Supporting Information

Copper-catalyzed enantioselective alkynylation of pyrazole-4,5-diones with terminal alkynes

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1. General Information

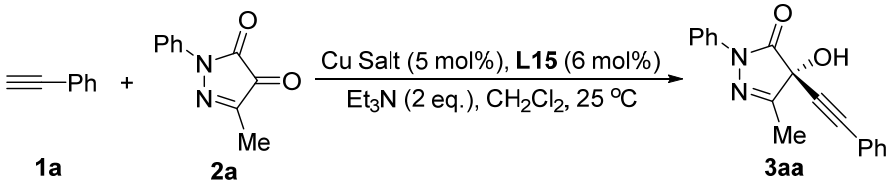
Melting points were taken on WRS-1B digital melting-point apparatus without correction. Optical rotations were measured on a WZZ-2A digital polarimeter at the wavelength of the sodium D-line (589 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 spectrometer, and the chemical shifts were referenced to tetramethylsilane (δ = 0.00 ppm) for ^{1}H NMR and central $CDCl_3$ resonance (δ = 77.0 ppm) or central $(CD_3)_2CO$ resonance (δ = 29.84 ppm) for ^{13}C NMR. IR spectra were recorded on Nicolet Magna-1 550 spectrometer. High Resolution Mass spectra (HRMS) were recorded on Micromass GCT with Electron Spray Ionization (ESI) resource. HPLC analysis was performed on Waters or PerkinElmer equipment using Daicel Chiralcel OD-H column or Chiralpak AD-H column.

Anhydrous solvents were distilled from CaH_2 (dichloromethane, ethyl acetate, acetonitrile), sodium (CH_3OH) or sodium-benzophenone (toluene, ether, THF) under N_2. Anhydrous DMF was dried over CaH_2 and distilled under reduced pressure. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 10-40 μm. Silica gel column chromatography was performed using silica gel (300-400 mesh).

Chiral cyclohexane-based *N*,*P*-ligands **L1-L15** were prepared according to literature procedures.[1] Pyrazole-4,5-diones were synthesized according to literature.[2]

2. Screening of Copper Salts for the Enantioselective Alkynylation

Table S1 Screening of copper salts for the enantioselective alkynylation[a]

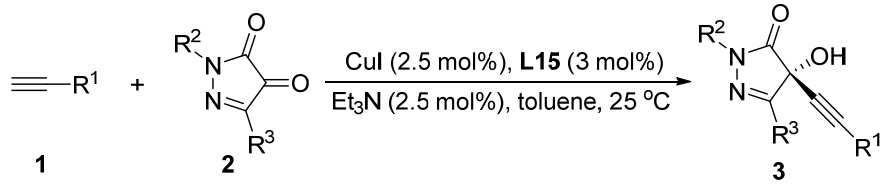


1a 2a 3aa

Entry	Cu Salt	Time (h)	Yield (%)[b]	Ee (%)[c]
1	CuI	4	86	95
2	CuBr	10	65	83
3	CuCl	12	53	80
4	CuOAc	12	14	46
5	$Cu(CH_3CN)_4BF_4$	8	62	74
6	$CuBr_2$	24	35	39
7	$Cu(OAc)_2$	24	74	83
8	$Cu(OTf)_2$	18	56	75

[a] The reactions were carried out with 0.24 mmol of phenylacetylene **1a**, 0.2 mmol of pyrazole-4,5-dione **2a**, 5 mol% of Cu salt, 6 mol% of chiral ligand **L15** and 0.4 mmol of Et_3N in 2 mL of CH_2Cl_2 at 25 °C. [b] Isolated yield. [c] The ee values were determined by chiral HPLC analysis.

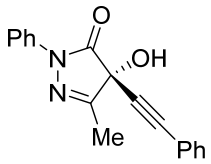
3. General Procedure for the Enantioselective Alkynylation



1 2 3

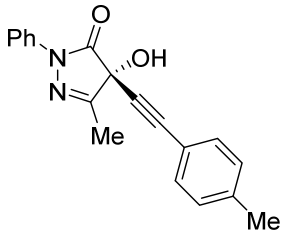
CuI (0.005 mmol, 1.0 mg) were added to a flame-dried Schlenk tube equipped a stir bar under N_2 atmosphere. Ligand **L15** (0.006 mmol, 3.2 mg) in 1 mL toluene was added to the tube via a syringe, and the mixture was stirred for an hour at 25 °C. Then pyrazole-4,5-dione **2** (0.2 mmol), terminal alkyne **1** (0.24 mmol), 1.0 mL toluene and Et_3N (0.005 mmol, 0.7 μL) were added, and the resulting mixture was stirred at this temperature until the reaction was completed (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (4:1 petroleum ether/EtOAc as eluent) to afford the desire product **3**.

(*R*)-4-hydroxy-5-methyl-2-phenyl-4-(phenylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3aa)



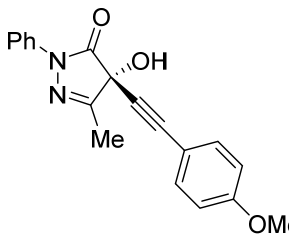
White solid, 98% yield, 96% ee, mp 161.4-161.7 ºC; $[\alpha]_D^{20}$ +399.0 (*c* 1.42, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.86 (m, 2H), 7.41-7.37 (m, 4H), 7.33-7.29 (m, 1H), 7.25-7.18 (m, 3H), 4.94 (t, J = 6.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 158.9, 137.3, 132.1, 129.4, 128.9, 128.2, 125.6, 120.7, 119.0, 88.8, 81.6, 73.0, 13.0; IR (KBr, cm^{-1}): *v* 3333, 2227, 1709, 1596, 1503, 1361, 1267, 1127, 1051, 754, 687, 578; HRMS (ESI) calcd for $C_{18}H_{14}N_2NaO_2^+$ ($[M+Na]^+$): 313.0947, found: 313.0952; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 14.09 min (major), 17.97 min (minor).

(*R*)-4-hydroxy-5-methyl-2-phenyl-4-(*p*-tolylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ba)



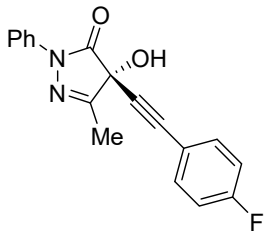
White solid, 96% yield, 96% ee, mp 147.7-148.4 ºC; $[\alpha]_D^{20}$ +390.3 (*c* 1.17, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.87 (m, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 4.42 (s, 1H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 158.6, 139.9, 137.4, 132.1, 129.1, 128.9, 125.5, 118.9, 117.7, 89.2, 81.0, 72.9, 21.6, 13.0; IR (KBr, cm^{-1}): *v* 3312, 2223, 1709, 1594, 1499, 1364, 1269, 1121, 817, 751, 685, 644, 518; HRMS (ESI) calcd for $C_{19}H_{16}N_2NaO_2^+$ ($[M+Na]^+$): 327.1104, found: 327.1100; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 16.57 min (minor), 18.57 min (major).

(*R*)-4-hydroxy-4-((4-methoxyphenyl)ethynyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3ca)



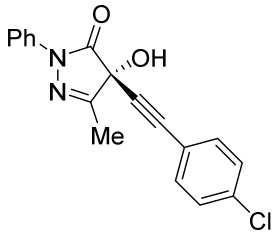
White solid, 98% yield, 95% ee, mp 148.9-149.1 ºC; $[\alpha]_D^{20}$ +400.0 (*c* 1.26, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.86 (m, 2H), 7.42-7.36 (m, 4H), 7.20 (t, J = 7.2 Hz, 1H), 6.79 (dt, J = 8.8, 2.0 Hz, 2H), 4.60 (s, 1H), 3.79 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 160.5, 158.8, 137.4, 133.8, 128.9, 125.5, 118.9, 114.0, 112.7, 89.1, 80.4, 73.0, 55.3, 13.0; IR (KBr, cm^{-1}): *v* 3398, 2223, 1709, 1604, 1508, 1364, 1252, 1174, 1027, 833, 751, 689, 653; HRMS (ESI) calcd for $C_{19}H_{16}N_2NaO_3^+$ ($[M+Na]^+$): 343.1053, found: 343.1042; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 25.61 min (minor), 30.13 min (major).

(*R*)-4-((4-fluorophenyl)ethynyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3da)



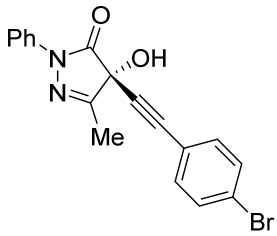
White solid, 99% yield, 95% ee, mp 156.2-156.7 °C; $[\alpha]_D^{20}$ +357.1 (*c* 1.22, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 7.6 Hz, 2H), 7.44-7.38 (m, 4H), 7.22 (t, J = 7.2 Hz, 1H), 6.97 (t, J = 8.4 Hz, 2H), 4.71 (s, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 163.2 (d, J = 250.2 Hz), 158.6, 137.3, 134.3, 128.9, 125.6, 118.9, 116.8 (d, J = 3.3 Hz), 115.7 (d, J = 22.0 Hz), 87.9, 81.4, 72.9, 13.0; IR (KBr, cm^{-1}): ν 3464, 2223, 1709, 1594, 1504, 1368, 1224, 1129, 838, 755, 689, 538; HRMS (ESI) calcd for $C_{18}H_{14}FN_2O_2^+$ ($[M+H]^+$): 309.1034, found: 309.1032; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 16.29 min (major), 19.22 min (minor).

(*R*)-4-((4-chlorophenyl)ethynyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3ea)



White solid, 98% yield, 95% ee, mp 165.0-165.9 °C; $[\alpha]_D^{20}$ +381.4 (*c* 1.28, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.26-7.20 (m, 3H), 4.91 (s, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 158.6, 137.3, 135.7, 133.3, 128.9, 128.7, 125.7, 119.2, 118.9, 87.7, 82.6, 72.9, 13.1; IR (KBr, cm^{-1}): ν 3424, 2223, 1709, 1635, 1491, 1368, 1265, 1133, 1088, 751, 681, 579; HRMS (ESI) calcd for $C_{18}H_{13}{}^{35}ClN_2NaO_2^+$ ($[M+Na]^+$): 347.0558, found: 347.0558; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 19.03 min (major), 20.63 min (minor).

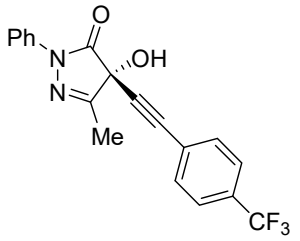
(*R*)-4-((4-bromophenyl)ethynyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3fa)



White solid, 96% yield, 91% ee, mp 180.5-181.0 °C; $[\alpha]_D^{20}$ +301.3 (*c* 1.42, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.86 (m, 2H), 7.42-7.38 (m, 4H), 7.28-7.26 (m, 2H), 7.22 (t, J = 7.2 Hz, 1H), 4.90 (s, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 158.6, 137.3, 133.5, 131.6, 128.9, 125.7, 124.1, 119.7, 118.9, 87.8, 82.7, 72.9, 13.1; IR (KBr, cm^{-1}): ν 3452, 2219, 1713, 1594, 1482, 1372, 1265, 1129, 1010, 829, 752, 689; HRMS (ESI) calcd for $C_{18}H_{13}{}^{79}BrN_2NaO_2^+$ ($[M+Na]^+$): 391.0053, found: 391.0071; HPLC analysis (Daicel Chiralpak AD-H

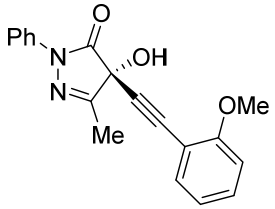
column, λ = 254 nm, eluent: 95: 5 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 41.76 min (major), 45.83 min (minor).

(*R*)-4-hydroxy-5-methyl-2-phenyl-4-((4-(trifluoromethyl)phenyl)ethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ga)



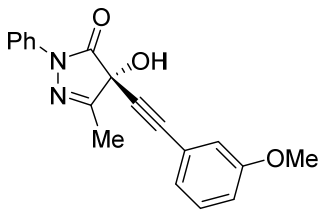
White solid, 98% yield, 96% ee, mp 164.7-165.7 °C; $[\alpha]_D^{20}$ +317.3 (*c* 1.41, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 4H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.16 (s, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 158.6, 137.2, 132.4, 131.2 (q, *J* = 32.3 Hz), 129.0, 125.8, 125.2 (q, *J* = 3.6 Hz), 124.5, 123.6 (q, *J* = 270.8 Hz), 119.0, 87.3, 83.9, 73.0, 13.1; IR (KBr, cm^{-1}): *v* 3324, 2227, 1713, 1598, 1499, 1367, 1322, 1170, 1121, 1064, 842, 751, 682; HRMS (ESI) calcd for $C_{19}H_{13}F_3N_2NaO_2^+$ ([M+Na]$^+$): 381.0821, found: 381.0838; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 23.58 min (major), 25.95 min (minor).

(*R*)-4-hydroxy-4-((2-methoxyphenyl)ethynyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3ha)



White solid, 97% yield, 96% ee, mp 139.3-139.9 °C; $[\alpha]_D^{20}$ +357.0 (*c* 1.24, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.87 (m, 2H), 7.41-7.37 (m, 3H), 7.31 (td, *J* = 8.0, 1.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.87-6.82 (m, 2H), 4.56 (s, 1H), 3.83 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 160.7, 158.7, 137.5, 134.0, 131.1, 128.8, 125.4, 120.4, 118.9, 110.6, 110.0, 85.7, 85.5, 73.0, 55.7, 13.0; IR (KBr, cm^{-1}): *v* 3320, 2218, 1705, 1594, 1491, 1364, 1265, 1121, 1018, 751, 694, 648; HRMS (ESI) calcd for $C_{19}H_{16}N_2NaO_3^+$ ([M+Na]$^+$): 343.1053, found: 343.1051; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 27.07 min (major), 37.08 min (minor).

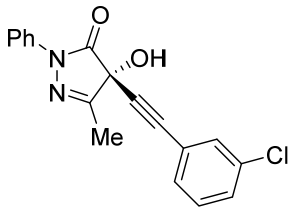
(*R*)-4-hydroxy-4-((3-methoxyphenyl)ethynyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3ia)



White solid, 96% yield, 97% ee, mp 119.0-119.3 °C; $[\alpha]_D^{20}$ +373.4 (*c* 1.23, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90-7.87 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.23-7.16 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.96-6.95 (m, 1H), 6.91-6.89

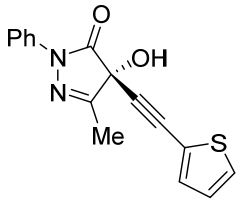
(m, 1H), 4.61 (s, 1H), 3.75 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 159.2, 158.6, 137.4, 129.4, 128.9, 125.6, 124.7, 121.7, 118.9, 116.6, 116.4, 88.8, 81.3, 72.9, 55.3, 13.1; IR (KBr, cm^{-1}): ν 3333, 2227, 1705, 1598, 1499, 1364, 1294, 1211, 1117, 1042, 756, 689, 579; HRMS (ESI) calcd for $C_{19}H_{16}N_2KO_3^+$ ([M+K]$^+$): 359.0793, found: 359.0797; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 18.64 min (major), 24.86 min (minor).

(*R*)-4-((3-chlorophenyl)ethynyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3ja)



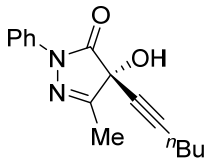
White solid, 98% yield, 97% ee, mp 178.9-179.3 °C; $[\alpha]_D^{20}$ +372.3 (*c* 1.27, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.86 (m, 2H), 7.43-7.39 (m, 3H), 7.33-7.30 (m, 2H), 7.24-7.18 (m, 2H), 4.91 (s, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 158.6, 137.3, 134.2, 132.0, 130.2, 129.8, 129.6, 128.9, 125.7, 122.4, 119.0, 87.3, 82.8, 72.9, 13.0; IR (KBr, cm^{-1}): ν 3460, 2227, 1705, 1590, 1499, 1368, 1265, 191, 1121, 1055, 801, 755, 685; HRMS (ESI) calcd for $C_{18}H_{13}{}^{35}ClN_2NaO_2^+$ ([M+Na]$^+$): 347.0558, found: 347.0567; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 12.30 min (major), 17.54 min (minor).

(*R*)-4-hydroxy-5-methyl-2-phenyl-4-(thiophen-2-ylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ka)



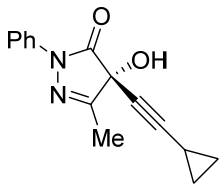
White solid, 95% yield, 84% ee, mp 119.2-120.4 °C; $[\alpha]_D^{20}$ +369.4 (*c* 1.13, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.86 (m, 2H), 7.42-7.38 (m, 2H), 7.31 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.28 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.96 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.61 (s, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 158.4, 137.3, 134.2, 129.0, 128.9, 127.1, 125.6, 120.5, 119.0, 85.4, 82.4, 73.0, 13.1; IR (KBr, cm^{-1}): ν 3469, 2219, 1709, 1594, 1503, 1364, 1273, 1187, 1117, 845, 755, 689, 648; HRMS (ESI) calcd for $C_{16}H_{12}N_2NaO_2S^+$ ([M+Na]$^+$): 319.0512, found: 319.0512; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 16.53 min (major), 22.67 min (minor).

(*R*)-4-(hex-1-yn-1-yl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3la)



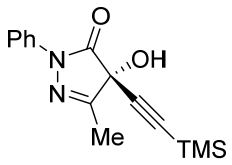
White solid, 83% yield, 97% ee, mp 93.3-94.7 ºC; $[\alpha]_D^{20}$ +276.8 (*c* 0.89, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.84 (m, 2H), 7.41-7.36 (m, 2H), 7.21-7.17 (m, 1H), 4.14 (s, 1H), 2.27-2.24 (m, 5H), 1.54-1.47 (m, 2H), 1.43-1.34 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 158.9, 137.4, 128.8, 125.4, 118.8, 90.8, 73.4, 72.6, 30.0, 21.9, 18.5, 13.5, 12.8; IR (KBr, cm^{-1}): ν 3420, 2231, 1705, 1630, 1504, 1363, 1269, 1117, 1079, 755, 689, 566; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2^+$ ($[M+H]^+$): 271.1441, found: 271.1448; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 9.23 min (major), 11.94 min (minor).

(*R*)-4-(cyclopropylethynyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3ma)



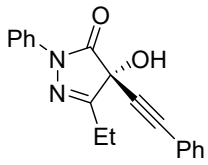
White solid, 91% yield, 84% ee, mp 98.8-99.2 ºC; $[\alpha]_D^{20}$ +248.7 (*c* 0.93, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.85 (m, 2H), 7.42-7.37 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 3.96 (s, 1H), 2.25 (s, 3H), 1.33-1.27 (m, 1H), 0.85-0.79 (m, 2H), 0.78-0.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 158.7, 137.5, 128.9, 125.4, 118.8, 94.0, 72.5, 68.4, 12.9, 8.7, -0.5; IR (KBr, cm^{-1}): ν 3481, 2227, 1709, 1594, 1499, 1364, 1277, 1113, 928, 842, 755, 689; HRMS (ESI) calcd for $C_{15}H_{14}N_2NaO_2^+$ ($[M+Na]^+$): 277.0947, found: 277.0953; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 12.12 min (major), 16.85 min (minor).

(*R*)-4-hydroxy-5-methyl-2-phenyl-4-((trimethylsilyl)ethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3na)



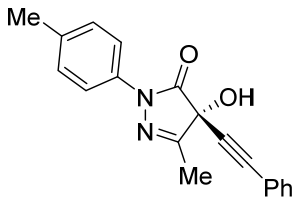
White solid, 82% yield, 98% ee, mp 126.5-126.9 ºC; $[\alpha]_D^{20}$ +311.5 (*c* 0.94, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.87 (dd, J = 8.4, 1.2 Hz, 2H), 7.43-7.39 (m, 2H), 7.23-7.19 (m, 1H), 3.74 (s, 1H), 2.27 (s, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 158.0, 137.4, 128.9, 125.5, 118.8, 96.9, 95.7, 72.6, 12.8, -0.5; IR (KBr, cm^{-1}): ν 3472, 2165, 1708, 1598, 1508, 1364, 1252, 1117, 846, 755, 689; HRMS (ESI) calcd for $C_{15}H_{18}N_2NaO_2Si^+$ ($[M+Na]^+$): 309.1030, found: 309.1046; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 6.65 min (major), 8.13 min (minor).

(*R*)-5-ethyl-4-hydroxy-2-phenyl-4-(phenylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ab)



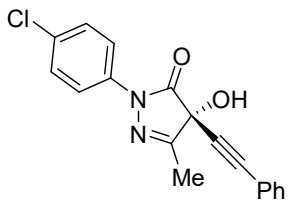
White solid, 97% yield, 94% ee, mp 136.8-137.3 °C; $[\alpha]_D^{20}$ +325.6 (*c* 1.18, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 7.6 Hz, 2H), 7.46-7.39 (m, 4H), 7.37-7.34 (m, 1H), 7.31-7.28 (m, 2H), 7.21 (t, J = 7.2 Hz, 1H), 4.15 (s, 1H), 2.75 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 162.2, 137.5, 132.1, 129.5, 128.9, 128.3, 125.5, 120.8, 118.9, 88.8, 82.0, 72.9, 21.1, 9.6; IR (KBr, cm^{-1}): ν 3431, 2227, 1713, 1627, 1495, 1368, 1191, 1121, 1047, 751, 689; HRMS (ESI) calcd for $C_{19}H_{16}N_2NaO_2^+$ ($[M+Na]^+$): 327.1104, found: 327.1130; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 15.11 min (major), 20.71 min (minor).

(*R*)-4-hydroxy-5-methyl-4-(phenylethynyl)-2-(*p*-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ac)



White solid, 98% yield, 96% ee, mp 144.8-146.3 °C; $[\alpha]_D^{20}$ +382.1 (*c* 0.36, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.74 (dt, J = 8.8, 2.0 Hz, 2H), 7.46-7.43 (m, 2H), 7.38-7.33 (m, 1H), 7.31-7.27 (m, 2H), 7.20 (d, J = 8.4 Hz, 2H), 4.36 (br, 1H), 2.35 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 158.4, 135.3, 135.0, 132.2, 129.5, 129.4, 128.3, 120.8, 119.0, 88.8, 81.8, 72.8, 21.0, 13.0; IR (KBr, cm^{-1}): ν 3433, 2223, 1711, 1617, 1498, 1377, 1236, 1132, 1027, 751, 687; HRMS (ESI) calcd for $C_{19}H_{17}N_2O_2^+$ ($[M+H]^+$): 305.1285, found: 305.1300; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 18.70 min (major), 33.48 min (minor).

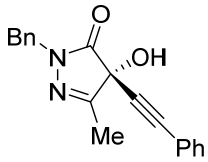
(*R*)-2-(4-chlorophenyl)-4-hydroxy-5-methyl-4-(phenylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ad)



White solid, 98% yield, 94% ee, mp 161.6-162.0 °C; $[\alpha]_D^{20}$ +323.6 (*c* 0.51, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.86 (dt, J = 8.8, 2.0 Hz, 2H), 7.46-7.44 (m, 2H), 7.39-7.34 (m, 3H), 7.32-7.28 (m, 2H), 4.27 (br, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 158.8, 136.0, 132.2, 130.7, 129.7, 129.0, 128.4, 120.6, 120.0, 89.2, 81.4, 72.8, 13.0; IR (KBr, cm^{-1}): ν 3429, 2227, 1703, 1597, 1495, 1372, 1235, 1157, 827, 751, 689, 539; HRMS (ESI) calcd for $C_{18}H_{14}ClN_2O_2^+$ ($[M+H]^+$): 325.0738, found: 325.0741; HPLC analysis (Daicel

Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 18.31 min (major), 26.10 min (minor).

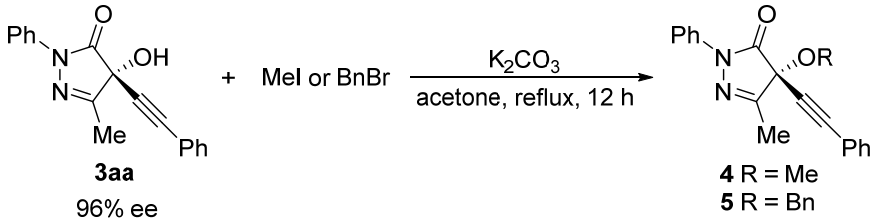
(*R*)-2-benzyl-4-hydroxy-5-methyl-4-(phenylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ae)



White solid, 95% yield, 69% ee, mp 110.7-111.3 °C; $[\alpha]_D^{20}$ +191.1 (*c* 0.90, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.40 (m, 2H), 7.36-7.31 (m, 1H), 7.31-7.24 (m, 7H), 5.28 (br, 1H), 4.81 (s, 2H), 2.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.7, 158.8, 135.6, 132.1, 129.3, 128.7, 128.3, 128.0, 127.8, 121.0, 88.5, 81.8, 71.9, 48.2, 12.9; IR (KBr, cm^{-1}): ν 3379, 2223, 1709, 1607, 1504, 1368, 1256, 1139, 1027, 835, 751, 689; HRMS (ESI) calcd for $C_{19}H_{17}N_2O_2^+$ ($[M+H]^+$): 305.1285, found: 305.1299; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 23.91 min (major), 28.84 min (minor).

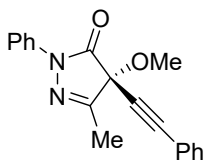
4. Transformation of Product 3aa

4.1 Alkylation of product **3aa**



Compound **3aa** (0.1 mmol, 29.0 mg) was dissolved in 2 mL acetone, then K_2CO_3 (0.15 mmol, 20.7 mg) and MeI or BnBr (0.15 mmol) were added. The reaction mixture was heated to reflux and stirred for 12 hours (monitored by TLC). The resulting mixture was concentrated and purified by silica-gel column chromatography (4:1 petroleum ether/EtOAc as eluent) to give the alkylated product **4** or **5**.

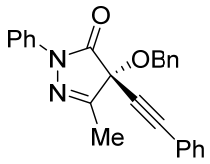
(*R*)-4-methoxy-5-methyl-2-phenyl-4-(phenylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (4)



Yellow oil, 94% yield, 96% ee; $[\alpha]_D^{20}$ +311.9 (*c* 0.66, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 2H), 7.53-7.50 (m, 2H), 7.44-7.31 (m, 5H), 7.23-7.19 (m, 1H), 3.68 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 157.2, 137.6, 132.3, 129.6, 128.9, 128.4, 125.4, 120.8, 118.8, 90.3, 79.5, 77.2, 53.3, 13.3; IR (KBr, cm^{-1}): ν 2237, 1711, 1607, 1485, 1378, 1231, 1124, 1087, 755, 687; HRMS (ESI) calcd for $C_{19}H_{17}N_2O_2^+$

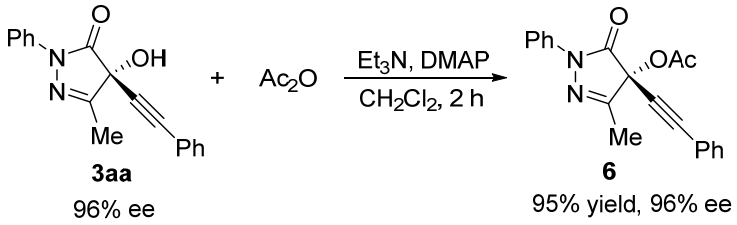
([M+H]$^+$): 305.1285, found: 305.1289; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 8.96 min (major), 9.71 min (minor).

(*R*)-4-(benzyloxy)-5-methyl-2-phenyl-4-(phenylethynyl)-2,4-dihydro-3*H*-pyrazol-3-one (5)



Yellow oil, 93% yield, 96% ee; $[\alpha]_D^{20}$ +260.9 (*c* 0.81, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92-7.89 (m, 2H), 7.51-7.49 (m, 2H), 7.44-7.28 (m, 10H), 7.23-7.19 (m, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7, 157.3, 137.6, 137.1, 132.3, 129.6, 128.9, 128.4×2, 128.2, 128.1, 125.4, 120.8, 118.8, 90.7, 79.8, 77.0, 68.0, 13.3; IR (KBr, cm^{-1}): *v* 2227, 1709, 1604, 1505, 1364, 1234, 1129, 838, 755, 689, 538; HRMS (ESI) calcd for $C_{25}H_{21}N_2O_2^+$ ([M+H]$^+$): 381.1598, found: 381.1604; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 14.49 min (minor), 22.90 min (major).

4.2 Acetylation of product **3aa**

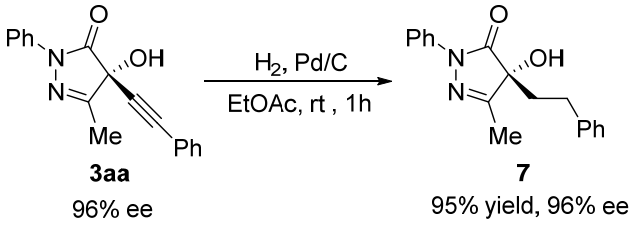


Compound **3aa** (0.1 mmol, 29.0 mg) was dissolved in 2 mL CH_2Cl_2, 0.5 mL acetic anhydride, 0.5 mL Et_3N and DMAP (0.01 mmol, 1.5 mg) were then added. The reaction mixture was stirred at room temperature for two hours (monitored by TLC). The resulting mixture was quenched with saturated $NaHCO_3$ and extracted with CH_2Cl_2 (5 mL × 2), then the organic layers were combined and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (5:1 petroleum ether/EtOAc as eluent) to give the acetylated product **6**.

Yellow oil, 95% yield, 96% ee; $[\alpha]_D^{20}$ +263.5 (*c* 0.96, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.85 (m, 2H), 7.52-7.49 (m, 2H), 7.44-7.31 (m, 5H), 7.23-7.19 (m, 1H), 2.24 (s, 3H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.6, 166.2, 154.1, 137.8, 132.3, 129.9, 128.9, 128.4, 125.6, 120.4, 119.1, 90.1, 77.8, 75.8, 20.1, 13.0; IR (KBr, cm^{-1}): *v* 2227, 1723, 1617, 1508, 1364, 1231, 1107, 842, 753, 687, 545; HRMS (ESI)

calcd for $C_{20}H_{16}NaN_2O_3^+$ ([M+H]$^+$): 355.1053, found: 355.1056; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 15.43 min (minor), 17.98 min (major).

4.3 Hydrogenation of product **3aa**

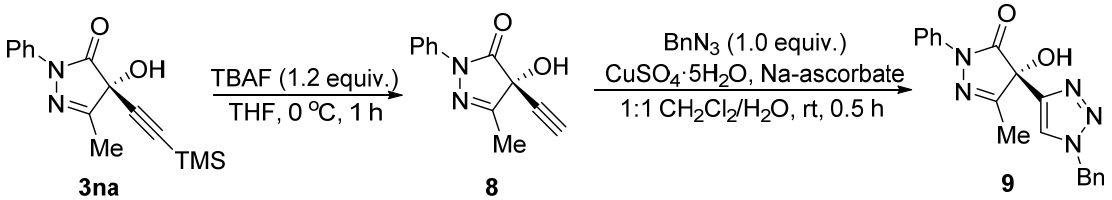


3aa 96% ee **7** 95% yield, 96% ee

Compound **3aa** (0.2 mmol, 58.1 mg) was dissolved in 2 mL EtOAc, and 10 mol% Pd Catalyst (10% w/w Pd/C) was added at room temperature. The reaction mixture was stirred under H_2 atmosphere (balloon). After the reaction was completed (monitored by TLC), the resulting mixture was filtered through a pad of celite to give the hydrogenation product **7**.

White solid, 95% yield, 96% ee, mp 119.5-120.4 °C; $[\alpha]_D^{20}$ +155.4 (*c* 0.56, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.80 (m, 2H), 7.38-7.33 (m, 2H), 7.26-7.22 (m, 2H), 7.20-7.16 (m, 2H), 7.13-7.11 (m, 2H), 4.06 (s, 1H), 2.61-2.47 (m, 2H), 2.34-2.27 (m, 1H), 2.15 (s, 3H), 2.13-2.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.7, 162.1, 139.8, 137.4, 128.9, 128.5, 128.3, 126.3, 125.4, 118.8, 79.9, 37.6, 28.7, 13.1; IR (KBr, cm^{-1}): *v* 3493, 1696, 1594, 1499, 1364, 1261, 1121, 1014, 755, 689, 504; HRMS (ESI) calcd for $C_{18}H_{18}N_2NaO_2^+$ ([M+Na]$^+$): 317.1260, found: 317.1278; HPLC analysis (Daicel Chiralpak AD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 18.95 min (minor), 20.60 min (major).

5. Transformation of Product 3na



3na **8** **9**

Compound **3na** (0.15 mmol, 43.0 mg) was dissolved in 2 mL THF and TBAF (1.2 equiv., 1M solution in THF) was added dropwise at 0 °C. The reaction was stirred at this temperature for an hour (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 (5 mL × 2), then the organic layers were combined and dried over anhydrous Na_2SO_4. After removal of the solvent under

reduced pressure, the residue was purified by silica-gel column chromatography (3:1 petroleum ether/EtOAc as eluent) to give the TMS deprotected alkyne **8**. Semi-solid, 99% yield, 98% ee; $[\alpha]_D^{20}$ +215.9 (*c* 0.64, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.77-7.75 (m, 2H), 7.34-7.29 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 4.88 (br, 1H), 2.64 (s, 1H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 158.4, 137.2, 128.9, 125.7, 119.0, 77.4, 76.9, 72.3, 12.8; IR (KBr, cm^{-1}): *v* 3435, 2231, 1715, 1597, 1501, 1362, 1270, 1169, 756, 693, 640; HRMS (ESI) calcd for $C_{12}H_{10}N_2NaO_2^+$ ($[M+Na]^+$): 237.0634, found: 237.0638; HPLC analysis (Daicel Chiralpak OD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate: 0.9 mL/min): t_R = 9.91 min (minor), 13.13 min (major).

The TMS deprotected alkyne **8** (0.15 mmol, 32.0 mg), $CuSO_4 \cdot H_2O$ (0.0075 mmol, 2.0 mg), Na-ascorbate (0.0225 mmol, 4.6 mg) and 1:1 CH_2Cl_2/H_2O (4 mL) was added to a vial equipped with a magnetic stirring bar. Benzyl azide (0.15 mmol, 20.0 mg) was added dropwise and the mixture was stirred at room temperature for 30 minutes (monitored by TLC). The resulting mixture was quenched with saturated NH_4Cl and extracted with dichloromethane (10 mL × 2), then the organic layers were combined and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (15:1 CH_2Cl_2/EtOAc as eluent) to afford compound **9**. Yellow solid, 95% yield, 98% ee, mp 187.8-189.2 °C; $[\alpha]_D^{20}$ +79.6 (*c* 0.60, CH_3OH); ^1H NMR ($(CD_3)_2CO$, 400 MHz): δ 8.19 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.44-7.37 (m, 7H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.36 (s, 0.4H), 5.67 (s, 2H), 2.21 (s, 3H); ^{13}C NMR ($(CD_3)_2CO$, 100 MHz): δ 172.3, 162.1, 145.4, 139.2, 136.6, 129.7, 129.6, 129.2, 129.0, 125.6, 124.5, 118.9, 77.4, 54.4, 13.8; IR (KBr, cm^{-1}): *v* 3433, 1732, 1631, 1503, 1400, 1223, 1187, 1125, 750, 713, 690; HRMS (ESI) calcd for $C_{19}H_{17}N_5NaO_2^+$ ($[M+Na]^+$): 370.1274, found: 370.1275; HPLC analysis (Daicel Chiralpak OD-H column, λ = 254 nm, eluent: 90:10 *n*-hexane/2-propanol, flow rate:1.0 mL/min): t_R = 36.73 min (minor), 41.31 min (major).

6. References

1. (a) H.-L. Song, K. Yuan and X.-Y. Wu, *Chem. Commun.,* 2011, **47**, 1012; (b) R. Rexiti, J. Lu, G. Wang, F. Sha and X.-Y. Wu, *Tetrahedron: Asymmetry,* 2016, **27**, 923; (c) T.-C. Kang, L.-P. Wu, F. Sha and X.-Y. Wu, *Tetrahedron,* 2018, **74**, 1017; (d) R. Rexiti, Z.-G. Zhang, J. Lu, F. Sha and X.-Y. Wu, *J. Org. Chem.,* 2019, **84**, 1330.
2. U. Kaya, P. Chauhan, S. Mahajan, K. Deckers, A. Valkonen, K. Rissanen and D. Enders, *Angew. Chem., Int. Ed.,* 2017, **56**, 15358.

7. X-ray Structure and Crystal Data for Product 3ha

The single crystal of product **3ha** was obtained by crystallization from EtOAc, and its configuration was determined as *R*-configuration by X-ray crystallography with Cu target (the data have been deposited in CCDC with number 1906329). The configuration of other alkynylation products **3** were assigned by analogy.

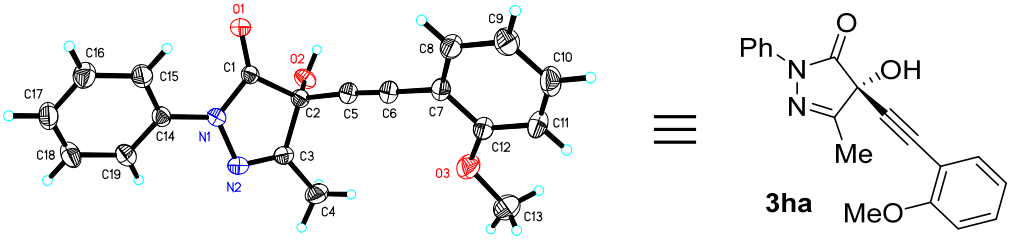
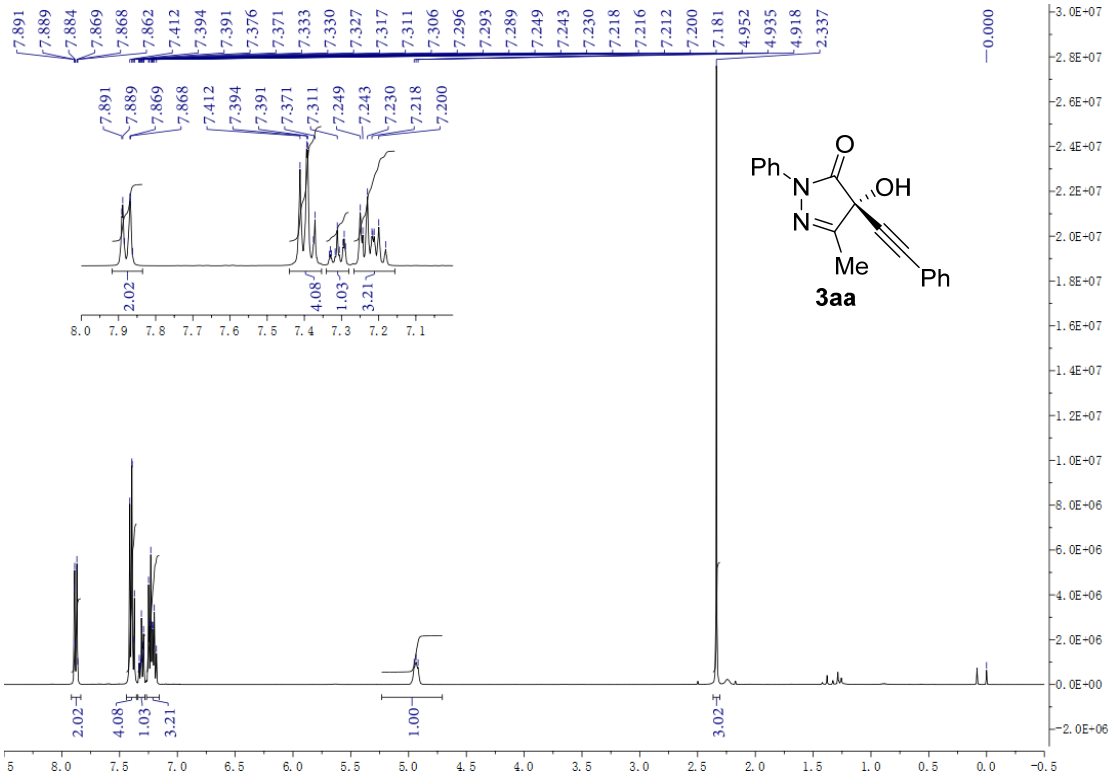


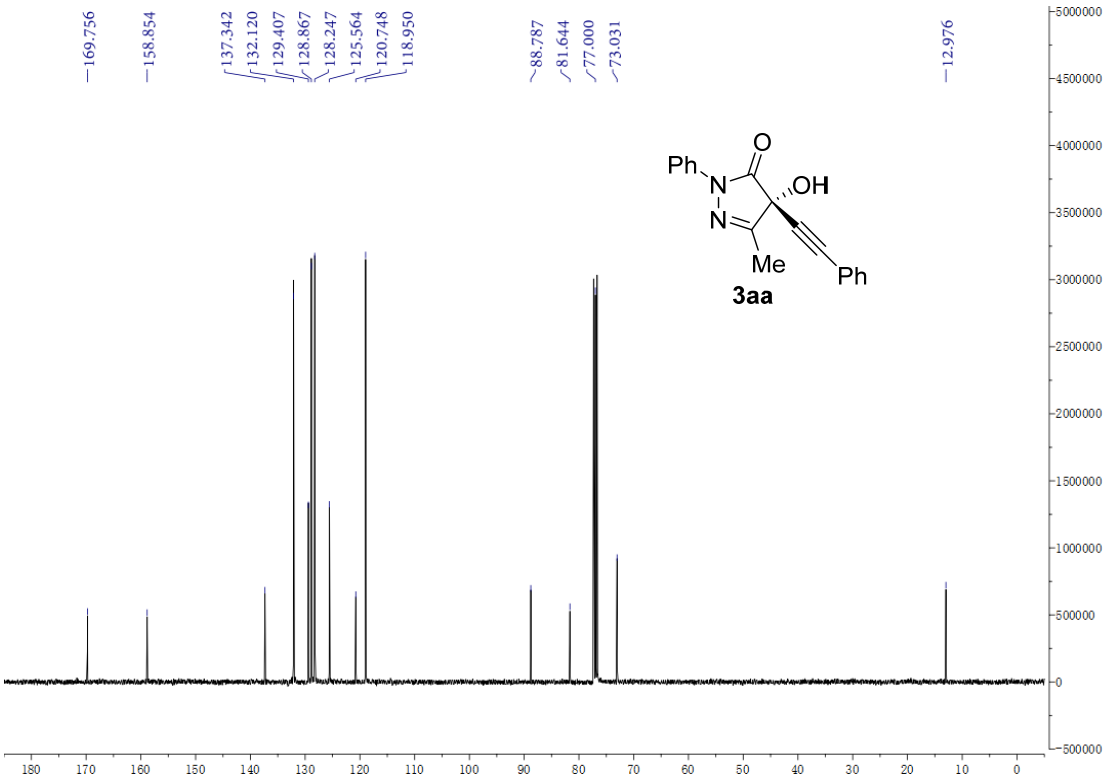
Table S2 Crystal data and structure refinement for **3ha**

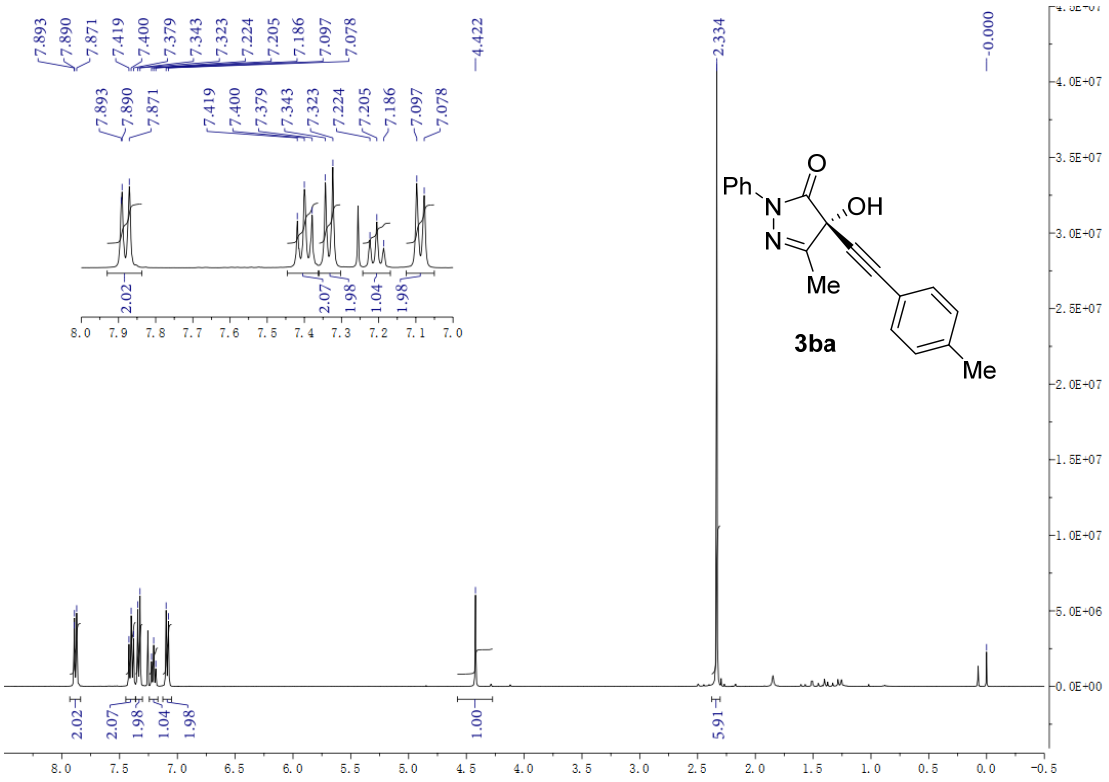
Identification code	**3ha**	
Empirical formula	$C_{19}H_{16}N_2O_3$	
Formula weight	320.34	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.2047(2) Å	a= 90°.
	b = 4.92460(10) Å	b= 110.4420(10)°.
	c = 14.6571(3) Å	g = 90°.
Volume	825.46(3) $Å^3$	
Z	2	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.721 mm^{-1}	
F(000)	336	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	9.573 to 67.485°.	
Index ranges	-13<=h<=14, -5<=k<=5, -17<=l<=16	
Reflections collected	12251	

Independent reflections	2826 [R(int) = 0.0345]
Completeness to theta = 67.679°	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5740
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2826 / 1 / 221
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0859
R indices (all data)	R1 = 0.0315, wR2 = 0.0865
Absolute structure parameter	0.03(7)
Extinction coefficient	0.059(13)
Largest diff. peak and hole	0.141 and -0.128 e.$Å^{-3}$

8. Copies of NMR Spectra for Products 3-9



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Me
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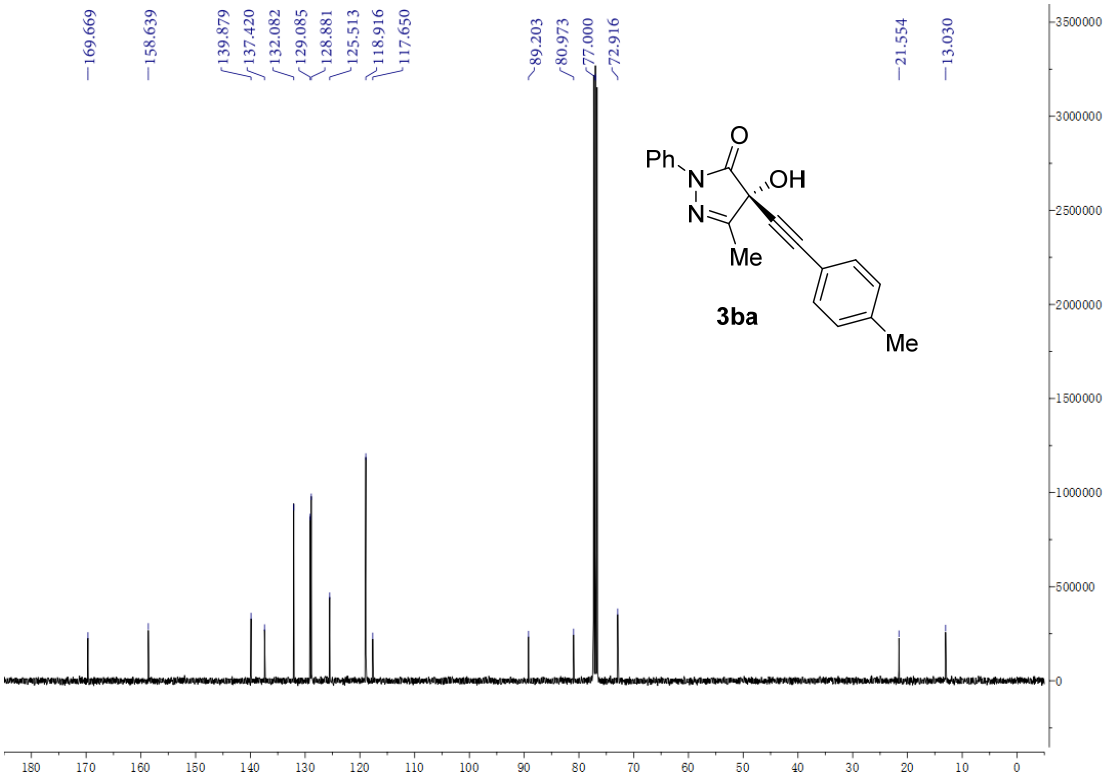
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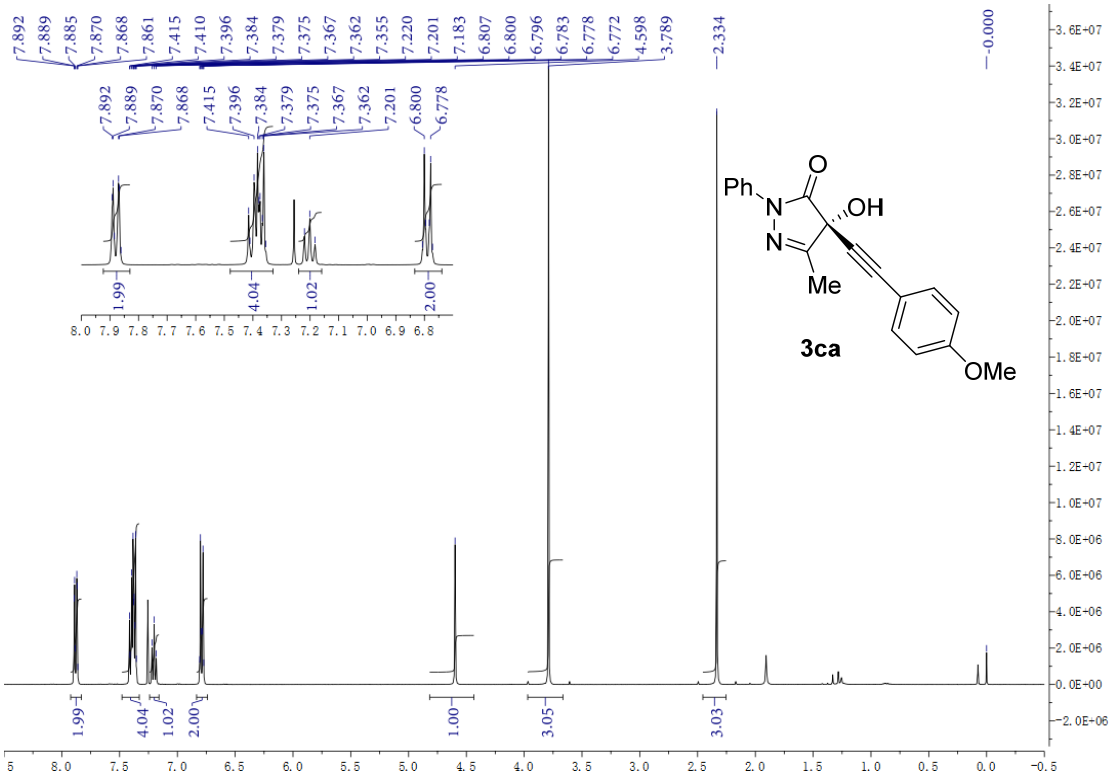
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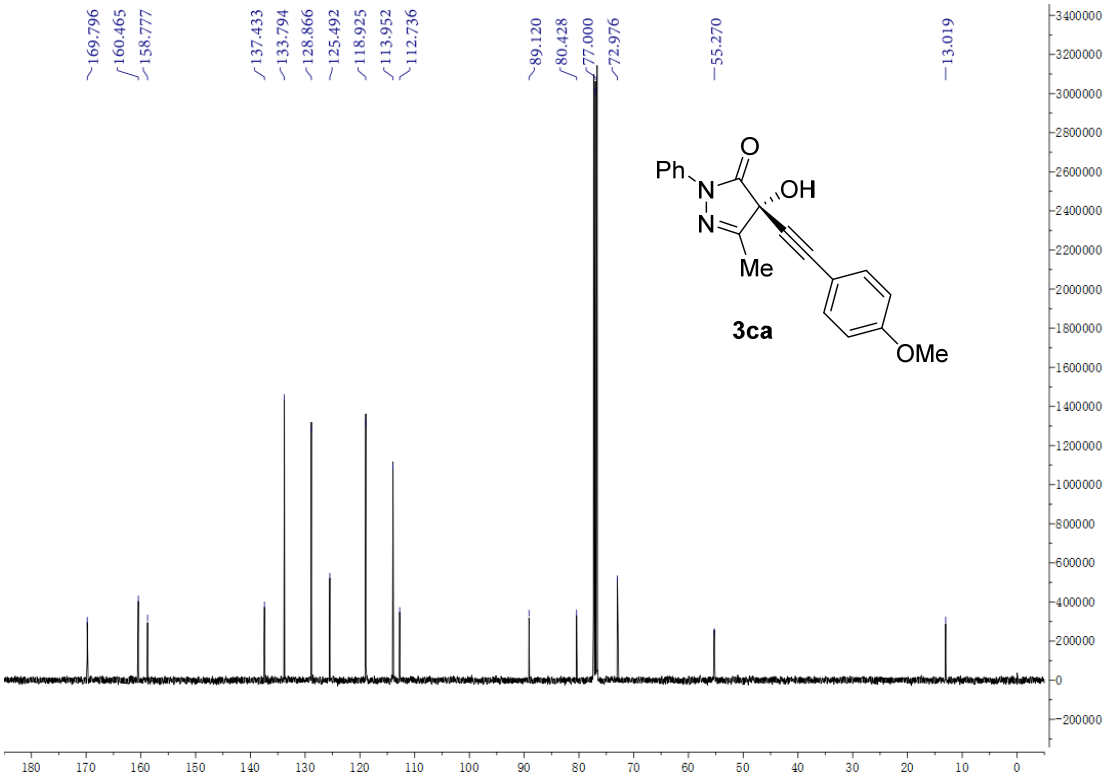
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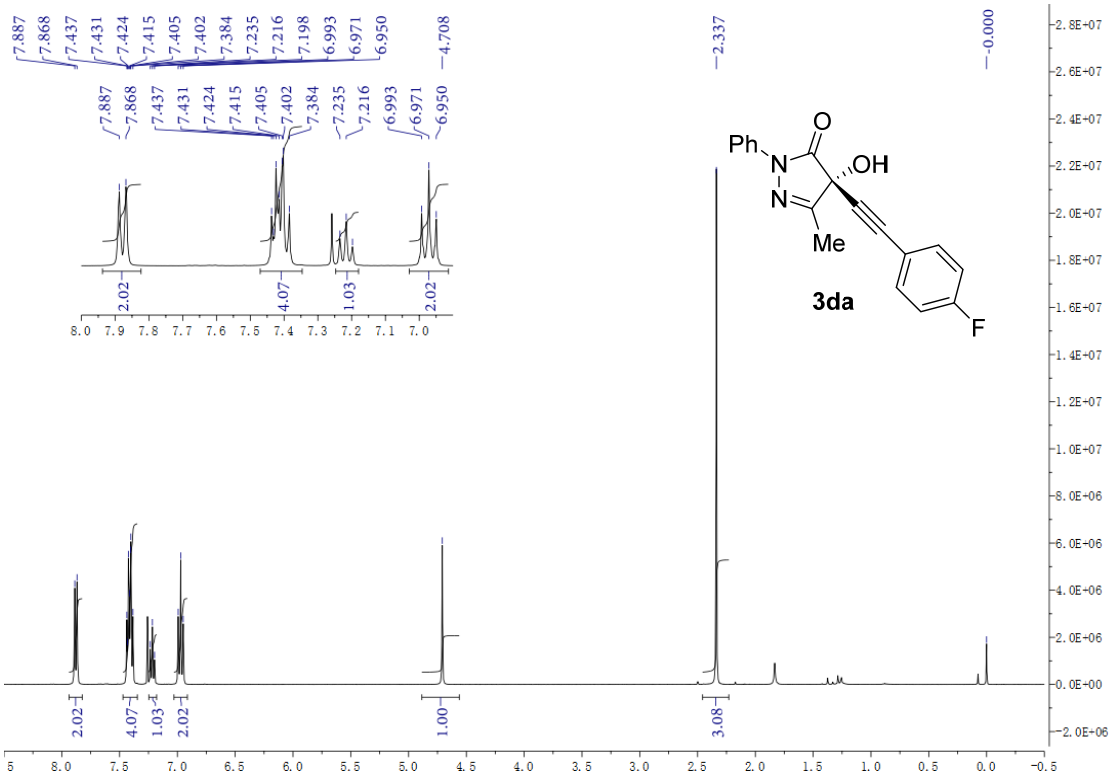
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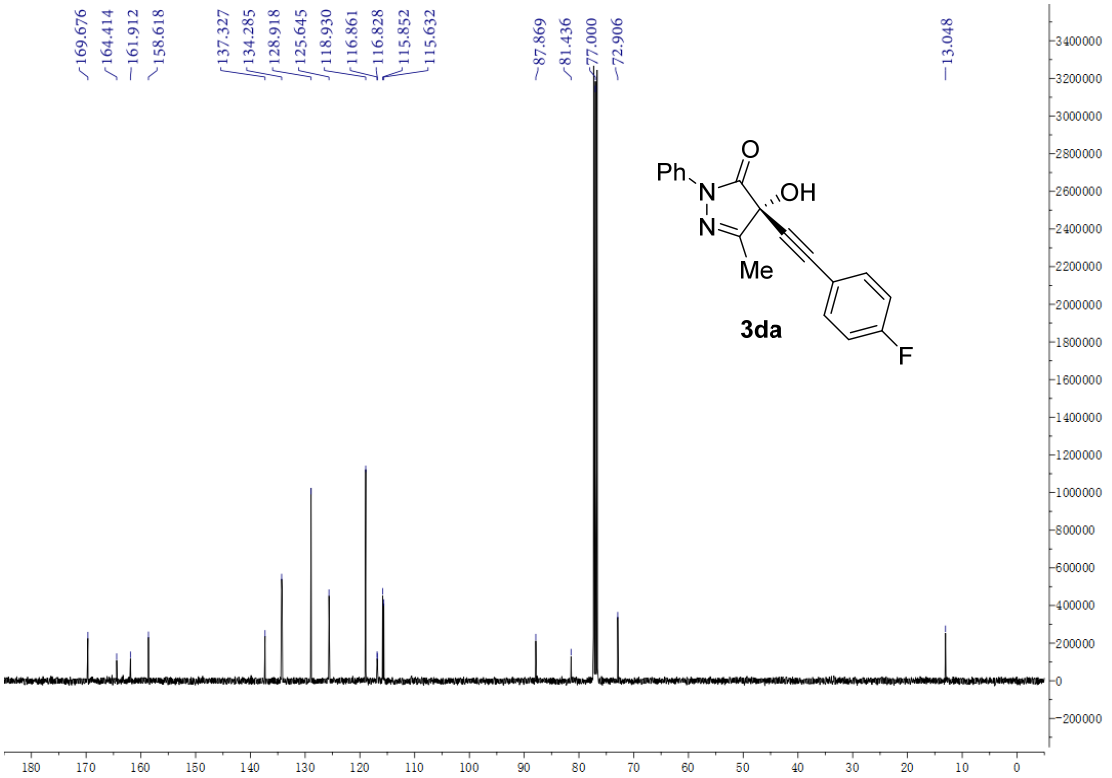
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F
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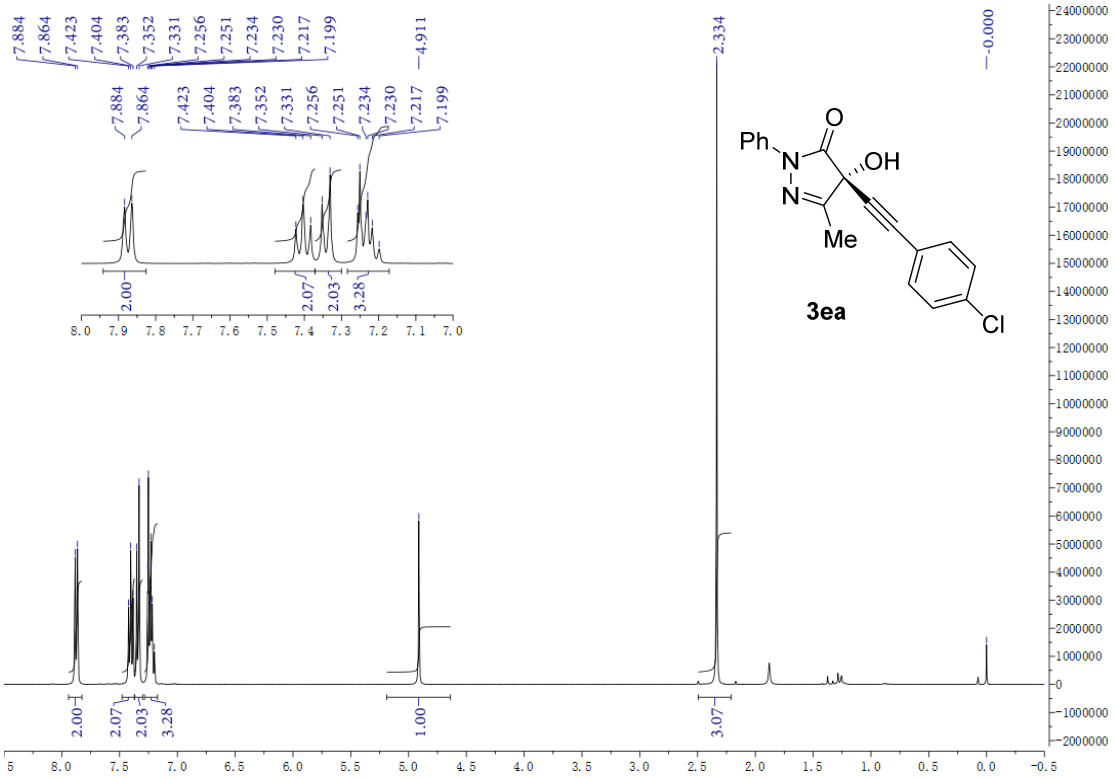
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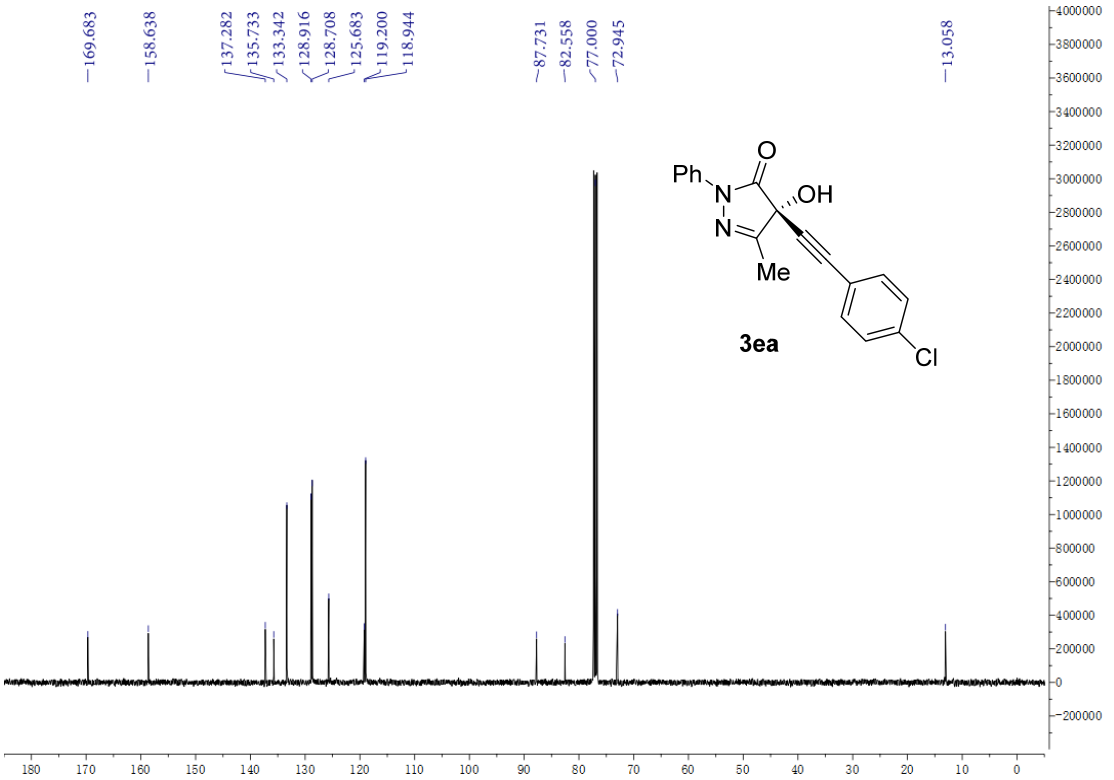
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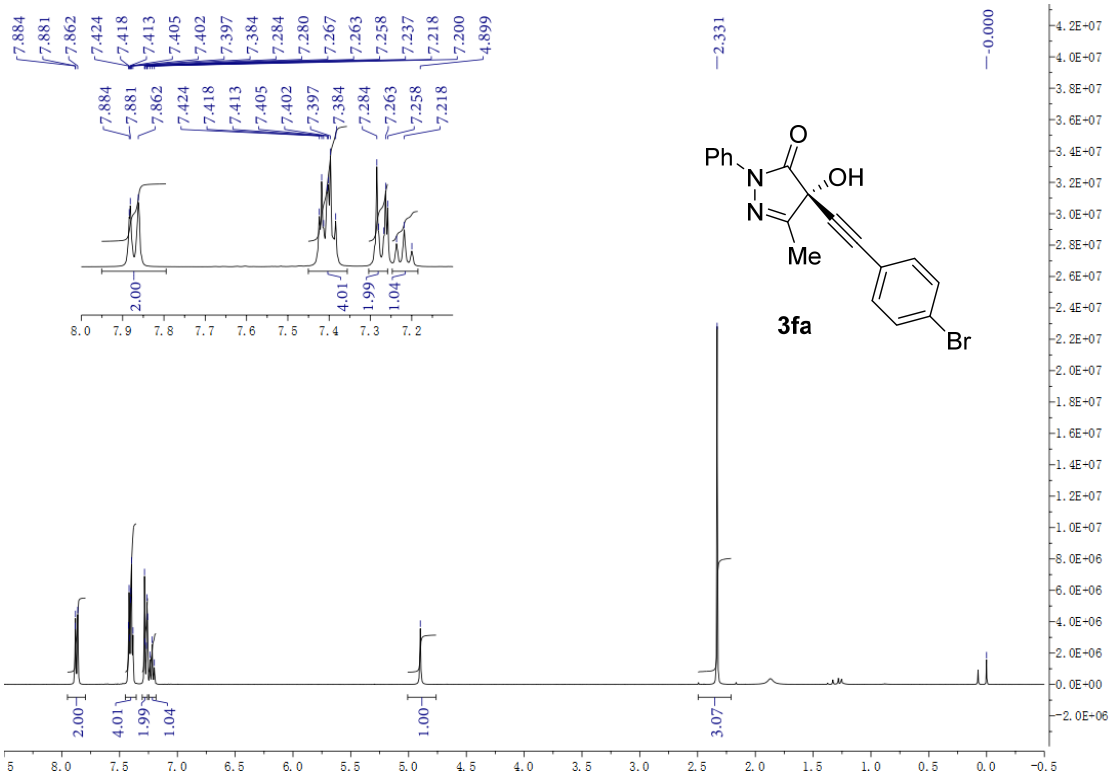
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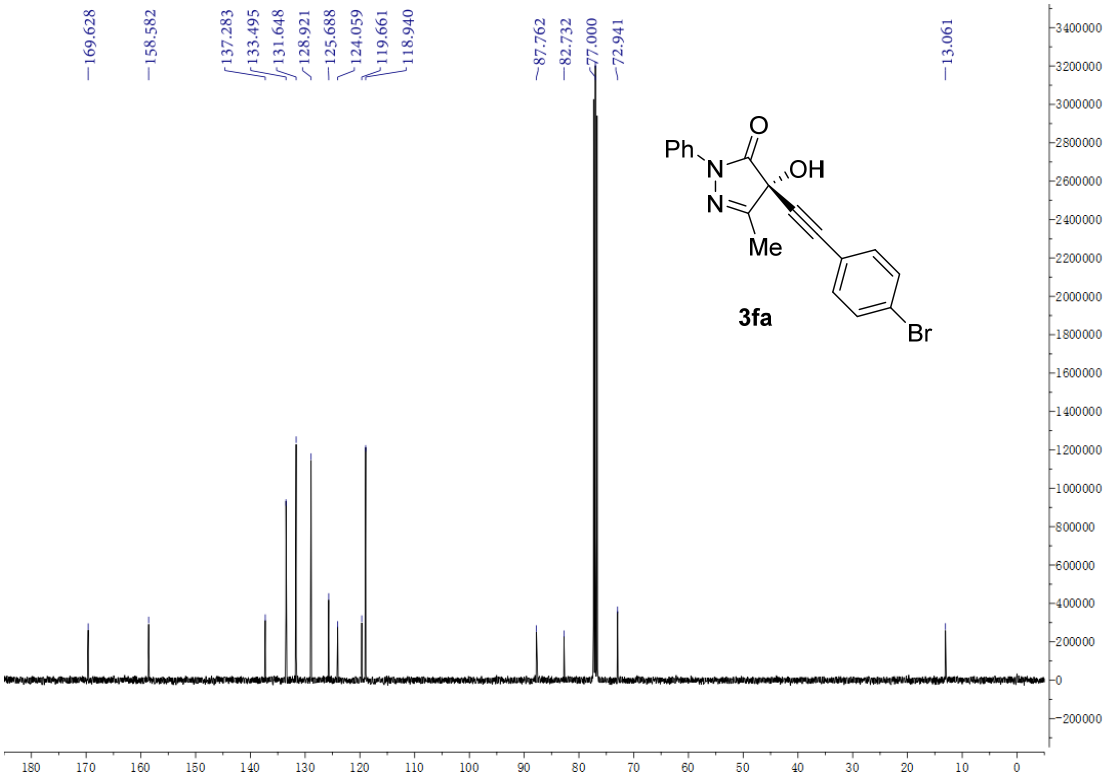
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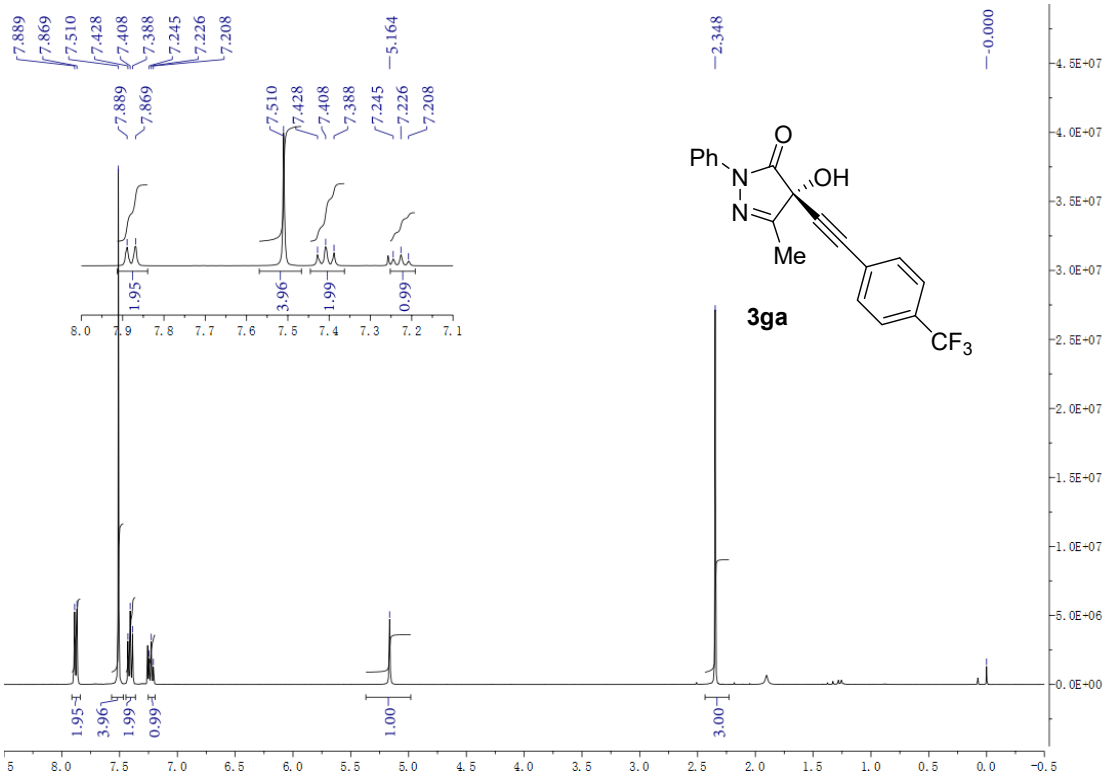
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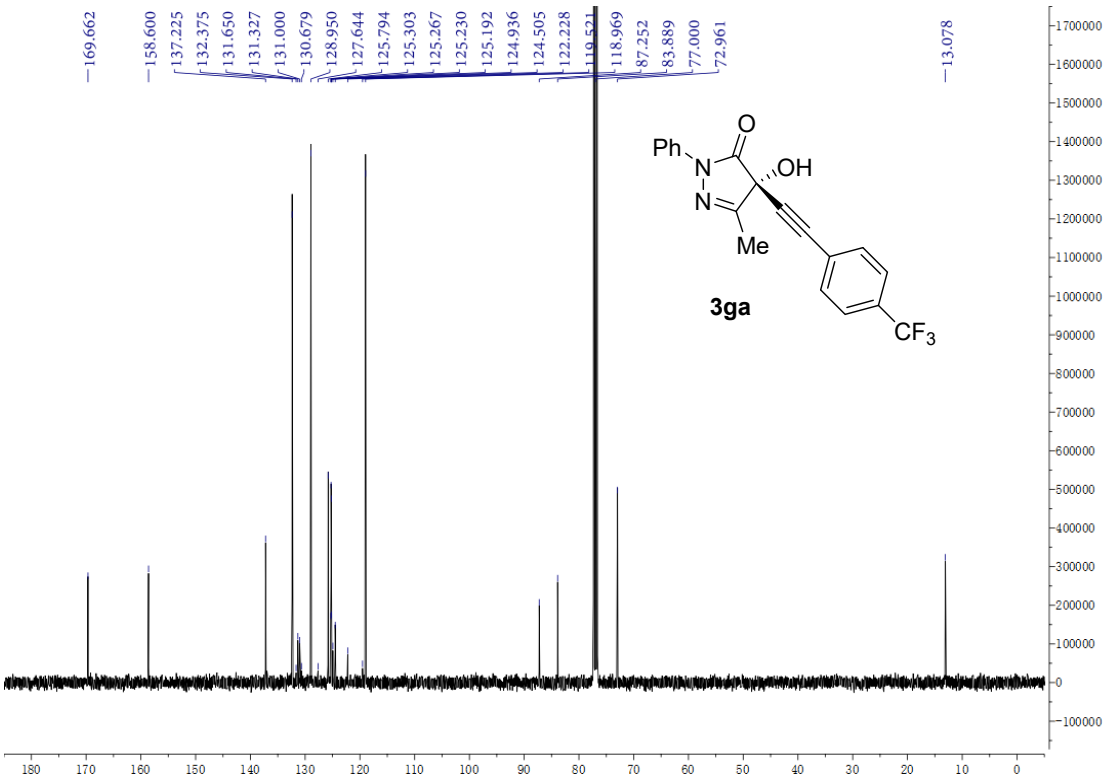
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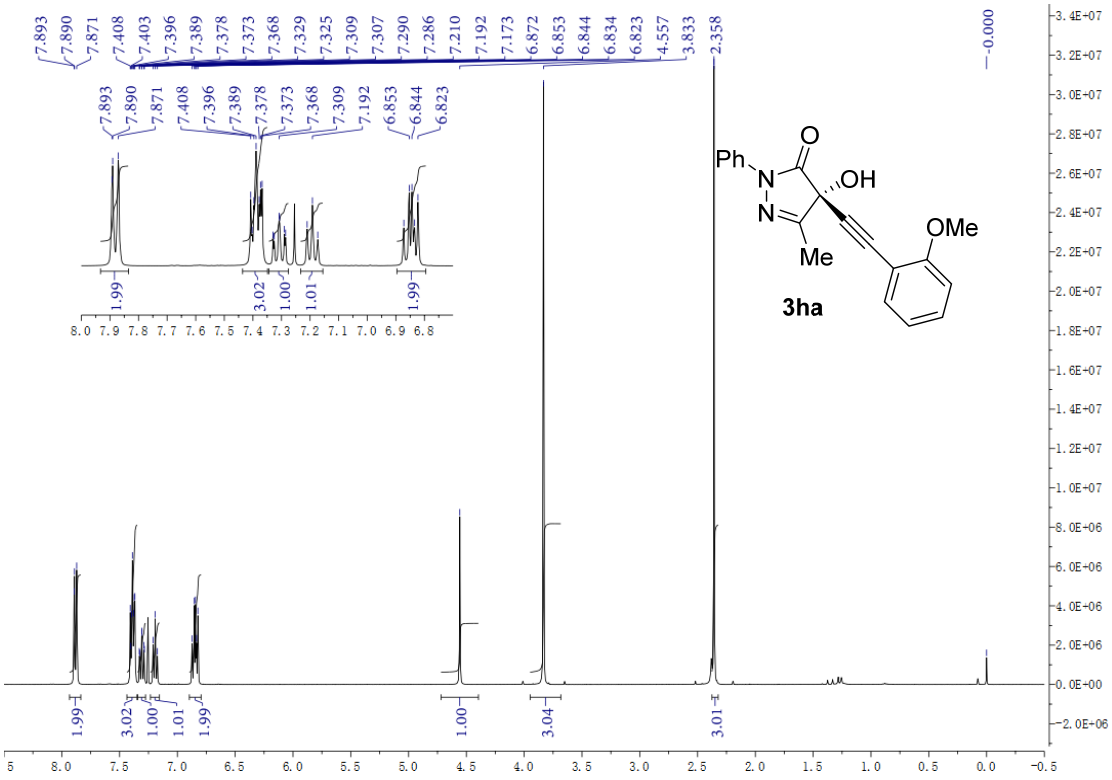
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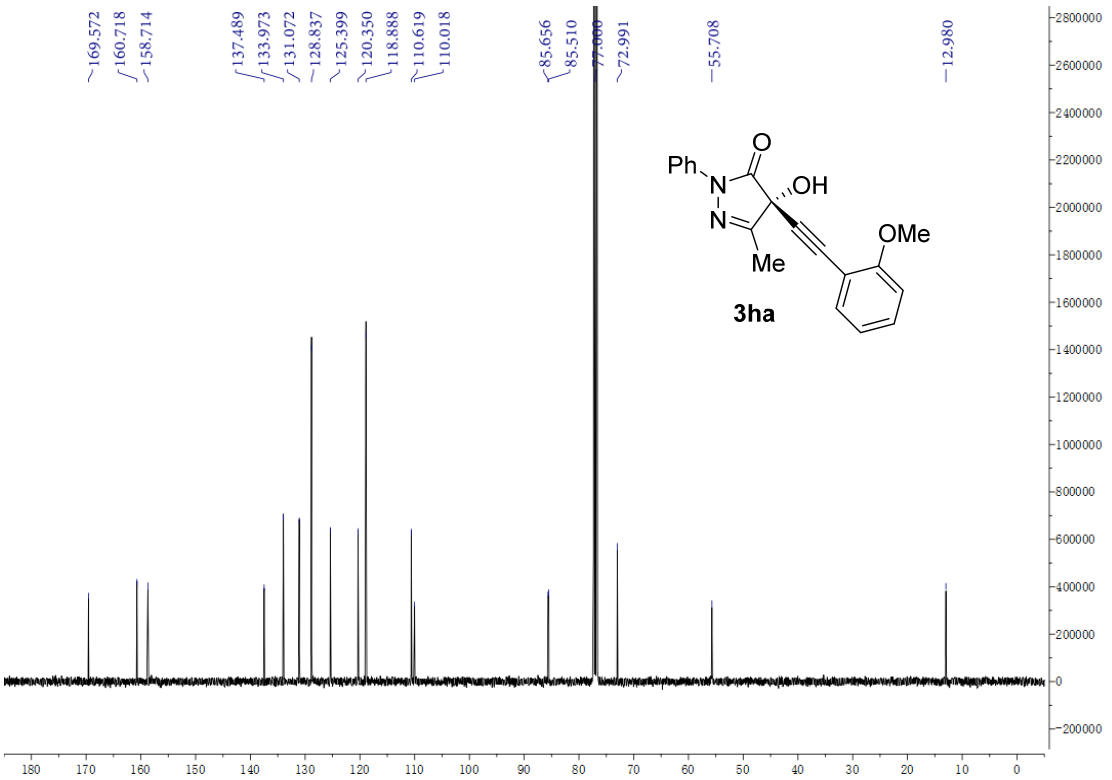
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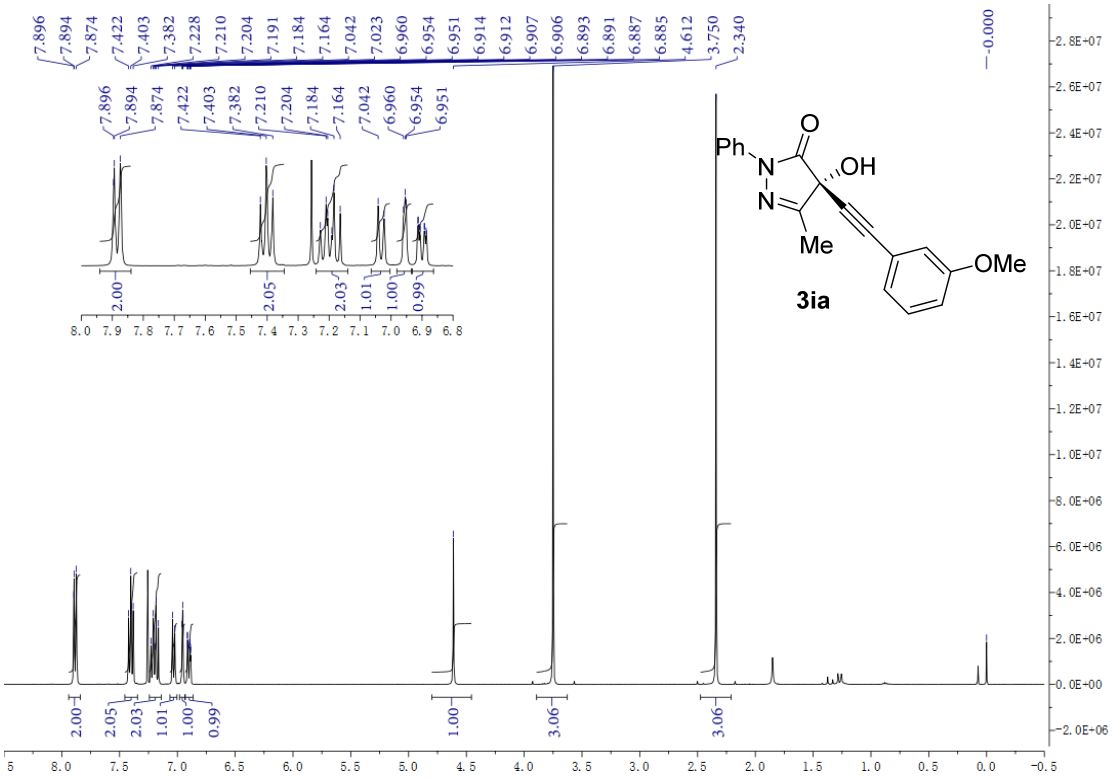
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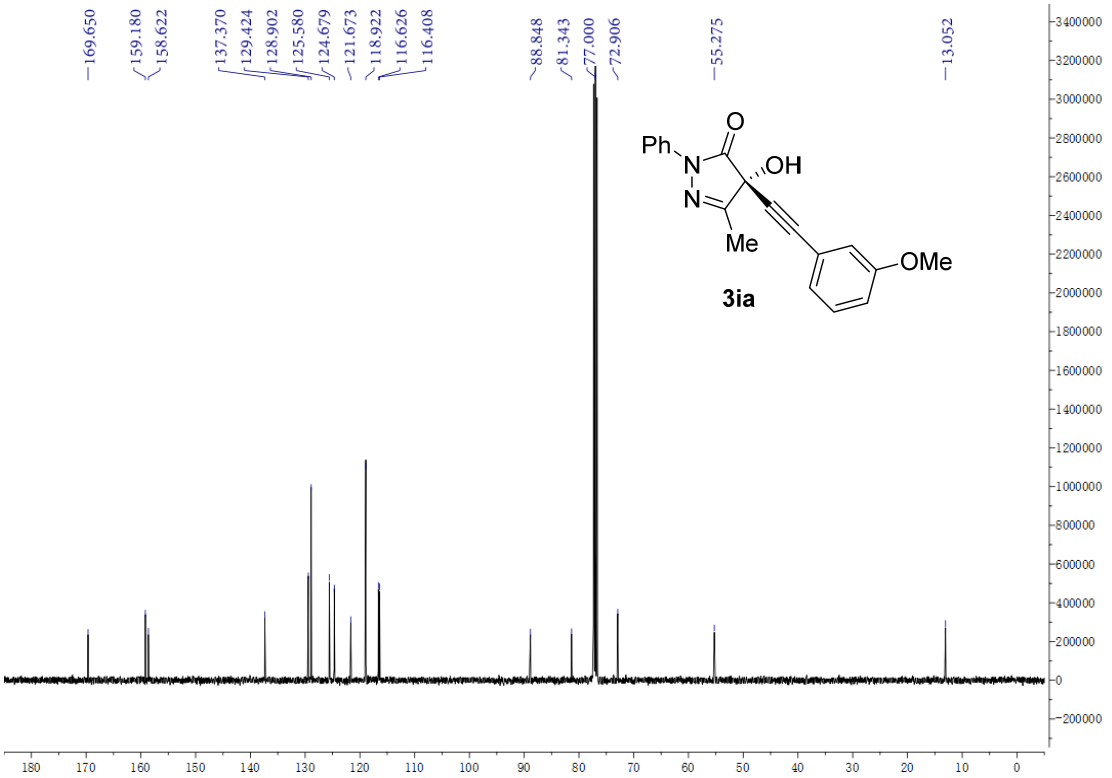
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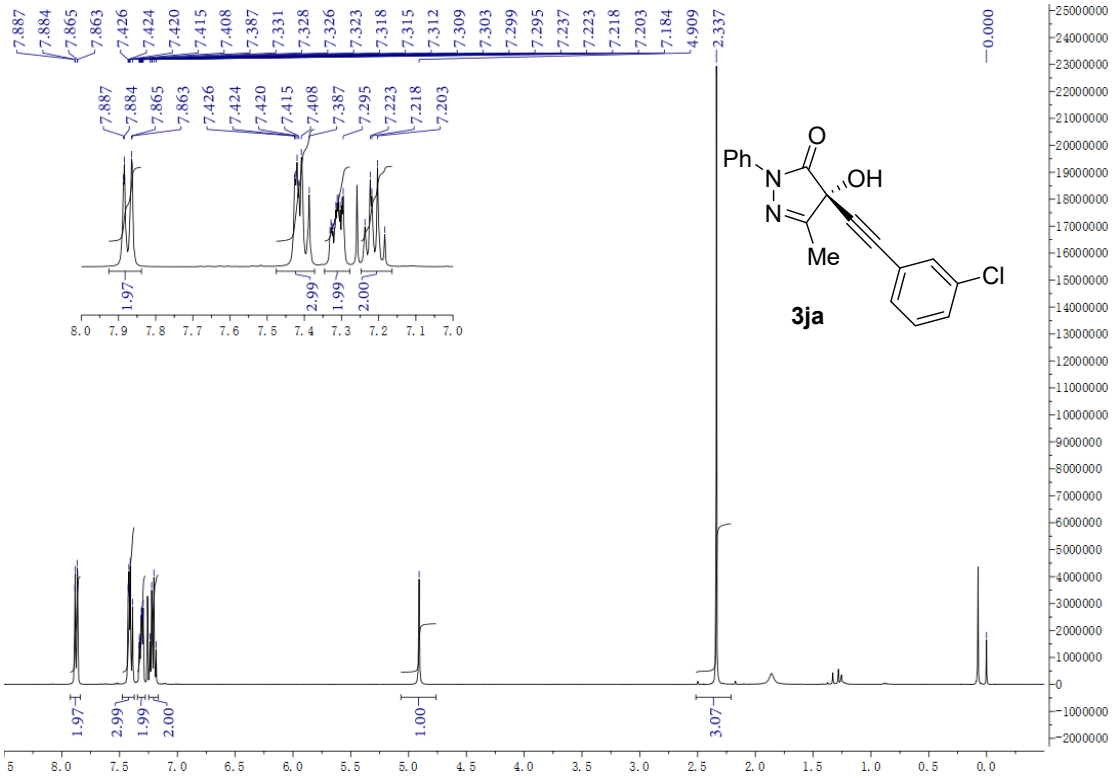
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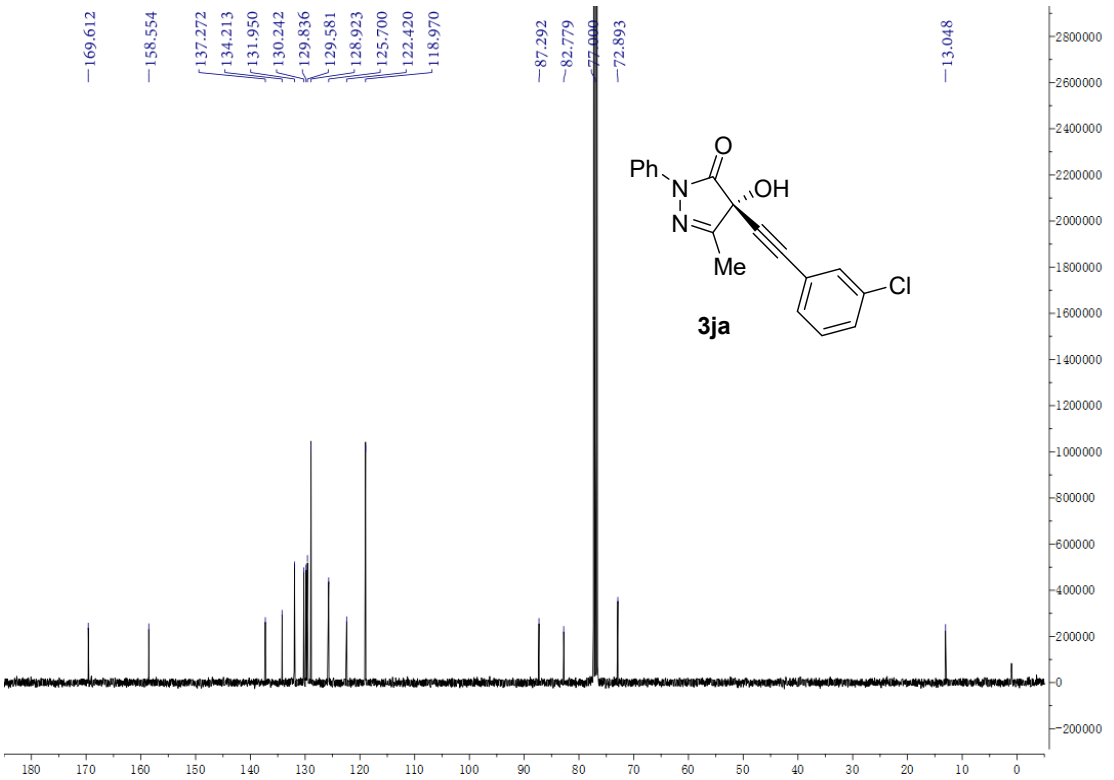
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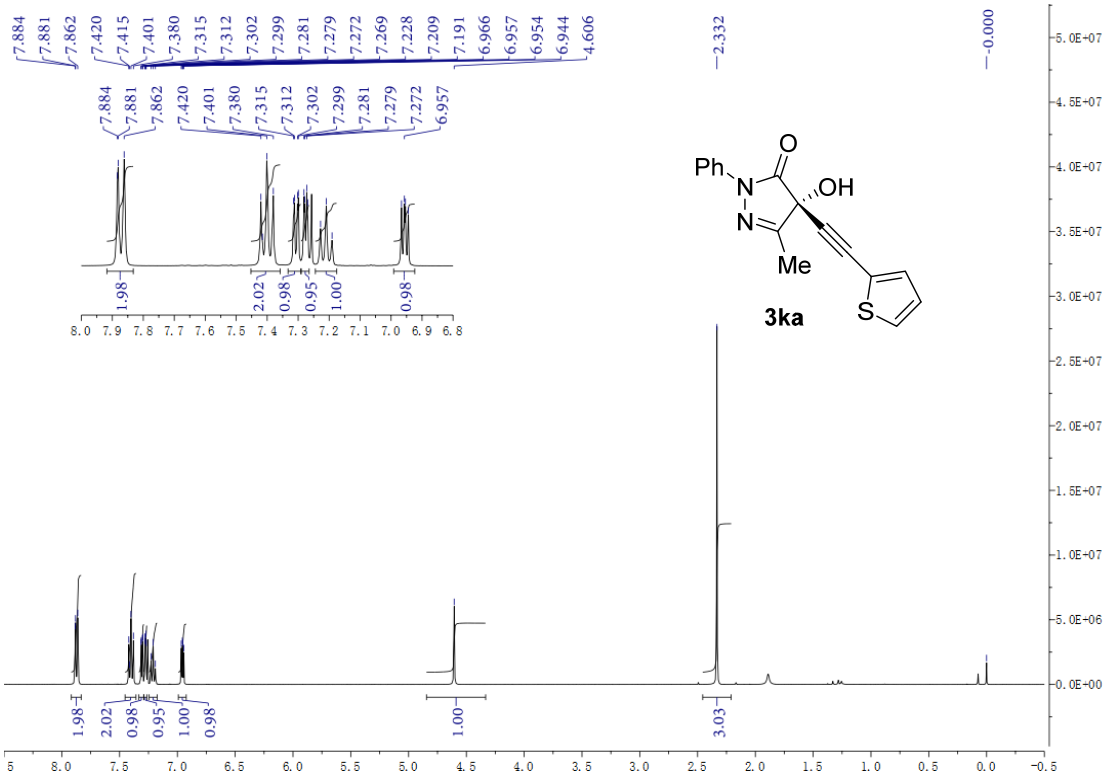
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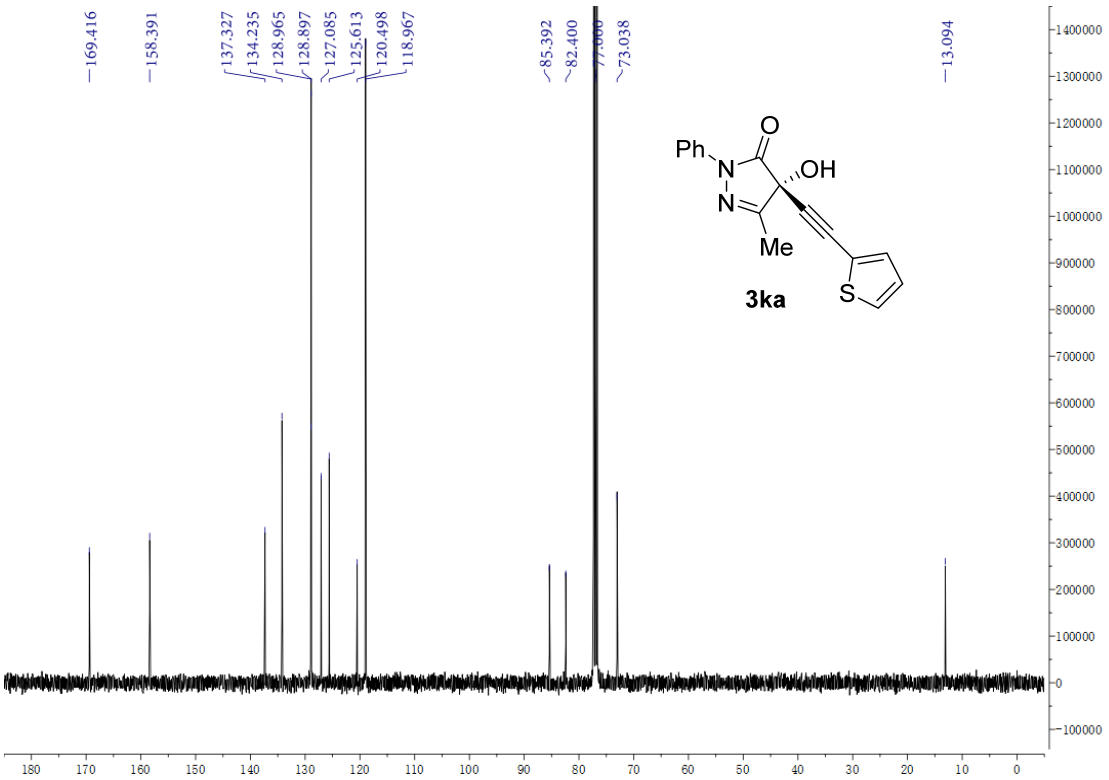
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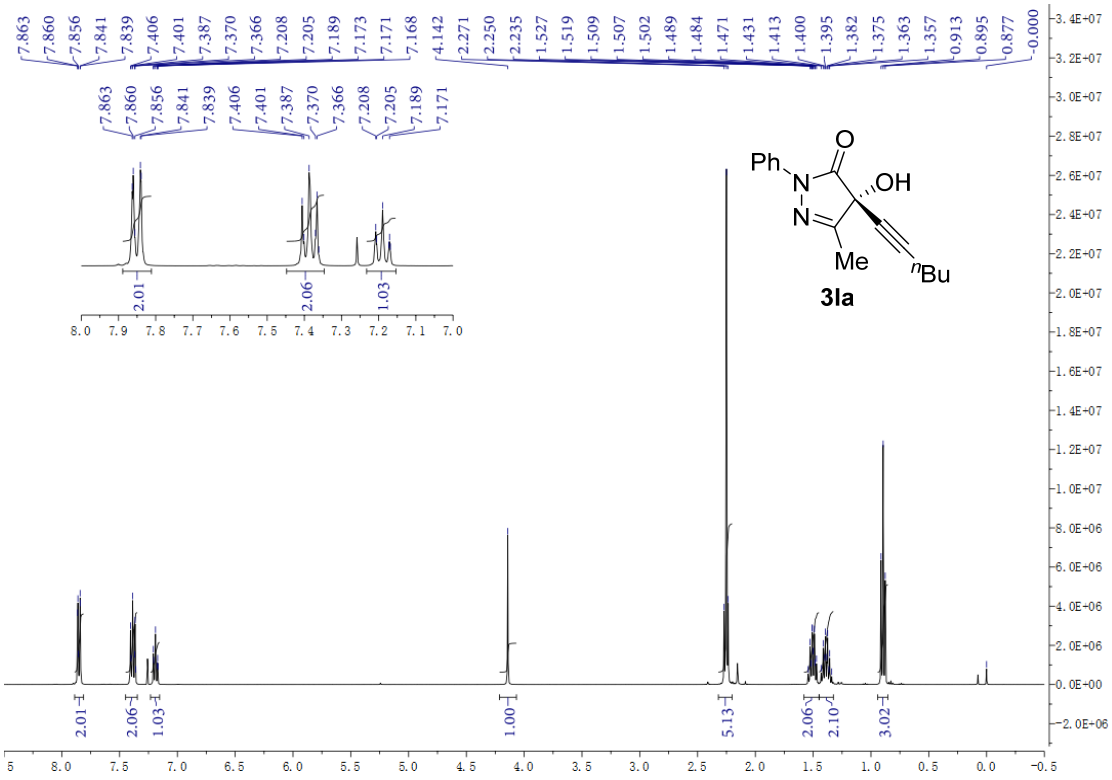
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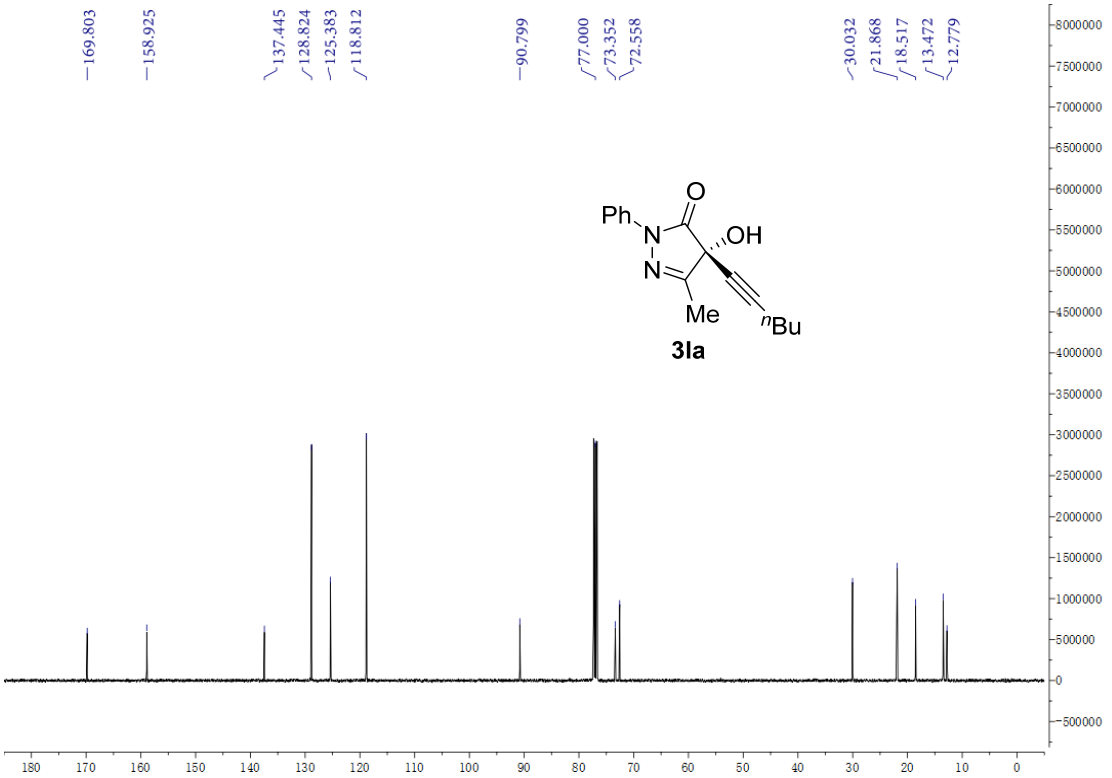
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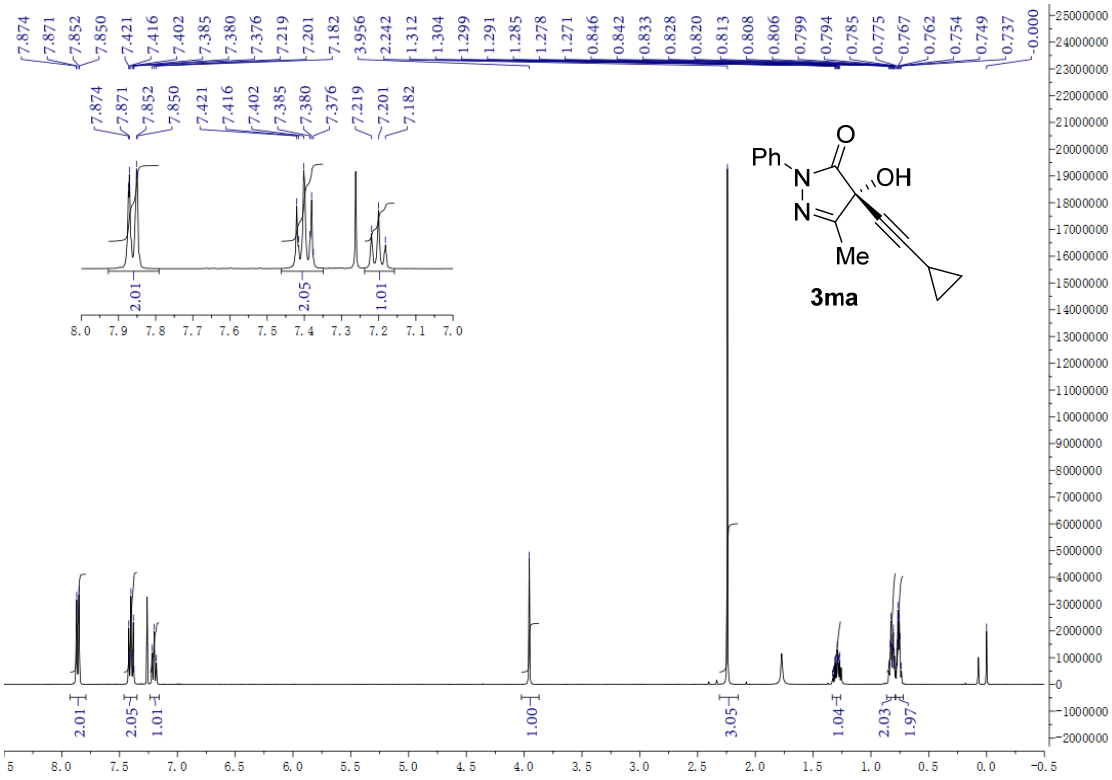
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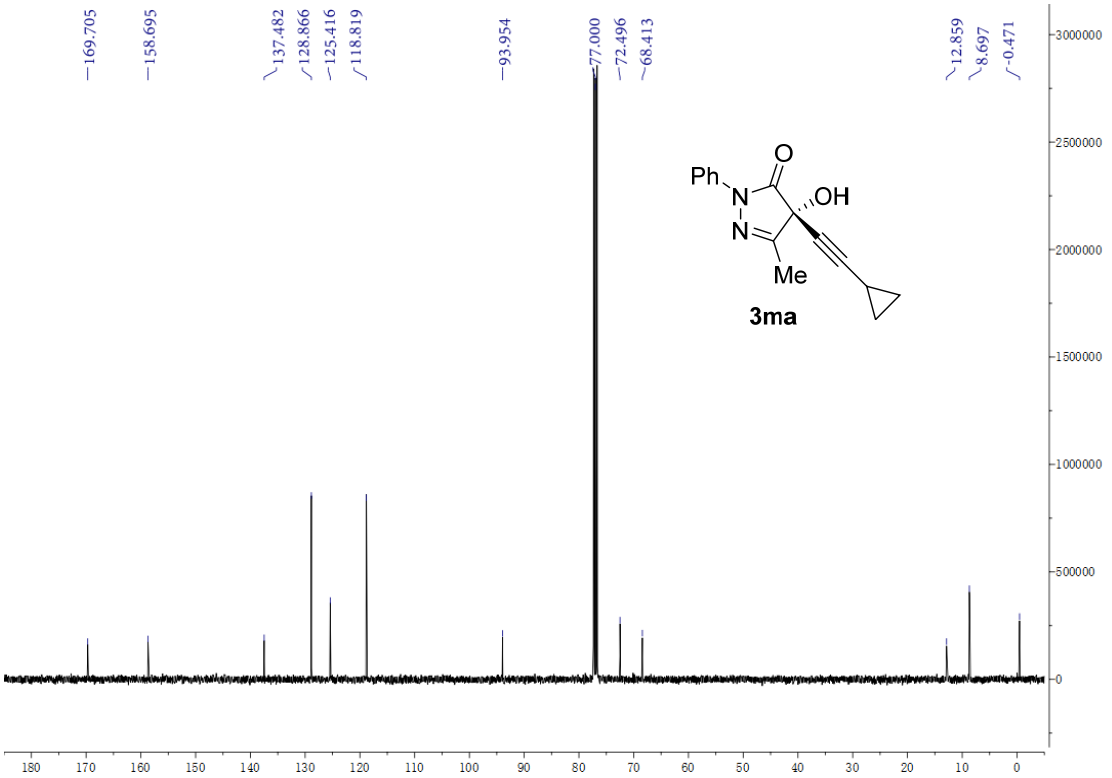
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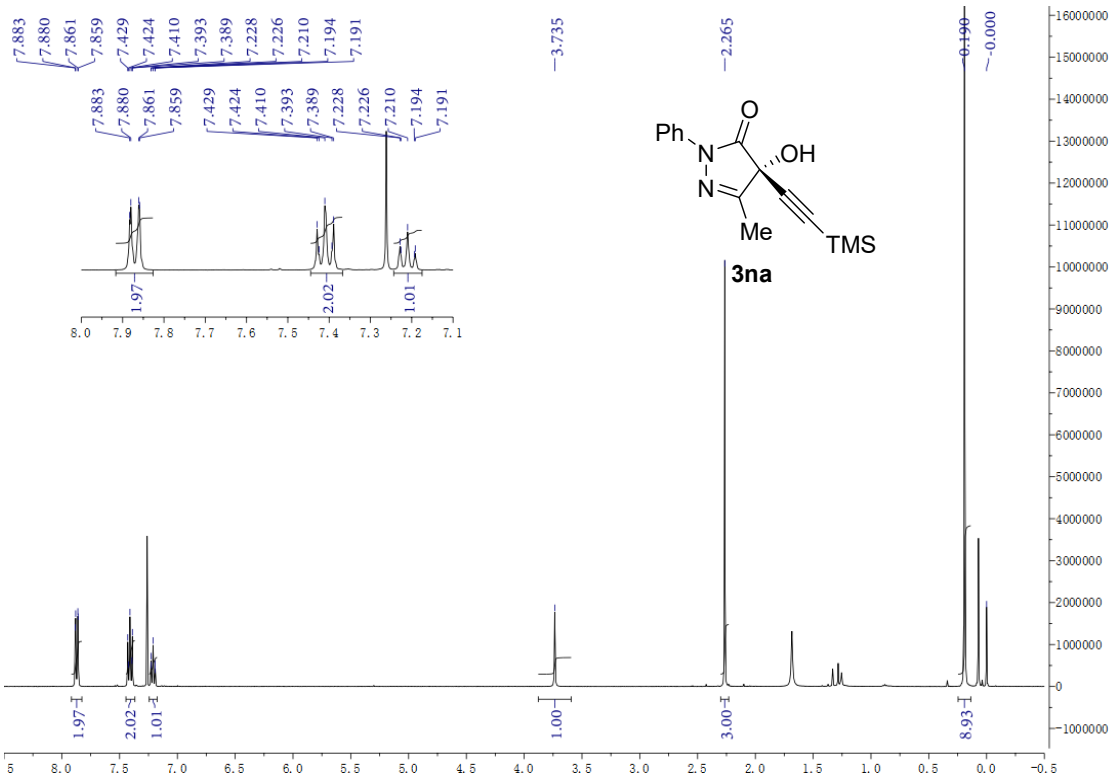
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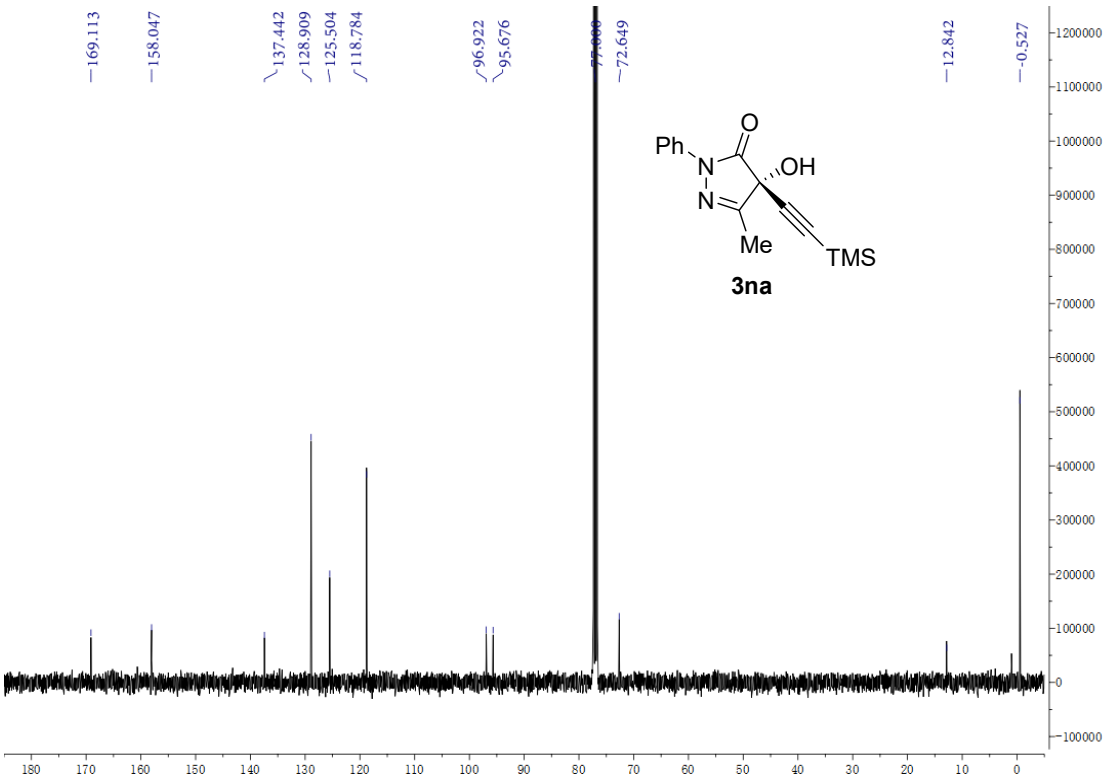
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TMS
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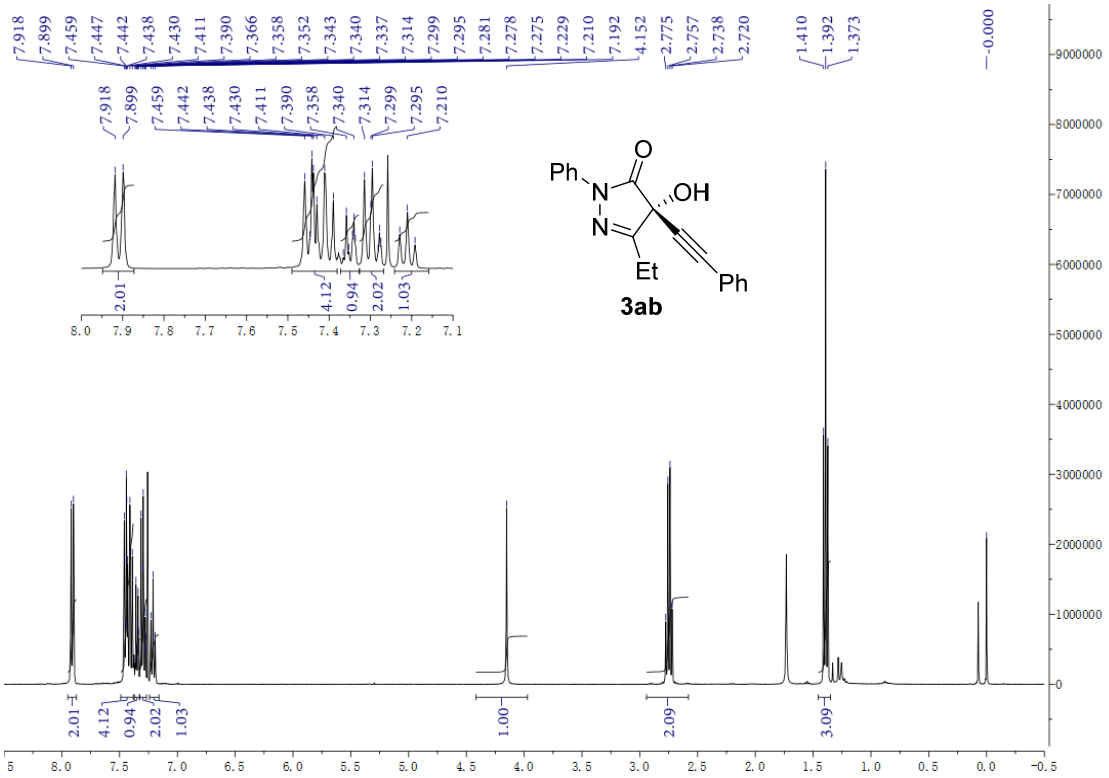
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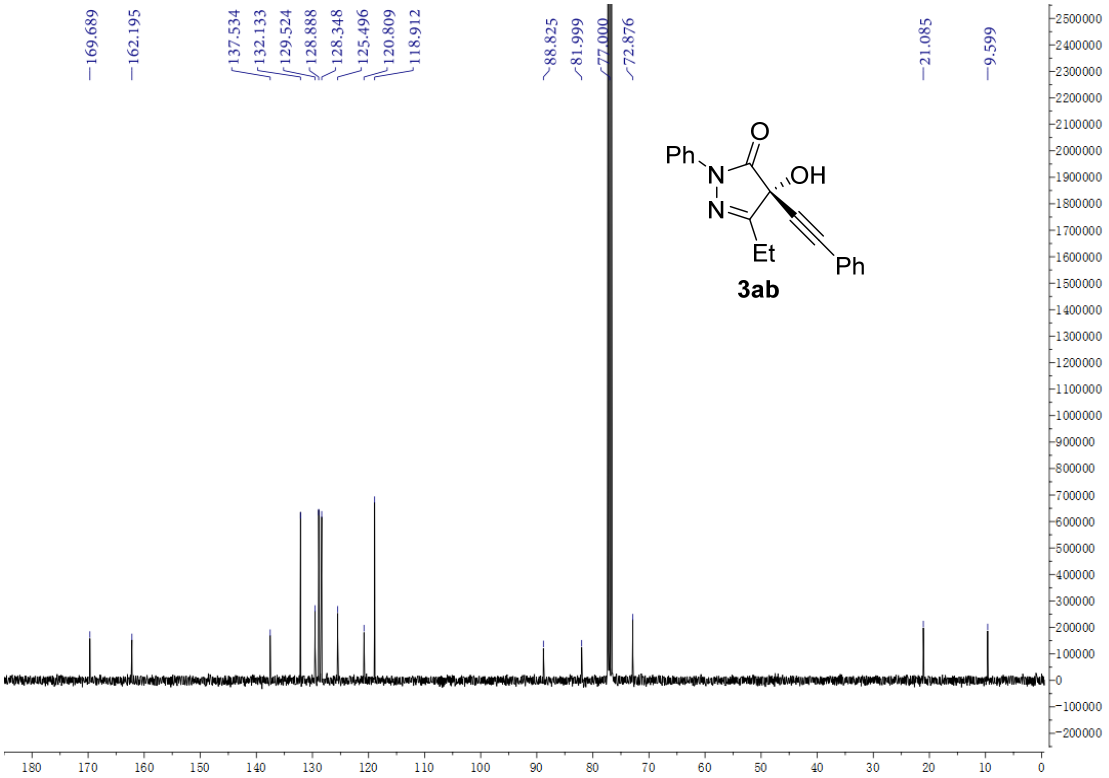
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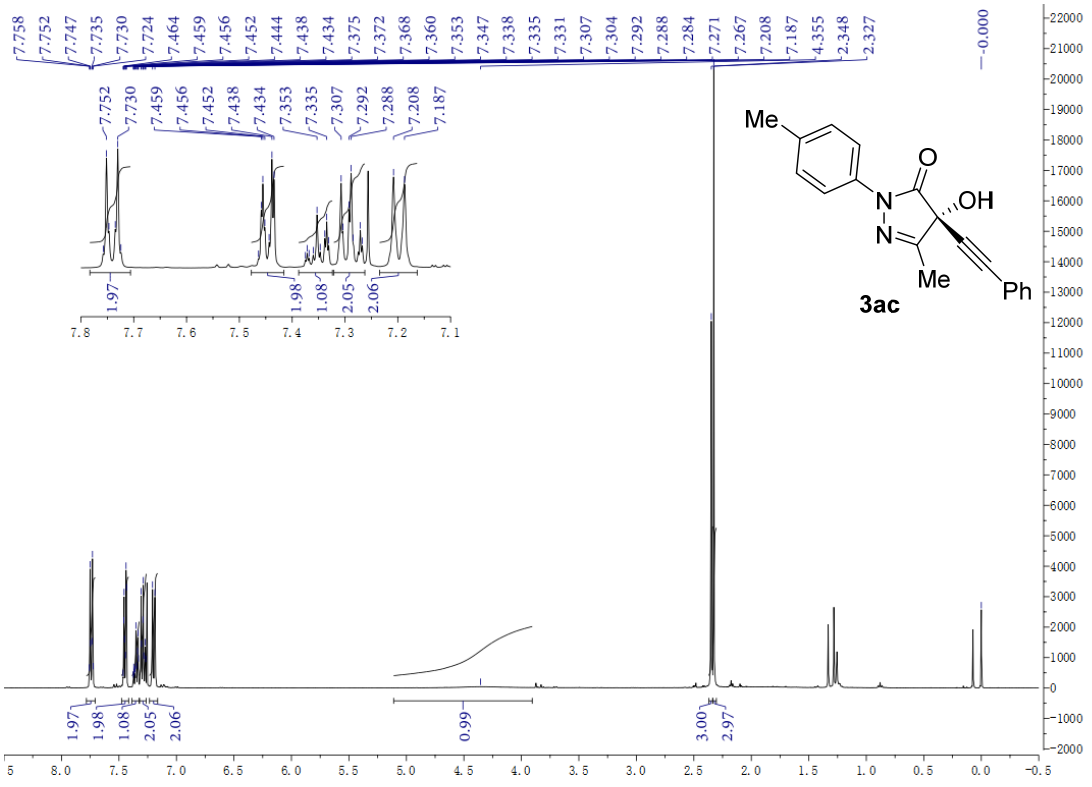
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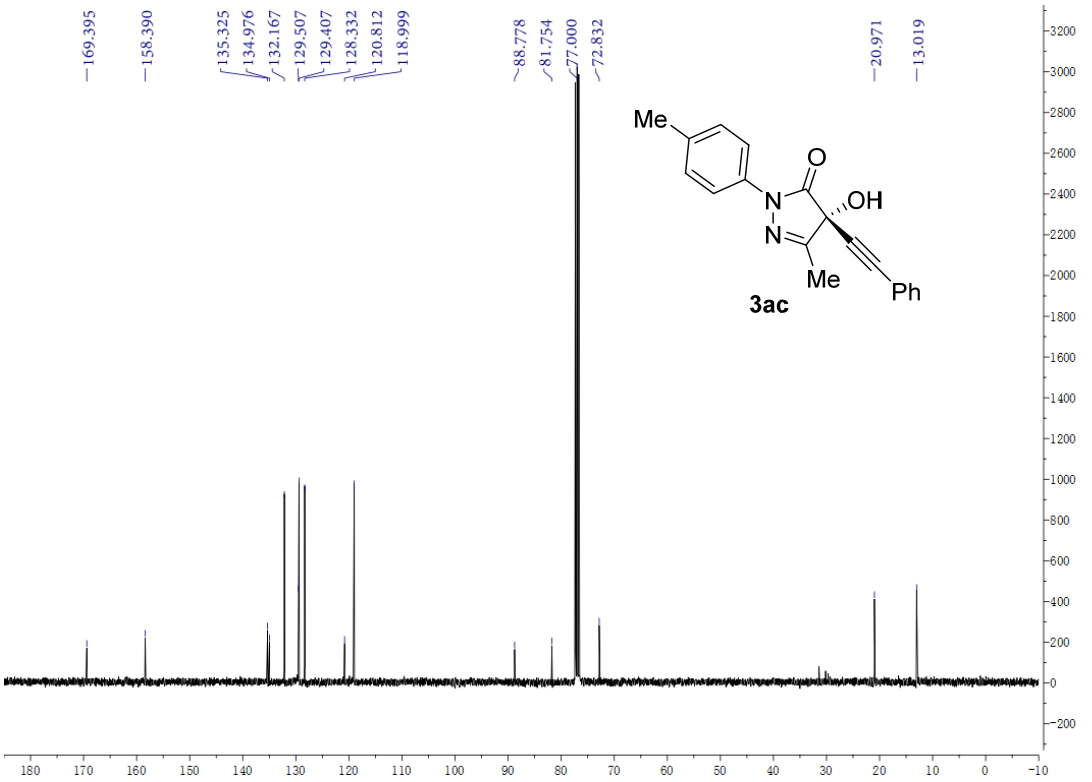
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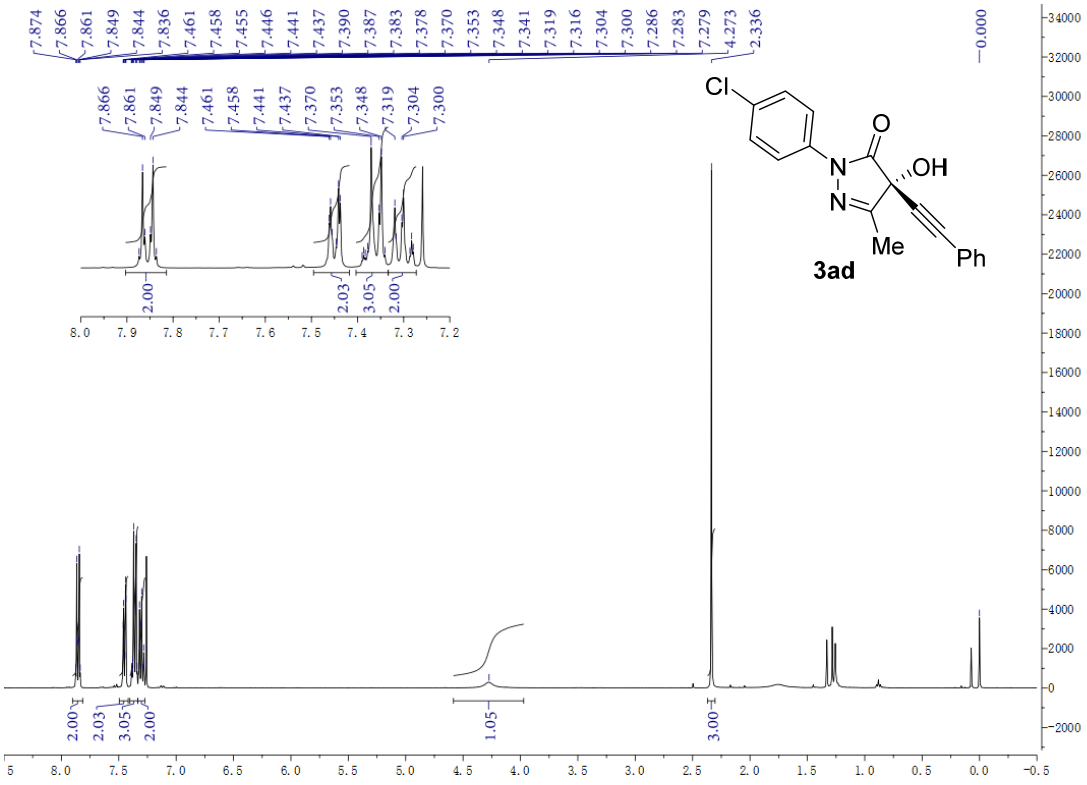
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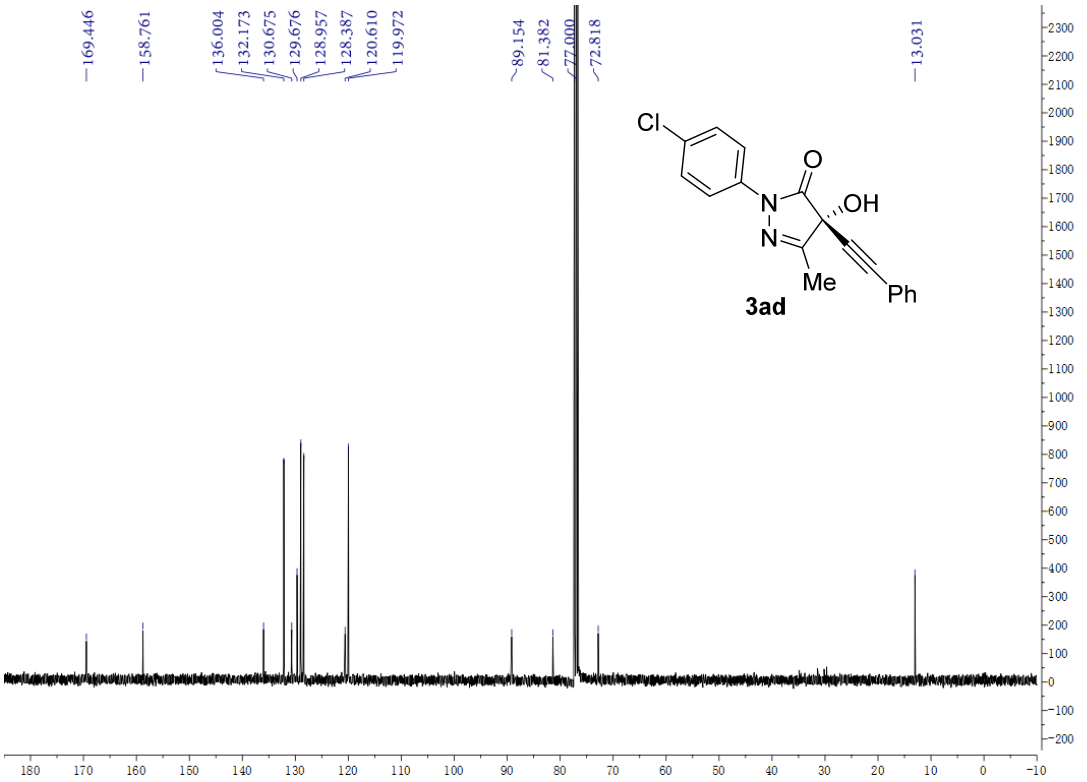
1.05
3.00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Ph
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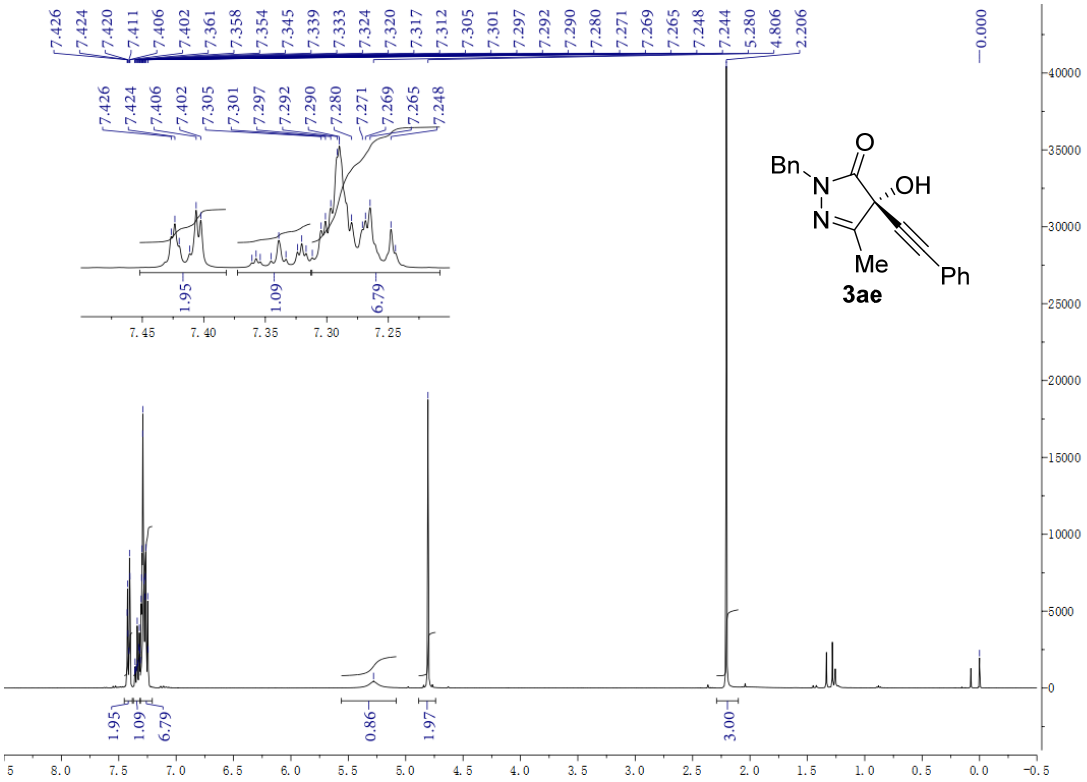
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7.292
7.290
7.280
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7.244
5.280
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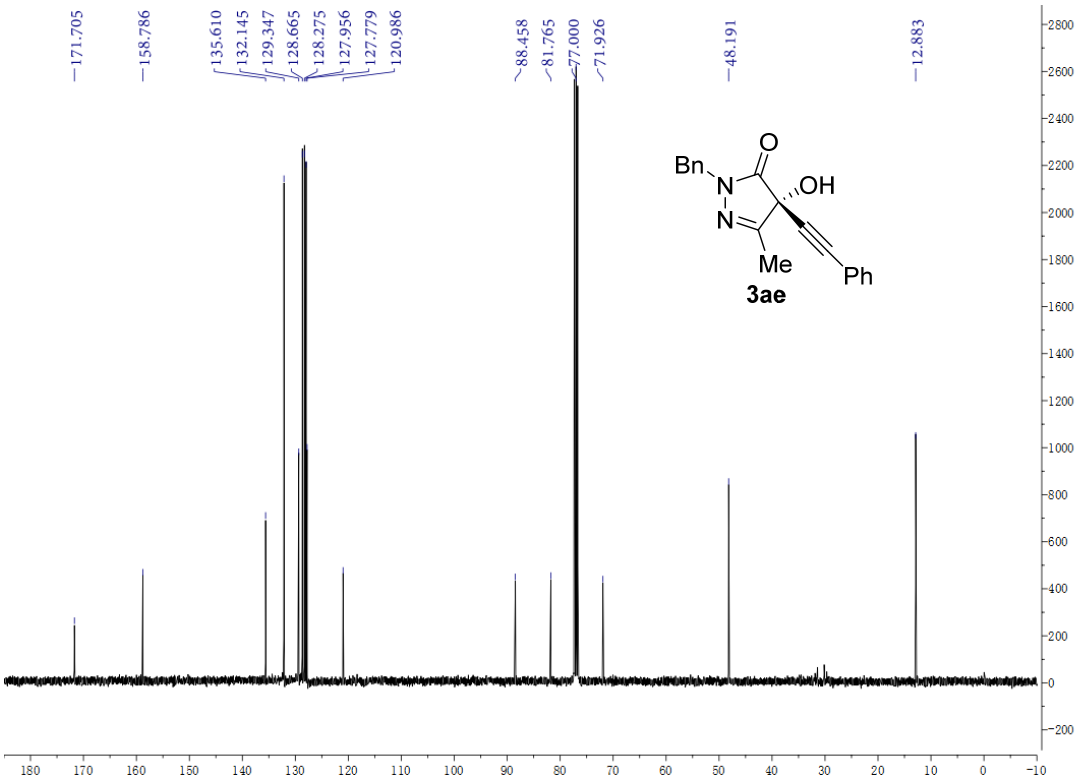
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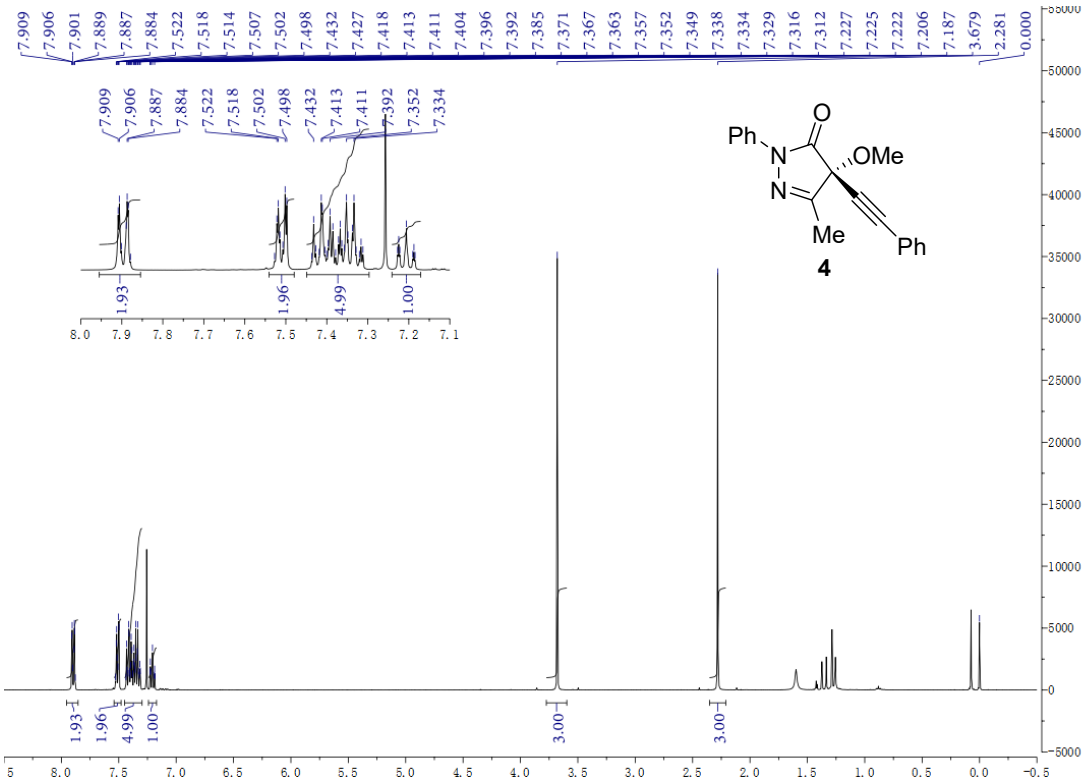
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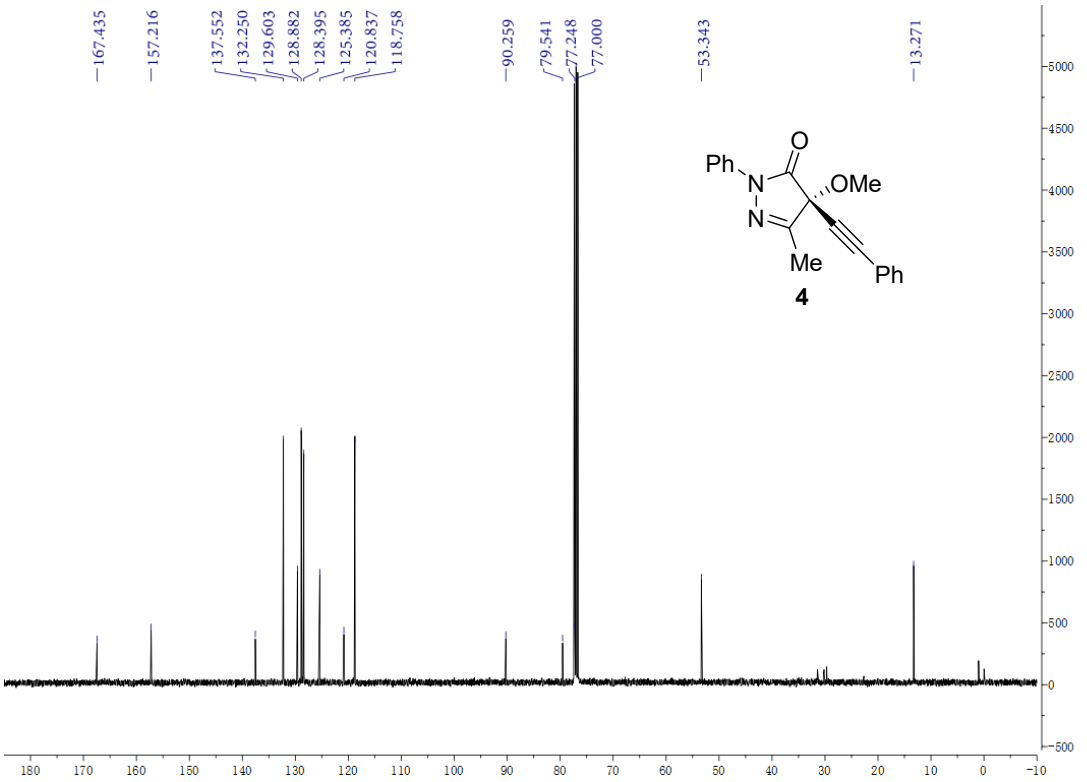
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O
OMe
Me
Ph
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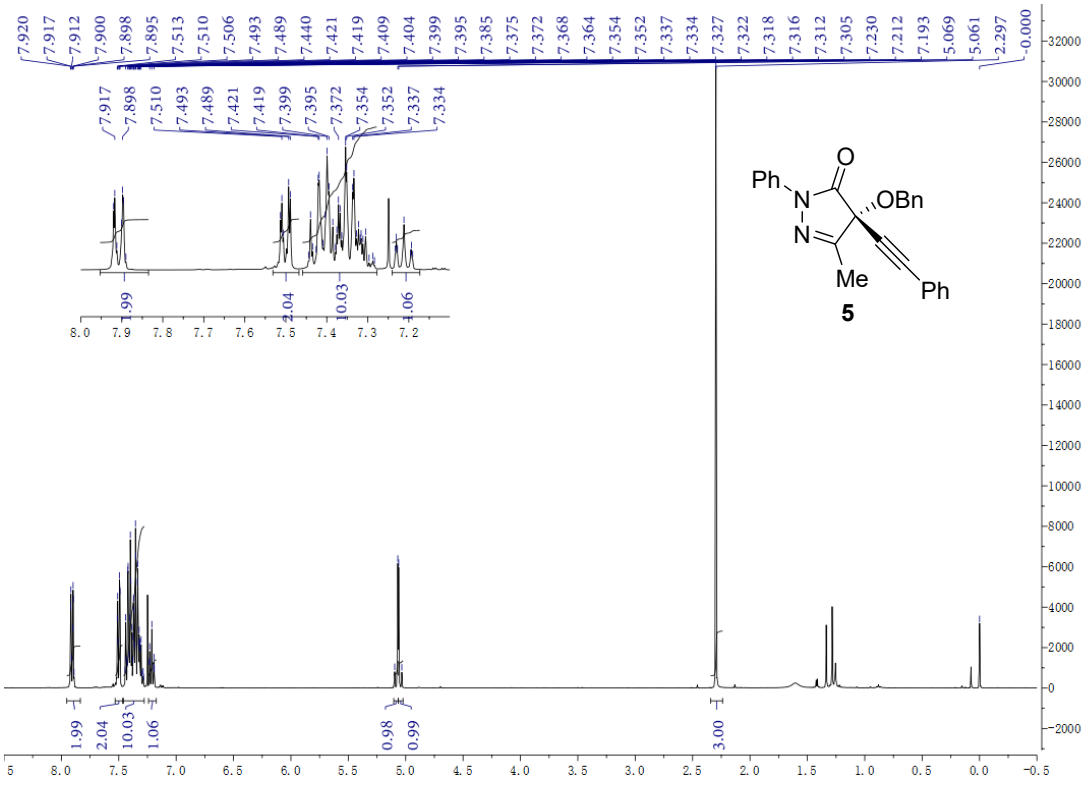
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OBn
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Ph
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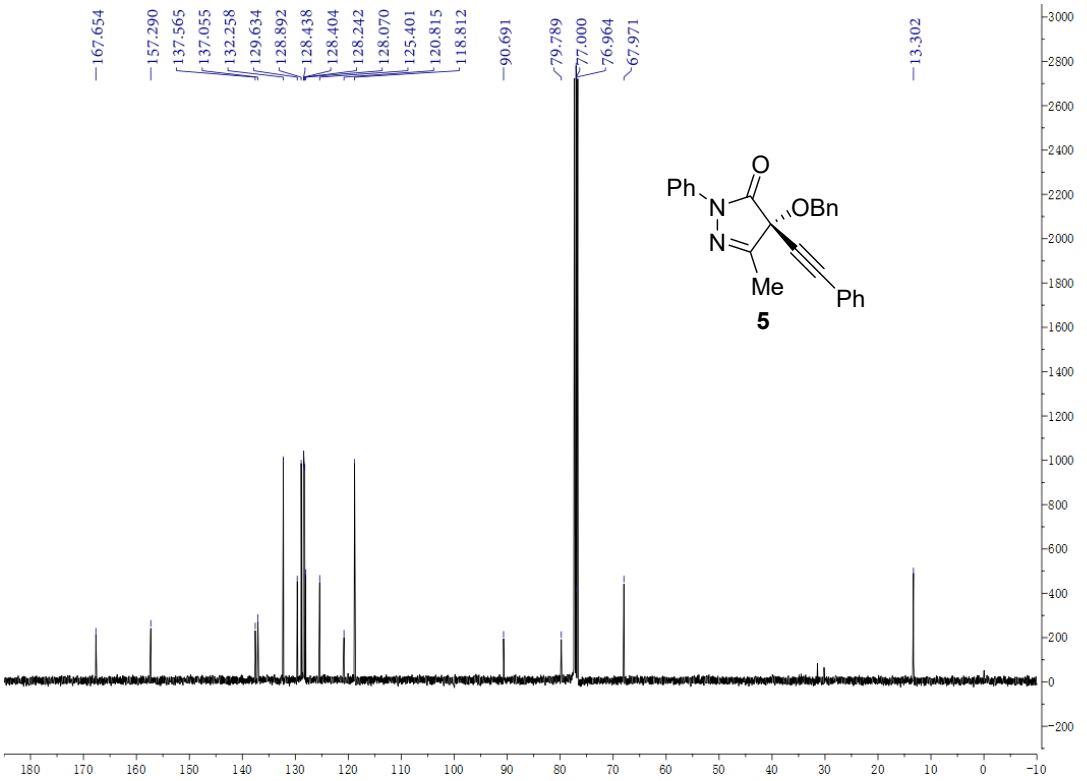
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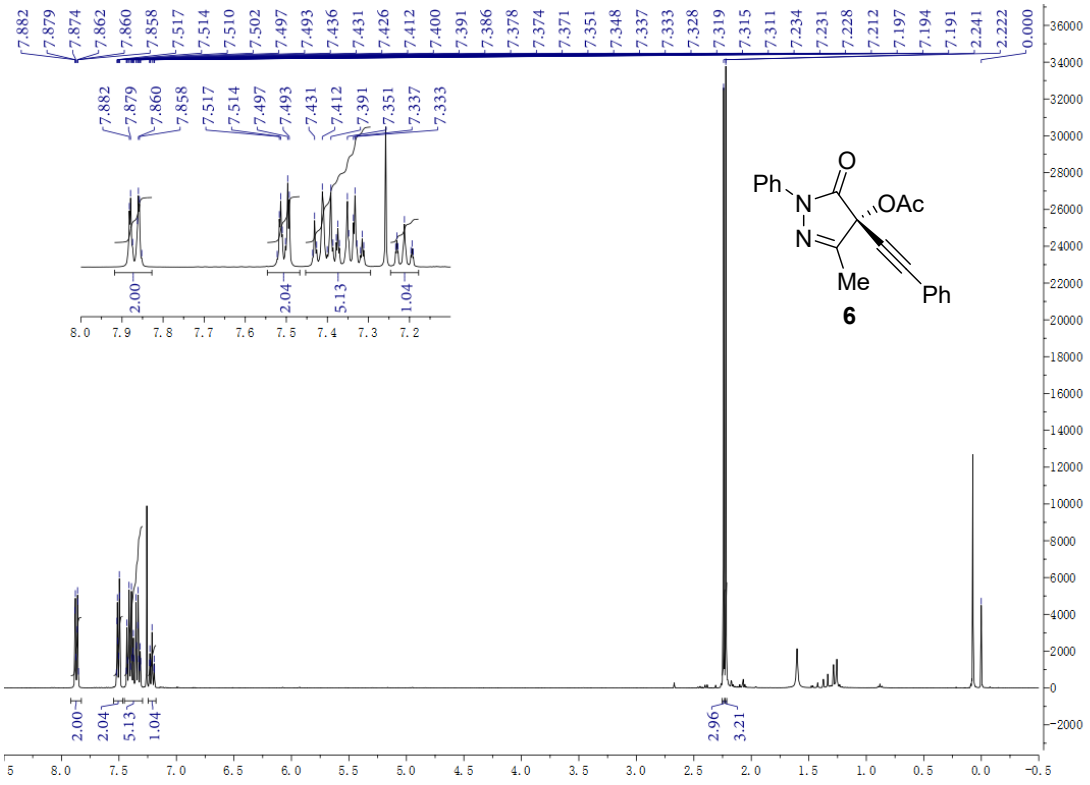
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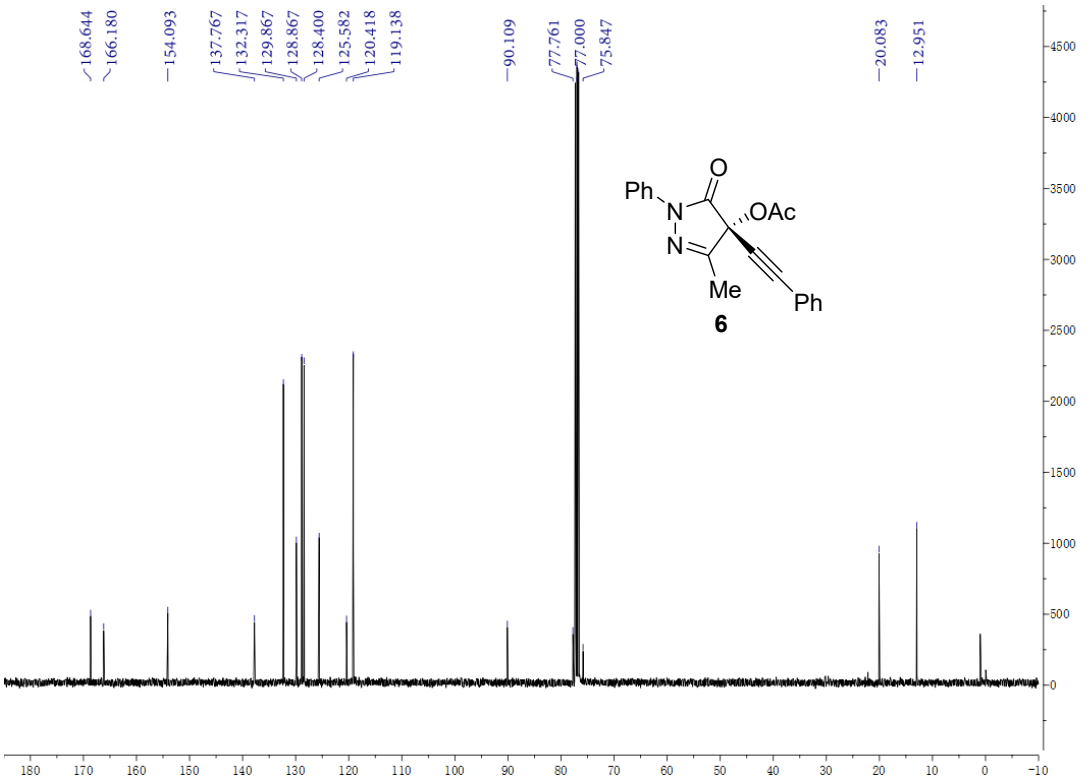
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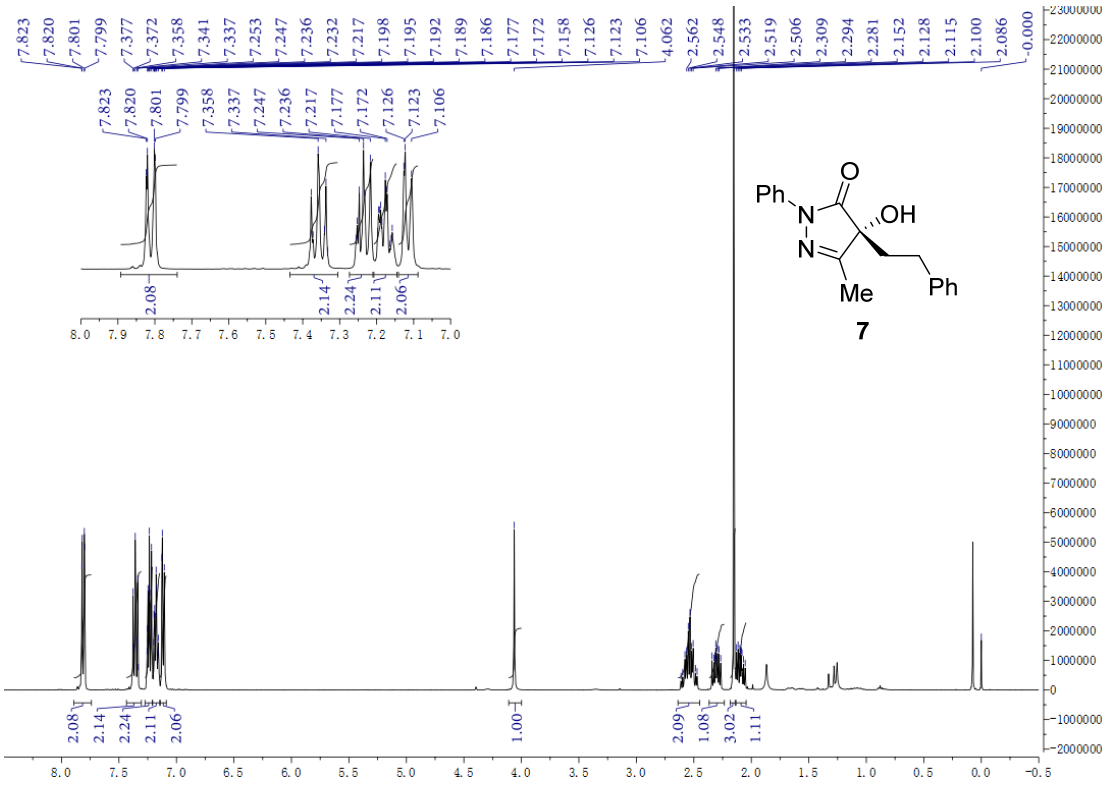
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Ph
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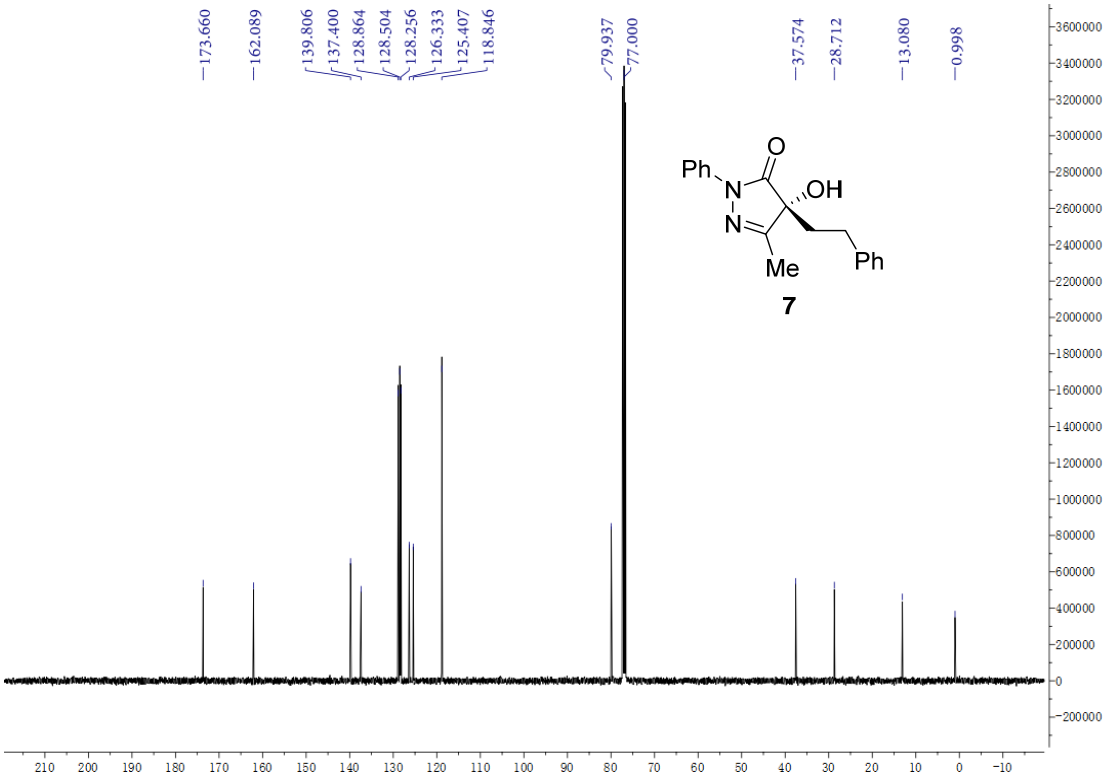
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Ph
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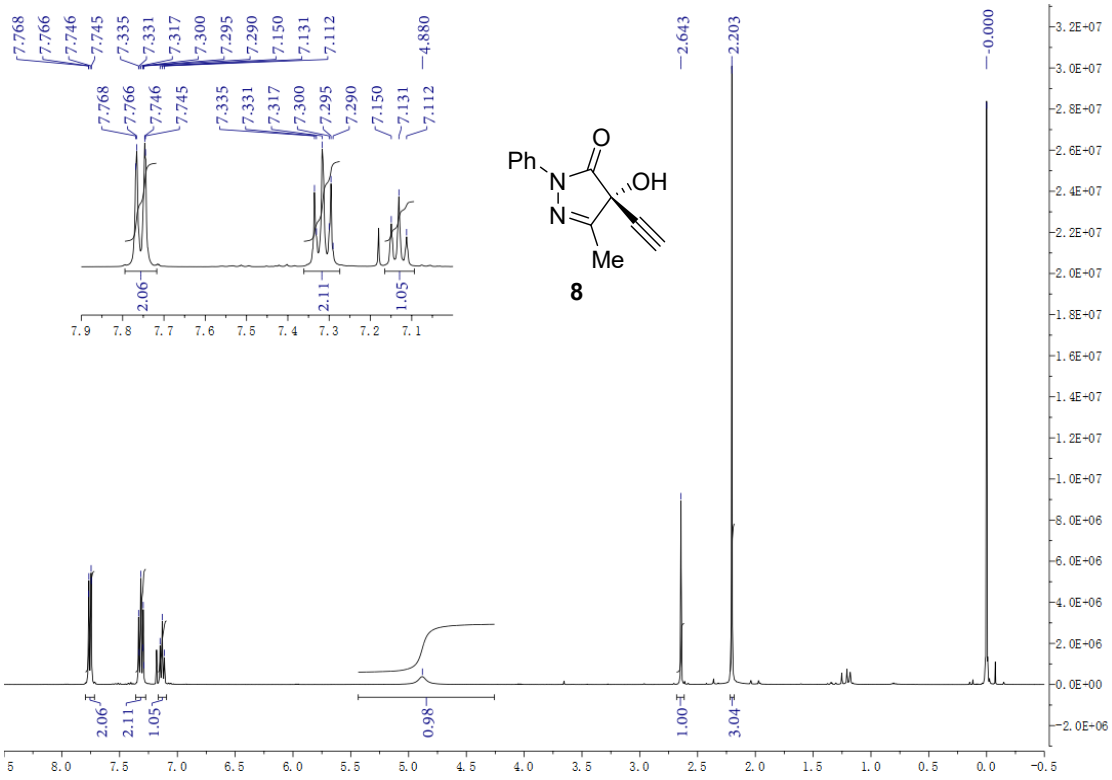
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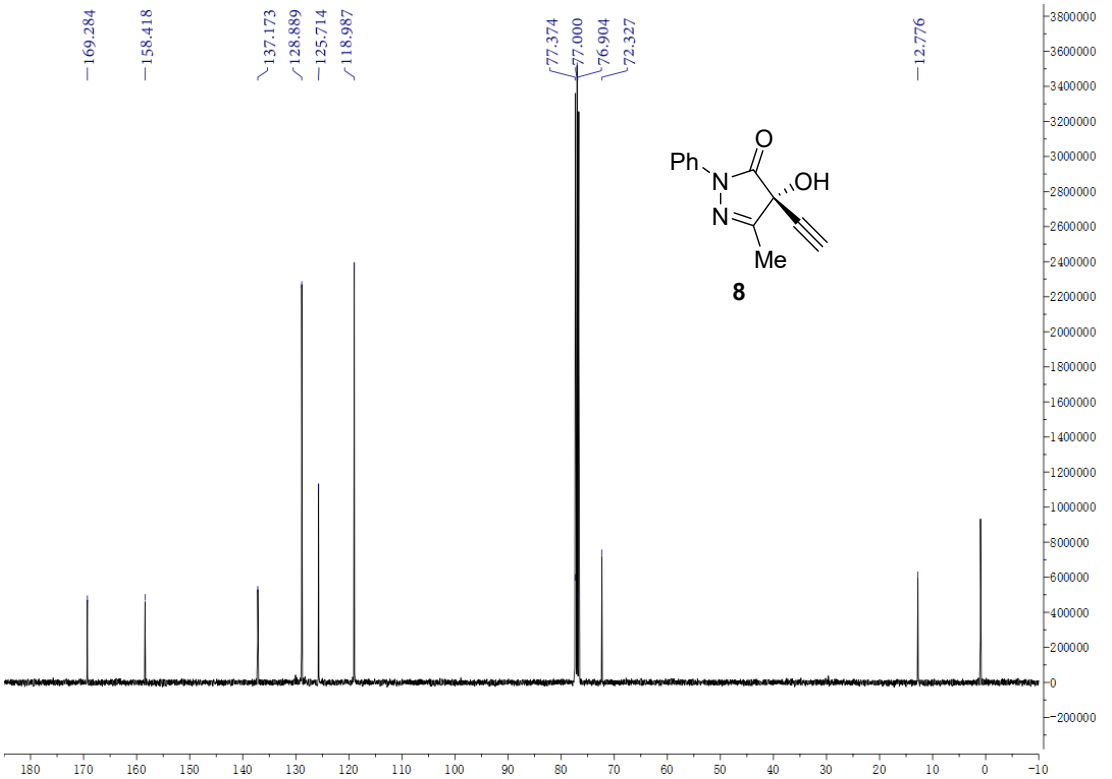
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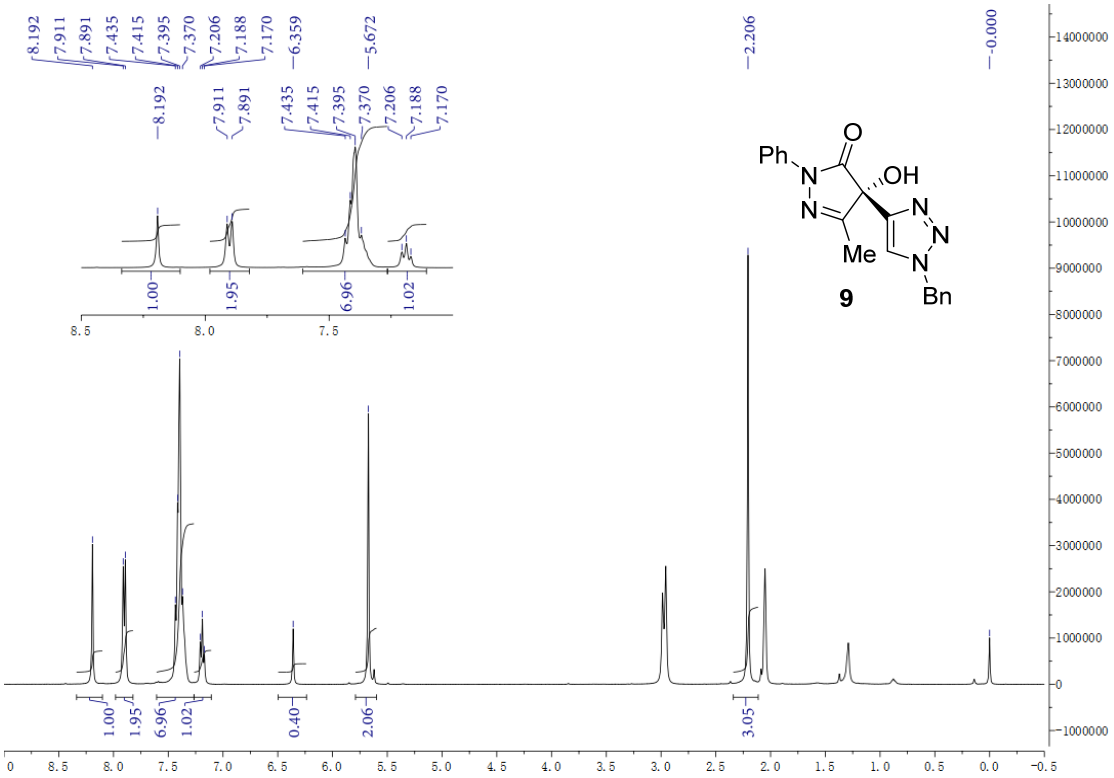
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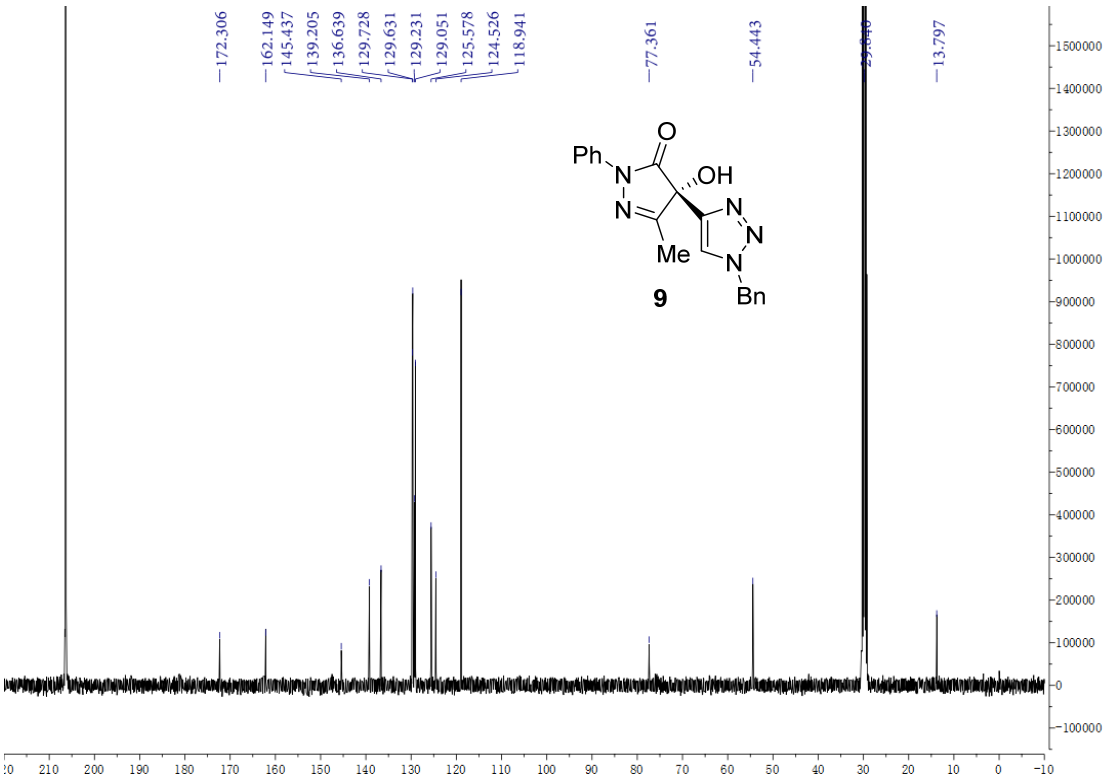
3.05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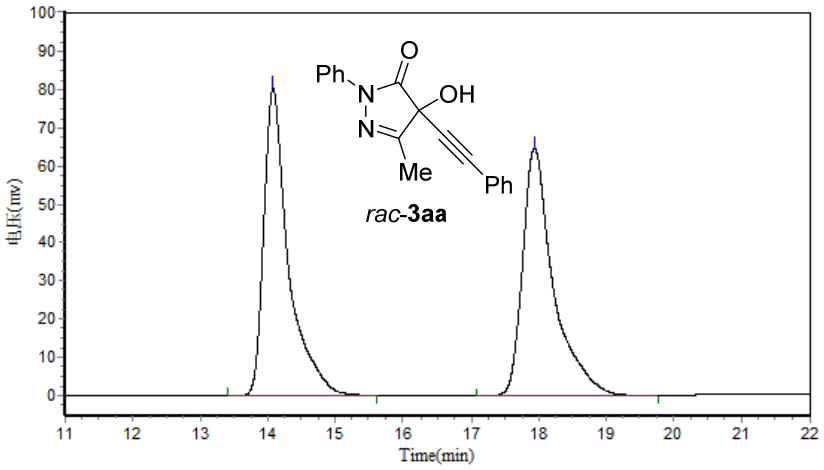
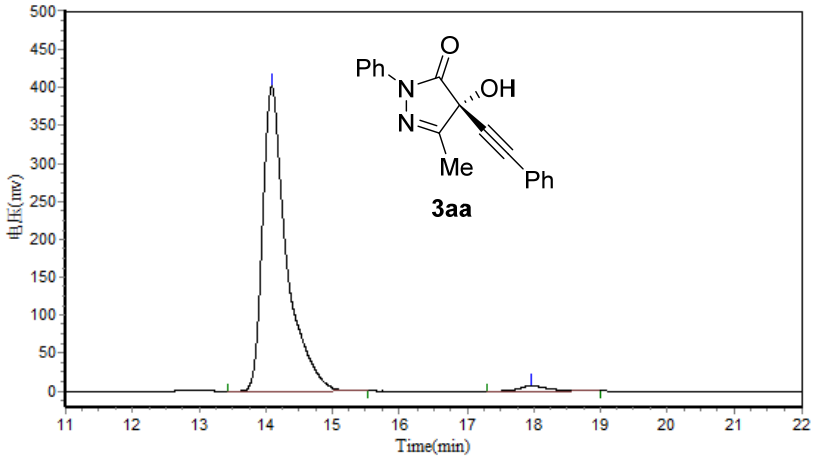
9

9. Copies of HPLC Chromatograms for Products 3-9



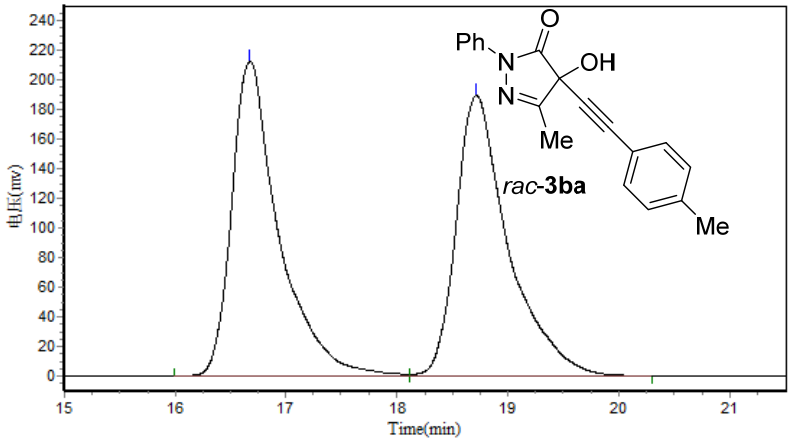
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.078	80333.672	2036151.375	50.0122
2		17.933	64547.094	2035161.500	49.9878
Total			144880.766	4071312.875	100.0000



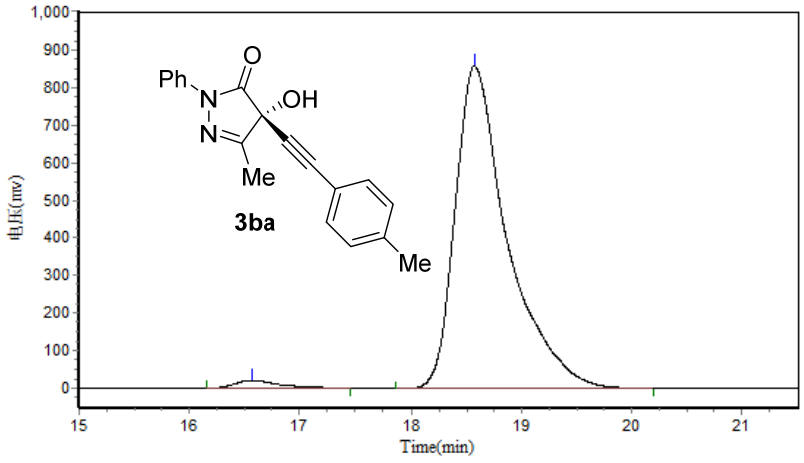
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.090	401604.531	9943041.000	98.0052
2		17.965	6665.117	202384.406	1.9948
Total			408269.648	10145425.406	100.0000



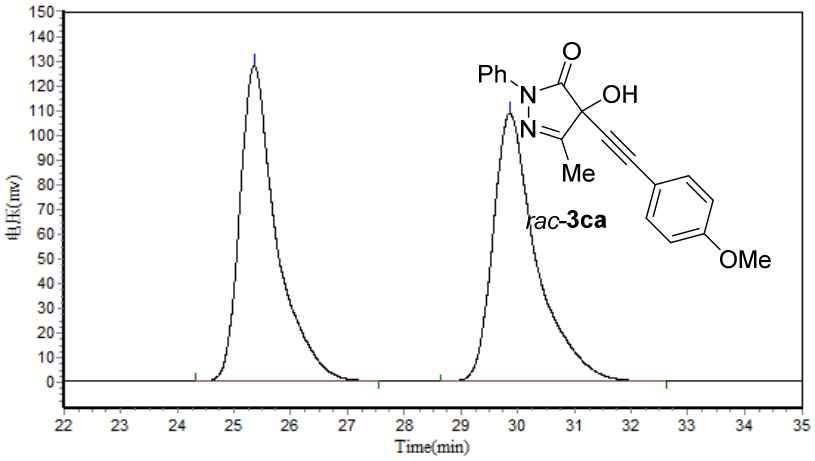
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.675	212759.672	6268517.000	50.2986
2		18.713	189560.141	6194083.000	49.7014
Total			402319.813	12462600.000	100.0000



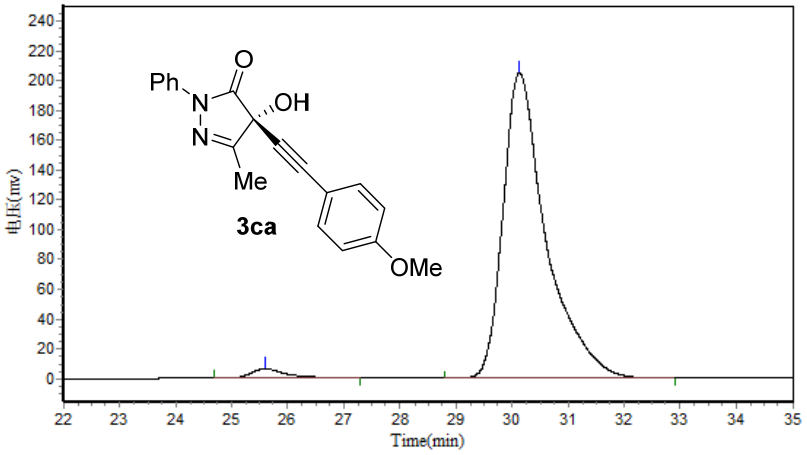
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.568	20992.684	575313.063	2.0077
2		18.573	855952.688	28080336.000	97.9923
Total			876945.371	28655649.063	100.0000



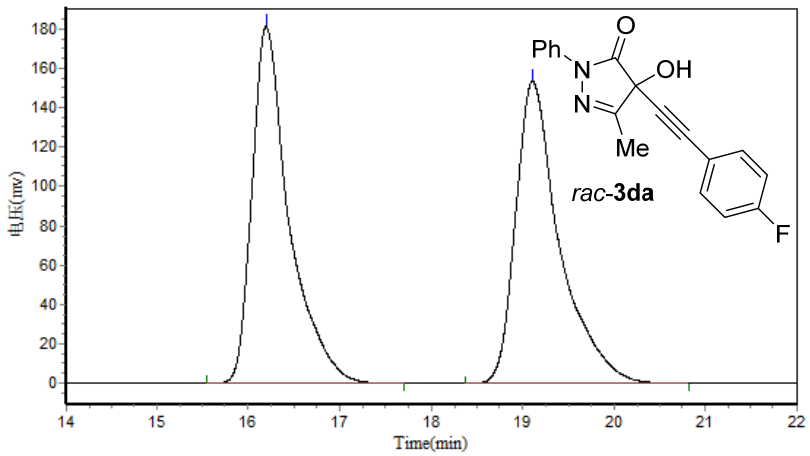
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.355	127504.250	5727900.500	49.9801
2		29.852	108384.883	5732450.500	50.0199
Total			235889.133	11460351.000	100.0000



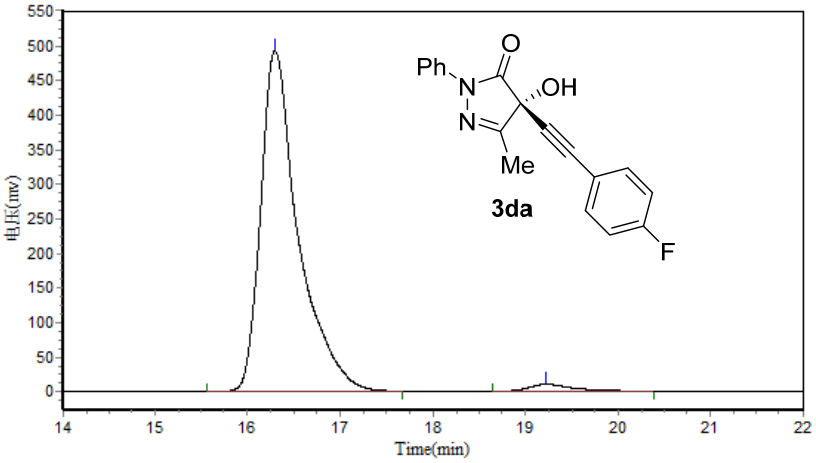
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.607	6412.614	287131.406	2.5645
2		30.130	204984.016	10909351.000	97.4355
Total			211396.629	11196482.406	100.0000



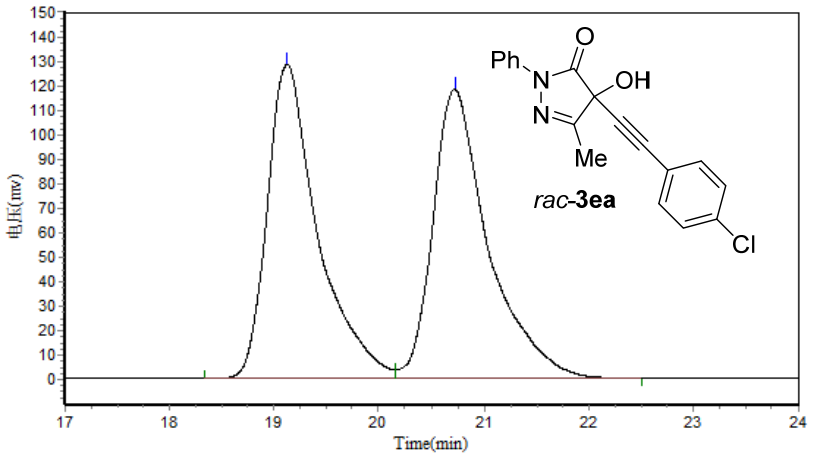
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.193	180725.906	5123718.000	49.9437
2		19.107	153093.406	5135260.000	50.0563
Total			333819.313	10258978.000	100.0000



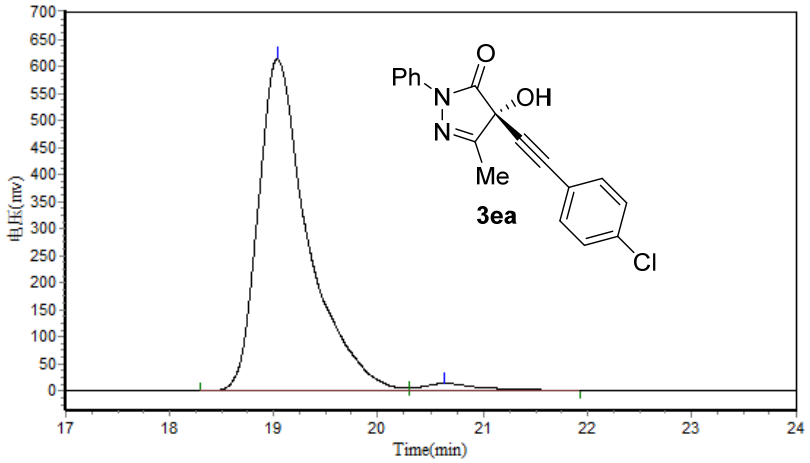
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.293	491569.219	13927364.000	97.7138
2		19.223	9865.667	325853.625	2.2862
Total			501434.886	14253217.625	100.0000



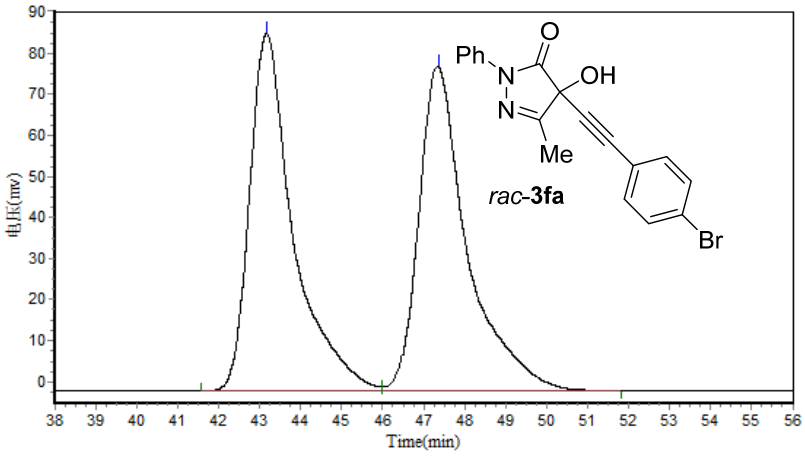
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.125	128292.023	4292167.000	49.7556
2		20.720	118075.992	4334337.500	50.2444
Total			246368.016	8626504.500	100.0000



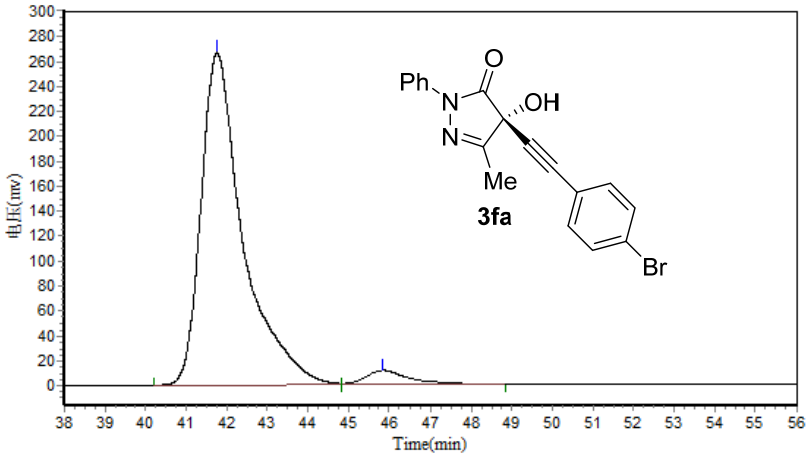
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.032	612447.938	20355826.000	97.6018
2		20.633	13109.904	500178.406	2.3982
Total			625557.842	20856004.406	100.0000



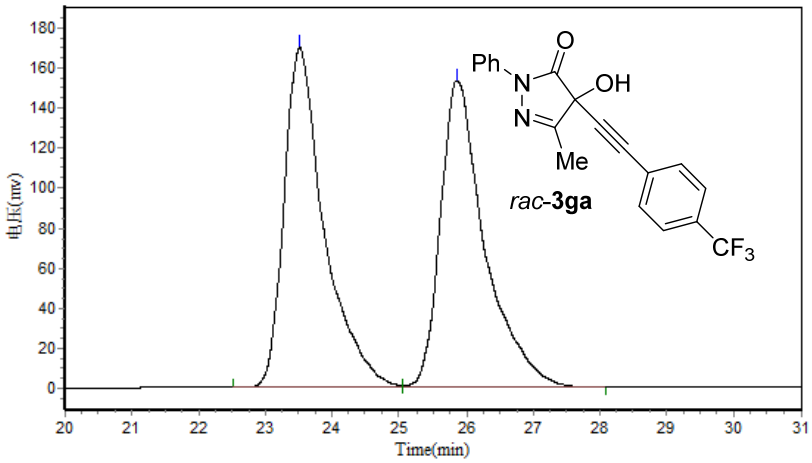
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		43.167	86832.922	6445017.000	49.9774
2		47.343	78931.242	6450857.500	50.0226
Total			165764.164	12895874.500	100.0000



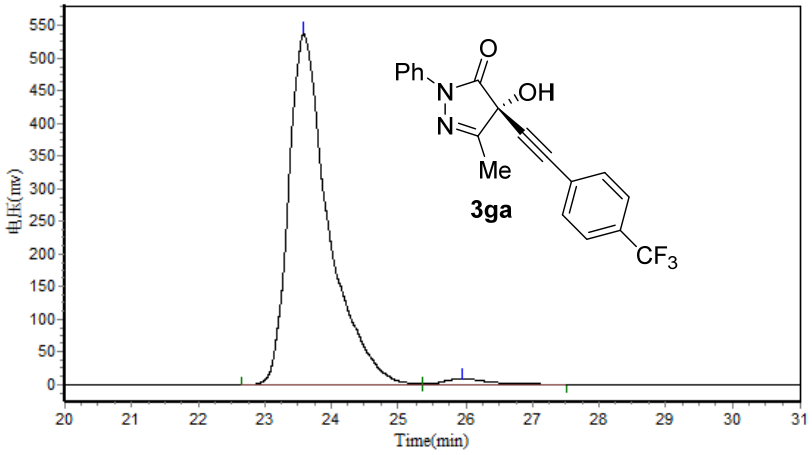
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		41.762	266498.469	19101374.000	95.4741
2		45.828	11535.145	905495.188	4.5259
Total			278033.613	20006869.188	100.0000



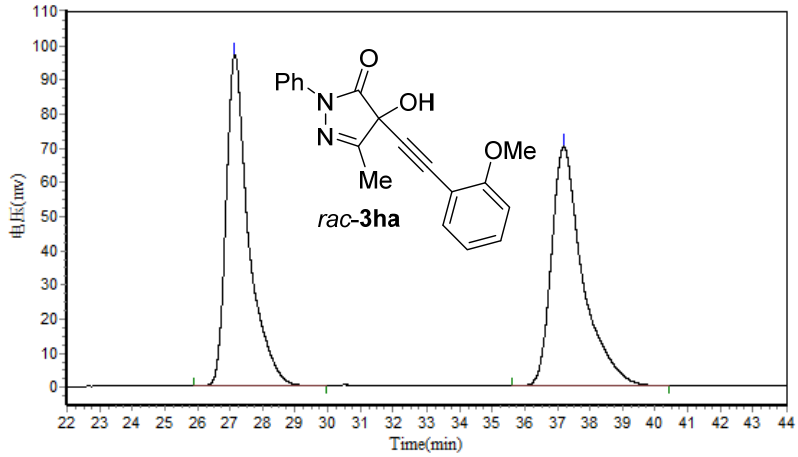
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.513	169165.547	7064934.000	50.1229
2		25.848	152324.922	7030289.000	49.8771
Total			321490.469	14095223.000	100.0000



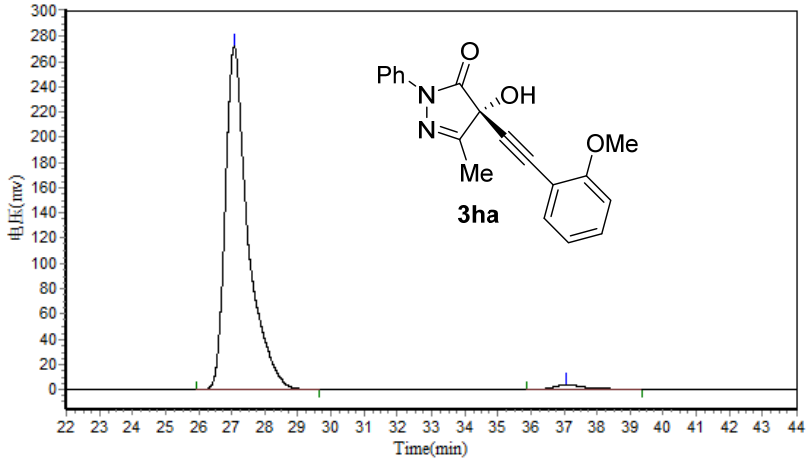
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.582	537400.250	22236196.000	98.1673
2		25.947	9128.371	415141.469	1.8327
Total			546528.621	22651337.469	100.0000



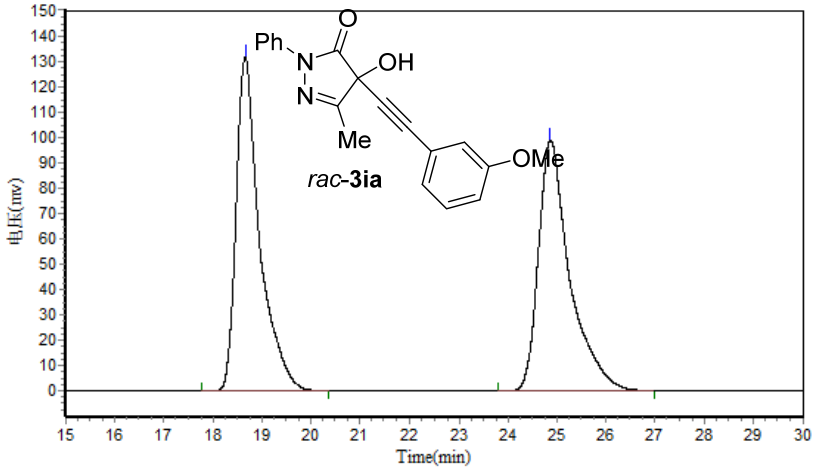
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.140	96749.922	4604043.500	49.8461
2		37.192	70040.461	4632473.500	50.1539
Total			166790.383	9236517.000	100.0000



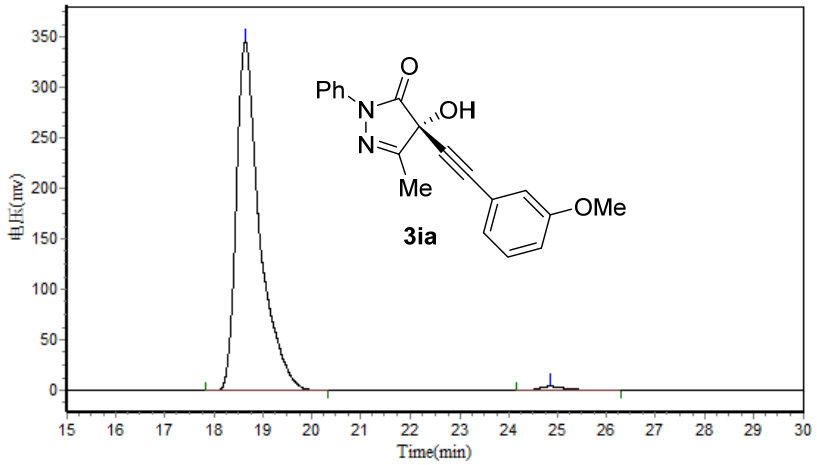
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.068	271770.563	12917063.000	98.1874
2		37.077	3651.862	238457.703	1.8126
Total			275422.425	13155520.703	100.0000



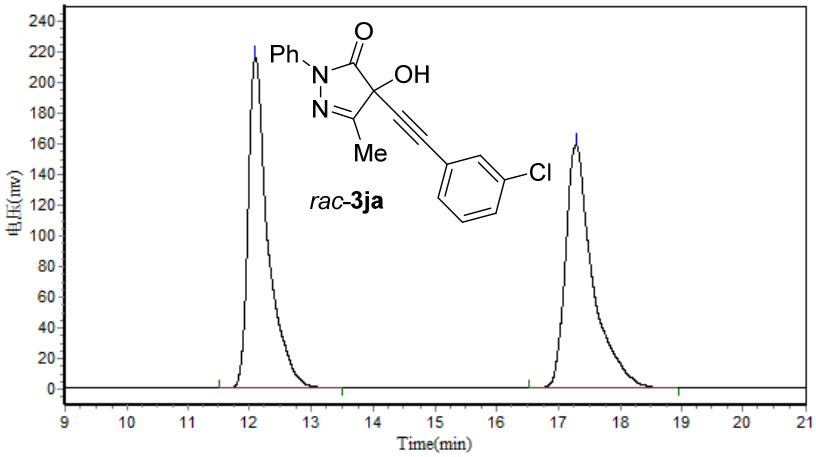
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.662	132020.734	4397318.000	50.0914
2		24.862	98910.953	4381263.000	49.9086
Total			230931.688	8778581.000	100.0000



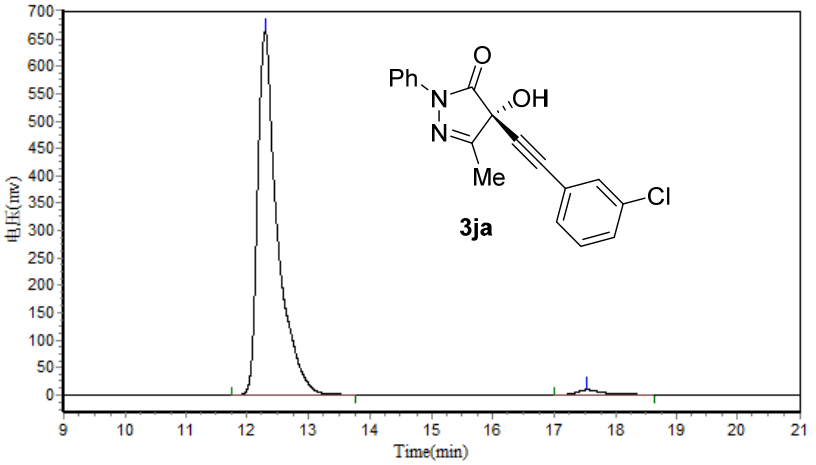
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.643	346333.375	11508675.000	98.4202
2		24.858	4288.868	184731.203	1.5798
Total			350622.243	11693406.203	100.0000



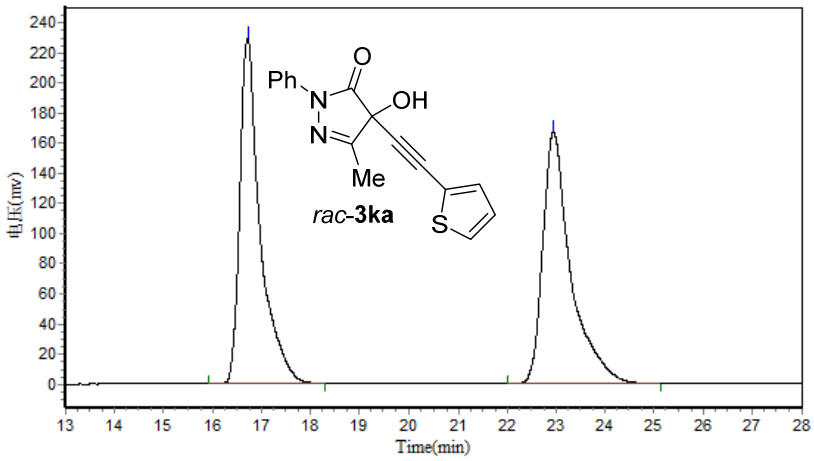
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.093	216218.016	4830387.000	49.8332
2		17.283	159014.281	4862720.500	50.1668
Total			375232.297	9693107.500	100.0000



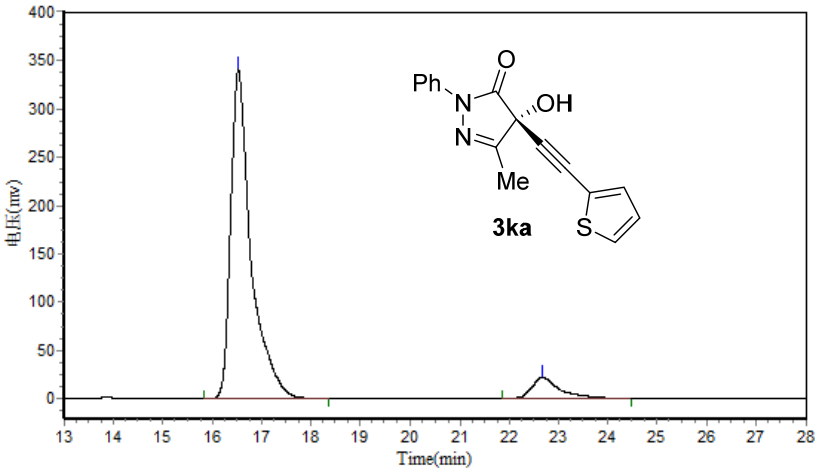
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.295	663953.438	14883798.000	98.2792
2		17.542	8762.340	260600.344	1.7208
Total			672715.777	15144398.344	100.0000



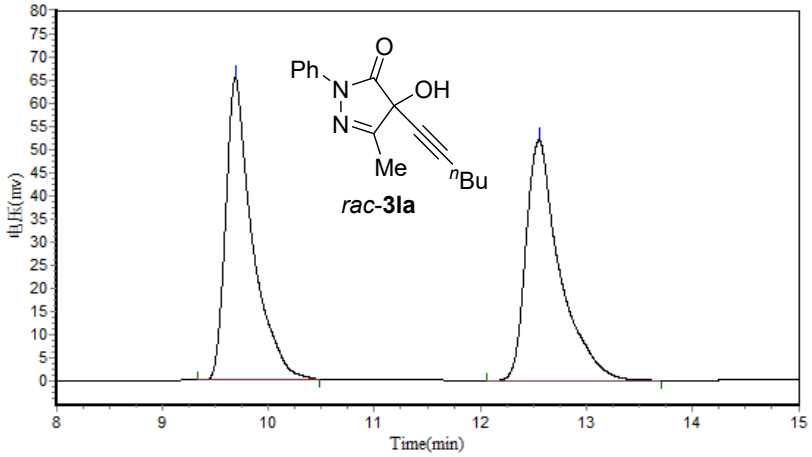
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.720	229177.875	6616649.500	50.0264
2		22.940	166637.672	6609654.500	49.9736
Total			395815.547	13226304.000	100.0000



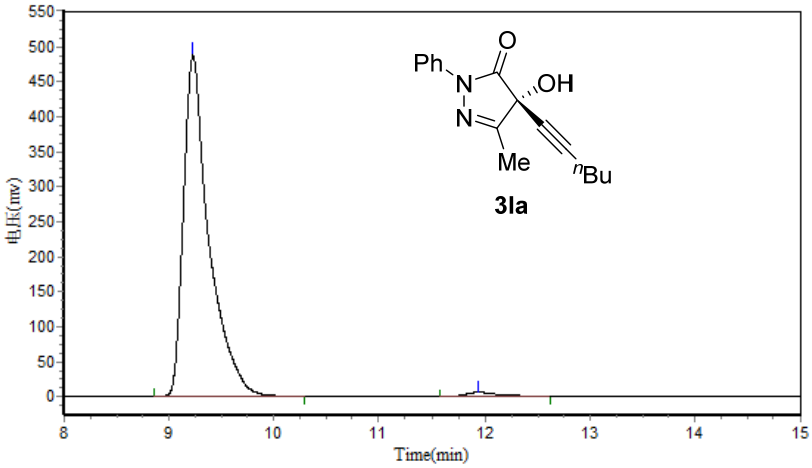
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.527	340691.500	9677251.000	92.1291
2		22.670	21282.416	826762.438	7.8709
Total			361973.916	10504013.438	100.0000



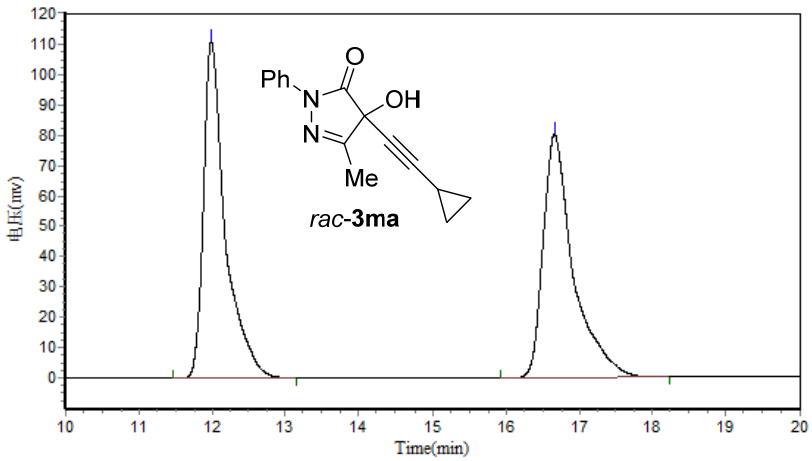
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.688	65365.449	1144350.875	49.8330
2		12.550	52013.387	1152021.375	50.1670
Total			117378.836	2296372.250	100.0000



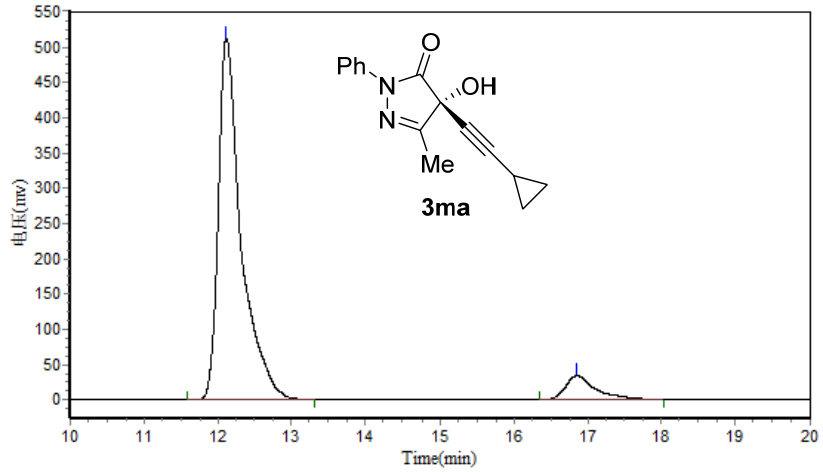
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.228	487155.594	8207610.500	98.5825
2		11.937	5758.765	118017.898	1.4175
Total			492914.359	8325628.398	100.0000



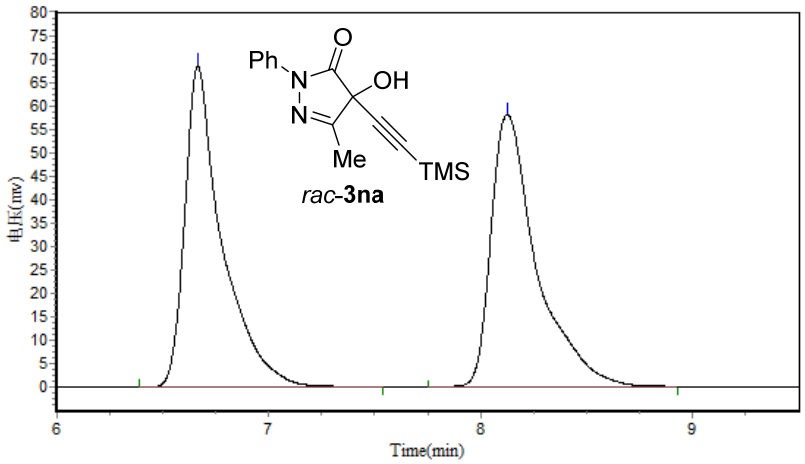
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.987	110870.695	2278578.250	49.8711
2		16.658	80295.133	2290355.000	50.1289
Total			191165.828	4568933.250	100.0000



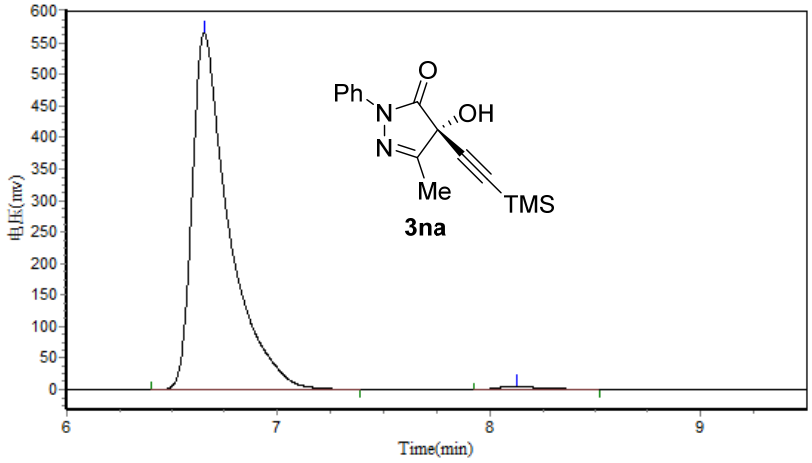
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.117	512524.719	10989708.000	91.9602
2		16.852	33530.004	960793.375	8.0398
Total			546054.723	11950501.375	100.0000



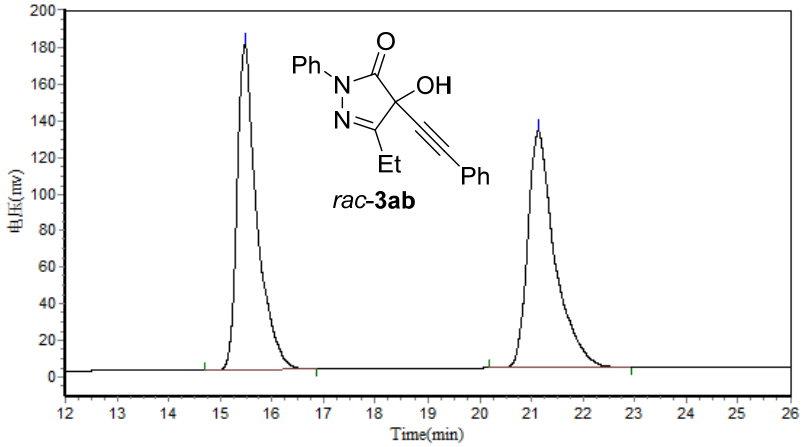
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.667	68631.039	840375.625	49.0365
2		8.123	58217.082	873400.000	50.9635
Total			126848.121	1713775.625	100.0000



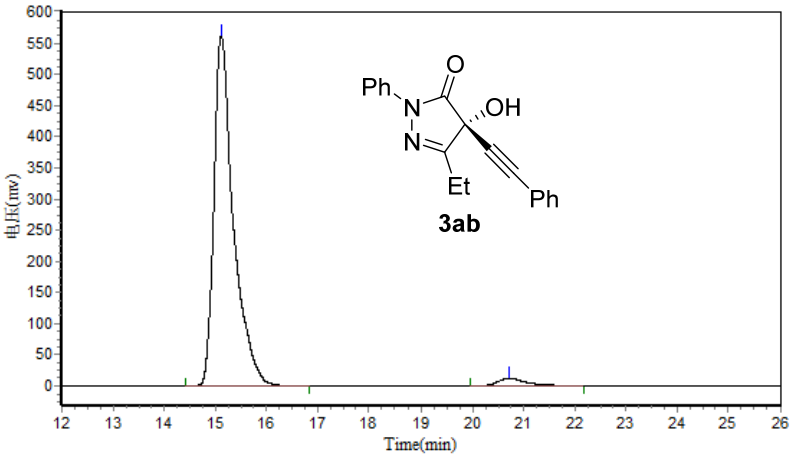
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.652	566147.000	6826869.000	98.9432
2		8.127	5466.911	72914.055	1.0568
Total			571613.911	6899783.055	100.0000



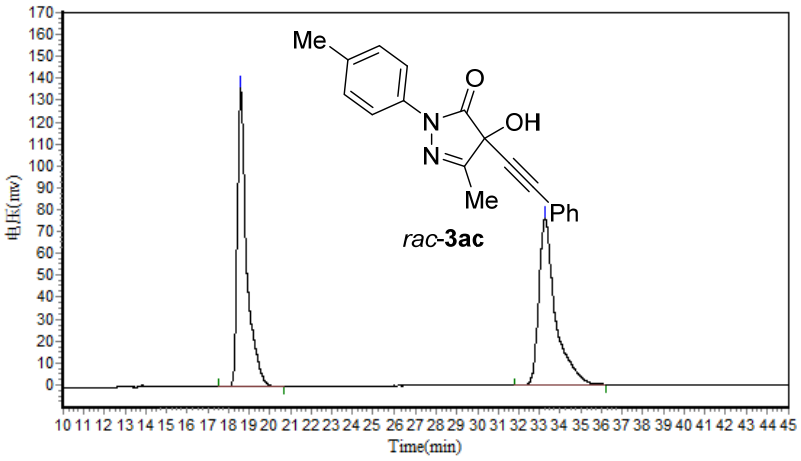
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.478	177150.875	4713900.500	50.0642
2		21.133	129358.367	4701802.500	49.9358
Total			306509.242	9415703.000	100.0000



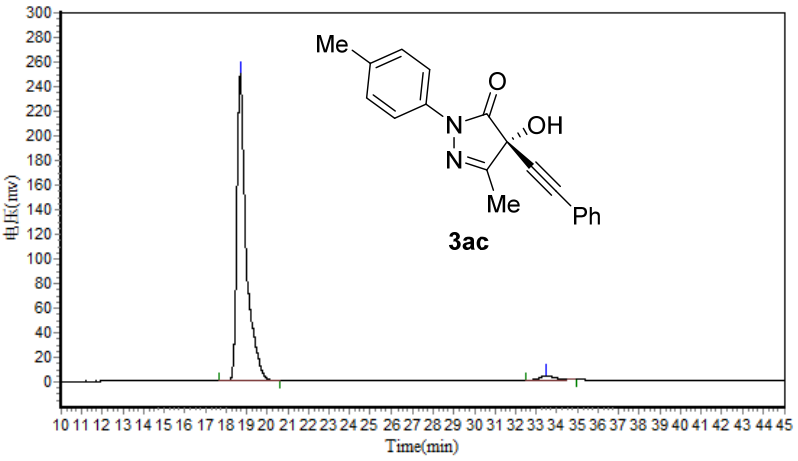
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.112	560992.563	14842653.000	97.1113
2		20.710	12211.498	441514.969	2.8887
Total			573204.061	15284167.969	100.0000



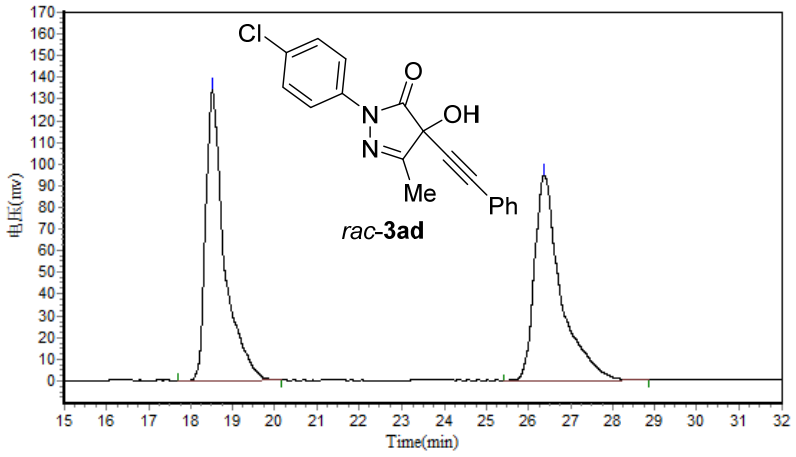
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.588	136101.172	4256654.500	50.2001
2		33.258	75976.523	4222711.500	49.7999
Total			212077.695	8479366.000	100.0000



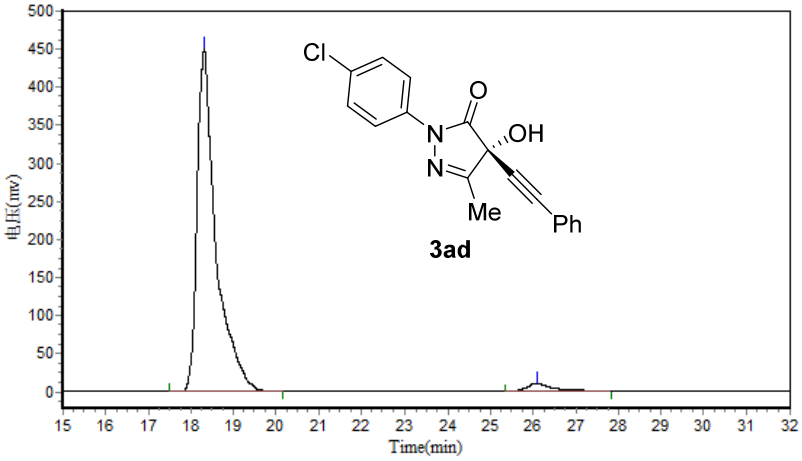
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.700	249991.547	7814573.000	97.9845
2		33.482	3237.434	160745.250	2.0155
Total			253228.981	7975318.250	100.0000



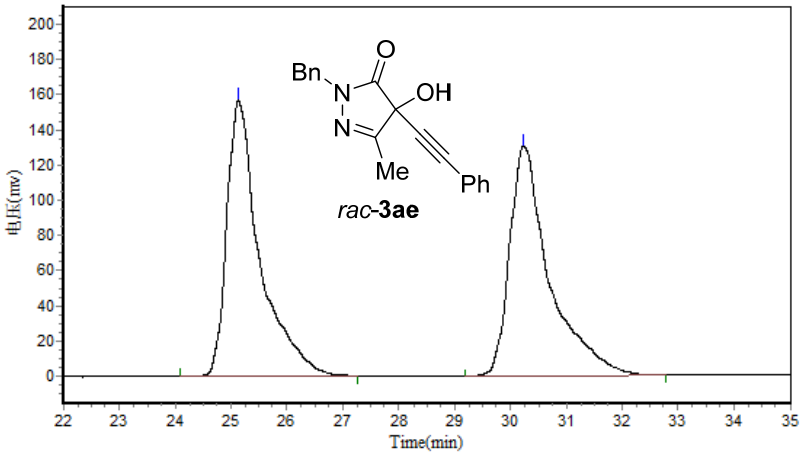
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.513	133772.313	4114594.750	50.0316
2		26.368	94425.438	4109397.500	49.9684
Total			228197.750	8223992.250	100.0000



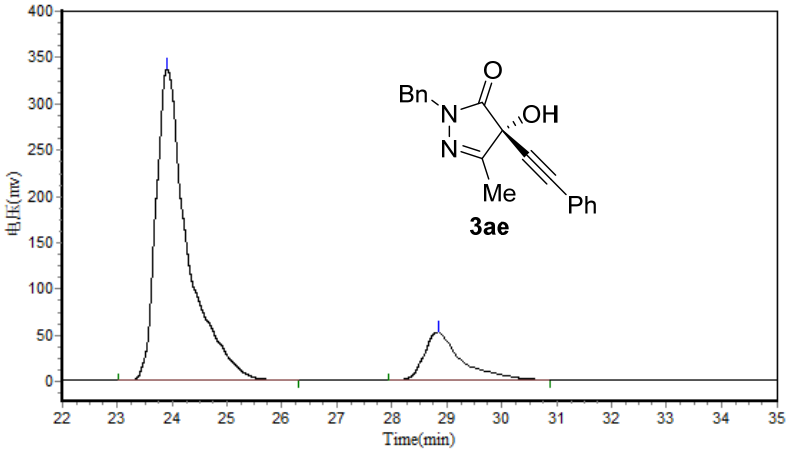
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.312	449928.844	13712996.000	97.0815
2		26.097	9619.534	412242.594	2.9185
Total			459548.378	14125238.594	100.0000



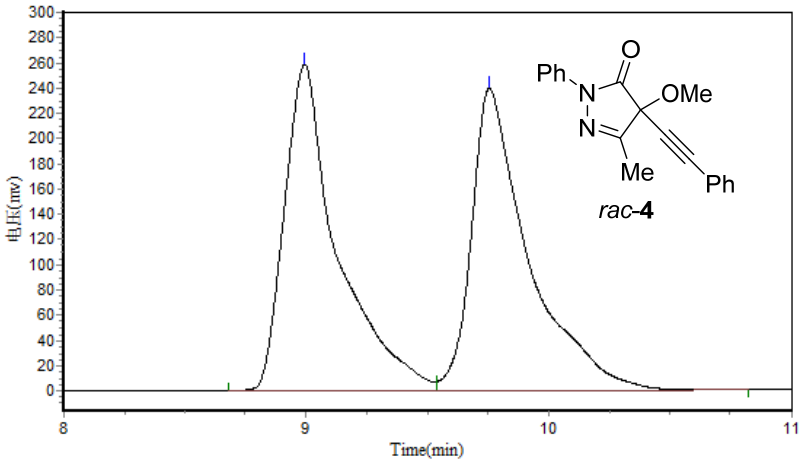
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.133	156978.219	6448222.000	50.0804
2		30.233	130521.094	6427507.500	49.9196
Total			287499.313	12875729.500	100.0000



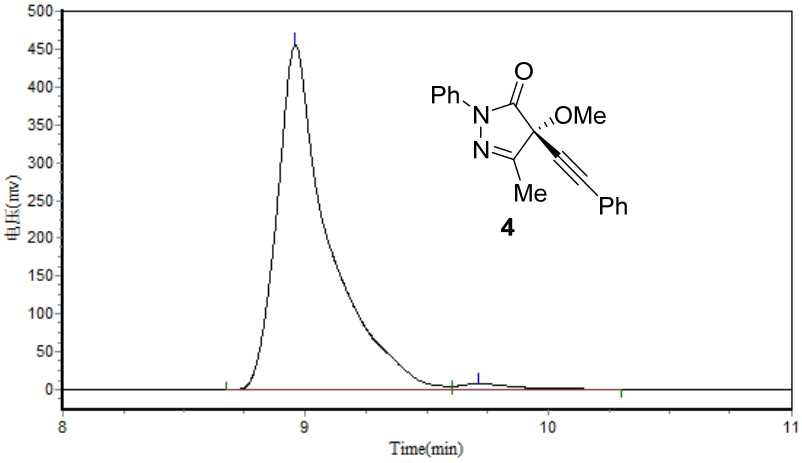
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.905	336091.406	13430984.000	84.4362
2		28.843	51988.586	2475672.750	15.5638
Total			388079.992	15906656.750	100.0000



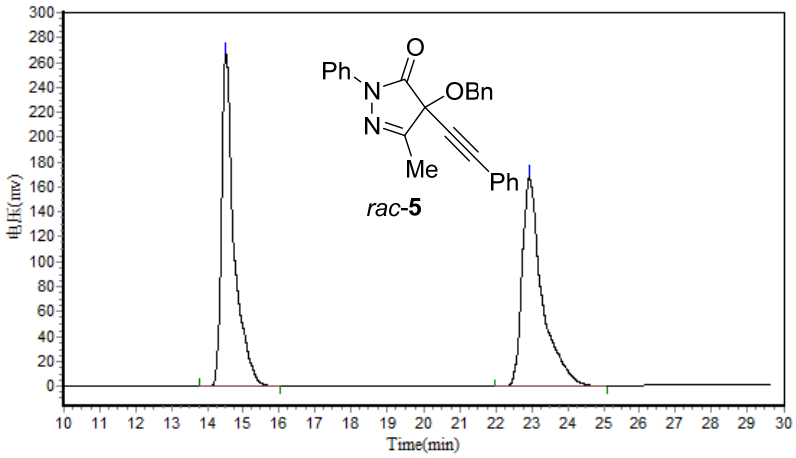
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.995	257919.828	3916434.250	50.1308
2		9.753	239182.922	3896001.500	49.8692
Total			497102.750	7812435.750	100.0000



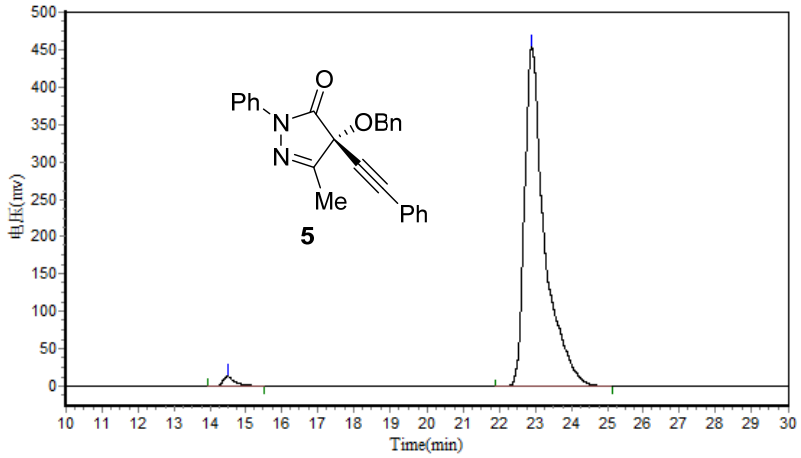
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.960	454657.938	6779685.000	98.2155
2		9.712	7762.086	123181.430	1.7845
Total			462420.023	6902866.430	100.0000



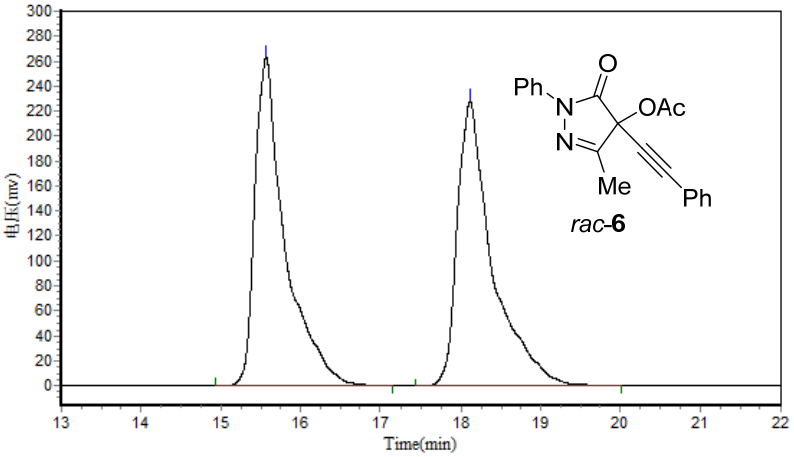
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.510	266364.438	6482047.500	50.0794
2		22.927	167465.906	6461500.000	49.9206
Total			433830.344	12943547.500	100.0000



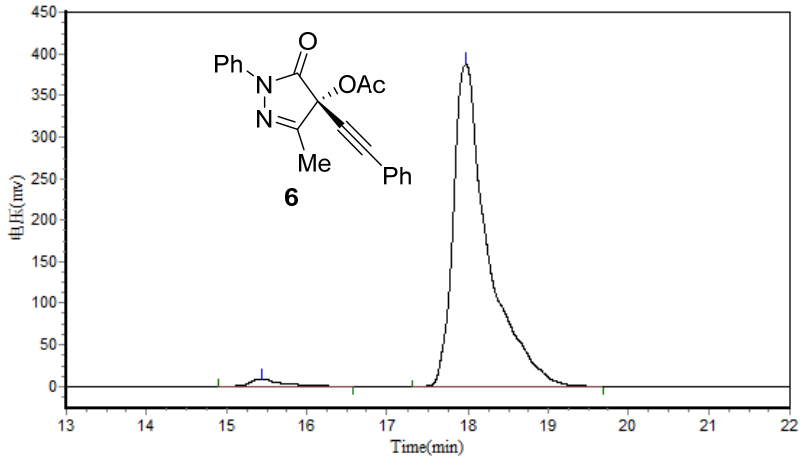
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.490	12718.264	302608.813	1.7038
2		22.897	452852.594	17458070.000	98.2962
Total			465570.857	17760678.813	100.0000



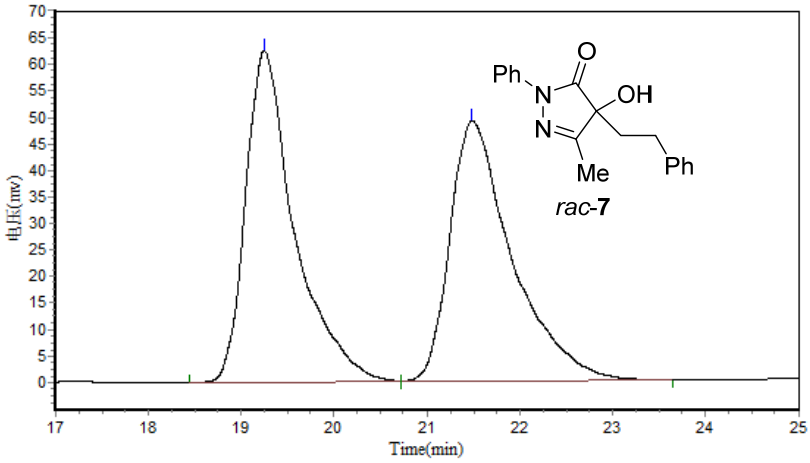
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.570	262924.156	6879550.500	49.9539
2		18.112	227673.906	6892240.000	50.0461
Total			490598.063	13771790.500	100.0000



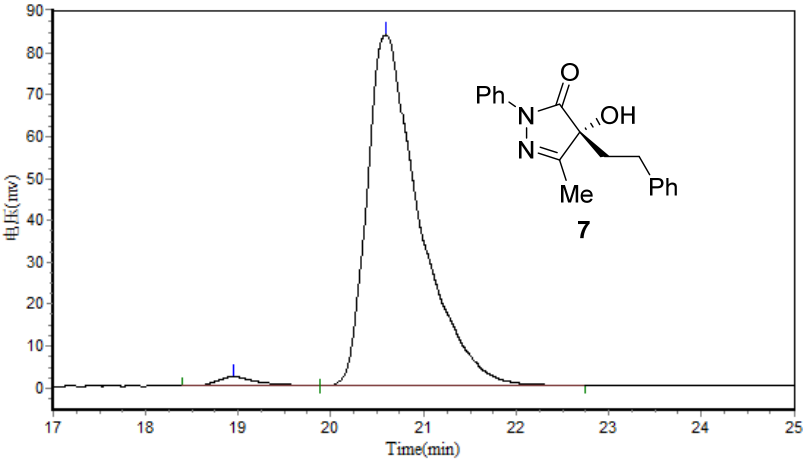
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.433	9036.122	235753.891	1.9923
2		17.975	386755.125	11597614.000	98.0077
Total			395791.247	11833367.891	100.0000



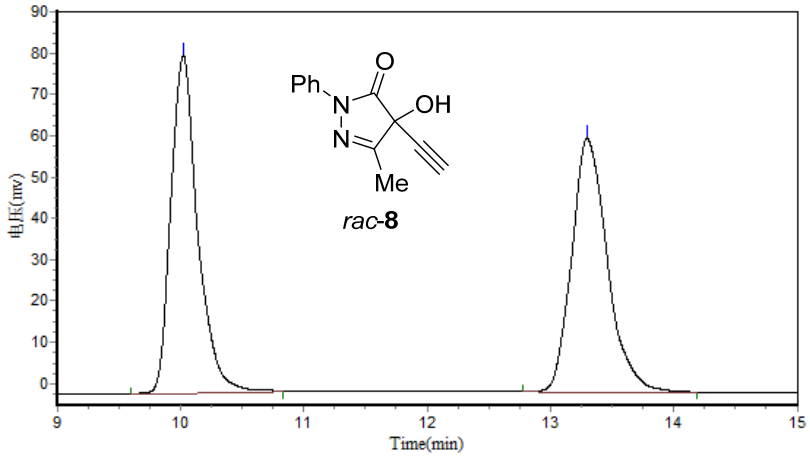
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.248	62428.730	2288758.000	50.1929
2		21.483	49030.859	2271169.250	49.8071
Total			111459.590	4559927.250	100.0000



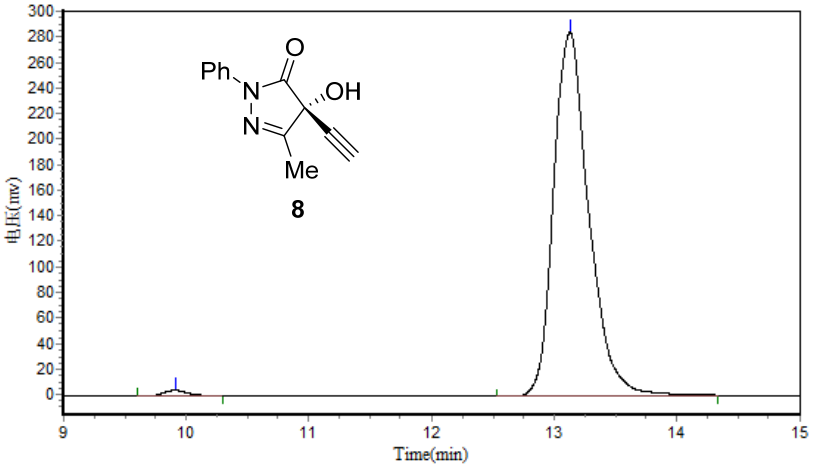
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.947	2187.551	68224.172	2.0529
2		20.603	83737.188	3255039.750	97.9471
Total			85924.739	3323263.922	100.0000



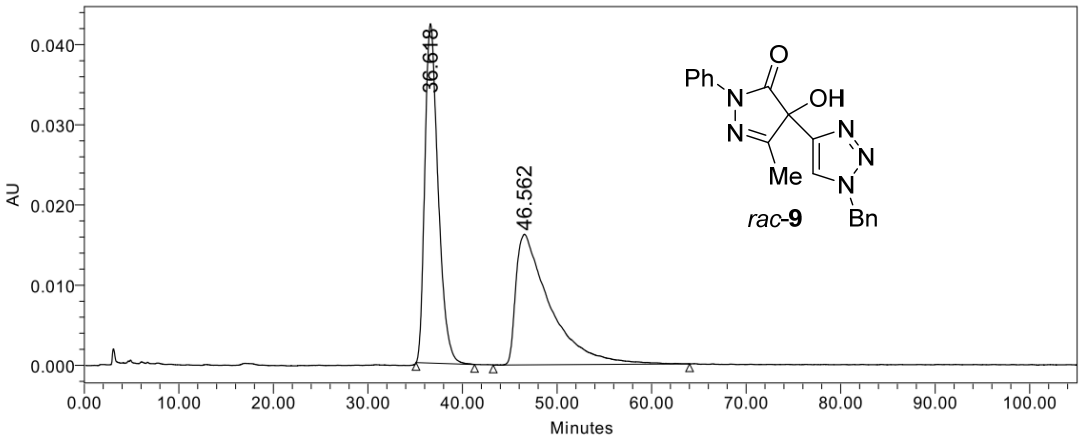
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.023	81580.195	1229105.875	49.8910
2		13.295	61503.141	1234474.875	50.1090
Total			143083.336	2463580.750	100.0000

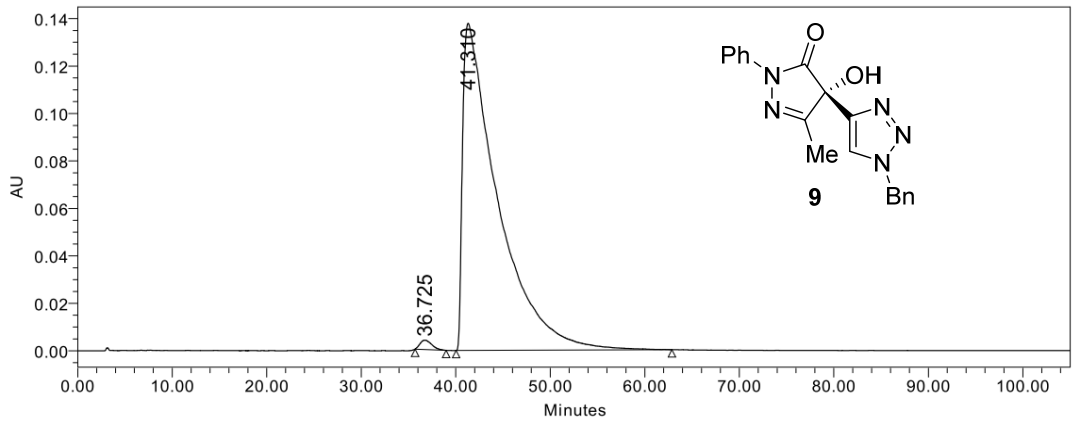


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.912	4441.852	64529.602	1.1229
2		13.128	284558.719	5681999.500	98.8771
Total			289000.571	5746529.102	100.0000



	RT	Area	% Area	Height
1	36.618	4140432	50.27	42324
2	46.562	4096122	49.73	16283



	RT	Area	% Area	Height
1	36.725	337873	0.94	3948
2	41.310	35526704	99.06	137826