Supporting Information

Intramolecular Dehydrogenative C–S Coupling of Thioamides to Form 1,3-Benzothiazines under Metal-Free Conditions

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1. General information

All the reactions were carried out under an air atmosphere using glassware without being predried. Hexafluoroisopropanol, [hydroxy(tosyloxy)iodo]benzene and diphenylphosphine oxide, were obtained from commercial sources and used without further purification. Column chromatography was performed on silica gel (200-300 mesh) using analytical pure EtOAc, dichloromethane and petroleum ether. NMR spectra were recorded in $CDCl_3$ on 400 MHz or 500 MHz spectrometers. ^1H NMR chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (0 ppm) or residual $CHCl_3$ (7.26 ppm). ^{13}C NMR chemical shifts are reported relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. Mass spectra were obtained on an Ultima Global spectrometer with an ESI source. Melting points are uncorrected.

Experimental procedure

2. General procedure for the synthesis of starting materials

The starting materials, thioamides **1a-s**[1], **1t**[2], **1u-w**[3], **1x**[4], **1y-aa**[5] , hypervalent iodines **2b**[6], **2c** [7], were prepared according to literature procedure.

3. References

[1] L.-R. Wen, Y.-X. Sun, J.-W. Zhang, W.-S. Guo and M. Li, *Green Chem.*, 2018, **20**, 125-129.

[2] T. Guntreddi, R. Vanjari and K. N. Singh, *Org. Lett.*, 2014, **16**, 3624-3627.

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[4] C. N. Kapanda, G. G. Muccioli, G. Labar, N. Draoui, D. M. Lambert and J. H. Poupaert, *Med. Chem. Res.*, 2009, **18**, 243-254.

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[6] J.-H. Chun, S. Telu, S. Lu, V. W. Pike, *Org. Biomol. Chem*., 2013, **11**, 5094-5099.

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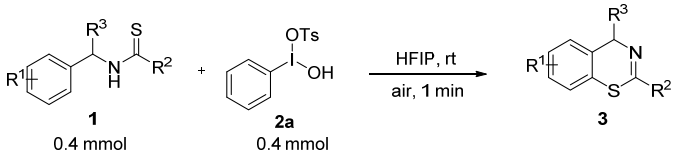
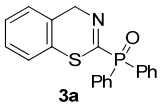
4. General procedure for the synthesis of 4*H*-benzo[*e*][1,3]thiazine



To a solution of thioamide **1** (0.4 mmol) in HFIP (4 mL) was added HTIB **2a** (157 mg, 0.4 mmol). The reaction mixture was stirred at room temperature under an air atmosphere for 1 min. Then the mixture was quenched with saturated $NaHCO_3$ (10 mL) and extracted with DCM (3 ×

10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent, followed by purification on silica gel, provided product 4*H*-benzo[*e*][1,3]thiazine **3**.

(4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3a)



3a

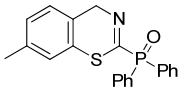
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3a** as a white solid (119 mg, 85%). Mp: 155-157 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82−7.78 (m, 4H), 7.57−7.53 (m, 2H), 7.47−7.43 (m, 4H), 7.34−7.30 (m, 1H), 7.28−7.27 (m, 3H), 4.78 (d, J = 2.8 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2 (d, $^1J_{PC}$ = 128.7 Hz, 1C), 132.5 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.1 (d, $^1J_{PC}$ = 105.7 Hz, 2C), 129.8 (s, 1C), 129.2 (s, 1C), 128.5 (s, 2C), 128.4 (s, 2C), 128.0 (s, 1C), 127.9 (s, 1C), 127.0 (s, 1C), 126.4 (s, 1C), 58.0 (d, $^3J_{PC}$ = 17.5 Hz, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{20}H_{17}NOPS$, 350.0768, found 350.0772.

(7-methyl-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3b)



3b

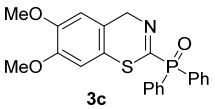
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3b** as a white solid (121 mg, 83%). Mp: 144-146 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82−7.77 (m, 4H), 7.56−7.51 (m, 2H), 7.46−7.42 (m, 4H), 7.16−7.12 (m, 1H), 7.09−7.08 (m, 2H), 4.74 (d, J = 2.7 Hz, 2H), 2.34 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (d, $^1J_{PC}$ = 128.7 Hz, 1C), 138.2 (s, 1C), 132.4 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.2 (d, $^1J_{PC}$ = 105.6 Hz, 2C), 129.1 (s, 1C), 128.7 (s, 1C), 128.5 (s, 2C), 128.4 (s, 2C), 127.7 (s, 1C), 126.4 (s, 1C), 126.2 (s, 1C), 58.0 (d, $^3J_{PC}$ = 17.6 Hz, 1C), 21.0 (s, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{21}H_{19}NOPS$, 364.0925, found 364.0923.

(6,7-dimethoxy-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3c)



3c

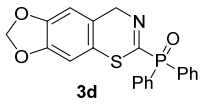
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3c** as a white solid (74 mg, 45%). Mp: 202-204 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (dd, J = 11.8, 7.9 Hz, 4H), 7.54−7.52 (m, 2H), 7.45−7.43 (m, 4H), 6.74 (d, J = 8.6 Hz, 2H), 4.71 (s, 2H), 3.84 (d, J = 25.2 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4 (d, $^1J_{PC}$ = 128.9 Hz, 1C), 149.4 (s, 1C), 148.9 (s, 1C), 132.4 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.3 (d, $^1J_{PC}$ = 105.7 Hz, 2C), 128.5 (s, 2C), 128.4 (s, 2C), 121.2 (s, 1C), 120.7 (s, 1C), 110.0 (s, 1C), 109.2 (s, 1C), 57.8 (d, $^3J_{PC}$ = 17.7 Hz, 1C), 56.1 (s, 2C).

HRMS (ESI-TOF, [M + Na]$^+$): calcd for $C_{22}H_{20}NO_3PSNa$, 432.0799, found 432.0794.

(8*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*e*][1,3]thiazin-6-yl)diphenylphosphine oxide (3d)



3d

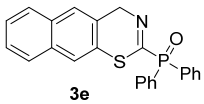
The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to provide **3d** as a white solid (123 mg, 78%). Mp: 126-128 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (dd, J = 12.0, 7.8 Hz, 4H), 7.55−7.52 (m, 2H), 7.46−7.43 (m, 4H), 6.73 (d, J = 9.7 Hz, 2H), 5.95 (s, 2H), 4.64 (d, J = 1.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6 (d, $^1J_{PC}$ = 128.1 Hz, 1C), 148.3 (s, 1C), 147.6 (s, 1C), 132.4 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.1 (d, $^1J_{PC}$ = 105.8 Hz, 2C), 128.5 (s, 2C), 128.4 (s, 2C), 122.9 (s, 1C), 122.0 (s, 1C), 107.4 (s, 1C), 106.6 (s, 1C), 101.6 (s, 1C), 58.2 (d, $^3J_{PC}$ = 17.0 Hz, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{21}H_{17}NO_3PS$, 394.0667, found 394.0671.

(4*H*-naphtho[2,3-*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3e)



3e

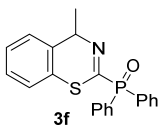
The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to provide **3e** as a yellow solid (128 mg, 80%). Mp: 163-165 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 7.8 Hz, 1H), 7.83−7.77 (m, 6H), 7.52−7.47 (m, 4H), 7.43−7.40 (m, 4H), 7.33 (d, J = 8.3 Hz, 1H), 4.92 (d, J = 2.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7 (d, $^1J_{PC}$ = 128.2 Hz, 1C), 132.8 (s, 1C), 132.4 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.2 (d, $^1J_{PC}$ = 105.9 Hz, 2C), 129.7 (s, 1C), 128.5 (s, 2C), 128.4 (s, 2C), 128.3 (s, 1C), 128.1 (s, 1C), 126.8 (s, 1C), 126.7 (s, 1C), 126.4 (s, 1C), 126.3 (s, 1C), 124.9 (s, 1C), 123.4 (s, 1C), 58.9 (d, $^3J_{PC}$ = 17.3 Hz, 1C).

HRMS (ESI-TOF, [M + Na]$^+$): calcd for $C_{24}H_{18}NOSPNa$, 422.0744, found 422.0744.

(4-methyl-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3f)



3f

The crude product was purified by silica gel column chromatography (petroleum ether/ethyl

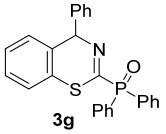
acetate = 30:1, v/v) to provide **3f** as a white solid (93 mg, 64%). Mp: 100-102 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87−7.78 (m, 4H), 7.55−7.52 (m, 2H), 7.46−7.42 (m, 4H), 7.35−7.32 (m, 1H), 7.28−7.23 (m, 3H), 4.75−4.71 (m, 1H), 1.64 (d, J = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6 (d, $^1J_{PC}$ = 130.2 Hz, 1C), 132.8 (s, 1C), 132.3 (s, 2C), 132.0 (s, 4C), 130.5 (d, $^1J_{PC}$ = 105.3, 1C), 130.1 (d, $^1J_{PC}$ = 105.1, 1C), 129.0 (s, 1C), 128.4 (s, 2C), 128.3 (s, 2C), 128.2 (s, 1C), 127.3 (s, 1C), 126.6 (s, 1C), 125.7 (s, 1C), 61.4 (d, $^3J_{PC}$ = 16.6 Hz, 1C), 18.0 (s, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{21}H_{19}NOPS$, 364.0925, found 364.0927.

diphenyl(4-phenyl-4*H*-benzo[*e*][1,3]thiazin-2-yl)phosphine oxide (3g)



3g

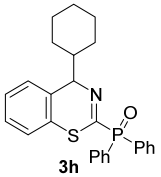
The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1, v/v) to provide **3g** as a white solid (105 mg, 62%). Mp: 170-172 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, J = 12.1, 7.3 Hz, 2H), 7.74 (dd, J = 12.1, 7.4 Hz, 2H), 7.52 (q, J = 8.0 Hz, 2H), 7.46−7.31 (m, 10H), 7.28−7.22 (m, 2H), 6.83−6.80 (m, 1H), 5.41 (d, J = 3.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6 (d, $^1J_{PC}$ = 128.1 Hz, 1C), 139.2 (s, 2C), 132.5 (s, 1C), 132.4 (s, 1C), 132.3 (s, 1C), 132.2 (s, 1C), 132.1 (s, 1C), 132.0 (s, 1C), 131.9 (s, 1C), 130.6 (d, $^1J_{PC}$ = 105.4 Hz, 1C), 130.2 (d, $^1J_{PC}$ = 105.7 Hz, 1C), 129.8 (s, 1C), 128.5 (s, 2C), 128.5 (s, 2C), 128.5 (s, 1C), 128.4 (s, 1C), 128.3 (s, 1C), 128.1 (s, 1C), 127.7 (s, 1C), 127.6 (s, 1C), 127.3 (s, 1C), 126.6 (s, 1C), 69.8 (d, $^3J_{PC}$ = 16.8 Hz, 1C).

HRMS (ESI-TOF, [M + Na]$^+$): calcd for $C_{26}H_{20}NOPSNa$, 448.0901, found 448.0899.

(4-cyclohexyl-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3h)



3h

The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1, v/v) to provide **3h** as a white solid (121 mg, 70%). Mp: 116-118 ºC.

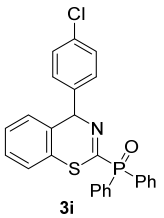
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88−7.81 (m, 4H), 7.53−7.51 (m, 2H), 7.46−7.43 (m, 4H), 7.29−7.26 (m, 1H), 7.23−7.19 (m, 2H), 7.10 (d, J = 7.4 Hz, 1H), 4.95 (d, J = 7.5 Hz, 1H), 1.85−1.84 (m, 1H), 1.61−1.57 (m, 4H), 1.32 (d, J = 11.5 Hz, 1H), 1.03−0.99 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6 (d, $^1J_{PC}$ = 132.8 Hz, 1C), 132.3 (s, 1C), 132.2 (s, 1C),

132.1 (s, 1C), 132.0 (s, 1C), 131.9 (s, 1C), 131.8 (s, 1C), 131.0 (d, $^{1}J_{PC}$ = 106.4 Hz, 1C), 129.9 (d, $^{1}J_{PC}$ = 103.6 Hz, 1C), 129.6 (s, 2C), 128.5 (s, 1C), 128.4 (s, 1C), 128.3 (s, 1C), 128.2 (s, 1C), 128.1 (s, 1C), 127.5 (s, 1C), 127.2 (s, 1C), 126.6 (s, 1C), 71.3 (d, $^{3}J_{PC}$ = 16.7 Hz, 1C), 40.5 (s, 1C), 30.4 (s, 1C), 29.4 (s, 1C), 26.2 (s, 1C), 26.0 (s, 1C), 25.8 (s, 1C).

HRMS (ESI-TOF, [M + H]$^{+}$): calcd for $C_{26}H_{27}NOPS$, 432.1551, found 432.1546.

(4-(4-chlorophenyl)-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3i)



3i

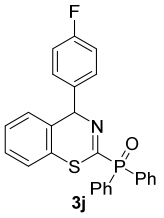
The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to provide **3i** as a light yellow solid (95 mg, 52%). Mp: 181-183 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (dd, J = 12.1, 7.5 Hz, 2H), 7.73 (dd, J = 12.2, 7.5 Hz, 2H), 7.54 (dd, J = 15.3, 7.9 Hz, 2H), 7.47−7.34 (m, 8H), 7.29−7.27 (m, 1H), 7.25−7.24 (m, 2H), 6.82 (d, J = 7.9 Hz, 1H), 5.34 (d, J = 3.1Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1 (d, $^{1}J_{PC}$ = 127.0 Hz, 1C), 137.6 (s, 1C), 133.5 (s, 1C), 132.5 (s, 1C), 132.4 (s, 1C), 132.1 (s, 1C), 132.0 (s, 2C), 131.9 (s, 1C), 131.8 (s, 1C), 130.3 (d, $^{1}J_{PC}$ = 105.8 Hz, 1C), 129.9 (d, $^{1}J_{PC}$ = 105.8 Hz, 1C), 129.8 (s, 2C), 129.7 (s, 1C), 128.6 (s, 2C), 128.5 (s, 1C), 128.5 (s, 1C), 128.4 (s, 1C), 128.3 (s, 1C), 128.2 (s, 1C), 127.8 (s, 1C), 127.0 (s, 1C), 126.6 (s, 1C), 69.1 (d, $^{3}J_{PC}$ = 16.7 Hz, 1C).

HRMS (ESI-TOF, [M + H]$^{+}$): calcd for $C_{26}H_{20}NOPSCl$, 460.0692, found 460.0687.

(4-(4-fluorophenyl)-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3j)



3j

The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to provide **3j** as a white solid (71 mg, 40%). Mp: 185-187 ºC.

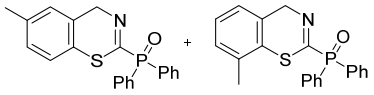
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90−7.85 (m, 2H), 7.72 (dd, J = 12.2, 7.3 Hz, 2H), 7.53 (q, J = 7.8 Hz, 2H), 7.47−7.36 (m, 5H), 7.30−7.26 (m, 4H), 7.06 (t, J = 8.6 Hz, 2H), 6.83−6.81 (m, 1H), 5.38 (d, J = 3.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9 (d, $^{1}J_{PC}$ = 127.4 Hz, 1C), 162.2 (d, $^{1}J_{FC}$ = 246.3 Hz, 1C), 135.0 (s, 1C), 132.5 (s, 1C), 132.4 (s, 1C), 132.3 (s, 1C), 132.2 (s, 1C), 132.1 (s, 1C), 131.9 (s,

1C), 131.8 (s, 1C), 130.5 (d, $^{1}J_{PC}$ = 105.6 Hz, 1C), 130.2 (s, 1C), 130.1 (s, 1C), 130.0 (d, $^{1}J_{PC}$ = 105.8 Hz, 1C), 129.7 (s, 1C), 128.6 (s, 1C), 128.5 (s, 1C), 128.4 (s, 1C), 128.3 (s, 1C), 128.2 (s, 1C), 127.8 (s, 1C), 127.1 (s, 1C), 126.6 (s, 1C), 115.4 (d, $^{2}J_{FC}$ = 21.4, 2C), 69.1 (d, $^{3}J_{PC}$ = 16.8 Hz, 1C).

HRMS (ESI-TOF, [M + H]$^{+}$): calcd for $C_{26}H_{20}NOFSP$, 444.0987, found 444.0984.

(6-methyl-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3k/3k')



3k/3k', ratio 4.4:1

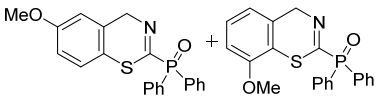
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3k/3k'** as a white solid (135 mg, 93%). Mp: 131-132 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81−7.77 (m, 4.91H), 7.55−7.52 (m, 2.45H), 7.46−7.42 (m, 4.91H), 7.22 (t, *J* = 7.4 Hz, 0.23H), 7.16−7.14 (m, 1H), 7.11 (t, *J* = 7.7 Hz, 0.45H), 7.09−7.08 (m, 2H), 4.74 (m, 2.45H), 2.34 (s, 3H), 2.30 (s, 0.68H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4 (d, $^{1}J_{PC}$ = 129.0 Hz, 1C), 138.1 (s, 1C), 132.4 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.1 (d, $^{1}J_{PC}$ = 105.6 Hz, 2C), 129.1 (s, 1C), 128.9 (s, 1C), 128.7 (s, 1C), 128.5 (s, 2C), 128.4 (s, 2C), 127.6 (s, 1C), 126.1 (s, 1C), 57.9 (d, $^{3}J_{PC}$ = 17.2 Hz, 1C), 21.0 (s, 1C).

HRMS (ESI-TOF, [M + H]$^{+}$): calcd for $C_{21}H_{19}NOPS$, 364.0925, found 364.0920.

(6-methoxy-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3l/3n)



3l/3n, ratio 3.2:1

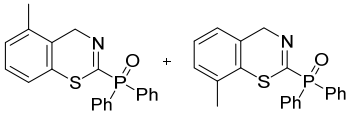
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3l/3n** as a white solid (126 mg, 83%). Mp: 110-112 ºC.

^{1}H NMR (400 MHz, DMSO): δ 7.77−7.69 (m, 5.26H), 7.64−7.62 (m, 2.62H), 7.56−7.55 (m, 5.26H), 7.38−7.34 (m, 0.31H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 7.02−6.99 (m, 0.62H), 6.95−6.93 (m, 1H), 4.81−4.79 (m, 2.62H), 3.81 (s, 0.93H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, DMSO): δ 165.3 (d, $^{1}J_{PC}$ = 128.1 Hz, 1C), 160.2 (s, 1C), 133.9 (s, 2C), 132.6 (s, 2C), 132.3 (s, 2C), 130.9 (s, 1C), 130.7 (d, $^{1}J_{PC}$ = 104.7 Hz, 2C), 128.5 (s, 2C), 128.3 (s, 2C), 126.8 (s, 1C), 119.9 (s, 1C), 114.1 (s, 1C), 112.2 (s, 1C), 57.6 (d, $^{3}J_{PC}$ = 17.1 Hz, 1C), 55.1 (s, 1C).

HRMS (ESI-TOF, [M + H]$^{+}$): calcd for $C_{21}H_{19}NO_2PS$, 380.0874, found 380.0874.

(5-methyl-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3m/3k')



3m/3k', ratio 1:10

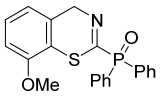
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3m/3k'** as a white solid (126 mg, 87%). Mp: 118-120 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82−7.76 (m, 4.4H), 7.54 (t, J = 7.4 Hz, 2.2H), 7.46−7.42 (m, 4.4H), 7.22 (t, J = 7.4 Hz, 1H), 7.15−7.10 (m, 2.3H), 4.80 (d, J = 2.7 Hz, 0.2H), 4.75 (d, J = 2.6 Hz, 2H), 2.43 (s, 0.3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, $^1J_{PC}$ = 128.8 Hz, 1C), 138.1 (s, 1C), 132.4 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.1 (d, $^1J_{PC}$ = 105.5 Hz, 2C), 129.1 (s, 1C), 128.7 (s, 1C), 128.5 (s, 2C), 128.4 (s, 2C), 127.6 (s, 1C), 126.7 (s, 1C), 126.1 (s, 1C), 57.9 (d, $^3J_{PC}$ = 17.3 Hz, 1C), 21.0 (s, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{21}H_{19}NOPS$, 364.0925, found 364.0927.

(5-methoxy-4*H*-benzo[*e*][1,3]thiazin-2-yl)diphenylphosphine oxide (3n)



3n

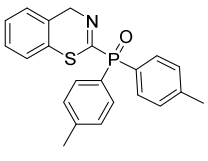
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3n** as a white solid (93 mg, 61%). Mp: 163-165 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, J = 12.0, 7.7 Hz, 4H), 7.58−7.56 (m, 2H), 7.50−7.46 (m, 4H), 7.30 (t, J = 7.9 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 4.82 (d, J = 2.4 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2 (d, $^1J_{PC}$ = 128.8 Hz, 1C), 154.8 (s, 1C), 132.4 (s, 2C), 132.1 (s, 2C), 132.0 (s, 2C), 130.4 (d, $^1J_{PC}$ = 105.2 Hz, 2C), 129.5 (s, 1C), 128.6 (s, 1C), 128.5 (s, 2C), 128.4 (s, 2C), 119.2 (s, 1C), 118.0 (s, 1C), 109.3 (s, 1C), 57.4 (d, $^3J_{PC}$ = 17.6 Hz, 1C), 55.9 (s, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{21}H_{19}NO_2PS$, 380.0874, found 380.0869.

(4*H*-benzo[*e*][1,3]thiazin-2-yl)di-p-tolylphosphine oxide (3o)



3o

The crude product was purified by silica gel column chromatography (dichloromethane/ethyl

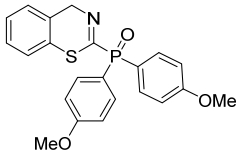
acetate = 15:1, v/v) to provide **3o** as a white solid (130 mg, 86%). Mp: 158-160 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (dd, J = 12.0, 8.1 Hz, 4H), 7.33−7.29 (m, 1H), 7.28−7.24 (m, 7H), 4.76 (d, J = 2.7 Hz, 2H), 2.38 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5 (d, $^1J_{PC}$ = 128.0 Hz, 1C), 143.0 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.0 (s, 1C), 129.2 (s, 4C), 129.1 (s, 2C), 127.9 (s, 1C), 127.8 (s, 1C), 127.3 (s, 1C), 126.9 (s, 1C),126.4 (s, 1C), 57.9 (d, $^3J_{PC}$ = 17.1 Hz, 1C), 21.6 (s, 2C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{22}H_{21}NOPS$, 378.1081, found 378.1078.

(4*H*-benzo[*e*][1,3]thiazin-2-yl)bis(4-methoxyphenyl)phosphine oxide (3p)



3p

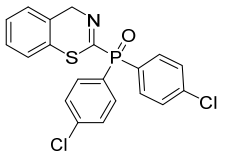
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3p** as a white solid (151 mg, 92%). Mp: 178-180 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, J = 11.6 Hz, 8.7 Hz, 4H), 7.33−7.30 (m, 1H), 7.29−7.27 (m, 3H), 6.95 (dd, J = 8.8, 2.2 Hz, 4H), 4.76 (d, J = 2.5 Hz, 2H), 3.83 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.8 (d, $^1J_{PC}$ = 128.5 Hz, 1C), 162.8 (s, 2C), 133.9 (s, 2C), 133.8 (s, 2C), 130.0 (s, 1C), 129.3 (s, 1C), 127.9 (s, 1C), 127.8 (s, 1C), 127.0 (s, 1C), 126.4 (s, 1C), 121.3 (d, $^1J_{PC}$ = 113.1 Hz, 2C), 114.1 (s, 2C), 114.0 (s, 2C), 57.9 (d, $^3J_{PC}$ = 17.3 Hz, 1C), 55.3 (s, 2C).

HRMS (ESI-TOF, [M + Na]$^+$): calcd for $C_{22}H_{20}NO_3PSNa$, 432.0799, found 432.0797.

(4*H*-benzo[*e*][1,3]thiazin-2-yl)bis(4-chlorophenyl)phosphine oxide (3q)



3q

The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3q** as a white solid (133 mg, 80%). Mp: 143-145 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (dd, J = 11.7, 8.4 Hz, 4H), 7.43 (dd, J = 8.3, 2.1 Hz, 4H), 7.35−7.31 (m, 1H), 7.28−7.27 (m, 3H), 4.77 (d, J = 2.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9 (d, $^1J_{PC}$ = 131.8 Hz, 1C), 139.4 (s, 2C), 133.3 (s, 2C), 133.2 (s, 2C), 129.4 (s, 2C), 129.0 (s, 2C), 128.9 (s, 2C), 128.3 (d, $^1J_{PC}$ = 107.6 Hz, 2C), 128.2 (s, 1C), 128.0 (s, 1C), 127.1 (s, 1C), 126.4 (s, 1C), 57.9 (d, $^3J_{PC}$ = 17.8 Hz, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{20}H_{15}NOPSCl_2$, 417.9989, found 417.9991.

(4*H*-benzo[*e*][1,3]thiazin-2-yl)bis(4-fluorophenyl)phosphine oxide (3r)

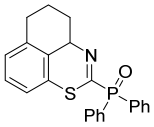
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3r** as a white solid (94 mg, 61%). Mp: 138-140 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81−7.76 (m, 4H), 7.34−7.29 (m, 1H), 7.27−7.26 (m, 3H), 7.15−7.11 (m, 4H), 4.76 (d, J = 2.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4 (d, $^1J_{FC}$ = 254.4 Hz, 2C), 165.1 (d, $^1J_{PC}$ = 131.6 Hz, 1C), 134.6 (s, 1C), 134.5 (s, 2C), 134.4 (s, 1C), 129.5 (s, 1C), 129.0 (s, 1C), 128.2 (s, 1C), 128.0 (s, 1C), 127.0 (s, 1C), 126.4 (s, 1C), 125.9 (d, $^1J_{PC}$ = 110.2 Hz, 2C), 116.0 (dd, $^2J_{FC}$ = 21.3, 13.8 Hz, 4C), 57.9 (d, $^3J_{PC}$ = 17.8 Hz, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{20}H_{15}NOF_2PS$, 386.0580, found 386.0575.

diphenyl(3a,4,5,6-tetrahydronaphtho[1,8-*de*][1,3]thiazin-2-yl)phosphine oxide (3s)



3s

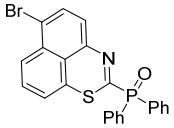
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3s** as a light yellow solid (143 mg, 92%). Mp: 166-168 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (dd, J = 12.0, 7.4 Hz, 2H), 7.78 (dd, J = 12.2, 7.5 Hz, 2H), 7.57−7.54 (m, 1H), 7.52−7.45 (m, 3H), 7.42−7.38 (m, 2H), 7.15−7.11 (m, 3H), 3.71 (dd, J = 13.0, 6.5 Hz, 1H), 2.81 (t, J = 6.0 Hz, 2H), 2.67−2.61 (m, 1H), 2.48−2.41 (m, 1H), 2.05−1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5 (d, $^1J_{PC}$ = 128.2 Hz, 1C), 138.1 (s, 1C), 132.3 (s, 2C), 131.8 (s, 1C), 131.7 (s, 1C), 130.9 (s, 1C), 130.8 (s, 1C), 130.1 (s, 1C), 129.9 (s, 1C), 129.7 (d, $^1J_{PC}$ = 177.6 Hz, 2C), 128.4 (s, 2C), 128.3 (s, 2C), 128.2 (s, 1C), 126.9 (s, 1C), 124.1 (s, 1C), 62.2 (d, $^3J_{PC}$ = 15.9 Hz, 1C), 31.1 (s, 1C), 29.6 (s, 1C), 21.3 (s, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{23}H_{21}NOPS$, 390.1081, found 390.1082.

(6-bromonaphtho[1,8-*de*][1,3]thiazin-2-yl)diphenylphosphine oxide (3t)



3t

The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 8:1, v/v) to provide **3t** as a light red solid (174 mg, 94%). Mp: 206-208 ºC.

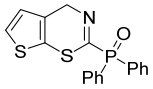
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82 (d, J = 7.7 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.25 (s, 1H), 8.04 (dd, J = 12.7, 7.4 Hz, 4H), 7.70−7.64 (m, 2H), 7.59−7.56 (m, 2H), 7.53−7.49 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.3 (d, $^1J_{PC}$ = 128.1 Hz, 1C), 151.8 (d, $^3J_{PC}$ = 20.8 Hz, 1C), 134.3 (s, 2C), 132.6 (s, 2C), 131.9 (s, 2C), 131.8 (s, 2C), 131.2 (d, $^1J_{PC}$ = 109.3 Hz, 1C), 129.8 (d, $^1J_{PC}$ = 103.1 Hz, 1C), 128.7 (s, 2C), 128.6 (s, 2C), 128.1 (s, 1C), 127.8 (s, 1C), 127.7 (s, 1C),

124.4 (s, 2C), 122.5 (s, 2C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{23}H_{16}NOPSBr$, 463.9874, found 463.9862.

diphenyl(4*H*-thieno[3,2-*e*][1,3]thiazin-2-yl)phosphine oxide (3u)



3u

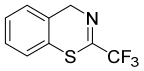
The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 15:1, v/v) to provide **3u** as a white solid (121 mg, 85%). Mp: 108-110 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (dd, J = 12.2, 7.3 Hz, 4H), 7.57−7.54 (m, 2H), 7.48−7.45 (m, 4H), 7.33 (d, J = 5.2 Hz, 1H), 6.83 (d, J = 5.1 Hz, 1H), 4.99 (d, J = 2.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0 (d, $^1J_{PC}$ = 130.7 Hz, 1C), 132.5 (s, 2C), 132.0 (s, 2C), 131.9 (s, 2C), 130.0 (d, $^1J_{PC}$ = 105.8 Hz, 2C), 128.5 (s, 2C), 128.4 (s, 2C), 126.7 (s, 1C), 125.9 (s, 1C), 125.1 (s, 1C), 124.7 (s, 1C), 53.2 (d, $^3J_{PC}$ = 17.9 Hz, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{18}H_{15}NOPS_2$, 356.0333, found 356.0330.

2-(trifluoromethyl)-4*H*-benzo[*e*][1,3]thiazine (3v)



3v

The crude product was purified by silica gel column chromatography (petroleum ether) to provide **3v** as a light yellow oil (70 mg, 81%).

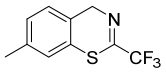
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.30 (m, 4H), 4.78 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.6 (q, $^2J_{FC}$ = 38.4 Hz, 1C), 129.0 (s, 1C), 128.4 (s, 1C), 128.2 (s, 1C), 127.7 (s, 1C), 127.3 (s, 1C), 126.7 (s, 1C), 118.8 (q, $^1J_{FC}$ =277.4 Hz, 1C), 55.9 (s, 1C).

^{19}F NMR (376 MHz, $CDCl_3$): δ -69.6.

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_9H_7F_3NS$, 218.0251, found 218.0251.

7-methyl-2-(trifluoromethyl)-4*H*-benzo[*e*][1,3]thiazine (3w)



3w

The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 500:1, v/v) to provide **3w** as a light yellow oil (69 mg, 75%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.22−7.18 (m, 1H), 7.17−7.13 (m, 2H), 4.75 (s, 2H), 2.37 (d, J = 8.2 Hz, 3H).

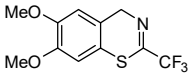
^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8 (q, $^2J_{FC}$ = 38.7 Hz, 1C), 138.7 (s, 1C), 129.0 (s, 1C), 128.0 (s, 1C), 127.0 (s, 1C), 126.4 (s, 1C), 124.2 (s, 1C), 118.9 (q, $^1J_{FC}$ = 277.5 Hz, 1C), 55.9 (s,

1C), 20.9 (s, 1C).

^{19}F NMR (376 MHz, $CDCl_3$): δ -69.7.

HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{10}H_9F_3NS$, 232.0408, found 232.0406.

6,7-dimethoxy-2-(trifluoromethyl)-4*H*-benzo[*e*][1,3]thiazine (3x)



3x

The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100:1, v/v) to provide **3x** as a white solid (85 mg, 77%). Mp: 99-101 ºC.

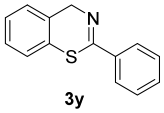
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (s, 2H), 4.72 (s, 2H), 3.87 (d, J = 8.0 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8 (q, $^2J_{FC}$ = 38.2 Hz, 1C), 149.6 (s, 1C), 149.1 (s, 1C), 120.9 (s, 1C), 118.9 (q, $^1J_{FC}$ = 277.5 Hz, 1C), 118.3 (s, 1C), 110.2 (s, 1C), 109.3 (s, 1C), 56.1 (s, 2C), 55.7 (s, 1C).

^{19}F NMR (376 MHz, DMSO): δ -68.8.

HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{11}H_{11}F_3NO_2S$, 278.0463, found 278.0464.

2-phenyl-4*H*-benzo[*e*][1,3]thiazine (3y)[8]



3y

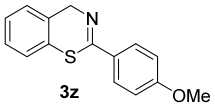
The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) to provide **3y** as a light yellow solid (74 mg, 82%). Mp: 41-42 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 7.3 Hz, 2H), 7.47−7.37 (m, 4H), 7.33−7.27 (m, 3H), 4.78 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6 (s, 1C), 136.9 (s, 1C), 131.3 (s, 1C), 131.1 (s, 1C), 130.9 (s, 1C), 128.4 (s, 2C), 127.7 (s, 2C), 127.4 (s, 2C), 126.8 (s, 1C), 126.5 (s, 1C), 56.7 (s, 1C).

[8] W. R. Bowman, H. Heaney, B. M. Jordan, *Tetrahedron* **1991**, *47*, 10119-10128.

2-(4-methoxyphenyl)-4*H*-benzo[*e*][1,3]thiazine (3z)



3z

The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1, v/v) to provide **3z** as a white solid (69 mg, 68%). Mp: 78-80 ºC.

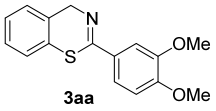
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.6 Hz, 2H), 7.40−7.39 (m, 1H), 7.34−7.28 (m, 3H), 6.94 (d, J = 8.6 Hz, 2H), 4.76 (s, 2H), 3.85 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0 (s, 1C), 161.0 (s, 1C), 131.7 (s, 1C), 131.1 (s, 1C), 129.6 (s, 1C), 129.4 (s, 2C), 127.5 (s, 1C), 127.4 (s, 1C), 126.8 (s, 1C), 126.6 (s, 1C), 113.8 (s, 2C),

56.6 (s, 1C), 55.4 (s, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{15}H_{14}NOS$, 256.0796, found 256.0800.

2-(3,4-dimethoxyphenyl)-4*H*-benzo[*e*][1,3]thiazine (3aa)



3aa

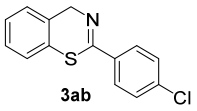
The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to provide **3aa** as a light yellow solid (83 mg, 73%). Mp: 120-122 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 8.4 Hz, 1H), 7.59 (s, 1H), 7.40−7.39 (m, 1H), 7.32−7.28 (m, 3H), 6.89 (d, J = 8.4 Hz, 1H), 4.76 (s, 2H), 3.94 (d, J = 16.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0 (s, 1C), 151.6 (s, 1C), 148.9 (s, 1C), 131.7 (s, 1C), 131.1 (s, 1C), 129.7 (s, 1C), 127.4 (s, 2C), 126.7 (s, 1C), 126.5 (s, 1C), 121.3 (s, 1C), 110.2 (s, 1C), 109.9 (s, 1C), 56.5 (s, 1C), 55.9 (s, 2C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{16}H_{16}NO_2S$, 286.0902, found 286.0905.

2-(4-chlorophenyl)-4*H*-benzo[*e*][1,3]thiazine (3ab)



3ab

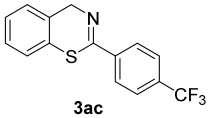
The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1, v/v) to provide **3ab** as a white solid (66 mg, 64%). Mp: 122-124 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.5 Hz, 2H), 7.41−7.38 (m, 3H), 7.34−7.29 (m, 3H), 4.79 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5 (s, 1C), 137.3 (s, 1C), 135.4 (s, 1C), 131.2 (s, 1C), 130.6 (s, 1C), 129.0 (s, 2C), 128.7 (s, 2C), 127.6 (s, 2C), 126.9 (s, 1C), 126.6 (s, 1C), 56.7 (s, 1C).

HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{14}H_{11}NSCl$, 260.0301, found 260.0307.

2-(4-(trifluoromethyl)phenyl)-4*H*-benzo[*e*][1,3]thiazine (3ac)



3ac

The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100:1, v/v) to provide **3ac** as a light yellow solid (88 mg, 75%). Mp: 76-78 ºC

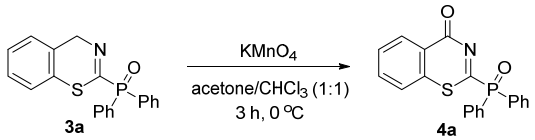
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.39−7.37 (m, 1H), 7.36−7.28 (m, 3H), 4.82 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4 (s, 1C), 140.1 (s, 1C), 132.7 (q, $^2J_{FC}$ = 32.6 Hz, 1C), 130.8 (s, 1C), 130.3 (s, 1C), 128.0 (s, 2C), 127.8 (s, 1C), 127.7 (s, 1C), 126.9 (s, 1C), 126.6 (s, 1C), 125.4 (q, $^3J_{FC}$ = 3.8 Hz, 2C), 123.8 (q, $^1J_{FC}$ = 272.4 Hz, 1C), 56.9 (s, 1C).

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7.

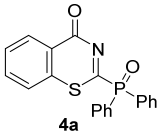
HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{15}H_{11}F_3NS$, 294.0564, found 294.0571.

5. Oxidation experiment



To a solution of $KMnO_4$ (190 mg, 1.2 mmol) in acetone (5 mL) and $CHCl_3$ (5 mL) was added **3a** (140 mg, 0.4 mmol). The reaction mixture was stirred at 0 °C under an air atmosphere for 3 h. Then, $CHCl_3$ (5 mL) was added, and the precipitated MnO_2 was removed by filtration. The solvent was evaporated and the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to provide **4a** as a white solid (87 mg, 60%). Mp: 185-187 °C.

2-(diphenylphosphoryl)-4*H*-benzo[*e*][1,3]thiazin-4-one (4a)

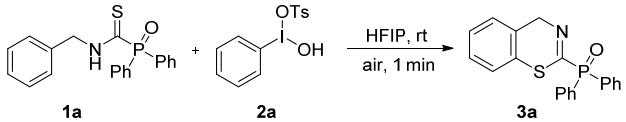


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50−8.48 (m, 1H), 8.08−8.04 (m, 4H), 7.72−7.65 (m, 2H), 7.62−7.55 (m, 3H), 7.54−7.49 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8 (d, $^1J_{PC}$ = 115.8 Hz, 1C), 167.1 (s, 1C), 166.9 (s, 1C), 136.0 (s, 1C), 133.1 (s, 2C), 132.3 (s, 2C), 132.2 (s, 2C), 131.0 (s, 1C), 130.8 (s, 1C), 128.9 (s, 2C), 128.8 (d, $^1J_{PC}$ = 106.2 Hz, 2C), 128.7 (s, 2C), 126.7 (s, 1C), 121.4 (s, 1C).

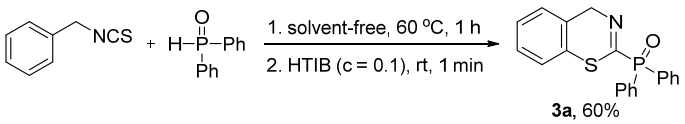
HRMS (ESI-TOF, [M + H]$^+$): calcd for $C_{20}H_{15}NO_2PS$, 364.0561, found 364.0558.

6. Gram scale synthesis



To a solution of *N*-benzyl-1-(diphenylphosphoryl)methanethioamide **1a** (2.106 g, 6 mmol) in HFIP (60 mL) was added HTIB **2a** (2.352 g, 6 mmol). The reaction mixture was stirred at room temperature under an air atmosphere for 1 min. The mixture was quenched with saturated $NaHCO_3$ (60 mL) and extracted with DCM (3 × 60 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. Evaporation of the solvent, followed by purification on silica gel, provided product **3a** (1.571 g, 75%).

7. One-pot reaction



3a, 60%

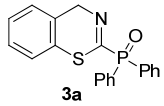
To a 15 mL sealed tube was charged with a mixture of (isothiocyanatomethyl)benzene (60 mg, 0.4 mmol) and diphenylphosphine oxide (81 mg, 0.4 mmol). The reaction mixture was stirred at 60 °C for 1 h. After completion, the mixture was cooled to room temperature, added with HFIP (4.0 mL) and HTIB **2a** (157 mg, 0.4 mmol). The reaction mixture was stirred at room temperature under an air atmosphere for 1 min. Then, the mixture was quenched with saturated $NaHCO_3$ (10 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent, followed by purification on silica gel, provided product **3a** (84 mg, 60%).

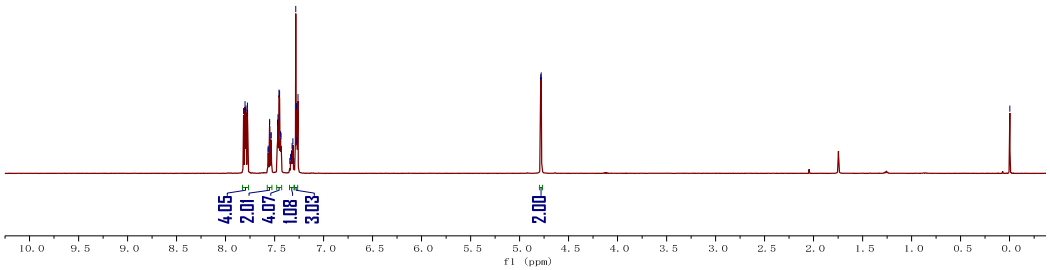
8. Radical inhibition experiment

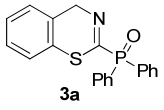
To a solution of **1a** (140 mg, 0.4 mmol) in HFIP (4.0 mL) was added TEMPO (63 mg, 0.4 mmol) and HTIB **2a** (157 mg, 0.4 mmol). The reaction mixture was stirred at room temperature under an air atmosphere for 1 min. The mixture was quenched with saturated $NaHCO_3$ (10 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent, followed by purification on silica gel, provided product **3a** (95 mg, 68%).

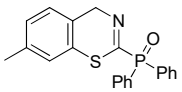
To a solution of **1a** (141 mg, 0.4 mmol) in HFIP (4.0 mL) was added 1,1-diphenylethylene (72 mg, 0.4 mmol) and HTIB **2a** (157 mg, 0.4 mmol). The reaction mixture was stirred at room temperature under an air atmosphere for 1 min. The mixture was quenched with saturated $NaHCO_3$ (10 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. Evaporation of the solvent, followed by purification on silica gel, provided product **3a** (101 mg, 72%).

9. ^{1}H NMR and ^{13}C NMR spectra

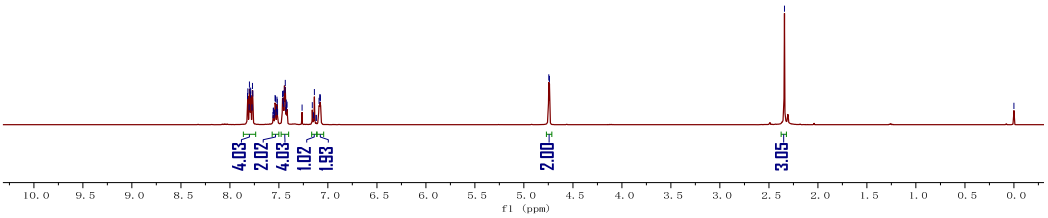


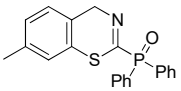




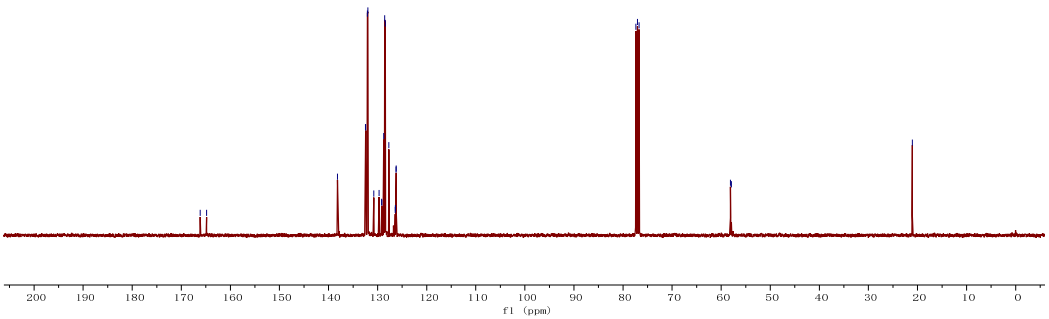


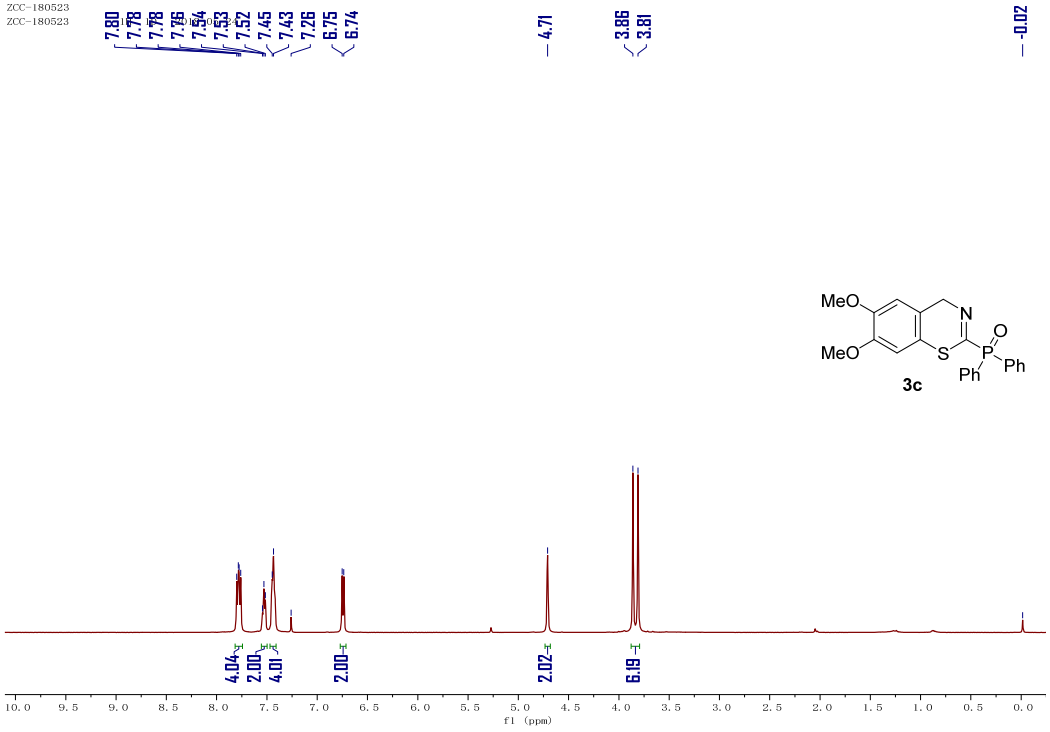
3b





3b

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7.26
6.75
6.74
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3.86
3.81
-0.02
MeO
MeO
N
S
O
P
Ph
Ph
Ph
3c
4.04
2.00
4.01
2.00
2.02
6.19
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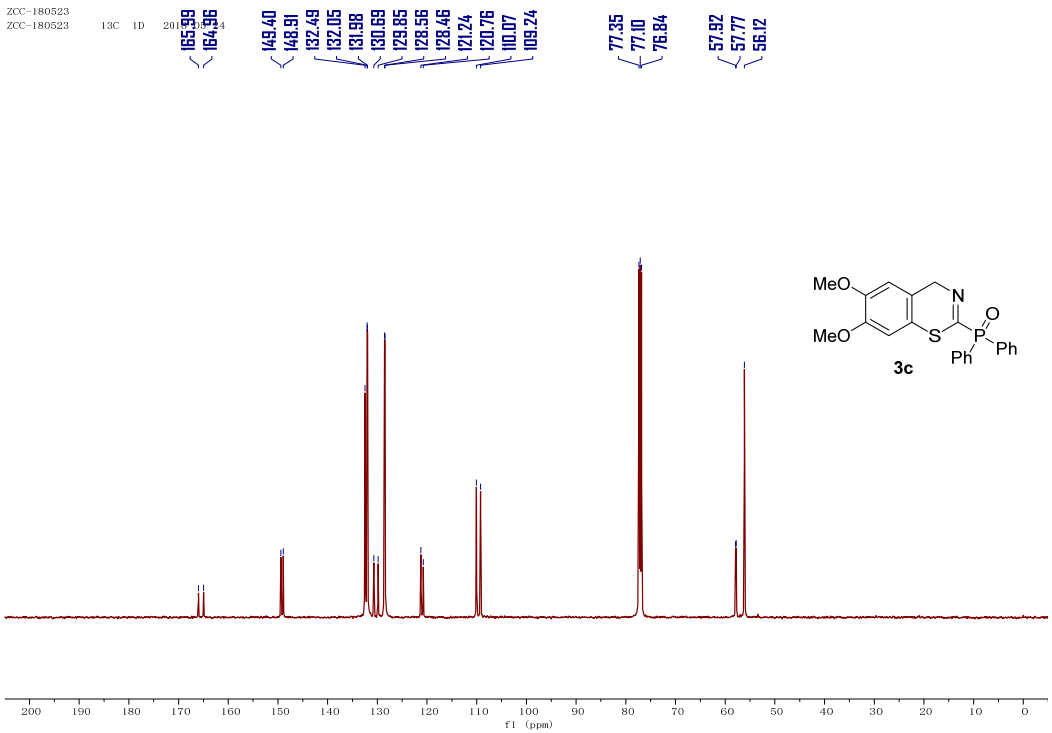
f1 (ppm)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ZCC-180523
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120.76
110.07
109.24
77.35
77.10
76.84
57.92
57.77
56.12
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MeO
N
S
O
P
Ph
Ph
Ph
3c
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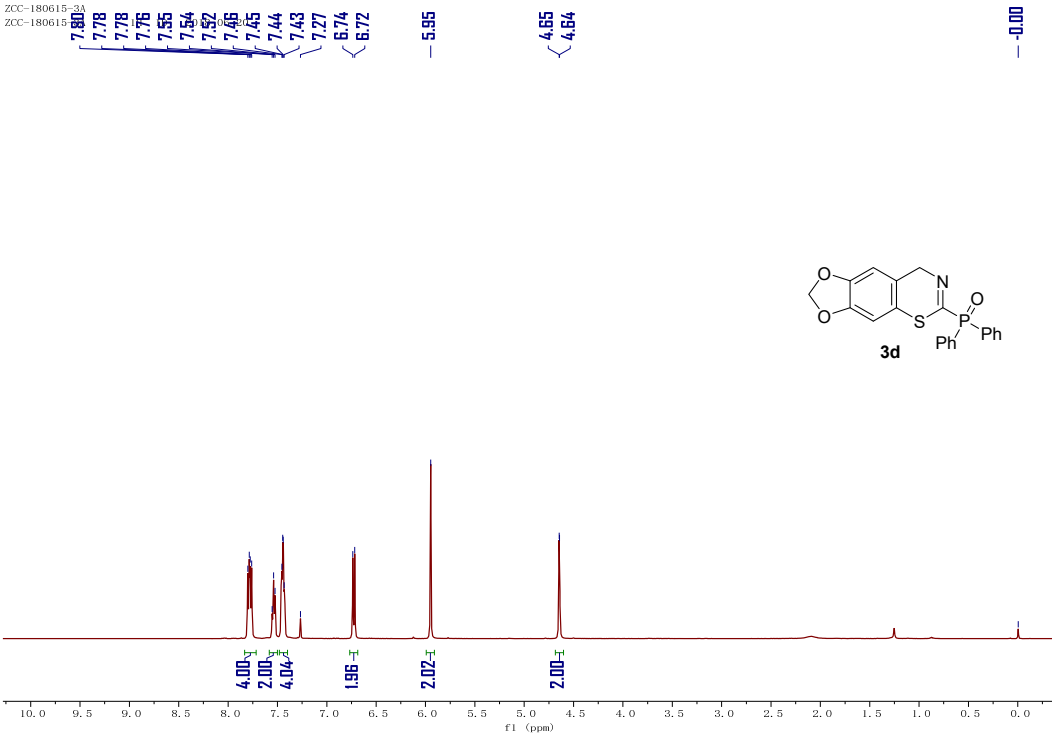
f1 (ppm)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6.72
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3d
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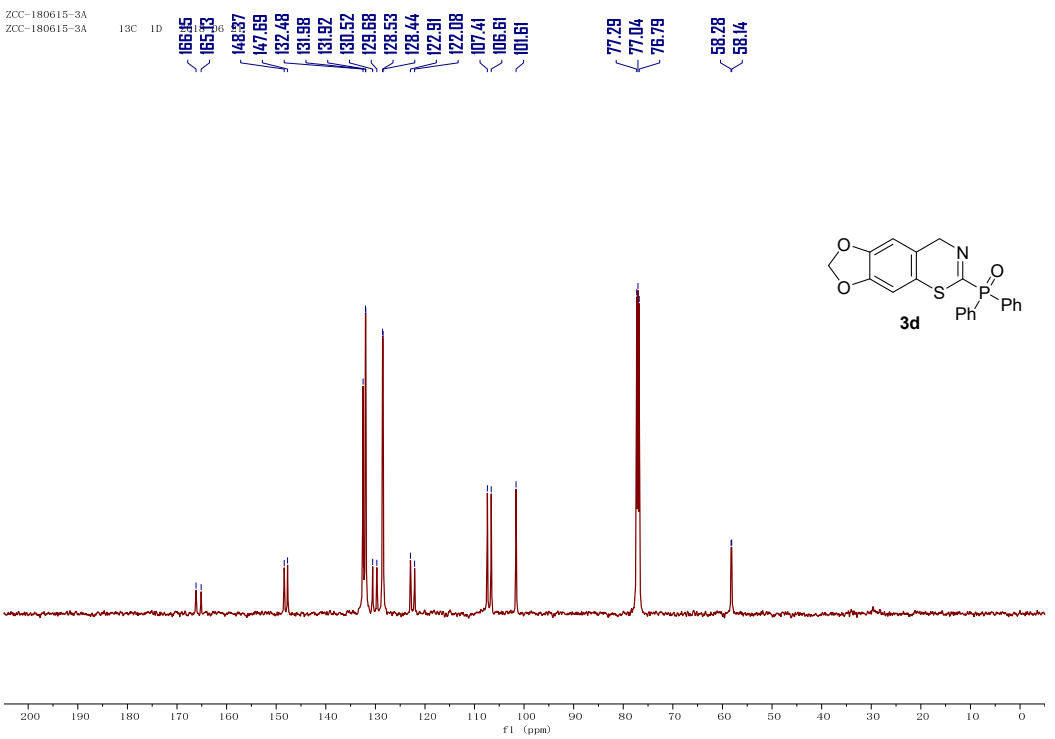
2.00
4.04
1.96
2.02
2.00
f1 (ppm)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ZCC-180615-3A 13C 1D
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130.52
129.68
128.53
128.44
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122.08
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106.61
101.61
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77.04
76.79
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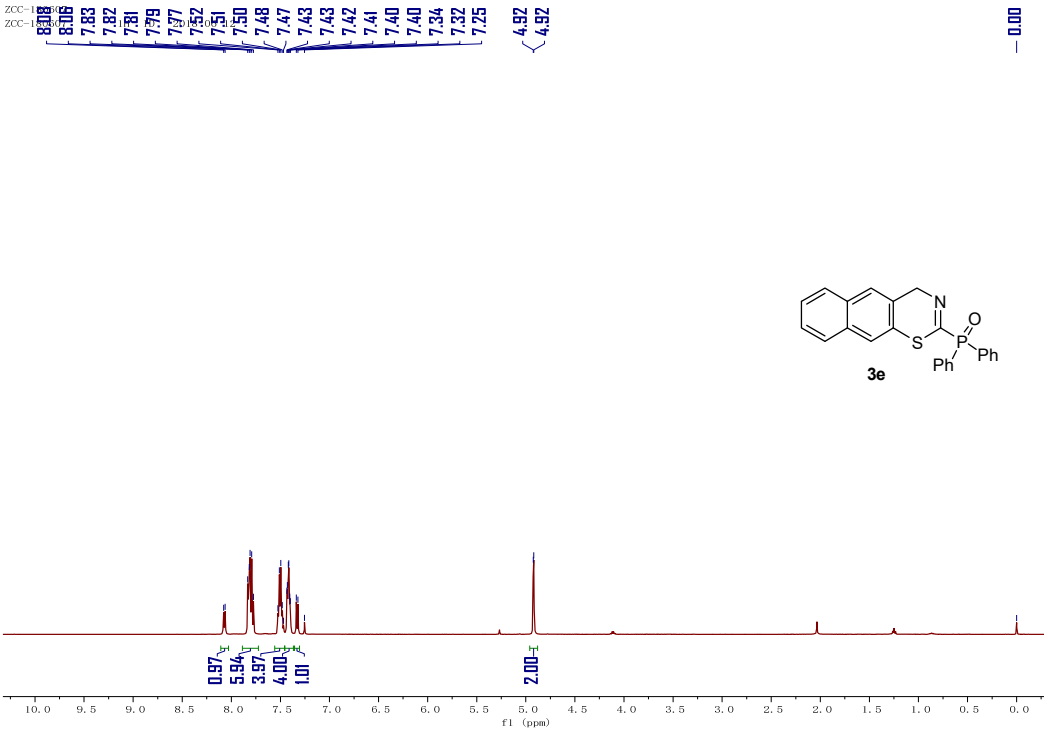
58.14
3d
f1 (ppm)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7.32
7.25
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4.92
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O
P
Ph
Ph
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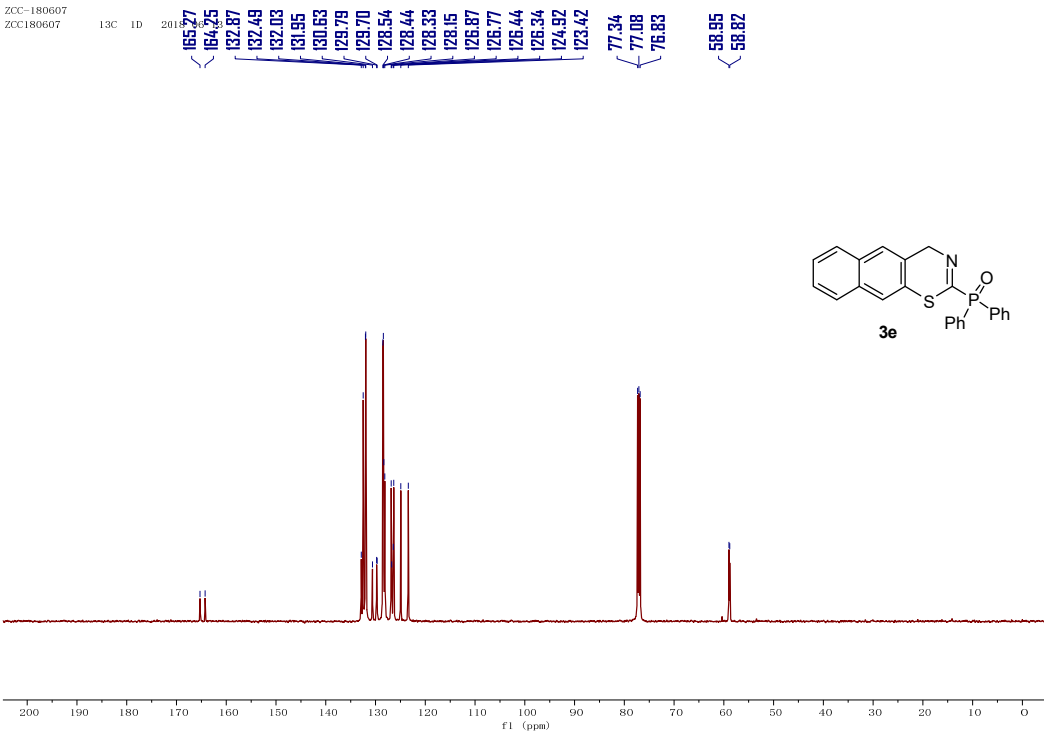
f1 (ppm)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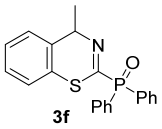
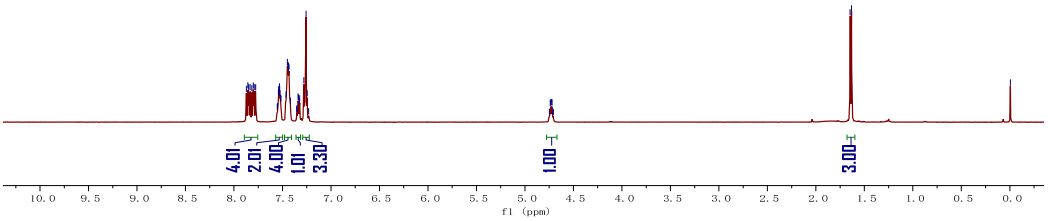
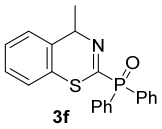
Ph
Ph
3e
f1 (ppm)

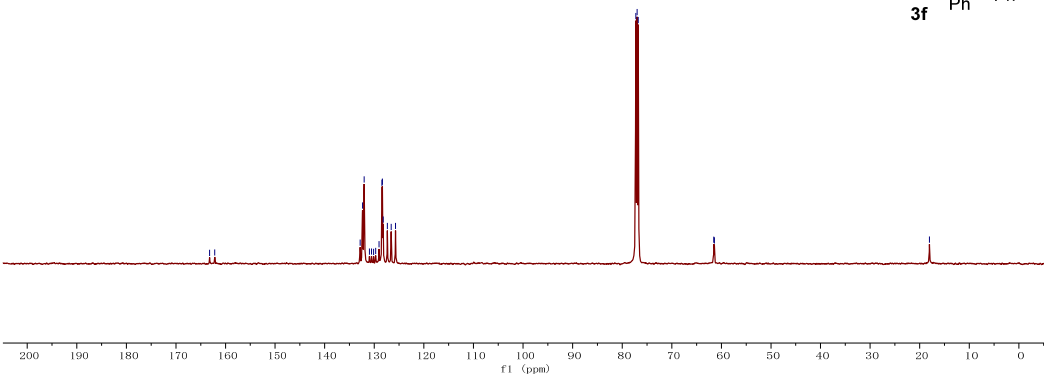


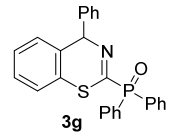
3f



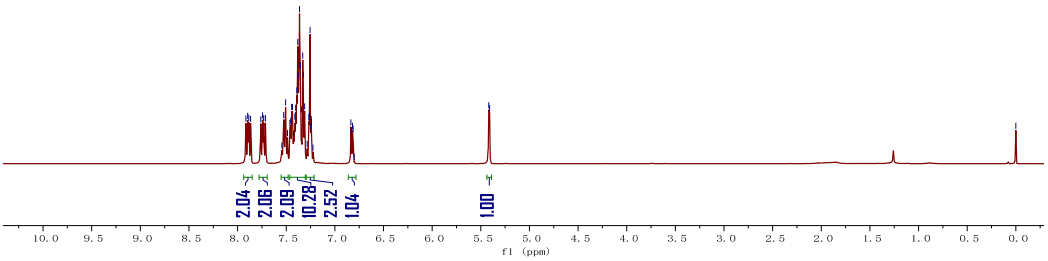


3f





3g



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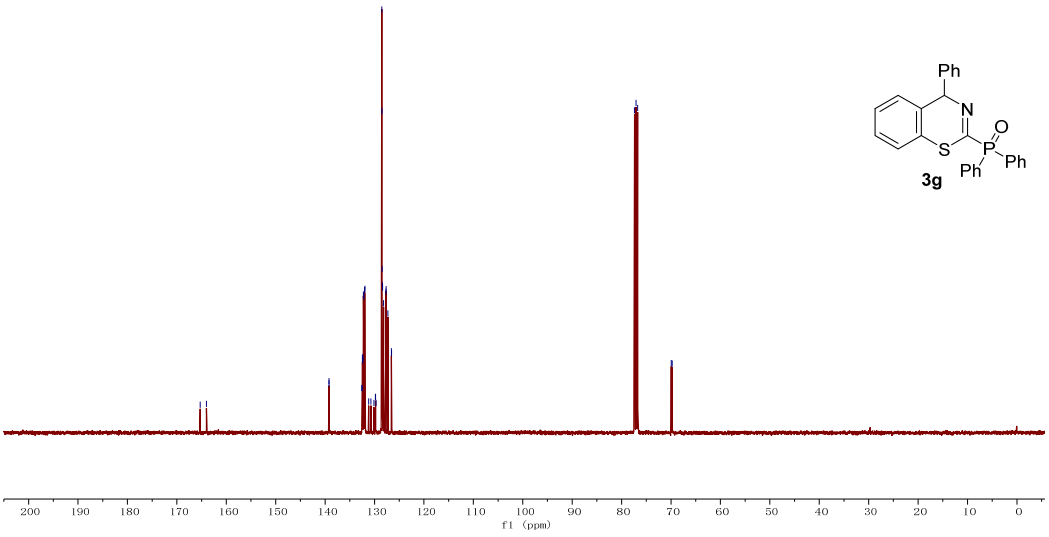

3g


ZCC-180524
ZCC-180524
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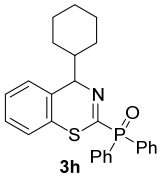
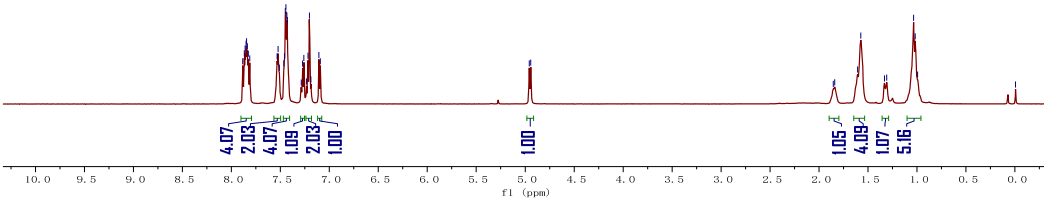

N
O
S
P
Ph
Ph

3h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9.0
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6.0
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4.0
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2.5
2.0
1.5
1.0
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f1 (ppm)


ZCC-180524
ZCC-180524
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132.09
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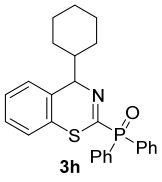
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Ph
Ph

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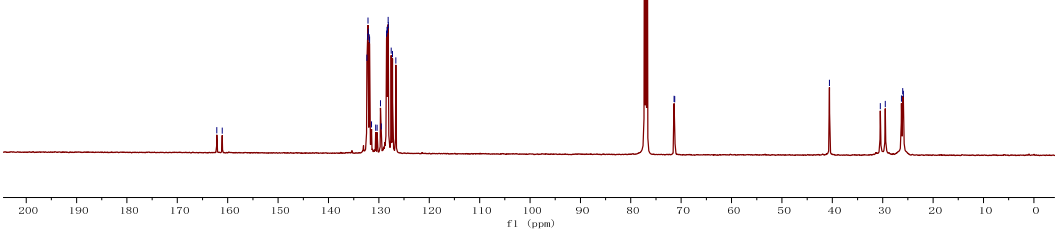
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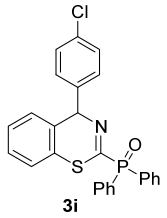
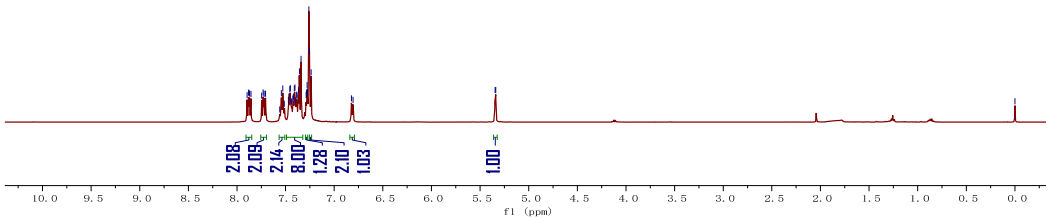
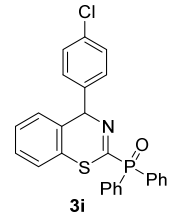
0
f1 (ppm)


Cl
N
S
O
P
Ph
Ph

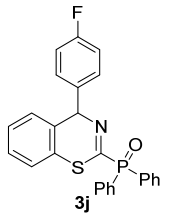
3i


2.08
2.05
2.14
8.00
1.28
2.10
1.03
1.00
f1 (ppm)

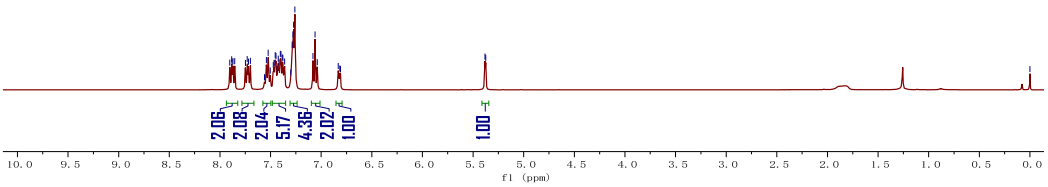

Cl
N
S
O
P
Ph
Ph

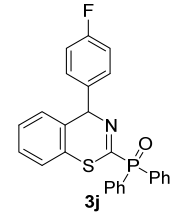
3i

f1 (ppm)

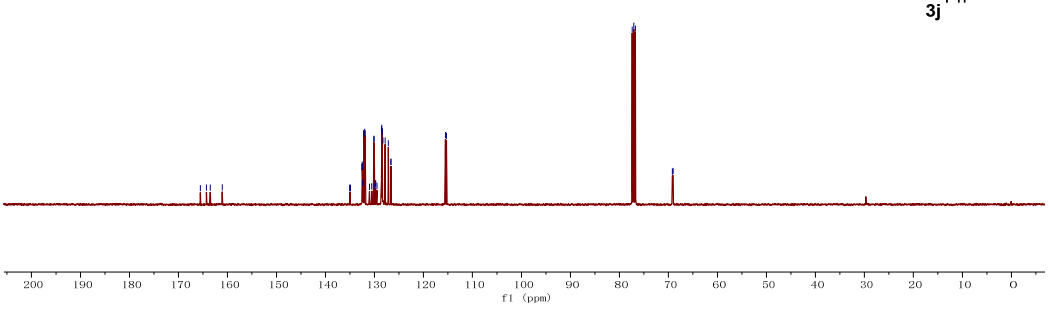

F
N
O
S
P
Ph
Ph

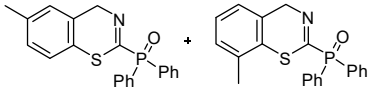
3j


2.06
2.08
2.04
5.17
4.38
2.02
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

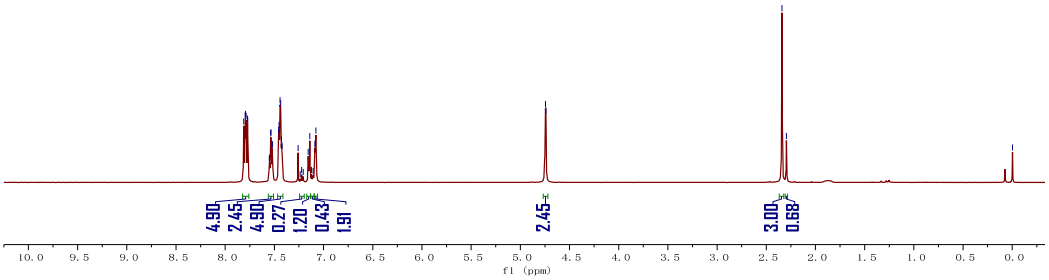

F
N
O
S
P
Ph
Ph

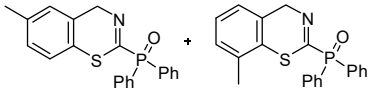
3j


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

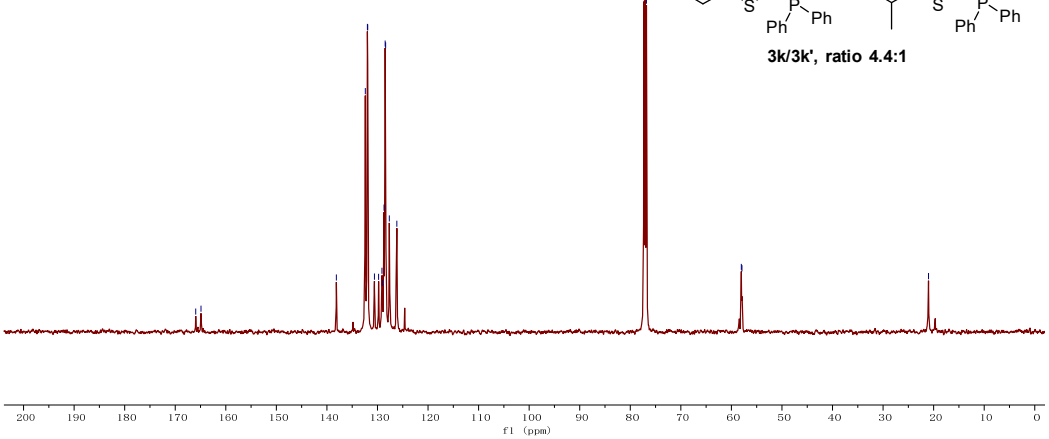


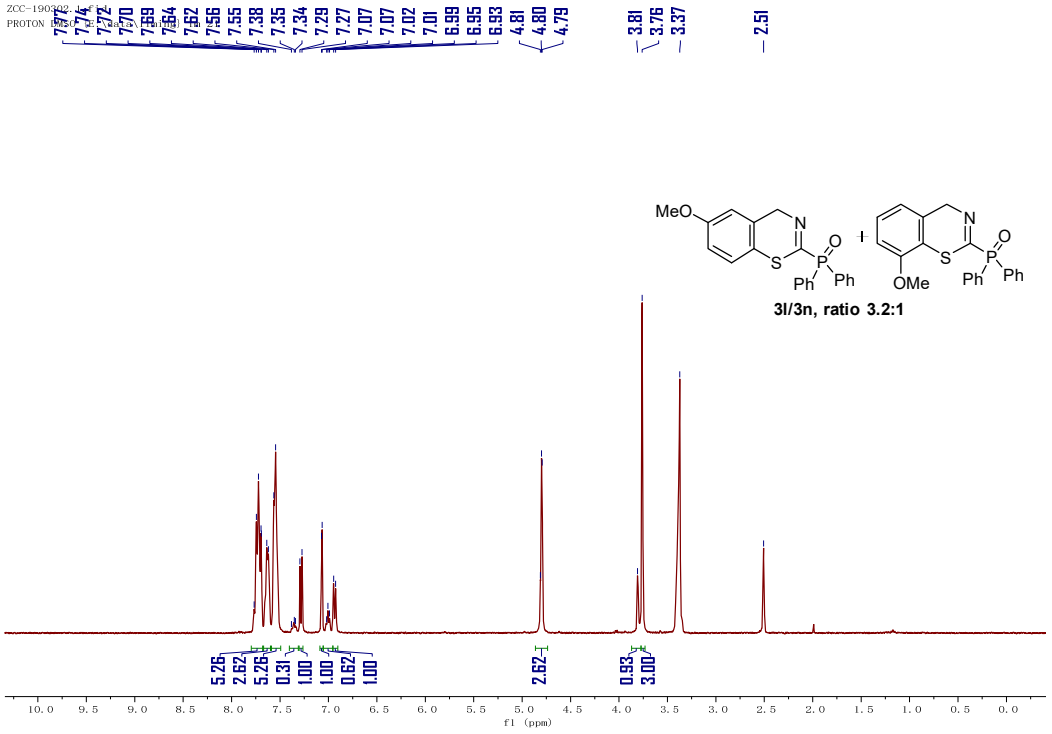
3k/3k', ratio 4.4:1

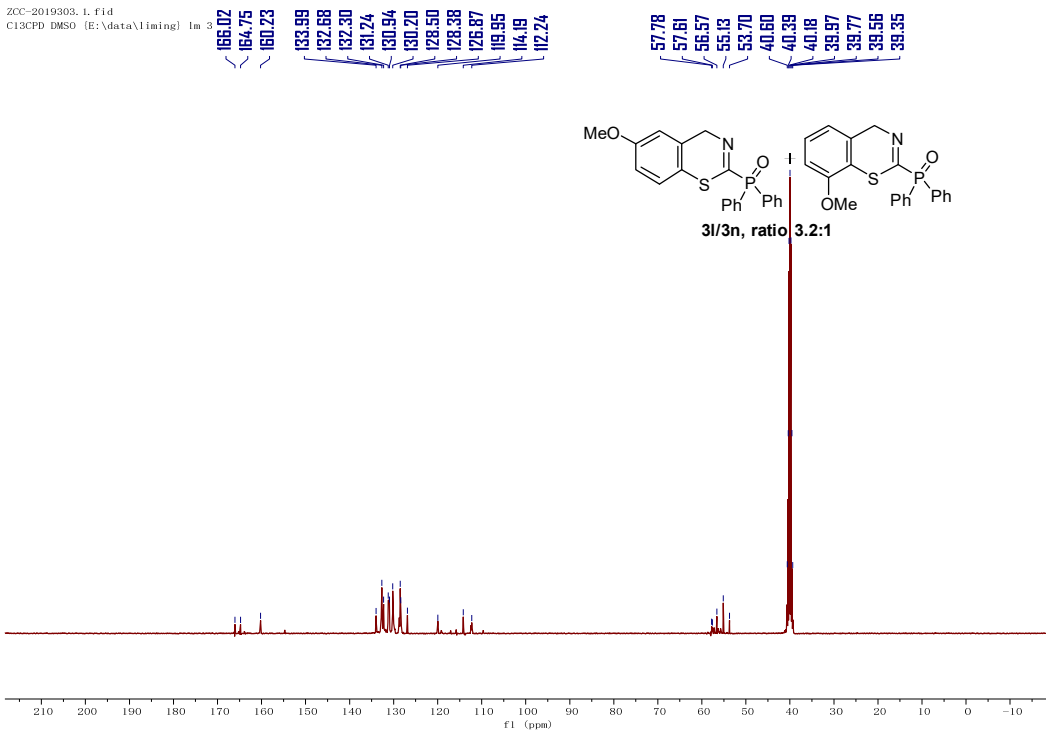


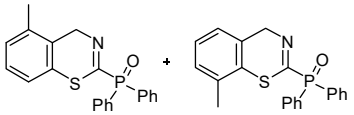


3k/3k', ratio 4.4:1

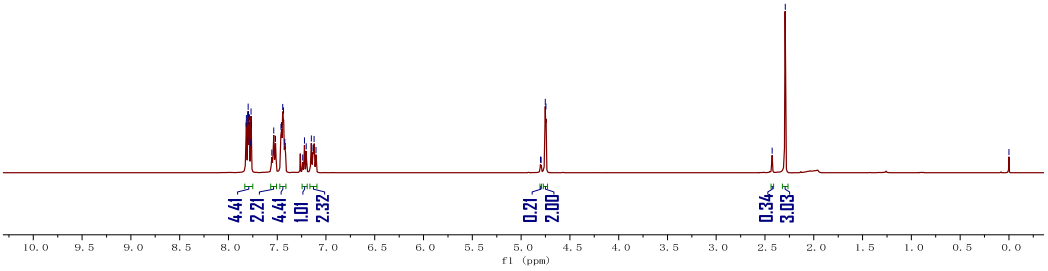


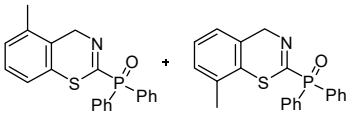

MeO
N
S
O
P
Ph
Ph
OMe
3l/3n, ratio 3.2:1
f1 (ppm)


MeO
N
S
O
P
Ph
Ph
OMe
3l/3n, ratio 3.2:1
f1 (ppm)

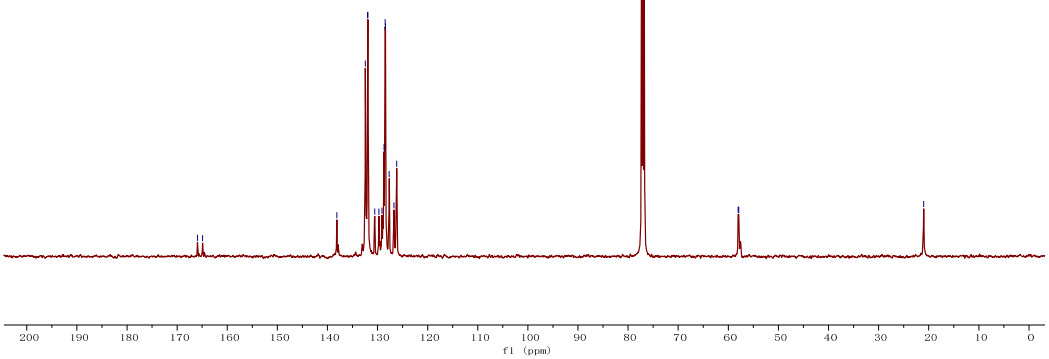


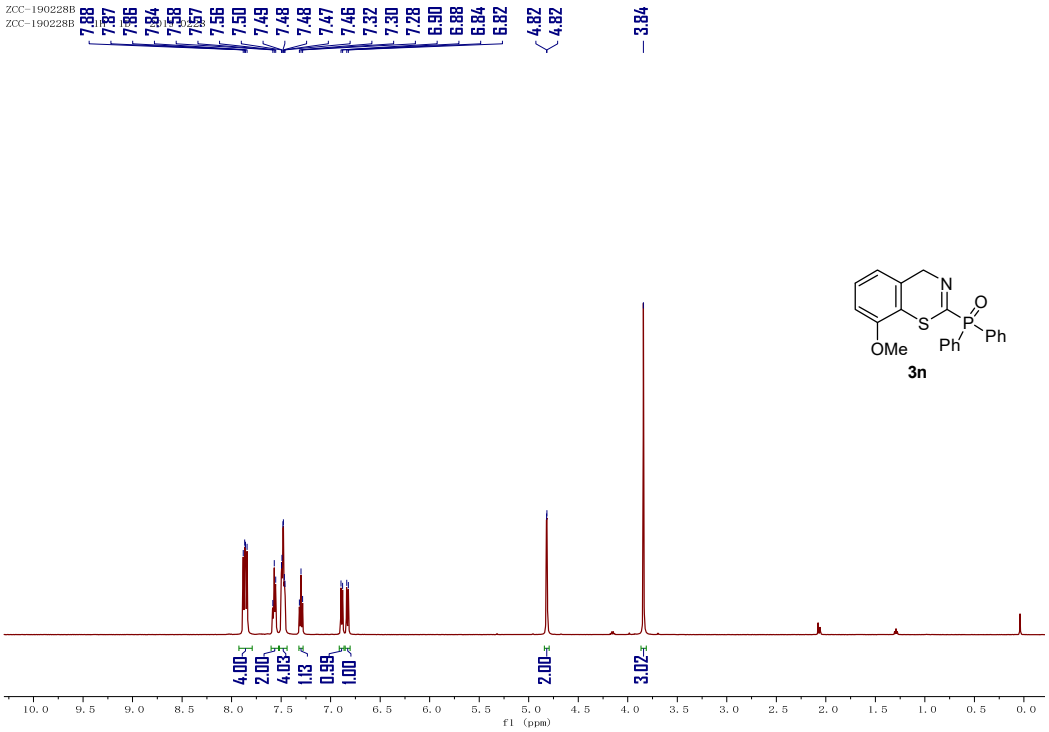
3m/3k', ratio 1:10

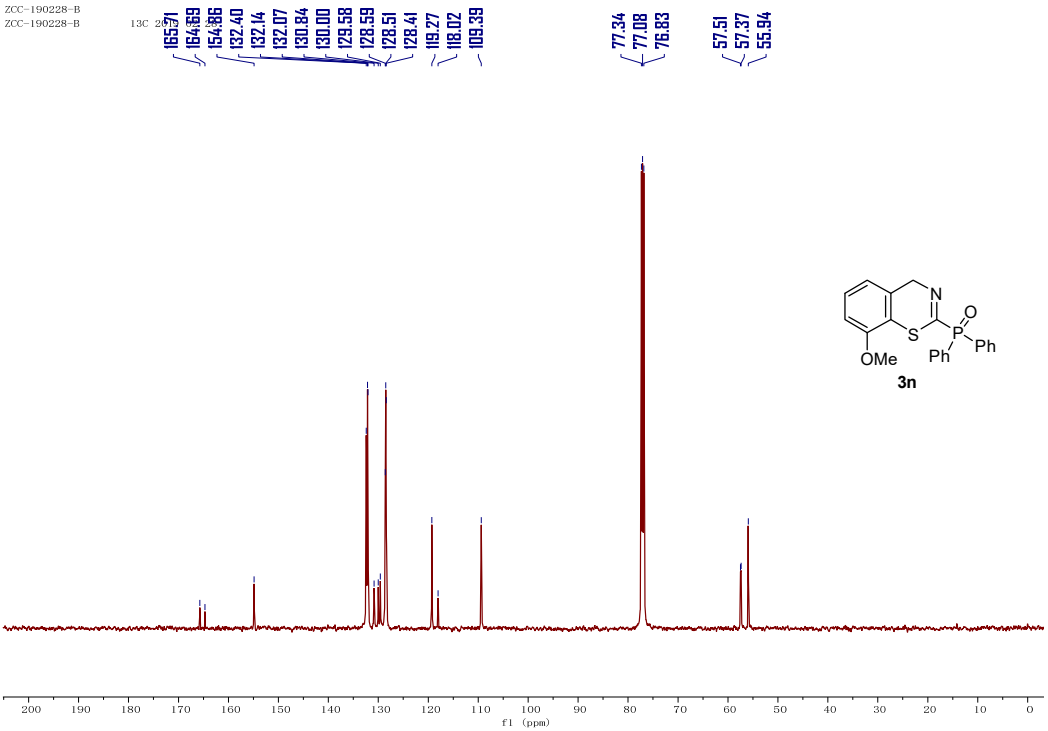


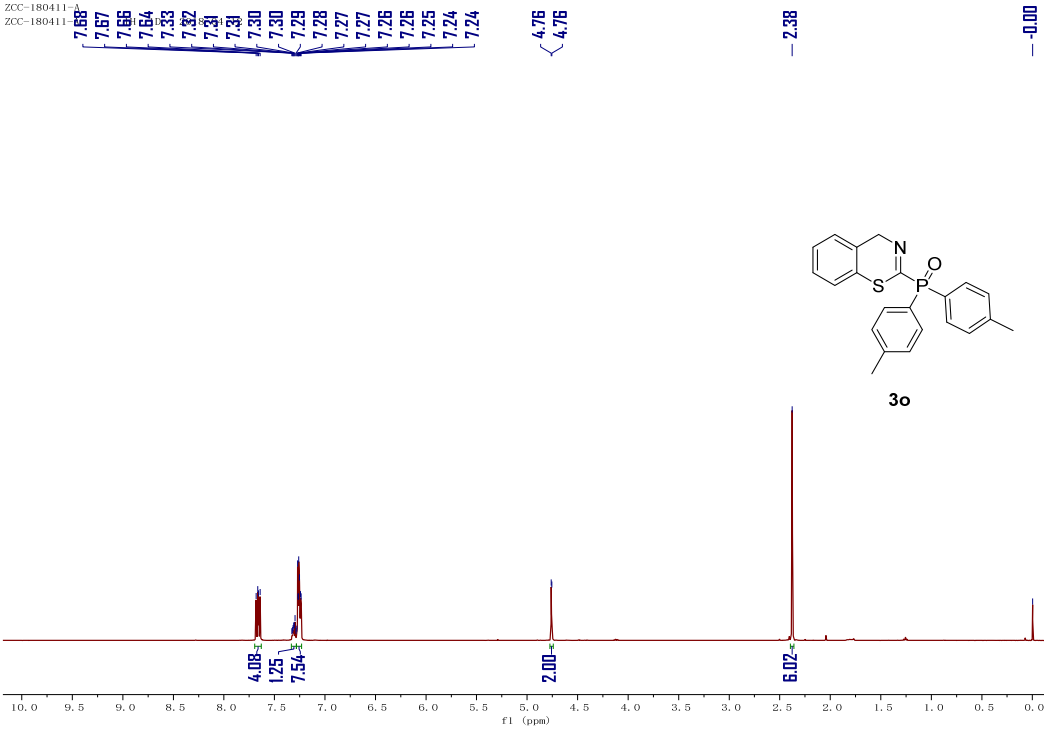


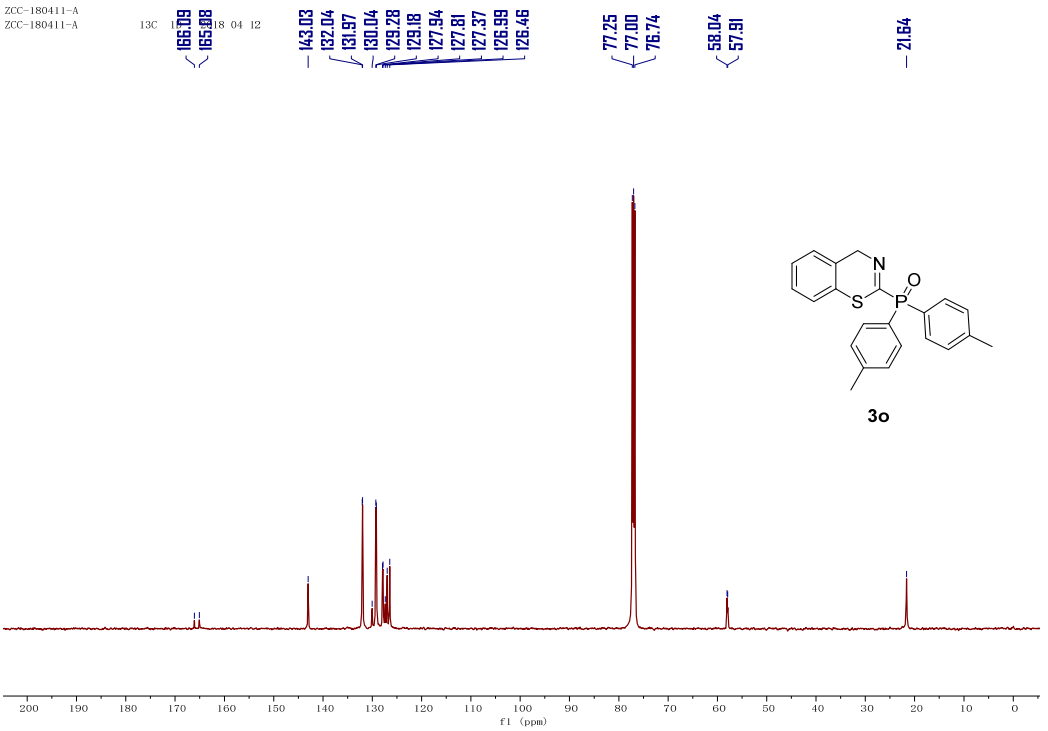
3m/3k', ratio 1:10

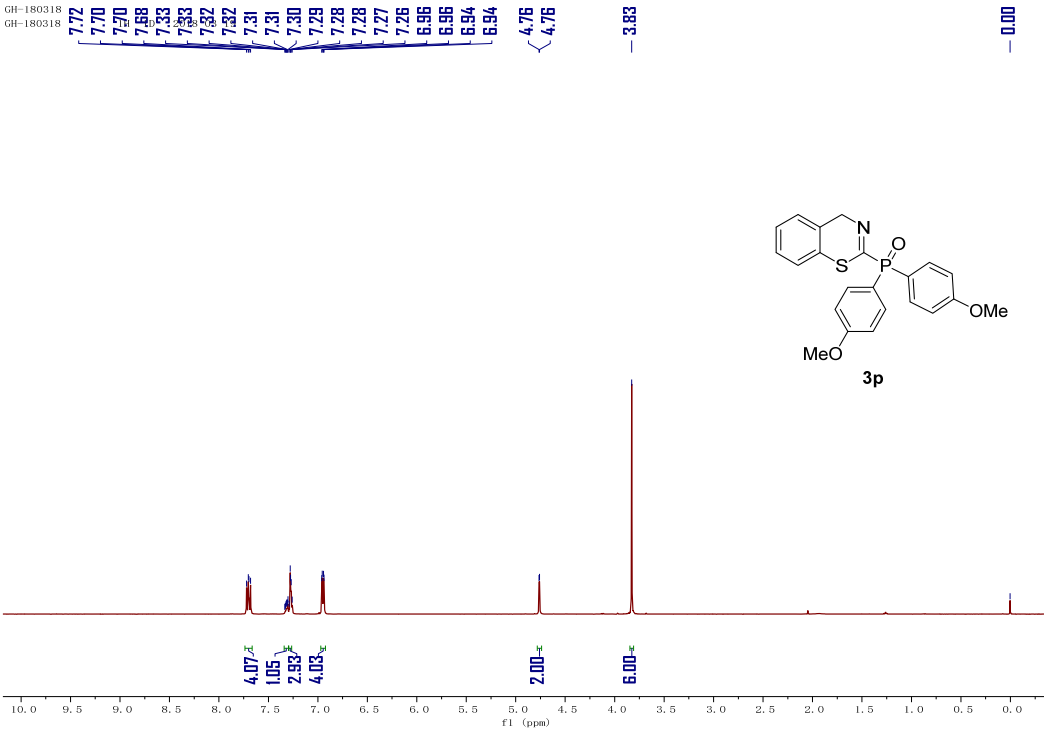


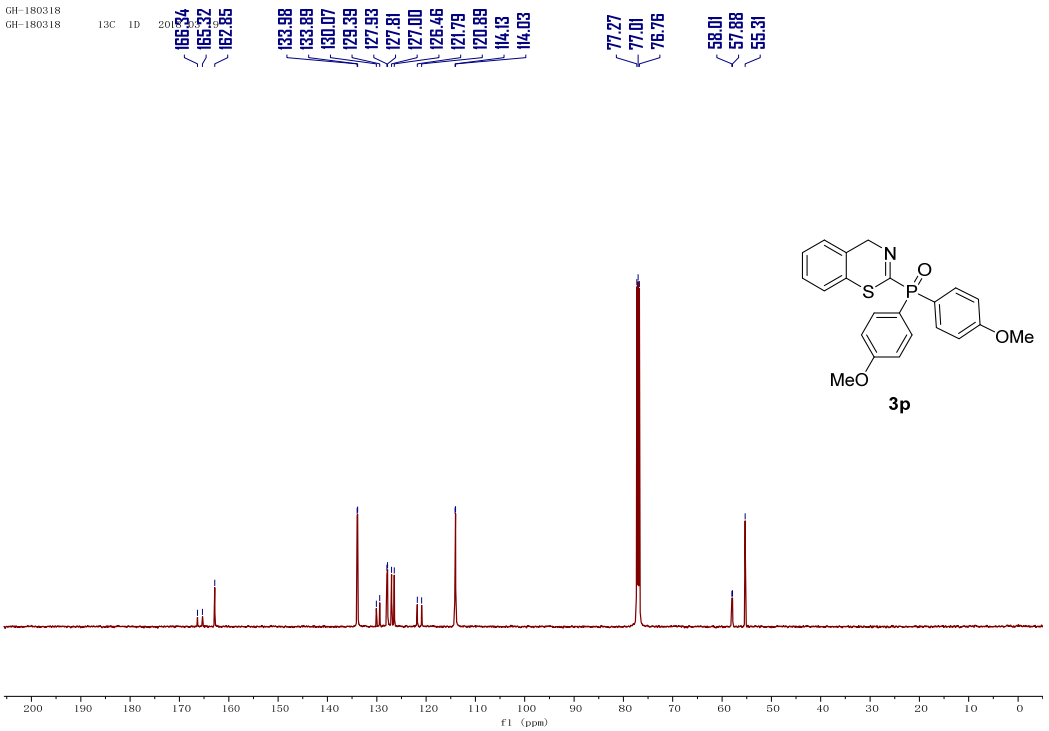

ZCC-190228B
ZCC-190228B
7.88
7.87
7.86
7.84
7.58
7.57
7.56
7.50
7.49
7.48
7.48
7.47
7.46
7.32
7.30
7.28
6.90
6.88
6.84
6.82
4.82
4.82
3.84
4.00
2.00
4.03
1.13
0.99
1.00
2.00
3.02
f1 (ppm)
OMe
Ph
Ph
O
P
S
N
3n

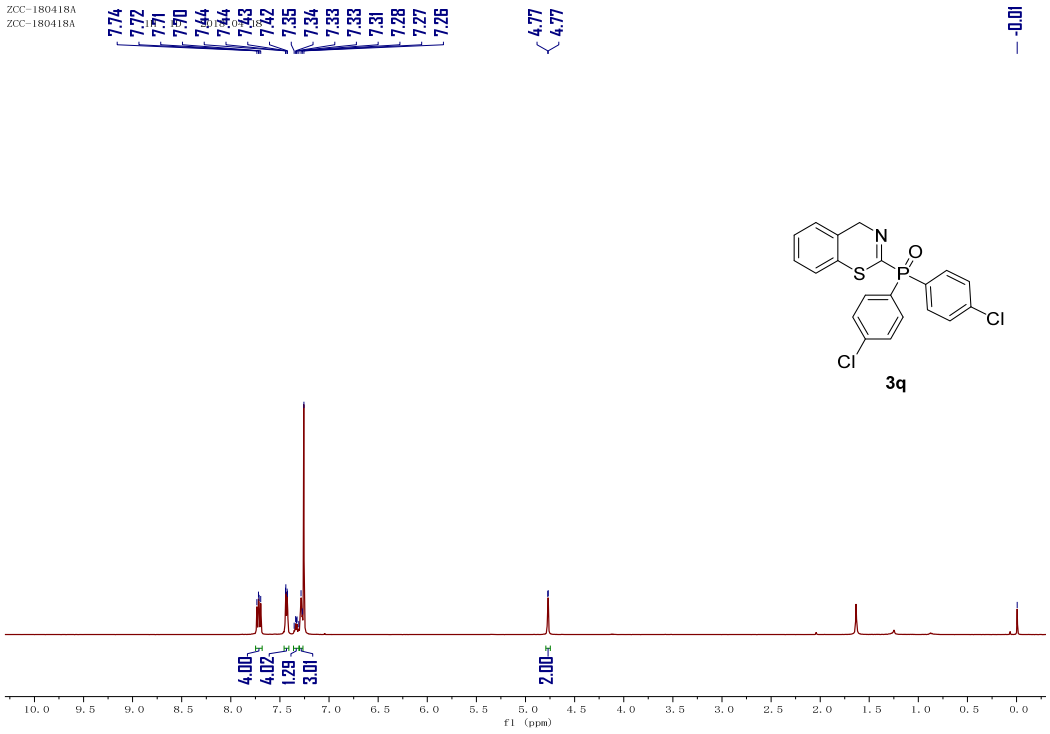

ZCC-190228-B
ZCC-190228-B
165.71
164.69
154.86
132.40
132.14
132.07
130.84
130.00
129.58
128.59
128.51
128.41
119.27
118.02
109.39
77.34
77.08
76.83
57.51
57.37
55.94
f1 (ppm)
OMe
Ph
Ph
O
P
S
N
3n

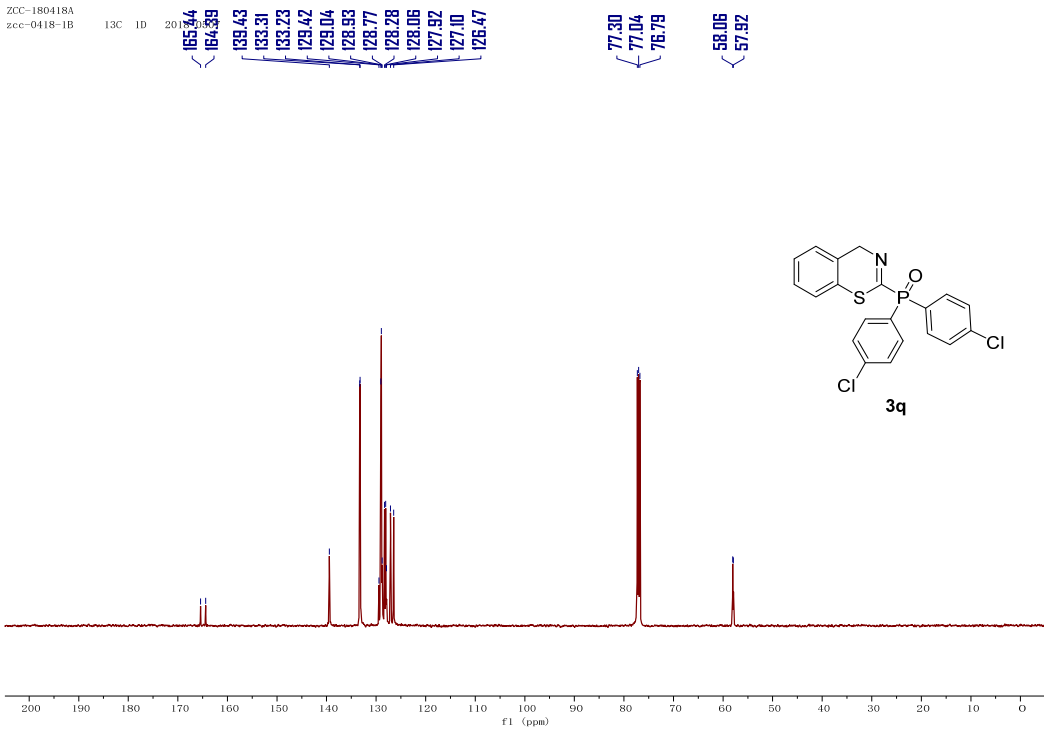

ZCC-180411-A
ZCC-180411-A
7.68
7.67
7.66
7.64
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
4.76
4.76
2.38
-0.00
3o
4.08
1.25
7.54
2.00
6.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


ZCC-180411-A
ZCC-180411-A
166.09
165.88
143.03
132.04
131.97
130.04
129.28
129.18
127.94
127.81
127.37
126.99
126.46
77.25
77.00
76.74
58.04
57.91
21.64
3o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

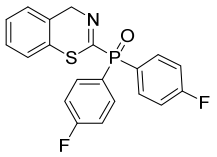

GH-180318
7.72
7.70
7.70
7.68
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.26
6.96
6.96
6.94
6.94
4.76
4.76
3.83
0.00
N
S
P
O
OMe
MeO
3p
4.07
1.05
2.93
4.03
2.00
6.00
f1 (ppm)


GH-180318
GH-180318
13C 1D
166.34
165.32
162.85
133.98
133.89
130.07
129.39
127.93
127.81
127.00
126.46
121.79
120.89
114.13
114.03
77.27
77.01
76.76
58.01
57.88
55.31
N
S
P
O
OMe
MeO
3p
f1 (ppm)

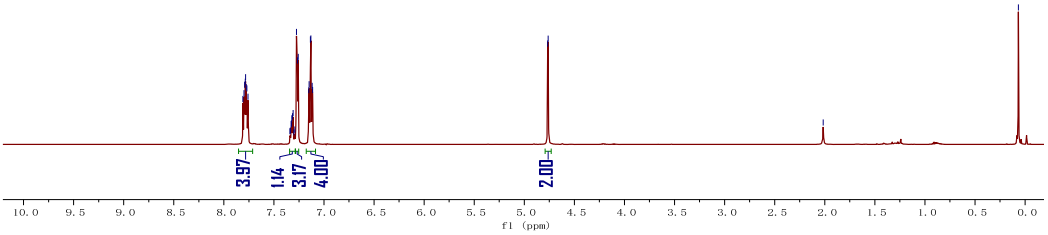

ZCC-180418A
ZCC-180418A
7.74
7.72
7.71
7.70
7.44
7.44
7.43
7.42
7.35
7.34
7.33
7.33
7.31
7.28
7.27
7.26
4.77
4.77
-0.01
N
O
S
P
Cl
Cl
3q
4.00
4.02
1.29
3.01
2.00
f1 (ppm)


ZCC-180418A
zcc-0418-1B
13C 1D
165.44
164.39
139.43
133.31
133.23
129.42
129.04
128.93
128.77
128.28
128.06
127.92
127.10
126.47
77.30
77.04
76.79
58.06
57.92
N
O
S
P
Cl
Cl
3q
f1 (ppm)

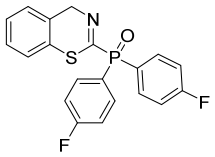

ZCC-180427
ZCC-180427
7.81
7.80
7.79
7.79
7.78
7.78
7.77
7.76
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.27
7.27
7.26
7.15
7.15
7.14
7.13
7.12
7.11
4.77
4.76
2.01
0.07


N
O
S
P
F
F

3r

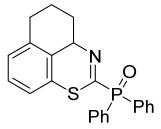

3.97
1.14
3.17
4.00
2.00
f1 (ppm)


ZCC-180427
ZCC-180327
166.46
165.71
164.66
164.44
134.59
134.51
134.43
129.53
129.00
128.23
128.02
127.08
126.46
126.34
125.47
116.19
116.08
116.02
115.91
77.29
77.03
76.78
58.03
57.89

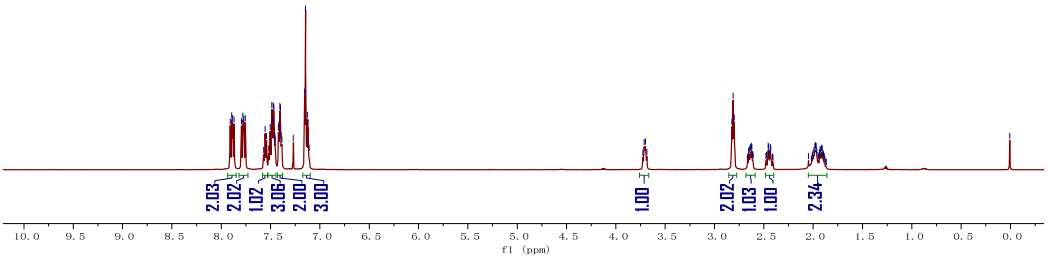

N
O
S
P
F
F

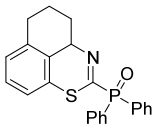
3r

f1 (ppm)

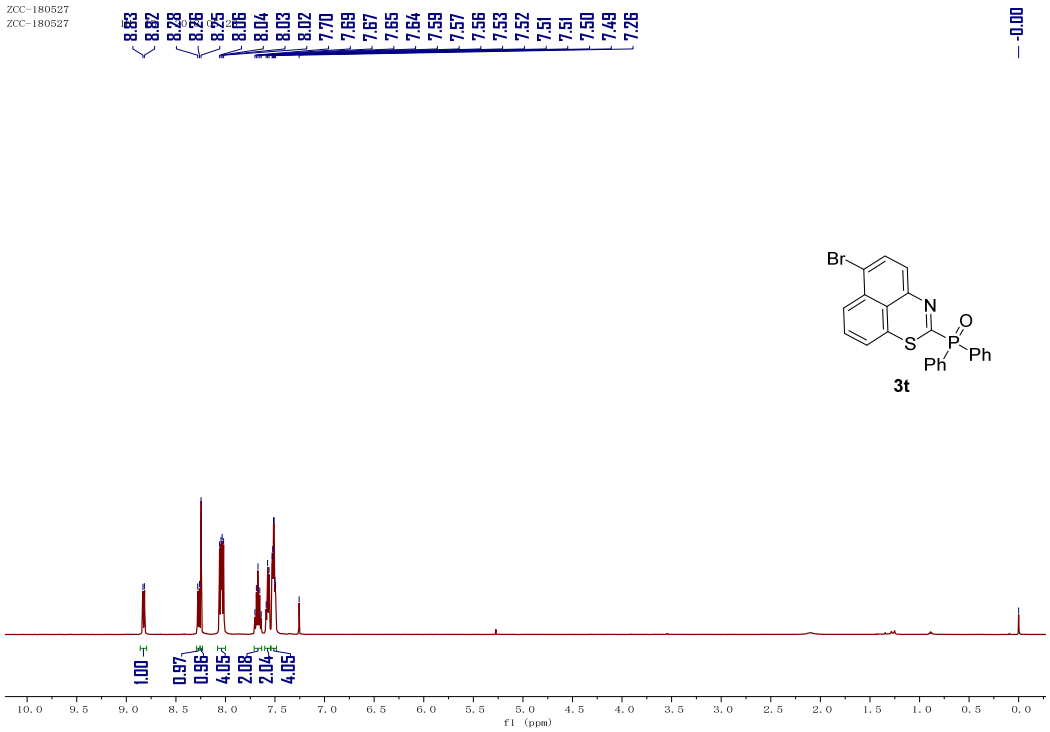


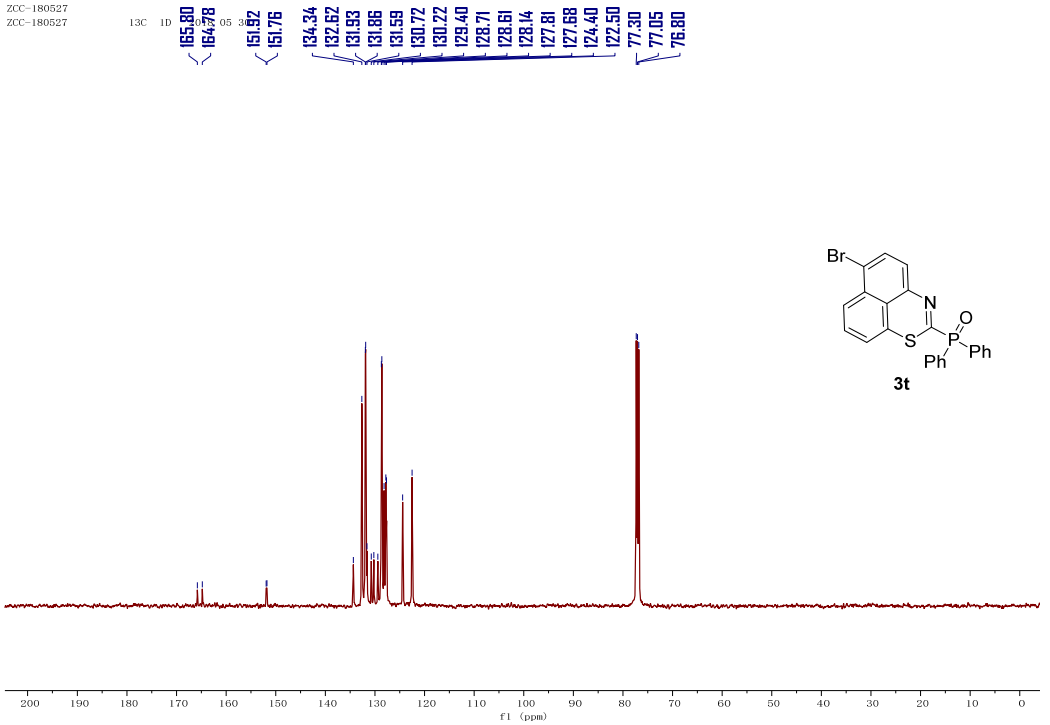
3s

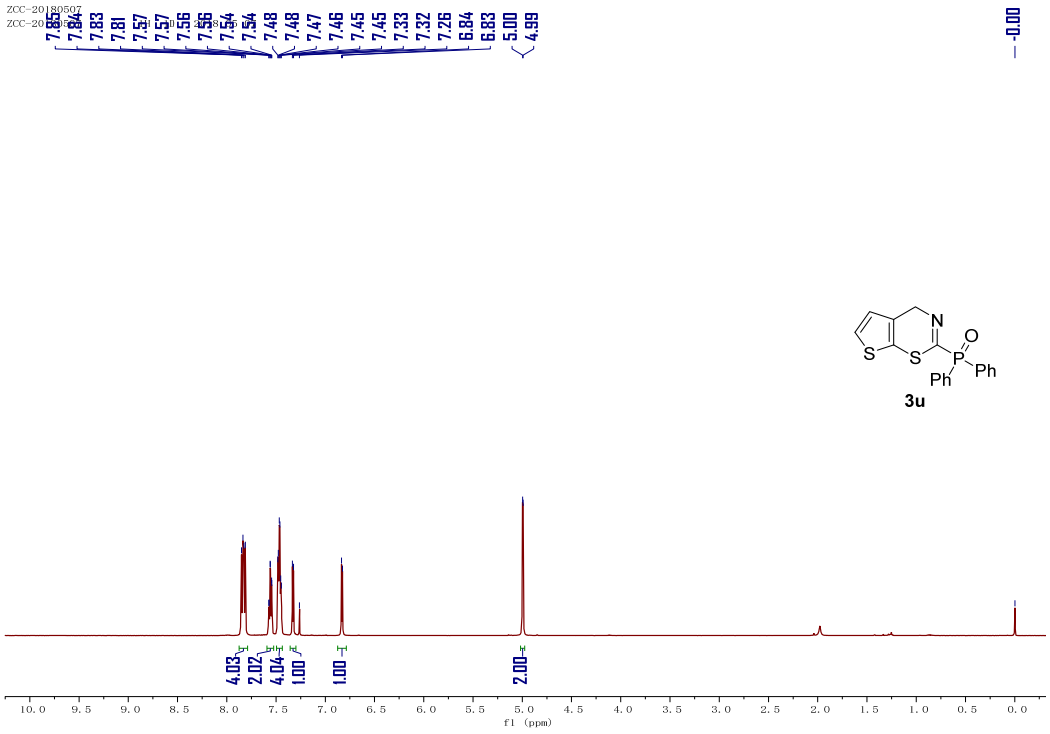


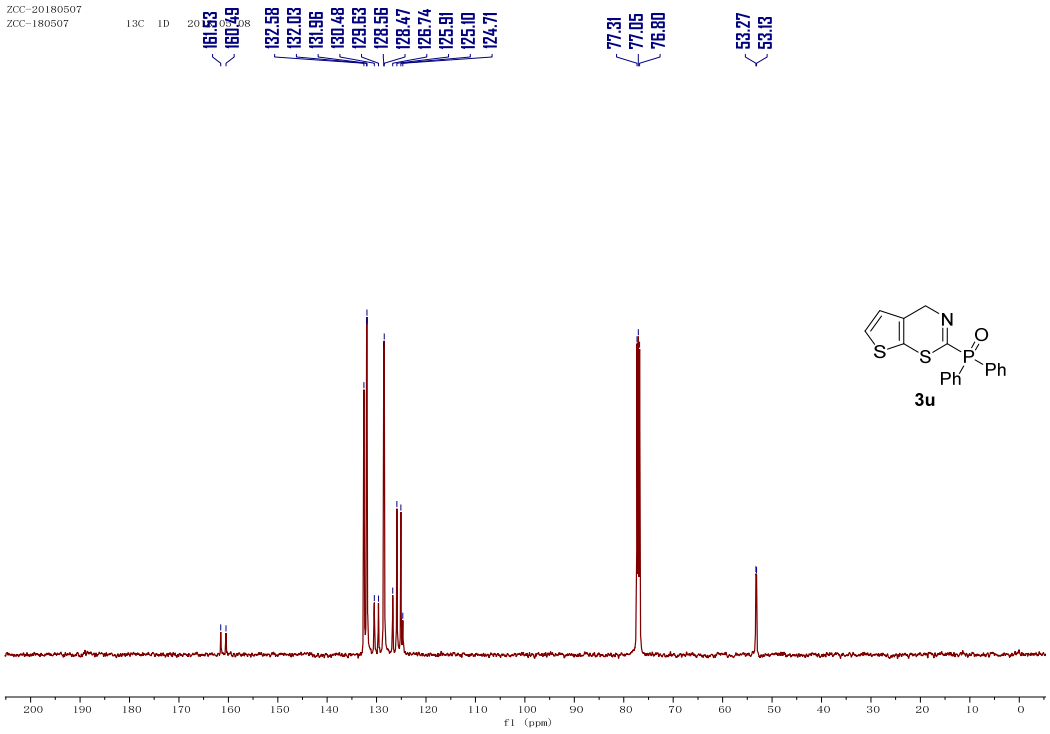


3s

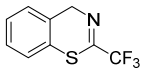

ZCC-180527
ZCC-180527
8.83
8.82
8.28
8.26
8.25
8.06
8.04
8.03
8.02
7.70
7.69
7.67
7.65
7.64
7.59
7.57
7.56
7.53
7.52
7.51
7.51
7.50
7.49
7.26
-0.00
Br
N
S
O
P
Ph
Ph
3t
1.00
0.97
0.96
4.05
2.08
2.04
4.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ZCC-180527
ZCC-180527
13C 1D
165.80
164.78
151.92
151.76
134.34
132.62
131.93
131.86
131.59
130.72
130.22
129.40
128.71
128.61
128.14
127.81
127.68
124.40
122.50
77.30
77.05
76.80
Br
N
S
O
P
Ph
Ph
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

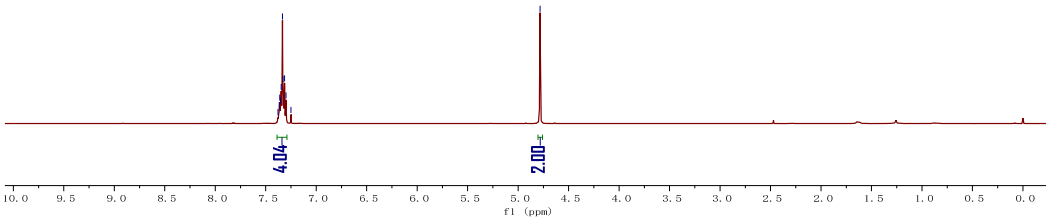

ZCC-20180507
7.85
7.84
7.83
7.81
7.57
7.57
7.56
7.56
7.54
7.54
7.48
7.48
7.47
7.46
7.45
7.45
7.33
7.32
7.26
6.84
6.83
5.00
4.99
-0.00
N
O
S
S
P
Ph
Ph
3u
4.03
2.02
4.04
1.00
1.00
2.00
f1 (ppm)


ZCC-20180507
ZCC-180507
13C 1D
161.53
160.49
132.58
132.03
131.96
130.48
129.63
128.56
128.47
126.74
125.91
125.10
124.71
77.31
77.05
76.80
53.27
53.13
N
O
S
S
P
Ph
Ph
3u
f1 (ppm)

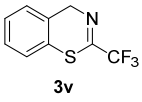

ZCC-180628
ZCC-180628 1H 1D 2018
7.38
7.37
7.36
7.35
7.35
7.33
7.33
7.31
7.30
7.25
4.78


N
S
CF3

3v


4.04
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


ZCC-180628
ZCC-180628 13C 1D 2018
154.08
153.78
153.47
153.17
129.02
128.48
128.23
127.78
127.35
126.74
122.17
119.96
117.75
115.55
77.24
76.99
76.73
55.93

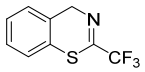

N
S
CF3

3v

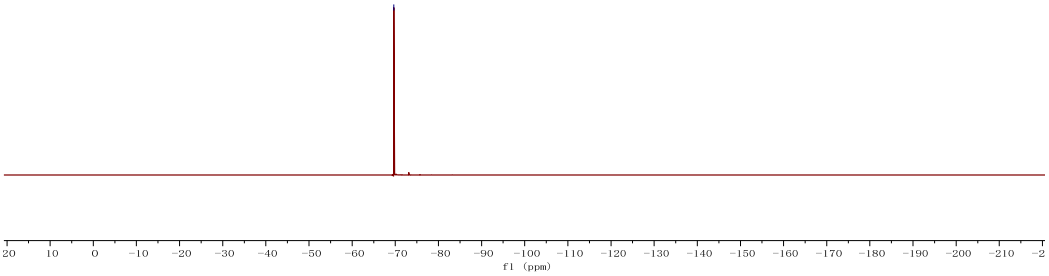
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

20190222-A.1.fid
F19 CDCl3 {E:\data\liming} lm 6

-69.64



3v

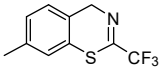


ZCC-180702
ZCC-180702 1H 1D 2018 07 02

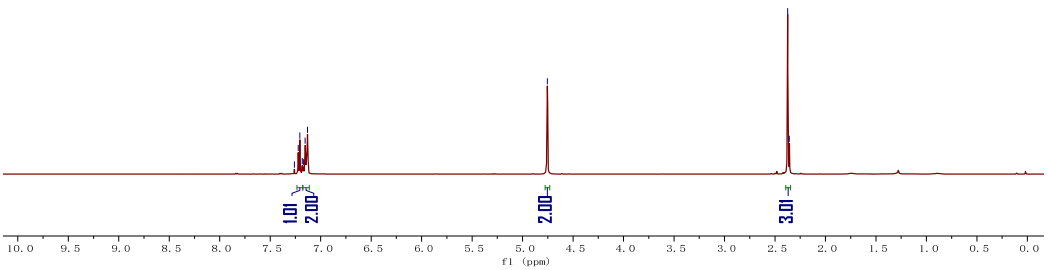
7.26
7.22
7.21
7.18
7.17
7.15
7.13

4.75

2.37
2.36

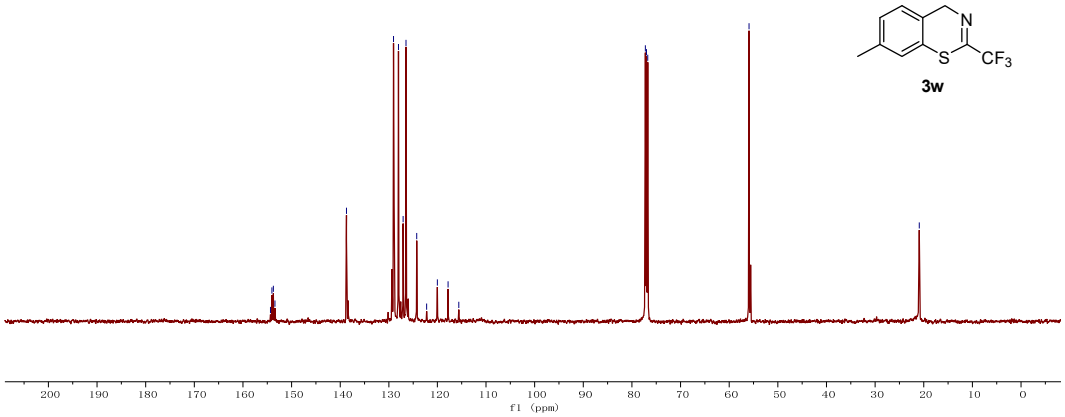


3w



ZCC-180702
ZCC-180702 13C 1D 2018 07 05

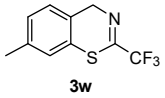
154.34
154.03
153.73
153.42
138.71
129.02
128.00
127.06
126.45
124.25
122.21
120.01
117.80
116.59
77.25
77.00
76.75
55.91
20.92



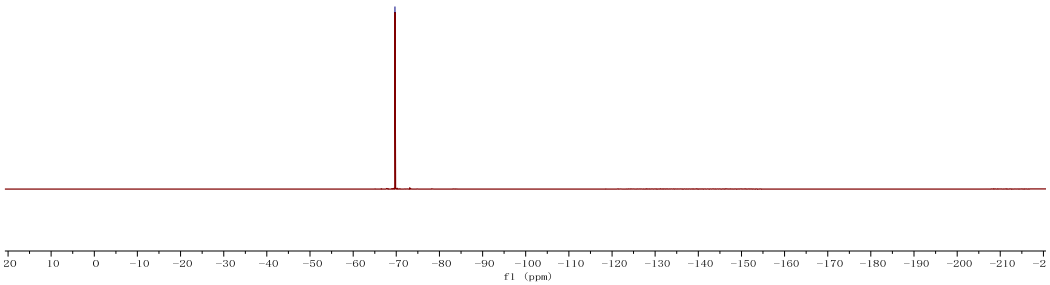
3w

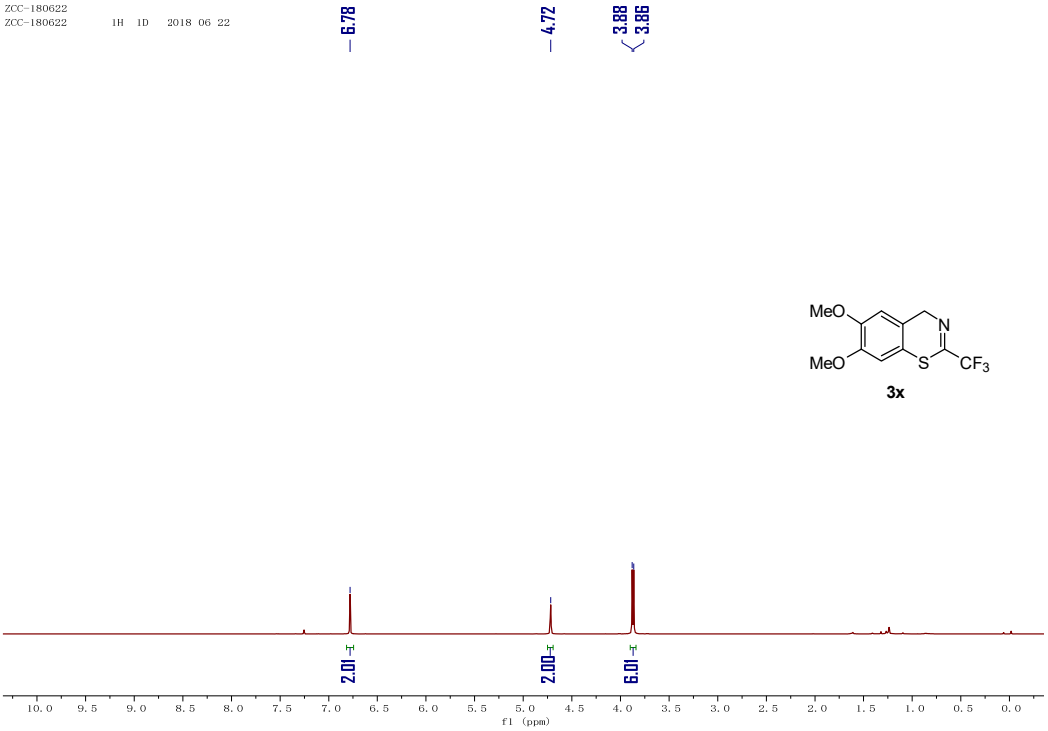
20190222-B.1.fid
F19 CDC13 {E:\data\liming} lm 7

-69.70

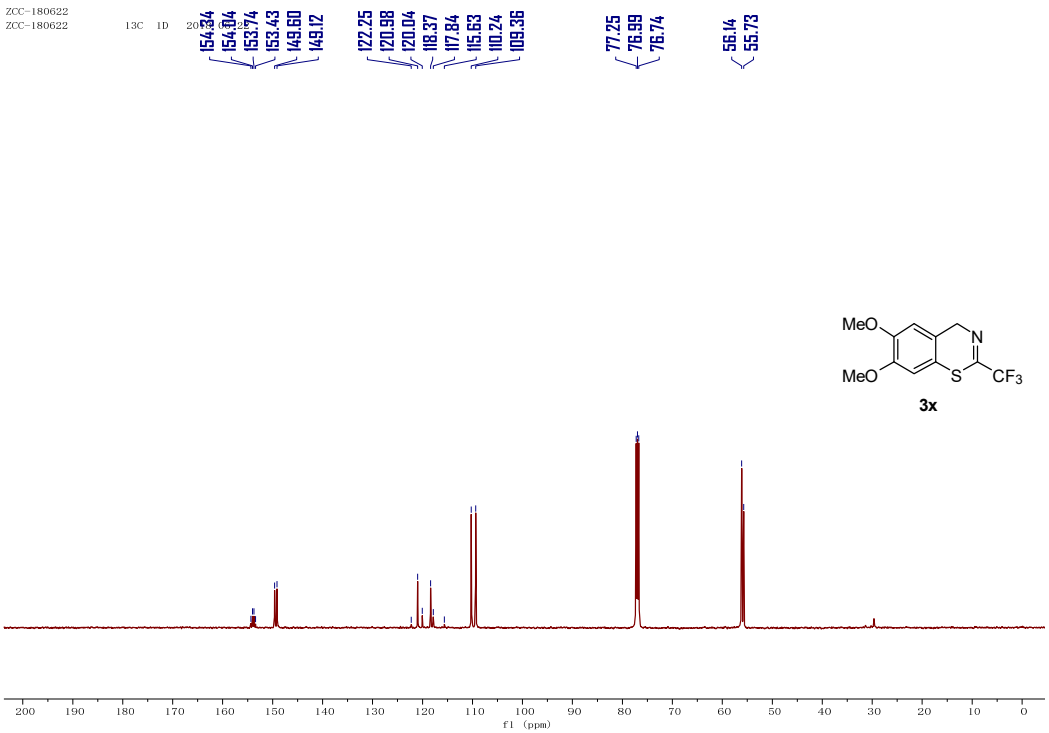


3w




ZCC-180622
ZCC-180622 1H 1D 2018 06 22
6.78
4.72
3.88
3.86
MeO
MeO
N
S
CF3
2.01
2.00
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

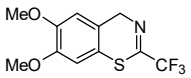
3x


ZCC-180622
ZCC-180622 13C 1D
154.34
154.04
153.74
153.43
149.60
149.12
122.25
120.98
120.04
118.37
117.84
115.63
110.24
109.36
77.25
76.99
76.74
56.14
55.73
MeO
MeO
N
S
CF3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

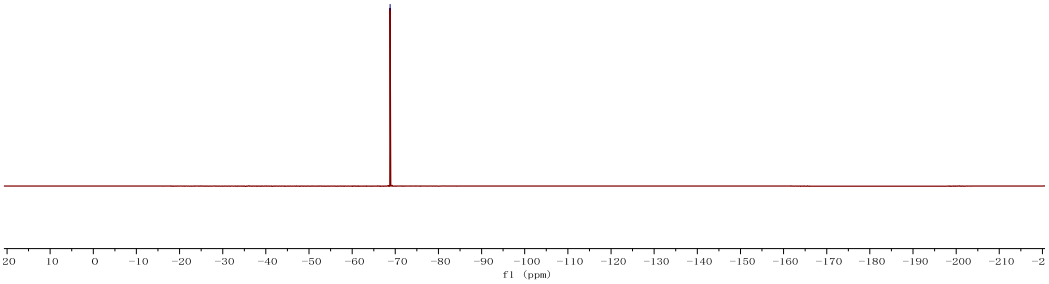
3x

zcc-190226.1.fid
F19 DMSO {E:\data\liming} lm 18

-68.80



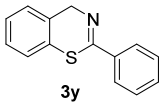
3x



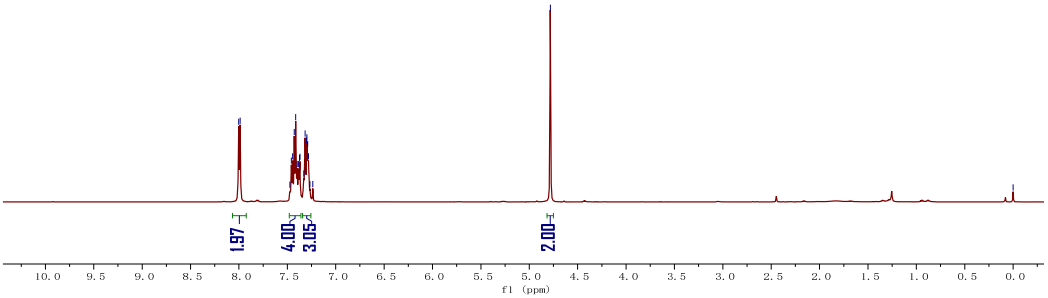
ZCC-180522-A
ZCC-180522-A 1H 1D 2018

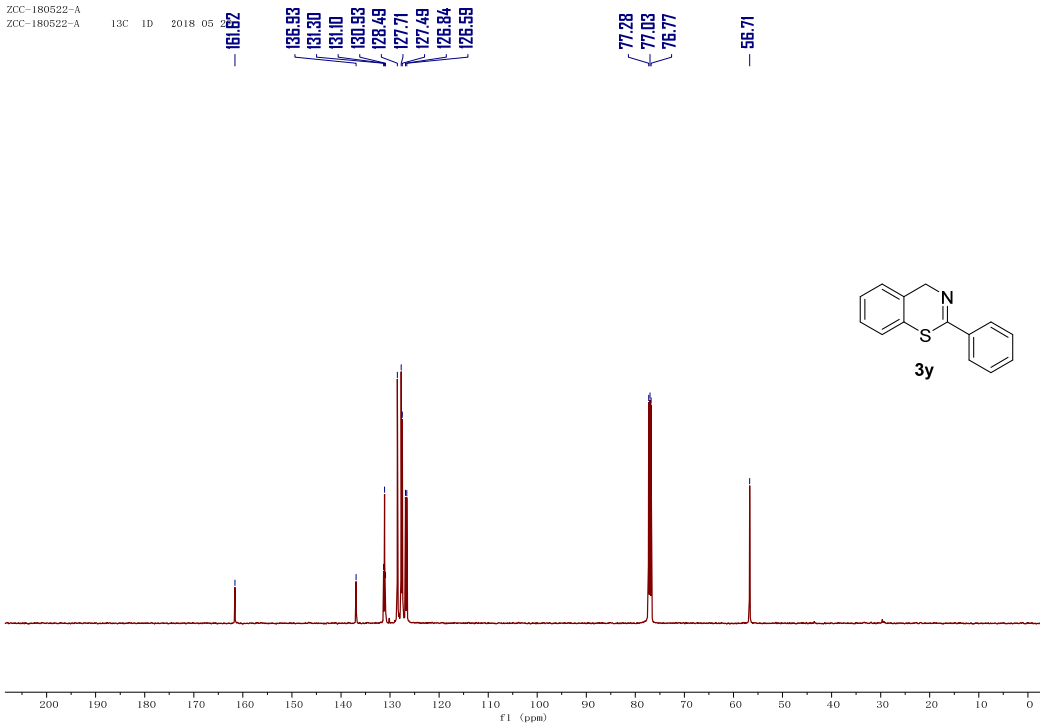
8.00 7.99 7.47 7.46 7.44 7.43 7.41 7.40 7.39 7.37 7.37 7.33 7.32 7.30 7.30 7.29 7.28 7.27 7.24 4.78

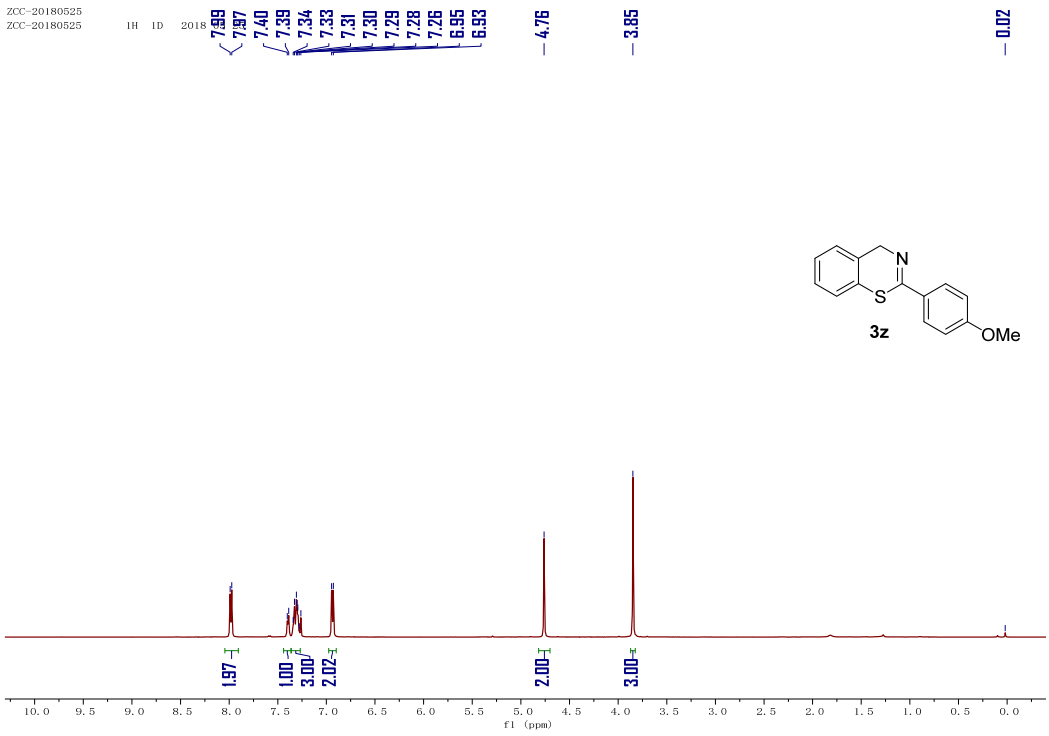
0.00

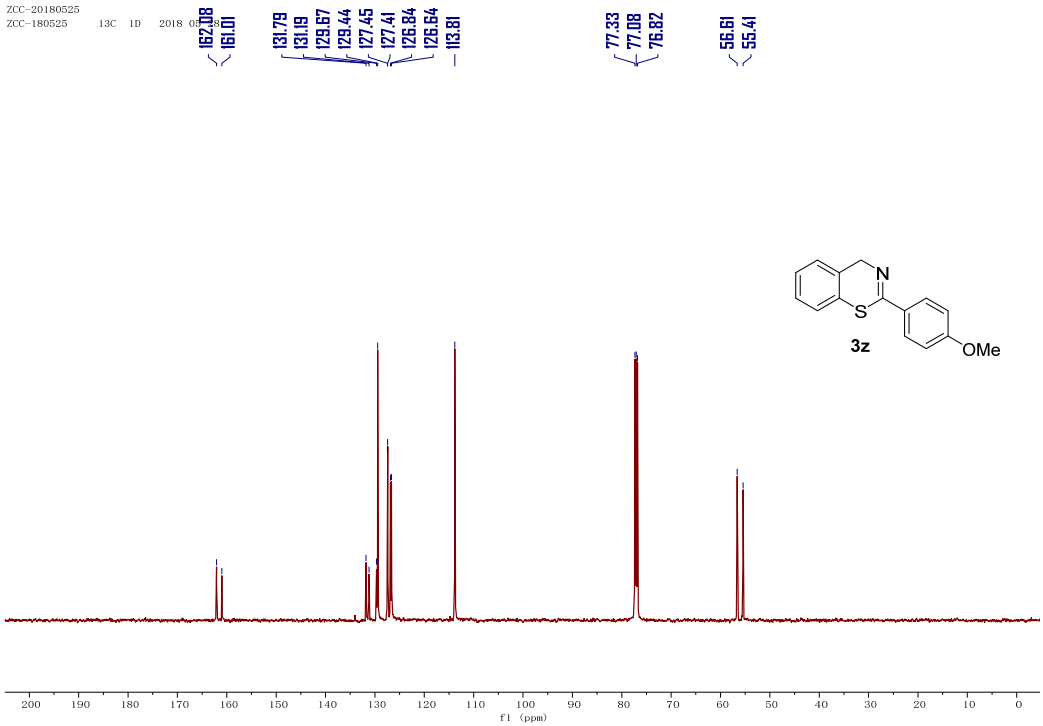


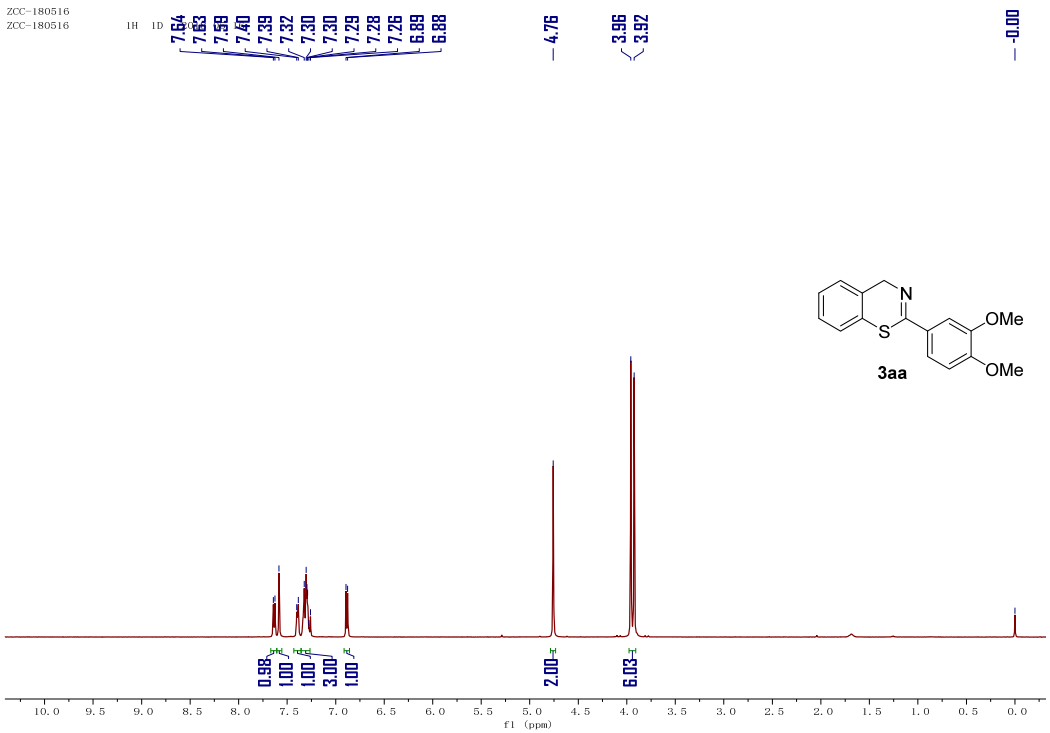
3y

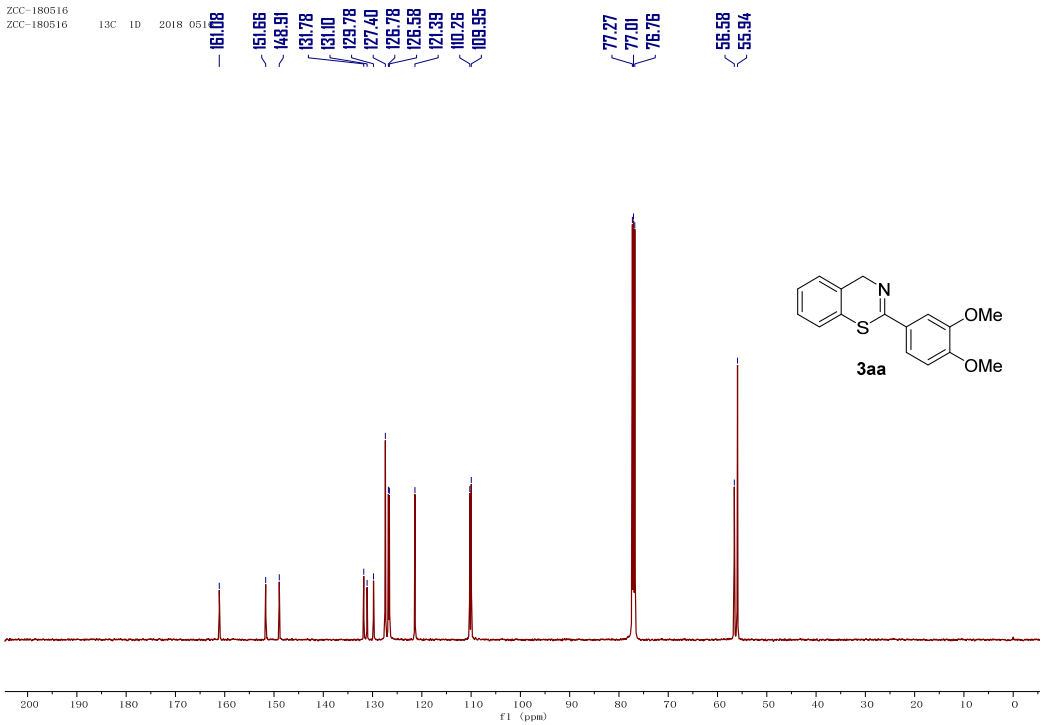


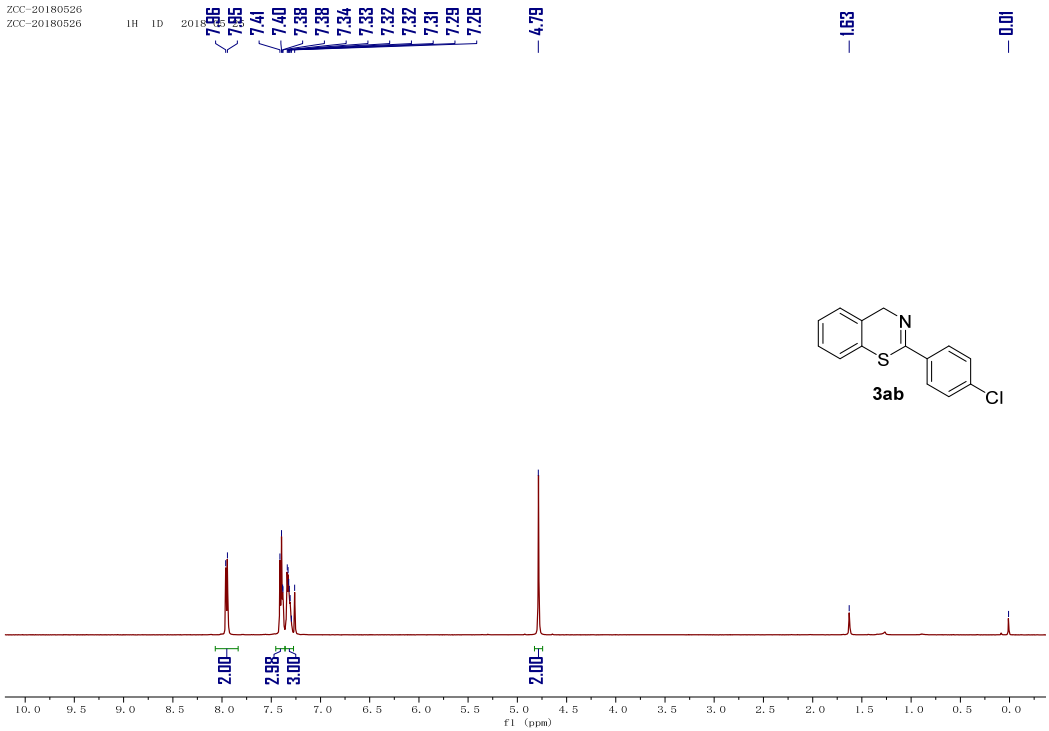

ZCC-180522-A
ZCC-180522-A 13C 1D 2018 05 25
161.62
136.93
131.30
131.10
130.93
128.49
127.71
127.49
126.84
126.59
77.28
77.03
76.77
56.71
N
S
3y
f1 (ppm)

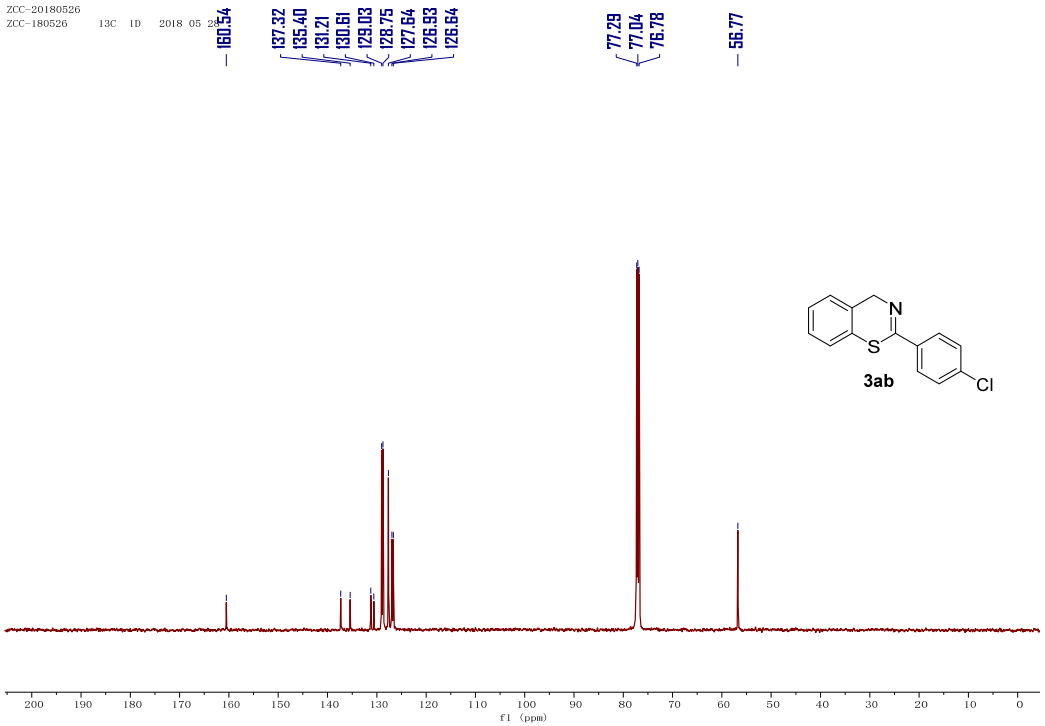

ZCC-20180525
ZCC-20180525 1H 1D 2018
7.99
7.97
7.40
7.39
7.34
7.33
7.31
7.30
7.29
7.28
7.26
6.95
6.93
4.76
3.85
0.02
N
S
3z
OMe
1.97
1.00
3.00
2.02
2.00
3.00
f1 (ppm)

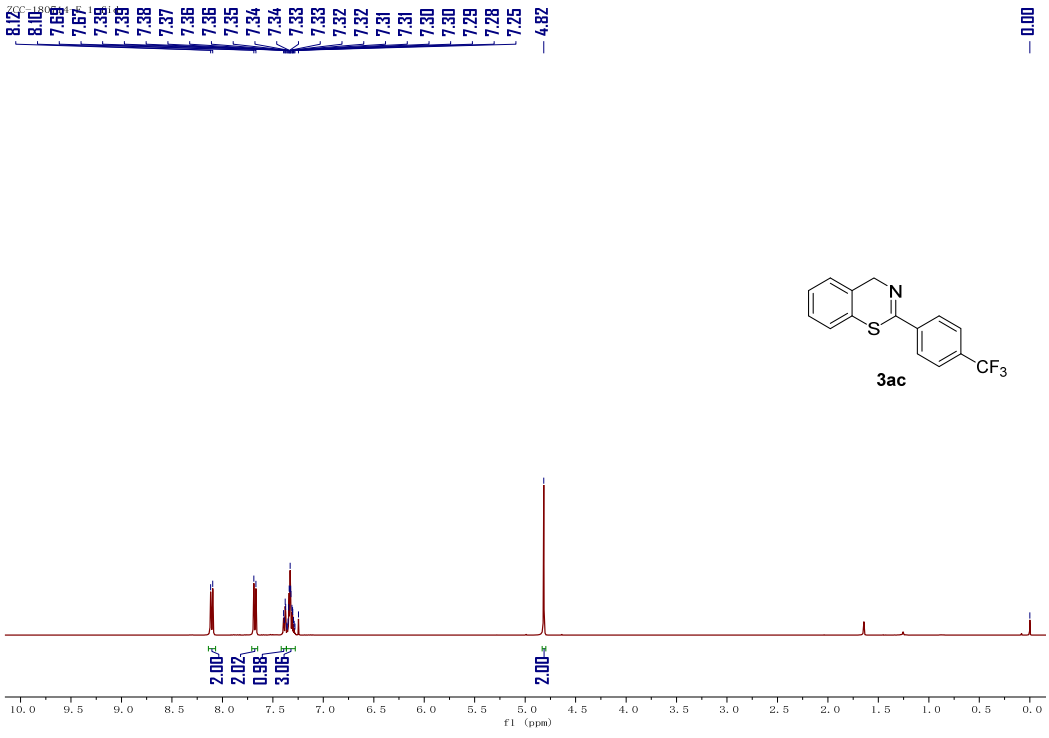

ZCC-20180525
ZCC-180525 13C 1D
162.08
161.01
131.79
131.19
129.67
129.44
127.45
127.41
126.84
126.64
113.81
77.33
77.08
76.82
56.61
55.41
N
S
OMe
3z
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


ZCC-180516
ZCC-180516 1H 1D
7.64
7.63
7.58
7.40
7.39
7.32
7.30
7.30
7.29
7.28
7.26
6.89
6.88
4.76
3.96
3.92
0.00
N
S
OMe
OMe
3aa
0.98
1.00
1.00
3.00
1.00
2.00
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


ZCC-180516
ZCC-180516 13C 1D
161.08
151.66
148.91
131.78
131.10
129.78
127.40
126.78
126.58
121.39
110.26
109.95
77.27
77.01
76.76
56.58
55.94
N
S
OMe
OMe
3aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

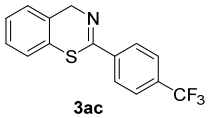

ZCC-20180526
ZCC-20180526 1H 1D
7.96
7.95
7.41
7.40
7.38
7.38
7.34
7.33
7.32
7.32
7.31
7.29
7.26
4.79
1.53
0.01
N
S
Cl
3ab
2.00
2.98
3.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


ZCC-20180526
ZCC-180526 13C 1D 2018 05 25
160.54
137.32
135.40
131.21
130.61
129.03
128.75
127.64
126.93
126.64
77.29
77.04
76.78
56.77
N
S
Cl
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.12
8.10
7.68
7.67
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.25
4.82
0.00
N
S
CF3
3ac
2.00
2.02
0.98
3.06
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

ZCC-180714-E.2.fid

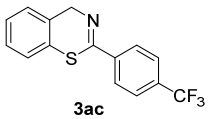
160.40
140.11
140.10
133.20
132.88
132.56
132.23
130.89
130.34
128.02
127.80
127.73
126.99
126.64
125.54
125.51
125.47
125.43
125.23
122.52
119.81
77.35
77.04
76.72
56.90



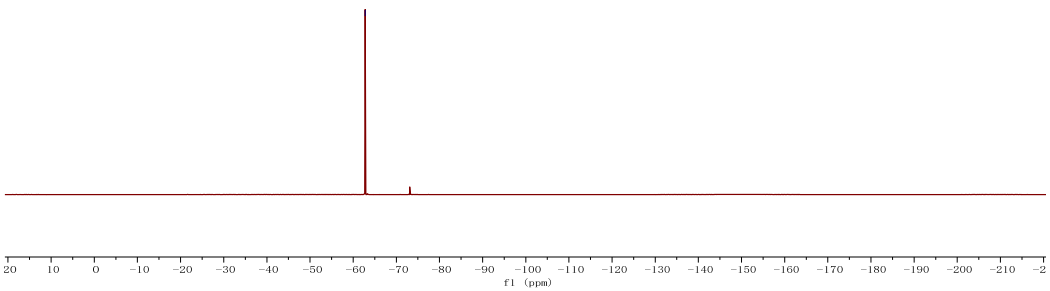
3ac

20190222-D.l.l.1r
F19 CDC13 {E:\data\liming} 1m 9

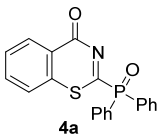
-62.79



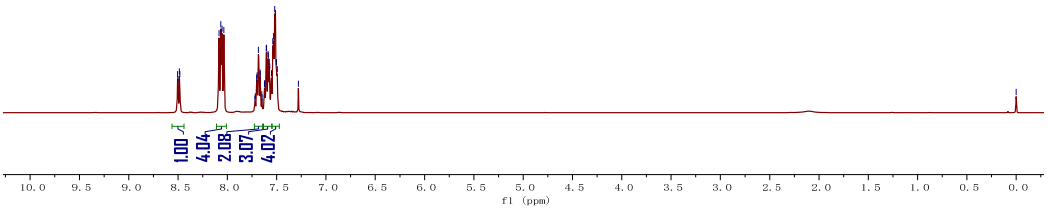
3ac



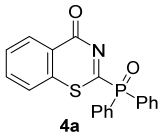

8.50
8.50
8.49
8.48
8.08
8.07
8.06
8.05
8.04
7.72
7.72
7.70
7.70
7.69
7.67
7.67
7.65
7.65
7.62
7.62
7.61
7.60
7.59
7.58
7.58
7.57
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.28
0.00


O
N
S
O
P
Ph
Ph

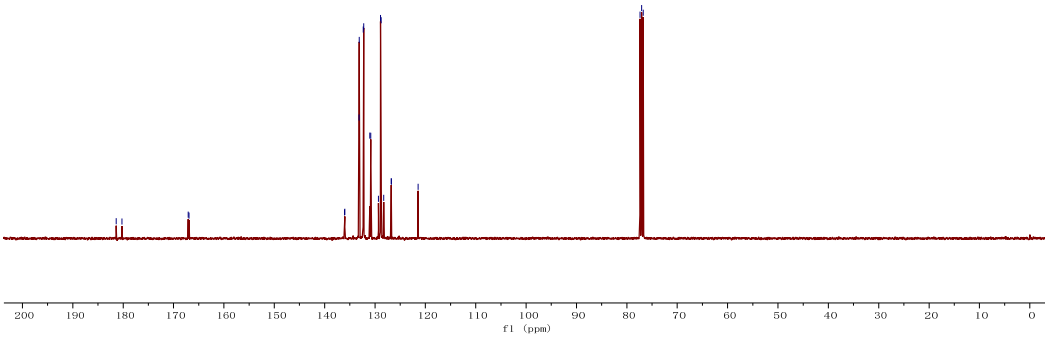
4a


1.00
4.04
2.08
3.07
4.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ZZC-180907-A.1.fid
181.40
180.25
167.10
166.93
136.04
135.99
133.16
133.13
132.34
132.24
131.03
130.86
129.31
128.90
128.77
128.26
126.79
126.75
121.45
77.40
77.08
76.76


O
N
S
O
P
Ph
Ph

4a


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)