

Supplementary Information

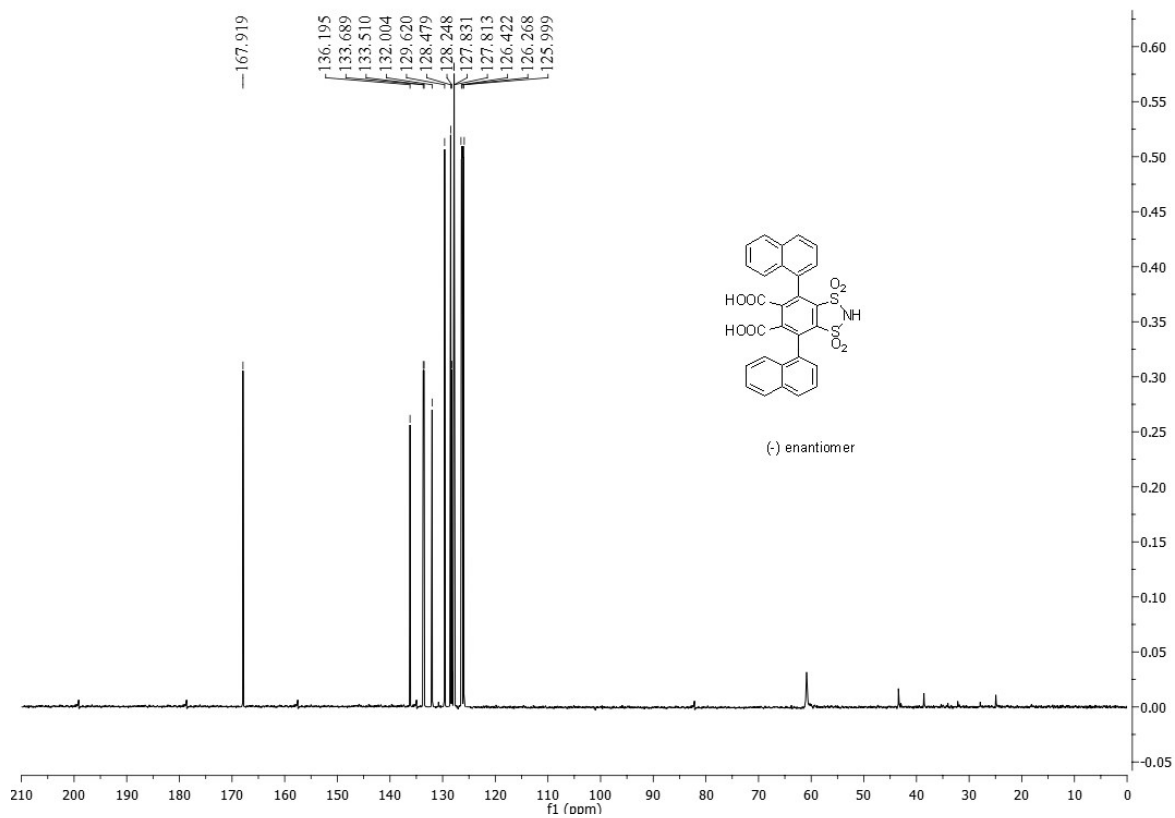
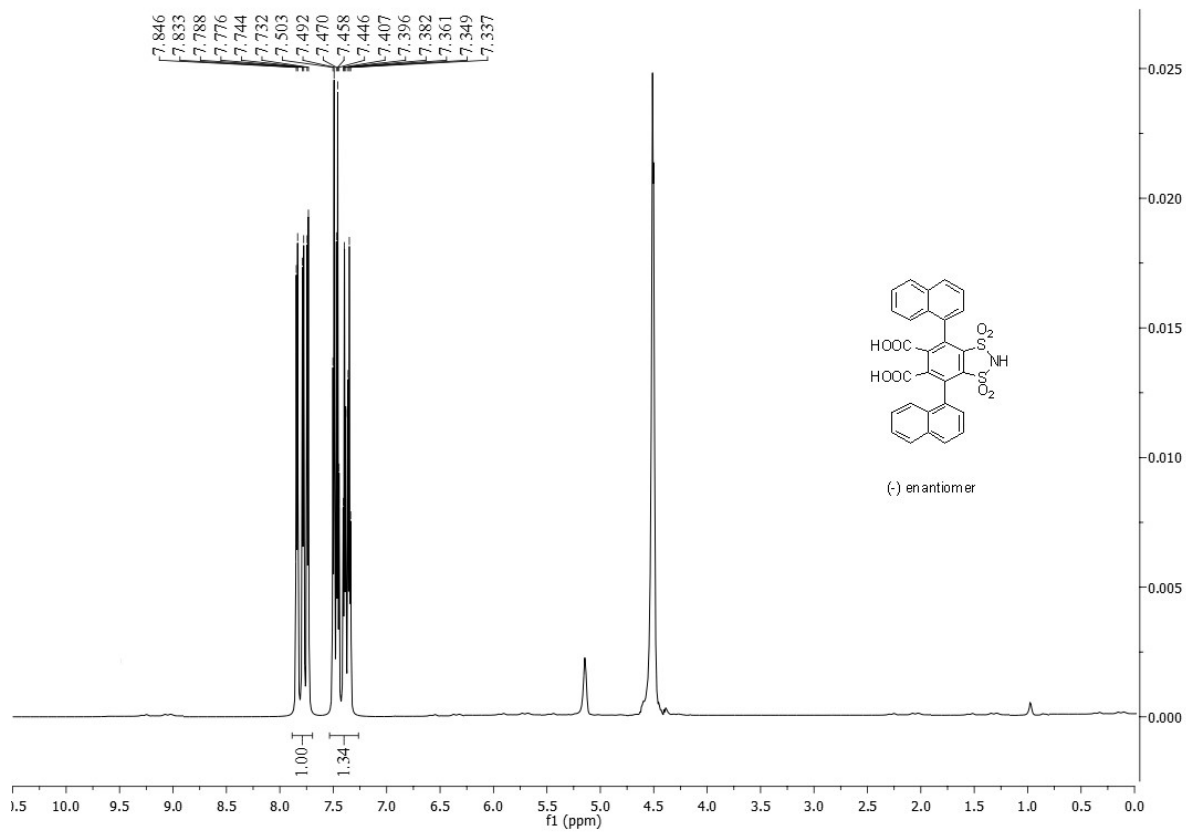
Silica gel-immobilized chiral 1,2-benzenedisulfonimide: a Brønsted acid heterogeneous catalyst for enantioselective Passerini reaction

Achille Antenucci, Francesco Marra and Stefano Dughera

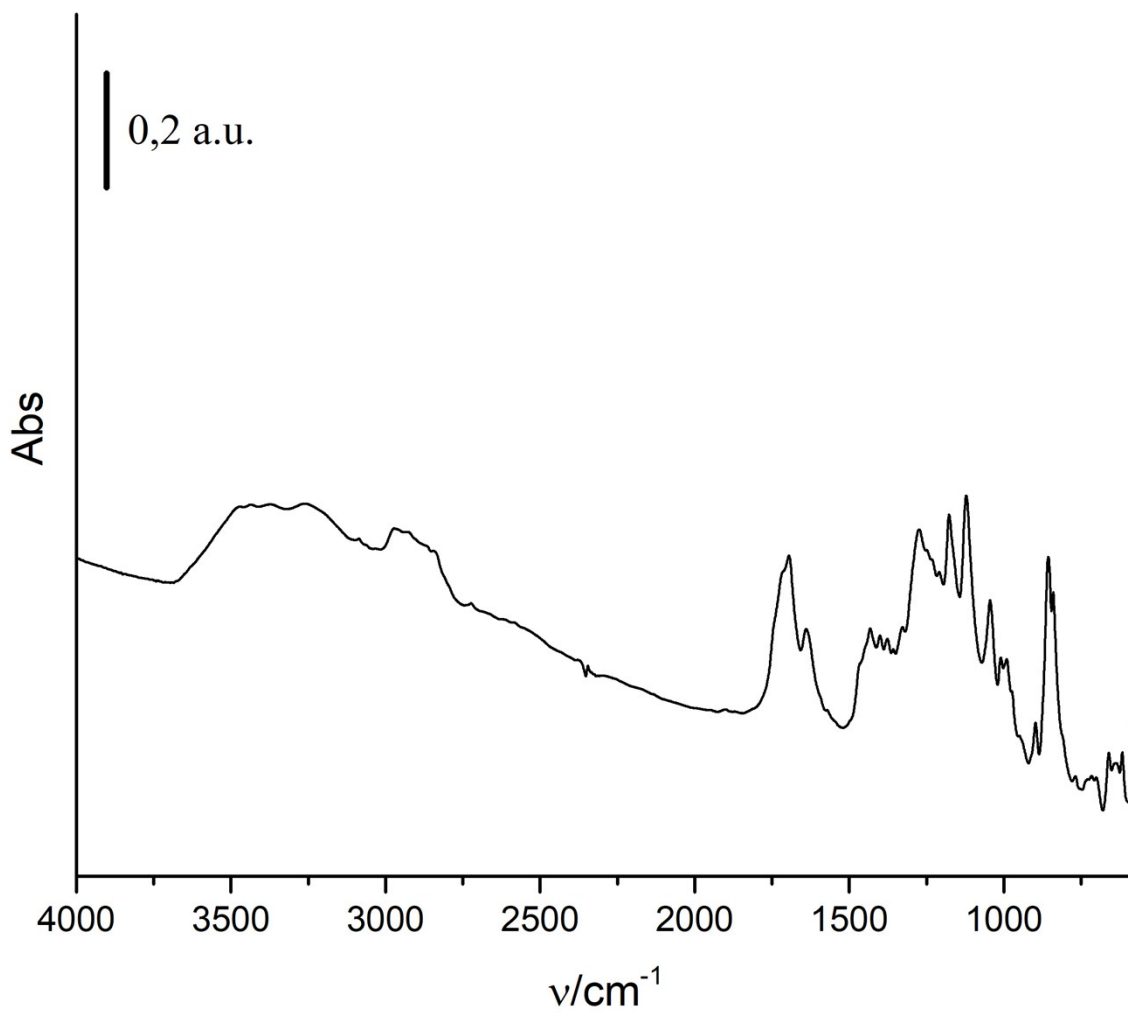
INDEX

1. NMR spectra of 4,5-dicarboxy-3,6-bis(1-naphthyl)-1,2-benzenedisulfonimide (10); pag. 2
2. IR spectra of 4,5-dicarboxy-3,6-bis(1-naphthyl)-1,2-benzenedisulfonimide (10); pag. 3
3. IR spectrum of 3-aminopropyl functionalized silica gel (7); pag. 4
4. IR spectrum of solide residue of reaction carried out without EDCM; pag. 5
5. Table. Scope of the Passerini reaction carried out in DES without chiral heterogeneous catalyst 11; pag. 6
6. Spectra, HPLC diagrams and physical properties of adducts 15; pag. 8
7. IR and NMR spectra of urea/choline chloride DES; pag. 59

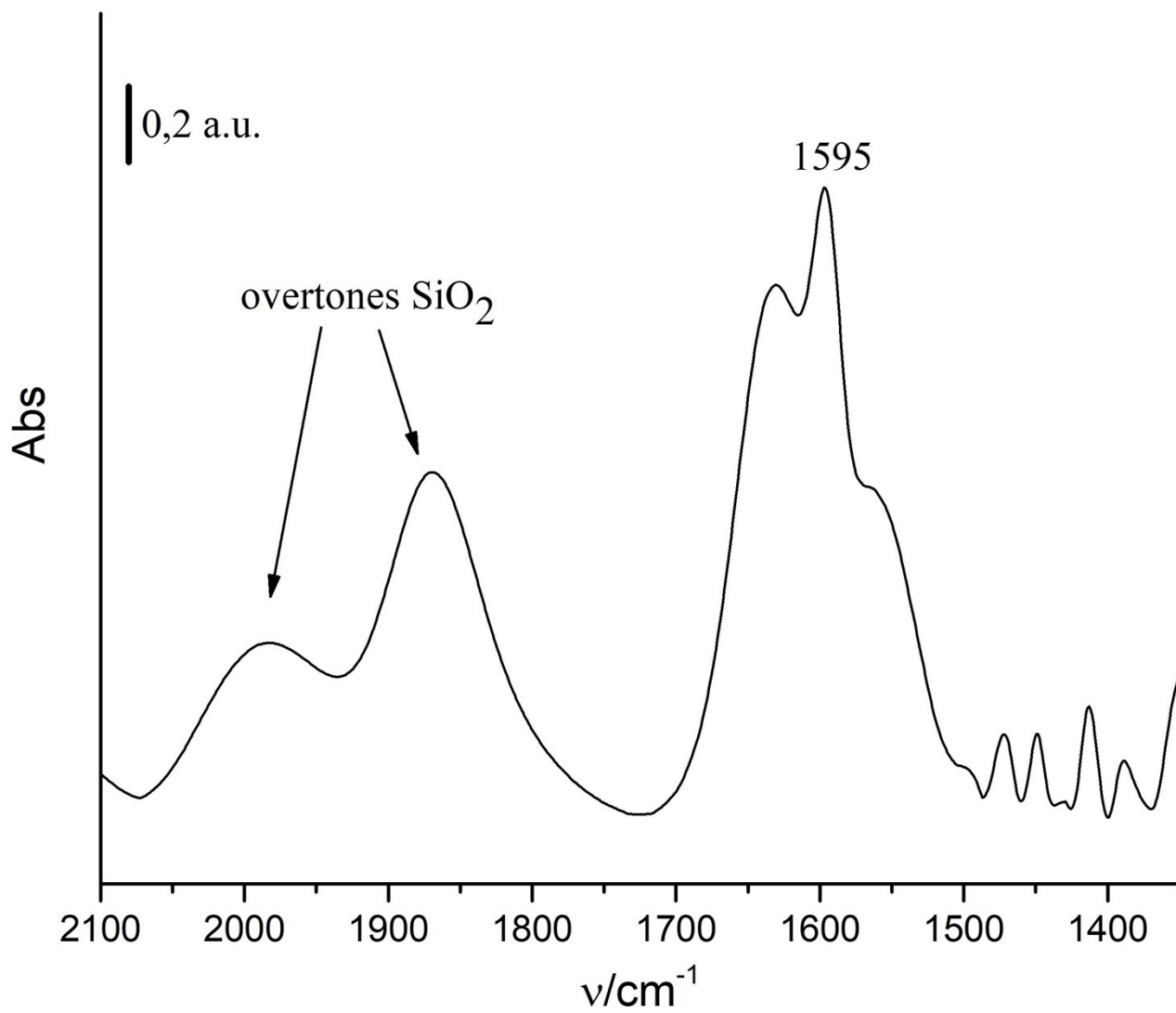
NMR spectra of 4,5-dicarboxy-3,6-bis(1-naphthyl)-1,2-benzenedisulfonimide (10)



IR spectrum of 4,5-dicarboxy-3,6-bis(1-naphthyl)-1,2-benzenedisulfonimide (10)



IR spectrum of 3-aminopropyl functionalized silica gel (7)



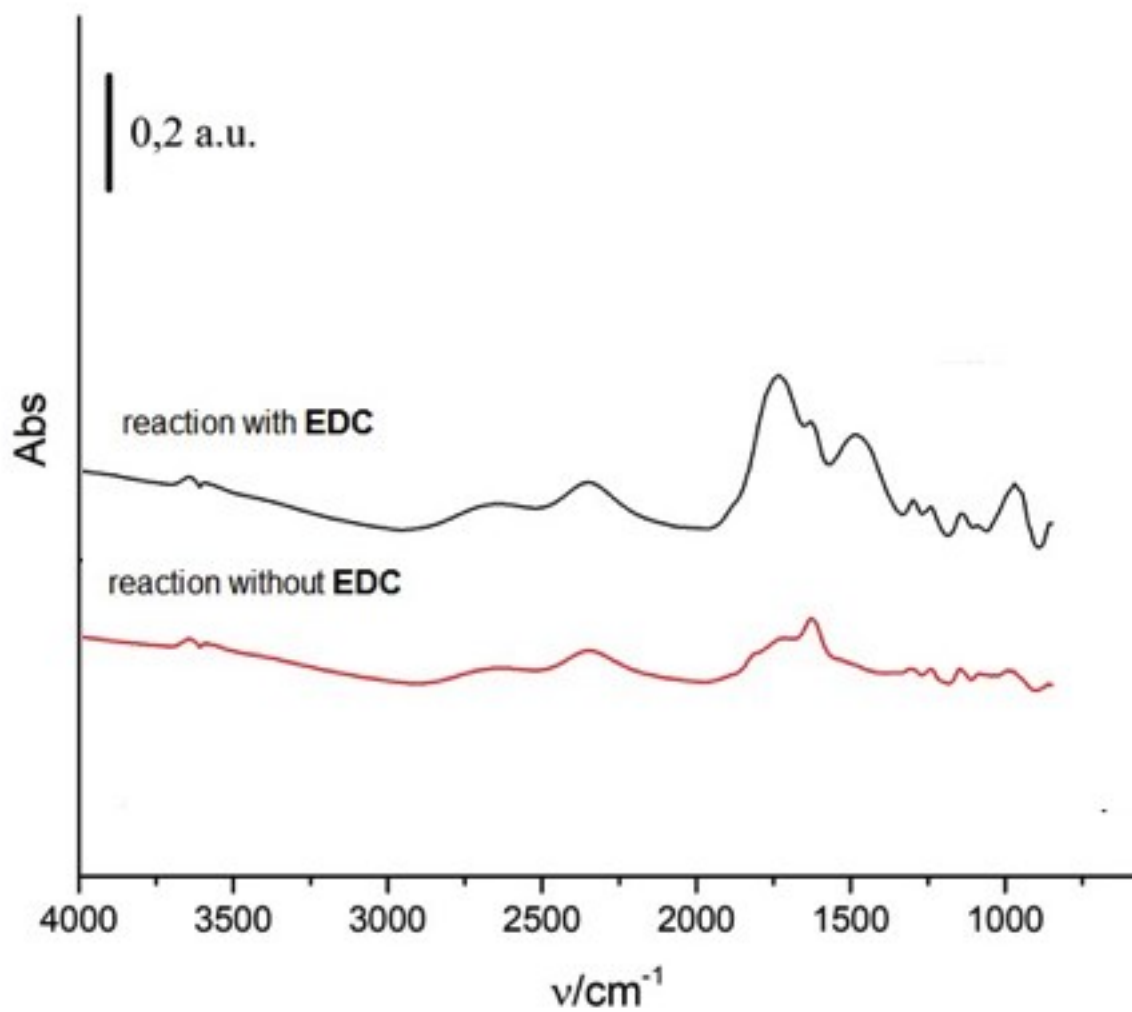


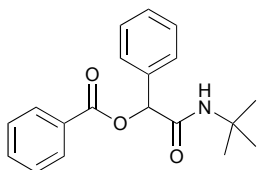
Table. Scope of the Passerini reaction carried out in DES without chiral heterogeneous catalyst **11**.

$ \begin{array}{c} \text{R}_1\text{---COOH} + \text{R}_2\text{---CHO} + \text{R}_3\text{---NC} \xrightarrow{\text{U/CC}} \text{R}_1\text{---C(=O)---O---CH(R}_2\text{)---C(=O)---N---R}_3 \\ \mathbf{12} \qquad \qquad \mathbf{13} \qquad \qquad \mathbf{14} \qquad \qquad \qquad \qquad \mathbf{15} \end{array} $						
Entry	R ₁ in RCOOH 12	R ₂ in RCHO 13	R ₃ in RNC 14	Time (h)	15	Yield (%) ^a
1	Ph; 12a	Ph; 13a	<i>t</i> -Bu; 14a	36	15a	91
2	Ph; 12a	3-NO ₂ C ₆ H ₄ ; 13b	<i>t</i> -Bu; 14a	38	15b	95
3	Ph; 12a	4-MeOC ₆ H ₄ ; 13c	<i>t</i> -Bu; 14a	40	15c	83
4	Ph; 12a	4-ClC ₆ H ₄ ; 13d	<i>t</i> -Bu; 14a	32	15d	98
5	Ph; 12a	4-MeC ₆ H ₄ ; 13e	<i>t</i> -Bu; 14a	34	15e	85
6	Ph; 12a	PhCH=CH; 13f	<i>t</i> -Bu; 14a	42	15f	84
7	Ph; 12a	<i>i</i> -Pr; 13g	<i>t</i> -Bu; 14a	38	15g	91
8	4-NO ₂ C ₆ H ₄ ; 12b	Ph; 13a	<i>t</i> -Bu; 14a	30	15h	86
9	4-MeOC ₆ H ₄ ; 12c	Ph; 13a	<i>t</i> -Bu; 14a	48	15i	84
10	4-ClC ₆ H ₄ ; 12d	Ph; 13a	<i>t</i> -Bu; 14a	36	15j	92
11	Me; 12e	Ph; 13a	<i>t</i> -Bu; 14a	30	15k	86
12	PhCH ₂ ; 12f	Ph; 13a	<i>t</i> -Bu; 14a	34	15l	90
13	3-Pyridyl; 12g	4-ClC ₆ H ₄ ; 13d	<i>t</i> -Bu; 14a	36	15m	82

14	Ph; 12a	Ph; 13a	2-Naphthyl; 14b	36	15n	86
15	Ph; 12a	4-ClC ₆ H ₄ ; 13d	2-Naphthyl; 14b	32	15o	83
16	Me; 12e	3-NO ₂ C ₆ H ₄ ; 13b	2-Naphthyl; 14b	32	15p	88
17	Me; 12e	<i>i</i> -Pr; 13g	2-Naphthyl; 14b	30	15q	87
18	Ph; 12a	PhCOMe; 13h	<i>t</i> -Bu; 14a	48 ^b	15r	-

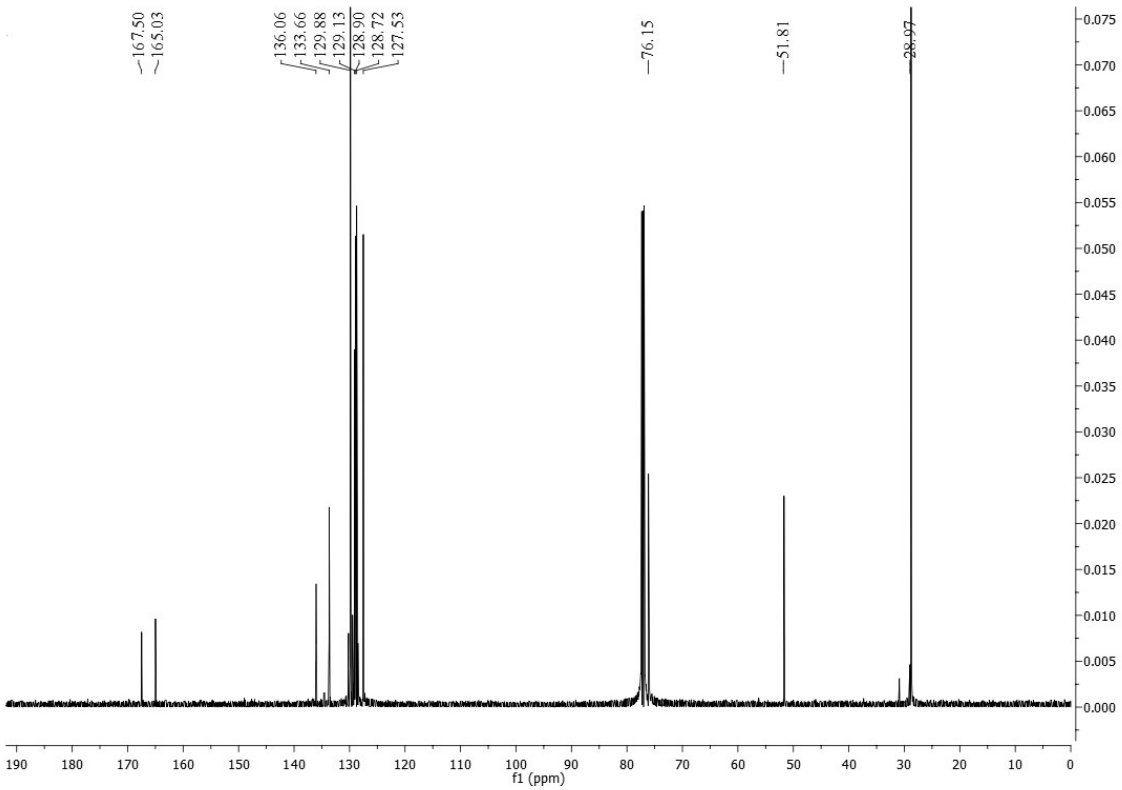
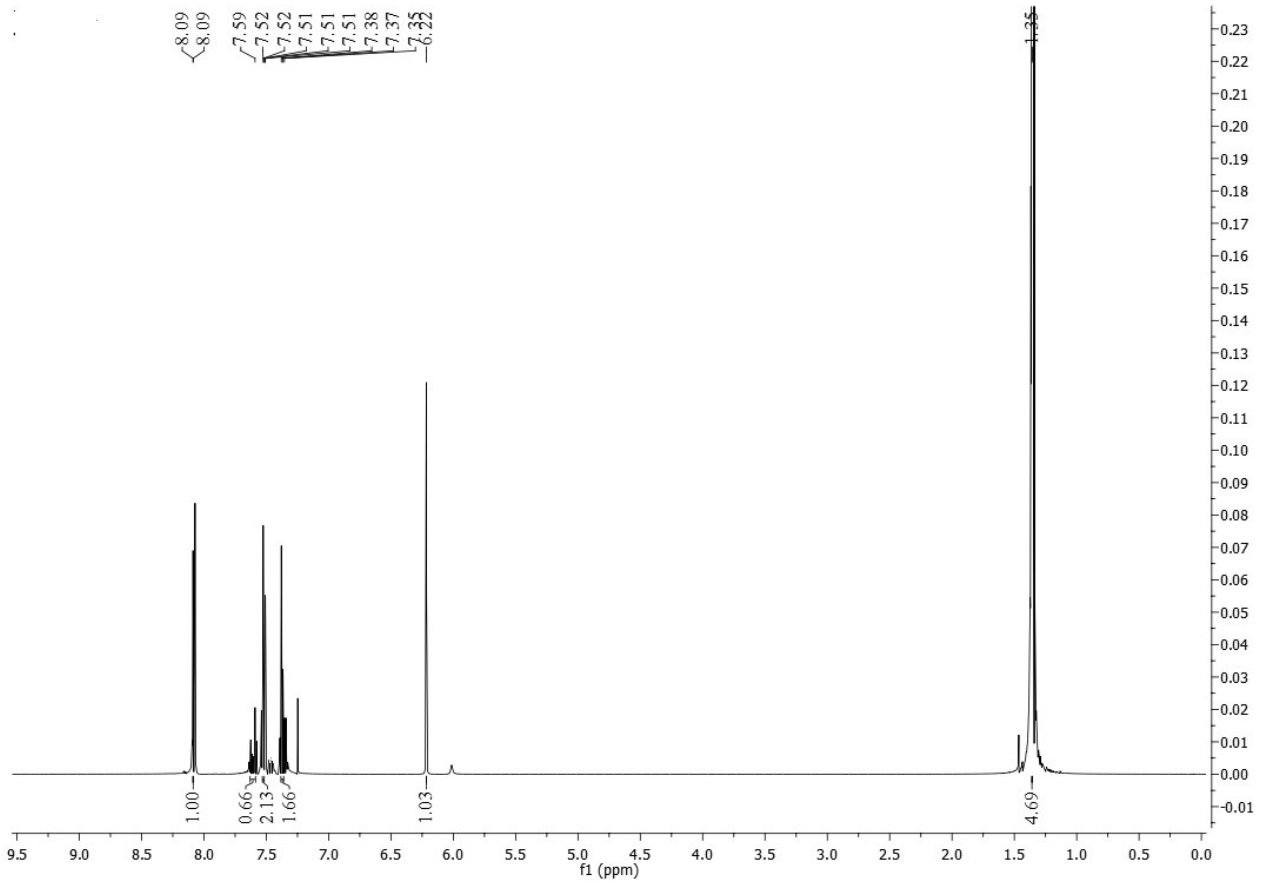
^a Yields refer to pure and isolated **15**. Times and yields refer to the reactions carried out with 1 mmol of **12a**, **13a**, **14a**.^b After 48 h, GC-MS analyses showed the presence of unreacted **12a**, **13h** and **14a**. **15r** was detected only in traces ; *m/z*: 325 (M⁺).

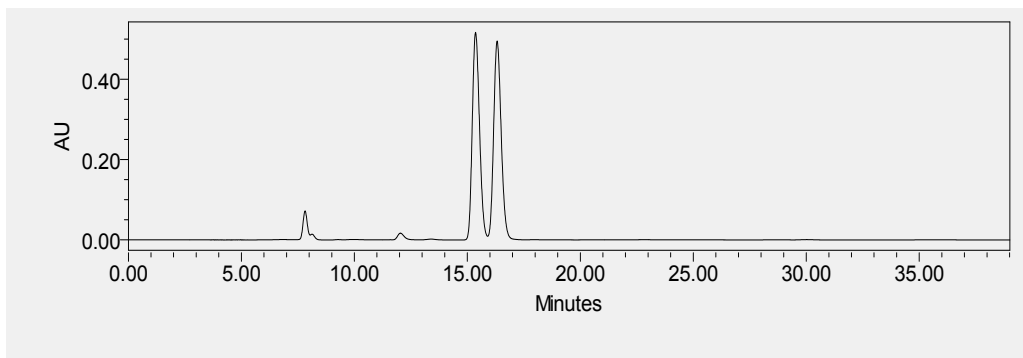
2-(*tert*-Butylamino)-2-oxo-1-phenylethyl benzoate (15a):



White solid (270 mg, 87% yield); mp 151–152 °C (from EtOH; lit. 150–151°C). 94.8% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 30/70, 1.0 mL/min, $\lambda = 230$ nm, t_R (minor) = 15.4 min, t_R (major) = 16.3 min]. $\nu_{\max}/\text{cm}^{-1}$ 3283 (NH), 1729, 1648 (CO). δ_H (600 MHz, CDCl_3) 8.09–8.08 (m, 2H), 7.63–7.59 (m, 1H), 7.52–7.51 (m, 4H), 7.39–7.35 (m, 3H), 6.22 (s, 2H), 1.36 (s, 9H). δ_C (150 MHz, CDCl_3) 167.5, 165.0, 136.1, 133.7, 129.9, 129.2, 129.1, 128.9, 128.7, 127.5, 76.1, 51.8, 28.9. m/z : 311 (M^+ , 1%), 212 (45), 105 (100). HRMS (ESI, m/z): 312.16 ($M+H^+$).

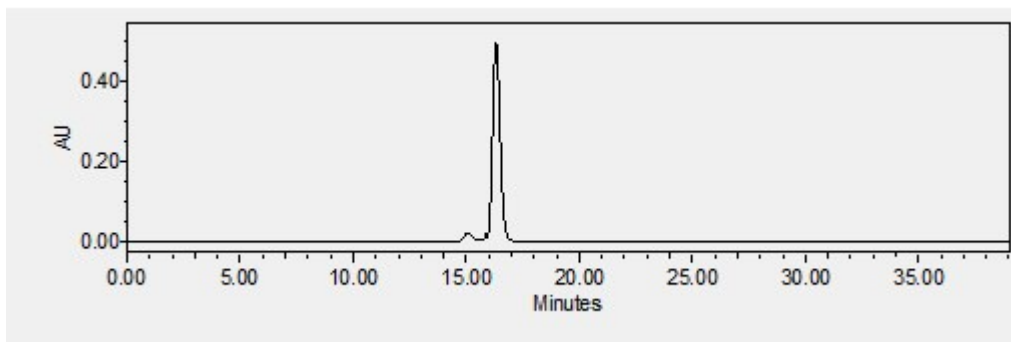
L. A. Polindara-Garcia and E. Juaristi, *Eur. J. Org. Chem.*, 2016, 1095–1102.





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
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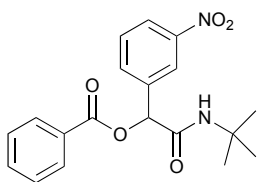
2-(*tert*-butylamino)-2-oxo-1-phenylethyl benzoate (15a): racemate



Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	15.392	412375	2.59	775	bb			Unknown	
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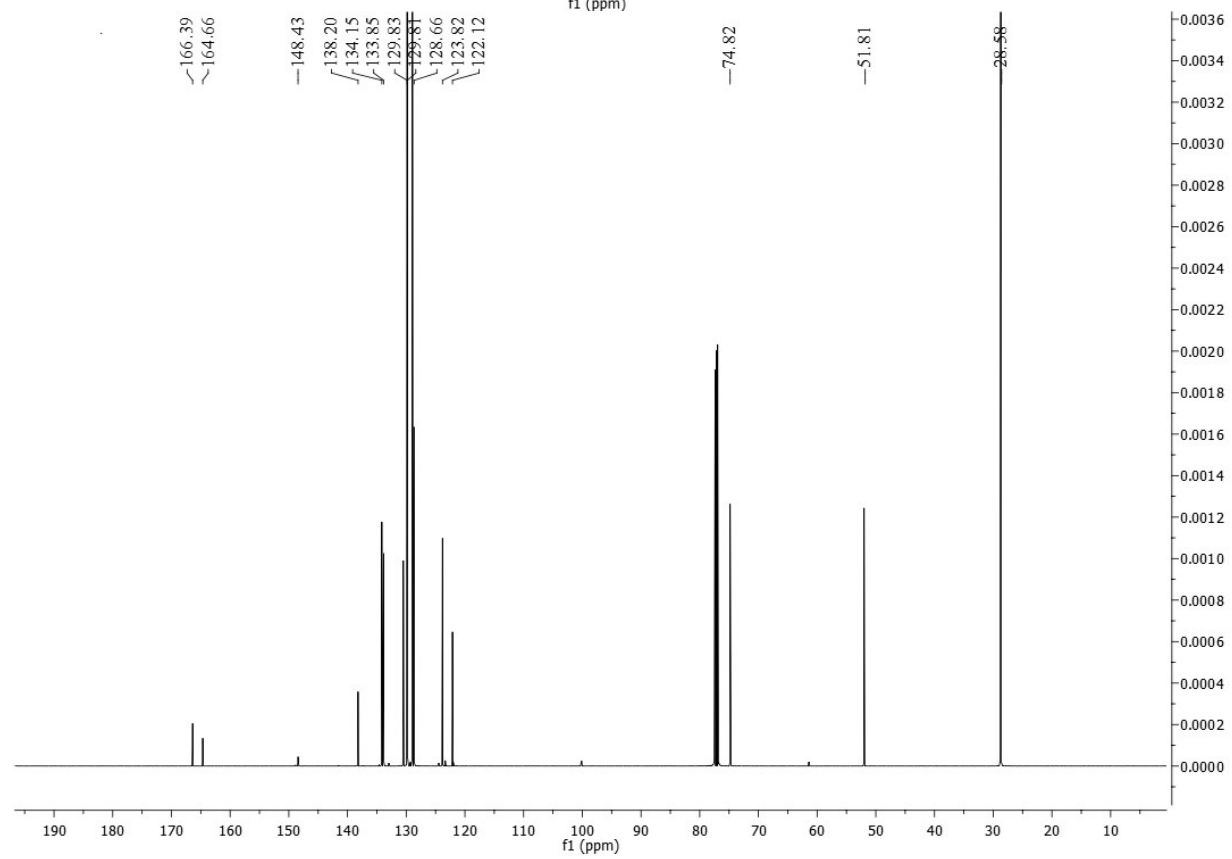
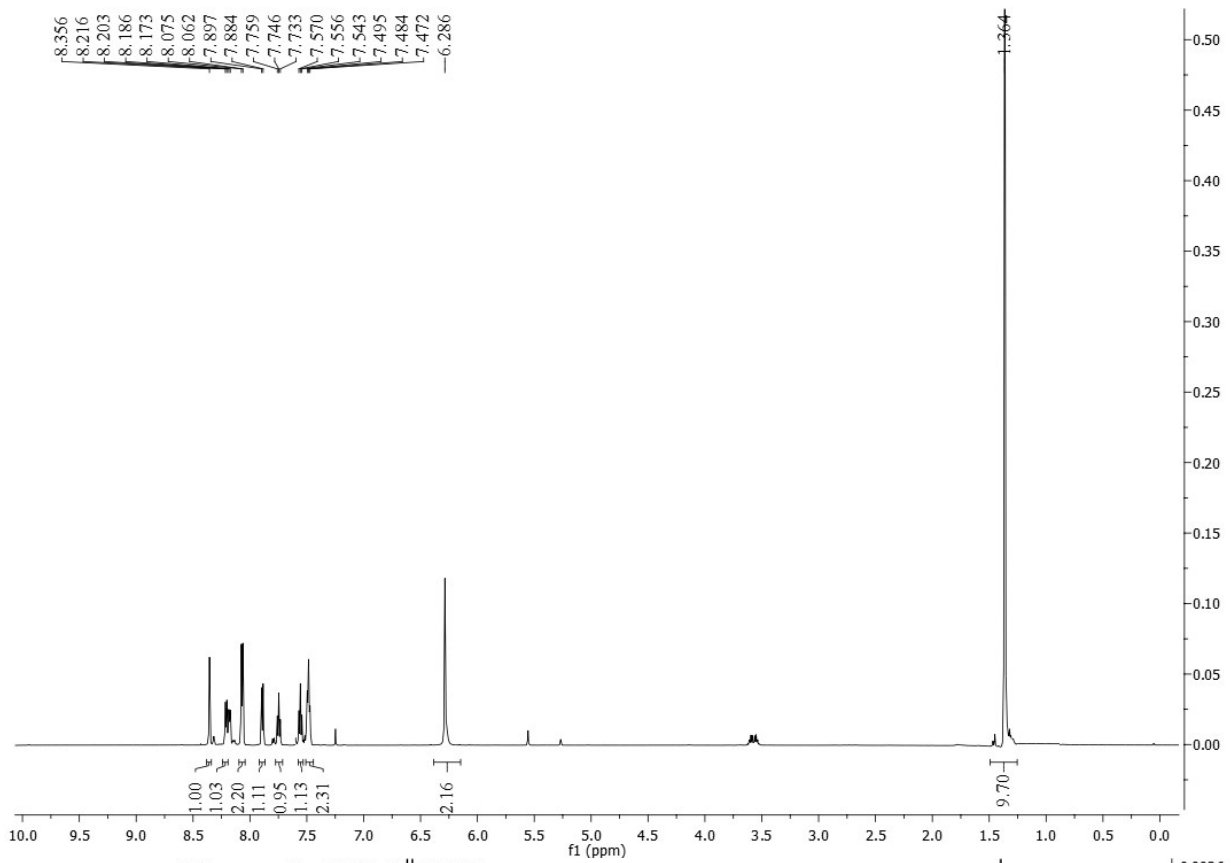
2-(*tert*-butylamino)-2-oxo-1-phenylethyl benzoate (15a): in the presence of chiral catalyst 11.

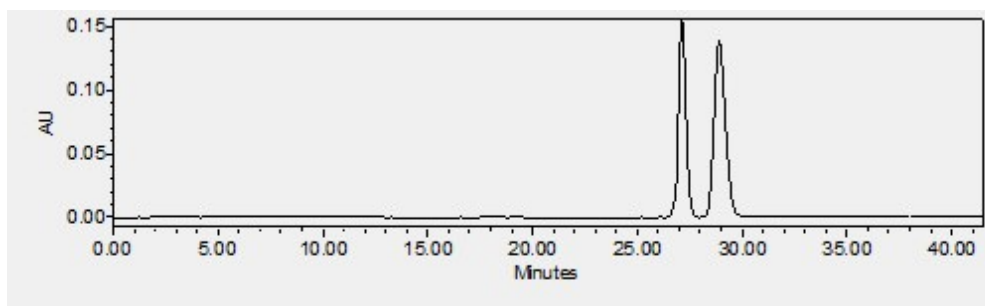
2-(*tert*-butylamino)-1-(3-nitrophenyl)-2-oxoethyl benzoate (15b):



White solid (332 mg, 93% yield); mp 166–167 °C (from EtOH; lit. 163–165°C). 96.4% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 15/85, 1.0 mL/min, λ = 230 nm, t_R (minor) = 26.6 min, t_R (major) = 28.9 min]. $\nu_{\max}/\text{cm}^{-1}$ 3294 (NH), 1731, 1645 (CO). δ_H (600 MHz, CDCl_3) 8.36 (s, 1H), 8.22–8.17 (m, 1H), 8.07 (d, J = 7.8 Hz, 2H), 7.89 (d, J = 7.8 Hz, 1H), 7.75 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 8.4 Hz, 1H), 7.49–7.47 (m, 2H), 6.28 (s, 2H), 1.36 (s, 9H). δ_C (150 MHz, CDCl_3) 166.4, 164.7, 148.4, 138.2, 134.1, 133.8, 129.83, 129.81, 128.8, 128.7, 123.8, 122.1, 74.7, 51.8, 28.6. m/z : 356 (M^+ , 1%), 135 (55), 105 (100). HRMS (ESI, m/z): 357.15 ($M+H^+$).

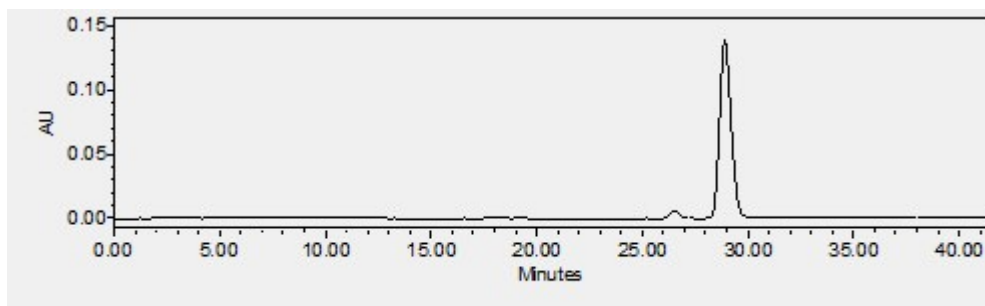
X. Fan, Y. Li, X. Zhang, G. Qu and J. Wang, *Can. J. Chem.*, 2006, **84**, 794–799.





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
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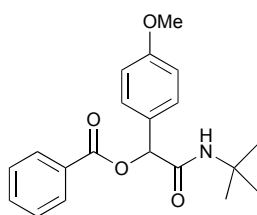
2-(*tert*-butylamino)-2-oxo-1-(3-nitrophenyl)ethyl benzoate (15b): racemate



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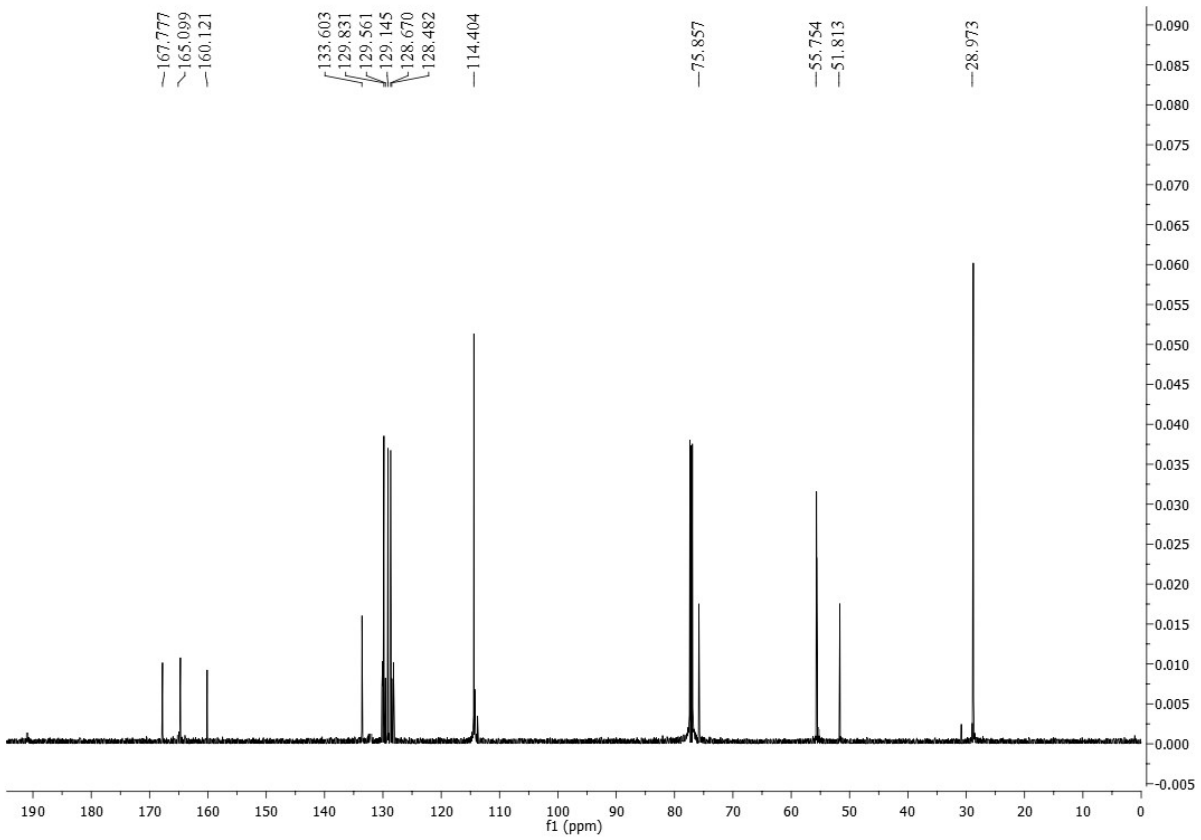
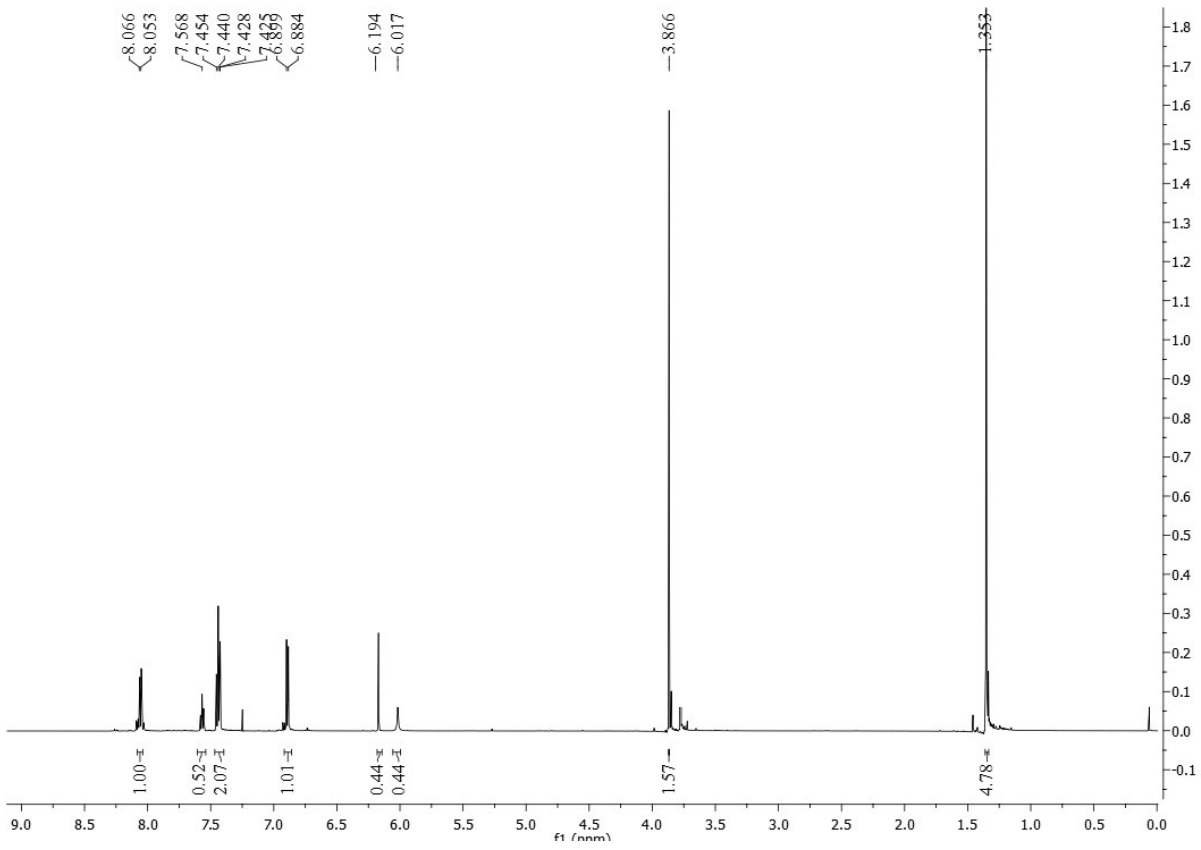
2-(*tert*-butylamino)-2-oxo-1-(3-nitrophenyl)ethyl benzoate (15b): in the presence of chiral catalyst 11.

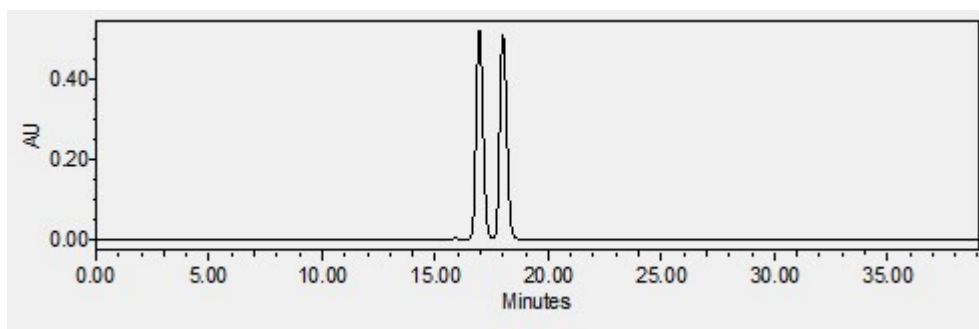
2-(*tert*-butylamino)-1-(4-methoxyphenyl)-2-oxoethyl benzoate (15c) :



White solid (291 mg, 85% yield); mp 147–148 °C (from EtOH; lit. 149–150°C). 96.8% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 10/90, 1.0 mL/min, λ = 214 nm, t_R (minor) = 18.9 min, t_R (major) = 19.9 min. $\nu_{\max}/\text{cm}^{-1}$ 3284 (NH), 1728, 1654 (CO). δ_H (600 MHz, CDCl_3) 8.06 (d, J = 7.8 Hz, 2H), 7.58–7.56 (m, 1H), 7.46–7.42 (m, 4H), 6.89 (d, J = 9.0 Hz, 2H), 6.19 (s, 1H), 6.02 (br s, 1H), 3.86 (s, 3H), 1.35 (s, 9H). δ_C (150 MHz, CDCl_3) 167.8, 165.0, 160.1, 133.6, 129.8, 129.6, 129.1, 128.7, 128.5, 114.4, 75.9, 55.7, 51.8, 28.9. m/z : 341 (M^+ , 1%), 242 (45), 105 (100). HRMS (ESI, m/z): 342.18 ($M+H^+$).

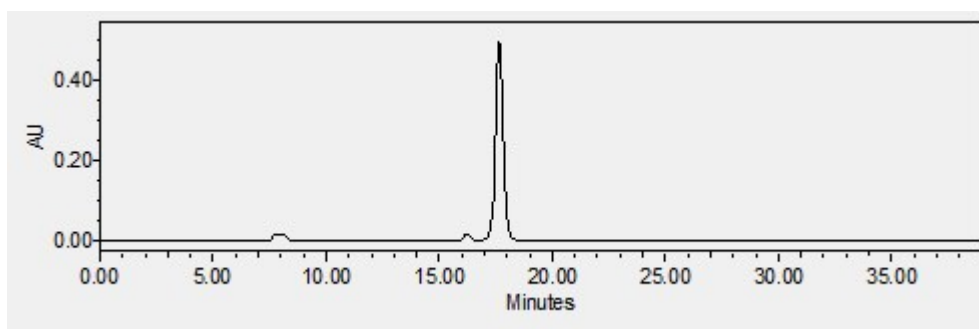
L. A. Polindara-Garcia and E. Juaristi, *Eur. J. Org. Chem.*, 2016, 1095–1102.





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	17.010	8923946	50.96	365176	bb			Unknown	
2	18.115	8587991	49.04	349168	bb			Unknown	

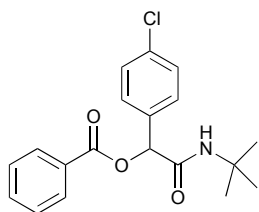
2-(*tert*-butylamino)-2-oxo-1-(4-methoxyphenyl)ethyl benzoate (15c): racemate



Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	18.885	128663	1.56	451	bb			Unknown	
2	19.890	8139009	98.34	355473	bb			Unknown	

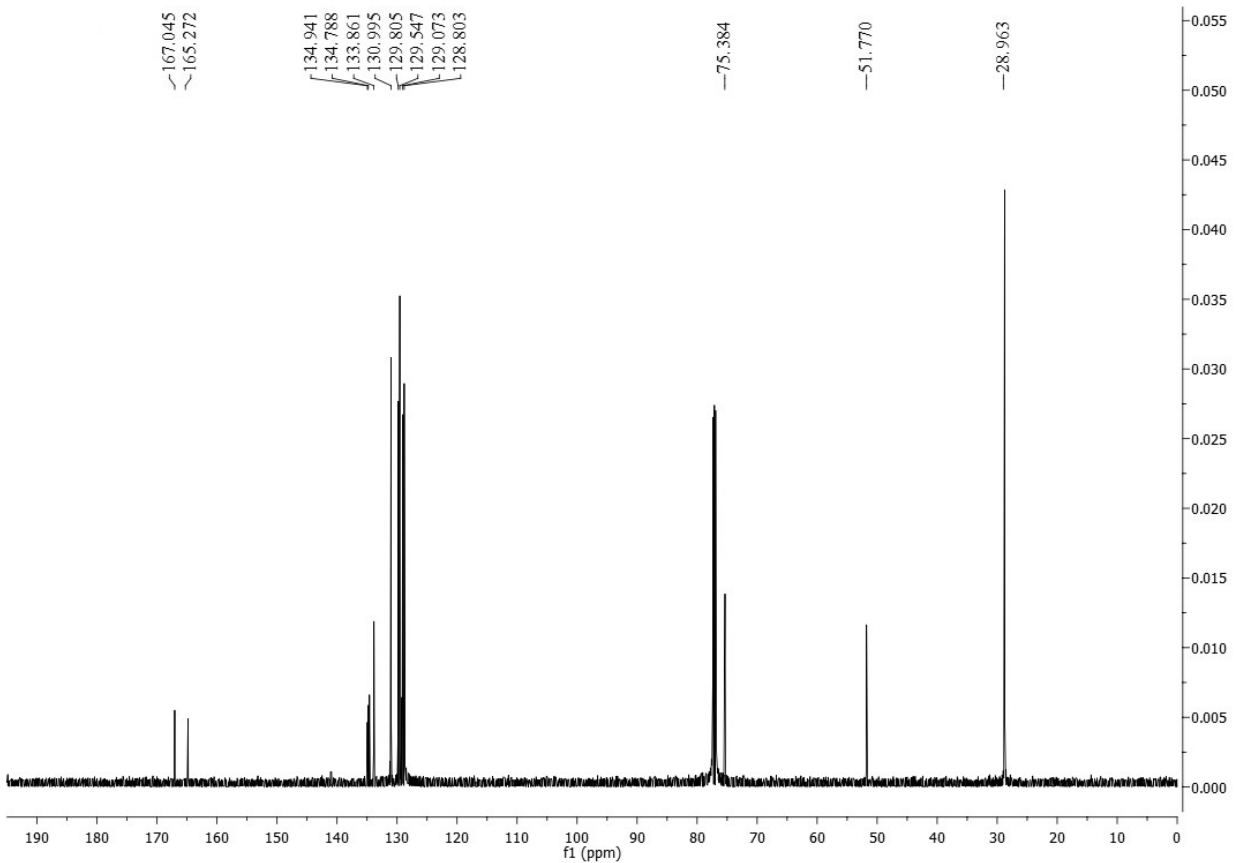
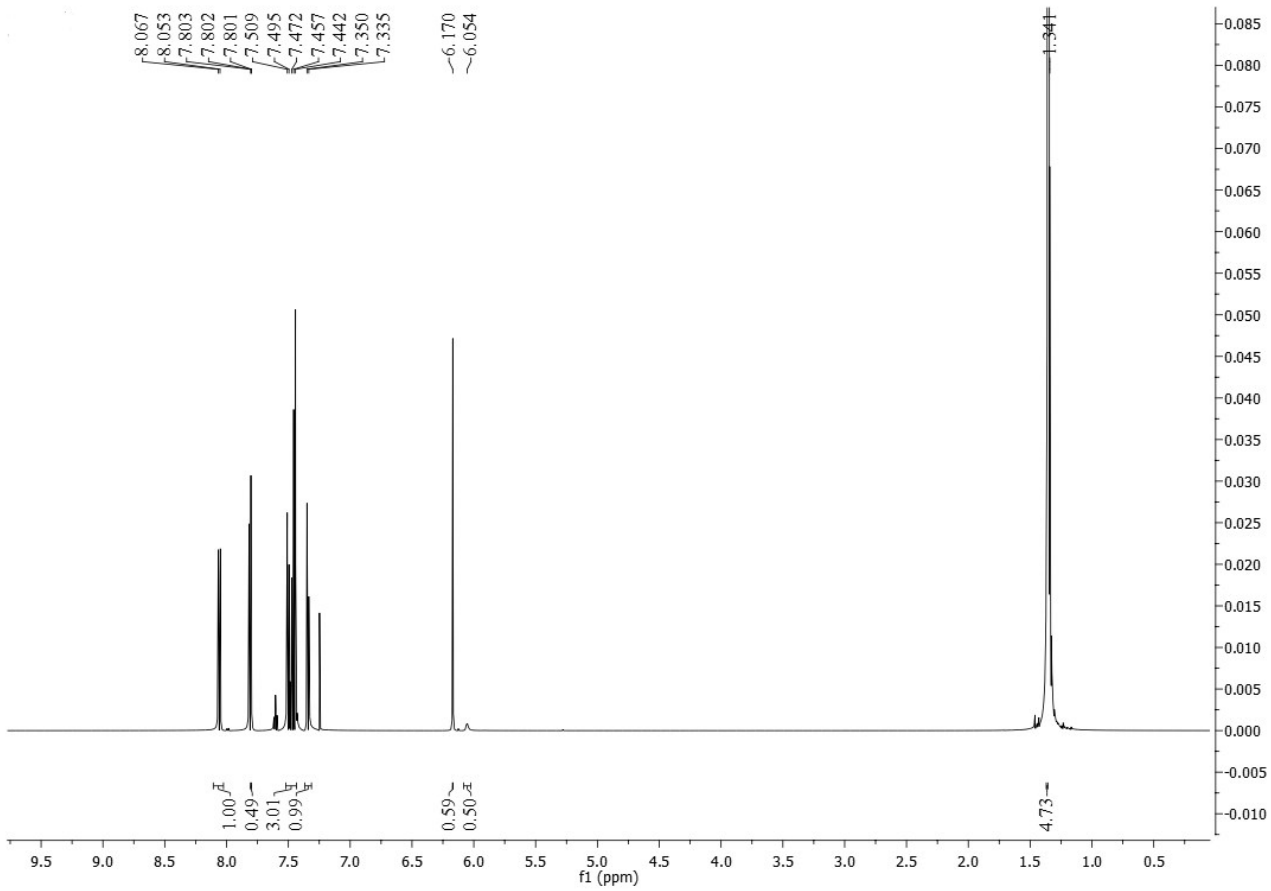
2-(*tert*-butylamino)-2-oxo-1-(4-methoxyphenyl)ethyl benzoate (15c): in the presence of chiral catalyst 11.

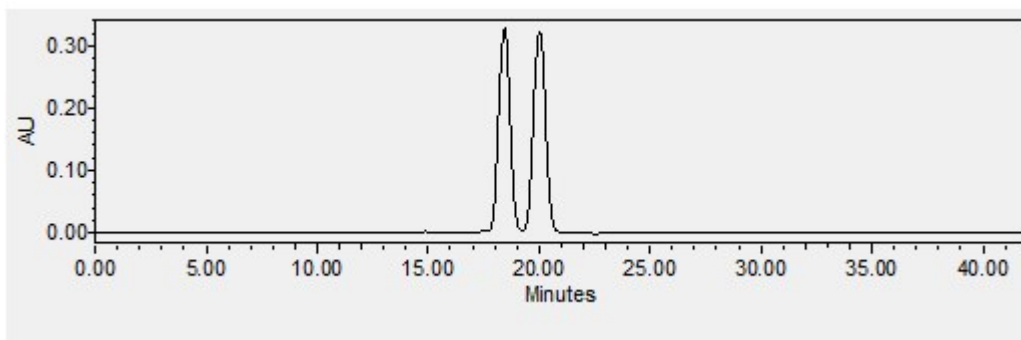
2-(tert-butylamino)-1-(4-chlorophenyl)-2-oxoethyl benzoate (15d) :



White solid (322 mg, 93% yield); mp 151–152 °C (from EtOH; lit. 150–151°C). 96.9% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, $\lambda = 254$ nm, t_R (minor) = 18.8 min, t_R (major) = 19.8 min. $\nu_{\max}/\text{cm}^{-1}$ 3281 (NH), 1728, 1651 (CO). δ_H (600 MHz, CDCl_3) 8.06 (d, $J = 8.4$ Hz, 2H), 7.81–7.80 (m, 1H), 7.51–7.44 (m, 4H), 7.34 (d, $J = 8.4$ Hz, 2H), 6.17 (s, 1H), 6.06 (br s, 1H), 1.34 (s, 9H). δ_C (150 MHz, CDCl_3). 167.0, 165.2, 134.9, 134.8, 133.9, 130.9, 129.8, 129.5, 129.1, 128.8, 75.4, 51.7, 28.9. m/z : 345 (M^+ , 1%), 246 (35), 105 (100). HRMS (ESI, m/z): 346.12 ($M+H^+$).

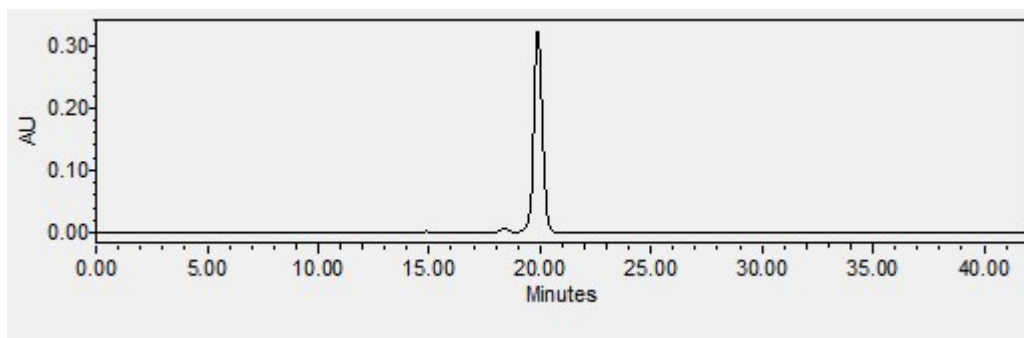
L. A. Polindara-Garcia and E. Juaristi, *Eur. J. Org. Chem.*, 2016, 1095–1102.





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.999	4045807	48.96	1077602	bb			Unknown	
2		20.107	4217634	51.04	1055291	bb			Unknown	

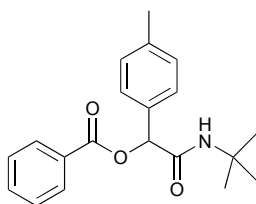
2-(*tert*-butylamino)-1-(4-chlorophenyl)-2-oxoethyl benzoate (15d): racemate



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.807	128663	1.56	1251	bb			Unknown	
2		19.799	8139009	98.44	1055183	bb			Unknown	

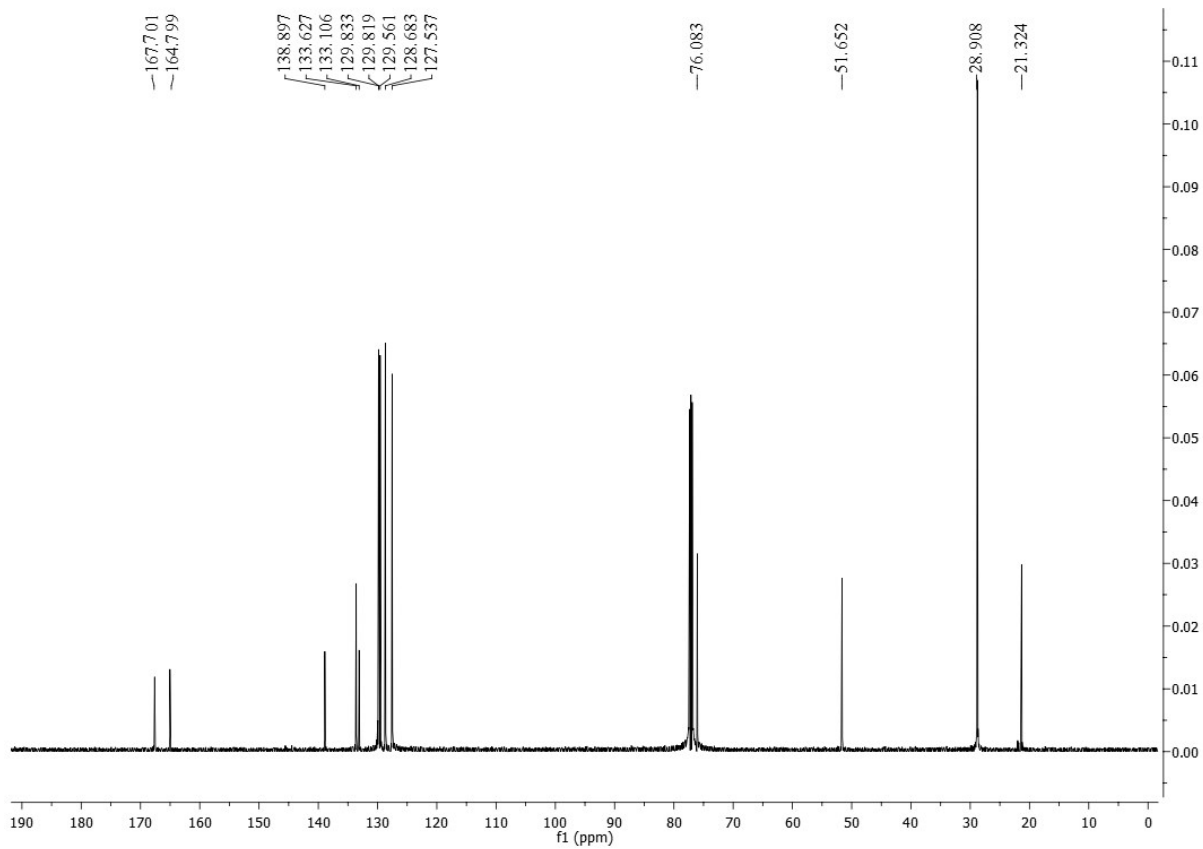
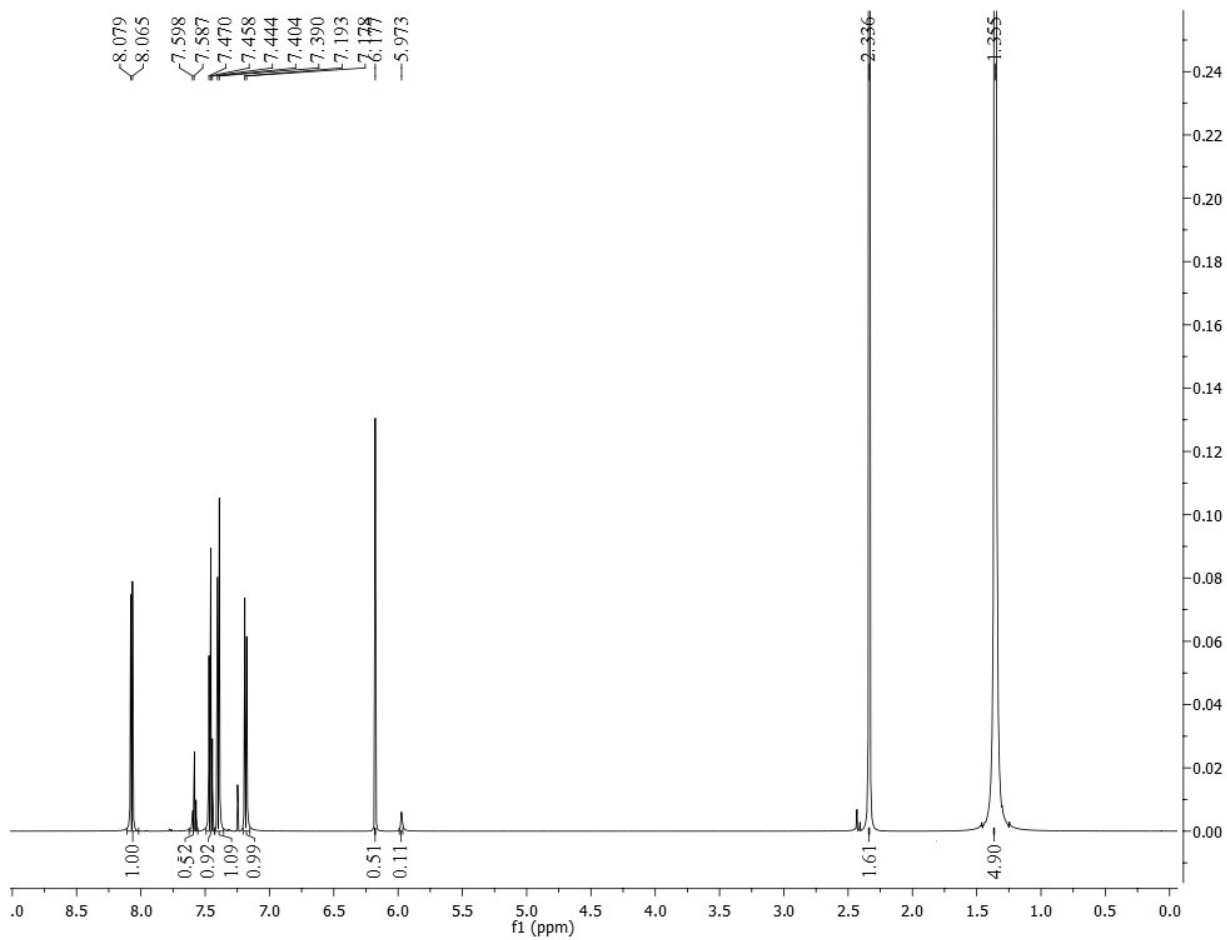
2-(*tert*-butylamino)-1-(4-chlorophenyl)-2-oxoethyl benzoate (15d): in the presence of chiral catalyst 11.

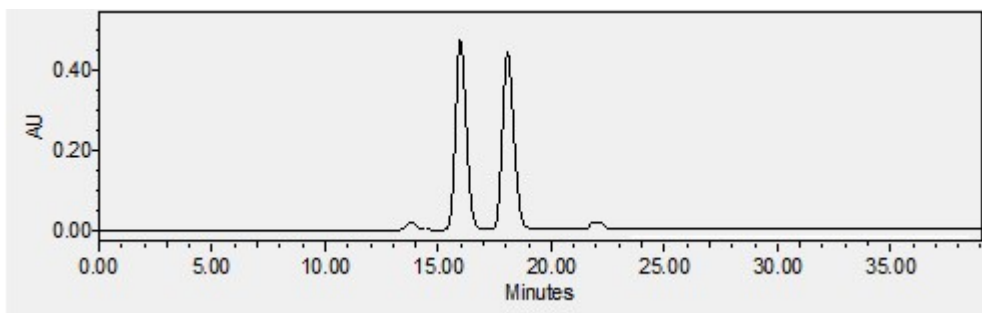
2-(tert-butylamino)-2-oxo-1-(4-tolyl)ethyl benzoate (15e):



White solid (282 mg, 87% yield); mp 157–158 °C (from EtOH; lit. 157–158°C). 97.6% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, $\lambda = 214$ nm, t_R (minor) = 16.9 min, t_R (major) = 18.0 min. $\nu_{\max}/\text{cm}^{-1}$ 3282 (NH), 1719, 1653 (CO). δ_H (600 MHz, CDCl_3). 8.06 (d, $J = 8.4$ 2H), 7.59–7.58 (m, 1H), 7.47–7.44 (m, 2H), 7.40–7.39 (m, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.18 (s, 1H), 5.97 (br s, 1H), 2.34 (s, 3H), 1.36 (s, 9H). δ_C (150 MHz, CDCl_3) 167.7, 164.8, 138.9, 133.6, 133.1, 129.8, 129.6, 128.7, 127.5, 76.1, 51.6, 28.9, 21.3. m/z : 325 (M^+ , 1%), 266 (55), 105 (100). HRMS (ESI, m/z): 326.19 ($M+H^+$).

L. A. Polindara-Garcia and E. Juaristi, *Eur. J. Org. Chem.*, 2016, 1095–1102.





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.065	11176566	49.35	325050	bb			Unknown	
2		18.118	11468735	50.65	307841	bb			Unknown	

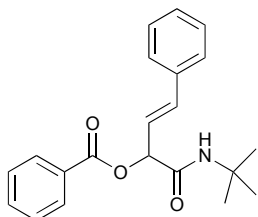
2-(*tert*-butylamino)-2-oxo-1-(4-tolyl)ethyl benzoate (15e): racemate



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.294	169151	1.19	575	bb			Unknown	
2		18.009	14033694	98.81	321843	bb			Unknown	

2-(*tert*-butylamino)-2-oxo-1-(4-tolyl)ethyl benzoate (15e): in the presence of chiral catalyst 11.

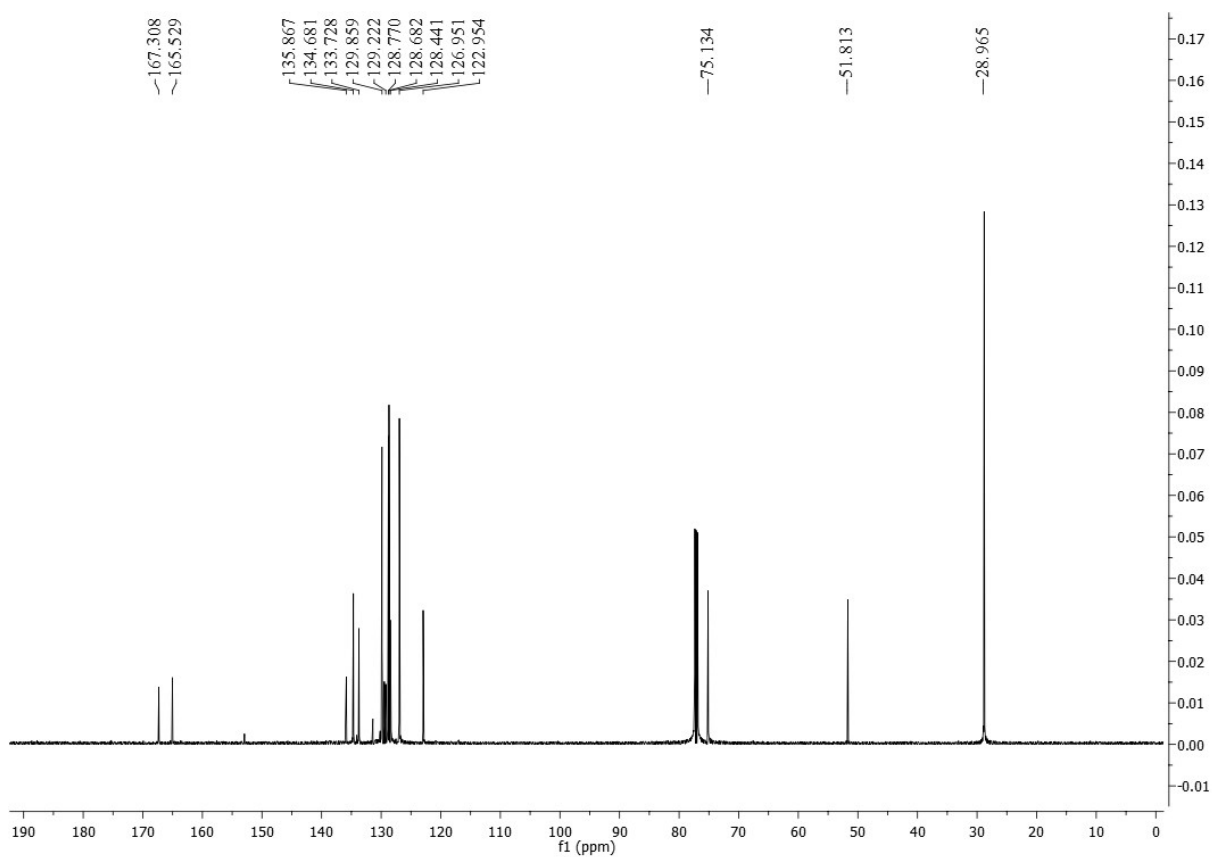
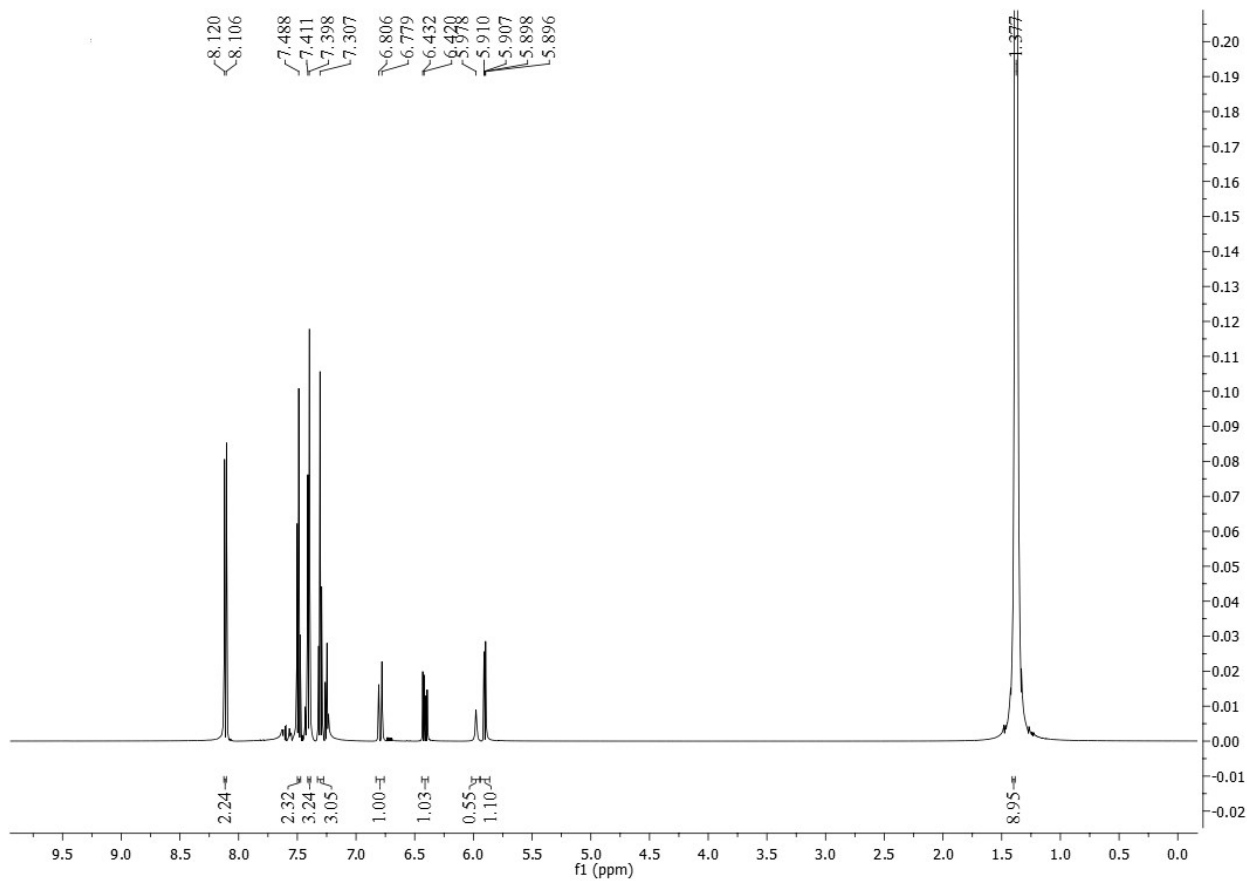
(E)-1-(tert-butylamino)-1-oxo-4-phenylbut-3-en-2-yl benzoate (15f):

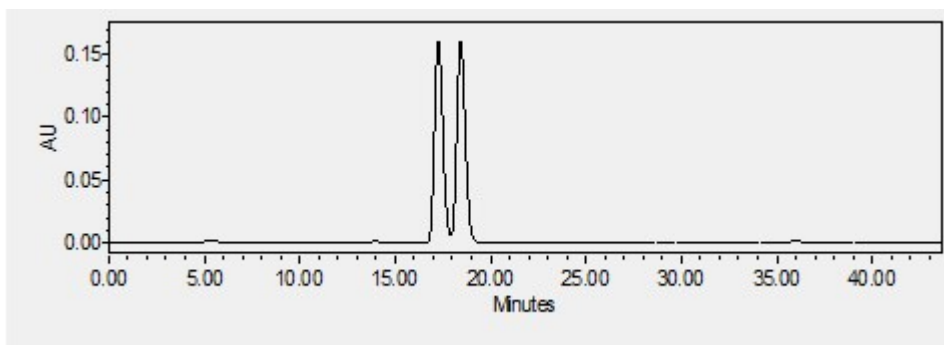


White solid (289 mg, 86% yield); mp 145–146°C (from EtOH). Found: C, 74.51; H, 6.52; N 4.31. Calc. for C₂₁H₂₃NO₃: C, 74.75; H, 6.87; N, 4.15. 92.7% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, λ = 230 nm, t_R (minor) = 17.4 min, t_R (major) = 18.6 min. $\nu_{\max}/\text{cm}^{-1}$ 3278 (NH), 1724, 1661 (CO). δ_{H} (600 MHz, CDCl₃) 8.12–8.11 (m, 2H), 7.50–7.47 (m, 2H), 7.41–7.39 (m, 3H), 7.31–7.29 (m, 3H), 6.79 (d, $J = 16.2$ Hz, 1H), 6.41 (dd, $J_1 = 16.2$ Hz, $J_2 = 7.2$ Hz, 1H), 5.98 (br s, 1H), 5.90 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.8$ Hz, 1H), 1.38 (s, 9H). δ_{C} (150 MHz, CDCl₃) 167.3, 165.5, 135.9, 134.7, 133.7, 129.9, 129.2, 128.8, 128.7, 128.4, 126.9, 122.9, 75.1, 51.2, 28.9. m/z : 337 (M⁺, 1%), 238 (20), 105 (100). HRMS (ESI, m/z): 338.18 (M+H⁺).

15f is known in the literature, however no physical and spectral data are reported.

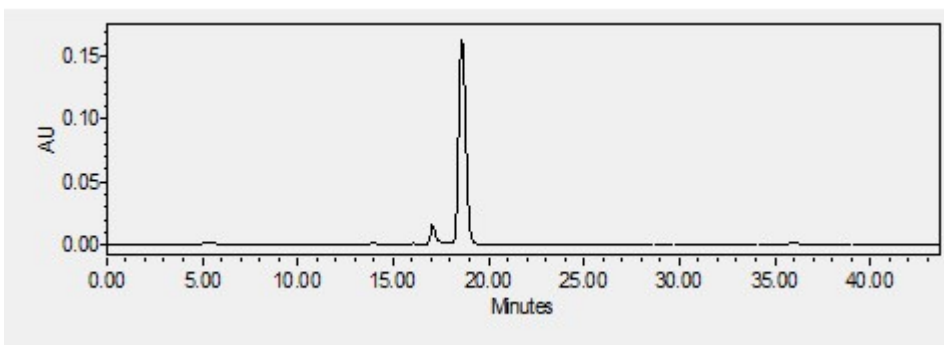
H. Yu, T. Gai, W. L. Sun and M. S. Zhang, *Chin. Chem. Lett.*, 2011, **22**, 379–381.





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.995	8128663	49.97	318451	bb			Unknown	
2		18.890	8139009	50.03	315473	bb			Unknown	

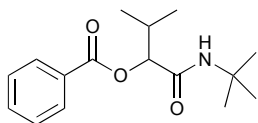
**(E)-1-(tert-butylamino)-1-oxo-3-phenylbut-3-en-2-yl benzoate (15f):
racemate**



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.359	323946	3.63	676	bb			Unknown	
2		18.599	8587991	96.37	319168	bb			Unknown	

(E)-1-(tert-butylamino)-1-oxo-4-phenylbut-3-en-2-yl benzoate (15f): in the presence of chiral catalyst 11.

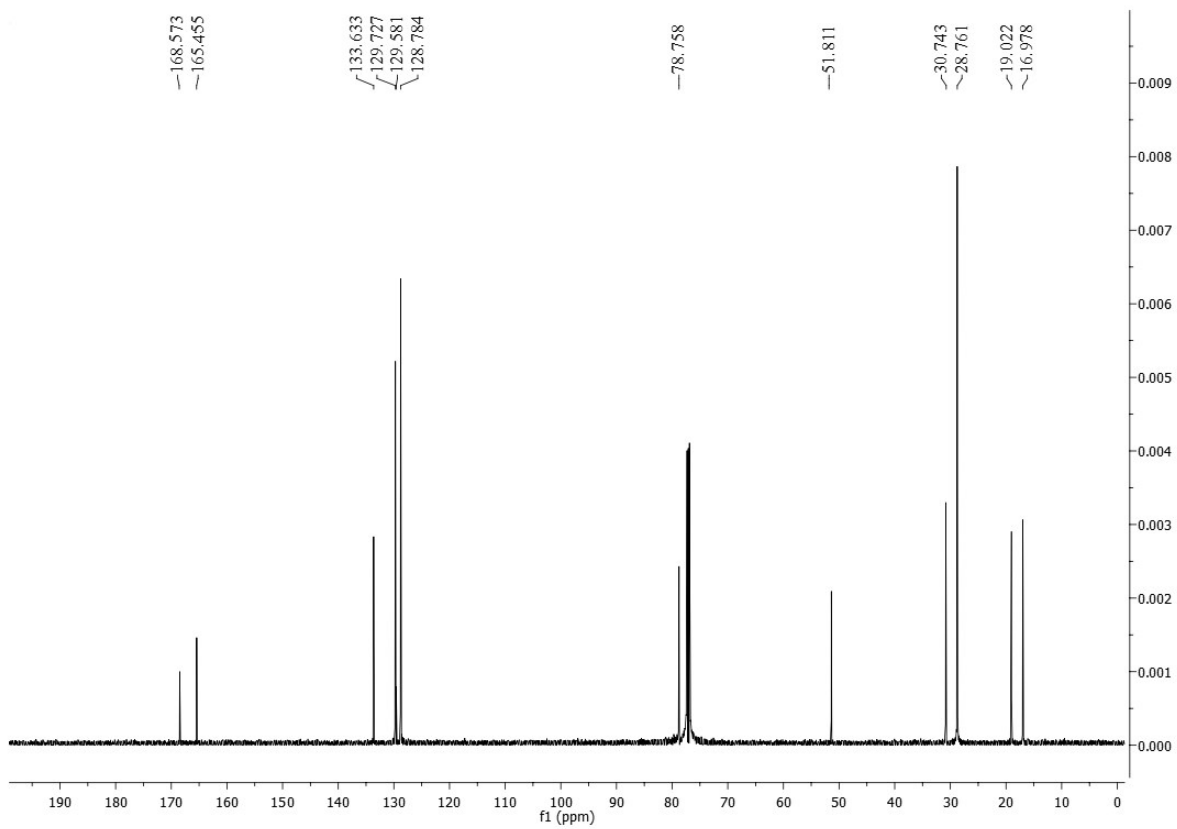
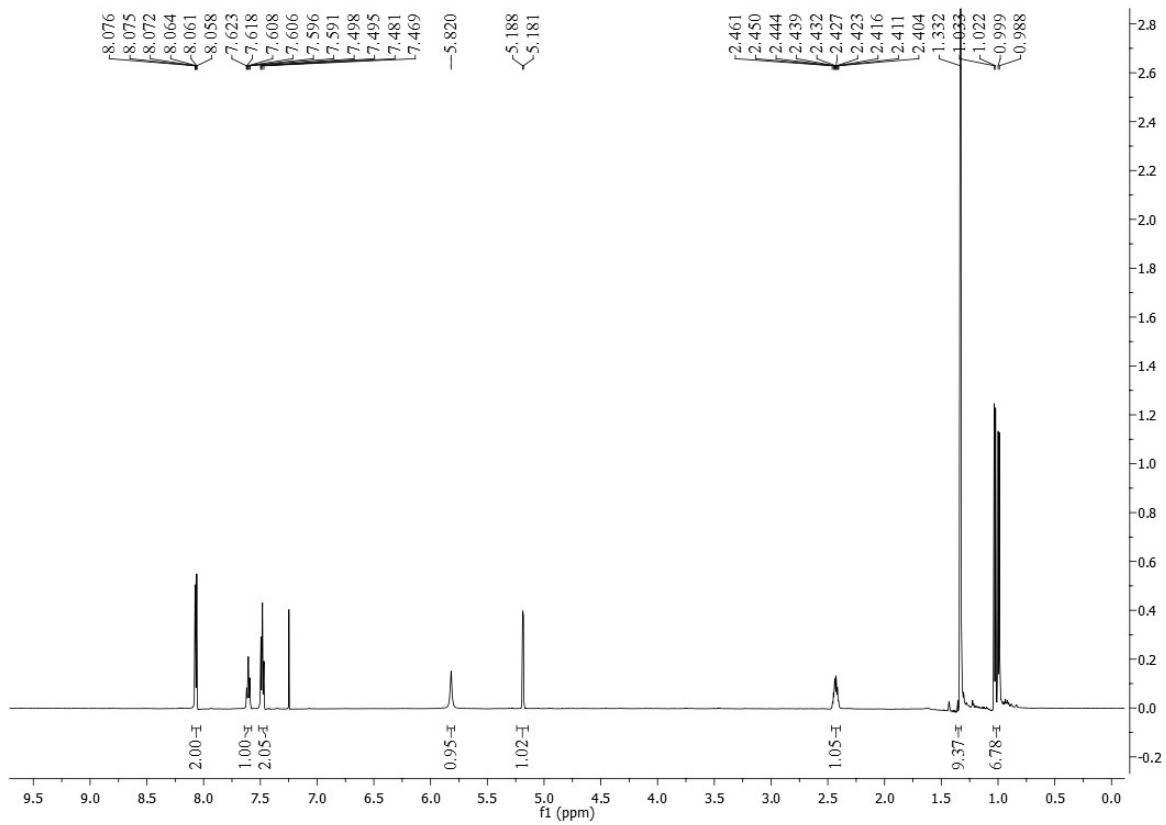
1-(*tert*-butylamino)-3-methyl-1-oxobut-2-yl benzoate (15g):

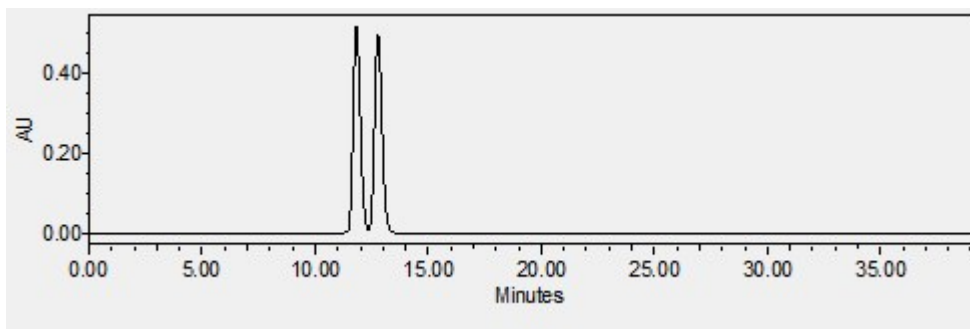


White solid (241 mg, 87% yield); mp 155–156°C (from EtOH). Found: C, 68.99; H, 8.52; N 4.88. Calc. for C₁₆H₂₃NO₃: C, 69.29; H, 8.36; N, 5.05. 95.5% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, λ = 230 nm, t_R (minor) = 11.5 min, t_R (major) = 13.1 min. $\nu_{\max}/\text{cm}^{-1}$ 3278 (NH), 1724, 1661 (CO). δ_{H} (600 MHz, CDCl₃) 8.07–8.06 (m, 2H), 8.07–8.06 (m, 2H), 7.62–7.59 (m, 1H), 7.49–7.46 (m, 2H), 5.82 (br s, 1H), 5.18 (d, $J=4.2$ Hz, 1H), 2.46–2.40 (m, 1H), 1.33 (s, 9H), 1.02 (d, $J=6.6$ Hz, 3H), 0.98 (d, $J=6.6$ Hz, 3H). δ_{C} (150 MHz, CDCl₃) 168.5, 165.4, 133.6, 129.7, 129.6, 128.7, 78.7, 51.8, 30.7, 28.7, 19.0, 16.9. m/z : 277 (M⁺, 1%), 178 (20), 123 (25), 105 (100). HRMS (ESI, m/z): 278.18 (M+H⁺).

15g is known in the literature, however no physical and spectral data are reported.

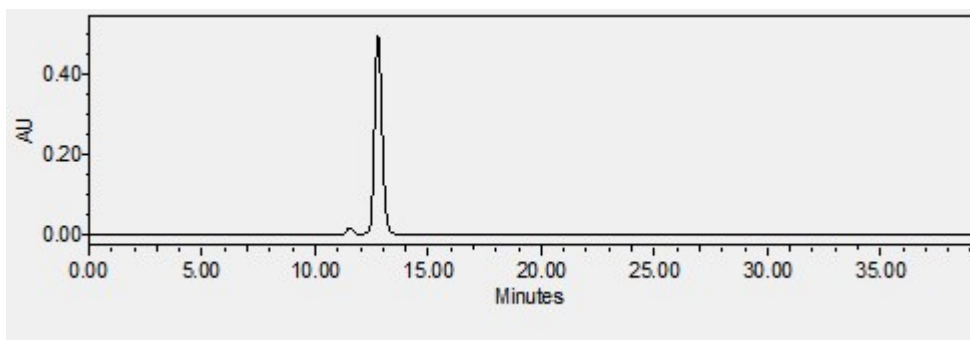
A. J. Clark, Y. S. S. Al Faiyz, D. Patel and M. J. Broadhurst, *Tetrahedron Lett.*, 2001, **42**, 2007–2009.





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.834	13848262	49.82	699175	bb			Unknown	
2		13.134	13945773	50.18	669843	bb			Unknown	

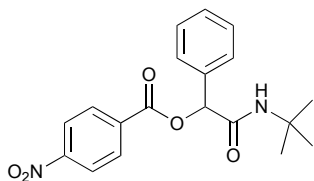
1-(*tert*-butylamino)-3-methyl-1-oxobut-2-yl benzoate (15g): racemate



Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
	11.508	651329	2.23	875	bb			Unknown	
	13.086	28500124	97.77	667746	bb			Unknown	

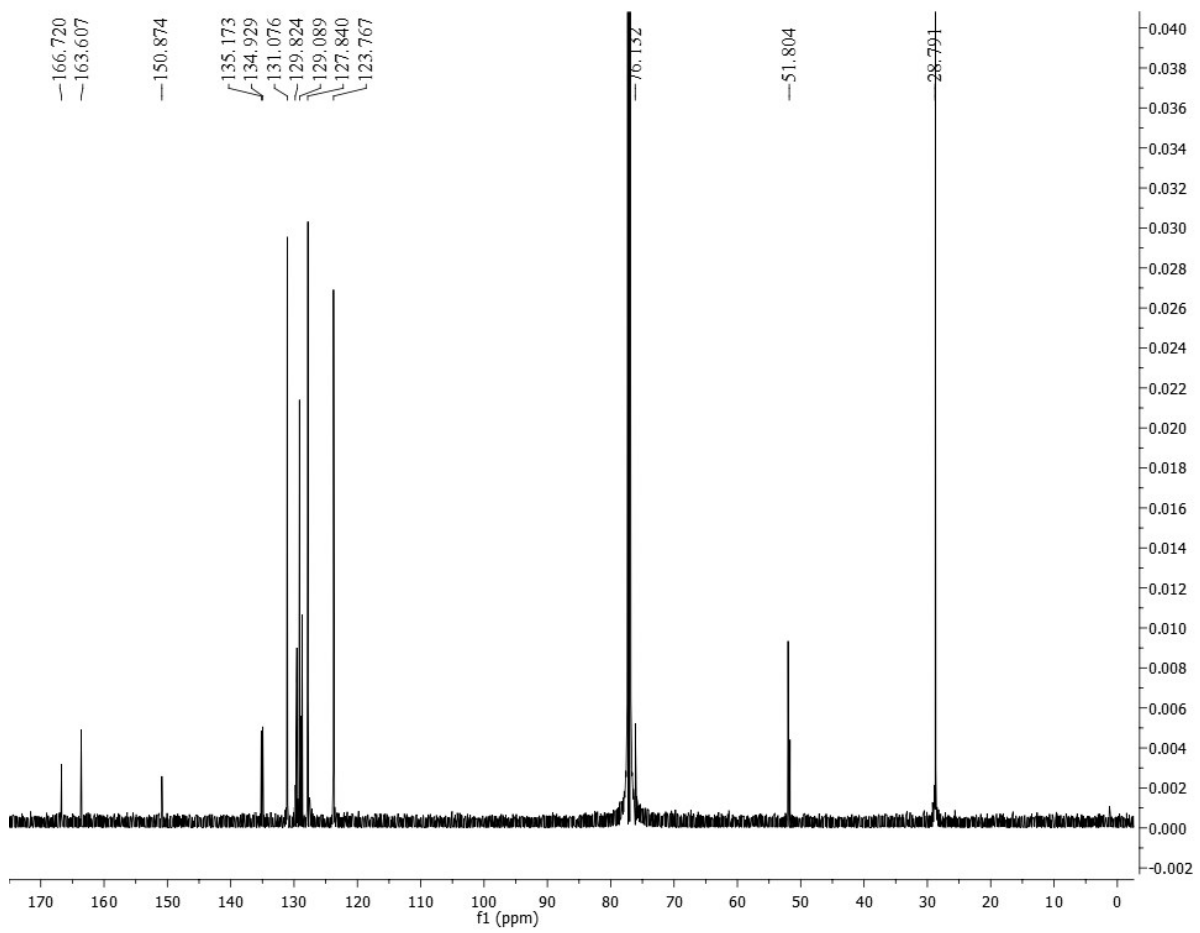
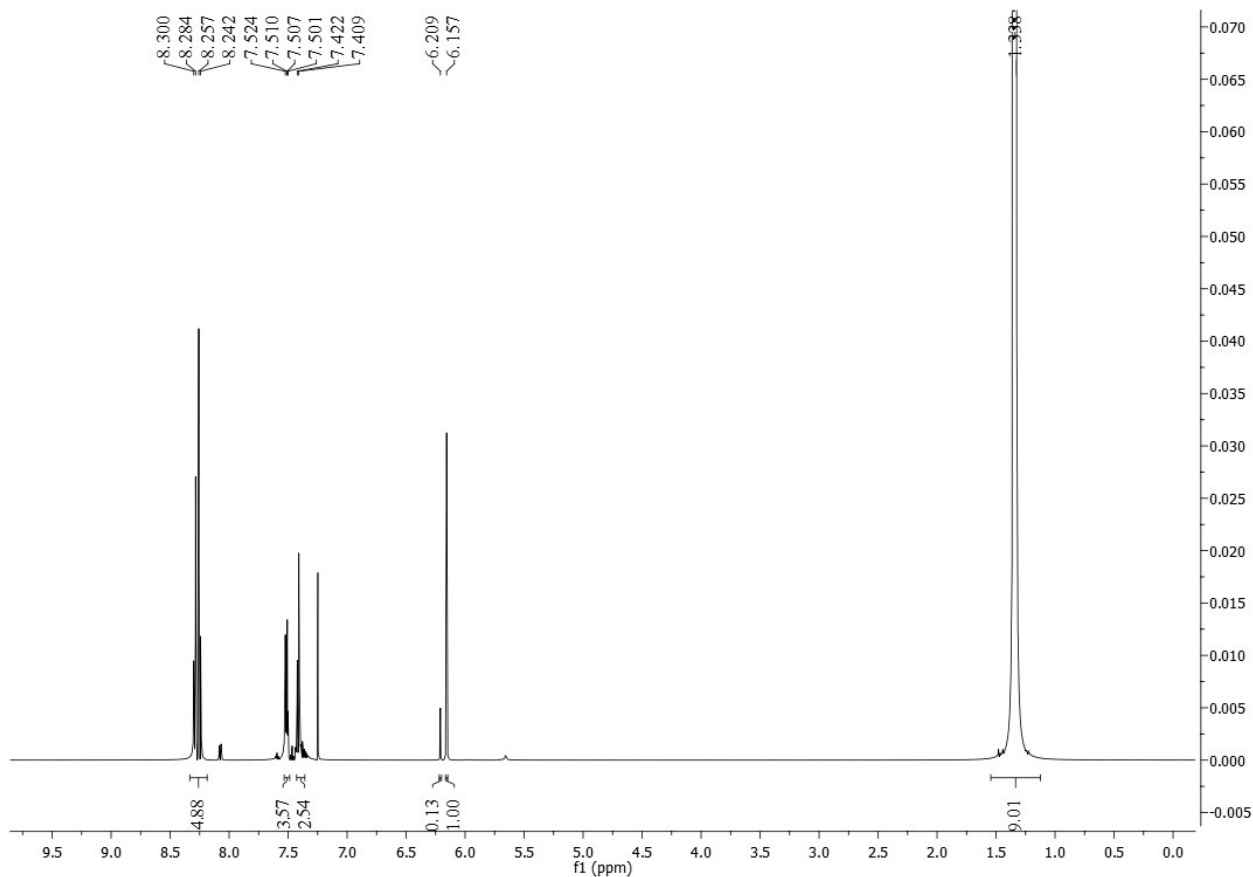
1-(*tert*-butylamino)-3-methyl-1-oxobut-2-yl benzoate (15g): in the presence of chiral catalyst 11.

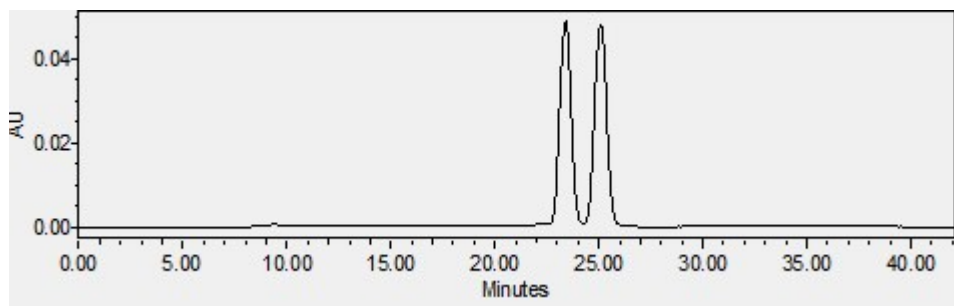
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-nitrobenzoate (15h):



White solid (300 mg, 84% yield); mp 137–138 °C (from EtOH; lit. 136–137°C). 95.5% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 10/90, 1.0 mL/min, $\lambda = 254$ nm, t_R (minor) = 23.7 min, t_R (major) = 25.8 min. $\nu_{\max}/\text{cm}^{-1}$ 3290 (NH), 1727, 1650 (CO). δ_H (600 MHz, CDCl_3) 8.30–8.24 (m, 4H), 7.52–7.50 (m, 3H), 7.42–7.41 (m, 2H), 6.21 (br s, 1H) 6.16 (s, 1H), 1.34 (s, 9H). δ_C (150 MHz, CDCl_3) 166.7, 163.6, 150.8, 135.1, 134.9, 131.1, 129.8, 129.1, 127.8, 123.7, 76.1, 51.8, 28.8. m/z : 356 (M^+ , 1%), 257 (65), 150 (100). HRMS (ESI, m/z): 357.15 ($M+H^+$).

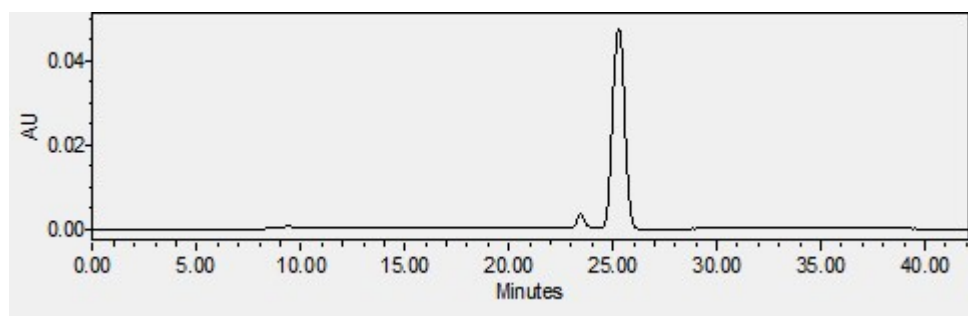
L. A. Polindara-Garcia and E. Juaristi, *Eur. J. Org. Chem.*, 2016, 1095–1102.





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
	19.846	3996129	49.88	1047602	bb			Unknown	
	21.541	4015433	50.12	1035292	bb			Unknown	

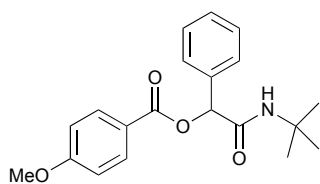
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-nitrobenzoate (15h): racemate



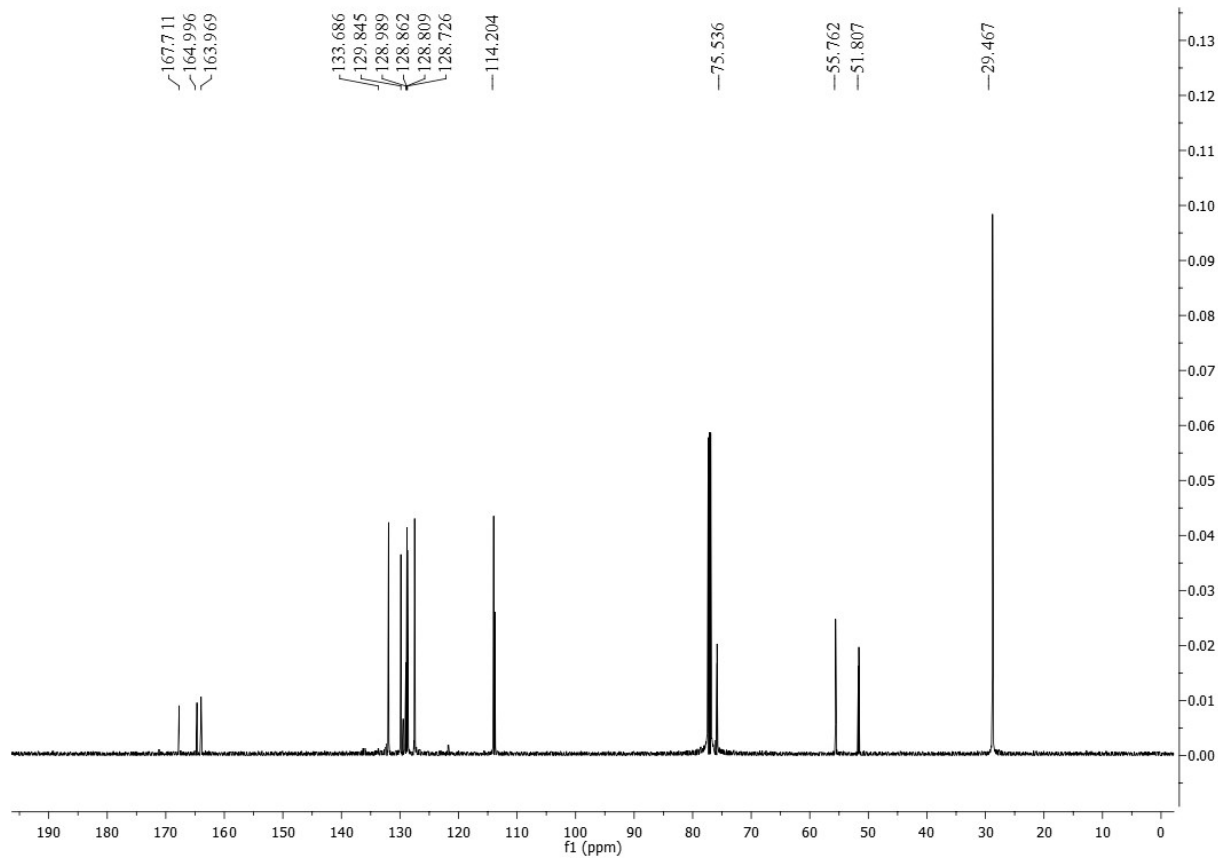
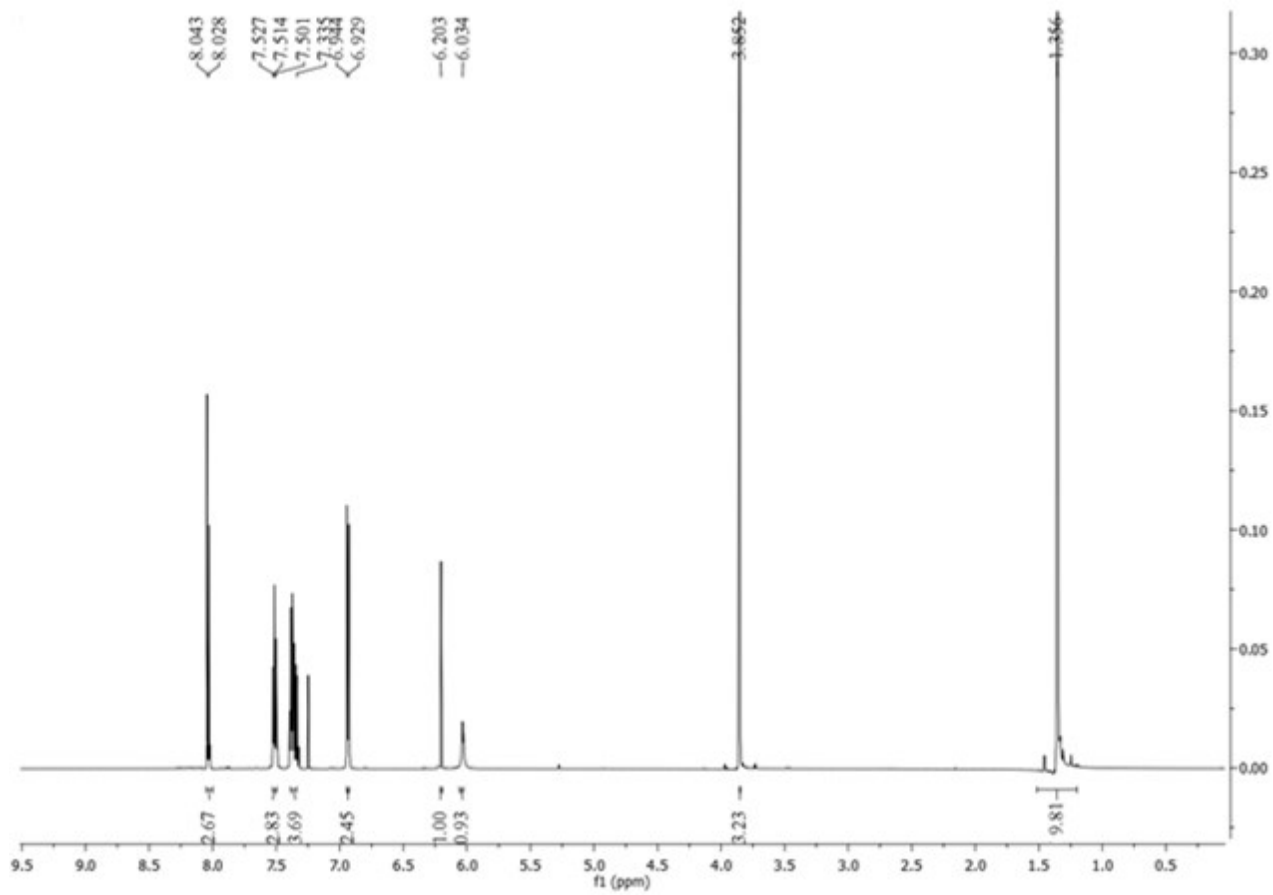
Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	23.646	120490	2.25	1060	bb			Unknown	
2	25.881	5238635	97.75	1056782	bb			Unknown	

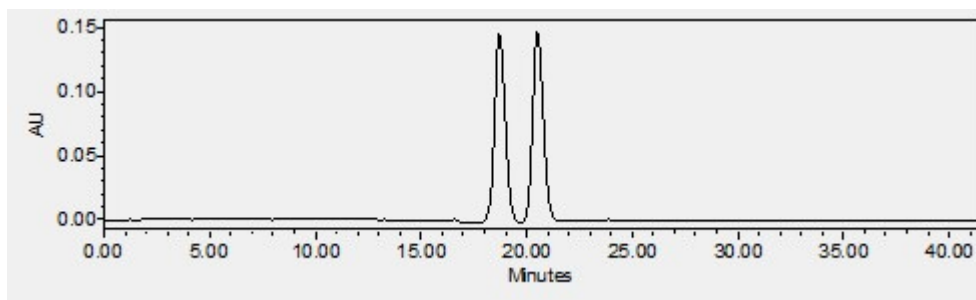
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-nitrobenzoate (15h): in the presence of chiral catalyst 11.

2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-methoxybenzoate (15i):



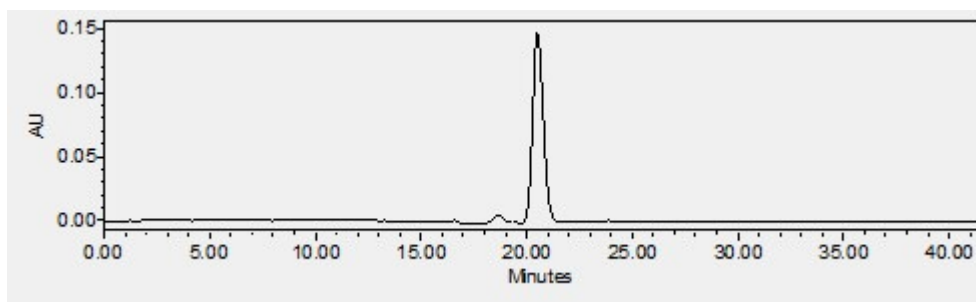
White solid (298 mg, 87% yield); mp 147–148 °C (from EtOH). Found: C, 70.65; H, 6.71; N 4.29. Calc. for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. 95.9% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (minor) = 18.8 min, t_R (major) = 20.8 min. $\nu_{\max}/\text{cm}^{-1}$ 3281 (NH), 1729, 1654 (CO). δ_H (600 MHz, $CDCl_3$) 8.03 (d, J = 9.0 Hz, 2H), 7.52–7.50 (m, 2H), 7.39–7.32 (m, 3H), 6.93 (d, J = 9.0 Hz, 2H), 6.20 (s, 1H), 6.03 (br s, 1H), 3.85 (s, 3H), 1.36 (s, 9H). δ_C (150 MHz, $CDCl_3$) 167.8, 164.9, 163.9, 133.7, 129.8, 128.9, 128.86, 128.80, 128.7, 114.3, 75.5, 55.7, 51.8, 29.5. m/z : 341 (M^+ , 1%), 242 (15), 135 (100). HRMS (ESI, m/z): 342.17 ($M+H^+$).





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.521	22884556	49.92	316771	bb			Unknown	
2		20.994	22958899	50.08	317841	bb			Unknown	

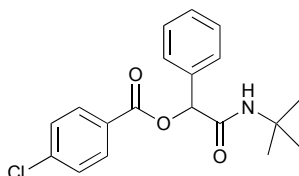
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-methoxybenzoate (15i): racemate



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.774	270012	2.07	550	bb			Unknown	
2		20.845	12768735	97.93	318913	bb			Unknown	

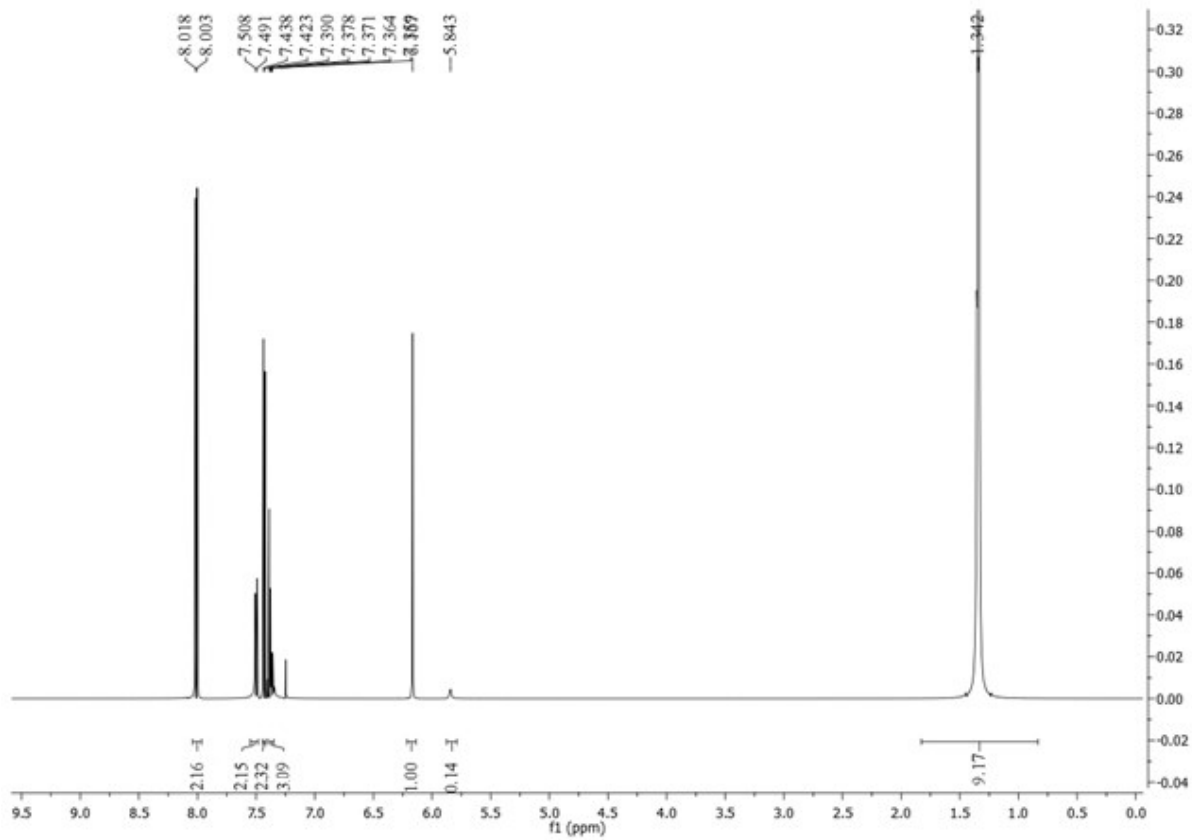
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-methoxybenzoate (15i): in the presence of chiral catalyst 11.

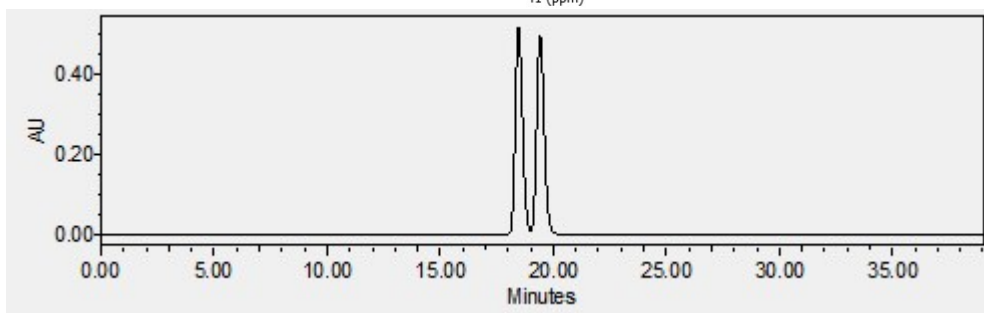
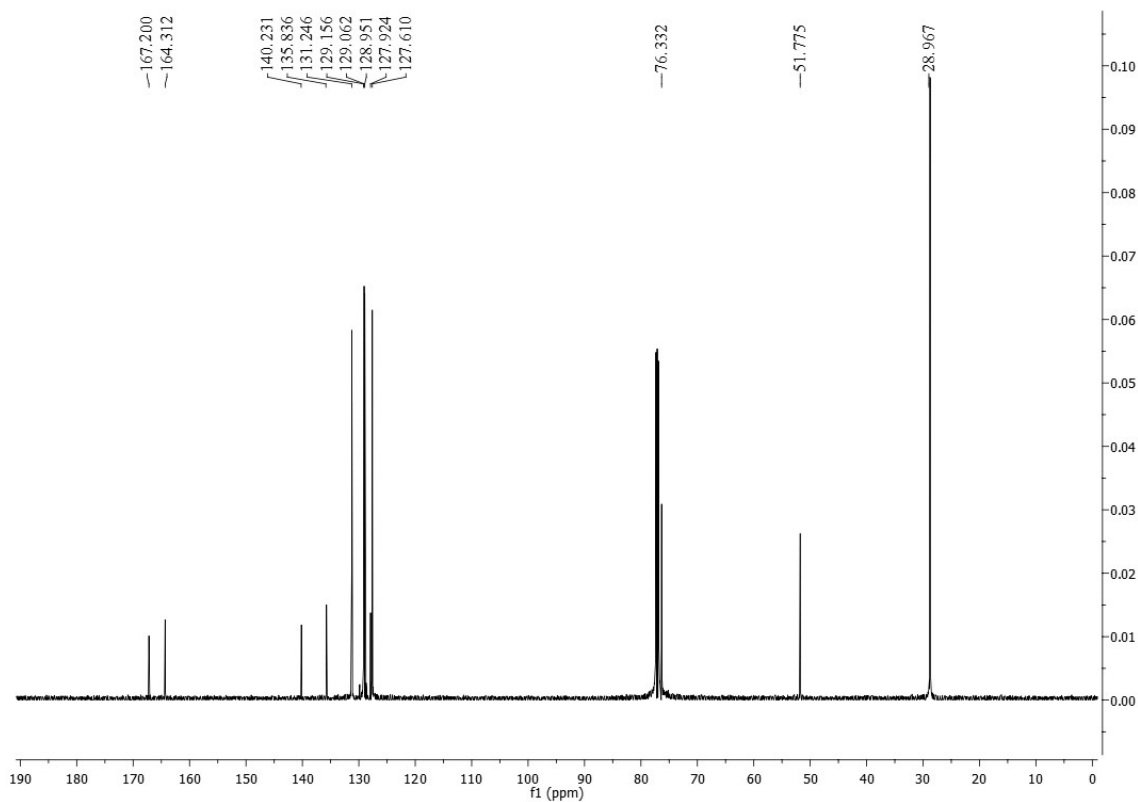
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-chlorobenzoate (15j):



White solid (312 mg, 90% yield); mp 139–140°C (from EtOH; lit. 142–143 °C). 96.8% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 10/90, 1.0 mL/min, $\lambda = 230$ nm, t_R (minor) = 18.9 min, t_R (major) = 19.9 min. $\nu_{\max}/\text{cm}^{-1}$ 3281 (NH), 1729, 1654 (CO). δ_H (600 MHz, CDCl_3) 8.01 (d, $J = 9.0$ Hz, 2H), 7.51–7.49 (m, 2H), 7.42 (d, $J = 9.0$ Hz, 2H), 7.39–7.35 (m, 3H), 6.17 (s, 1H), 5.84 (br s, 1H), 1.34 (s, 9H). δ_C (150 MHz, CDCl_3) 167.2, 164.3, 140.2, 135.8, 131.2, 129.1, 129.0, 128.9, 127.9, 127.6, 76.3, 51.7, 28.9. m/z : 345 (M^+ , 1%), 246 (35), 139 (100). HRMS (ESI, m/z): 346.13 ($M+H^+$).

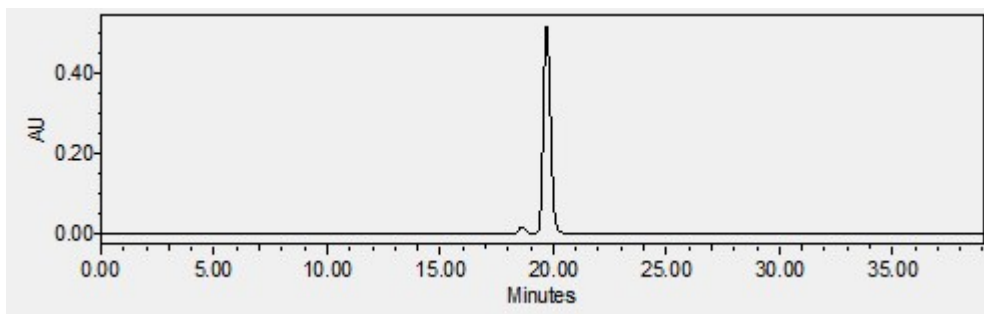
L. A. Polindara-Garcia and E. Juaristi, *Eur. J. Org. Chem.*, 2016, 1095–1102.





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	18.364	14969151	49.89	699175	bb			Unknown	
2	19.556	15034694	50.11	669843	bb			Unknown	

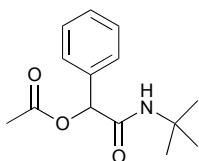
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-chlorobenzoate (15j): racemate.



Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	18.869	329151	1.62	305	bb			Unknown	
2	19.995	20039595	98.38	626555	bb			Unknown	

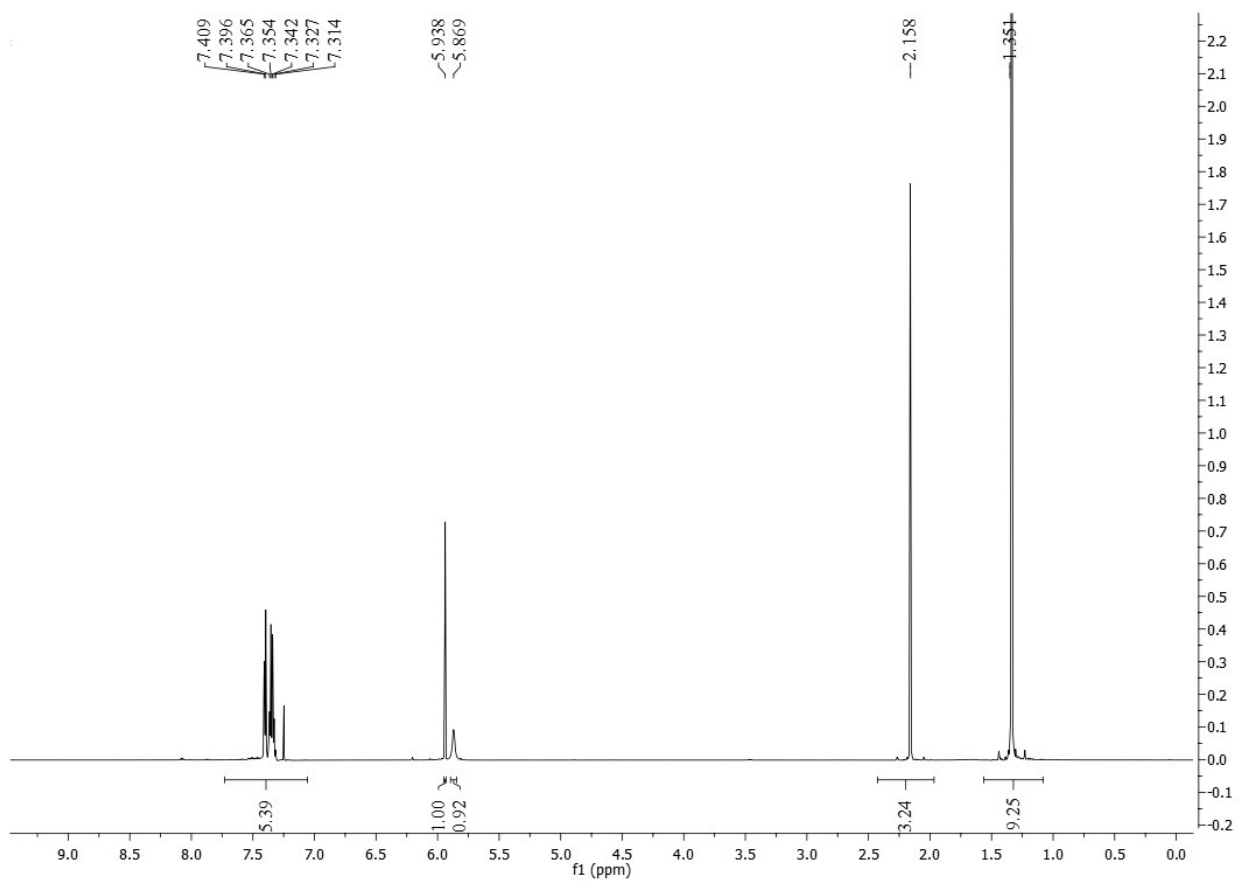
2-(*tert*-butylamino)-2-oxo-1-phenylethyl 4-chlorobenzoate (15j): in the presence of chiral catalyst 11.

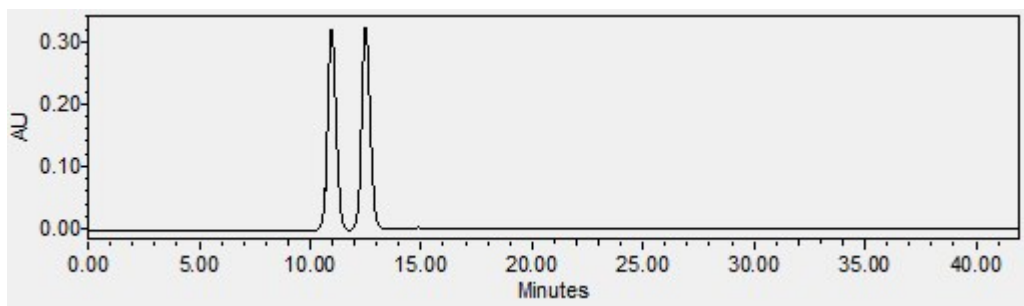
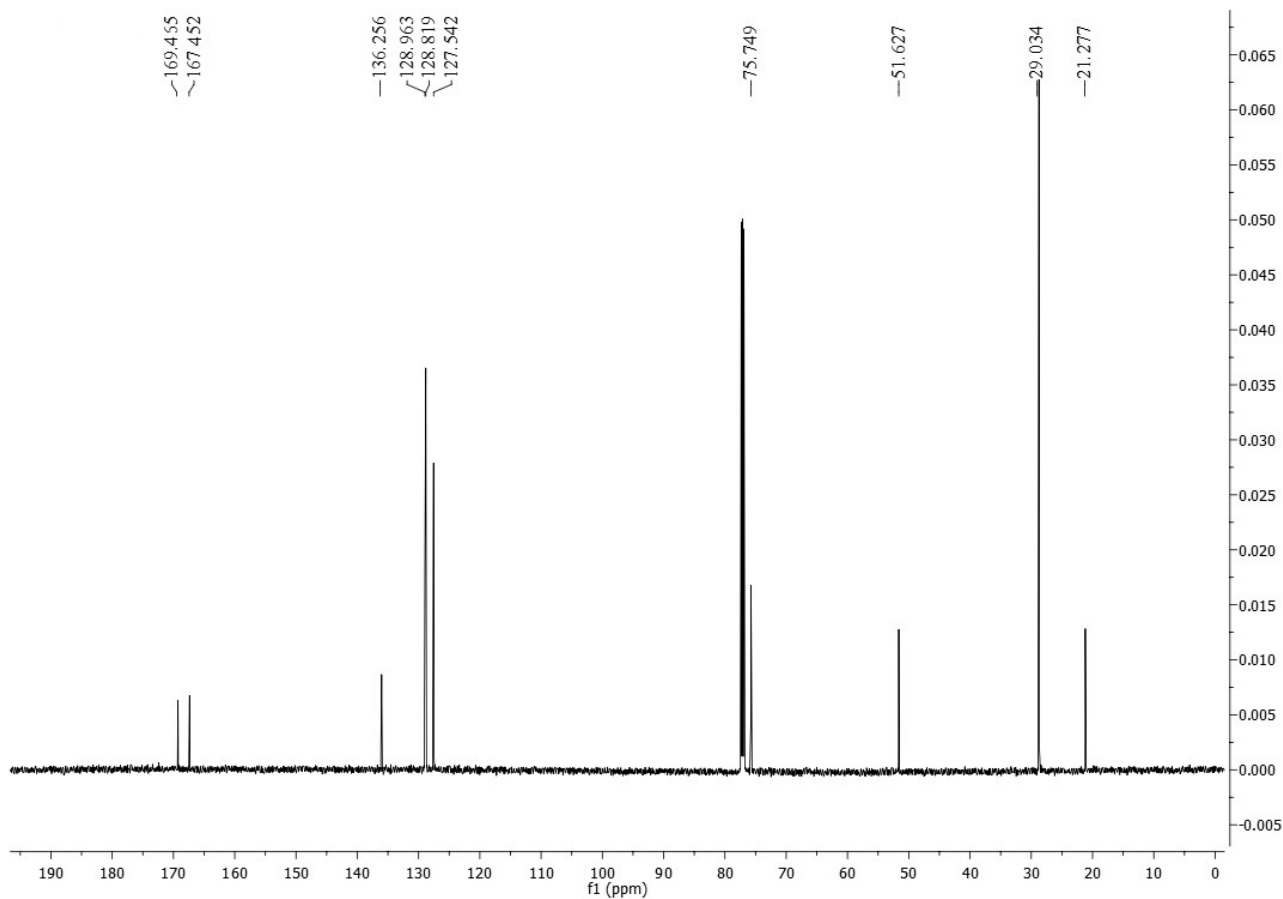
2-(*tert*-butylamino)-2-oxo-1-phenylethyl acetate (15k):



White solid (215 mg, 86% yield); mp 79–80°C (from EtOH; lit. 77 °C). 96.5% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 10/90, 1.0 mL/min, $\lambda = 214$ nm, t_R (minor) = 11.1 min, t_R (major) = 12.9 min. $\nu_{\max}/\text{cm}^{-1}$ 3283 (NH), 1721, 1650 (CO). δ_H (600 MHz, CDCl_3) 7.49–7.31 (m, 5H), 5.94 (s, 1H), 5.87 (br s, 1H), 2.16 (s, 3H), 1.35 (s, 9H). δ_C (150 MHz, CDCl_3) 169.4, 167.4, 136.2, 128.9, 128.8, 127.5, 75.7, 51.6, 29.0, 21.3. m/z : 249 (M^+ , 1%), 150 (70), 107 (100), 57 (35), 43 (35). HRMS (ESI, m/z): 250.14 ($M+H^+$).

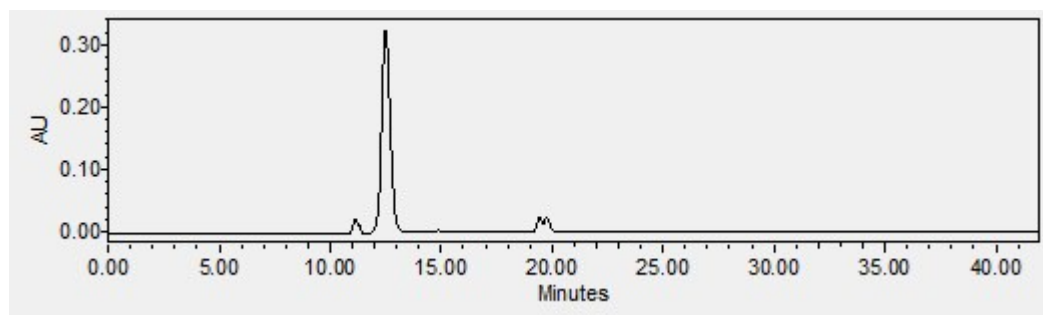
T. Nguansavanah and J. Zhu, *Angew. Chem. Int. Ed.*, 2006, **45**, 3495–3497.





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	11.095	5371234	50.04	799158	bb			Unknown	
2	12.976	5362908	49.96	800156	bb			Unknown	

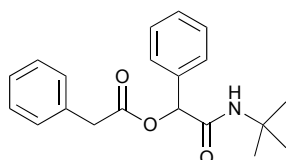
2-(*tert*-butylamino)-2-oxo-1-phenylethyl acetate (15k): racemate



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.105	11125	1.75	497	bb			Unknown	
2		12.987	623212	98.25	789157	bb			Unknown	

2-(*tert*-butylamino)-2-oxo-1-phenylethyl acetate (15k): in the presence of chiral catalyst 11.

2-(*tert*-butylamino)-2-oxo-1-phenylethyl 2-phenylacetate (15l):

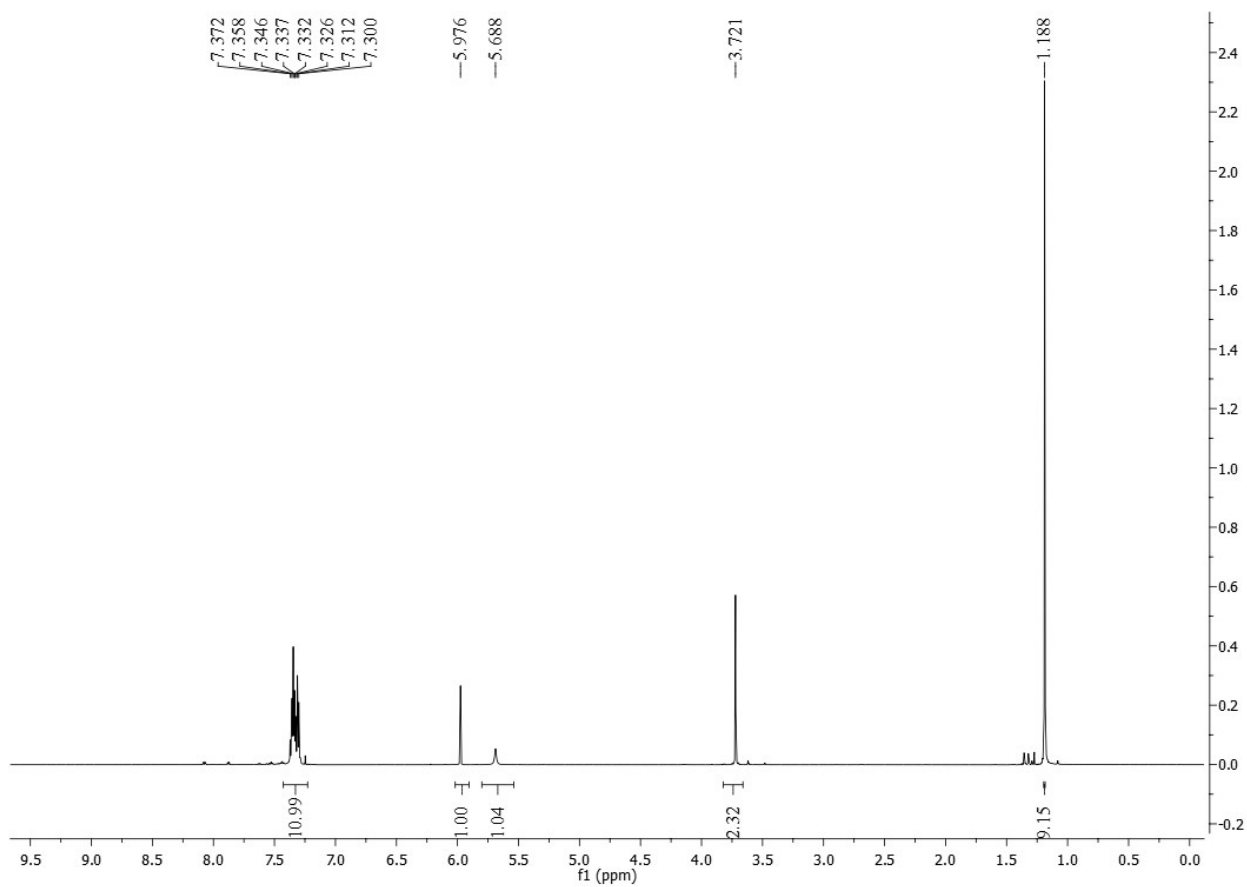


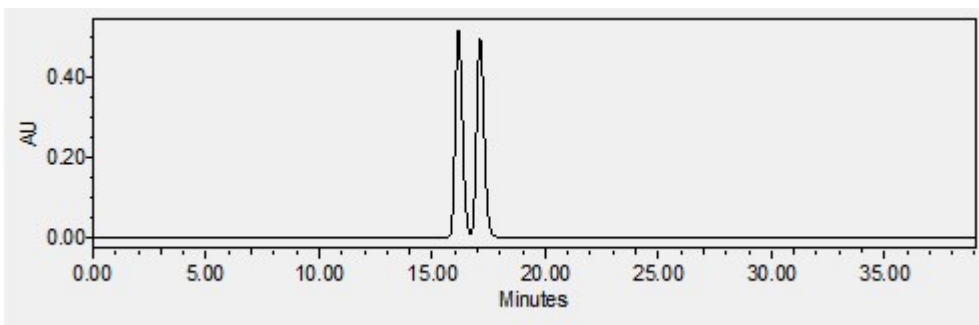
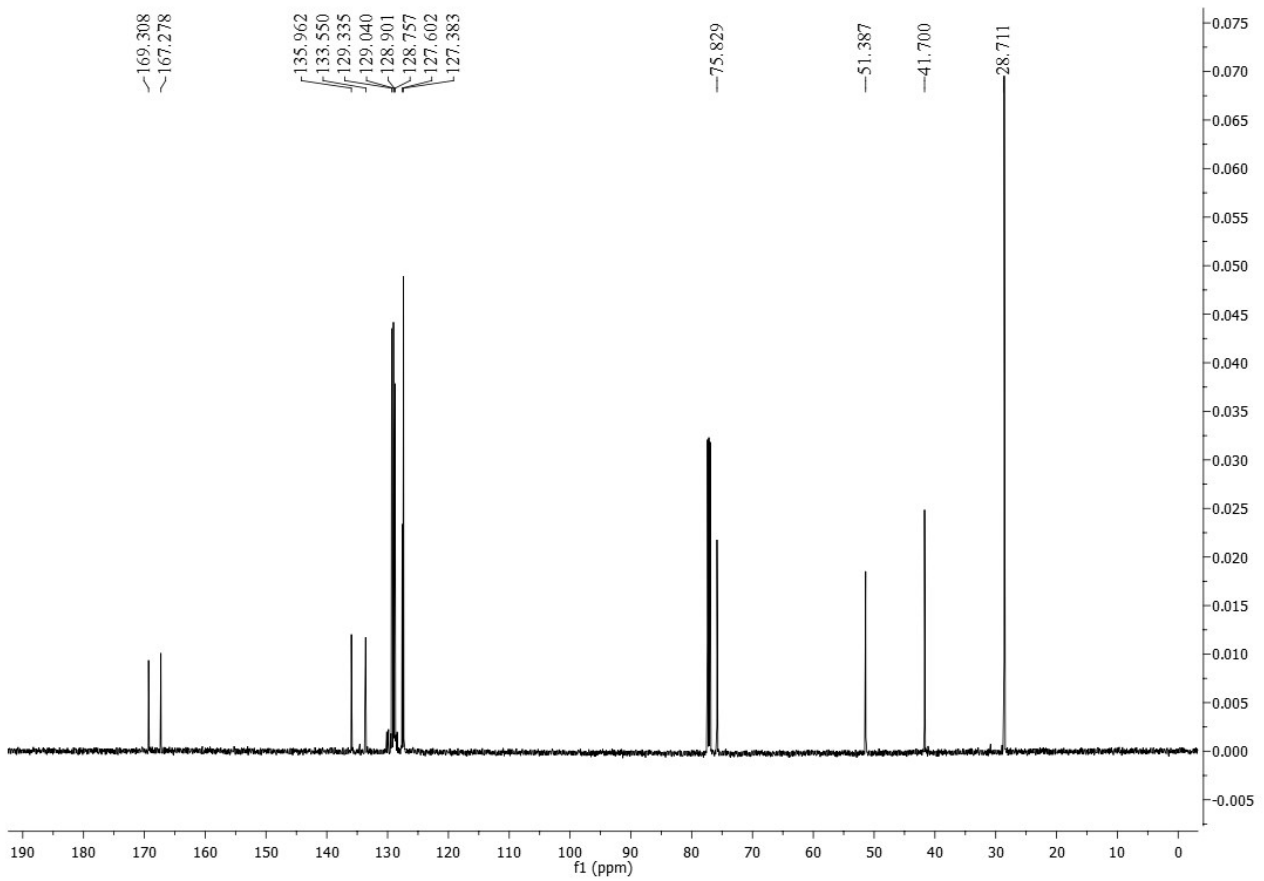
White solid (285 mg, 87% yield); mp 100–101°C (from EtOH). Found: C, 73.61; H, 7.40; N 4.35. Calc. for C₂₀H₂₃NO₃: C, 73.82; H, 7.12; N, 4.30. 93.1% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 10/90, 1.0 mL/min, λ = 214 nm, t_R (minor) = 16.4 min, t_R (major) = 17.6 min. ν_{max}/cm⁻¹ 3277 (NH), 1719, 1650 (CO). δ_H (600 MHz, CDCl₃) 7.37–7.30 (m, 10H), 5.97 (s, 1H), 5.68 (br s, 1H), 3.72 (s, 2H), 1.19 (s, 9H). δ_C (150 MHz, CDCl₃) 169.3,

167.3, 135.9, 133.5, 129.3, 129.0, 128.9, 128.7, 127.6, 127.4, 75.8, 51.4, 41.7, 28.7. m/z : 325 (M^+ , 1%), 226 (40), 91 (100). HRMS (ESI, m/z): 326.18 ($M+H^+$).

15I is known in the literature, however no physical and spectral data are reported.

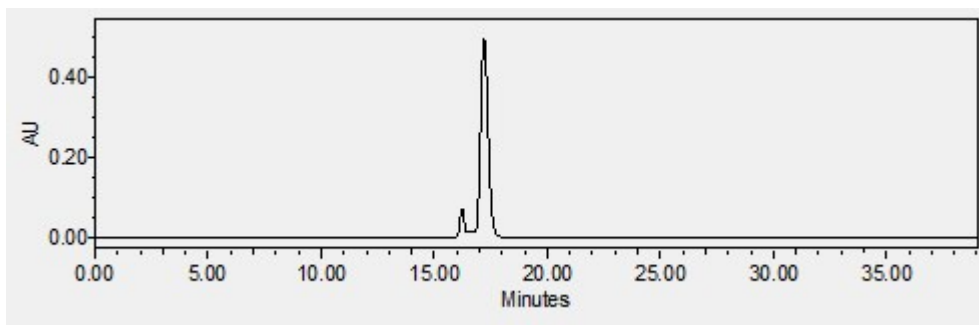
T. Bousquet, M. Jida, M. Soueidan, R. Deprez-Poulain, F. Agbossou-Niedercorn and L. Pelinski, *Tetrahedron Lett.*, 2012, **53**, 306–308.





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	16.124	15768161	50.05	599145	bb			Unknown	
2	17.116	15734127	49.95	598875	bb			Unknown	

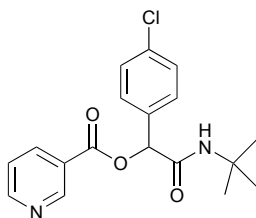
2-(*tert*-butylamino)-2-oxo-1-phenylethyl phenylacetate (15l): racemate



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.378	901121	3.47	775	bb			Unknown	
2		17.556	25037695	96.53	589843	bb			Unknown	

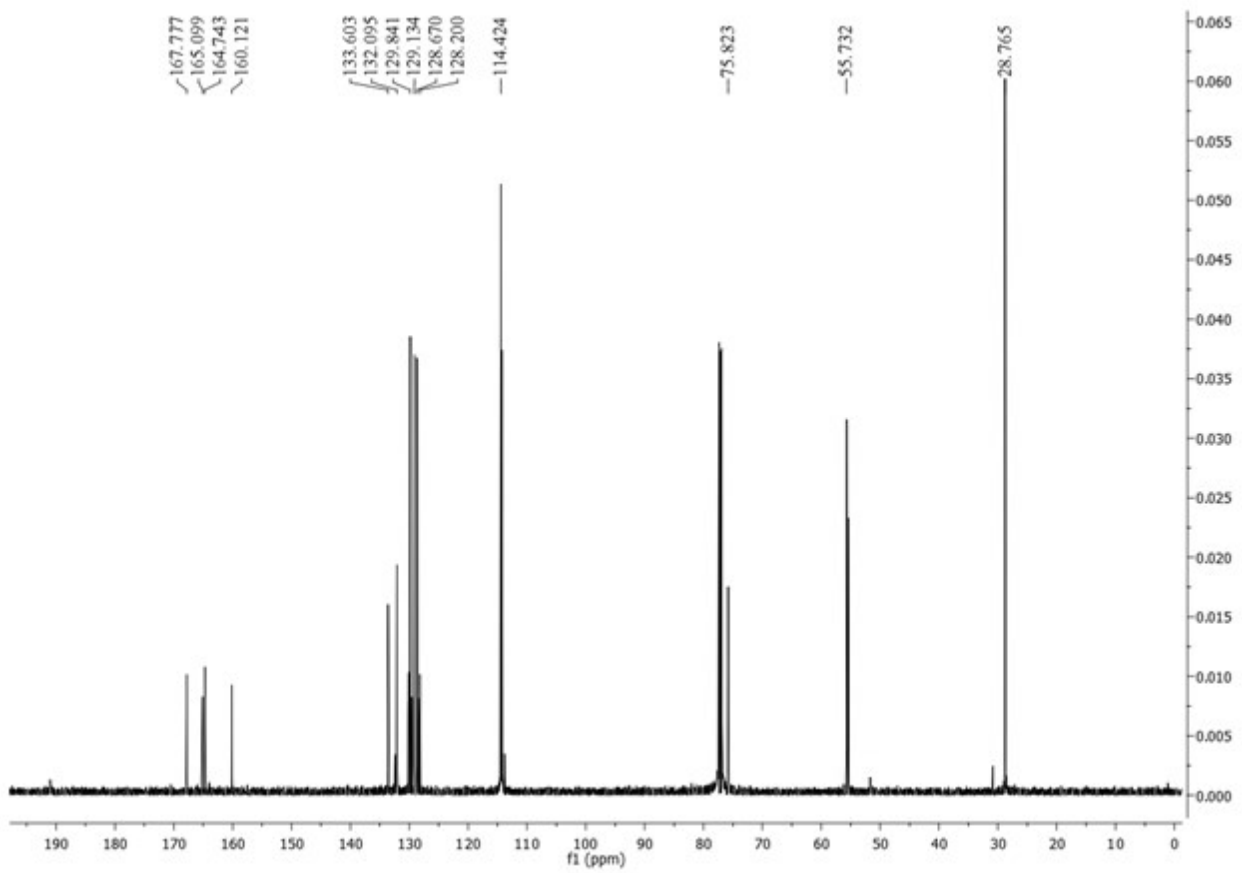
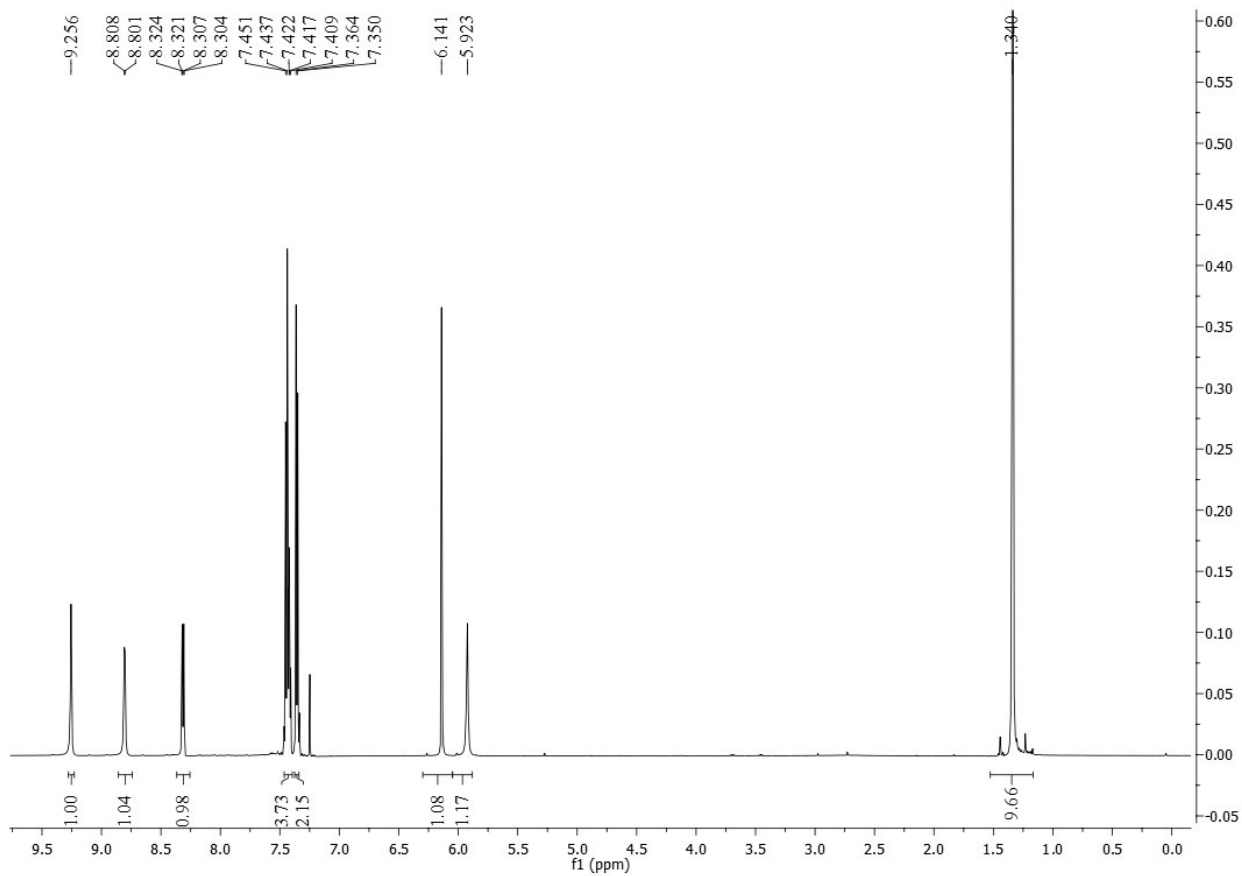
2-(*tert*-butylamino)-2-oxo-1-phenylethyl phenylacetate (15l): in the presence of chiral catalyst **11**.

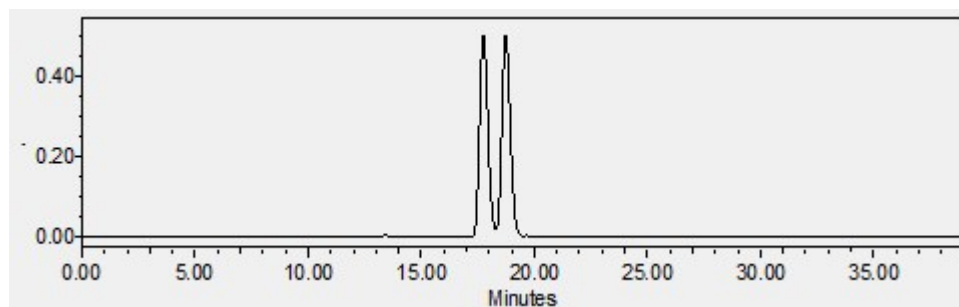
2-(*tert*-butylamino)-1-(4-chlorophenyl)-2-oxoethyl pyridin-3-carboxylate (15m):



White solid (270 mg, 78% yield); mp 169–170°C (from EtOH). Found: C, 62.59; H, 5.48; N 8.15. Calc. for $C_{18}H_{19}ClN_2O_3$: C, 62.34; H, 5.52; N, 8.08. 96.5% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 10/90, 1.0 mL/min, λ = 230 nm, t_R (minor) = 17.9 min, t_R (major) = 19.1 min. ν_{max}/cm^{-1} 3278 (NH), 1719, 1650 (CO). δ_H (600 MHz, $CDCl_3$) 9.26 (s, 1H), 8.80 (d, J = 4.2 Hz, 1H), 8.32–8.30 (m, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.42–7.41 (m, 1H), 7.35 (d, J = 8.4 Hz, 2H), 6.14 (s, 1H), 5.92 (br s, 1H), 1.34 (s, 9H). δ_C (150 MHz, $CDCl_3$) 167.7, 165.1, 164.7,

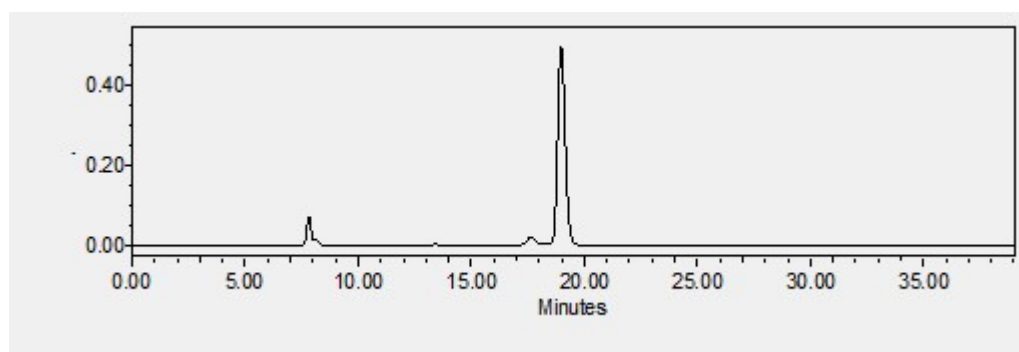
160.1, 133.6, 132.1, 129.8, 129.1, 128.7, 128.2, 114.4, 75.8, 55.7, 28.7. m/z : 346 (M^+ , 1%), 247 (50), 106 (100). HRMS (ESI, m/z): 347.11 ($M+H^+$).





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.995	9328774	49.99	419451	bb			Unknown	
2		19.003	9330125	50.01	419577	bb			Unknown	

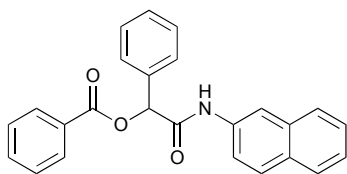
2-(*tert*-butylamino)-1-(4-chlorophenyl)-2-oxoethyl pyridin-3-carboxylate (15m): racemate



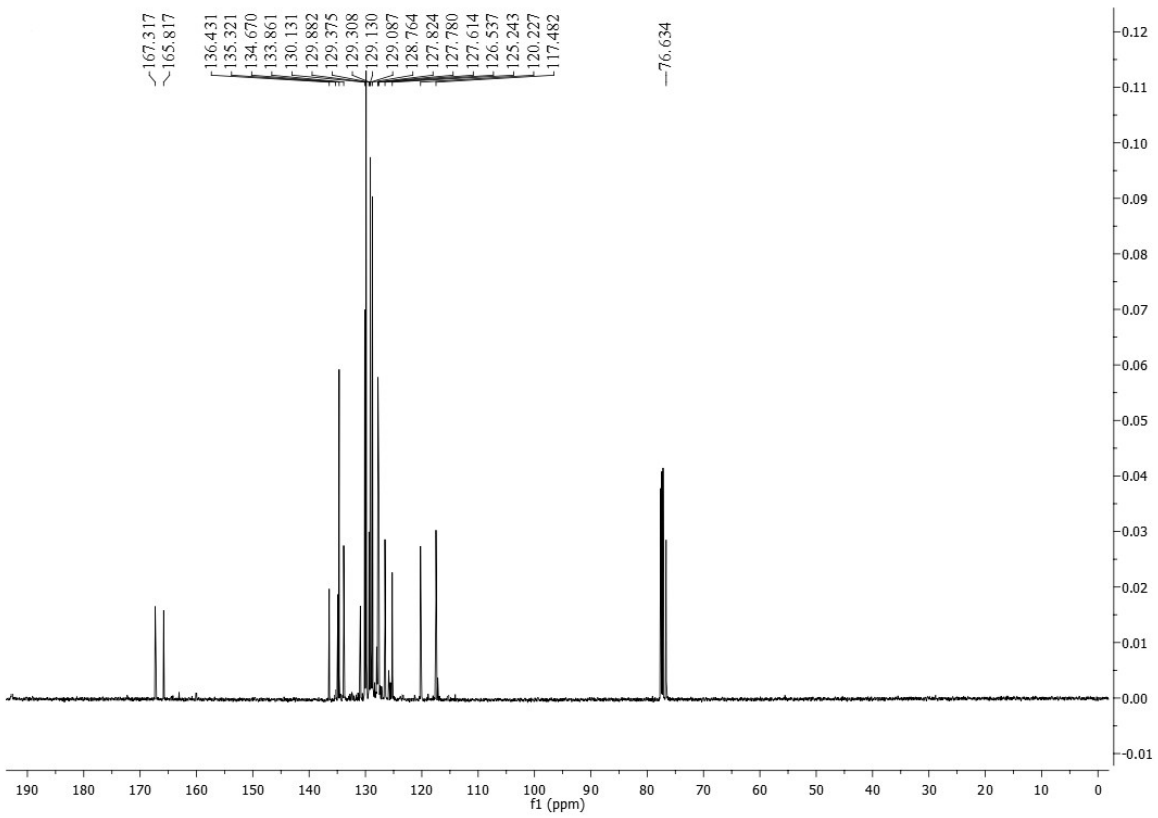
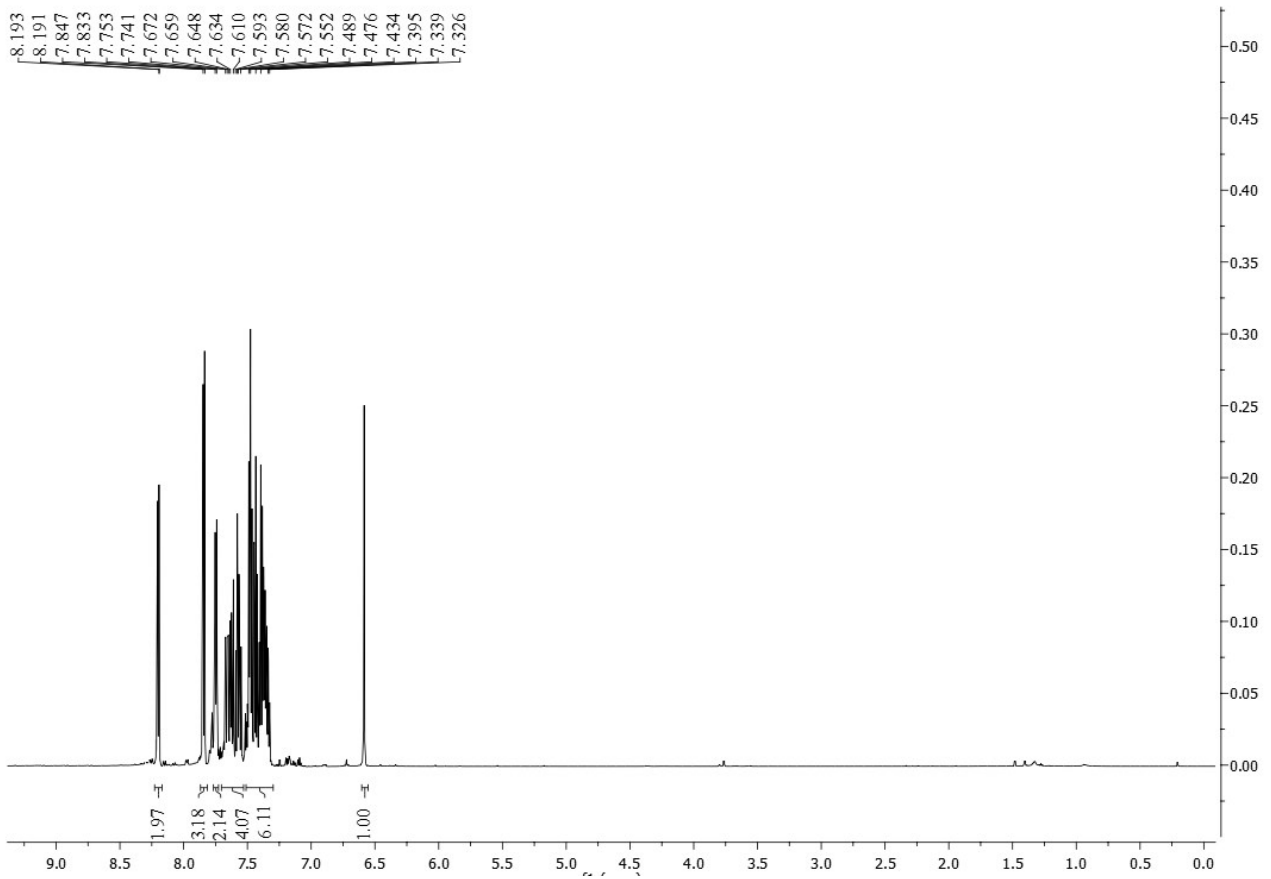
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.986	461121	1.74	305	bb			Unknown	
2		19.118	26037695	98.26	423567	bb			Unknown	

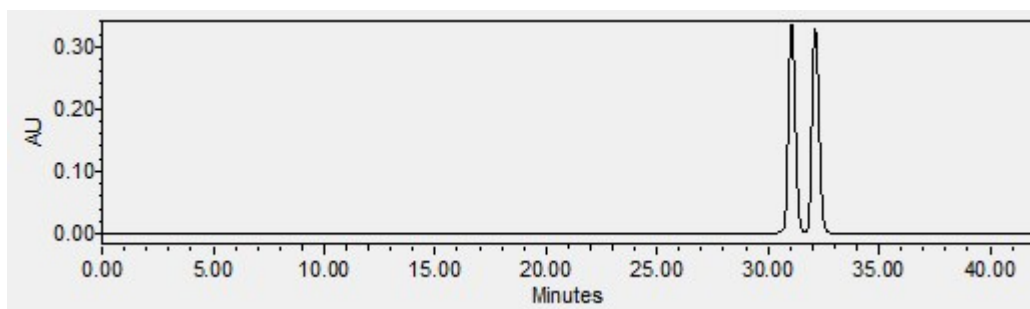
2-(*tert*-butylamino)-1-(4-chlorophenyl)-2-oxoethyl pyridin-3-carboxylate (15m): in the presence of chiral catalyst 11.

2-(2-naphthylamino)-2-oxo-1-phenylethyl benzoate (15n):



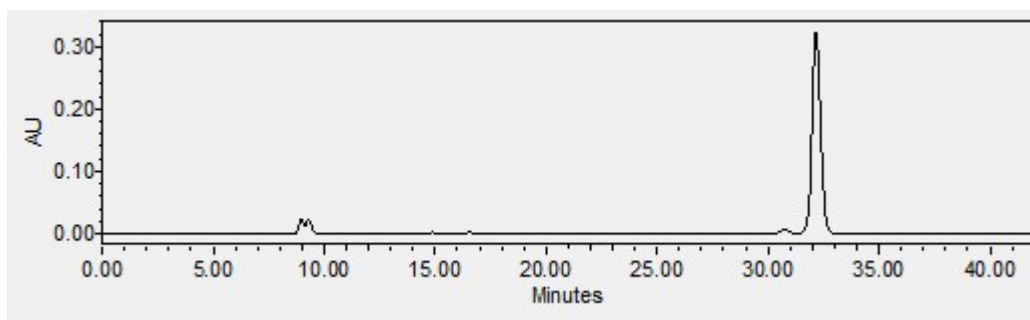
White waxy solid (330 mg, 87% yield). Found: C, 79.01; H, 4.38; N 3.49. Calc. for $C_{25}H_{19}NO_3$: C, 78.72; H, 5.02; N, 3.67. 98.4% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, $\lambda = 230$ nm, t_R (minor) = 30.6 min, t_R (major) = 32.3 min. ν_{max}/cm^{-1} 3274 (NH), 1739, 1651 (CO). δH (600 MHz, $CDCl_3$) 8.193–8.191 (m, 2H), 7.84–7.83 (m, 3H), 7.75–7.74 (m, 2H), 7.67–7.55 (m, 4H), 7.48–7.32 (m, 6H), 6.58 (s, 1H). δC (150 MHz, $CDCl_3$) 167.3, 165.8, 136.4, 135.3, 134.6, 133.8, 130.1, 129.8, 129.4, 129.3, 129.1, 129.0, 128.7, 127.8, 127.7, 127.6, 126.5, 125.4, 120.2, 117.8, 76.6. m/z : 381 (M^+ , 1%), 142 (60), 105 (100). HRMS (ESI, m/z): 382.14 ($M+H^+$).





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		31.056	9293946	51.97	276287	bb			Unknown	
2		32.688	8587991	48.03	260279	bb			Unknown	

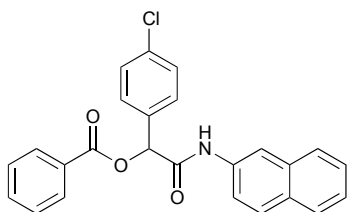
2-(2-naphthylamino)-2-oxo-1-phenylethyl benzoate (15n): racemate



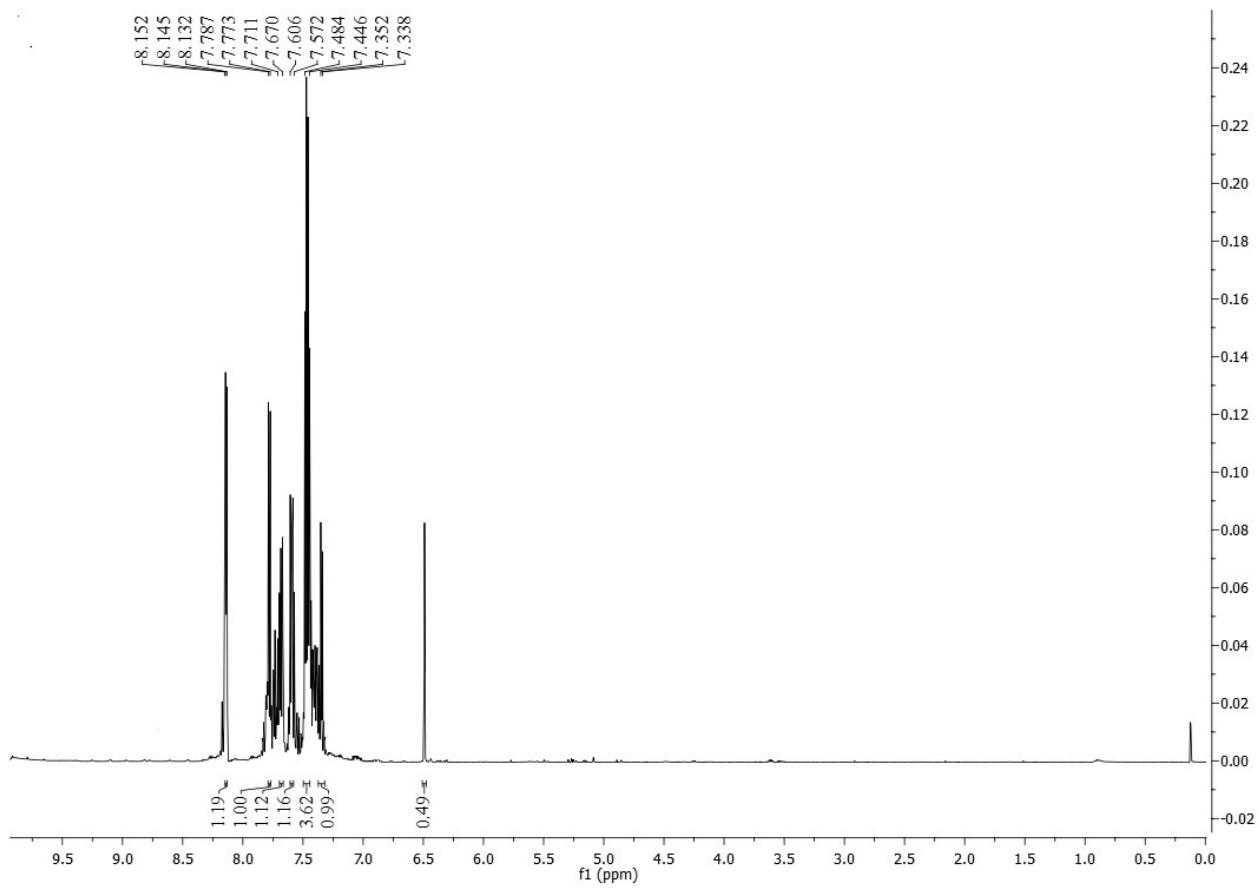
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		30.665	67775	0.82	251	bb			Unknown	
2		32.375	8238128	99.18	264334	bb			Unknown	

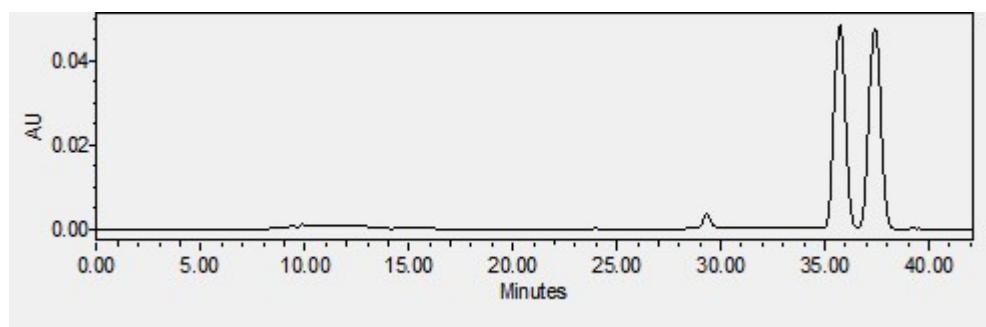
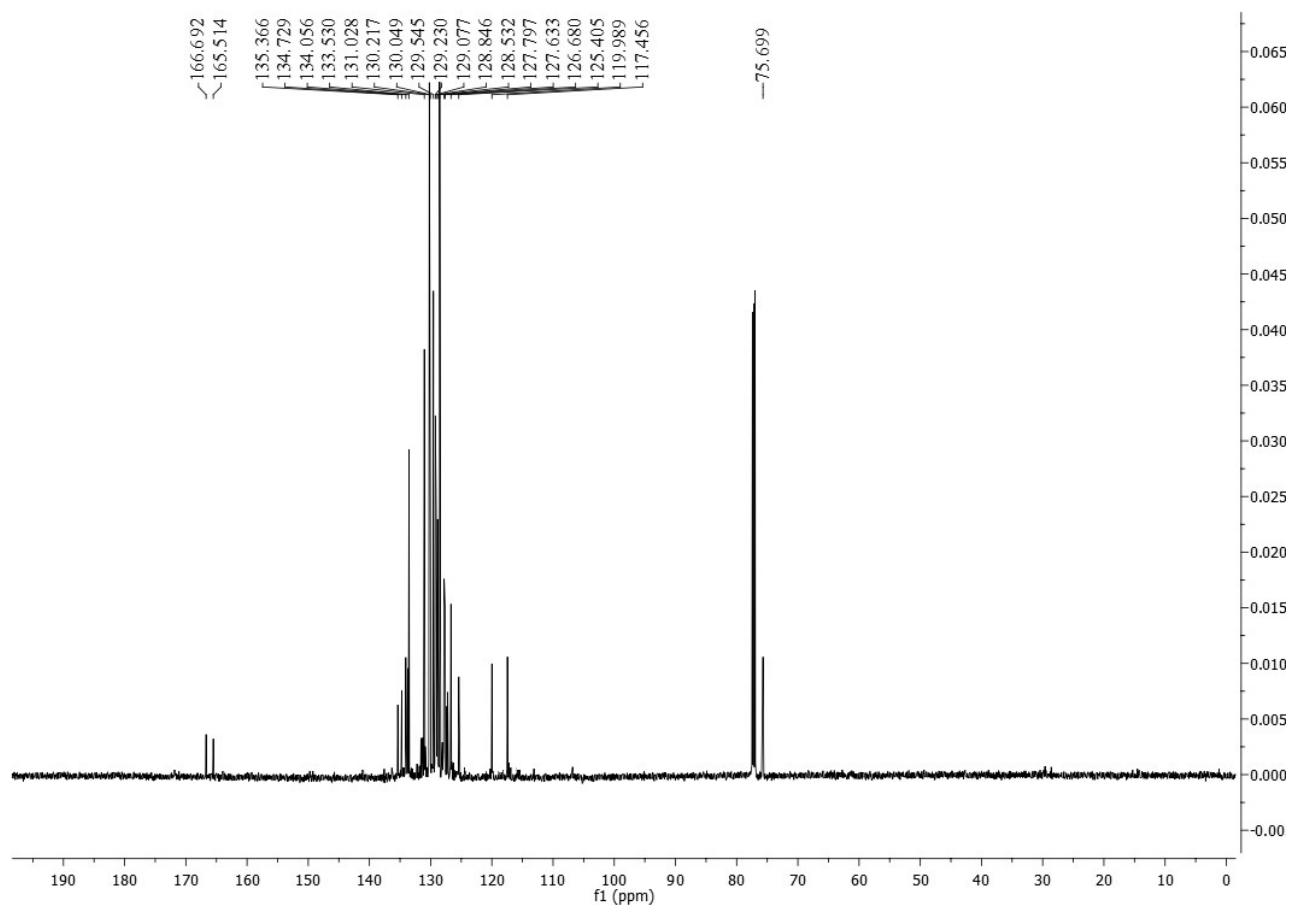
2-(2-naphthylamino)-2-oxo-1-phenylethyl benzoate (15n): in the presence of chiral catalyst 11.

1-(4-chlorophenyl)-2-(2-naphthylamino)-2-oxoethyl benzoate (15o):



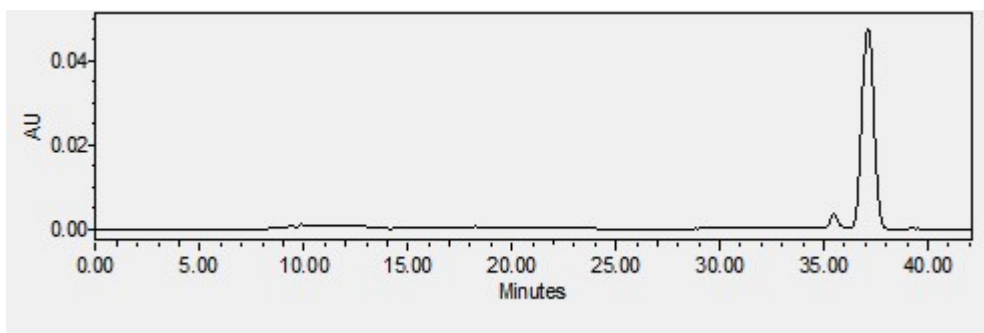
White waxy solid (345 mg, 83% yield). Found: C, 72.34; H, 4.27; N 3.31. Calc. for $C_{25}H_{18}ClNO_3$: C, 72.20; H, 4.36; N, 3.37. 95.3% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (minor) = 35.6 min, t_R (major) = 37.3 min. ν_{max}/cm^{-1} 3268 (NH), 1719, 1654 (CO). δ_H (600 MHz, $CDCl_3$) 8.15–8.13 (m, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.73–7.71 (m, 2H), 7.60–7.57 (m, 2H), 7.48–7.44 (m, 6H), 7.34 (d, J = 8.4 Hz, 2H), 6.49 (s, 1H). δ_C (150 MHz, $CDCl_3$) 166.9, 165.5, 135.3, 134.7, 134.0, 133.5, 131.0, 130.2, 130.0, 129.5, 129.2, 129.0, 128.8, 128.5, 127.7, 127.6, 126.6, 125.4, 119.9, 117.4, 74.7. m/z : 415 (M^+ , 1%), 142 (32), 105 (100). HRMS (ESI, m/z): 416.11($M+H^+$).





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	35.996	4045807	48.96	218871	bb			Unknown	
2	37.992	4217634	51.04	216640	bb			Unknown	

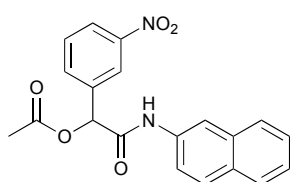
1-(4-chlorophenyl)-2-(2-naphthylamino)-2-oxoethyl benzoate (15o): racemate



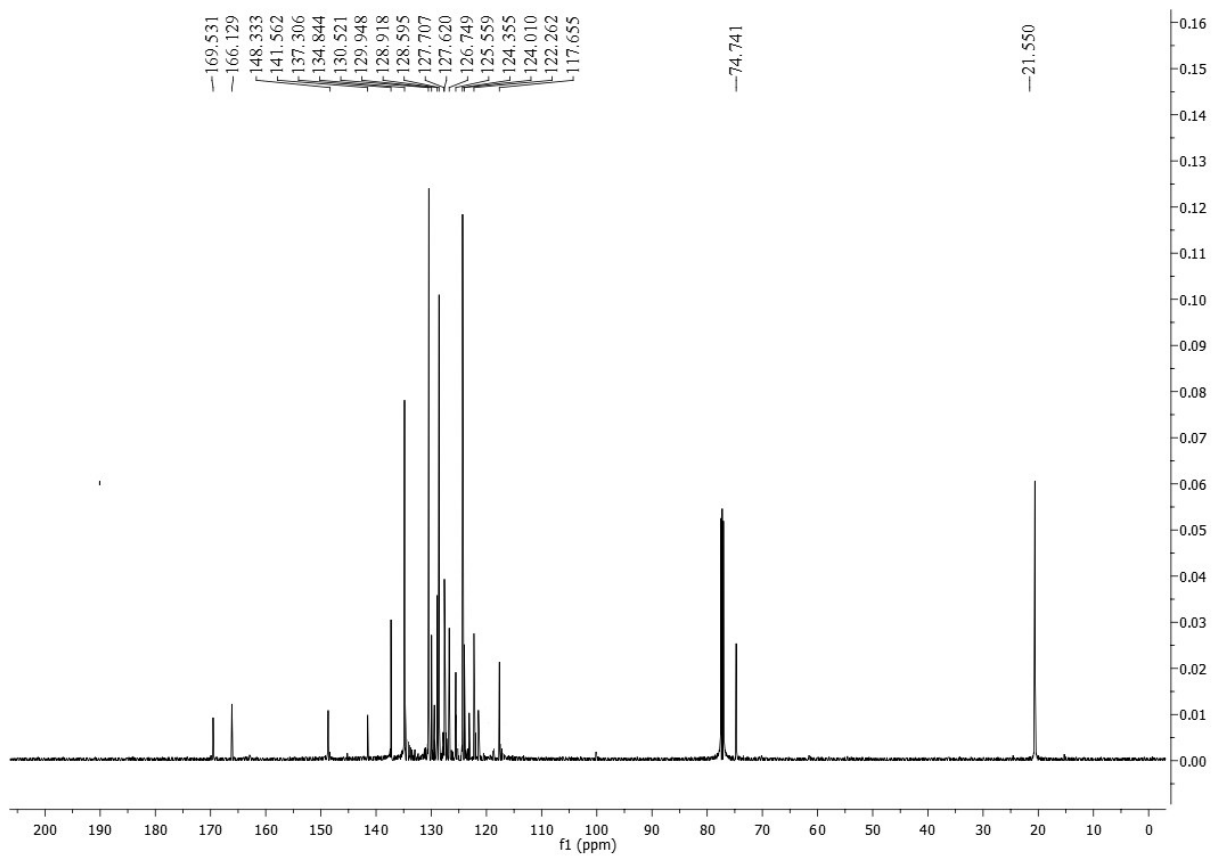
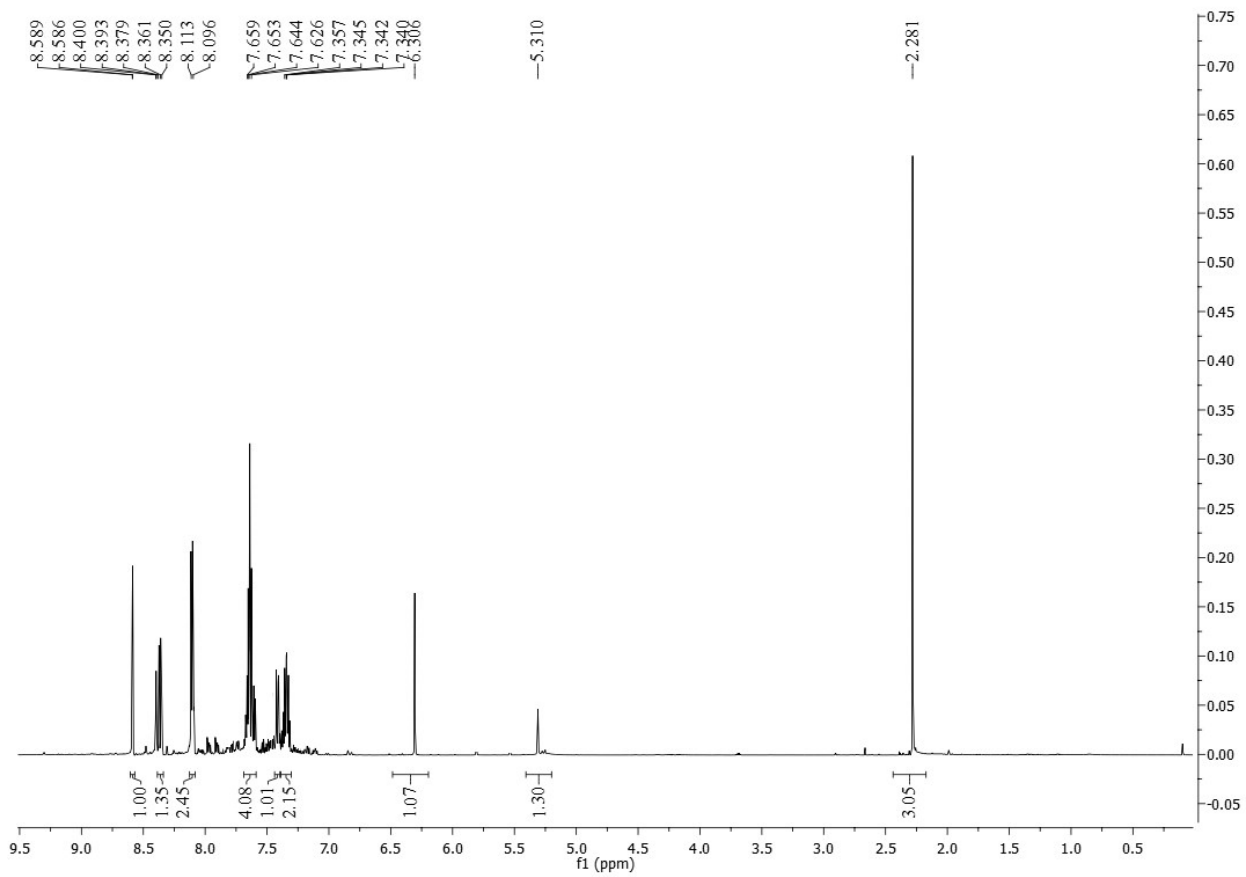
Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	35.627	199775	2.36	388	bb			Unknown	
2	37.273	8263441	97.64	234638	bb			Unknown	

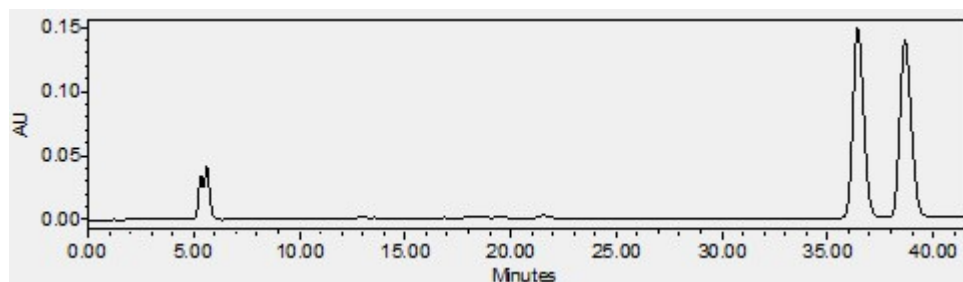
1-(4-chlorophenyl)-2-(2-naphthylamino)-2-oxoethyl benzoate (15o): in the presence of chiral catalyst 11.

2-(2-naphthylamino)-1-(3-nitrophenyl)-2-oxoethyl acetate (15p):



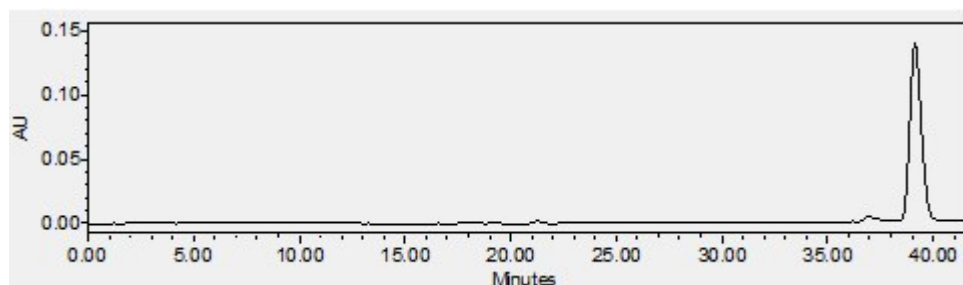
White waxy solid (305 mg, 84% yield). Found: C, 66.12; H, 4.28; N 8.00. Calc. for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69. 97.6% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, $\lambda = 230$ nm, t_R (minor) = 37.1 min, t_R (major) = 39.1 min. ν_{max}/cm^{-1} 3274 (NH), 1739, 1651 (CO). δH (600 MHz, $CDCl_3$) 8.58–8.56 (m, 1H), 8.40–8.37 (m, 1H), 8.36–8.35 (m, 2H), 7.66–7.63 (m, 4H), 7.35–7.345 (m, 1H), 7.342–7.340 (m, 2H), 6.31 (s, 1H) 5.31 (br s, 1H), 2.28 (s, 3H). δC (150 MHz, $CDCl_3$) 169.5, 166.1, 148.3, 141.5, 137.3, 134.8, 130.5, 129.9, 128.9, 128.6, 127.7, 127.6, 126.7, 125.5, 124.3, 124.0, 122.2, 117.6, 74.7, 21.5. m/z : 364 (M^+ , 10%), 142 (100), 43 (80). HRMS (ESI, m/z): 365.10 ($M+H^+$).





Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	36.525	22287677	49.67	785949	bb			Unknown	
2	39.010	22579835	50.33	727913	bb			Unknown	

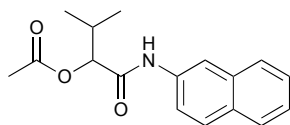
2-(2-naphthylamino)-1-(3-nitrophenyl)-2-oxoethyl acetate (15p): racemate



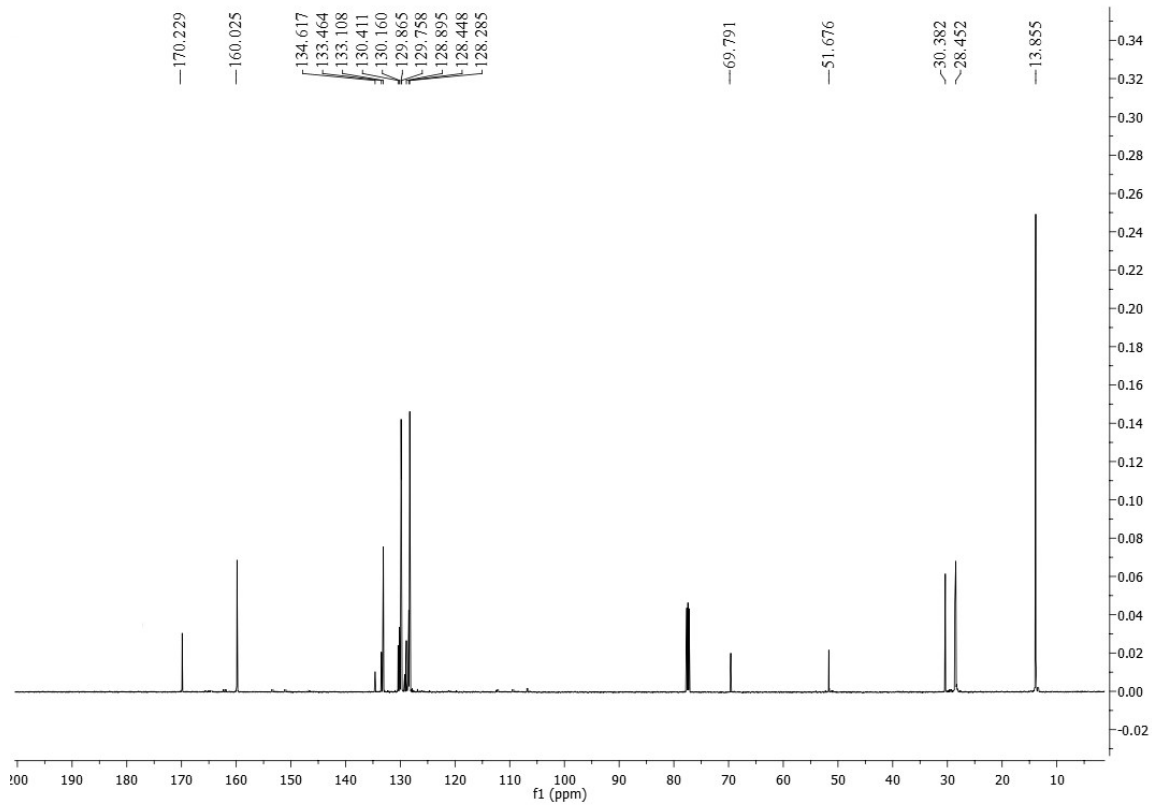
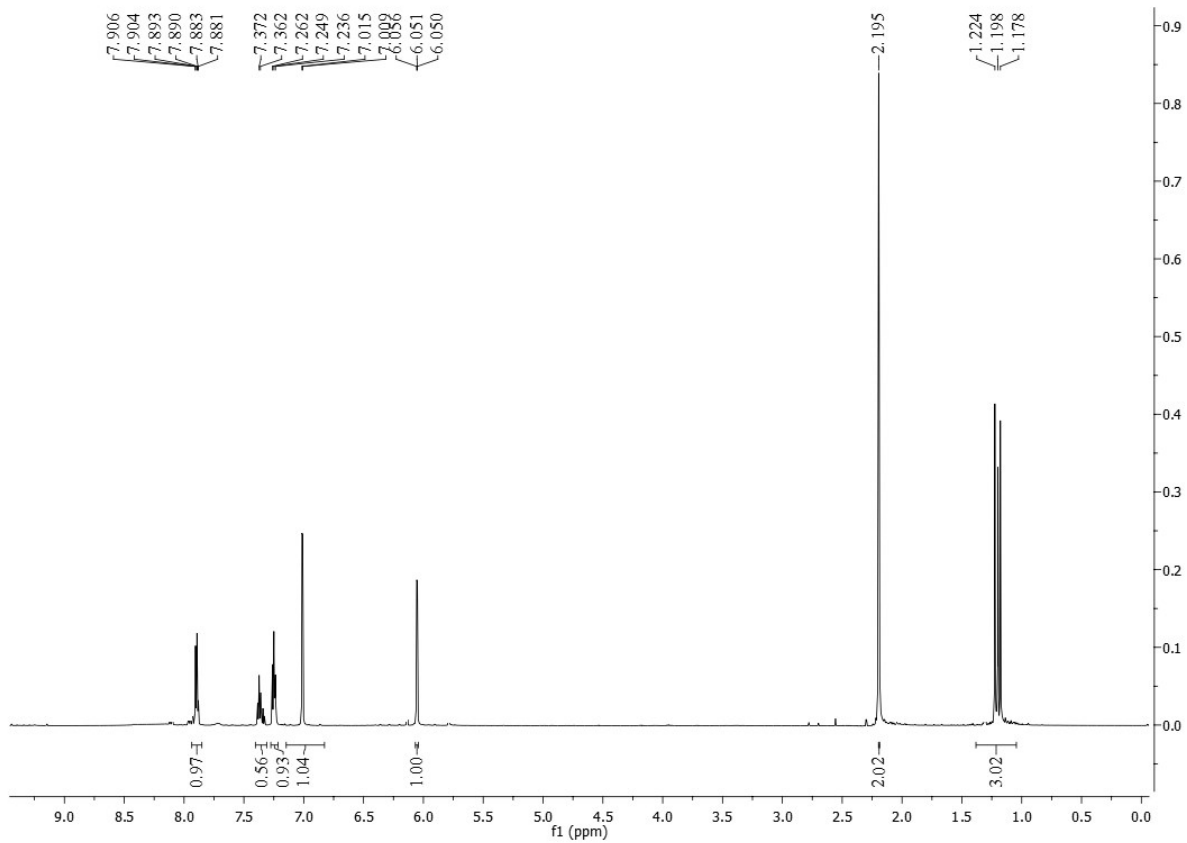
Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1	37.125	176566	1.21	250	bb			Unknown	
2	39.018	14466813	98.79	716952	bb			Unknown	

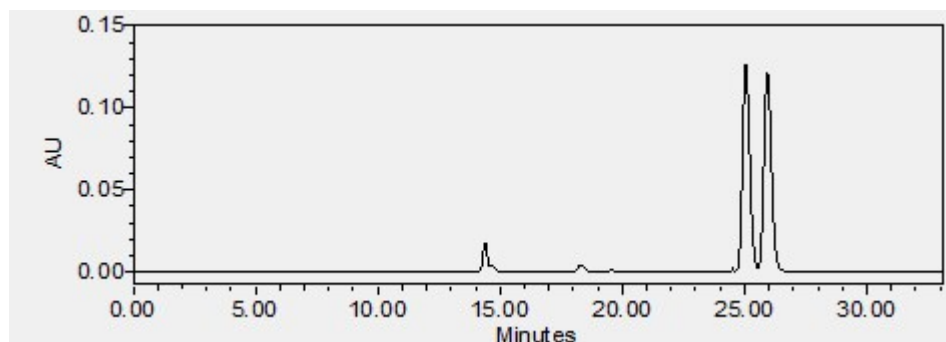
2-(2-naphthylamino)-1-(3-nitrophenyl)-2-oxoethyl acetate (15p): in the presence of chiral catalyst 11.

3-methyl-1-(2-naphthylamino)-1-oxobut-2-yl acetate (15q):



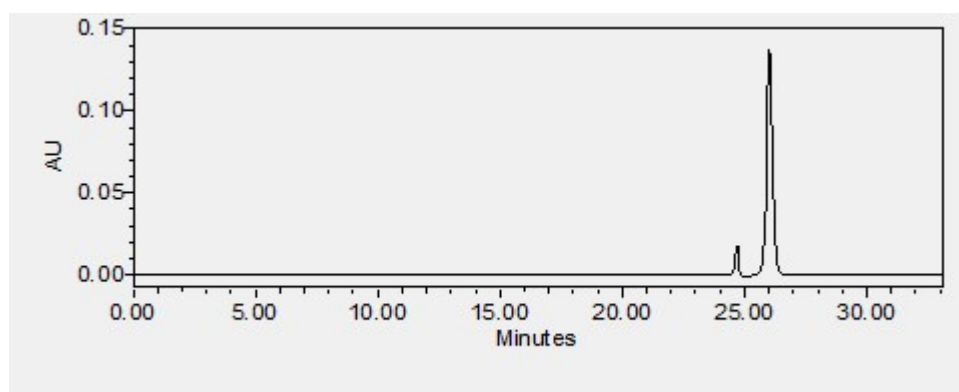
White waxy solid (245 mg, 86% yield). Found: C, 72.00; H, 6.62; N 4.97. Calc. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. 96.1% ee, determined by chiral stationary phase HPLC analysis (Daicel Chiralpack IG-SFC) isopropanol/hexane = 20/80, 1.0 mL/min, $\lambda = 214$ nm, t_R (minor) = 24.8 min, t_R (major) = 25.1 min. ν_{max}/cm^{-1} 3281 (NH), 1716, 1655 (CO). δ_H (600 MHz, $CDCl_3$) 7.90–7.88 (m, 2H), 7.37–7.36 (m, 1H), 7.26–7.23 (m, 2H), 7.01–7.00 (m, 2H), 6.054 (d, $J = 3.6$, 1H), 6.050 (br s, 1H), 2.19 (s, 4H), 1.22–1.17 (m, 6H). δ_C (150 MHz, $CDCl_3$) 170.2, 160.0, 134.6, 133.4, 133.1, 130.4, 130.1, 129.8, 129.7, 128.9, 128.4, 128.2, 69.8, 51.7, 30.4, 28.4, 13.8. m/z : 285 (M^+ , 30%), 142 (100), 43 (20). HRMS (ESI, m/z): 286.14 ($M+H^+$).





	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		25.008	6080262	50.14	288825	bb			Unknown	
2		26.121	6045805	49.86	279754	bb			Unknown	

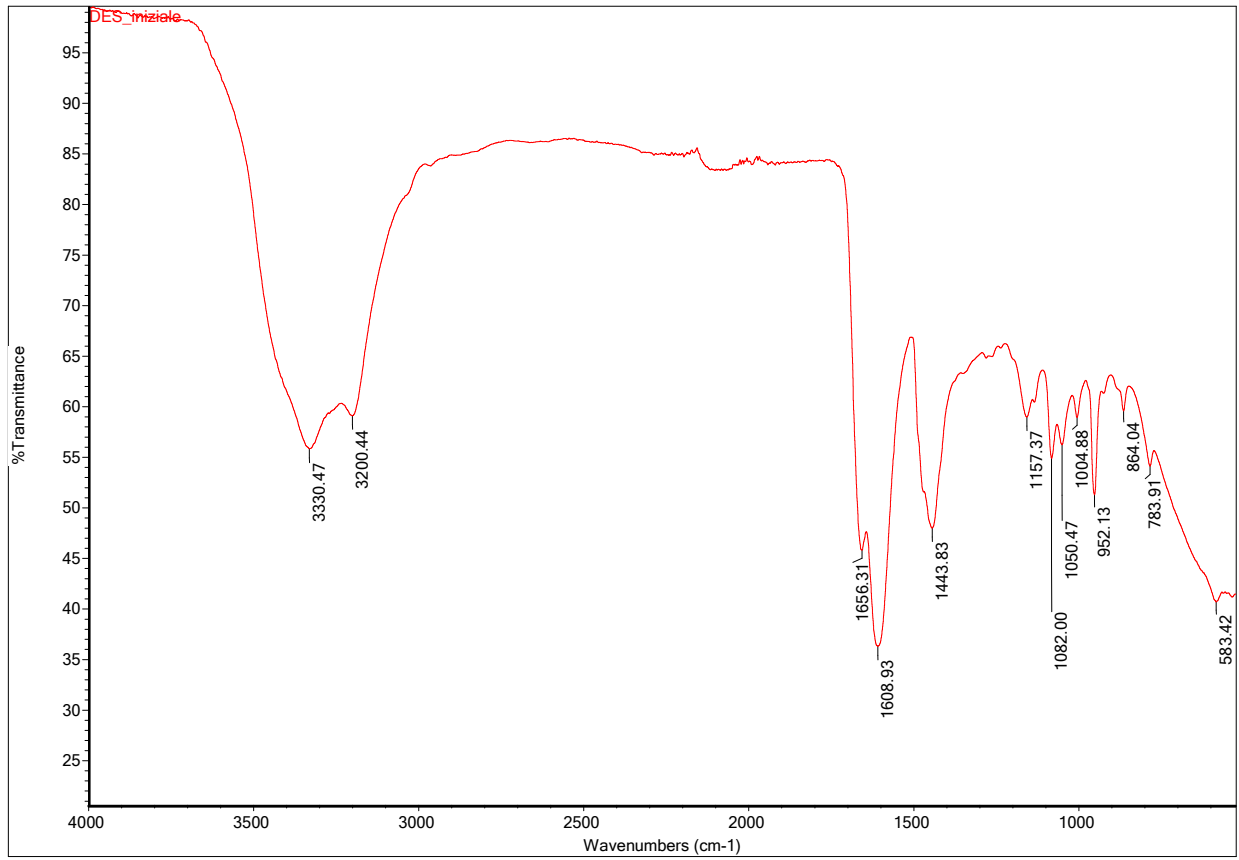
3-methyl-1-(2-naphthylamino)-1-oxobut-2-yl acetate (15q): racemate



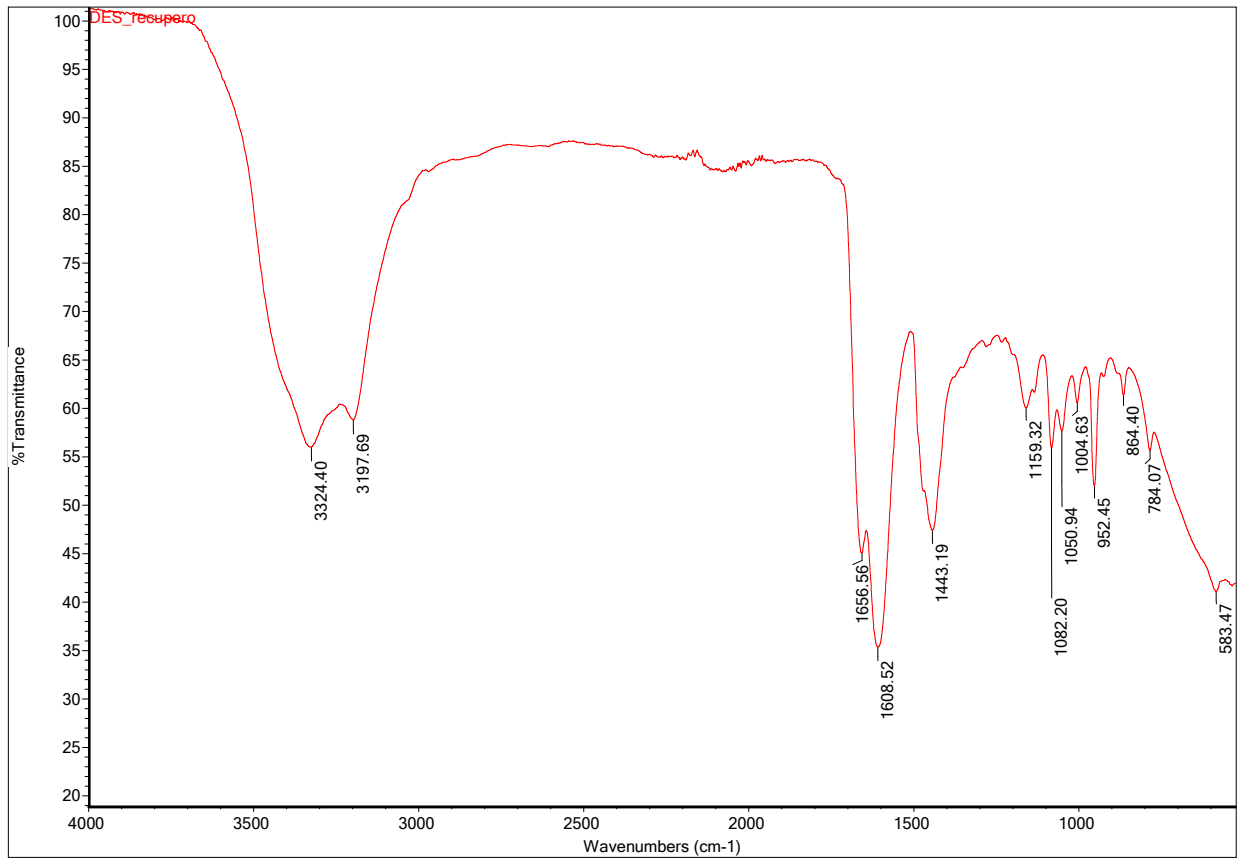
	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		24.475	185555	1.97	951	bb			Unknown	
2		25.107	9237137	98.03	290582	bb			Unknown	

3-methyl-1-(2-naphthylamino)-1-oxobut-2-yl acetate (15q): in the presence of chiral catalyst 11.

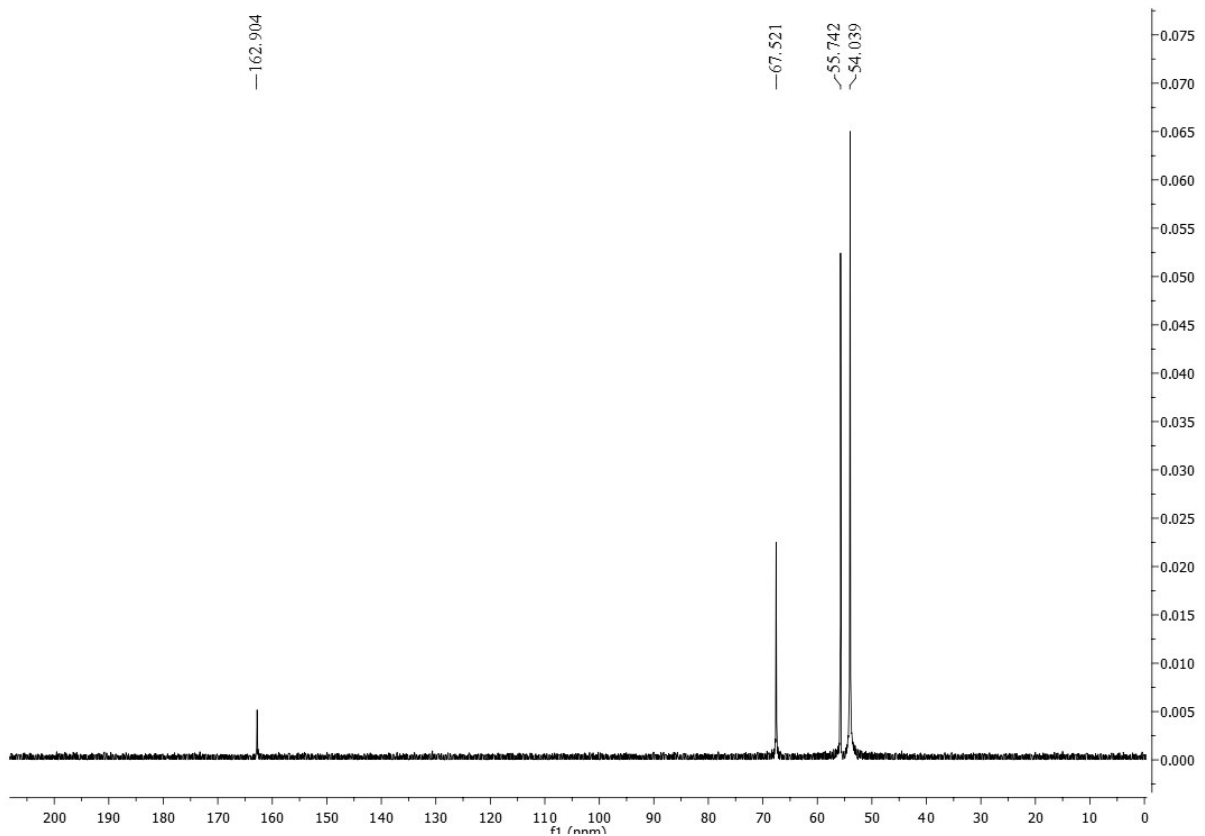
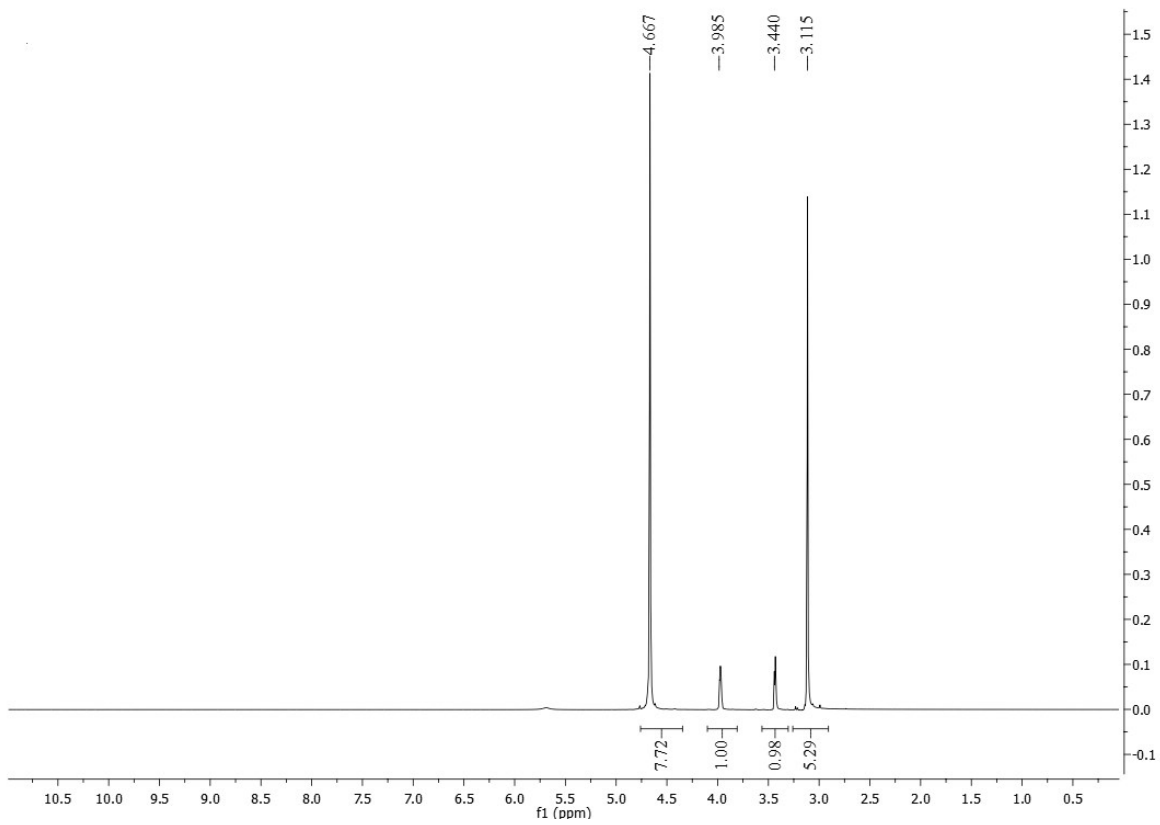
Starting urea/choline chloride DES



Recovered urea/choline chloride DES



Starting urea/choline Chloride DES; spectra recorded in D₂O



Recovered urea/choline chloride DES. Spectra recorded in D₂O

