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Synthesis of 1,4-Diazepinone Derivatives via a Domino Aza-Michael/S_N2 Cyclization of 1-Azadienes with α-Halogenoacetamides

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General Information

All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 400 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Melting points were determined on a Stuard SMP3 melting apparatus. X-ray crystallographic data were collected using a Bruker APEX-II CCD.

General procedure for preparation of 1-Azadienes 1[1]

1-azadienes were prepared by the reported procedure.

General procedure for preparation of α-Halohydroxamates 2[2]

α-halohydroxamates were prepared by the reported procedure.

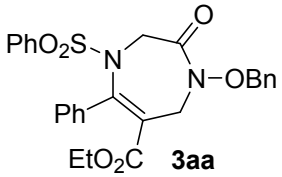
General Procedure for the Preparation of 3, 5 and 7

Under a nitrogen atmosphere, 1-azadiene (0.1 mmol) in CH_3CN (2 mL) was added to the mixed systems of N-alkoxy α-halogenoacetamide (0.15 mmol) and Na_2CO_3 (0.3 mmol). Then the reaction solution was vigorously stirred at room temperature and monitored by TLC. After the reaction was complete, the solutions were concentrated under reduced pressure and the mixture was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to furnish the corresponding product.

[1] H. Liu, Q. Zhang, L. Wang, X. Tong, *Chem. - Eur. J.*, 2010, **16**, 1968.
[2] C. S. Jeffrey, K. L. Barnes, J. A. Eickhoff, C. R. Carson, *J. Am. Chem. Soc.*, 2011, **133**, 7688.

Characterization Data for the Products 3, 5, 7 and 8.

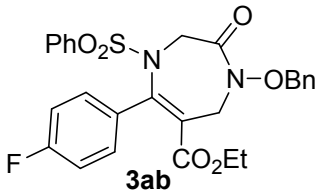
ethyl 4-(benzyloxy)-3-oxo-7-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3aa)



3aa

White solid (95%, 53.3mg), mp = 92 – 94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 3H), 7.32 - 730 (m, 3H), 7.27 – 7.15 (m, 5H), 7.08 (t, *J* = 7.3 Hz, 2H), 6.95 – 6.93 (m, 2H), 4.89 (s, 2H), 4.47 (s, 4H), 3.82 (q, *J* = 6.9 Hz, 2H), 0.77 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9 164.2, 152.1, 139.5, 134.8, 134.3, 133.1, 129.9, 129.8, 129.2, 129.0, 128.9, 128.7, 127.9, 127.0, 126.3, 76.9, 61.4, 54.5, 51.2, 13.4. HRMS calcd for $C_{27}H_{27}N_2O_6S^+$ $[M+H]^+$ 507.1584, found 507.1575.

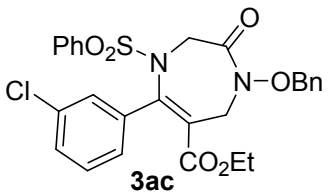
ethyl 4-(benzyloxy)-7-(4-fluorophenyl)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ab)



3ab

White solid (72%, 37.7mg), mp = 96 – 98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 3H), 7.35 – 7.29 (m, 3H), 7.28 – 7.19 (m, 4H), 6.96 – 6.91 (m, 2H), 6.82 – 6.72 (m, 2H), 4.89 (s, 2H), 4.46 (s, 2H), 4.44 (s, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 , 163.2, 162.57 (d, *J* = 251.8 Hz), 149.9, 138.6, 133.7, 132.2, 130.25 (d, *J* = 8.6 Hz), 129.47 (d, *J* = 3.6 Hz), 128.0, 127.9, 127.6, 125.9, 125.2, 114.1, 113.9, 75.9, 60.5, 53.4, 50.2, 12.5. HRMS calcd for $C_{27}H_{26}FN_2O_6S^+$ $[M+H]^+$ 525.1490, found 525.1482.

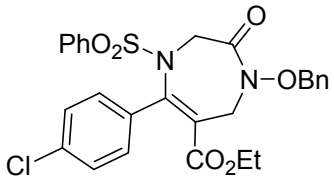
ethyl 4-(benzyloxy)-7-(3-chlorophenyl)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ac)



3ac

White solid (71%, 38.4mg), mp = 120 – 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 1H), 7.44 – 7.36 (m, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.20 (m, 5H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.93 – 6.82 (m, 2H), 4.89 (s, 2H), 4.45 (s, 2H), 4.44 (s, 2H), 3.85 (q, *J* = 7.1 Hz, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 163.4, 149.0, 138.2, 134.9, 133.7, 132.9, 132.4, 128.9, 128.8, 128.1, 128.1, 128.1, 127.9, 127.6, 126.6, 125.8, 125.8, 75.9, 60.6, 53.4, 50.2, 12.4. HRMS calcd for $C_{27}H_{26}ClN_2O_6S^+$ $[M+H]^+$ 541.1195, found 541.1185.

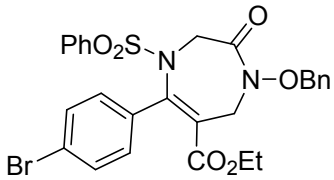
ethyl 4-(benzyloxy)-7-(4-chlorophenyl)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ad)



3ad

White solid (75%, 40.6mg), mp = 100 – 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 1H), 7.43 – 7.36 (m, 2H), 7.37 – 7.28 (m, 3H), 7.32 – 7.20 (m, 2H), 7.25 – 7.17 (m, 2H), 7.10 – 7.01 (m, 2H), 6.94 – 6.83 (m, 2H), 4.88 (s, 2H), 4.46 (s, 2H), 4.43 (s, 2H), 3.86 (q, *J* = 7.1 Hz, 2H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 163.2, 149.7, 138.5, 135.1, 133.7, 132.3, 131.9, 129.5, 128.8, 128.0, 127.9, 127.6, 127.1, 125.9, 125.4, 75.9, 60.5, 53.4, 50.2, 12.5. HRMS calcd for $C_{27}H_{26}ClN_2O_6S^+$ $[M+H]^+$ 541.1195, found 541.1182.

ethyl 4-(benzyloxy)-7-(4-bromophenyl)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ae)

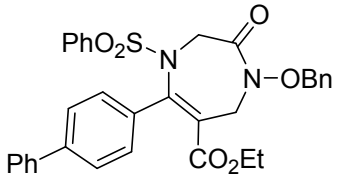


3ae

White solid (68%, 39.8mg), mp = 104 – 106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 3H), 7.37 – 7.26 (m, 3H), 7.30 – 7.17 (m, 2H), 7.20 – 7.12 (m, 2H), 7.12 – 7.03 (m, 2H), 6.97 – 6.90 (m, 2H), 4.90 (s, 2H), 4.47 (s, 2H), 4.47 (s, 2H), 3.82 (q, *J* = 7.1 Hz, 2H), 0.76 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.2, 151.1, 138.5, 133.7, 133.2, 132.0, 128.9, 128.8, 128.2, 127.9, 127.9, 127.6, 126.9, 125.9, 125.3, 75.9, 60.4, 53.4, 50.2, 12.3. HRMS calcd for

$C_{27}H_{26}BrN_2O_6S^+$ [M+H]$^+$ 585.0689, found 585.0680.

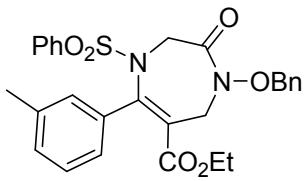
ethyl 7-([1,1'-biphenyl]-4-yl)-4-(benzyloxy)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3af)



3af

White solid (85%, 49.5mg), mp = 120 – 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.43 – 7.38 (m, 5H), 7.36 – 7.27 (m, 6H), 7.24 – 7.20 (m, 2H), 7.22 – 7.14 (m, 2H), 7.04 – 6.97 (m, 2H), 4.92 (s, 2H), 4.52 (s, 2H), 4.49 (s, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 0.81 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.1, 150.9, 141.7, 139.0, 138.7, 133.7, 132.1, 132.0, 128.8, 128.7, 128.0, 127.9, 127.9, 127.7, 127.0, 126.0, 125.4, 125.2, 60.4, 53.5, 50.2, 12.4. HRMS calcd for $C_{33}H_{31}N_2O_6S^+$ [M+H]$^+$ 583.1897, found 538.1885.

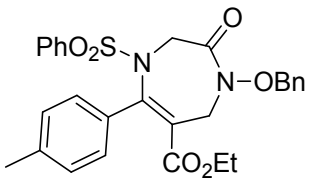
ethyl 4-(benzyloxy)-3-oxo-1-(phenylsulfonyl)-7-(*m*-tolyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ah)



3ah

Yellow oil (85%, 44.2mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.33 – 7.26 (m, 4H), 7.24 – 7.12 (m, 4H), 7.08 – 6.95 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 4.90 (s, 2H), 4.47 (s, 4H), 3.84 (q, *J* = 6.8 Hz, 2H), 2.05 (s, 3H), 0.78 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.2, 151.3, 138.6, 136.5, 133.7, 132.9, 132.0, 129.7, 128.8, 128.5, 127.9, 127.8, 127.6, 126.8, 126.0, 125.8, 125.0, 75.9, 60.3, 53.5, 50.2, 20.0, 12.4. HRMS calcd for $C_{28}H_{29}N_2O_6S^+$ [M+H]$^+$ 521.1741, found 521.1732.

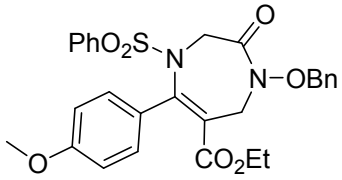
ethyl 4-(benzyloxy)-3-oxo-1-(phenylsulfonyl)-7-(*p*-tolyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ai)



3ai

White solid (84%, 43.7mg), mp = 68 – 70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.31 – 7.26 (m, 4H), 7.24 – 7.16 (m, 3H), 6.91 – 6.77 (m, 4H), 4.88 (s, 2H), 4.46 (s, 2H), 4.45 (s, 2H), 3.85 (q, *J* = 7.0 Hz, 2H), 2.26 (s, 3H), 0.82 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.1, 151.5, 139.3, 138.7, 133.8, 131.9, 130.4, 128.7, 128.2, 127.9, 127.8, 127.8, 127.6, 127.5, 126.0, 124.6, 75.8, 60.3, 53.4, 50.2, 20.4, 12.5. HRMS calcd for $C_{28}H_{29}N_2O_6S^+$ [M+H] $^+$ 521.1741, found 521.1730.

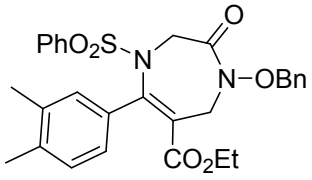
ethyl 4-(benzyloxy)-7-(4-methoxyphenyl)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3aj)



3aj

Yellow solid (90%, 48.3mg), mp = 66 – 68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.34 – 7.26 (m, 4H), 7.28 – 7.21 (m, 2H), 7.19 (s, 1H), 6.88 – 6.85 (m, 2H), 6.62 – 6.51 (m, 2H), 4.88 (s, 2H), 4.45 (s, 4H), 3.87 (q, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 163.0, 160.2, 151.4, 138.8, 133.8, 132.0, 129.9, 128.7, 127.9, 127.6, 126.0, 125.4, 123.7, 112.3, 75.8, 60.3, 54.4, 53.4, 50.2, 12.6. HRMS calcd for $C_{28}H_{29}N_2O_7S^+$ [M+H] $^+$ 537.1690, found 537.1680.

ethyl 4-(benzyloxy)-7-(3,4-dimethylphenyl)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ak)

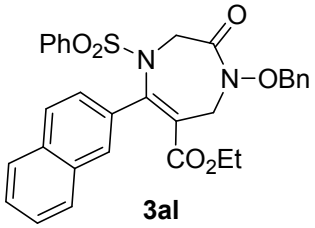


3ak

White solid (91%, 48.6mg), mp = 58 – 60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H),

7.36 – 7.24 (m, 4H), 7.24 – 7.17 (m, 3H), 6.90 – 6.83 (m, 1H), 6.73 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.57 (s, 1H), 4.90 (s, 2H), 4.47 (s, 2H), 4.45 (s, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 2.16 (s, 3H), 1.94 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.0, 151.6, 138.6, 138.0, 135.0, 133.7, 131.9, 130.4, 129.0, 128.8, 128.1, 127.9, 127.7, 127.6, 126.2, 126.0, 124.3, 75.8, 60.3, 53.5, 50.2, 18.7, 18.5, 12.5. HRMS calcd for $C_{29}H_{31}N_2O_6S^+$ $[M+H]^+$ 535.1897, found 535.1895.

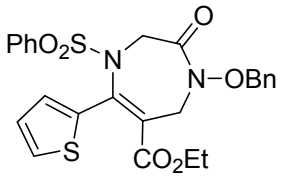
ethyl 4-(benzyloxy)-7-(naphthalen-2-yl)-3-oxo-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3al)



3al

White solid (86%, 47.9mg), mp = 60 – 62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.36 (m, 5H), 7.36 – 7.28 (m, 4H), 7.28 – 7.19 (m, 1H), 7.11 – 7.01 (m, 3H), 6.99 – 6.91 (m, 2H), 4.92 (s, 2H), 4.56 (s, 2H), 4.53 (s, 2H), 3.81 (q, *J* = 7.1 Hz, 2H), 0.66 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 163.2, 151.2, 138.4, 133.7, 132.6, 132.0, 131.2, 130.4, 128.8, 128.2, 127.9, 127.7, 127.6, 127.4, 126.6, 126.4, 126.4, 125.9, 125.5, 125.4, 125.1, 75.9, 60.4, 53.6, 50.3, 12.4. HRMS calcd for $C_{31}H_{29}N_2O_6S^+$ $[M+H]^+$ 557.1741, found 557.1728.

ethyl 4-(benzyloxy)-3-oxo-1-(phenylsulfonyl)-7-(thiophen-2-yl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3am)

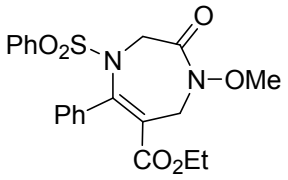


3am

Yellow solid (88%, 45.1mg), mp = 62 – 64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 1H), 7.43 – 7.29 (m, 4H), 7.33 – 7.28 (m, 5H), 7.30 – 7.23 (m, 1H), 6.88 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.80 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.89 (s, 2H), 4.44 (s, 2H), 4.40 (s, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 162.8, 143.5, 138.6, 134.5, 133.7, 132.2, 130.1, 128.7, 128.5, 128.0, 127.9, 127.6, 126.08, 126.0, 125.7, 75.8, 60.6, 52.7, 50.3, 12.6. HRMS calcd for

$C_{25}H_{25}N_2O_6S_2^+$ [M+H]$^+$ 513.1149, found 513.1141.

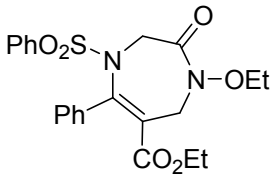
ethyl 4-methoxy-3-oxo-7-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ba)



3ba

White solid (86%, 37.0mg), mp = 120 – 122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 1H), 7.29 – 7.25 (m, 1H), 7.23 – 7.13 (m, 4H), 7.12 – 7.08 (m, 2H), 7.02 – 6.95 (m, 2H), 4.66 (s, 2H), 4.47 (s, 2H), 3.90 (q, *J* = 6.9 Hz, 2H), 3.71 (s, 3H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.6, 151.5, 138.4, 133.3, 132.1, 129.0, 128.3, 127.9, 126.9, 126.0, 125.5, 61.1, 60.5, 53.4, 48.7, 12.4. HRMS calcd for $C_{21}H_{23}N_2O_6S^+$ [M+H]$^+$ 431.1271, found 431.1263.

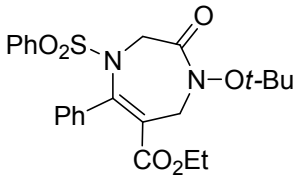
ethyl 4-ethoxy-3-oxo-7-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ca)



3ca

Colorless oil (90%, 40.0mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 1H), 7.31 – 7.22 (m, 1H), 7.25 – 7.13 (m, 4H), 7.14 – 7.06 (m, 2H), 7.01 – 6.95 (m, 2H), 4.66 (s, 2H), 4.47 (s, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 0.80 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.0, 151.3, 138.5, 133.3, 132.0, 128.9, 128.2, 127.9, 126.9, 126.0, 125.5, 69.2, 60.5, 53.4, 49.6, 12.5, 12.4. HRMS calcd for $C_{22}H_{25}N_2O_6S^+$ [M+H]$^+$ 445.1428, found 445.1418.

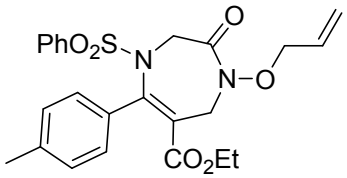
ethyl 4-(*tert*-butoxy)-3-oxo-7-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3da)



3da

White solid (91%, 43.0mg), mp = 174 – 176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 1H), 7.26 – 7.09 (m, 5H), 7.09 – 6.99 (m, 2H), 6.97 – 6.89 (m, 2H), 4.56 (s, 2H), 4.46 (s, 2H), 3.81 (q, *J* = 7.1 Hz, 2H), 1.30 (s,9H), 0.72 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 165.7, 149.2, 139.0, 133.7, 131.9, 128.5, 128.5, 127.8, 126.8, 125.9, 122.9, 82.9, 60.3, 53.8, 53.2, 26.0, 12.3. HRMS calcd for $C_{24}H_{29}N_2O_6S^+$ $[M+H]^+$ 473.1741, found 473.1731.

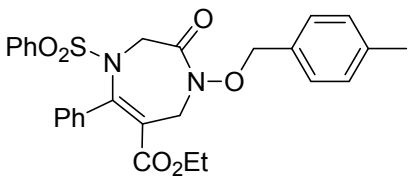
ethyl 4-(allyloxy)-3-oxo-1-(phenylsulfonyl)-7-(*p*-tolyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ei)



3ei

White solid (80%, 37.6mg), mp = 72 – 74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 1H), 7.26 – 7.14 (m, 4H), 6.94 – 6.80 (m, 4H), 5.95 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.35 – 5.18 (m, 2H), 4.62 (s, 2H), 4.45 (s, 2H), 4.38 (dt, *J* = 6.7, 1.1 Hz, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 162.8, 151.8, 139.4, 138.6, 132.0, 130.8, 130.3, 128.2, 127.8, 127.5, 126.0, 124.7, 120.5, 74.8, 60.4, 53.4, 50.0, 20.4, 12.5. HRMS calcd for $C_{24}H_{27}N_2O_6S^+$ $[M+H]^+$ 471.1584, found 471.1575.

ethyl 4-((4-methylbenzyl)oxy)-3-oxo-7-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3fa)

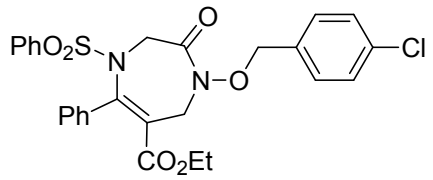


3fa

White solid (87%, 45.3mg), mp = 104 – 106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 1H), 7.38 – 7.31 (m, 2H), 7.32 – 7.16 (m, 6H), 7.20 – 7.04 (m, 3H), 6.98 – 6.89 (m, 2H), 4.86 (s, 2H),

4.48 (s, 2H), 4.45 (s, 2H), 3.83 (q, *J* = 7.1 Hz, 2H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.5, 151.2, 138.4, 133.9, 133.2, 132.3, 132.1, 130.1, 128.9, 128.2, 127.9, 127.8, 126.9, 126.0, 125.0, 74.9, 60.4, 53.4, 50.2, 12.3. HRMS calcd for $C_{28}H_{29}N_2O_6S^+$ $[M+H]^+$ 521.1741, found 521.1732.

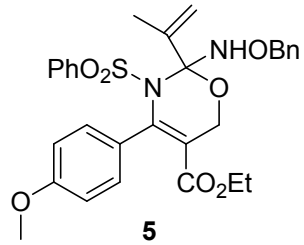
ethyl 4-((4-chlorobenzyl)oxy)-3-oxo-7-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (3ga)



3ga

White solid (86%, 46.5mg), mp = 115 – 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (tt, *J* = 7.0, 1.6 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.27 – 7.17 (m, 2H), 7.20 – 7.03 (m, 7H), 6.97 – 6.90 (m, 2H), 4.85 (s, 2H), 4.47 (s, 2H), 4.46 (s, 2H), 3.82 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 0.77 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.9, 151.1, 138.5, 137.8, 133.2, 132.0, 130.7, 128.9, 128.8, 128.3, 128.1, 127.9, 126.9, 125.9, 125.5, 60.3, 53.4, 50.2, 20.3, 12.3. HRMS calcd for $C_{27}H_{26}ClN_2O_6S^+$ $[M+H]^+$ 541.1195, found 541.1197.

ethyl 2-((benzyloxy)amino)-4-(4-methoxyphenyl)-3-(phenylsulfonyl)-2-(prop-1-en-2-yl)-3,6-dihydro-2*H*-1,3-oxazine-5-carboxylate (5)

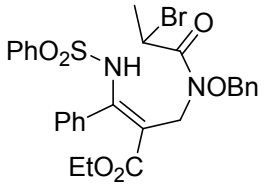


5

Colorless oil (89%, 50.2mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 7.46 – 7.37 (m, 1H), 7.39 – 7.32 (m, 2H), 7.31 – 7.22 (m, 5H), 7.10 – 7.03 (m, 2H), 6.82 – 6.74 (m, 2H), 6.66 – 6.58 (m, 2H), 5.10 (dt, *J* = 3.1, 1.4 Hz, 2H), 4.32 (s, 2H), 4.31 (s, 2H), 3.73 (s, 3H), 1.77 (t, *J* = 1.2 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 168.1, 159.7, 152.7, 139.3, 138.8, 133.1, 131.9, 130.6, 127.8, 127.7, 127.6, 127.5, 126.4, 122.0, 116.8, 112.2, 104.4, 75.8, 60.4, 54.3, 42.4, 18.7, 13.1. HRMS calcd for $C_{30}H_{31}N_2O_7S^-$ $[M-H]^-$ 563.1857, found 563.1860.

(*E*)-ethyl 2-((*N*-(benzyloxy)-2-bromopropanamido)methyl)-3-phenyl-3-

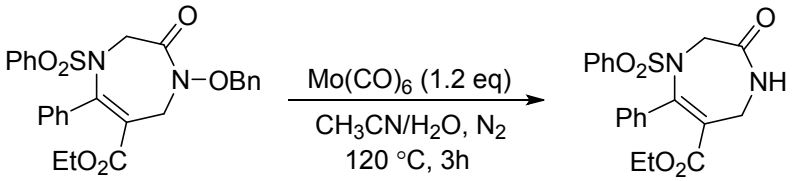
(phenylsulfonamido)acrylate (7)



7

White solid (61%, 36.7mg), mp = 126 – 128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 7.47 – 7.39 (m, 1H), 7.37 – 7.23 (m, 8H), 7.17 – 7.09 (m, 4H), 6.91 (d, *J* = 7.5 Hz, 2H), 4.54 (dd, *J* = 27.9, 11.6 Hz, 3H), 4.35 – 4.06 (m, 4H), 1.44 (d, *J* = 6.7 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 167.9, 152.8, 138.8, 132.5, 132.0, 129.7, 129.0, 129.0, 128.1, 127.9, 127.8, 127.7, 126.9, 126.4, 104.2, 60.7, 41.5, 35.9, 20.0, 13.0. HRMS calcd for $C_{28}H_{28}BrN_2O_6S^-$ [M-H] $^-$ 601.0831, found 601.0842.

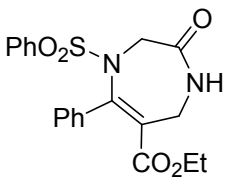
Transformations of the product 3aa



3aa **8**

Under argon atmosphere, the compound **3aa** (50.7 mg, 0.1 mmol) and $Mo(CO)_6$ (31.7mg, 0.12 mmol) were added sequentially to a tube. After adding CH_3CN/H_2O (9:1, 2mL) to the reaction system, the reaction mixture was stirred at 120 °C for 3 h. Then, the reaction mixture was filtered and concentrated. The resulting residue was purified by flash column chromatography (EtOAc:PE = 1:1) to afford the product **8** in 96% yield (38.4 mg).

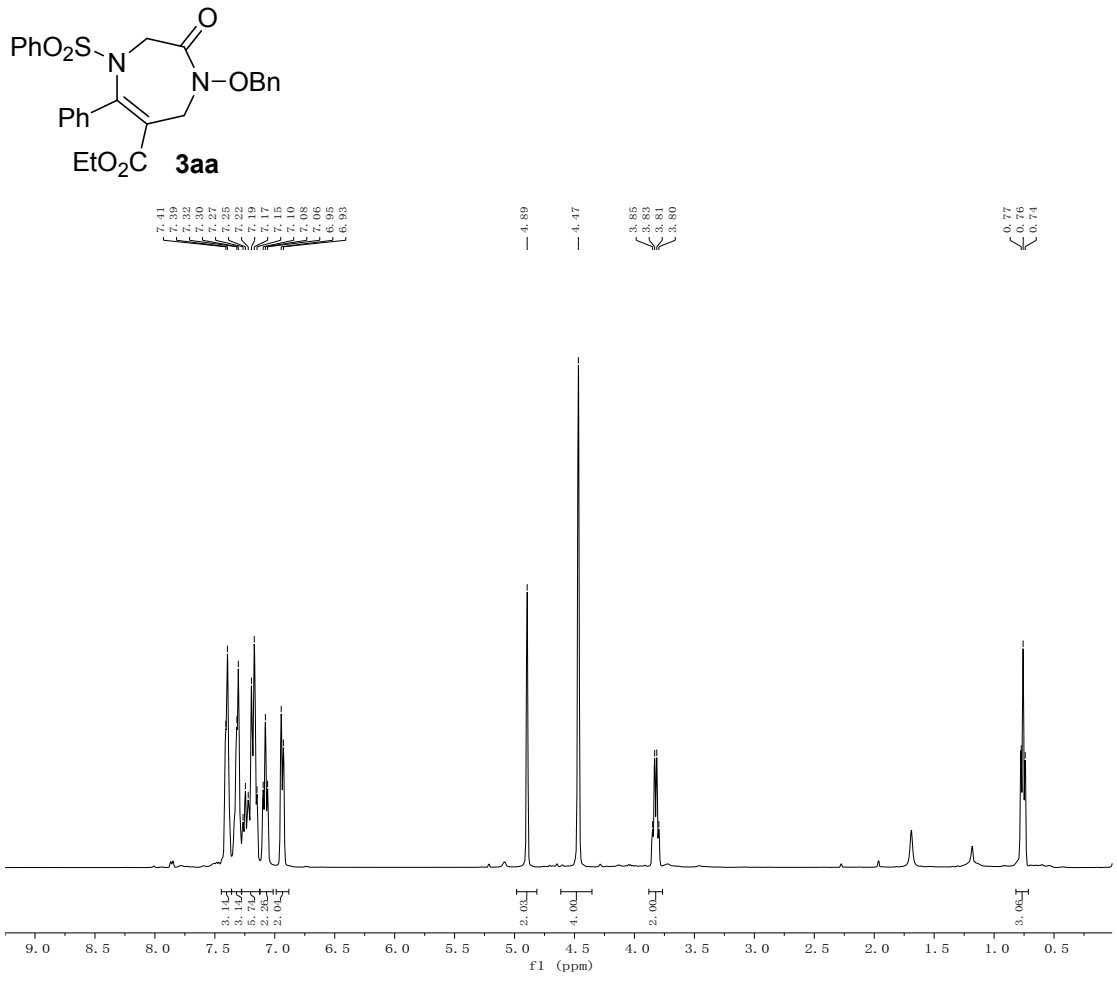
ethyl 3-oxo-7-phenyl-1-(phenylsulfonyl)-2,3,4,5-tetrahydro-1*H*-1,4-diazepine-6-carboxylate (8)

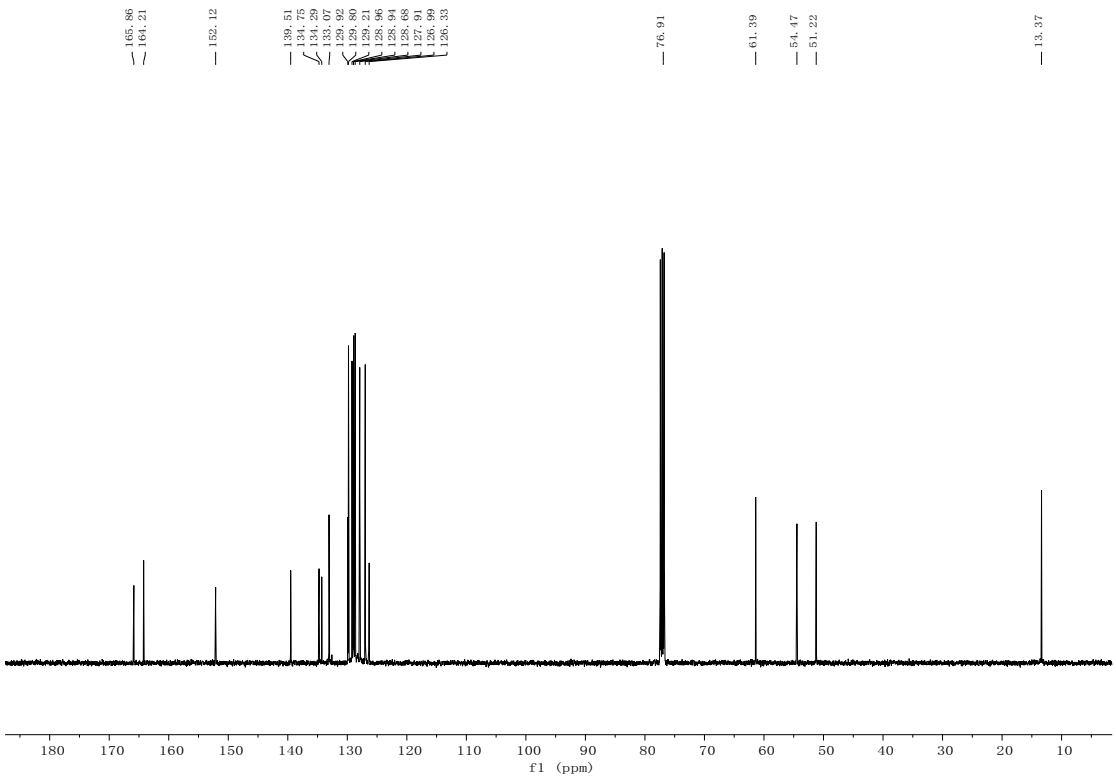


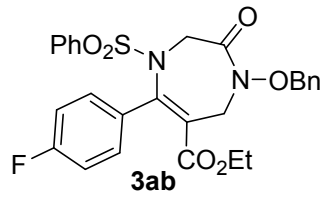
8

White solid, mp = 170 – 172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (tt, *J* = 7.1, 1.6 Hz, 1H), 7.28 – 7.17 (m, 1H), 7.22 – 7.14 (m, 2H), 7.18 – 7.10 (m, 2H), 7.12 – 7.03 (m, 2H), 6.99 – 6.94 (m, 2H),

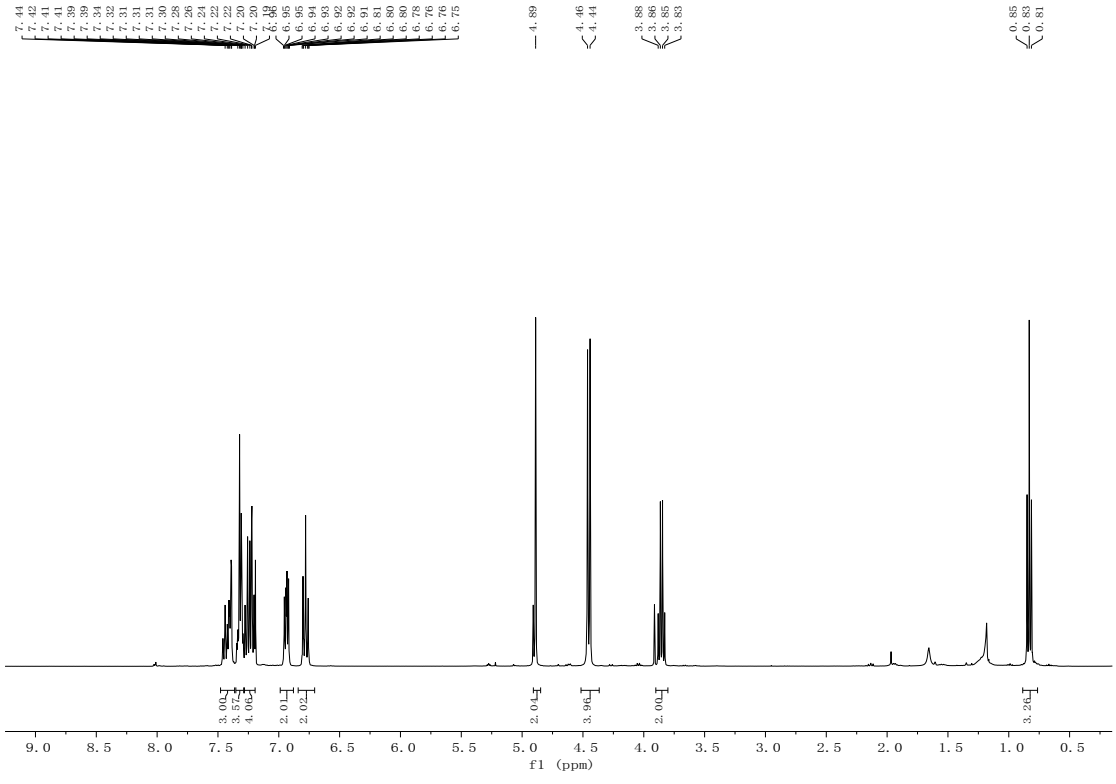
4.44 (s, 2H), 4.27 (d, J = 5.1 Hz, 2H), 3.88 (q, J = 7.1 Hz, 2H), 0.79 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 165.1, 150.7, 138.6, 133.3, 131.8, 128.7, 128.4, 128.1, 127.8, 126.8, 125.8, 60.3, 52.4, 39.4, 12.4. HRMS calcd for $C_{20}H_{21}N_2O_5S^+$ $[M+H]^+$ 401.1165, found 401.1160.

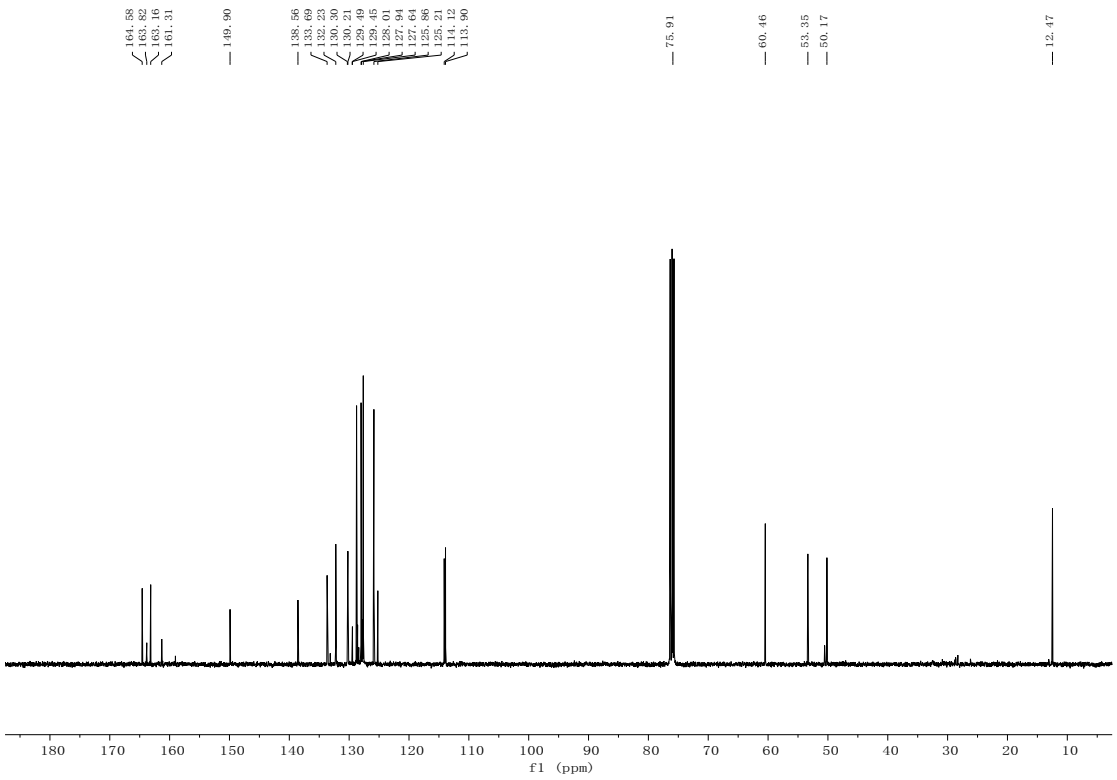


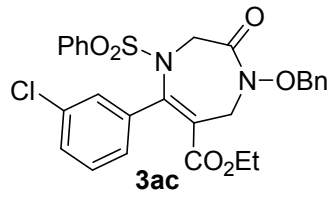

165.86
164.21
152.12
139.51
134.75
134.29
133.07
129.92
129.80
129.21
128.96
128.94
128.68
127.91
126.99
126.33
76.91
61.39
54.47
51.22
13.37
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

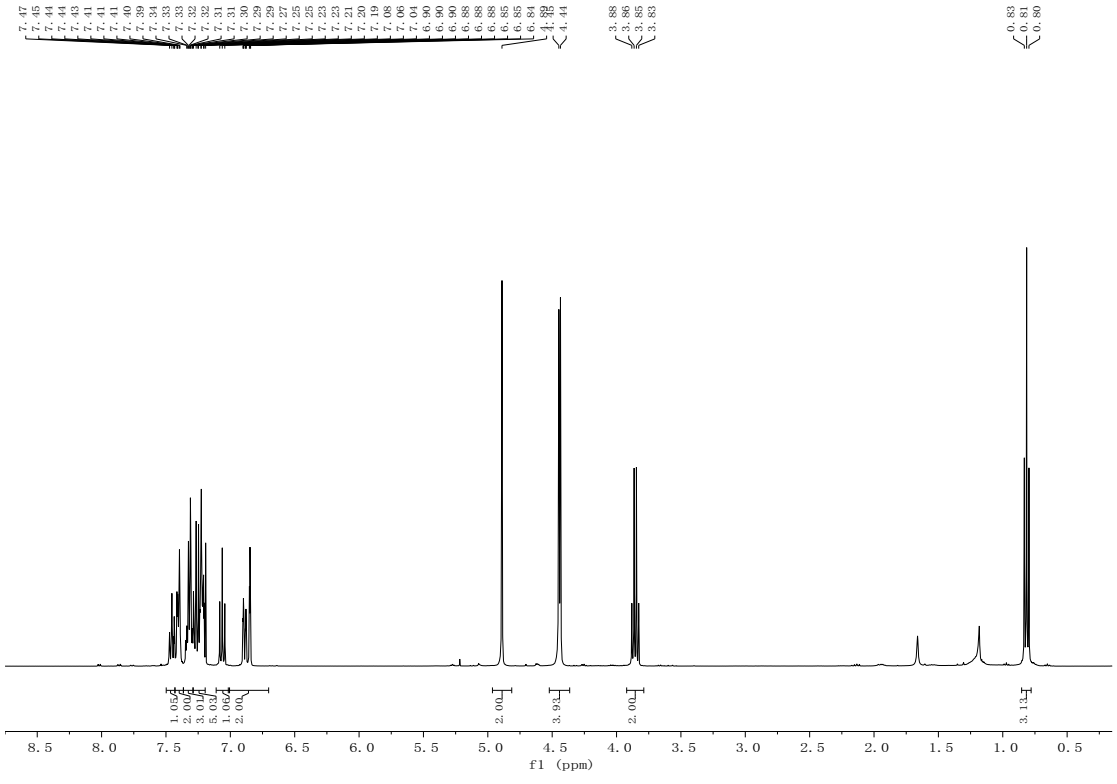

PhO2S
N
O
N−OBn
F
CO2Et

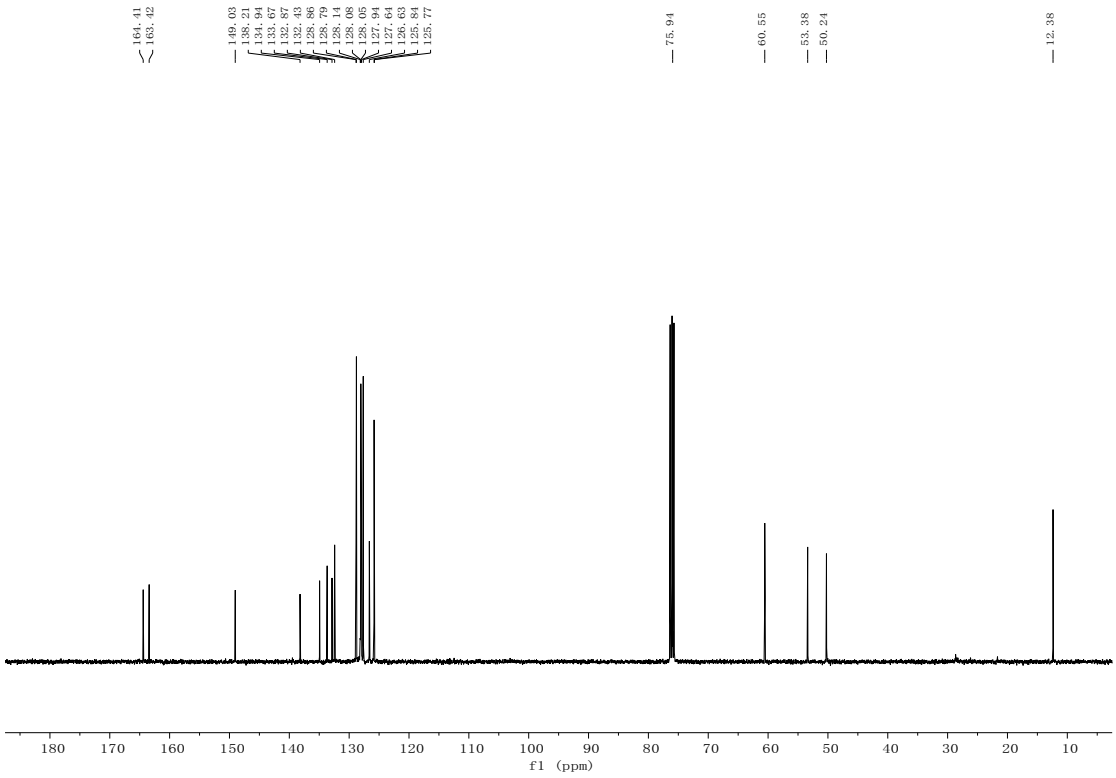
3ab

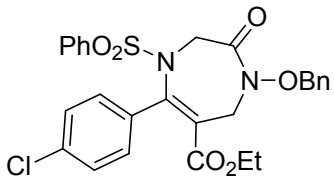

7.44
7.42
7.41
7.41
7.39
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7.34
7.32
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7.31
7.30
7.28
7.26
7.24
7.22
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7.20
6.98
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6.95
6.94
6.93
6.92
6.92
6.91
6.81
6.80
6.80
6.78
6.76
6.76
6.75
4.89
4.46
4.44
3.88
3.86
3.85
3.83
0.85
0.83
0.81
3.00
3.57
4.06
2.01
2.02
2.04
3.96
2.00
3.26
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
f1 (ppm)


164.58
163.82
163.16
161.31
149.90
138.56
135.69
132.23
130.30
130.21
129.49
129.45
128.01
127.94
127.64
125.86
125.21
114.12
113.90
75.91
60.46
53.35
50.17
12.47
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

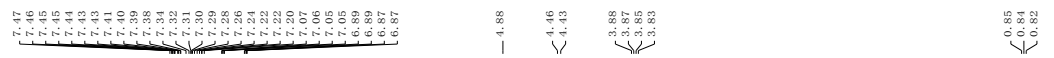

PhO2S
N
O
N−OBn
Cl
CO2Et
3ac

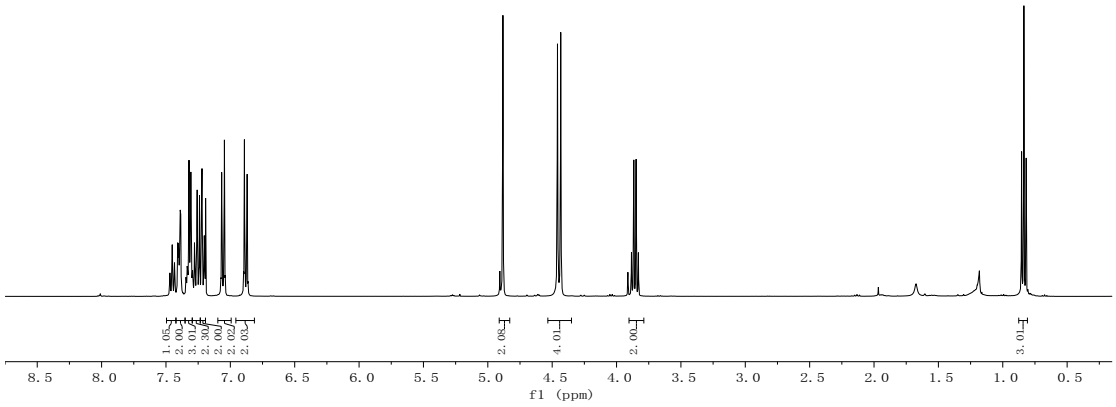

7.47
7.45
7.44
7.44
7.43
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7.41
7.40
7.39
7.34
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7.32
7.31
7.31
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7.29
7.27
7.25
7.23
7.23
7.21
7.20
7.19
7.08
7.06
7.04
6.90
6.90
6.90
6.88
6.88
6.88
6.85
6.85
6.84
4.45
4.44
3.88
3.86
3.85
3.83
0.83
0.81
0.80
1.05
2.00
3.01
5.03
1.06
2.00
2.07
3.93
2.00
3.13
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
f1 (ppm)

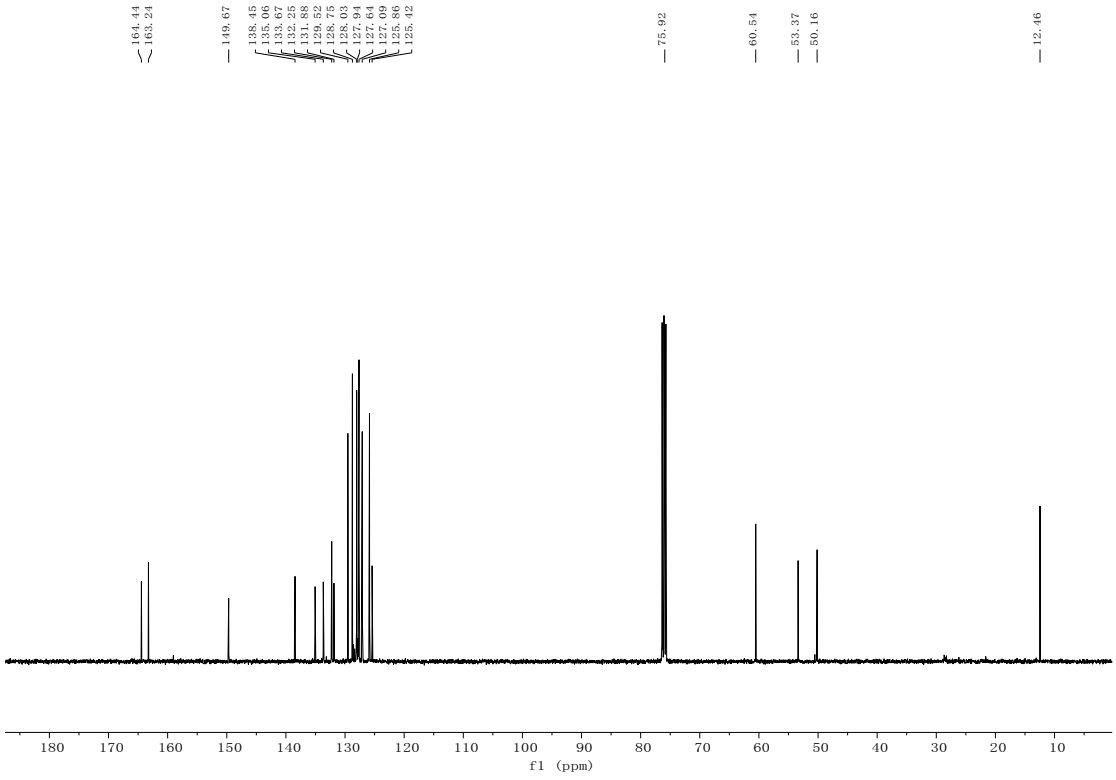

164.41
163.42
149.03
138.21
134.94
133.67
132.87
132.43
128.86
128.79
128.14
128.08
128.05
127.94
127.64
126.63
125.84
125.77
75.94
60.55
53.38
50.24
12.38
180
170
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150
140
130
120
110
100
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70
60
50
40
30
20
10
f1 (ppm)

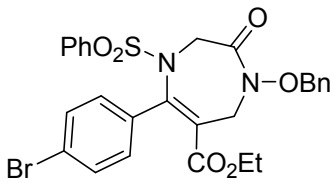

PhO2S
N
O
N−OBn
Cl
CO2Et

3ad

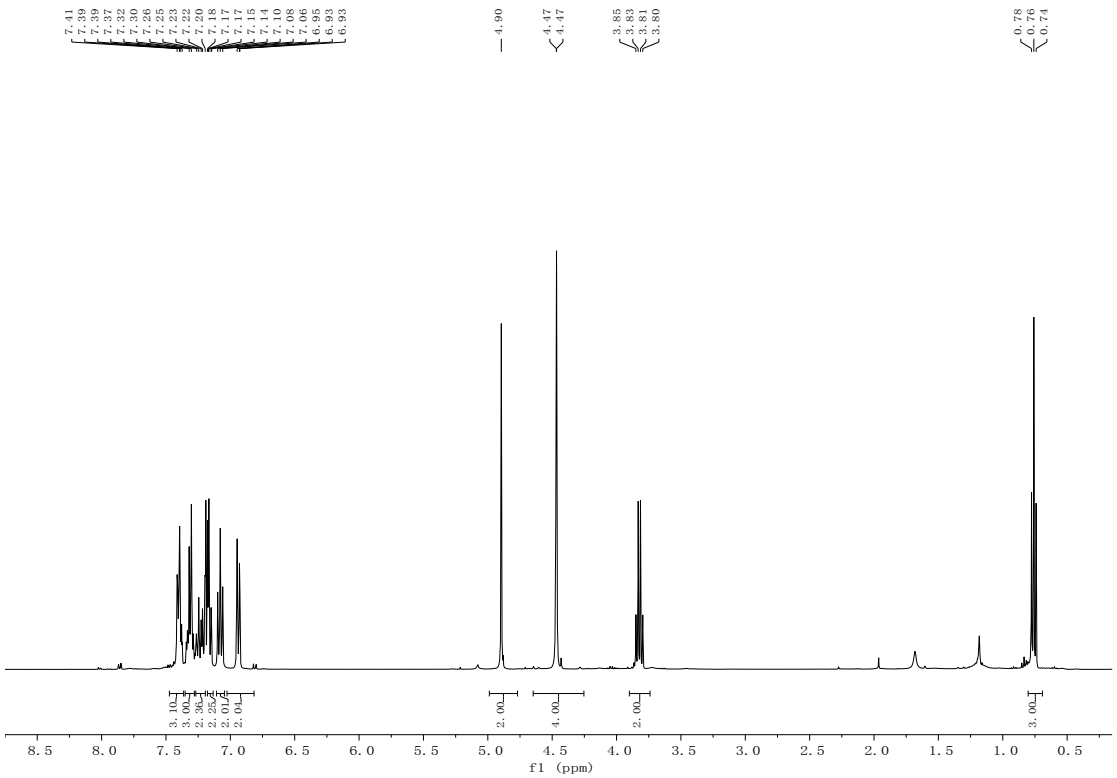

7.47
7.46
7.45
7.45
7.44
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7.34
7.32
7.31
7.30
7.29
7.28
7.26
7.24
7.22
7.20
7.07
7.06
7.05
6.89
6.89
6.87
6.87
4.88
4.46
4.43
3.88
3.87
3.85
3.83
0.85
0.84
0.82

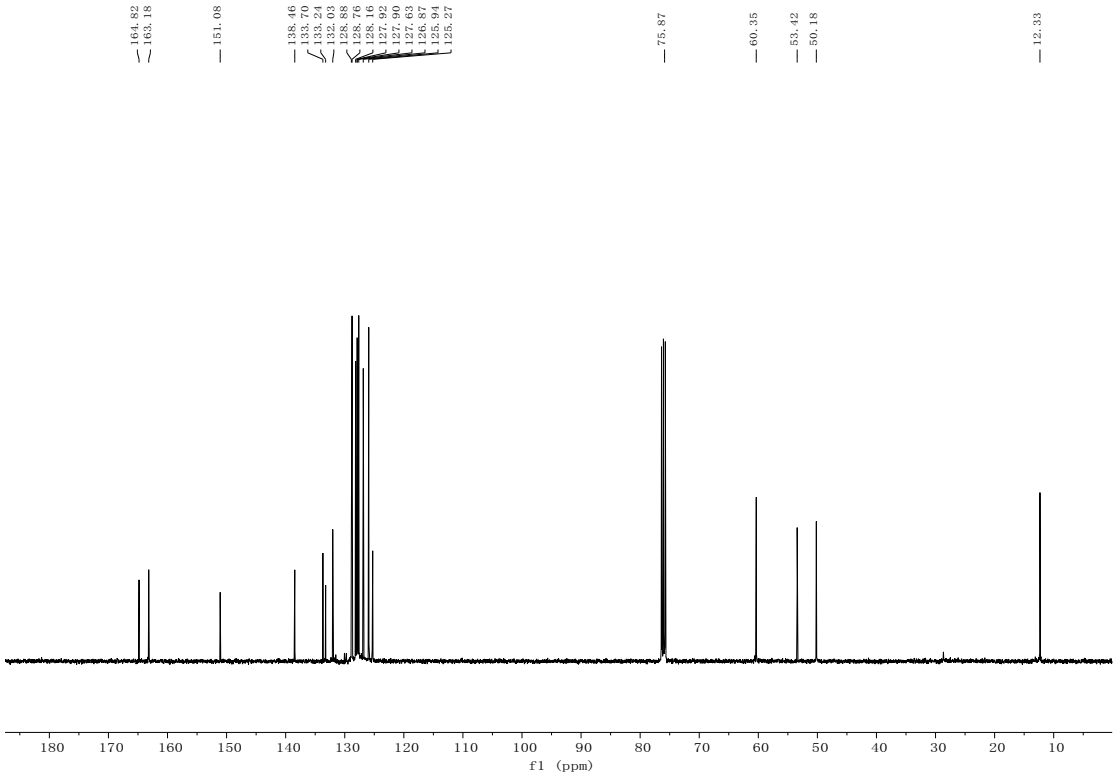

1.05
2.00
3.01
2.30
2.00
2.02
2.03
2.08
4.01
2.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

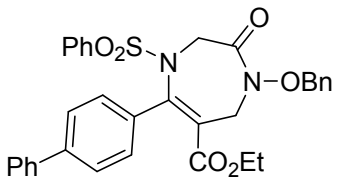

164.44
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128.03
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125.42
75.92
60.54
53.37
50.16
12.46
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100
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f1 (ppm)


PhO2S
N
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N−OBn
Br
CO2Et

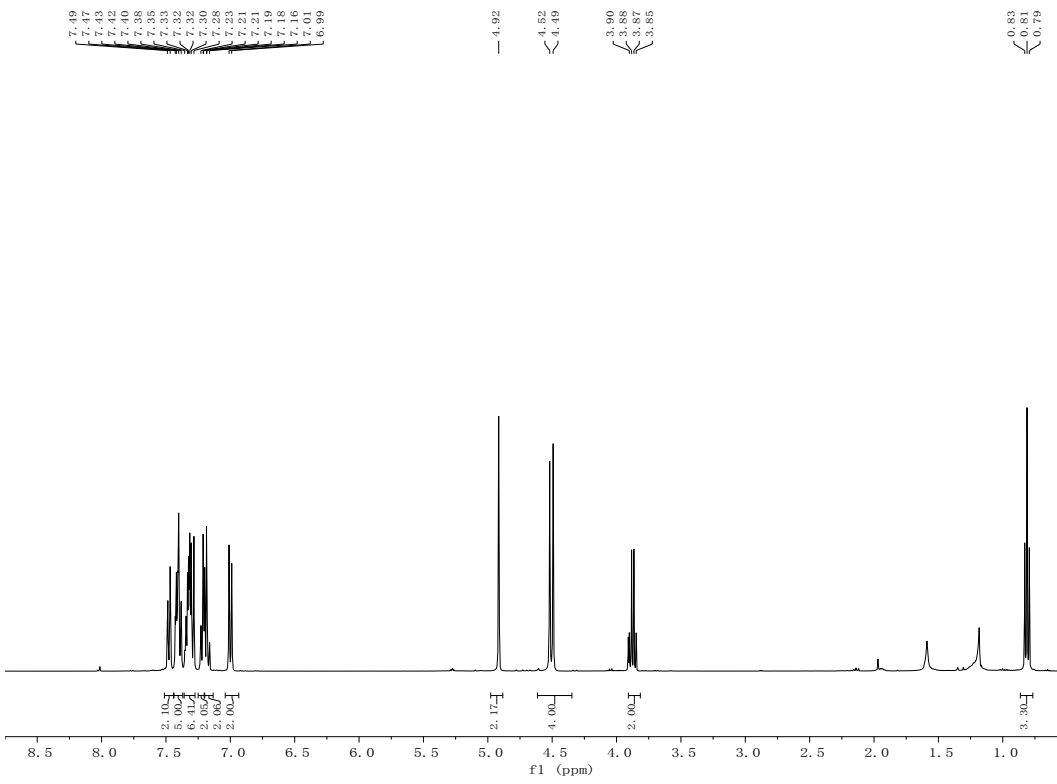
3ae

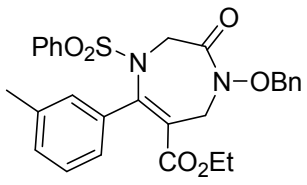

7.41
7.39
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7.37
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7.25
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7.22
7.20
7.18
7.17
7.17
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7.10
7.08
7.06
6.95
6.93
6.93
4.90
4.47
4.47
3.85
3.83
3.81
3.80
0.78
0.76
0.74
3.10
3.00
2.38
2.25
2.01
2.04
2.00
4.00
2.00
3.00
f1 (ppm)


164.82
163.18
151.08
138.46
133.70
133.24
132.03
128.88
128.76
128.16
127.92
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126.87
125.94
125.27
75.87
60.35
53.42
50.18
12.33
f1 (ppm)

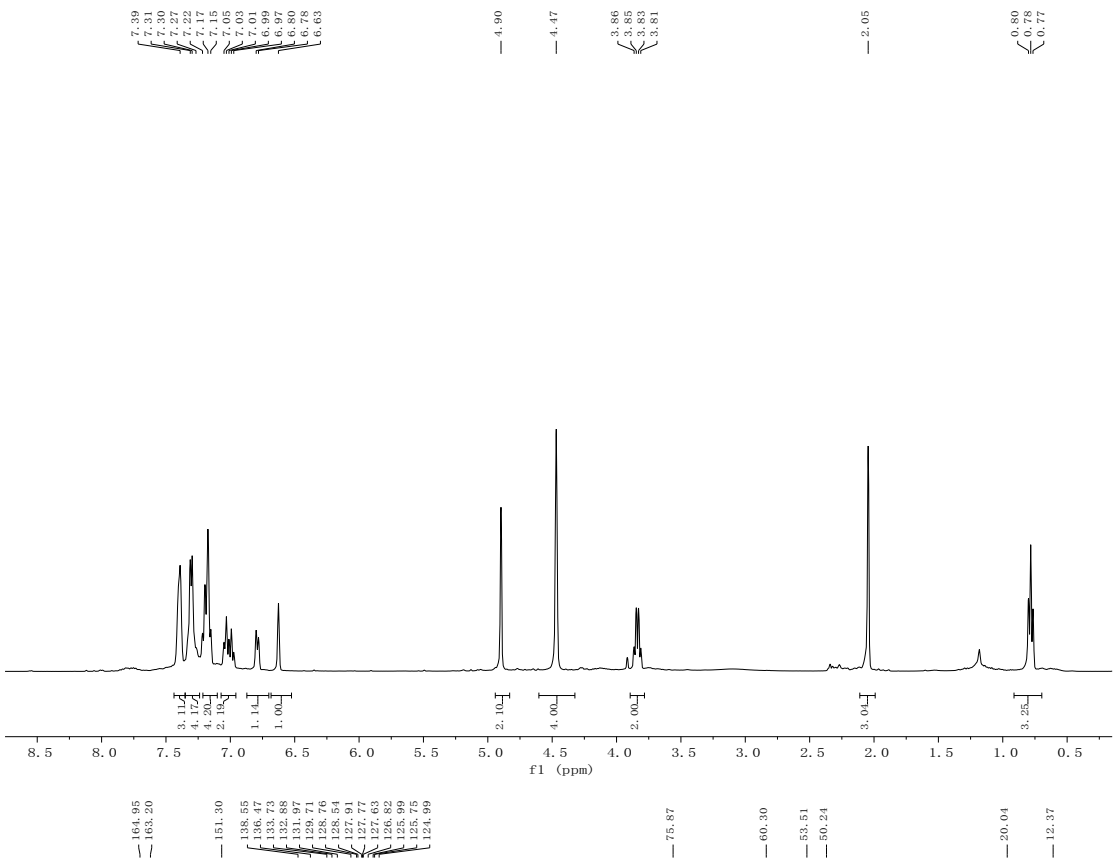

PhO2S
N
O
N−OBn
Ph
CO2Et

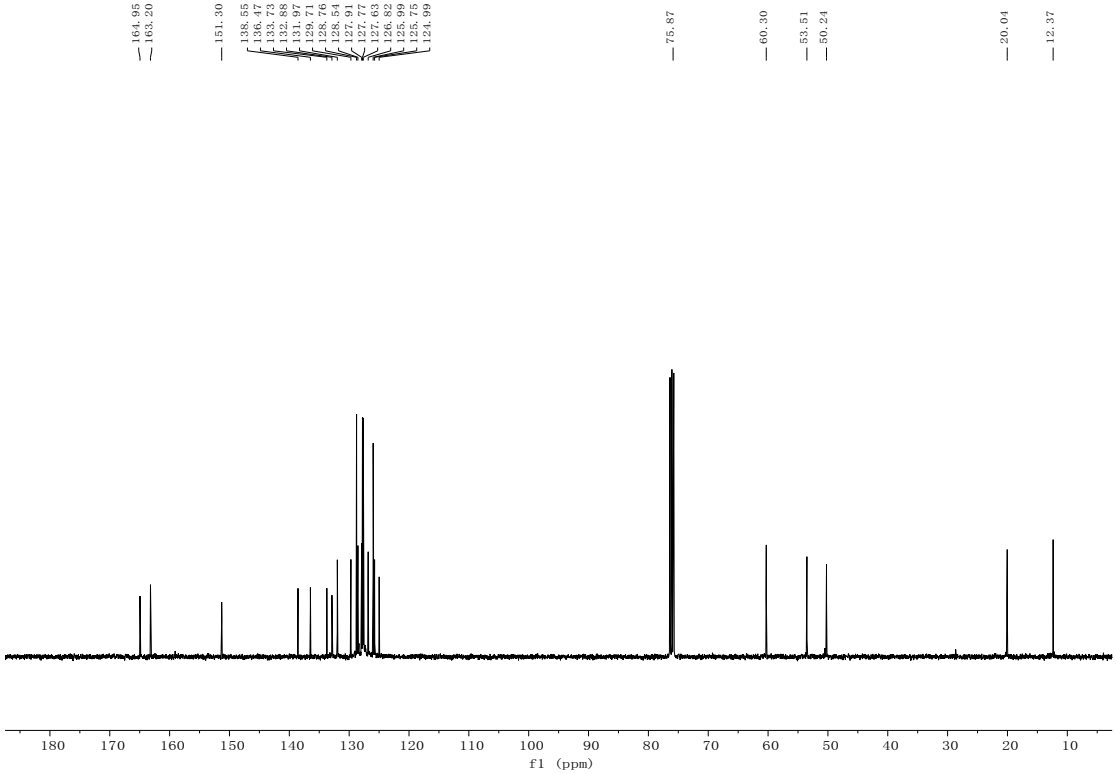
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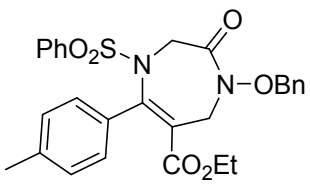

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7.33
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7.28
7.23
7.21
7.21
7.19
7.18
7.16
7.01
6.99
4.92
4.52
4.49
3.90
3.88
3.87
3.85
0.83
0.81
0.79
2.10
5.00
6.41
2.05
2.06
2.00
2.17
4.00
2.00
3.30
f1 (ppm)
164.77
163.06
150.90
141.73
138.98
138.65
133.72
132.07
131.98
128.78
128.70
127.97
127.93
127.88
127.65
126.98
125.97
125.42
125.20
60.42
53.48
50.19
12.42
f1 (ppm)


PhO2S
N
O
N−OBn
CO2Et

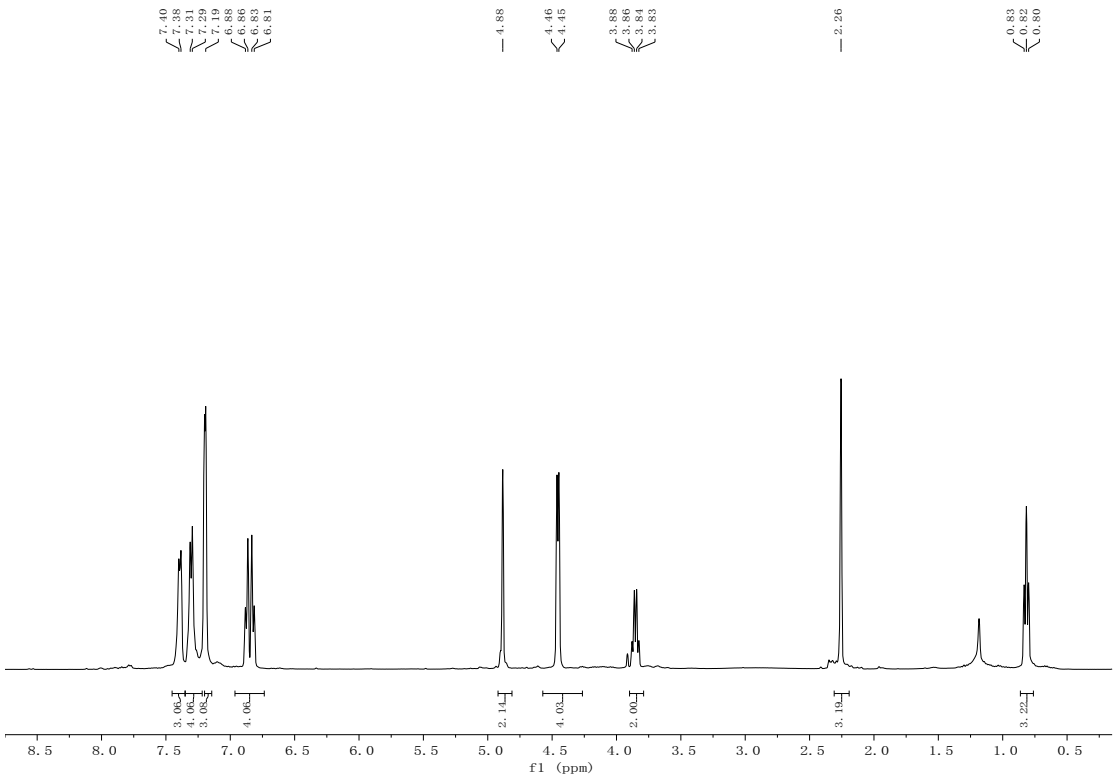
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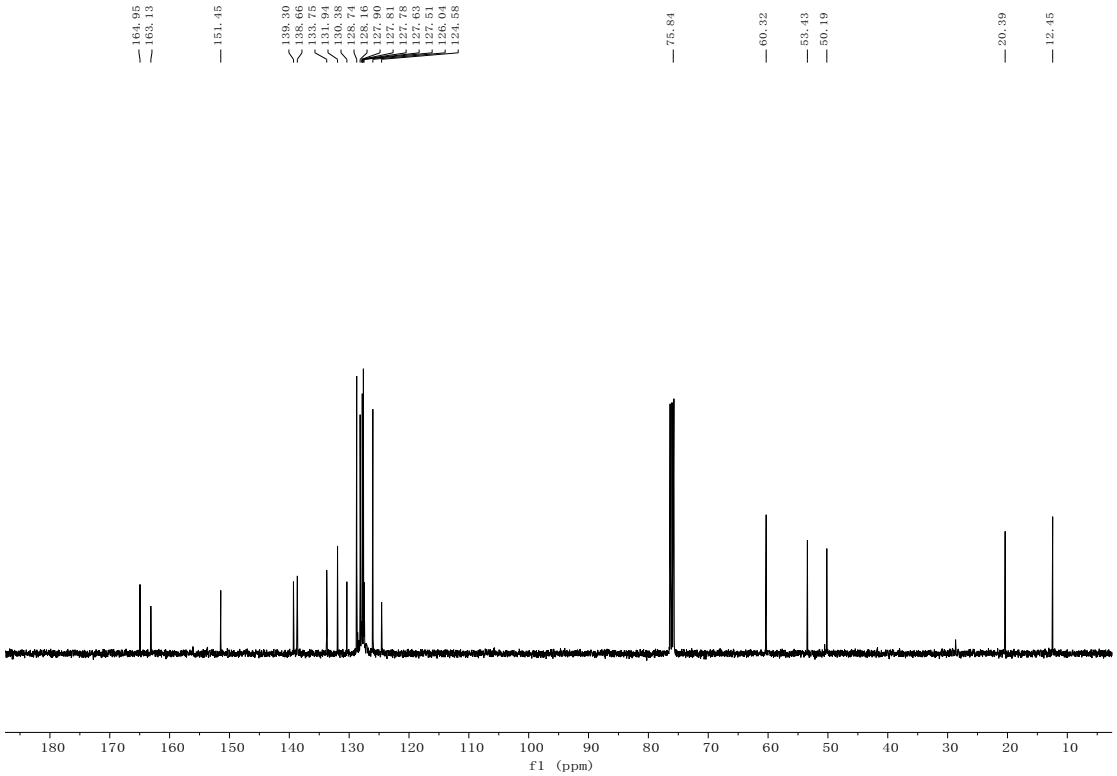

7.39
7.31
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7.17
7.15
7.05
7.03
7.01
6.99
6.97
6.80
6.78
6.63
4.90
4.47
3.86
3.85
3.83
3.81
2.05
0.80
0.78
0.77
3.11
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2.19
1.14
1.00
2.10
4.00
2.00
3.04
3.25
f1 (ppm)

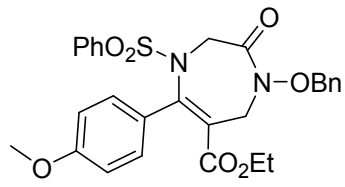

164.95
163.20
151.30
138.55
136.47
133.73
132.88
131.97
129.71
128.76
128.54
127.91
127.77
127.63
126.82
125.99
125.75
124.99
75.87
60.30
53.51
50.24
20.04
12.37
f1 (ppm)


PhO2S
N
O
N−OBn
CO2Et

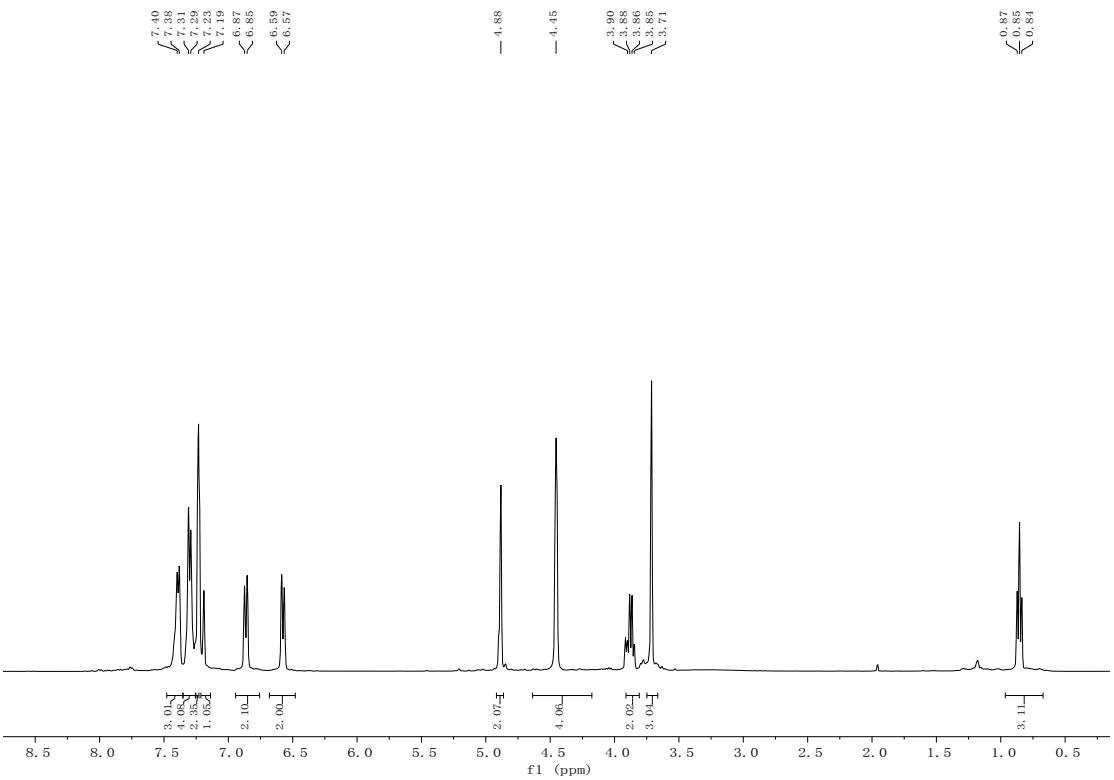
3ai

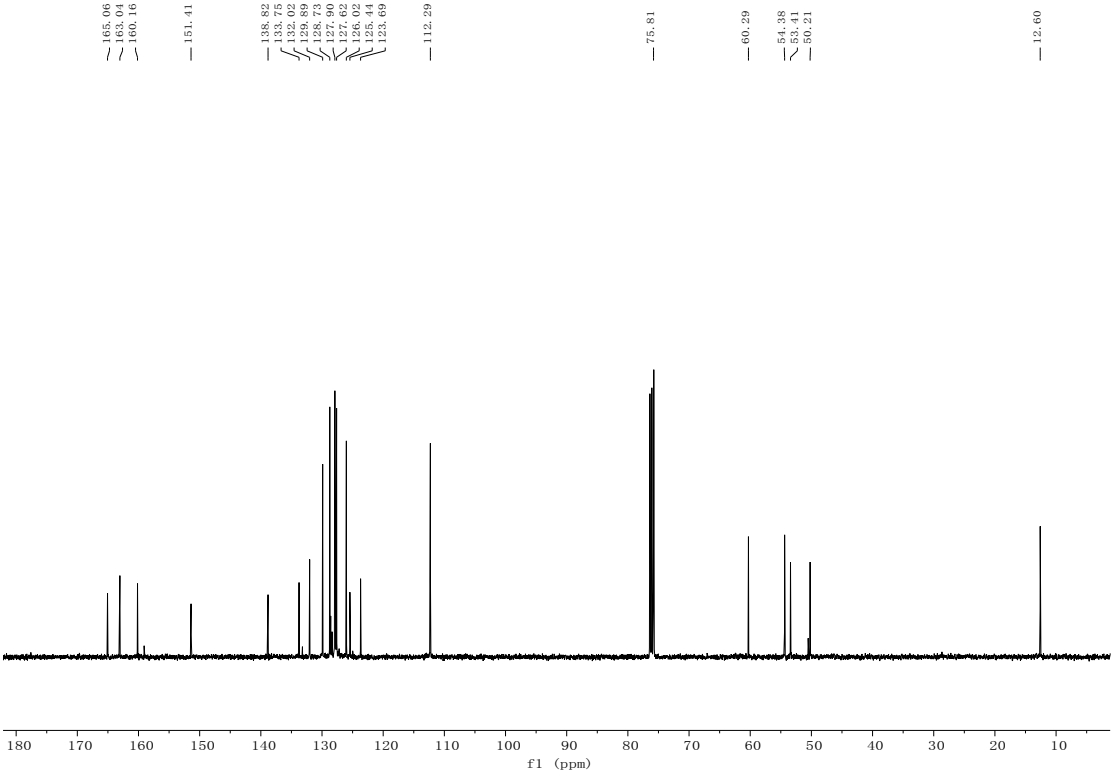

7.40
7.38
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6.88
6.86
6.83
6.81
4.88
4.46
4.45
3.88
3.86
3.84
3.83
2.26
0.83
0.82
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4.06
3.08
4.06
2.14
4.03
2.00
3.19
3.22
f1 (ppm)

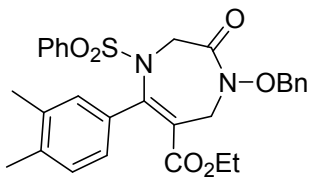

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163.13
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133.75
131.94
130.38
128.74
128.16
127.90
127.81
127.78
127.63
127.51
126.04
124.58
75.84
60.32
53.43
50.19
20.39
12.45
f1 (ppm)


PhO2S
N
O
N−OBn
O
CO2Et

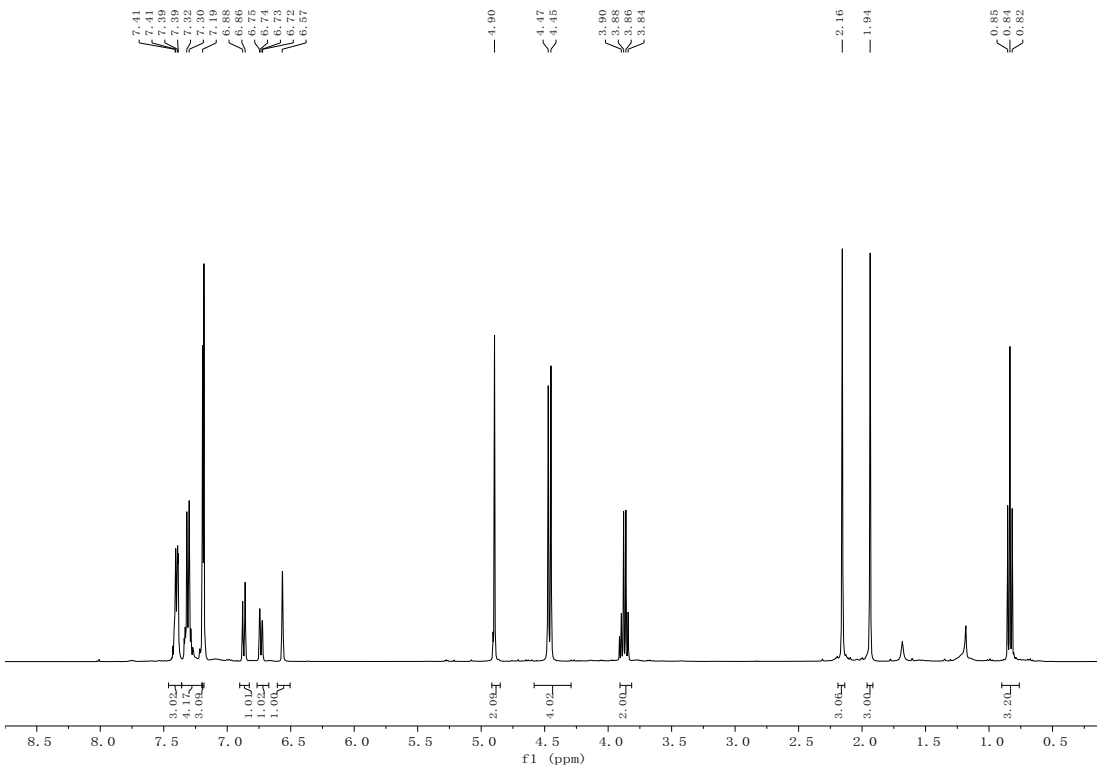
3aj

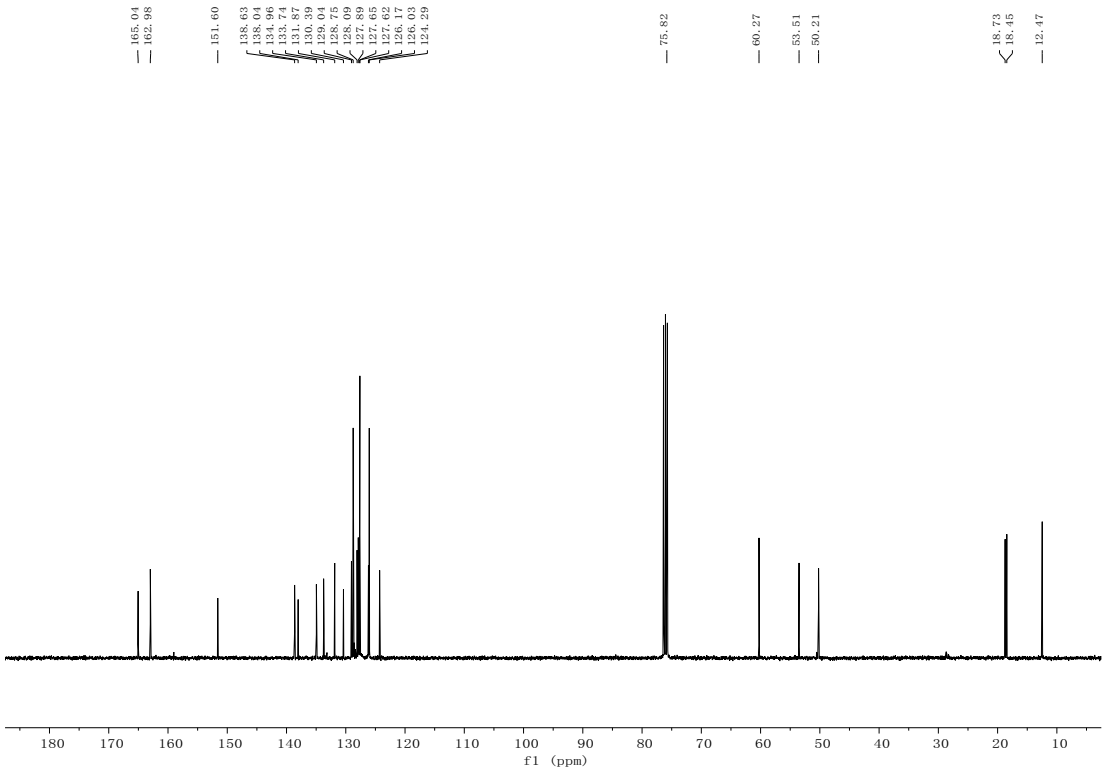

7.40
7.38
7.31
7.29
7.23
7.19
6.87
6.85
6.59
6.57
4.88
4.45
3.90
3.88
3.86
3.85
3.71
0.87
0.85
0.84
3.01
4.08
2.35
1.05
2.10
2.00
2.07
4.06
2.02
3.04
3.11
f1 (ppm)

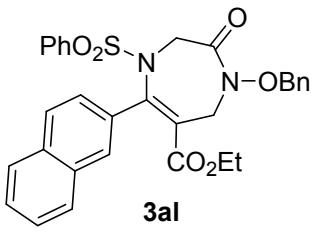

165.06
163.04
160.16
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133.75
132.02
129.89
128.73
127.90
127.62
126.02
125.44
123.69
112.29
75.81
60.29
54.38
53.41
50.21
12.60
f1 (ppm)


PhO2S
N
O
N−OBn
CO2Et

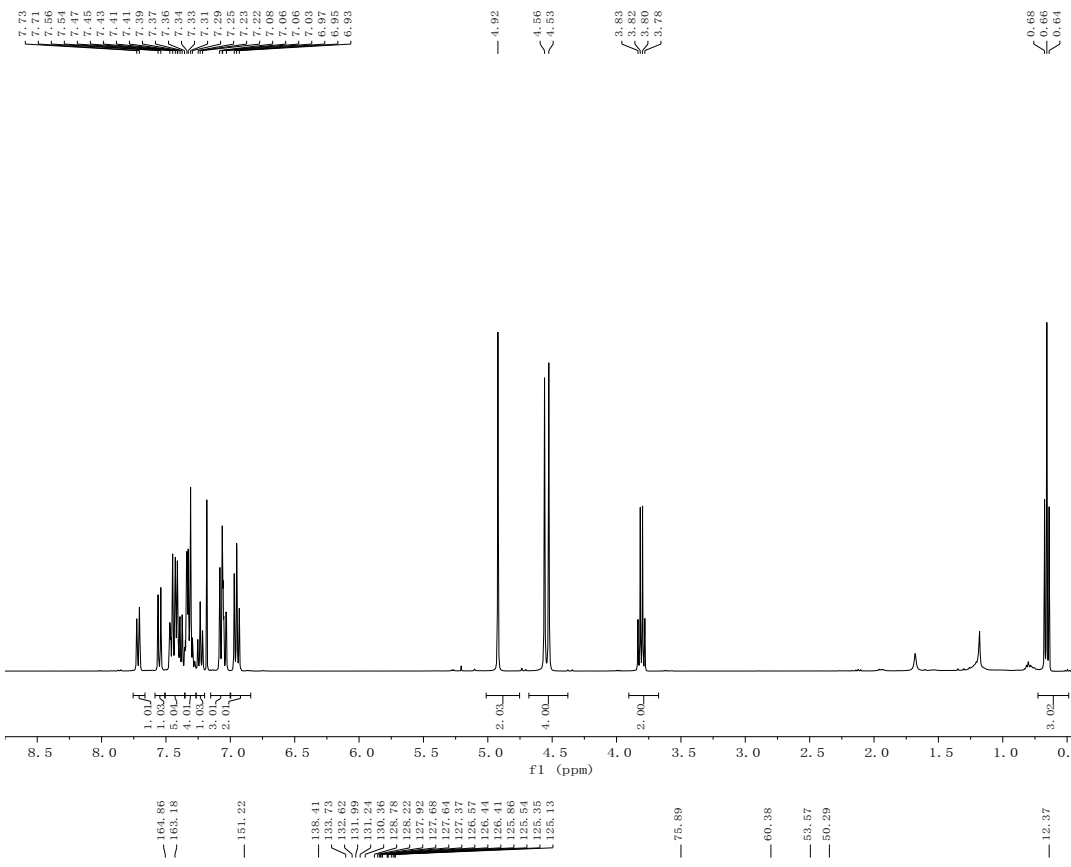
3ak

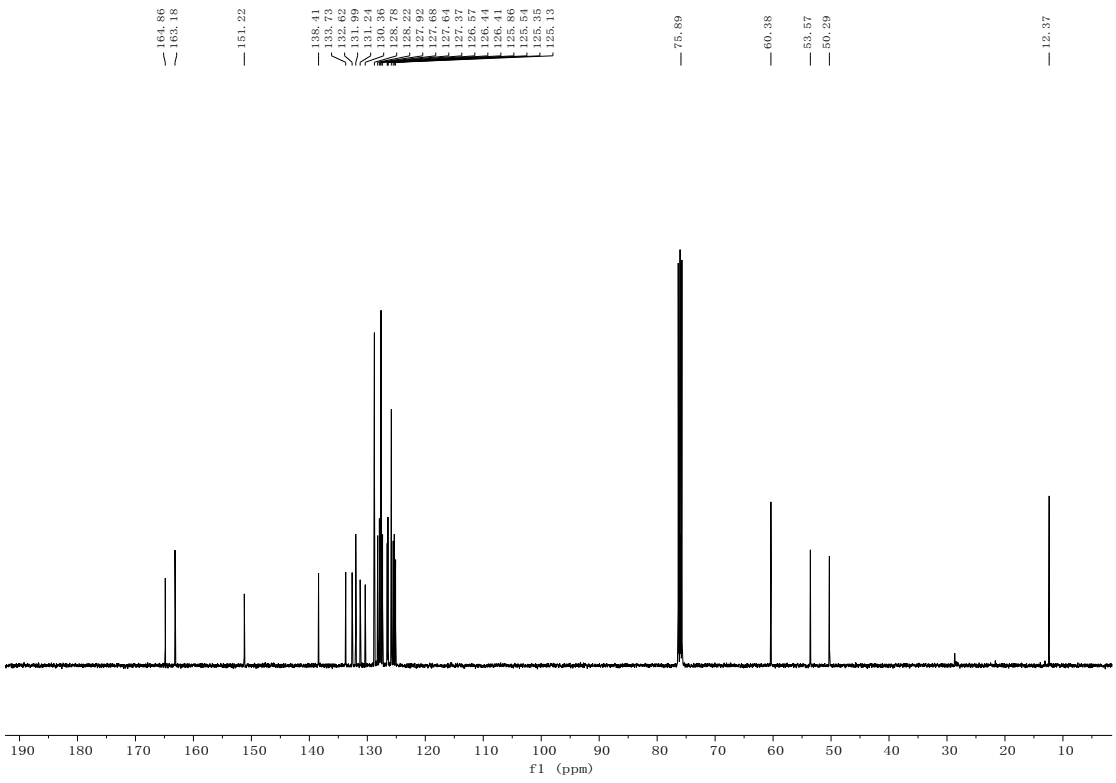

7.41
7.41
7.39
7.39
7.32
7.30
7.19
6.88
6.86
6.75
6.74
6.73
6.72
6.57
4.90
4.47
4.45
3.90
3.88
3.86
3.84
2.16
1.94
0.85
0.84
0.82
3.02
4.17
3.04
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1.02
1.00
2.05
4.02
2.00
3.06
3.00
3.20
f1 (ppm)

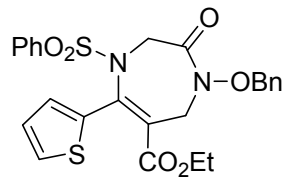

165.04
162.98
151.60
138.63
138.04
134.96
133.74
131.87
130.39
129.04
128.75
128.09
127.89
127.65
127.62
126.17
126.03
124.29
75.82
60.27
53.51
50.21
18.73
18.45
12.47
f1 (ppm)


PhO2S
N
O
N−OBn
CO2Et

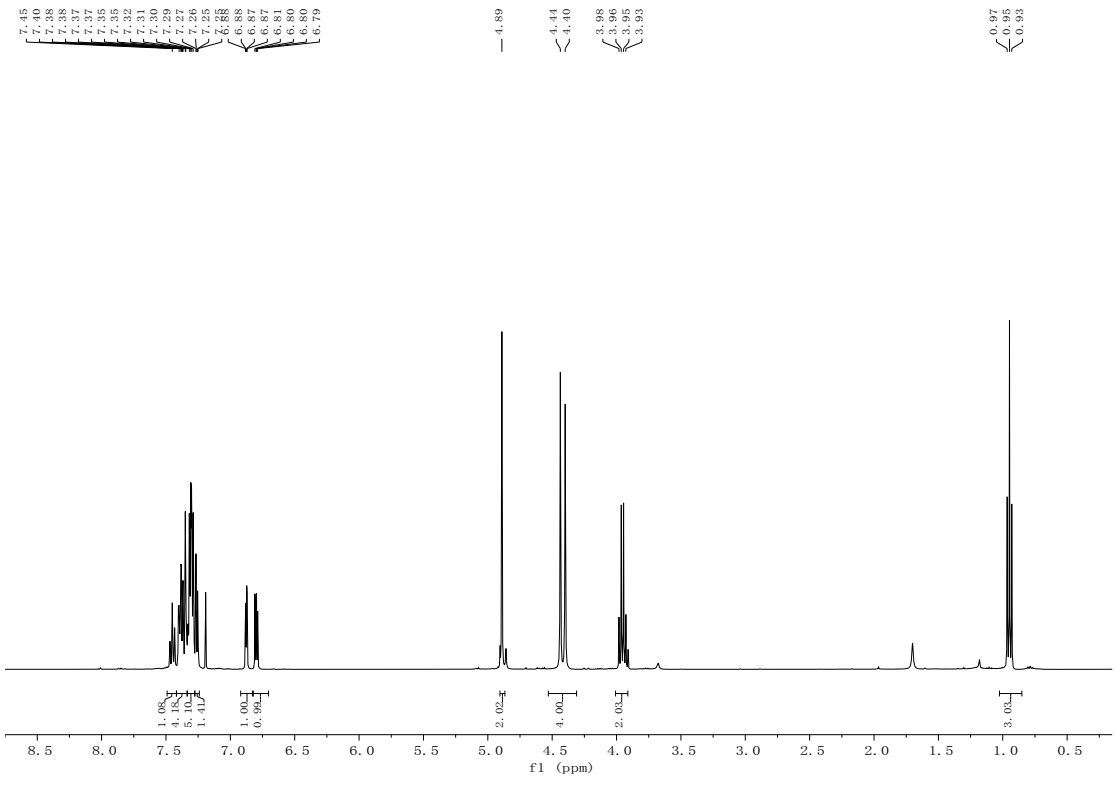
3al

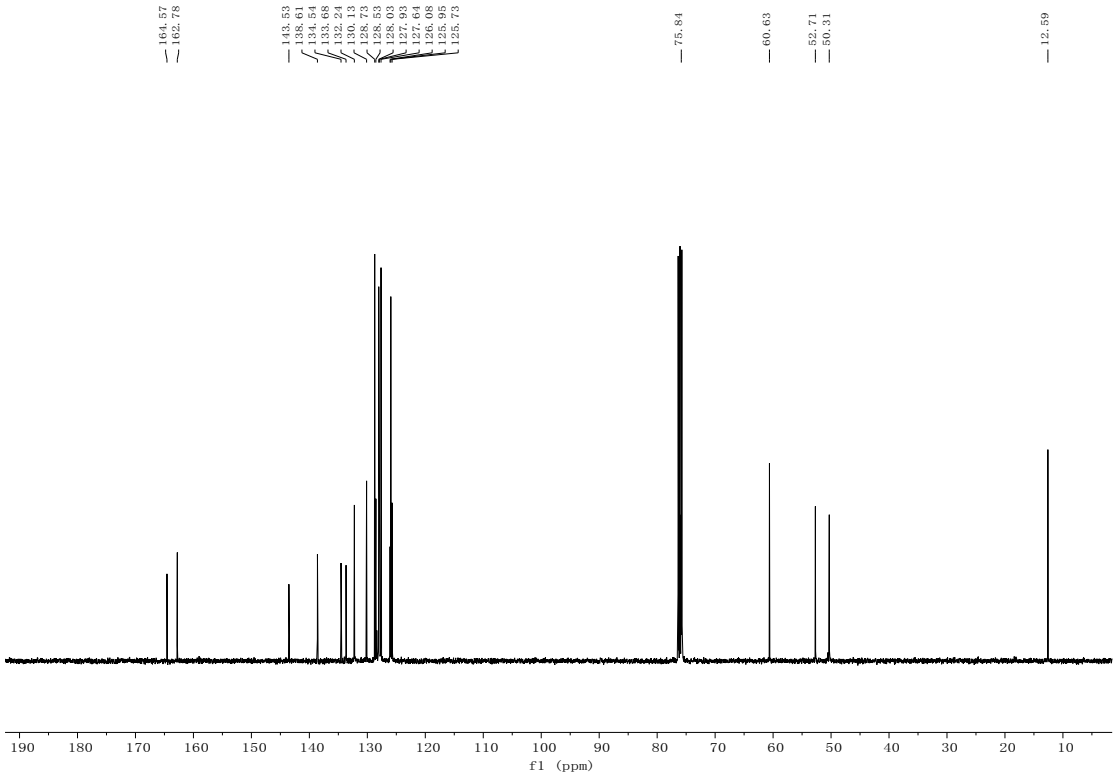


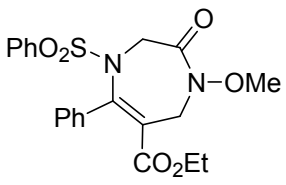




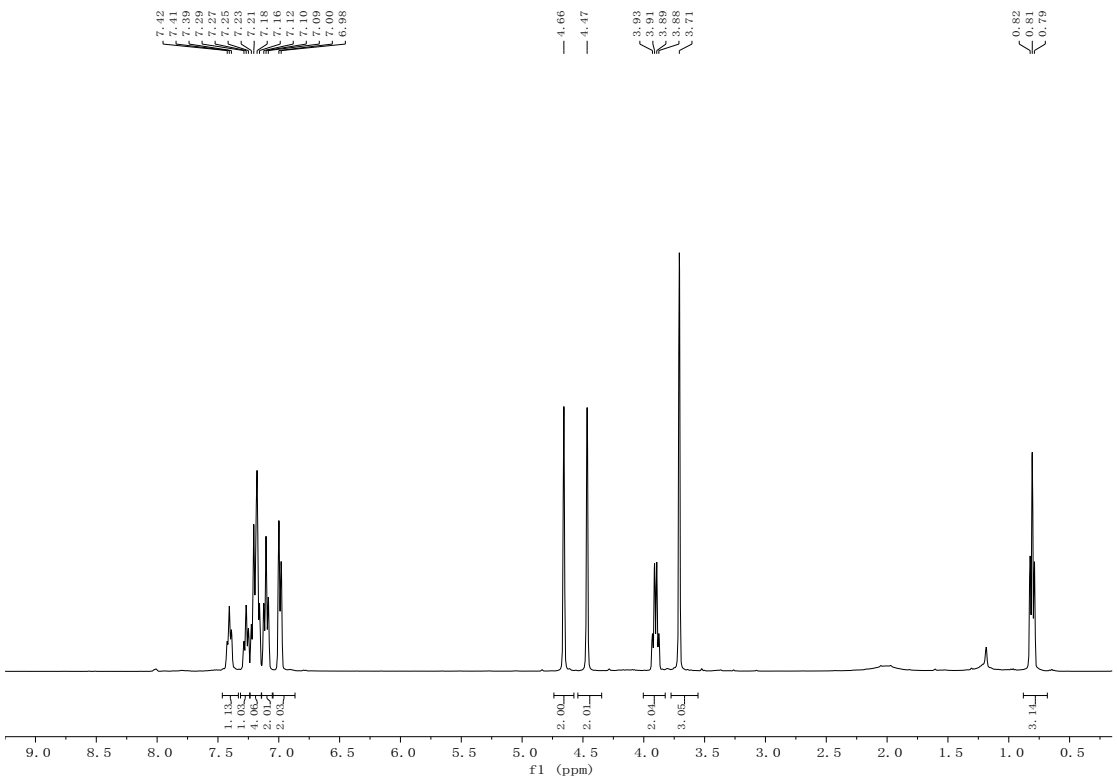
3am

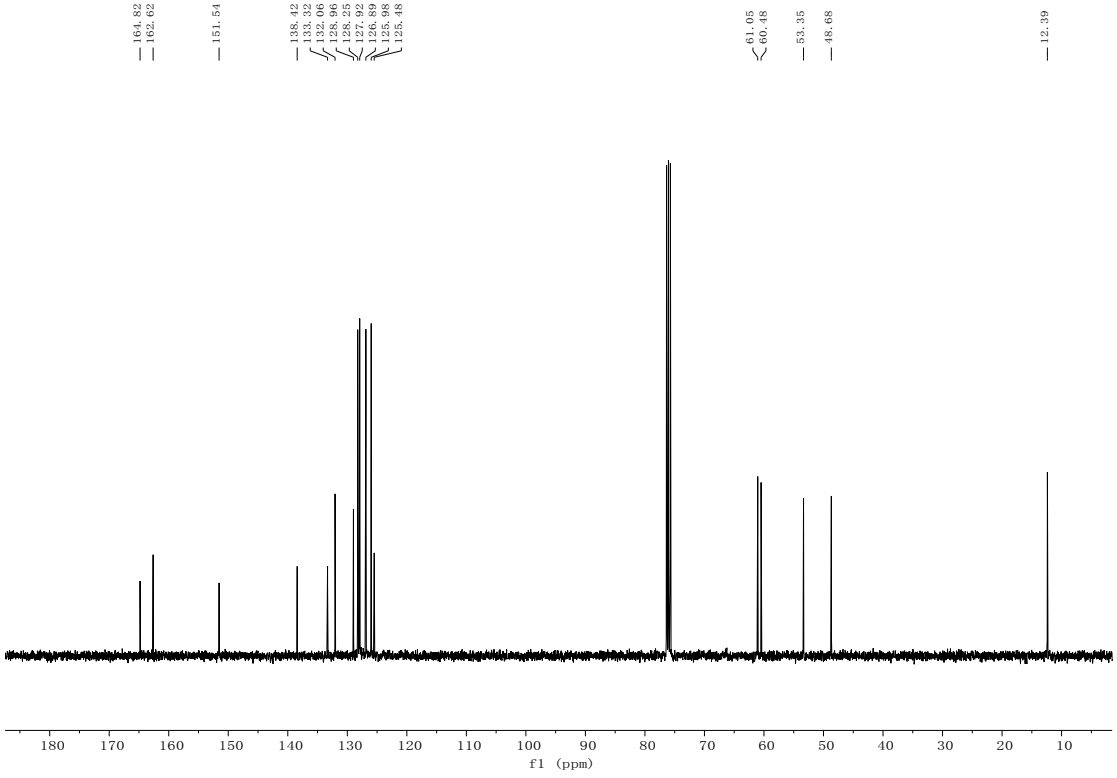

7.45
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7.35
7.35
7.32
7.31
7.30
7.29
7.27
7.26
7.25
6.88
6.87
6.87
6.81
6.80
6.80
6.79
4.89
4.44
4.40
3.98
3.96
3.95
3.93
0.97
0.95
0.93
1.08
4.18
5.10
1.41
1.00
0.99
2.02
4.00
2.03
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

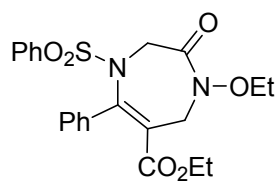

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132.24
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128.73
128.53
128.03
127.93
127.64
126.08
125.95
125.73
75.84
60.63
52.71
50.31
12.59
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


PhO2S
N
O
N−OMe
Ph
CO2Et

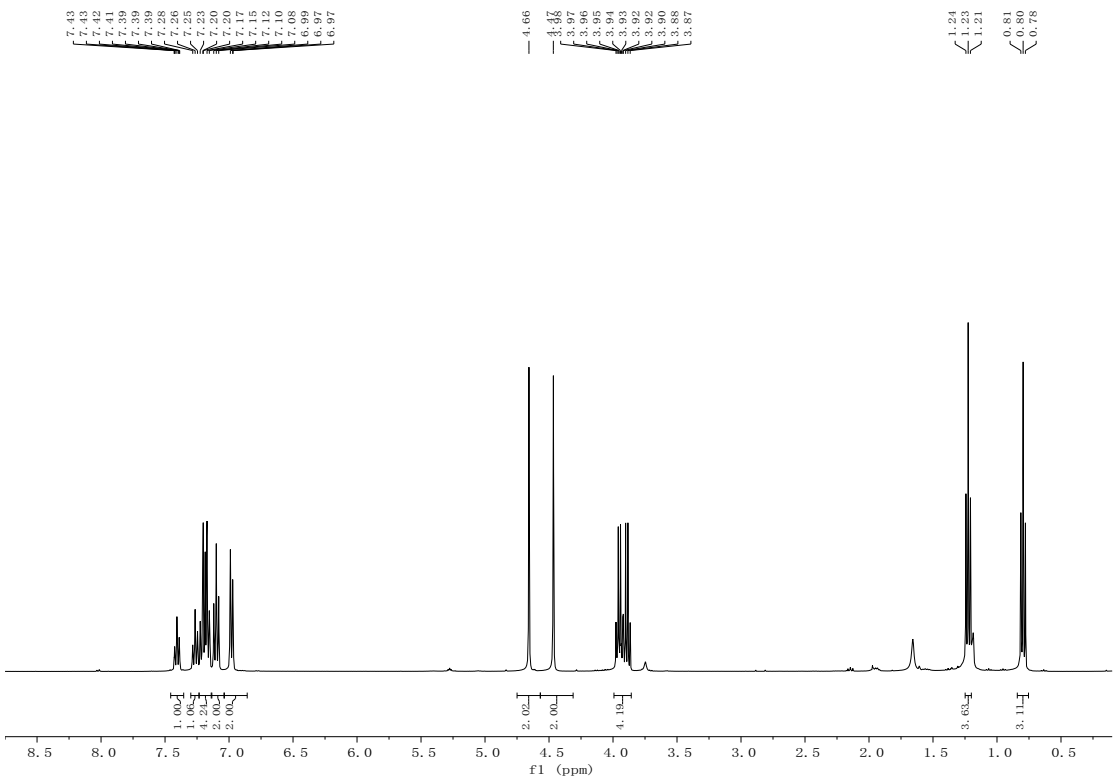
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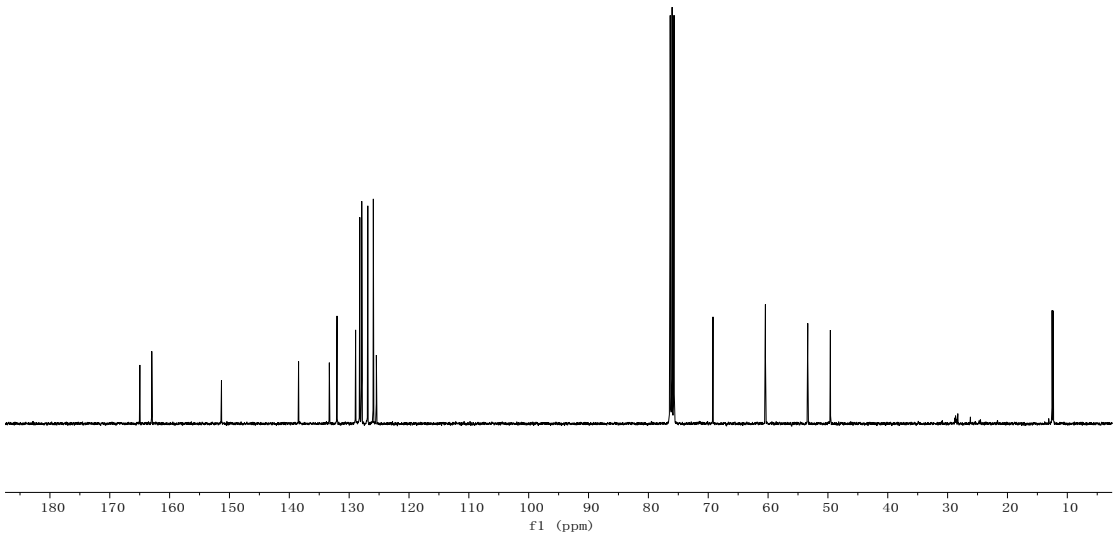

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7.09
7.00
6.98
4.66
4.47
3.93
3.91
3.89
3.88
3.71
0.82
0.81
0.79
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4.06
2.01
2.03
2.00
2.01
2.04
3.05
3.14
f1 (ppm)

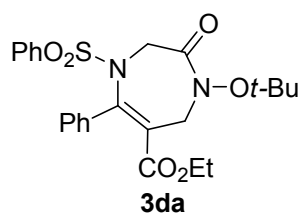

164.82
162.62
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133.32
132.06
128.96
128.25
127.92
126.89
125.98
125.48
61.05
60.48
53.35
48.68
12.39
f1 (ppm)


PhO2S
N
O
N−OEt
Ph
CO2Et

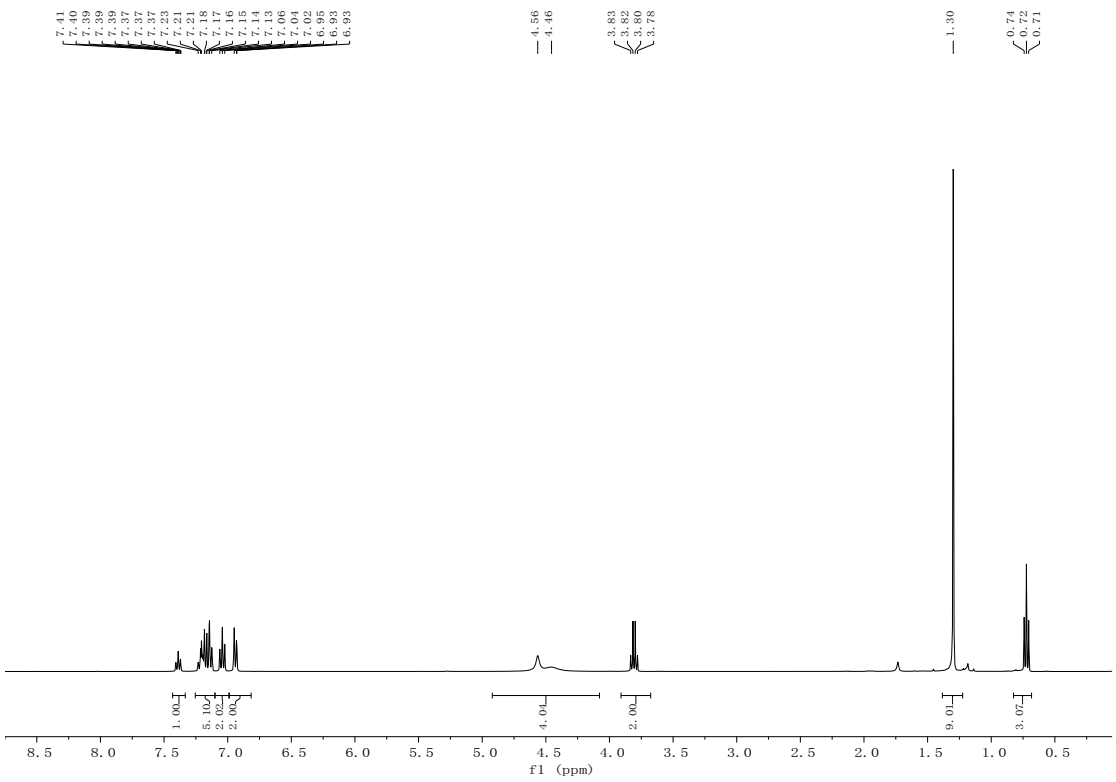
3ca

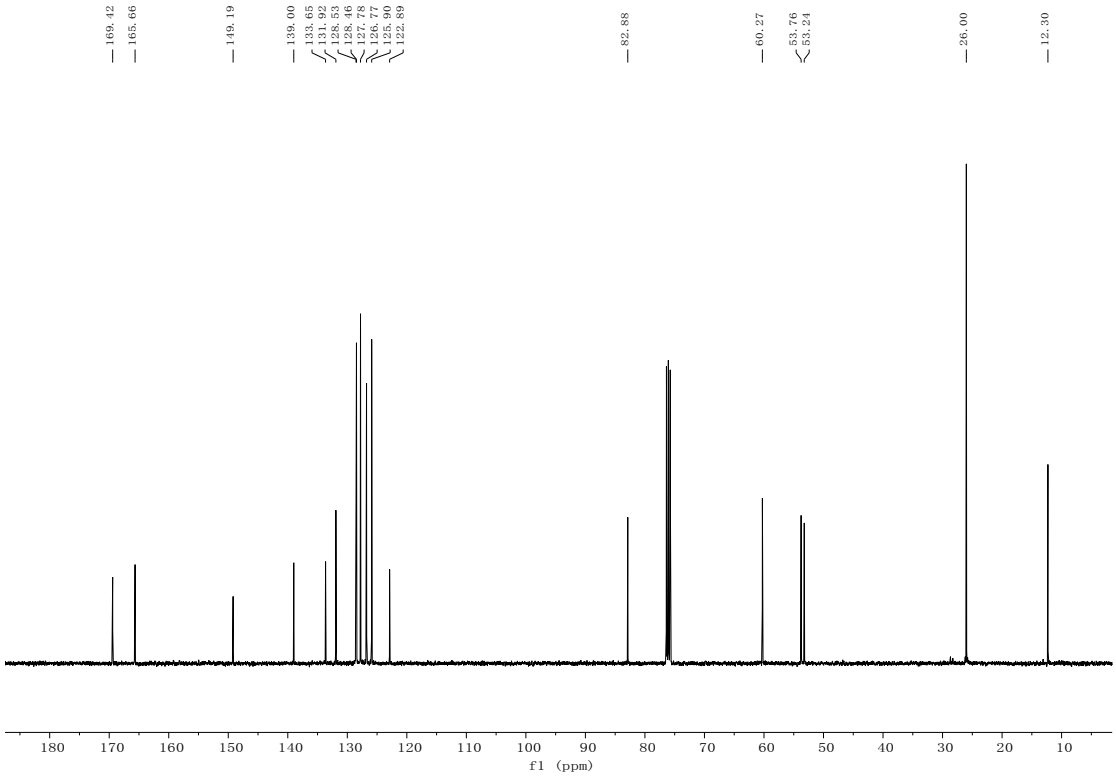


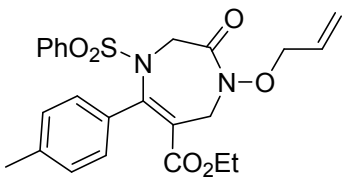




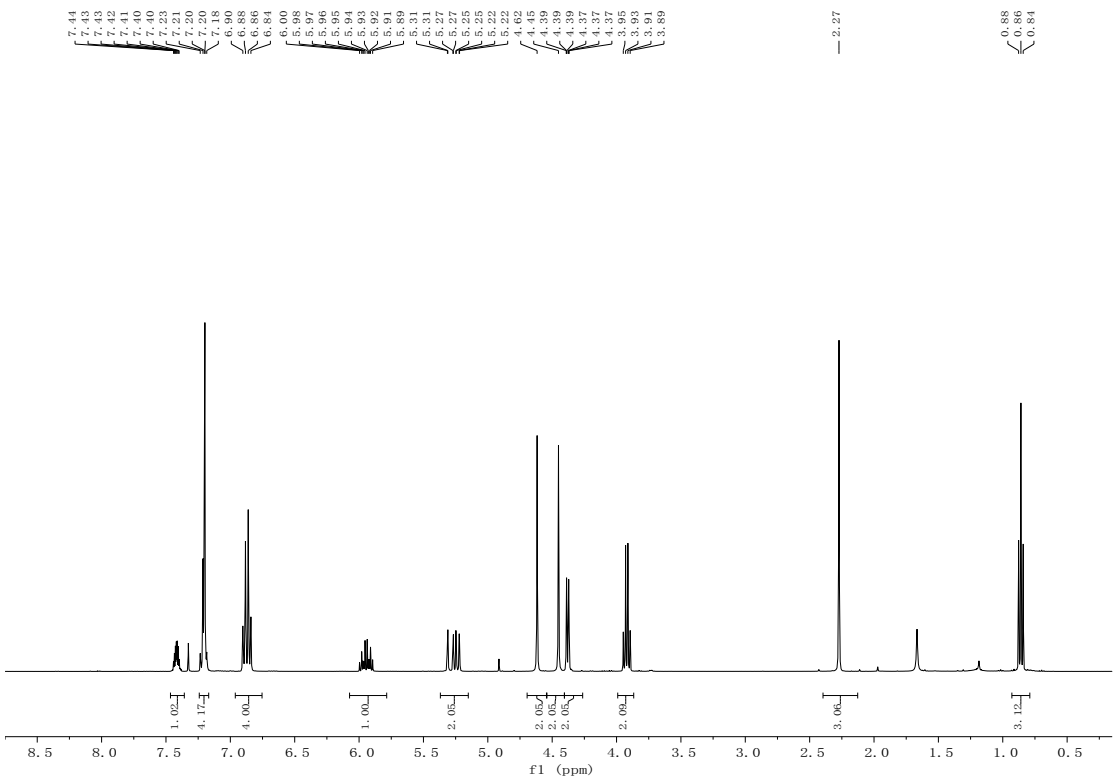
3da

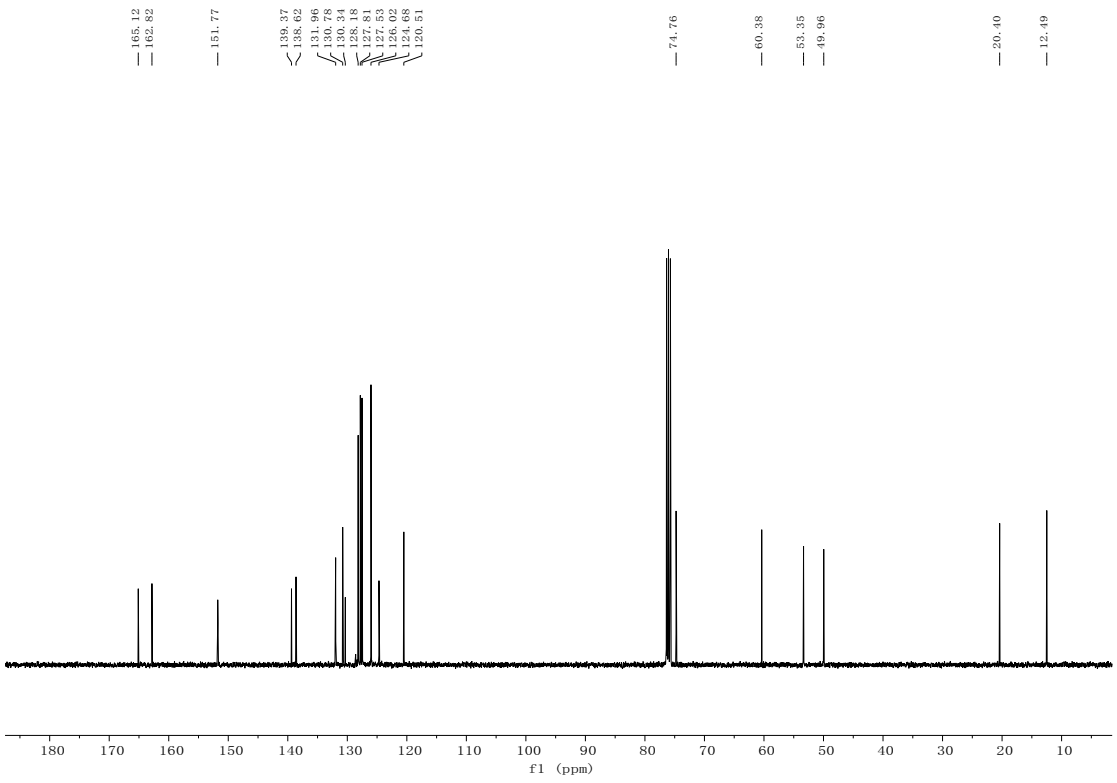

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7.39
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7.37
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7.21
7.18
7.17
7.16
7.15
7.14
7.13
7.06
7.04
7.02
6.95
6.93
6.93
4.56
4.46
3.83
3.82
3.80
3.78
1.30
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0.72
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1.00
5.10
2.02
2.00
4.04
2.00
9.01
3.07
f1 (ppm)

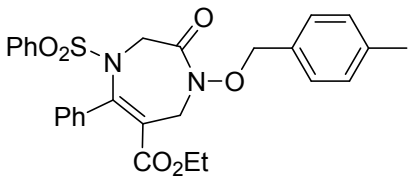

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128.53
128.46
127.78
126.77
125.90
122.89
82.88
60.27
53.76
53.24
26.00
12.30
f1 (ppm)


PhO2S
N
O
N–O
CO2Et

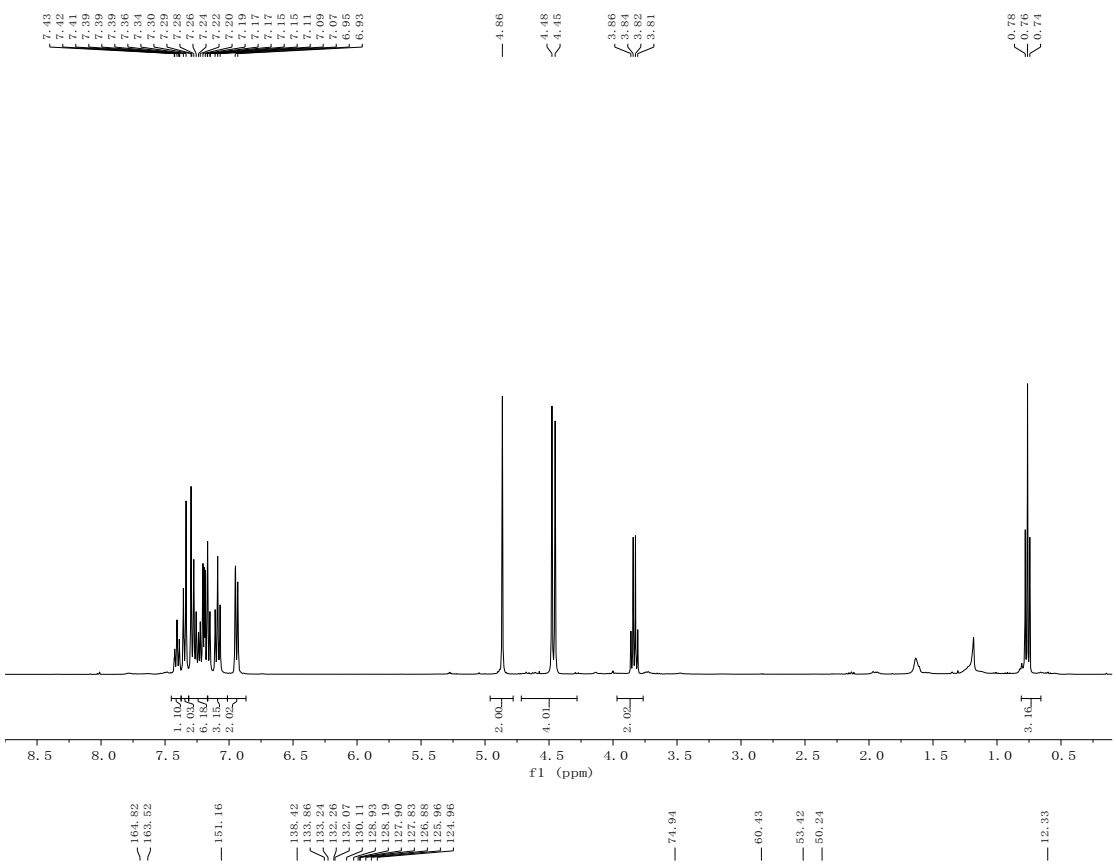
3ei

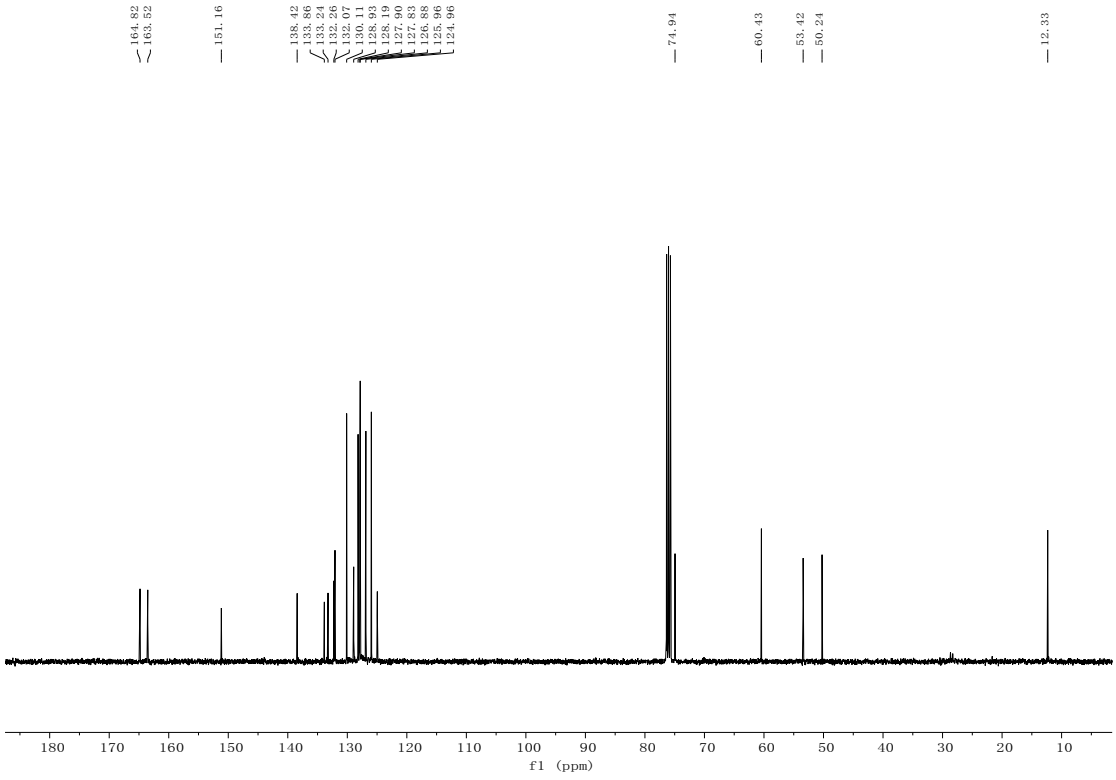

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6.88
6.86
6.84
6.00
5.98
5.97
5.96
5.95
5.94
5.93
5.92
5.91
5.89
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4.45
4.39
4.39
4.39
4.37
4.37
4.37
3.95
3.93
3.91
3.89
2.27
0.88
0.86
0.84
1.02
4.17
4.00
1.00
2.05
2.05
2.05
2.05
2.09
3.06
3.12
8.5
8.0
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7.0
6.5
6.0
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4.0
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3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

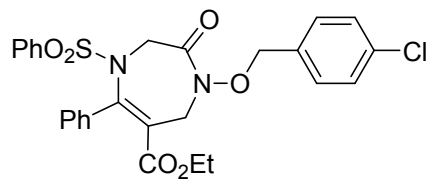

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74.76
60.38
53.35
49.96
20.40
12.49
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


PhO2S
N
O
N–O
Ph
CO2Et

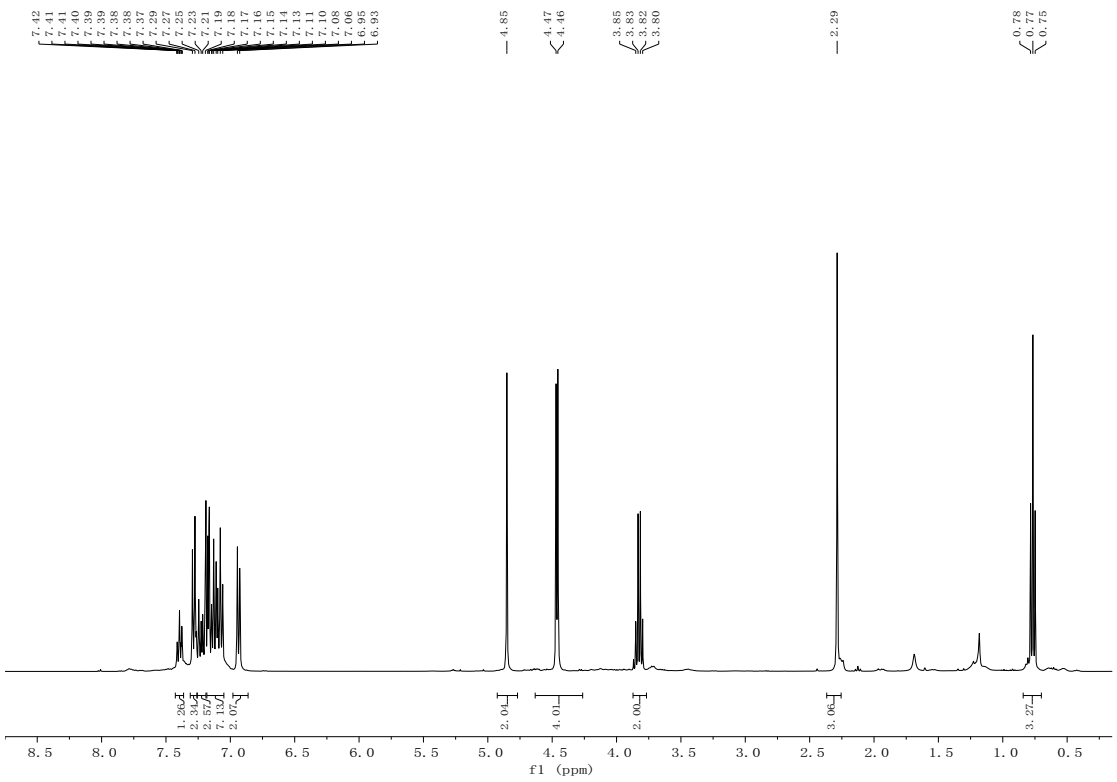
3fa

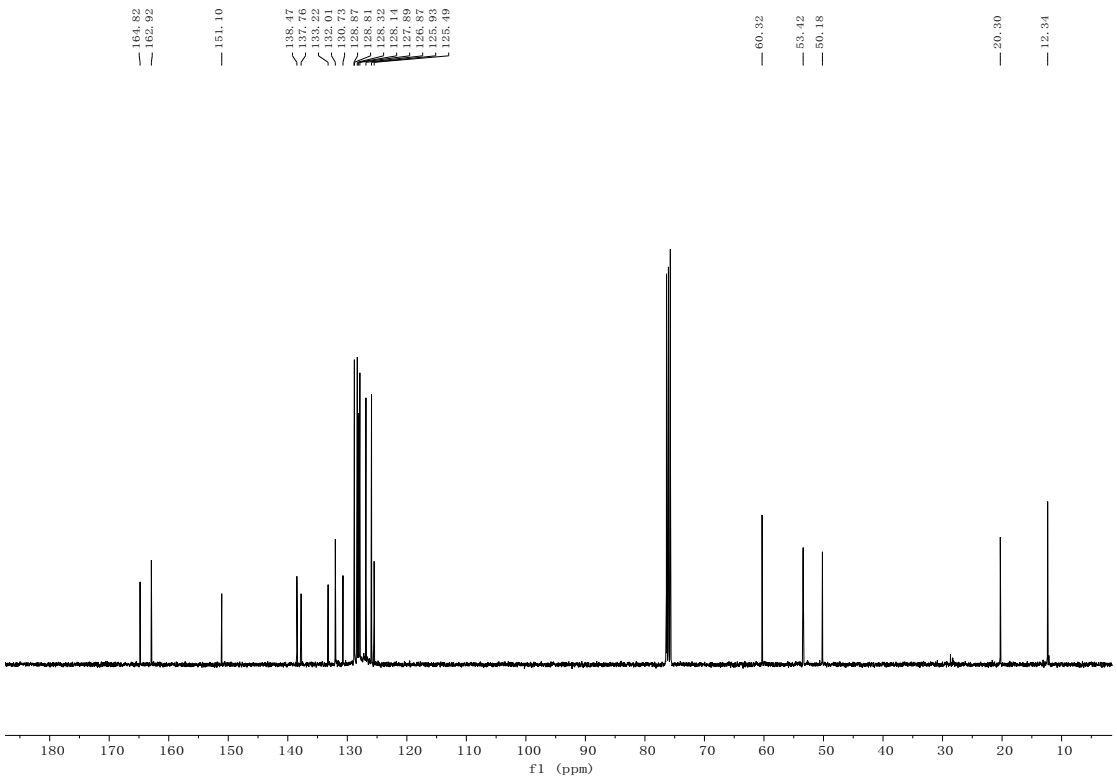

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7.24
7.22
7.20
7.19
7.17
7.17
7.15
7.15
7.11
7.09
7.07
6.95
6.93
4.86
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4.45
3.86
3.84
3.82
3.81
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0.76
0.74
1.10
2.03
6.18
3.15
2.02
2.00
4.01
2.02
3.16
f1 (ppm)

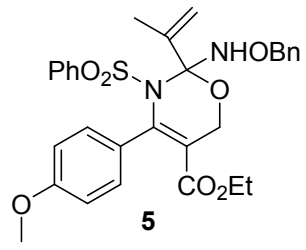

164.82
163.52
151.16
138.42
133.86
133.24
132.26
132.07
130.11
128.93
128.19
127.90
127.83
126.88
125.96
124.96
74.94
60.43
53.42
50.24
12.33
f1 (ppm)


PhO2S
N
O
N–O
Cl
Ph
CO2Et

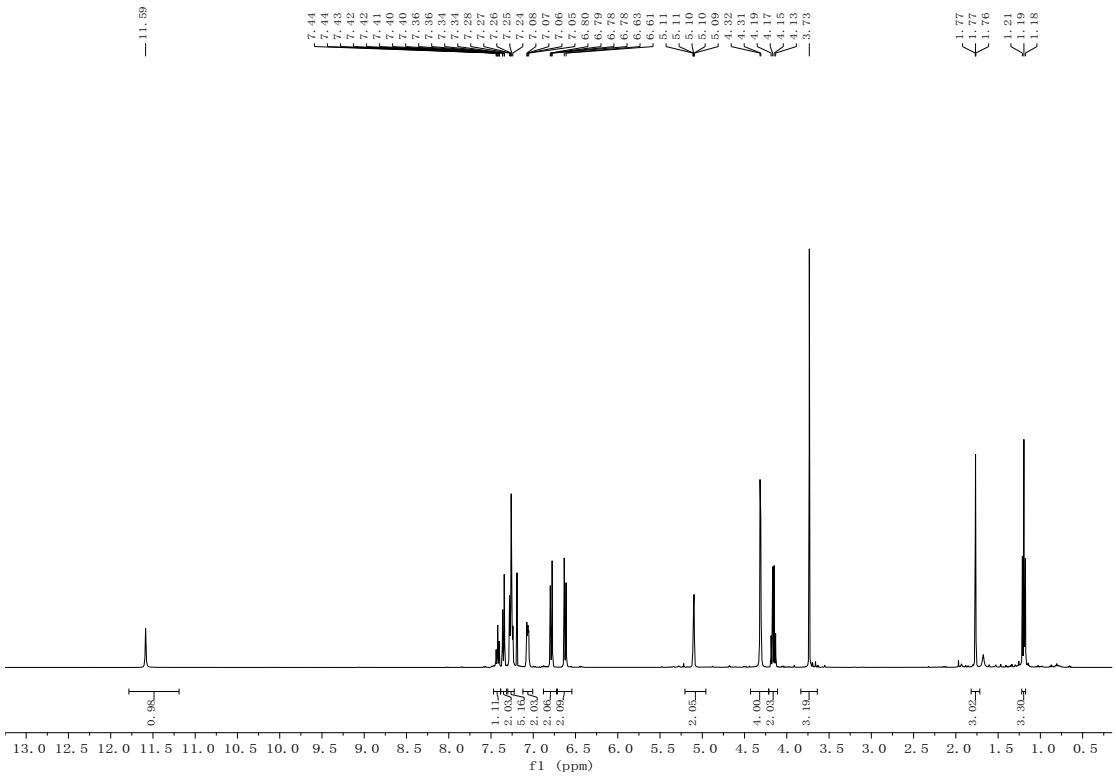
3ga

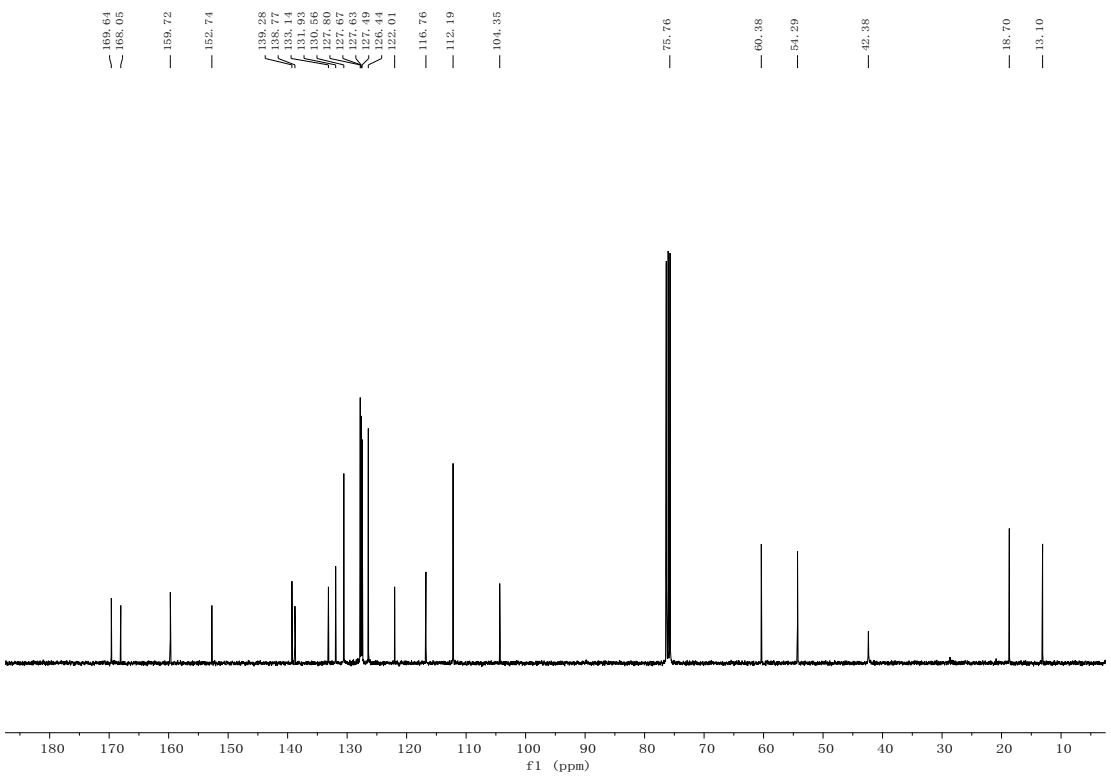

7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.29
7.27
7.25
7.23
7.21
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.11
7.10
7.08
7.06
6.95
6.93
4.85
4.47
4.46
3.85
3.83
3.82
3.80
2.29
0.78
0.77
0.75
1.26
2.34
2.57
7.13
2.07
2.04
4.01
2.00
3.06
3.27
f1 (ppm)

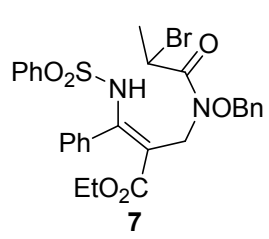

164.82
162.92
151.10
138.47
137.76
133.22
132.01
130.73
128.87
128.81
128.32
128.14
127.89
127.87
125.93
125.49
60.32
53.42
50.18
20.30
12.34
f1 (ppm)


PhO2S
N
O
NHOBn
CO2Et
O

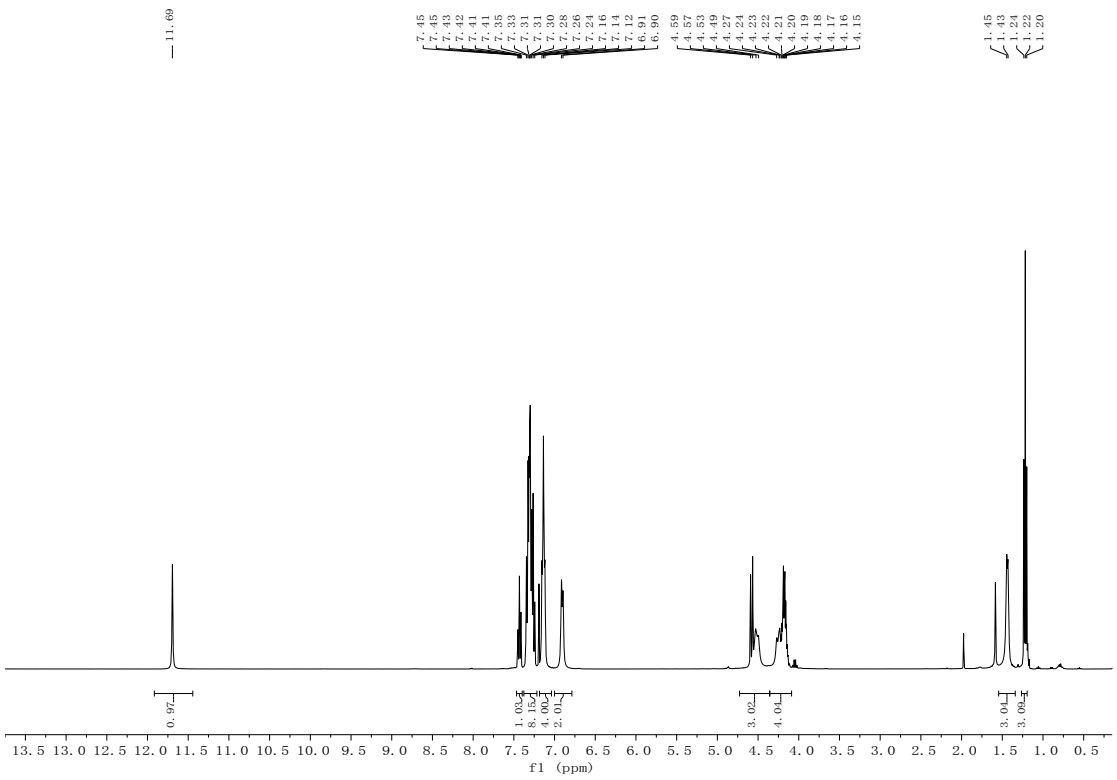
5

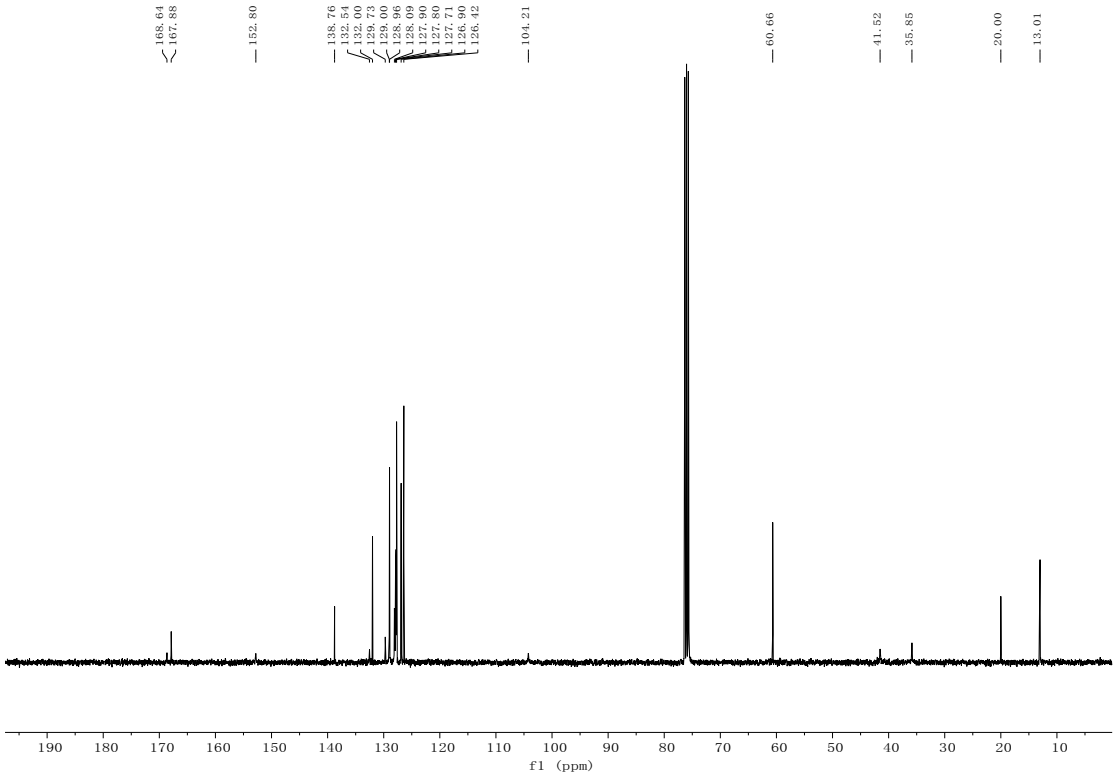


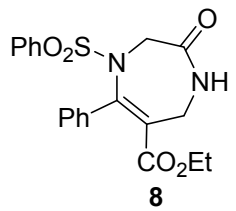




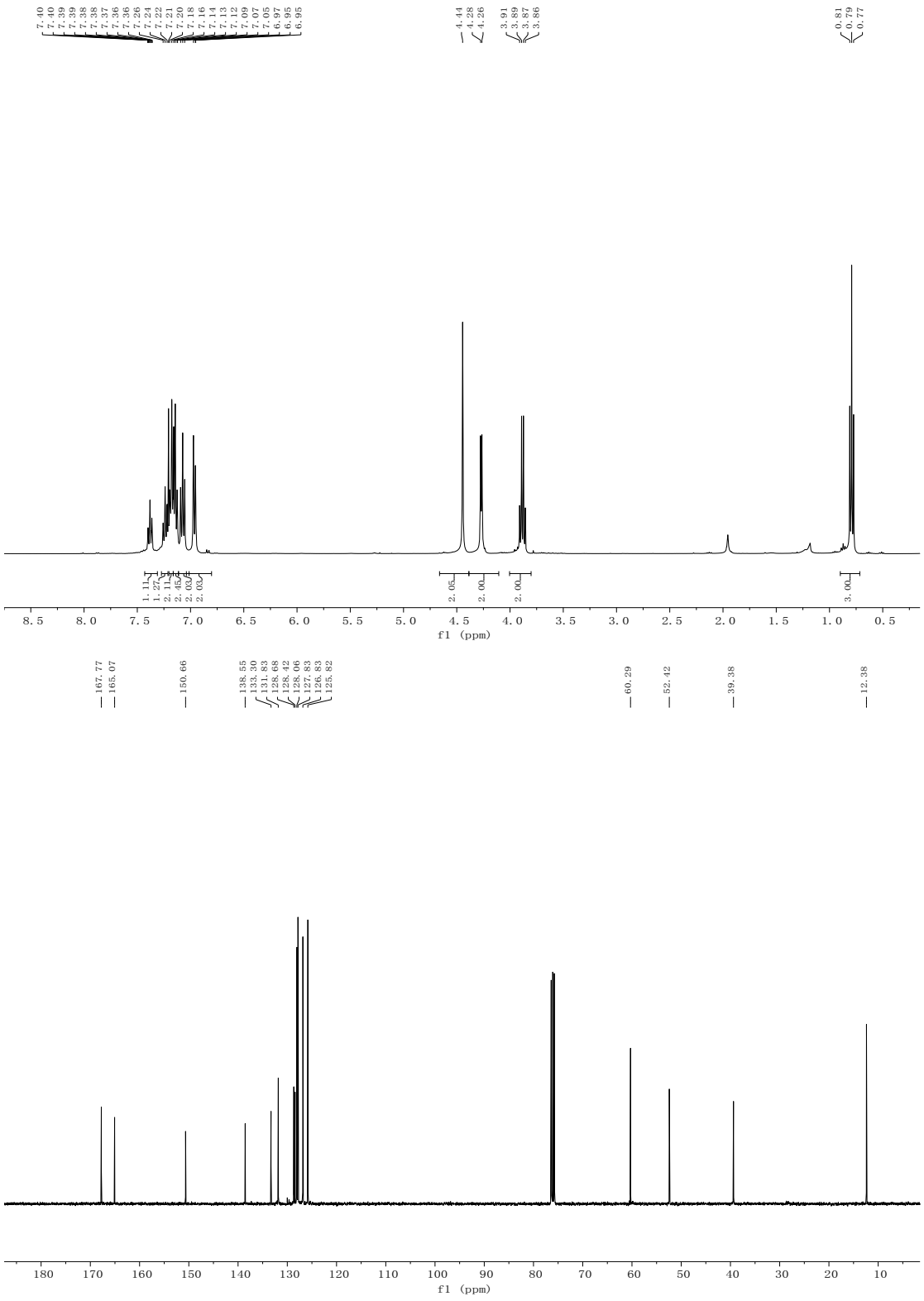
7


11.69
7.45
7.45
7.43
7.42
7.41
7.41
7.35
7.33
7.31
7.31
7.30
7.28
7.26
7.24
7.16
7.14
7.12
6.91
6.90
4.59
4.57
4.53
4.49
4.27
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
1.45
1.43
1.24
1.22
1.20
0.97
1.03
8.15
4.00
2.01
3.02
4.04
3.04
3.09
f1 (ppm)


168.64
167.88
152.80
138.76
132.54
132.00
129.73
129.00
128.96
128.09
127.90
127.80
127.71
126.90
126.42
104.21
60.66
41.52
35.85
20.00
13.01
f1 (ppm)


PhO2S
N
O
NH
Ph
CO2Et

8



X-Ray Crystallography Data

Crystallographic data for **3aa** and **7** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1970833 and 1975164. These data can be obtained free of

charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

X-Ray Crystallography Data of **3aa**

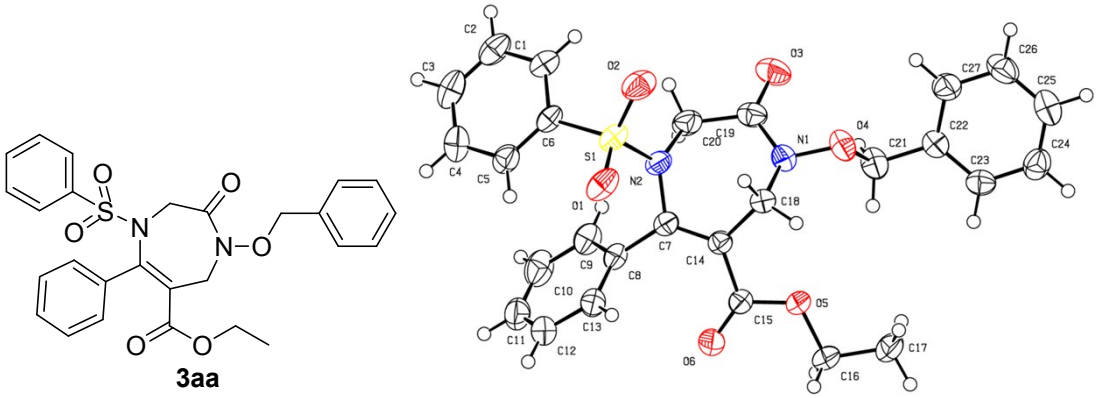


Table 1. Crystal data and structure refinement for **3aa**.

Identification code	**3aa**	
Empirical formula	C27 H26 N2 O6 S	
Formula weight	506.56	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8523(4) Å	α= 79.614(2)°.
	b = 10.2310(5) Å	β= 82.176(2)°.
	c = 14.4737(6) Å	γ = 76.804(2)°.
Volume	1249.14(10) $Å^3$	
Z	2	
Density (calculated)	1.347 Mg/m^3	
Absorption coefficient	0.175 mm^{-1}	
F(000)	532	
Crystal size	0.170 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.330 to 28.248°.	
Index ranges	-11<=h<=11, -13<=k<=13, -18<=l<=19	
Reflections collected	12452	
Independent reflections	6095 [R(int) = 0.0343]	
Completeness to theta = 25.242°	98.6 %	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	6095 / 0 / 326
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1053
R indices (all data)	R1 = 0.0565, wR2 = 0.1158
Extinction coefficient	n/a
Largest diff. peak and hole	0.247 and -0.302 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 20190909LI_ZNZ5256_28_3_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4662(2)	10939(2)	8326(1)	42(1)
C(2)	3381(2)	11818(2)	8692(1)	51(1)
C(3)	2323(2)	11312(2)	9367(1)	56(1)
C(4)	2526(2)	9937(2)	9692(1)	55(1)
C(5)	3809(2)	9041(2)	9338(1)	44(1)
C(6)	4856(2)	9555(2)	8656(1)	35(1)
C(7)	5439(2)	6762(2)	7288(1)	32(1)
C(8)	4009(2)	6580(2)	7914(1)	35(1)
C(9)	2634(2)	7555(2)	7798(1)	45(1)
C(10)	1298(2)	7417(2)	8395(2)	58(1)
C(11)	1327(2)	6339(2)	9115(2)	59(1)
C(12)	2687(2)	5386(2)	9251(1)	55(1)
C(13)	4019(2)	5498(2)	8645(1)	44(1)
C(14)	6340(2)	5929(2)	6716(1)	31(1)
C(15)	5900(2)	4687(2)	6518(1)	35(1)
C(16)	6577(2)	3030(2)	5487(1)	48(1)
C(17)	7674(2)	2805(2)	4626(1)	53(1)
C(18)	7827(2)	6299(2)	6215(1)	34(1)
C(19)	6884(2)	8724(2)	5502(1)	41(1)
C(20)	5760(2)	9014(2)	6368(1)	46(1)
C(21)	7948(2)	7074(2)	3857(1)	46(1)
C(22)	9203(2)	6997(2)	3049(1)	37(1)
C(23)	9519(2)	5933(2)	2538(1)	42(1)
C(24)	10691(2)	5870(2)	1799(1)	49(1)
C(25)	11544(2)	6870(2)	1568(1)	53(1)
C(26)	11223(2)	7944(2)	2068(1)	55(1)

C(27)	10057(2)	8011(2)	2806(1)	48(1)
N(1)	7549(2)	7416(1)	5426(1)	40(1)
N(2)	5905(2)	8027(1)	7237(1)	37(1)
O(1)	6782(2)	7203(1)	8807(1)	50(1)
O(2)	7636(1)	9198(1)	7812(1)	58(1)
O(3)	7028(2)	9669(1)	4875(1)	57(1)
O(4)	8677(1)	7232(1)	4651(1)	44(1)
O(5)	6766(1)	4280(1)	5753(1)	46(1)
O(6)	4912(2)	4133(1)	6950(1)	57(1)
S(1)	6453(1)	8440(1)	8166(1)	38(1)

Table 3. Bond lengths [Å] and angles [°] for 20190909LI_ZNZ5256_28_3_0m_a.

C(1)-C(2)	1.385(2)
C(1)-C(6)	1.389(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.375(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.379(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.389(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.378(2)
C(5)-H(5)	0.9500
C(6)-S(1)	1.7562(15)
C(7)-C(14)	1.346(2)
C(7)-N(2)	1.4327(19)
C(7)-C(8)	1.481(2)
C(8)-C(13)	1.385(2)
C(8)-C(9)	1.394(2)
C(9)-C(10)	1.385(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.372(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.378(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.385(2)

C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(15)	1.496(2)
C(14)-C(18)	1.507(2)
C(15)-O(6)	1.1943(19)
C(15)-O(5)	1.3328(18)
C(16)-O(5)	1.4510(18)
C(16)-C(17)	1.489(2)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-N(1)	1.4657(19)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-O(3)	1.2175(19)
C(19)-N(1)	1.352(2)
C(19)-C(20)	1.520(2)
C(20)-N(2)	1.464(2)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-O(4)	1.4422(19)
C(21)-C(22)	1.499(2)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.381(2)
C(22)-C(27)	1.388(2)
C(23)-C(24)	1.384(2)
C(23)-H(23)	0.9500
C(24)-C(25)	1.374(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.379(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.380(3)
C(26)-H(26)	0.9500
C(27)-H(27)	0.9500
N(1)-O(4)	1.4049(16)

N(2)-S(1)	1.6419(13)
O(1)-S(1)	1.4251(13)
O(2)-S(1)	1.4283(13)

C(2)-C(1)-C(6)	119.00(17)
C(2)-C(1)-H(1)	120.5
C(6)-C(1)-H(1)	120.5
C(3)-C(2)-C(1)	119.83(18)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	120.82(17)
C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	120.18(19)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	118.63(17)
C(6)-C(5)-H(5)	120.7
C(4)-C(5)-H(5)	120.7
C(5)-C(6)-C(1)	121.53(15)
C(5)-C(6)-S(1)	119.64(13)
C(1)-C(6)-S(1)	118.81(13)
C(14)-C(7)-N(2)	114.30(13)
C(14)-C(7)-C(8)	129.20(14)
N(2)-C(7)-C(8)	116.42(13)
C(13)-C(8)-C(9)	118.95(15)
C(13)-C(8)-C(7)	121.54(14)
C(9)-C(8)-C(7)	119.43(15)
C(10)-C(9)-C(8)	120.05(18)
C(10)-C(9)-H(9)	120.0
C(8)-C(9)-H(9)	120.0
C(11)-C(10)-C(9)	120.31(18)
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8
C(10)-C(11)-C(12)	120.22(18)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-C(13)	119.85(19)

C(11)-C(12)-H(12)	120.1
C(13)-C(12)-H(12)	120.1
C(12)-C(13)-C(8)	120.59(17)
C(12)-C(13)-H(13)	119.7
C(8)-C(13)-H(13)	119.7
C(7)-C(14)-C(15)	123.16(13)
C(7)-C(14)-C(18)	118.53(13)
C(15)-C(14)-C(18)	118.25(12)
O(6)-C(15)-O(5)	123.56(14)
O(6)-C(15)-C(14)	126.87(14)
O(5)-C(15)-C(14)	109.55(12)
O(5)-C(16)-C(17)	106.58(14)
O(5)-C(16)-H(16A)	110.4
C(17)-C(16)-H(16A)	110.4
O(5)-C(16)-H(16B)	110.4
C(17)-C(16)-H(16B)	110.4
H(16A)-C(16)-H(16B)	108.6
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(1)-C(18)-C(14)	112.68(12)
N(1)-C(18)-H(18A)	109.1
C(14)-C(18)-H(18A)	109.1
N(1)-C(18)-H(18B)	109.1
C(14)-C(18)-H(18B)	109.1
H(18A)-C(18)-H(18B)	107.8
O(3)-C(19)-N(1)	123.25(17)
O(3)-C(19)-C(20)	118.22(16)
N(1)-C(19)-C(20)	118.18(14)
N(2)-C(20)-C(19)	118.98(14)
N(2)-C(20)-H(20A)	107.6
C(19)-C(20)-H(20A)	107.6
N(2)-C(20)-H(20B)	107.6
C(19)-C(20)-H(20B)	107.6
H(20A)-C(20)-H(20B)	107.0

O(4)-C(21)-C(22)	105.87(12)
O(4)-C(21)-H(21A)	110.6
C(22)-C(21)-H(21A)	110.6
O(4)-C(21)-H(21B)	110.6
C(22)-C(21)-H(21B)	110.6
H(21A)-C(21)-H(21B)	108.7
C(23)-C(22)-C(27)	119.30(15)
C(23)-C(22)-C(21)	120.96(15)
C(27)-C(22)-C(21)	119.74(16)
C(22)-C(23)-C(24)	120.27(16)
C(22)-C(23)-H(23)	119.9
C(24)-C(23)-H(23)	119.9
C(25)-C(24)-C(23)	120.16(17)
C(25)-C(24)-H(24)	119.9
C(23)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	119.92(17)
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-C(27)	120.19(17)
C(25)-C(26)-H(26)	119.9
C(27)-C(26)-H(26)	119.9
C(26)-C(27)-C(22)	120.16(17)
C(26)-C(27)-H(27)	119.9
C(22)-C(27)-H(27)	119.9
C(19)-N(1)-O(4)	115.01(13)
C(19)-N(1)-C(18)	125.62(13)
O(4)-N(1)-C(18)	112.29(12)
C(7)-N(2)-C(20)	119.34(12)
C(7)-N(2)-S(1)	120.93(10)
C(20)-N(2)-S(1)	119.51(11)
N(1)-O(4)-C(21)	109.63(11)
C(15)-O(5)-C(16)	117.45(12)
O(1)-S(1)-O(2)	120.83(8)
O(1)-S(1)-N(2)	105.41(7)
O(2)-S(1)-N(2)	105.85(8)
O(1)-S(1)-C(6)	109.45(8)
O(2)-S(1)-C(6)	107.25(8)
N(2)-S(1)-C(6)	107.31(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 20190909LI_ZNZ5256_28_3_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	46(1)	33(1)	48(1)	-10(1)	-13(1)	-4(1)
C(2)	59(1)	37(1)	56(1)	-15(1)	-21(1)	7(1)
C(3)	53(1)	59(1)	54(1)	-26(1)	-14(1)	13(1)
C(4)	55(1)	66(1)	42(1)	-18(1)	1(1)	-4(1)
C(5)	56(1)	39(1)	37(1)	-9(1)	-7(1)	-4(1)
C(6)	38(1)	33(1)	37(1)	-13(1)	-12(1)	-1(1)
C(7)	37(1)	30(1)	30(1)	-4(1)	-9(1)	-5(1)
C(8)	37(1)	36(1)	34(1)	-12(1)	-4(1)	-6(1)
C(9)	41(1)	47(1)	47(1)	-13(1)	-10(1)	-1(1)
C(10)	36(1)	71(1)	70(1)	-31(1)	-3(1)	-3(1)
C(11)	53(1)	69(1)	62(1)	-33(1)	17(1)	-23(1)
C(12)	69(1)	51(1)	45(1)	-16(1)	14(1)	-20(1)
C(13)	51(1)	40(1)	38(1)	-9(1)	2(1)	-6(1)
C(14)	35(1)	29(1)	30(1)	-4(1)	-6(1)	-6(1)
C(15)	39(1)	33(1)	34(1)	-8(1)	-2(1)	-8(1)
C(16)	59(1)	40(1)	54(1)	-20(1)	5(1)	-22(1)
C(17)	59(1)	51(1)	57(1)	-27(1)	4(1)	-18(1)
C(18)	36(1)	31(1)	36(1)	-5(1)	-4(1)	-8(1)
C(19)	49(1)	38(1)	39(1)	1(1)	-11(1)	-16(1)
C(20)	64(1)	28(1)	44(1)	-1(1)	-7(1)	-5(1)
C(21)	39(1)	67(1)	39(1)	-12(1)	-4(1)	-19(1)
C(22)	34(1)	43(1)	34(1)	-2(1)	-7(1)	-9(1)
C(23)	46(1)	36(1)	44(1)	0(1)	-8(1)	-10(1)
C(24)	53(1)	42(1)	45(1)	-9(1)	-5(1)	2(1)
C(25)	43(1)	72(1)	41(1)	-5(1)	1(1)	-10(1)
C(26)	58(1)	71(1)	46(1)	-3(1)	-2(1)	-37(1)
C(27)	56(1)	51(1)	44(1)	-11(1)	-4(1)	-24(1)
N(1)	46(1)	42(1)	32(1)	-4(1)	1(1)	-12(1)
N(2)	50(1)	28(1)	34(1)	-6(1)	-7(1)	-7(1)
O(1)	60(1)	38(1)	51(1)	-13(1)	-26(1)	9(1)

O(2)	39(1)	53(1)	91(1)	-29(1)	-4(1)	-14(1)
O(3)	69(1)	46(1)	52(1)	11(1)	-8(1)	-21(1)
O(4)	38(1)	65(1)	33(1)	-7(1)	-1(1)	-19(1)
O(5)	57(1)	39(1)	48(1)	-20(1)	12(1)	-22(1)
O(6)	64(1)	59(1)	58(1)	-27(1)	20(1)	-35(1)
S(1)	36(1)	34(1)	48(1)	-15(1)	-12(1)	-1(1)

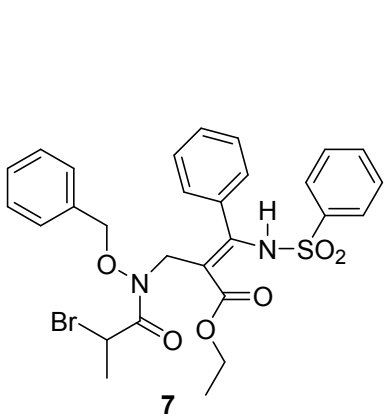
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for 20190909LI_ZNZ5256_28_3_0m_a.

	x	y	z	U(eq)
H(1)	5397	11278	7857	50
H(2)	3234	12768	8477	61
H(3)	1440	11917	9612	67
H(4)	1786	9602	10160	66
H(5)	3961	8093	9563	53
H(9)	2615	8314	7310	54
H(10)	357	8071	8304	69
H(11)	406	6251	9522	71
H(12)	2712	4653	9760	66
H(13)	4949	4828	8730	53
H(16A)	5490	3112	5351	58
H(16B)	6827	2261	6003	58
H(17A)	7368	3541	4109	79
H(17B)	7641	1934	4446	79
H(17C)	8735	2792	4758	79
H(18A)	8394	6564	6672	41
H(18B)	8497	5491	5975	41
H(20A)	5857	9896	6518	56
H(20B)	4689	9134	6192	56
H(21A)	7083	7859	3708	56
H(21B)	7529	6234	3995	56
H(23)	8930	5242	2693	50
H(24)	10907	5134	1451	58
H(25)	12354	6821	1064	64

H(26)	11806	8639	1905	66
H(27)	9839	8754	3148	58

Table 6. Torsion angles [°] for **3aa**.

X-Ray Crystallography Data of **7**



7

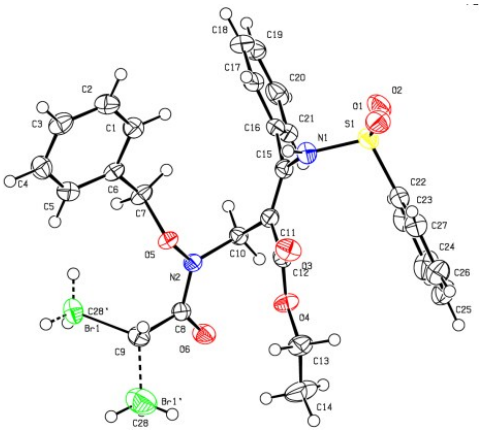


Table 1. Crystal data and structure refinement for **7**.

Identification code	**7**	
Empirical formula	C28 H29 Br N2 O6 S	
Formula weight	601.50	
Temperature	193(2) K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1845(6) Å	α= 62.147(2)°.
	b = 12.6592(8) Å	β= 77.425(2)°.
	c = 12.8148(8) Å	γ = 70.019(2)°.
Volume	1369.49(15) $Å^3$	
Z	2	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	2.064 mm^{-1}	
F(000)	620	
Crystal size	0.120 x 0.110 x 0.080 mm^3	
Theta range for data collection	3.402 to 54.027°.	
Index ranges	-12<=h<=12, -15<=k<=15, -15<=l<=15	
Reflections collected	18103	
Independent reflections	4998 [R(int) = 0.0494]	

Completeness to theta = 53.594°	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4998 / 0 / 347
Goodness-of-fit on F^2	1.160
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1144
R indices (all data)	R1 = 0.0513, wR2 = 0.1165
Extinction coefficient	n/a
Largest diff. peak and hole	0.546 and -0.505 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 20191229LI_ZNZ2846_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6220(3)	77(3)	6398(3)	33(1)
C(2)	7583(4)	-670(3)	6567(3)	37(1)
C(3)	8522(3)	-639(3)	5599(3)	37(1)
C(4)	8093(4)	152(3)	4468(3)	37(1)
C(5)	6731(3)	906(3)	4303(3)	32(1)
C(6)	5780(3)	869(3)	5264(3)	27(1)
C(7)	4272(3)	1607(3)	5106(3)	30(1)
C(8)	2448(3)	4578(3)	3560(3)	25(1)
C(9)	3654(3)	4776(3)	2617(3)	30(1)
C(10)	1825(3)	3396(3)	5696(2)	24(1)
C(11)	2539(3)	3312(3)	6656(3)	25(1)
C(12)	3146(3)	4350(3)	6329(3)	28(1)
C(13)	2853(4)	6513(3)	5140(3)	38(1)
C(14)	1879(5)	7526(3)	4226(4)	56(1)
C(15)	2689(3)	2345(3)	7741(3)	26(1)
C(16)	2062(3)	1302(3)	8168(2)	26(1)
C(17)	2919(3)	84(3)	8682(3)	32(1)
C(18)	2387(4)	-901(3)	9016(3)	42(1)
C(19)	996(4)	-702(3)	8894(3)	41(1)
C(20)	134(4)	489(3)	8423(3)	37(1)
C(21)	665(3)	1499(3)	8049(3)	29(1)
C(22)	1976(3)	4091(3)	9150(3)	31(1)
C(23)	677(4)	4546(3)	8689(3)	39(1)
C(24)	68(4)	5816(4)	8177(4)	48(1)

C(25)	736(4)	6623(3)	8137(3)	45(1)
C(26)	2028(4)	6159(3)	8596(3)	40(1)
C(27)	2657(3)	4898(3)	9097(3)	34(1)
Br(1)	4036(1)	3582(1)	1961(1)	38(1)
C(28)	3241(2)	6256(2)	1520(2)	61(1)
C(28')	4036(1)	3582(1)	1961(1)	38(1)
Br(1')	3241(2)	6256(2)	1520(2)	61(1)
N(1)	3559(3)	2236(2)	8542(2)	29(1)
N(2)	2759(2)	3594(2)	4619(2)	25(1)
O(1)	3970(3)	2235(2)	10362(2)	42(1)
O(2)	1796(3)	1817(2)	10272(2)	44(1)
O(3)	4165(2)	4273(2)	6733(2)	36(1)
O(4)	2411(2)	5395(2)	5523(2)	33(1)
O(5)	4168(2)	2894(2)	4797(2)	24(1)
O(6)	1260(2)	5268(2)	3383(2)	33(1)
S(1)	2827(1)	2483(1)	9724(1)	32(1)

Table 3. Bond lengths [Å] and angles [°] for 20191229LI_ZNZ2846_0m_a.

C(1)-C(2)	1.382(5)
C(1)-C(6)	1.391(4)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.385(5)
C(2)-H(2)	0.9500
C(3)-C(4)	1.384(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.384(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.384(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.500(4)
C(7)-O(5)	1.456(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-O(6)	1.221(4)
C(8)-N(2)	1.353(4)
C(8)-C(9)	1.521(4)

C(9)-Br(1')	1.709(3)
C(9)-C(28)	1.709(3)
C(9)-Br(1)	1.946(3)
C(9)-C(28')	1.946(3)
C(9)-H(9)	1.0000
C(10)-N(2)	1.464(4)
C(10)-C(11)	1.505(4)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(15)	1.352(4)
C(11)-C(12)	1.487(4)
C(12)-O(3)	1.213(4)
C(12)-O(4)	1.327(4)
C(13)-O(4)	1.461(3)
C(13)-C(14)	1.495(5)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-N(1)	1.428(4)
C(15)-C(16)	1.484(4)
C(16)-C(21)	1.388(4)
C(16)-C(17)	1.398(4)
C(17)-C(18)	1.377(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.382(5)
C(18)-H(18)	0.9500
C(19)-C(20)	1.373(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.394(4)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(22)-C(27)	1.388(5)
C(22)-C(23)	1.390(5)
C(22)-S(1)	1.763(3)
C(23)-C(24)	1.382(5)
C(23)-H(23)	0.9500

C(24)-C(25)	1.385(6)
C(24)-H(24)	0.9500
C(25)-C(26)	1.382(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.376(5)
C(26)-H(26)	0.9500
C(27)-H(27)	0.9500
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(28')-H(28D)	0.9800
C(28')-H(28E)	0.9800
C(28')-H(28F)	0.9800
N(1)-S(1)	1.655(3)
N(1)-H(1)	0.8800
N(2)-O(5)	1.407(3)
O(1)-S(1)	1.430(2)
O(2)-S(1)	1.428(2)

C(2)-C(1)-C(6)	120.7(3)
C(2)-C(1)-H(1A)	119.6
C(6)-C(1)-H(1A)	119.6
C(1)-C(2)-C(3)	119.9(3)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	119.7(3)
C(2)-C(3)-H(3)	120.1
C(4)-C(3)-H(3)	120.1
C(5)-C(4)-C(3)	120.2(3)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	120.5(3)
C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	119.0(3)
C(5)-C(6)-C(7)	121.4(3)
C(1)-C(6)-C(7)	119.5(3)
O(5)-C(7)-C(6)	108.4(2)

O(5)-C(7)-H(7A)	110.0
C(6)-C(7)-H(7A)	110.0
O(5)-C(7)-H(7B)	110.0
C(6)-C(7)-H(7B)	110.0
H(7A)-C(7)-H(7B)	108.4
O(6)-C(8)-N(2)	121.3(3)
O(6)-C(8)-C(9)	122.3(3)
N(2)-C(8)-C(9)	116.4(3)
C(8)-C(9)-Br(1')	110.6(2)
C(8)-C(9)-C(28)	110.6(2)
C(8)-C(9)-Br(1)	108.6(2)
C(28)-C(9)-Br(1)	109.92(18)
C(8)-C(9)-C(28')	108.6(2)
Br(1')-C(9)-C(28')	109.92(18)
C(8)-C(9)-H(9)	109.2
C(28)-C(9)-H(9)	109.2
Br(1)-C(9)-H(9)	109.2
N(2)-C(10)-C(11)	110.1(2)
N(2)-C(10)-H(10A)	109.6
C(11)-C(10)-H(10A)	109.6
N(2)-C(10)-H(10B)	109.6
C(11)-C(10)-H(10B)	109.6
H(10A)-C(10)-H(10B)	108.2
C(15)-C(11)-C(12)	120.4(3)
C(15)-C(11)-C(10)	123.7(3)
C(12)-C(11)-C(10)	115.8(2)
O(3)-C(12)-O(4)	123.8(3)
O(3)-C(12)-C(11)	125.8(3)
O(4)-C(12)-C(11)	110.4(3)
O(4)-C(13)-C(14)	105.5(3)
O(4)-C(13)-H(13A)	110.6
C(14)-C(13)-H(13A)	110.6
O(4)-C(13)-H(13B)	110.6
C(14)-C(13)-H(13B)	110.6
H(13A)-C(13)-H(13B)	108.8
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5

C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(11)-C(15)-N(1)	120.5(3)
C(11)-C(15)-C(16)	124.3(3)
N(1)-C(15)-C(16)	115.0(2)
C(21)-C(16)-C(17)	119.3(3)
C(21)-C(16)-C(15)	122.1(3)
C(17)-C(16)-C(15)	118.6(3)
C(18)-C(17)-C(16)	119.8(3)
C(18)-C(17)-H(17)	120.1
C(16)-C(17)-H(17)	120.1
C(17)-C(18)-C(19)	120.7(3)
C(17)-C(18)-H(18)	119.6
C(19)-C(18)-H(18)	119.6
C(20)-C(19)-C(18)	120.0(3)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	120.1(3)
C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.0
C(16)-C(21)-C(20)	120.1(3)
C(16)-C(21)-H(21)	120.0
C(20)-C(21)-H(21)	120.0
C(27)-C(22)-C(23)	120.7(3)
C(27)-C(22)-S(1)	119.2(2)
C(23)-C(22)-S(1)	120.0(3)
C(24)-C(23)-C(22)	119.1(3)
C(24)-C(23)-H(23)	120.4
C(22)-C(23)-H(23)	120.4
C(23)-C(24)-C(25)	120.4(3)
C(23)-C(24)-H(24)	119.8
C(25)-C(24)-H(24)	119.8
C(26)-C(25)-C(24)	119.9(3)
C(26)-C(25)-H(25)	120.0
C(24)-C(25)-H(25)	120.0
C(27)-C(26)-C(25)	120.4(3)
C(27)-C(26)-H(26)	119.8

C(25)-C(26)-H(26)	119.8
C(26)-C(27)-C(22)	119.5(3)
C(26)-C(27)-H(27)	120.2
C(22)-C(27)-H(27)	120.2
C(9)-C(28)-H(28A)	109.5
C(9)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(9)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(9)-C(28')-H(28D)	109.5
C(9)-C(28')-H(28E)	109.5
H(28D)-C(28')-H(28E)	109.5
C(9)-C(28')-H(28F)	109.5
H(28D)-C(28')-H(28F)	109.5
H(28E)-C(28')-H(28F)	109.5
C(15)-N(1)-S(1)	119.4(2)
C(15)-N(1)-H(1)	120.3
S(1)-N(1)-H(1)	120.3
C(8)-N(2)-O(5)	118.5(2)
C(8)-N(2)-C(10)	124.2(2)
O(5)-N(2)-C(10)	115.2(2)
C(12)-O(4)-C(13)	116.9(2)
N(2)-O(5)-C(7)	108.4(2)
O(2)-S(1)-O(1)	120.63(15)
O(2)-S(1)-N(1)	108.01(14)
O(1)-S(1)-N(1)	105.33(14)
O(2)-S(1)-C(22)	108.78(16)
O(1)-S(1)-C(22)	108.55(15)
N(1)-S(1)-C(22)	104.34(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 20191229LI_ZNZ2846_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(2)	31(2)	32(2)	-13(1)	0(1)	-8(1)
C(2)	35(2)	31(2)	36(2)	-7(1)	-8(1)	-7(1)
C(3)	26(2)	30(2)	49(2)	-16(2)	-5(1)	-3(1)
C(4)	32(2)	39(2)	37(2)	-18(2)	8(1)	-12(2)
C(5)	36(2)	28(2)	31(2)	-8(1)	-3(1)	-11(1)
C(6)	28(2)	20(1)	35(2)	-12(1)	-4(1)	-7(1)
C(7)	27(2)	22(1)	43(2)	-15(1)	-3(1)	-7(1)
C(8)	28(2)	24(1)	24(1)	-10(1)	-4(1)	-7(1)
C(9)	28(2)	32(2)	28(2)	-10(1)	-4(1)	-9(1)
C(10)	24(1)	24(1)	24(1)	-9(1)	0(1)	-8(1)
C(11)	24(1)	23(1)	27(2)	-12(1)	0(1)	-6(1)
C(12)	30(2)	31(2)	24(1)	-13(1)	2(1)	-11(1)
C(13)	49(2)	28(2)	43(2)	-14(2)	-1(2)	-21(2)
C(14)	76(3)	26(2)	66(3)	-11(2)	-23(2)	-16(2)
C(15)	24(1)	26(2)	26(1)	-12(1)	-1(1)	-5(1)
C(16)	32(2)	24(1)	21(1)	-8(1)	1(1)	-9(1)
C(17)	33(2)	27(2)	28(2)	-9(1)	0(1)	-4(1)
C(18)	58(2)	24(2)	35(2)	-7(1)	-2(2)	-10(2)
C(19)	59(2)	34(2)	33(2)	-11(1)	6(2)	-27(2)
C(20)	40(2)	46(2)	30(2)	-15(2)	5(1)	-24(2)
C(21)	32(2)	28(2)	26(2)	-9(1)	1(1)	-10(1)
C(22)	30(2)	37(2)	26(2)	-15(1)	0(1)	-8(1)
C(23)	30(2)	50(2)	48(2)	-29(2)	-3(2)	-11(2)
C(24)	33(2)	55(2)	58(2)	-32(2)	-15(2)	3(2)
C(25)	44(2)	38(2)	50(2)	-22(2)	-9(2)	2(2)
C(26)	38(2)	39(2)	47(2)	-22(2)	-3(2)	-10(2)
C(27)	28(2)	40(2)	35(2)	-17(1)	-5(1)	-8(1)
Br(1)	38(1)	47(1)	32(1)	-22(1)	0(1)	-11(1)
C(28)	51(1)	61(1)	50(1)	-11(1)	2(1)	-15(1)
C(28')	38(1)	47(1)	32(1)	-22(1)	0(1)	-11(1)
Br(1')	51(1)	61(1)	50(1)	-11(1)	2(1)	-15(1)
N(1)	26(1)	34(1)	29(1)	-15(1)	-3(1)	-7(1)
N(2)	23(1)	22(1)	24(1)	-9(1)	-2(1)	-2(1)

O(1)	51(2)	38(1)	34(1)	-14(1)	-18(1)	-5(1)
O(2)	55(2)	47(1)	32(1)	-15(1)	10(1)	-27(1)
O(3)	38(1)	40(1)	36(1)	-12(1)	-6(1)	-20(1)
O(4)	37(1)	23(1)	39(1)	-9(1)	-7(1)	-12(1)
O(5)	22(1)	19(1)	30(1)	-9(1)	-4(1)	-4(1)
O(6)	26(1)	33(1)	29(1)	-7(1)	-5(1)	-2(1)
S(1)	38(1)	33(1)	24(1)	-11(1)	-3(1)	-11(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 20191229LI_ZNZ2846_0m_a.

	x	y	z	U(eq)
H(1A)	5578	50	7064	39
H(2)	7875	-1204	7345	44
H(3)	9456	-1159	5711	44
H(4)	8736	178	3803	44
H(5)	6446	1453	3524	39
H(7A)	3925	1560	4469	36
H(7B)	3696	1268	5847	36
H(9)	4505	4633	2987	36
H(10A)	1566	2618	5963	29
H(10B)	957	4093	5530	29
H(13A)	3834	6396	4798	45
H(13B)	2782	6712	5814	45
H(14A)	2035	7357	3530	84
H(14B)	2054	8324	3997	84
H(14C)	909	7563	4553	84
H(17)	3867	-63	8800	39
H(18)	2981	-1727	9335	51
H(19)	636	-1389	9136	49
H(20)	-826	625	8351	44
H(21)	70	2322	7712	35
H(23)	215	3992	8726	47
H(24)	-814	6138	7851	58
H(25)	307	7495	7794	54

H(26)	2485	6714	8566	48
H(27)	3549	4581	9405	40
H(28A)	2341	6437	1228	91
H(28B)	3971	6332	870	91
H(28C)	3176	6846	1834	91
H(28D)	4192	2739	2603	56
H(28E)	4874	3638	1412	56
H(28F)	3235	3765	1536	56
H(1)	4475	2039	8409	35

Table 6. Torsion angles [°] for **7.**