Supporting Information

Multifunctionalization of Rh-carbynoids with Alcohol/carbamate and α-Propargylic-3-indolymethanol

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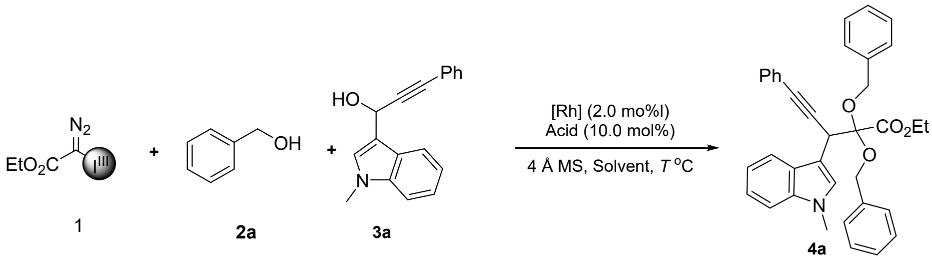
1.General Information

All reactions were carried out in oven-dried glassware. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 500/400 MHz spectrometer; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Enantioselectivity was determined on HPLC using Chiralpak IA, and OD-H column. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source) and (CI Source).

Anhydrous solvents, acids (including racemic phosphoric acid) and 4 Å molecular sieve were purchased from *Energy Chemical*. Chiral phosphoric acids were purchased from *Daicel*. Unless otherwise stated, all purchased reagents were used without further purification. 4 Å molecular sieve was dried in a Muffle furnace at 250 ℃ over 8 h. Hypervalent iodine reagent[1] and 3-indolymethanol[2] were prepared using the literature procedures.

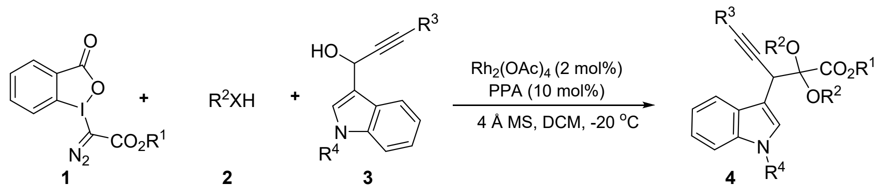
2. Experimental procedures

A: General procedure for optimization of conditions



The reactions were conducted on a 0.1 mmol scale: to a mixture of metal catalyst (2.0 mol %), acid catalyst (10.0 mol %), alcohol **2a** (0.40 mmol), α-propargylic-3-indolymethanol **3a** (0.1 mmol) and 4 Å MS (150 mg) in solvent (2.0 mL) was added diazo compound **1** (0.15 mmol) at indicated temperature, and the reaction was running for 2 h under these conditions. The solution was then concentrated in vacuum. And the residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/10) to give the product **4a**.

B: General procedure for the preparation of products 4



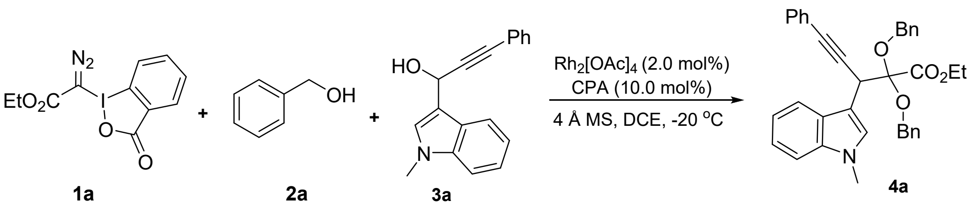
The reactions were conducted on a 0.1 mmol scale: to a solution of $Rh_2(OAc)_4$ (0.9 mg, 2.0 mol %), phosphoric acid (3.5 mg, 10.0 mol %), alcohol **2** (0.4 mmol), and 4 Å MS (150 mg) in DCM (1.0 mL) was added a solution of diazo compound **1** (0.15 mmol) and α-propargylic-3-indolymethanol **3** (0.1 mmol), in DCM (3.0 mL) via a syringe pump in 1 h under an argon atmosphere at indicate temperature. After completion of the addition, stirring was continued at indicate temperature for 0.5 h. The solution was concentrated in vacuum. And then the residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/10-1/6) to give the product **4**.

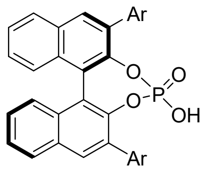
3. References

[1] a) Wang, Z.; Herraiz, A. G.; Del Hoyo, A. M.; Suero, M. G. Generating carbyne equivalents with photoredox catalysis. *Nature* **2018**, 554, 86; b) Weiss, R.; Seubert, J.; Hampel, F. D−Aryliodonio diazo compounds: SN reactions at the α-C atom as a novel reaction type for diazo compounds. *Angew. Chem. Int. Ed*. **1994**, 33, 1952.

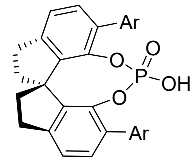
[2] a) Li, X.; Sun, J. *Angew. Chem. Int. Ed*. **2020**, 59, 17049-17054; b)Yue, C.; Na, F.; Fang, X.; Cao, Y.; Antilla, J. *Angew. Chem. Int. Ed*. **2018**, 57,11004-11008.

4. Preliminary Results of Optimizing Asymmetric Reaction Conditions





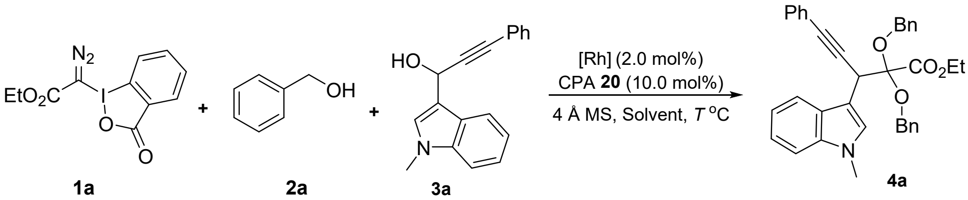
CPA 1: Ar = 2,4,6-(^{i}Pr)$_3$C$_6$H$_2$
CPA 2: Ar = 2,4,6-(Me)$_3$C$_6$H$_2$
CPA 3: Ar = 2,4,6-(cy)$_3$C$_6$H$_2$
CPA 4: Ar = 9-Phenanthryl
CPA 5: Ar = 9-anthryl
CPA 6: Ar = 1-pyreyl
CPA 7: Ar = 1-naphthyl
CPA 8: Ar = 2-naphthyl
CPA 9: Ar = Si(Ph)$_3$
CPA 10: Ar = 3,5-(Me)$_2$PC$_6$H$_3$
CPA 11: Ar = 3,5-(tBu)$_2$C$_6$H$_3$
CPA 12: Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$
CPA 13: Ar = 4-tBuPhC$_6$H$_4$
CPA 14: Ar = 4-CF$_3$PhC$_6$H$_4$
CPA 15: Ar = 4-OMePhC$_6$H$_4$



CPA 16: Ar = 2,4,6-(^{i}Pr)$_3$C$_6$H$_2$
CPA 17: Ar = 2,4,6-(Me)$_3$C$_6$H$_2$
CPA 18: Ar = 9-Phenanthryl
CPA 19: Ar = 9-anthryl
CPA 20: Ar = 1-pyreyl
CPA 21: Ar = Si(Ph)$_3$
CPA 22: Ar = 3,5-(Me)$_2$PC$_6$H$_3$
CPA 23: Ar = 3,5-(tBu)$_2$C$_6$H$_3$
CPA 24: Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$
CPA 25: Ar = 4-^{t}BuPhC$_6$H$_4$
CPA 26: Ar = 4-CF$_3$PhC$_6$H$_4$

Entry[a]	CPA	Yield (%)[b]	Ee (%)[c]
1	CPA 1	41	8
2	CPA 2	45	0
3	CPA 3	40	20
4	CPA 4	47	20
5	CPA 5	45	2
6	CPA 6	42	20
7	CPA 7	40	0
8	CPA 8	45	0
9	CPA 9	41	8
10	CPA 10	46	0
11	CPA 11	43	8
12	CPA 12	46	8
13	CPA 13	43	0
14	CPA 14	40	4
15	CPA 15	45	0
16	CPA 16	42	0
17	CPA 17	46	6
18	CPA 18	44	22
19	CPA 19	40	8
20	CPA 20	43	54
21	CPA 21	41	0
22	CPA 22	45	8
23	CPA 23	45	8
24	CPA 24	41	0
25	CPA 25	46	0
26	CPA 26	45	0

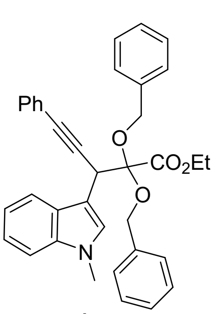
aThe reactions were conducted on a 0.1 mmol scale: to a solution of $Rh_2(OAc)_4$ (2.0 mol%), chiral phosphoric acid (10 mol%), **2a** (0.40 mmol), and 4 Å MS (150 mg) in DCE (1.0 mL) was added a solution of **1a** (0.15 mmol) and **3a** (0.1 mmol), in DCE (3.0 mL) via a syringe pump in 1 h under an argon atmosphere at -20 ^{o}C, and the reaction was running for 0.5 h under these conditions. bIsolated yield. cenantiomeric excess were determined by chiral high performance liquid chromatography (HPLC) analysis.



Entry[a]	Rh	Solvent	T/°C	Yield (%)[b]	Ee (%)[c]
1	$Rh_2(OAc)_4$	DCM	-20	55	54
2	$Rh_2(OAc)_4$	EA	-20	NR	--
3	$Rh_2(OAc)_4$	THF	-20	NR	--
4	$Rh_2(OAc)_4$	DCM	0	52	54
5	$Rh_2(OAc)_4$	DCM	25	40	54
6	$Rh_2(OAc)_4$	DCM	-30	32	53
7	$Rh_2(Oct)_4$	DCM	-20	52	54
8	$Rh_2(esp)_2$	DCM	-20	45	54

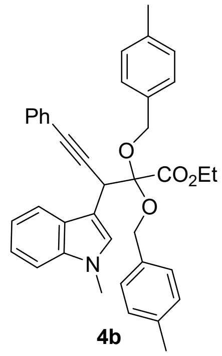
aThe reactions were conducted on a 0.1 mmol scale: to a solution of [Rh] (2.0 mol%), chiral phosphoric acid **20** (10 mol%), **2a** (0.40 mmol), and 4 Å MS (150 mg) in solvent (1.0 mL) was added a solution of **1a** (0.15 mmol) and **3a** (0.1 mmol), in same solvent (3.0 mL) via a syringe pump in 1 h under an argon atmosphere at indicated temperature, and the reaction was running for 0.5 h under these conditions. bIsolated yield. cenantiomeric excess were determined by chiral high performance liquid chromatography (HPLC) analysis.

5. NMR, HRMS(ESI) Data for Compounds 4, 5a, 6a



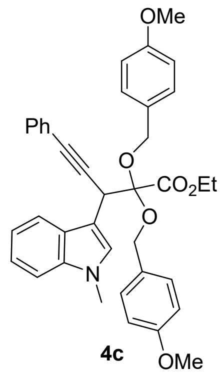
4a

ethyl 2,2-bis(benzyloxy)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4a**). Yellow oil, 44.5 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (t, *J* = 7.1 Hz, 3H), 3.70 (s, 3H), 3.93-4.07 (m, 2H),4.76-4.86 (m, 2H), 4.94 (d, *J* = 11.9 Hz, 1H), 5.09 (d, *J* = 10.1 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.18-7.21 (m, 2H), 7.25-7.35 (m, 12H), 7.42-7.45 (m, 4H), 7.85 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.74, 138.03, 137.90, 136.68, 131.51, 128.91, 128.23, 128.15, 128.14, 127.79, 127.38, 127.36, 127.33, 127.25, 123.71, 121.49, 120.13, 118.99, 109.05, 108.62, 102.84, 88.03, 83.96, 66.12, 65.58, 61.48, 37.22, 32.76, 13.80. HRMS (TOF MS ESI^{+}) calculated for $C_{36}H_{33}NO_4Na$ $[M+Na]^{+}$: 566.2302, Found: 566.2302.



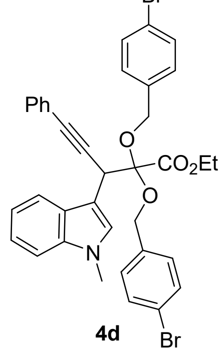
4b

ethyl 3-(1-methyl-1H-indol-3-yl)-2,2-bis((4-methylbenzyl)oxy)-5-phenylpent-4-ynoate (**4b**). Yellow oil, 47.5 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, *J* = 7.1 Hz, 3H), 2.32 (s, 6H), 3.70 (s, 3H), 3.89-4.03 (m, 2H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.86 (d, J = 11.6 Hz, 1H), 5.02 (d, *J* = 10.5 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 4H), 7.16-7.23 (m, 5H), 7.24-7.26 (m, 3H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.39-7.40 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.82, 137.01, 136.99, 136.69, 135.04, 134.92, 131.55, 128.92, 128.85, 128.13, 127.75, 127.49, 127.44, 127.42, 123.82, 121.47, 120.20, 118.98, 109.04, 108.74, 102.79, 88.14, 83.90, 66.02, 65.45, 61.43, 37.23, 32.81, 29.68, 21.16, 13.82. HRMS (TOF MS ESI^+) calculated for $C_{38}H_{37}NO_4Na$ $[M+Na]^+$: 594.2615, Found: 596.2610.



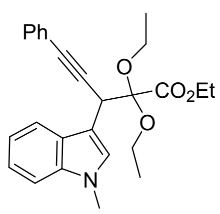
4c

ethyl 2,2-bis((4-methoxybenzyl)oxy)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4c**). Yellow oil, 51.3 mg, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06 (t, *J* = 7.1 Hz, 3H), 3.74 (s, 3H), 3.81 (s, 6H), 3.93-4.08 (m, 2H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 4.87 (d, J = 11.4 Hz, 1H), 5.03 (d, J = 11.4 Hz, 1H), 5.05 (s, 1H), 6.87 (t, *J* = 8.1 Hz, 4H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.19-7.22 (m, 2H), 7.27-7.30 (m, 6H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.43-7.44 (m, 2H), 7.84 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.82, 159.03, 158.99, 136.71, 131.55, 130.21, 130.10, 128.99, 128.93, 128.90, 128.14, 127.77, 127.44, 123.80, 121.48, 120.25, 118.97, 113.68, 113.59, 109.04, 108.77, 102.82, 88.12, 83.90, 65.89, 65.28, 61.44, 55.27, 37.26, 32.82, 13.84. HRMS (TOF MS ESI^+) calculated for $C_{38}H_{37}NO_6Na$ $[M+Na]^+$: 626.2513, Found: 626.2504.



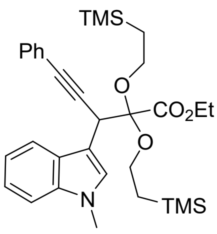
4d

ethyl 2,2-bis((4-bromobenzyl)oxy)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4d**). Yellow oil, 52.4 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (t, *J* = 7.1 Hz, 3H), 3.74 (s, 3H), 3.96-4.10 (m, 2H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.75 (d, *J* = 12.2 Hz, 1H), 4.83 (d, *J* = 12.2 Hz, 1H), 4.98 (d, *J* = 12.2 Hz, 1H), 5.04 (s, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.15-7.18 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.28-7.31 (m, 6H), 7.41-7.44 (m, 6H), 7.81 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.56, 136.97, 136.88, 136.75, 131.50, 131.36, 131.27, 128.91, 128.89, 128.82, 128.25, 128.00, 127.31, 123.50, 121.66, 121.27, 121.23, 120.12, 119.11, 109.17, 108.50, 103.05, 87.63, 84.14, 65.61, 65.03, 61.67, 37.24, 32.85, 13.85. HRMS (TOF MS ESI^+) calculated for $C_{36}H_{31}Br_2NO_4Na$ $[M+Na]^+$: 722.0512, Found: 722.0510.



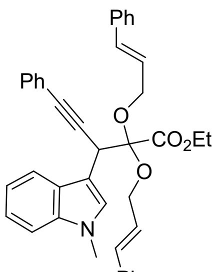
4e

ethyl 2,2-diethoxy-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4e**). Yellow oil, 33.5 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.0 Hz, 3H), 1.34 (t, J = 7.0 Hz, 3H), 3.57-3.63 (m, 1H), 3.71-3.77- 3.70 (m, 4H), 3.84-3.91 (m, 1H), 3.93-3.99 (m, 1H), 4.02-4.09 (m, 2H), 4.89 (s, 1H), 7.10 (t, J = 7.4 Hz, 1H), 7.17-7.21 (m, 2H), 7.25-7.29 (m, 4H), 7.41-7.42 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.21, 136.69, 131.53, 128.63, 128.08, 127.67, 127.52, 123.88, 121.41, 120.09, 118.87, 109.10, 109.03, 102.43, 88.14, 83.47, 61.31, 59.61, 59.01, 37.12, 32.82, 15.51, 15.25, 13.86. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{29}NO_4Na$ $[M+Na]^+$: 442.1989, Found: 442.1986.



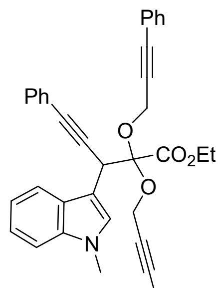
4f

ethyl 3-(1-methyl-1H-indol-3-yl)-5-phenyl-2,2-bis(2-(trimethylsilyl)ethoxy)pent-4-ynoate (**4f**). Yellow oil, 46.7 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.05 (s, 9H), 0.08 (s, 9H), 1.03 (t, J = 8.0 Hz, 3H), 1.10 (t, J = 7.1 Hz, 4H), 3.64-3.69 (m, 1H), 3.79-3.84 (m, 1H), 3.80 (s, 3H), 3.94-4.03 (m, 2H), 4.05-4.14 (m, 2H), 4.92 (s, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.30-7.31 (m, 5H), 7.44-7.46 (m, 2H), 7.87 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.74, 138.03, 137.90, 136.68, 131.51, 128.91, 128.23, 128.15, 128.14, 127.79, 127.38, 127.36, 127.33, 127.25, 123.71, 121.49, 120.13, 118.99, 109.05, 108.62, 102.84, 88.03, 83.96, 66.12, 65.58, 61.48, 37.22, 32.76, 13.80. HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{45}NO_4Si_2Na$ $[M+Na]^+$: 586.2780, Found: 586.2776.



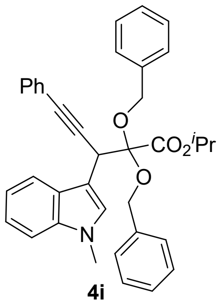
4g

ethyl 2,2-bis(cinnamyloxy)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4g**). Yellow oil, 44.6 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08 (t, J = 7.1 Hz, 3H), 3.75 (s, 3H), 3.97-4.11 (m, 2H), 4.33-4.37 (m, 1H), 4.44-4.48 (m, 1H), 4.61-4.65 (m, 1H), 4.71-4.75 (m, 1H), 5.02 (s, 1H), 6.28-6.33 (m, 1H), 6.39-6.44 (m, 1H), 6.64 (d, J = 15.9 Hz, 1H), 6.72 (d, J = 15.9 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.19-7.25 (m, 4H), 7.27-7.29 (m, 6H), 7.30-7.31 (m, 3H), 7.33-7.34 (m, 3H), 7.44-7.46 (m, 2H), 7.88 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.89, 136.81, 136.79, 136.74, 131.69, 131.61, 128.87, 128.48, 128.16, 127.83, 127.53, 127.46, 126.48, 126.45, 125.78, 125.46, 123.71, 121.56, 120.02, 119.10, 109.15, 108.79, 102.59, 88.01, 83.97, 64.96, 64.54, 61.62, 37.33, 32.89, 13.89. HRMS (TOF MS ESI$^+$) calculated for $C_{40}H_{37}NO_4Na$ $[M+Na]^+$: 618.2615, Found: 618.2610.



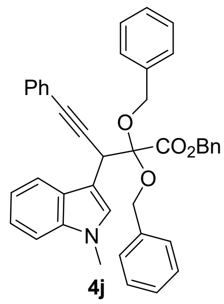
4h

ethyl 3-(1-methyl-1H-indol-3-yl)-5-phenyl-2,2-bis((3-phenylprop-2-yn-1-yl)oxy)pent-4-ynoate (**4h**). Yellow oil, 43.7 mg, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (t, J = 7.1 Hz, 3H), 3.75 (s, 3H), 3.95-4.01 (m, 1H), 4.04-4.10 (m, 1H), 4.68-4.76 (m, 2H), 4.93-5.01 (m, 2H), 5.02 (s, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.25-7.32 (m, 10H), 7.35 (s, 1H), 7.42-7.47 (m, 6H), 7.88 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.05, 136.69, 131.81, 131.68, 129.22, 128.40, 128.37, 128.21, 128.12, 127.89, 127.31, 123.53, 122.77, 122.71, 121.58, 119.93, 119.20, 109.15, 108.25, 102.69, 87.32, 86.06, 85.98, 85.28, 84.97, 84.38, 61.96, 53.85, 53.40, 37.19, 32.90, 13.79. HRMS (TOF MS ESI^{+}) calculated for $C_{40}H_{33}NO_4Na$ $[M+Na]^{+}$: 614.2302, Found: 614.2309.



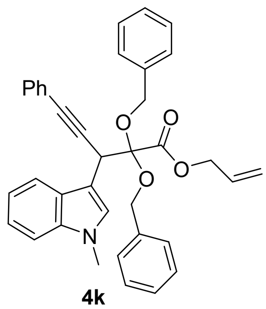
4i

isopropyl 2,2-bis(benzyloxy)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4i**). Yellow oil, 42.3 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (d, J = 6.3 Hz, 3H), 1.05 (d, J = 6.2 Hz, 3H), 3.71 (s, 3H), 4.75 (d, J = 11.9 Hz, 1H), 4.82-4.89 (m, 2H), 4.92 (d, J = 12.0 Hz, 1H), 5.05-5.08 (m, 2H), 7.06 (t, J = 7.5 Hz, 1H), 7.17-7.20 (m, 2H), 7.23-7.34 (m, 12H), 7.40-7.44 (m, 4H), 7.84 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.31, 138.14, 138.02, 136.69, 131.54, 128.92, 128.23, 128.14, 127.77, 127.53, 127.33, 127.31, 127.26, 123.77, 121.50, 120.34, 119.00, 108.98, 108.71, 102.71, 88.09, 83.97, 69.44, 66.11, 65.62, 37.14, 32.78, 21.48, 21.28. HRMS (TOF MS ESI^{+}) calculated for $C_{37}H_{35}NO_4Na$ $[M+Na]^{+}$: 580.2458, Found: 580.2450.



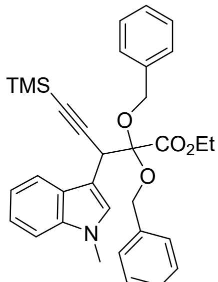
4j

benzyl 2,2-bis(benzyloxy)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4j**). Yellow oil, 47.2 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.74 (s, 3H), 4.38-4.43 (m, 1H),4.47-4.52 (m, 1H), 4.80 (d, J = 11.9 Hz, 1H), 4.87 (d, J = 11.9 Hz, 1H), 4.95 (d, J = 11.9 Hz, 1H), 5.10-5.13 (m, 3H), 5.20-5.24 (m, 1H), 5.67-5.75 (m, 1H), 7.09 (t, J = 7.9 Hz, 1H), 7.20-7.23 (m, 2H), 7.27-7.37 (m, 14H), 7.44-7.48 (m, 4H), 7.86 (d, J = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.44, 137.98, 137.86, 136.72, 131.57, 131.42, 129.00, 128.27, 128.19, 128.15, 127.82, 127.40, 127.38, 127.36, 127.33, 123.70, 121.52, 120.21, 119.04, 118.61, 109.09, 108.57, 103.04, 87.95, 84.02, 66.19, 66.04, 65.56, 37.30, 32.82. HRMS (TOF MS ESI^{+}) calculated for $C_{41}H_{35}NO_4Na$ $[M+Na]^{+}$: 628.2458, Found: 628.2455.



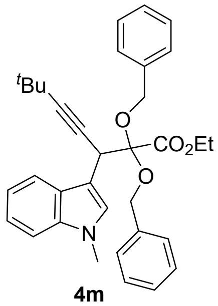
4k

allyl 2,2-bis(benzyloxy)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4k**). Yellow oil, 44.5 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.63 (s, 3H), 4.74 (d, J = 11.8 Hz, 1H), 4.81 (d, J = 11.8 Hz, 1H), 4.90-4.94 (m, 2H), 5.02 (d, J = 12.4 Hz, 1H), 5.08 (s, 1H), 5.11 (d, J = 11.8 Hz, 1H), 7.03-7.06 (m, 2H), 7.11 (d, J = 7.4 Hz, 2H), 7.17-7.20 (m, 3H), 7.23-7.24 (m, 3H), 7.27-7.32 (m, 8H), 7.37-7.39 (m, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.52, 137.91, 137.79, 136.74, 135.19, 131.59, 128.88, 128.28, 128.26, 128.25, 128.16, 128.13, 128.04, 127.81, 127.41, 127.39, 127.37, 127.35, 123.68, 121.53, 120.28, 119.06, 109.10, 108.55, 103.13, 87.87, 84.01, 67.10, 66.23, 65.49, 37.24, 32.75. HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{33}NO_4Na$ [M+Na]$^+$: 578.2302, Found: 578.2300.



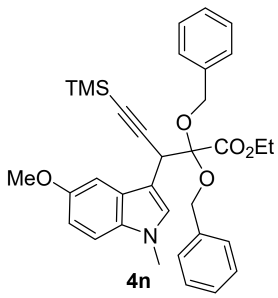
4l

ethyl 2,2-bis(benzyloxy)-3-(1-methyl-1H-indol-3-yl)-5-(trimethylsilyl)pent-4-ynoate (**4l**). Yellow oil, 43.1 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.16 (s, 9H), 1.04 (t, J = 7.1 Hz, 3H), 3.70 (s, 3H), 3.89-4.03 (m, 2H), 4.70 (d, J = 12.0 Hz, 1H), 4.80 (d, J = 12.0 Hz, 1H), 4.87-4.89 (m, 2H), 5.03 (d, J = 12.1 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 7.10 (s, 1H), 7.17 (t, J = 7.3 Hz, 1H), 7.22-7.24 (m, 2H), 7.28-7.35 (m, 7H), 7.41 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.67, 138.16, 137.98, 136.65, 128.88, 128.54, 128.45, 128.37, 128.22, 128.15, 128.08, 127.95, 127.34, 127.32, 127.29, 127.20, 127.10, 121.46, 120.16, 118.87, 109.02, 108.24, 104.39, 102.48, 88.54, 65.95, 65.57, 61.48, 37.52, 32.80, 13.82. HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{37}NO_4SiNa$ [M+Na]$^+$: 562.2385, Found: 562.2382.



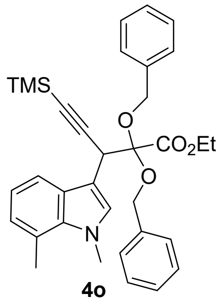
4m

ethyl 2,2-bis(benzyloxy)-6,6-dimethyl-3-(1-methyl-1H-indol-3-yl)hept-4-ynoate (**4m**). Yellow oil, 39.7 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ1.08 (t, J = 7.1 Hz, 3H), 1.25 (s, 9H), 3.70 (s, 3H), 3.93-4.06 (m, 2H), 4.70 (d, J = 12.0 Hz, 1H), 4.79 (d, J = 12.5 Hz, 2H), 4.85 (d, J = 12.0 Hz, 1H), 5.03 (d, J = 12.1 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 7.07 (s, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.23-7.28 (m, 3H), 7.30-7.35 (m, 6H), 7.42 (d, J = 7.7 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.93, 138.23, 138.19, 136.71, 128.78, 128.19, 128.09, 127.51, 127.28, 127.25, 127.21, 127.11, 121.32, 120.50, 118.69, 109.41, 108.93, 102.79, 92.16, 65.91, 65.45, 61.36, 36.60, 32.76, 30.97, 27.62, 13.87. HRMS (TOF MS ESI$^+$) calculated for $C_{34}H_{37}NO_4Na$ [M+Na]$^+$: 546.2615, Found: 546.2607.



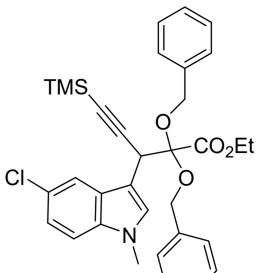
4n

ethyl 2,2-bis(benzyloxy)-3-(5-methoxy-1-methyl-1H-indol-3-yl)-5-(trimethylsilyl)pent-4-ynoate (**4n**). Yellow oil, 46.1 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.09 (t, *J* = 7.1 Hz, 3H), 3.59 (s, 3H), 3.68 (s, 3H), 3.97-4.09 (m, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.82-4.88 (m, 3H), 5.02 (d, *J* = 12.0 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.04 (s, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.25-7.35 (m, 8H), 7.43 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.76, 153.66, 138.16, 138.06, 132.10, 129.31, 128.24, 128.16, 127.66, 127.37, 127.32, 127.28, 127.14, 112.24, 109.78, 107.82, 104.21, 102.76, 101.85, 88.60, 66.02, 65.66, 61.47, 55.53, 37.90, 32.95, 13.89. HRMS (TOF MS ESI$^+$) calculated for $C_{34}H_{39}NO_5Si$ [M+Na]$^+$: 592.2490, Found: 592.2494.



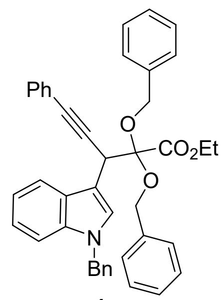
4o

ethyl 2,2-bis(benzyloxy)-3-(1,7-dimethyl-1H-indol-3-yl)-5-(trimethylsilyl)pent-4-ynoate (**4o**). Yellow oil, 47.0 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.12 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H), 2.67 (s, 3H), 3.91 (s, 3H), 3.86-3.93 (m, 1H), 3.97-4.02 (m, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.81 (s, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 5.01 (d, *J* = 12.1 Hz, 1H), 6.81 (d, *J* = 7.0 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 7.19-7.24 (m, 3H), 7.27-7.31 (m, 5H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.69, 138.20, 137.98, 135.30, 130.49, 128.42, 128.22, 128.15, 127.29, 127.28, 127.18, 127.07, 124.15, 120.94, 119.12, 118.08, 107.91, 104.49, 102.34, 88.40, 65.89, 65.56, 61.50, 37.27, 36.84, 19.72, 13.86. HRMS (TOF MS ESI$^+$) calculated for $C_{34}H_{39}NO_4SiNa$ [M+Na]$^+$: 576.2541, Found: 576.2549.



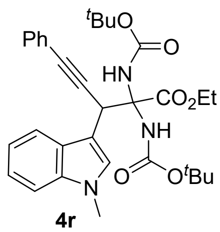
4p

ethyl 2,2-bis(benzyloxy)-3-(5-chloro-1-methyl-1H-indol-3-yl)-5-(trimethylsilyl)pent-4-ynoate (**4p**). Yellow oil, 35.5 mg, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.22 (s, 9H), 1.16 (t, *J* = 7.1 Hz, 3H), 3.69 (s, 3H), 3.97-4.10 (m, 2H), 4.74-4.86 (m, 4H), 5.02 (d, *J* = 11.8 Hz, 1H), 7.08 (s, 1H), 7.13-7.17 (m, 2H), 7.27-7.32 (m, 2H), 7.34-7.38 (m, 6H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.43, 137.86, 137.85, 135.16, 130.24, 128.29, 128.24, 127.43, 127.38, 127.33, 127.18, 124.92, 121.76, 119.93, 110.13, 107.99, 103.68, 102.58, 89.07, 66.03, 65.59, 61.58, 37.63, 32.98, 13.87, 0.13. HRMS (TOF MS ESI$^+$) calculated for $C_{33}H_{36}ClNO_4SiNa$ [M+Na]$^+$: 596.1995, Found: 596.1991.



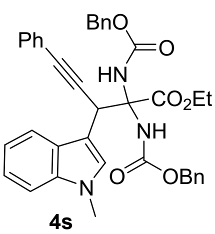
4q

ethyl 3-(1-benzyl-1H-indol-3-yl)-2,2-bis(benzyloxy)-5-phenylpent-4-ynoate (**4q**). Yellow oil, 50.1 mg, 81% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 1.0 (t, *J* = 7.1 Hz, 3H), 3.88-4.02 (m, 2H), 4.77 (d, *J* = 11.8 Hz, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.89 (d, *J* = 11.7 Hz, 1H), 5.07 (d, *J* = 10.9 Hz, 2H), 5.28 (s, 2H), 7.06-7.11 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.24-7.25 (m, 2H), 7.26-7.30 (m, 11H), 7.32-7.35 (m, 3H), 7.42-7.44 (m, 4H), 7.91 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.70, 137.92, 137.90, 137.45, 136.33, 131.57, 128.68, 128.38, 128.25, 128.19, 128.15, 127.83, 127.70, 127.51, 127.46, 127.40, 127.37, 127.34, 126.74, 123.70, 121.74, 120.47, 119.29, 109.56, 109.43, 102.93, 87.78, 84.12, 66.17, 65.59, 61.51, 50.03, 37.41, 13.80. HRMS (TOF MS ESI$^+$) calculated for $C_{42}H_{37}NO_4Na$ $[M+Na]^+$: 642.2615, Found: 642.2610.



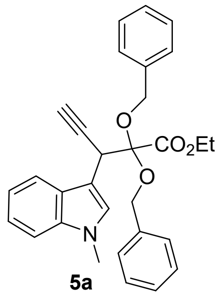
4r

ethyl 2,2-bis((tert-butoxycarbonyl)amino)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (**4r**). Yellow solid, m.p. = 68-70 °C, 39.3 mg, 70% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 1.26 (t, *J* = 7.0 Hz, 3H), 1.40 (s, 9H), 1.44 (s, 9H), 3.77 (s, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 5.35 (s, 1H), 6.22 (s, 2H), 7.04 (s, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.28-7.31 (m, 4H), 7.45-7.47 (m, 2H), 7.81 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.63, 154.07, 153.80, 136.83, 131.69, 128.91, 128.19, 128.04, 127.44, 123.31, 121.76, 119.60, 119.45, 109.45, 107.99, 86.72, 84.12, 80.16, 79.82, 72.84, 62.55, 36.62, 32.93, 28.17, 13.97. HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{39}N_3O_6Na$ $[M+Na]^+$: 584.2731, Found: 584.2725.



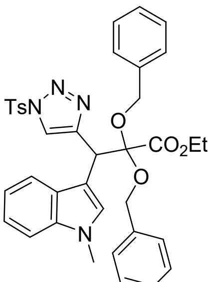
4s

ethyl 2,2-bis(((benzyloxy)carbonyl)amino)-3-(1-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (4s). Yellow solid, m.p. = 76-78 °C, 45.3 mg, 72% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.1 Hz, 3H), 3.69 (s, 3H), 4.18 (brs, 2H), 4.98 (d, *J* = 11.1 Hz, 1H), 5.14-5.15 (m, 3H), 5.46 (s, 1H), 6.45 (s, 1H), 6.59 (s, 1H), 6.92 (s, 1H), 7.04 (t, *J* = 7.1 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.26-7.30 (m, 3H), 7.31-7.36 (m, 11H), 7.43-7.45 (m, 2H), 7.75 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.81, 154.51, 154.25, 136.78, 136.19, 131.66, 129.00, 128.44, 128.41, 128.25, 128.20, 128.16, 128.11, 128.03, 127.91, 127.23, 123.01, 121.84, 119.58, 119.23, 109.53, 107.40, 86.18, 84.50, 73.07, 66.78, 66.64, 62.85, 36.39, 32.86, 13.80. HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{35}N_3O_6Na$ $[M+Na]^+$: 652.2418, Found: 652.2419.



5a

ethyl 2,2-bis(benzyloxy)-3-(1-methyl-1H-indol-3-yl)pent-4-ynoate (**5a**). Yellow oil, 85.0 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.1 Hz, 3H), 2.36 (d, *J* = 2.7 Hz, 1H), 3.69 (s, 3H), 3.89-4.03 (m, 2H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.84 (d, *J* = 2.6 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 11.9 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.21-7.25 (m, 4H), 7.27-7.33 (m, 5H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.58, 137.86, 137.74, 136.69, 128.90, 128.27, 128.16, 127.41, 127.39, 127.33, 127.30, 127.25, 121.59, 120.08, 119.03, 109.07, 108.25, 102.56, 82.04, 72.28, 66.23, 65.43, 61.57, 36.45, 32.81, 13.77. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{29}NO_4Na$ $[M+Na]^+$: 490.1989, Found: 490.1981.

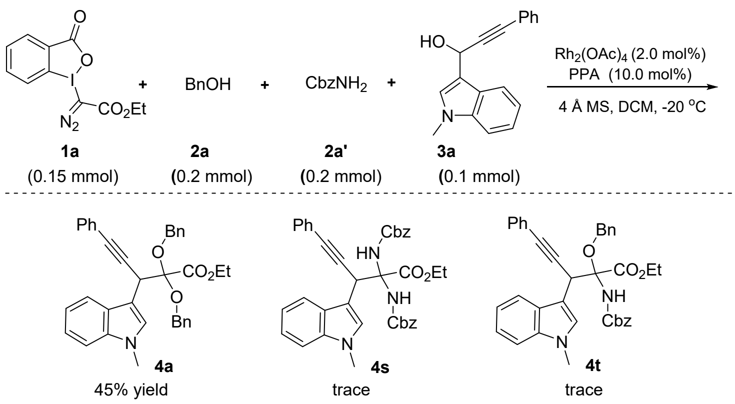


6a

ethyl 2,2-bis(benzyloxy)-3-(1-methyl-1H-indol-3-yl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propanoate (**6a**). Yellow oil, m.p. = 45-47 ^{o}C, 61.8 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.80 (t, *J* = 7.1 Hz, 3H), 2.31 (s, 3H), 3.62 (s, 3H), 3.78-3.88 (m, 2H), 4.57-4.67 (m, 4H), 5.38 (s, 1H), 6.89-6.92 (m, 1H), 7.06-7.09 (m, 1H), 7.12 (s, 1H), 7.14-7.17 (m, 6H), 7.19-7.27 (m, 7H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.75-7.77 (m, 2H), 8.05 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.21, 146.81, 146.68, 137.81, 137.53, 136.32, 133.30, 130.22, 129.09, 128.41, 128.31, 128.23, 127.53, 127.50, 127.48, 127.44, 127.31, 123.52, 121.50, 119.10, 119.02, 109.13, 109.06, 102.72, 66.40, 66.17, 61.44, 40.82, 32.83, 21.72, 13.52. HRMS (TOF MS ESI$^+$) calculated for $C_{37}H_{36}N_4O_6SNa$ $[M+Na]^+$: 687.2248, Found: 687.2244.

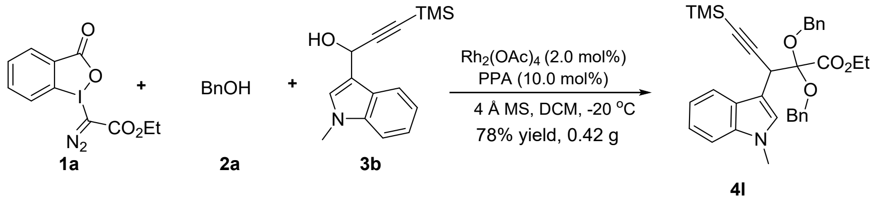
6. Four-component Trifunctionalization Reaction Using Different Nucleophiles

The reaction was conducted on a 0.1 mmol scale: to a solution of $Rh_2(OAc)_4$ (0.9 mg, 2.0 mol %), phosphoric acid (3.5 mg, 10 mol %), benzyl alcohol **2a** (0.2 mmol), $CbzNH_2$ **2a′** (0.2 mmol) and 4 Å MS (150 mg) in DCM (1.0 mL) was added a solution of diazo compound **1a** (0.15 mmol) and *α*-propargylic-3-indolymethanol **3a** (0.1 mmol), in DCM (3.0 mL) via a syringe pump in 1 h under an argon atmosphere at -20 ^{o}C. After diazo compound **1a** were completely consumed (monitored by TLC analysis), and then LCMS analysis was performed for reaction mixture. The molecular weight of the products **4a**, **4s**, **4t** were found on LCMS, however, almost only product **4a** was observed by TLC. The reaction mixture was concentrated in vacuum, the residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/10) to obtain the product **4a** as main product. *This result likely due to the nucleophilic attack of benzyl alcohol prior to the nucleophilic attack of* $CbzNH_2$*, which resulted in the di-oxonium ylide interception by α-propargylic-3-indolymethanol under the catalysis of phosphoric acid.*



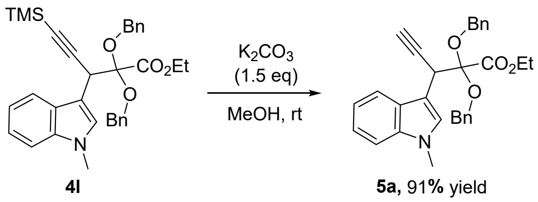
7. Procedures for Scale up and Derivations

A: Procedure for the scale-up synthesis of product 4l



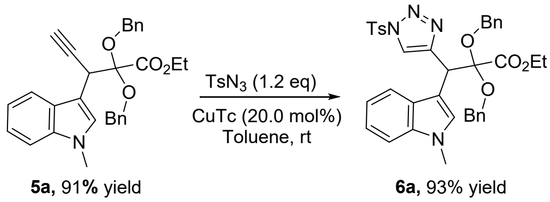
The reactions were conducted on a 1.0 mmol scale: to a solution of $Rh_2(OAc)_4$ (9 mg, 2.0 mol %), phosphoric acid (35 mg, 10.0 mol %), alcohol **2a** (4 mmol), and 4 Å MS (1500 mg) in DCM (10.0 mL) was added a solution of diazo compound **1a** (1.5 mmol) and α-propargylic-3-indolymethanol **3b** (1.0 mmol), in DCM (30.0 mL) via a syringe pump in 1 h under an argon atmosphere at indicate temperature. After completion of the addition, stirring was continued at indicate temperature for 0.5 h. The solution was concentrated in vacuum. And then the residue was purified by column chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1/10) to give the product **4l** in 78% yield.

B: General Procedure for the Synthesis of 5a



To a 10-mL oven-dried vial containing a magnetic stirring bar, propargylic indole derivative **4l** (107.8 mg, 0.2 mmol) in 5 mL of MeOH, was added K_2CO_3 (41.4 mg, 1.5 eq). the reaction mixture was stirred overnight at room temperature. After the propargylic indole derivative **4l** was completely consumed (indicated by TLC analysis), the crude reaction mixture concentrated in vacuo and the product was purified by column chromatography on silica gel without any additional treatment (Hexanes : EtOAc = 10:1) to give the pure products **5a** in 91% yield.

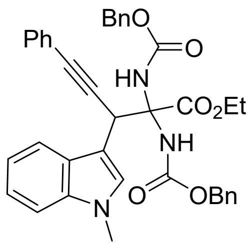
C: General Procedure for the Synthesis of 6a



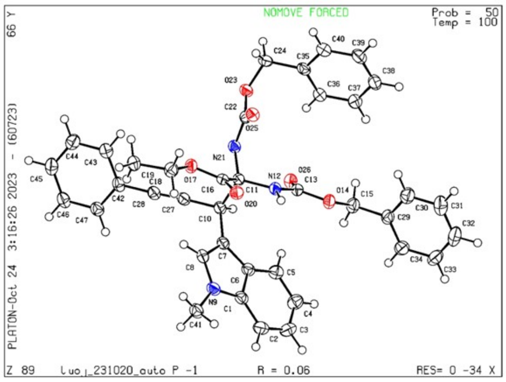
To a 10-mL oven-dried vial containing a magnetic stirring bar and CuTc (3.8 mg, 20.0 mol %) in 1.0 mL of toluene, was added propargylic indole derivative **5a** (47.0 mg, 0.1 mmol) and TsN_3 (23.6 mg, 0.12mmol) in 1.0 mL of toluene under argon atmosphere. The mixture was stirred 5h at room temperature. After propargylic indole derivative **5a** was completely consumed (monitored by TLC analysis), the crude reaction mixture concentrated in vacuo and the product was purified by column chromatography on silica gel without any additional treatment (Hexanes : EtOAc = 6:1) to give the pure products **6a** in 93% yield.

8. X-Ray crystallographic data for compounds 4s.

Single-crystal X-Ray difraction analysis of **4s**: The crystal of **4s** used for the single-crystal X-ray diffraction experiment was grown by slow evaporation of a solution of **4s** in dichloromethane and hexane at 25 ℃ . An ORTEP diagram of the crystal structure of **4s** is shown below (CCDC No: 2307507)



≡



Datablock: luoj_231020_auto

Bond precision: C-C = 0.0034 A Wavelength=1.54184

Cell: a=11.0033(5) b=12.5268(5) c=12.5483(5)
alpha=106.431(4) beta=91.810(4) gamma=103.462(4)

Temperature: 100 K

	Calculated	Reported
Volume	1604.57(13)	1604.57(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C38 H35 N3 O6	C38 H35 N3 O6
Sum formula	C38 H35 N3 O6	C38 H35 N3 O6
Mr	629.69	629.69
Dx,g cm-3	1.303	1.303
Z	2	2
Mu (mm-1)	0.721	0.721
F000	664.0	664.0
F000'	666.05	
h,k,lmax	13,15,15	13,15,15
Nref	6627	6200
Tmin,Tmax	0.841,0.930	0.862,1.000
Tmin'	0.805	

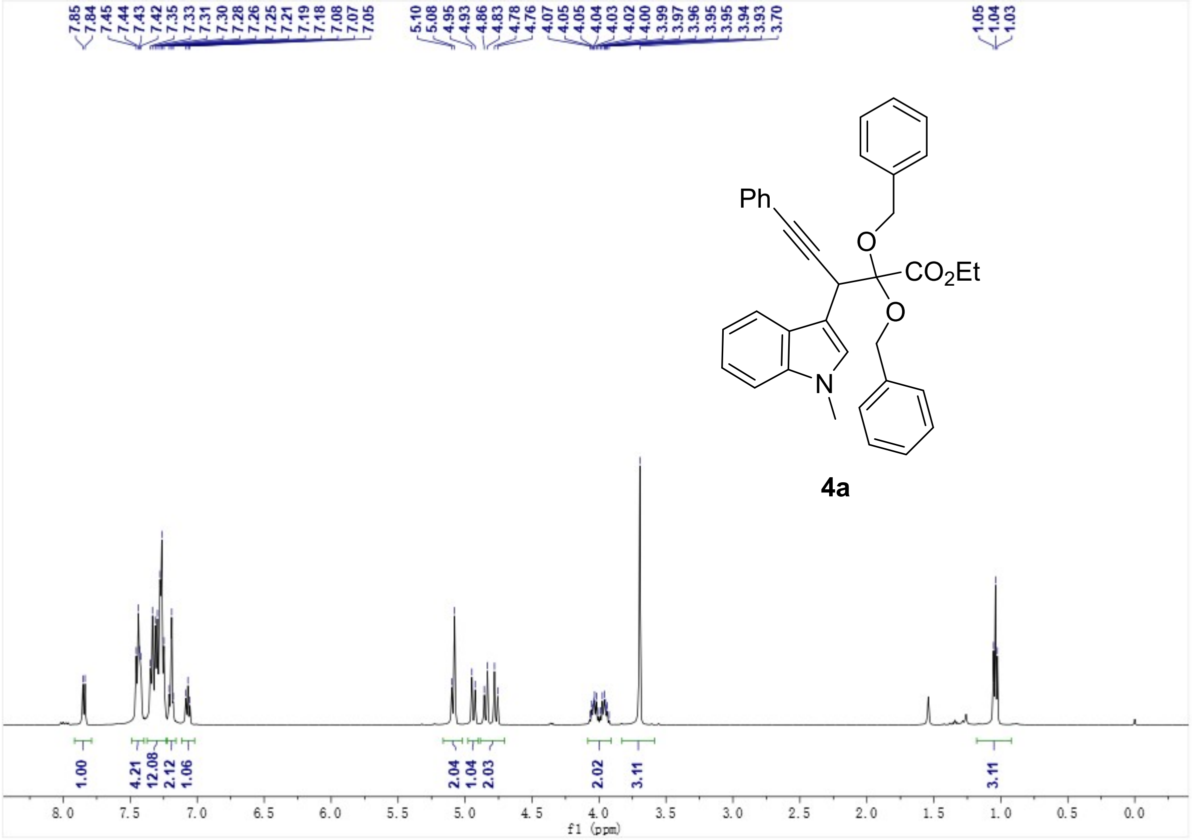
Correction method= # Reported T Limits: Tmin=0.862 Tmax=1.000
AbsCorr = MULTI-SCAN

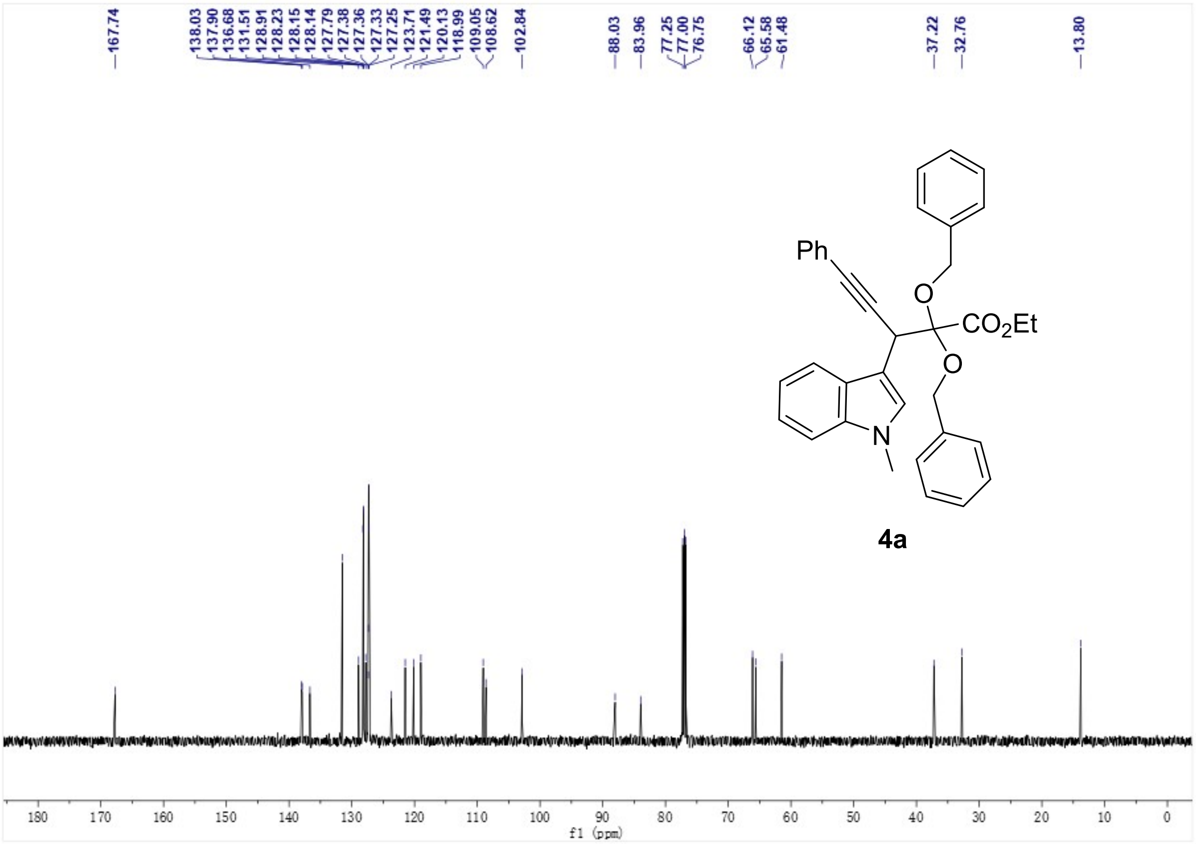
Data completeness= 0.936 Theta(max)= 75.230

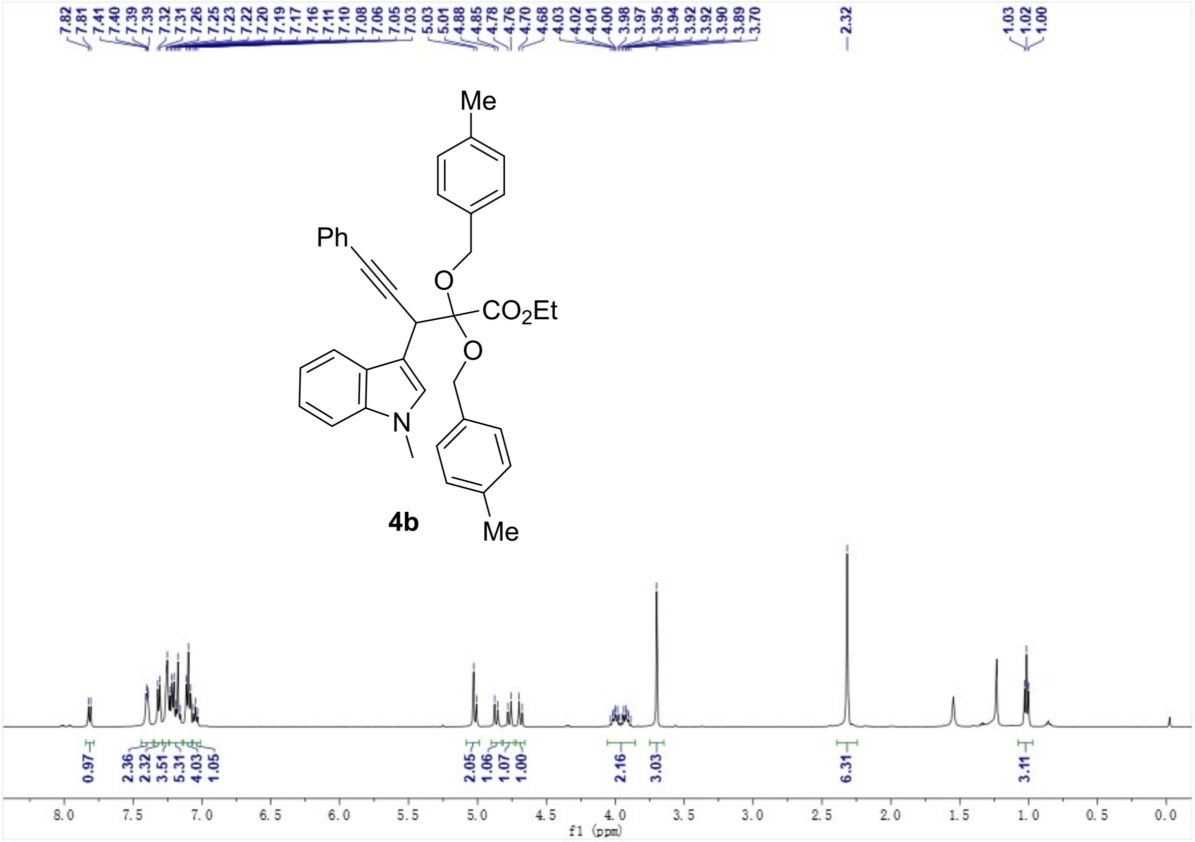
R(reflections)= 0.0636(4849) wR2(reflections)= 0.1885(6200)

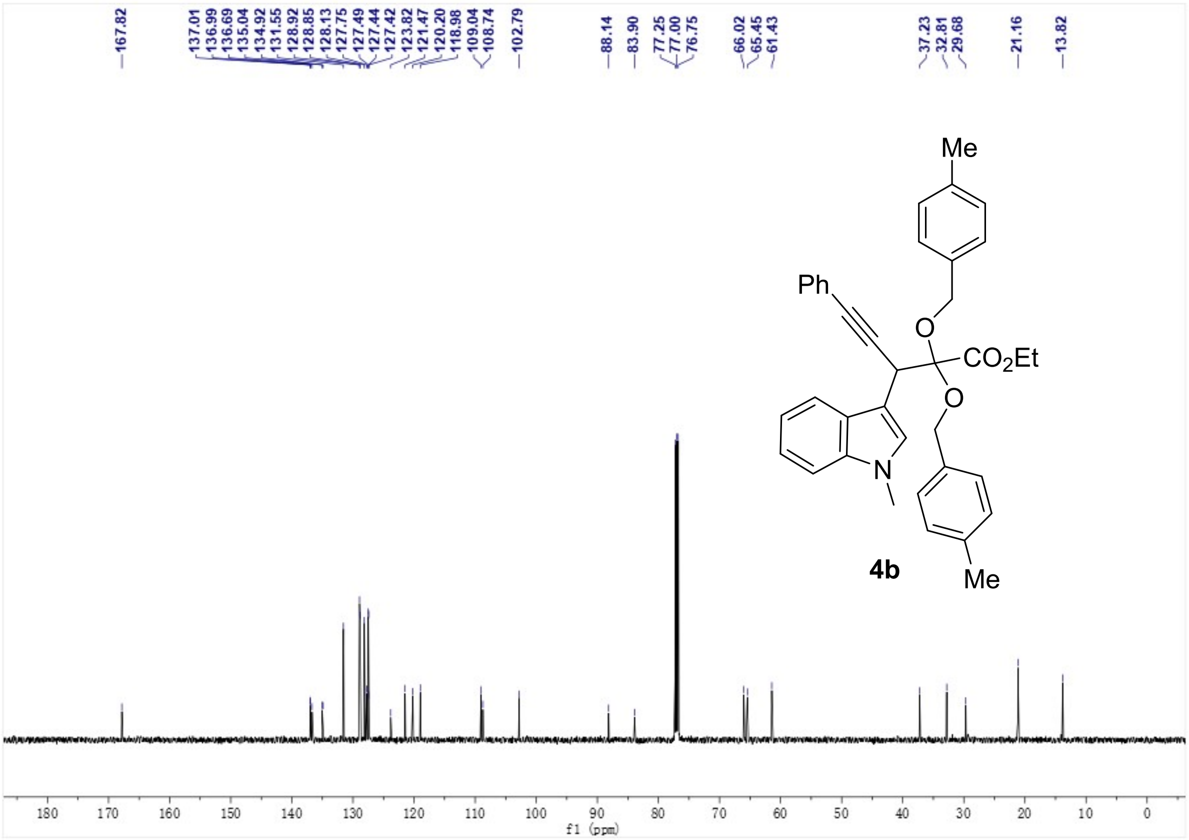
S = 1.038 Npar= 434

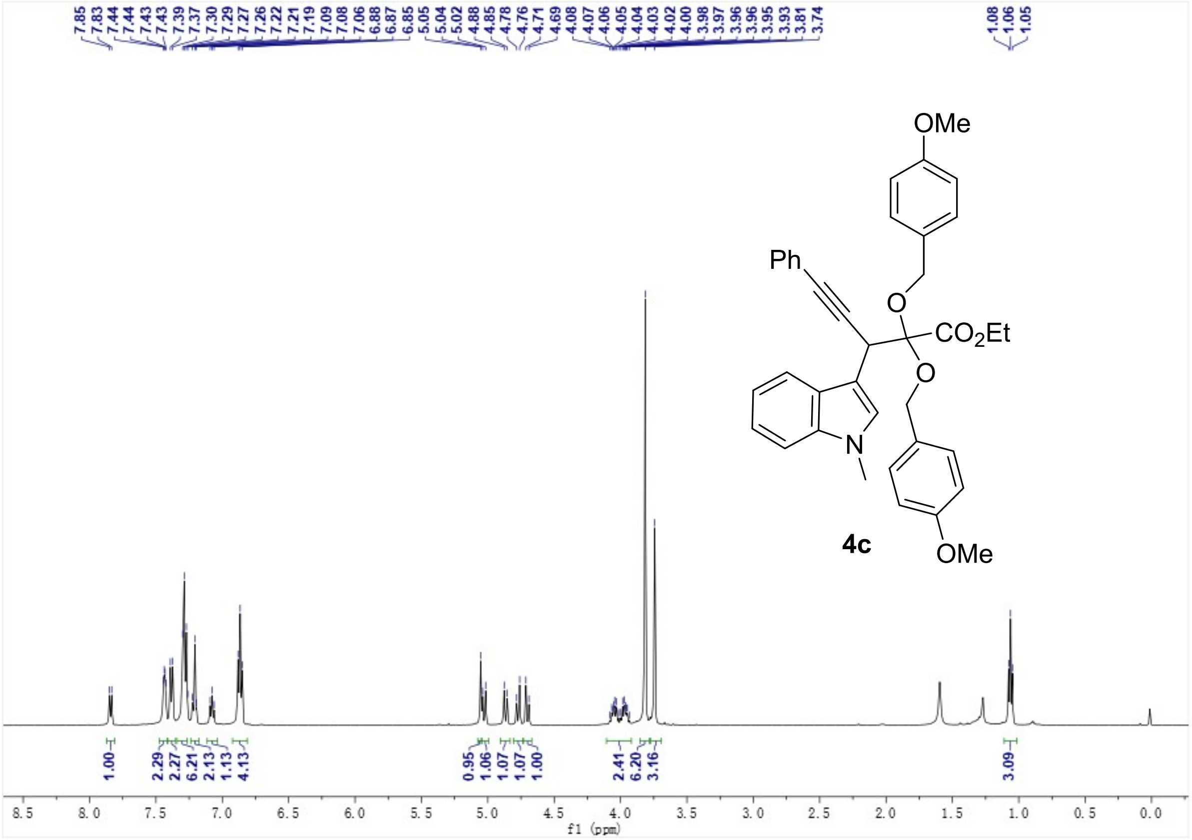
9. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Products 4, 5a, 6a







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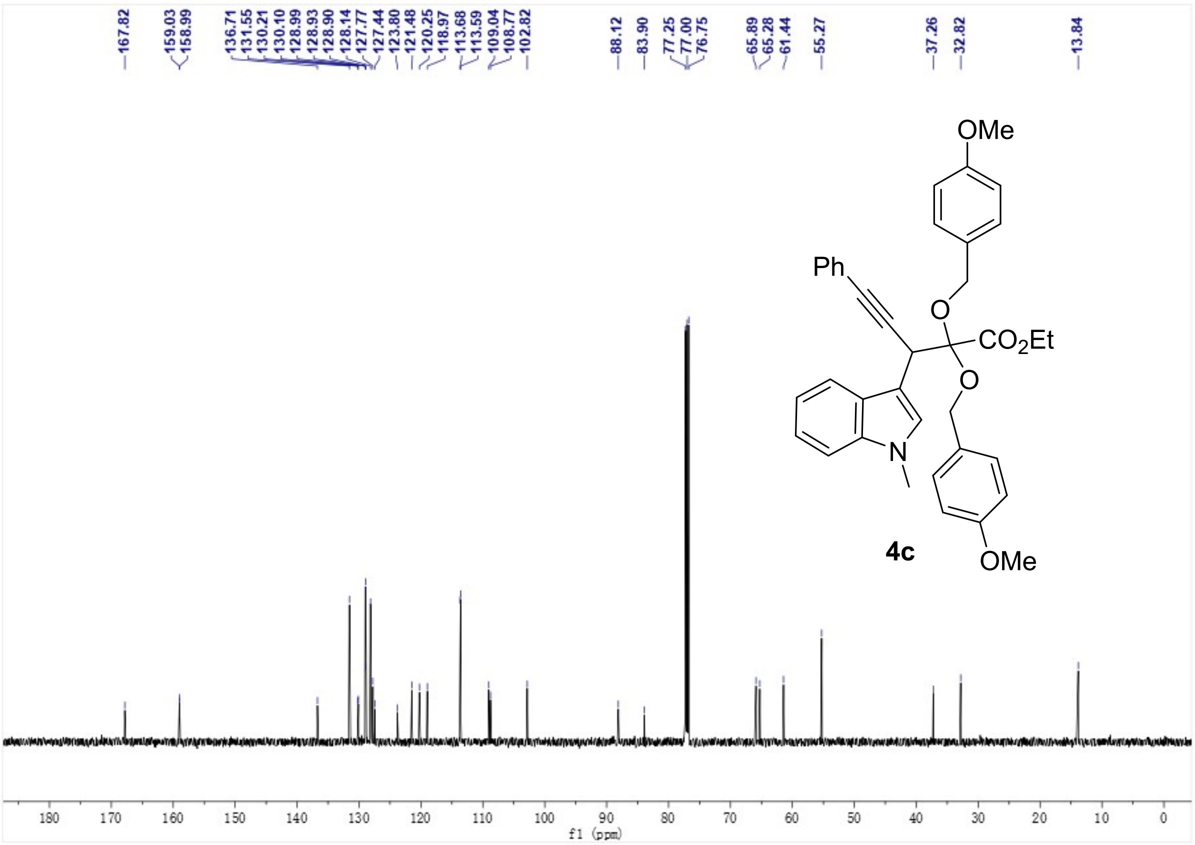
1.08 1.06 1.05
OMe
Ph
O
CO_2Et
O
N
4c
OMe
1.00 2.29 2.27 6.21 2.13 1.13 4.13 0.95 1.06 1.07 1.07 1.00 2.41 6.20 3.16 3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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88.12 83.90 77.25 77.00 76.75
65.89 65.28 61.44 55.27
37.26 32.82
13.84
OMe
Ph
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CO_2Et
O
N
4c
OMe
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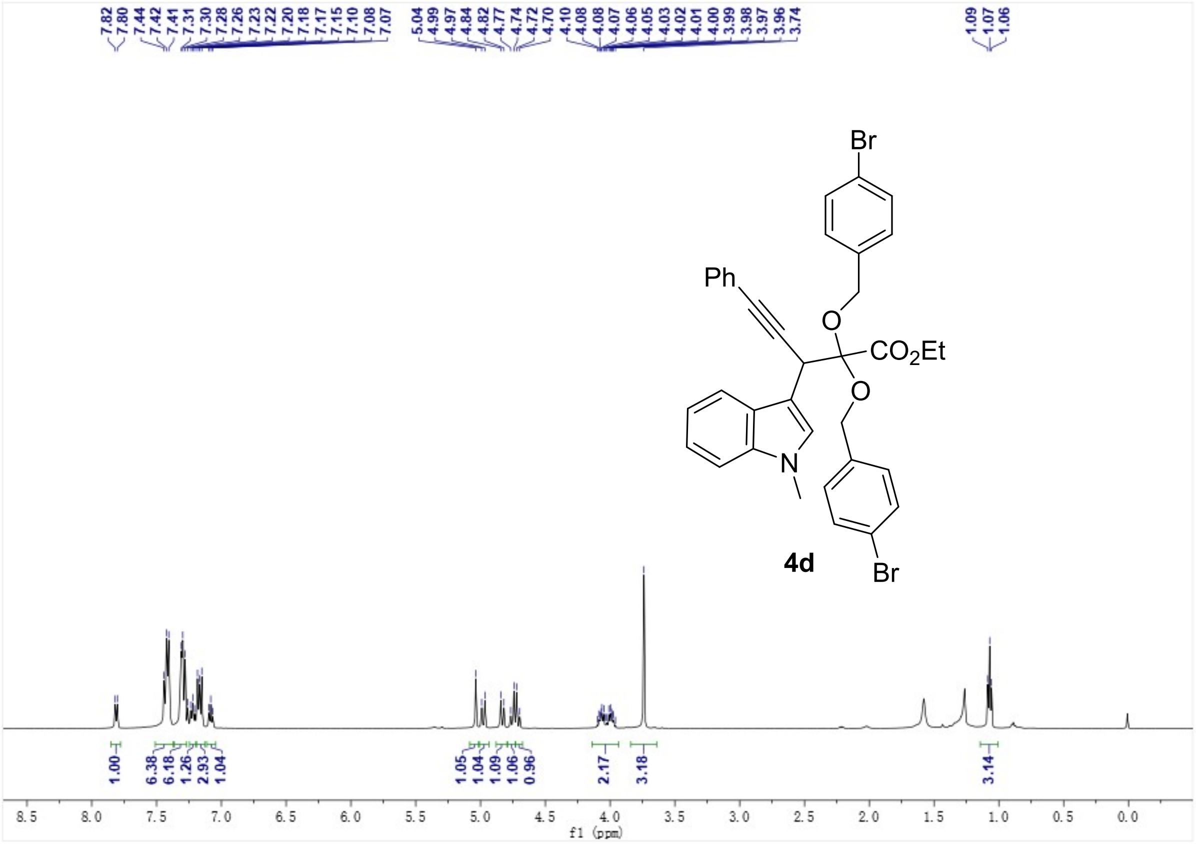
f1 (ppm)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7.15
7.10
7.08
7.07
5.04
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4.82
4.77
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4.72
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4.10
4.08
4.08
4.07
4.06
4.05
4.03
4.02
4.01
4.00
3.99
3.98
3.97
3.96
3.74
1.09
1.07
1.06
Br
Ph
O
CO2Et
O
N
Br
4d
1.00
6.38
6.18
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1.05
1.04
1.09
1.06
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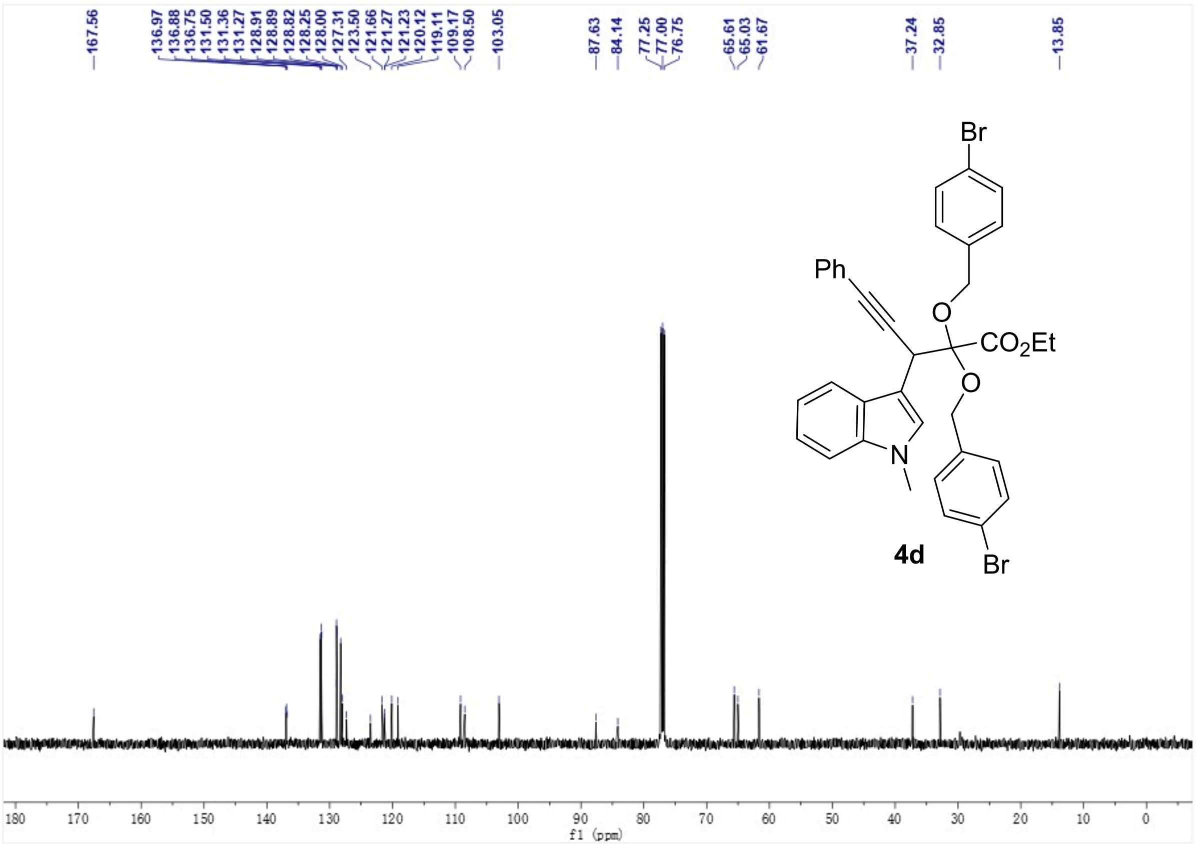
3.18
3.14
f1 (ppm)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119.11
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108.50
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77.00
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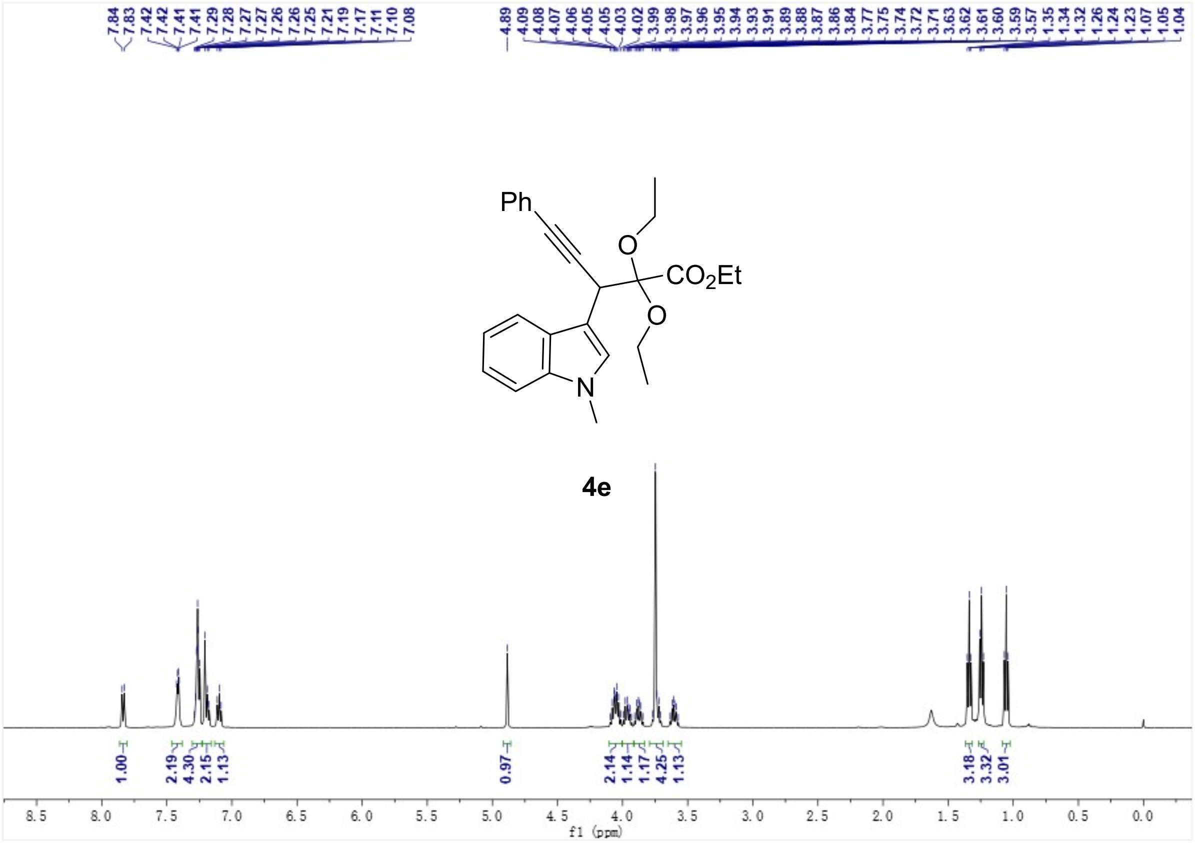
Br
4d
f1 (ppm)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Ph
O
CO_2Et
O
N
4e
1.00 2.19 4.30 2.15 1.13 0.97 2.14 1.14 1.17 4.25 1.13 3.18 3.32 3.01
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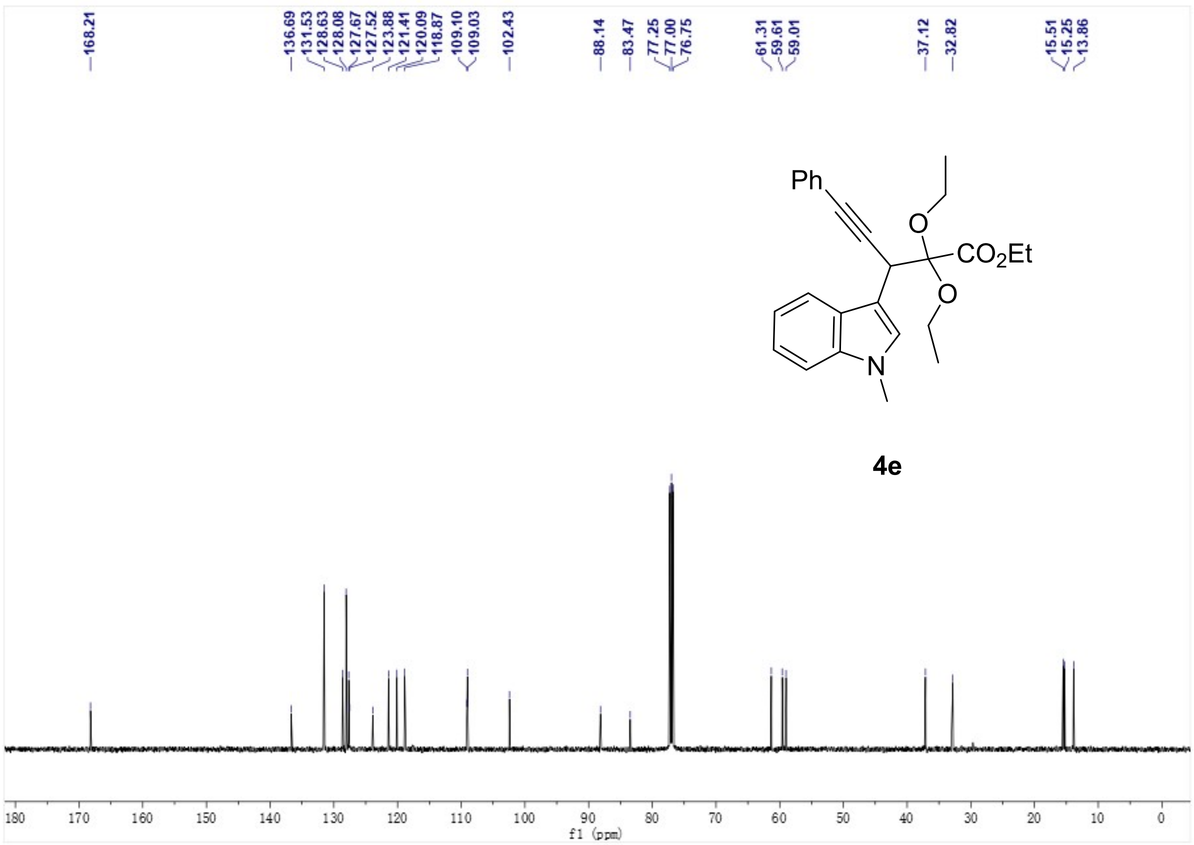
f1 (ppm)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88.14 83.47 77.25 77.00 76.75
61.31 59.61 59.01
37.12 32.82
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CO_2Et
O
N
4e
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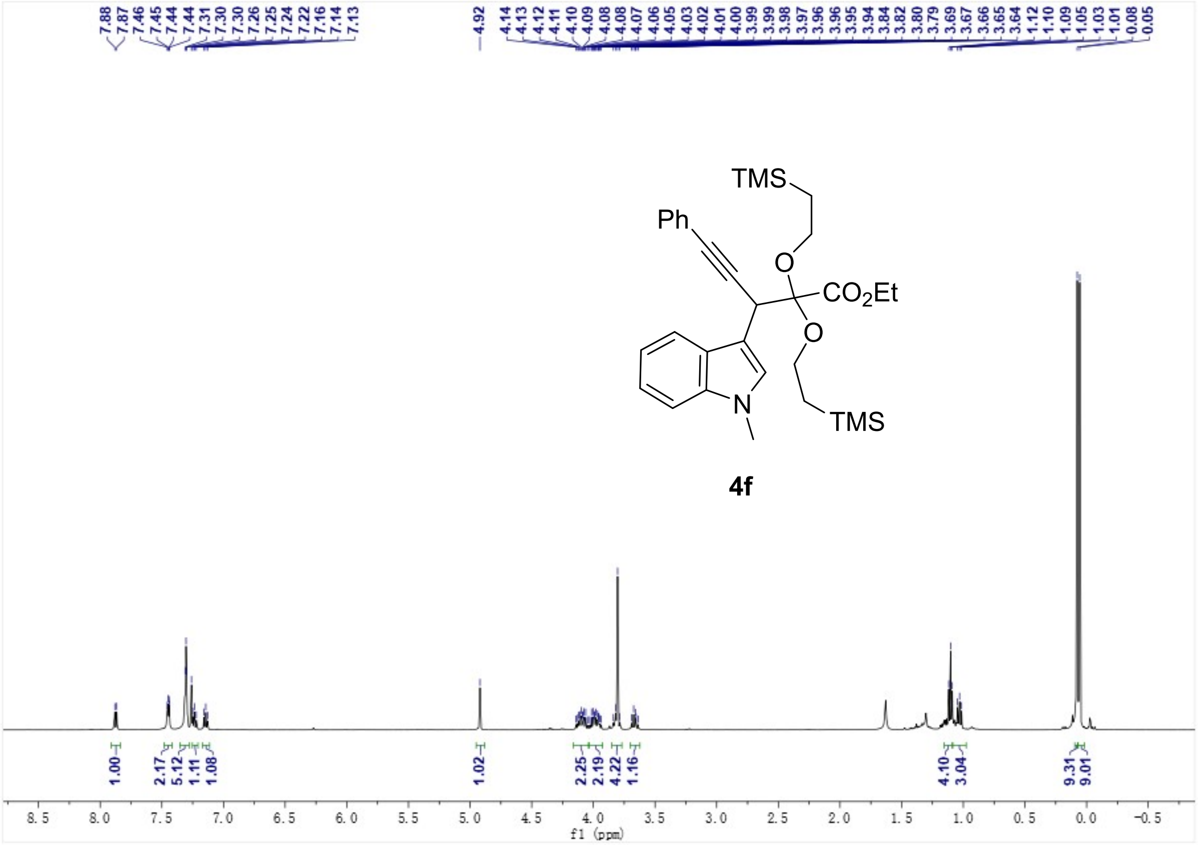
f1 (ppm)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Ph
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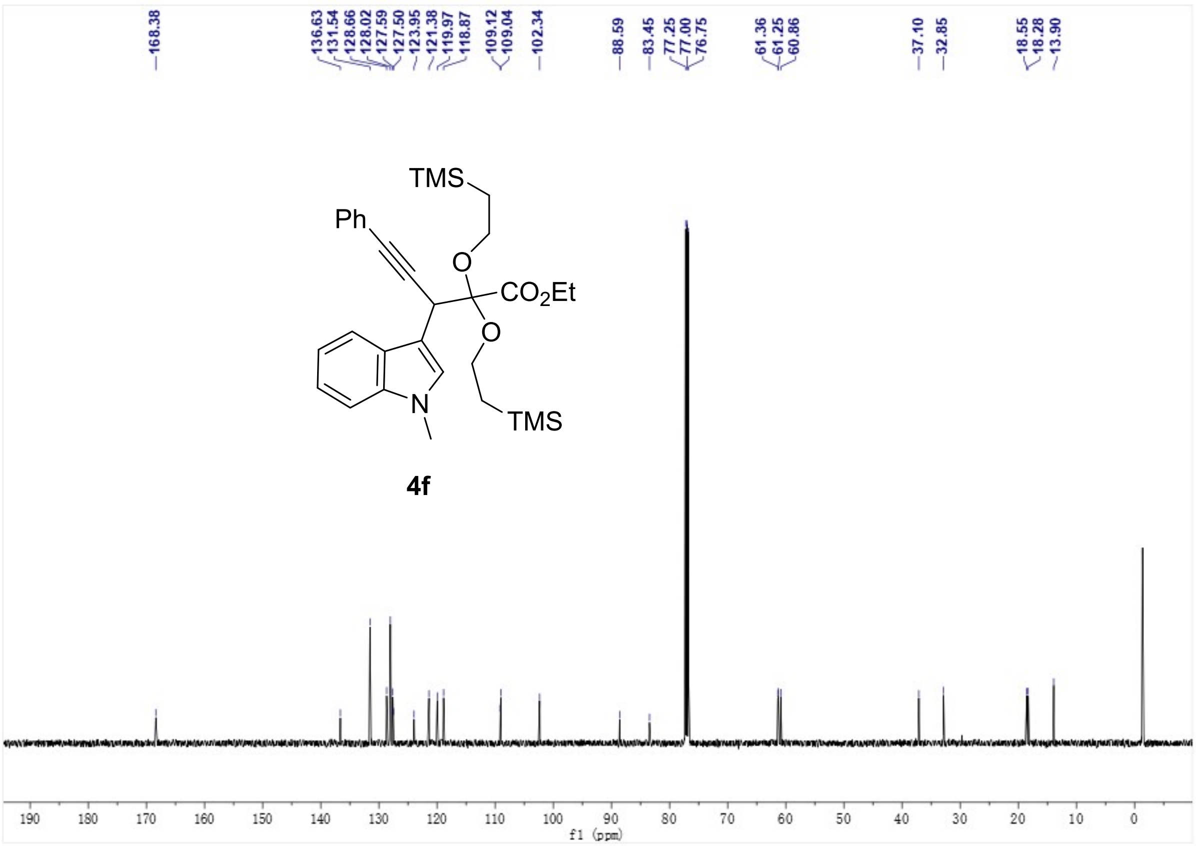
CO2Et
O
N
TMS
4f
f1 (ppm)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77.00
76.75
61.36
61.25
60.86
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Ph
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CO2Et
O
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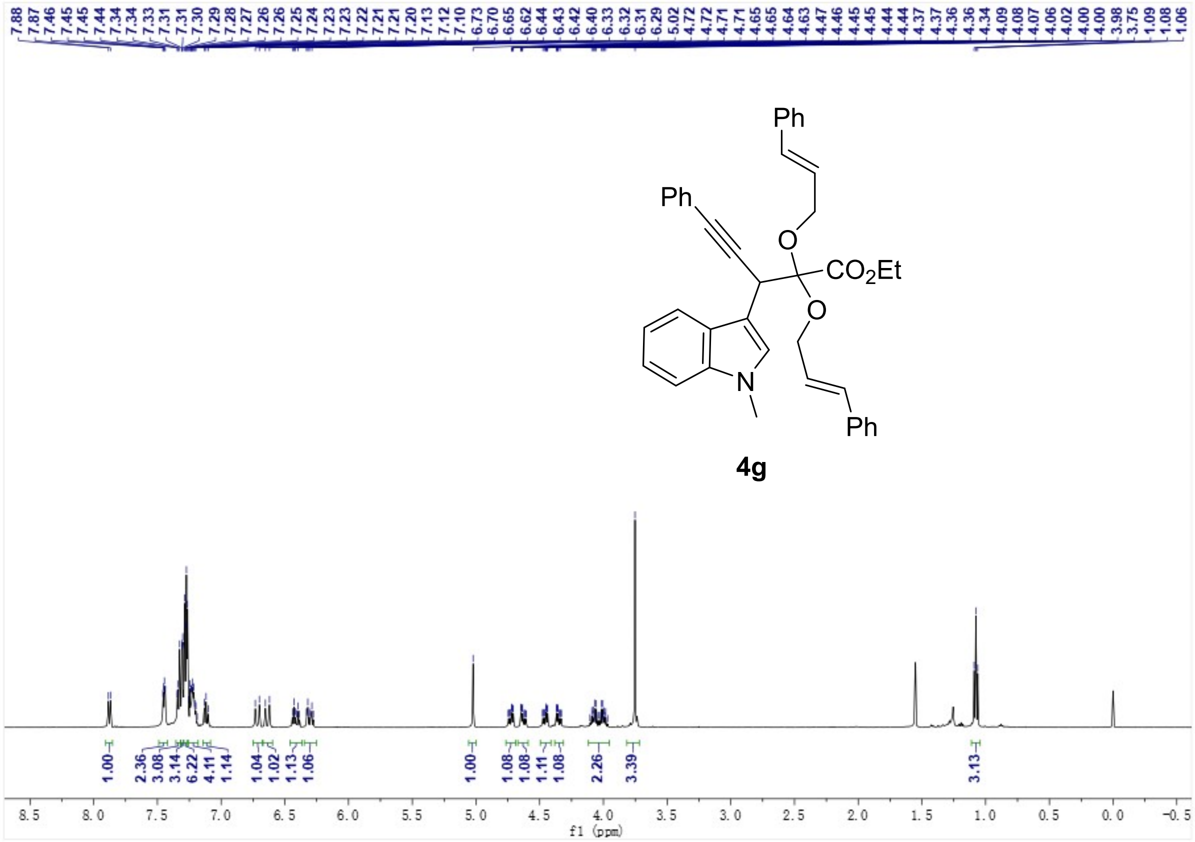
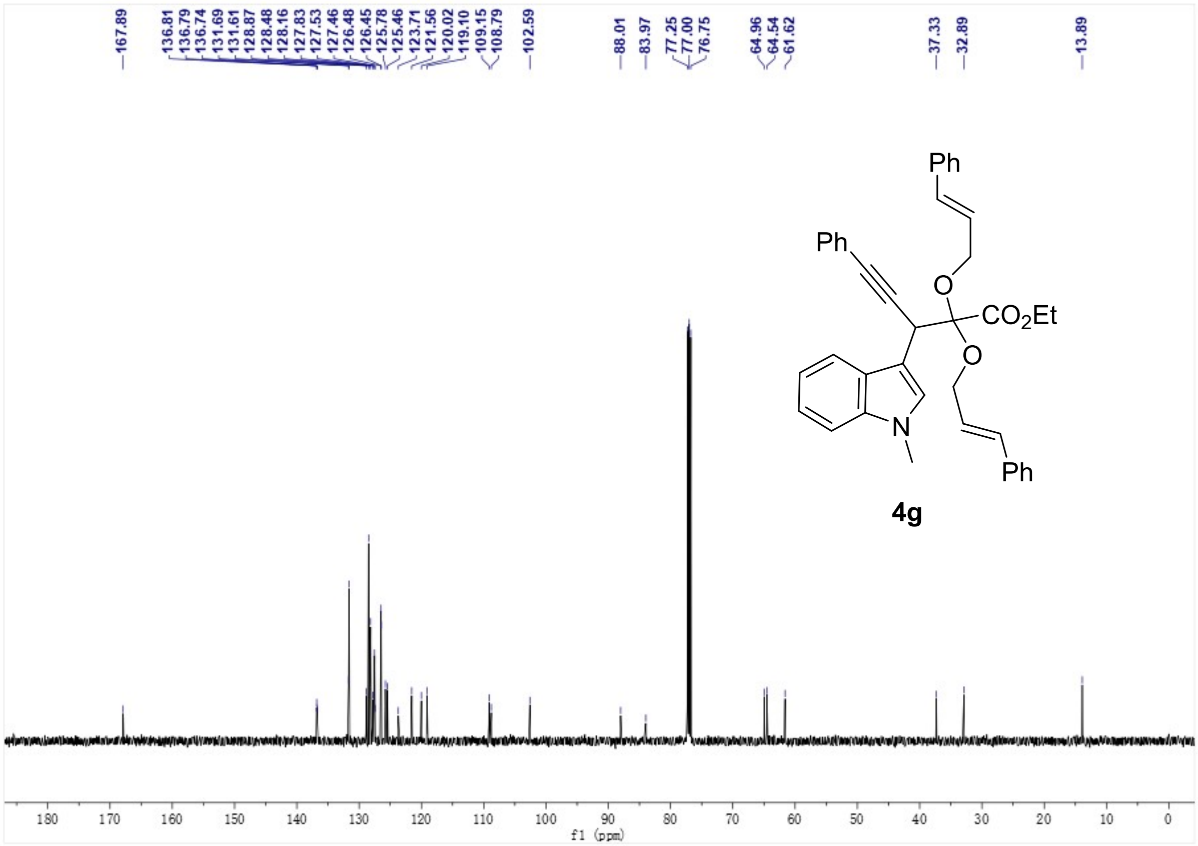
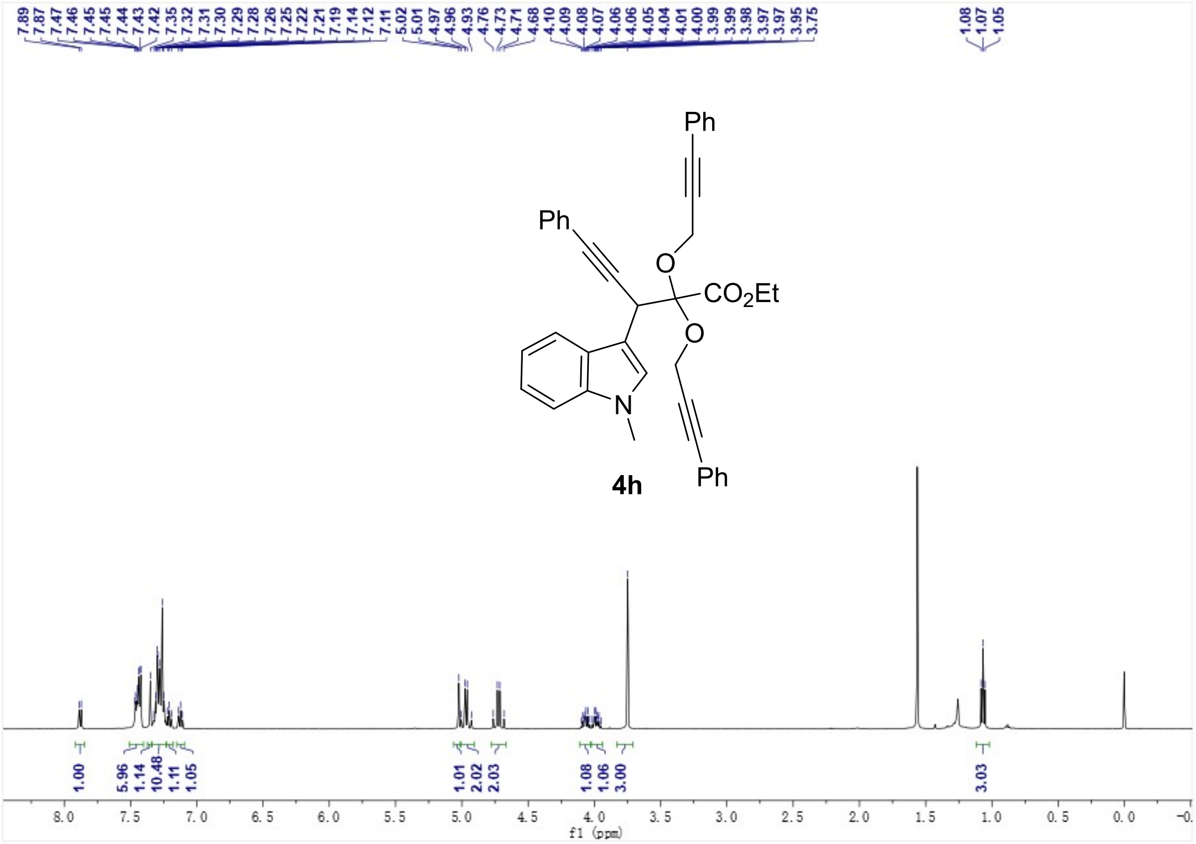
TMS
4f
f1 (ppm)

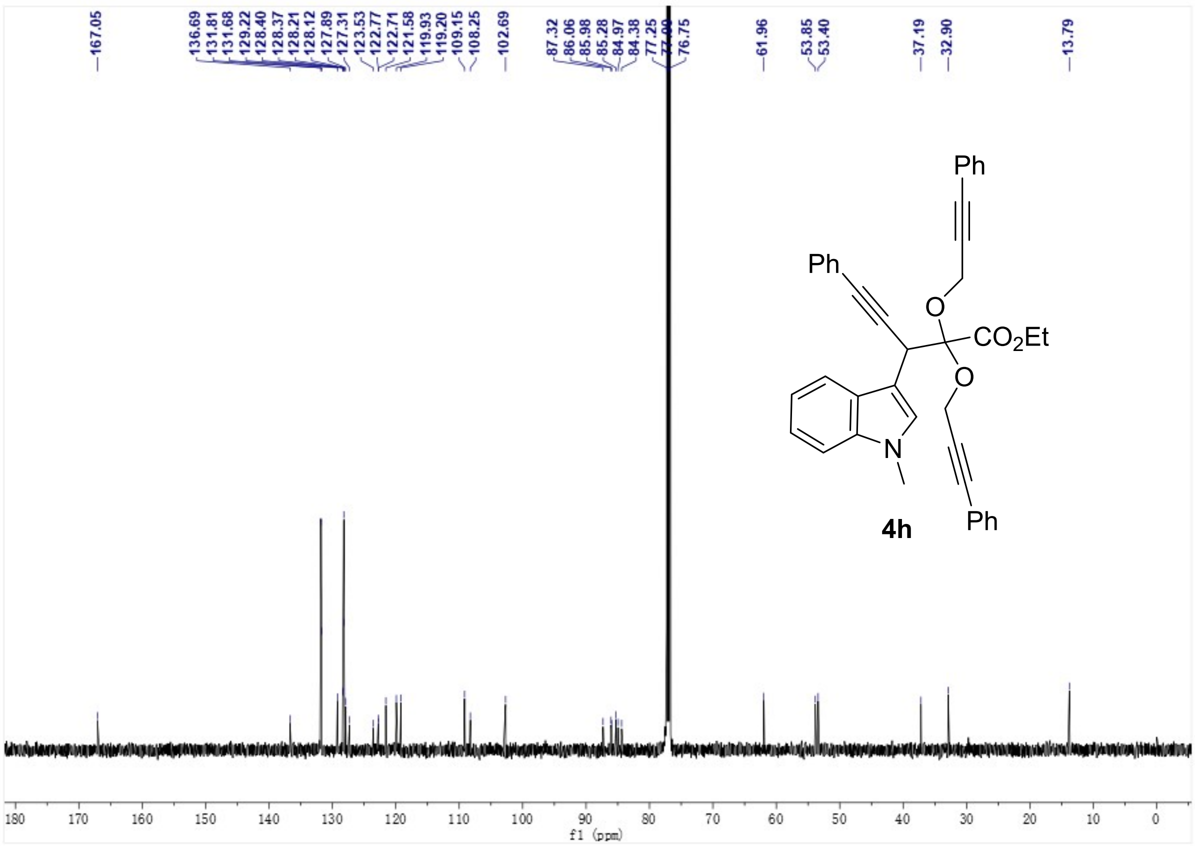


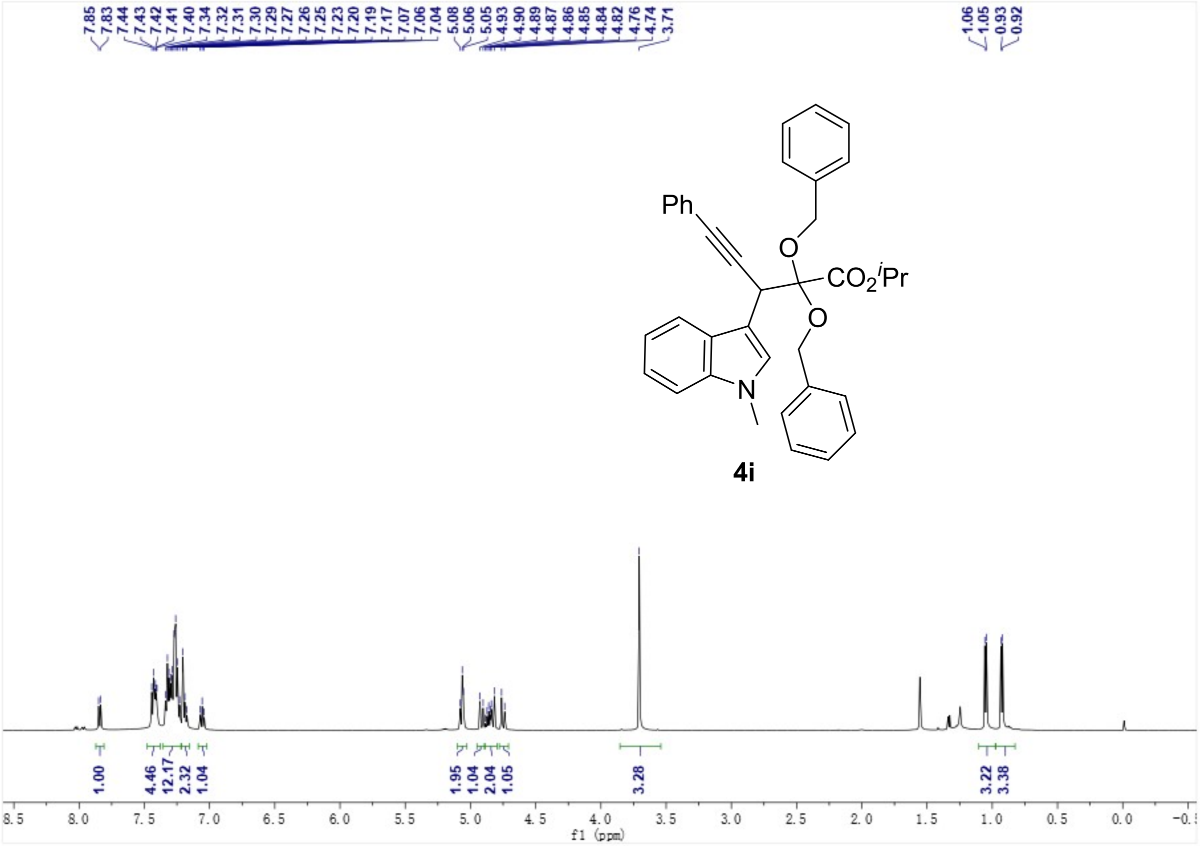
4g



4g



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7.06
7.04
5.08
5.06
5.05
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0.92
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CO2iPr
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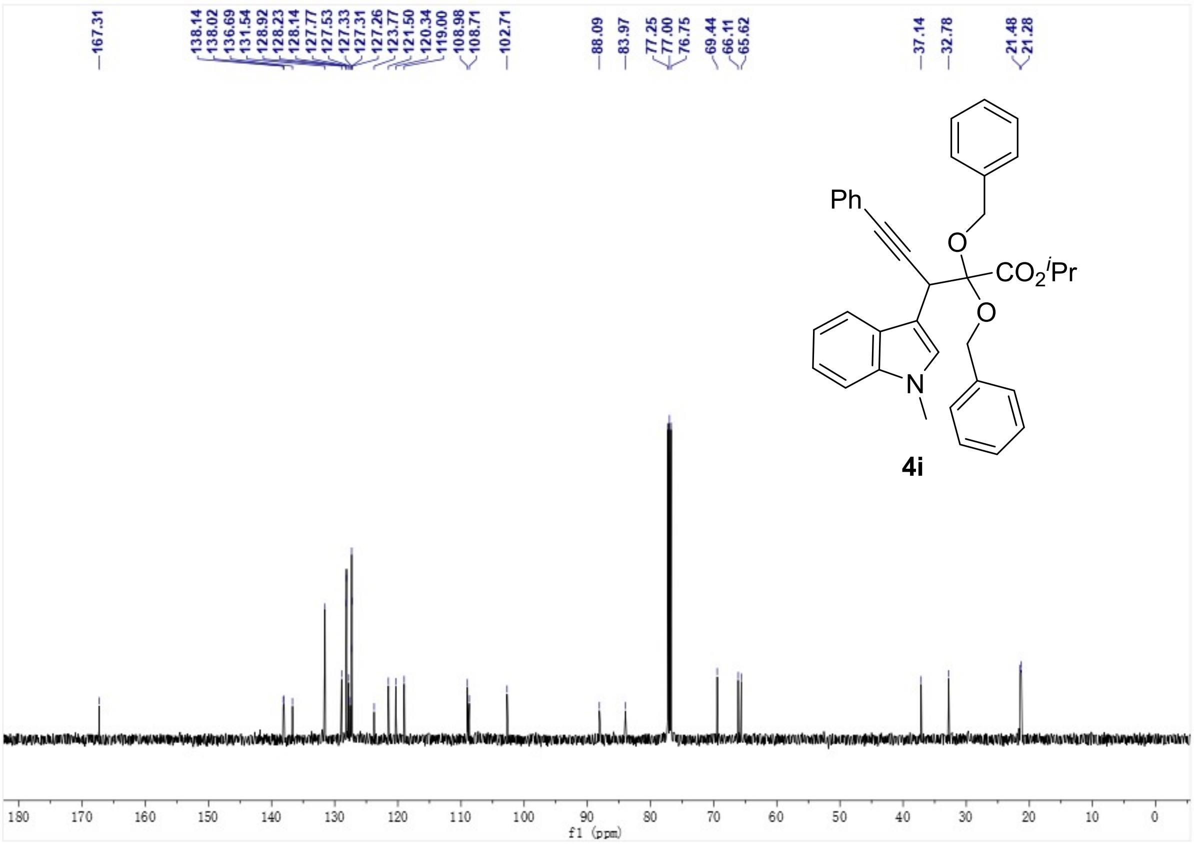
f1 (ppm)

4i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77.25
77.00
76.75
69.44
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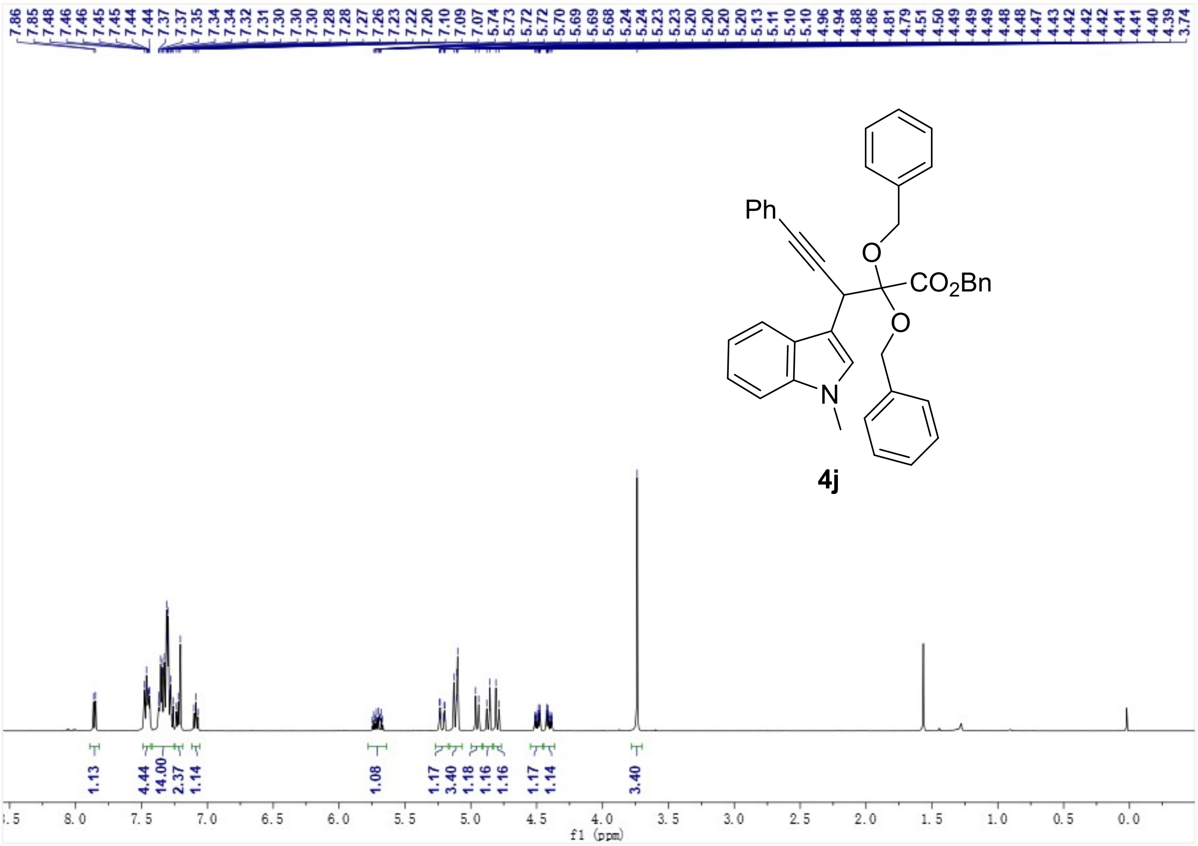
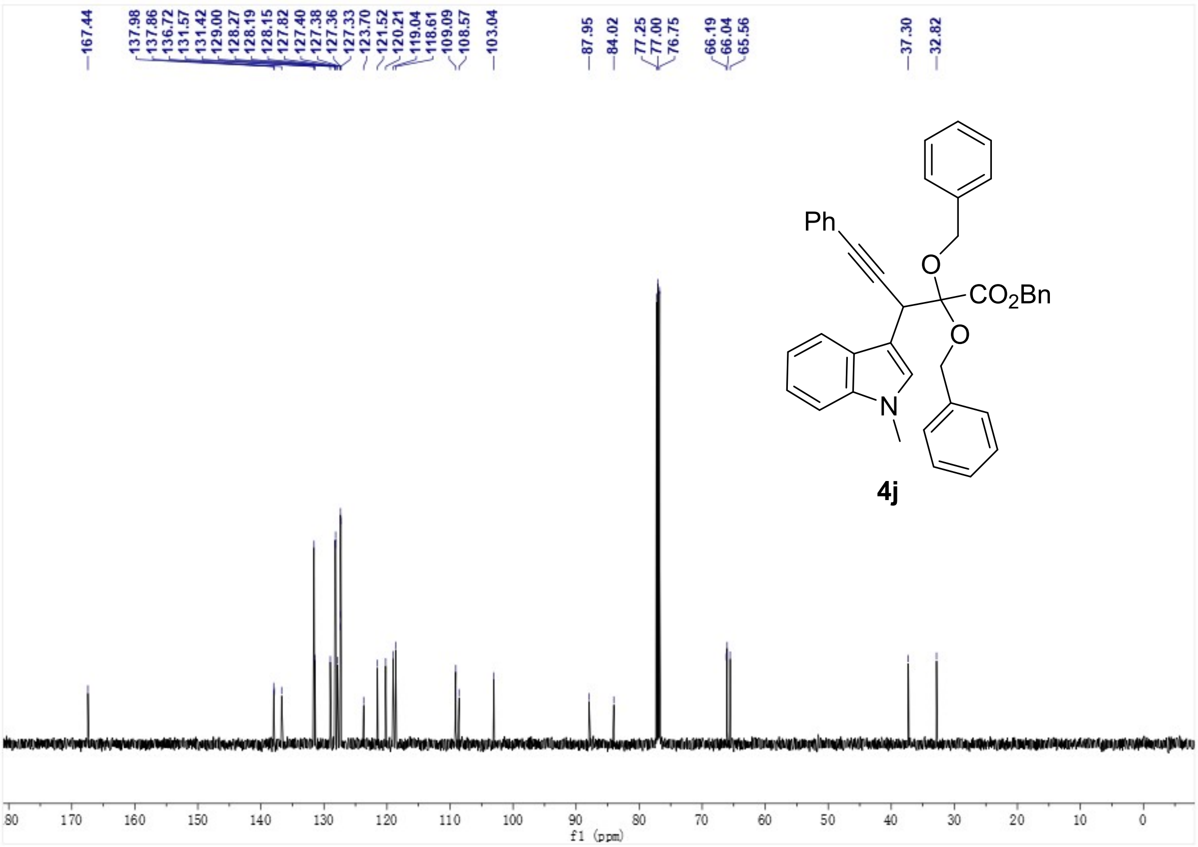
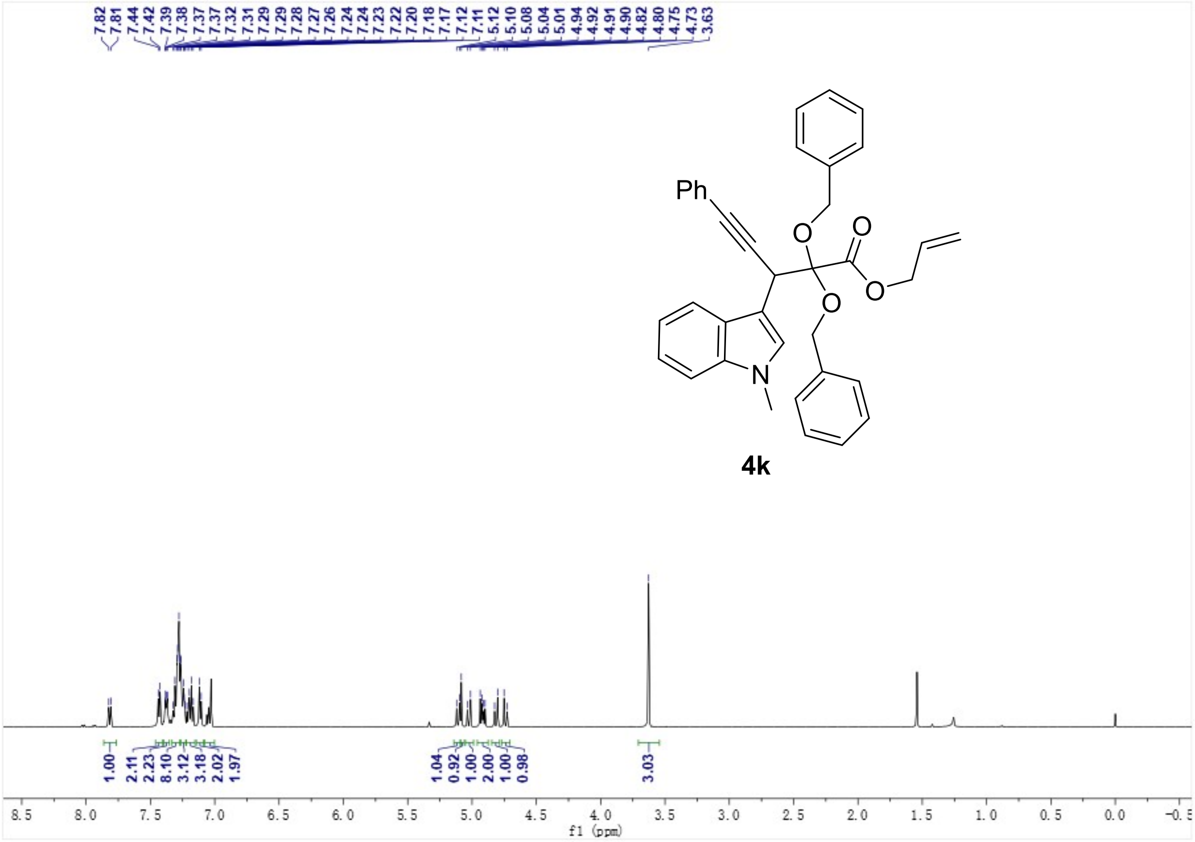
CO2iPr
O
N
f1 (ppm)

4i



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7.24
7.23
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7.18
7.17
7.12
7.11
5.12
5.10
5.08
5.04
5.01
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4.90
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Ph
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O
O
O
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4k
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8.10
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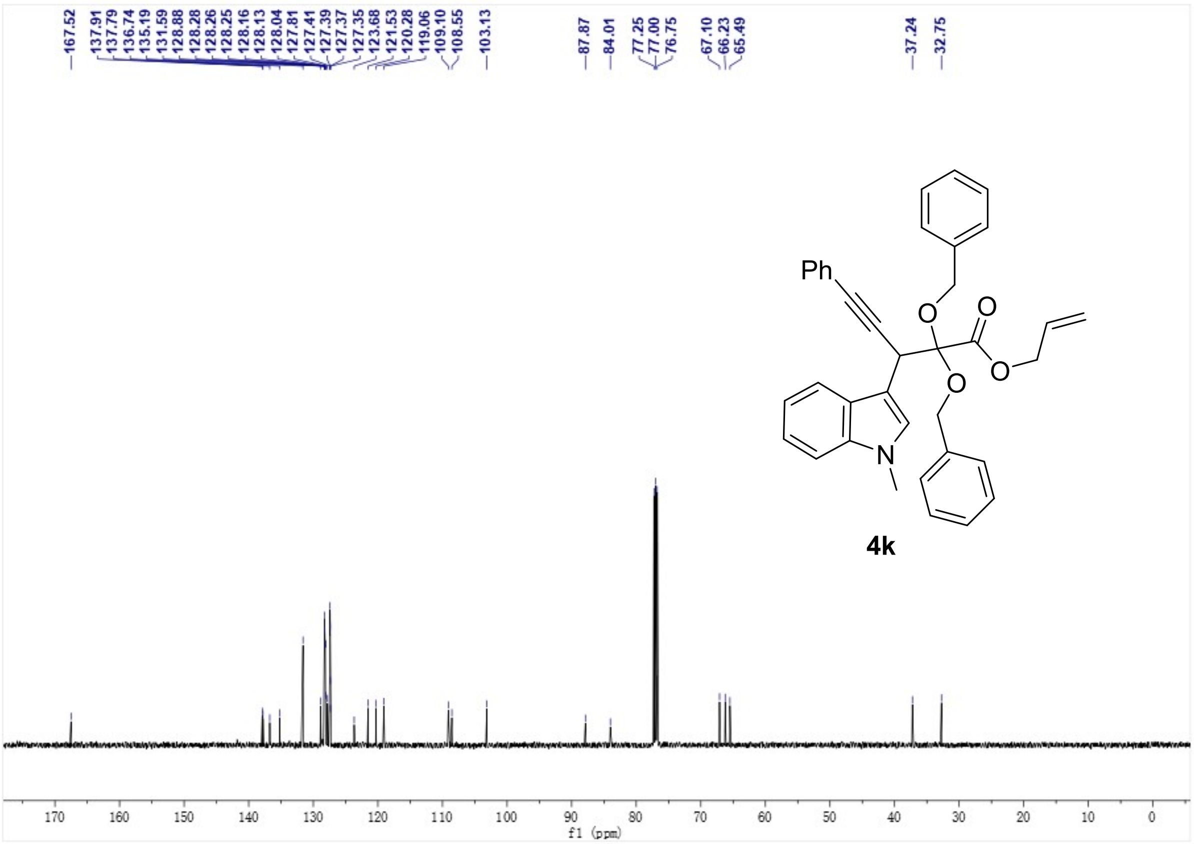
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127.39
127.37
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103.13
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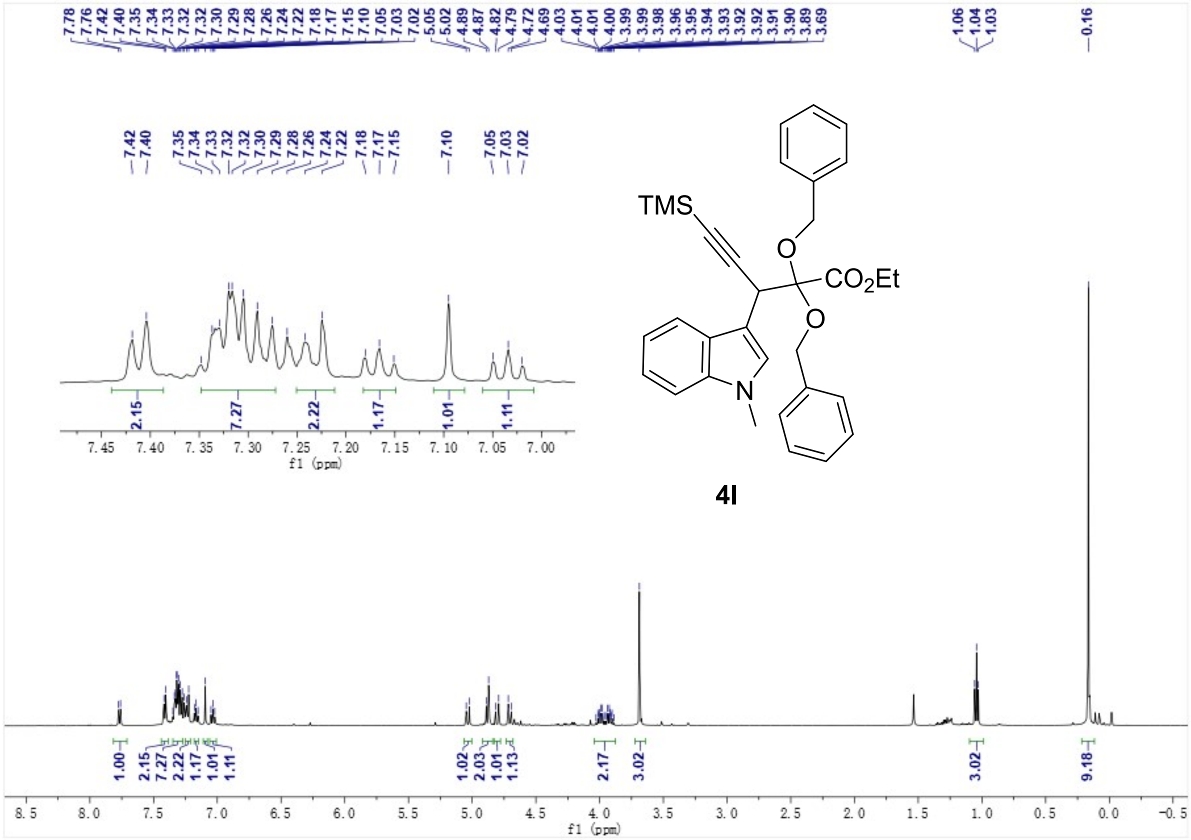
4k
f1 (ppm)



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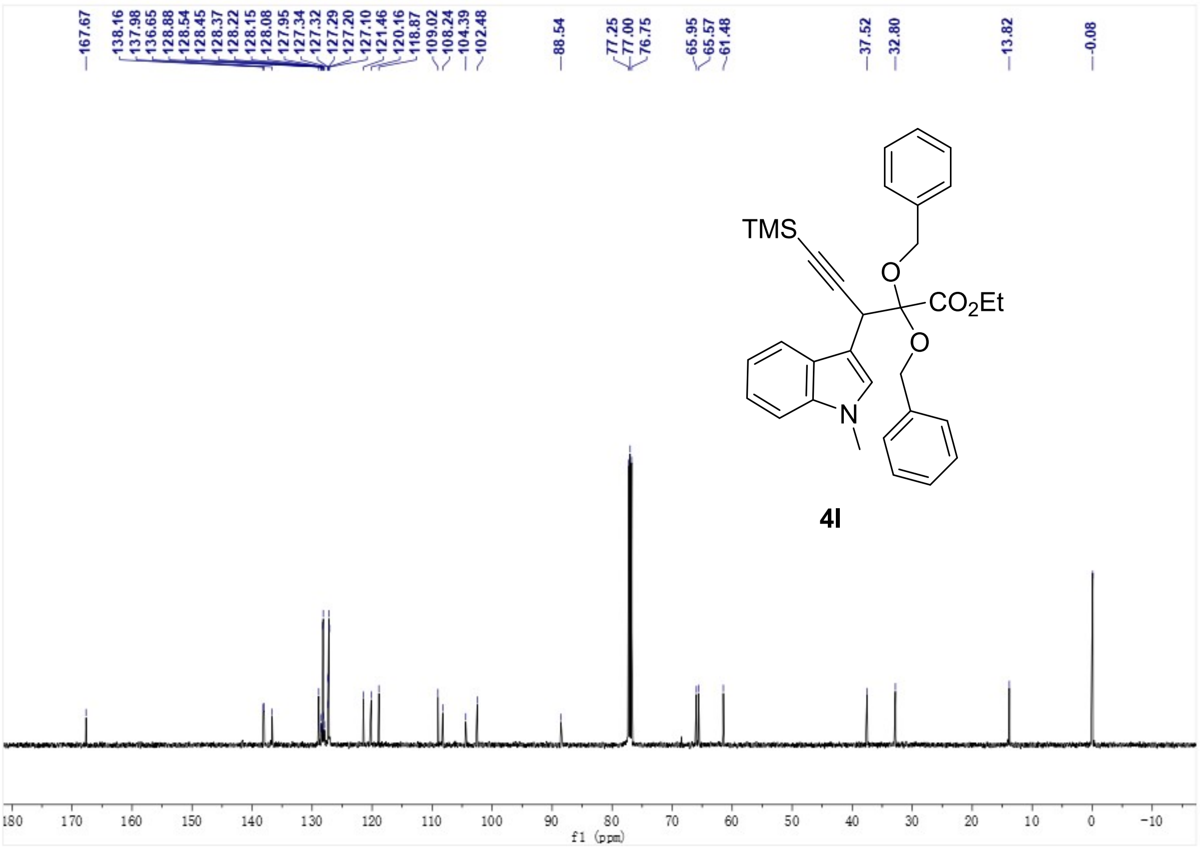

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N
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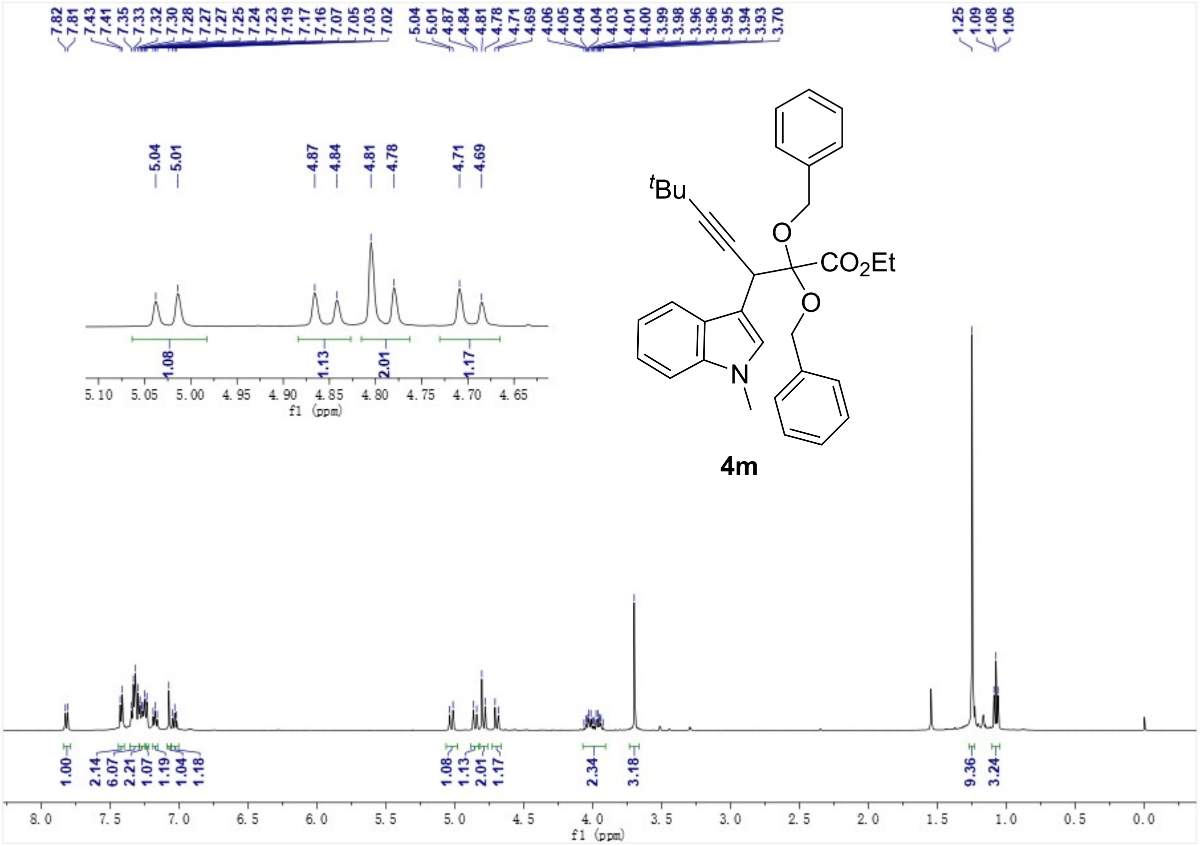
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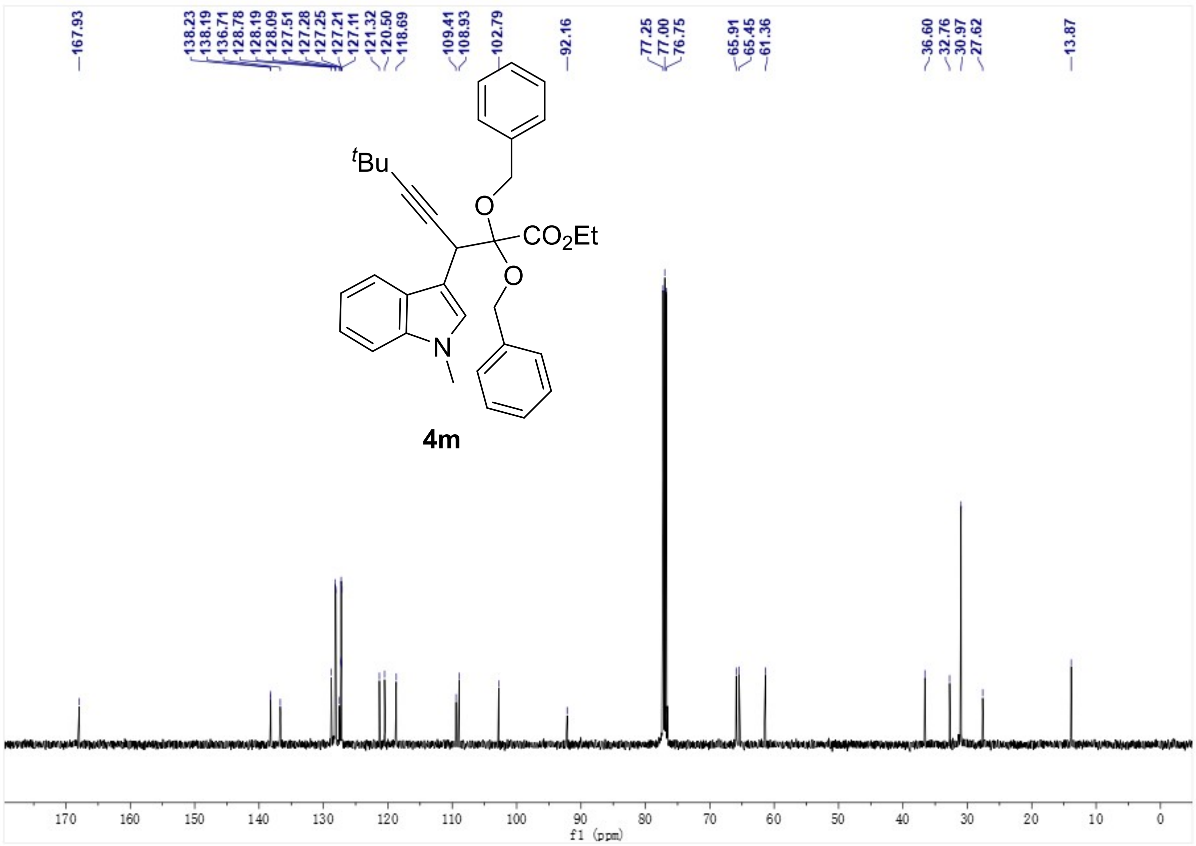
O
N
4m
f1 (ppm)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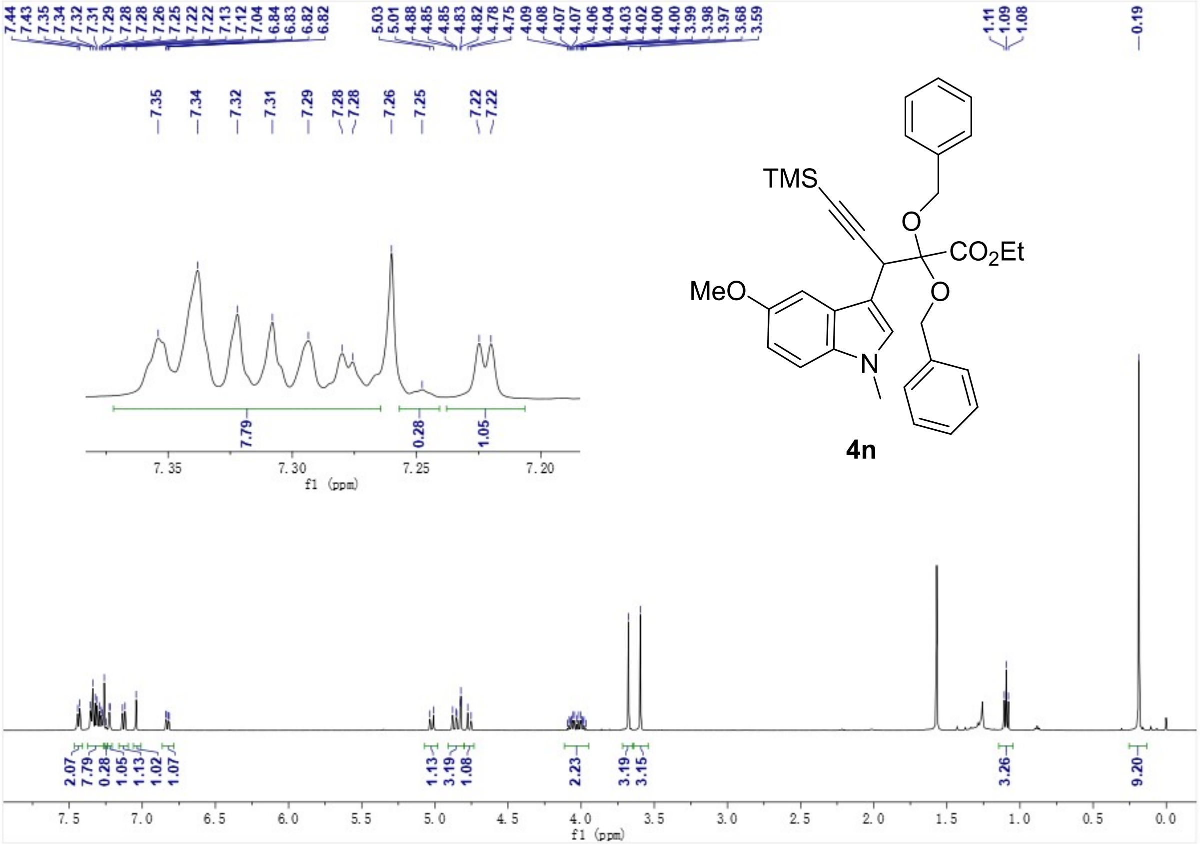
tBu
CO2Et
O
N
4m
f1 (ppm)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1.11 1.09 1.08
0.19
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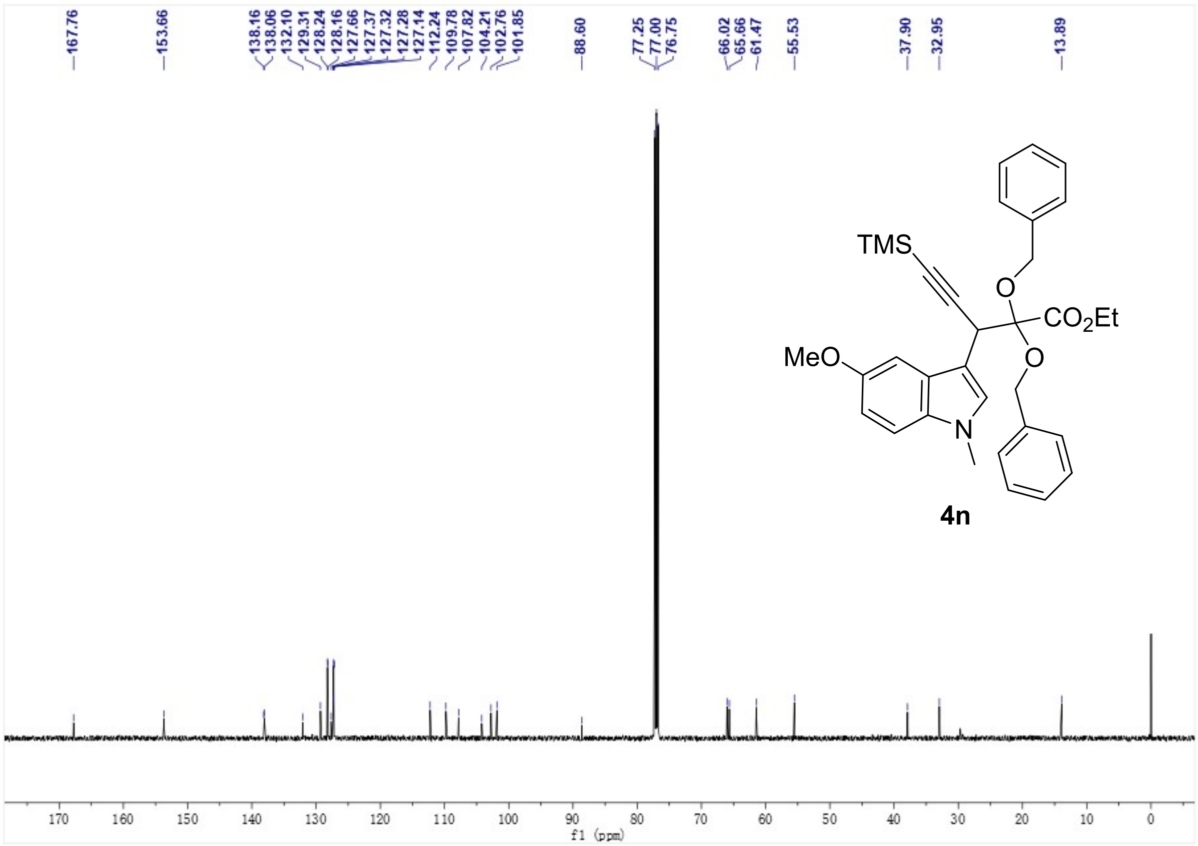
MeO
N
O
CO2Et
4n
7.79
0.28
1.05
f1 (ppm)
2.07 7.79 0.28 1.05 1.13 1.02 1.07
1.13 3.19 1.08
2.23
3.19 3.15
3.26
9.20
f1 (ppm)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88.60
77.25 77.00 76.75
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55.53
37.90 32.95
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MeO
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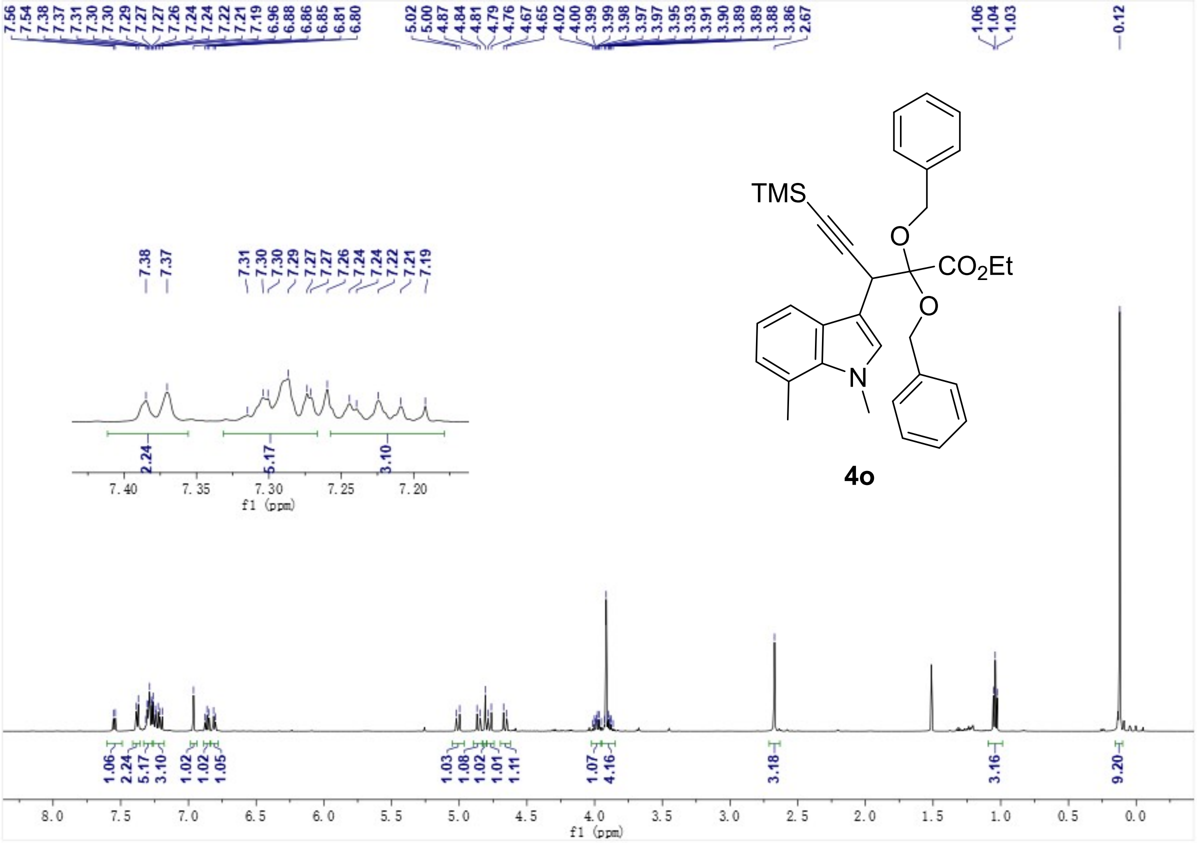
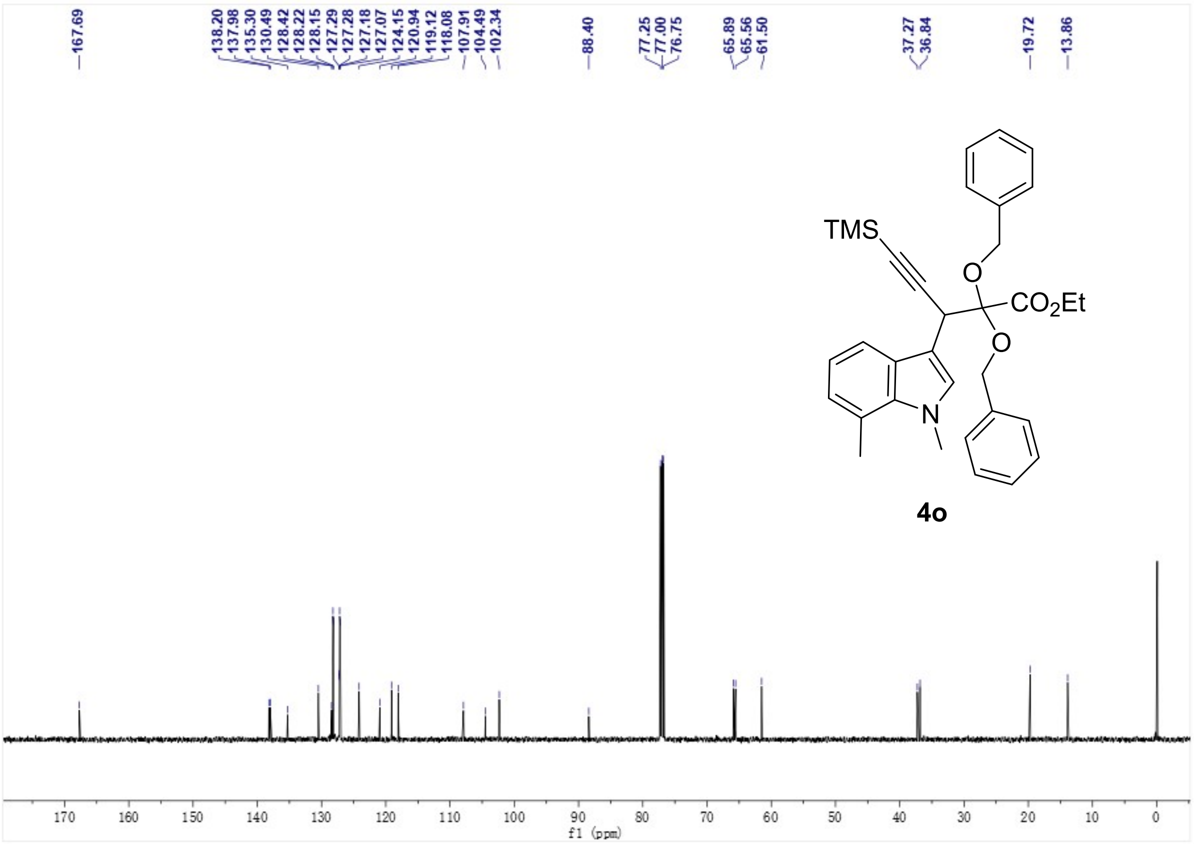
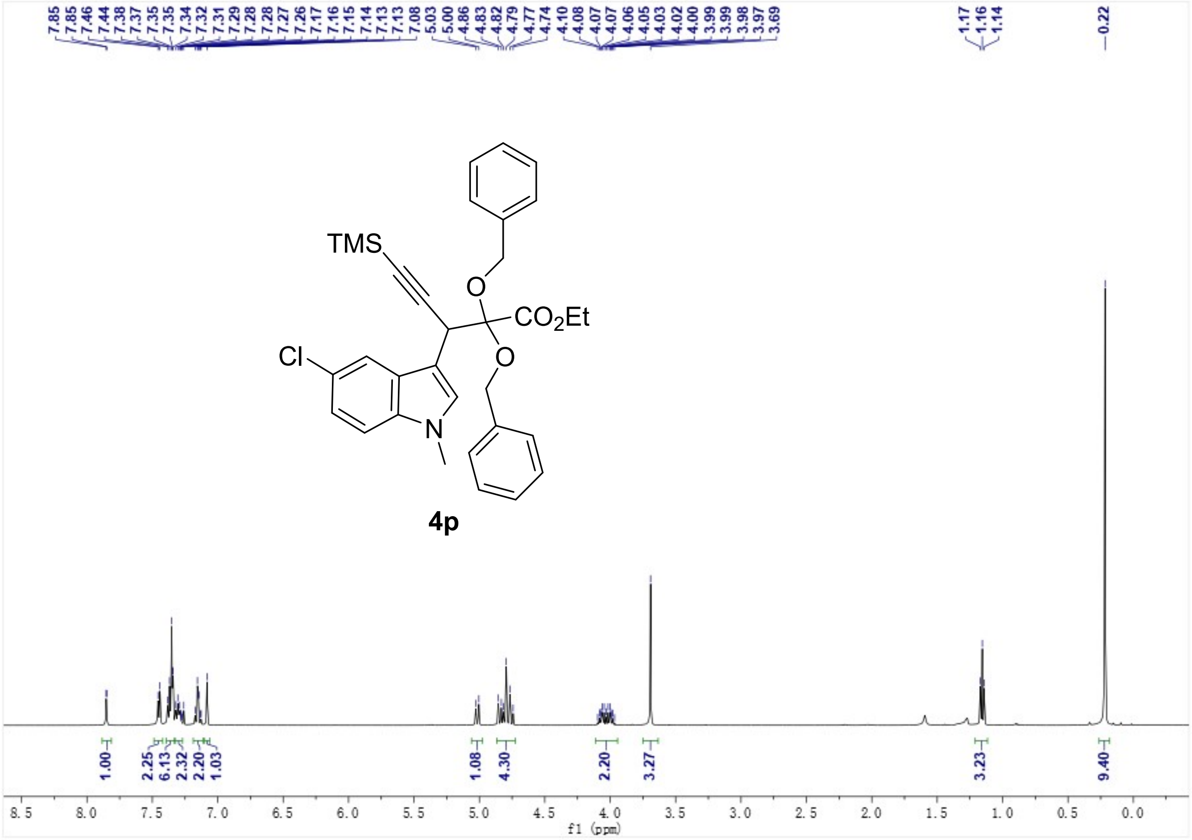
CO2Et
4n
f1 (ppm)



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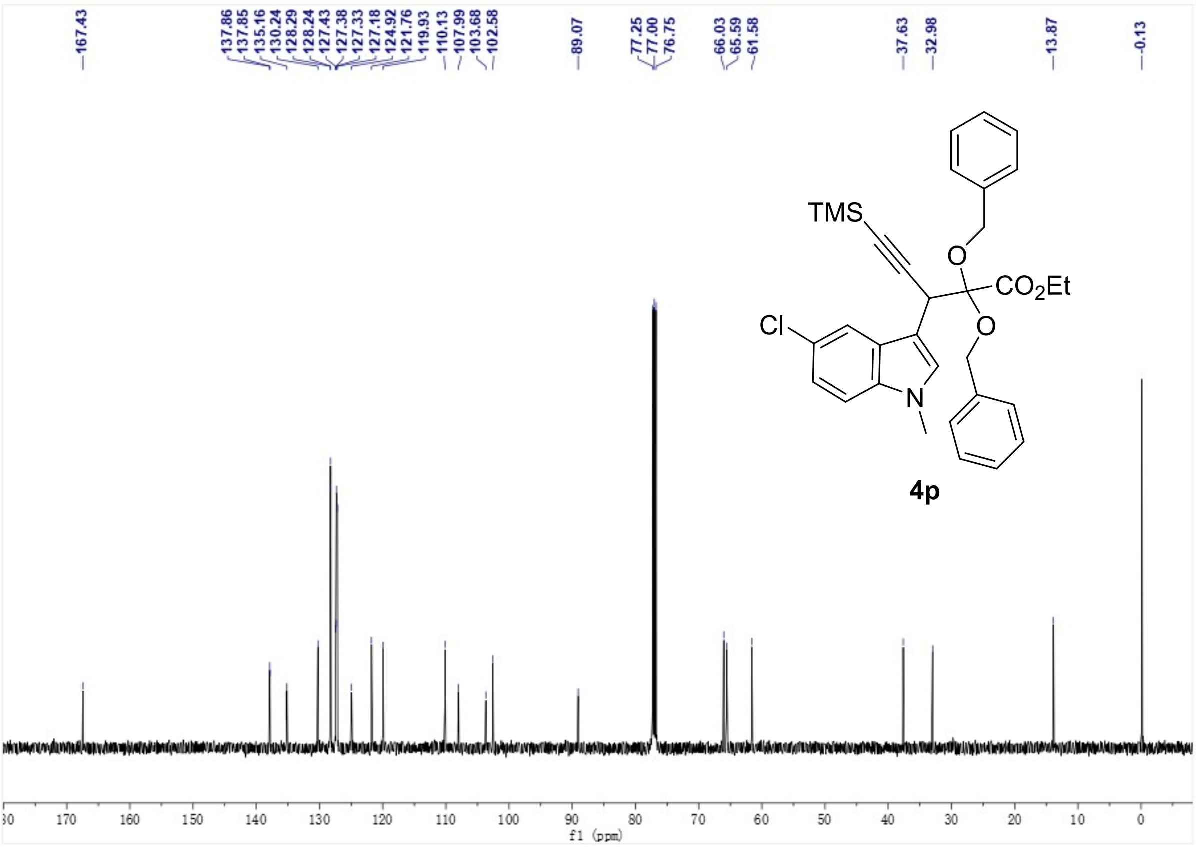
CO2Et
Cl
N
4p
f1 (ppm)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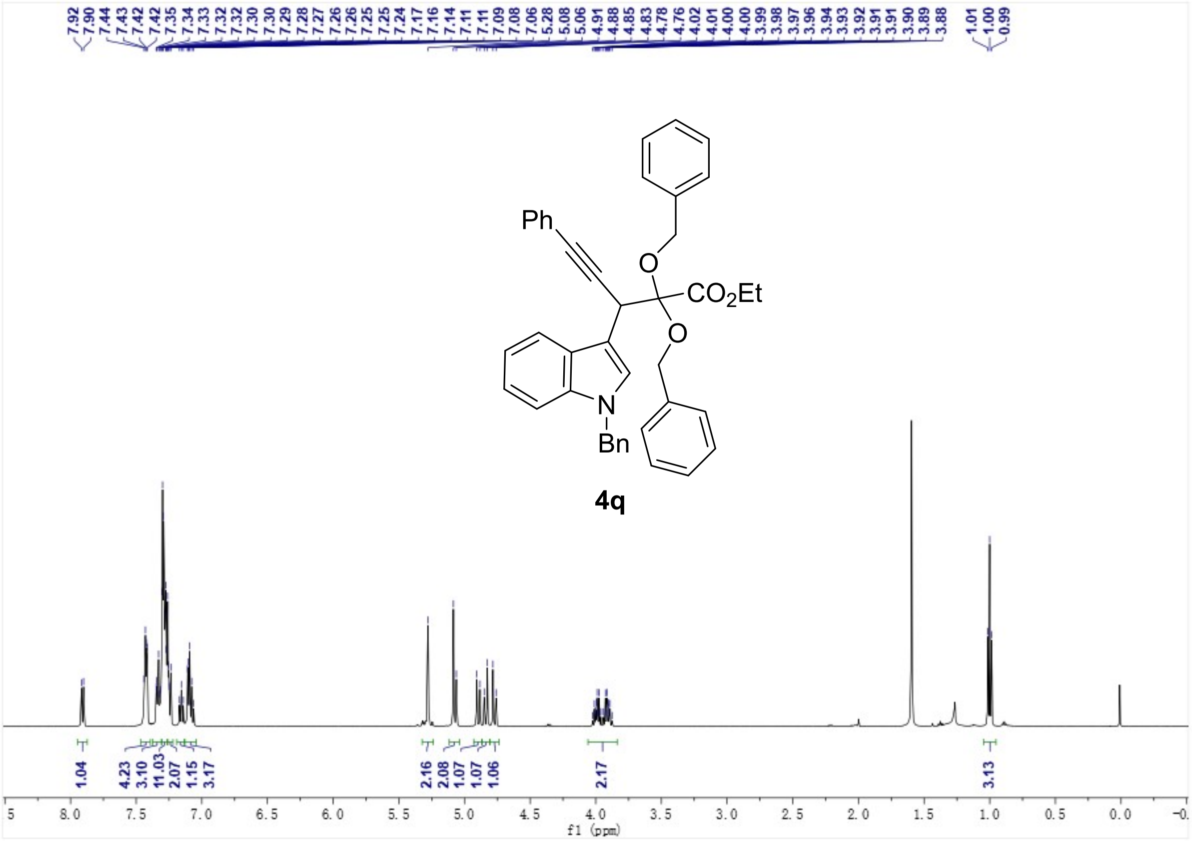
CO2Et
Cl
N
4p
f1 (ppm)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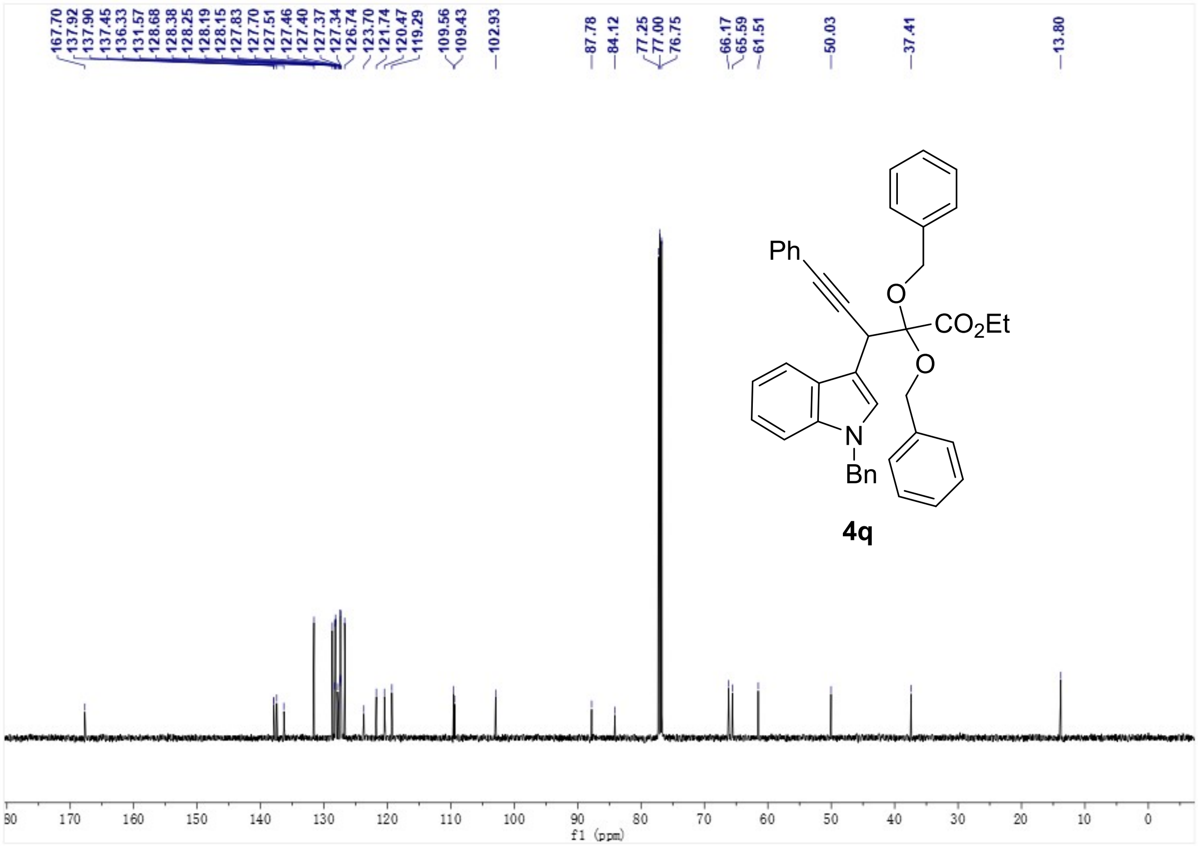
7.27
7.26
7.26
7.25
7.25
7.24
7.17
7.16
7.14
7.11
7.09
7.08
7.06
5.28
5.08
5.06
4.91
4.88
4.85
4.83
4.78
4.76
4.02
4.01
4.00
4.00
3.99
3.98
3.97
3.96
3.94
3.93
3.92
3.91
3.91
3.90
3.89
3.88
1.01
1.00
0.99
Ph
O
CO_2Et
O
N
Bn
4q
1.04
4.23
3.10
11.03
2.07
1.15
3.17
2.16
2.08
1.07
1.07
1.06
2.17
3.13
f1 (ppm)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127.46
127.40
127.37
127.34
126.74
123.70
121.74
120.47
119.29
109.56
109.43
102.93
87.78
84.12
77.25
77.00
76.75
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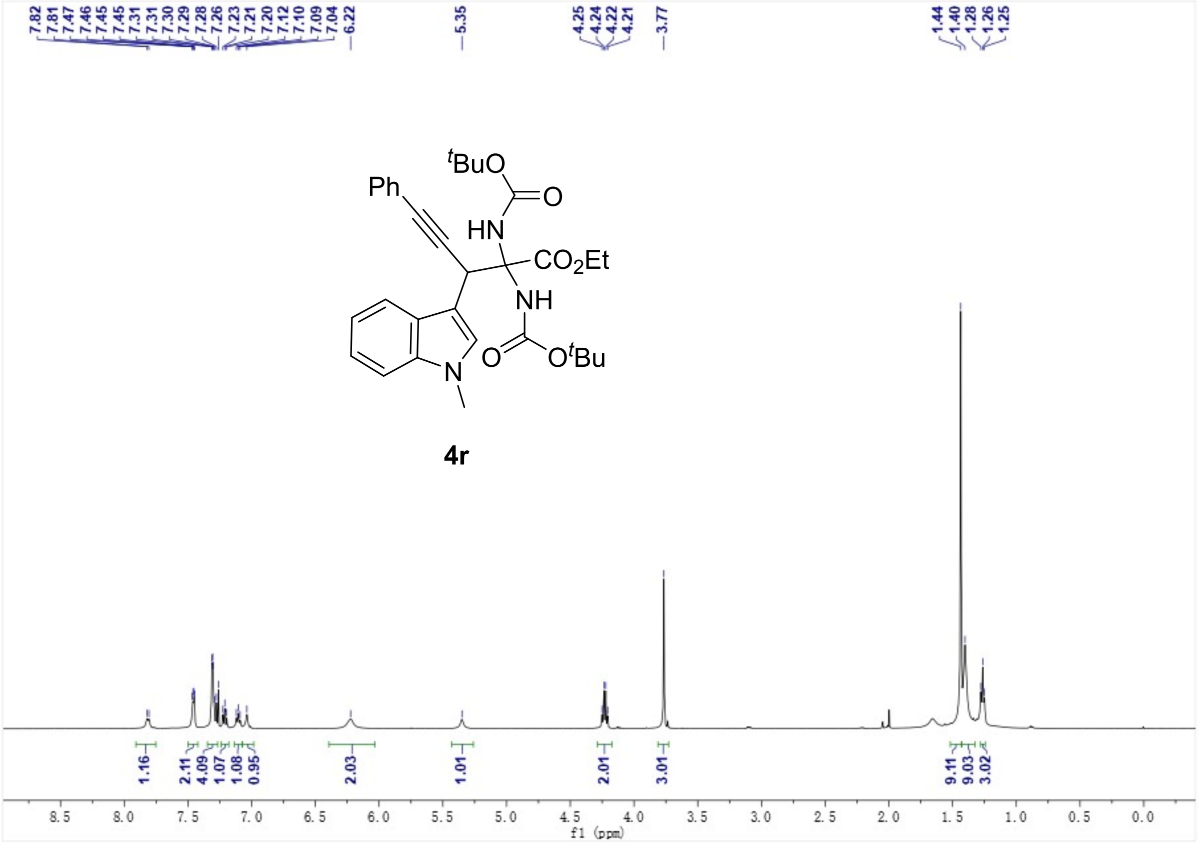
50.03
37.41
13.80
Ph
O
CO_2Et
O
N
Bn
4q
f1 (ppm)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7.20
7.12
7.10
7.09
7.04
6.22
5.35
4.25
4.24
4.22
4.21
3.77
1.44
1.40
1.28
1.26
1.25
tBuO
Ph
O
HN
CO2Et
NH
O
OtBu
N
4r
1.16
2.11
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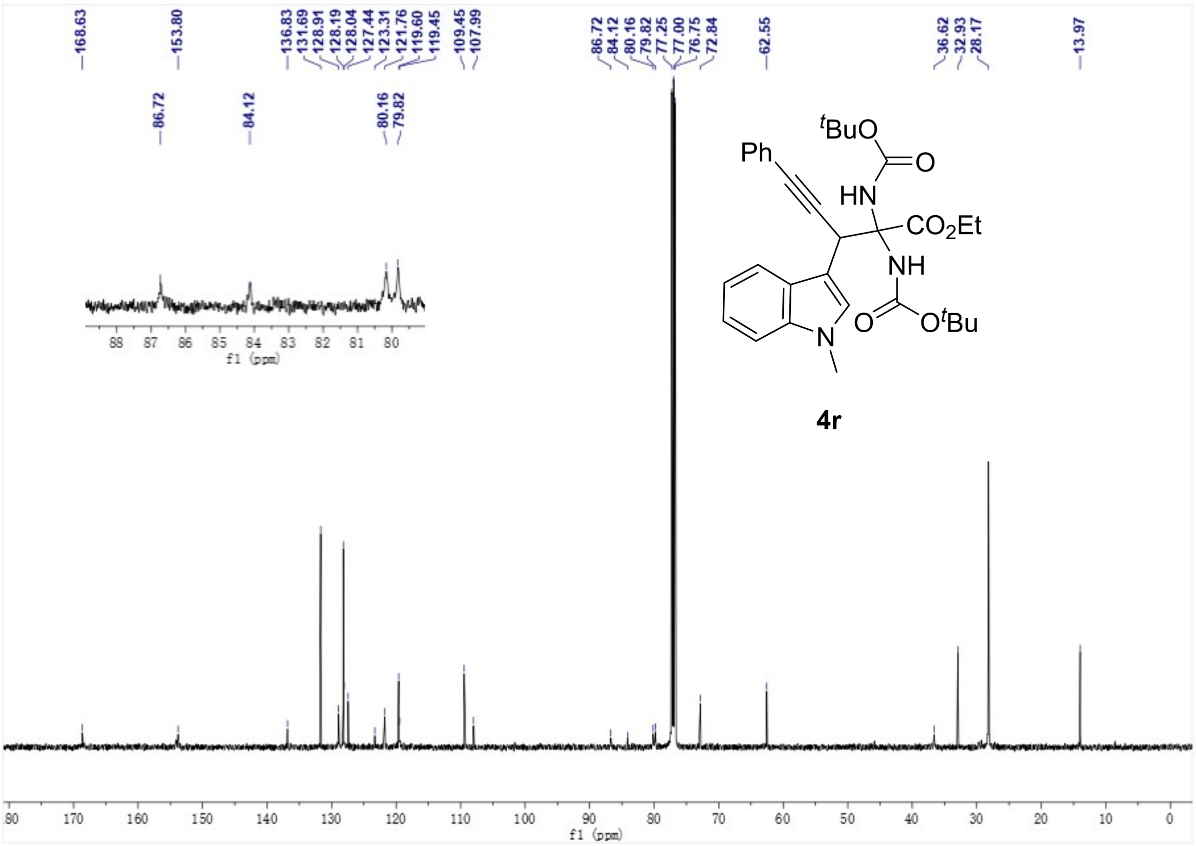
1.01
2.01
3.01
9.11
9.03
3.02
f1 (ppm)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107.99
86.72
84.12
80.16
79.82
77.25
77.00
76.75
72.84
62.55
36.62
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28.17
13.97
tBuO
Ph
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HN
CO2Et
NH
O
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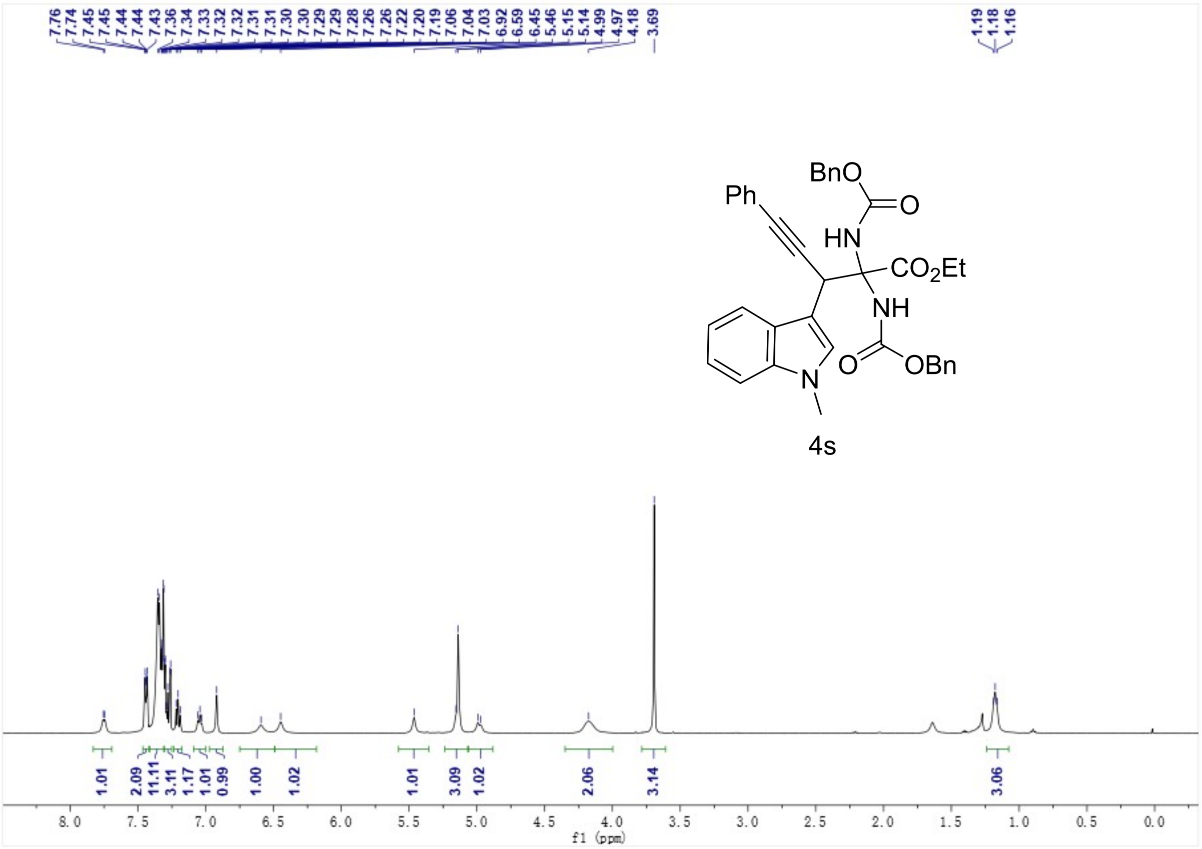
N
4r
f1 (ppm)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1.19 1.18 1.16
Ph
BnO
O
HN
CO2Et
NH
O
OBn
N
4s
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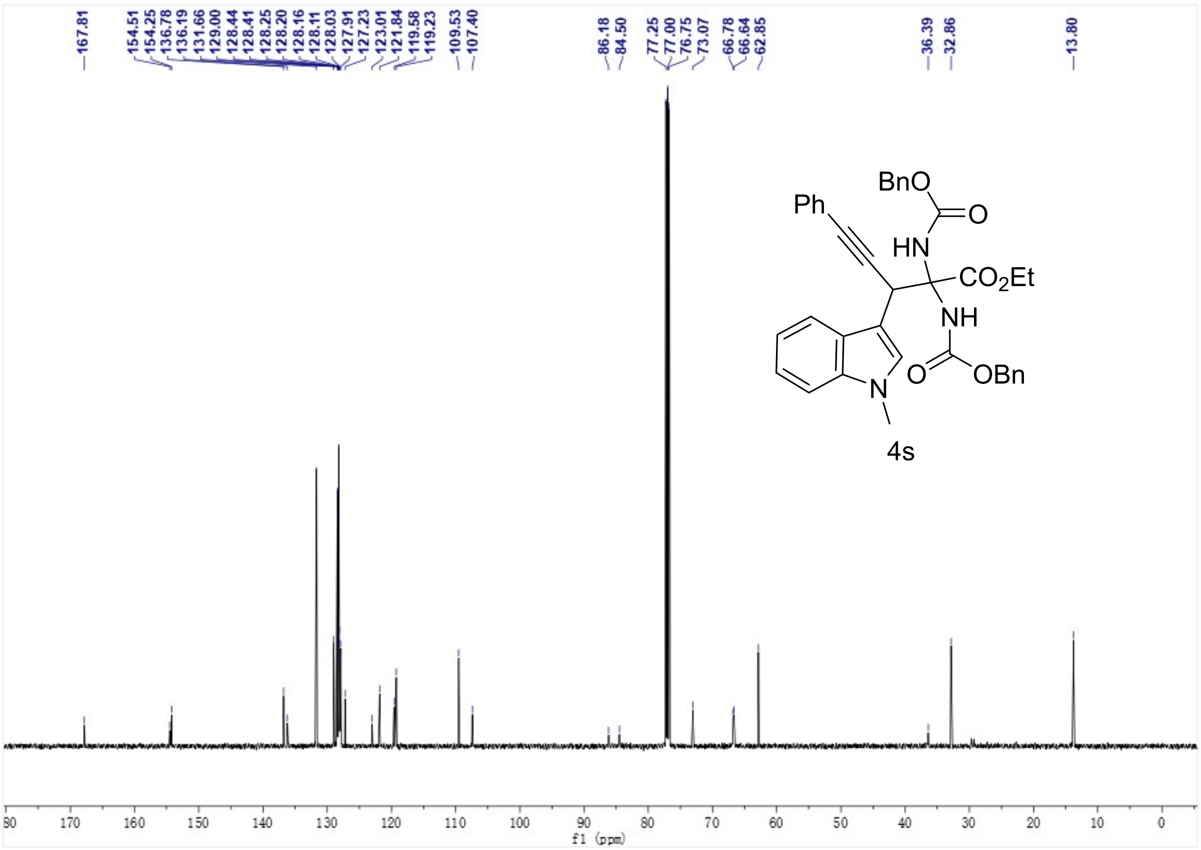
f1 (ppm)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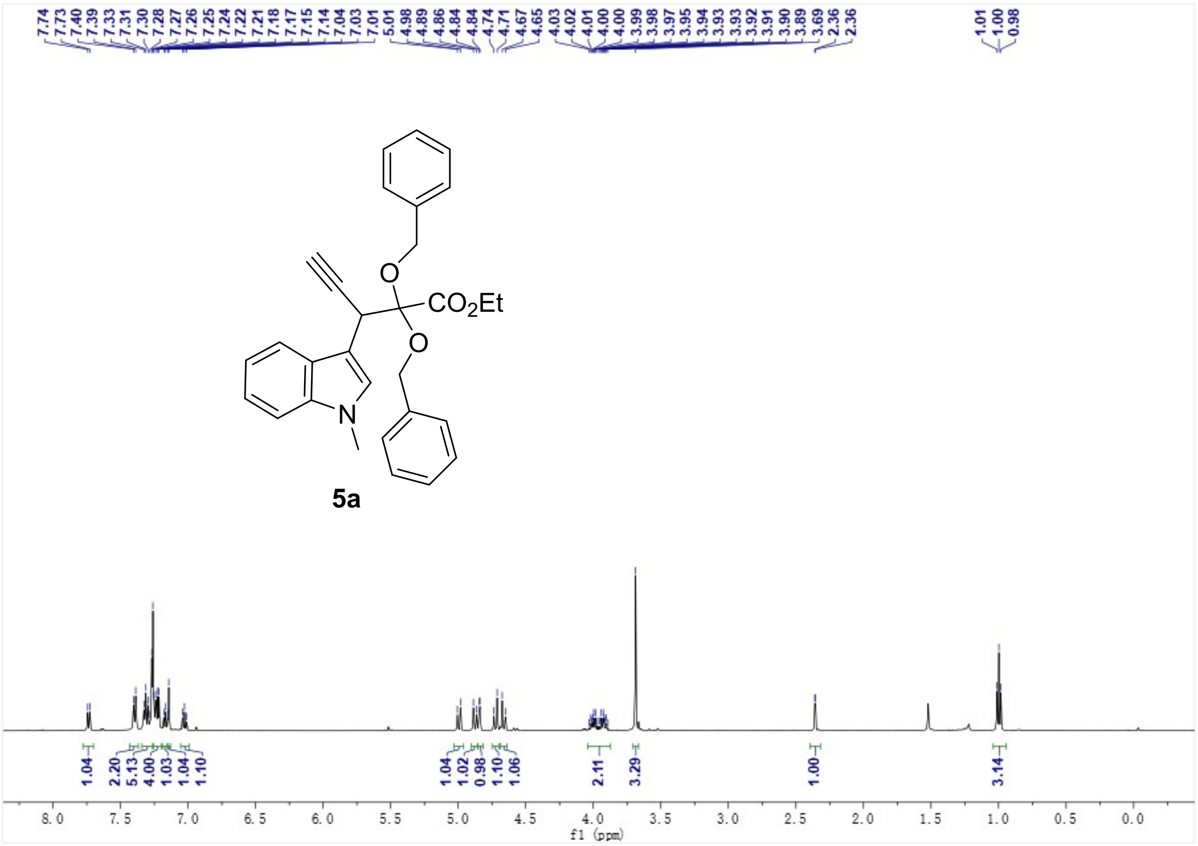
86.18 84.50
77.25 77.00 76.75 73.07 66.78 66.64 62.85
36.39 32.86
13.80
Ph
BnO
O
HN
CO2Et
NH
O
OBn
N
4s
f1 (ppm)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7.21
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7.17
7.15
7.14
7.04
7.03
7.01
5.01
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4.89
4.86
4.84
4.84
4.74
4.71
4.67
4.65
4.03
4.02
4.01
4.00
4.00
3.99
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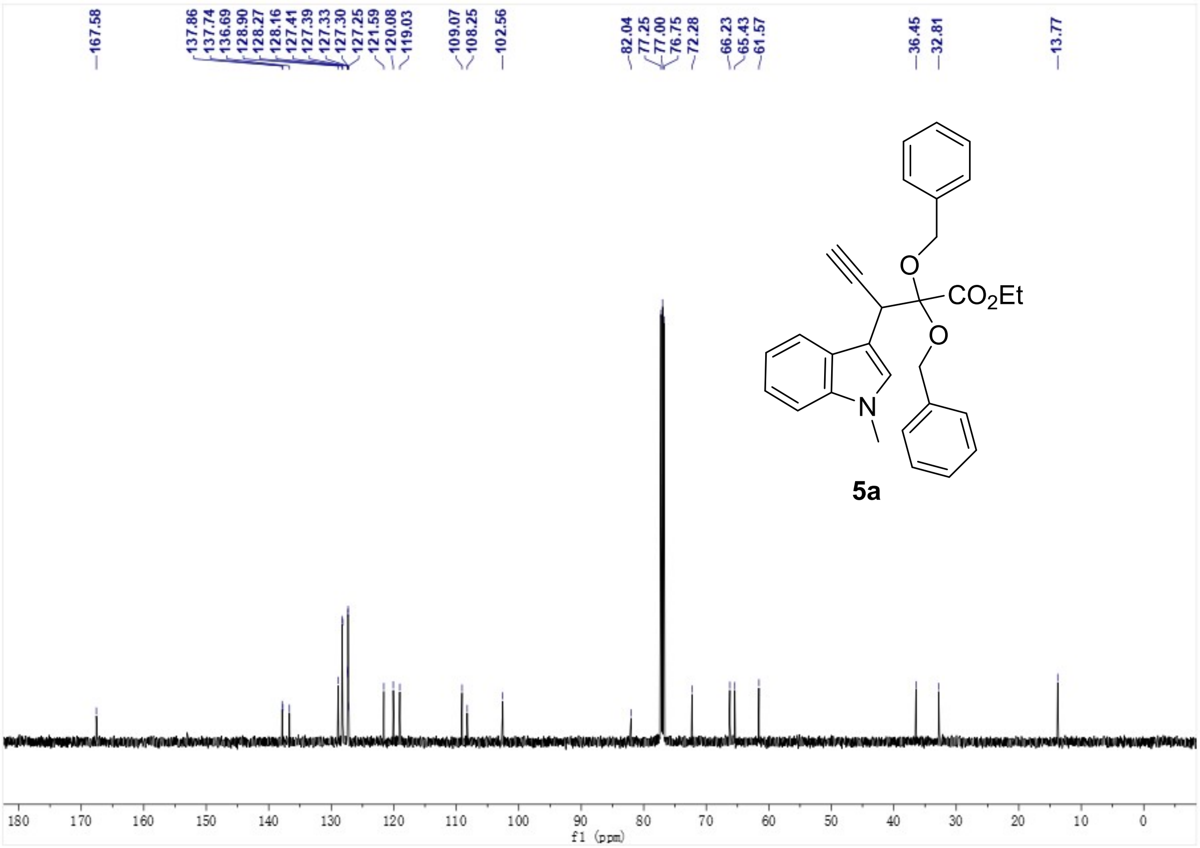
3.97
3.95
3.94
3.93
3.93
3.92
3.91
3.90
3.89
3.69
2.36
2.36
1.01
1.00
0.98
CO2Et
O
O
N
5a
1.04
2.20
5.13
4.00
1.03
1.04
1.10
1.04
1.02
0.98
1.10
1.06
2.11
3.29
1.00
3.14
f1 (ppm)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127.41
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127.33
127.30
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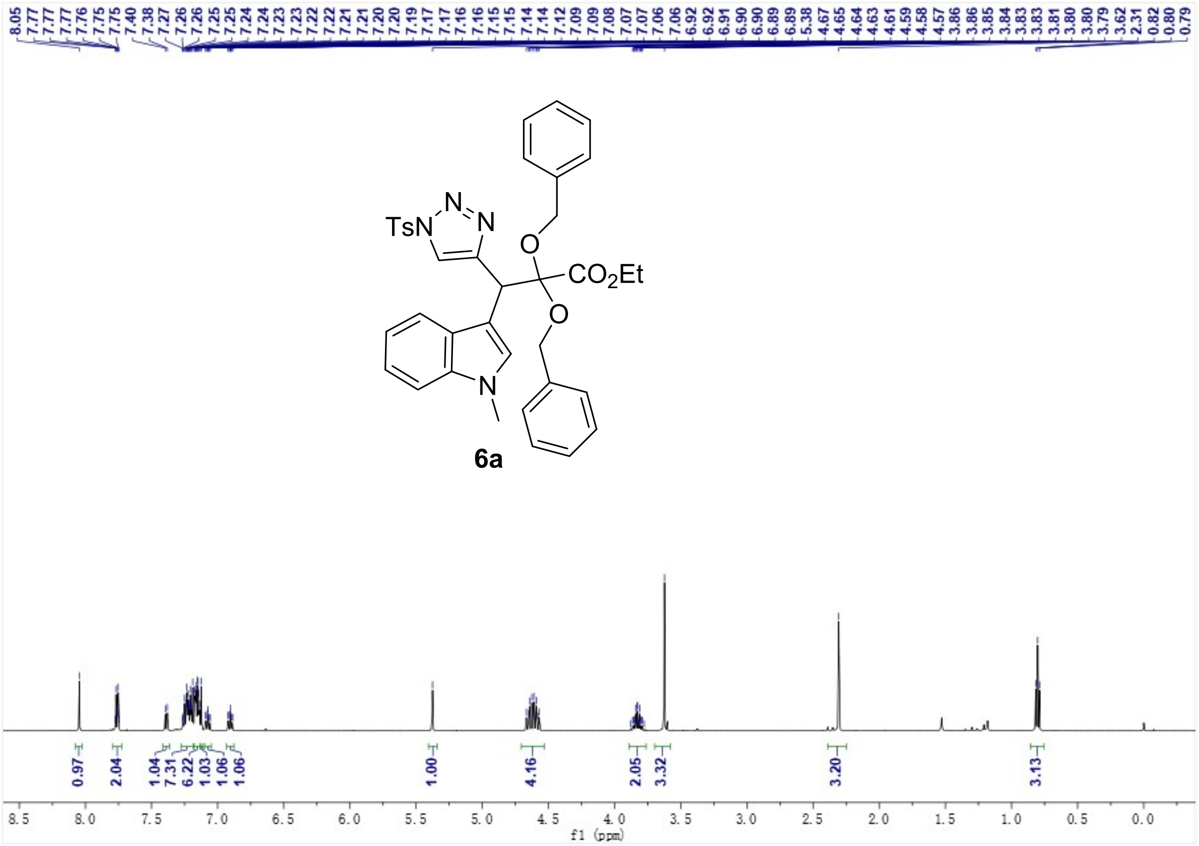
121.59
120.08
119.03
109.07
108.25
102.56
82.04
77.25
77.00
76.75
72.28
66.23
65.43
61.57
36.45
32.81
13.77
CO2Et
O
O
N
5a
f1 (ppm)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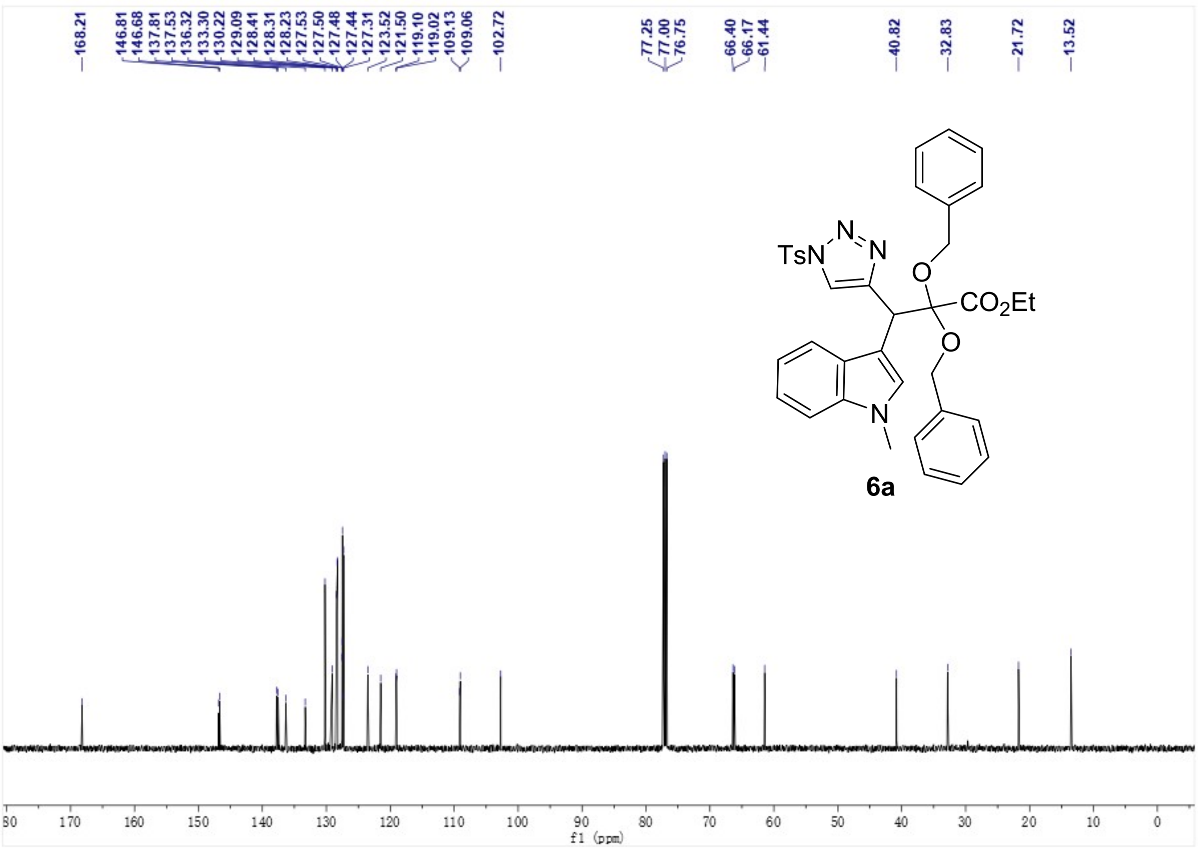
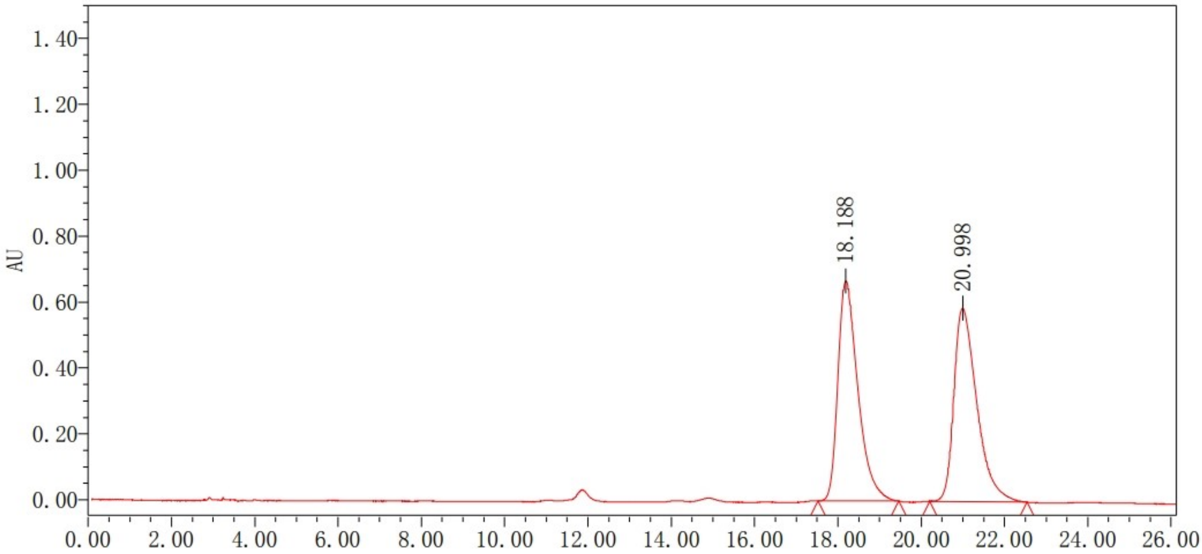
TsN N N O O CO2Et N
6a
0.97 2.04 1.04 7.31 6.22 1.03 1.06 1.06 1.00 4.16 2.05 3.32 3.20 3.13
f1 (ppm)

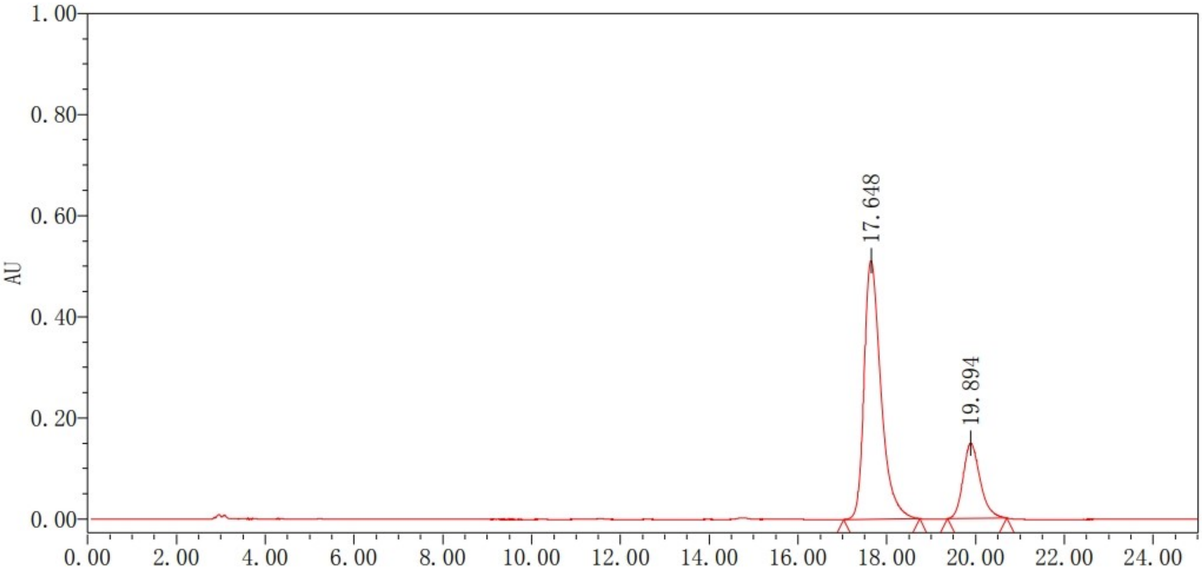

168.21 146.81 146.68 137.81 137.53 136.32 133.30 130.22 129.09 128.41 128.31 128.23 127.53 127.50 127.48 127.44 127.31 123.52 121.50 119.10 119.02 109.13 109.06 102.72 77.25 77.00 76.75 66.40 66.17 61.44 40.82 32.83 21.72 13.52
TsN N N O O CO2Et N
6a
f1 (ppm)

10. Copies of HPLC Spectra of Products 4a, 4s

HPLC chromatograms of **4a**



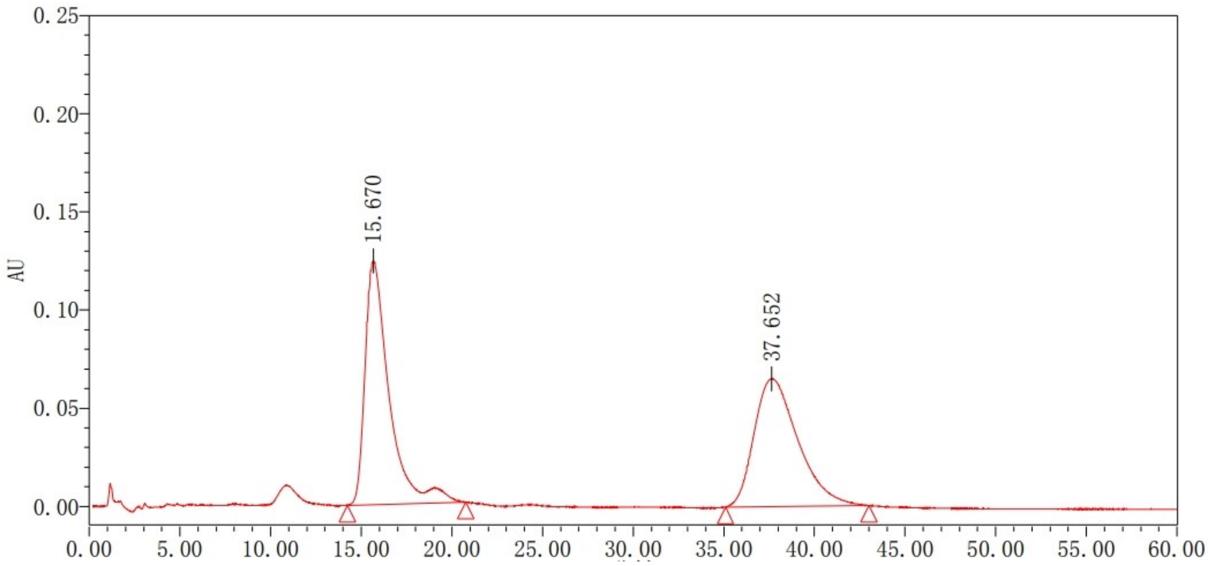
Peak#	Retention Time /min	Area / μ AU*s	Height / μ AU	Area (%)
1	18.188	22430987	666852	49.99
2	20.998	22440596	586258	50.01



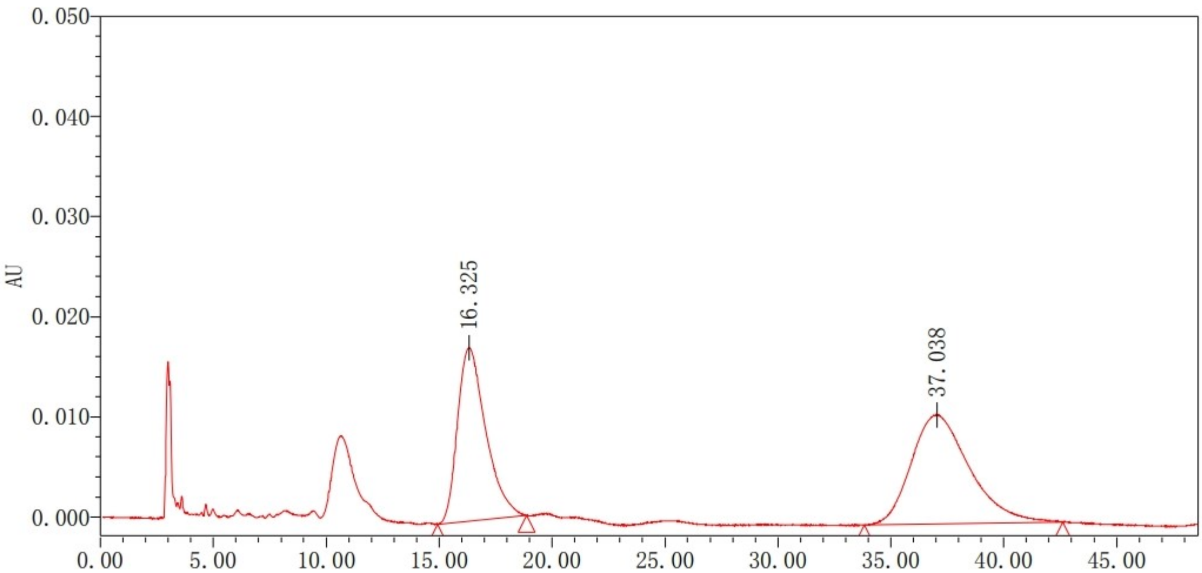
Peak#	Retention Time /min	Area / μ AU*s	Height / μ AU	Area (%)
1	17.648	13442458	511587	77.05
2	19.894	4004640	148837	22.95

HPLC conditions for determination of enantiomeric excess: Daicel Chiralcel IA, λ = 254.0 nm, hexane : 2-propanol = 98 : 2, flow rate = 1.0 mL/min, t_{major} = 17.6 min, t_{minor} = 19.9 min;

HPLC chromatograms of **4s**



Peak#	Retention Time /min	Area / μ AU*s	Height / μ AU	Area (%)
1	15.670	11526546	124094	51.36
2	37.652	10916998	65065	48.64



Peak#	Retention Time /min	Area / μ AU*s	Height / μ AU	Area (%)
1	16.325	1505152	17299	43.53
2	37.038	1952454	10902	56.47

HPLC conditions for determination of enantiomeric excess: Daicel Chiralcel OD-H, λ = 254.0 nm, hexane : 2-propanol = 80 : 20, flow rate = 1.0 mL/min, t_{minor} = 16.3 min, t_{major} = 37.0 min;