Supporting Information

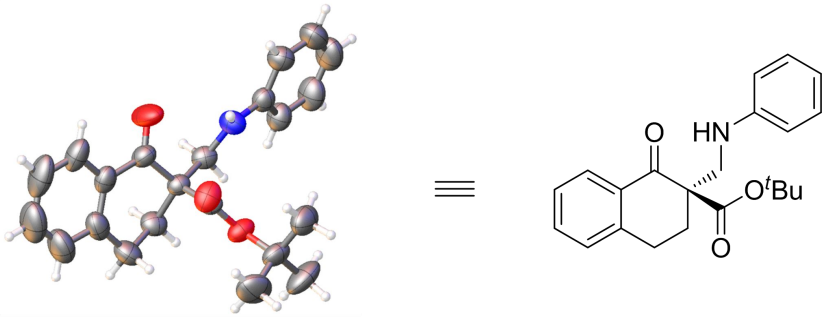
Contents:

1. General information

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomeric excesses (*ee*) were determined by chiral HPLC analysis on Daicel Chiralpak IC or IA in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). The $Ni(ClO_4)_2 \cdot 6H_2O$, $Mg(OTf)_2$ is commercially available, and used without further purification. The CH_2Cl_2 was purified by usual methods before use. The α-tetralone-derived β-keto esters **1** and amides **2** were prepared by previously reported methods.[1] 1,3,5-triaryl-1,3,5-triazinanes **3** were prepared according to reported methods.[2] The *N,N'*-dioxide ligands **L** were synthesized according to the method reported by our group.[3]

2. The X-ray data for 4a and 5a.

(1) The X-ray data for 4a



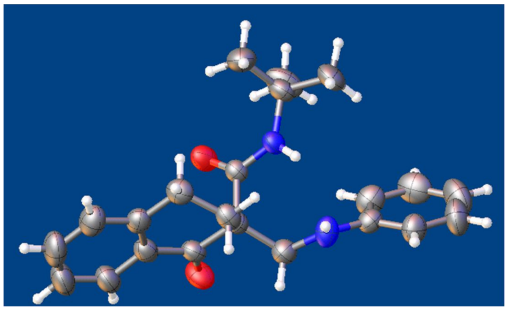
Single crystal of **4a** [$C_{22}H_{25}NO_3$] was obtained from the mixed solvents of ethyl acetate and petroleum ether. The absolute configuration is *R*. Mp 99–100 °C; $[\alpha]_D^{19}$ = 109.1 (c = 0.54, CH_2Cl_2). CCDC 1448521 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystal data and structure refinement for fxm-lxj.

Identification code	fxm-lxj
Empirical formula	$C_{22}H_{25}NO_3$

Formula weight	351.43
Temperature/K	217.05(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.05221(8)
b/Å	17.0223(3)
c/Å	19.5981(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2019.05(6)
Z	4
ρcalcg/cm^3	1.156
μ/mm^{-1}	0.610
F(000)	752.0
Crystal size/mm^3	0.7 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.024 to 134.104
Index ranges	$-7 \le h \le 4$, $-20 \le k \le 18$, $-19 \le l \le 23$
Reflections collected	10704
Independent reflections	3602 [R_{int} = 0.0285, R_{sigma} = 0.0203]
Data/restraints/parameters	3602/0/238
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1425
Final R indexes [all data]	R_1 = 0.0546, wR_2 = 0.1470
Largest diff. peak/hole / e Å^{-3}	0.24/-0.26
Flack parameter	0.05(9)

(2) The X-ray data for 5a



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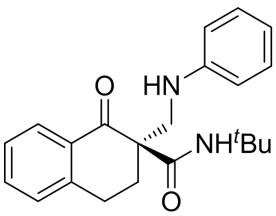


Single crystal of **5a** [$C_{22}H_{26}N_2O_2$] was obtained from the mixed solvents of ethyl acetate and petroleum ether. The absolute configuration is *R*. Mp 78–80 °C; $[\alpha]_D^{23}$ = 77.7 (c = 0.69, CH_2Cl_2). CCDC 1480808 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from

the Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

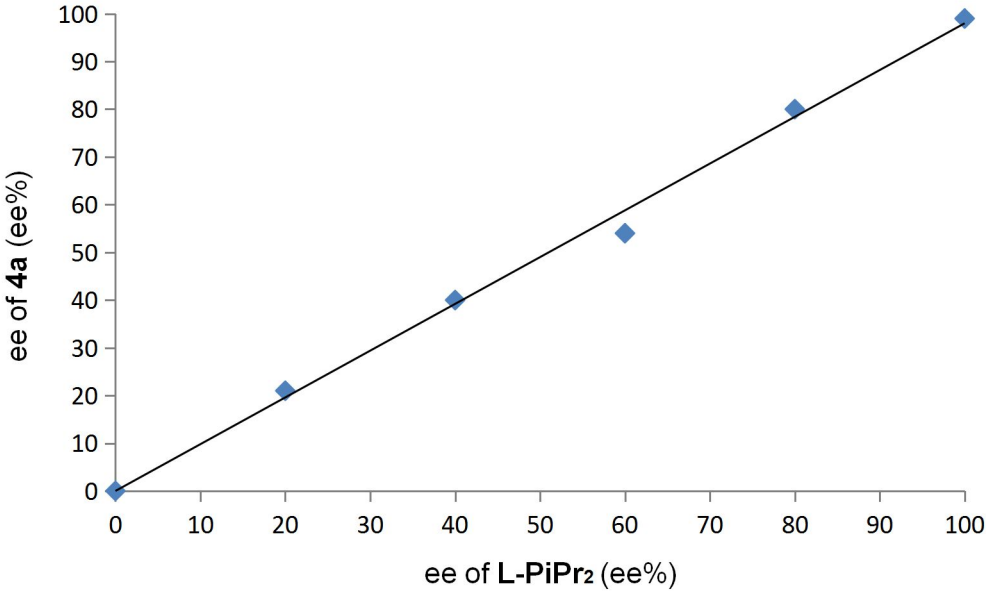
Table 2 Crystal data and structure refinement for fxm-lxj-nh-ph-5.

Identification code	fxm-lxj-nh-ph-5
Empirical formula	$C_{44}H_{52}N_4O_4$
Formula weight	700.89
Temperature/K	295.1(5)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.20362(17)
b/Å	10.9688(3)
c/Å	19.3712(4)
α/°	90
β/°	100.345(2)
γ/°	90
Volume/Å^3	1923.78(7)
Z	2
ρcalcg/cm^3	1.210
μ/mm^{-1}	0.613
F(000)	752.0
Crystal size/mm^3	0.6 × 0.3 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.282 to 145.172
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 12, -23 ≤ l ≤ 23
Reflections collected	18988
Independent reflections	6766 [R_{int} = 0.0289, R_{sigma} = 0.0263]
Data/restraints/parameters	6766/1/475
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1487
Final R indexes [all data]	R_1 = 0.0558, wR_2 = 0.1522
Largest diff. peak/hole / e Å^{-3}	0.24/-0.23
Flack parameter	0.04(12)

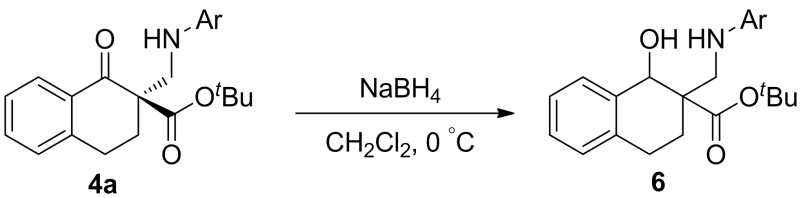
3. The nonlinear effect[4] between the *ee* value of the ligand L-PiPr$_2$ and the product 4a

To a dry reaction tube, the ligand (*S*)-**L-PiPr$_2$** (*x* mol% loading), (*R*)-**L-PiPr$_2$** (*y* mol% loading), $Ni(ClO_4)_2 \cdot 6H_2O$ (0.005 mmol, 1.8 mg), **1a** (0.1 mmol) and CH_2Cl_2 (1.0 mL) were added and stirred at 30 °C for 0.5 h. Then **3a** (0.034 mmol) were added, and the reaction was stirred at 0 °C for 8 h. The product **4a** was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1).

x/*y* (mol%)	*ee* of **L-PiPr$_2$** [%]	*ee* of **4a** [%]
0.25/0.25	0	0
0.30/0.20	20	21
0.35/0.15	40	40
0.40/0.10	60	54
0.45/0.05	80	80
0.50/0	100	99



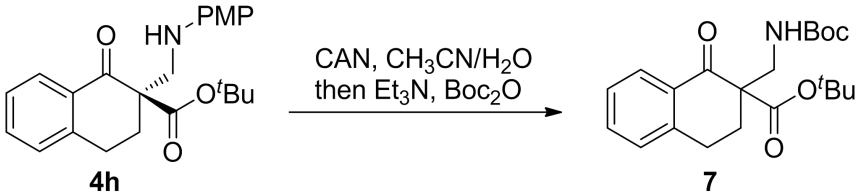
4. Typical experimental procedure for the reduction of 4a



$NaBH_4$ (8.4 mg, 0.22 mmol) was added to a solution of **4a** (70.3 mg, 0.2 mmol)

in 2 mL MeOH/CH_2Cl_2 (1:1) at 0 °C, and the mixture was stirred at 0 °C, and monitored by TLC. After 1 h, the mixture was quenched by saturated NH_4Cl aq. and extraction with ethyl acetate three times (10 mL), and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to afford **6** (70.0 mg, 99% yield) as a white solid.

5. Typical experimental procedure for the deprotection of 4h



4h **7**

$[Ce(NO_3)_6(NH_4)_2]$ (CAN; 274.1 mg, 0.5 mmol) in H_2O (2.0 mL) was added to a solution of **4h** (38.1 mg, 0.1 mmol) in CH_3CN (2.5 mL) at 0 °C. The solution was stirred at 0 °C. After 8 h, Et_3N (83.0 μL, 0.6 mmol) and Boc_2O (252.0 mg, 1.2 mmol) were added and the solution was stirred for another 18 h at 30 °C. Then saturated $NaHCO_3$ solution (3 mL) was added to the mixture and extracted three times with ethyl acetate (10 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether ethyl acetate = 10:1) to afford **7** (22.4 mg, 60% yield) as a yellow oil.

6. Reference

[1] C. Pan, X. Zeng, Y. Guan, X. Jiang, L. Li, H. Zhang, *Synlett.* **2011**, *3*, 425-429.

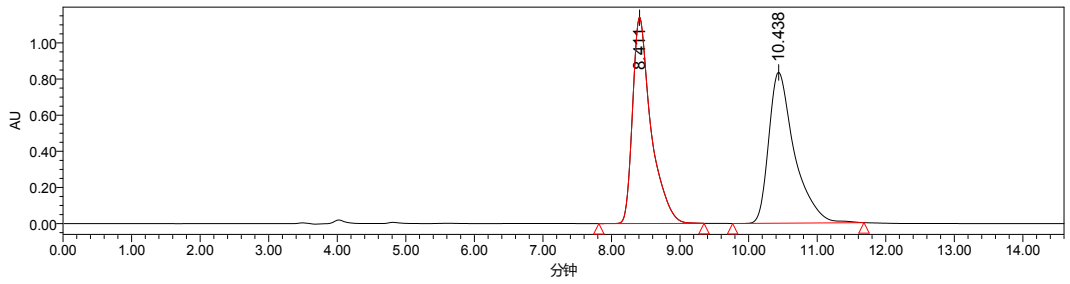
[2] *a*) C. A. Bischoff, F. Reinfeld, *Chem. Ber.* **1903**, *36*, 41-53; *b*) A. G. Giumanini, G. Verardo, E. Zangrando, L. Lassiani, *J. Prakt. Chem.* **1987**, *329*, 1087-1103; *c*) A. G. Giumanini, N. Toniutti, G. Verardo, M. Merli, *Eur. J. Org. Chem.* **1999**, 141-143; *d*) G. O. Jones, J. M. García, H. W. Horn, J. L. Hedrick, *Org. Lett.* **2014**, *16*, 5502-5505.

[3] *a*) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett* **2005**, 2445-2448; *b*) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie, X. M. Feng, *Angew. Chem. Int. Ed.* **2008**, *47*, 1308-1311; *c*) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu, X. M. Feng, *Org. Lett.* **2009**, *11*, 1401-1404.

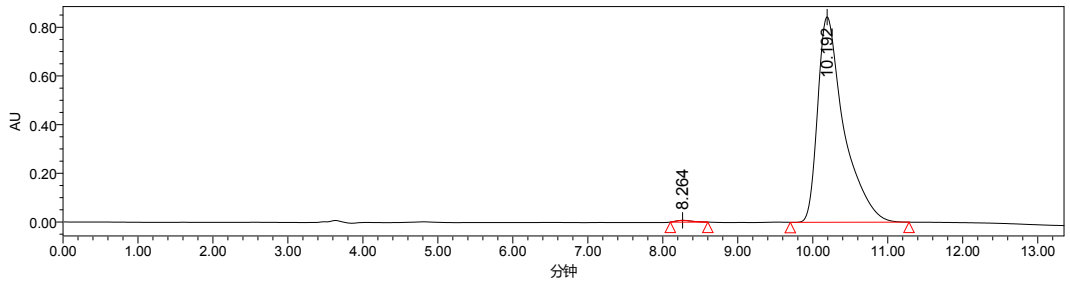
[4] *a*) C. Girard, H. B. Kagan, *Angew. Chem. Int. Ed.* **1998**, *37*, 2922-2959; *b*) H. B. Kagan, *Adv. Synth. Catal.* **2001**, *343*, 227-233; *c*) T. Satyanarayana, S. Abraham, H. B. Kagan, *Angew. Chem. Int. Ed.* **2009**, *48*, 456-494.

7. Characterization of the products

tert-butyl 1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4a**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 97% yield, 99% ee; mp 99–100 °C; $[\alpha]_D^{19}$ = 109.1 (c = 0.54, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 8.26 min (minor), 10.19 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.97 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.42–7.38 (m, 1H), 7.27–7.23 (t, *J* = 7.6 Hz, 1H), 7.15–7.13 (d, *J* = 8.0 Hz, 1H), 7.10–7.06 (t, *J* = 8.0 Hz, 2H), 6.60–6.58 (m, 3H), 4.56 (s, 1H), 3.63–3.60 (d, *J* = 13.2 Hz, 1H), 3.47–3.44 (d, *J* = 13.2 Hz, 1H), 3.05–3.00 (m, 1H), 2.98–2.83 (m, 1H), 2.46–2.41 (m, 1H), 2.21–2.13 (m, 1H), 1.20 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 170.4, 148.4, 142.8, 133.5, 132.6, 129.2, 128.7, 127.6, 126.8, 117.4, 113.2, 82.7, 59.4, 48.3, 30.8, 27.7, 26.2 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{25}NNaO_3$ ([M+Na^+]) = 374.1732, Found 374.1731.

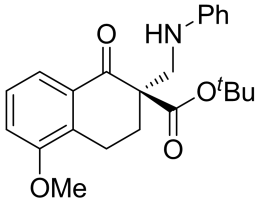


	Retention Time	% Area
1	8.411	49.54
2	10.438	50.46

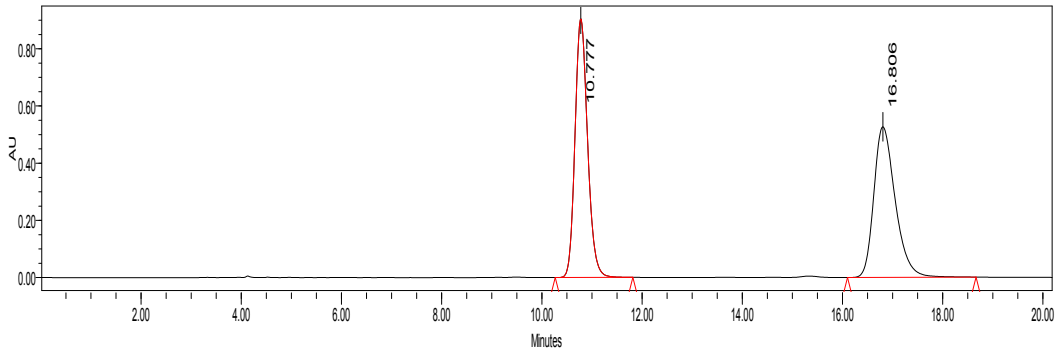


	Retention Time	% Area
1	8.264	0.48
2	10.192	99.52

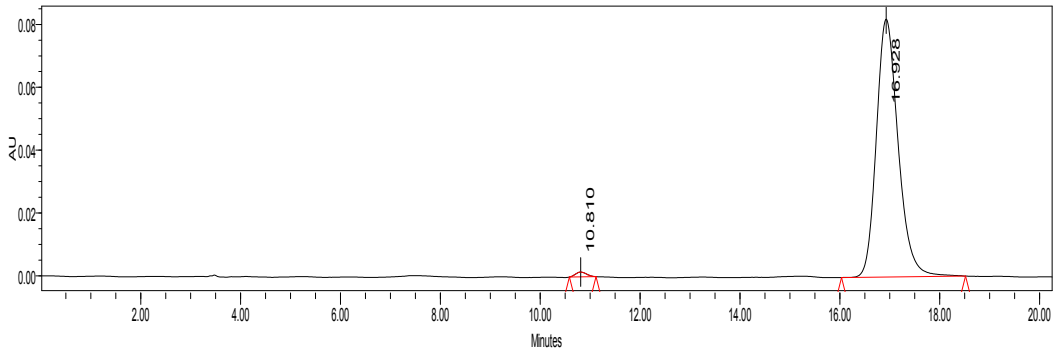
tert-butyl 5-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthal



-ene-2-carboxylate (**4b**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 83% yield, 98% ee; mp 117–119 °C; $[\alpha]_D^{19}$ = 121.7 (c = 0.63, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 10.81 min (minor), 16.93 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.58 (d, *J* = 8.0 Hz, 1H), 7.24–7.20 (t, *J* = 8.0 Hz, 1H), 7.09–7.05 (t, *J* = 7.8 Hz, 2H), 6.95–6.93 (d, *J* = 8.0 Hz, 1H), 6.61–6.58 (m, 3H), 4.55 (s, 1H), 3.77 (s, 3H), 3.61–3.58 (d, *J* = 12.8 Hz, 1H), 3.46–3.43 (d, *J* = 12.8 Hz, 1H), 3.02–2.95 (m, 1H), 2.73–2.64 (m, 1H), 2.48–2.42 (m, 1H), 2.12–2.04 (m, 1H), 1.19 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 170.4, 156.6, 148.5, 133.7, 131.8, 129.2, 127.1, 119.1, 117.4, 114.2, 113.2, 82.6, 58.9, 55.7, 48.2, 30.1, 27.7, 20.1 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{27}NNaO_4$ ([M+Na$^+$]) = 404.1838, Found 404.1837.

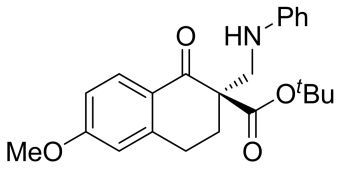


	Retention Time	% Area
1	10.777	50.30
2	16.806	49.70

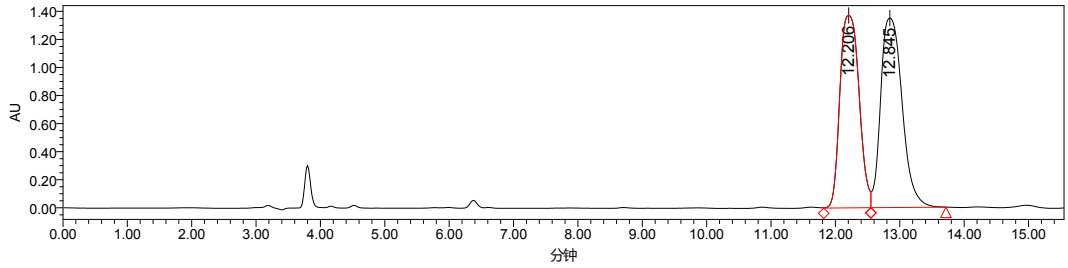


	Retention Time	% Area
1	10.810	0.94
2	16.928	99.06

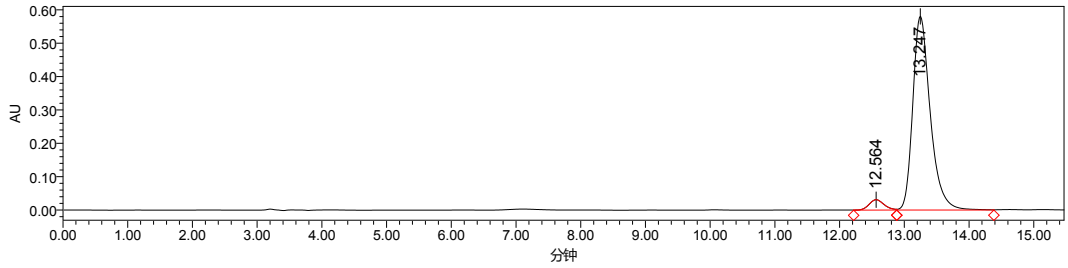
tert-butyl 6-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene



-2-carboxylate (**4c**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 90% yield, 91% ee; mp 79–80 °C; $[\alpha]_D^{19}$ = 108.0 (c = 0.68, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL/min, λ = 254 nm) retention time: 12.56 min (minor), 13.25 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.95 (d, *J* = 8.8 Hz, 1H), 7.09–7.05 (t, *J* = 8.0 Hz, 2H), 6.78–6.75 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.59–6.57 (m, 4H), 4.59 (s, 1H), 3.77 (s, 3H), 3.62–3.58 (d, *J* = 8.8 Hz, 1H), 3.45–3.42 (d, *J* = 8.8 Hz, 1H), 3.01–2.93 (m, 1H), 2.84–2.78 (m, 1H), 2.43–2.37 (m, 1H), 2.19–2.11 (m, 1H), 1.23 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 170.6, 163.7, 148.5, 145.4, 130.1, 129.2, 126.1, 117.3, 113.5, 113.2, 112.4, 82.5, 59.1, 55.5, 48.3, 30.9, 27.8, 26.6 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{27}NNaO_4$ ([M+Na$^+$]) = 404.1838, Found 404.1837.

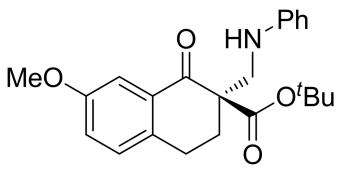


	Retention Time	% Area
1	12.206	47.51
2	12.845	52.49



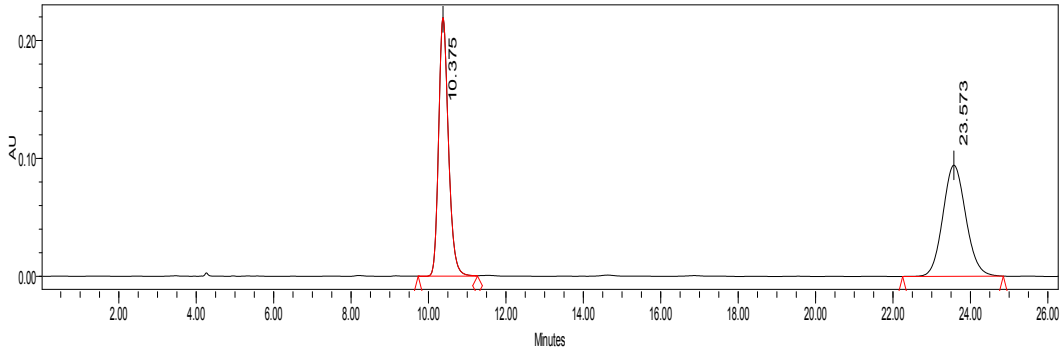
	Retention Time	% Area
1	12.564	4.39
2	13.247	95.61

tert-butyl 7-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene

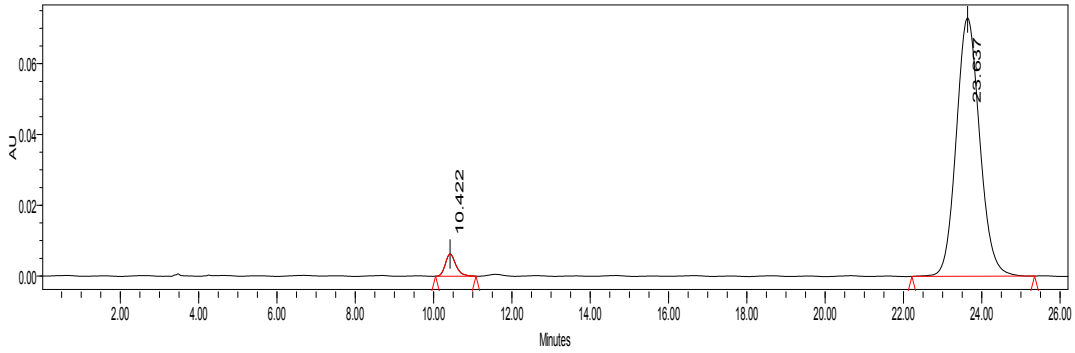


-2-carboxylate (**4d**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 90% yield, 92% ee; mp 78–80 °C; $[\alpha]_D^{19}$ = 127.6 (c = 0.68, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time:

10.42 min (minor), 23.64 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.45 (d, *J* = 2.8 Hz, 1H), 7.10–7.04 (m, 3H), 7.00–6.97 (m, 1H), 6.62–6.58 (m, 3H), 4.55 (s, 1H), 3.77 (s, 3H), 3.63–3.60 (d, *J* = 12.8 Hz, 1H), 3.46–3.43 (d, *J* = 12.8 Hz, 1H), 2.97–2.89 (m, 1H), 2.83–2.77 (m, 1H), 2.44–2.39 (m, 1H), 2.19–2.11 (m, 1H), 1.22 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 170.5, 158.5, 148.4, 135.4, 133.3, 129.9, 129.2, 122.0, 117.4, 113.2, 109.4, 82.7, 59.3, 55.5, 48.3, 31.1, 27.7, 25.4 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{27}NNaO_4$ ([M+Na$^+$]) = 404.1838, Found 404.1834.

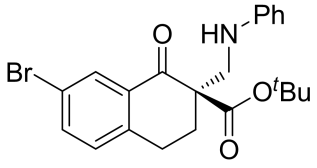


	Retention Time	% Area
1	10.375	49.91
2	23.573	50.09

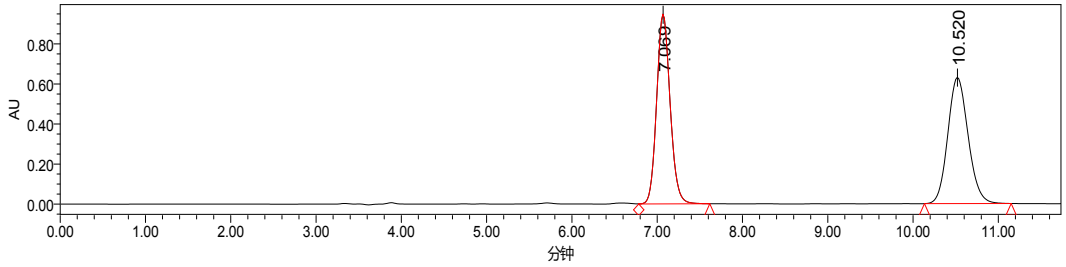


	Retention Time	% Area
1	10.422	3.76
2	23.637	96.24

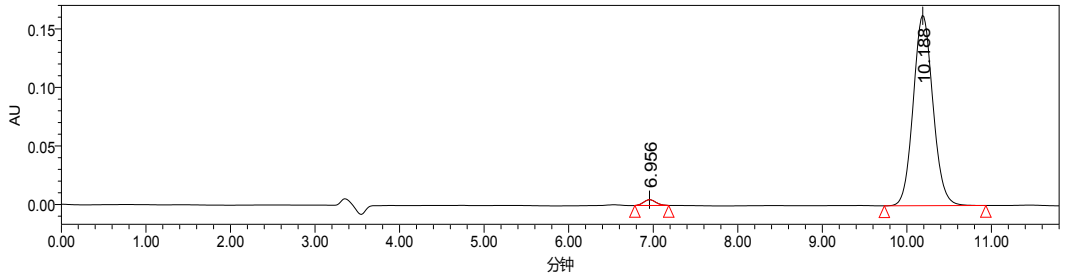
tert-butyl 7-bromo-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene -2-carboxylate (**4e**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 84% yield, 96% ee; mp 109–110 °C; $[\alpha]_D^{19}$ = 98.5 (c = 0.71, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 6.96 min (minor), 10.19 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–8.09 (d, *J* = 2.0 Hz, 1H), 7.51–7.49 (m, 1H), 7.10–7.03 (m, 3H), 6.61–6.58 (m, 3H), 4.46 (s, 1H), 3.64–3.61 (d, *J* = 12.8 Hz, 1H), 3.47–3.43 (d, *J* = 12.8 Hz, 1H), 2.97–2.78 (m, 2H),



2.45–2.40 (m, 1H), 2.19–2.11 (m, 1H), 1.22 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 170.1, 148.3, 141.5, 136.3, 134.1, 130.5, 130.3, 129.2, 120.8, 117.6, 113.2, 83.1, 59.3, 48.1, 30.6, 27.8, 25.8 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{24}{}^{78.9183}BrNNaO_3$ ([M+Na$^+$]) = 452.0837, Found 452.0814. HRMS (ESI-TOF) calcd for $C_{22}H_{24}{}^{80.9163}BrNNaO_3$ ([M+Na$^+$]) = 454.0817, Found 454.0805.

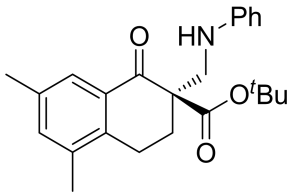


	Retention Time	% Area
1	7.069	49.85
2	10.520	50.15

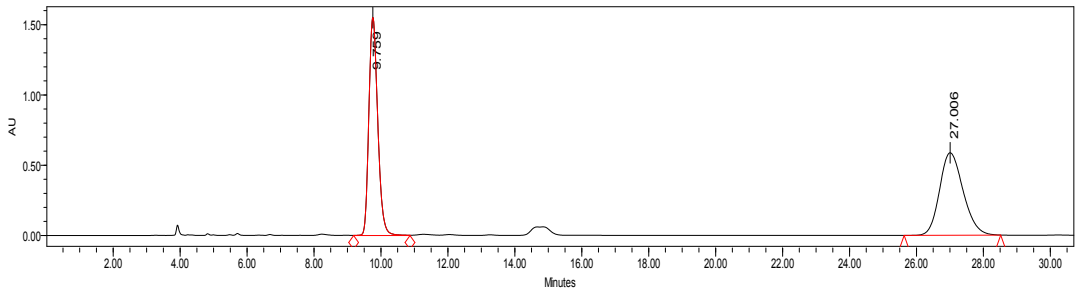


	Retention Time	% Area
1	6.956	1.82
2	10.188	98.18

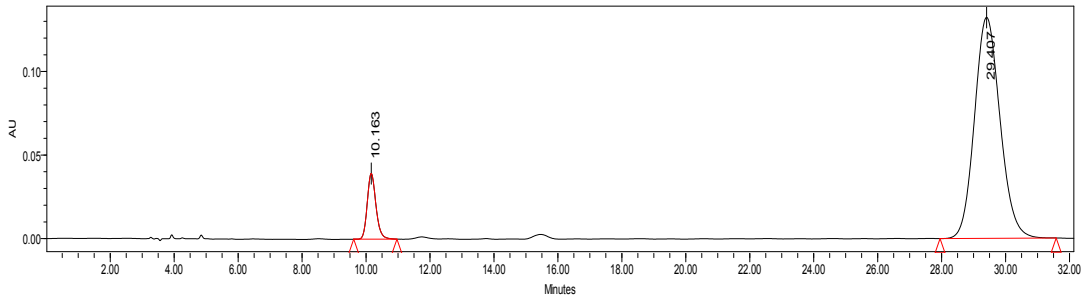
tert-butyl 5,7-dimethyl-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthal



-ene-2-carboxylate (**4f**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 98% yield, 81% ee; mp 138–140 °C; $[\alpha]_D^{19}$ = 86.8 (c = 0.74, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 10.16 min (minor), 29.41 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.11–7.05 (m, 3H), 6.60–6.58 (m, 1H), 4.57 (s, 1H), 3.61–3.57 (d, *J* = 12.8 Hz, 1H), 3.46–3.43 (d, *J* = 12.8 Hz, 1H), 2.82–2.67 (m, 1H), 2.48–2.43 (m, 1H), 2.26 (s, 3H), 2.16 (s, 3H) 2.13–2.07 (m, 1H), 1.19 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 169.4, 147.4, 137.1, 135.1, 135.0, 134.9, 131.6, 128.1, 124.5, 116.3, 112.1, 81.5, 57.7, 47.1, 29.1, 26.7, 22.2, 19.8, 18.2 ppm. HRMS (ESI-TOF) calcd for $C_{24}H_{29}NNaO_3$ ([M+Na$^+$]) = 402.2045, Found 402.2041.

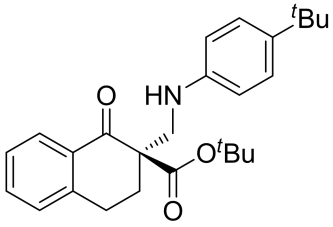


	Retention Time	% Area
1	9.759	49.94
2	27.006	50.06

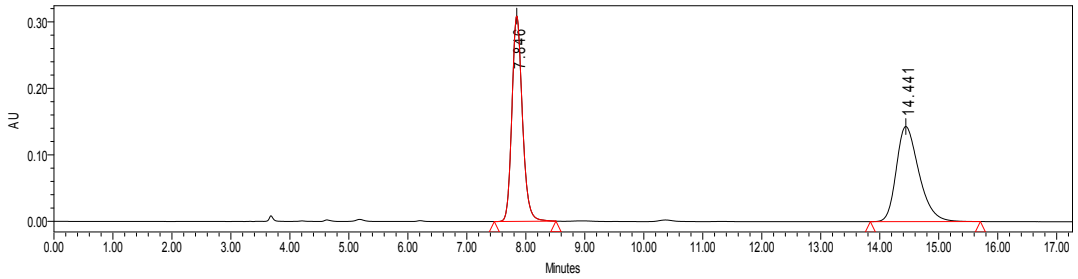


	Retention Time	% Area
1	10.163	9.22
2	29.407	90.78

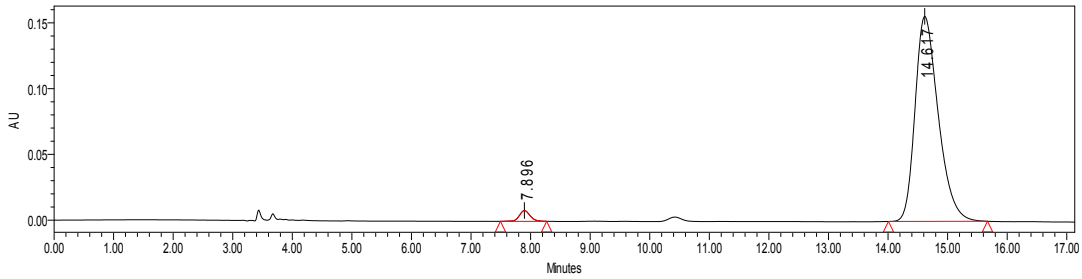
tert-butyl 2-(((4-(tert-butyl)phenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthal



-ene-2-carboxylate (**4g**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a yellow oil in 96% yield, 95% ee; $[\alpha]_D^{21}$ = 85.3 (c = 0.78, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 7.90 min (minor), 14.62 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.97 (m, 1H), 7.41–7.37 (m, 1H), 7.26–7.22 (m, 1H), 7.17–7.10 (m, 3H), 6.56–6.55 (m, 2H), 4.38 (s, 1H), 3.62–3.58 (d, *J* = 12.4 Hz, 1H), 3.45–3.42 (d, *J* = 12.4 Hz, 1H), 3.05–2.98 (m, 1H), 2.89–2.84 (m, 1H), 2.46–2.42 (m, 1H), 2.23–2.16 (m, 1H), 1.21–1.19 (m, 18H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 168.0, 143.6, 140.3, 137.7, 130.9, 130.1, 126.1, 125.1, 124.2, 123.4, 110.5, 80.1, 56.8, 46.0, 31.3, 29.0, 28.3, 25.2, 23.6 ppm. HRMS (ESI-TOF) calcd for $C_{26}H_{33}NNaO_3$ ([M+Na^+]) = 430.2358, Found 430.2356.

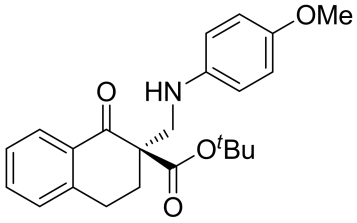


	Retention Time	% Area
1	7.846	50.00
2	14.441	50.00

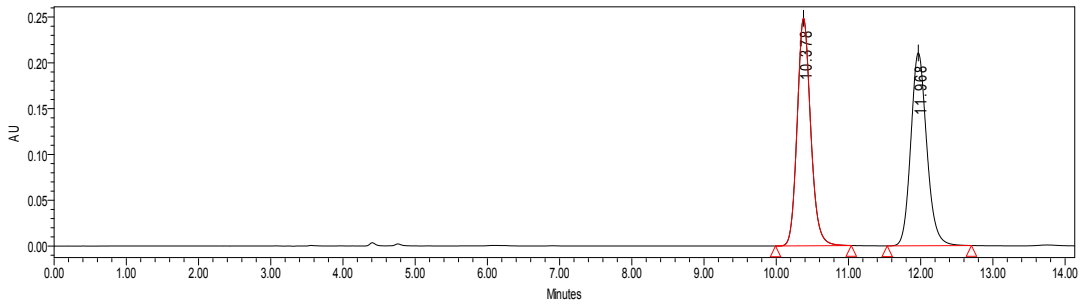


	Retention Time	% Area
1	7.896	2.39
2	14.617	97.61

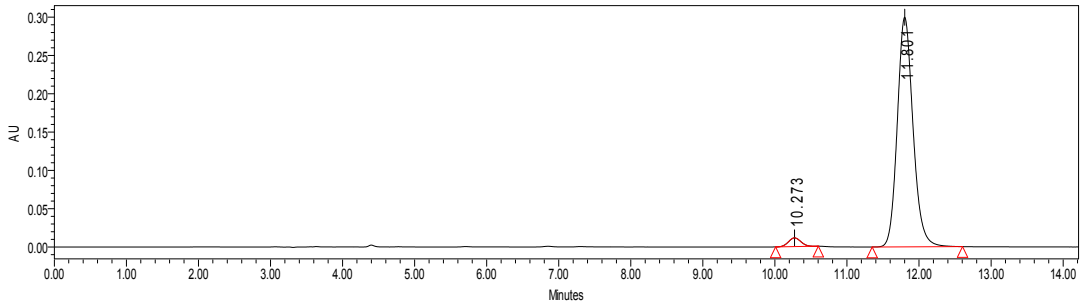
tert-butyl 2-(((4-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthal



-ene-2-carboxylate (**4h**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 91% yield, 94% ee; mp 106–108 °C; $[\alpha]_D^{22}$ = 91.6 (c = 0.69, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 7.90 min (minor), 14.62 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.97 (m, 1H), 7.42–7.38 (m, 1H), 7.27–7.23 (m, 1H), 7.15–7.13 (m, 1H), 6.70–6.68 (m, 2H), 6.58–6.56 (m, 2H), 4.30 (s, 1H), 3.66 (s, 3H), 3.54–3.51 (d, *J* = 12.8 Hz, 1H), 3.42–3.39 (d, *J* = 12.8 Hz, 1H), 3.05–2.96 (m, 1H), 2.89–2.83 (m, 1H), 2.45–2.40 (m, 1H), 2.22–2.14 (m, 1H), 1.22 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 170.5, 152.1, 142.8, 133.5, 132.6, 128.7, 127.6, 126.8, 114.8, 114.7, 82.6, 59.3, 55.8, 49.6, 30.9, 27.8, 26.2 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{27}NNaO_4$ ([M+Na$^+$]) = 404.1838, Found 404.1836.

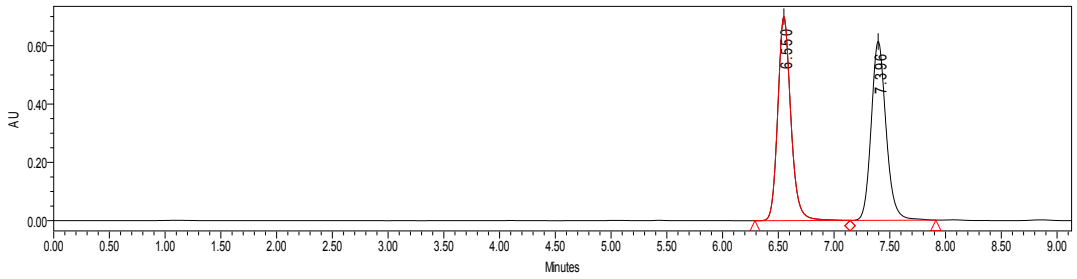


	Retention Time	% Area
1	10.378	49.99
2	11.968	50.01

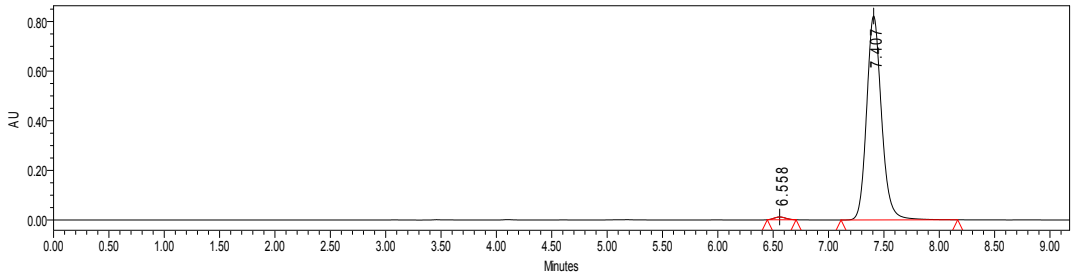


	Retention Time	% Area
1	10.273	2.92
2	11.801	97.08

tert-butyl 2-(((4-chlorophenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4i**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 95% yield, 98% ee; mp 138–140 °C; $[\alpha]_D^{22}$ = 108.9 (c = 0.73, CH_2Cl_2). HPLC (Chiralpak IA, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 6.56 min (minor), 7.41 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.96 (m, 1H), 7.43–7.39 (m, 1H), 7.27–7.24 (m, 1H), 7.16–7.14 (m, 1H), 7.02–7.00 (m, 2H), 6.52–6.50 (m, 2H), 4.63 (s, 1H), 3.57–3.54 (d, *J* = 12.8 Hz, 1H), 3.43–3.40 (d, *J* = 12.8 Hz, 1H), 3.05–2.96 (m, 1H), 2.90–2.83 (m, 1H), 2.43–2.38 (m, 1H), 2.16–2.09 (m, 1H), 1.19 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 170.3, 147.0, 142.7, 133.6, 132.6, 128.0, 129.70, 127.6, 126.9, 121.8, 114.2, 82.9, 59.2, 48.5, 30.9, 27.7, 26.2 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{24}{}^{34.9689}ClNNaO_3$ ([M+Na$^+$]) = 408.1342, Found 408.1341. HRMS (ESI-TOF) calcd for $C_{22}H_{24}{}^{36.9659}ClNNaO_3$ ([M+Na$^+$]) = 410.1313, Found 410.1289.

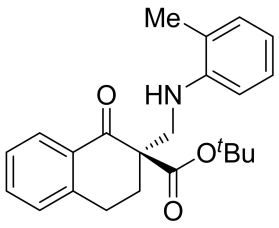


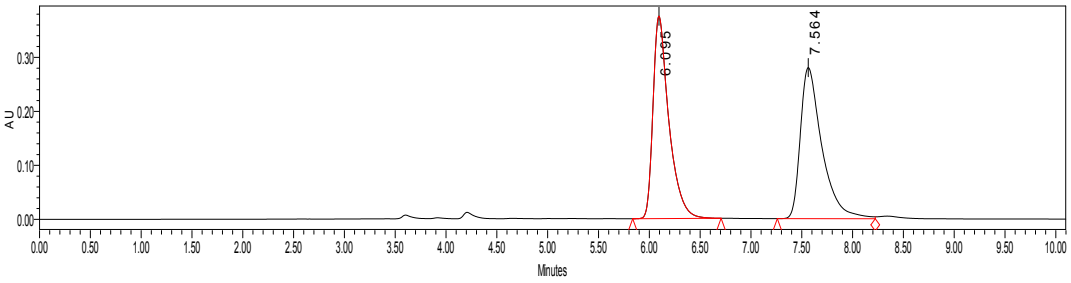
	Retention Time	% Area
1	6.550	50.00
2	7.396	50.00



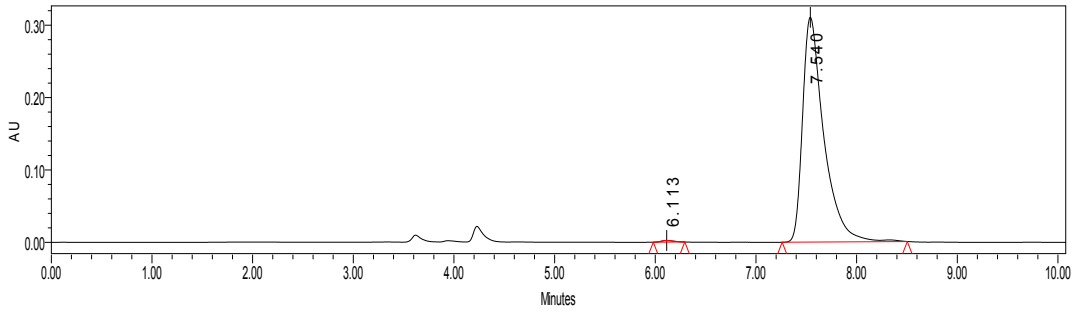
	Retention Time	% Area
1	6.558	1.04
2	7.407	98.96

tert-butyl 1-oxo-2-((o-tolylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4j**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 82% yield, 99% ee; mp 84–86 °C; $[\alpha]_D^{19}$ = 107.3 (c = 0.60, CH_2Cl_2). HPLC (Chiralpak ID, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 6.11 min (minor), 7.54 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.98 (m, 1H), 7.42–7.38 (m, 1H), 7.27–7.23 (m, 1H), 7.16–7.14 (m, 1H), 7.05–7.01 (m, 1H), 6.97–6.95 (m, 1H), 6.63–6.61 (m, 1H), 6.58–6.54 (m, 1H), 4.58 (s, 1H), 3.62–3.59 (d, *J* = 12.4 Hz, 1H), 3.49–3.45 (d, *J* = 12.4 Hz, 1H), 3.06–2.97 (m, 1H), 2.90–2.83 (m, 1H), 2.50–2.43 (m, 1H), 2.18–2.17 (m, 1H), 2.09(s, 3H), 1.19 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 170.4, 146.5, 142.7, 133.5, 132.6, 130.1, 128.7, 127.6, 127.0, 126.8, 122.7, 117.0, 109.9, 82.7, 59.0, 48.3, 31.1, 27.7, 26.2, 17.6 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{27}NNaO_3$ ([M+Na^+]) = 388.1889, Found 388.1887.



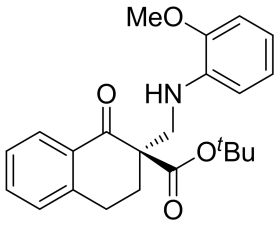


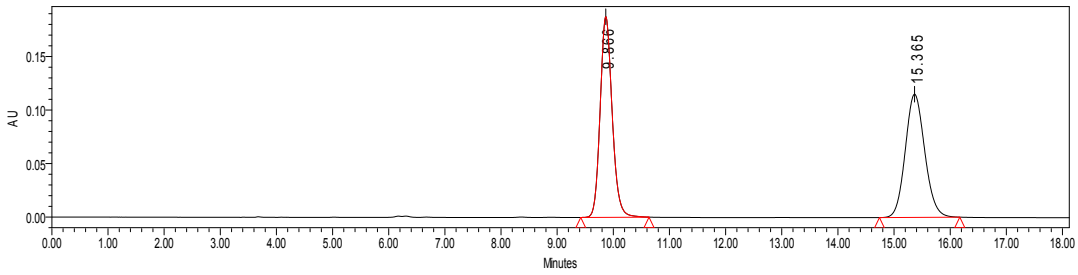
	Retention Time	% Area
1	6.095	49.56
2	7.564	50.44



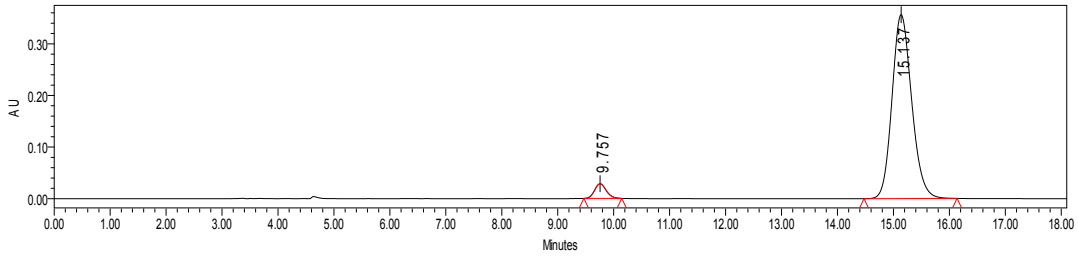
	Retention Time	% Area
1	6.113	0.43
2	7.540	99.57

tert-butyl 2-(((2-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene -2-carboxylate (**4k**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a yellow oil in 50% yield, 91% ee; $[\alpha]_D^{20}$ = 86.9 (c = 0.38, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 9.76 min (minor), 15.14 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.97 (m, 1H), 7.42–7.38 (m, 1H), 7.27–7.23 (m, 1H), 7.15–7.13 (m, 1H), 6.70–6.68 (m, 2H), 6.58–6.56 (m, 2H), 4.30 (s, 1H), 3.66 (s, 3H), 3.54–3.51 (d, *J* = 12.8 Hz, 1H), 3.42–3.39 (d, *J* = 12.8 Hz, 1H), 3.05–2.96 (m, 1H), 2.89–2.83 (m, 1H), 2.45–2.40 (m, 1H), 2.22–2.14 (m, 1H), 1.22 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 170.5, 152.1, 142.8, 133.5, 132.6, 128.7, 127.6, 126.8, 114.8, 114.7, 82.6, 59.3, 55.8, 49.6, 30.9, 27.8, 26.2 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{27}NNaO_4$ ([M+Na$^+$]) = 404.1838, Found 404.1837.



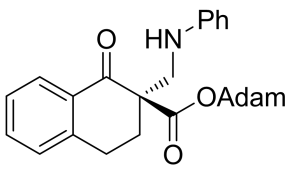


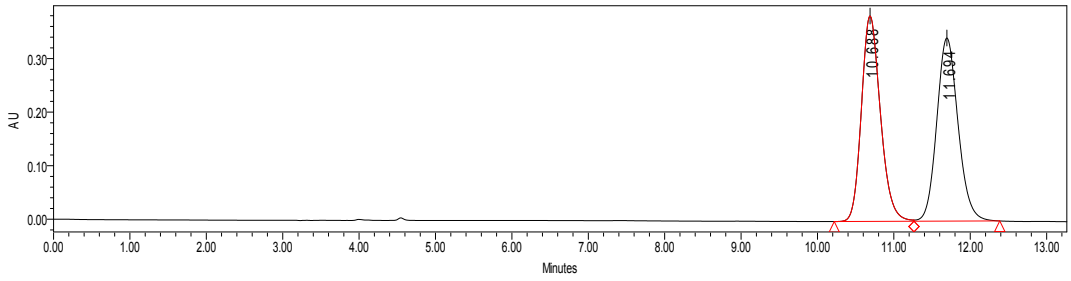
	Retention Time	% Area
1	9.866	50.12
2	15.365	49.88



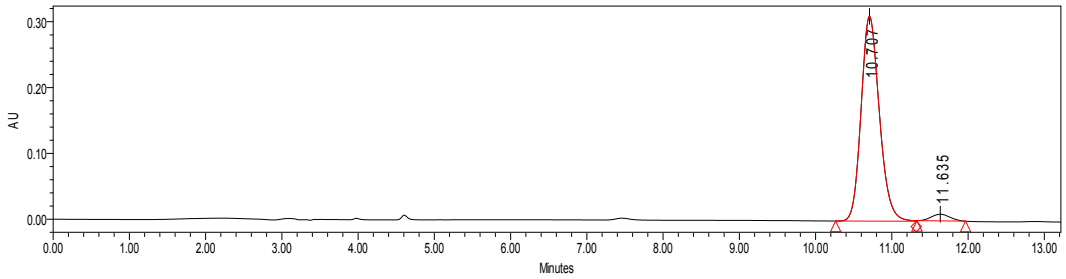
	Retention Time	% Area
1	9.757	4.54
2	15.137	95.46

Adamantan-1-yl 1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4l**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 99% yield, 93% ee; mp 101–102 °C; $[\alpha]_D^{20}$ = 83.8 (c = 0.86, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 10.71 min (major), 11.64 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.97 (d, *J* = 8.0 Hz, 1H), 7.42–7.38 (m, 1H), 7.26–7.23 (m, 1H), 7.15–7.13 (m, 1H), 7.10–7.06 (m, 2H), 6.61–6.58 (m, 3H), 4.49 (s, 1H), 3.64–3.61 (d, *J* = 12.0 Hz, 1H), 3.47–3.44 (d, *J* = 12.0 Hz, 1H), 3.07–2.98 (m, 1H), 2.88–2.82 (m, 1H), 2.45–2.40 (m, 1H), 2.20–2.14 (m, 1H), 1.98 (s, 3H), 1.84 (s, 6H), 1.48 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 170.1, 148.5, 142.8, 133.5, 132.7, 129.2, 128.7, 127.6, 126.8, 117.4, 113.2, 82.8, 59.5, 48.2, 41.0, 36.0, 30.9, 30.8, 26.2 ppm. HRMS (ESI-TOF) calcd for $C_{28}H_{31}NNaO_3$ ([M+Na$^+$]) = 452.2202, Found 452.2201.



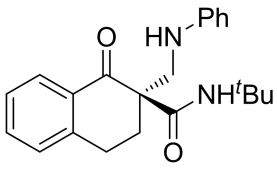


	Retention Time	% Area
1	10.688	50.03
2	11.694	49.97

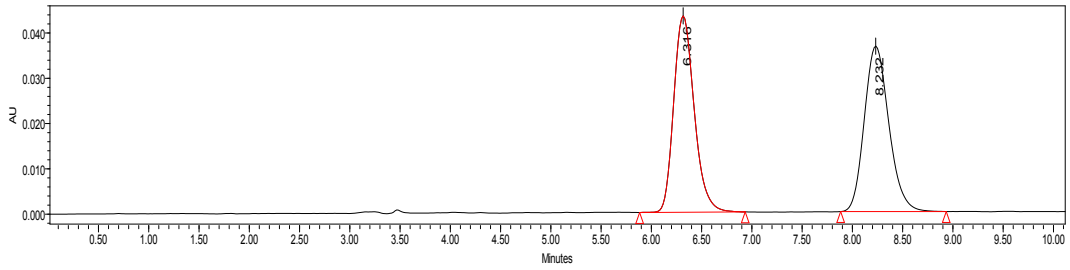


	Retention Time	% Area
1	10.707	96.76
2	11.635	3.24

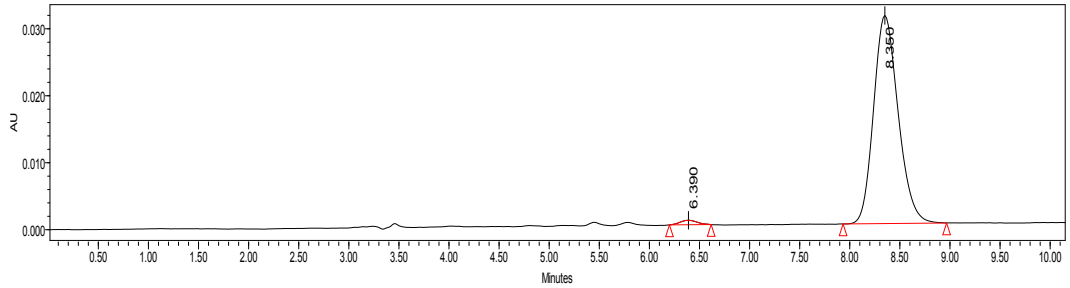
N-(*tert*-butyl)-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carbo



xamide (**5a**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 98% yield, 97% ee; mp 78–80 °C; $[\alpha]_D^{23}$ = 77.7 (c = 0.69, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 6.39 min (minor), 8.35 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.98 (d, *J* = 8.0 Hz, 1H), 7.45–7.42 (m, 1H), 7.27–7.24 (m, 1H), 7.18–7.15 (m, 1H), 7.09–7.05 (m, 2H), 6.63–6.59 (m, 1H), 6.56–6.54 (m, 2H), 6.41(s, 1H), 4.07 (s, 1H), 3.58–3.47 (dd, *J* = 30.0, 12.8 Hz, 2H), 3.08–3.00 (m, 1H), 2.83–2.76 (m, 1H), 2.68–2.63 (m, 1H), 2.18–2.11 (m, 1H), 1.16 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 167.3, 148.1, 144.8, 134.5, 131.7, 129.3, 128.9, 128.0, 126.8, 117.7, 113.0, 59.2, 51.6, 50.2, 29.4, 28.5, 26.0 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{26}N_2NaO_2$ ([M+Na$^+$]) = 373.1892, Found 373.1885.

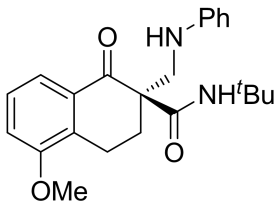


	Retention Time	% Area
1	6.316	49.78
2	8.232	50.22

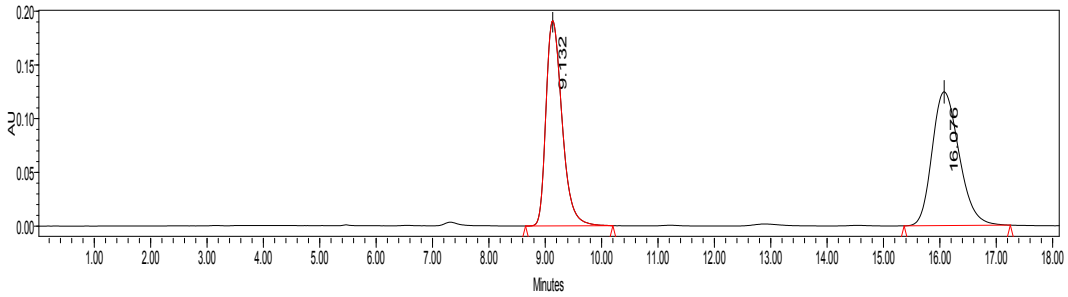


	Retention Time	% Area
1	6.390	1.47
2	8.350	98.53

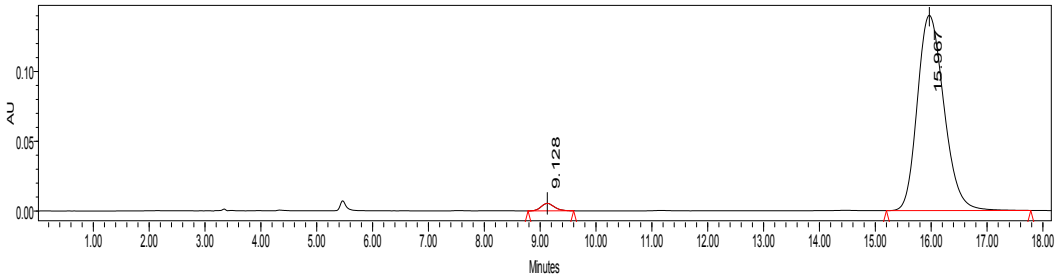
N-(*tert*-butyl)-5-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthal



ene-2-carboxamide (**5b**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 98% yield, 96% ee; mp 92–94 °C; $[\alpha]_D^{27}$ = 76.3 (c = 0.74, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 9.13 min (minor), 15.97 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (d, *J* = 7.6 Hz, 1H), 7.31–7.27 (m, 1H), 7.16–7.12 (m, 2H), 7.05–7.03 (m, 1H), 6.70–6.66 (m, 1H), 6.63–6.61 (m, 2H), 6.44 (s, 1H), 4.18(s, 1H), 3.85(s, 3H), 3.62–3.54 (dd, *J* = 22.8, 12.8 Hz, 2H), 3.02–2.83 (m, 2H), 2.71–2.65 (m, 1H), 2.22–2.15 (m, 1H), 1.22 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 167.6, 156.7, 148.1, 133.8, 132.6, 129.2, 127.0, 119.4, 117.6, 115.1, 113.0, 58.5, 55.7, 51.6, 49.8, 28.8, 28.5, 19.4 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{28}N_2NaO_3$ ([M+Na$^+$]) = 403.1998, Found 403.1991.

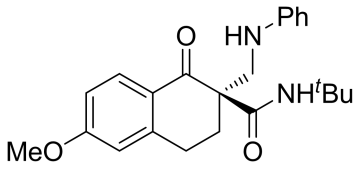


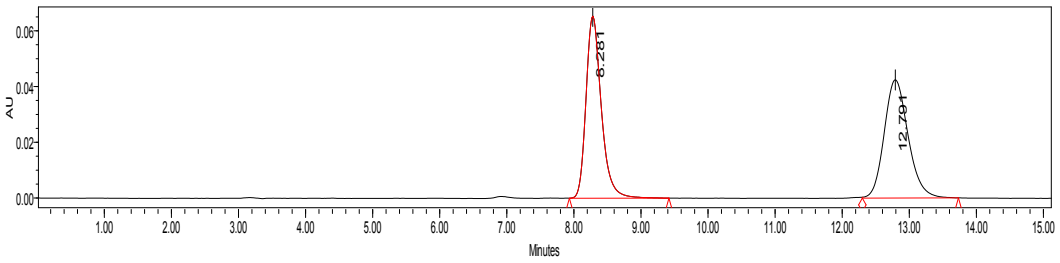
	Retention Time	% Area
1	9.132	47.79
2	16.076	52.21



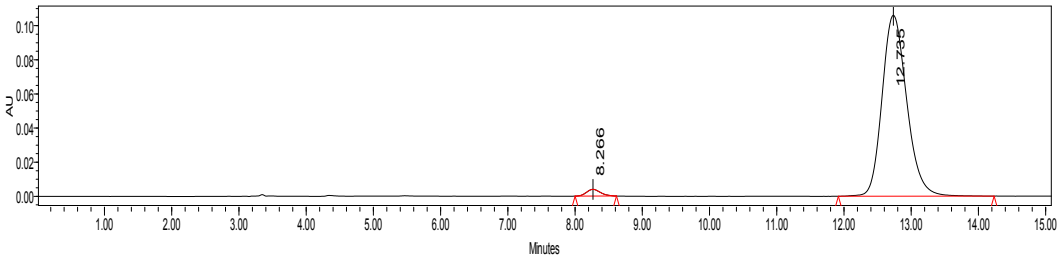
	Retention Time	% Area
1	9.128	1.87
2	15.967	98.13

N-(*tert*-butyl)-6-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5c**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 77% yield, 96% ee; mp 128–130 °C; $[\alpha]_D^{27}$ = 83.0 (c = 0.58, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 8.27 min (minor), 12.73 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.02 (d, *J* = 8.8 Hz, 1H), 7.16–7.12 (m, 2H), 6.86–6.83 (m, 1H), 6.68–6.61 (m, 4H), 6.55 (s, 1H), 4.15 (s, 1H), 3.86 (s, 3H), 3.65–3.52 (m, 2H), 3.12–3.04 (m, 1H), 2.85–2.79 (m, 1H), 2.74–2.69 (m, 1H), 2.22–2.15 (m, 1H), 1.24 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 167.5, 164.5, 148.2, 147.6, 130.7, 129.2, 125.3, 117.5, 113.8, 112.9, 112.3, 58.9, 55.6, 51.5, 50.4, 29.4, 28.5, 26.5 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{28}N_2NaO_3$ ([M+Na$^+$]) = 403.1998, Found 403.1995.



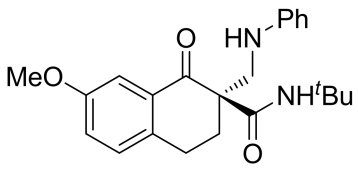


	Retention Time	% Area
1	8.281	49.57
2	12.791	50.43

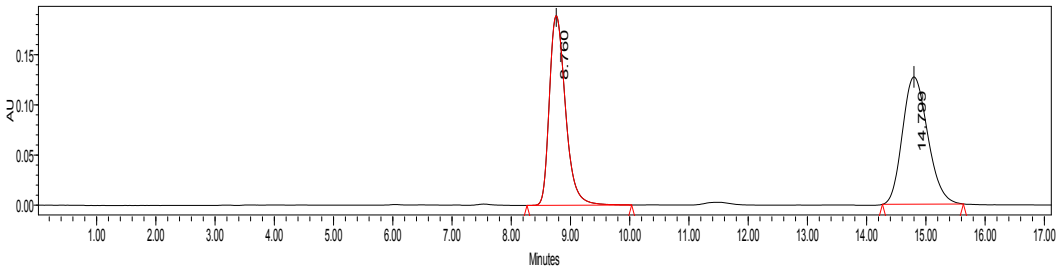


	Retention Time	% Area
1	8.266	2.08
2	12.735	97.92

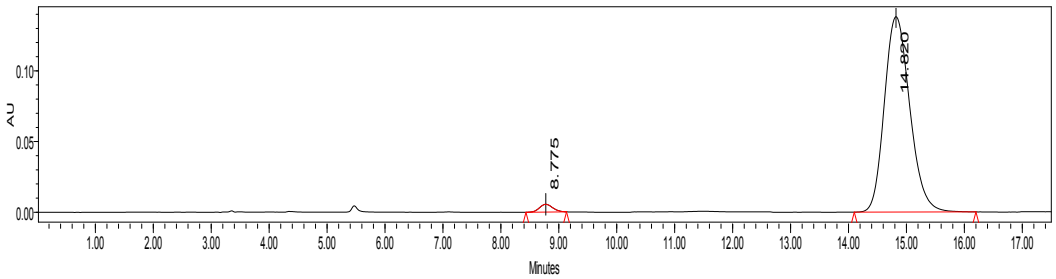
N-(*tert*-butyl)-7-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthal



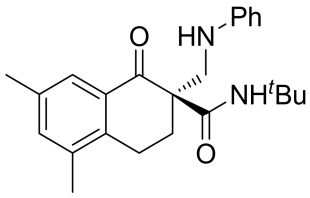
ene-2-carboxamide (**5d**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 95% yield, 96% ee; mp 150–152 °C; $[\alpha]_D^{27}$ = 79.7 (c = 0.72, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 8.78 min (minor), 14.82 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.52 (d, *J* = 2.8 Hz, 1H), 7.16–7.08 (m, 4H), 6.70–6.67 (m, 1H), 6.64–6.62 (m, 2H), 6.47 (s, 1H), 4.16 (s, 1H), 3.85 (s, 3H), 3.65–3.54 (dd, *J* = 29.2, 12.4 Hz, 2H), 3.08–3.00 (m, 1H), 2.85–2.78 (m, 1H), 2.72–2.67 (m, 1H), 2.25–2.17 (m, 1H), 1.25 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 167.4, 158.4, 148.1, 137.4, 132.4, 130.1, 129.3, 122.8, 117.7, 113.0, 109.9, 59.0, 55.5, 51.6, 50.2, 29.7, 28.5, 25.2 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{28}N_2NaO_3$ ([M+Na$^+$]) = 403.1998, Found 403.1991.



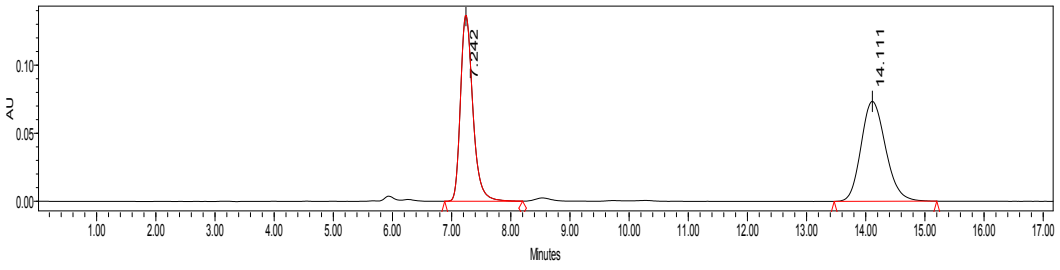
	Retention Time	% Area
1	8.760	48.64
2	14.799	51.36



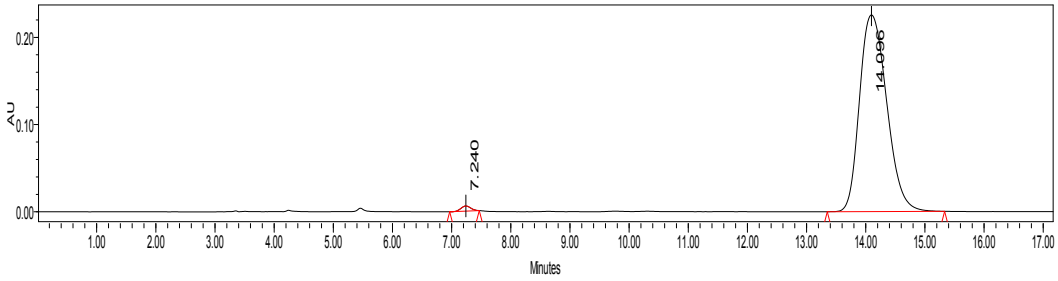
	Retention Time	% Area
1	8.775	2.05
2	14.820	97.95



N-(*tert*-butyl)-5,7-dimethyl-1-oxo-2-((phenylamino)methyl) -1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5e**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 75% yield, 98% ee; mp 152–154 °C; $[\alpha]_D^{27}$ = 67.7 (c = 0.57, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 7.24 min (minor), 14.10 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.22 (s, 1H), 7.16–7.12 (m, 2H), 6.70–6.66 (m, 1H), 6.63–6.61 (m, 2H), 6.46 (s, 1H), 4.17 (s, 1H), 3.63–3.52 (m, 2H), 2.92–2.77 (m, 2H), 2.73–2.67 (m, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 2.23–2.17 (m, 1H), 1.23 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 167.6, 148.1, 140.3, 136.9, 136.4, 135.9, 131.6, 129.2, 125.9, 117.6, 113.0, 58.5, 51.6, 50.0, 28.8, 28.5, 22.7, 20.9, 19.2 ppm. HRMS (ESI-TOF) calcd for $C_{24}H_{30}N_2NaO_2$ ([M+Na$^+$]) = 401.2205, Found 401.2199.

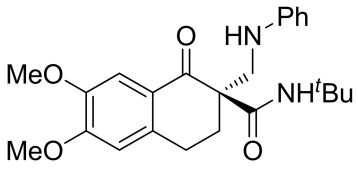


	Retention Time	% Area
1	7.242	48.38
2	14.111	51.62

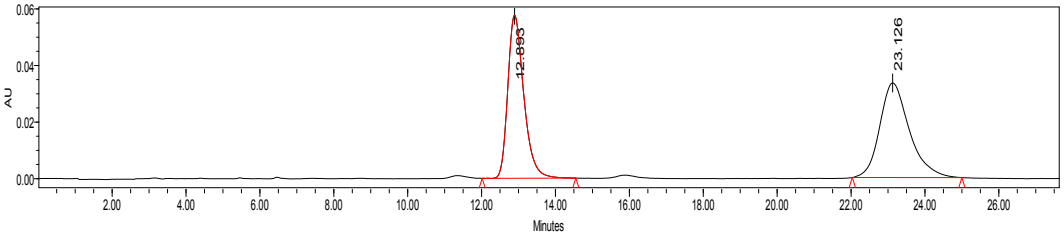


	Retention Time	% Area
1	7.240	0.93
2	14.096	99.07

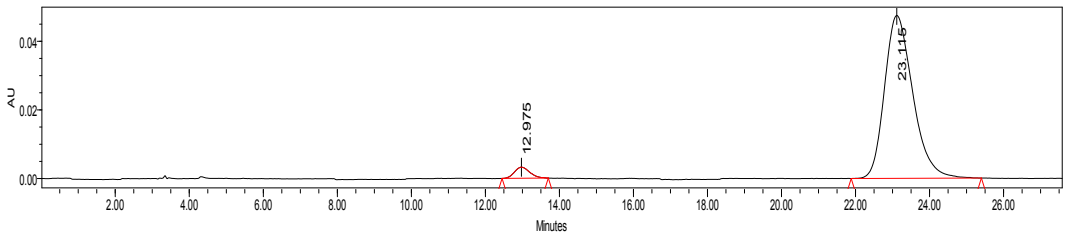
N-(*tert*-butyl)-6,7-dimethoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronapht



halene-2-carboxamide (**5f**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a yellow oil in 71% yield, 93% ee; $[\alpha]_D^{27}$ = 85.2 (c = 0.58, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 12.98 min (minor), 23.12 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.16–7.13 (m, 2H), 6.70–6.66 (m, 1H), 6.64–6.62 (m, 3H), 6.56 (s, 1H), 4.16 (s, 1H), 3.94–3.93 (d, *J* = 3.6 Hz, 6H), 3.65–3.53 (dd, *J* = 34.4, 12.4 Hz, 2H), 3.10–3.02 (m, 1H), 2.82–2.68 (m, 2H), 2.25–2.18 (m, 1H), 1.25 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 167.6, 154.6, 148.1, 140.2, 129.2, 124.8, 117.6, 113.0, 110.1, 109.1, 58.5, 56.2, 56.0, 51.5, 50.3, 29.6, 28.5, 25.9 ppm. HRMS (ESI-TOF) calcd for $C_{24}H_{30}N_2NaO_4$ ([M+Na$^+$]) = 433.2103, Found 433.2107.

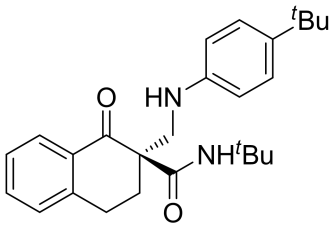


	Retention Time	% Area
1	12.893	48.21
2	23.126	51.79

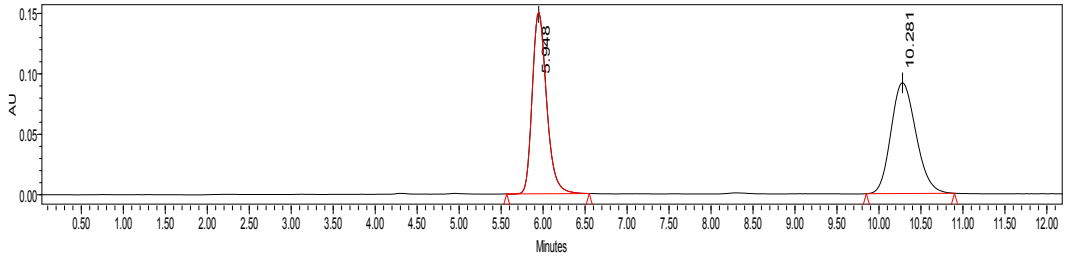


	Retention Time	% Area
1	12.975	3.53
2	23.115	96.47

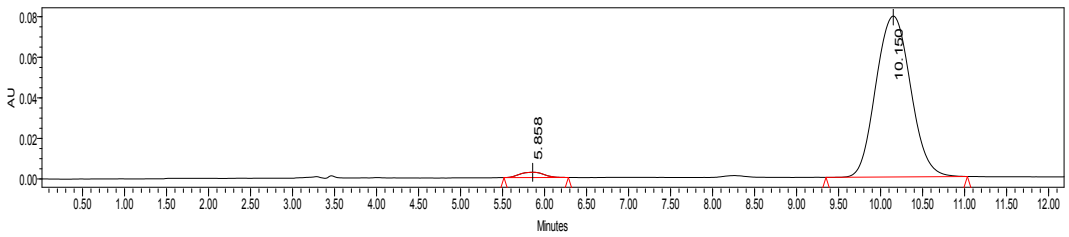
N-(*tert*-butyl)-2-(((4-(tert-butyl)phenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronapht



halene-2-carboxamide (**5g**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 95% yield, 95% ee; mp 106–108 °C; $[\alpha]_D^{27}$ = 76.7 (c = 0.78, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 5.86 min (minor), 10.15 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 1H), 7.52–7.48 (m, 1H), 7.34–7.30 (m, 1H), 7.24–7.22 (m, 1H), 7.19–7.17 (m, 2H), 6.60–6.58 (m, 2H), 6.53 (s, 1H), 4.04 (s, 1H), 3.64–3.52 (dd, *J* = 34.8, 12.4 Hz, 2H), 3.16–3.08 (m, 1H), 2.91–2.84 (m, 1H), 2.76–2.70 (m, 1H), 2.27–2.20 (m, 1H), 1.26–1.24 (m, 18H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 167.4, 145.7, 144.8, 140.5, 134.4, 131.7, 128.8, 128.0, 126.8, 126.0, 112.8, 59.2, 51.6, 50.6, 33.9, 31.6, 29.3, 28.5, 26.0 ppm. HRMS (ESI-TOF) calcd for $C_{26}H_{34}N_2NaO_2$ ([M+Na$^+$]) = 429.2518, Found 429.2512.



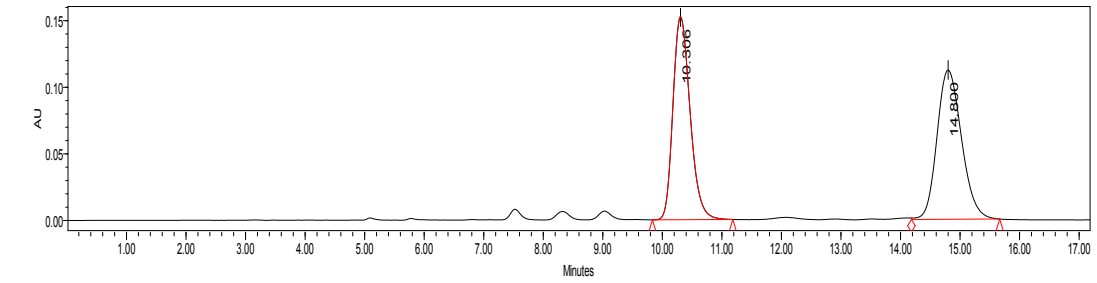
	Retention Time	% Area
1	5.948	48.40
2	10.281	51.60



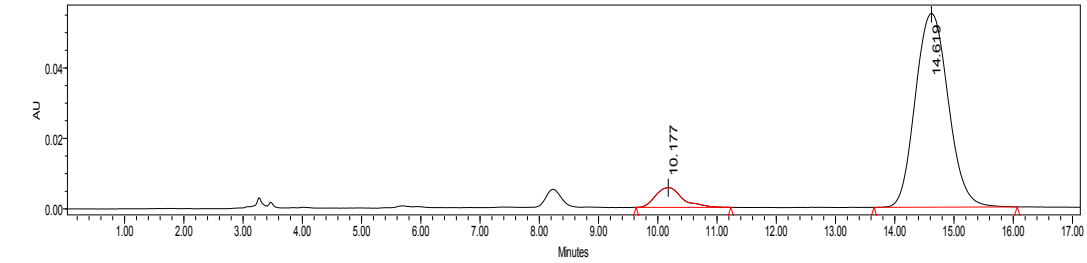
	Retention Time	% Area

1	5.858	2.24
2	10.150	97.76

N-(*tert*-butyl)-2-(((4-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5h**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 87% yield, 84% ee; mp 137–138 °C; $[\alpha]_D^{28}$ = 68.1 (c = 0.66, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 10.12 min (minor), 14.62 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 1H), 7.53–7.48 (m, 1H), 7.35–7.31 (m, 1H), 7.25–7.23 (m, 1H), 6.76–6.74 (m, 2H), 6.61–6.58 (m, 3H), 3.73 (s, 3H), 3.60–3.49 (dd, *J* = 30.8, 12.8 Hz, 2H), 3.16–3.08 (m, 1H), 2.91–2.84 (m, 1H), 2.74–2.69 (m, 1H), 2.27–2.20 (m, 1H), 1.25 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 167.6, 152.3, 144.7, 142.3, 134.4, 131.8, 128.8, 128.0, 126.8, 114.8, 114.5, 59.2, 55.8, 51.6, 51.5, 29.4, 28.5, 26.0 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{28}N_2NaO_3$ ([M+Na$^+$]) = 403.1998, Found 403.2000.



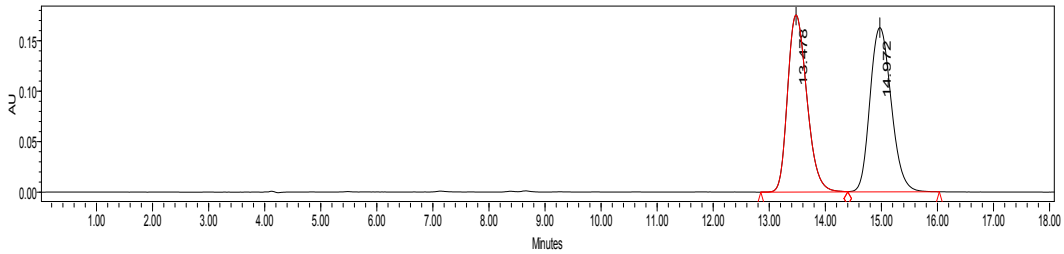
	Retention Time	% Area
1	10.306	48.74
2	14.800	51.26



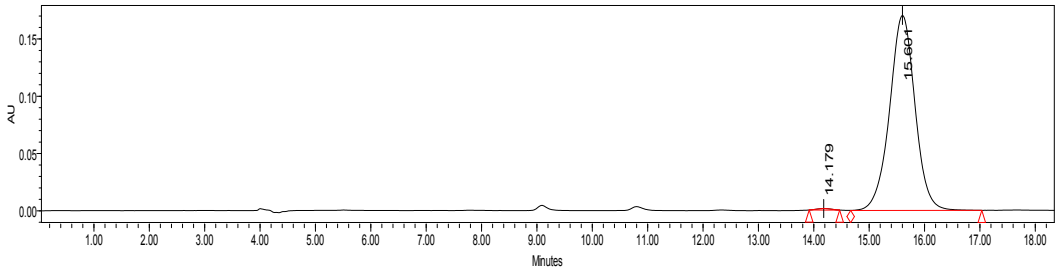
	Retention Time	% Area
1	10.177	7.71
2	14.619	92.29

N-(*tert*-butyl)-1-oxo-2-((o-tolylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5i**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a yellow oil in 96% yield, 98% ee; $[\alpha]_D^{28}$ = 75.9 (c = 0.70, CH_2Cl_2). HPLC (Chiralpak IC,

hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 14.18 min (minor), 15.60 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 1H), 7.54–7.50 (m, 1H), 7.36–7.32 (m, 1H), 7.26–7.24 (m, 1H), 7.11–7.07 (m, 1H), 7.05–7.03 (m, 1H), 6.66–6.59 (m, 3H), 4.19 (s, 1H), 3.63–3.56 (m, 2H), 3.15–3.07 (m, 1H), 2.93–2.86 (m, 1H), 2.81–2.75 (m, 1H), 2.26–2.19 (m, 1H), 2.15 (s, 3H), 1.25 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 167.5, 146.0, 144.8, 134.5, 131.7, 130.1, 128.9, 128.1, 127.1, 126.9, 122.4, 117.1, 109.7, 58.5, 51.6, 49.9, 29.6, 28.5, 26.0, 17.5 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{28}N_2NaO_2$ ([M+Na$^+$]) = 387.2048, Found 387.2041.

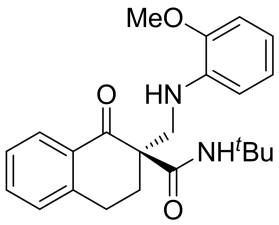


	Retention Time	% Area
1	13.478	49.49
2	14.972	50.51

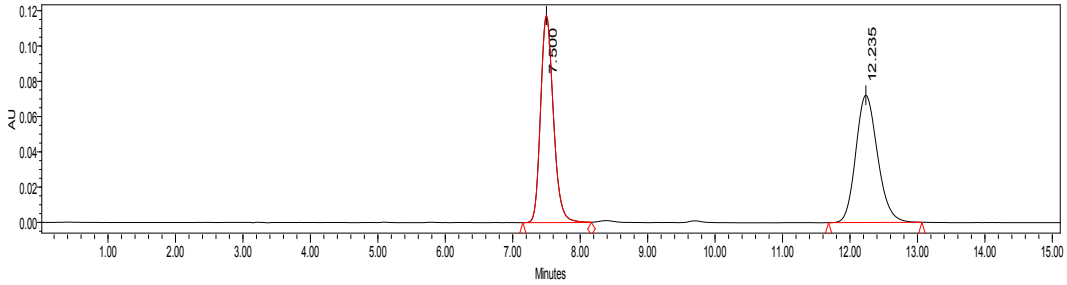


	Retention Time	% Area
1	14.179	0.44
2	15.601	99.56

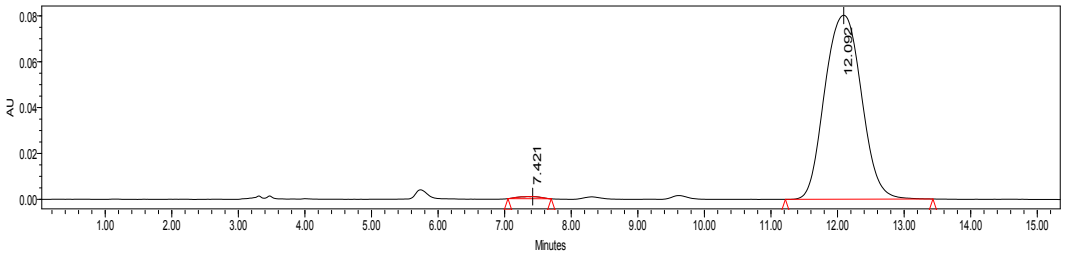
N-(*tert*-butyl)-2-(((2-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5j**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a yellow oil in 97% yield, 99% ee; $[\alpha]_D^{28}$ = 86.8 (c = 0.74, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 7.42 min (minor), 12.09 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 1H), 7.52–7.47 (m, 1H), 7.34–7.30 (m, 1H), 7.25–7.22 (m, 1H), 6.85–6.81 (m, 1H), 6.75–6.73 (m, 1H), 6.66–6.62 (m, 2H), 6.55 (s, 1H), 4.68 (s, 1H), 3.81 (s, 3H), 3.70–3.66 (m, 1H), 3.61–3.57 (m, 1H), 3.19–3.11 (m, 1H), 2.91–2.85 (m, 1H), 2.80–2.74 (m, 1H), 2.27–2.20 (m, 1H), 1.24 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 167.2, 146.9, 144.8, 138.0, 134.3, 131.8, 128.8, 128.0, 126.7, 121.2,



116.7, 110.1, 109.6, 59.4, 55.5, 51.5, 50.1, 29.3, 28.5, 26.1 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{28}N_2NaO_3$ ([M+Na$^+$]) = 403.1998, Found 403.1994.

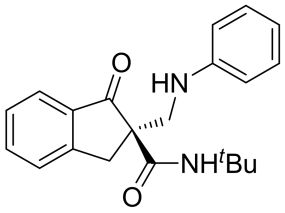


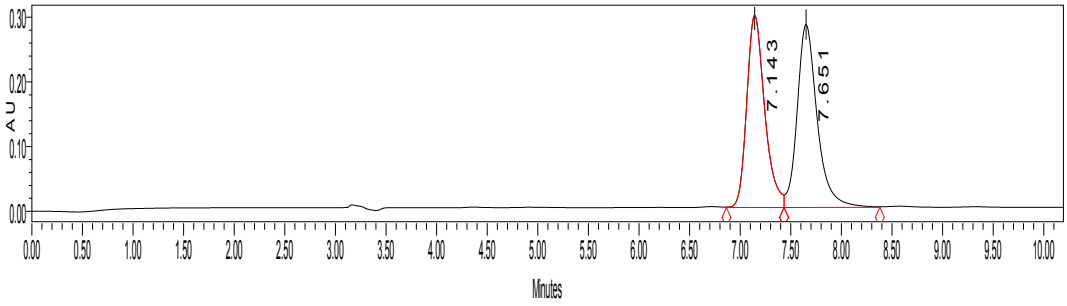
	Retention Time	% Area
1	7.500	48.83
2	12.235	51.17



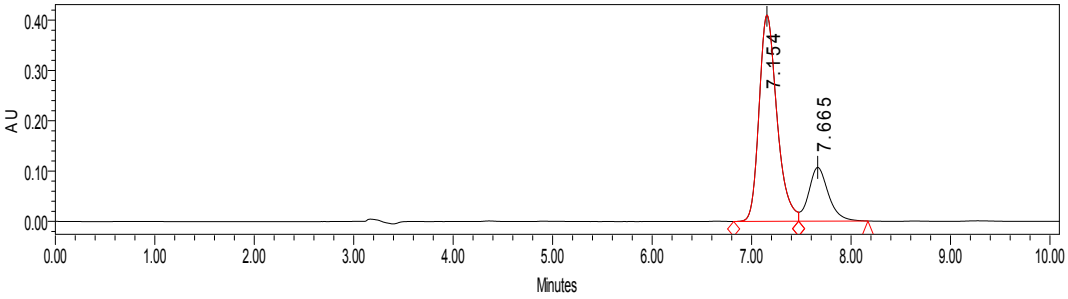
	Retention Time	% Area
1	7.421	0.74
2	12.092	99.26

N-(*tert*-butyl)-1-oxo-2-((phenylamino)methyl)-2,3-dihydro-1H-indene-2-carboxamide (**5k**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a yellow solid in 99% yield, 55% ee; mp 122–124 °C; $[\alpha]_D^{23}$ = -4.5 (c = 0.67, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) retention time: 7.15 min (major), 7.67 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.67 (d, *J* = 7.6 Hz, 1H), 7.58–7.54 (t, *J* = 7.4 Hz, 1H), 7.40–7.38 (d, *J* = 7.6 Hz, 1H), 7.34–7.30 (t, *J* = 7.4 Hz, 1H), 7.08–7.04 (t, *J* = 7.4 Hz, 2H), 6.64–6.60 (t, *J* = 7.2 Hz, 1H), 6.52–6.50 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 1H), 3.86–3.82 (d, *J* = 18.0 Hz, 1H), 3.51–3.46 (m, 1H), 3.37–3.34 (m, 1H), 3.16–3.12 (d, *J* = 18.0 Hz, 1H), 1.22 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.4, 167.5, 153.7, 147.6, 136.2, 134.9, 129.3, 127.7, 126.7, 124.6, 118.0, 113.0, 61.4, 52.0, 51.4, 34.9, 28.5 ppm. HRMS (ESI-TOF) calcd for $C_{21}H_{24}N_2NaO_2$ ([M+Na$^+$]) = 359.1735, Found 359.1736.



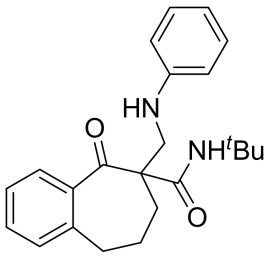


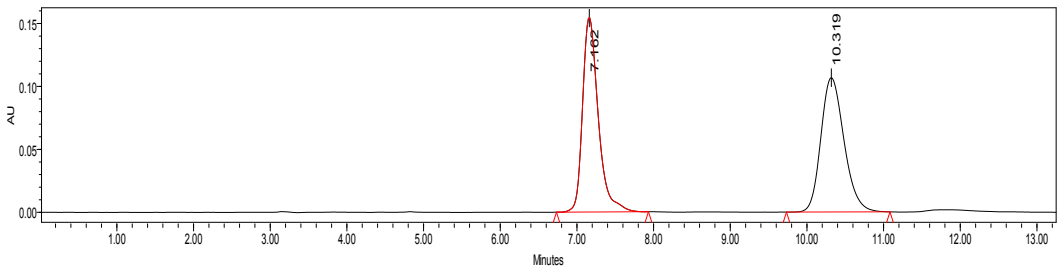
	Retention Time	% Area
1	7.143	48.46
2	7.651	51.54



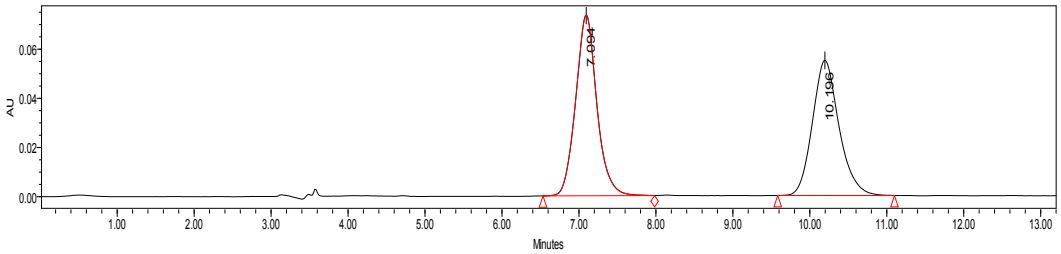
	Retention Time	% Area
1	7.154	77.65
2	7.665	22.35

N-(*tert*-butyl)-5-oxo-6-((phenylamino)methyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxamide (**5l**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 92% yield, 0% ee; mp 94–95 °C. HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 7.09 min, 10.20 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.36 (m, 2H), 7.29–7.25 (m, 1H), 7.16–7.12 (m, 3H), 6.75 (s, 1H), 6.71–6.68 (m, 1H), 6.62–6.60 (m, 2H), 4.11 (s, 1H), 3.67–3.62 (m, 1H), 3.55–3.51 (m, 1H), 2.81–2.75 (m, 2H), 2.50–2.44 (m, 1H), 2.34–2.26 (m, 1H), 1.79–1.71 (m, 2H), 1.23 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.0, 167.1, 147.8, 139.8, 139.0, 132.4, 129.2, 128.7, 127.9, 126.8, 117.9, 113.3, 62.8, 53.3, 51.4, 31.8, 28.6, 28.4, 23.2 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{28}N_2NaO_2$ ([M+Na$^+$]) = 387.2048, Found 387.2048.



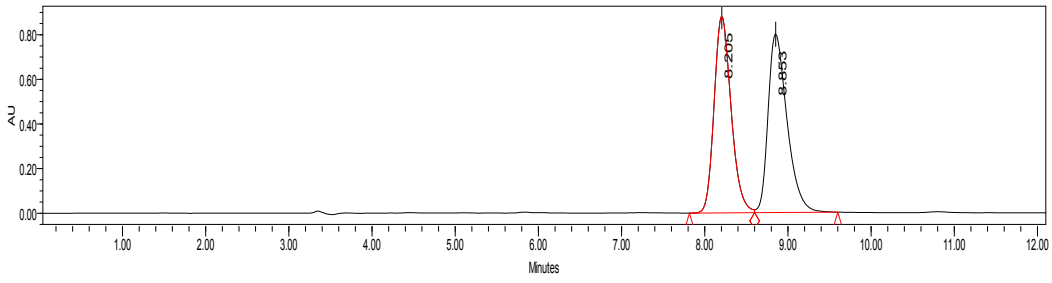


	Retention Time	% Area
1	7.162	49.53
2	10.319	50.47

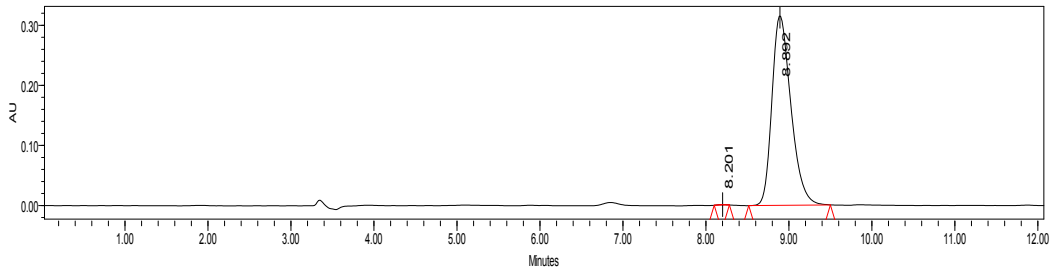


	Retention Time	% Area
1	7.094	51.61
2	10.196	48.39

tert-butyl-1-hydroxy-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**6**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a white solid in 99% yield, 99% ee; mp 116–118 °C; $[\alpha]_D^{23}$ = 94.4 (c = 0.34, CH_2Cl_2). HPLC (Chiralpak IC, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL/min, λ = 254 nm) retention time: 8.20 min (minor), 8.89 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.62–7.60 (d, *J* = 7.6 Hz, 1H), 7.25–7.14 (m, 4H), 7.07–7.05 (m, 1H), 6.70–6.63 (m, 3H), 4.77–4.75 (d, *J* = 9.2 Hz, 1H), 4.63 (s, 1H), 3.70–3.68 (d, *J* = 10.0 Hz, 1H), 3.59–3.56 (d, *J* = 12.0 Hz, 1H), 3.38–3.35 (d, *J* = 12.0 Hz, 1H), 2.88–2.77 (m, 2H), 2.29–2.25 (m, 1H), 1.91–1.84 (m, 1H), 1.32 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 148.4, 138.7, 134.8, 129.2, 128.3, 127.3, 127.1, 126.5, 117.5, 113.1, 82.2, 74.3, 51.3, 51.2, 27.9, 27.9, 26.0 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{27}NNaO_3$ ([M+Na$^+$]) = 376.1889, Found 376.1883.

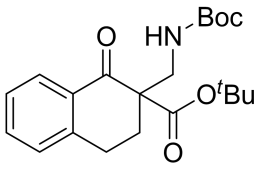


	Retention Time	% Area
1	8.205	49.70
2	8.853	50.30

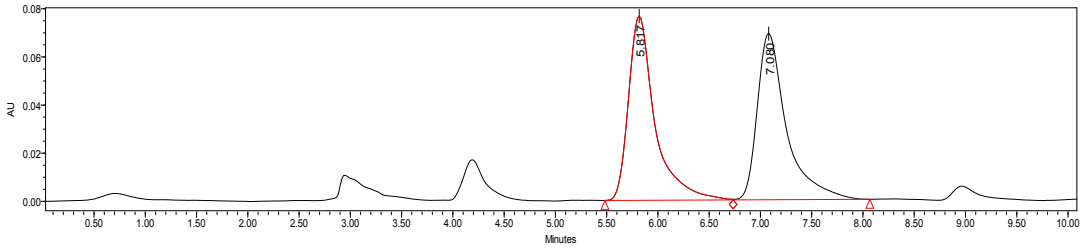


	Retention Time	% Area
1	8.201	0.11
2	8.892	99.89

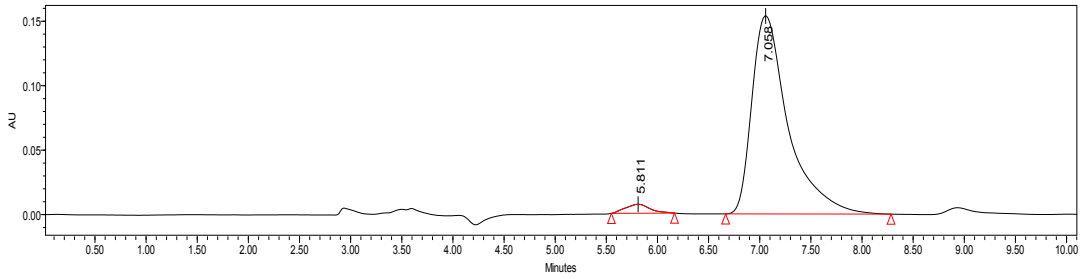
tert-butyl 2-(((tert-butoxycarbonyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthal



-ene-2-carboxylate (**7**): Purified by flash chromatography (petroleum ether: EtOAc = 10:1) to afford a yellow oil in 60% yield, 94% ee; $[\alpha]_D^{23}$ = 45.5 (c = 0.45, CH_2Cl_2). HPLC (Chiralpak IA, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) retention time: 5.81 min (minor), 7.06 min (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.02 (d, *J* = 8.0 Hz, 1H), 7.50–7.46 (m, 1H), 7.34–7.30 (m, 1H), 7.24–7.22 (m, 1H), 6.79 (s, 1H), 3.80–3.75 (m, 1H), 3.49–3.45 (m, 1H), 3.03 (m, 2H), 2.49–2.46 (m, 1H), 2.18–2.13 (m, 1H), 1.42 (s, 9H), 1.37 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 148.3, 137.5, 134.9, 129.2, 128.4, 128.0, 127.5, 126.4, 118.1, 113.9, 81.8, 71.6, 50.6, 47.4, 27.9, 26.6, 25.5 ppm. HRMS (ESI-TOF) calcd for $C_{21}H_{29}NNaO_5$ ([M+Na^+]) = 398.1943, Found 398.1940.

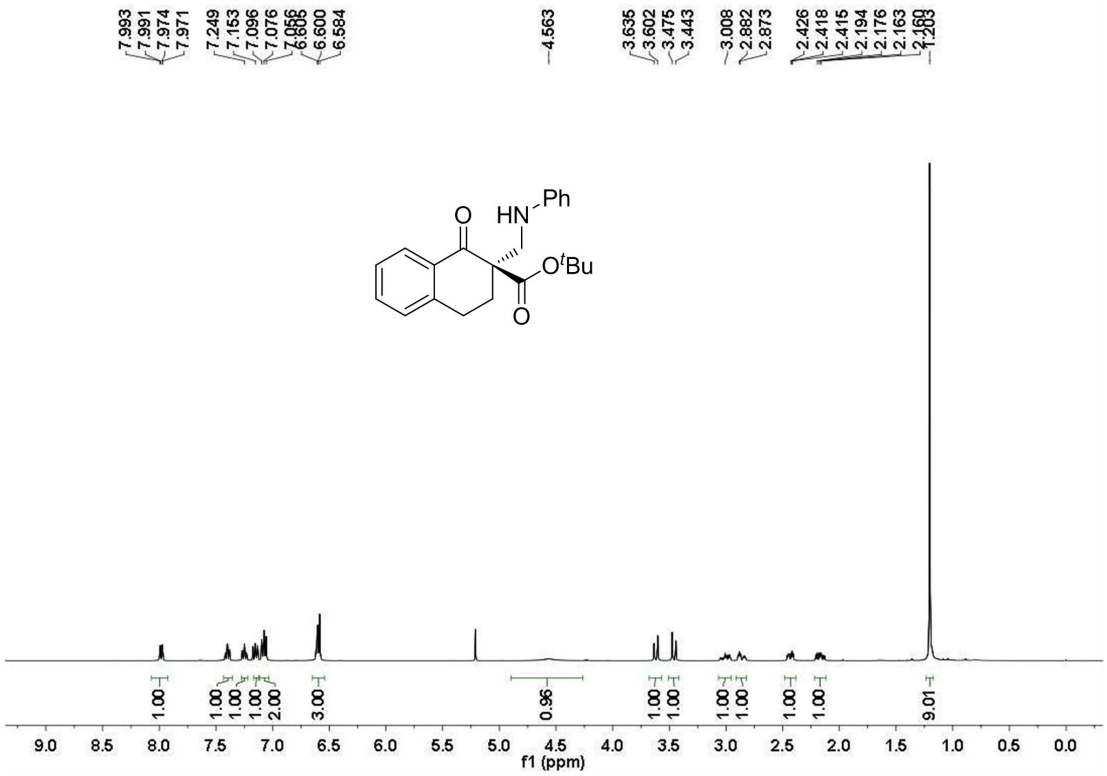


	Retention Time	% Area
1	5.817	50.14
2	7.080	49.86



	Retention Time	% Area
1	5.811	2.95
2	7.058	97.05

8. Copies of NMR spectra for the reaction products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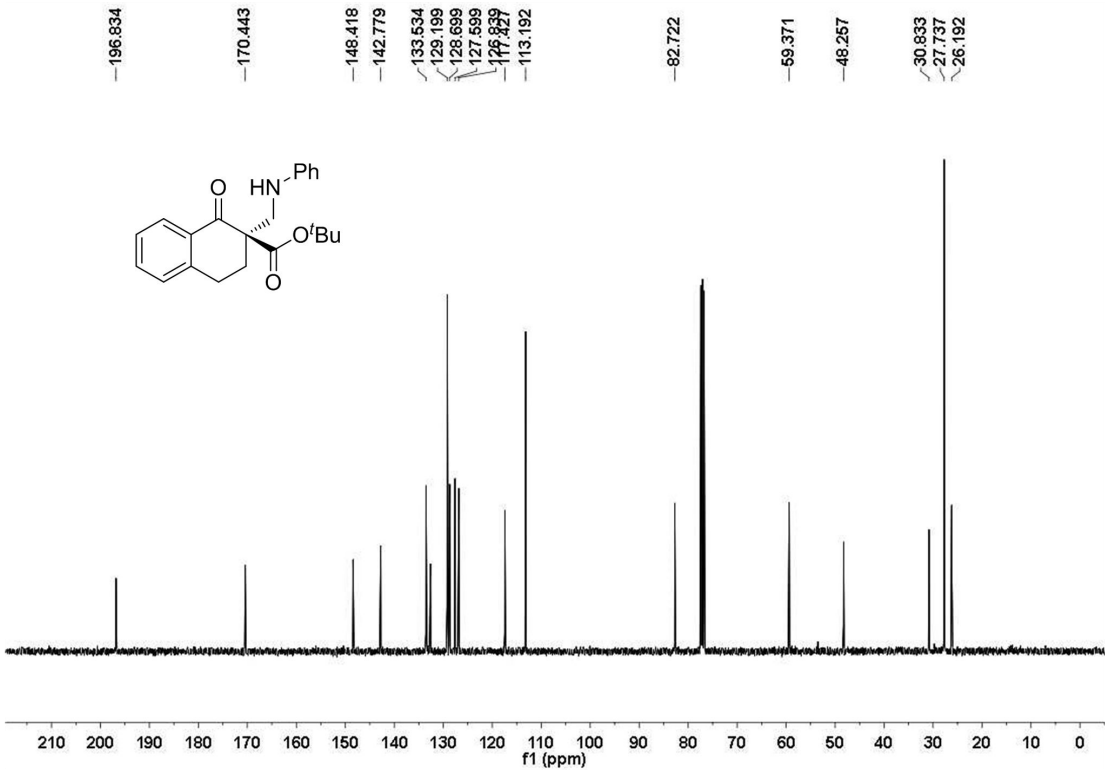
3.635
3.602
3.475
3.443
3.008
2.882
2.873
2.426
2.418
2.415
2.194
2.176
2.163
1.283
HN
Ph
O
O
O
tBu
1.00
1.00
1.00
1.00
2.00
3.00
0.96
1.00
1.00
1.00
1.00
1.00
1.00
9.01
f1 (ppm)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133.534
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128.699
127.599
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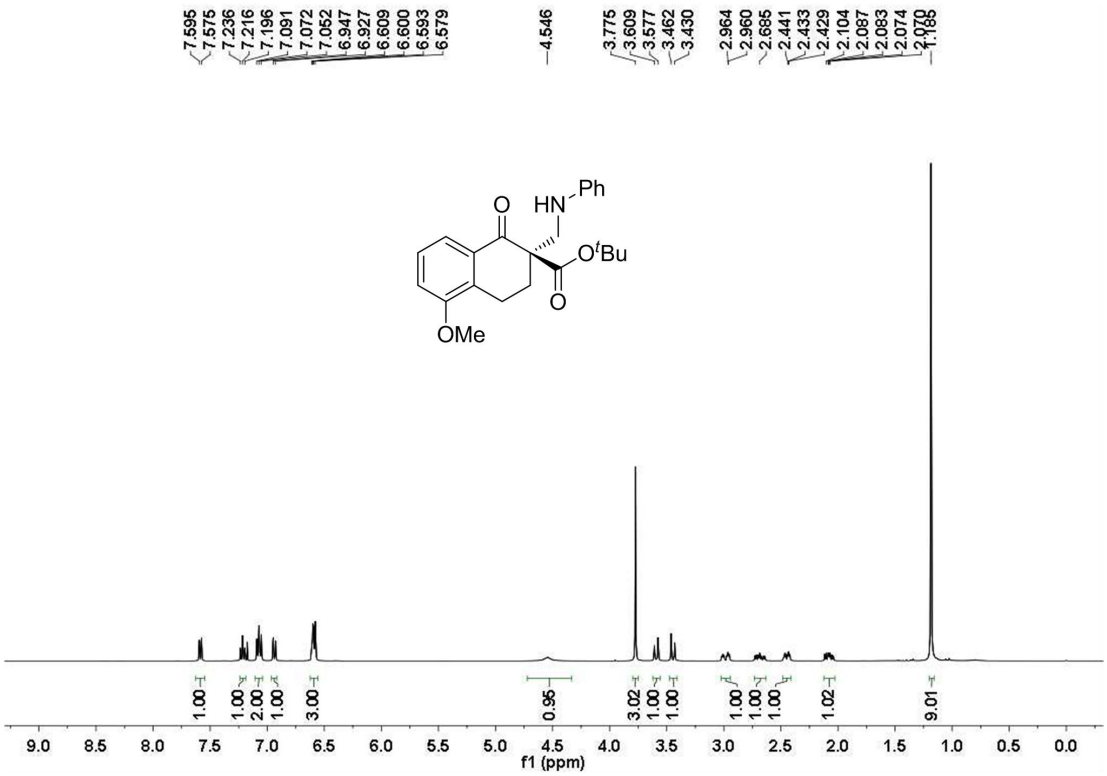
27.737
26.192
HN
Ph
O
O
O
tBu
f1 (ppm)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7.091
7.072
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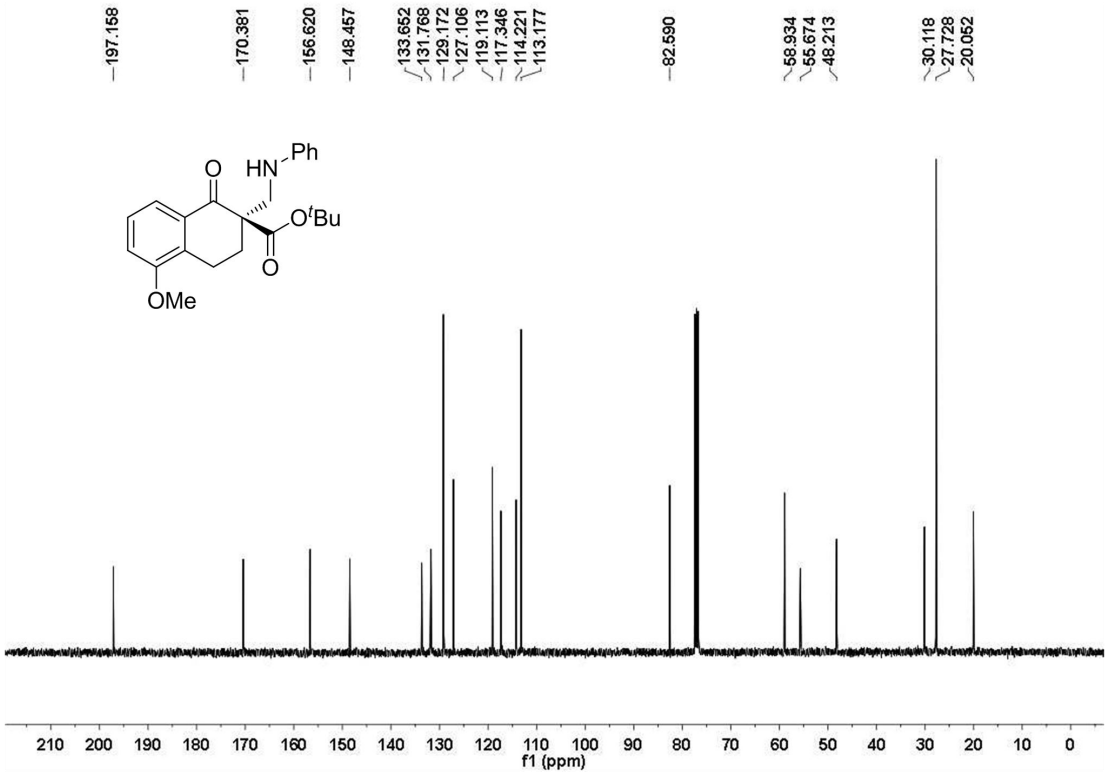
6.927
6.609
6.600
6.593
6.579
4.546
3.775
3.609
3.577
3.462
3.430
2.964
2.960
2.685
2.441
2.433
2.429
2.104
2.087
2.083
2.074
1.185
O
HN
Ph
O
tBu
O
OMe
1.00
1.00
2.00
1.00
3.00
0.95
3.02
1.00
1.00
1.00
1.00
1.00
1.02
9.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.172
127.106
119.113
117.346
114.221
113.177
82.590
58.934
55.674
48.213
30.118
27.728
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HN
Ph
O
tBu
O
OMe
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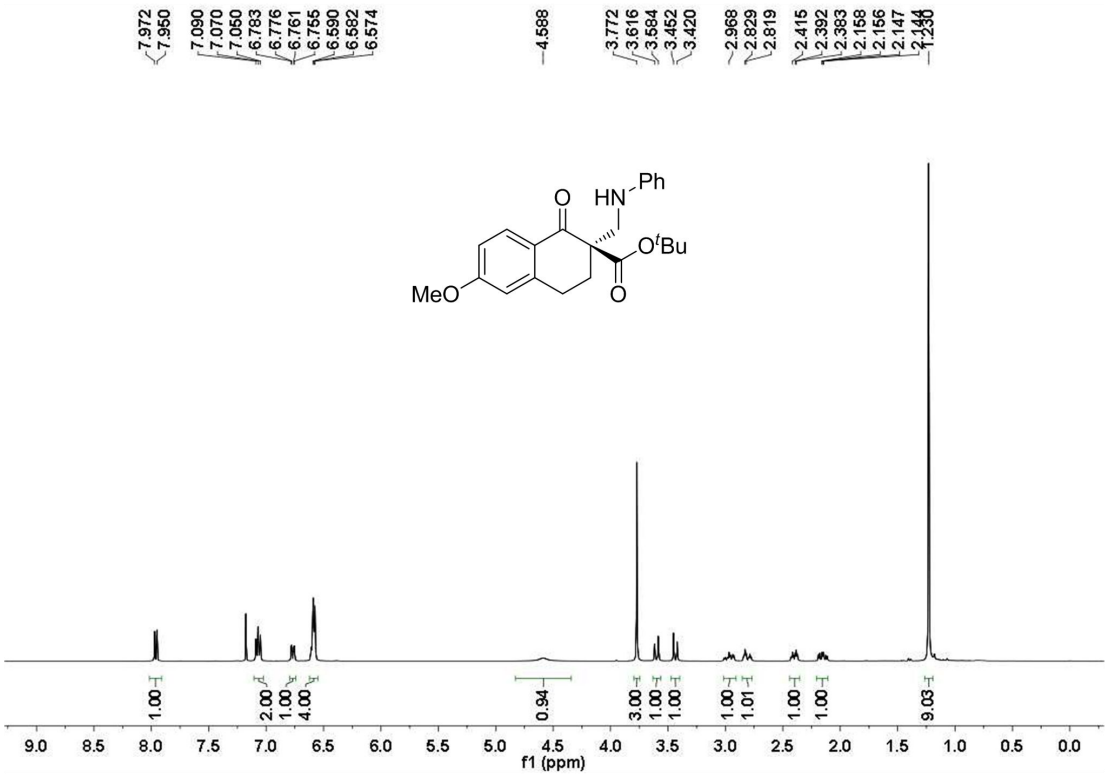
f1 (ppm)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6.574
4.588
3.772
3.616
3.584
3.452
3.420
2.968
2.829
2.819
2.415
2.392
2.383
2.158
2.156
2.147
2.144
1.230
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Ph
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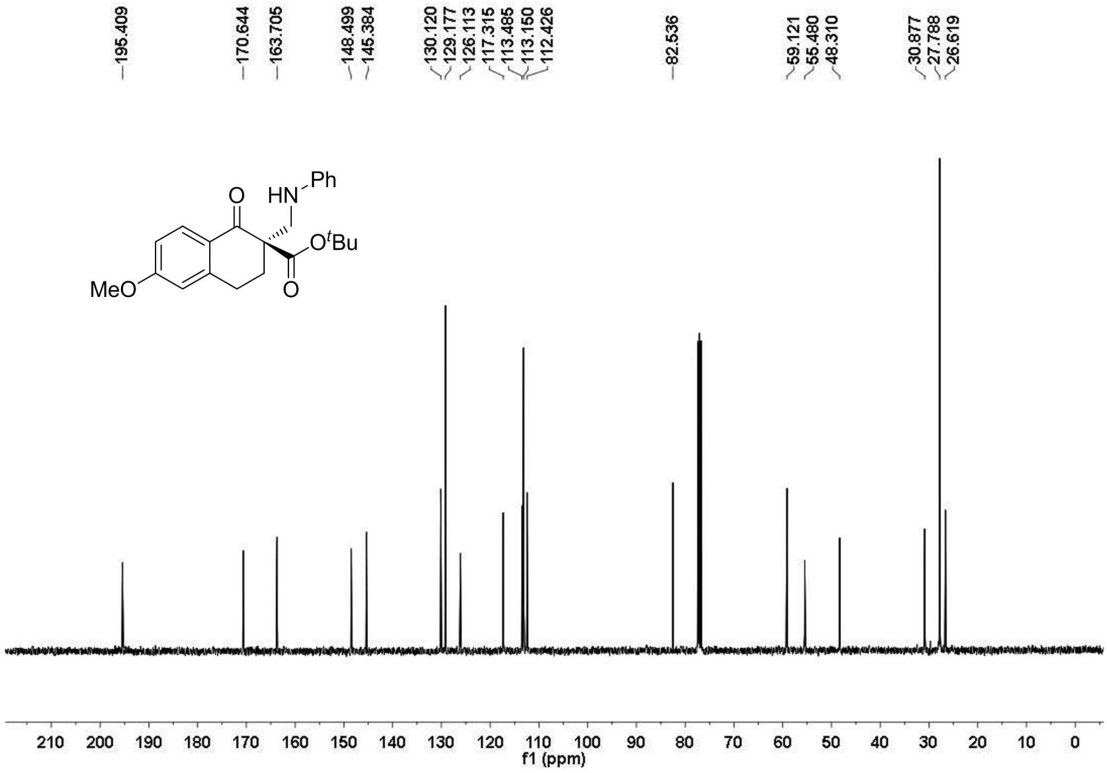
O
tBu
MeO
O
1.00
2.00
1.00
4.00
0.94
3.00
1.00
1.00
1.00
1.01
1.00
1.00
9.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.113
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113.485
113.150
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82.536
59.121
55.480
48.310
30.877
27.788
26.619
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O
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MeO
O
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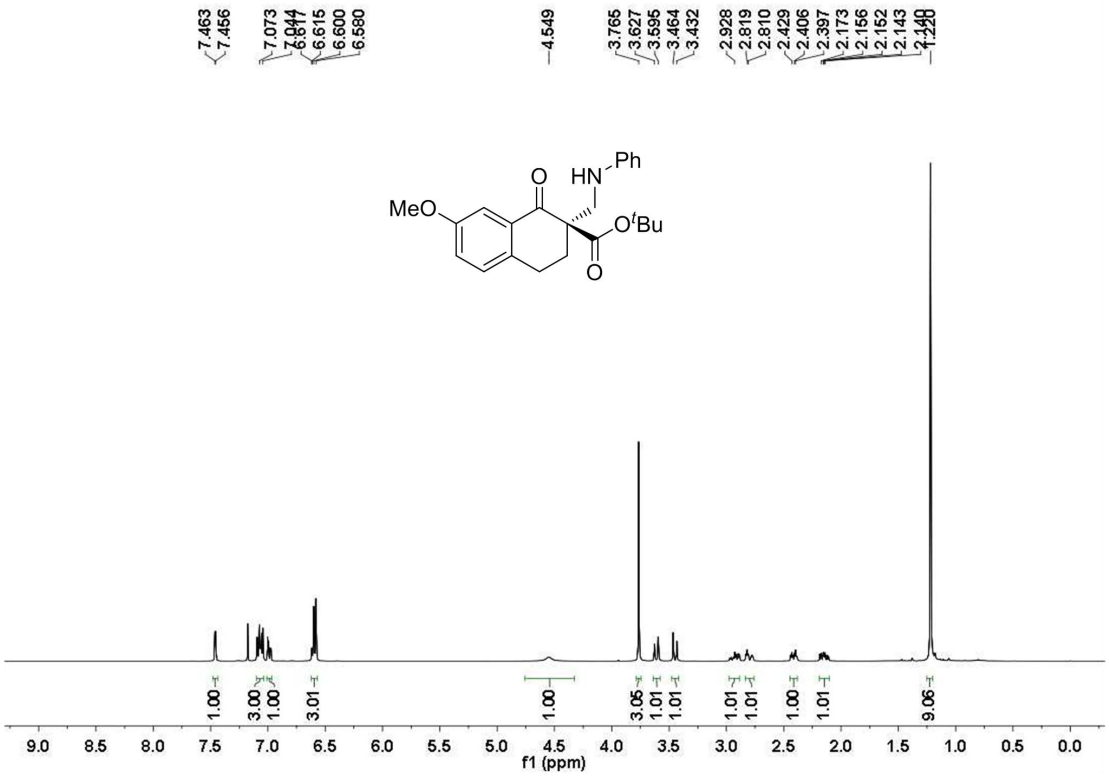
f1 (ppm)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6.580
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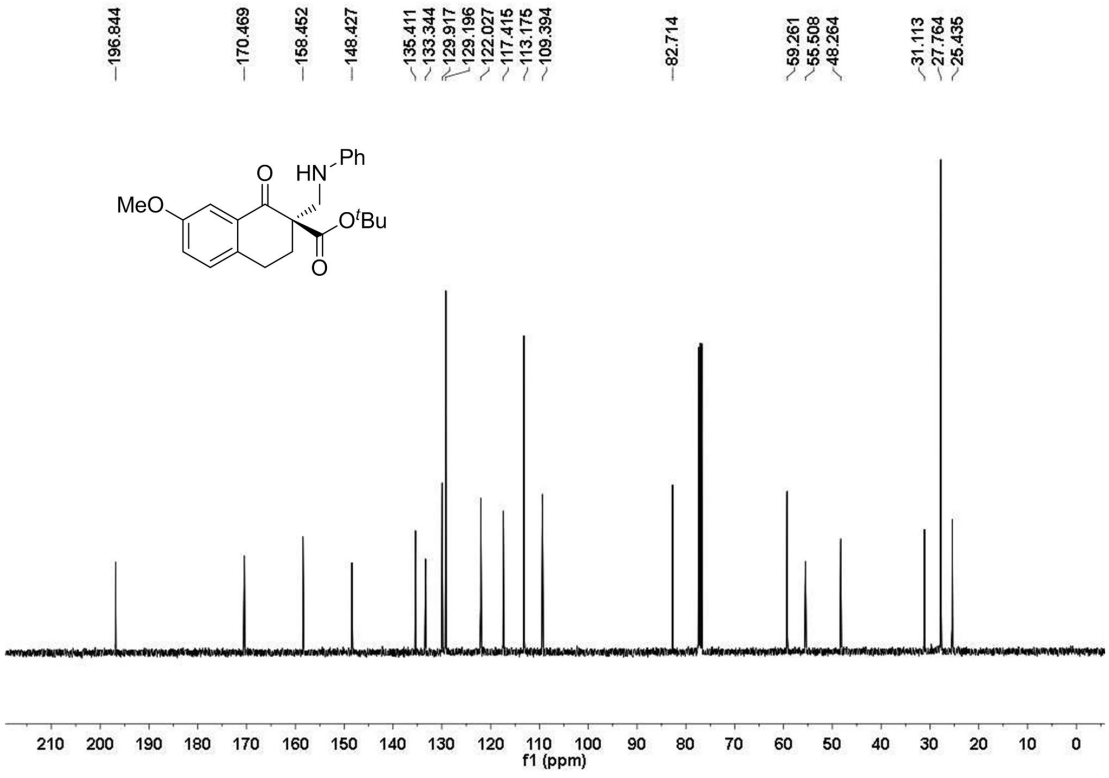
3.627
3.595
3.464
3.432
2.928
2.819
2.810
2.429
2.406
2.397
2.173
2.156
2.152
2.143
1.220
O
HN
Ph
MeO
O^{t}Bu
O
1.00
3.00
1.00
3.01
1.00
3.05
1.01
1.01
1.01
1.01
1.00
1.01
9.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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82.714
59.261
55.508
48.264
31.113
27.764
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Ph
MeO
O^{t}Bu
O
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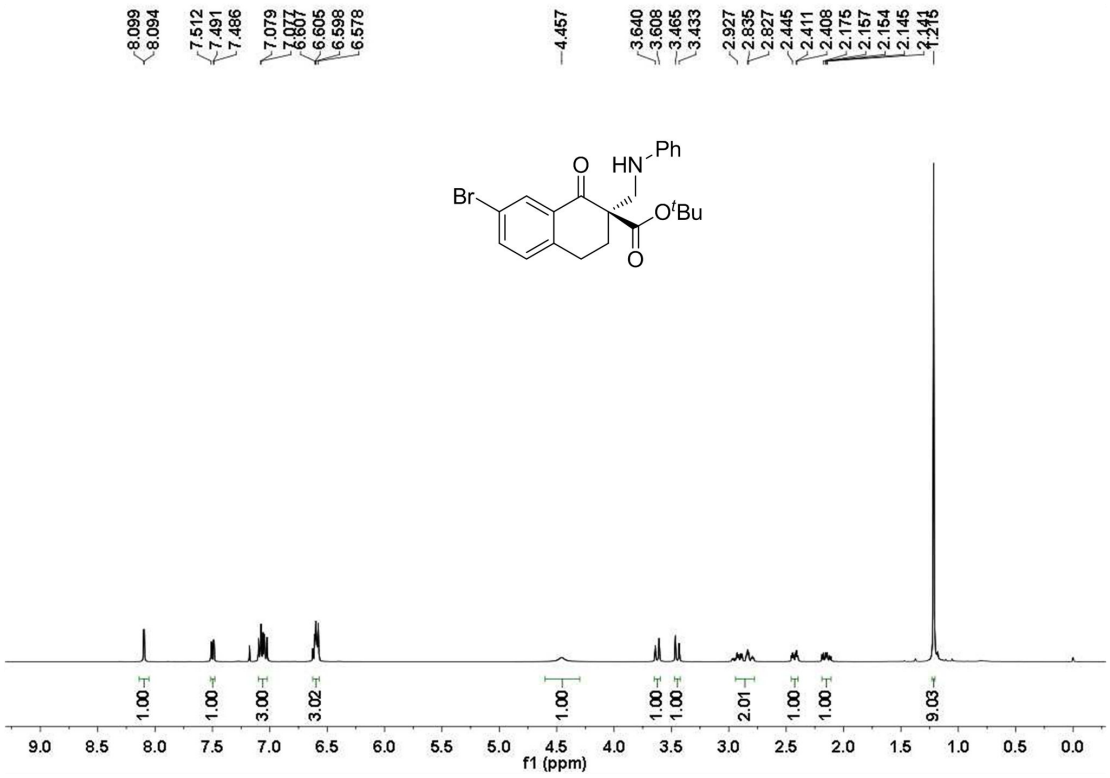
f1 (ppm)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2.835
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2.408
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2.157
2.154
2.145
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Ph
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O
tBu
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1.00
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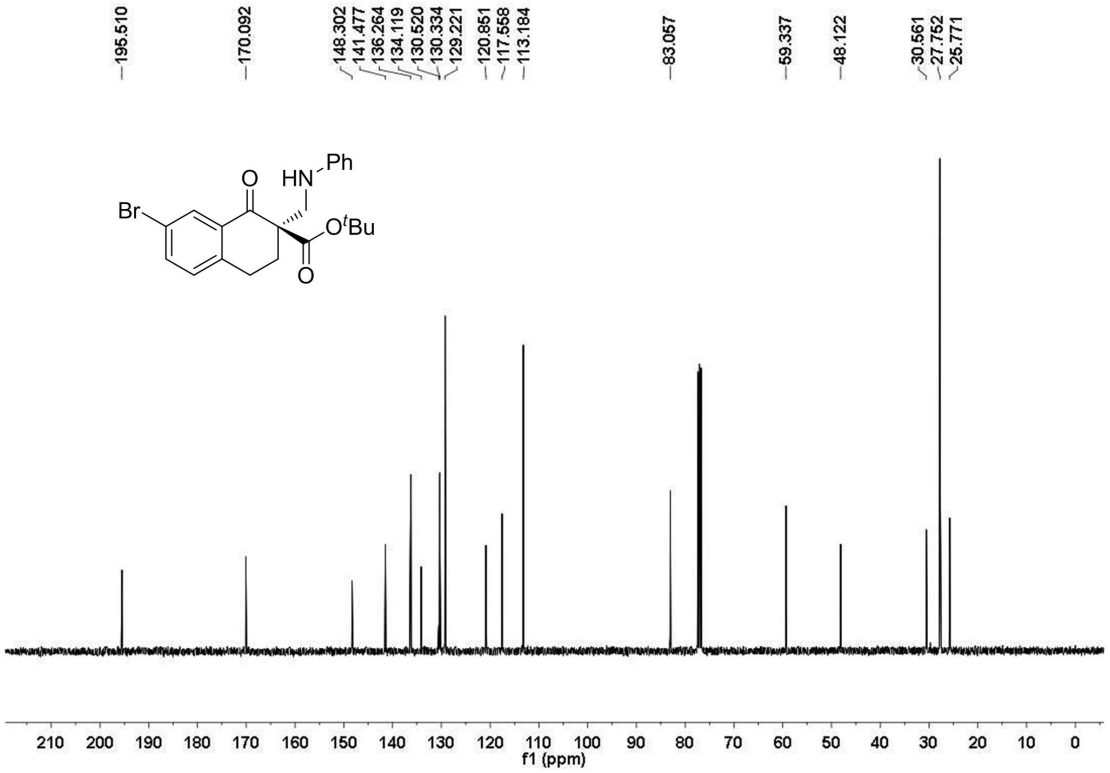
3.02
1.00
1.00
1.00
2.01
1.00
1.00
9.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.334
129.221
120.851
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113.184
83.057
59.337
48.122
30.561
27.752
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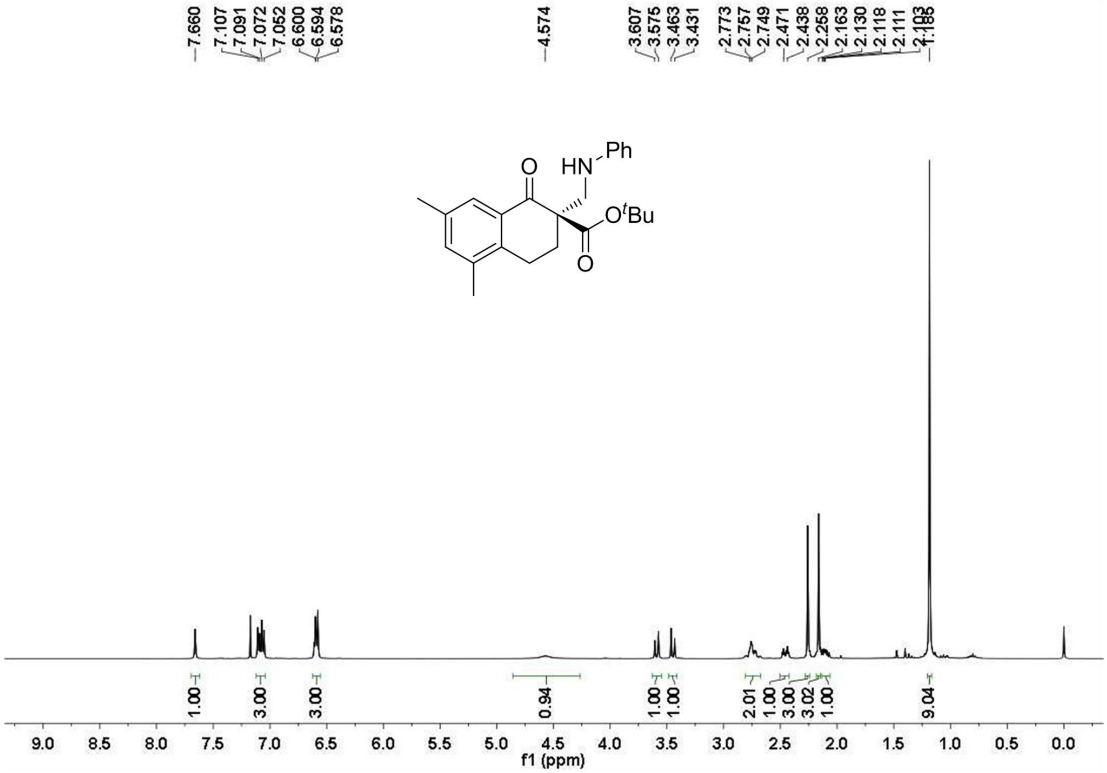
Br
O
HN
Ph
O
O
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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2.773
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2.471
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O
HN
Ph
O
O
tBu
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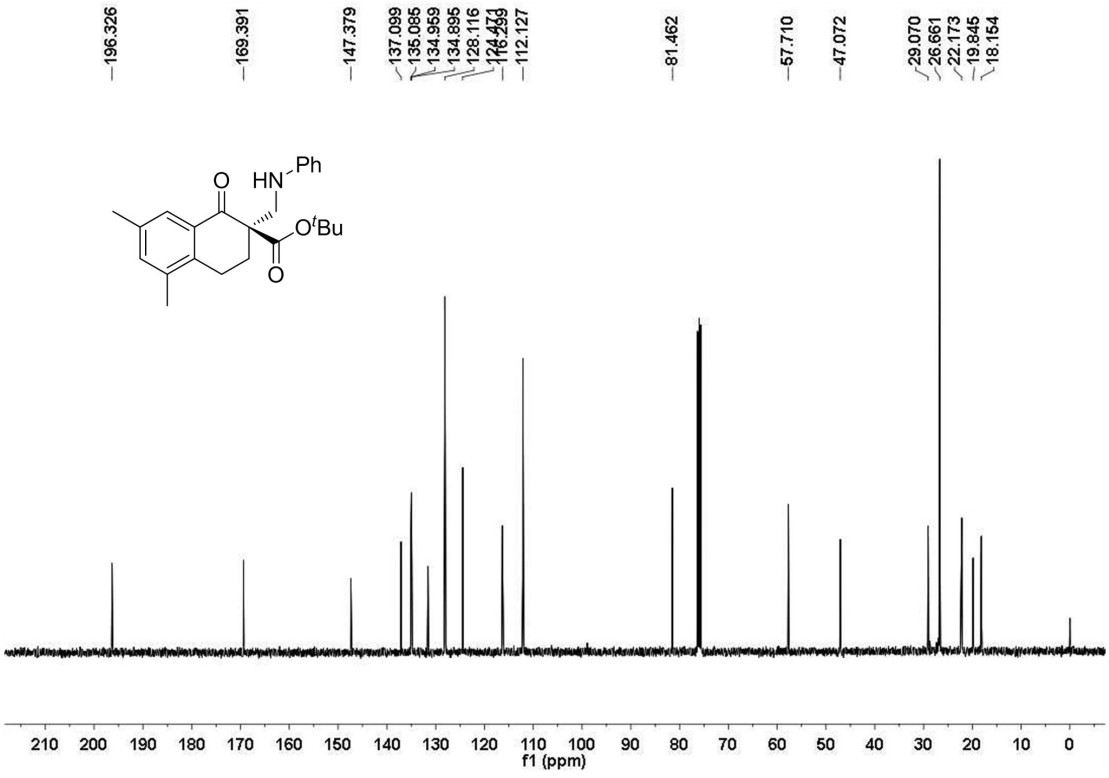
f1 (ppm)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Ph
O
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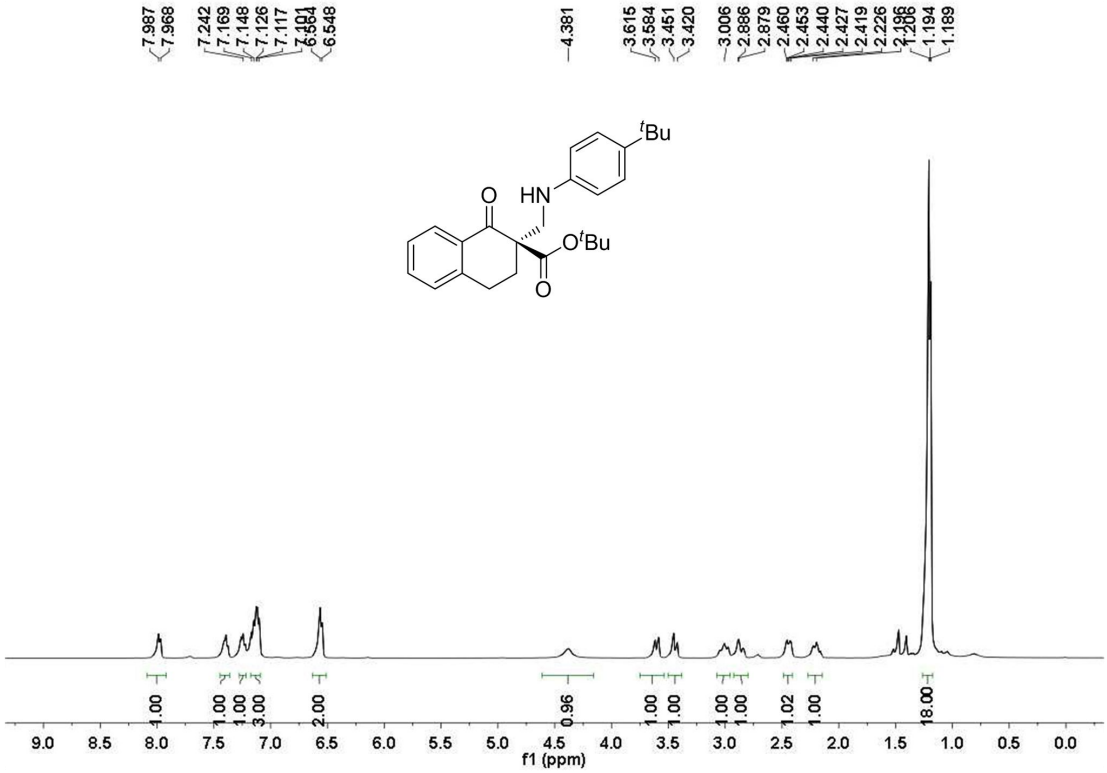
tBu
f1 (ppm)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3.584
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2.419
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2.196
2.186
1.206
1.194
1.189
tBu
HN
O
OtBu
O
1.00
1.00
1.00
3.00
2.00
0.96
1.00
1.00
1.00
1.00
1.02
1.00
18.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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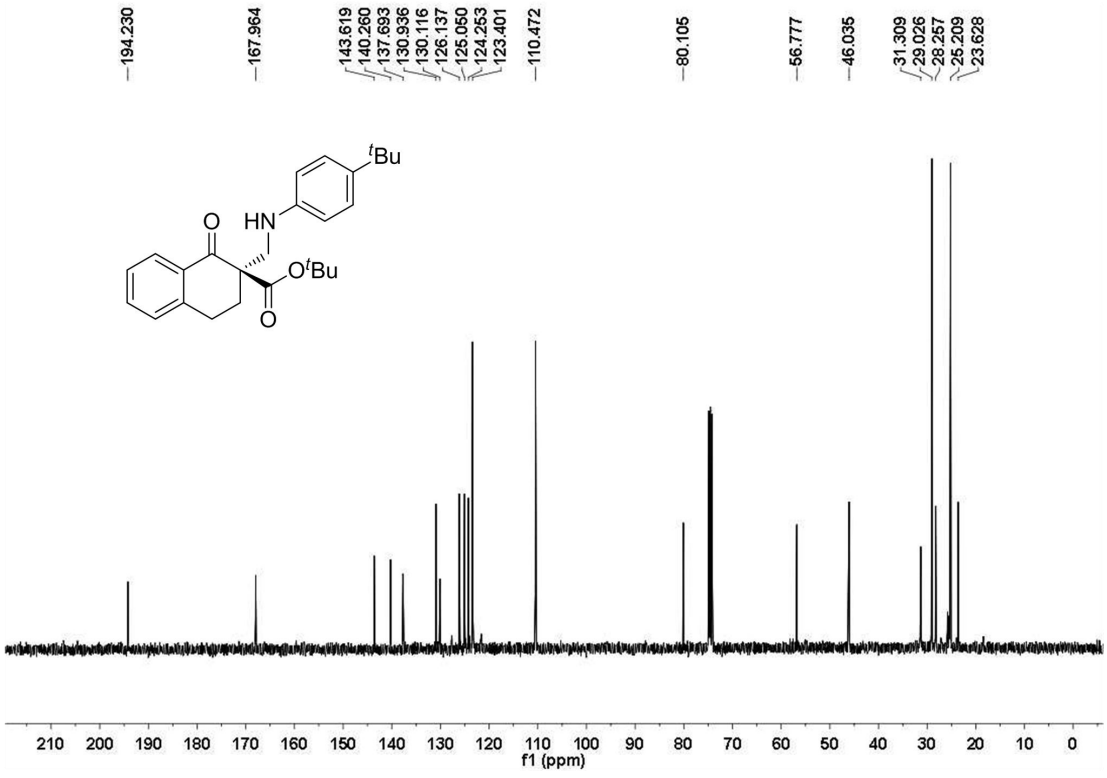
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167.964
143.619
140.260
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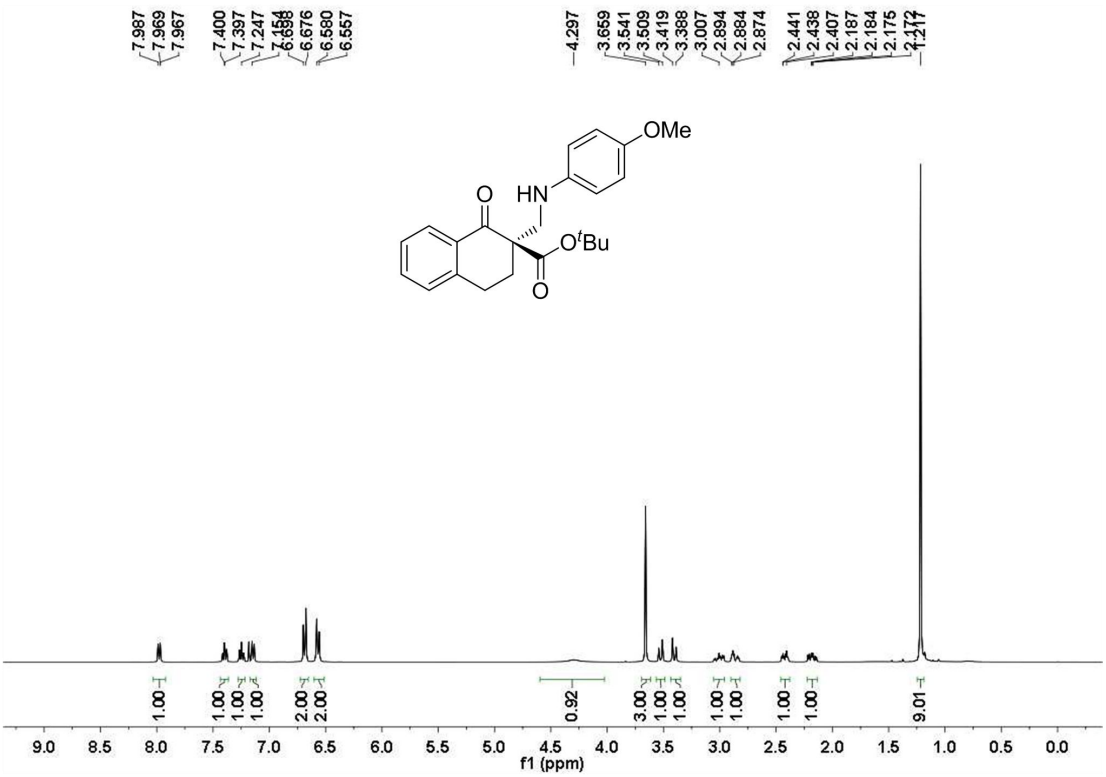
130.936
130.116
126.137
125.050
124.253
123.401
110.472
80.105
56.777
46.035
31.309
29.026
28.257
25.209
23.628
tBu
HN
O
OtBu
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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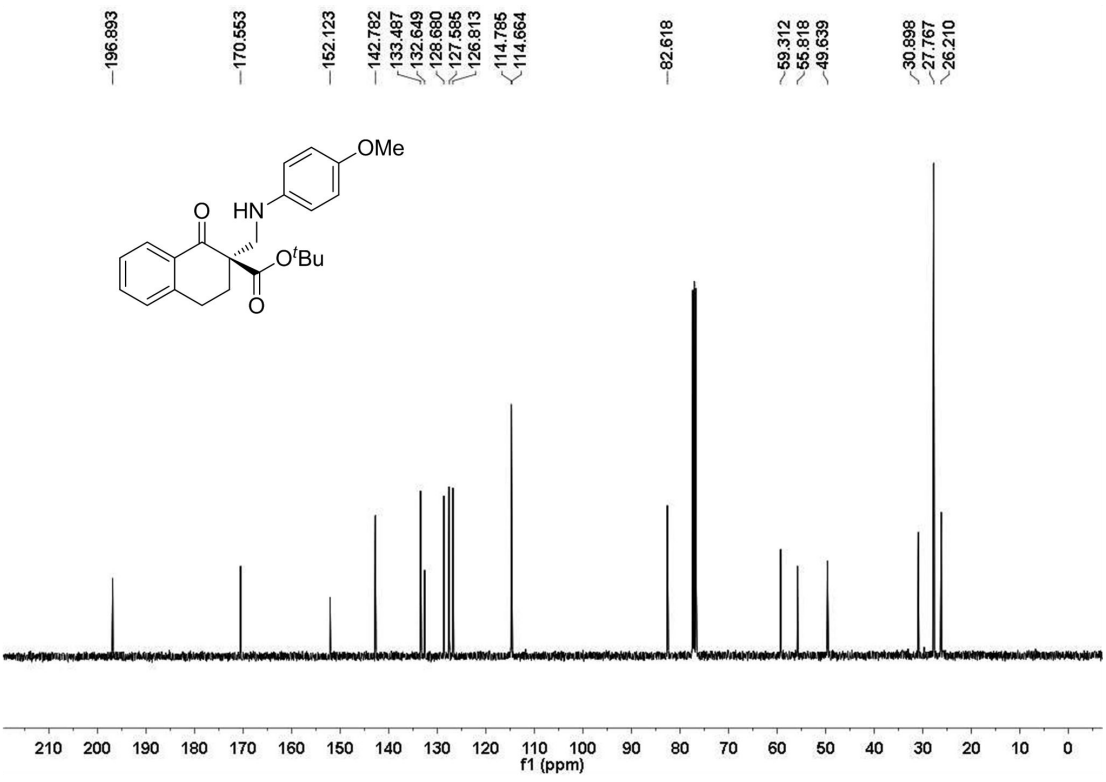
7.969
7.967
7.400
7.397
7.247
6.676
6.580
6.557
4.297
3.659
3.541
3.509
3.419
3.388
3.007
2.894
2.884
2.874
2.441
2.438
2.407
2.187
2.184
2.175
1.217
OMe
HN
O
O
O
O
tBu
1.00
1.00
1.00
1.00
2.00
2.00
0.92
3.00
1.00
1.00
1.00
1.00
1.00
1.00
9.01
f1 (ppm)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152.123
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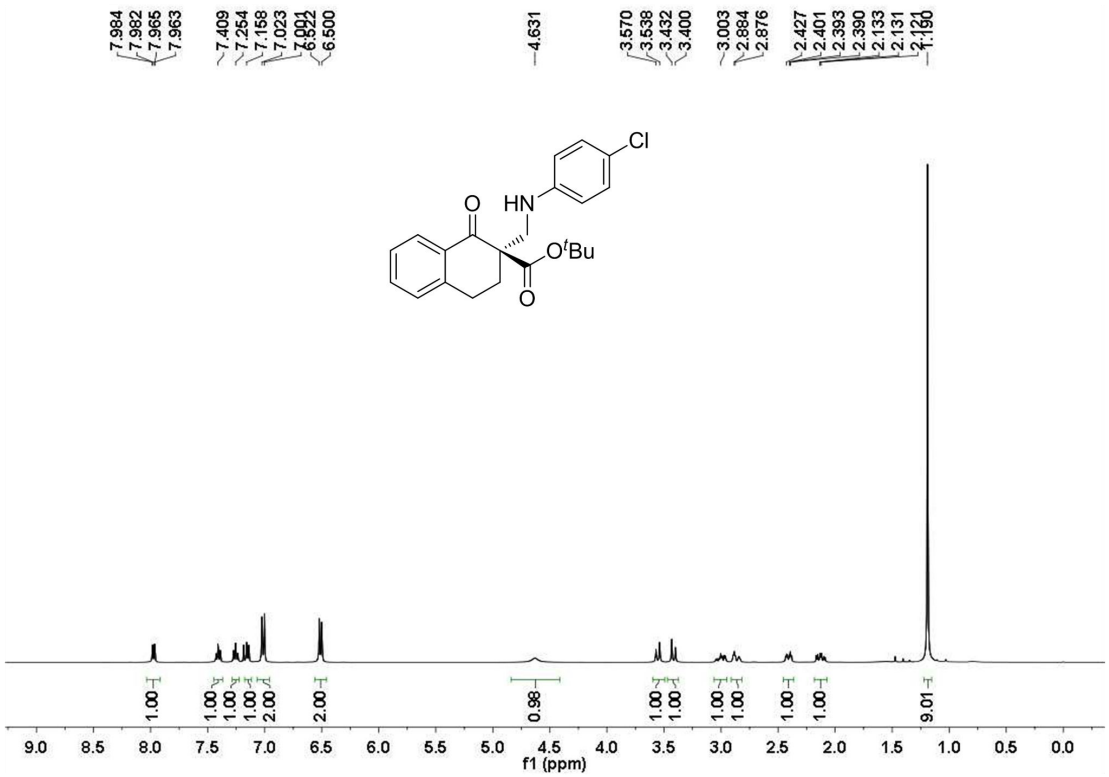
128.680
127.585
126.813
114.785
114.664
82.618
59.312
55.818
49.639
30.898
27.767
26.210
OMe
HN
O
O
O
O
tBu
f1 (ppm)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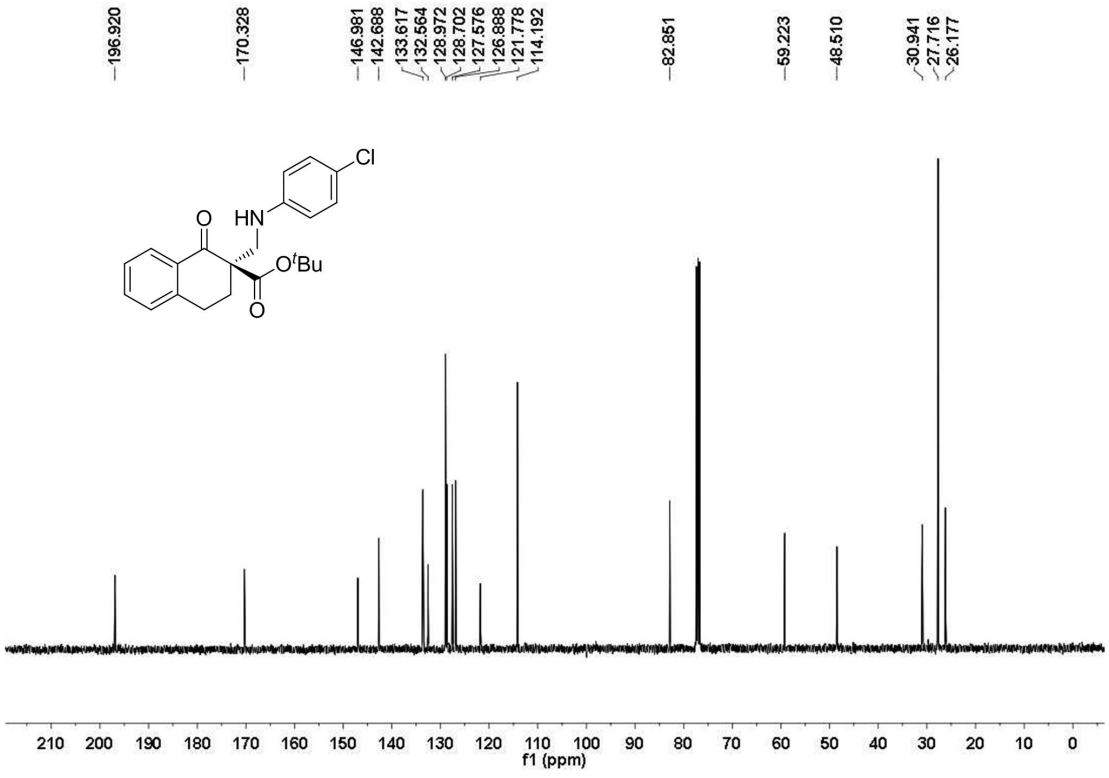
7.982
7.965
7.963
7.409
7.254
7.158
7.023
7.001
6.822
6.500
4.631
3.570
3.538
3.432
3.400
3.003
2.884
2.876
2.427
2.401
2.393
2.390
2.133
2.131
2.121
1.190
Cl
HN
O
O
O
tBu
1.00
1.00
1.00
1.00
2.00
2.00
0.98
1.00
1.00
1.00
1.00
1.00
1.00
9.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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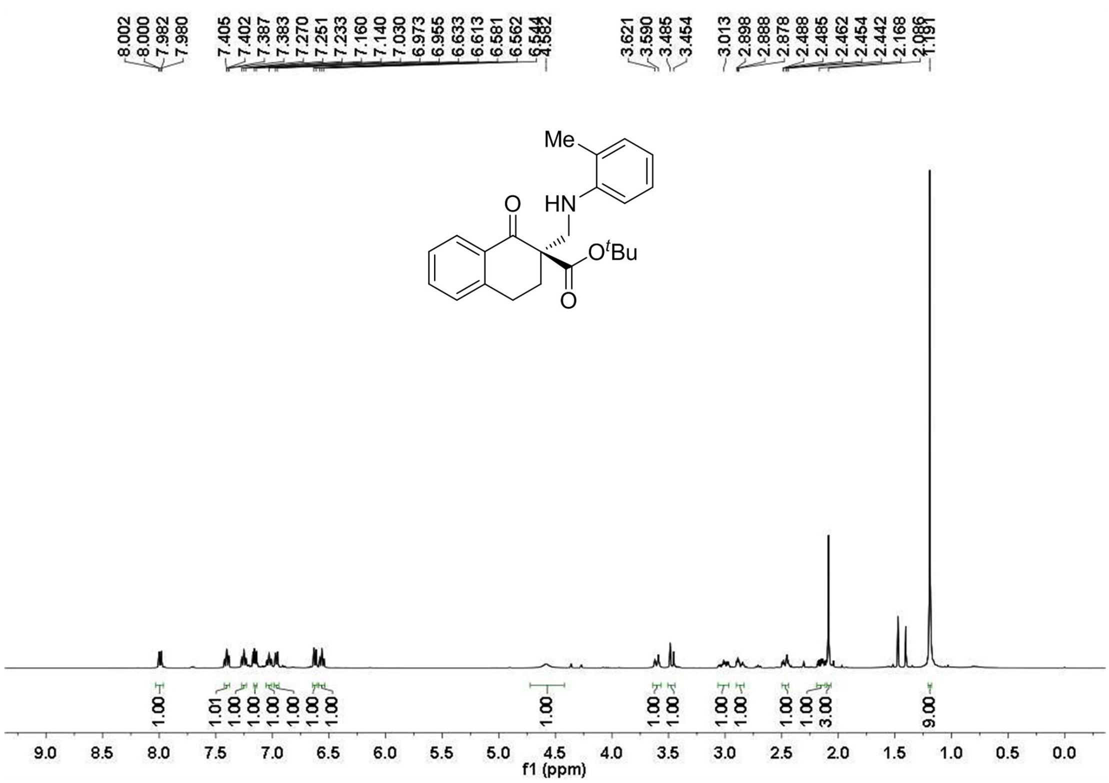
146.981
142.688
133.617
132.564
128.972
128.702
127.576
126.888
121.778
114.192
82.851
59.223
48.510
30.941
27.716
26.177
Cl
HN
O
O
O
tBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.000
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7.980
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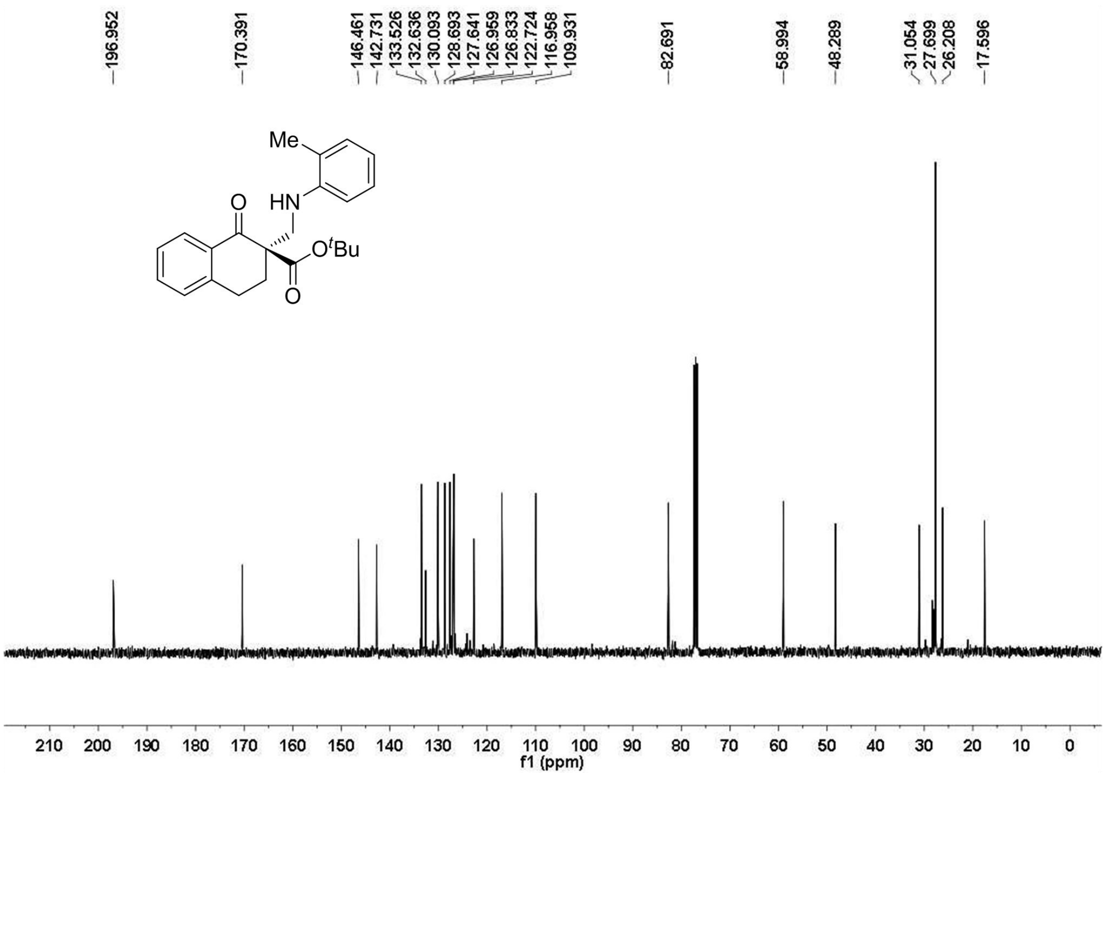
7.402
7.387
7.383
7.270
7.251
7.233
7.160
7.140
7.030
6.973
6.955
6.633
6.613
6.581
6.562
6.544
4.582
3.621
3.590
3.485
3.454
3.013
2.898
2.888
2.878
2.488
2.485
2.462
2.454
2.442
2.168
2.086
1.191
Me
HN
O
O^{t}Bu
O
1.00
1.01
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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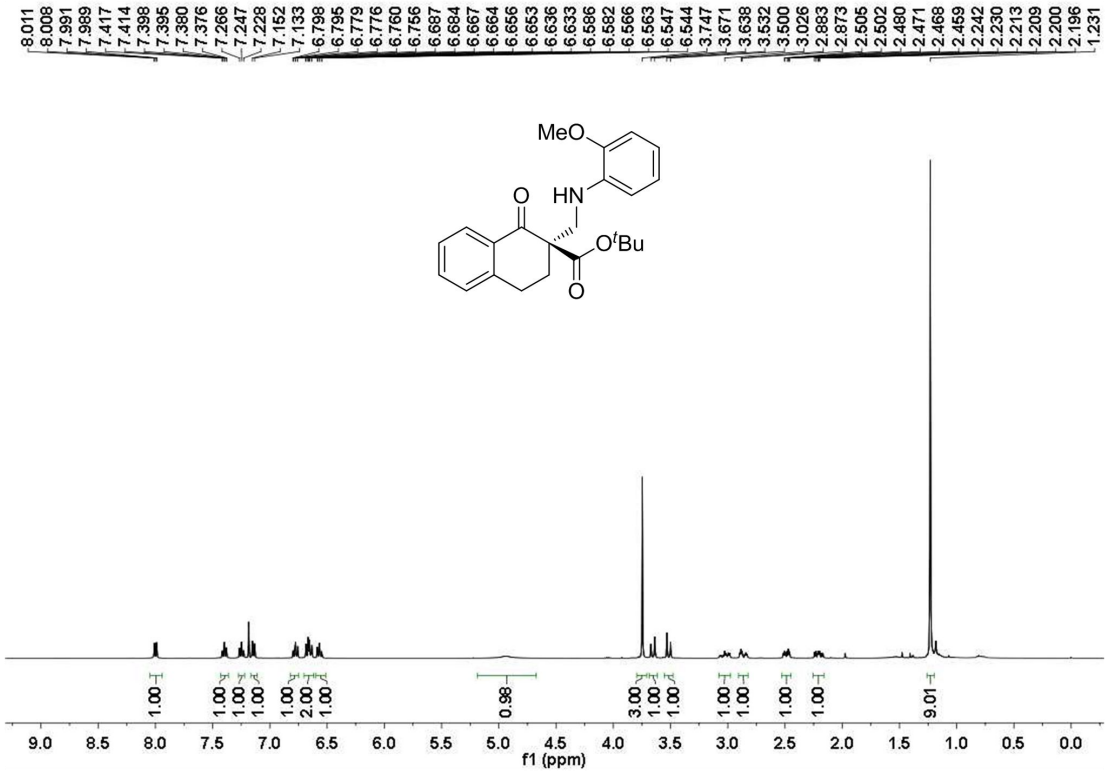
146.461
142.731
133.526
132.636
130.093
128.693
127.641
126.959
126.833
122.724
116.958
109.931
82.691
58.994
48.289
31.054
27.699
26.208
17.596
Me
HN
O
O^{t}Bu
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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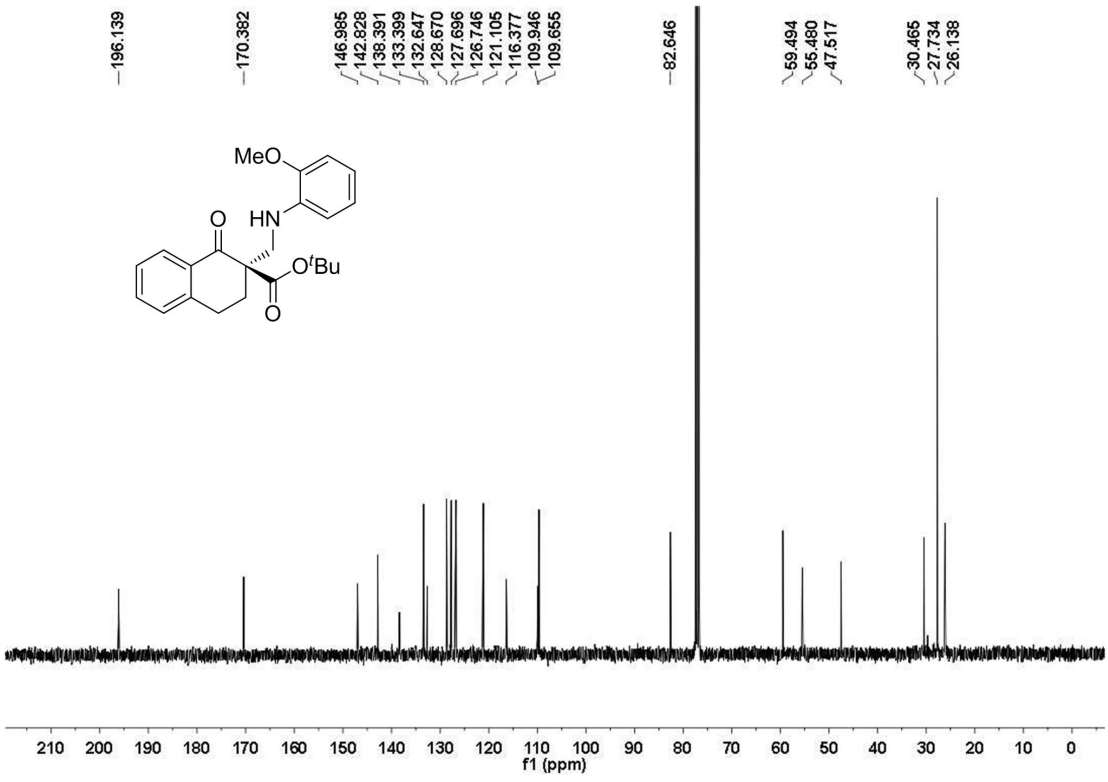
8.008
7.991
7.989
7.417
7.414
7.398
7.395
7.380
7.376
7.266
7.247
7.228
7.152
7.133
6.798
6.795
6.779
6.776
6.760
6.756
6.687
6.684
6.667
6.664
6.656
6.653
6.636
6.633
6.586
6.582
6.566
6.563
6.547
6.544
3.747
3.671
3.638
3.532
3.500
3.026
2.883
2.873
2.505
2.502
2.480
2.471
2.468
2.459
2.242
2.230
2.213
2.209
2.200
2.196
1.231
MeO
HN
O
O
O
O
t
Bu
1.00
1.00
1.00
1.00
2.00
1.00
0.98
3.00
1.00
1.00
1.00
1.00
1.00
1.00
9.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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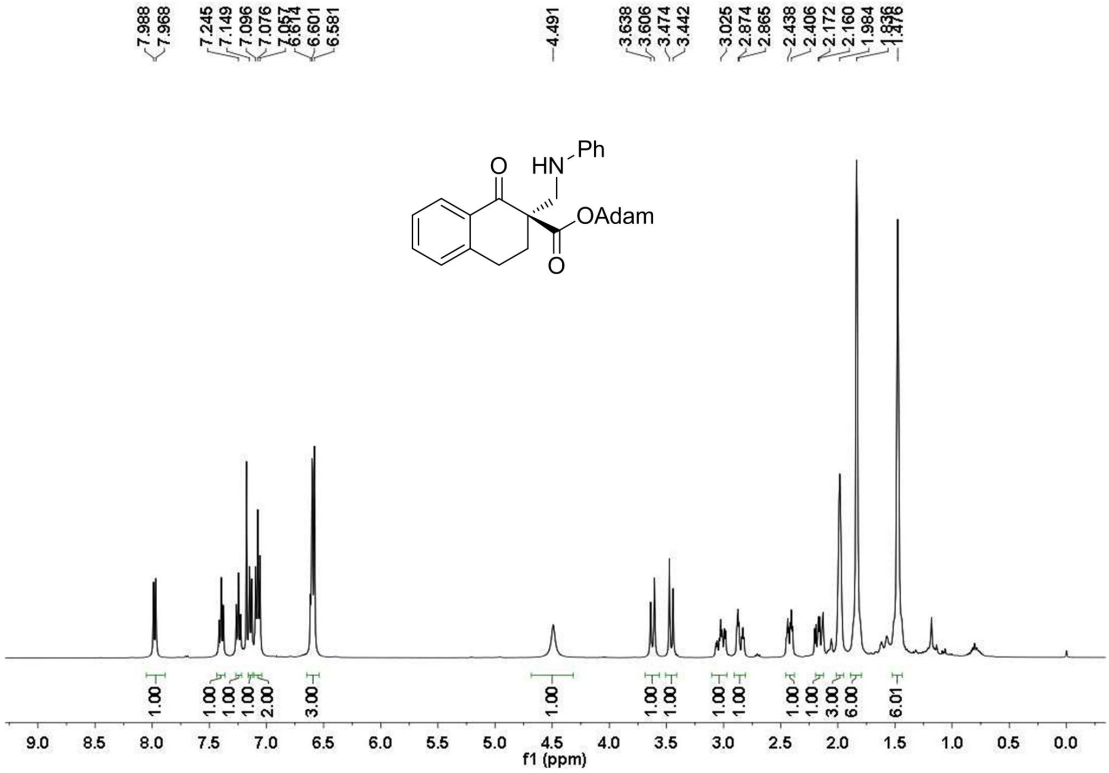
146.985
142.828
138.391
133.399
132.647
128.670
127.696
126.746
121.105
116.377
109.946
109.655
82.646
59.494
55.480
47.517
30.465
27.734
26.138
MeO
HN
O
O
O
O
t
Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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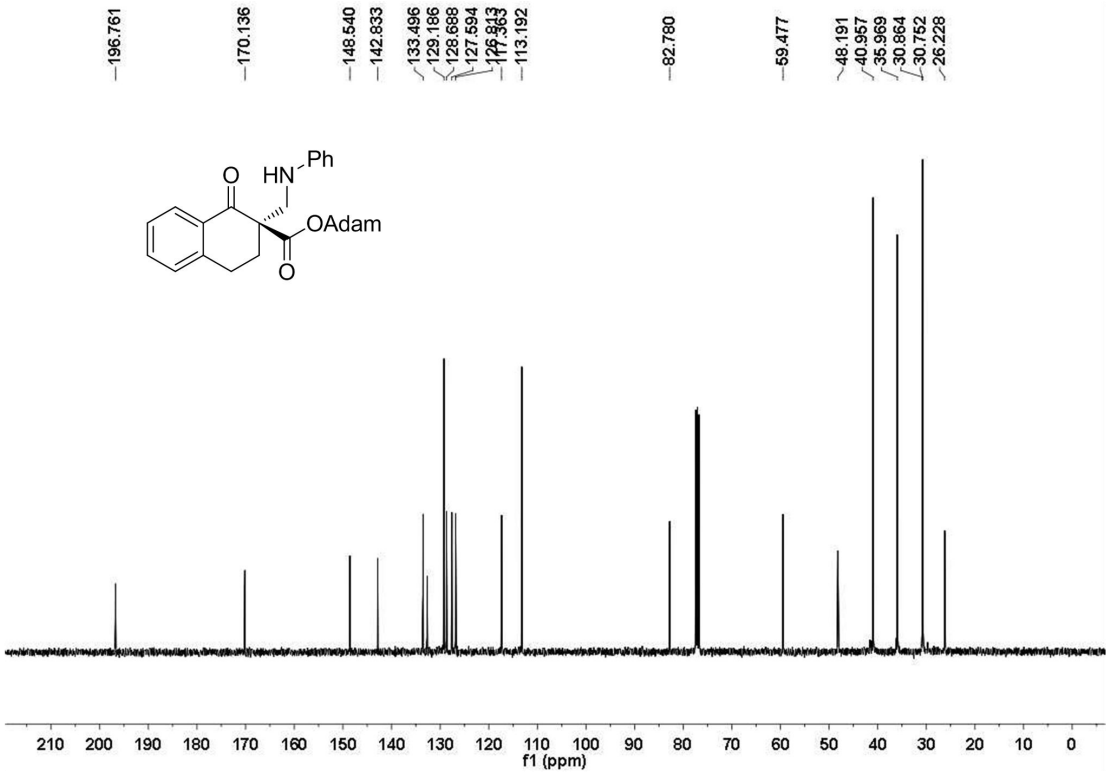
7.149
7.096
7.076
7.057
6.814
6.601
6.581
4.491
3.638
3.606
3.474
3.442
3.025
2.874
2.865
2.438
2.406
2.172
2.160
1.984
1.836
1.476
HN
Ph
O
OAdam
O
1.00
1.00
1.00
1.00
2.00
3.00
1.00
1.00
1.00
1.00
1.00
3.00
6.00
6.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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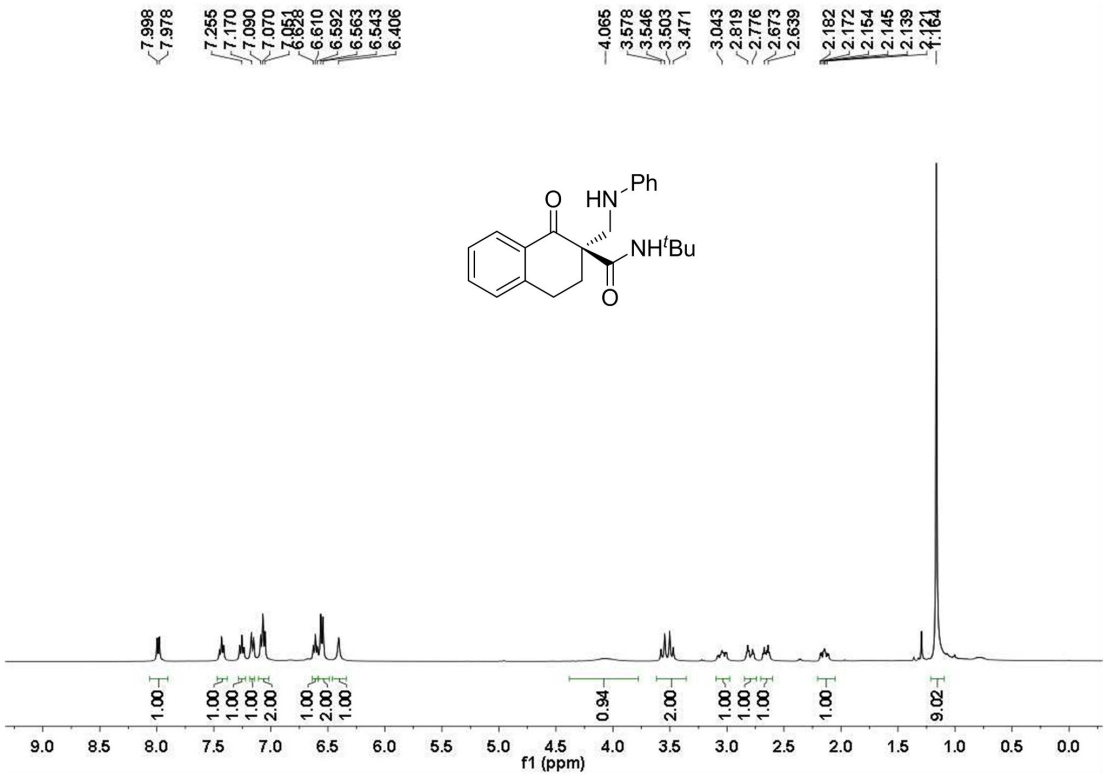
133.496
129.186
128.688
127.594
126.813
117.363
113.192
82.780
59.477
48.191
40.957
35.969
30.864
30.752
26.228
HN
Ph
O
OAdam
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.978
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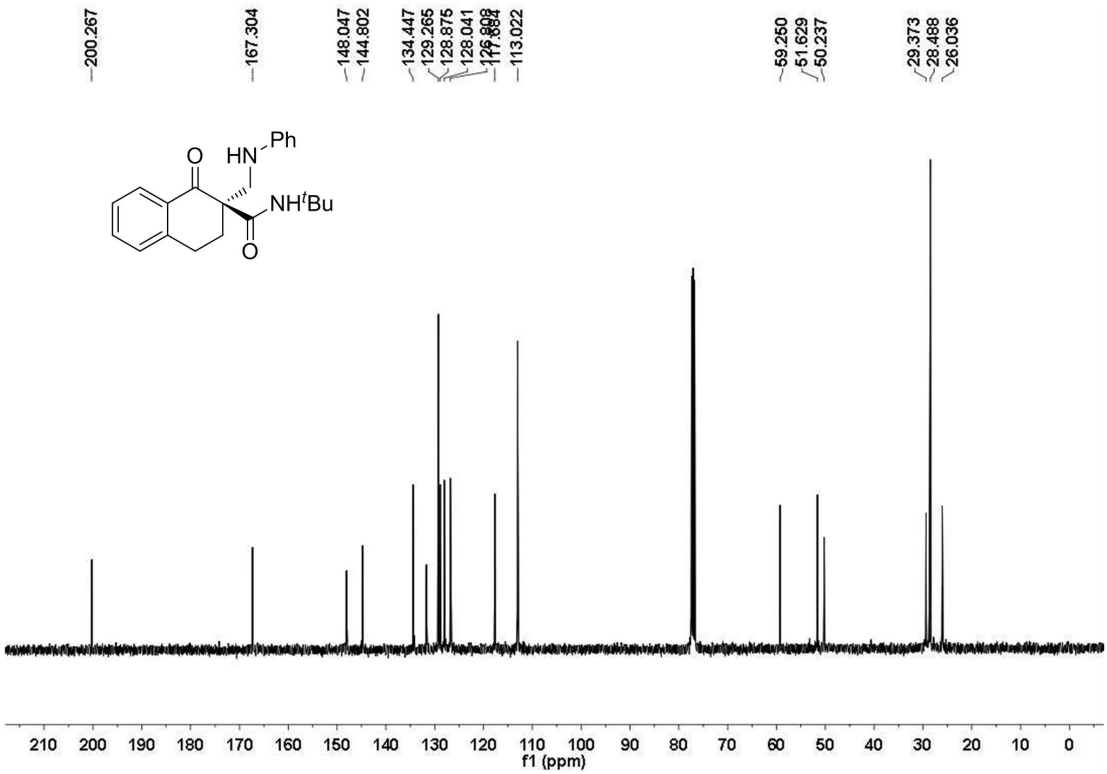
7.090
7.070
6.610
6.592
6.563
6.543
6.406
4.065
3.578
3.546
3.503
3.471
3.043
2.819
2.776
2.673
2.639
2.182
2.172
2.154
2.145
2.139
2.121
2.104
O
HN
Ph
NH^{t}Bu
O
1.00
1.00
1.00
2.00
1.00
2.00
1.00
0.94
2.00
1.00
1.00
1.00
1.00
9.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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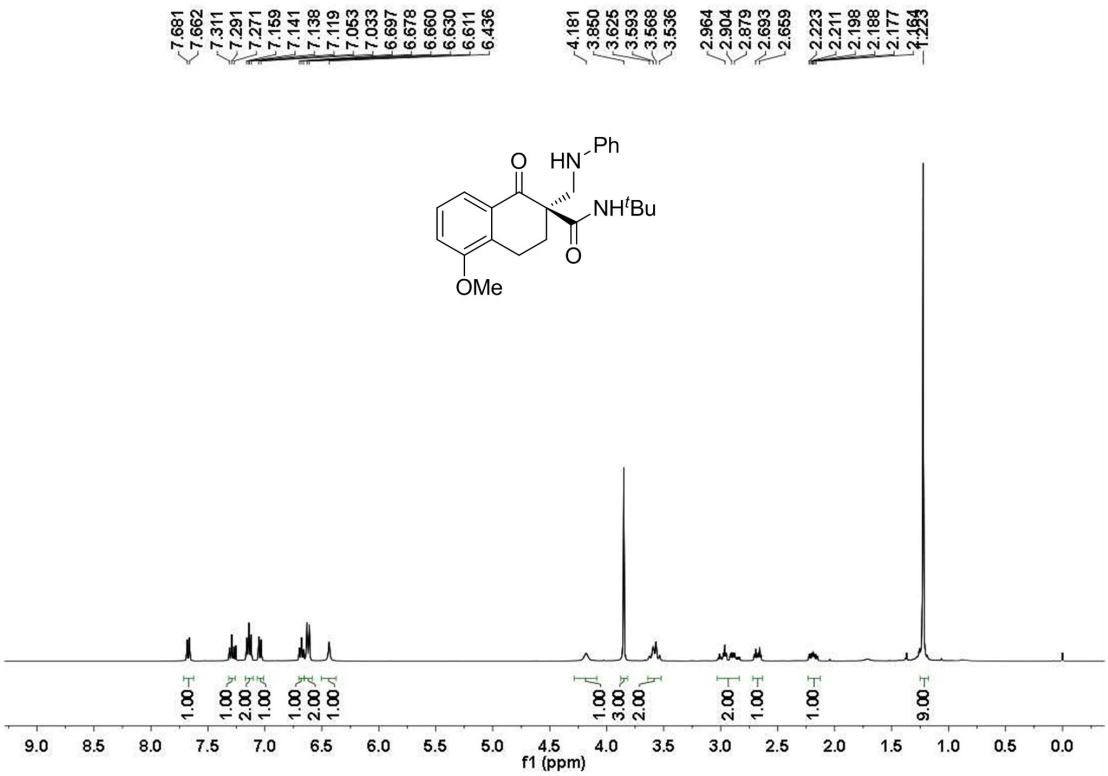
129.265
128.875
128.041
113.022
59.250
51.629
50.237
29.373
28.488
26.036
O
HN
Ph
NH^{t}Bu
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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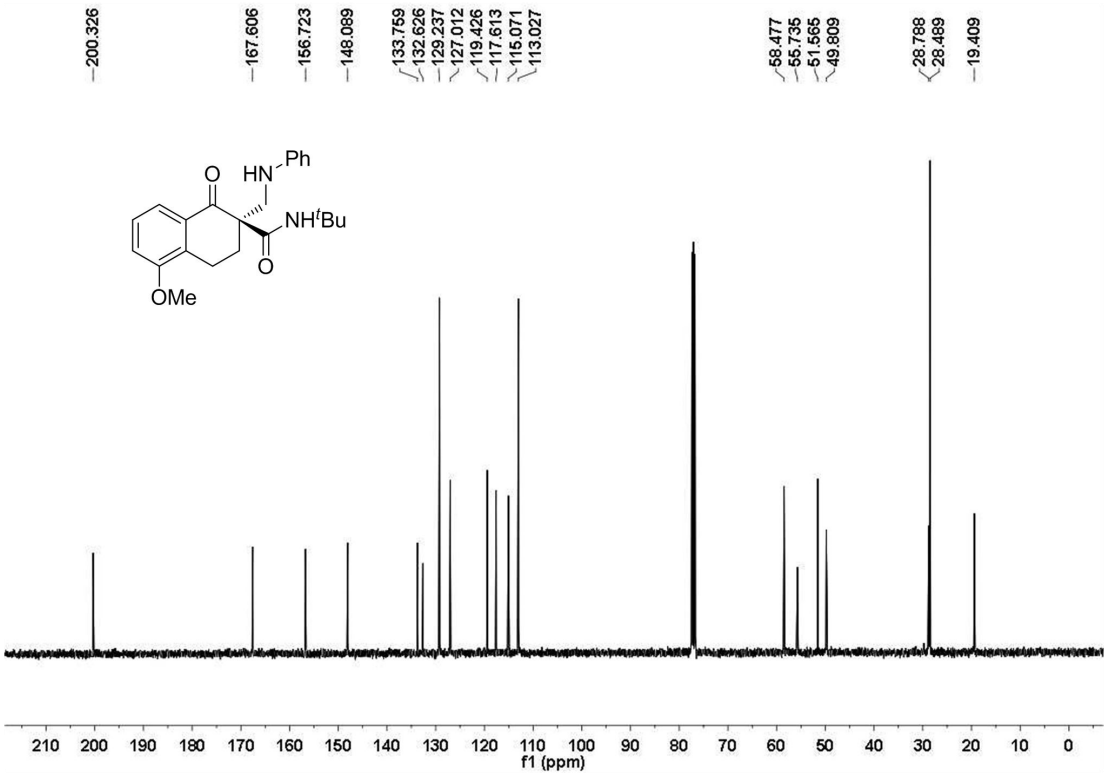
7.271
7.159
7.141
7.138
7.119
7.053
7.033
6.697
6.678
6.660
6.630
6.611
6.436
4.181
3.850
3.625
3.593
3.568
3.536
2.964
2.904
2.879
2.693
2.659
2.223
2.211
2.198
2.188
2.177
2.164
1.223
O
HN
Ph
NHtBu
O
OMe
1.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
3.00
2.00
2.00
1.00
1.00
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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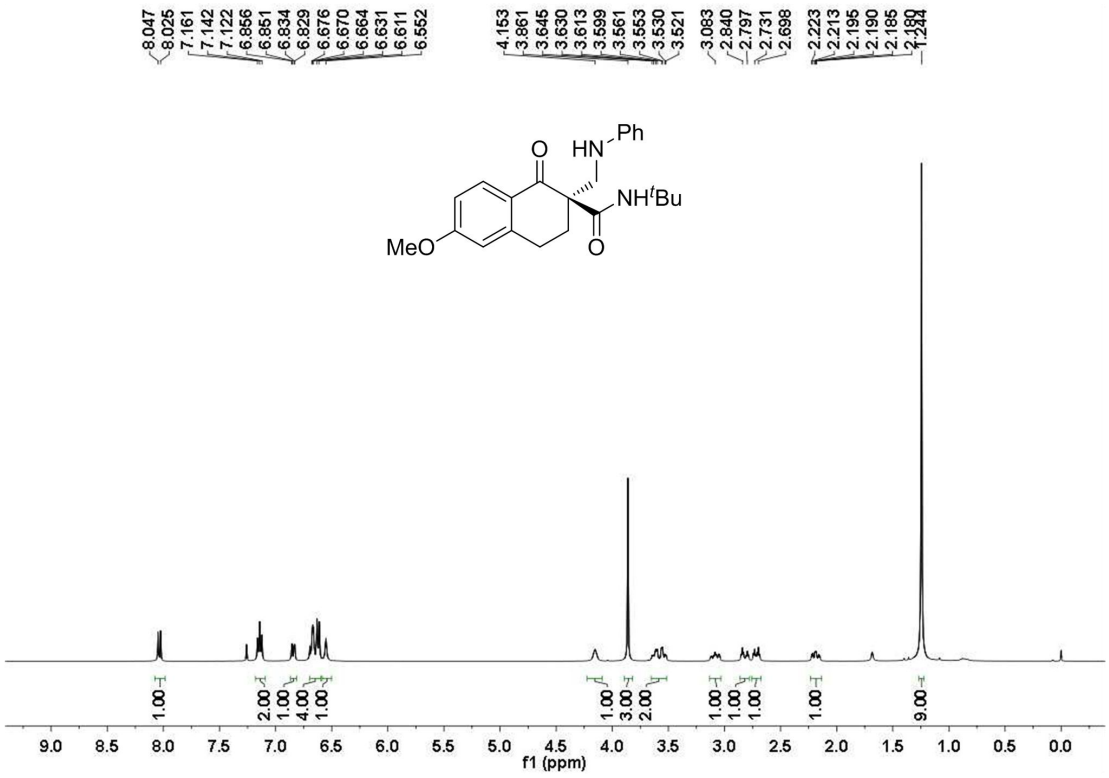
129.237
127.012
119.426
117.613
115.071
113.027
58.477
55.735
51.565
49.809
28.788
28.489
19.409
O
HN
Ph
NHtBu
O
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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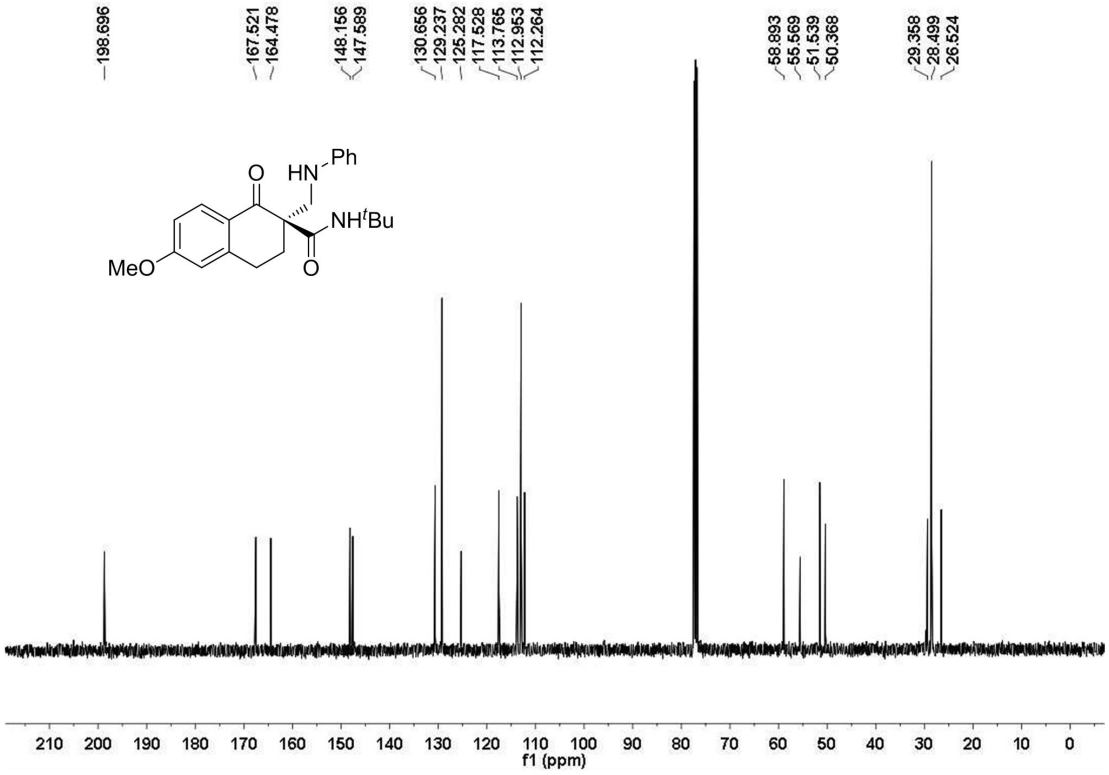
6.851
6.834
6.829
6.676
6.670
6.664
6.631
6.611
6.552
4.153
3.861
3.645
3.630
3.613
3.599
3.561
3.553
3.530
3.521
3.083
2.840
2.797
2.731
2.698
2.223
2.213
2.195
2.190
2.185
2.180
1.244
HN
Ph
O
NH^{t}Bu
O
MeO
1.00
2.00
1.00
4.00
1.00
1.00
3.00
2.00
1.00
1.00
1.00
1.00
9.00
f1 (ppm)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167.521
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148.156
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130.656
129.237
125.282
117.528
113.765
112.953
112.264
58.893
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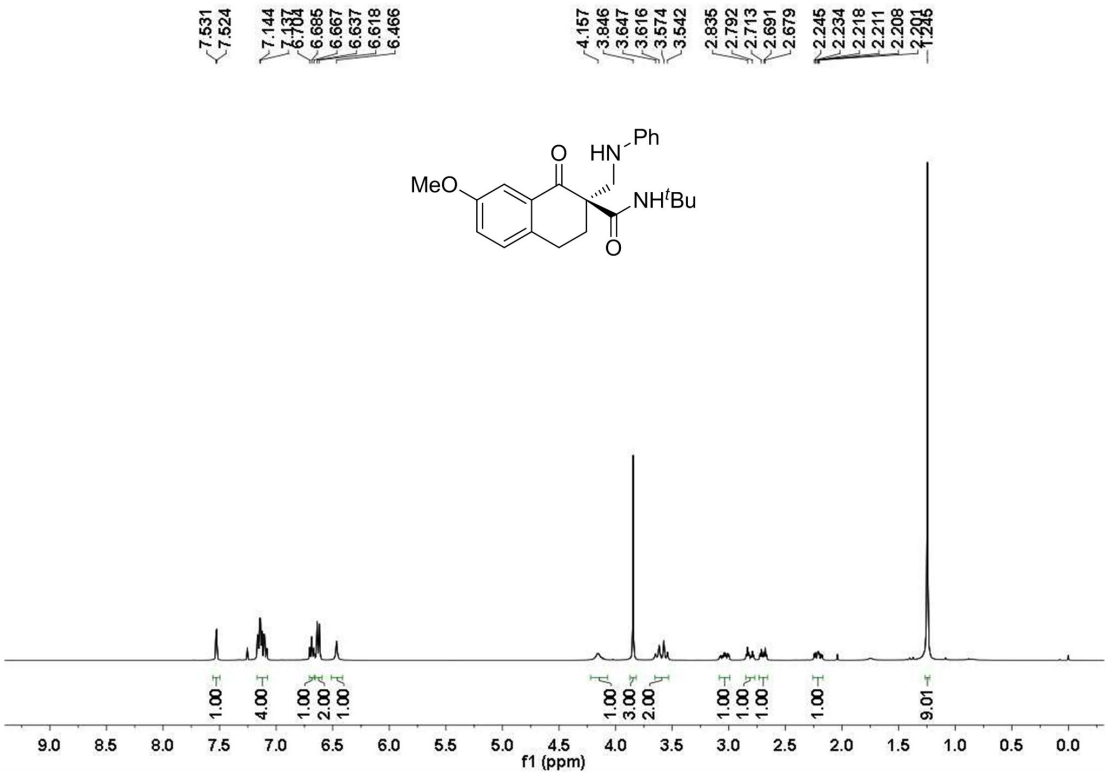
51.539
50.368
29.358
28.499
26.524
HN
Ph
O
NH^{t}Bu
O
MeO
f1 (ppm)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7.144
7.137
7.131
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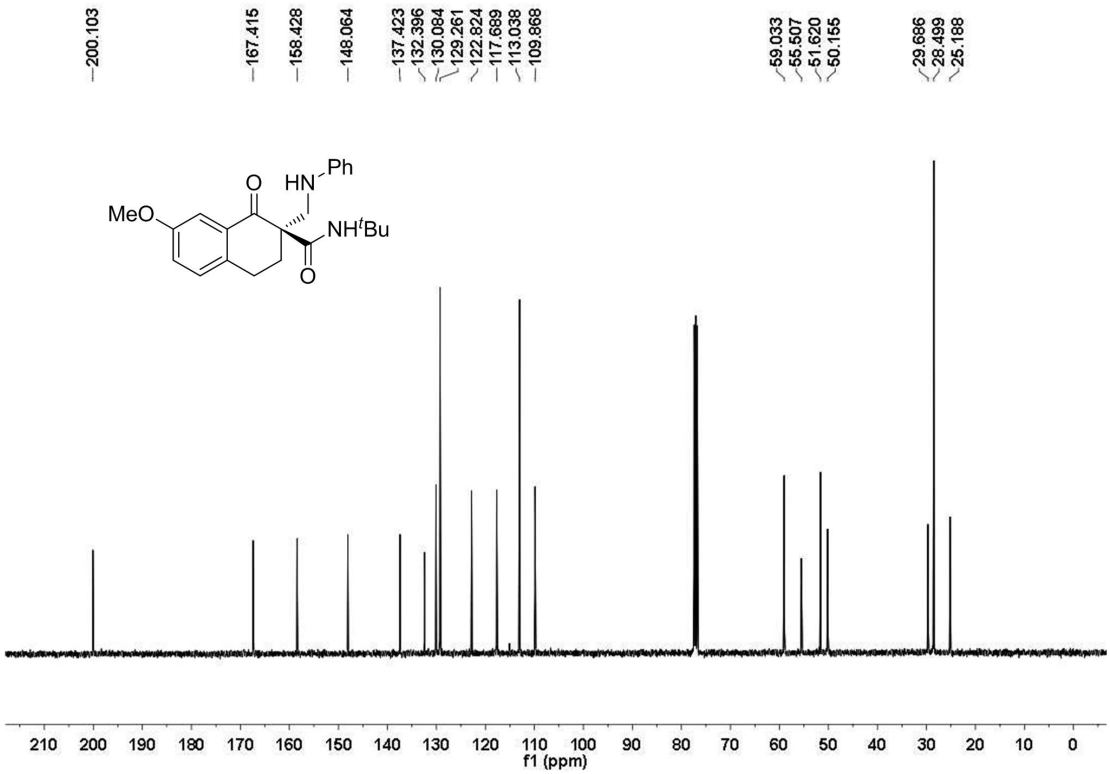
6.667
6.637
6.618
6.466
4.157
3.846
3.647
3.616
3.574
3.542
2.835
2.792
2.713
2.691
2.679
2.245
2.234
2.218
2.211
2.208
2.201
1.245
MeO
O
HN
Ph
NH^{t}Bu
O
1.00
4.00
1.00
2.00
1.00
1.00
3.00
2.00
1.00
1.00
1.00
1.00
9.01
f1 (ppm)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129.261
122.824
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113.038
109.868
59.033
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51.620
50.155
29.686
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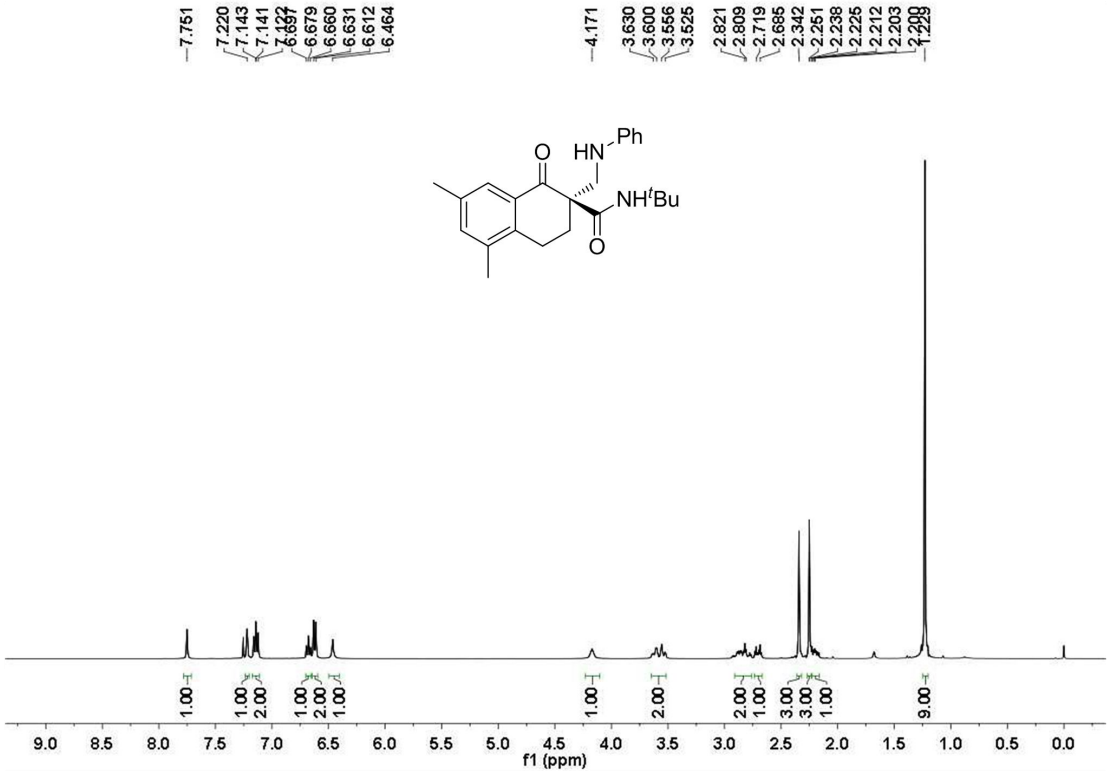
25.188
MeO
O
HN
Ph
NH^{t}Bu
O
f1 (ppm)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6.612
6.464
4.171
3.630
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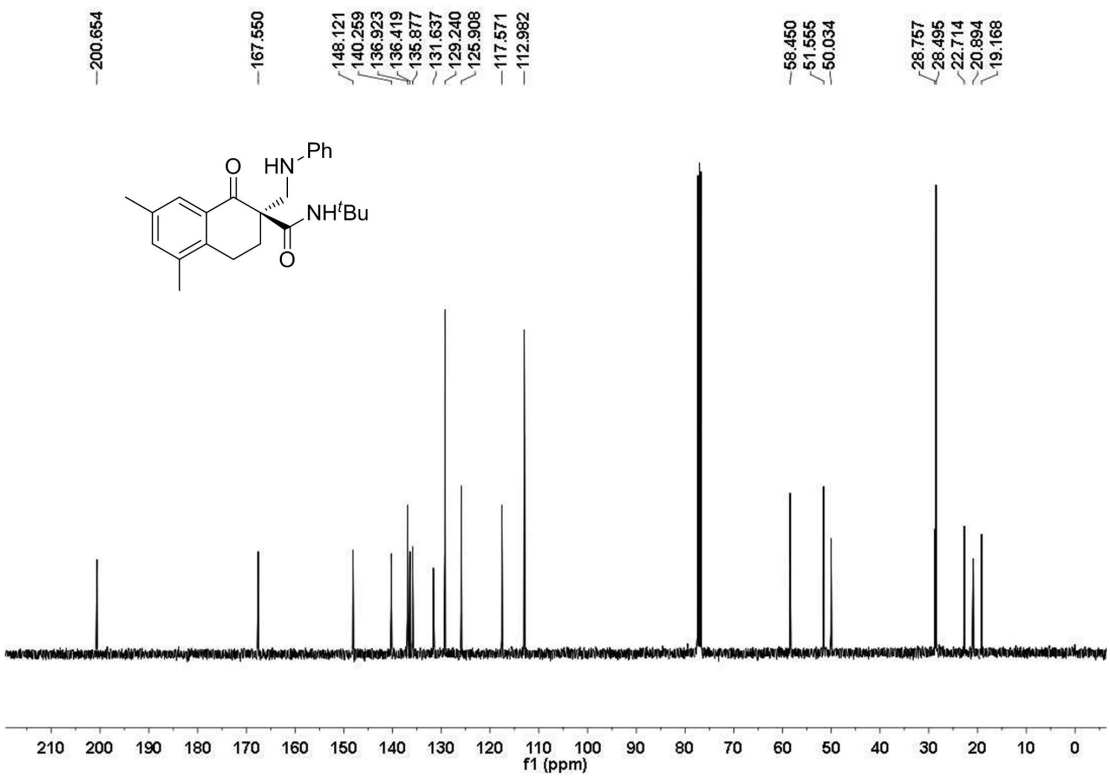
3.556
3.525
2.821
2.809
2.719
2.685
2.342
2.251
2.238
2.225
2.212
2.203
1.229
O
HN
Ph
NH^{t}Bu
O
1.00
1.00
2.00
1.00
2.00
1.00
1.00
2.00
2.00
1.00
3.00
3.00
1.00
9.00
f1 (ppm)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131.637
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112.982
58.450
51.555
50.034
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28.495
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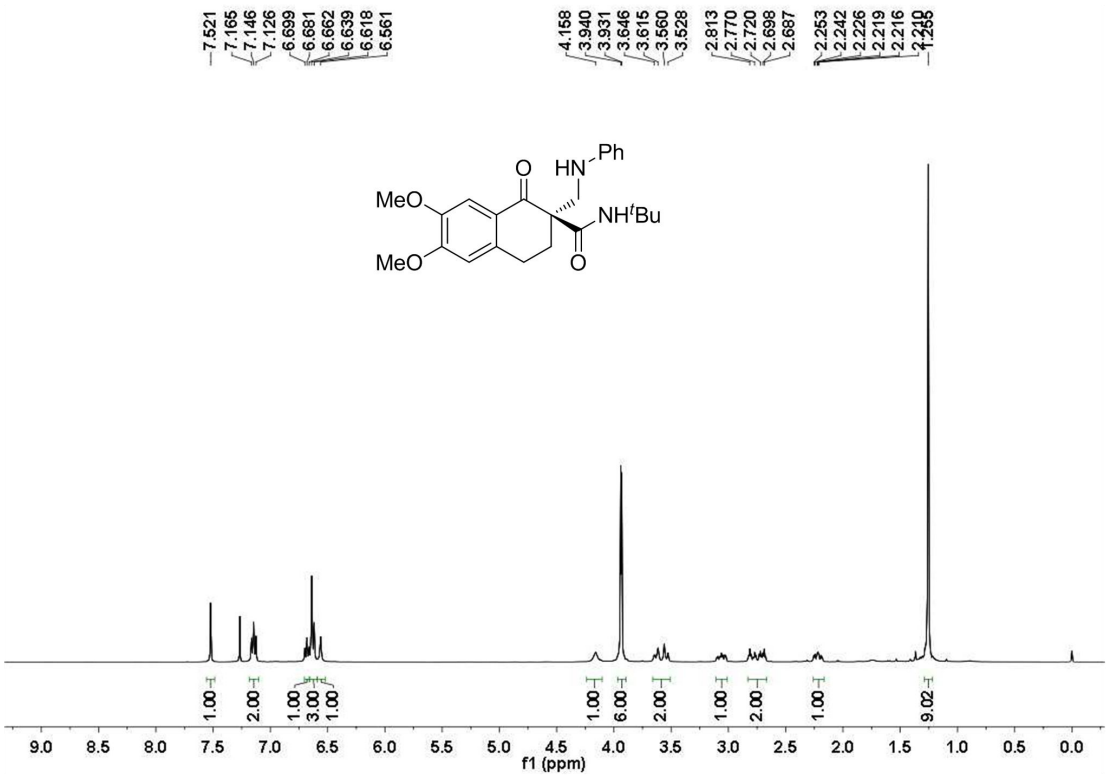
20.894
19.168
O
HN
Ph
NH^{t}Bu
O
f1 (ppm)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7.126
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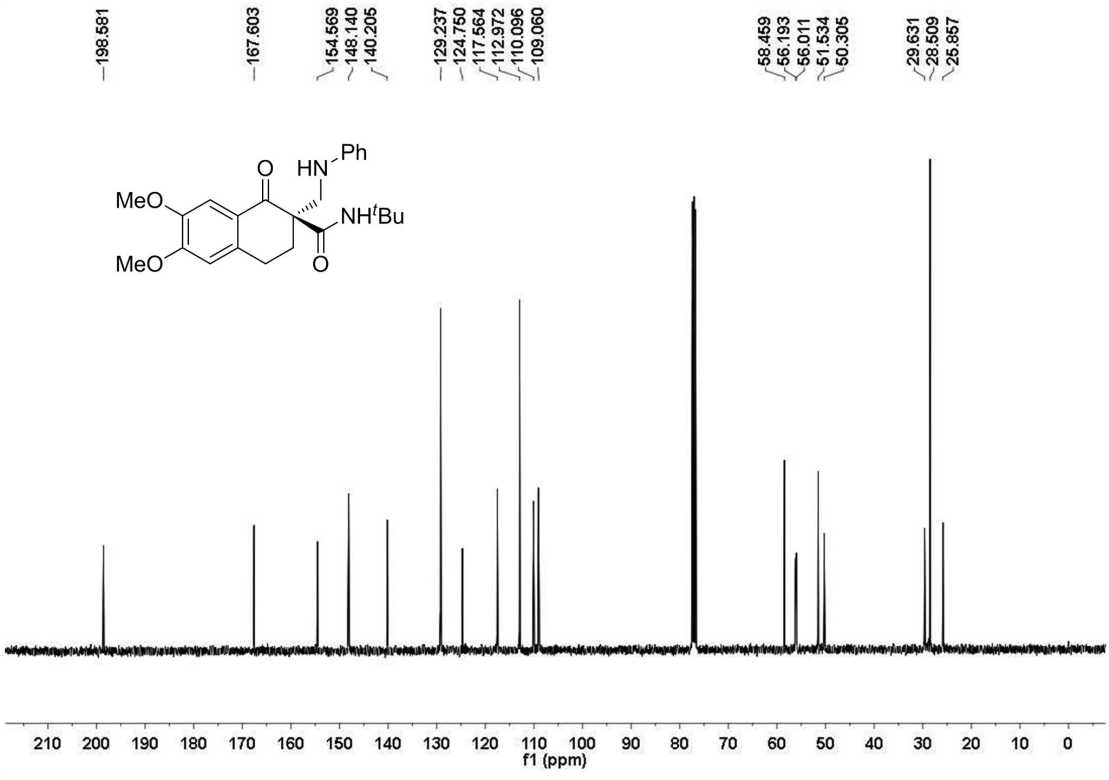
6.681
6.662
6.639
6.618
6.561
4.158
3.940
3.931
3.646
3.615
3.560
3.528
2.813
2.770
2.720
2.698
2.687
2.253
2.242
2.226
2.219
2.216
2.210
1.255
O
HN
Ph
MeO
NHtBu
MeO
O
1.00
2.00
1.00
3.00
1.00
1.00
6.00
2.00
1.00
2.00
1.00
9.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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148.140
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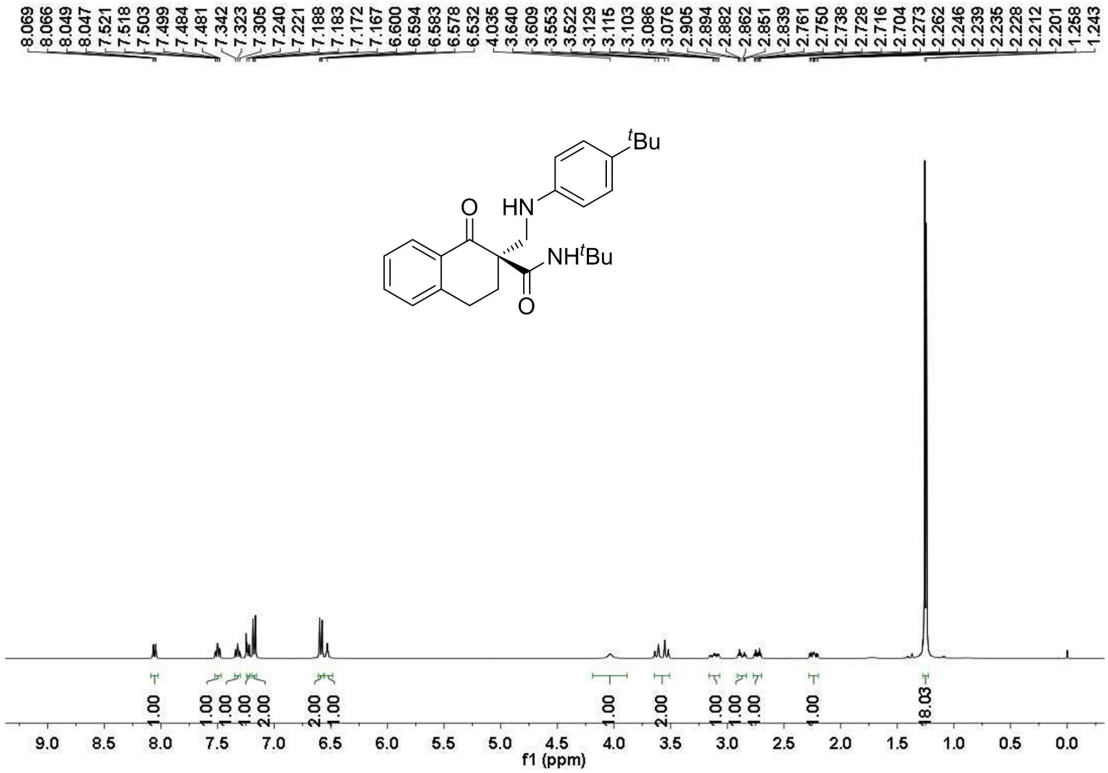
129.237
124.750
117.564
112.972
110.096
109.060
58.459
56.193
56.011
51.534
50.305
29.631
28.509
25.857
O
HN
Ph
MeO
NHtBu
MeO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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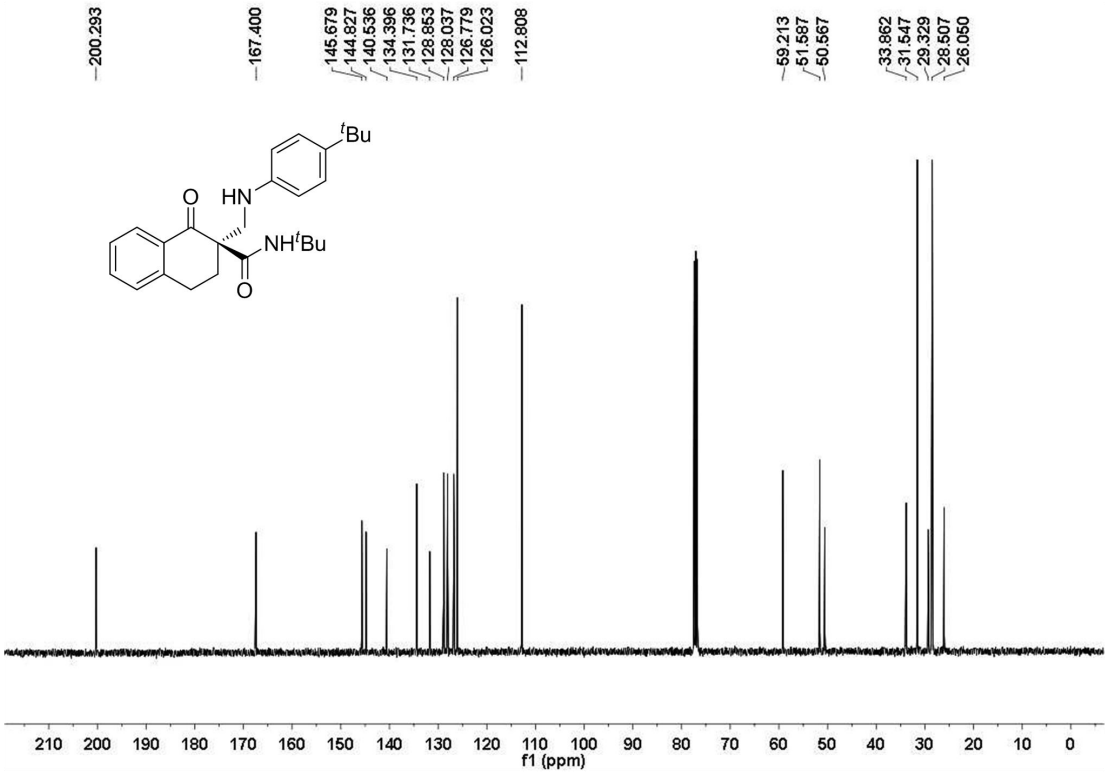
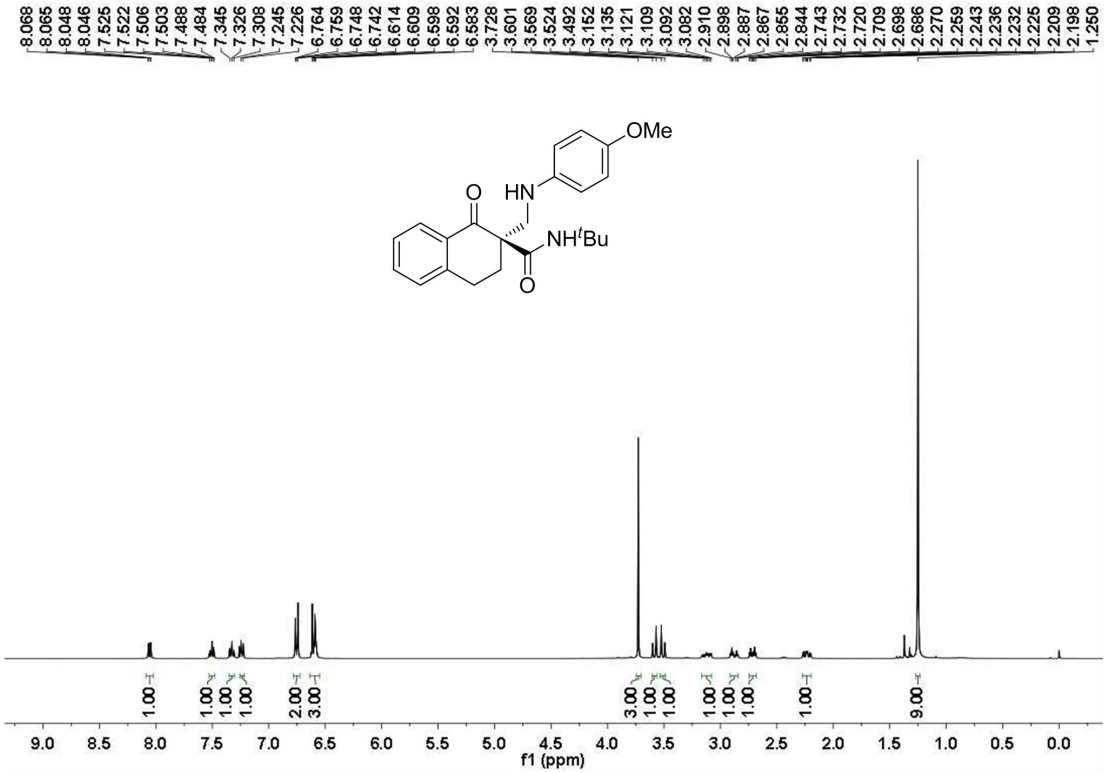
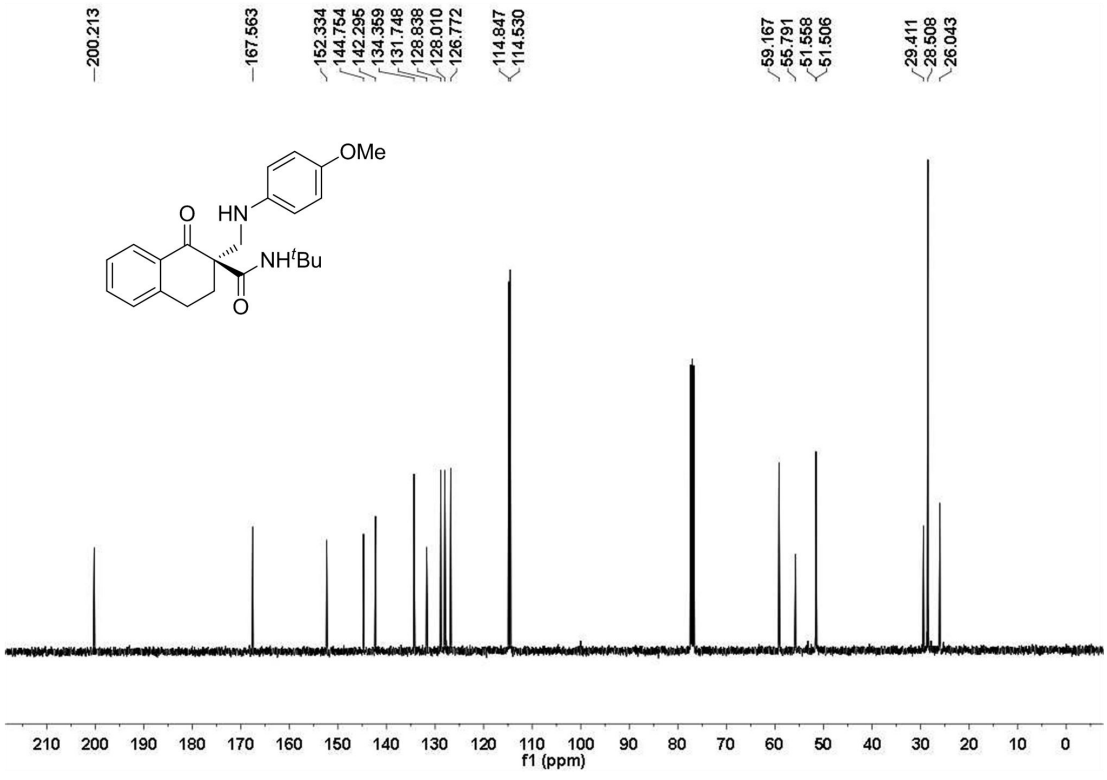
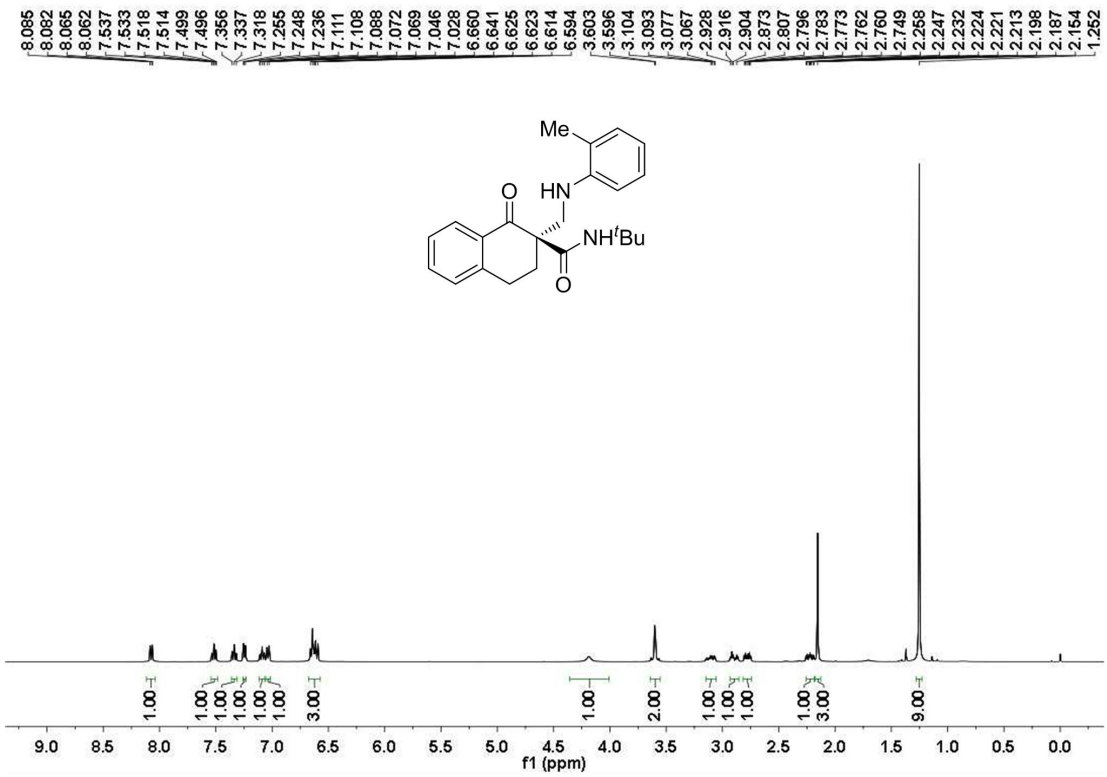
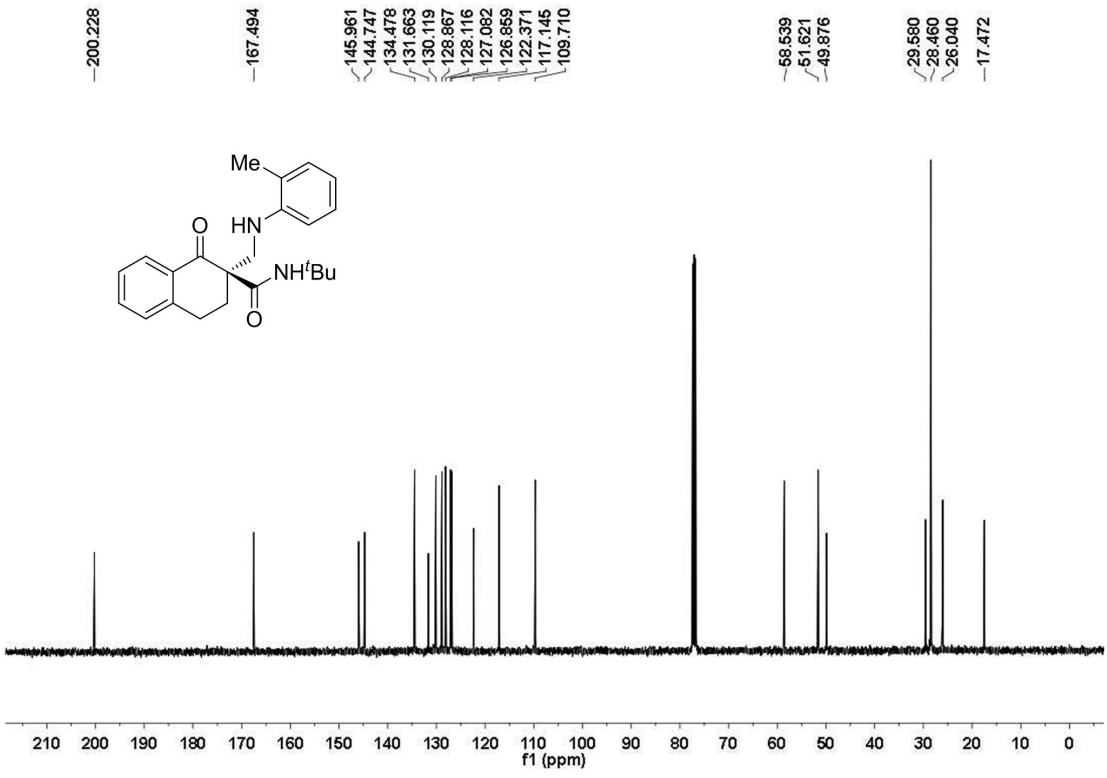
8.066
8.049
8.047
7.521
7.518
7.503
7.499
7.484
7.481
7.342
7.323
7.305
7.240
7.221
7.198
7.183
7.172
7.167
6.600
6.594
6.583
6.578
6.532
4.035
3.640
3.609
3.553
3.522
3.129
3.115
3.103
3.086
3.076
2.905
2.894
2.882
2.862
2.851
2.839
2.761
2.750
2.738
2.728
2.716
2.704
2.273
2.262
2.246
2.239
2.235
2.228
2.212
2.201
1.268
1.243
tBu
HN
O
NHtBu
O
1.00
1.00
1.00
1.00
2.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
18.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

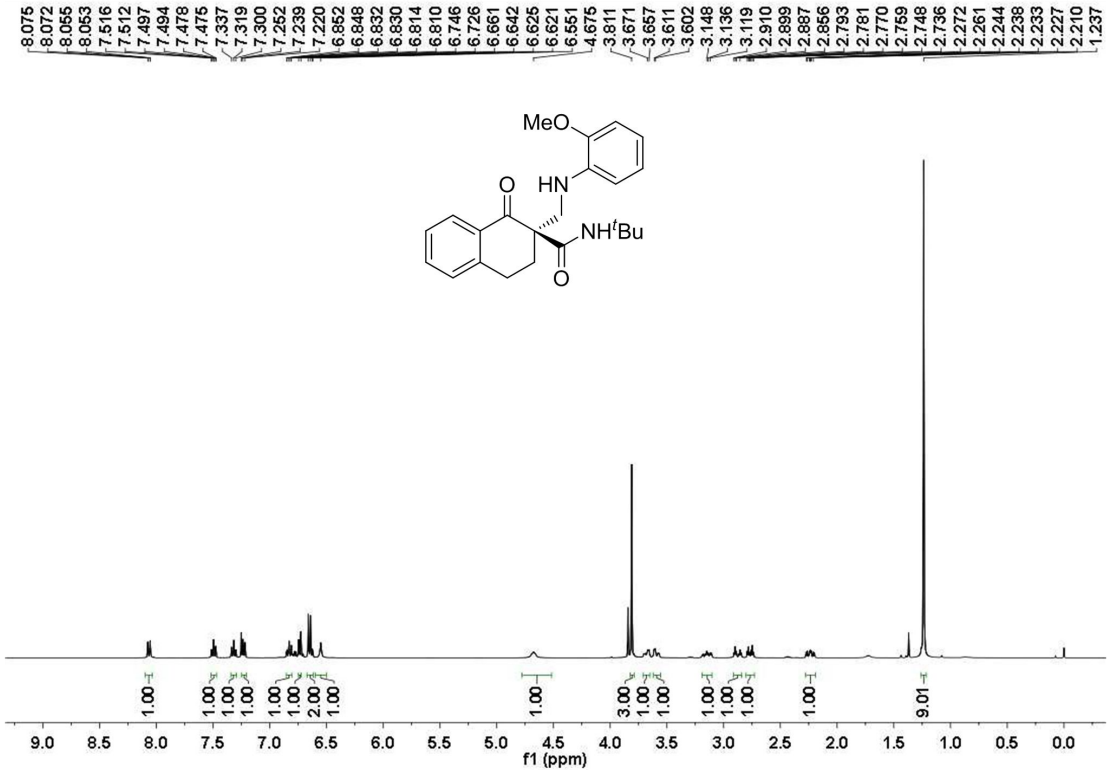

200.293
167.400
145.679
144.827
140.536
134.396
131.736
128.853
128.037
126.779
126.023
112.808
59.213
51.587
50.567
33.862
31.547
29.329
28.507
26.050
tBu
HN
O
NHtBu
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

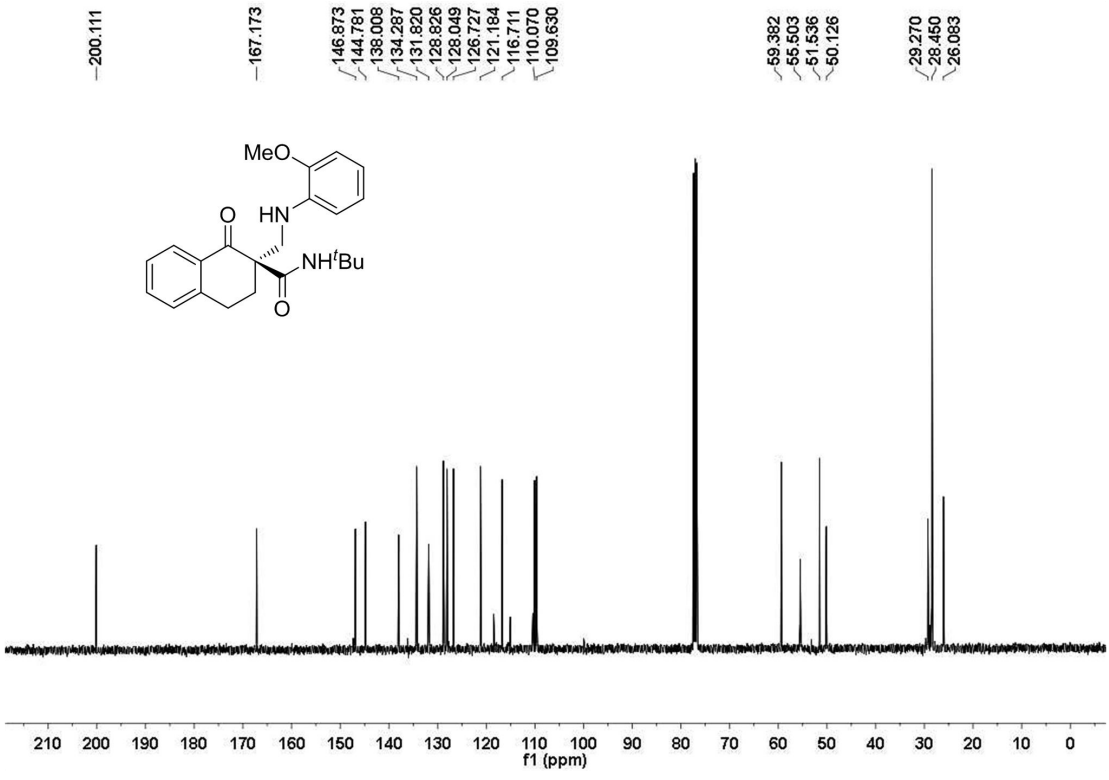

8.068
8.065
8.048
8.046
7.525
7.522
7.506
7.503
7.488
7.484
7.345
7.326
7.308
7.245
7.226
6.764
6.759
6.748
6.742
6.614
6.609
6.598
6.592
6.583
3.728
3.601
3.569
3.524
3.492
3.152
3.135
3.121
3.109
3.092
3.082
2.910
2.898
2.887
2.867
2.855
2.844
2.743
2.732
2.720
2.709
2.698
2.686
2.270
2.259
2.243
2.236
2.232
2.225
2.209
2.198
1.250
OMe
HN
O
NH^{t}Bu
O
1.00
1.00
1.00
1.00
2.00
3.00
3.00
1.00
1.00
1.00
1.00
1.00
1.00
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

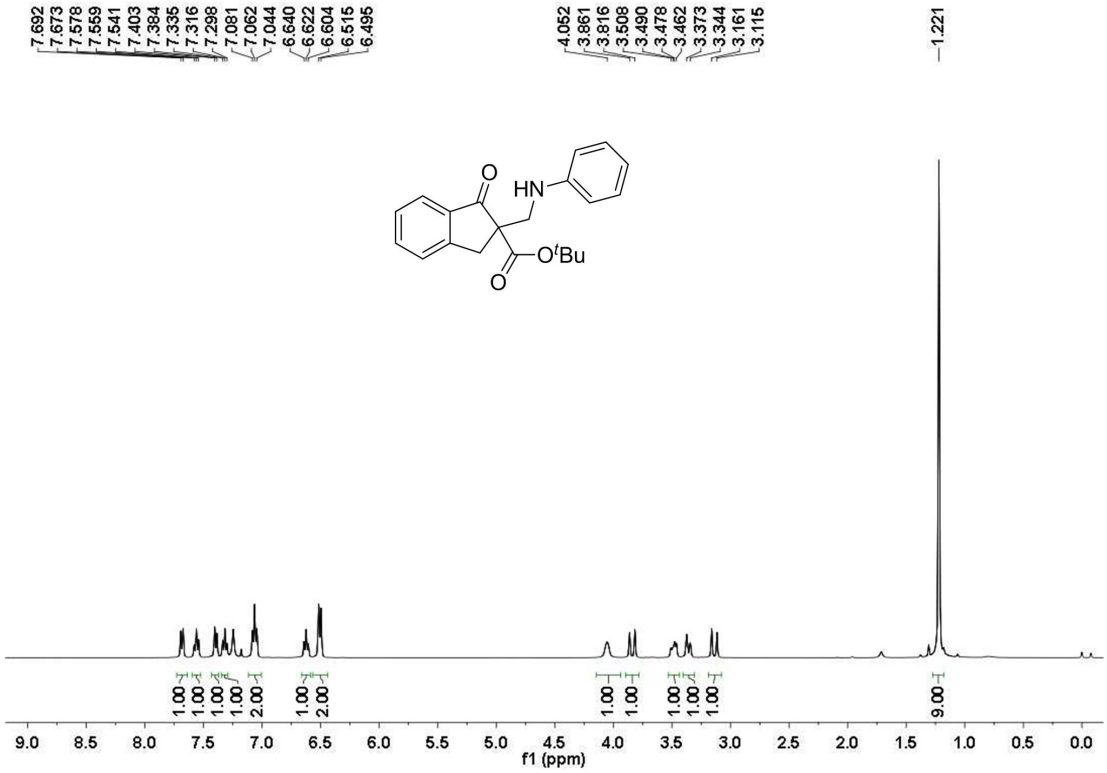

200.213
167.563
152.334
144.754
142.295
134.359
131.748
128.838
128.010
126.772
114.847
114.530
59.167
55.791
51.558
51.506
29.411
28.508
26.043
OMe
HN
O
NH^{t}Bu
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

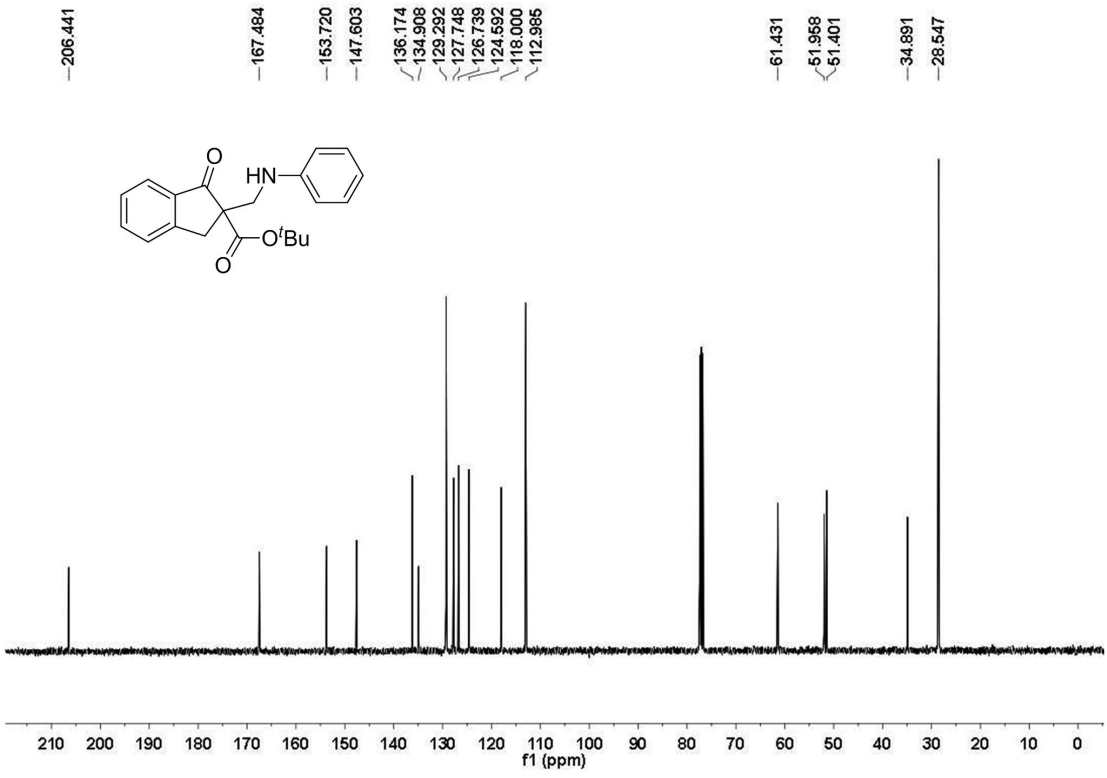

8.085
8.082
8.065
8.062
7.537
7.533
7.518
7.514
7.499
7.496
7.356
7.337
7.318
7.255
7.248
7.236
7.111
7.108
7.088
7.072
7.069
7.046
7.028
6.660
6.641
6.625
6.623
6.614
6.594
3.603
3.596
3.104
3.093
3.077
3.067
2.928
2.916
2.904
2.873
2.807
2.796
2.783
2.773
2.762
2.760
2.749
2.258
2.247
2.232
2.224
2.221
2.213
2.198
2.187
2.154
1.252
Me
HN
O
NH^{t}Bu
O
1.00
1.00
1.00
1.00
1.00
3.00
1.00
2.00
1.00
1.00
1.00
3.00
9.00
f1 (ppm)

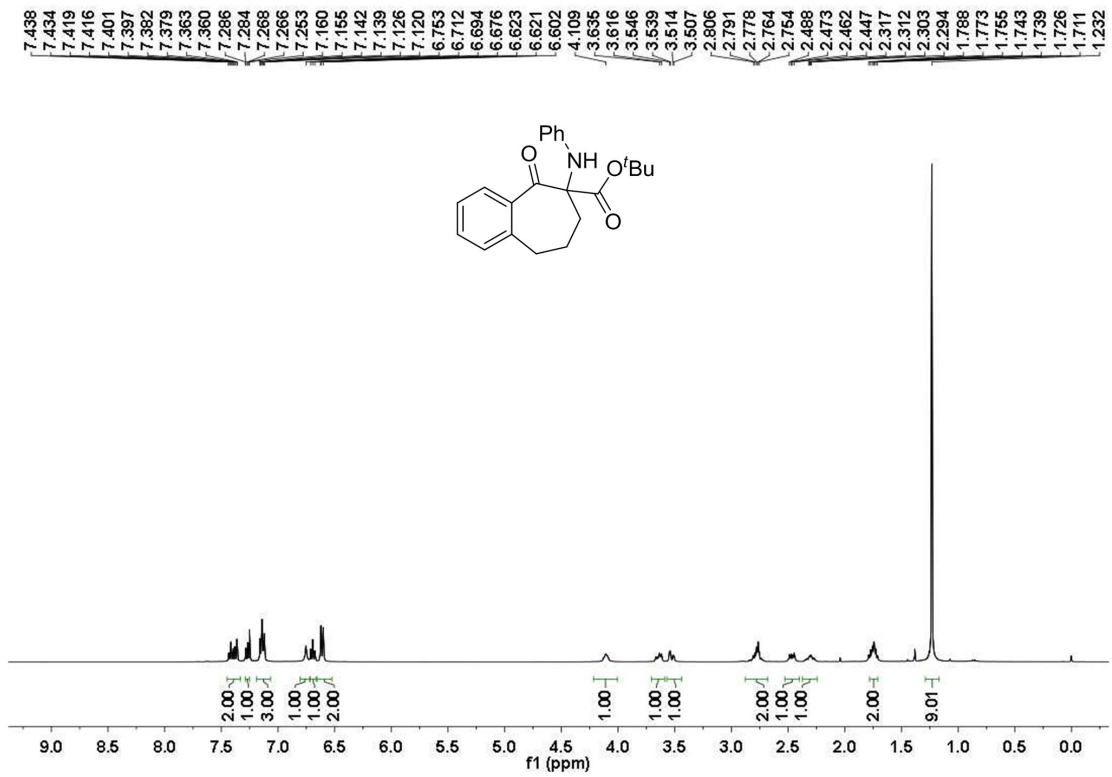

200.228
167.494
145.961
144.747
134.478
131.663
130.119
128.867
128.116
127.082
126.859
122.371
117.145
109.710
58.539
51.621
49.876
29.580
28.460
26.040
17.472
Me
HN
O
NH^{t}Bu
O
f1 (ppm)

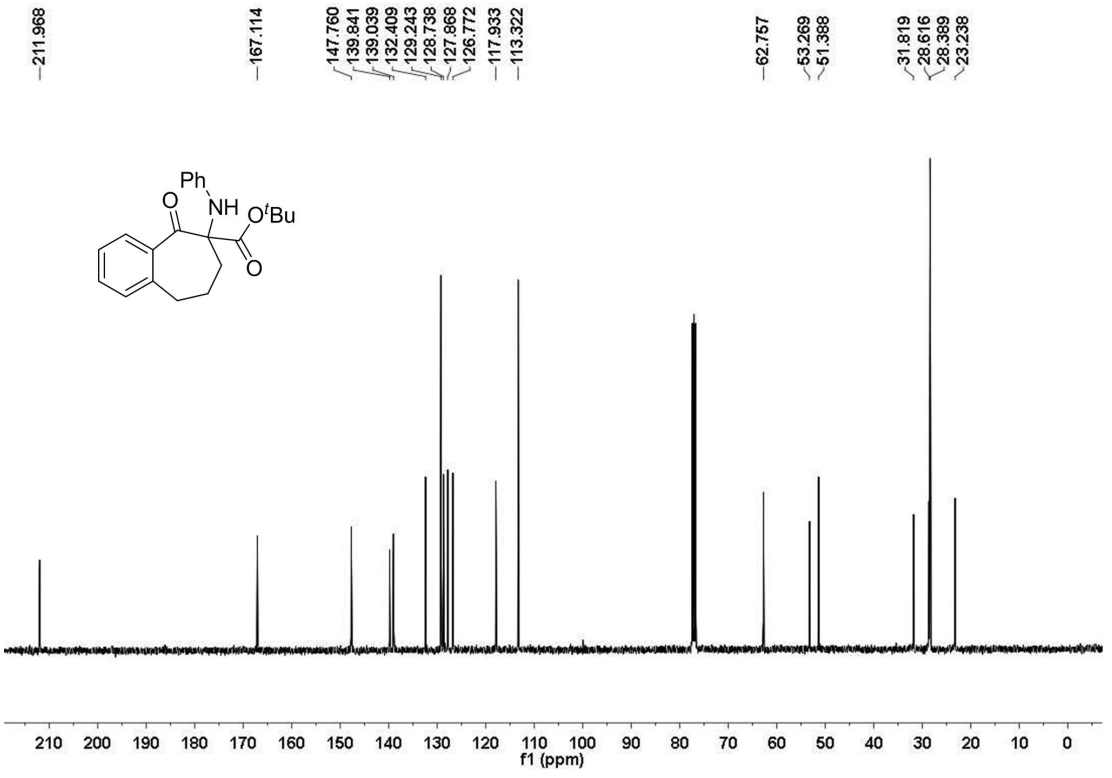

8.075
8.072
8.055
8.053
7.516
7.512
7.497
7.494
7.478
7.475
7.337
7.319
7.300
7.252
7.239
7.220
6.852
6.848
6.832
6.830
6.814
6.810
6.746
6.726
6.661
6.642
6.625
6.621
6.551
4.675
3.811
3.671
3.657
3.611
3.602
3.148
3.136
3.119
2.910
2.899
2.887
2.856
2.793
2.781
2.770
2.759
2.748
2.736
2.272
2.261
2.244
2.238
2.233
2.227
2.210
1.237
MeO
HN
O
NH^{t}Bu
O
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
3.00
1.00
1.00
1.00
1.00
1.00
1.00
9.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

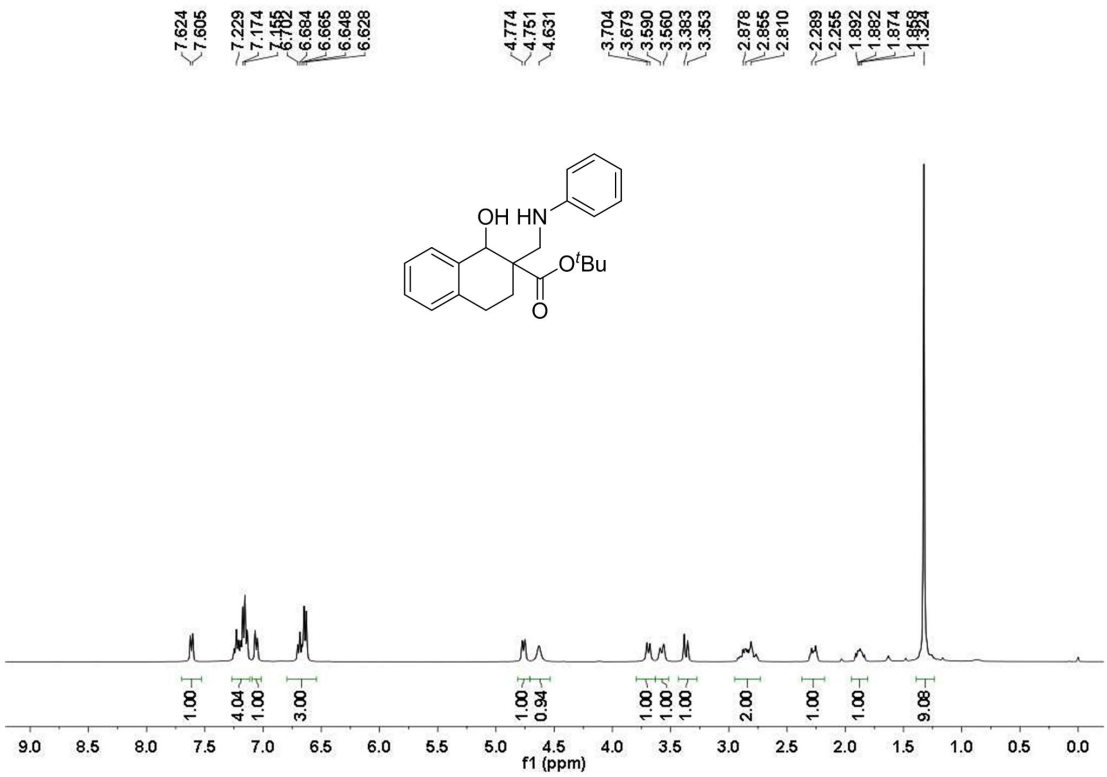

200.111
167.173
146.873
144.781
138.008
134.287
131.820
128.826
128.049
126.727
121.184
116.711
110.070
109.630
59.382
55.503
51.536
50.126
29.270
28.450
26.083
MeO
HN
O
NH^{t}Bu
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

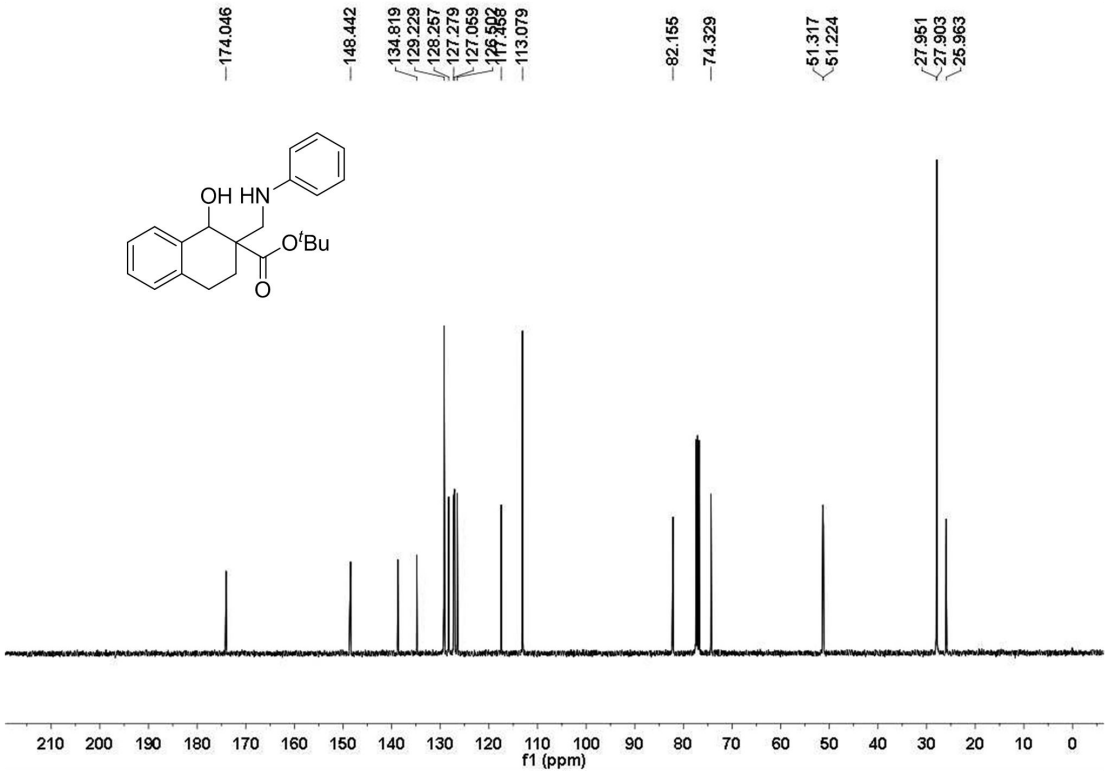

7.692
7.673
7.578
7.559
7.541
7.403
7.384
7.335
7.316
7.298
7.081
7.062
7.044
6.640
6.622
6.604
6.515
6.495
4.052
3.861
3.816
3.508
3.490
3.478
3.462
3.373
3.344
3.161
3.115
1.221
O
HN
O
O^{t}Bu
1.00
1.00
1.00
1.00
2.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

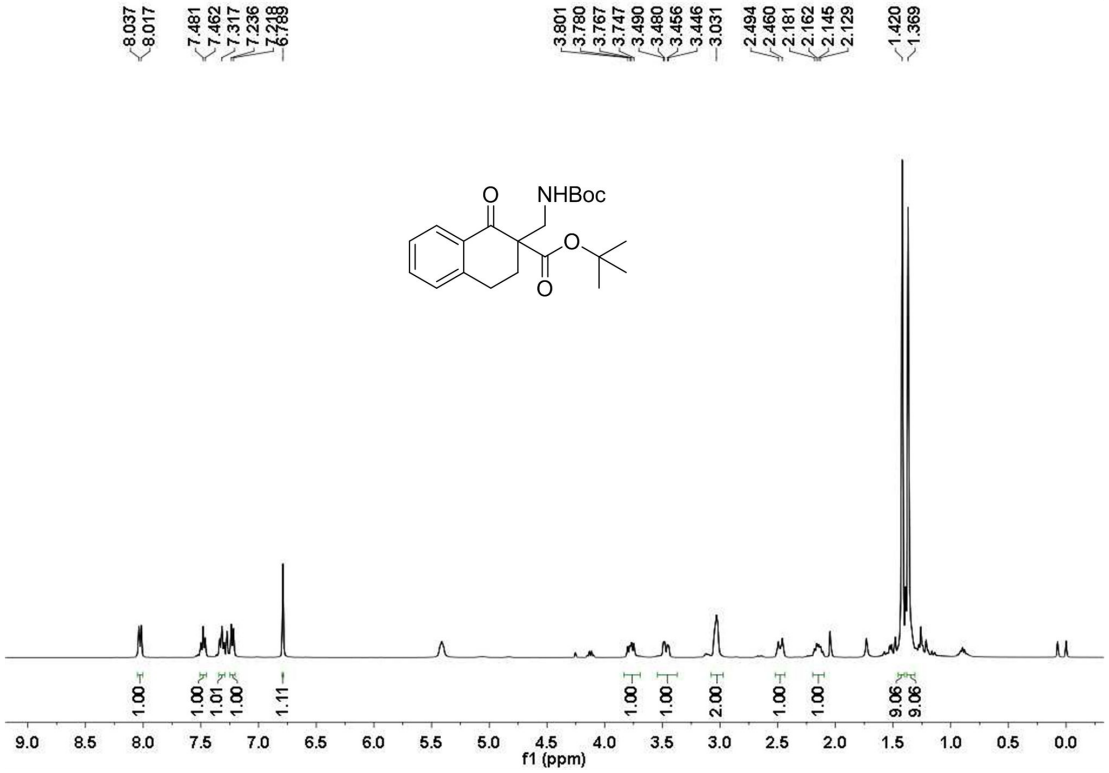

206.441
167.484
153.720
147.603
136.174
134.908
129.292
127.748
126.739
124.592
118.000
112.985
61.431
51.958
51.401
34.891
28.547
O
HN
O
O^{t}Bu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

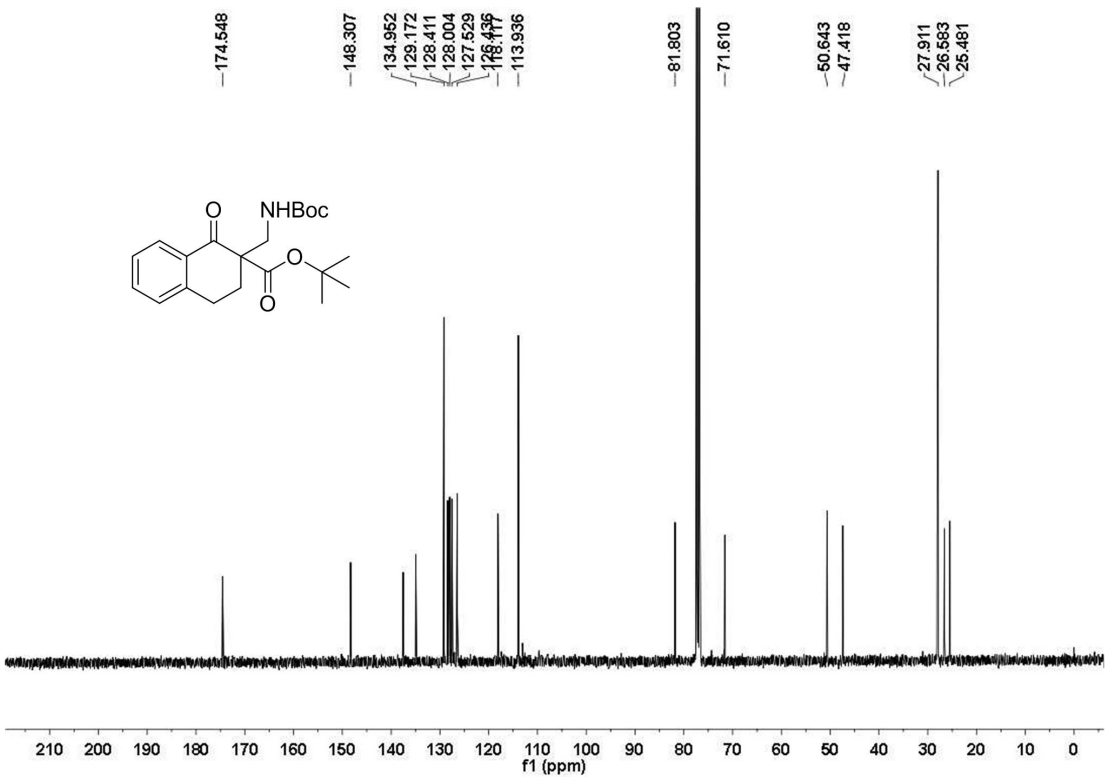

7.438
7.434
7.419
7.416
7.401
7.397
7.382
7.379
7.363
7.360
7.286
7.284
7.268
7.266
7.253
7.160
7.155
7.142
7.139
7.126
7.120
6.753
6.712
6.694
6.676
6.623
6.621
6.602
4.109
3.635
3.616
3.546
3.539
3.514
3.507
2.806
2.791
2.778
2.764
2.754
2.488
2.473
2.462
2.447
2.317
2.312
2.303
2.294
1.788
1.773
1.755
1.743
1.739
1.726
1.711
1.232
Ph
NH
O
O
O
tBu
2.00
1.00
3.00
1.00
1.00
2.00
1.00
1.00
1.00
2.00
1.00
1.00
2.00
9.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


211.968
167.114
147.760
139.841
139.039
132.409
129.243
128.738
127.868
126.772
117.933
113.322
62.757
53.269
51.388
31.819
28.616
28.389
23.238
Ph
NH
O
O
O
tBu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

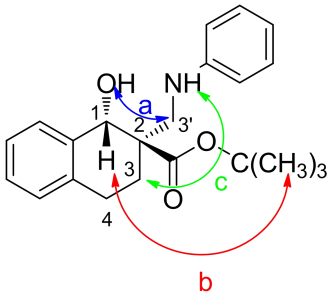

7.624
7.605
7.229
7.174
6.684
6.665
6.648
6.628
4.774
4.751
4.631
3.704
3.679
3.590
3.560
3.383
3.353
2.878
2.855
2.810
2.289
2.255
1.892
1.882
1.874
1.324
OH HN
O^{t}Bu
O
1.00
4.04
1.00
3.00
1.00
0.94
1.00
1.00
1.00
2.00
1.00
1.00
9.08
f1 (ppm)

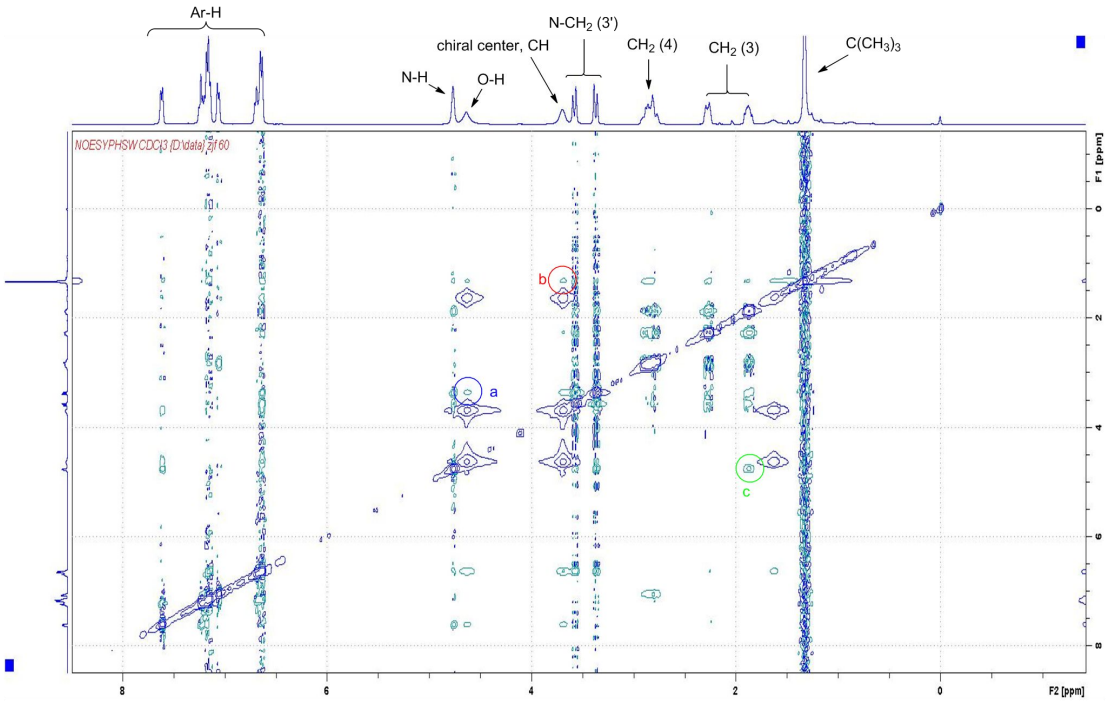

174.046
148.442
134.819
129.229
128.257
127.279
127.059
113.079
82.155
74.329
51.317
51.224
27.951
27.903
25.963
OH HN
O^{t}Bu
O
f1 (ppm)


8.037
8.017
7.481
7.462
7.317
7.236
3.801
3.780
3.767
3.747
3.490
3.480
3.456
3.446
3.031
2.494
2.460
2.181
2.162
2.145
2.129
1.420
1.369
O
NHBoc
O
O
1.00
1.00
1.01
1.00
1.11
1.00
1.00
2.00
1.00
1.00
9.06
9.06
f1 (ppm)


174.548
148.307
134.952
129.172
128.411
128.004
127.529
113.936
81.803
71.610
50.643
47.418
27.911
26.583
25.481
O
NHBoc
O
O
f1 (ppm)

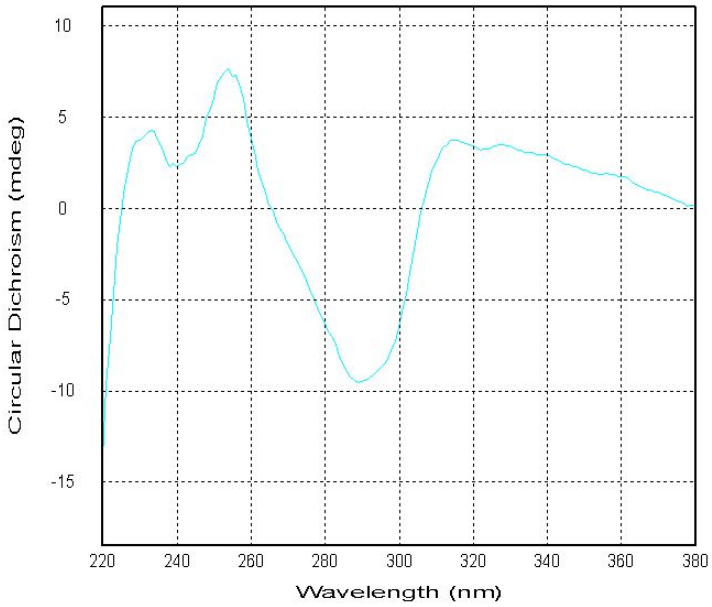
9. The NOESY spectra of 6

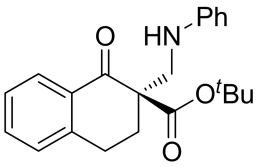




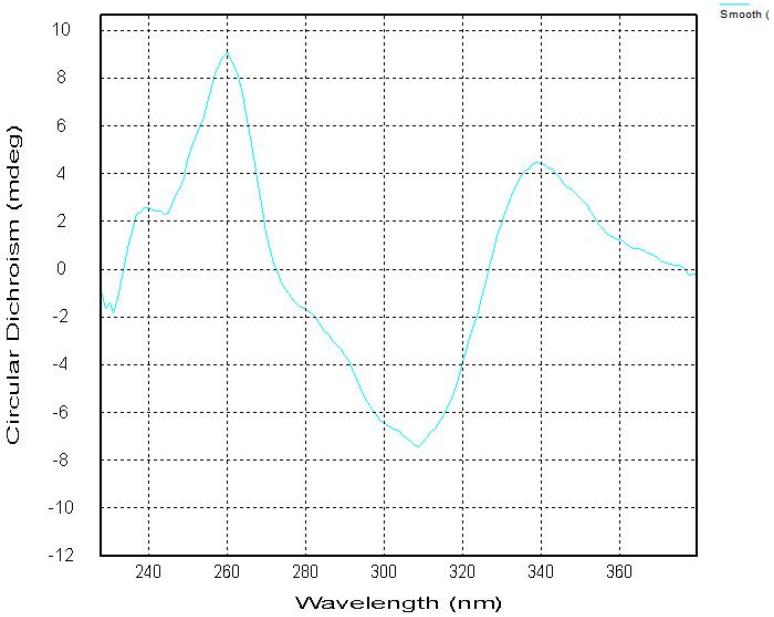
10. CD information of the products

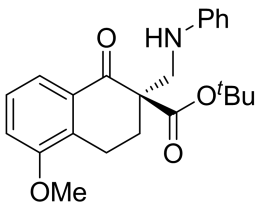
tert-butyl 1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4a**)**:**



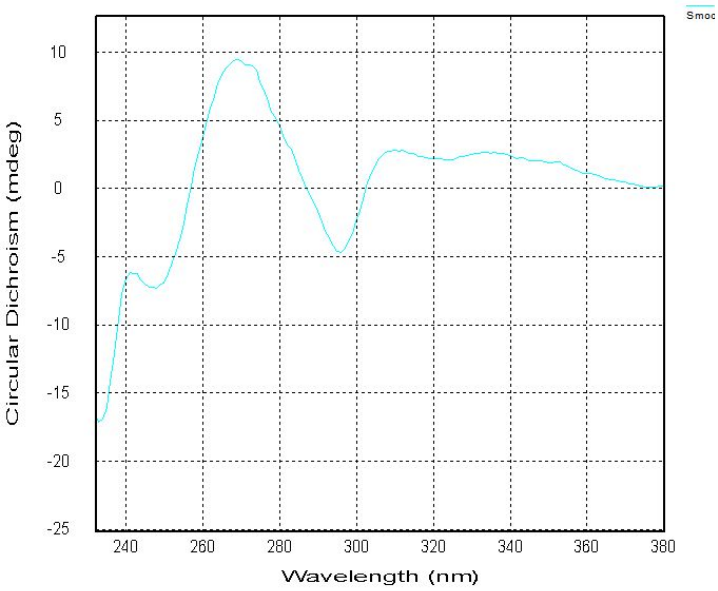


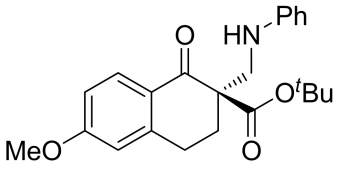
tert-butyl 5-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthal-ene-2-carboxylate (**4b**):



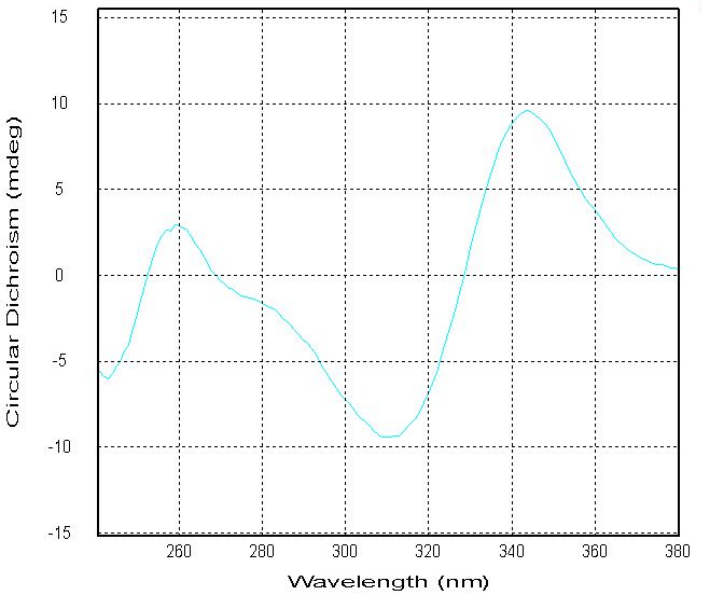


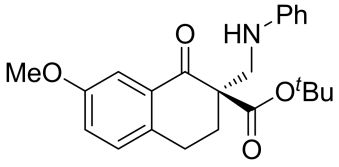
tert-butyl 6-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene -2-carboxylate (**4c**):



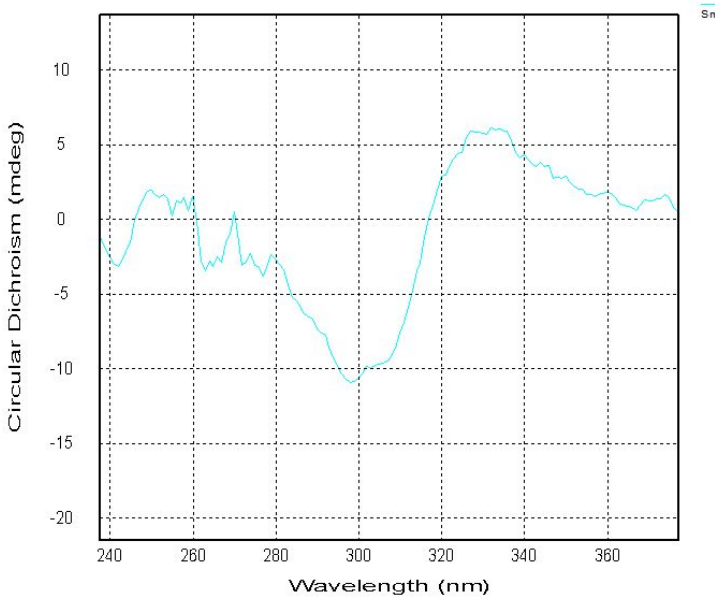


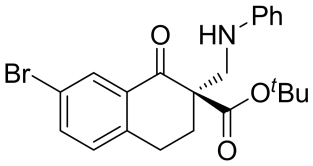
tert-butyl 7-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene -2-carboxylate (**4d**):



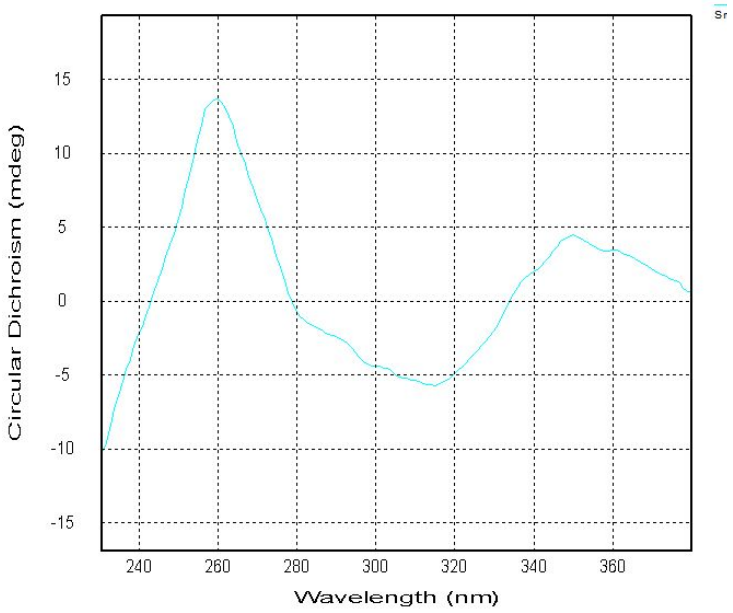


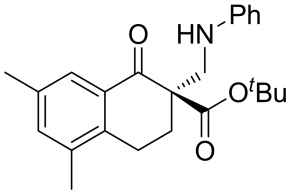
tert-butyl 7-bromo-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene -2-carboxylate (**4e**):



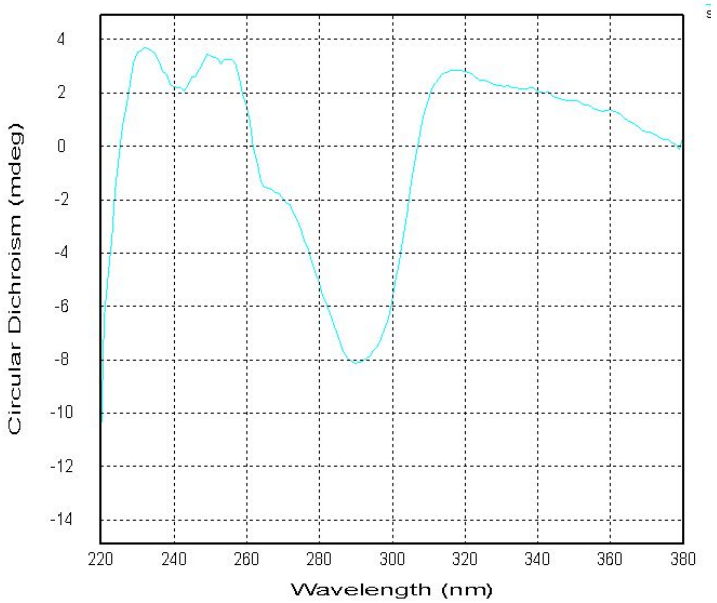


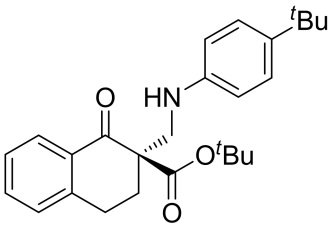
tert-butyl 5,7-dimethyl-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthal -ene-2-carboxylate (**4f**):



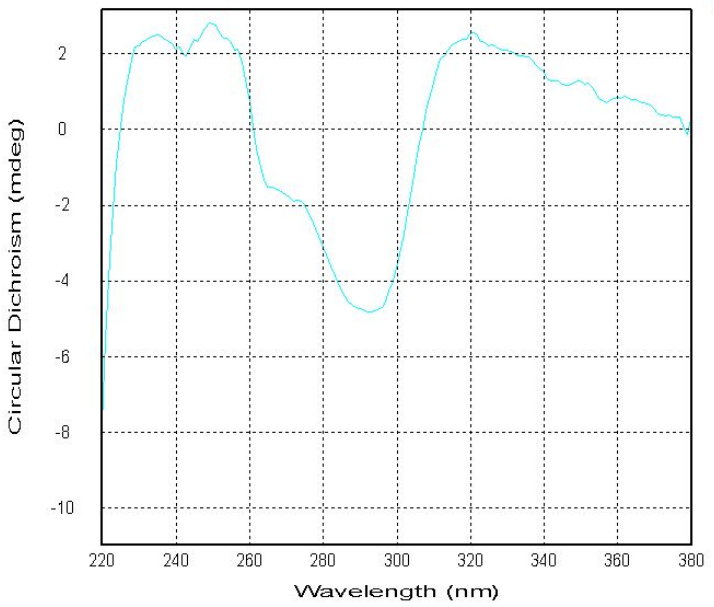


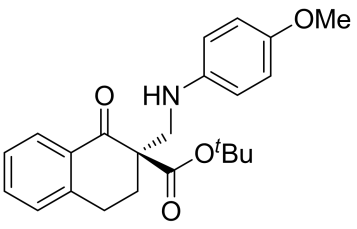
tert-butyl 2-(((4-(tert-butyl)phenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthal
-ene-2-carboxylate (**4g**):



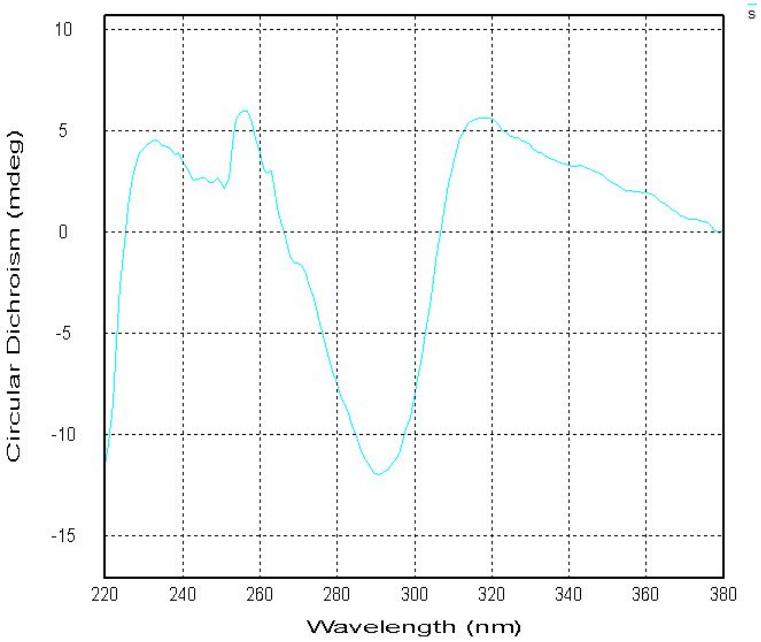


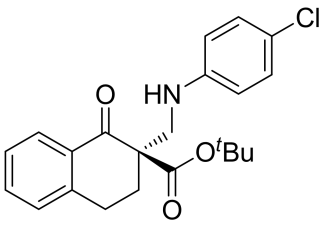
tert-butyl 2-(((4-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthal
-ene-2-carboxylate (**4h**):



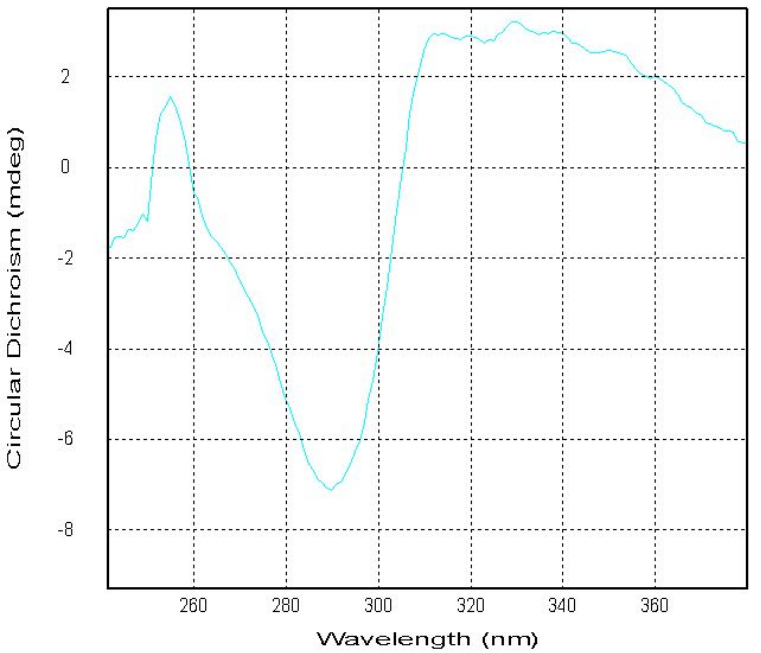


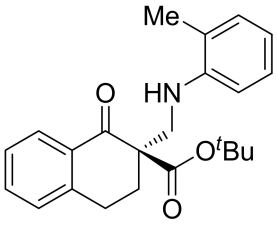
tert-butyl 2-(((4-chlorophenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4i**):



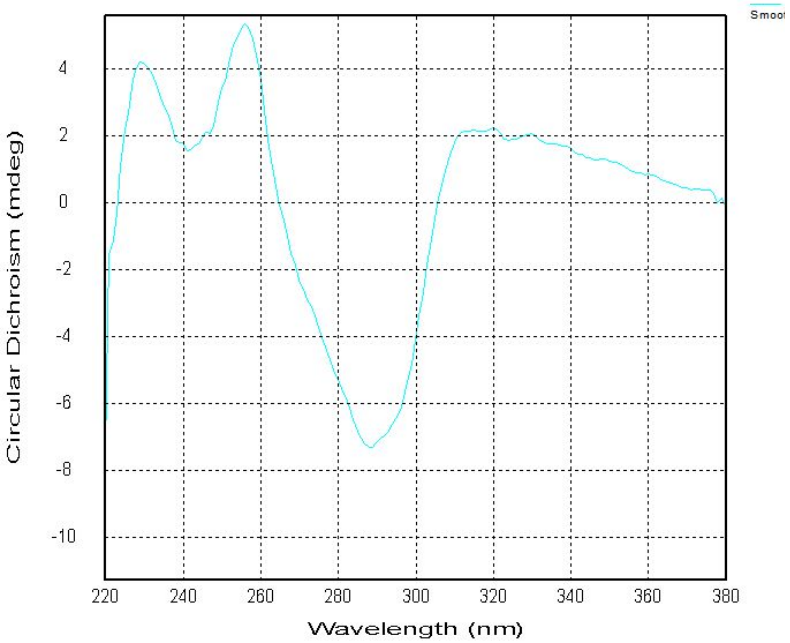


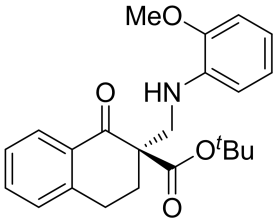
tert-butyl 1-oxo-2-((o-tolylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4j**):



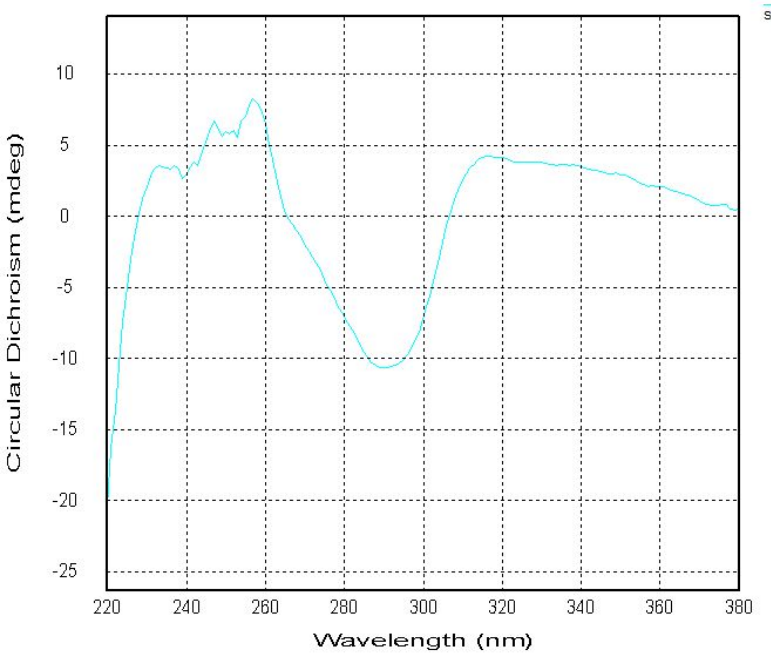


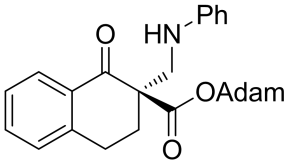
tert-butyl 2-(((2-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene -2-carboxylate (**4k**):



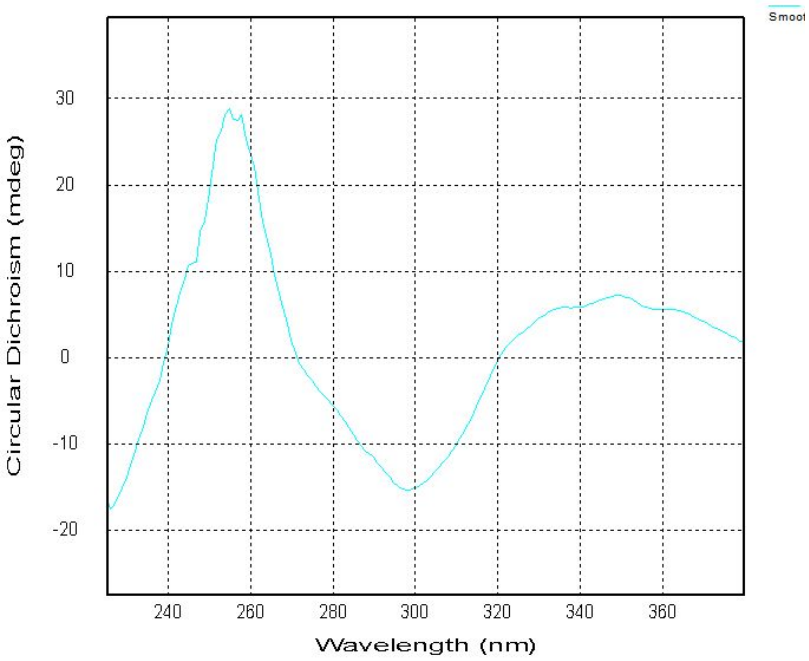


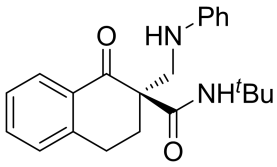
Adamantan-1-yl 1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**4l**):



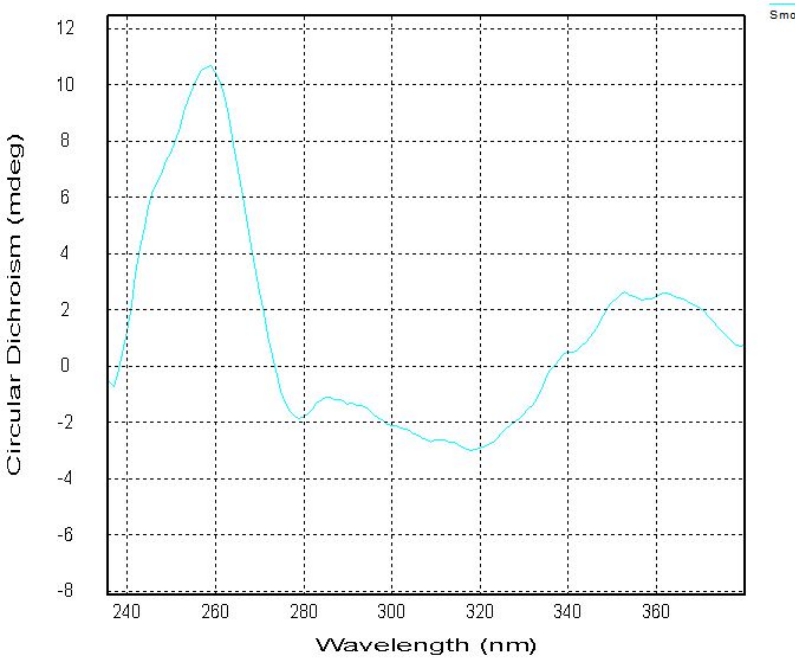


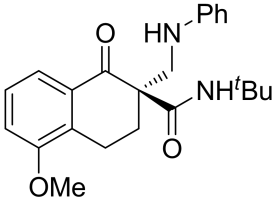
N-(*tert*-butyl)-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5a**):



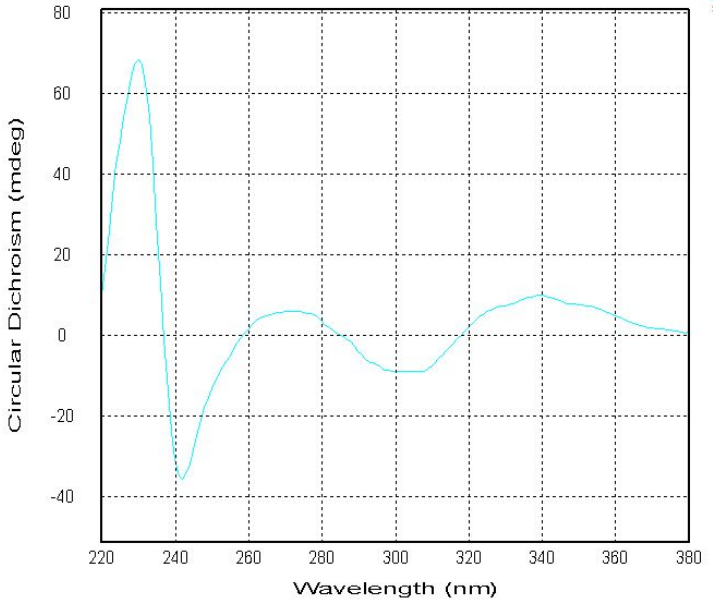


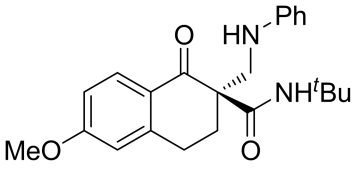
N-(*tert*-butyl)-5-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5b**):



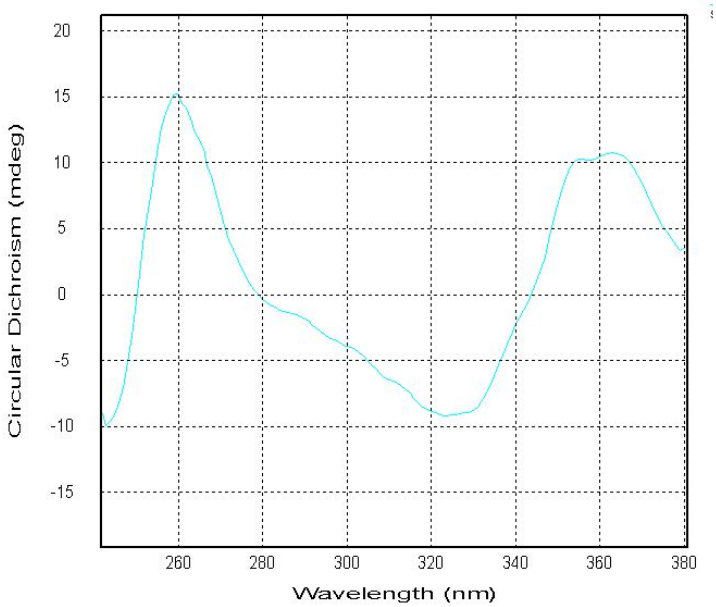


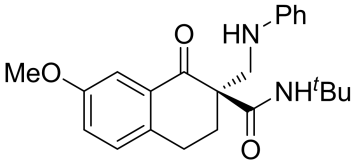
N-(*tert*-butyl)-6-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5c**):



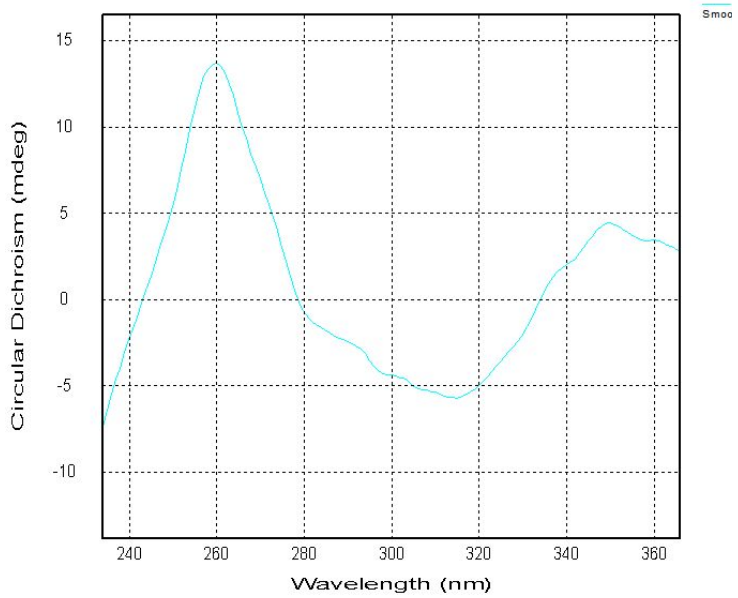


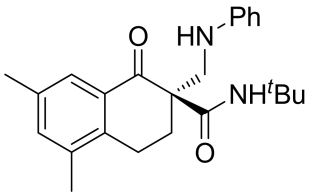
N-(*tert*-butyl)-7-methoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5d**):



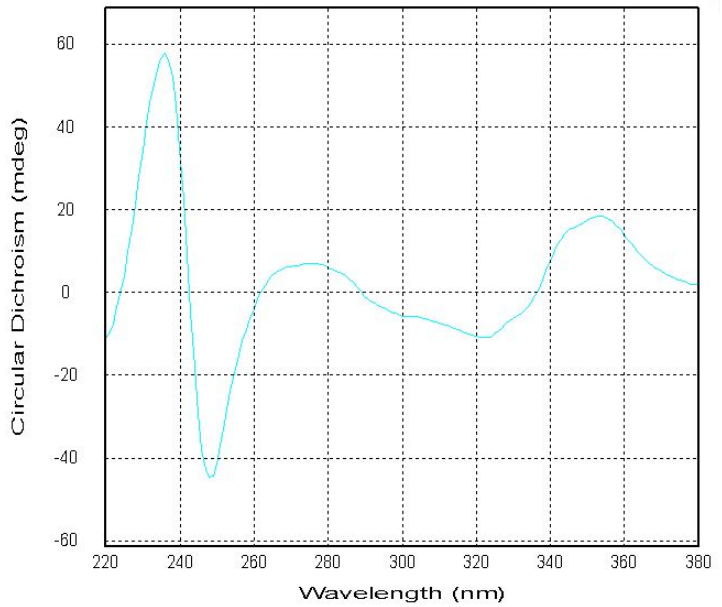


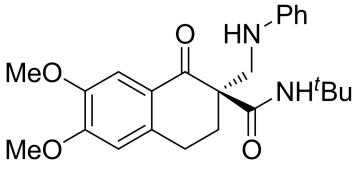
N-(*tert*-butyl)-5,7-dimethyl-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5e**):



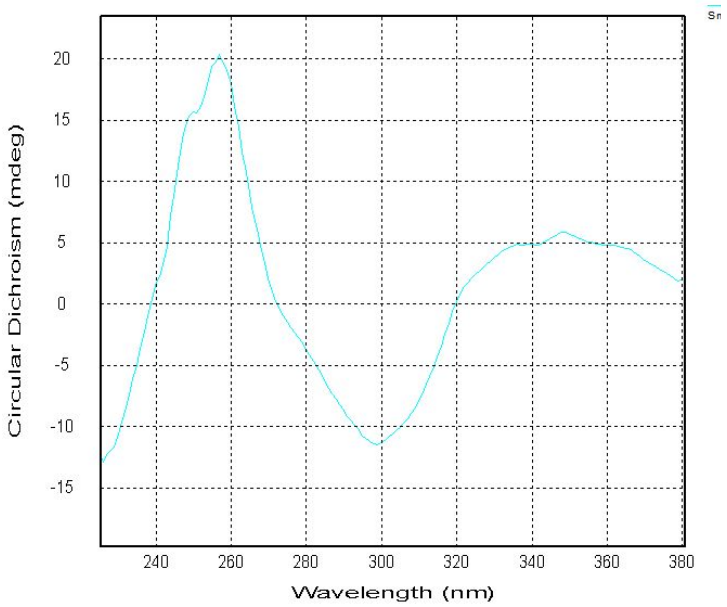


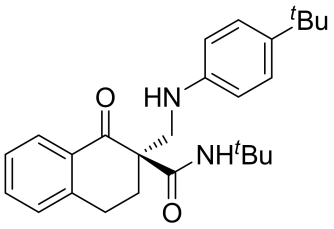
N-(*tert*-butyl)-6,7-dimethoxy-1-oxo-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5f**):



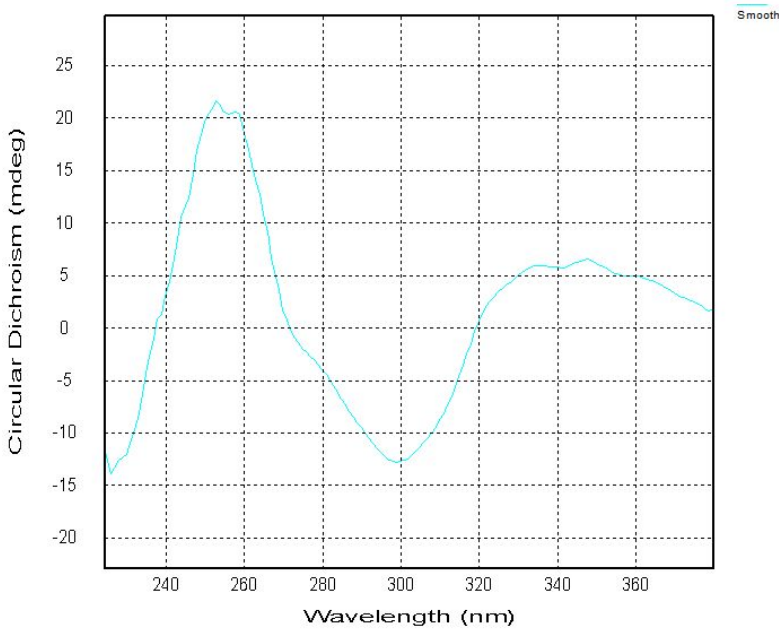


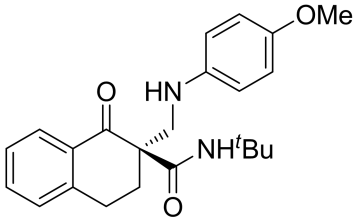
N-(*tert*-butyl)-2-(((4-(tert-butyl)phenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronapht halene-2-carboxamide (**5g**):



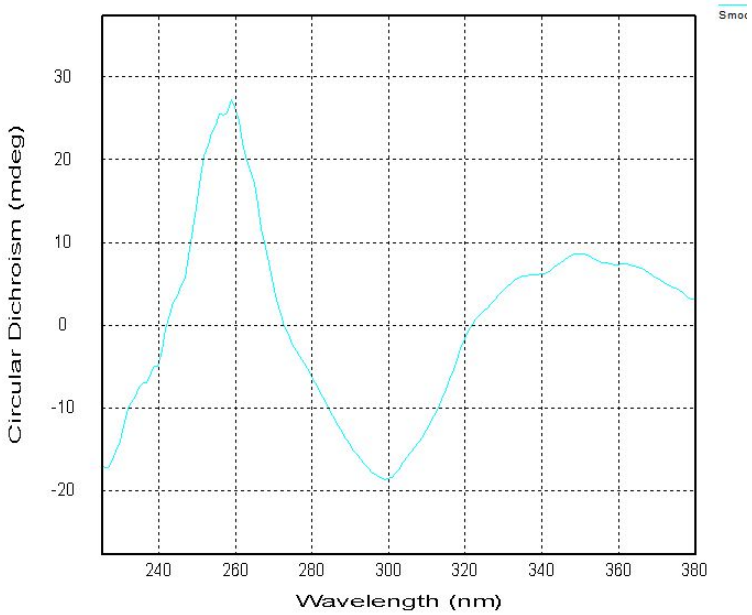


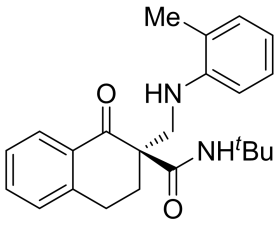
N-(*tert*-butyl)-2-(((4-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthal ene-2-carboxamide (**5h**):



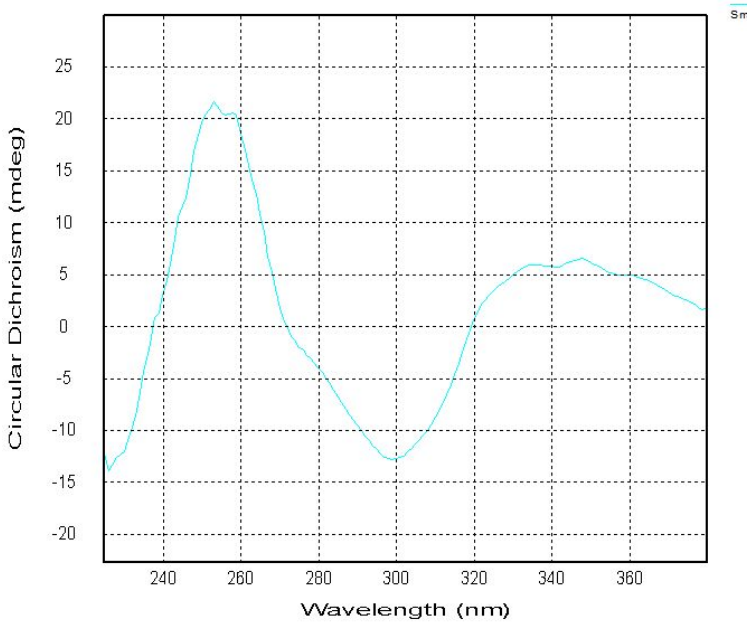


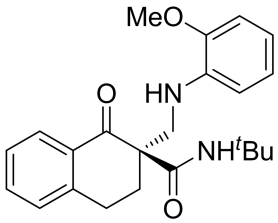
N-(*tert*-butyl)-1-oxo-2-((o-tolylamino)methyl)-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5i**):





N-(*tert*-butyl)-2-(((2-methoxyphenyl)amino)methyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxamide (**5j**):





N-(*tert*-butyl)-1-oxo-2-((phenylamino)methyl)-2,3-dihydro-1H-indene-2-carboxamide (**5k**):