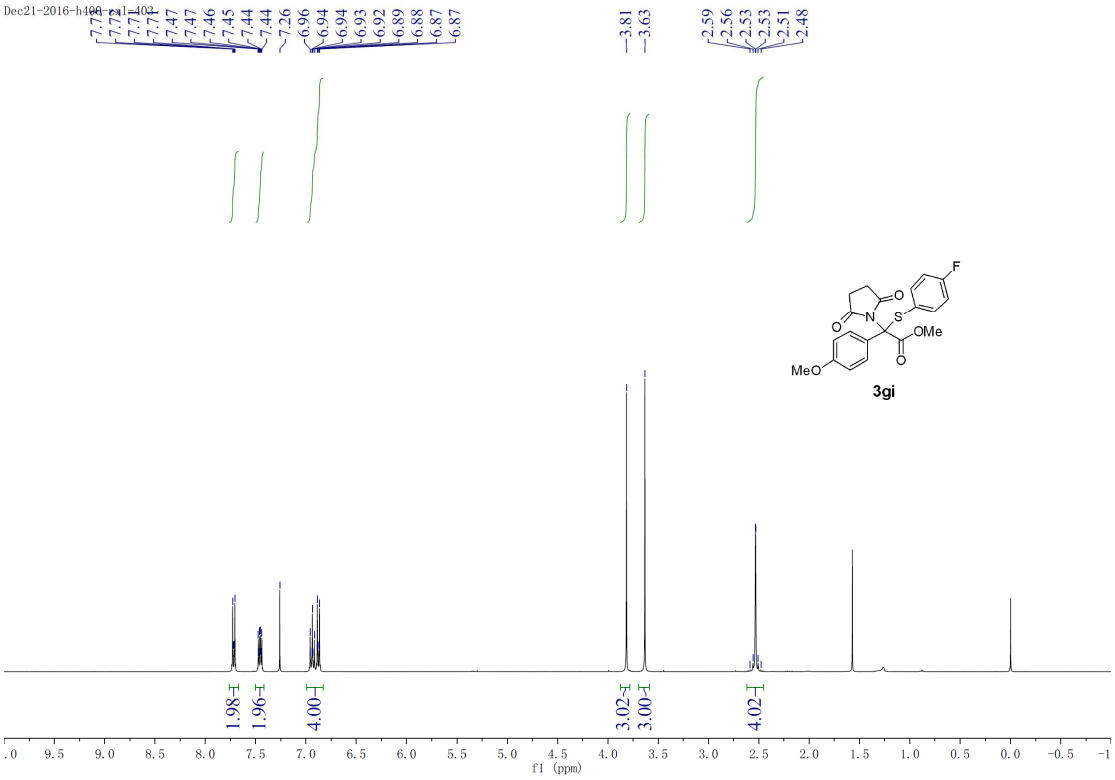
3gf

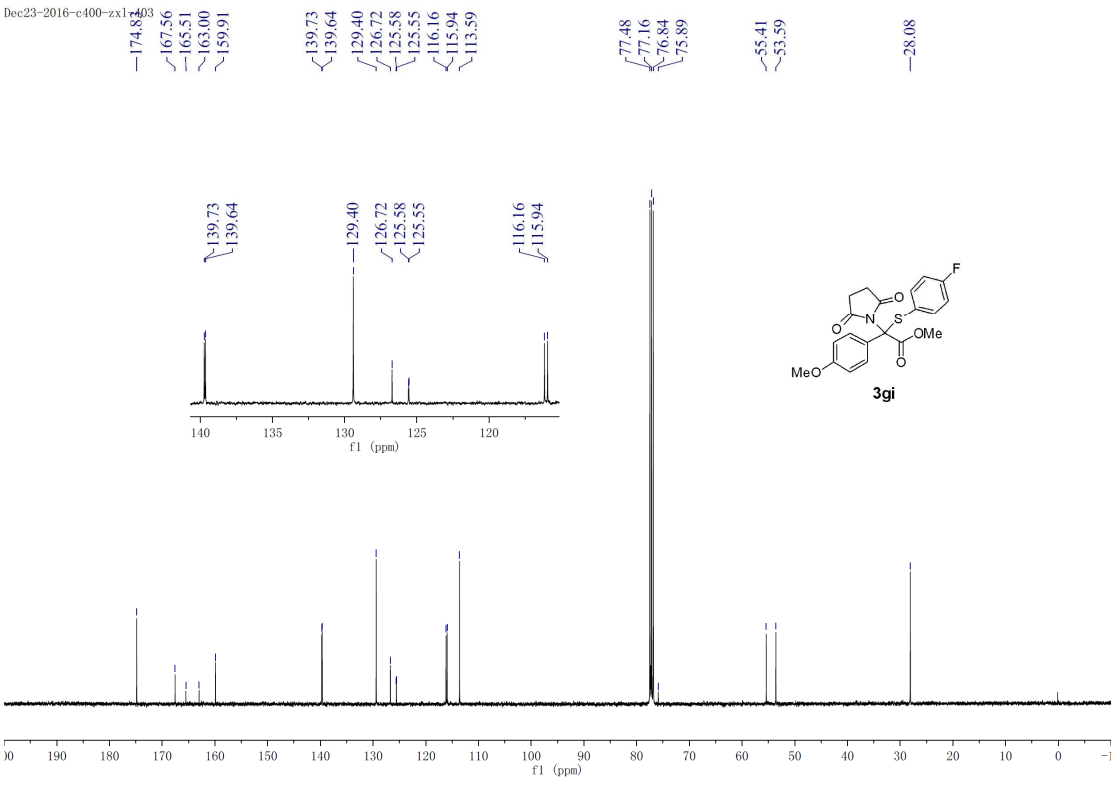

7.77
7.76
7.69
7.38
7.36
7.35
7.33
7.32
7.31
7.26
6.89
6.88
6.87
6.86
6.85
5.29
3.81
3.63
2.66
2.59
2.57
2.54
2.51
2.49
Br
O
N
S
OMe
MeO
3gg
2.01
4.03
2.00
3.01
3.01
4.00
f1 (ppm)

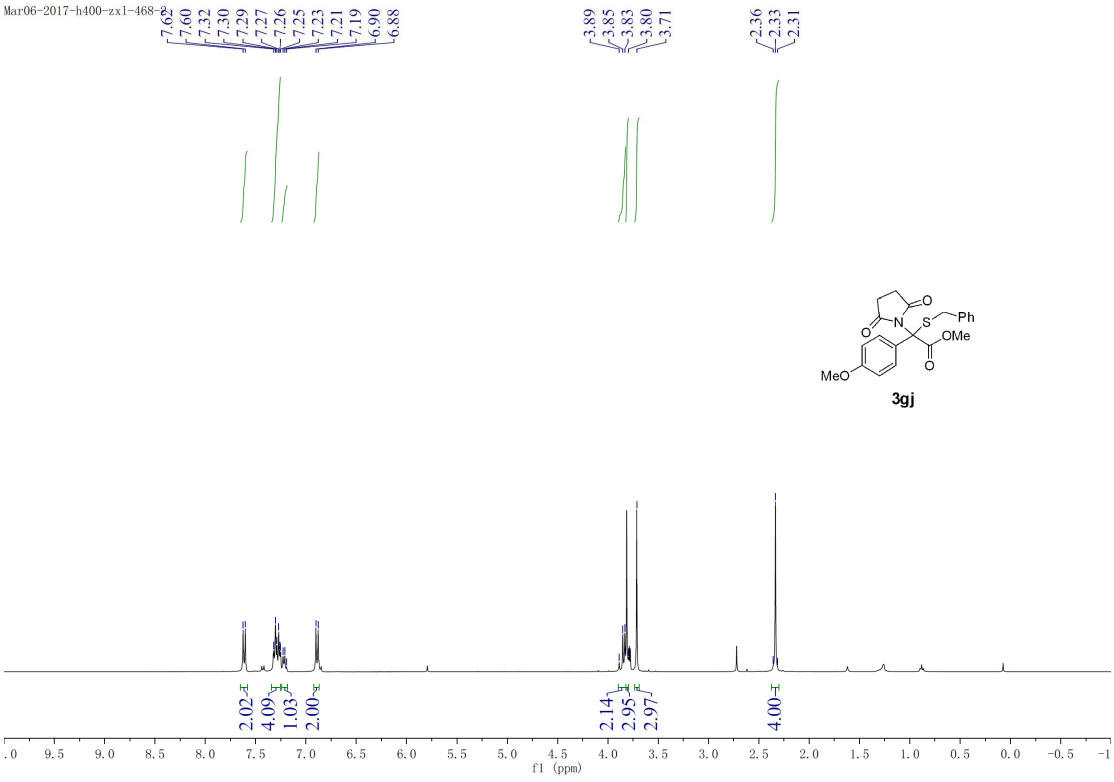

174.84
167.41
159.92
138.85
132.02
129.45
129.28
126.65
125.23
113.58
77.48
77.16
76.84
75.78
55.41
53.60
28.09
Br
O
N
S
OMe
MeO
3gg
f1 (ppm)

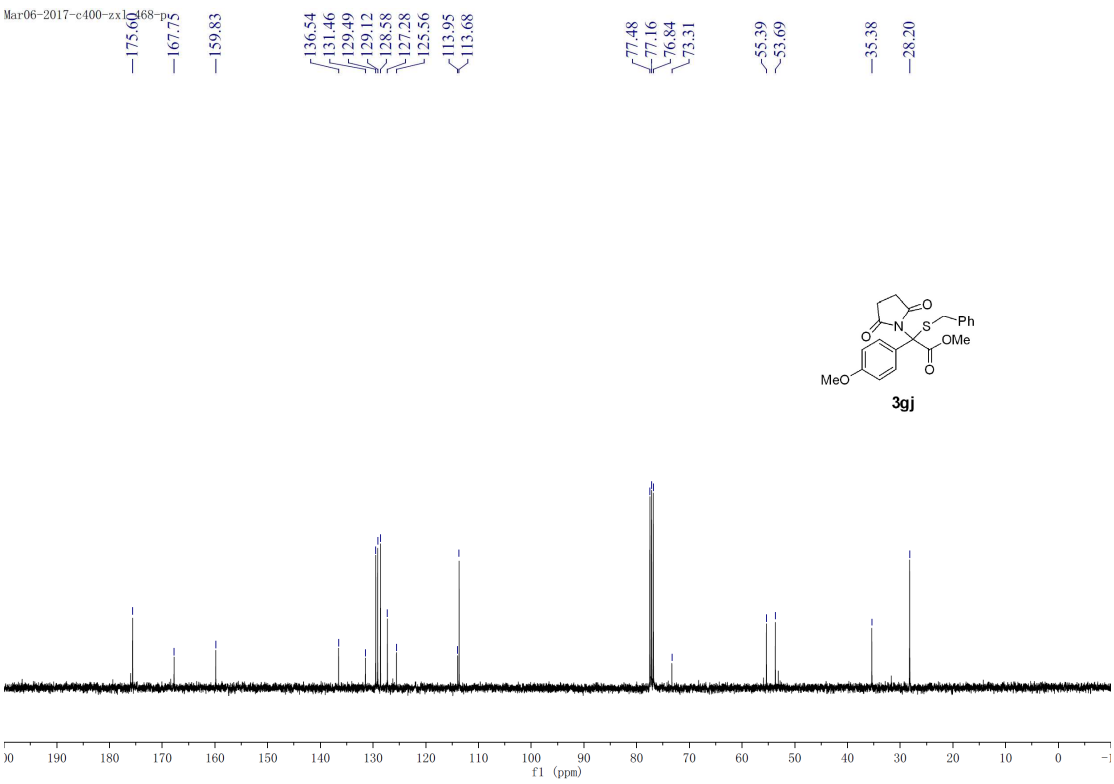

7.74
7.73
7.71
7.70
7.40
7.40
7.38
7.38
7.26
7.22
7.22
7.21
7.20
6.88
6.88
6.87
6.86
5.29
3.81
3.63
2.59
2.56
2.54
2.51
2.48
Cl
O
O
N
S
OMe
O
MeO
3gh
2.01
2.01
2.01
2.03
3.03
3.00
4.04
f1 (ppm)

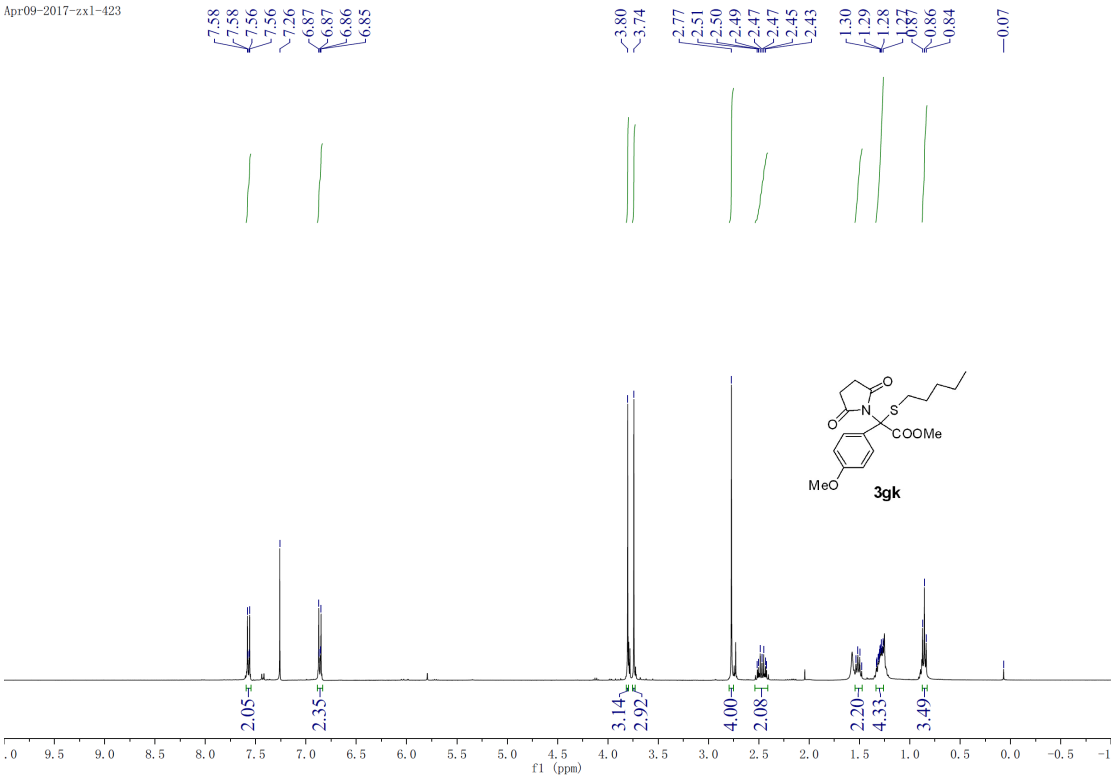

174.85
167.44
159.91
138.66
136.90
129.43
129.04
128.65
126.65
113.58
77.48
77.16
76.84
75.85
55.40
53.59
28.08
Cl
O
O
N
S
OMe
O
MeO
3gh
f1 (ppm)

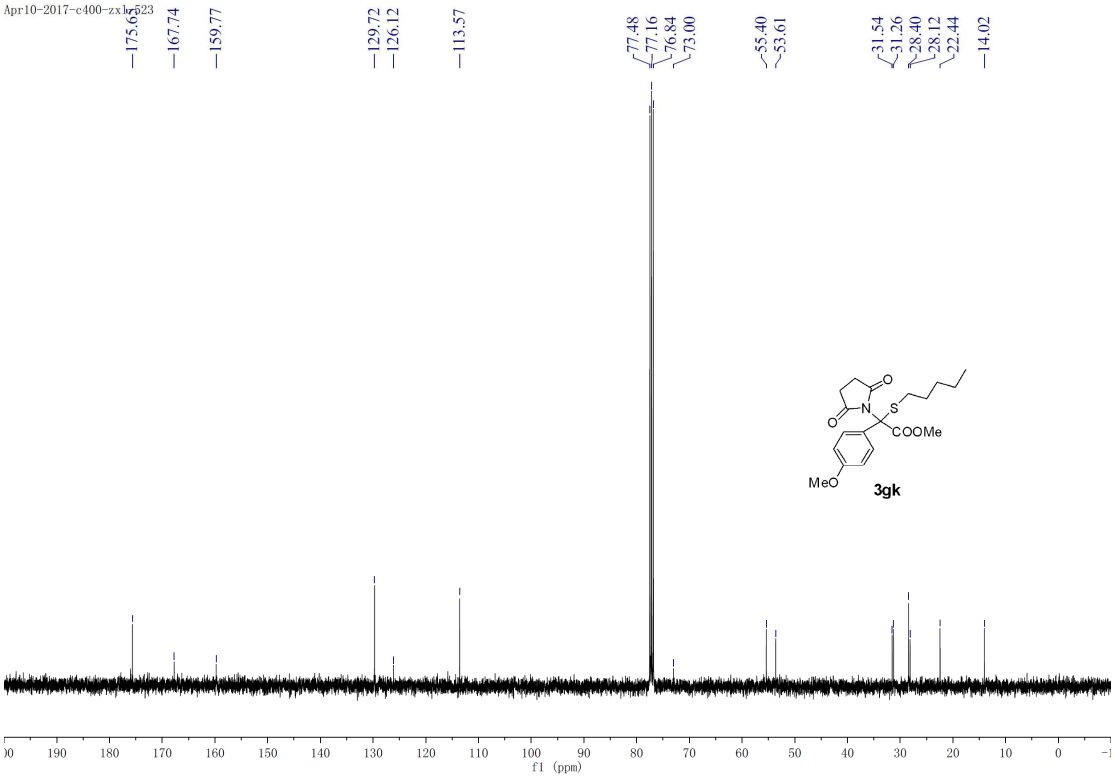

Dec21-2016-h400-zxl-103
7.77
7.77
7.77
7.77
7.47
7.47
7.46
7.45
7.44
7.44
7.26
6.96
6.94
6.94
6.93
6.92
6.89
6.88
6.87
6.87
3.81
3.63
2.59
2.56
2.53
2.53
2.51
2.48
F
O
O
N
S
OMe
O
MeO
3gi
1.98
1.96
4.00
3.02
3.00
4.02
f1 (ppm)

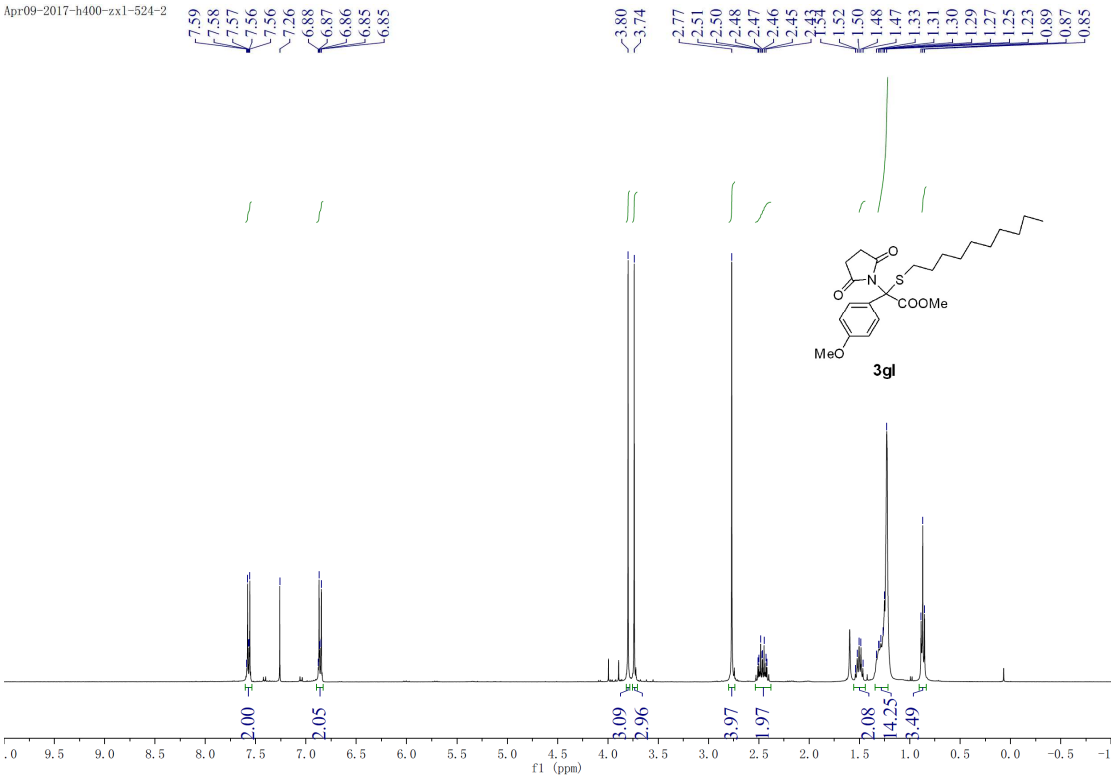

Dec23-2016-c400-zxl-103
174.83
167.56
165.51
163.00
159.91
139.73
139.64
129.40
126.72
125.58
125.55
116.16
115.94
113.59
77.48
77.16
76.84
75.89
55.41
53.59
28.08
F
O
O
N
S
OMe
O
MeO
3gi
f1 (ppm)

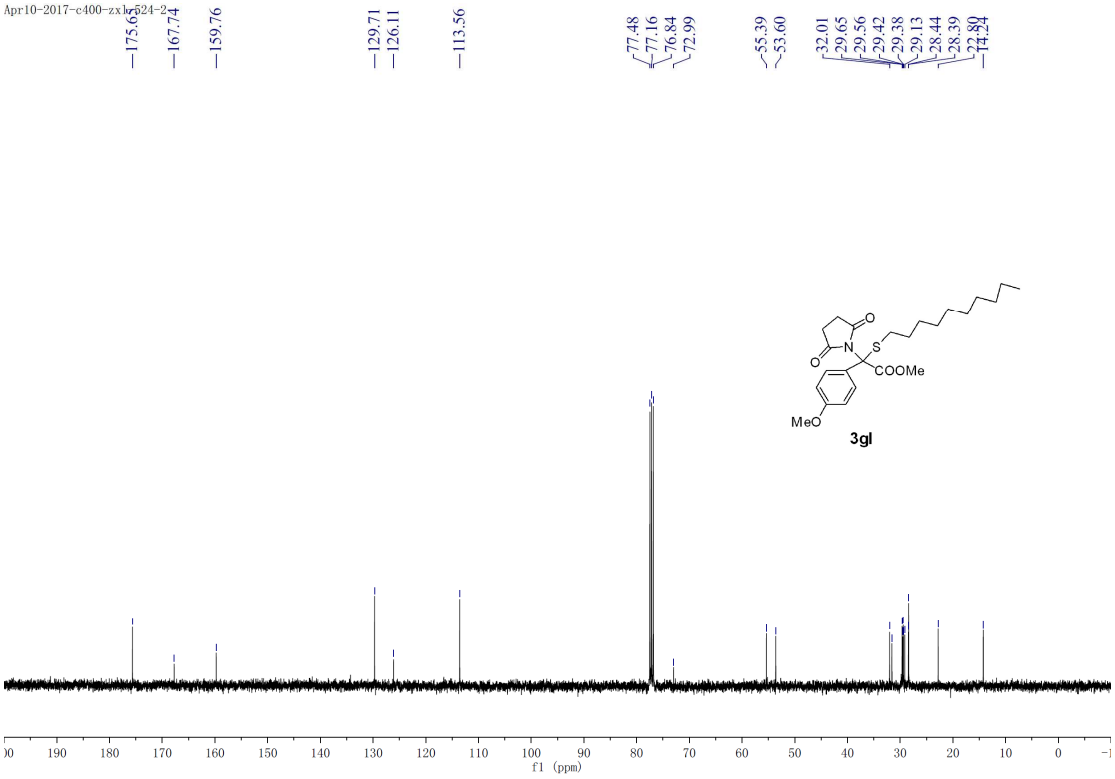

Mar06-2017-h400-zxl-468-p
7.62
7.60
7.32
7.30
7.29
7.27
7.26
7.25
7.23
7.21
7.19
6.90
6.88
3.89
3.85
3.83
3.80
3.71
2.36
2.33
2.31
Ph
S
N
O
OMe
MeO
3gj
2.02
4.09
1.03
2.00
2.14
2.95
2.97
4.00
f1 (ppm)

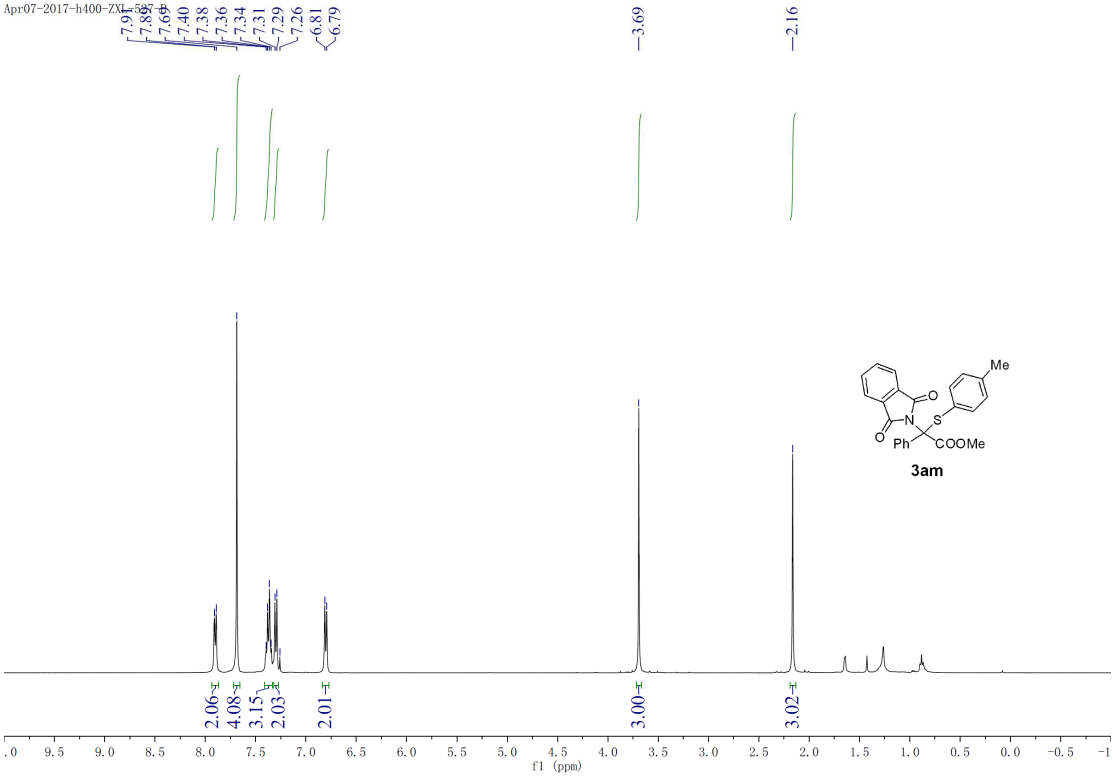

Mar06-2017-c400-zxl-468-p
175.60
167.75
159.83
136.54
131.46
129.49
129.12
128.58
127.28
125.56
113.95
113.68
77.48
77.16
76.84
73.31
55.39
53.69
35.38
28.20
Ph
S
N
O
OMe
MeO
3gj
f1 (ppm)

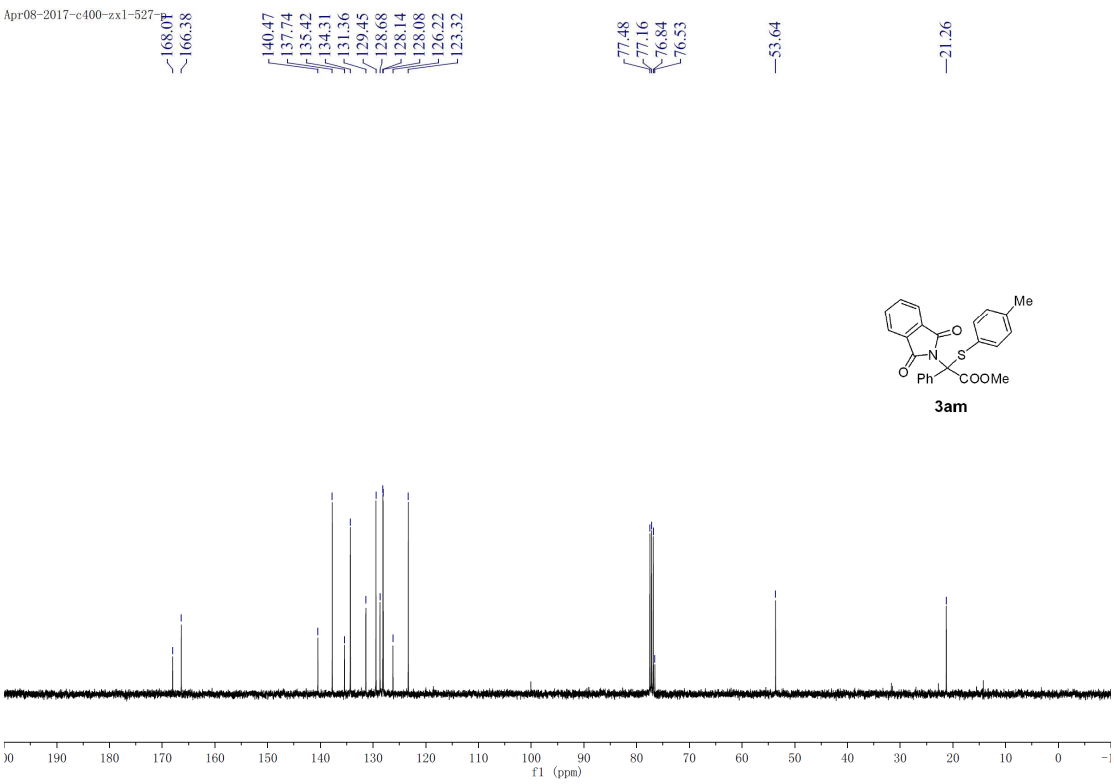

Apr09-2017-zx1-423
7.58
7.58
7.56
7.56
7.26
6.87
6.87
6.86
6.85
3.80
3.74
2.77
2.51
2.50
2.49
2.47
2.47
2.45
2.43
1.30
1.29
1.28
0.87
0.86
0.84
0.07
COOMe
MeO
3gk
2.05
2.35
3.14
2.92
4.00
2.08
2.20
4.33
3.49
f1 (ppm)

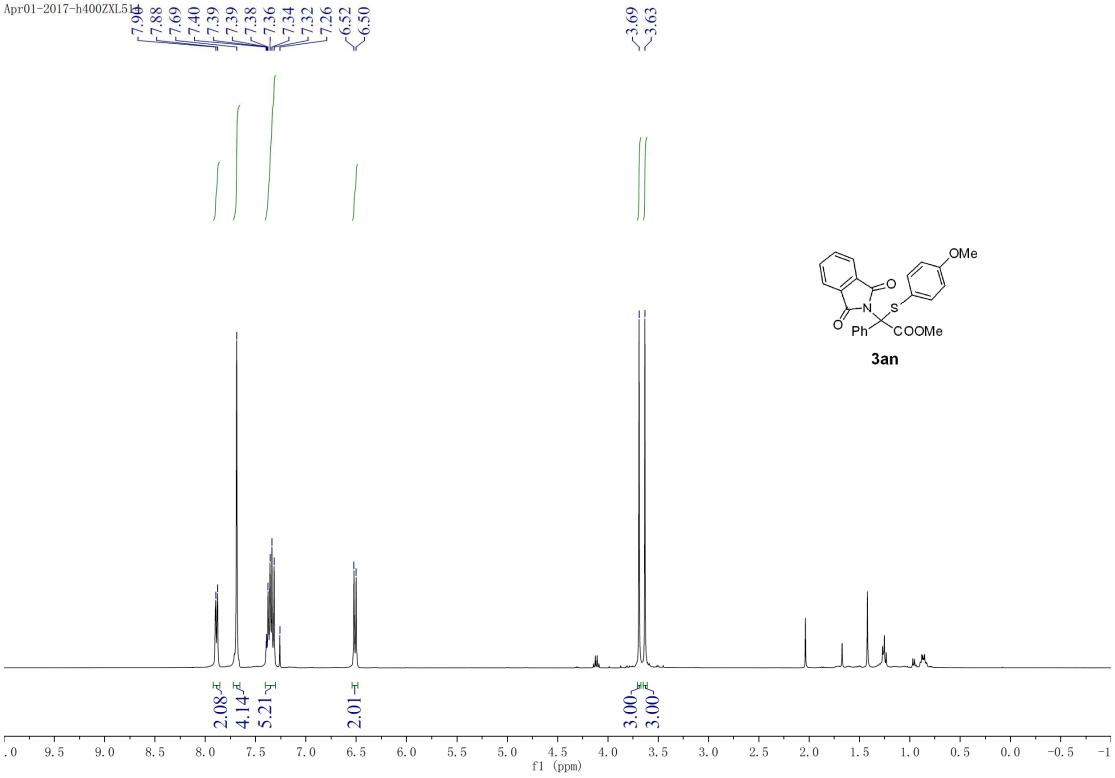

Apr10-2017-c400-zxl-523
175.65
167.74
159.77
129.72
126.12
113.57
77.48
77.16
76.84
73.00
55.40
53.61
31.54
31.26
28.40
28.12
22.44
14.02
COOMe
MeO
3gk
f1 (ppm)

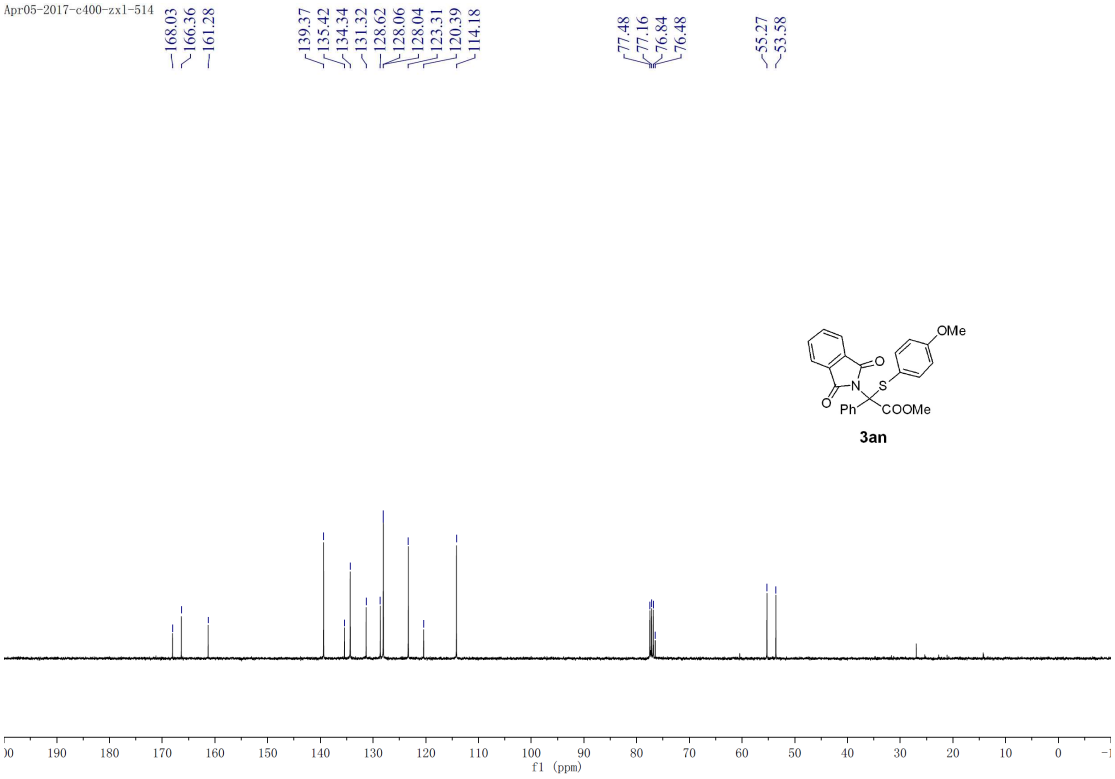

Apr09-2017-h400-zxl-524-2
7.59
7.58
7.57
7.56
7.56
7.26
6.88
6.87
6.86
6.85
6.85
3.80
3.74
2.77
2.51
2.50
2.48
2.47
2.46
2.45
2.43
1.54
1.52
1.50
1.48
1.47
1.33
1.31
1.30
1.29
1.27
1.25
1.23
0.89
0.87
0.85
2.00
2.05
3.09
2.96
3.97
1.97
2.08
14.25
3.49
f1 (ppm)
O
O
N
S
COOMe
MeO
3gl

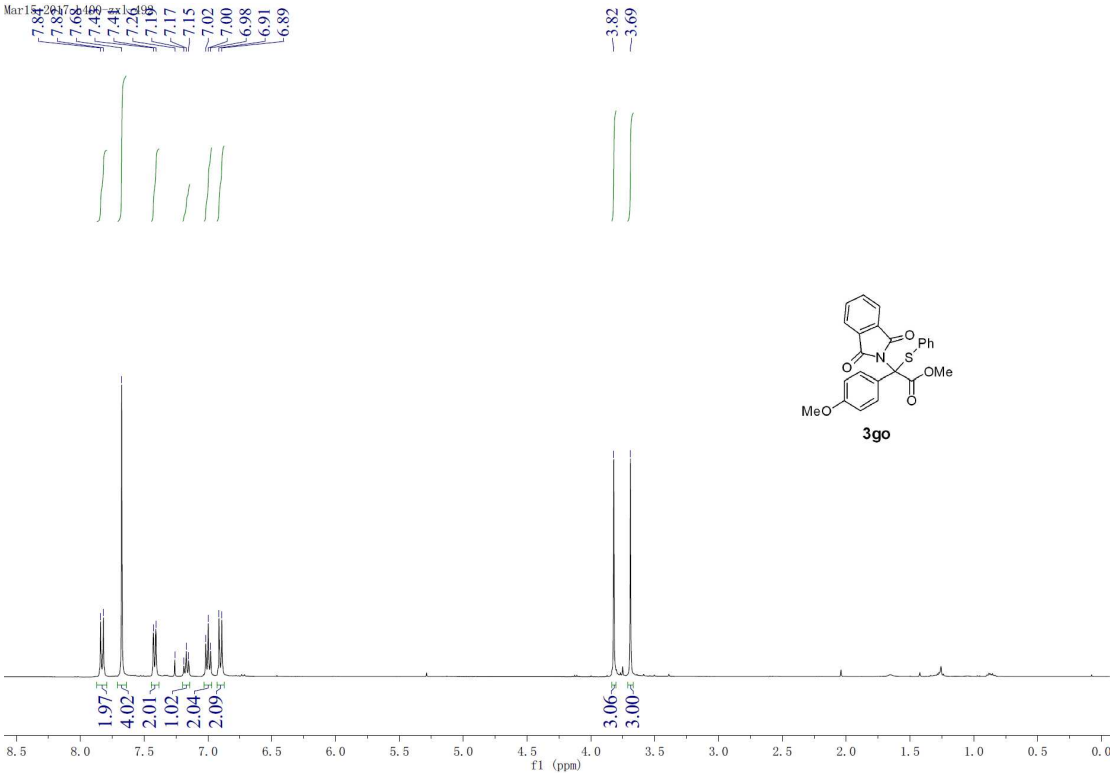

Apr10-2017-c400-zxl-524-2
175.65
167.74
159.76
129.71
126.11
113.56
77.48
77.16
76.84
72.99
55.39
53.60
32.01
29.65
29.56
29.42
29.38
29.13
28.44
28.39
22.80
14.24
f1 (ppm)
O
O
N
S
COOMe
MeO
3gl

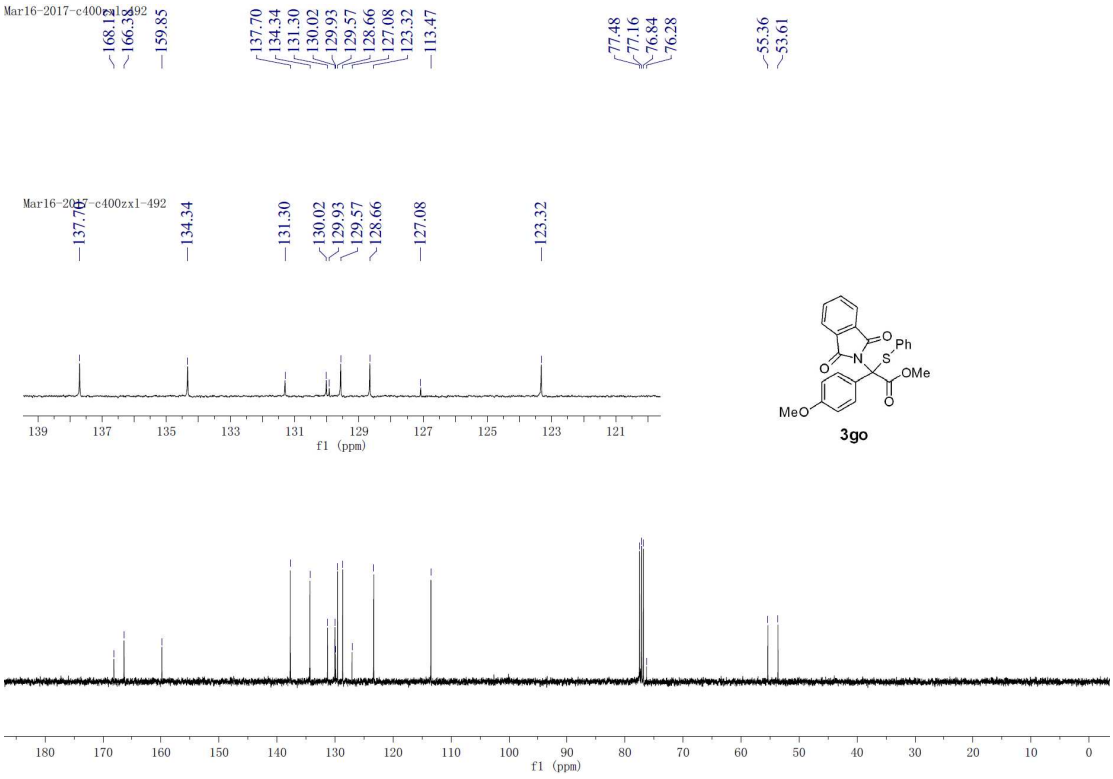

Apr07-2017-h400-ZXL-527
7.91
7.89
7.69
7.40
7.38
7.36
7.34
7.31
7.29
7.26
6.81
6.79
3.69
2.16
2.06
4.08
3.15
2.03
2.01
3.00
3.02
f1 (ppm)
Me
O
N
S
O
Ph
COOMe
3am

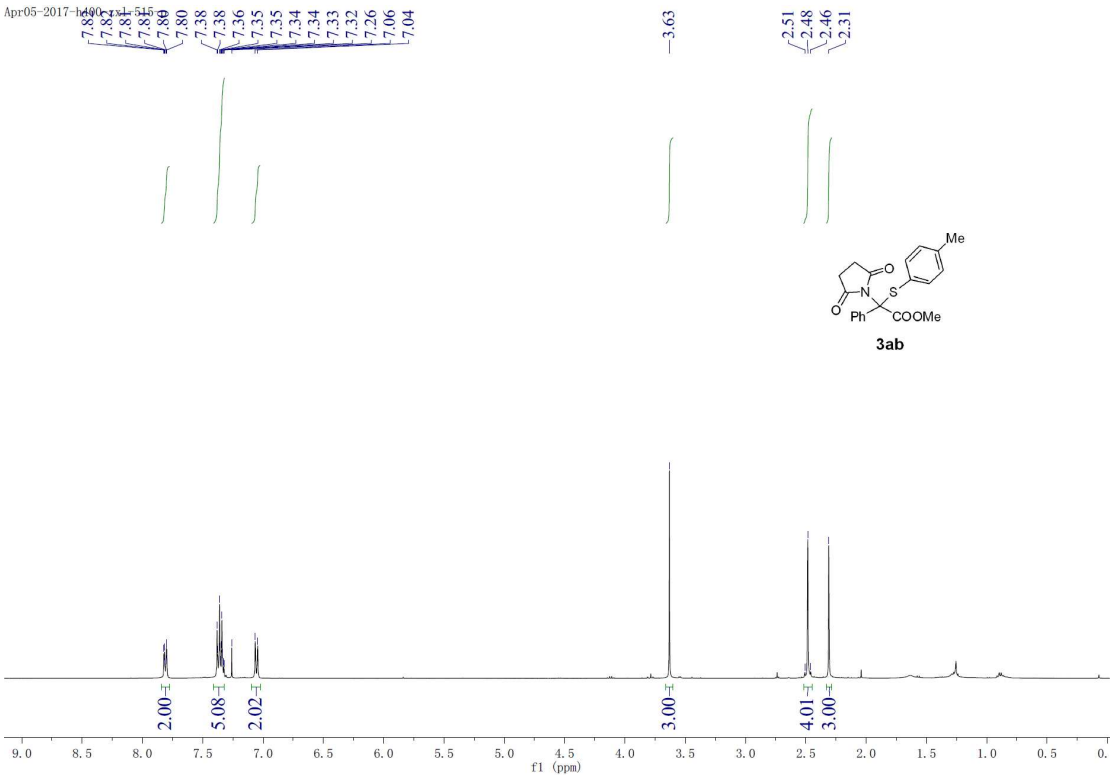

Apr08-2017-c400-zxl-527
168.07
166.38
140.47
137.74
135.42
134.31
131.36
129.45
128.68
128.14
128.08
126.22
123.32
77.48
77.16
76.84
76.53
53.64
21.26
f1 (ppm)
Me
O
N
S
O
Ph
COOMe
3am

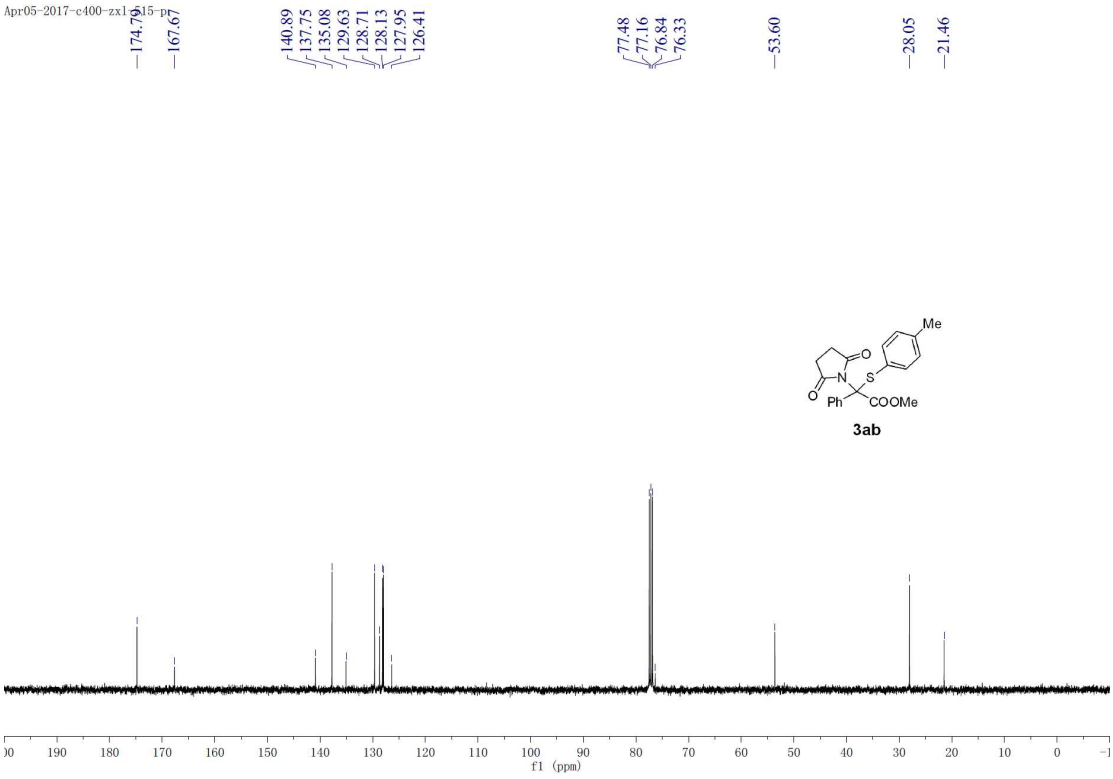

Apr01-2017-h400ZXL514
7.90
7.88
7.69
7.40
7.39
7.39
7.38
7.36
7.34
7.32
7.26
6.52
6.50
3.69
3.63
OMe
O
N
S
O
Ph
COOMe
3an
2.08
4.14
5.21
2.01
3.00
3.00
f1 (ppm)

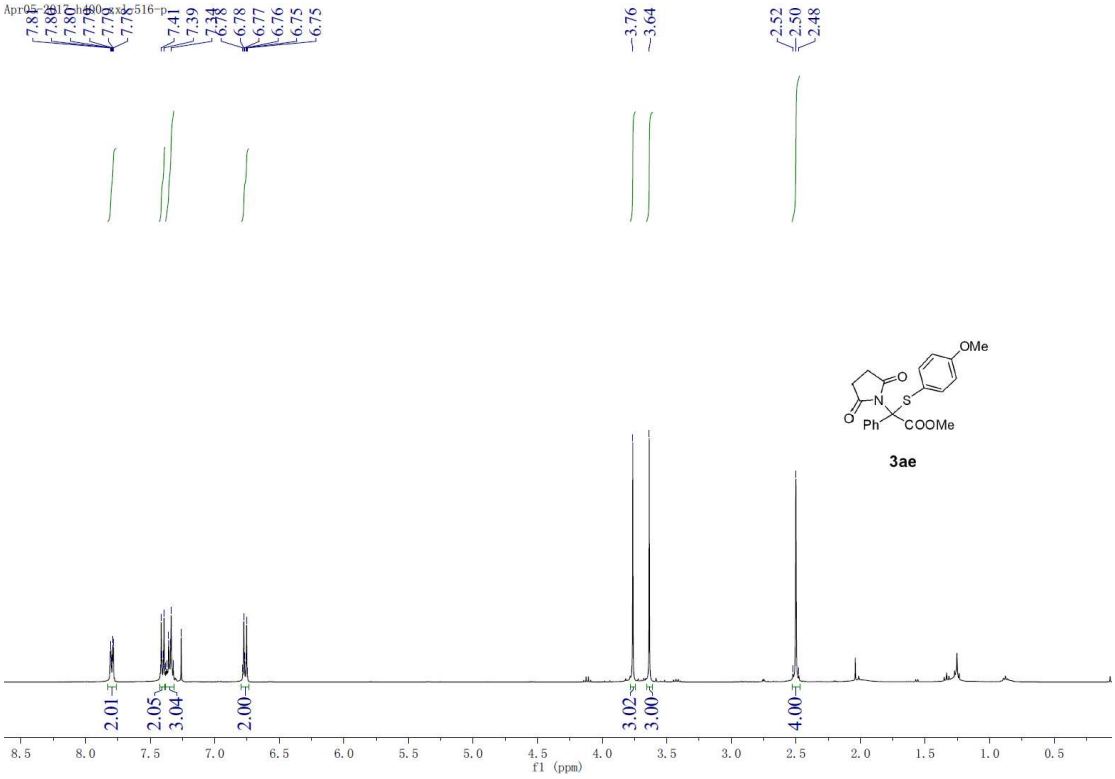

Apr05-2017-c400-zxl-514
168.03
166.36
161.28
139.37
135.42
134.34
131.32
128.62
128.06
128.04
123.31
120.39
114.18
77.48
77.16
76.84
76.48
55.27
53.58
OMe
O
N
S
O
Ph
COOMe
3an
f1 (ppm)

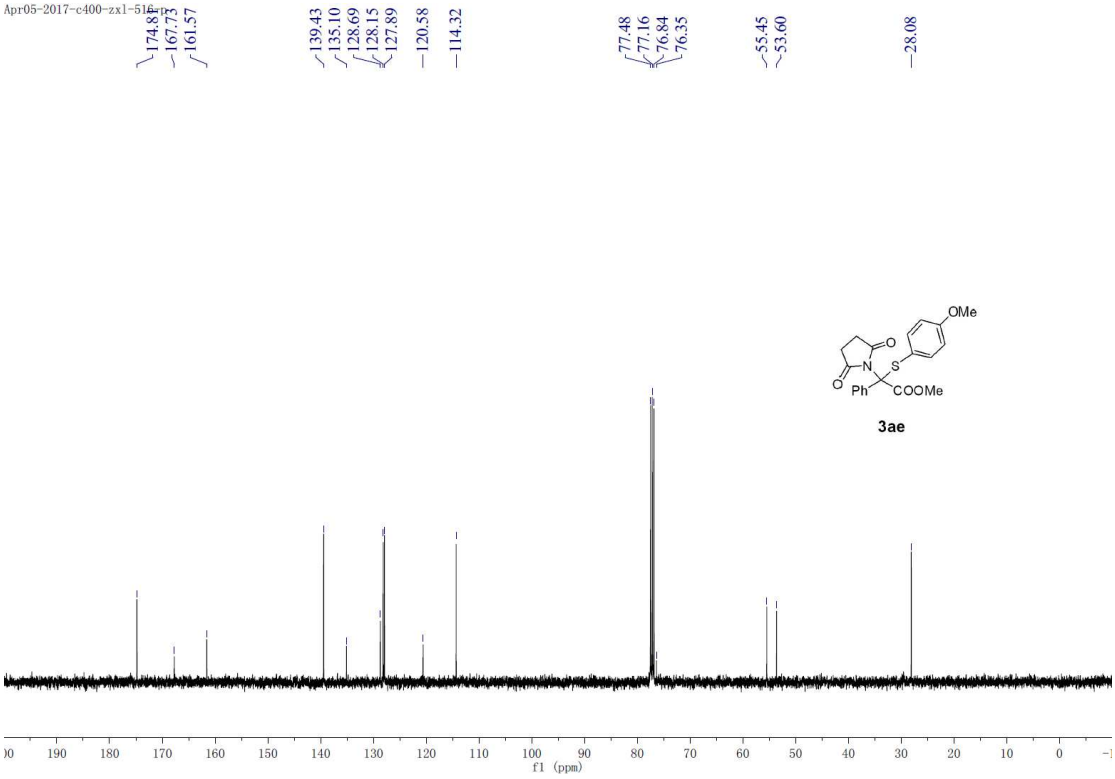

7.89
7.88
7.68
7.44
7.26
7.19
7.17
7.15
7.02
7.00
6.98
6.91
6.89
3.82
3.69
Ph
S
N
O
OMe
MeO
3go
1.97
4.02
2.01
1.02
2.04
2.09
3.06
3.00
f1 (ppm)

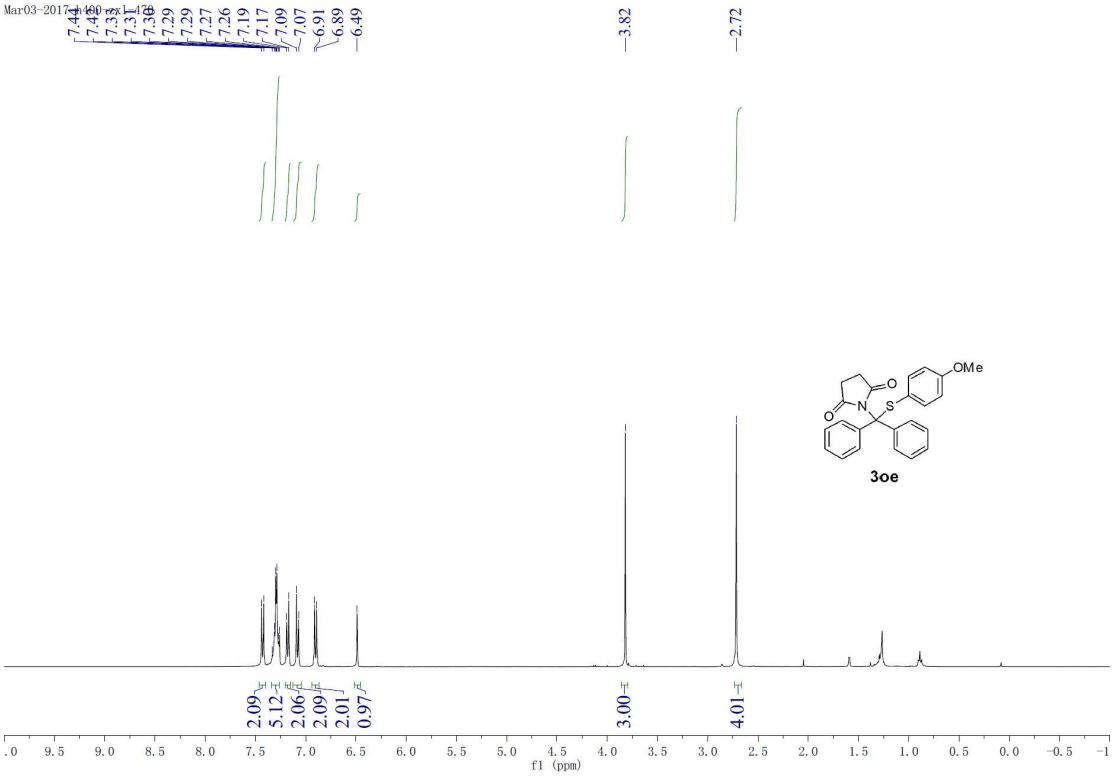

168.12
166.32
159.85
137.70
134.34
131.30
130.02
129.93
129.57
128.66
127.08
123.32
113.47
77.48
77.16
76.84
76.28
55.36
53.61
Ph
S
N
O
OMe
MeO
3go
f1 (ppm)

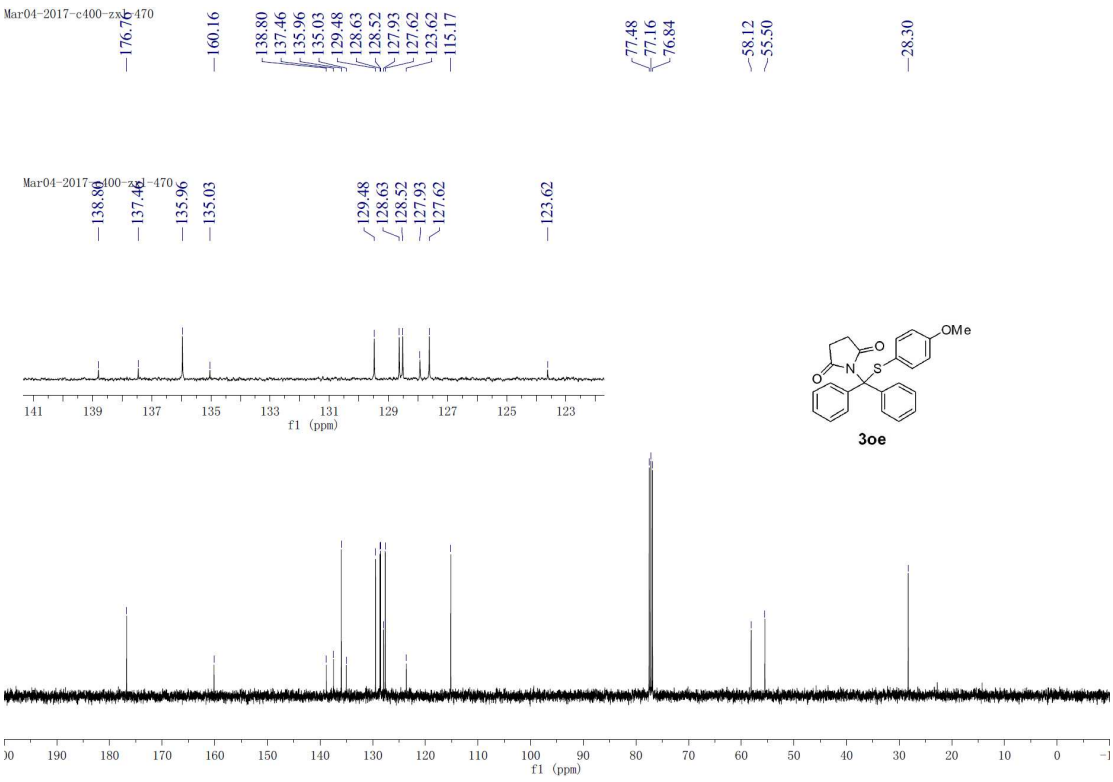

Apr05-2017-h400-zxl-515
7.85
7.84
7.81
7.80
7.80
7.80
7.38
7.36
7.35
7.34
7.34
7.33
7.32
7.26
7.06
7.04
3.63
2.51
2.48
2.46
2.31
Me
O
N
S
O
Ph
COOMe
3ab
2.00
5.08
2.02
3.00
4.01
3.00
f1 (ppm)

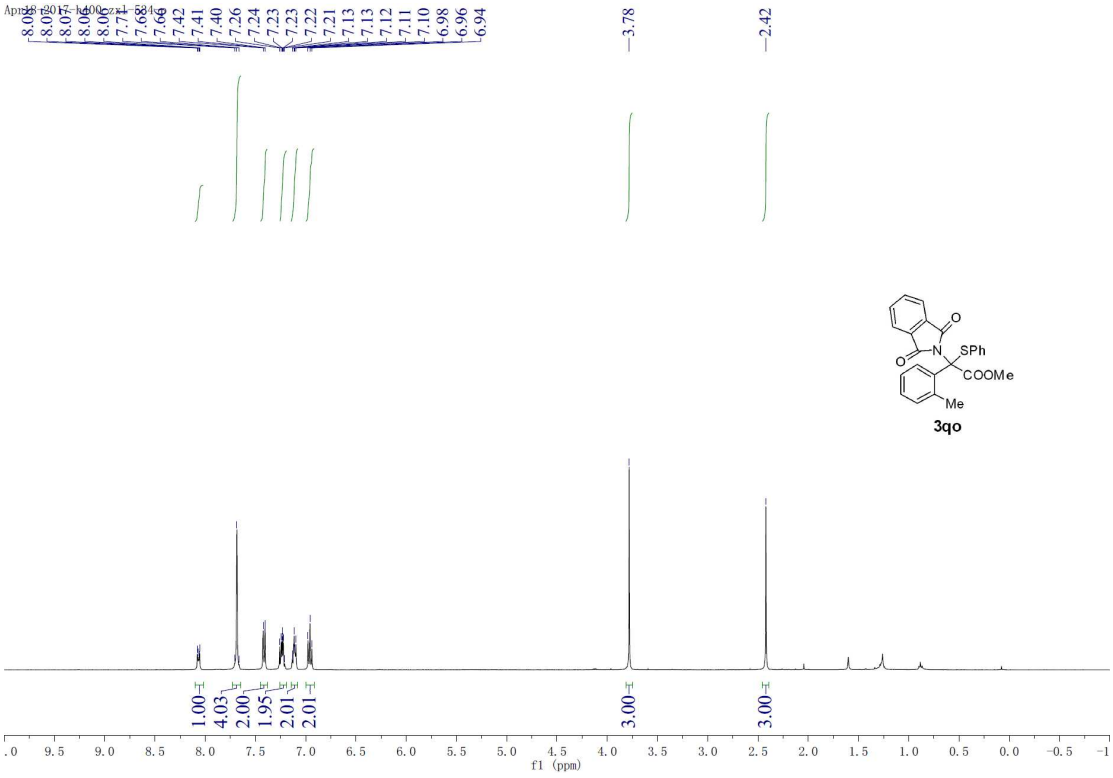

Apr05-2017-c400-zxl-515-pr
174.79
167.67
140.89
137.75
135.08
129.63
128.71
128.13
127.95
126.41
77.48
77.16
76.84
76.33
53.60
28.05
21.46
Me
O
N
S
O
Ph
COOMe
3ab
f1 (ppm)

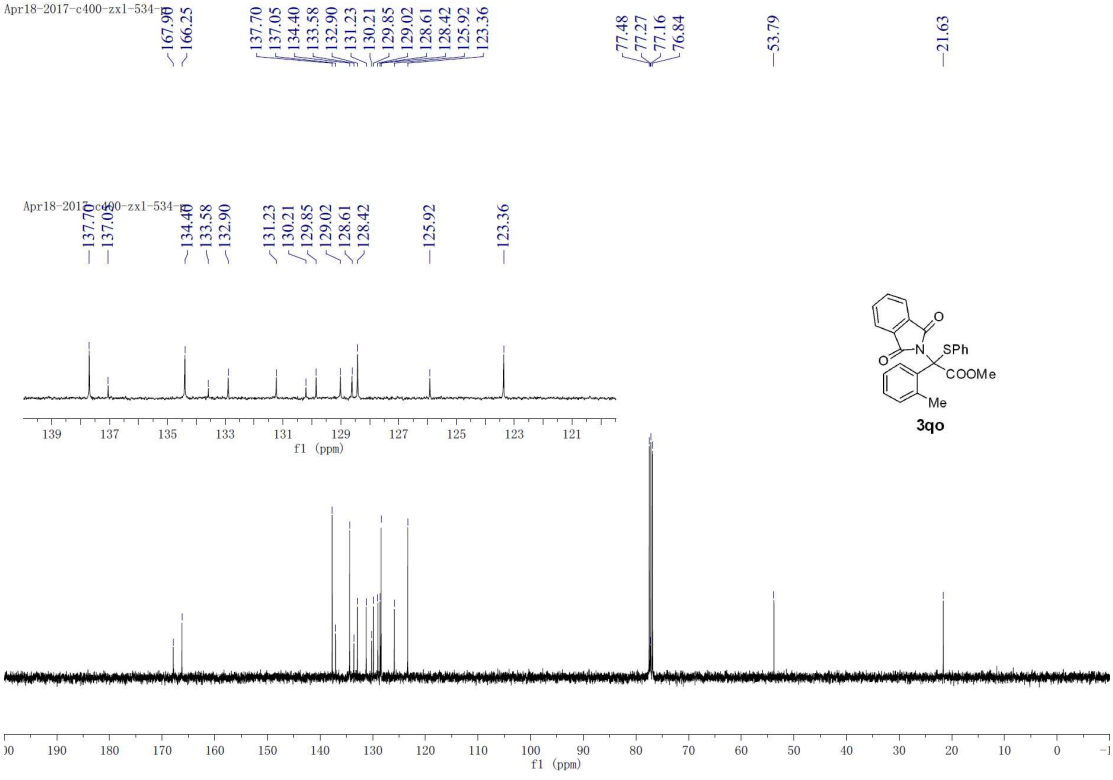

7.85
7.80
7.79
7.41
7.39
7.34
6.78
6.77
6.76
6.75
3.76
3.64
2.52
2.50
2.48
OMe
O
N
S
Ph
COOMe
3ae
2.01
2.05
3.04
2.00
3.02
3.00
4.00
f1 (ppm)

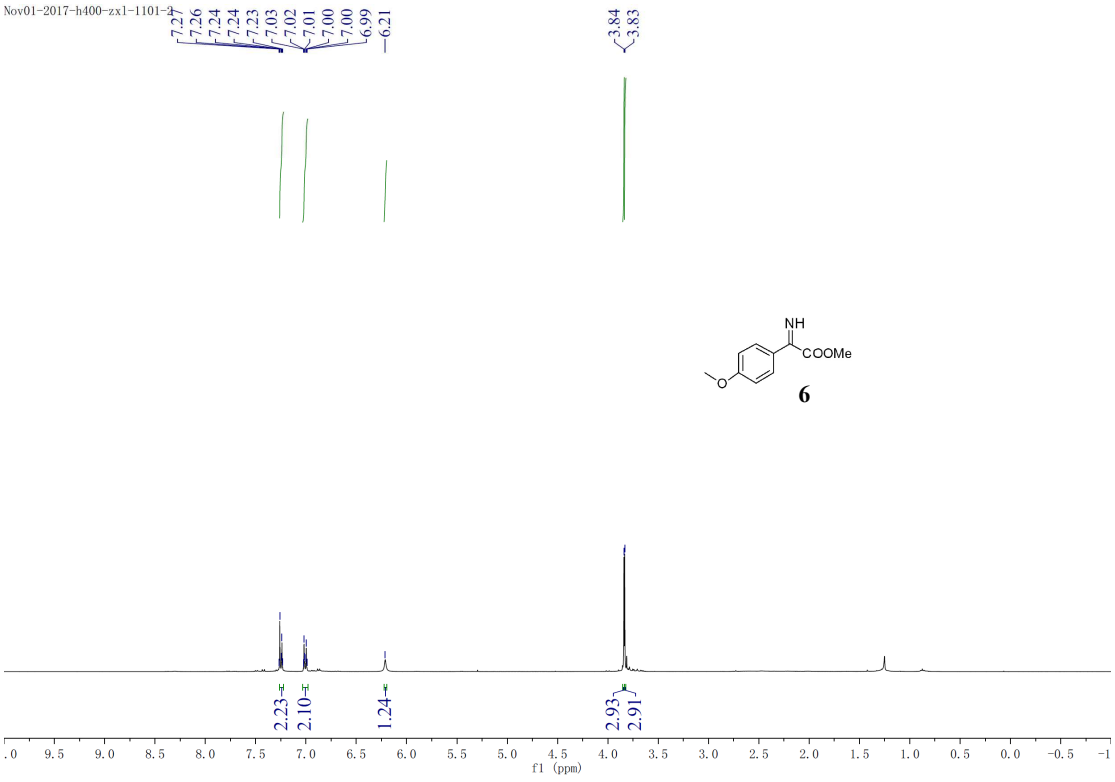

174.81
167.73
161.57
139.43
135.10
128.69
128.15
127.89
120.58
114.32
77.48
77.16
76.84
76.35
55.45
53.60
28.08
OMe
O
N
S
Ph
COOMe
3ae
f1 (ppm)


Mar03-2017-c400-zxl-470
7.44
7.43
7.33
7.31
7.30
7.29
7.29
7.27
7.26
7.19
7.17
7.09
7.07
6.91
6.89
6.49
3.82
2.72
OMe
O
N
S
O
3oe
2.09
5.12
2.06
2.09
2.01
0.97
3.00
4.01
f1 (ppm)

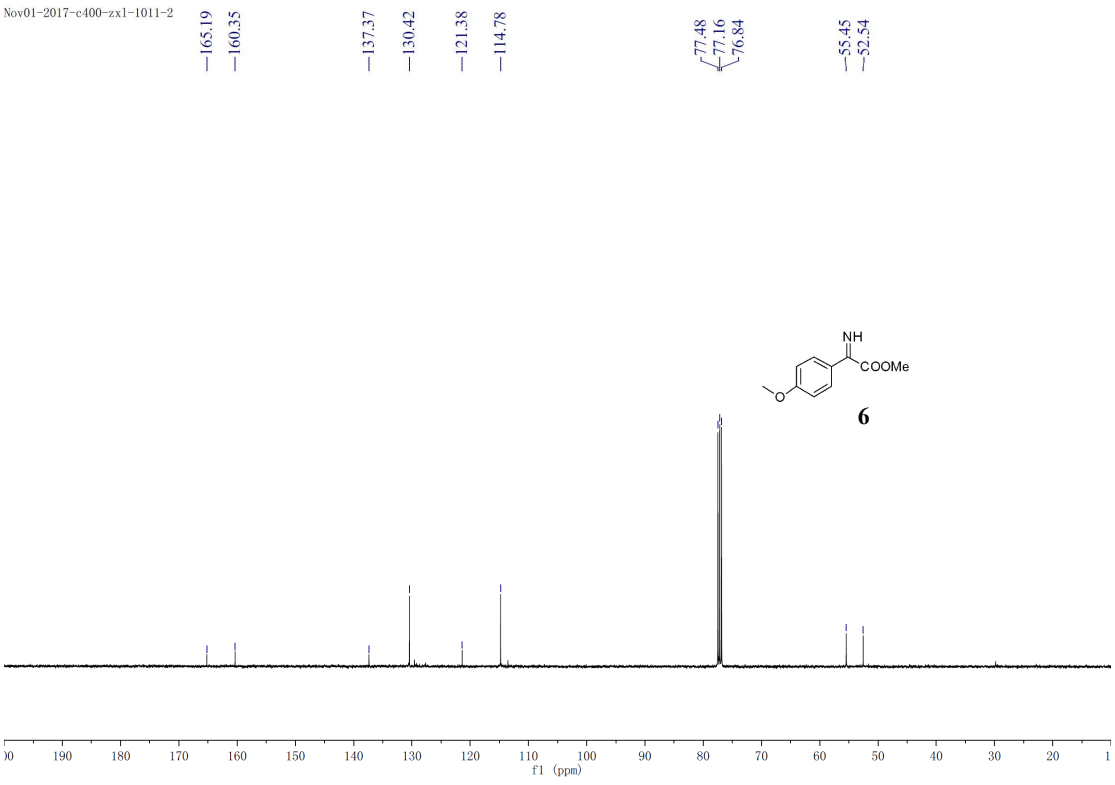

Mar04-2017-c400-zxl-470
176.76
160.16
138.80
137.46
135.96
135.03
129.48
128.63
128.52
127.93
127.62
123.62
115.17
77.48
77.16
76.84
58.12
55.50
28.30
Mar04-2017-c400-zxl-470
138.80
137.46
135.96
135.03
129.48
128.63
128.52
127.93
127.62
123.62
f1 (ppm)
OMe
O
N
S
O
3oe
f1 (ppm)


8.08
8.07
8.07
8.06
8.06
7.71
7.68
7.66
7.42
7.41
7.40
7.26
7.24
7.23
7.23
7.22
7.21
7.13
7.13
7.12
7.11
7.10
6.98
6.96
6.94
3.78
2.42
SPh
COOMe
Me
3qo
1.00
4.03
2.00
1.95
2.01
2.01
3.00
3.00
f1 (ppm)


Apr18-2017-c400-zx1-534-
167.90
166.25
137.70
137.05
134.40
133.58
132.90
131.23
130.21
129.85
129.02
128.61
128.42
125.92
123.36
77.48
77.27
77.16
76.84
53.79
21.63
SPh
COOMe
Me
3qo
f1 (ppm)


Nov01-2017-h400-zxl-1101-2
7.27
7.26
7.24
7.24
7.23
7.03
7.02
7.01
7.00
7.00
6.99
6.21
3.84
3.83
NH
COOMe
O
2.23
2.10
1.24
2.93
2.91
f1 (ppm)

6


Nov01-2017-c400-zxl-1011-2
165.19
160.35
137.37
130.42
121.38
114.78
77.48
77.16
76.84
55.45
52.54
NH
COOMe
O
f1 (ppm)

6