Reversal Enantioselective Friedel–Crafts C3-Alkylation of Pyrrole by Slightly Tuning the Amide Units of N,N′-Dioxide Ligands

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Supporting Information

1. General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR and ^{13}C DEPT 135 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. Enantiomer excesses were determined by chiral HPLC analysis on Daicel Chiralcel ODH, ASH, IB, 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). All the solvents were purified by usual methods before use. CD spectra were determined by Chirascan CD (MeOH as the solvent) which was purchased from Applied photophysics Ltd. Silica gel for Thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd.

2. General procedure for *N,N'*-dioxide preparation

The *N,N'*-dioxide ligands **L** were synthesized by the same procedure in the literature.[1]

3. Typical procedure for the asymmetric Friedel–Crafts alkylation

Procedure A:

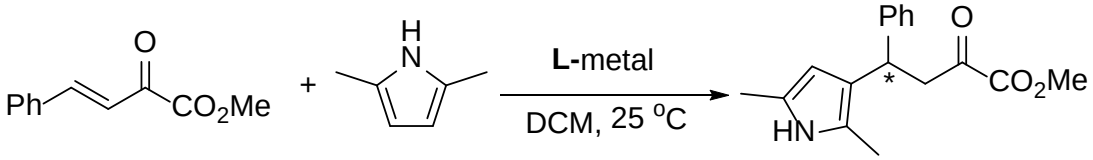
In a test tube, **L-RaPr$_2$** (7.0 mg, 0.01 mmol) and Ni(OTf)$_2$ (3.6 mg, 0.01 mmol) were added. Then β,γ-unsaturated α-ketoester **1a** (19.0 mg, 0.1 mmol) and toluene (0.5 mL) were added at N_2 atmosphere. After stirred at 35 ^{o}C for 0.5 hour, the reaction mixture was cooled to –20 ^{o}C and pyrrole **2a** (3.0 equiv., 21 uL) was added under stirring. The reaction mixture was stirred at –20 ^{o}C until β,γ-unsaturated α-ketoester **1a** was consumed (determined by TLC). After flash column chromatography on silica gel (eluent: AcOEt/Pet = 1/4), the pure product **3a** was obtained for HPLC analysis (Daicel Chiralcel IB).

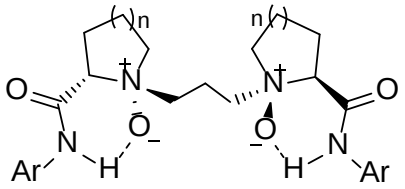
Procedure B:

In a test tube, **L-Ra*m*Bu$_2$** (7.6 mg, 0.01 mmol) and Ni(OTf)$_2$ (3.6 mg, 0.01 mmol) were added. Then β,γ-unsaturated α-ketoester **1a** (19.0 mg, 0.1 mmol) and CH_2Cl_2 (0.5 mL) were added at N_2 atmosphere. After stirred at 35 ^{o}C for 0.5 hour, the reaction mixture was cooled to –20 ^{o}C and pyrrole **2a** (3.0 equiv., 21 uL) was added under stirring. The reaction mixture was stirred at –20 ^{o}C until β,γ-unsaturated α-ketoester **1a** was consumed (determined by TLC). After flash column chromatography on silica gel (eluent: AcOEt/Pet = 1/4), the pure product **3a** was obtained for HPLC analysis (Daicel Chiralcel IB).

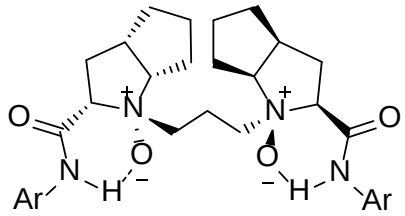
4. Optimization of the asymmetric reaction conditions

4.1 Screening of metal salts and chiral ligands[a]





L-PiPh: Ar = C_6H_5, n = 2
L-PiMe$_2$: Ar = 2,6-$Me_2C_6H_3$, n = 2
L-PiEt$_2$: Ar = 2,6-$Et_2C_6H_3$, n = 2
L-PiPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$, n = 2
L-Pi*m*Me$_2$: Ar = 3,5-$Me_2C_6H_3$, n = 2
L-Pi*m*Bu$_2$: Ar = 3,5-*t*$Bu_2C_6H_3$, n = 2
L-PrPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$, n =1
L-Pr*m*Bu$_2$: Ar = 3,5-*t*$Bu_2C_6H_3$, n = 1



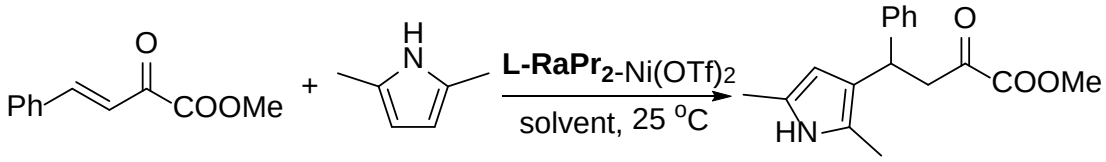
L-RaPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$
L-Ra*m*Bu$_2$: Ar = 3,5-*t*$Bu_2C_6H_3$

Entry	Metal salt	**L**	t [h]	Yield [%][b]	*ee* [%][c]
1	$Sc(OTf)_3$	**L-PiPh**	12	11	14
2	$Cu(OTf)_2$	**L-PiPh**	12	N.D.	N.D.
3	$Mg(OTf)_2$	**L-PiPh**	12	56	14
4	$La(OTf)_3$	**L-PiPh**	12	50	12
5	$Ni(OTf)_2$	**L-PiPh**	12	74	15
6	$Ni(OTf)_2$	**L-PiMe$_2$**	12	83	16
7	$Ni(OTf)_2$	**L-PiEt$_2$**	12	84	22
8	$Ni(OTf)_2$	**L-PiPr$_2$**	12	85	55
9	$Ni(OTf)_2$	**L-PrPr$_2$**	12	60	70

10	$Ni(OTf)_2$	**L-RaPr$_2$**	12	79	80
11	$Y(OTf)_3$	**L-RaPr$_2$**	15	96	28
12	$La(OTf)_2$	**L-RaPr$_2$**	15	81	51
13	$Ni(acac)_2$	**L-RaPr$_2$**	15	N.R.	-
14	$Fe(BF_4)_2 \cdot 6H_2O$	**L-RaPr$_2$**	15	N.R.	-
15	$Co(BF_4)_2 \cdot 6H_2O$	**L-RaPr$_2$**	15	99	76
16	$Ni(BF_4)_2 \cdot 6H_2O$	**L-RaPr$_2$**	15	84	80
17	$Ni(ClO_4)_2 \cdot 6H_2O$	**L-RaPr$_2$**	15	79	80
18	$Ni(OTf)_2$	**L-Pi*m*Me$_2$**	15	62	51 (–)
19[d]	$Ni(OTf)_2$	**L-Pi*m*Bu$_2$**	24	92	92 (–)
20[d]	$Ni(OTf)_2$	**L-Pr*m*Bu$_2$**	24	75	93 (–)
21[d]	$Ni(OTf)_2$	**L-Ra*m*Bu$_2$**	24	95	95 (–)

[a] Reaction conditions: **L**-metal (1:1, 10 mol%), **1a** (0.1 mmol), and **2a** (0.3 mmol) in CH_2Cl_2 (0.5 mL) at 25 °C. [b] Isolated yield. [c] Determined by chiral HPLC. And (–) referred to the optical rotation which is opposite to the others. [d] At -20 °C.

4.2 Optimization of the reaction solvents[a]

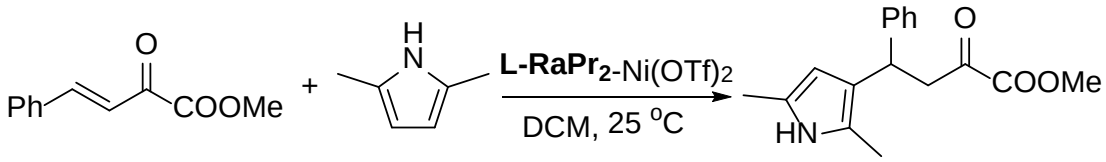


1a **2a** **3a**

Entry	solvent	t [h]	Yield [%][b]	*ee* [%][c]
1	CH_2Cl_2	12	79	80
2	THF	18	33	83
3	EtOH	18	74	83
4	EtOAc	18	60	86
5	toluene	18	70	90
6	DCE	18	75	85
7	$CHCl_3$	18	69	82

[a] Reaction conditions: **L-RaPr$_2$**-Ni(OTf)$_2$ (1:1, 10 mol%), **1a** (0.1 mmol), and **2a** (0.3 mmol) in solvent (0.5 mL) at 25 ^{o}C. [b] Isolated yield. [c] Determined by chiral HPLC.

4.3 Optimization of the ratio of ligand to metal salt [a]

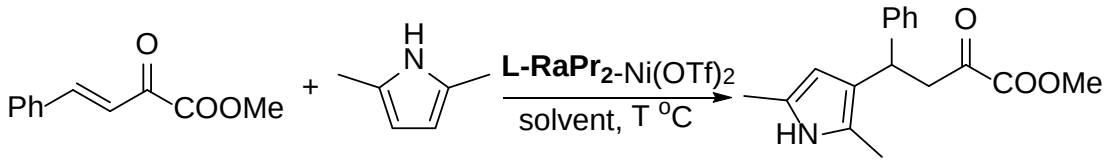


1a **2a** **3a**

Entry	**L-RaPr$_2$**/Ni(OTf)$_2$	Yield [%][b]	*ee* [%][c]
1	2/1	78	82
2	1.2/1	76	82
4	1/1.2	80	81
5	1/2	79	80

[a] Reaction conditions: **L-RaPr$_2$**-Ni(OTf)$_2$ (10 mol%), **1a** (0.1 mmol), and **2a** (0.3 mmol) in DCM (0.5 mL) at 25 ^{o}C for 18 h. [b] Isolated yield. [c] Determined by chiral HPLC.

4.4 Optimization of the reaction temperature.[a]

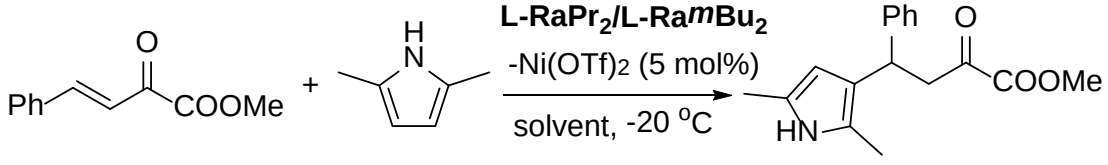


1a **2a** **3a**

Entry	Temperature [°C]	solvent	Yield [%][b]	*ee* [%][c]
1	0	DCM	76	83
2	–20	DCM	86	88
3	–20	DCE	87	90
4	–20	toluene	92	92
5	–30	toluene	61	86

[a] Reaction conditions: **L-RaPr$_2$**-Ni(OTf)$_2$ (1:1, 10 mol%), **1a** (0.1 mmol), and **2a** (0.3 mmol) in solvent (0.5 mL) for 18 h. [b] Isolated yield. [c] Determined by chiral HPLC.

4.4 Optimization of the catalyst loading.[a]



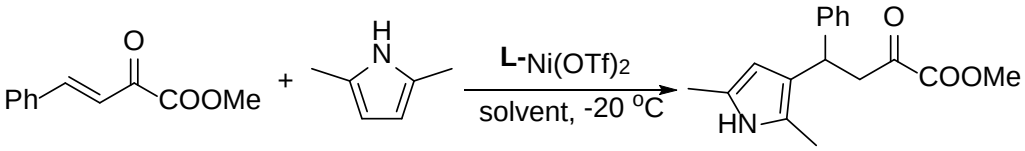
1a **2a** **3a**

Entry	**L**	Time (h)	Yield [%][b]	*ee* [%][c]

1	**L-RaPr$_2$**	24	67	91
2	**L-RaPr$_2$**	48	82	91
3	**L-Ra*m*Bu$_2$**	24	65	-93
4	**L-Ra*m*Bu$_2$**	48	86	-93

[a] Reaction conditions: **L-RaPr$_2$/L-Ra*m*Bu$_2$**-Ni(OTf)$_2$ (1:1, 5 mol%), **1a** (0.2 mmol), and **2a** (0.6 mmol) in solvent (1.0 mL) at -20 ^{o}C . [b] Isolated yield. [c] Determined by chiral HPLC.

5. Experimental procedure for the gram-scale synthesis of 3a.



system A: L-RaPr$_2$-Ni(OTf)$_2$, toluene

950 mg	1.0 mL	1.2870 g, 90% yield, 92% ee

system B: L-Ra*m*Bu$_2$-Ni(OTf)$_2$, DCM

950 mg	1.0 mL	1.2796 g, 90% yield, -96% ee

System A:

To a 100 mL dried flask containing Ni(OTf)$_2$ (180 mg, 0.5 mmol), **L-RaPr$_2$** (360 mg, 0.5 mmol), and β,γ-unsaturated α-ketoester **1a** (5.0 mmol, 0.95 g) was added 25 mL of toluene under N_2 atmosphere. After stirred at 35 ^{o}C for 1 hour, pyrrole **2a** (3.0 equiv, 1.0 mL) was added. The reaction continued stirring at –20 ^{o}C for 48 h.

Workup: The reaction solvent was evaporated under reduced pressure, then the concentrated mixture was purified by flash chromatography on silica gel (AcOEt : Pet

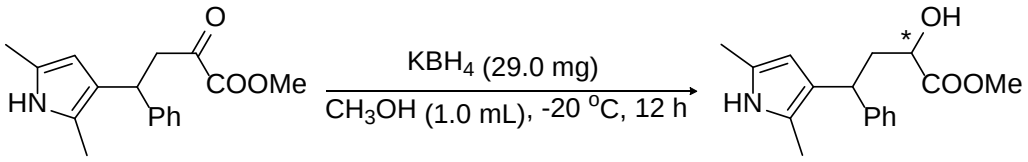
= 1:10) to afford the desired product **3a** as a light yellow oil (1.2870 g, 90% yield, 92% ee).

System B:

To a 100 mL dried flask containing $Ni(OTf)_2$ (180 mg, 0.5 mmol), **L-Ra*m*Bu$_2$** (380 mg, 0,5 mmol), and β,γ-unsaturated α-ketoester **1a** (5.0 mmol, 0.95 g) was added 25 mL of toluene under N_2 atmosphere. After stirred at 35 ^oC for 1 hour, pyrrole **2a** (3.0 equiv, 1.0 mL) was added. The reaction continued stirring at –20 ^oC for 48 h.

Workup: The reaction solvent was evaporated under reduced pressure, then the concentrated mixture was purified by flash chromatography on silica gel (AcOEt : Pet = 1:10) to afford the desired product **3a** as a light yellow oil (1.2796 g, 90% yield, -96% ee).

6. Experimental procedure for the hydrogenation of 3a.



3a **6**

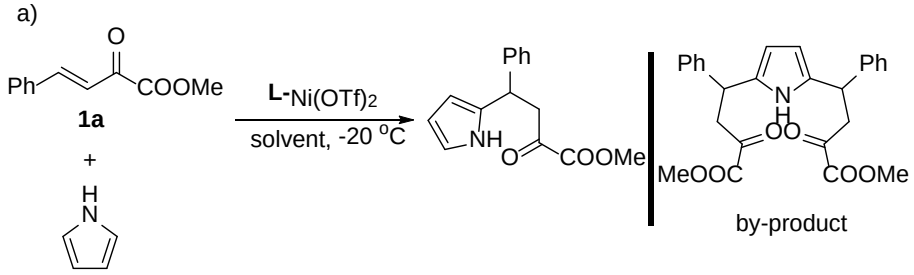
0.2 mmol, 91% *ee*	75% yield, 55:45 d.r., 91% *ee* for major isomer; 91% *ee* for minor isomer.
0.2 mmol, -94% *ee*	80% yield, 55:45 d.r., -92% *ee* for major isomer; -93% *ee* for minor isomer.

B: To a solution of the adduct **3a** (67.0 mg, 0.20 mmol) in CH_3OH (1.0 mL) was added KBH_4 (29.0 mg) at −20 ^oC under stirring. After 12 hours, the reaction mixture was allowed to warm to 0 ^oC and kept stirring for 3 h. Then, saturated NH_4Cl aqueous solution was added to quench the reaction. The mixture was extracted with CH_2Cl_2,

drying over Na_2SO_4. After evaporation of the solvents, the reduction product **6** was purified on silica gel chromatography (AcOEt : Pet = 1 : 3).

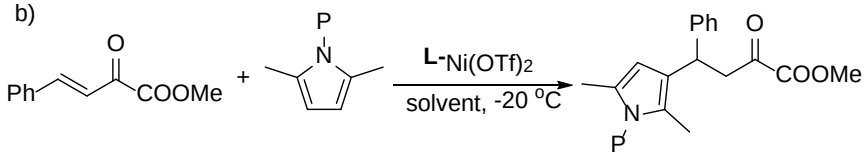
7. Control experiments and study on mechanism:

a)



system **L-RaPr$_2$-**Ni(OTf)$_2$: 76% yield, 99% ee; system **L-Ra*m*Bu$_2$-**Ni(OTf)$_2$: 72% yield, 11% ee.

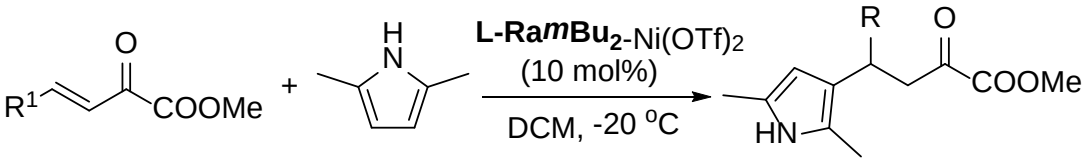
b)



P = Me, system **L-RaPr$_2$-**Ni(OTf)$_2$: 76% yield, 90% ee; system **L-Ra*m*Bu$_2$-**Ni(OTf)$_2$: 72% yield, -92% ee.

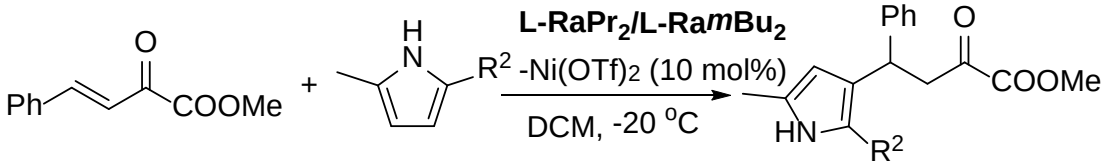
P = Ts, no reaction for both catalytic system.

It indicated that there was no interaction between the NH of pyrrole with the catalysts.



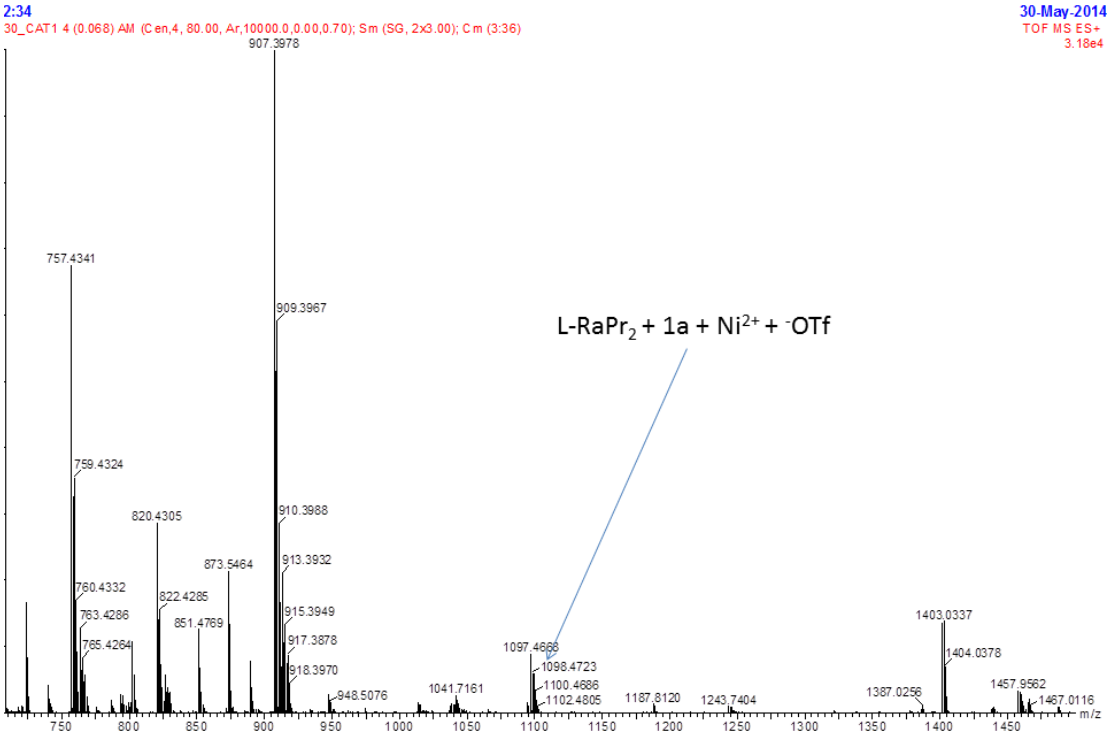
1 **2a** **3**

R^1 = 2Cl-C_6H_4, 91% yield with -67% ee for 26h;
R^1 = 2Br-C_6H_4, 78% yield with -60% ee for 20h;
R^1 = c-hexyl, 84% yield with -20% ee for 26h.



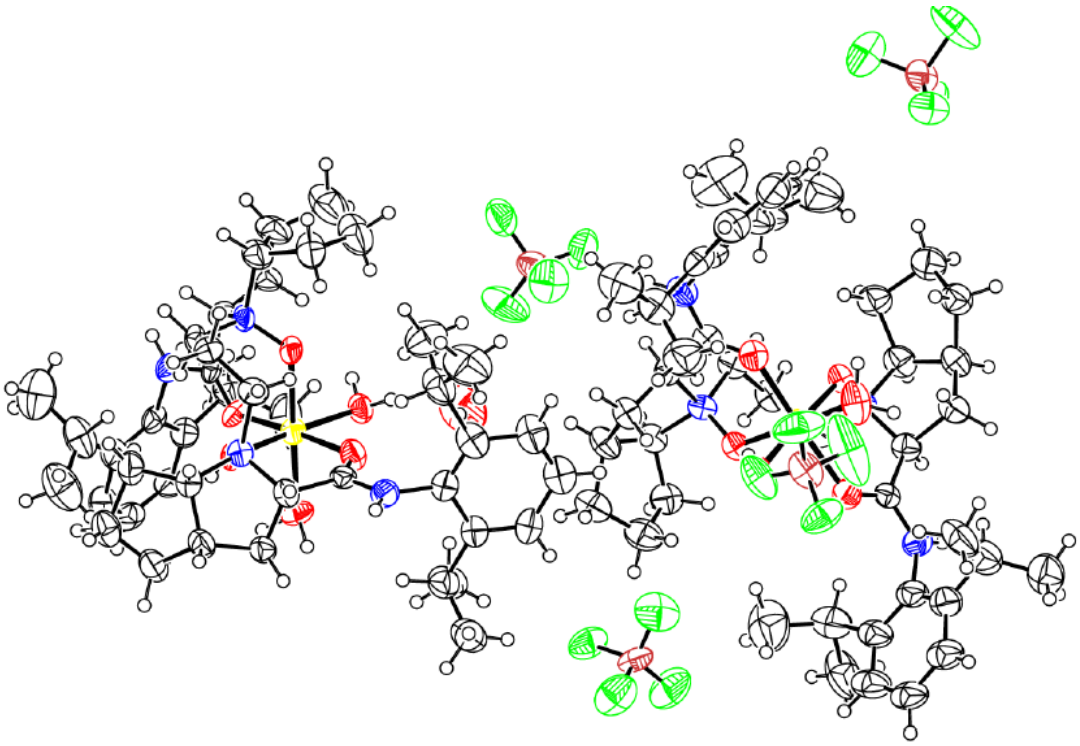
R^2 = CHO or COOEt, no reaction.

It implied that the steric hindrance and electron nature of the nucleophiles was also crucial for the facial selection.

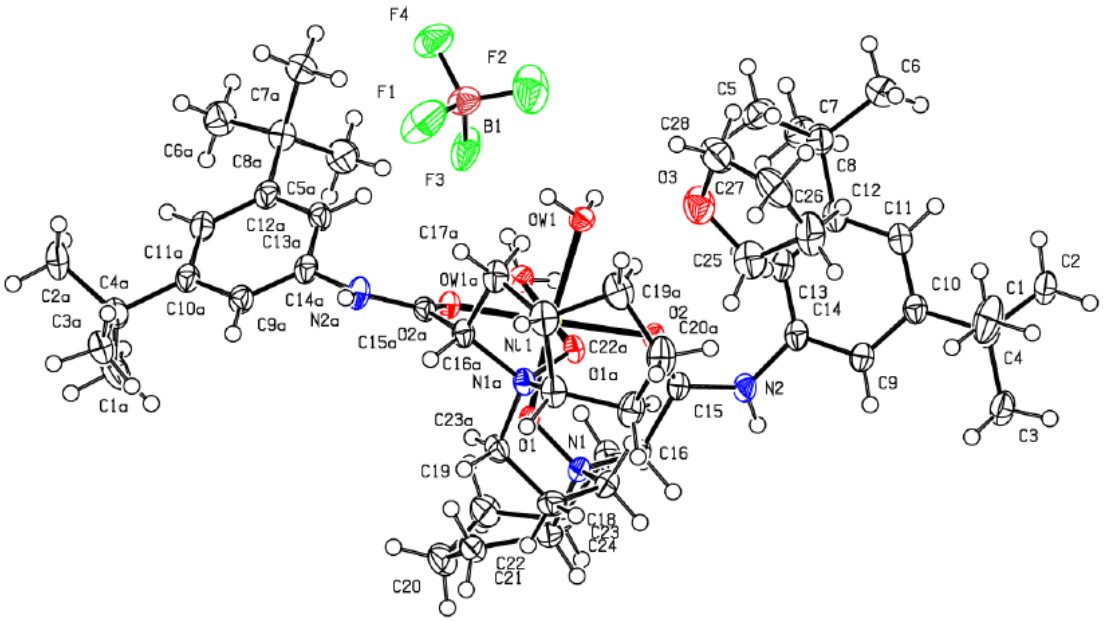


HRMS for substrate coordinated to catalyst **L-RaPr$_2$**-Ni(OTf)$_2$.

Data for X-ray of **L-RaPr$_2$**-Ni(BF$_4$)$_2$•6H$_2$O and **L-Ra*m*Bu$_2$**-Ni(BF$_4$)$_2$•6H$_2$O

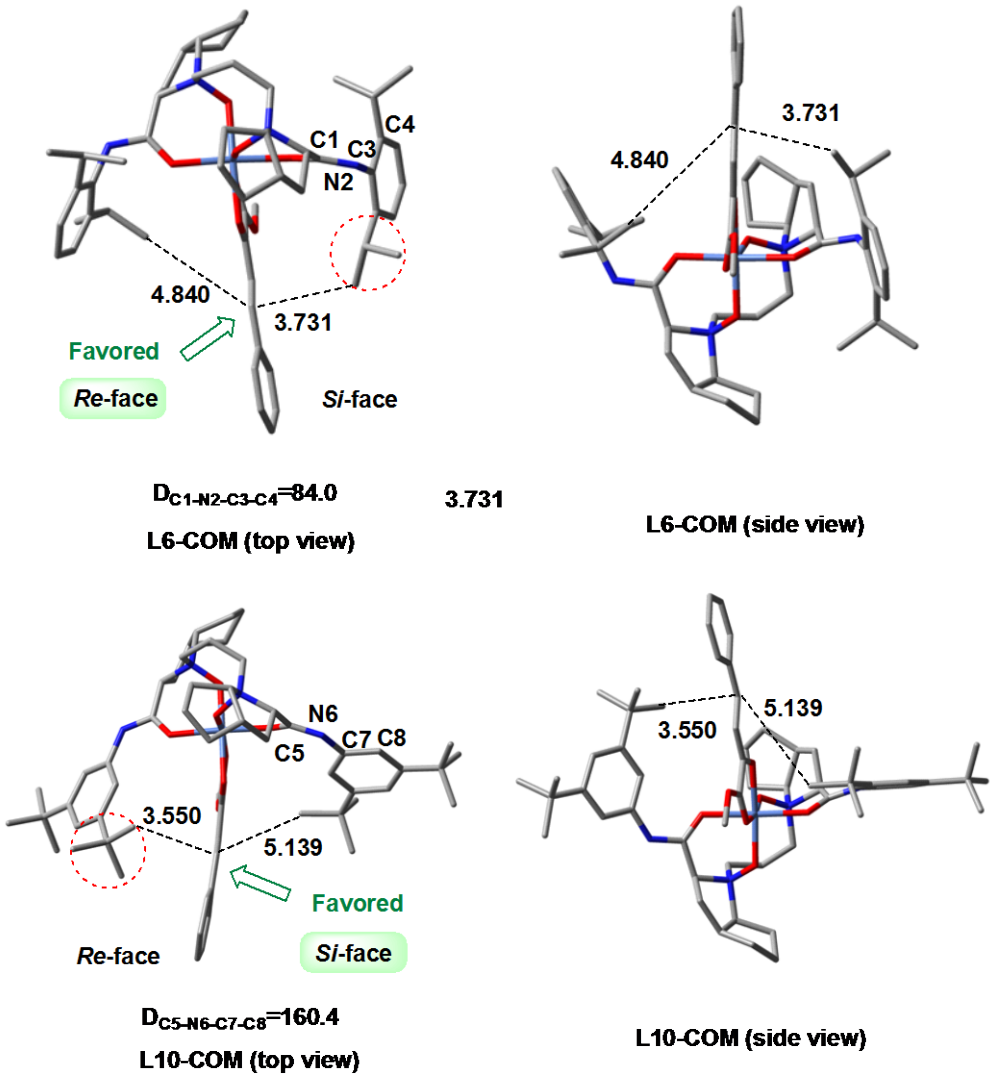


This figure was for X-ray of **L-RaPr$_2$**-Ni(BF$_4$)$_2$•6H$_2$O. CCDC 1035849 contain the supplementary crystallographic data for the **L-RaPr$_2$**-Ni(BF$_4$)$_2$•6H$_2$O. These data can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.



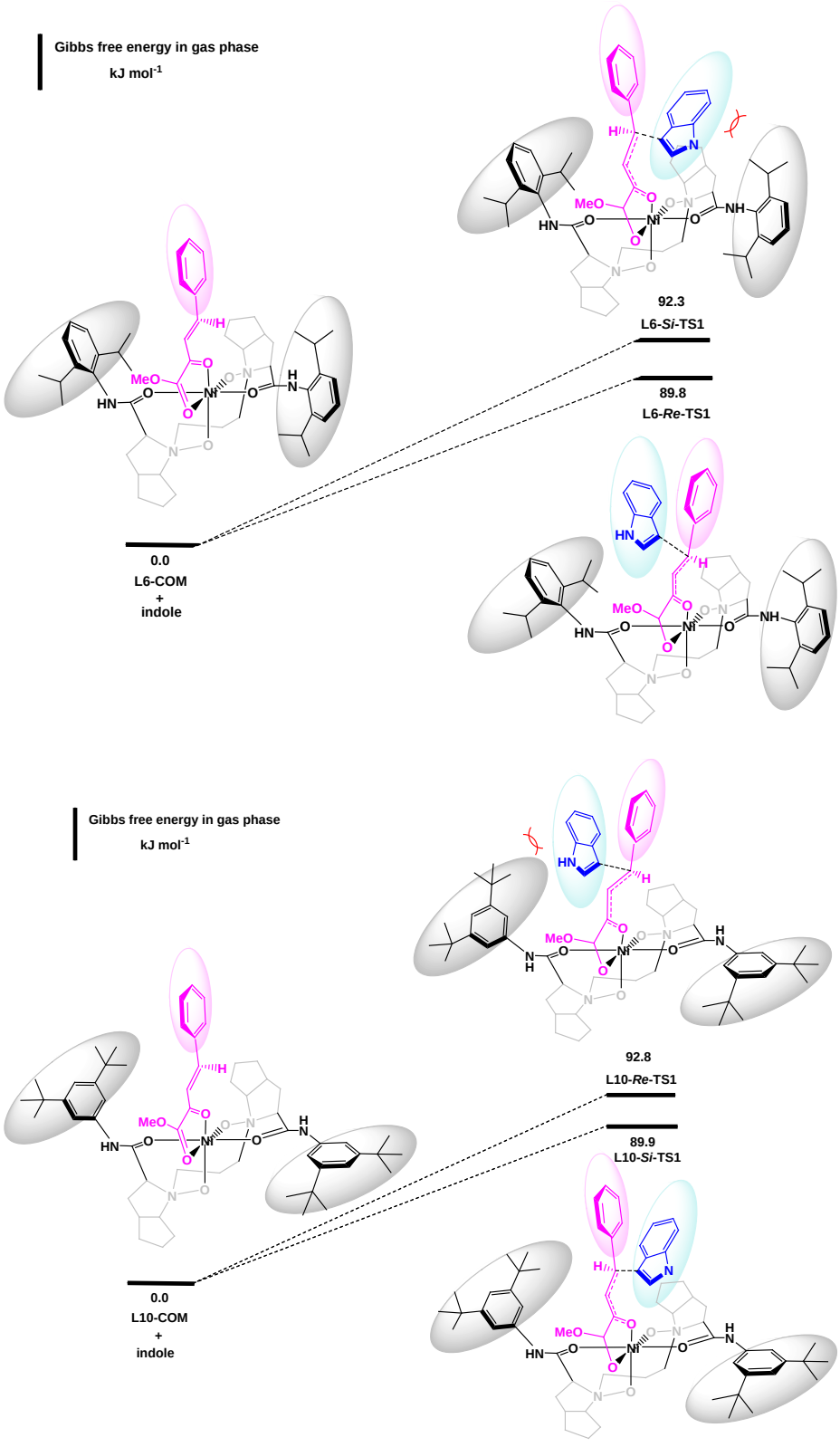
This figure was for X-ray of **L-Ra*m*Bu$_2$**-Ni(BF$_4$)$_2$•6H$_2$O. CCDC 1035929 contain the supplementary crystallographic data for the **L-Ra*m*Bu$_2$**-Ni(BF$_4$)$_2$•6H$_2$O. These data can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculation:



Structure of *N*.*N*′-dioxide-nickel complex coordinated to substrate

This calculation can also well explain the origin of the enantioselectivity. The results of calculation indicated that the plane of *N*,*N*′-dioxide dipolar amide and phenyl ring was near-vertical.as for the steric hinderance effect at the 2,6-position on the phenyl ring of L6-COM (dihedral DC1-N2-C3-C4 was 84.0 ^{o}C). Simultaneously, because the blocking effect of isopropyl at 2,6-position on the right phenyl ring, it is unfavored when indole attacked the Si face of the carbon carbon double bond. However, the phenyl ring nearly lied on the same planar with the *N*,*N*′-dioxide dipolar amide units (dihedral DC1-N2-C3-C4 was 160.4 ^{o}C). Because of the sterically hindered tertiary butyl at 3,5-position on the left phenyl ring, it hindeded indole attacking the Re face of substrate. Wherefore, it was advantage to afford S-configuration adduct.

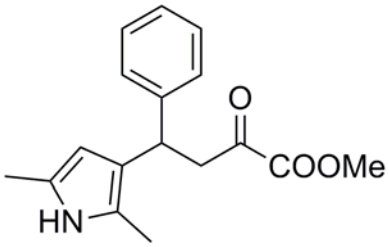


The calculated pathway of the first step of the reaction. Bond lengths are in Å and the relative free energies in gas phase ΔG_{gas} are in kcal mol^{-1}.

The calculated results show that transition state L6-Si-Ts1 is more stable than L6-Re-Ts1 which lead to indole favored Si face attack. Meanwhile, transition state L10-Re-Ts1 is more stable than L10-Si-Ts1 which Re face attack is more favored.

8. The analytical and spectral characterization data of the products

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-phenylbutanoate



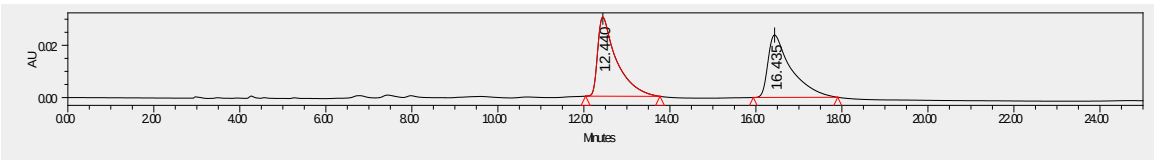
($C_{17}H_{19}NO_3$) (+)-enantiomer (Table 2, entry 1): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford a yellow oil in 88% yield with 95% ee. $[\alpha]^{14.3}_D$ = +13.9 (c = 0.33, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 12.507 min, tr (minor) = 16.637 min.

(-)-enantiomer (Table 2, entry 1): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 88% yield with 95% ee. $[\alpha]^{14.1}_D$ = –10.7 (c = 0.46, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 16.496 min, tr (minor) = 12.645 min.

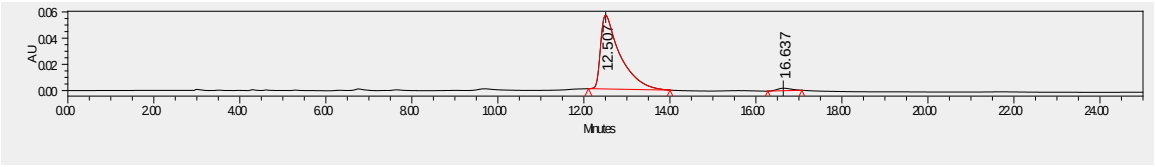
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.26 (m, 2H), 7.16 (m, 3H), 5.73 (d, *J* = 2.0 Hz, 1H), 4.45 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.52 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.45 – 3.39 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.95, 161.27, 144.67, 128.42, 127.33, 126.04, 125.30, 121.90, 120.47, 104.59, 52.80, 46.22, 37.47, 12.98, 11.03.

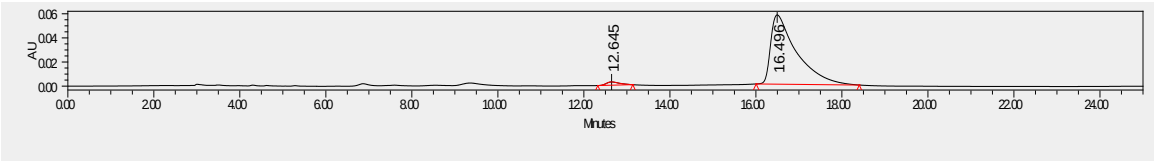
HRMS (ESI-TOF) calcd for $C_{17}H_{19}NO_3$ ([M+Na^+]) = 308.1263. Found 308.1263.



	Retention Time	Area	% Area
1	12.440	918370	50.72
2	16.435	892377	49.28

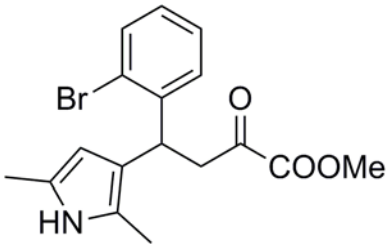


	Retention Time	Area	% Area
1	12.507	1772002	97.62
2	16.637	43265	2.38



	Retention Time	Area	% Area
1	12.645	58647	2.39
2	16.496	2397290	97.61

Methyl 4-(2-bromophenyl)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate



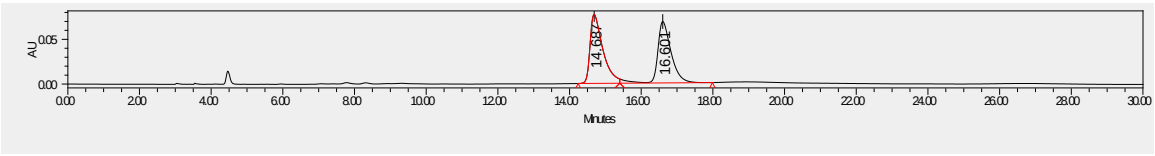
($C_{17}H_{18}BrNO_3$) (-)-enantiomer (Table 2, entry 6): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 80% yield with 98% ee. $[\alpha]^{12.6}_D$ = –41.9 (c = 0.41, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 14.511 min, tr (minor) = 16.733 min.

(+)-enantiomer (Table 2, entry 6): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 78% yield with 60% ee. The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 16.410 min, tr (minor) = 14.719 min.

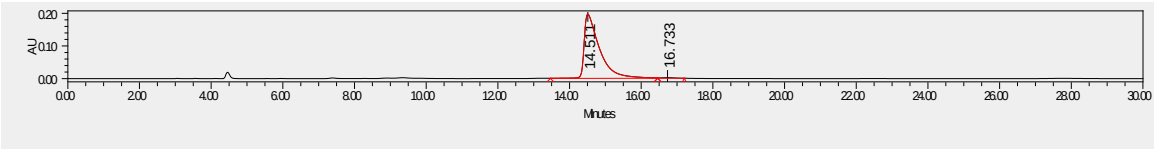
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 1H), 7.44 (s, 1H), 7.37 (m, 1H), 7.23 (m, 1H), 7.02 (m, 1H), 5.72 (d, *J* = 2.0 Hz, 1H), 4.93 (dd, *J* = 9.6, 5.6 Hz, 1H), 3.81 (s, 3H), 3.56 (dd, *J* = 17.2, 9.6 Hz, 1H), 3.28 (dd, *J* = 17.2, 5.6 Hz, 1H), 2.16 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.21, 161.18, 143.55, 132.86, 128.91, 127.64, 125.41, 123.85, 122.74, 118.86, 104.82, 52.86, 45.82, 36.50, 13.03, 11.31.

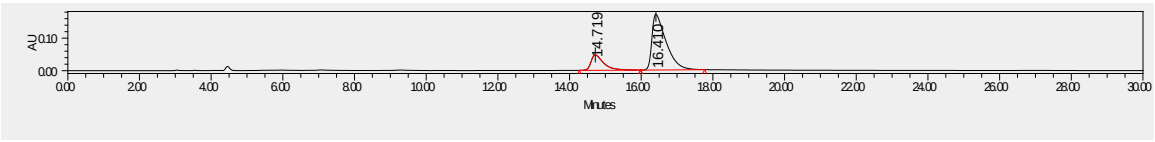
HRMS (ESI-TOF) calcd for $C_{17}H_{18}BrNO_3$ ([M+Na^+]) = 386.0368. Found 386.0370.



	Retention Time	Area	% Area
1	14.687	1904398	51.42
2	16.601	1799364	48.58

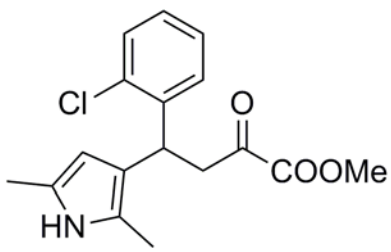


	Retention Time	Area	% Area
1	14.511	5859460	99.15
2	16.733	50160	0.85



	Retention Time	Area	% Area
1	14.719	1165457	19.81
2	16.410	4717066	80.19

Methyl 4-(2-chlorophenyl)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate



($C_{17}H_{18}ClNO_3$) (-)-enantiomer (Table 2, entry 5): Prepared according to general procedure A. After 24 h, the crude material

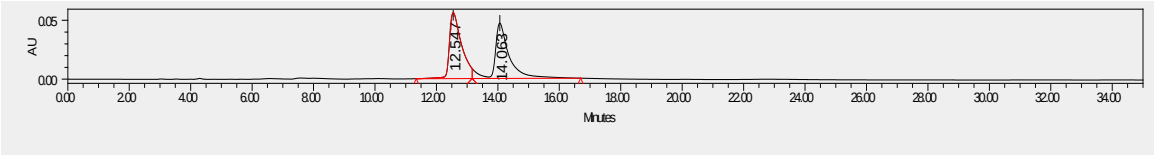
was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 84% yield with 99% ee. $[\alpha]^{14.3}_{D}$ = -18.2 (c = 0.52, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 12.456 min, tr (minor) = 14.123 min.

(+)-enantiomer (Table 2, entry 5): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 91% yield with 67% ee. $[\alpha]^{14.4}_{D}$ = +16.4 (c = 0.47, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 13.923 min, tr (minor) = 12.607 min.

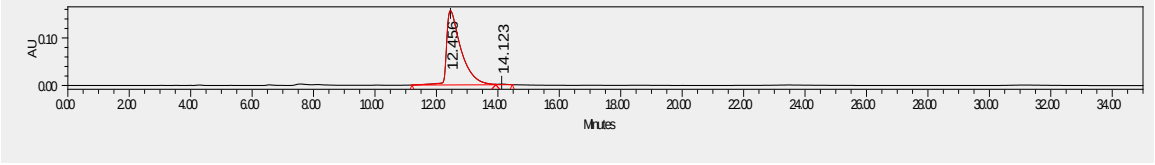
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.37 (m, 1H), 7.31 (m, 1H), 7.19 (m, 1H), 7.12 – 7.08 (m, 1H), 5.72 (d, *J* = 2.4 Hz, 1H), 4.96 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.81 (s, 3H), 3.57 (dd, *J* = 17.2, 9.2 Hz, 1H), 3.30 (dd, *J* = 17.2, 6.0 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.30, 161.19, 141.91, 133.05, 129.54, 128.63, 127.30, 126.98, 125.41, 122.67, 118.84, 104.80, 52.85, 45.61, 33.66, 13.02, 11.13.

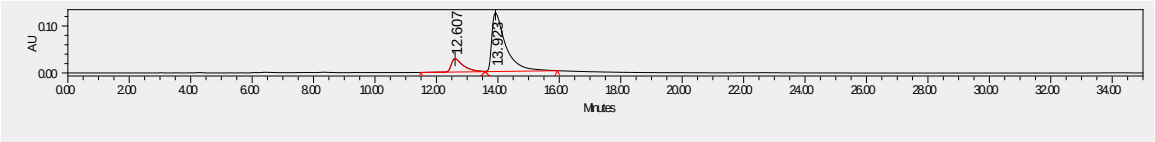
HRMS (ESI-TOF) calcd for $C_{17}H_{18}ClNO_3$ ([M+Na^+]) = 342.0873. Found 342.0871.



	Retention Time	Area	% Area
1	12.547	1542797	50.09
2	14.063	1537489	49.91

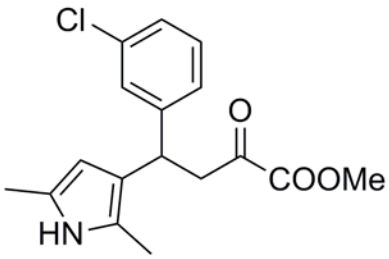


	Retention Time	Area	% Area
1	12.456	5098824	99.47
2	14.123	26989	0.53



	Retention Time	Area	% Area
1	12.607	775441	16.50
2	13.923	3925335	83.50

Methyl 4-(3-chlorophenyl)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate



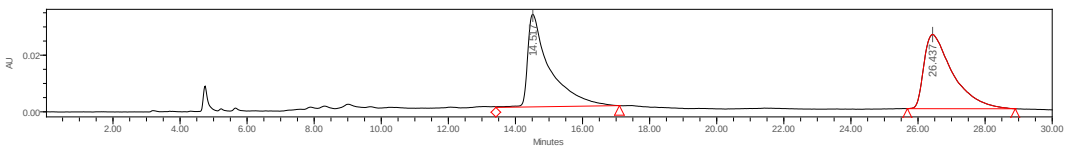
($C_{17}H_{18}ClNO_3$) (+)-enantiomer (Table 2, entry 7): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 89% yield with 90% ee. $[\alpha]^{16.1}_D$ = +18.8 (c = 0.32, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 14.174 min, tr (minor) = 25.833 min.

(-)-enantiomer (Table 2, entry 7): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 93% yield with 90% ee. $[\alpha]^{16.2}_D$ = -13.9 (c = 0.46, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 24.392 min, tr (minor) = 13.952 min.

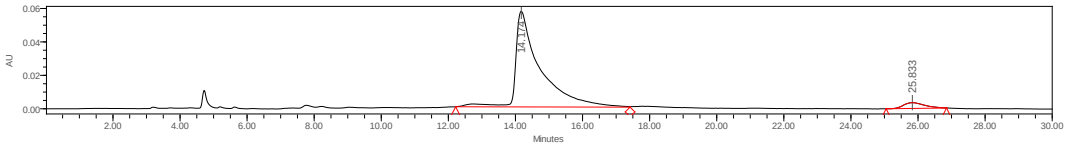
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.20 – 7.09 (m, 4H), 5.72 (d, *J* = 2.4 Hz, 1H), 4.42 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.52 (dd, *J* = 17.6, 8.4 Hz, 1H), 3.43 – 3.37 (dd, *J* = 17.6, 7.2 Hz, 2H), 2.17 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.46, 161.12, 146.82, 134.12, 129.67, 127.56, 126.26, 125.59, 125.55, 122.07, 119.75, 104.42, 52.90, 46.02, 37.08, 12.97, 11.02.

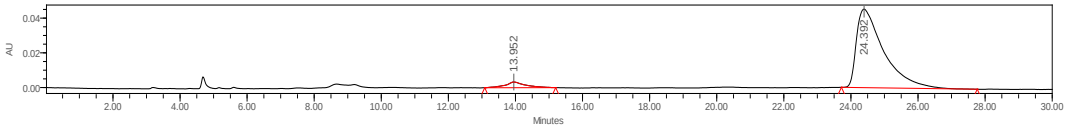
HRMS (ESI-TOF) calcd for $C_{17}H_{18}ClNO_3$ ([M+Na^+]) = 342.0873. Found 342.0870.



	Retention Time	Area	% Area
1	14.517	1493913	48.88
2	26.437	1562485	51.12

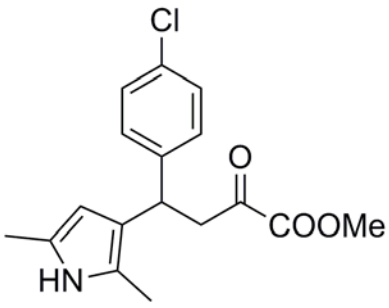


	Retention Time	Area	% Area
1	14.174	2918925	95.15
2	25.833	148824	4.85



	Retention Time	Area	% Area
1	13.952	134940	5.01
2	24.392	2557110	94.99

Methyl 4-(4-chlorophenyl)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate



($C_{17}H_{18}ClNO_3$) (+)-enantiomer (Table 2, entry 8): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 94% yield with 93% ee. $[\alpha]^{14.0}_D$ = +14.1 (c = 0.55, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 11.630 min, tr (minor) = 20.790 min.

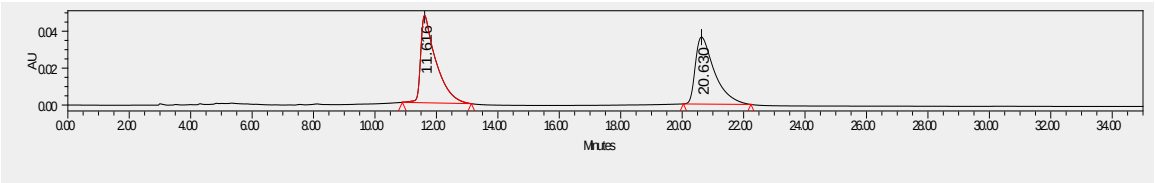
(-)-enantiomer (Table 2, entry 8): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 95% yield with 93% ee. $[\alpha]^{13.7}_D$ = -12.1 (c = 0.57, CH_2Cl_2); The ee was

determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 20.506 min, tr (minor) = 11.682 min.

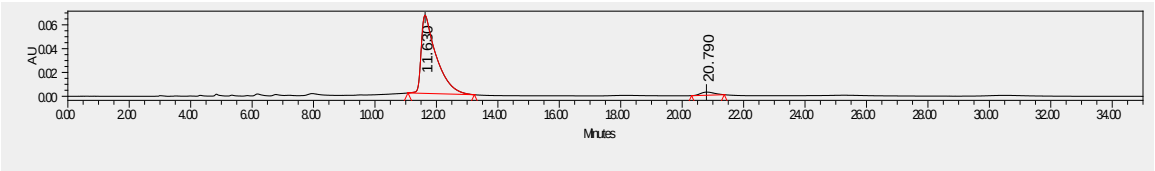
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.24 – 7.18 (m, 4H), 5.71 (d, *J* = 2.4 Hz, 1H), 4.43 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.50 (dd, *J* = 17.6, 8.0 Hz, 1H), 3.42 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.60, 161.16, 143.22, 131.67, 128.74, 128.49, 125.49, 121.96, 120.04, 104.40, 52.89, 46.05, 36.80, 12.96, 11.01.

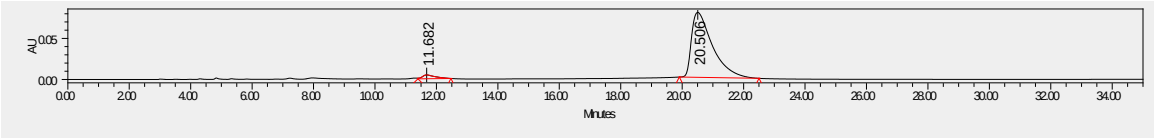
HRMS (ESI-TOF) calcd for $C_{17}H_{18}ClNO_3$ ([M+Na^+]) = 342.0873. Found 342.0874.



	Retention Time	Area	% Area
1	11.616	1629235	51.01
2	20.630	1564969	48.99

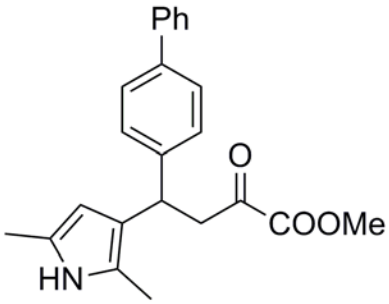


	Retention Time	Area	% Area
1	11.630	2234410	96.49
2	20.790	81353	3.51



	Retention Time	Area	% Area
1	11.682	134092	3.45
2	20.506	3754328	96.55

Methyl 4-([1,1'-biphenyl]-4-yl)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate



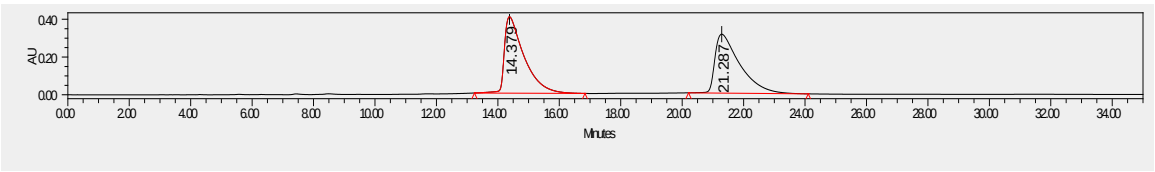
($C_{23}H_{23}NO_3$) (+)-enantiomer (Table 2, entry 11): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 92% yield with 91% ee. $[\alpha]^{14.7}_D$ = +25.5 (c = 0.51, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 14.290 min, tr (minor) = 21.585 min.

(-)-enantiomer (Table 2, entry 11): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 91% yield with 94% ee. $[\alpha]^{14.8}_D$ = -26.5 (c = 0.58, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 21.171 min, tr (minor) = 14.634 min.

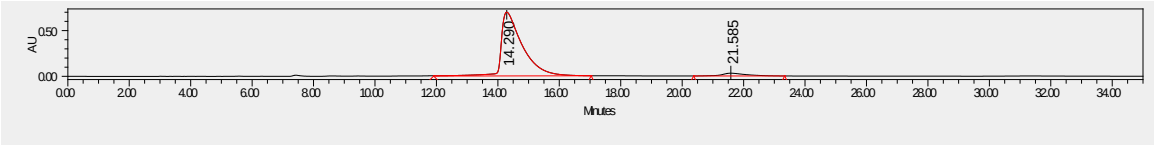
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.50 (m, 2H), 7.41 (m, 2H), 7.38 – 7.32 (m, 3H), 5.79 (d, *J* = 2.4 Hz, 1H), 4.52 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.58 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.52 – 3.46 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.19 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.91, 161.26, 143.79, 140.95, 138.91, 128.64, 127.72, 127.19, 126.97, 126.94, 125.42, 121.94, 120.39, 104.52, 52.83, 46.18, 37.12, 13.00, 11.06.

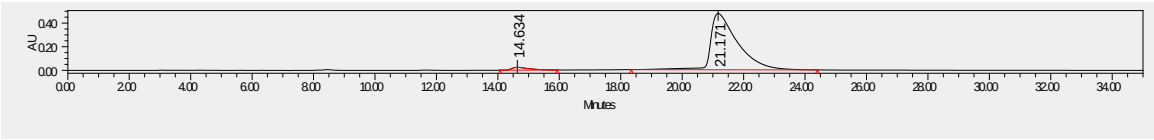
HRMS (ESI-TOF) calcd for $C_{23}H_{23}NO_3$ ([M+Na^+]) = 384.1576. Found 384.1581.



	Retention Time	Area	% Area
1	14.379	17941340	50.57
2	21.287	17536098	49.43

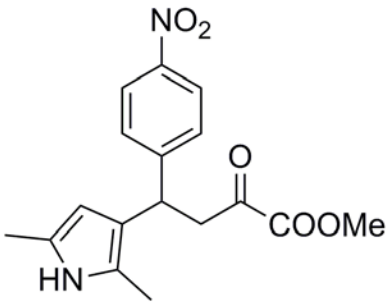


	Retention Time	Area	% Area
1	14.290	33126079	95.23
2	21.585	1657857	4.77



	Retention Time	Area	% Area
1	14.634	934597	3.12
2	21.171	29056793	96.88

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-4-(4-nitrophenyl)-2-oxobutanoate



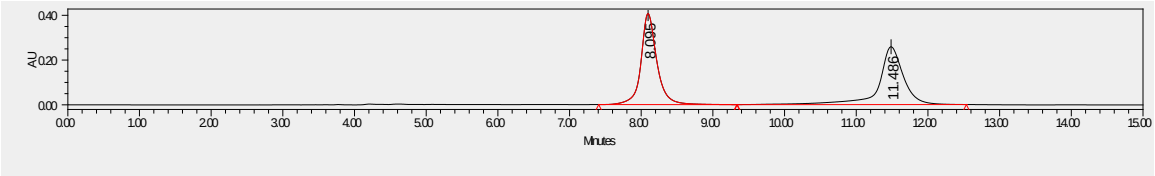
($C_{17}H_{18}N2O_5$) (+)-enantiomer (Table 2, entry 9): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 92% yield with 88% ee. $[\alpha]^{13.9}_D$ = +28.1 (c = 0.34, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 70:30, 1.0 mL/min, 254 nm, tr (major) = 8.321min, tr (minor) = 12.097 min.

(-)-enantiomer (Table 2, entry 9): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 89% yield with 92% ee. $[\alpha]^{14.2}_D$ = -33.4 (c = 0.40, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 70:30, 1.0 mL/min, 254 nm, tr (major) = 11.967 min, tr (minor) = 8.377 min.

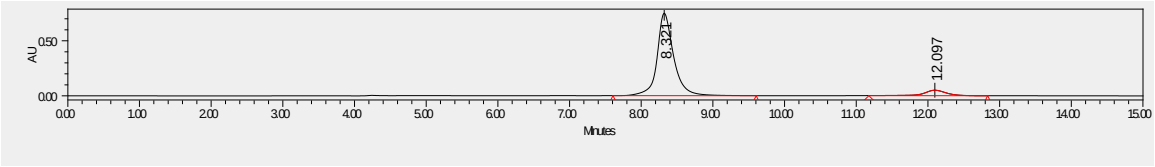
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 2H), 7.53 (s, 1H), 7.43 (m, 2H), 5.71 (d, *J* = 2.4 Hz, 1H), 4.55 (t, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 3.56 (dd, *J* = 18.0, 7.6 Hz, 1H), 3.47 (dd, *J* = 18.0, 7.6 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.02, 160.98, 152.39, 146.20, 128.25, 125.92, 123.76, 122.30, 119.05, 104.23, 53.02, 45.63, 12.92, 11.01.

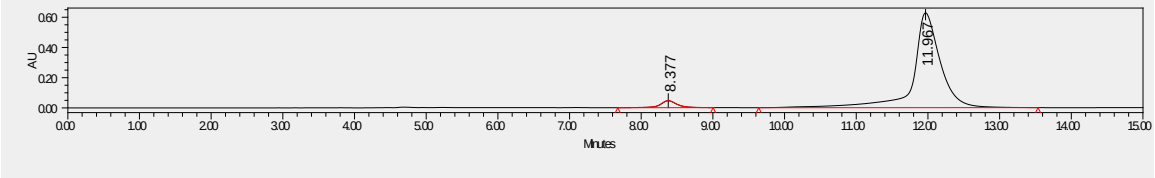
HRMS (ESI-TOF) calcd for $C_{17}H_{18}N2O_5$ ([M+Na^+]) = 353.1113. Found 353.1116.



	Retention Time	Area	% Area
1	8.095	6248698	50.22
2	11.486	6194093	49.78

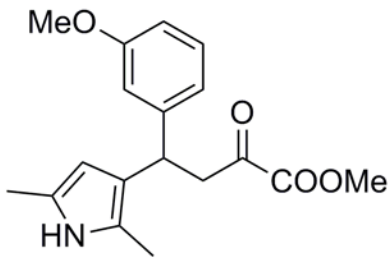


	Retention Time	Area	% Area
1	8.321	12037298	91.58
2	12.097	1107321	8.42



	Retention Time	Area	% Area
1	8.377	738161	4.29
2	11.967	16458506	95.71

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-4-(3-methoxyphenyl)-2-oxobutanoate



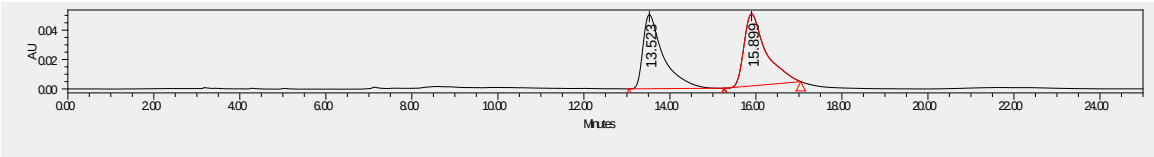
($C_{18}H_{21}NO_4$) (+)-enantiomer (Table 2, entry 12): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 82% yield with 93% ee. $[\alpha]^{13.3}_D$ = +13.5 (c = 0.36, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IC column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 13.473 min, tr (minor) = 15.961 min.

(-)-enantiomer (Table 2, entry 12): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 95% yield with 93% ee. $[\alpha]^{13.4}_D$ = -14.0 (c = 0.40, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IC column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 15.844 min, tr (minor) = 13.601 min.

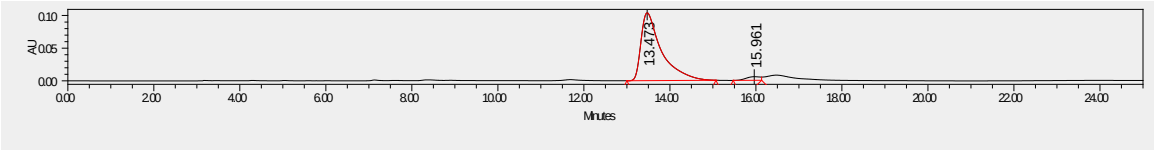
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.18 (m, 1H), 6.85 (m, 2H), 6.69 (m, 1H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.43 (t, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.52 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.42 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.16 (s, 3H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.87, 161.25, 159.53, 146.38, 129.39, 125.32, 121.90, 120.28, 119.74, 113.45, 111.01, 104.53, 55.07, 52.81, 46.16, 37.45, 12.98, 11.03.

HRMS (ESI-TOF) calcd for $C_{18}H_{21}NO_4$ ([M+Na^+]) = 338.1368. Found 338.1368.

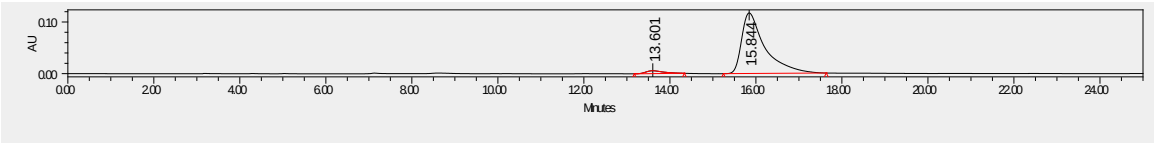


	Retention Time	Area	% Area
1	13.523	1659061	48.59
2	15.899	1755028	51.41



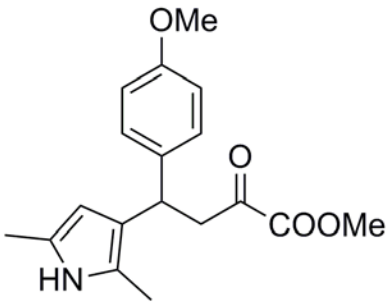
	Retention Time	Area	% Area
1	13.473	3422616	96.46

2	15.961	125538	3.54



	Retention Time	Area	% Area
1	13.601	156757	3.44
2	15.844	4396365	96.56

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-4-(4-methoxyphenyl)-2-oxobutanoate



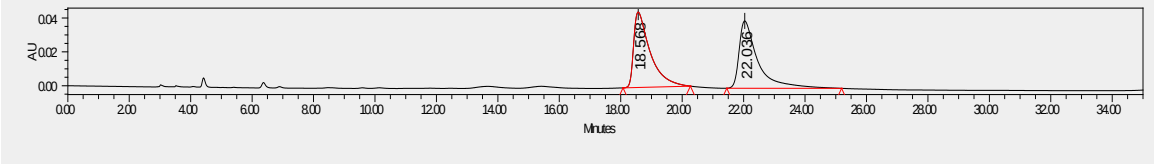
($C_{18}H_{21}NO_4$) (+)-enantiomer (Table 2, entry 13): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 81% yield with 96% ee. $[\alpha]^{12.5}_D$ = +9.6 (c = 0.42, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 18.516 min, tr (minor) = 22.293 min.

(-)-enantiomer (Table 2, entry 13): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 78% yield with 94% ee. $[\alpha]^{12.7}_D$ = -11.1 (c = 0.35, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 21.924min, tr (minor) = 18.889 min.

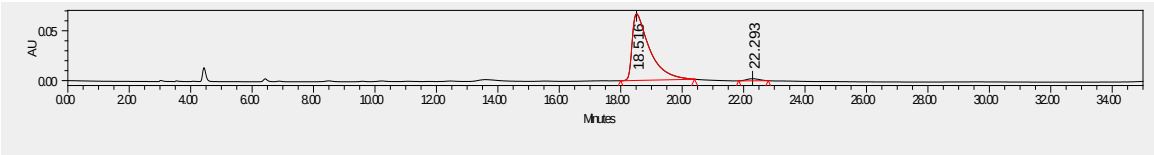
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.18 (m, 2H), 6.79 (m, 2H), 5.72 (d, *J* = 2.0 Hz, 1H), 4.40 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.48 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.40 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.07, 161.30, 157.75, 136.89, 128.26, 125.26, 121.73, 120.81, 113.75, 104.53, 55.17, 52.80, 46.42, 36.70, 12.99, 11.03.

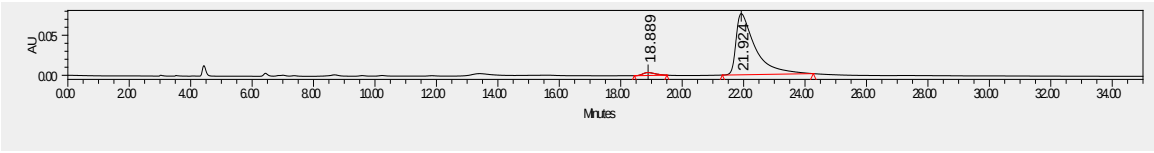
HRMS (ESI-TOF) calcd for $C_{18}H_{21}NO_4$ ([M+Na^+]) = 338.1368. Found 338.1367.



	Retention Time	Area	% Area
1	18.568	1661562	49.58
2	22.036	1689744	50.42

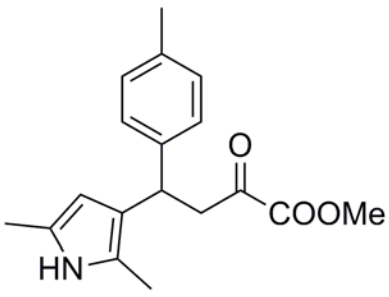


	Retention Time	Area	% Area
1	18.516	2636943	97.80
2	22.293	59268	2.20



	Retention Time	Area	% Area
1	18.889	102380	2.99
2	21.924	3325034	97.01

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-(p-tolyl)butanoate



($C_{18}H_{21}NO_3$) (+)-enantiomer (Table 2, entry 10): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 90% yield with 93% ee. $[\alpha]^{16.0}_{D}$ = +17.1 (c = 0.47, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr

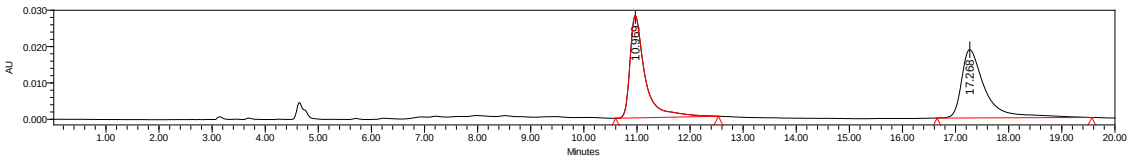
(major) = 11.142 min, tr (minor) = 17.824 min.

(-)-enantiomer (Table 2, entry 10): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 93% yield with 93% ee. $[\alpha]^{16.1}_{D}$ = -17.1 (c = 0.41, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 17.625 min, tr (minor) = 11.250 min.

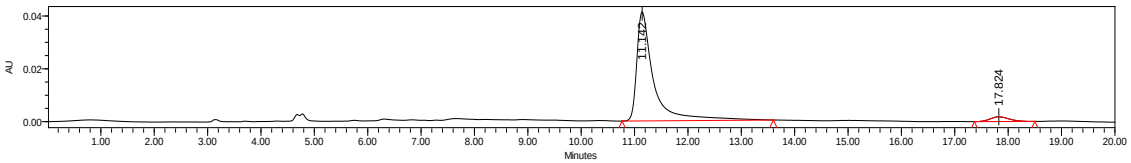
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.17 (m, 2H), 7.07 (m, 2H), 5.72 (d, *J* = 2.4 Hz, 1H), 4.42 (t, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.51 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.41 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.28 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.05, 161.29, 141.67, 135.47, 129.08, 127.15, 125.25, 121.77, 120.67, 104.55, 52.78, 46.27, 37.07, 20.92, 12.99, 11.02.

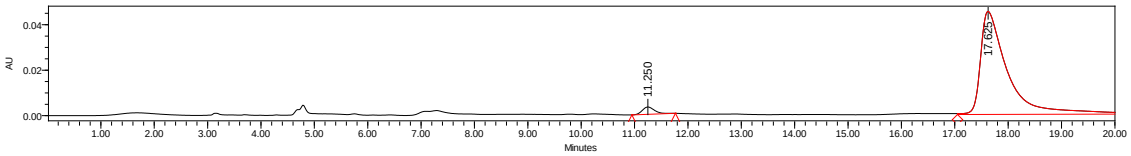
HRMS (ESI-TOF) calcd for $C_{18}H_{21}NO_3$ ([M+Na^+]) = 322.1419. Found 322.1420.



	Retention Time	Area	% Area
1	10.969	556776	49.01
2	17.268	579364	50.99

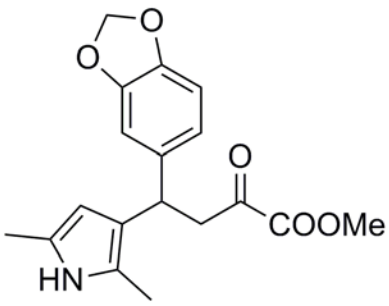


	Retention Time	Area	% Area
1	11.142	903584	95.31
2	17.824	44477	4.69



	Retention Time	Area	% Area
1	11.250	51614	3.11
2	17.625	1606023	96.89

Methyl 4-(benzo[d][1,3]dioxol-5-yl)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate



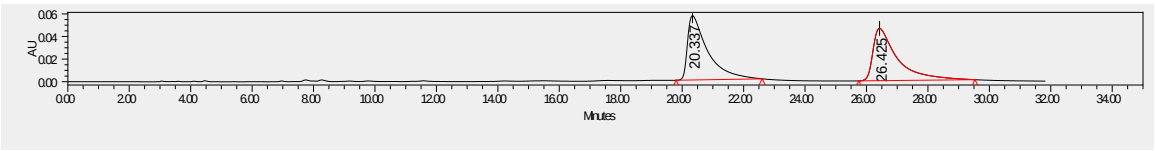
($C_{18}H_{19}NO_5$) (+)-enantiomer (Table 2, entry 20): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 85% yield with 92% ee. $[\alpha]^{14.3}_D$ = +12.5 (c = 0.24, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 20.444 min, tr (minor) = 26.811 min.

(-)-enantiomer (Table 2, entry 20): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 90% yield with 95% ee. $[\alpha]^{14.5}_D$ = -14.7 (c = 0.41, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 26.291 min, tr (minor) = 20.702 min.

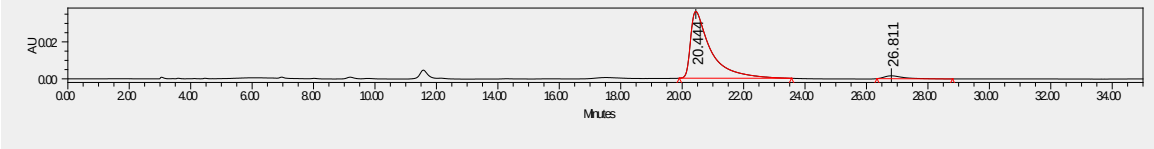
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 6.77 – 6.68 (m, 3H), 5.88 (d, *J* = 2.4 Hz, 2H), 5.72 (d, *J* = 2.0 Hz, 1H), 4.38 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.47 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.41 – 3.35 (dd, *J* = 17.2, 7.6 Hz, 1H), 2.17 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.83, 161.23, 147.56, 145.67, 138.78, 125.35, 121.80, 120.56, 120.11, 108.02, 107.96, 104.40, 100.75, 52.83, 46.38, 37.17, 12.97, 11.01.

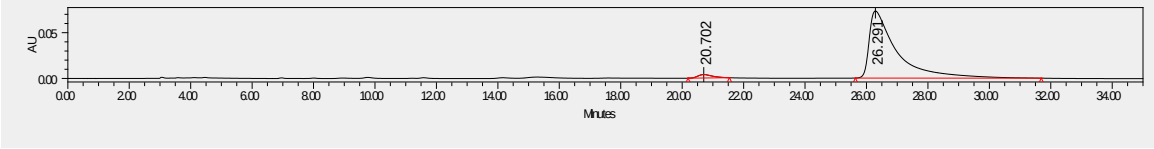
HRMS (ESI-TOF) calcd for $C_{18}H_{19}NO_5$ ([M+Na^+]) = 352.1161. Found 352.1163.



	Retention Time	Area	% Area
1	20.337	2592161	50.34
2	26.425	2556911	49.66

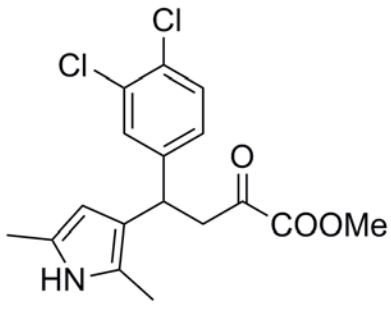


	Retention Time	Area	% Area
1	20.444	1659421	96.11
2	26.811	67108	3.89



	Retention Time	Area	% Area
1	20.702	125163	2.67
2	26.291	4561159	97.33

Methyl 4-(3,4-dichlorophenyl)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate



($C_{17}H_{17}Cl_2NO_3$) (+)-enantiomer (Table 2, entry 14): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 90% yield with 91% ee. $[\alpha]^{20.2}_D$ = +17.5 (c = 0.54, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 7.415min, tr (minor) = 12.370 min.

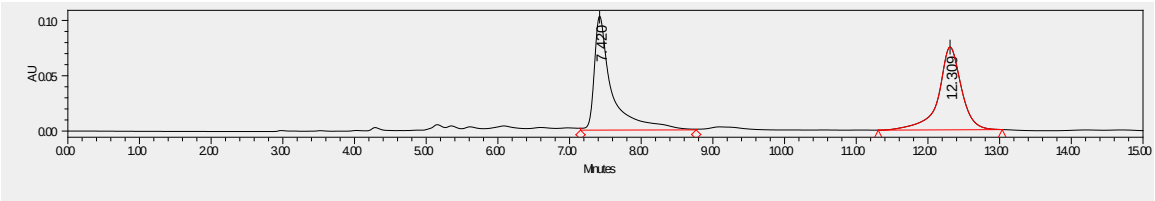
(-)-enantiomer (Table 2, entry 14): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 92% yield with 92% ee. $[\alpha]^{20.4}_D$ = -19.3 (c = 0.43, CH_2Cl_2); The ee was

determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 12.238 min, tr (minor) = 7.437 min.

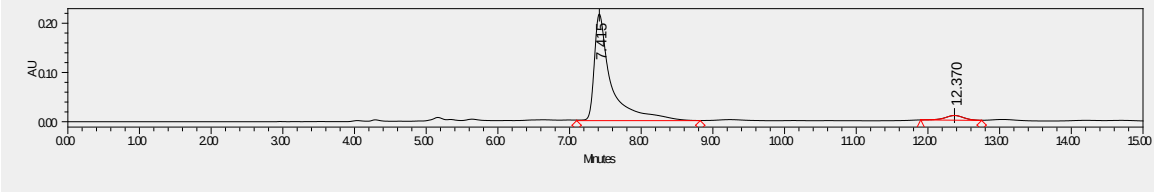
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.34 (m, 1H), 7.31 (m, 1H), 7.11 (m, 1H), 5.69 (d, *J* = 2.0 Hz, 1H), 4.40 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.50 (dd, *J* = 17.6, 7.6 Hz, 1H), 3.39 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.22, 161.06, 145.11, 132.24, 130.29, 129.93, 129.42, 126.88, 125.72, 122.13, 119.41, 104.30, 52.96, 45.90, 36.55, 12.95, 11.03.

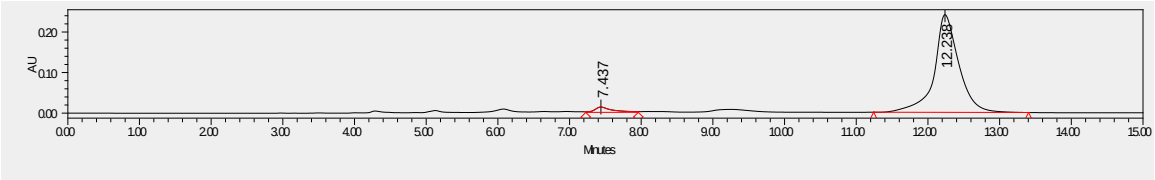
HRMS (ESI-TOF) calcd for $C_{17}H_{17}Cl_2NO_3$ ([M+Na^+]) = 376.0483. Found 376.0486.



	Retention Time	Area	% Area
1	7.420	1768260	51.62
2	12.309	1657506	48.38

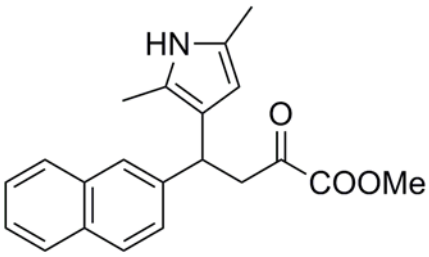


	Retention Time	Area	% Area
1	7.415	3565636	95.30
2	12.370	175933	4.70



	Retention Time	Area	% Area
1	7.437	228929	3.83
2	12.238	5742041	96.17

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-4-(naphthalen-2-yl)-2-oxobutanoate



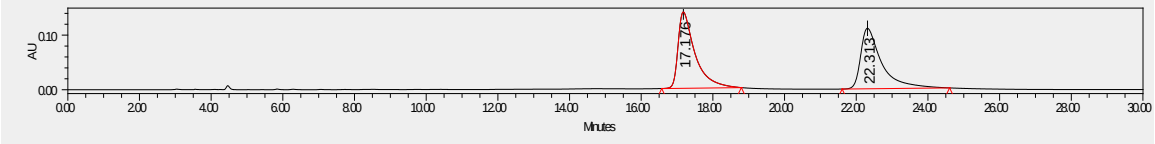
($C_{21}H_{21}NO_3$) (+)-enantiomer (Table 2, entry 16): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 89% yield with 93% ee. $[\alpha]^{12.8}_D$ = +31.3 (c = 0.48, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 17.129 min, tr (minor) = 22.549 min.

(-)-enantiomer (Table 2, entry 16): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 89% yield with 94% ee. $[\alpha]^{13.0}_D$ = -39.8 (c = 0.37, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 22.165 min, tr (minor) = 17.383 min.

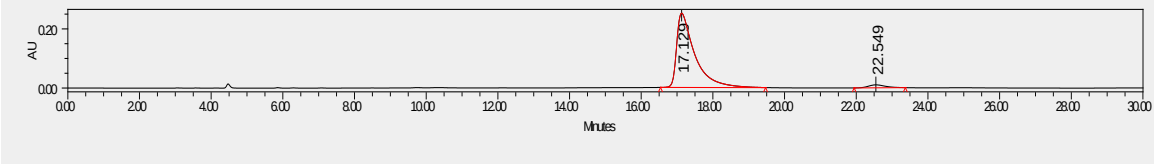
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 4H), 7.46 – 7.38 (m, 4H), 5.79 (d, *J* = 2.4 Hz, 1H), 4.64 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.62 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.58 – 3.52 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.18 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.90, 161.27, 142.09, 133.42, 132.05, 128.14, 127.70, 127.47, 126.30, 125.83, 125.33, 125.28, 125.20, 122.07, 120.33, 104.73, 52.82, 45.99, 37.59, 12.99, 11.09.

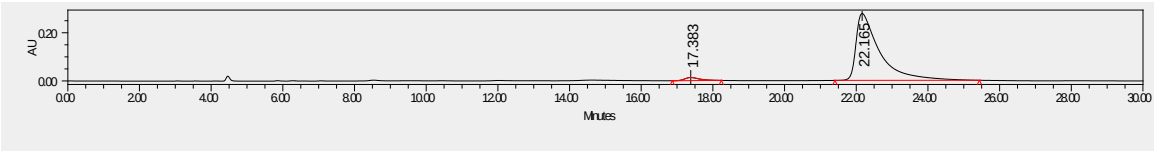
HRMS (ESI-TOF) calcd for $C_{21}H_{21}NO_3$ ([M+Na^+]) = 358.1419. Found 358.1416.



	Retention Time	Area	% Area
1	17.176	4597445	50.47
2	22.313	4511146	49.53

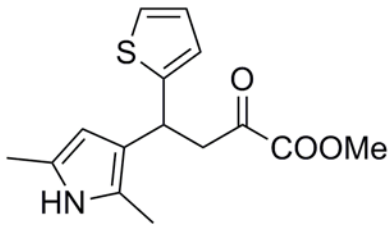


	Retention Time	Area	% Area
1	17.129	8800828	96.44
2	22.549	325283	3.56



	Retention Time	Area	% Area
1	17.383	371108	2.83
2	22.165	12753263	97.17

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-(thiophen-2-yl)butanoate



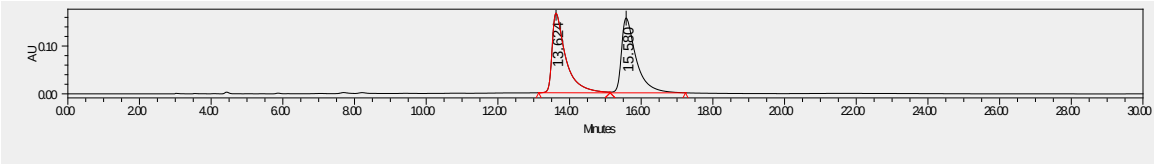
($C_{15}H_{17}NO_3S$) (+)-enantiomer (Table 2, entry 17): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 84% yield with 92% ee. $[\alpha]^{12.7}_D$ = +11.6 (c = 0.34, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 13.507 min, tr (minor) = 15.695 min.

(-)-enantiomer (Table 2, entry 17): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 95% yield with 93% ee. $[\alpha]^{12.7}_D$ = -13.4 (c = 0.31, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 15.426 min, tr (minor) = 13.746 min.

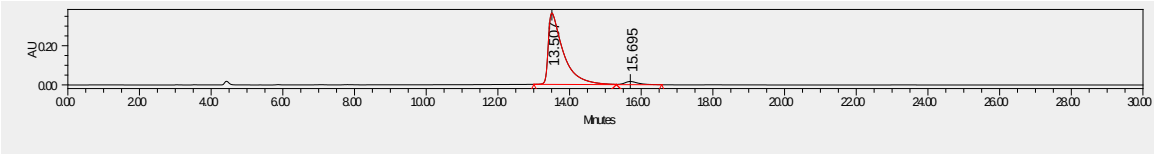
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.09 (m, 1H), 6.92 – 6.78 (m, 2H), 5.74 (d, *J* = 2.0 Hz, 1H), 4.72 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.55 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.48 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.17 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.33, 161.08, 149.36, 126.49, 125.50, 123.39, 123.33, 122.13, 120.27, 104.39, 52.88, 47.22, 32.79, 13.01, 10.97.

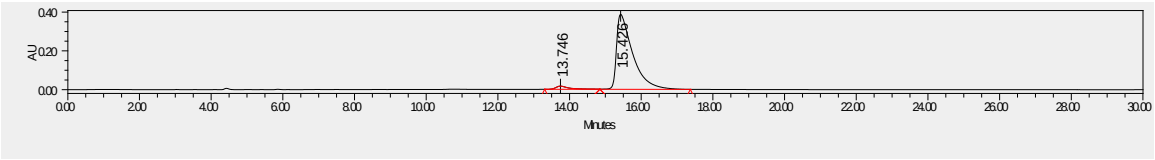
HRMS (ESI-TOF) calcd for $C_{15}H_{17}NO_3S$ ([M+Na^+]) = 314.0826. Found 314.0824.



	Retention Time	Area	% Area
1	13.624	4425001	49.95
2	15.580	4434472	50.05

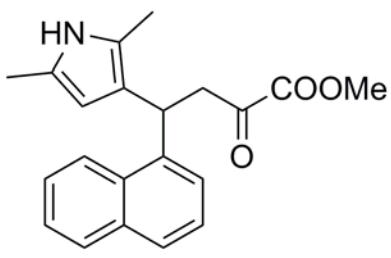


	Retention Time	Area	% Area
1	13.507	10552675	96.16
2	15.695	421793	3.84



	Retention Time	Area	% Area
1	13.746	447255	3.57
2	15.426	12084271	96.43

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-4-(naphthalen-1-yl)-2-oxobutanoate



($C_{21}H_{21}NO_3$) (+)-enantiomer (Table 2, entry 15): Prepared according to general procedure A. After 24 h, the crude material

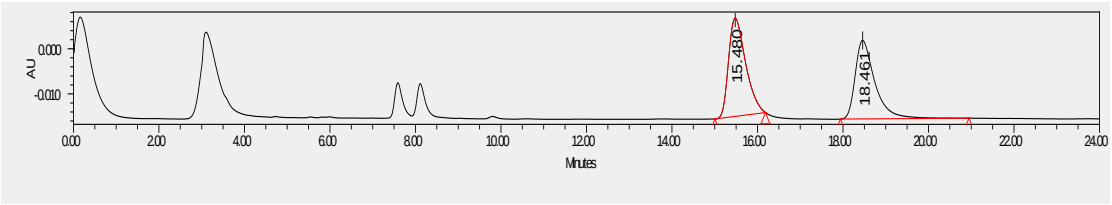
was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 79% yield with 95% ee. $[\alpha]^{14.5}_{D}$ = -27.9 (c = 0.36, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 15.394 min, tr (minor) = 18.506 min.

(-)-enantiomer (Table 2, entry 15): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 80% yield with 91% ee. $[\alpha]^{14.9}_{D}$ = +22.58 (c = 0.33, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 18.333 min, tr (minor) = 15.510 min.

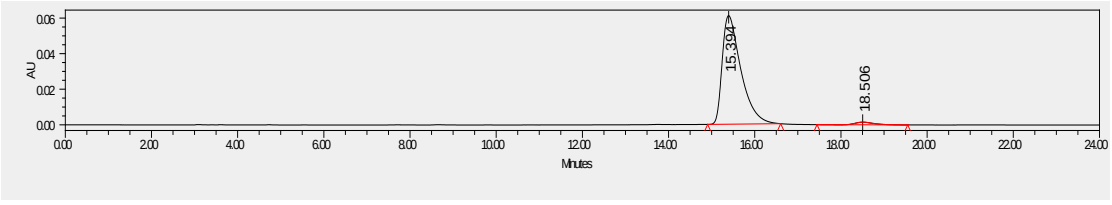
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (m, 1H), 7.83 (m, 1H), 7.68 (m, 1H), 7.56 – 7.31 (m, 5H), 5.73 (m, 1H), 5.30 (dd, *J* = 9.6, 5.2 Hz, 1H), 3.78 (s, 3H), 3.67 (dd, *J* = 17.2, 9.6 Hz, 1H), 3.43 (dd, *J* = 17.2, 5.2 Hz, 1H), 2.13 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.19, 161.51, 140.69, 134.15, 131.29, 129.11, 127.10, 126.29, 125.70, 125.60, 125.46, 124.64, 123.41, 122.18, 120.06, 105.82, 53.06, 46.64, 33.17, 13.26, 11.48.

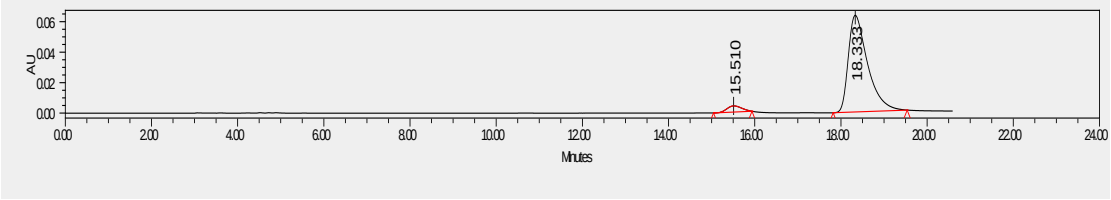
HRMS (ESI-TOF) calcd for $C_{21}H_{21}NO_3$ ([M+H$^+$]) = 336.1600. Found 336.1602.



	Retention Time	Area	% Area
1	15.480	602322	51.99
2	18.461	556311	48.01

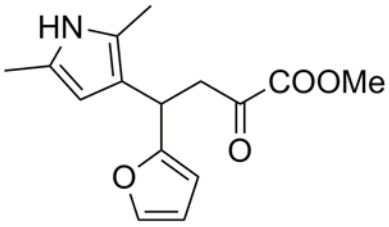


	Retention Time	Area	% Area
1	15.394	1835262	97.62
2	18.506	44728	2.38



	Retention Time	Area	% Area
1	15.510	96452	4.68
2	18.333	1966568	95.32

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-4-(furan-2-yl)-2-oxobutanoate



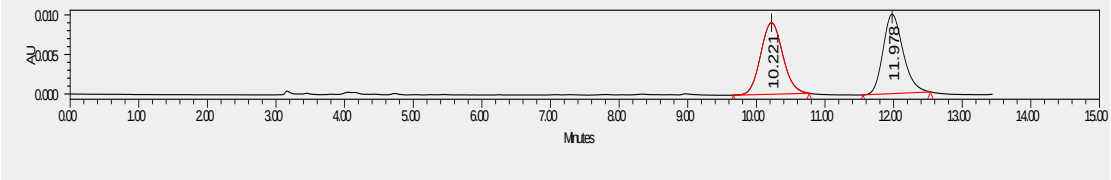
($C_{15}H_{17}NO_3S$) (+)-enantiomer (Table 2, entry 18): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 94% yield with 92% ee. $[\alpha]^{13.8}_D$ = +21.6 (c = 0.50, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IC column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 10.226 min, tr (minor) = 12.012 min.

(-)-enantiomer (Table 2, entry 18): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 95% yield with 96% ee. $[\alpha]^{14.1}_D$ = -28.1 (c = 0.47, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IC column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 11.954 min, tr (minor) = 10.212 min.

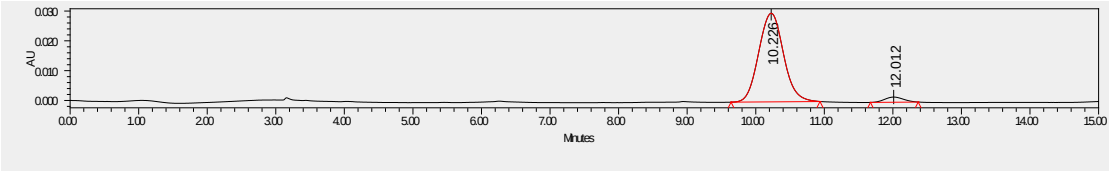
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.26 (s, 1H), 6.22 (m, 1H), 5.97 (m, 1H), 5.67 (m, 1H), 4.49 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.48 (dd, *J* = 17.2, 6.8 Hz, 1H), 3.36 (dd, *J* = 17.2, 8.0 Hz, 1H), 2.15 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.59, 161.29, 157.41, 141.39, 125.68, 122.63, 118.16, 110.22, 105.21, 105.05, 53.11, 44.77, 31.69, 13.21, 11.16.

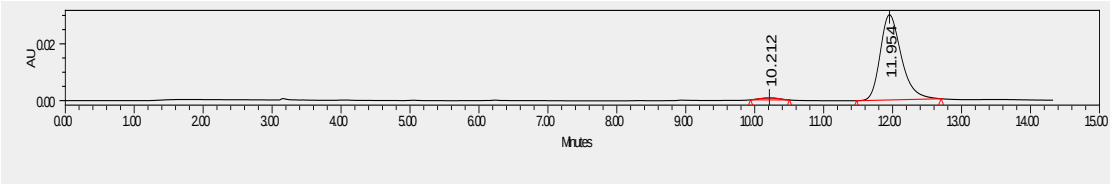
HRMS (ESI-TOF) calcd for $C_{15}H_{17}NO_3S$ ([M+Na^+]) = 298.1055. Found 298.1060.



	Retention Time	Area	% Area
1	10.221	202988	49.95
2	11.978	203397	50.05

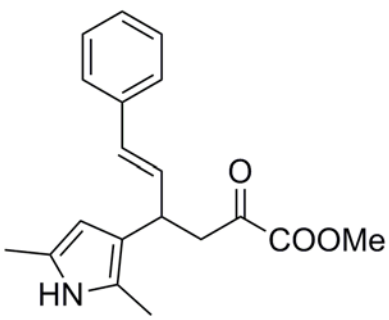


	Retention Time	Area	% Area
1	10.226	745437	95.77
2	12.012	32937	4.23



	Retention Time	Area	% Area
1	10.212	13473	2.07
2	11.954	638112	97.93

Methyl (E)-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-6-phenylhex-5-enoate



($C_{19}H_{21}NO_3$) (+)-enantiomer (Table 2, entry 19): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil

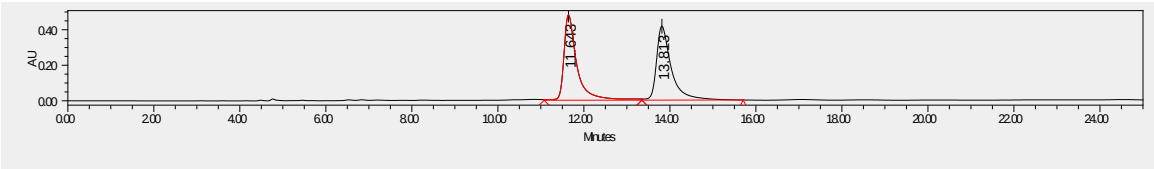
in 68% yield with 94% ee. $[\alpha]^{13.6}_{D}$ = +29.0 (c = 0.26, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 11.604 min, tr (minor) = 13.871min.

(-)-enantiomer (Table 2, entry 19): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 95% yield with 91% ee. $[\alpha]^{13.7}_{D}$ = -28.0 (c = 0.40, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 13.765 min, tr (minor) = 11.691 min.

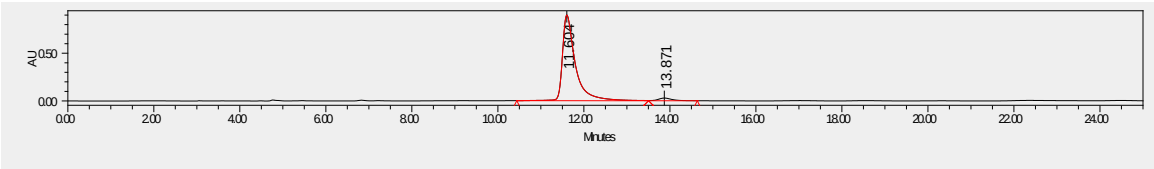
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.30 (m, 3H), 7.17 (m, 2H), 6.38 (m, 1H), 6.26 (m, 1H), 5.71 (d, *J* = 2.0 Hz, 1H), 3.99 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.79 (s, 3H), 3.28 (dd, *J* = 14.8, 5.6 Hz, 1H), 3.23 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.18 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.15, 161.33, 137.25, 132.53, 128.88, 128.35, 127.03, 126.18, 125.50, 122.09, 119.19, 104.34, 52.83, 45.31, 35.53, 12.95, 11.06.

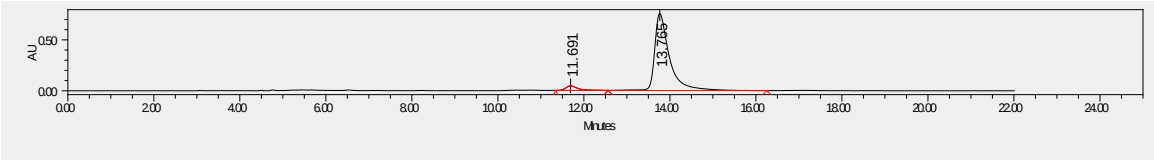
HRMS (ESI-TOF) calcd for $C_{19}H_{21}NO_3$ ([M+Na^+]) = 334.1419. Found 334.1421.



	Retention Time	Area	% Area
1	11.643	10101541	50.50
2	13.813	9899711	49.50

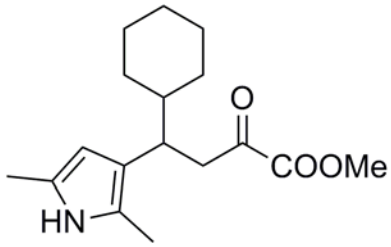


	Retention Time	Area	% Area
1	11.604	18688624	96.89
2	13.871	599547	3.11



	Retention Time	Area	% Area
1	11.691	895677	4.71
2	13.765	18115863	95.29

Methyl 4-cyclohexyl-4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxobutanoate

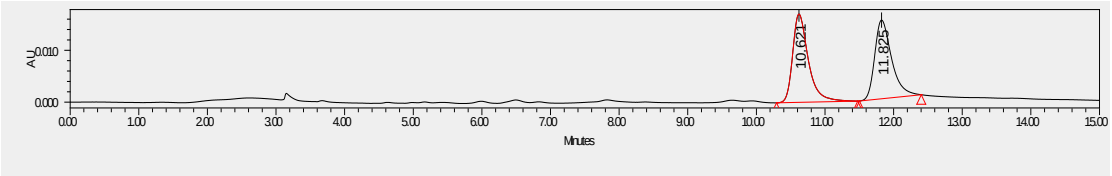


($C_{17}H_{25}NO_3$) (-)-enantiomer (Table 2, entry 21): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 78% yield with 86% ee. $[\alpha]^{16.5}_{D}$ = -1.5 (c = 0.32, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 95:5, 1.0 mL/min, 254 nm, tr (major) = 10.609 min, tr (minor) = 11.861 min.

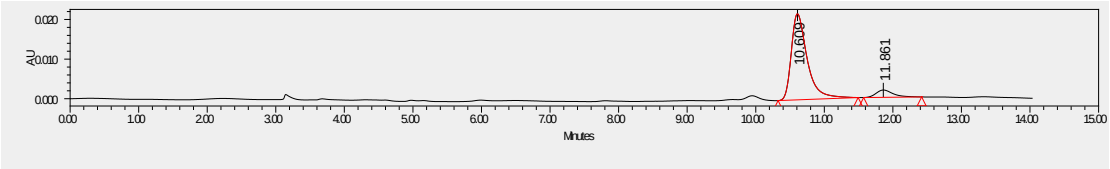
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 5.54 (d, *J* = 2.0 Hz, 1H), 3.74 (s, 3H), 3.08 – 3.03 (m, 2H), 2.86 (dd, *J* = 14.2, 8.0 Hz, 1H), 2.15 (s, 3H), 2.07 (s, 3H), 1.78 – 1.56 (m, 7H), 1.22 – 1.03 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.81, 161.55, 125.00, 122.50, 119.45, 104.78, 52.58, 43.53, 43.38, 37.91, 31.26, 30.34, 26.42, 26.39, 13.03, 11.03.

HRMS (ESI-TOF) calcd for $C_{17}H_{25}NO_3$ ([M+Na^+]) = 314.1732. Found 314.1731.

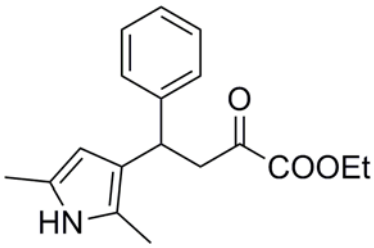


	Retention Time	Area	% Area
1	10.621	270757	51.09
2	11.825	259168	48.91



	Retention Time	Area	% Area
1	10.609	350743	91.71
2	11.861	31724	8.29

Ethyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-phenylbutanoate



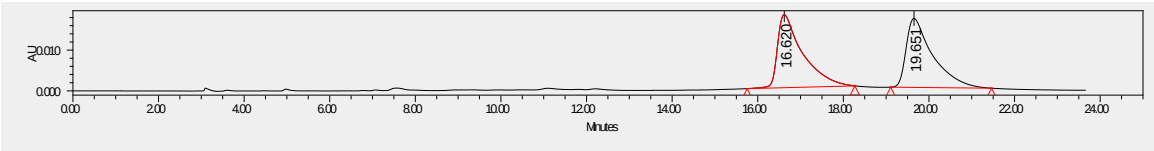
($C_{18}H_{21}NO_3$) (+)-enantiomer (Table 2, entry 2): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 84% yield with 95% ee. $[\alpha]^{16.1}_{D}$ = +10.7 (c = 0.40, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 16.362 min, tr (minor) = 19.613 min.

(-)-enantiomer (Table 2, entry 2): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 85% yield with 96% ee. $[\alpha]^{16.2}_{D}$ = -12.1 (c = 0.34, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 19.369 min, tr (minor) = 16.647min.

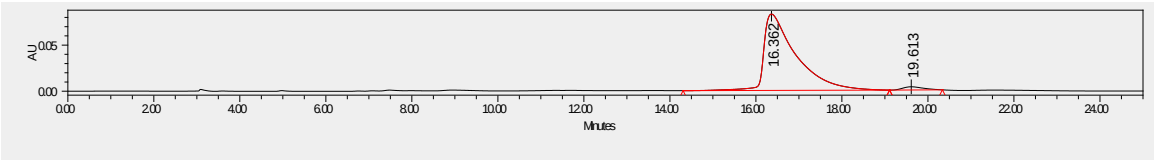
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.28 (m, 2H), 7.23 (m, 2H), 7.15 – 7.11 (m, 1H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.44 (t, *J* = 7.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.51 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.41 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.41, 160.91, 144.73, 128.41, 127.35, 126.02, 125.26, 121.89, 120.52, 104.63, 62.26, 46.16, 37.56, 13.92, 12.99, 11.04.

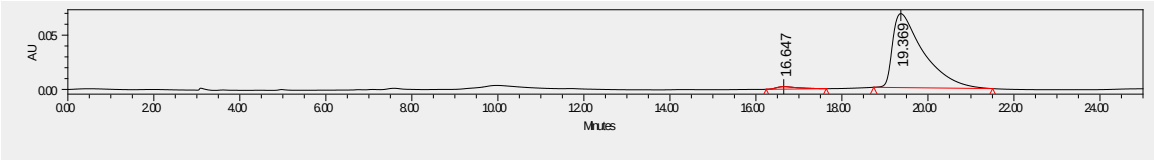
HRMS (ESI-TOF) calcd for $C_{18}H_{21}NO_3$ ([M+Na^+]) = 322.1419. Found 322.1417.



	Retention Time	Area	% Area
1	16.620	731150	50.14
2	19.651	726971	49.86

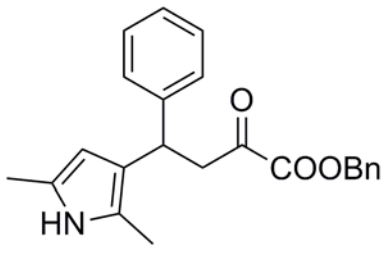


	Retention Time	Area	% Area
1	16.362	4292365	97.35
2	19.613	117017	2.65



	Retention Time	Area	% Area
1	16.647	78502	2.26
2	19.369	3400269	97.74

Benzyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-phenylbutanoate



($C_{23}H_{23}NO_3$) (+)-enantiomer (Table 2, entry 3): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 91% yield with 92% ee. $[\alpha]^{19.9}_D$ = +7.4 (c = 0.47, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 25.775 min, tr (minor) = 29.644 min.

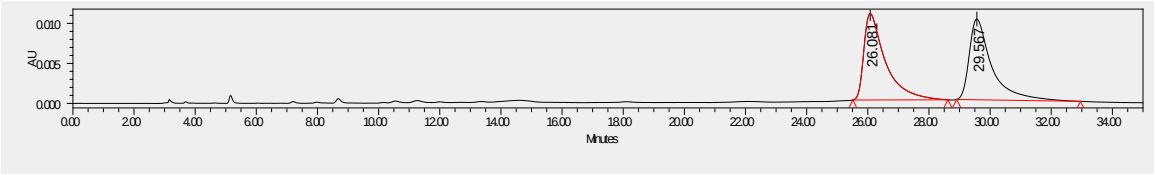
(-)-enantiomer (Table 2, entry 3): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1)

to afford the little yellow oil in 89% yield with 97% ee. $[\alpha]^{20.0}_{D}$ = -6.5 (c = 0.44, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 29.302 min, tr (minor) = 26.230min.

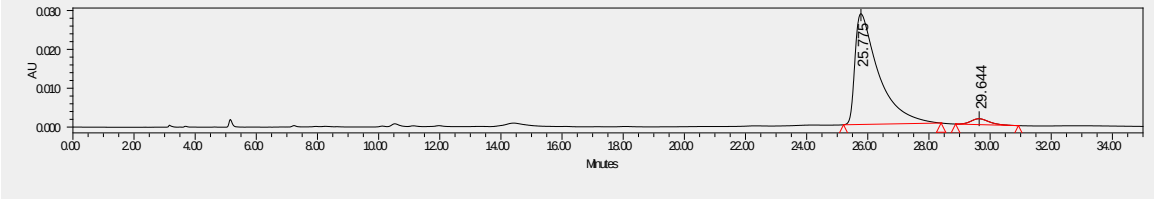
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 6H), 7.25 (m, 2H), 7.15 (m, 1H), 5.73 (d, *J* = 2.4 Hz, 1H), 5.21 (s, 2H), 4.48 – 4.40 (t, *J* = 7.6 Hz, 1H), 3.53 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.45 – 3.39 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.15 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.04, 160.68, 144.64, 134.51, 128.66, 128.61, 128.55, 128.41, 127.32, 126.04, 125.28, 121.88, 120.42, 104.63, 67.72, 46.31, 37.59, 12.98, 11.00.

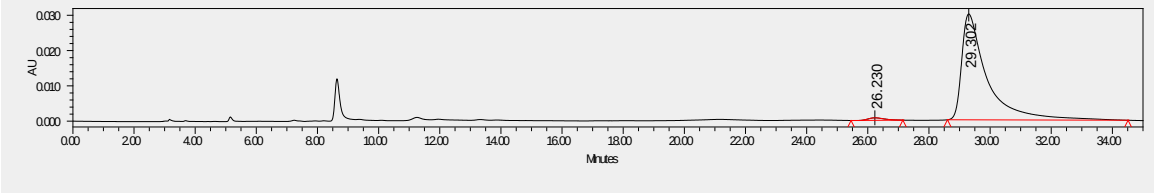
HRMS (ESI-TOF) calcd for $C_{23}H_{23}NO_3$ ([M+Na^+]) = 384.1575. Found 384.1576.



	Retention Time	Area	% Area
1	26.081	528669	50.55
2	29.567	517105	49.45

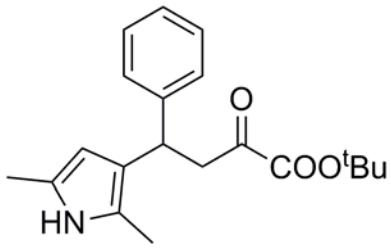


	Retention Time	Area	% Area
1	25.775	1527489	96.02
2	29.644	63376	3.98



	Retention Time	Area	% Area
1	26.230	26198	1.49
2	29.302	1731399	98.51

tert-Butyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-phenylbutanoate



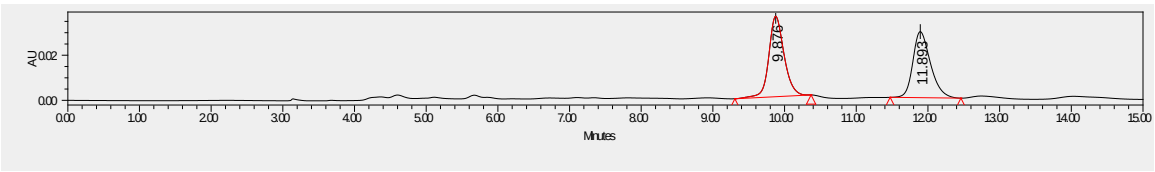
($C_{20}H_{25}NO_3$) (+)-enantiomer (Table 2, entry 4): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 89% yield with 96% ee. $[\alpha]^{16.8}_D$ = +6.5 (c = 0.47, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 11.815 min, tr (minor) = 9.908 min.

(-)-enantiomer (Table 2, entry 4): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 89% yield with 93% ee. $[\alpha]^{17.0}_D$ = -11.0 (c = 0.48, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 9.845 min, tr (minor) = 11.921 min.

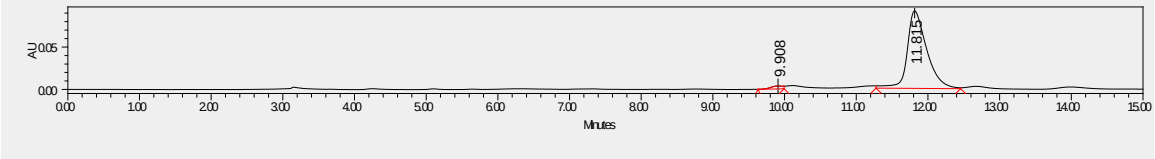
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.28 (m, 3H), 7.24 – 7.19 (m, 1H), 7.15 – 7.11 (m, 1H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.42 (t, *J* = 7.6 Hz, 1H), 3.46 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.35 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.50, 160.35, 144.90, 128.38, 127.36, 125.96, 125.17, 121.81, 120.63, 104.67, 83.64, 45.96, 37.75, 27.69, 13.00, 11.04.

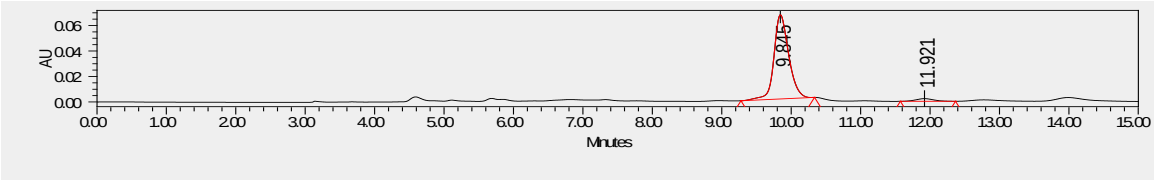
HRMS (ESI-TOF) calcd for $C_{20}H_{25}NO_3$ ([M+Na$^+$]) = 350.1732. Found 350.1732.



	Retention Time	Area	% Area
1	9.876	526219	51.26
2	11.893	500410	48.74

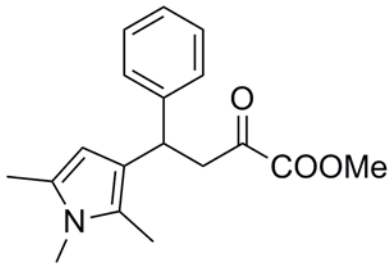


	Retention Time	Area	% Area
1	9.908	39671	2.24
2	11.815	1728145	97.76



	Retention Time	Area	% Area
1	9.845	974370	96.36
2	11.921	36827	3.64

Methyl 2-oxo-4-phenyl-4-(1,2,5-trimethyl-1H-pyrrol-3-yl)butanoate



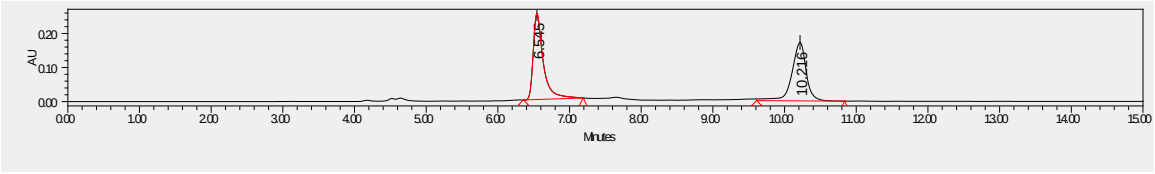
($C_{18}H_{21}NO_3$) (+)-enantiomer : Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 6:1) to afford the little yellow oil in 85% yield with 90% ee. $[\alpha]^{22.5}_D$ = +6.8 (c = 0.51, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 10.630 min, tr (minor) = 6.658 min.

(-)-enantiomer : Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 6:1) to afford the little yellow oil in 84% yield with 93% ee. $[\alpha]^{22.4}_D$ = -7.4 (c = 0.51, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IB column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 6.609 min, tr (minor) = 10.410 min.

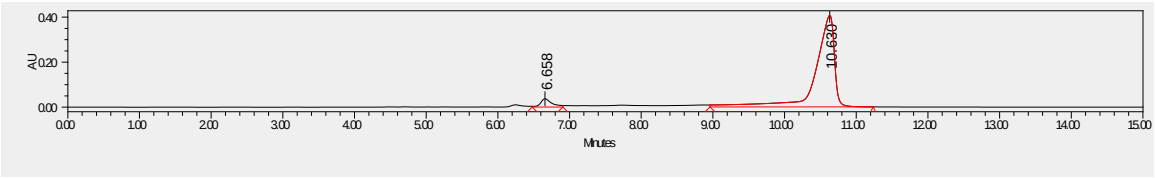
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 3H), 7.24 (m, 1H), 7.16 – 7.11 (m, 1H), 5.76 (s, 1H), 4.49 (t, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.52 (dd, *J* = 16.8, 8.0 Hz, 1H), 3.47 – 3.41 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.15 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.95, 161.31, 144.88, 128.43, 127.36, 127.08, 126.01, 123.72, 119.60, 103.63, 52.77, 46.39, 37.75, 30.08, 12.46, 10.10.

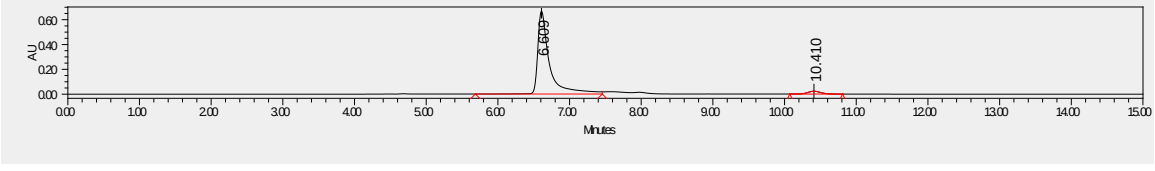
HRMS (ESI-TOF) calcd for $C_{18}H_{21}NO_3$ ([M+Na^+]) = 322.1419. Found 322.1416.



	Retention Time	Area	% Area
1	6.545	2452157	50.75
2	10.216	2380053	49.25



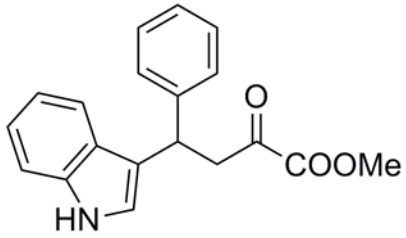
	Retention Time	Area	% Area
1	6.658	402493	5.22
2	10.630	7304005	94.78



	Retention Time	Area	% Area
1	6.609	7587546	96.35

2	10.410	287770	3.65

Methyl 4-(1H-indol-3-yl)-2-oxo-4-phenylbutanoate



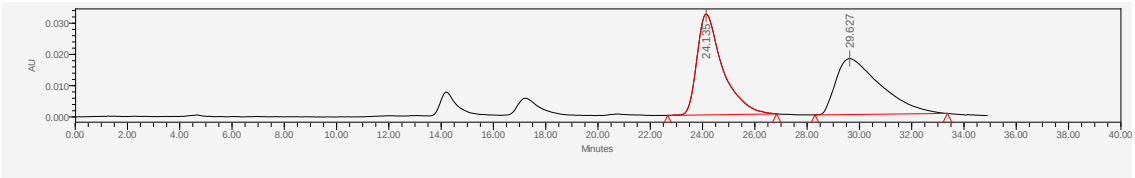
($C_{19}H_{17}NO_3$) (*R*)-enantiomer (Scheme 1, **5a**): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 93% yield with 92% ee. $[\alpha]^{24.4}_D$ = -39.3 (c = 0.57, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 80:20, 0.7 mL/min, 254 nm, tr (major) = 23.992 min, tr (minor) = 30.440 min.

(*S*)-enantiomer (Scheme 1, **5a**): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 83% yield with 72% ee. $[\alpha]^{24.5}_D$ = +34.3 (c = 0.51, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel OD-H column (hexane/2-propanol 80:20, 0.7 mL/min, 254 nm, tr (major) = 29.888 min, tr (minor) = 24.530 min.

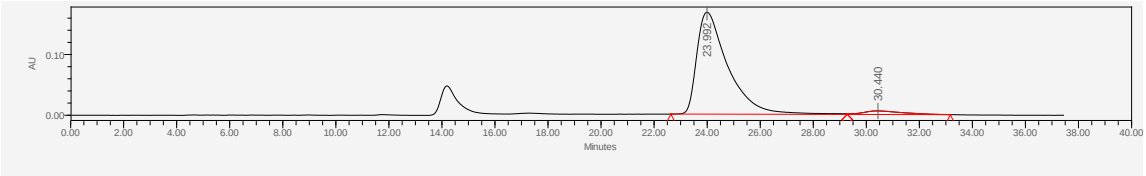
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 6.0 Hz, 3H), 7.28 (m, 2H), 7.17 (dd, *J* = 16.0, 8.0 Hz, 2H), 7.03 (m, 2H), 4.93 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.70 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.61 (dd, *J* = 16.8, 8.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.60, 161.26, 143.13, 136.51, 128.51, 127.74, 126.57, 126.36, 122.27, 121.48, 119.50, 119.37, 118.28, 111.12, 52.91, 45.61, 37.69.

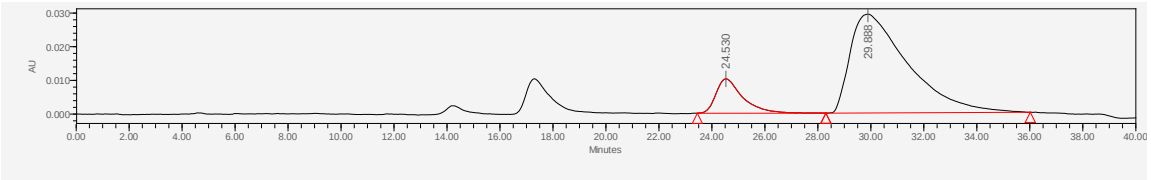
HRMS (ESI-TOF) calcd for $C_{19}H_{17}NO_3$ ([M+Na^+]) = 330.1106. Found 330.1101.



	Retention Time	Area	% Area
1	24.135	2196613	50.80
2	29.627	2127324	49.20

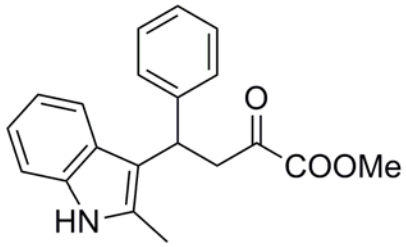


	Retention Time	Area	% Area
1	23.992	13708421	95.77
2	30.440	604903	4.23



	Retention Time	Area	% Area
1	24.530	716726	13.91
2	29.888	4437172	86.09

Methyl 4-(2-methyl-1H-indol-3-yl)-2-oxo-4-phenylbutanoate



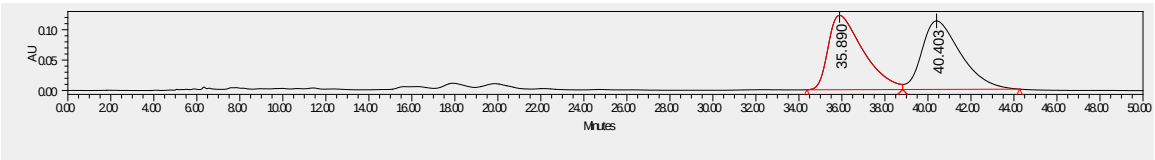
($C_{20}H_{19}NO_3$) (+)-enantiomer (Scheme 1, **5b**): Prepared according to general procedure A. After 48h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 95% yield with 93% ee.$[\alpha]^{22.3}D$ = +37.1 (c = 0.61, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel OJ-H column (hexane/2-propanol 70:30, 0.7 mL/min, 254 nm, tr (major) = 34.441 min, tr (minor) = 40.123 min.

(-)-enantiomer (Scheme 1, **5b**): Prepared according to general procedure B. After 48 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 99% yield with 94% ee.$[\alpha]^{22.3}{}_D$ = -35.1 (c = 0.64, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel OJ-H column (hexane/2-propanol 70:30, 0.7 mL/min, 220 nm, tr (major) = 38.365 min, tr (minor) = 35.456 min.

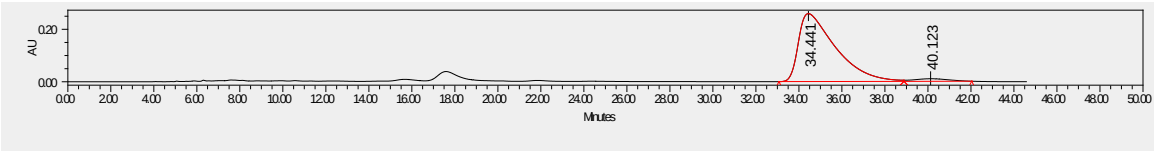
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.34 (m, 2H), 7.28 (m, 2H), 7.24 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.08 (m, 1H), 7.01 (m, 1H), 4.92 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.93 (dd, *J* = 16.8, 9.2 Hz, 1H), 3.72 (dd, *J* = 17.2, 6.0 Hz, 1H), 3.65 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.99, 160.97, 143.06, 135.36, 132.10, 128.36, 127.27, 127.08, 126.16, 120.90, 119.27, 119.05, 112.25, 110.36, 52.73, 43.92, 36.15, 12.11.

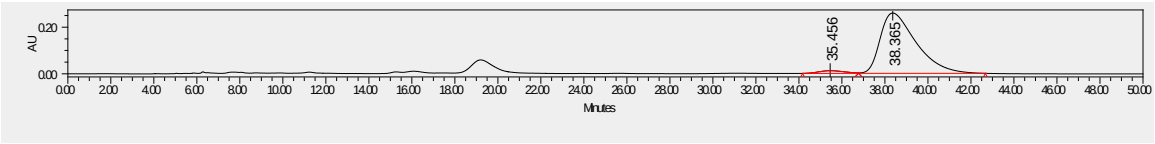
HRMS (ESI-TOF) calcd for $C_{20}H_{19}NO_3$ ([M+Na^+]) = 344.1262. Found 344.1258.



	Retention Time	Area	% Area
1	35.890	13861703	49.47
2	40.403	14159559	50.53

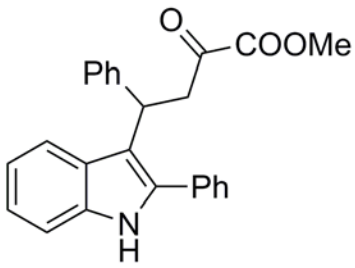


	Retention Time	Area	% Area
1	34.441	30982475	96.61
2	40.123	1088577	3.39



	Retention Time	Area	% Area
1	35.456	958685	3.09
2	38.365	30030526	96.91

Methyl 4-(2-methyl-1H-indol-3-yl)-2-oxo-4-phenylbutanoate



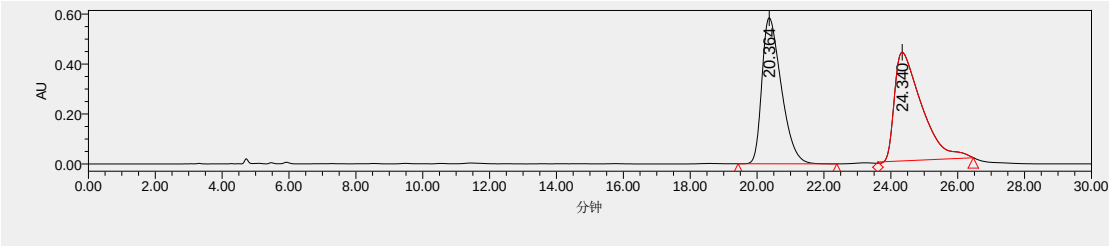
($C_{25}H_{21}NO_3$) (+)-enantiomer (Scheme 1, **5c**): Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 90% yield with 95% ee.$[\alpha]^{22.3}D$ = +36.5 (c = 0.52, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol 80:20, 1.0 mL/min, 254 nm, tr (major) = 24.783 min, tr (minor) = 20.524 min.

(+)-enantiomer (Scheme 1, **5c**): Prepared according to general procedure B. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 96% yield with 33% ee. The ee was determined by HPLC analysis using a chiralcel AD-H column (hexane/2-propanol 80:20, 1.0 mL/min, 254 nm, tr (major) = 25.892 min, tr (minor) = 20.306 min.

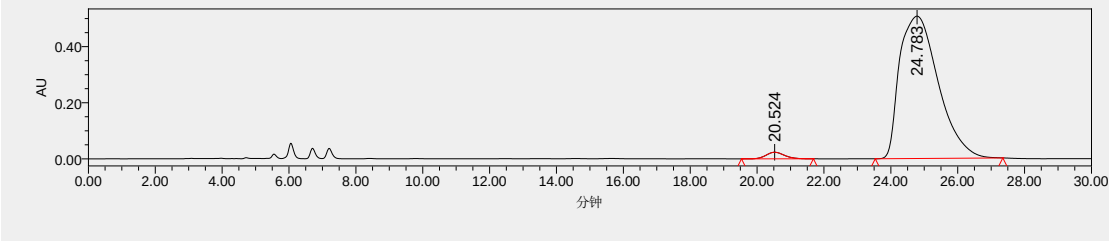
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (m, 1.25H), 7.62 – 7.51 (m, 1.64H), 7.52 – 7.46 (m, 2.05H), 7.46 – 7.37 (m, 3.89H), 7.36 – 7.30 (m, 3.27H), 7.27 (m, 1.89H), 7.23 – 7.12 (m, 3H), 7.09 – 6.94 (m, 1.32H), 6.46 (dd, *J* = 8.0, 4.0 Hz, 0.26H), 5.73 (dd, *J* = 12.0, 4.0 Hz, 1H), 5.08 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.11 (q, *J* = 8.0 Hz, 0.12H), 3.85 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.79 (s, 0.72H), 3.72 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.56 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.61, 166.11, 160.95, 143.39, 142.58, 139.28, 136.17, 136.01, 132.67, 128.81, 128.79, 128.65, 128.51, 128.25, 128.04, 127.62, 127.38, 127.30, 126.29, 126.10, 122.19, 120.83, 120.61, 119.85, 119.65, 115.30, 112.94, 111.09, 111.02, 52.65, 44.86, 36.53.

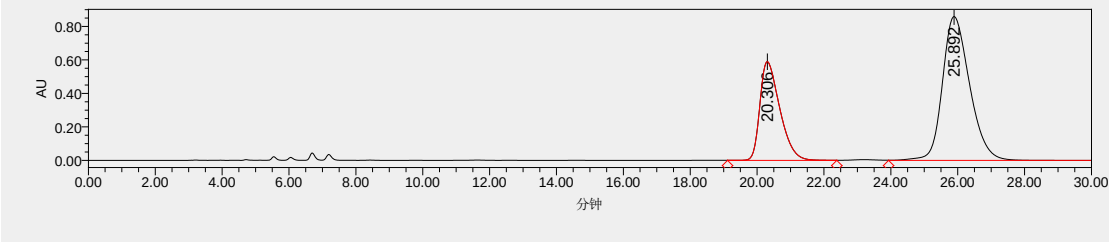
HRMS (ESI-TOF) calcd for $C_{25}H_{21}NO_3$ ($[M+H^+]$) = 384.1599. Found 384.1596.



	Retention Time	Area	% Area
1	20.364	23572127	48.90
2	24.340	24631324	51.10

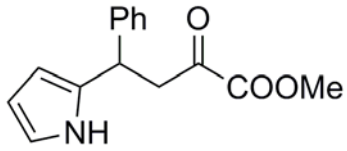


	Retention Time	Area	% Area
1	20.524	892479	2.14
2	24.783	40819947	97.86



	Retention Time	Area	% Area
1	20.306	24311920	33.37
2	25.892	48538638	66.63

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-phenylbutanoate

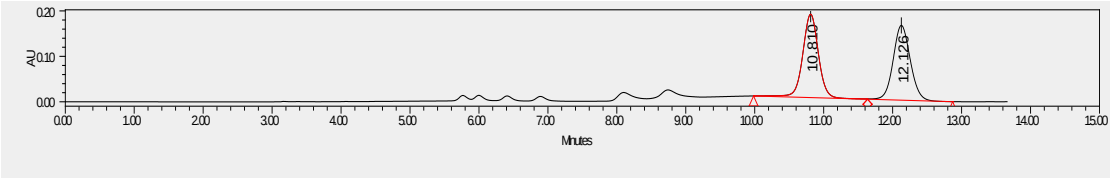


($C_{15}H_{15}NO_3$) (-)-enantiomer: Prepared according to general procedure A. After 24 h, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford the little yellow oil in 76% yield with 99% ee. $[\alpha]^{25.5}_{D}$ = -61.1 (c = 0.26, CH_2Cl_2); The ee was determined by HPLC analysis using a chiralcel IC column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 10.882 min, tr (minor) = 12.126 min.

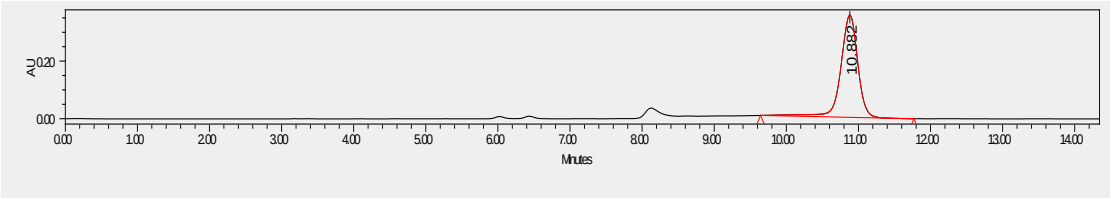
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.33 – 7.27 (m, 2H), 7.22 (m, 3H), 6.62 (d, *J* = 1.2 Hz, 1H), 6.10 (dd, *J* = 5.6, 2.8 Hz, 1H), 5.95 (s, 1H), 4.60 (t, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.67 (dd, *J* = 18.0, 7.6 Hz, 1H), 3.45 (dd, *J* = 18.0, 6.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.48, 161.02, 141.92, 133.15, 128.77, 127.85, 127.10, 117.45, 108.09, 105.50, 53.04, 45.45, 38.93.

HRMS (ESI-TOF) calcd for $C_{15}H_{15}NO_3$ ([M+Na^+]) = 280.0949. Found 280.0953.

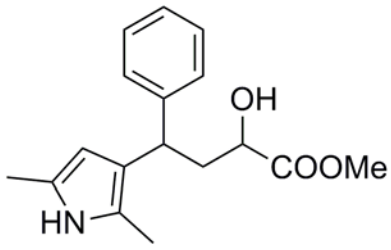


	Retention Time	Area	% Area
1	10.810	2896341	50.48
2	12.126	2841042	49.52



	Retention Time	Area	% Area
1	10.882	5833183	100.00

Methyl 4-(2,5-dimethyl-1H-pyrrol-3-yl)-2-oxo-4-phenylbutanoate



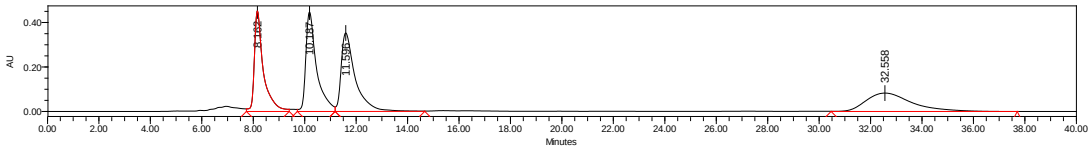
($C_{17}H_{21}NO_3$): little yellow oil in 75% yield with 92% ee for major isomer; 93% ee for minor isomer; 56:44 d.r.. The ee and d.r. was determined by HPLC analysis using a chiralcel ASH column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 8.223, 10.353 min, tr (minor) = 33.772, 11.979 min.

(Scheme 2b): little yellow oil in 80% yield with 91% ee for major isomer; 91% ee for minor isomer; 57:43 d.r.. The ee and d.r. was determined by HPLC analysis using a chiralcel ASH column (hexane/2-propanol 90:10, 1.0 mL/min, 254 nm, tr (major) = 12.138, 34.548 min, tr (minor) = 10.497, 8.306 min.

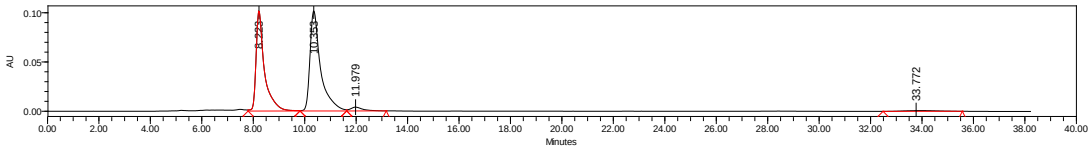
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.35 – 7.24 (m, 4H), 7.15 (m, 1H), 5.80 (s, 1H), 4.20 – 4.10 (m, 1.48H), 4.02 (dd, *J* = 8.8, 3.6 Hz, 0.55H), 3.72 (s, 1.36H), 3.69 (s, 1.63H), 2.77 (s, 1H), 2.51 – 2.42 (m, 1H), 2.21 (s, 1.40H), 2.19 (s, 1.67H), 2.14 (s, 1.39H), 2.12 (s, 1.66H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.09, 175.80, 146.09, 144.98, 128.39, 128.25, 127.75, 127.47, 125.82, 125.66, 125.27, 124.98, 122.64, 121.88, 121.55, 120.08, 104.71, 104.56, 69.09, 68.87, 52.31, 52.25, 41.30, 41.18, 38.14, 13.06, 12.95, 11.02, 10.97.

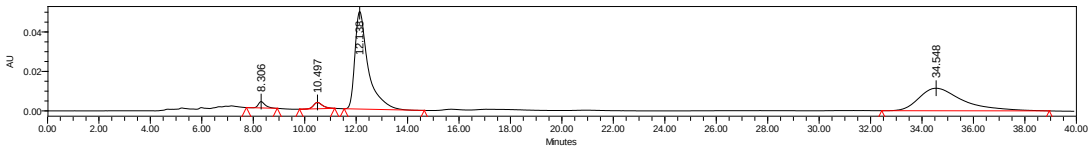
HRMS (ESI-TOF) calcd for $C_{17}H_{21}NO_3$ ([M+Na^+]) = 310.1419. Found 310.1417.



	Retention Time	Area	% Area
1	8.162	11015783	23.08
2	10.187	13009079	27.25
3	11.596	13455171	28.18
4	32.558	10258962	21.49



	Retention Time	Area	% Area
1	8.223	2301928	42.49
2	10.353	2922236	53.94
3	11.979	125267	2.31
4	33.772	67924	1.25



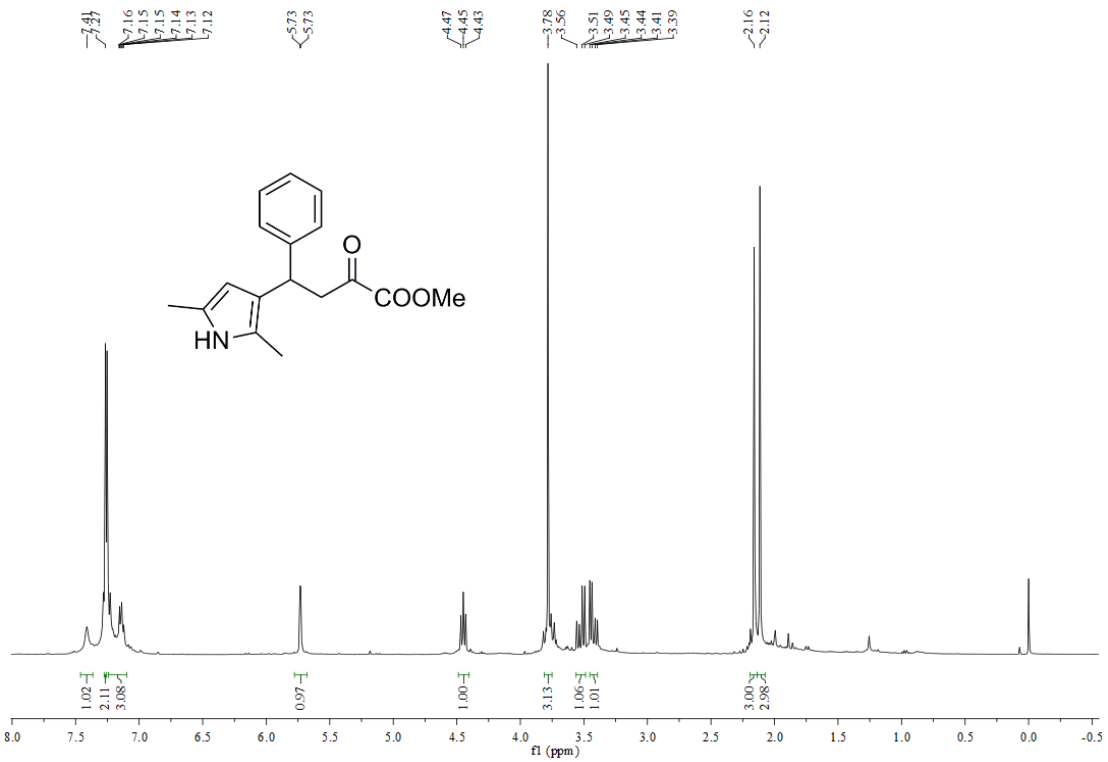
	Retention Time	Area	% Area

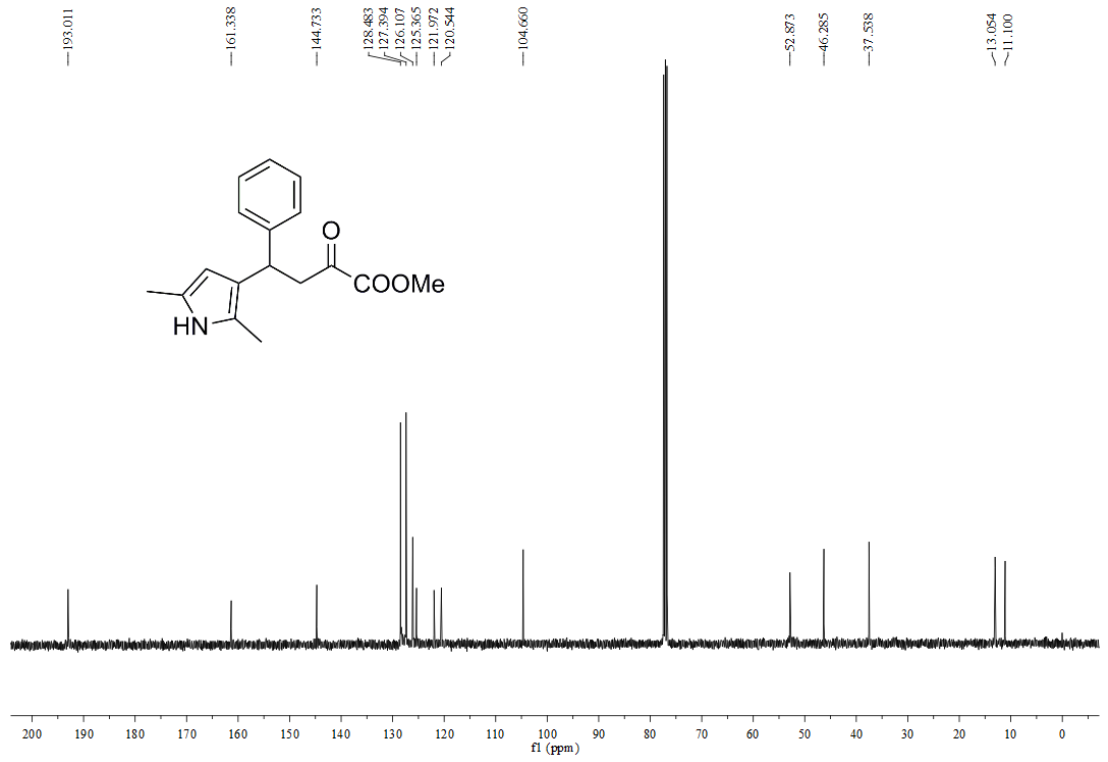
1	8.306	60923	1.86
2	10.497	79241	2.42
3	12.138	1776434	54.34
4	34.548	1352260	41.37

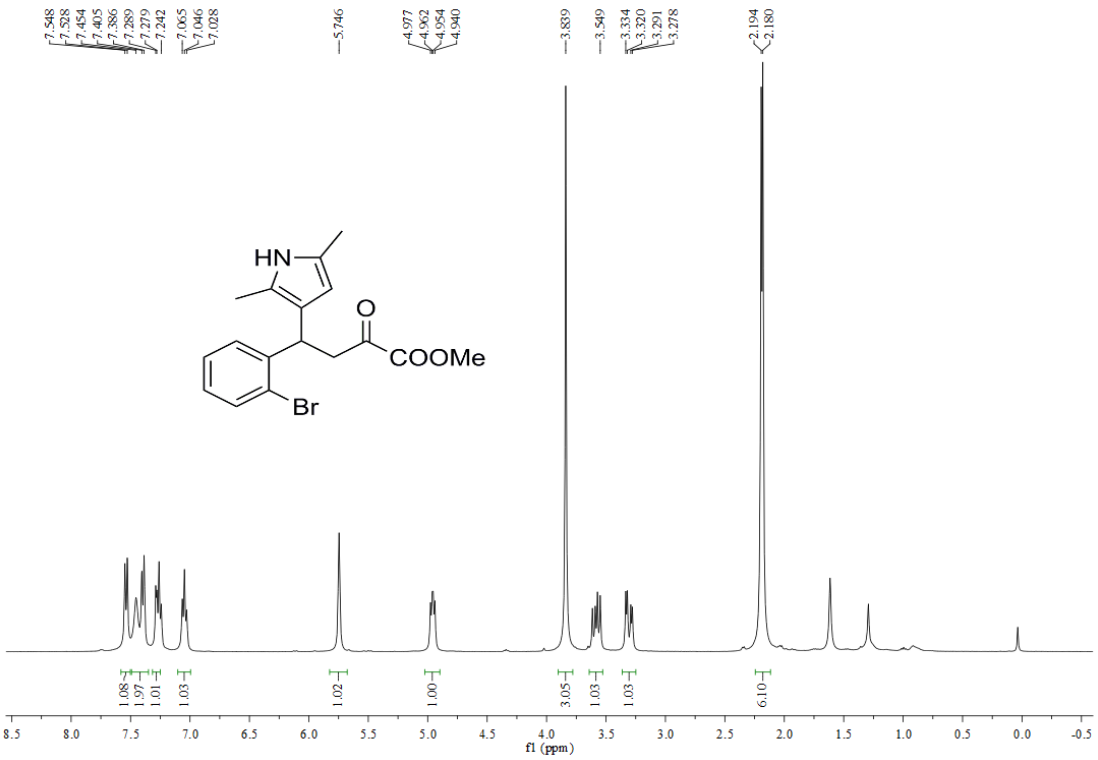
9. References

(1) a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett* **2005**, 2445; b) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie, X. M. Feng, *Angew. Chem.* **2008**, *120*, 1328-1331; *Angew. Chem. Int. Ed.* **2008**, *47*, 1308-1311; c) K. Zheng, B. Qin, X. H. Liu, X. M. Feng, *J. Org. Chem.* **2007**, *72*, 8478; d) X. Zhang, D. H. Chen, X. H. Liu, X. M. Feng, *J. Org. Chem.* **2007**, *72*, 5227; e) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu, X. M. Feng, *Org. Lett.* **2009**, *11*, 1401.

Copies of NMR spectra for the products



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7.046
7.028
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4.962
4.954
4.940
3.839
3.549
3.334
3.320
3.291
3.278
2.194
2.180
HN
O
COOMe
Br
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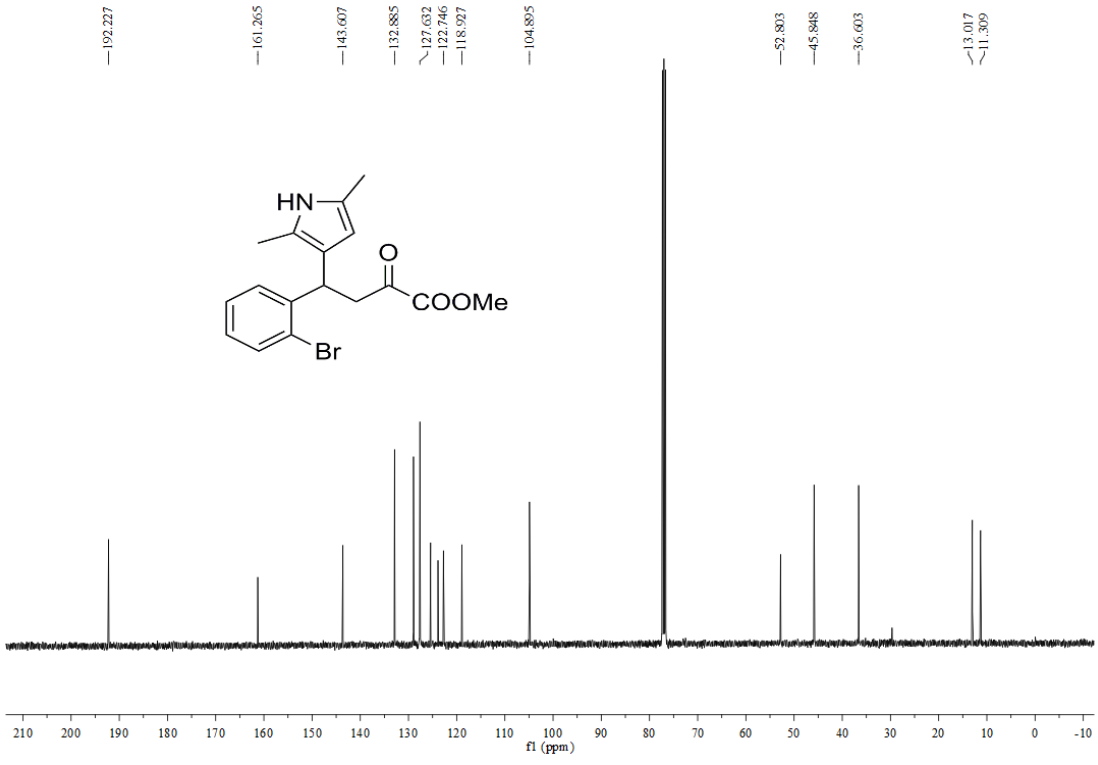
1.01
1.03
1.02
1.00
3.05
1.03
1.03
6.10
f1 (ppm)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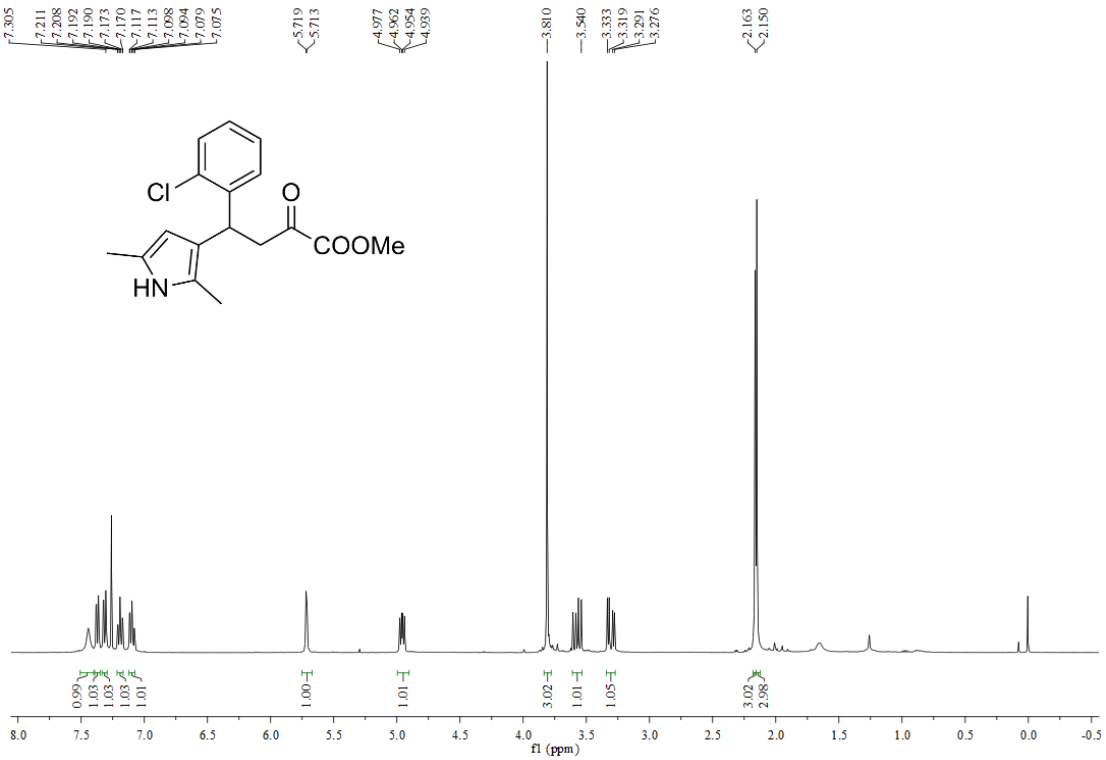
O
COOMe
Br
f1 (ppm)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7.075
5.719
5.713
4.977
4.962
4.954
4.939
3.810
3.540
3.333
3.319
3.291
3.276
2.163
2.150
Cl
O
COOMe
HN
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1.01
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1.01
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1.05
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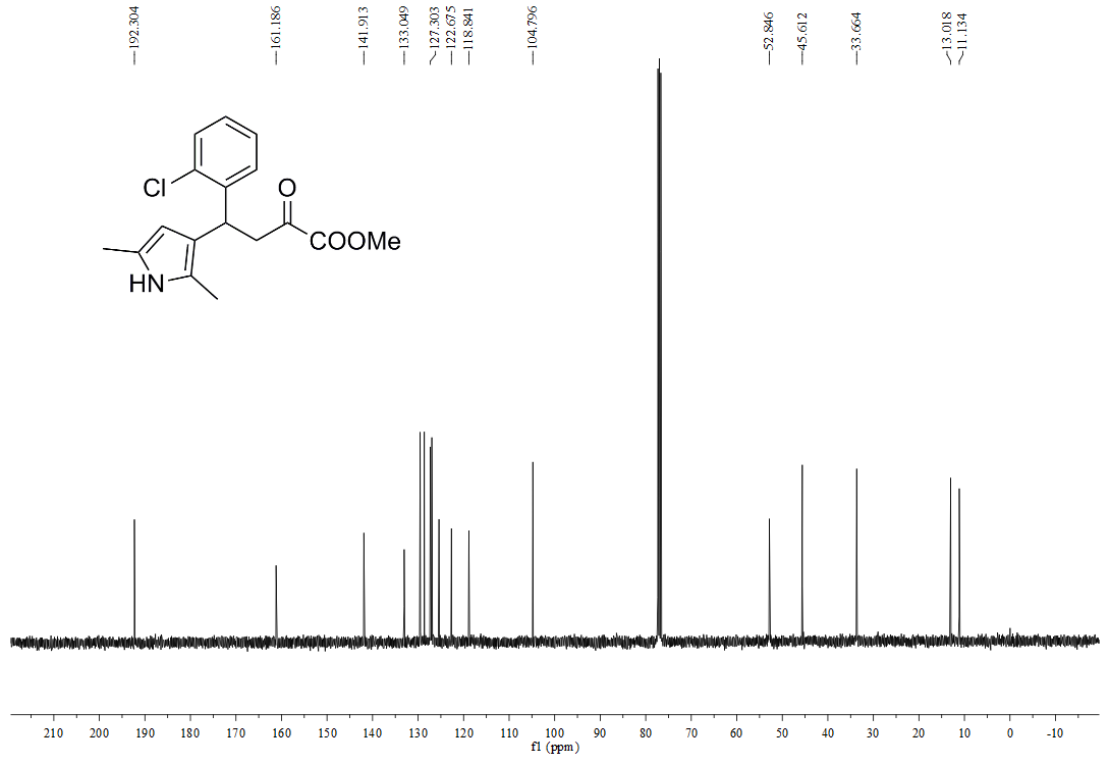
f1 (ppm)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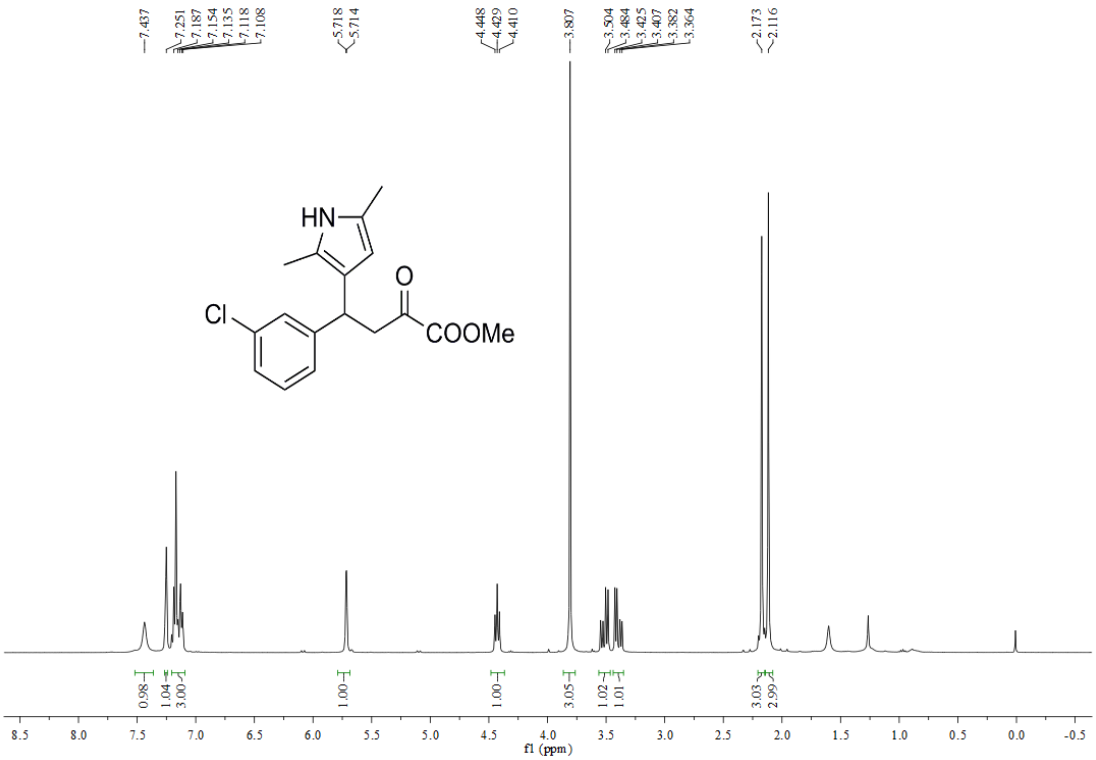
11.134
Cl
O
COOMe
HN
f1 (ppm)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4.429
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3.807
3.504
3.484
3.425
3.407
3.382
3.364
2.173
2.116
HN
O
Cl
COOMe
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1.00
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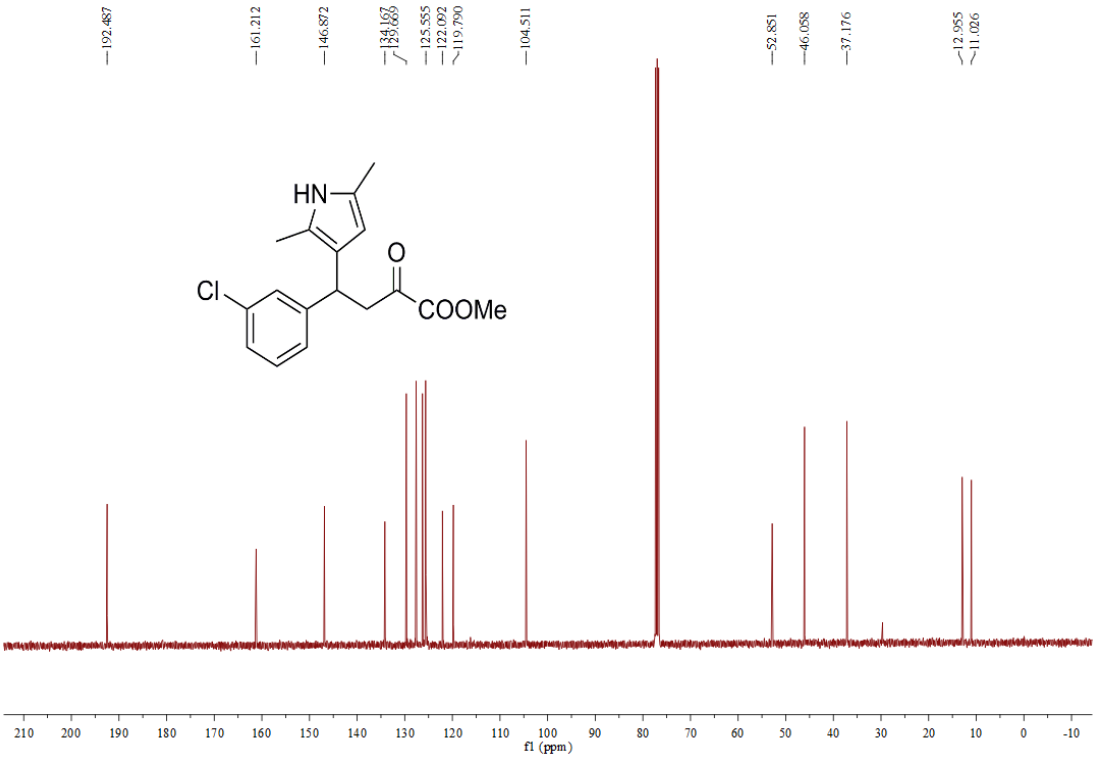
f1 (ppm)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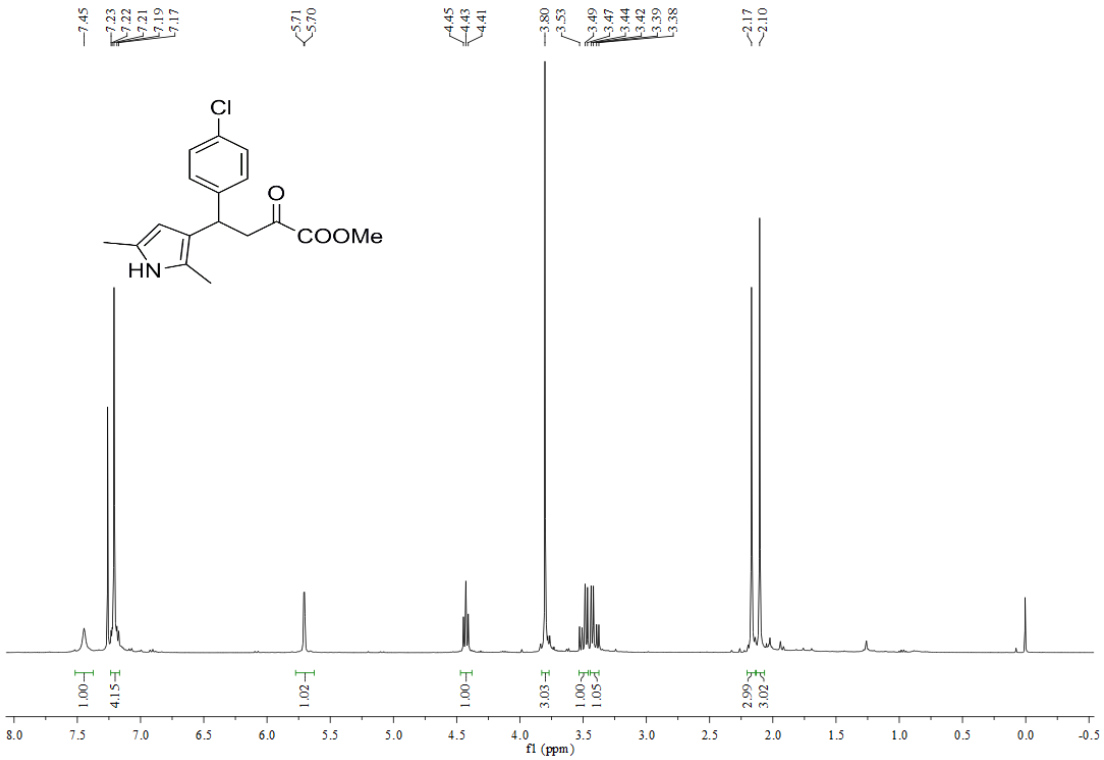
Cl
COOMe
f1 (ppm)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3.53
3.49
3.47
3.44
3.42
3.39
3.38
2.17
2.10
Cl
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1.05
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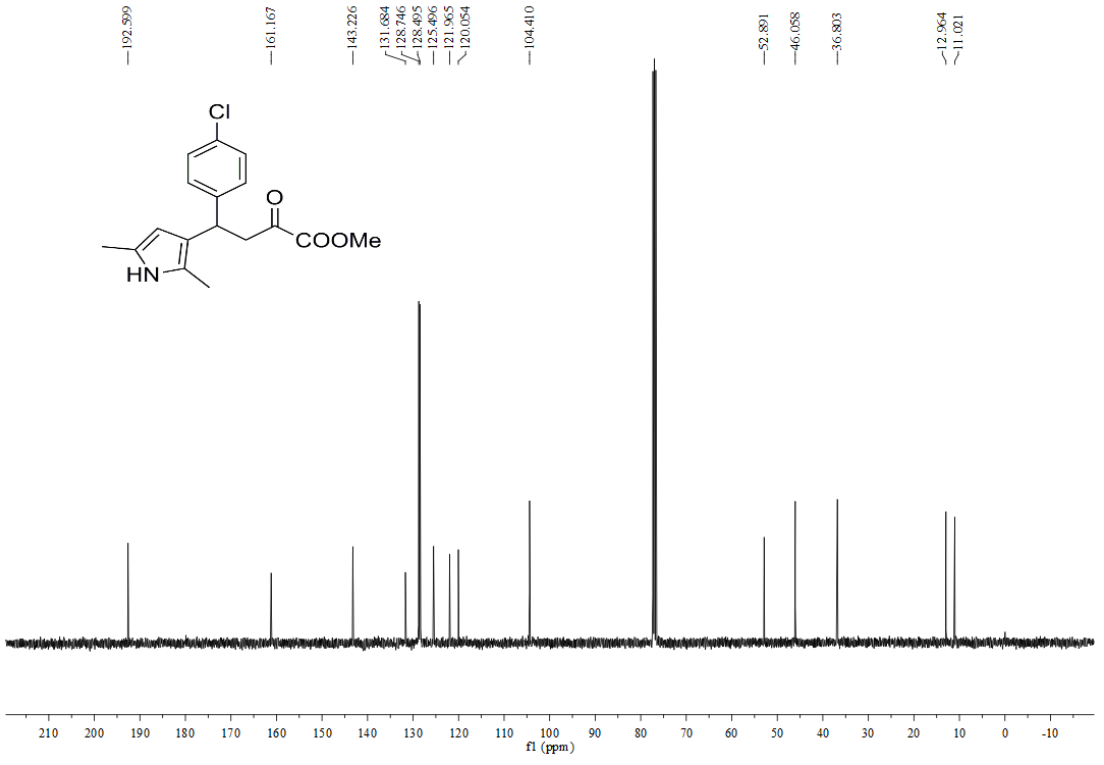
3.02
f1 (ppm)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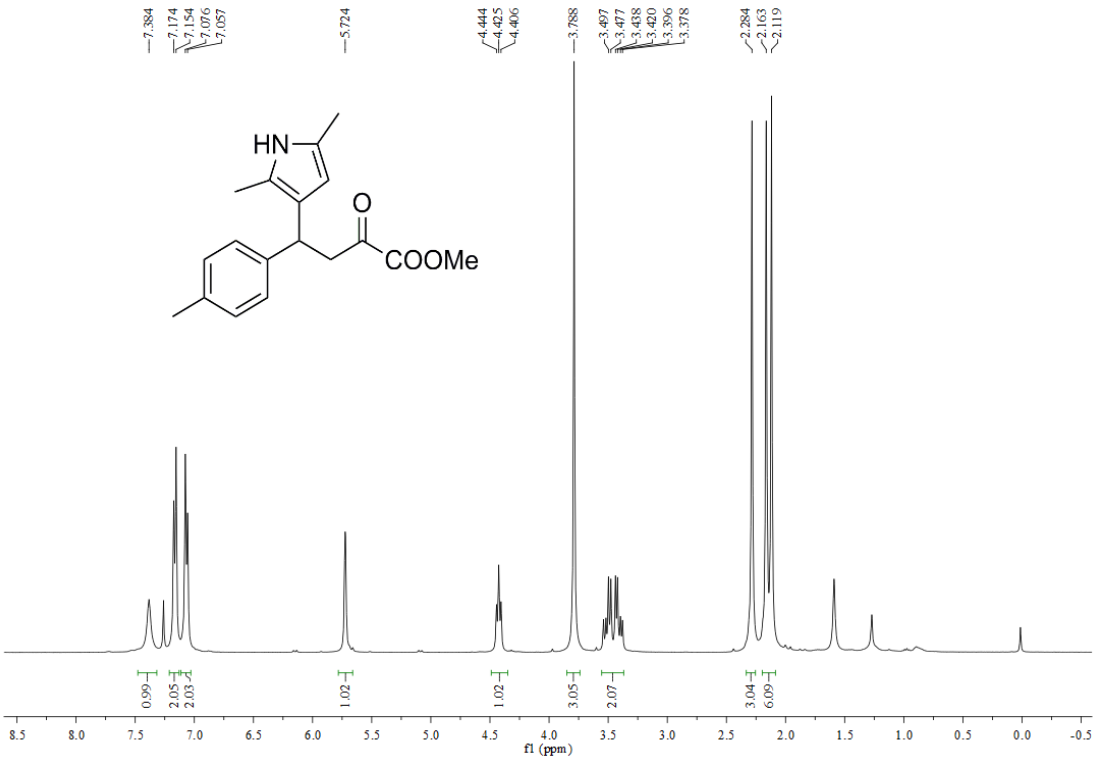
O
COOMe
HN
f1 (ppm)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3.420
3.396
3.378
2.284
2.163
2.119
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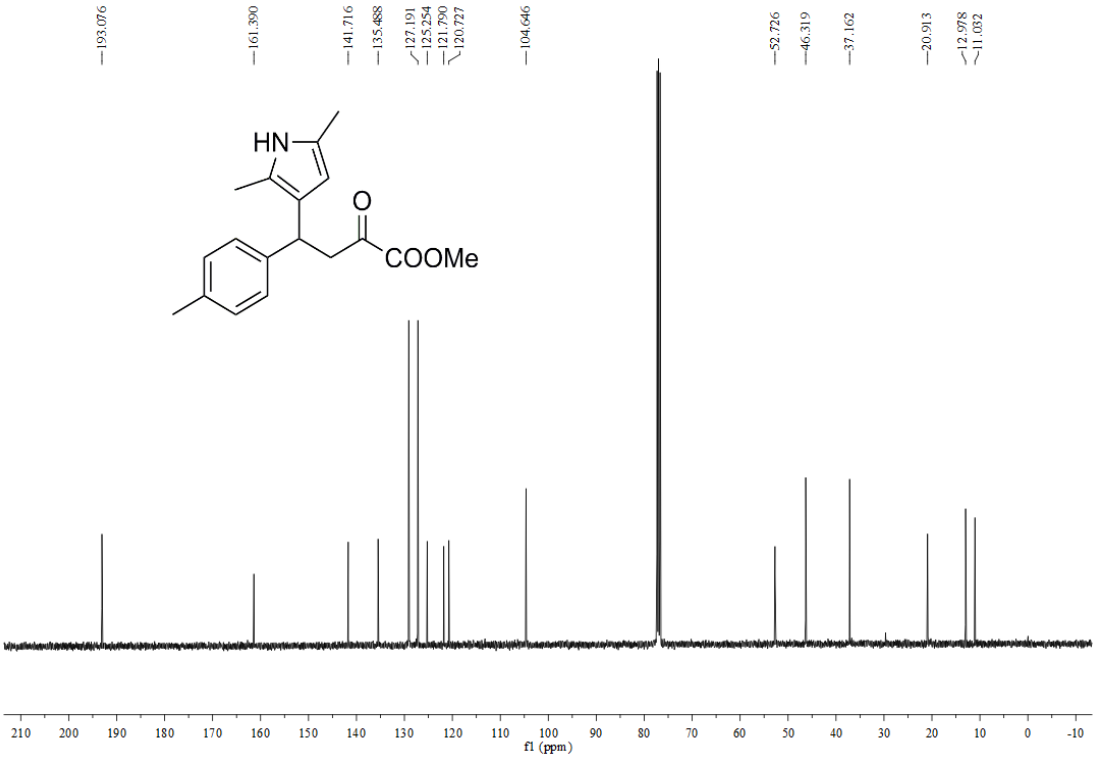
f1 (ppm)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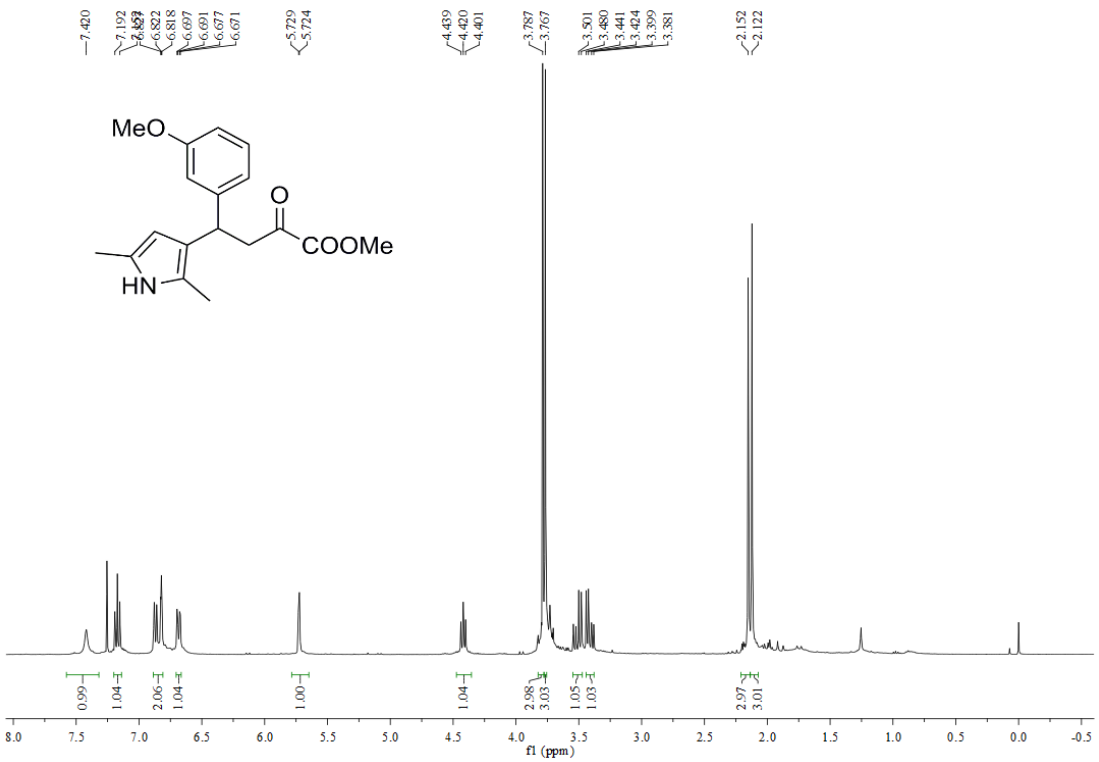
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3.787
3.767
3.501
3.480
3.441
3.424
3.399
3.381
2.152
2.122
MeO
O
COOMe
HN
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1.00
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1.03
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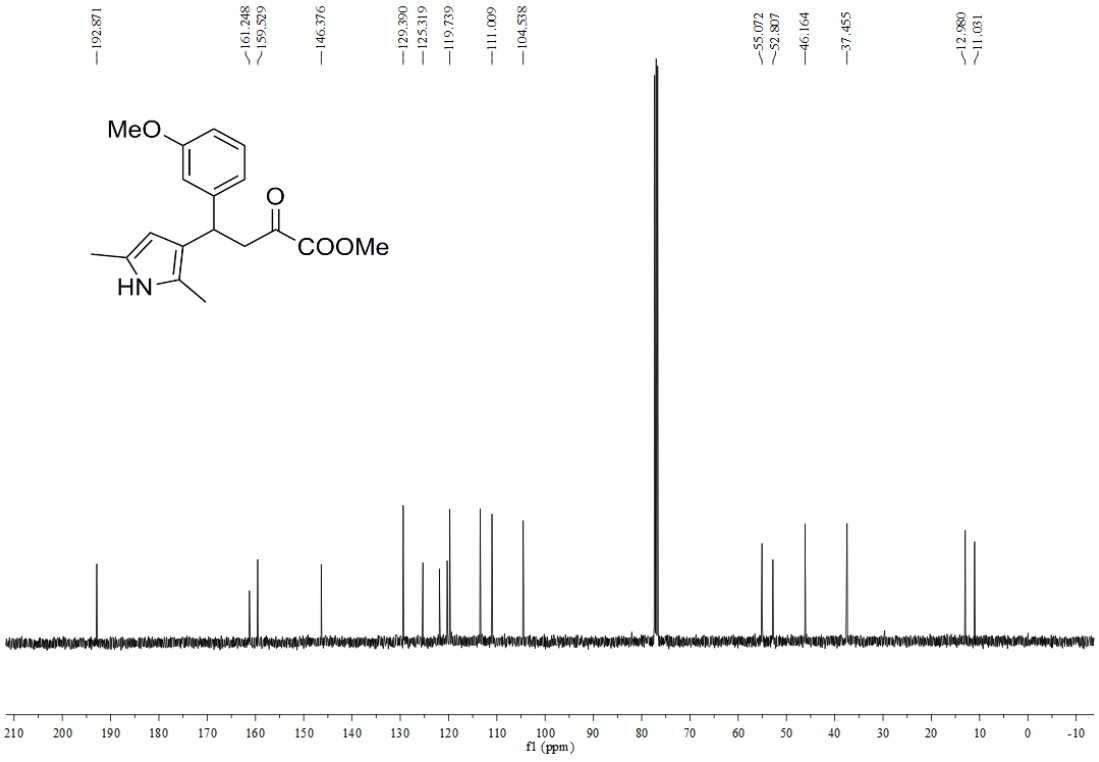
3.01
f1 (ppm)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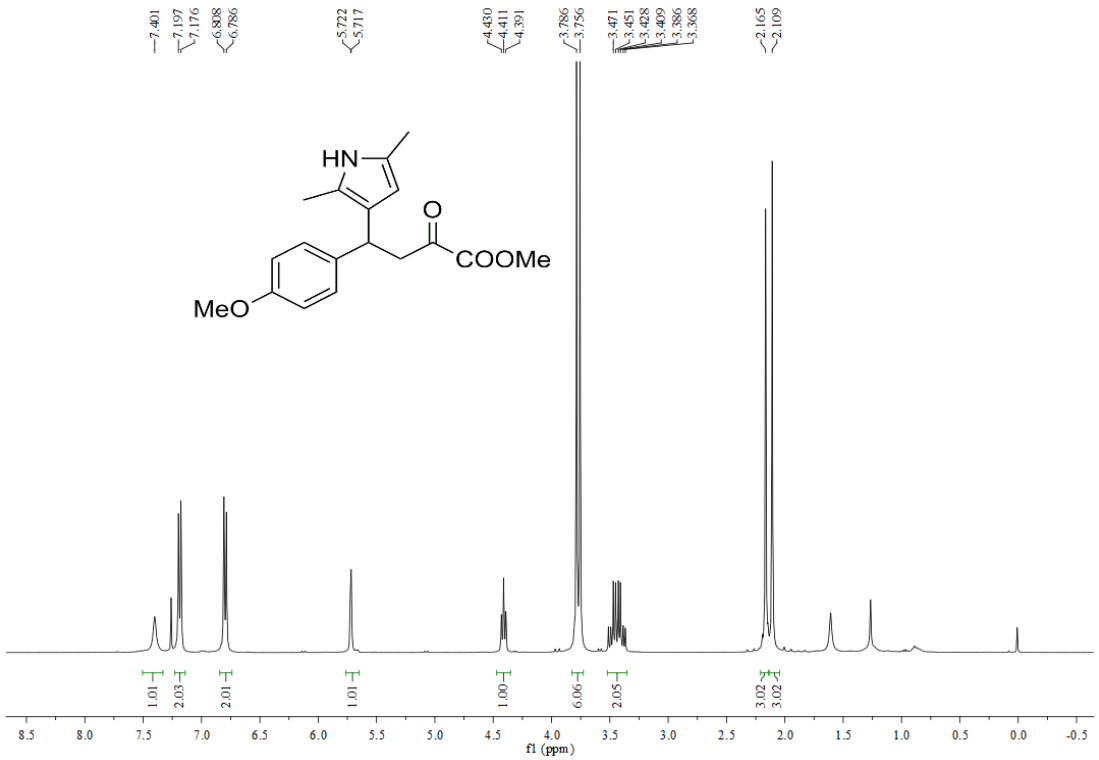
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3.451
3.428
3.409
3.386
3.368
2.165
2.109
HN
O
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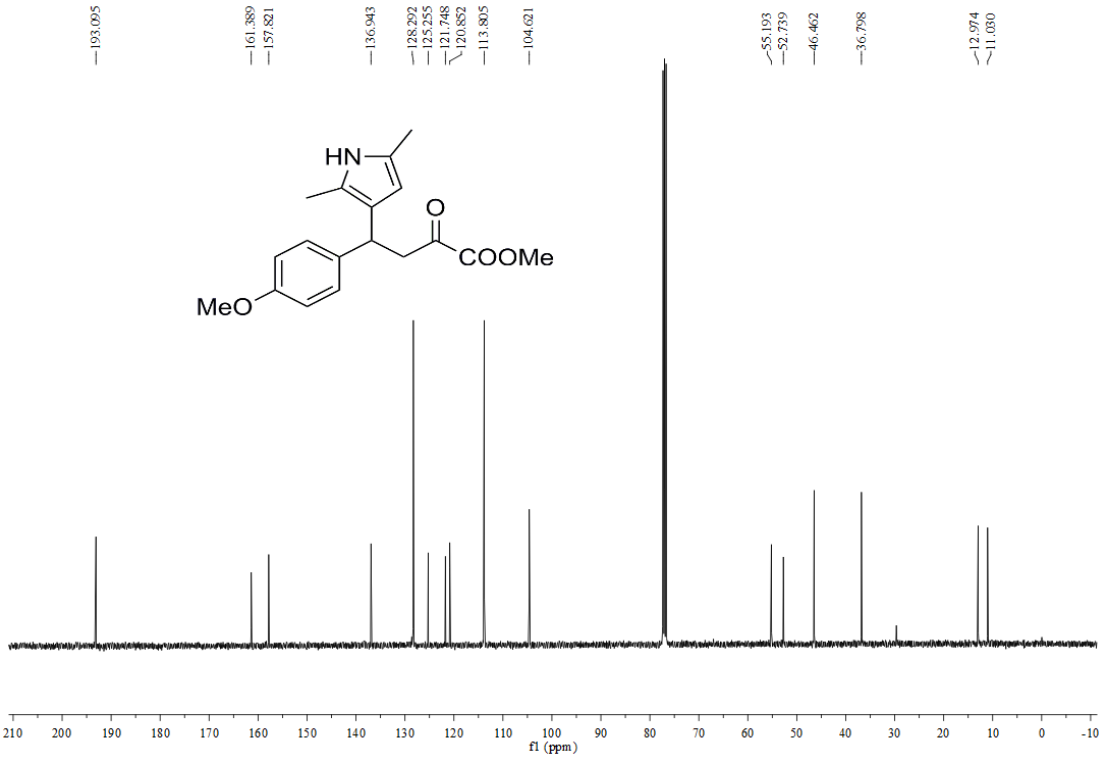
2.05
3.02
3.02
f1 (ppm)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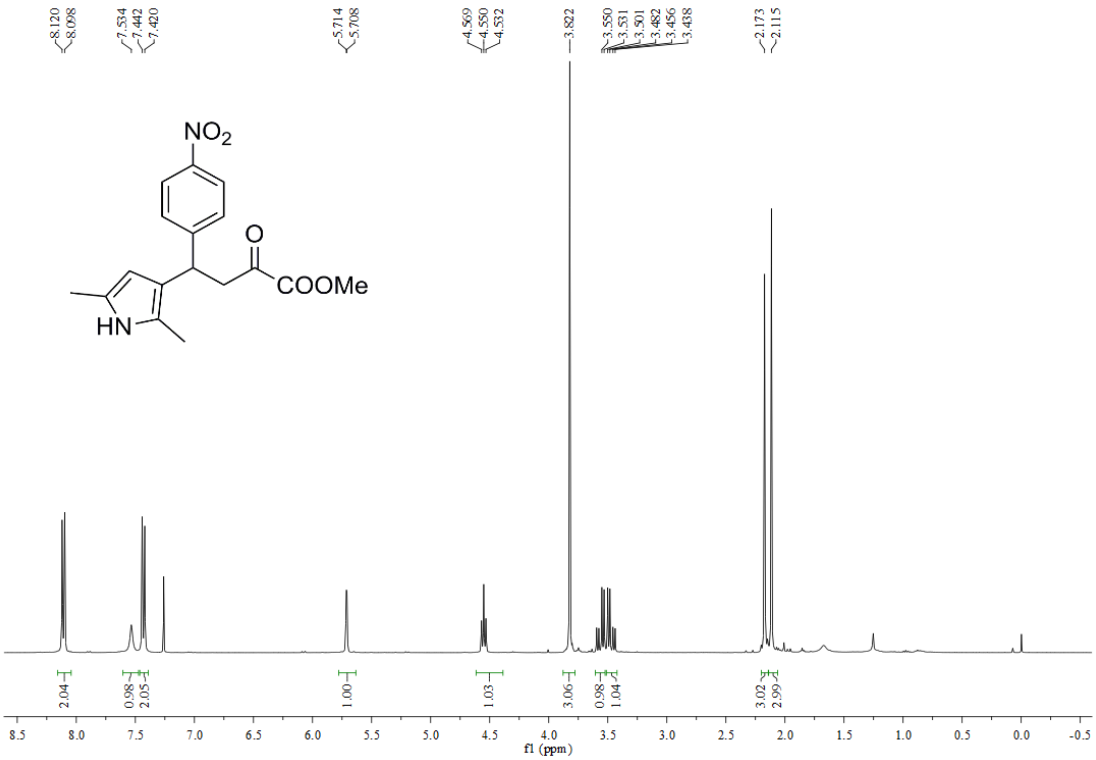
f1 (ppm)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3.501
3.482
3.456
3.438
2.173
2.115
NO2
O
COOMe
HN
2.04
0.98
2.05
1.00
1.03
3.06
0.98
1.04
3.02
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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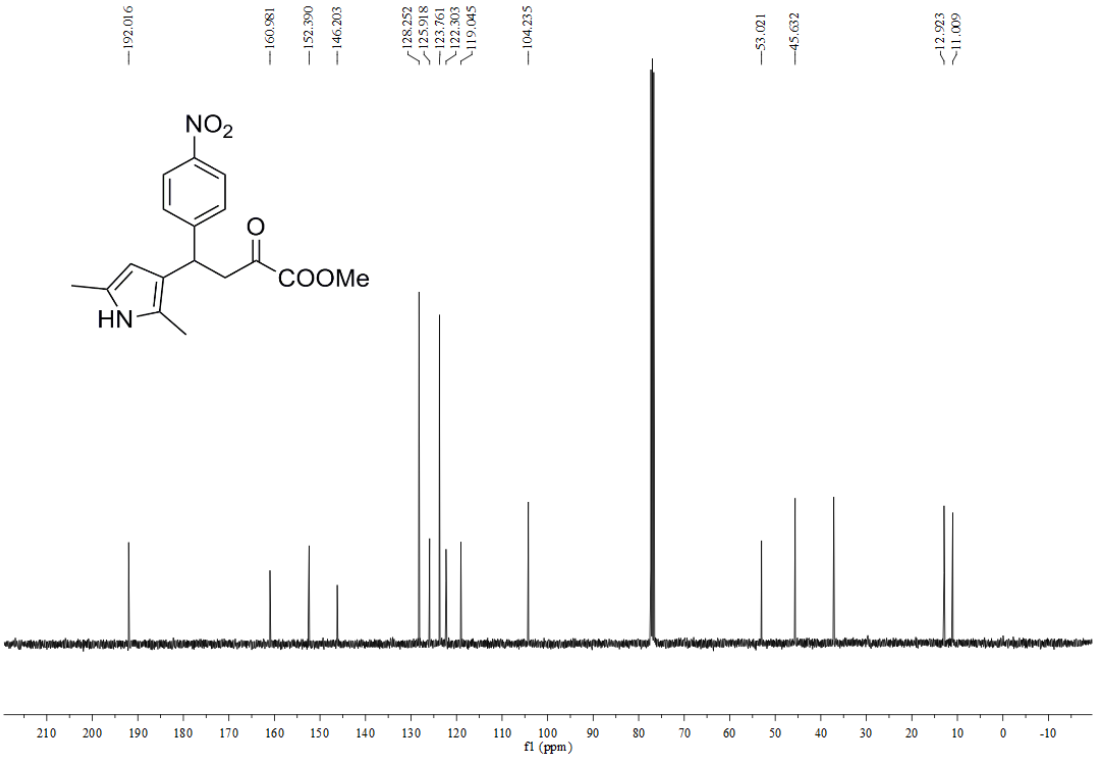
f1 (ppm)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12.923
11.009
NO2
O
COOMe
HN
210
200
190
180
170
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150
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110
100
90
80
70
60
50
40
30
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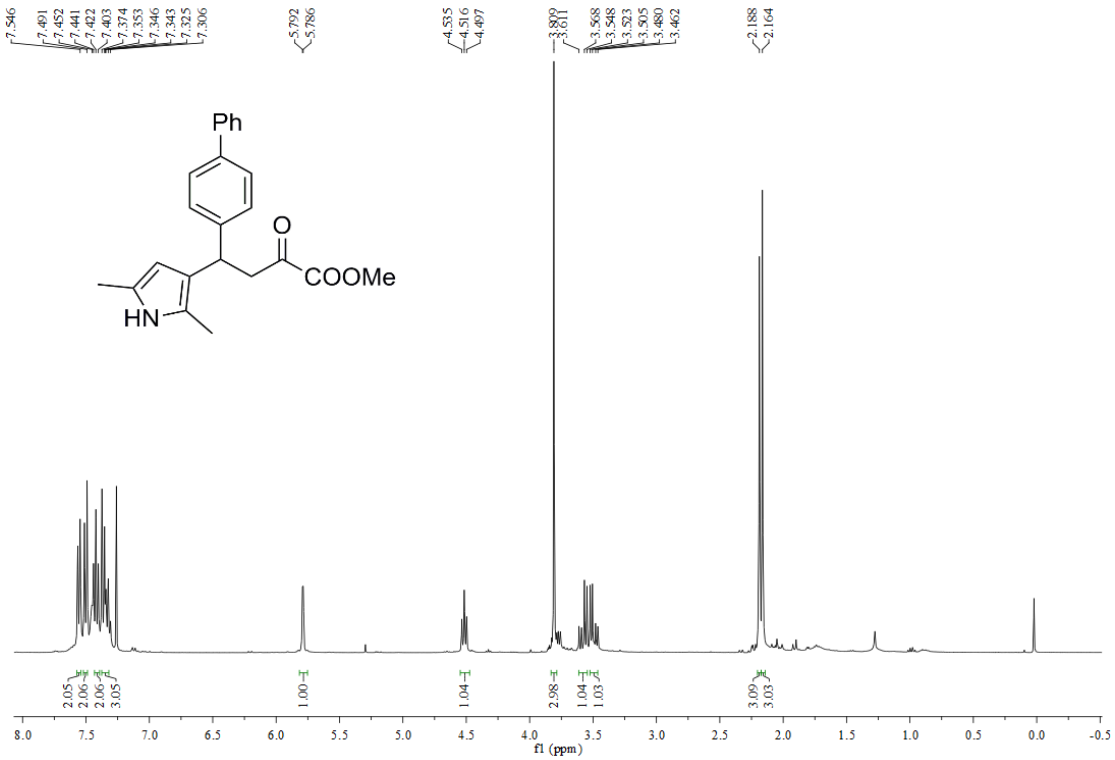
f1 (ppm)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3.609
3.611
3.568
3.548
3.523
3.505
3.480
3.462
2.188
2.164
Ph
O
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HN
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2.06
2.06
3.05
1.00
1.04
2.98
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1.03
3.09
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7.5
7.0
6.5
6.0
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5.0
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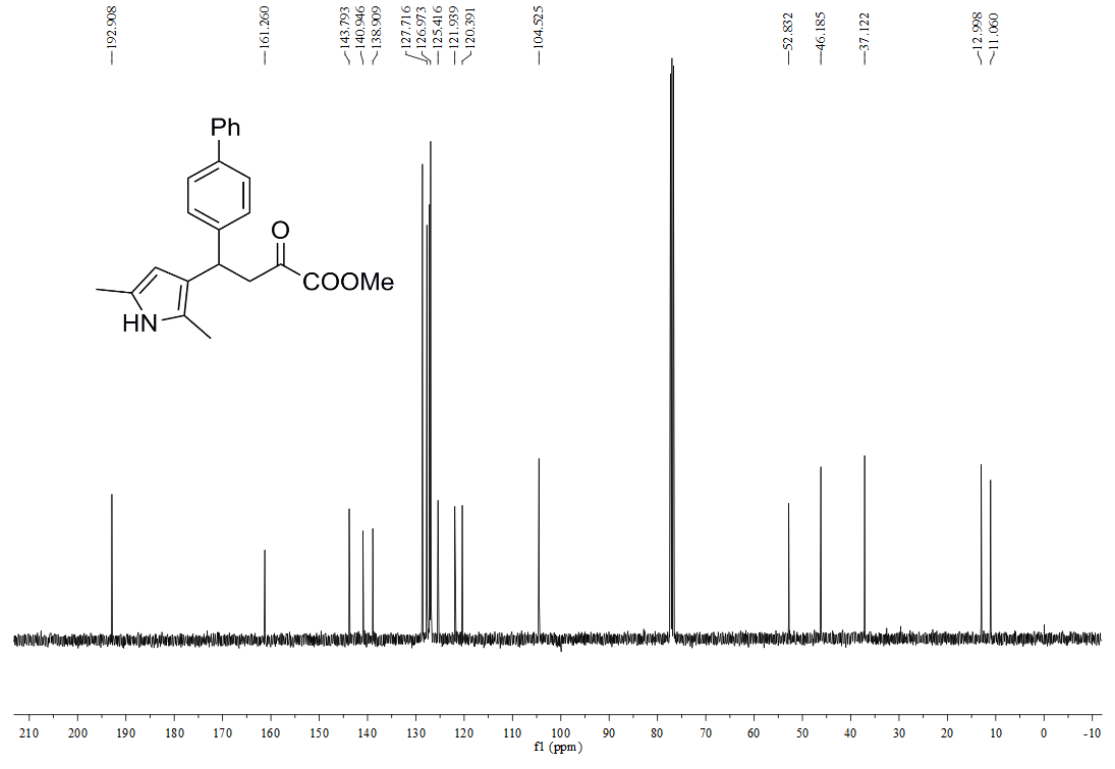
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37.122
12.998
11.060
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O
COOMe
HN
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200
190
180
170
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100
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60
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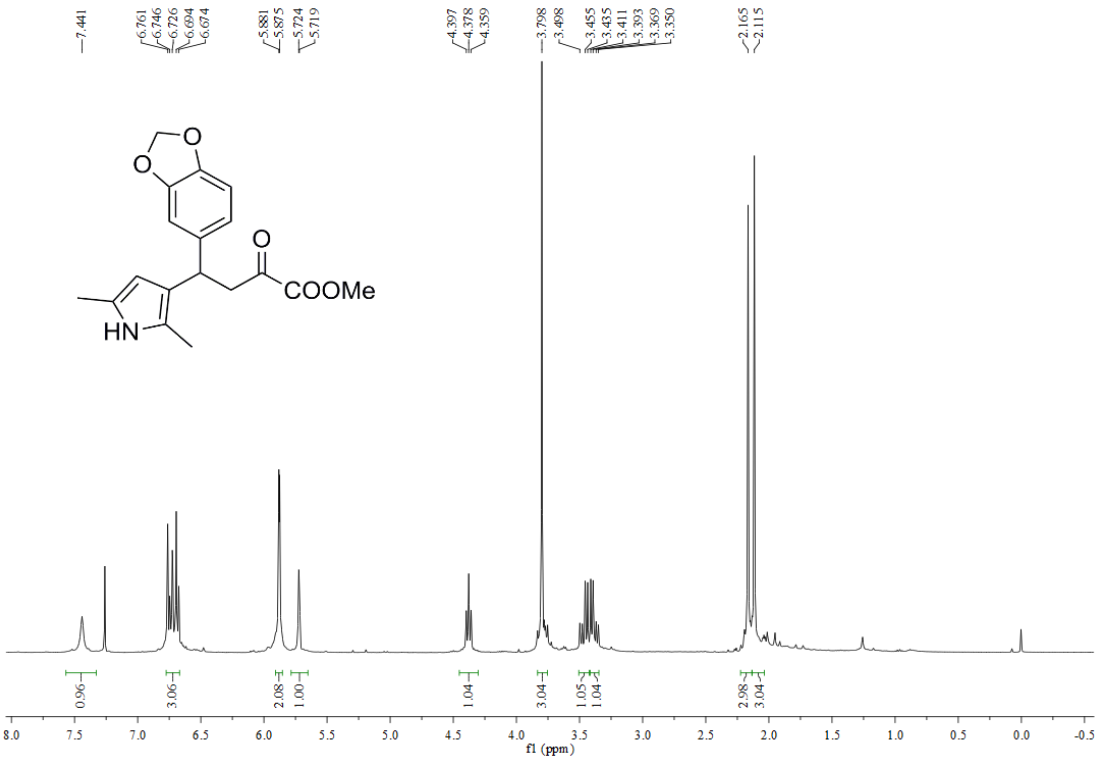
40
30
20
10
0
-10
f1 (ppm)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4.359
3.798
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3.455
3.435
3.411
3.393
3.369
3.350
2.165
2.115
O
O
O
COOMe
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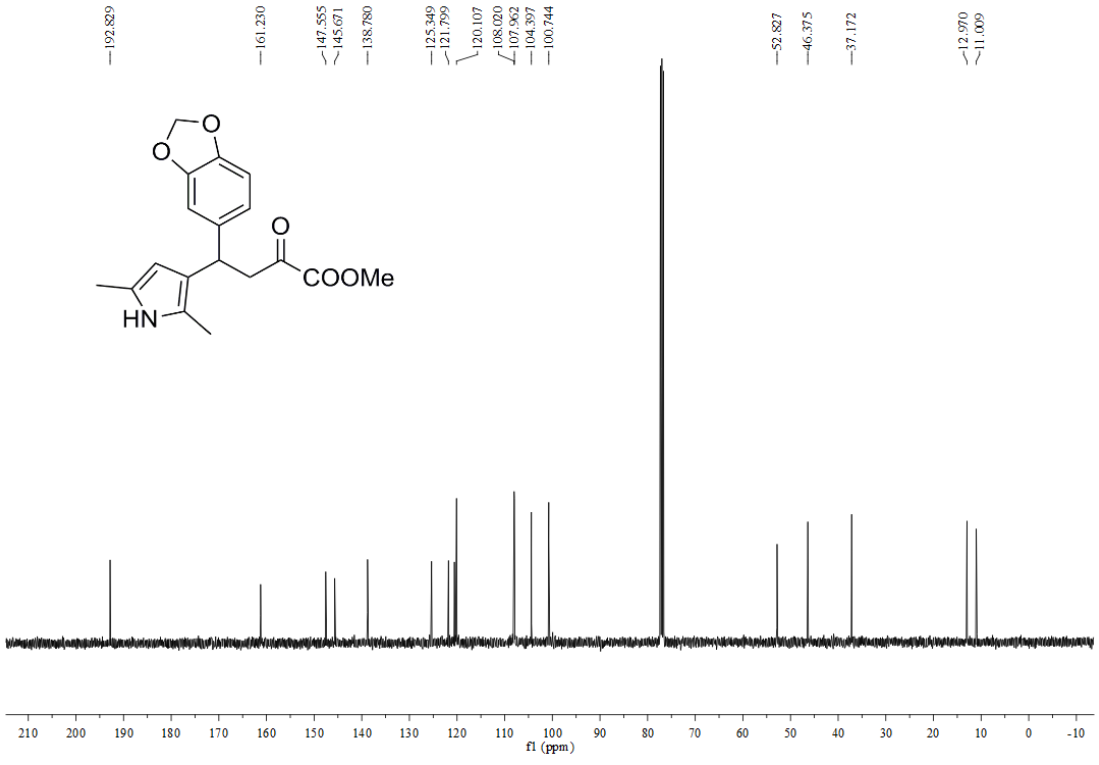
2.98
3.04
f1 (ppm)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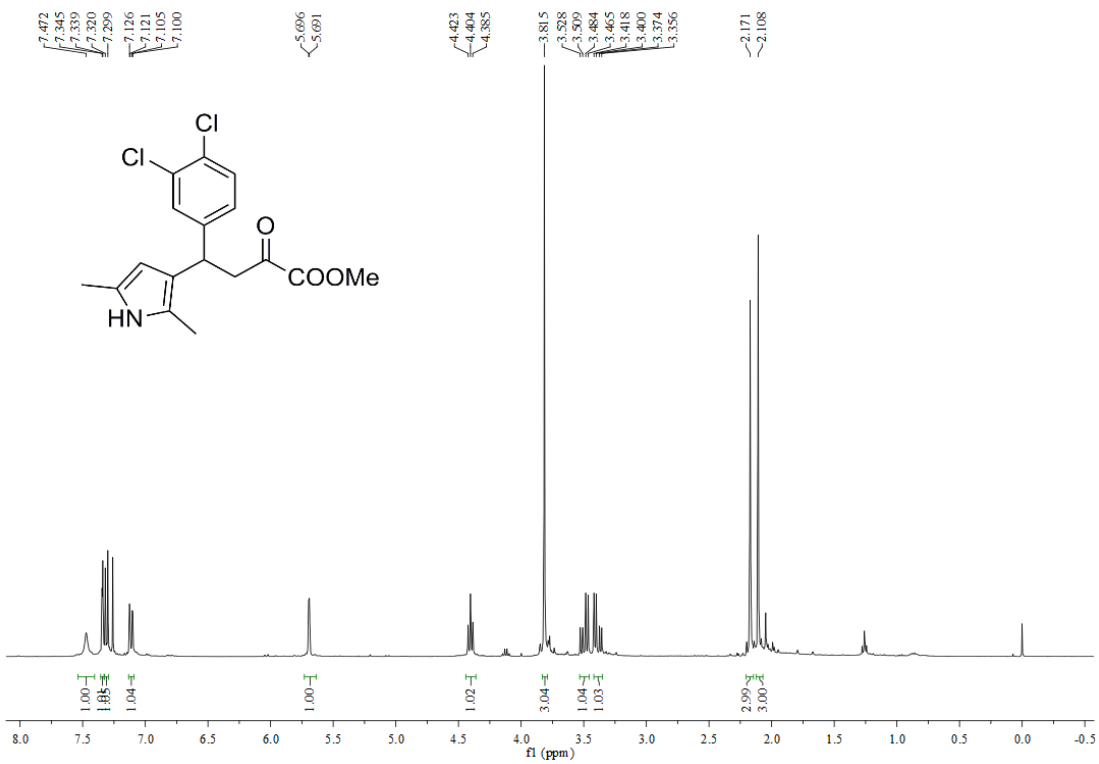
O
O
O
COOMe
HN
f1 (ppm)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2.108
Cl
Cl
O
COOMe
HN
1.00
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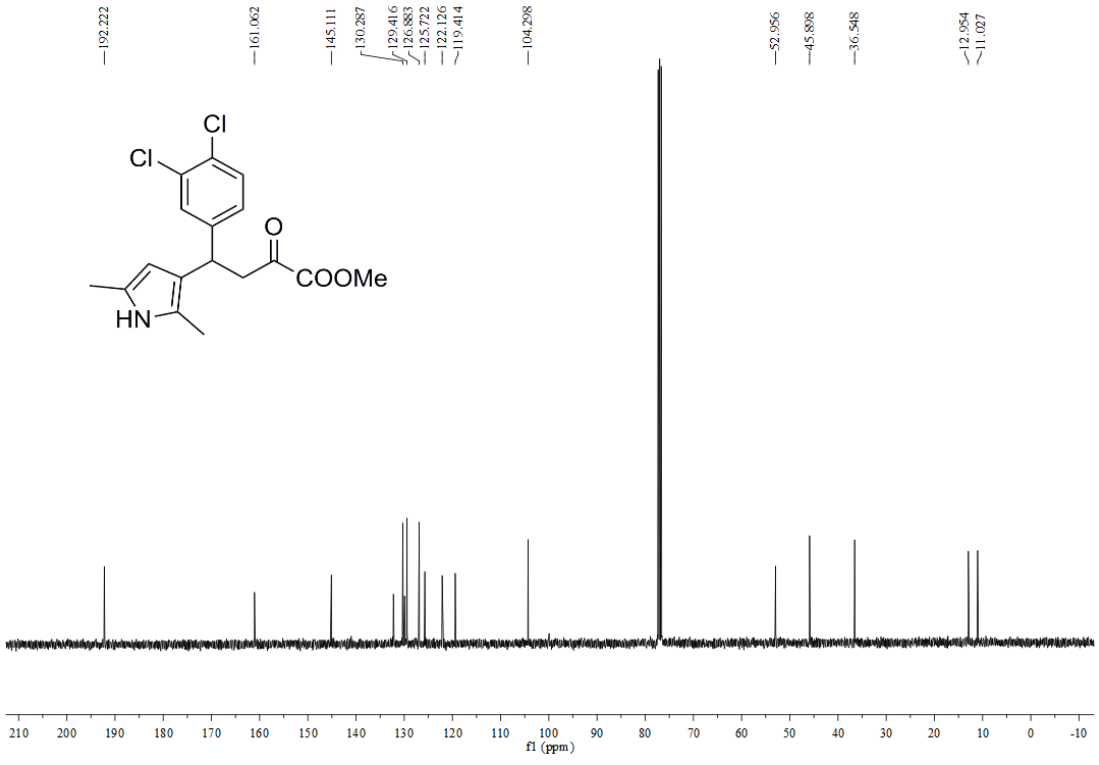
1.84
1.04
1.00
1.02
3.04
1.04
1.03
2.99
3.00
f1 (ppm)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126.883
125.722
122.126
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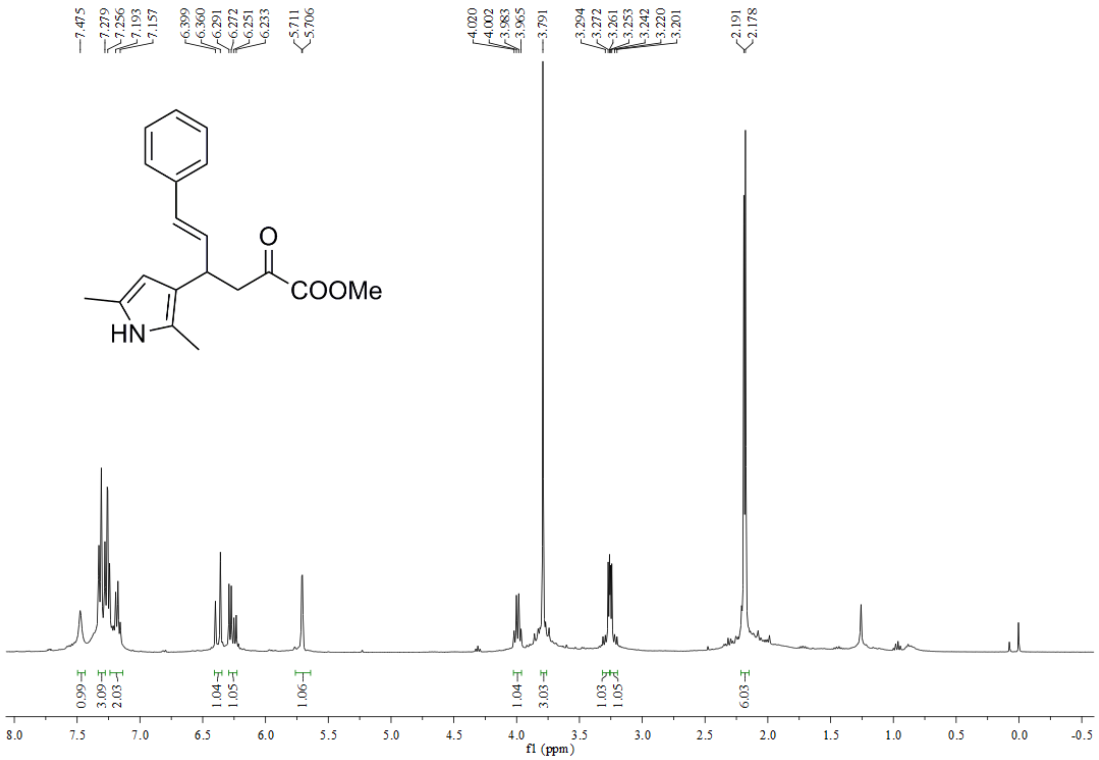
45.898
36.548
12.954
11.027
Cl
Cl
O
COOMe
HN
f1 (ppm)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7.193
7.157
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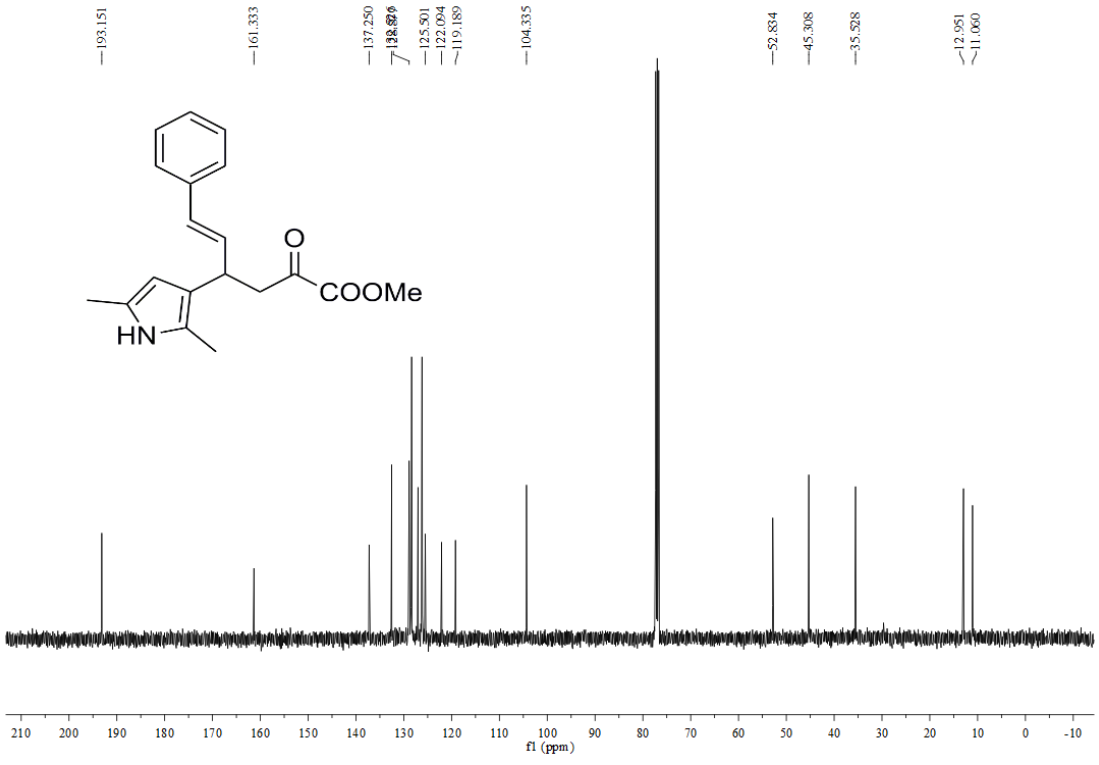
6.360
6.291
6.272
6.251
6.233
5.711
5.706
4.020
4.002
3.983
3.965
3.791
3.294
3.272
3.261
3.253
3.242
3.220
3.201
2.191
2.178
O
COOMe
HN
0.99
3.09
2.03
1.04
1.05
1.06
1.04
3.03
1.03
1.05
6.03
f1 (ppm)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161.333
137.250
125.501
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104.335
52.834
45.308
35.528
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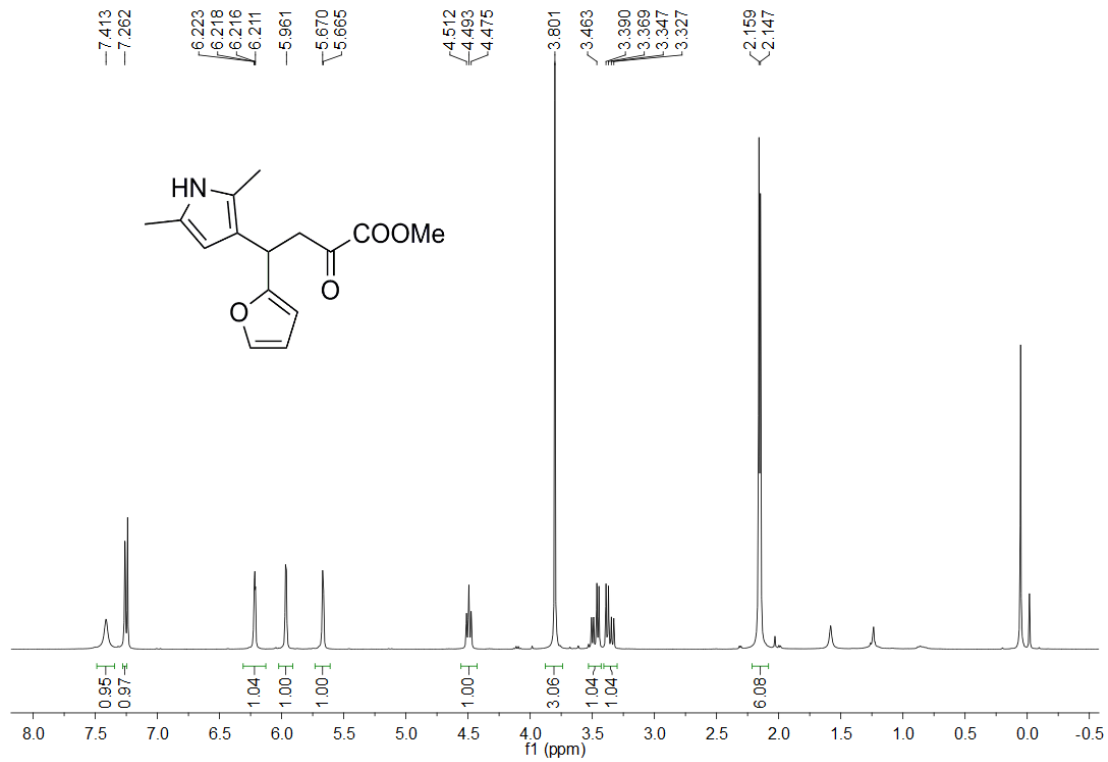
11.060
O
COOMe
HN
f1 (ppm)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7.262
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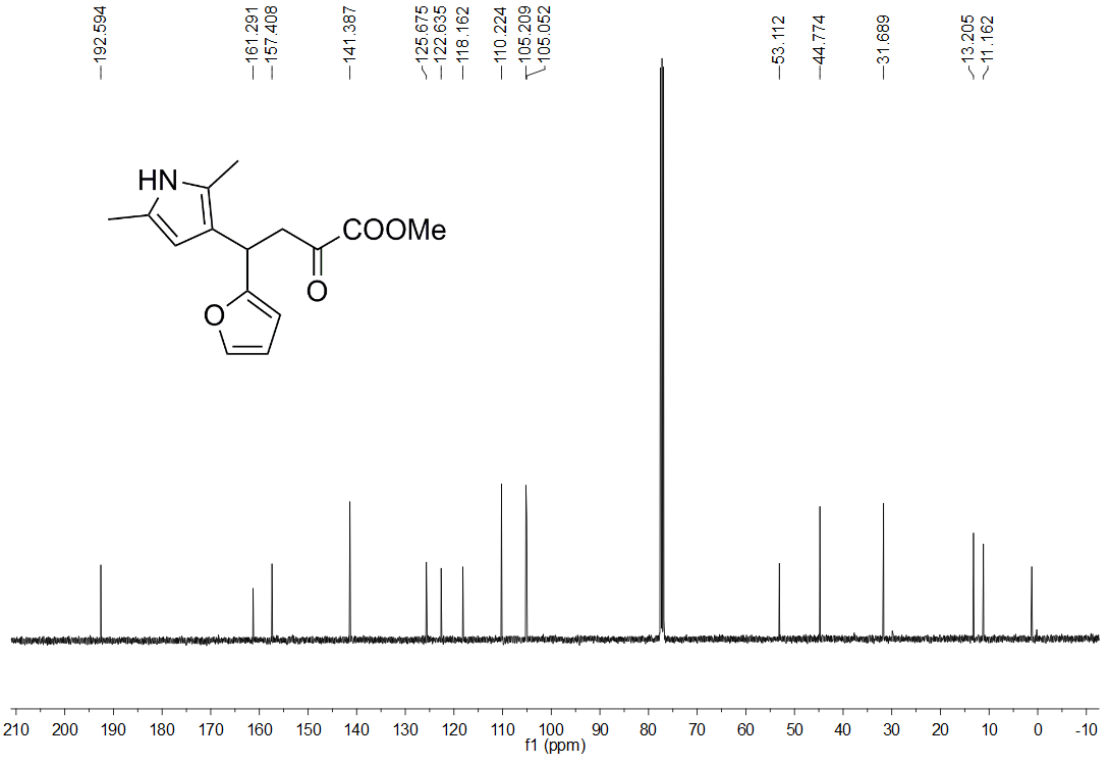
6.218
6.216
6.211
5.961
5.670
5.665
4.512
4.493
4.475
3.801
3.463
3.390
3.369
3.347
3.327
2.159
2.147
HN
COOMe
O
O
0.95
0.97
1.04
1.00
1.00
1.00
3.06
1.04
1.04
6.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.635
118.162
110.224
105.209
105.052
53.112
44.774
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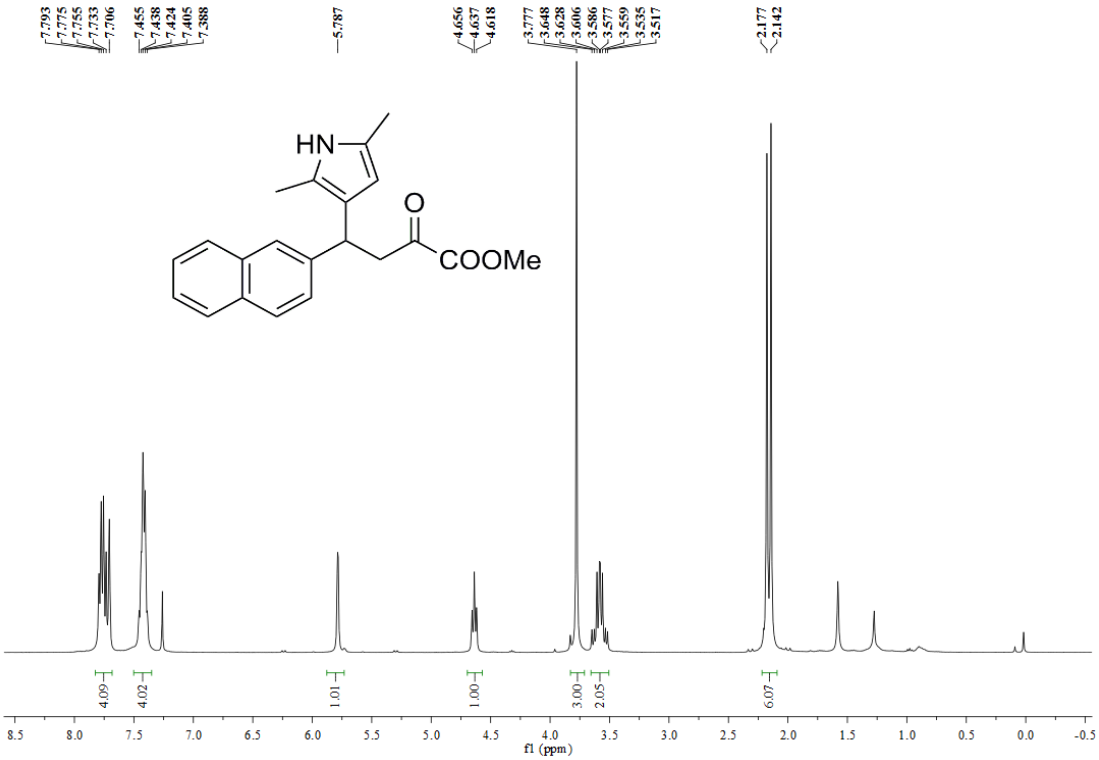
13.205
11.162
HN
COOMe
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.424
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7.388
5.787
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4.637
4.618
3.777
3.648
3.628
3.606
3.586
3.577
3.559
3.535
3.517
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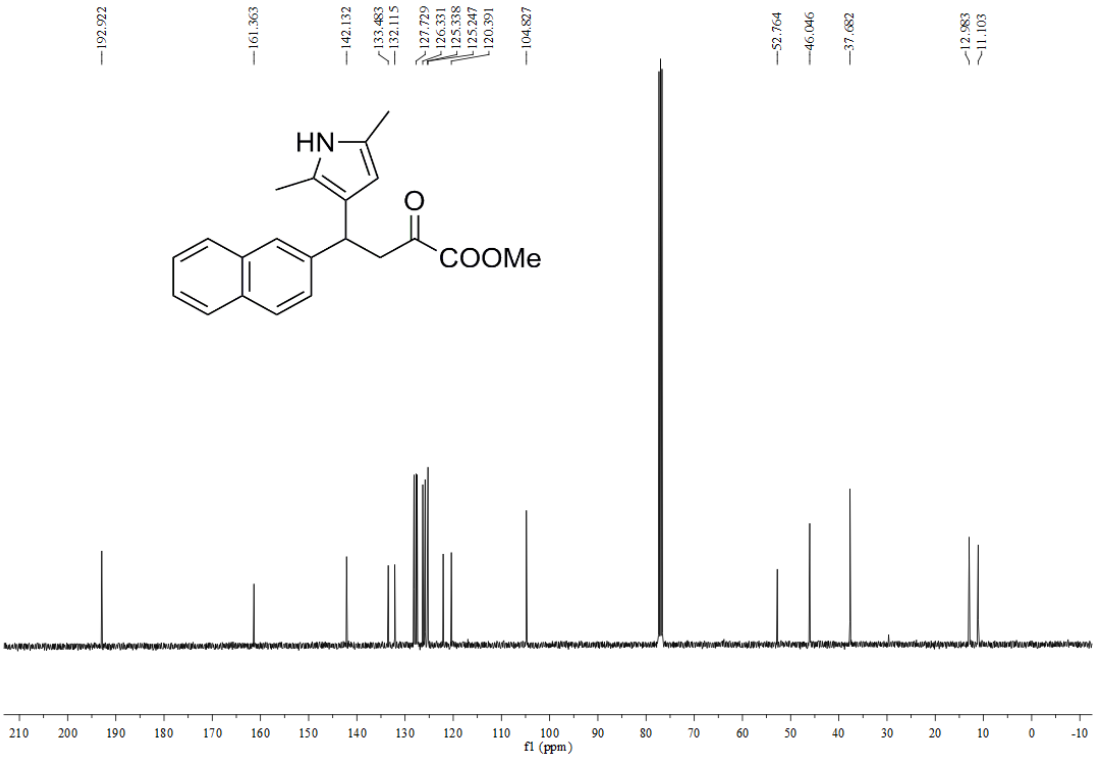
2.142
HN
O
COOMe
4.09
4.02
1.01
1.00
3.00
2.05
6.07
f1 (ppm)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142.132
133.483
132.115
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126.331
125.338
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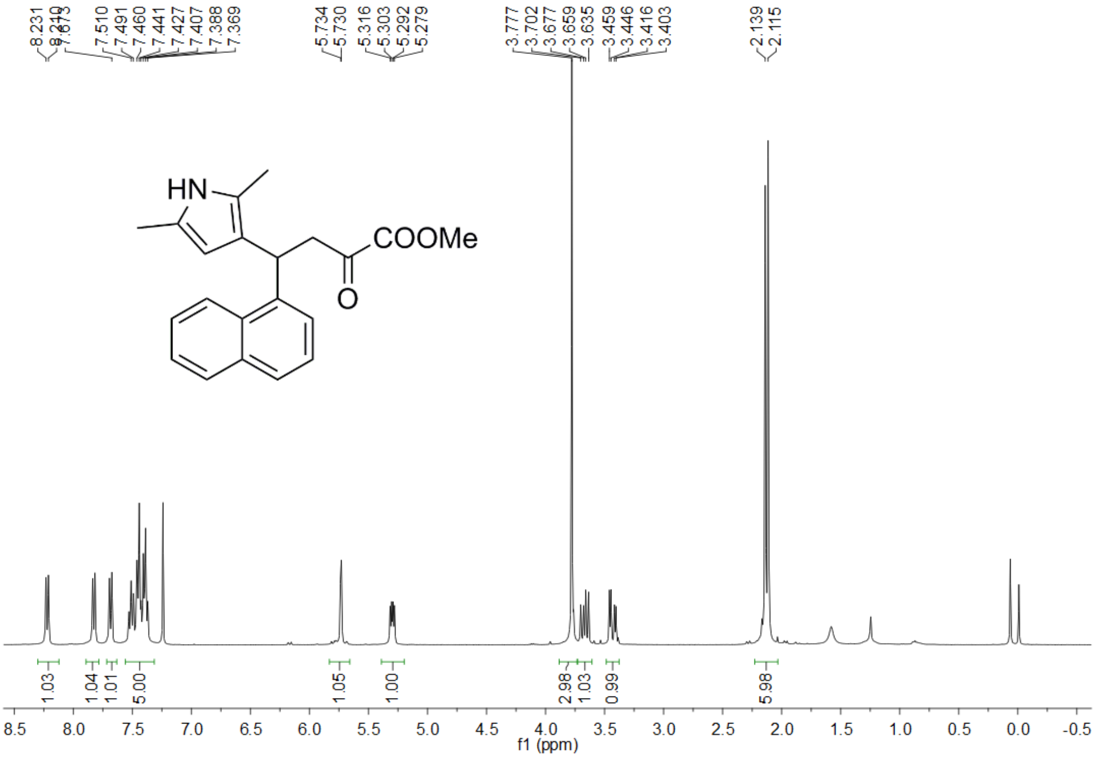
52.764
46.046
37.682
12.983
11.103
HN
O
COOMe
f1 (ppm)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8.210
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7.491
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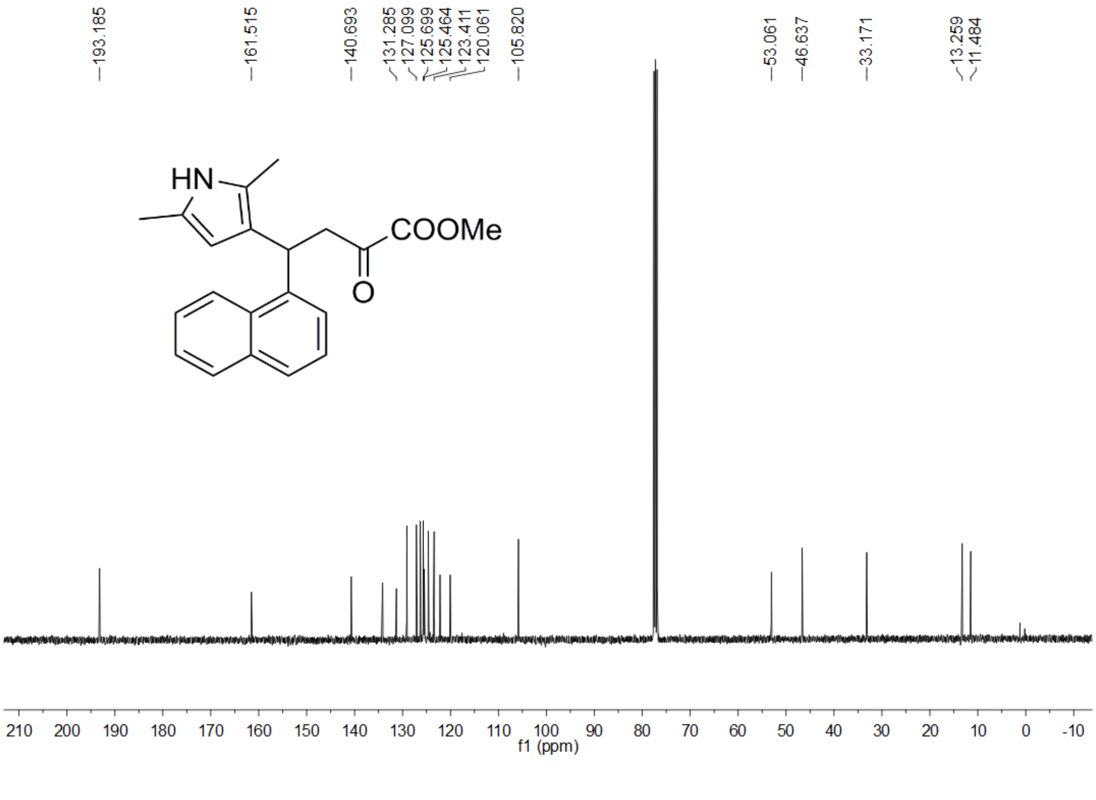
7.441
7.427
7.407
7.388
7.369
5.734
5.730
5.316
5.303
5.292
5.279
3.777
3.702
3.677
3.659
3.635
3.459
3.446
3.416
3.403
2.139
2.115
HN
COOMe
O
1.03
1.04
1.01
5.00
1.05
1.00
2.98
1.03
0.99
5.98
f1 (ppm)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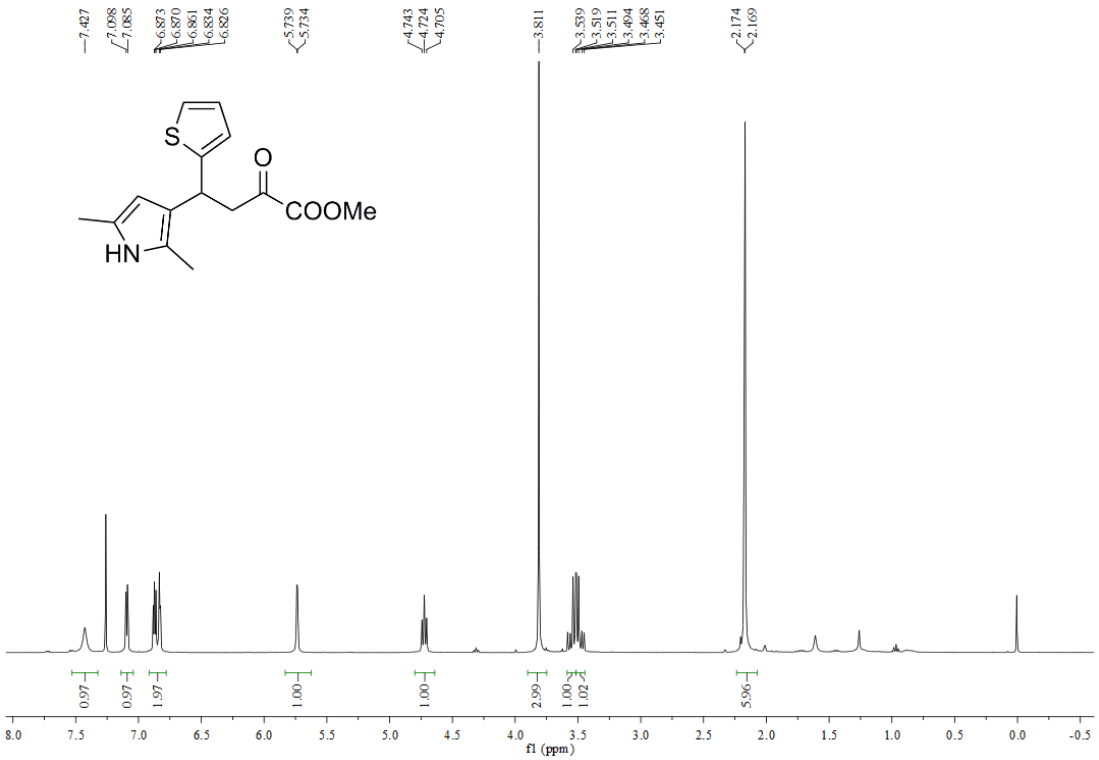
140.693
131.285
127.099
125.699
125.464
123.411
120.061
105.820
53.061
46.637
33.171
13.259
11.484
HN
COOMe
O
f1 (ppm)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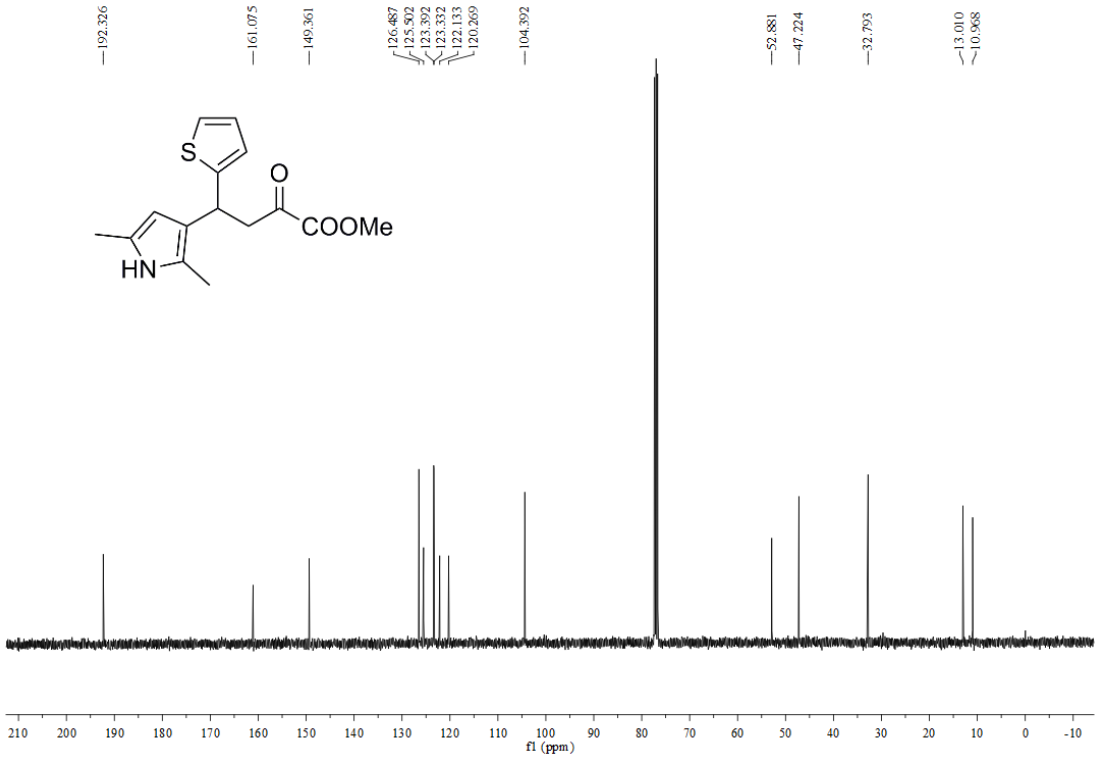
7.098
7.085
6.873
6.870
6.861
6.834
6.826
5.739
5.734
4.743
4.724
4.705
3.811
3.539
3.519
3.511
3.494
3.468
3.451
2.174
2.169
S
O
COOMe
HN
0.97
0.97
1.97
1.00
1.00
2.99
1.00
1.02
5.96
f1 (ppm)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123.332
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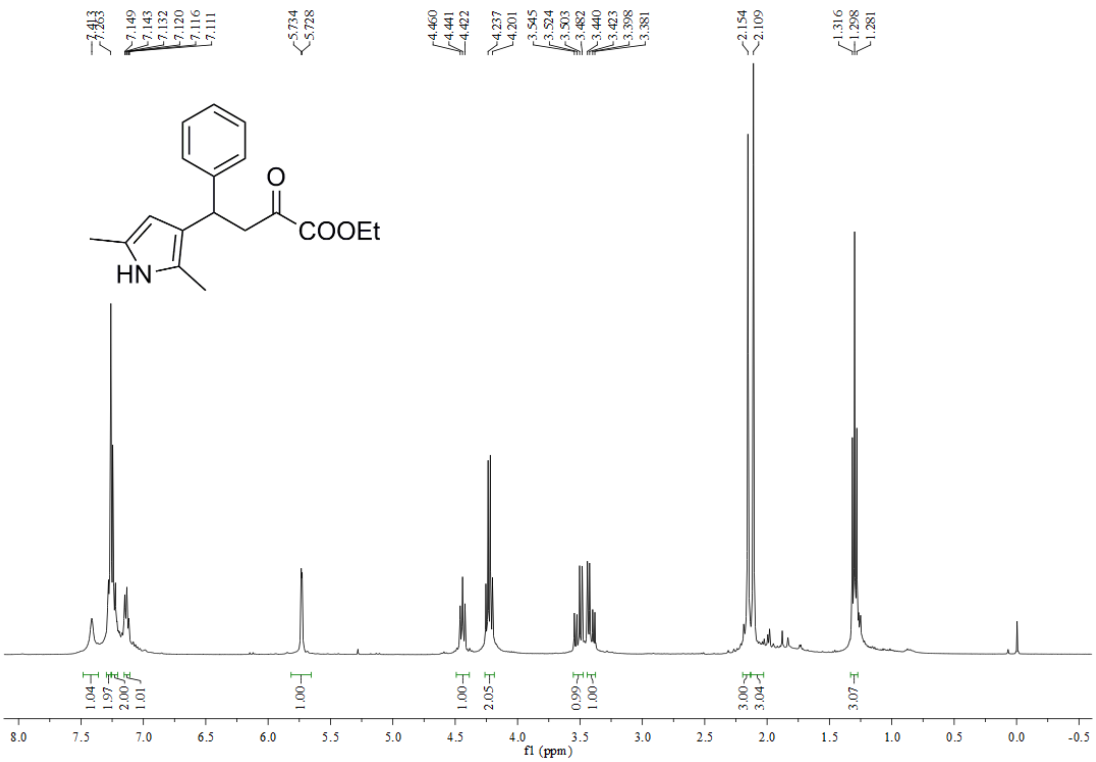
47.224
32.793
13.010
10.968
S
O
COOMe
HN
f1 (ppm)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7.143
7.132
7.120
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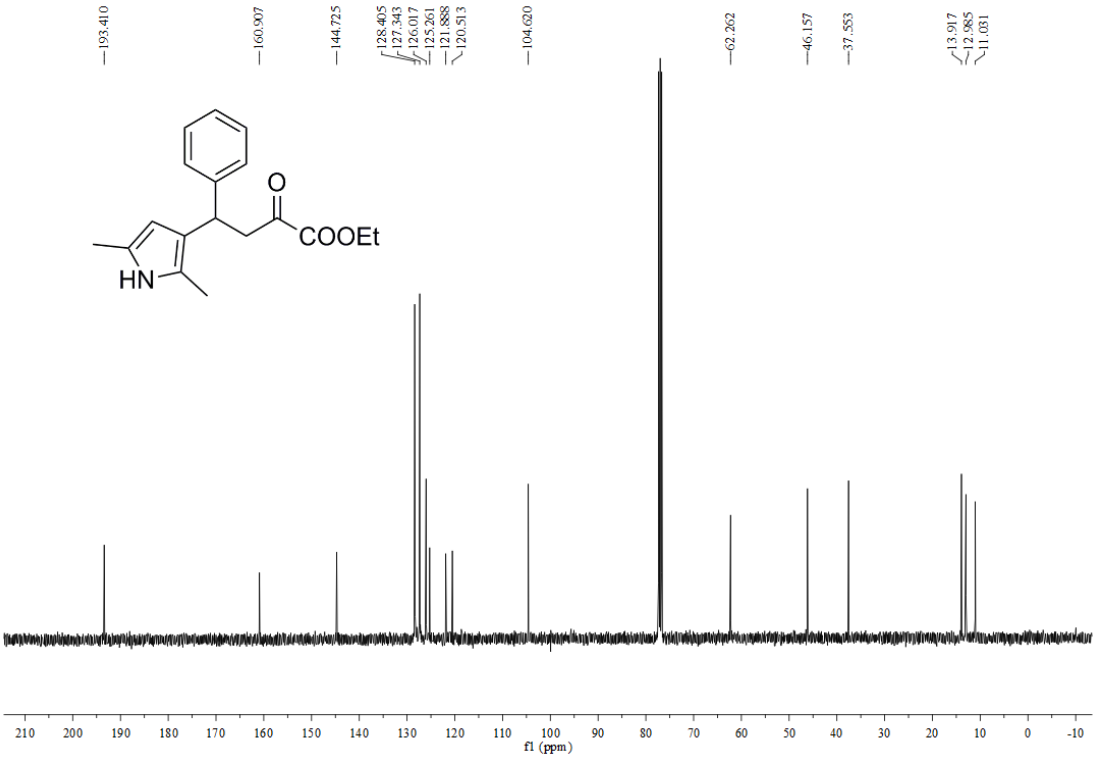
7.111
5.734
5.728
4.460
4.441
4.422
4.237
4.201
3.545
3.524
3.503
3.482
3.440
3.423
3.398
3.381
2.154
2.109
1.316
1.298
1.281
O
COOEt
HN
1.04
1.97
2.00
1.01
1.00
1.00
2.05
0.99
1.00
3.00
3.04
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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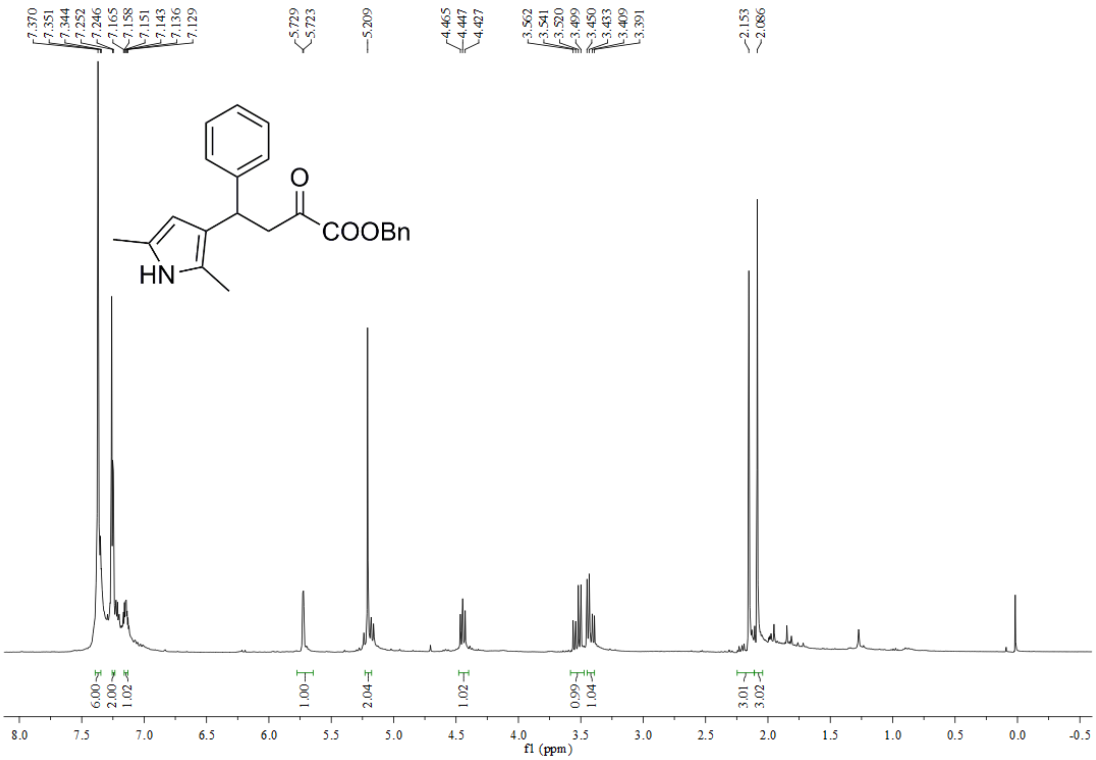
127.343
126.017
125.261
121.888
120.513
104.620
62.262
46.157
37.553
13.917
12.985
11.031
O
COOEt
HN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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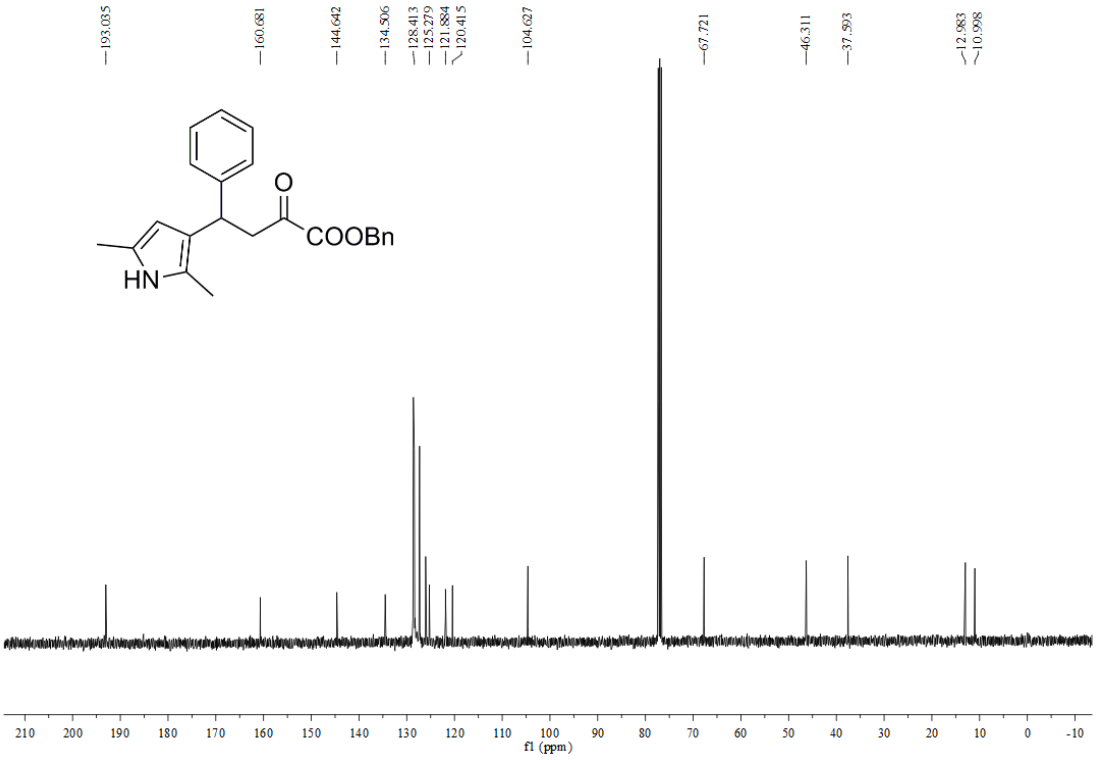
7.158
7.151
7.143
7.136
7.129
5.729
5.723
5.209
4.465
4.447
4.427
3.562
3.541
3.520
3.499
3.450
3.433
3.409
3.391
2.153
2.086
O
COOBn
HN
6.00
2.00
1.02
1.00
2.04
1.02
0.99
1.04
3.01
3.02
f1 (ppm)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67.721
46.311
37.993
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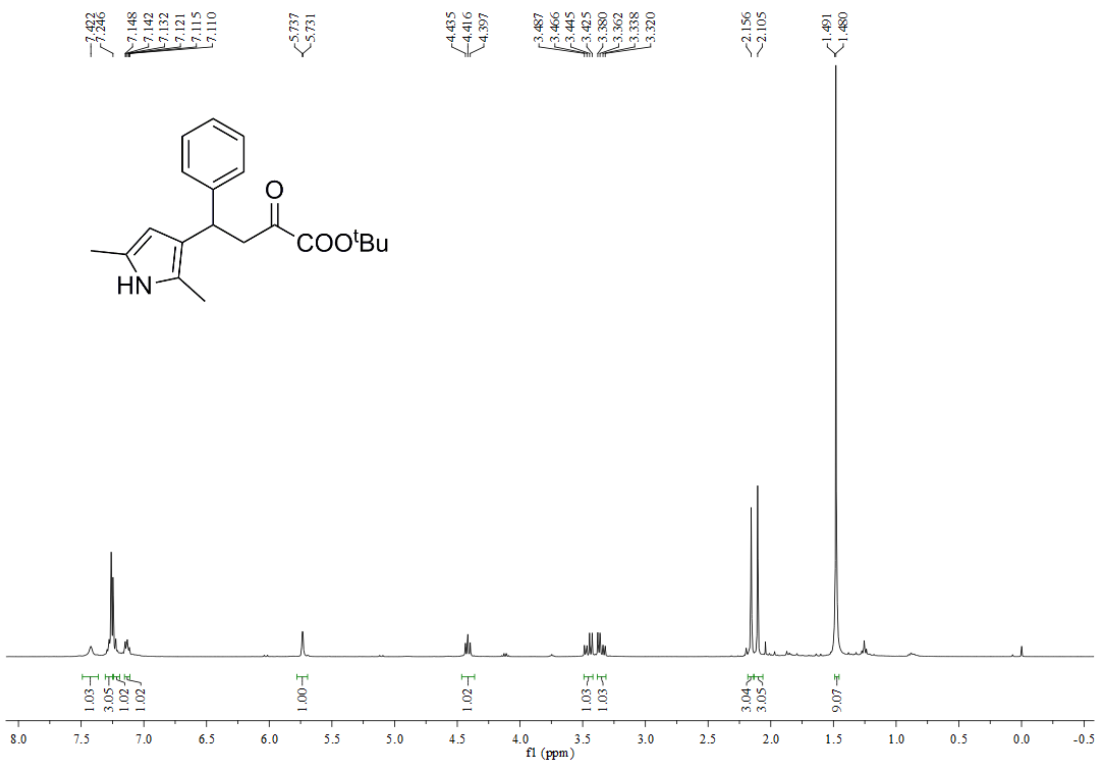
10.998
O
COOBn
HN
f1 (ppm)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7.110
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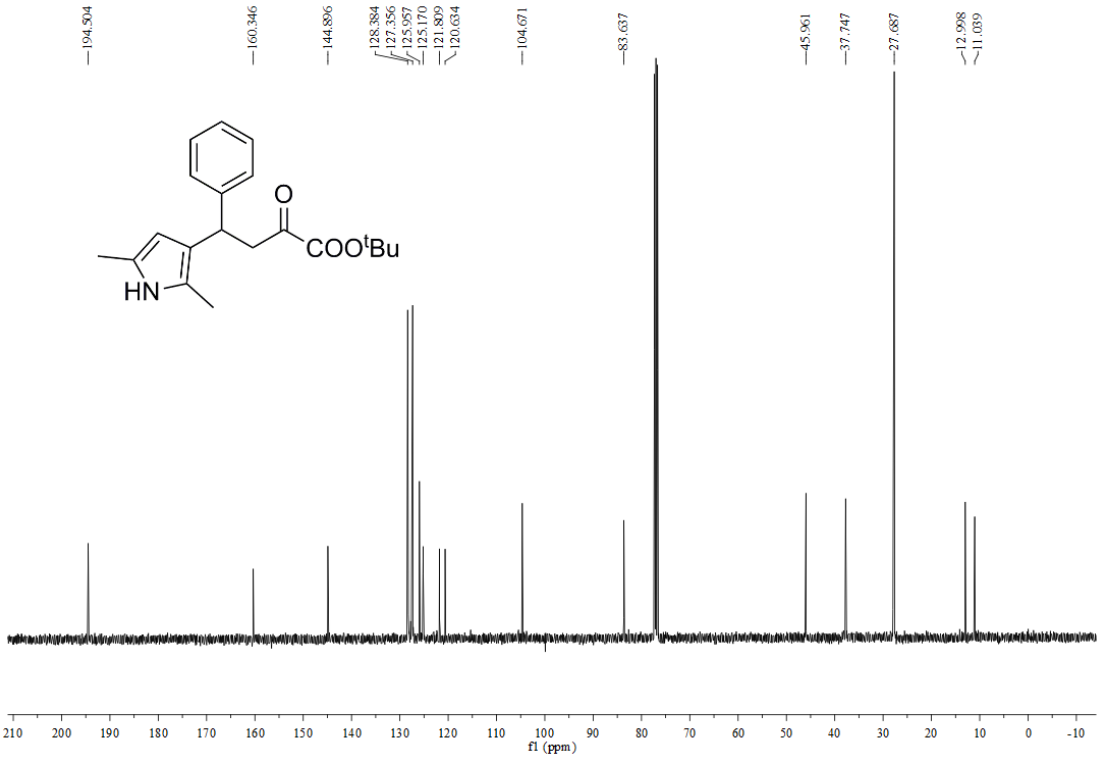
5.731
4.435
4.416
4.397
3.487
3.466
3.445
3.425
3.380
3.362
3.338
3.320
2.156
2.105
1.491
1.480
O
COO^{t}Bu
HN
1.03
3.05
1.02
1.02
1.00
1.02
1.03
1.03
3.04
3.05
9.07
f1 (ppm)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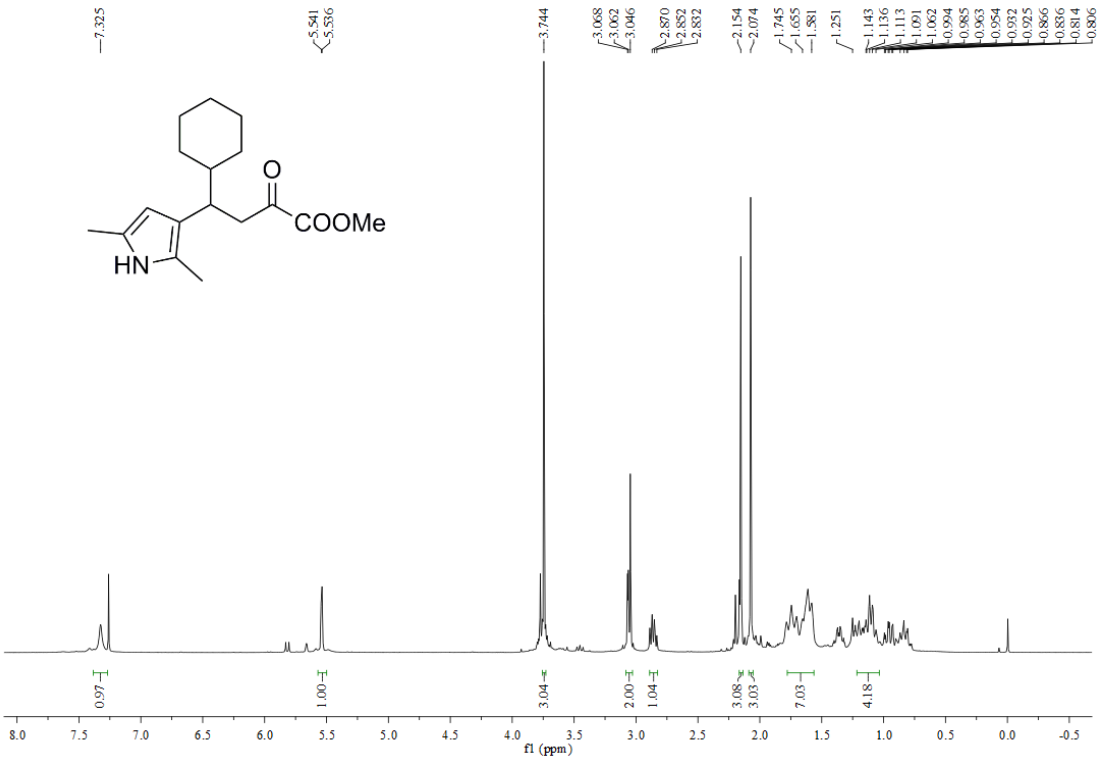
11.039
O
COO^{t}Bu
HN
f1 (ppm)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1.745
1.655
1.581
1.251
1.143
1.136
1.113
1.091
1.062
0.994
0.985
0.963
0.954
0.932
0.925
0.866
0.836
0.814
0.806
O
COOMe
HN
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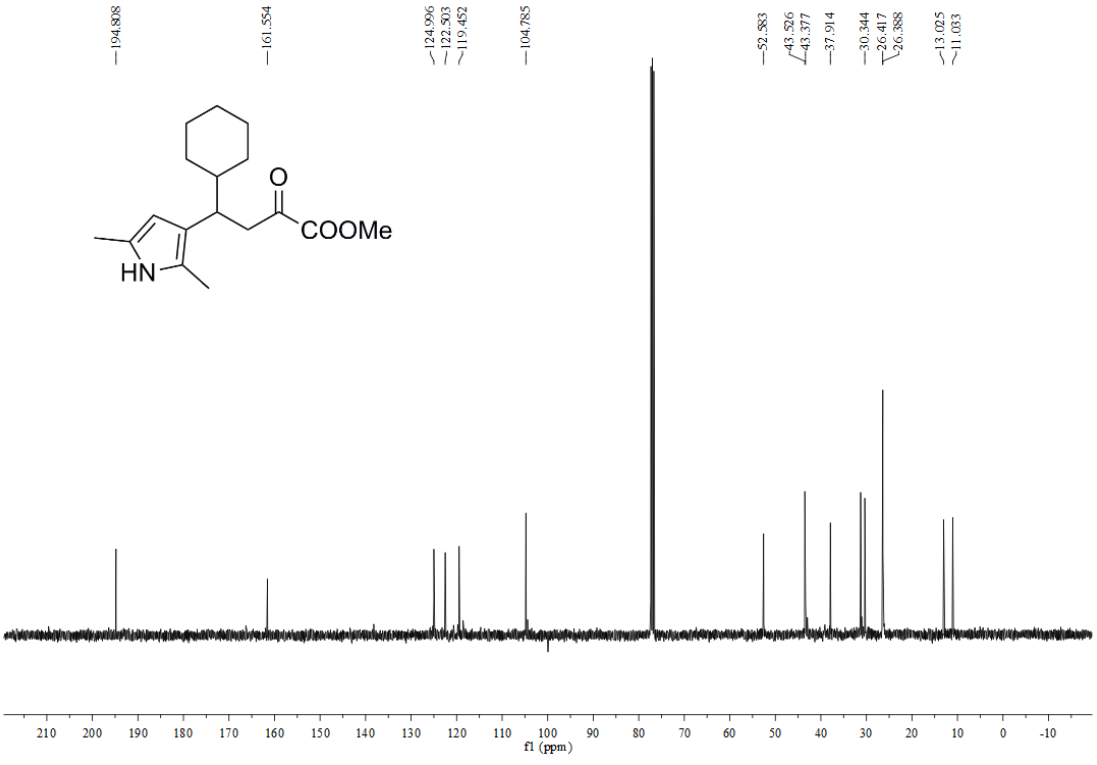
2.00
1.04
3.08
3.03
7.03
4.18
f1 (ppm)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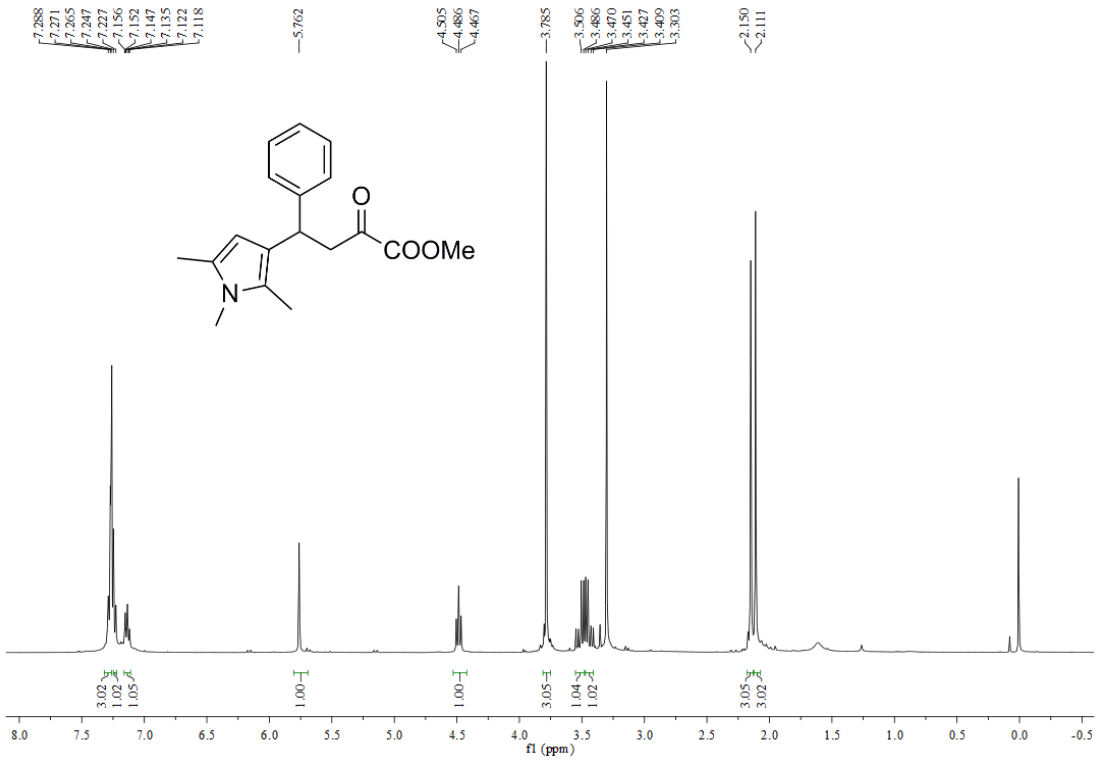
26.417
26.388
13.025
11.033
O
COOMe
HN
f1 (ppm)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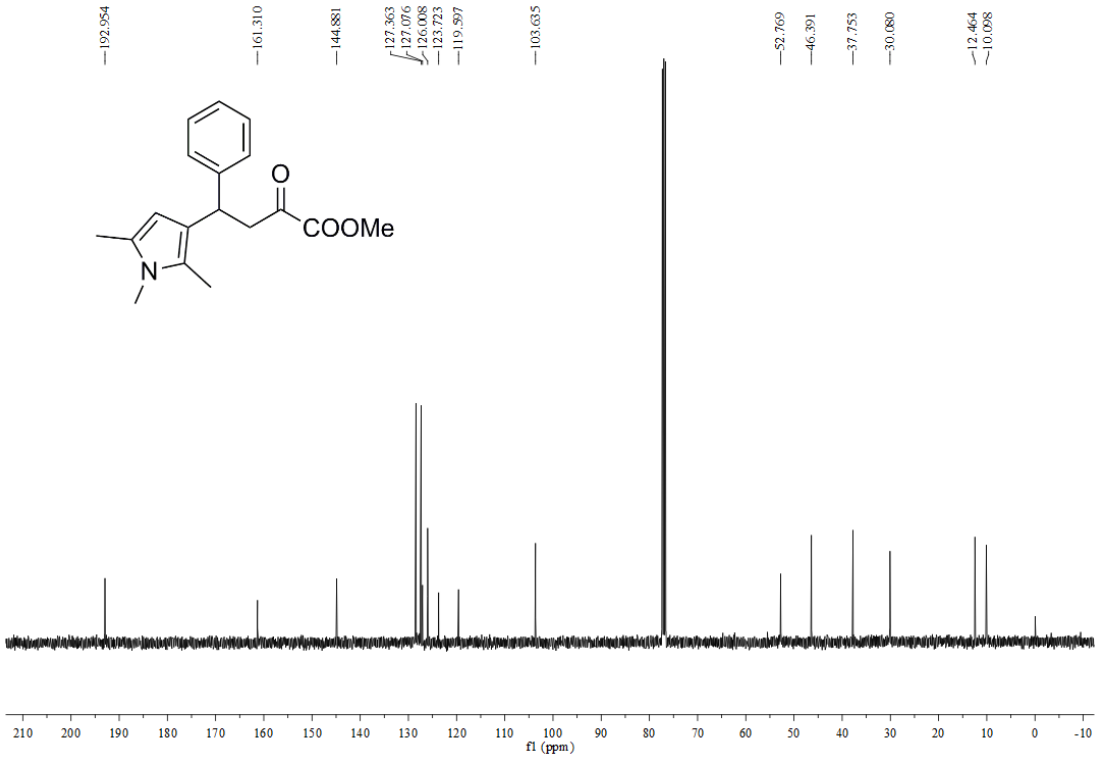
7.247
7.227
7.156
7.152
7.147
7.135
7.122
7.118
5.762
4.505
4.486
4.467
3.785
3.506
3.486
3.470
3.451
3.427
3.409
3.303
2.150
2.111
O
COOMe
N
3.02
1.02
1.05
1.00
1.00
3.05
1.04
1.02
3.05
3.02
f1 (ppm)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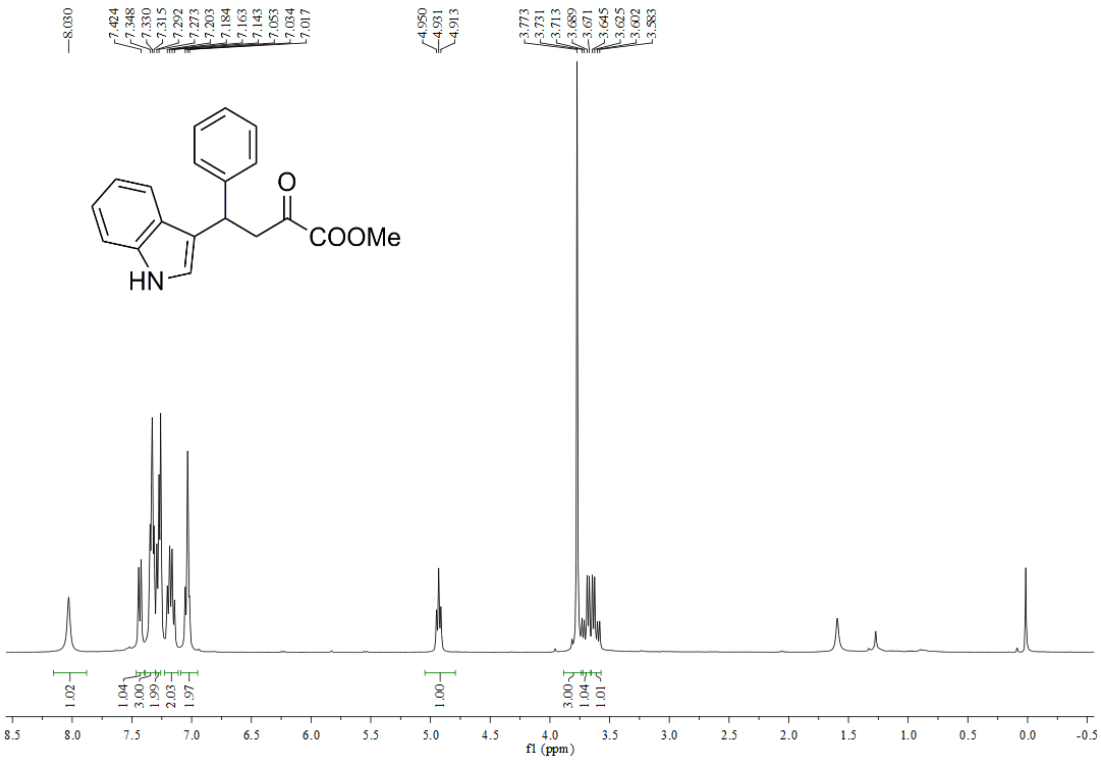
10.098
O
COOMe
N
f1 (ppm)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7.143
7.053
7.034
7.017
4.950
4.931
4.913
3.773
3.731
3.713
3.689
3.671
3.645
3.625
3.602
3.583
O
COOMe
HN
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3.00
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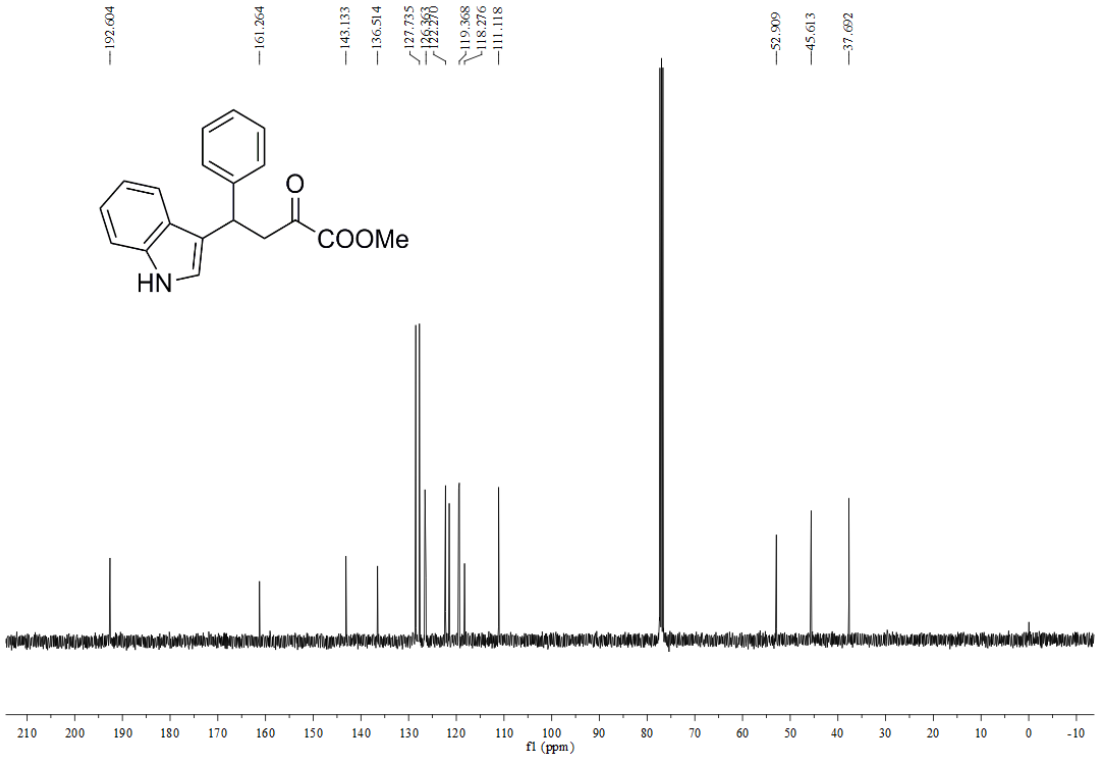
2.03
1.97
1.00
3.00
1.04
1.01
f1 (ppm)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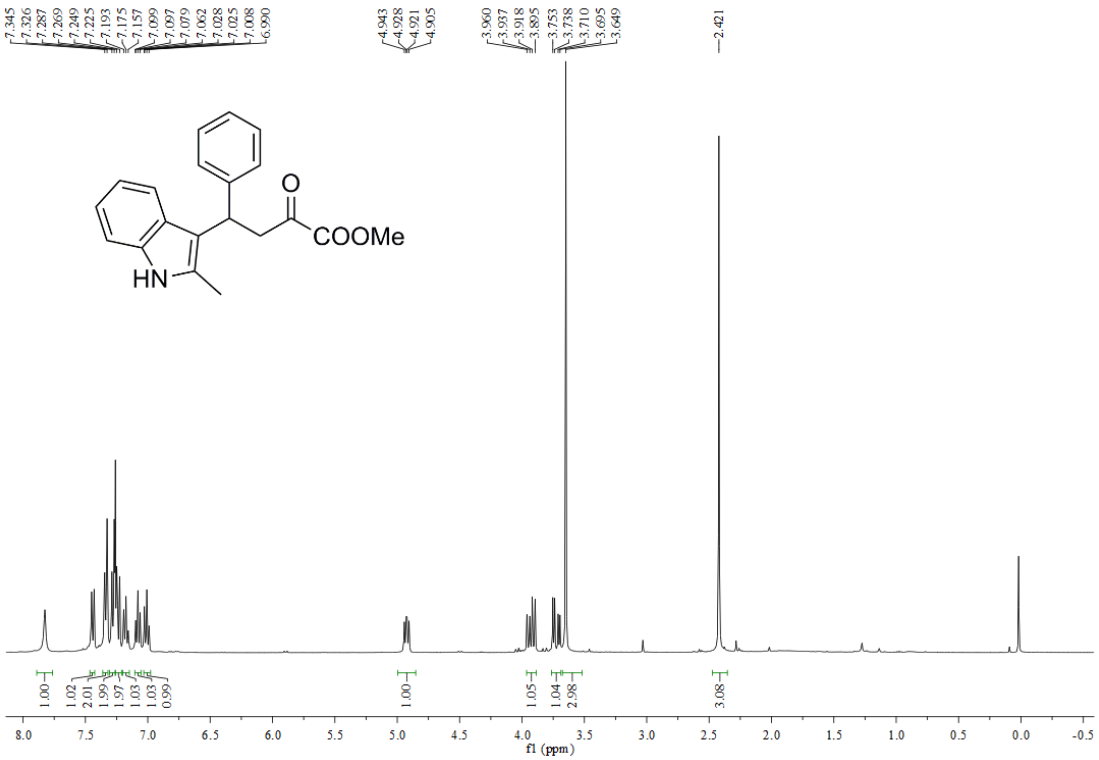
COOMe
HN
f1 (ppm)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7.062
7.028
7.025
7.008
6.990
4.943
4.928
4.921
4.905
3.960
3.937
3.918
3.895
3.753
3.738
3.710
3.695
3.649
2.421
O
COOMe
HN
1.00
1.02
2.01
1.99
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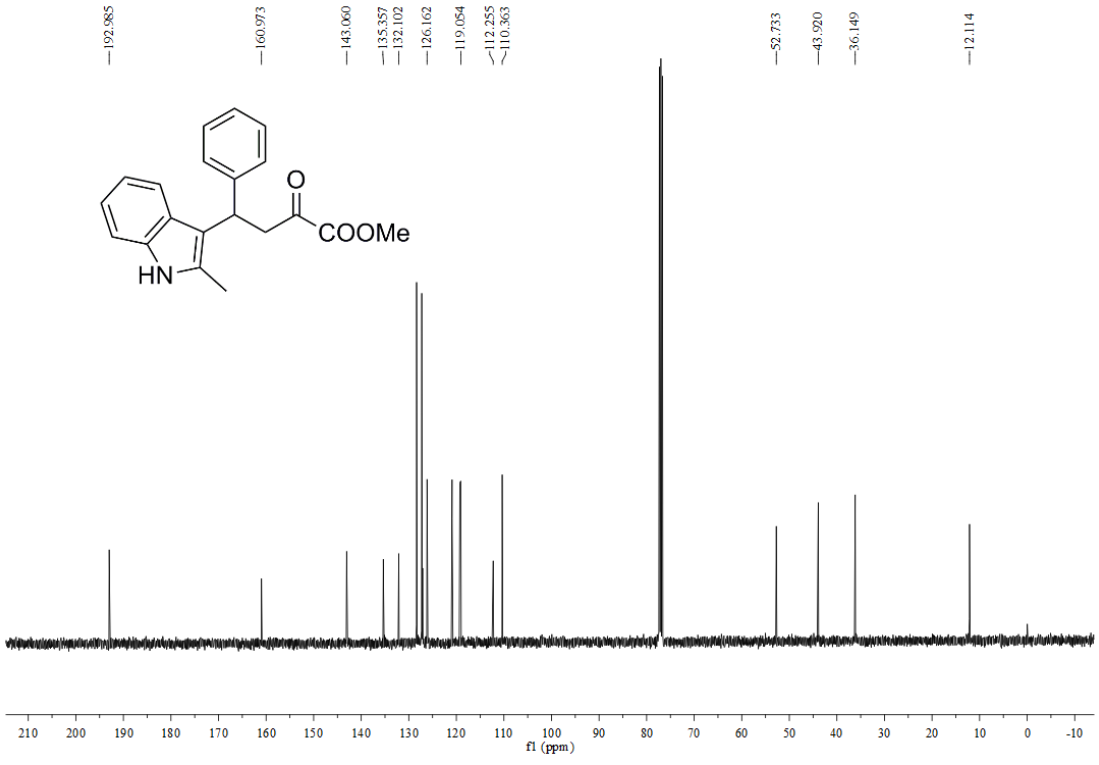
1.03
1.03
0.99
1.00
1.05
1.04
2.98
3.08
f1 (ppm)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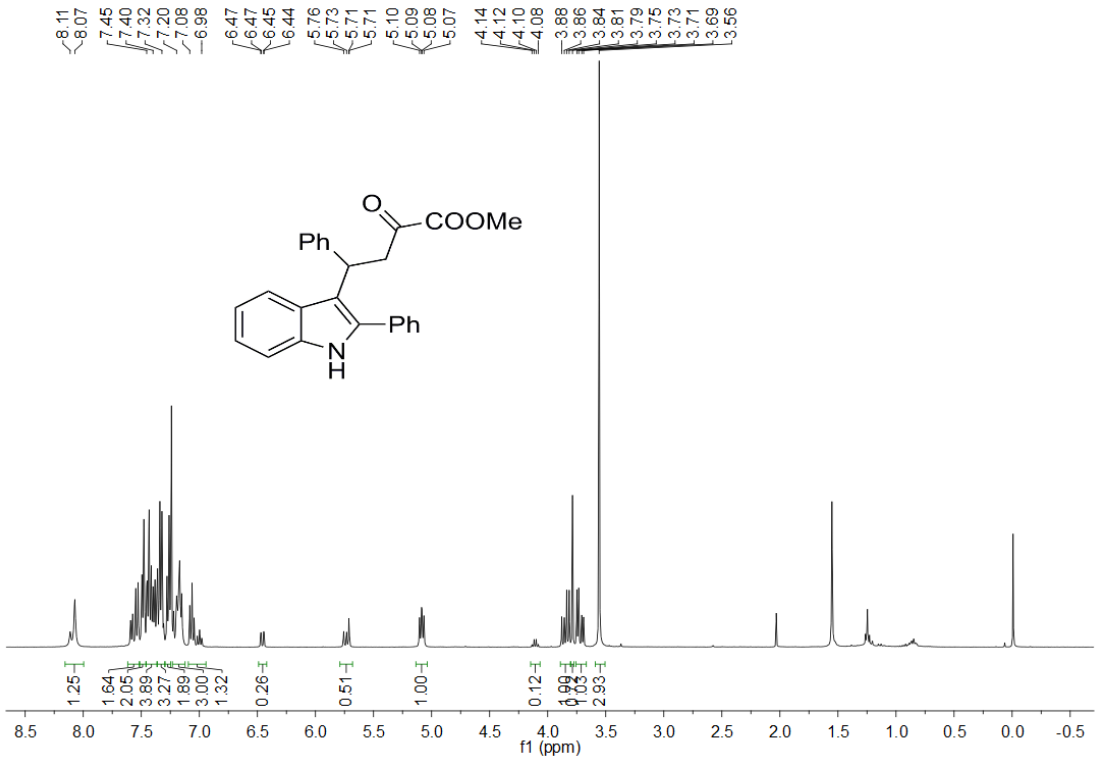
COOMe
HN
f1 (ppm)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5.76
5.73
5.71
5.71
5.10
5.09
5.08
5.07
4.14
4.12
4.10
4.08
3.88
3.86
3.84
3.81
3.79
3.75
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3.71
3.69
3.56
O
COOMe
Ph
Ph
N
H
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1.64
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3.00
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1.00
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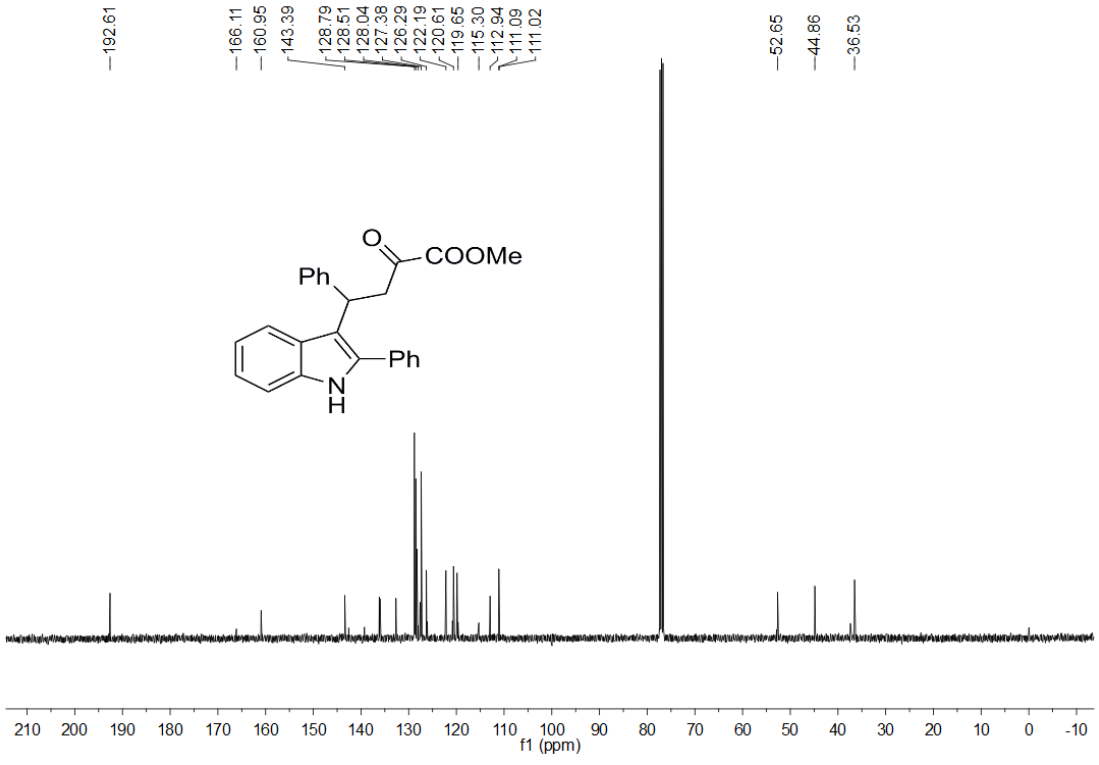
f1 (ppm)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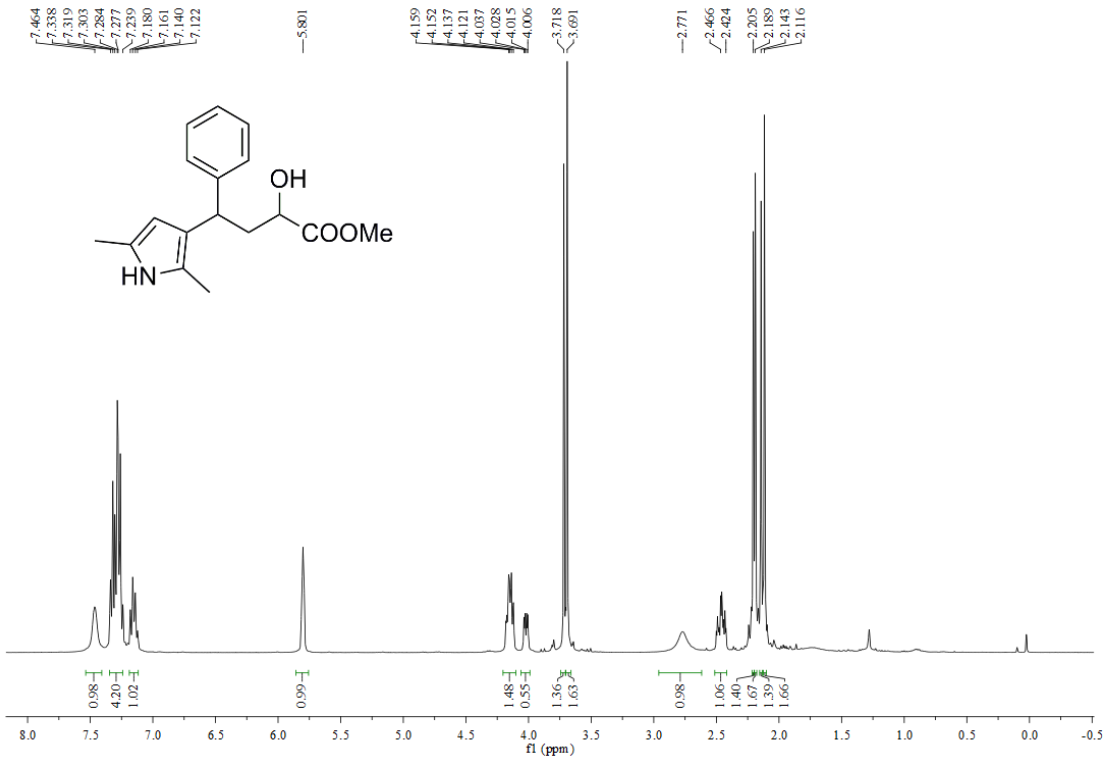
111.02
52.65
44.86
36.53
O
COOMe
Ph
Ph
N
H
f1 (ppm)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4.159
4.152
4.137
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4.015
4.006
3.718
3.691
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2.424
2.205
2.189
2.143
2.116
OH
COOMe
HN
0.98
4.20
1.02
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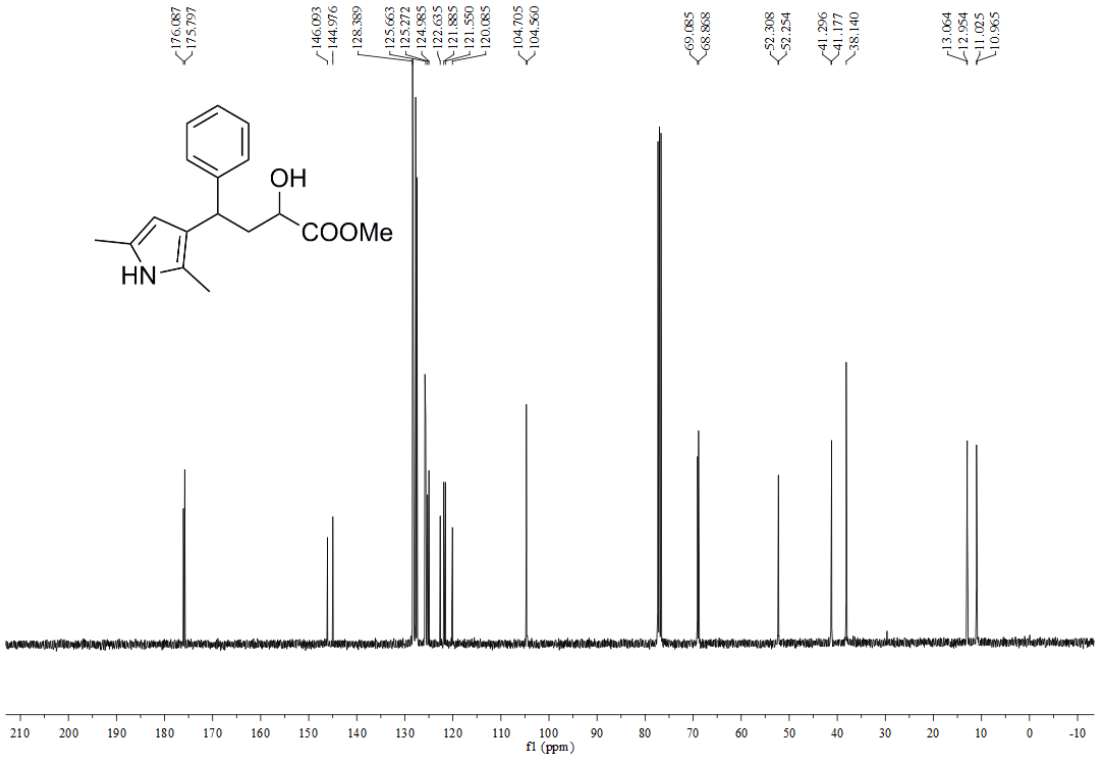
1.66
f1 (ppm)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OH
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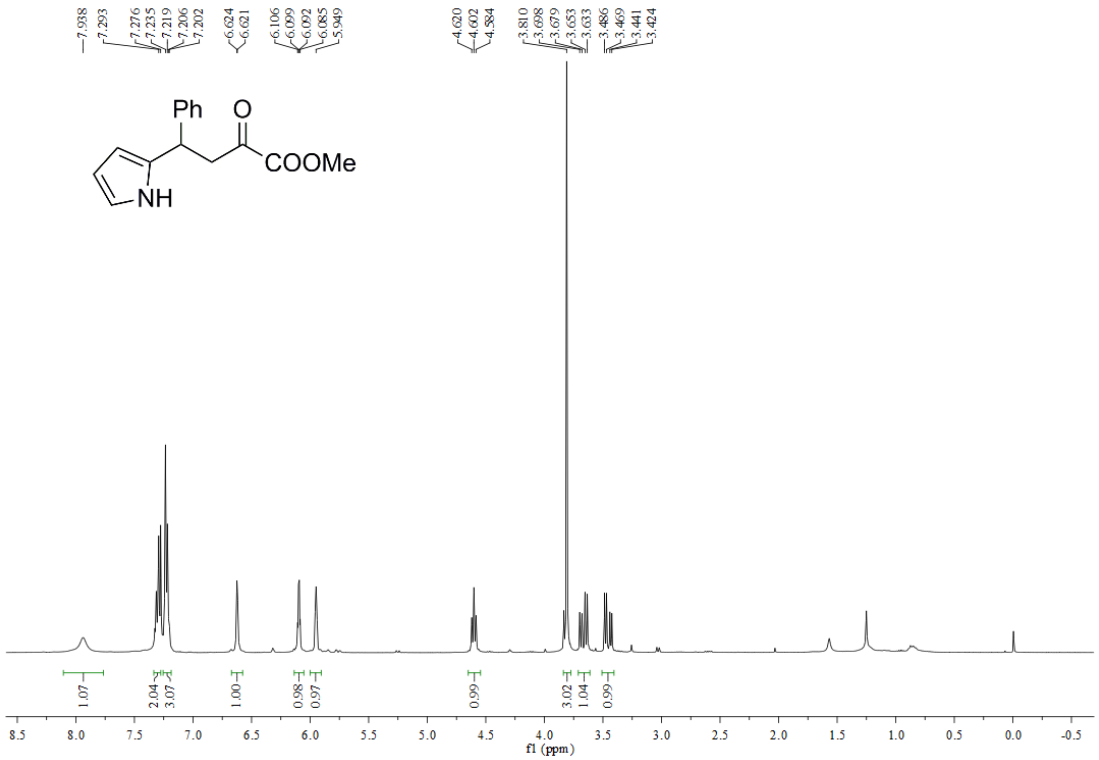
HN
f1 (ppm)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4.602
4.584
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3.653
3.633
3.486
3.469
3.441
3.424
Ph
O
COOMe
NH
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1.00
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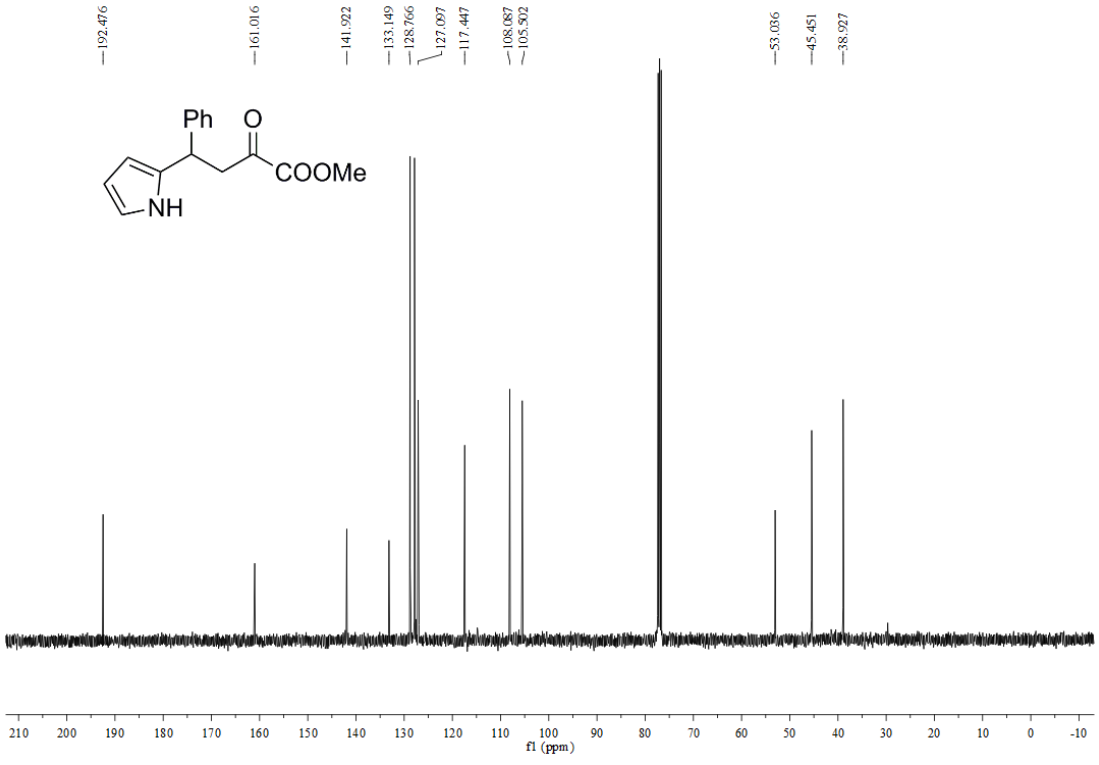
0.99
3.02
1.04
0.99
f1 (ppm)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127.097
117.447
108.087
105.502
53.036
45.451
38.927
Ph
O
COOMe
NH
f1 (ppm)

Computational details：

All calculations were performed by use of the density functional theory (DFT) in the Gaussian 09 programs.[1] The geometries were optimized using UM06[2] method. The LanL2DZ basis set and the corresponding effective core potential (ECP) was used for nickel atoms, and 6-31G(d) was used for all the other atoms, namely UM06/[6-31G(d), LanL2DZ].[3] Frequency calculations at the same level were performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). The relative Gibbs free energies in gas phase were used in the discussion.

Table S1 The relative energies of the stationary points calculated at the UM06/[6-31G(d), LanL2DZ] level.

species	**G_{gas} [a] (a.u.)**	**ΔG_r [b] (kJ mol^{-1})**	**Imaginary frequency (cm^{-1})**	**Number of Imaginary frequency**
Indole	-363.44008	-	-	0
L6-COM	-3013.65535	-	-	0
Indole + L6-COM	-3377.09543	0.0	-	-
L6-*Re*-TS1	-3377.06029	89.8	-331	1
L6-*Si*-TS1	-3377.06122	92.3	-288	1
L10-COM	-3170.67397	-	-	0
Indole + L10-COM	-3534.11405	0.0	-	-
L10-*Re*-TS1	-3534.07979	92.8	-265	1
L10-*Si*-TS1	-3534.07870	89.9	-319	1

[a] Gibbs free energies (a.u.) in gas phase calculated at the UM06/[6-31G(d), LanL2DZ] level.

[b] Related Gibbs free energies (kJ mol^{-1}) in gas phase.

XYZ Coordinates for the species considered

Indole

Zero-point correction= 0.129434 (a.u.)
Thermal correction to Gibbs Free Energy= 0.099085 (a.u.)
Sum of electronic and zero-point Energies= -363.409733 (a.u.)
Sum of electronic and thermal Free Energies= -363.440082 (a.u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.247078	-0.668053	-0.001009
2	6	0	-0.249038	0.748385	-0.000720
3	6	0	0.979140	1.423546	-0.000225
4	6	0	2.151339	0.689196	0.000636
5	6	0	2.127648	-0.716477	0.000511
6	6	0	0.931637	-1.413527	-0.000541
7	6	0	-2.381168	0.030701	0.000760

8	6	0	-1.619794	1.163093	0.000324
9	1	0	1.006236	2.512558	-0.001096
10	1	0	3.110312	1.204499	0.000876
11	1	0	3.067175	-1.266398	0.001367
12	1	0	0.911951	-2.502719	0.000344
13	1	0	-3.458201	-0.084890	0.001504
14	1	0	-1.991538	2.180591	0.000662
15	7	0	-1.561228	-1.078257	-0.001127
16	1	0	-1.873453	-2.037029	0.005810

L6-COM

Zero-point correction= 1.215593 (a.u.)
Thermal correction to Gibbs Free Energy= 1.119541(a.u.)
Sum of electronic and zero-point Energies= -3013.559296(a.u.)
Sum of electronic and thermal Free Energies= -3013.655349(a.u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.658802	-0.474624	6.463267
2	6	0	0.376491	1.948226	-1.042572
3	6	0	0.648617	3.328810	-1.264780
4	6	0	1.077364	4.119009	-0.237320
5	6	0	1.364246	5.523953	-0.278697
6	8	0	-0.157369	-0.136453	-2.090299
7	1	0	0.506759	3.716381	-2.270291
8	1	0	1.221421	3.625655	0.728625
9	6	0	1.143750	6.313057	-1.426406
10	6	0	1.883768	6.136069	0.878188
11	6	0	2.186788	7.487406	0.887302
12	6	0	1.442198	7.662499	-1.412538
13	6	0	1.966644	8.250304	-0.257974
14	1	0	0.727462	5.863558	-2.326879
15	1	0	2.055127	5.529752	1.767476
16	1	0	2.593940	7.950690	1.782885
17	1	0	2.202495	9.312516	-0.253473
18	1	0	1.267618	8.267781	-2.298915
19	8	0	-2.004800	0.008115	0.055485
20	8	0	-0.065153	-0.853107	1.982694
21	8	0	-0.708842	-2.520587	-0.422972
22	8	0	1.843562	-1.261620	-0.150515
23	7	0	-1.229575	-1.100799	2.646657
24	7	0	0.051828	-3.593507	-0.069529

25	7	0	3.576297	-2.613599	-0.619117
26	1	0	3.872301	-3.555976	-0.855893
27	7	0	-3.783906	1.018890	0.966895
28	1	0	-4.288166	1.260929	1.814589
29	6	0	-2.635707	0.340823	1.066951
30	6	0	-2.199688	0.057826	2.490253
31	1	0	-3.089752	-0.227059	3.075089
32	6	0	-1.474236	1.203581	3.184653
33	1	0	-2.172346	2.011592	3.435042
34	1	0	-0.702372	1.608066	2.516754
35	6	0	-0.854035	0.522942	4.413422
36	1	0	-1.438838	0.757517	5.314233
37	6	0	-0.945313	-1.001092	4.165853
38	1	0	-1.824349	-1.453665	4.644388
39	6	0	-1.883828	-2.395274	2.224448
40	1	0	-2.251795	-2.231134	1.208129
41	1	0	-2.738475	-2.540612	2.898832
42	6	0	-0.996799	-3.632001	2.271685
43	1	0	-1.652016	-4.480288	2.025062
44	1	0	-0.668338	-3.816161	3.305118
45	6	0	0.263098	-3.690799	1.420619
46	1	0	0.934728	-2.870435	1.684228
47	1	0	0.775207	-4.646303	1.598743
48	6	0	-0.580086	-4.851294	-0.712640
49	6	0	-0.162719	-4.736807	-2.197291
50	6	0	0.982216	-3.714704	-2.253200
51	1	0	1.832960	-4.041919	-2.861866
52	1	0	0.637981	-2.743929	-2.633939
53	6	0	1.388342	-3.574685	-0.792422
54	1	0	1.906341	-4.489654	-0.461726
55	6	0	2.267246	-2.378544	-0.476542
56	6	0	4.597309	-1.620492	-0.386467
57	6	0	4.904355	-0.701065	-1.396743
58	6	0	5.924082	0.216538	-1.136920
59	1	0	6.194711	0.946505	-1.898853
60	6	0	6.602151	0.210077	0.073360
61	6	0	6.262759	-0.704228	1.063337
62	1	0	6.797220	-0.691142	2.011485
63	6	0	5.248455	-1.636513	0.857533
64	6	0	-4.348477	1.379796	-0.309926
65	6	0	-4.073643	2.658462	-0.820016
66	6	0	-4.663480	3.000608	-2.035378
67	1	0	-4.495049	3.987809	-2.459761
68	6	0	-5.467425	2.094630	-2.718990

69	6	0	-5.686285	0.824097	-2.207373
70	1	0	-6.305763	0.120432	-2.761906
71	6	0	-5.131543	0.435774	-0.986240
72	1	0	0.191757	-5.723227	-2.528410
73	1	0	-0.100417	-5.698032	-0.203206
74	6	0	4.806741	-2.564296	1.969780
75	1	0	4.348868	-3.459044	1.516021
76	6	0	4.149528	-0.641898	-2.707140
77	1	0	3.477593	-1.513682	-2.759119
78	6	0	3.727503	-1.868122	2.807654
79	1	0	2.894308	-1.496428	2.191012
80	1	0	3.333488	-2.551875	3.574684
81	1	0	4.157728	-0.997587	3.324281
82	6	0	5.947480	-3.040221	2.861744
83	1	0	5.583810	-3.795661	3.569453
84	1	0	6.764276	-3.484794	2.280370
85	1	0	6.366748	-2.220527	3.460140
86	6	0	5.075745	-0.699987	-3.919050
87	1	0	4.491147	-0.724596	-4.847749
88	1	0	5.729220	0.180733	-3.970802
89	1	0	5.718341	-1.588472	-3.897418
90	6	0	3.272384	0.611285	-2.747139
91	1	0	2.669974	0.628735	-3.667516
92	1	0	2.606970	0.639885	-1.872642
93	1	0	3.884272	1.524014	-2.736332
94	6	0	-5.347479	-0.968972	-0.464511
95	1	0	-5.022786	-1.000784	0.588812
96	6	0	-3.197650	3.632171	-0.057094
97	1	0	-2.384700	3.051346	0.418776
98	6	0	-3.998974	4.323496	1.048016
99	1	0	-4.822238	4.905422	0.611597
100	1	0	-4.446295	3.611200	1.754940
101	1	0	-3.366085	5.013371	1.621405
102	6	0	-2.541736	4.679874	-0.949219
103	1	0	-1.806167	5.258080	-0.374229
104	1	0	-2.024047	4.220615	-1.803596
105	1	0	-3.275288	5.396822	-1.342181
106	6	0	-6.815067	-1.387791	-0.496164
107	1	0	-7.189099	-1.484681	-1.523859
108	1	0	-6.942749	-2.366418	-0.016138
109	1	0	-7.456189	-0.666544	0.024943
110	6	0	-4.482910	-1.964619	-1.242911
111	1	0	-3.414739	-1.701837	-1.203045
112	1	0	-4.613819	-2.978430	-0.836146

113	1	0	-4.782205	-1.993978	-2.300742
114	1	0	7.401093	0.927530	0.249964
115	1	0	-5.923684	2.383827	-3.663823
116	6	0	-2.104314	-4.905843	-0.675118
117	1	0	-2.480536	-5.670840	0.014266
118	1	0	-2.485037	-3.927154	-0.359715
119	6	0	-1.457858	-4.391951	-2.933461
120	1	0	-1.639280	-3.308177	-2.865966
121	1	0	-1.431225	-4.670573	-3.993037
122	6	0	0.374072	-1.611480	4.628096
123	1	0	0.232470	-2.534869	5.201959
124	1	0	0.988624	-1.831960	3.747642
125	6	0	0.628220	0.773681	4.693386
126	1	0	1.173733	0.846024	3.739884
127	1	0	0.804923	1.692642	5.263779
128	6	0	1.046874	-0.491798	5.434470
129	1	0	2.132938	-0.621058	5.503373
130	6	0	-2.513018	-5.150643	-2.134839
131	1	0	-2.466401	-6.223797	-2.369814
132	1	0	-3.538048	-4.821018	-2.341455
133	6	0	-0.067787	1.076186	-2.220030
134	8	0	0.481957	1.348872	0.041086
135	8	0	-0.327626	1.731313	-3.321128
136	6	0	-0.765687	0.952019	-4.451426
137	1	0	-0.992396	1.674775	-5.234451
138	1	0	0.037838	0.278658	-4.764813
139	1	0	-1.652517	0.372604	-4.178790
140	28	0	-0.090244	-0.680420	-0.004512

L6-*Re*-TS1

Zero-point correction= 1.348472 (a.u.)
Thermal correction to Gibbs Free Energy= 1.247746 (a.u.)
Sum of electronic and zero-point Energies= -3376.960496 (a.u.)
Sum of electronic and thermal Free Energies= -3377.061222 (a.u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.721785	0.065280	6.230398
2	8	0	-2.674387	0.951534	0.175870
3	8	0	-0.865828	-0.431609	1.958324
4	8	0	-2.661542	-1.873626	0.047855
5	8	0	0.212236	-1.928035	-0.226730

6	7	0	-1.845324	0.025379	2.787353
7	7	0	-2.403254	-3.110895	0.540677
8	7	0	1.011437	-3.990487	-0.613588
9	1	0	0.796099	-4.979242	-0.698461
10	7	0	-3.149619	3.005347	0.937011
11	1	0	-3.166422	3.640899	1.728518
12	6	0	-2.663189	1.770886	1.101493
13	6	0	-2.136106	1.489567	2.497671
14	1	0	-2.914486	1.785870	3.221479
15	6	0	-0.814284	2.159309	2.855024
16	1	0	-0.941187	3.241508	2.980671
17	1	0	-0.096765	1.983691	2.040704
18	6	0	-0.406230	1.436775	4.145902
19	1	0	-0.661588	2.053330	5.019797
20	6	0	-1.257215	0.144901	4.210217
21	1	0	-2.129648	0.252832	4.868622
22	6	0	-3.102660	-0.808196	2.714202
23	1	0	-3.538076	-0.614847	1.730211
24	1	0	-3.776905	-0.419768	3.489854
25	6	0	-2.905230	-2.303687	2.925368
26	1	0	-3.912910	-2.744080	2.916442
27	1	0	-2.524476	-2.489899	3.940226
28	6	0	-1.991187	-3.087801	1.992880
29	1	0	-0.983360	-2.664187	2.014226
30	1	0	-1.952949	-4.135681	2.320520
31	6	0	-3.633608	-4.001693	0.241637
32	6	0	-3.492339	-4.304780	-1.267625
33	6	0	-2.040519	-3.974859	-1.648242
34	1	0	-1.553165	-4.760230	-2.238929
35	1	0	-1.977785	-3.032079	-2.207465
36	6	0	-1.353336	-3.817667	-0.295953
37	1	0	-1.228558	-4.807827	0.172758
38	6	0	0.006012	-3.138988	-0.352865
39	6	0	2.387449	-3.597717	-0.777286
40	6	0	2.830283	-3.222615	-2.054998
41	6	0	4.200119	-3.005856	-2.222312
42	1	0	4.588236	-2.752573	-3.207493
43	6	0	5.078395	-3.136935	-1.152296
44	6	0	4.599151	-3.429901	0.118333
45	1	0	5.294328	-3.500461	0.953541
46	6	0	3.239711	-3.664858	0.335844
47	6	0	-3.684430	3.440533	-0.329229
48	6	0	-2.824605	4.108186	-1.215747
49	6	0	-3.368998	4.544089	-2.422427

50	1	0	-2.744300	5.080206	-3.134445
51	6	0	-4.700526	4.294088	-2.735967
52	6	0	-5.509793	3.587889	-1.858347
53	1	0	-6.543301	3.378416	-2.131221
54	6	0	-5.017894	3.138832	-0.631197
55	1	0	-3.693517	-5.374679	-1.420193
56	1	0	-3.497136	-4.894857	0.866303
57	6	0	2.710905	-3.912391	1.732660
58	1	0	1.762108	-4.466252	1.645990
59	6	0	1.874160	-3.095590	-3.222619
60	1	0	0.883444	-2.824324	-2.819161
61	6	0	2.399449	-2.570182	2.407921
62	1	0	1.674550	-1.971623	1.835306
63	1	0	1.994727	-2.739293	3.416704
64	1	0	3.317862	-1.971352	2.516043
65	6	0	3.649452	-4.740230	2.603798
66	1	0	3.149712	-5.011978	3.541620
67	1	0	3.964006	-5.665980	2.106802
68	1	0	4.552629	-4.178724	2.878477
69	6	0	1.736458	-4.431447	-3.953666
70	1	0	1.020607	-4.352211	-4.782194
71	1	0	2.702943	-4.743052	-4.373082
72	1	0	1.394897	-5.235103	-3.286828
73	6	0	2.279286	-1.990002	-4.192155
74	1	0	1.488701	-1.827578	-4.936437
75	1	0	2.456447	-1.038192	-3.669195
76	1	0	3.187496	-2.247171	-4.753451
77	6	0	-5.896885	2.313666	0.285857
78	1	0	-5.394666	2.231029	1.264092
79	6	0	-1.370566	4.349448	-0.863256
80	1	0	-1.028130	3.488893	-0.262418
81	6	0	-1.219984	5.616030	-0.018201
82	1	0	-1.547230	6.496465	-0.588625
83	1	0	-1.819620	5.587642	0.902238
84	1	0	-0.170930	5.774140	0.267979
85	6	0	-0.460159	4.433095	-2.083737
86	1	0	0.592960	4.453496	-1.770483
87	1	0	-0.592056	3.575306	-2.757422
88	1	0	-0.636936	5.349592	-2.663044
89	6	0	-7.257991	2.961146	0.527976
90	1	0	-7.862575	2.991502	-0.388191
91	1	0	-7.827871	2.386071	1.268913
92	1	0	-7.160169	3.989777	0.896241
93	6	0	-6.061526	0.893968	-0.265987

94	1	0	-5.090349	0.399349	-0.412859
95	1	0	-6.669980	0.285429	0.418563
96	1	0	-6.577598	0.912906	-1.236315
97	1	0	6.148810	-3.010103	-1.313104
98	1	0	-5.106643	4.646075	-3.682466
99	6	0	-4.984940	-3.320837	0.440834
100	1	0	-5.532596	-3.722444	1.301529
101	1	0	-4.822644	-2.247448	0.595363
102	6	0	-4.599953	-3.482657	-1.928642
103	1	0	-4.254439	-2.447552	-2.067368
104	1	0	-4.897711	-3.880252	-2.905605
105	6	0	-0.325548	-0.984491	4.636785
106	1	0	-0.788594	-1.671302	5.355254
107	1	0	-0.026226	-1.548717	3.744419
108	6	0	1.038099	0.952267	4.279518
109	1	0	1.419794	0.634688	3.294939
110	1	0	1.714134	1.719927	4.674449
111	6	0	0.904876	-0.259635	5.195725
112	1	0	1.797452	-0.896138	5.211304
113	6	0	-5.718610	-3.526082	-0.892691
114	1	0	-6.213190	-4.507980	-0.909931
115	1	0	-6.494347	-2.769920	-1.058540
116	28	0	-1.247415	-0.476468	-0.012058
117	6	0	5.137860	1.129627	1.173271
118	6	0	3.817305	1.537678	1.426067
119	6	0	3.593946	2.563225	2.342965
120	6	0	4.687327	3.135999	2.981474
121	6	0	5.994093	2.709583	2.707507
122	6	0	6.244011	1.697014	1.790149
123	6	0	3.807488	-0.086792	-0.167664
124	6	0	2.955302	0.820064	0.495819
125	1	0	2.582868	2.920135	2.543169
126	1	0	4.532103	3.933476	3.705184
127	1	0	6.828571	3.182882	3.219860
128	1	0	7.258220	1.371627	1.568006
129	1	0	3.556608	-0.805911	-0.944411
130	1	0	1.891860	0.606448	0.649509
131	7	0	5.073347	0.123733	0.199462
132	1	0	5.875747	-0.332929	-0.218551
133	6	0	0.540881	0.978449	-1.560513
134	6	0	1.751603	1.498074	-1.948873
135	6	0	2.575933	2.150034	-0.973716
136	6	0	3.851106	2.768865	-1.351312
137	8	0	-1.288844	-0.419848	-2.152823

138	1	0	2.080733	1.406240	-2.980910
139	1	0	2.009034	2.719744	-0.226978
140	6	0	4.696392	2.184819	-2.305099
141	6	0	4.258054	3.952744	-0.722981
142	6	0	5.478709	4.536485	-1.033154
143	6	0	5.917898	2.765977	-2.614242
144	6	0	6.313346	3.939687	-1.974086
145	1	0	4.393905	1.258971	-2.798611
146	1	0	3.600732	4.420089	0.010476
147	1	0	5.779947	5.459114	-0.541747
148	1	0	7.272059	4.393699	-2.216513
149	1	0	6.566061	2.308461	-3.359140
150	6	0	-0.348903	0.269157	-2.544346
151	8	0	0.099630	0.989466	-0.355823
152	8	0	-0.062161	0.449253	-3.814093
153	6	0	-0.921079	-0.202502	-4.760705
154	1	0	-0.501226	0.018329	-5.742555
155	1	0	-0.934176	-1.282878	-4.575490
156	1	0	-1.937623	0.193164	-4.674868

L6-*Si*-TS1

Zero-point correction= 1.348850 (a.u.)
Thermal correction to Gibbs Free Energy= 1.248642(a.u.)
Sum of electronic and zero-point Energies= -3376.960077(a.u.)
Sum of electronic and thermal Free Energies= -3377.060285(a.u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.279915	1.585132	6.231455
2	8	0	-2.416897	1.267156	-0.153842
3	8	0	-1.100390	0.186040	2.141216
4	8	0	-2.842591	-1.572137	0.388577
5	8	0	-0.037702	-1.945232	0.486460
6	7	0	-2.125411	0.854670	2.734016
7	7	0	-2.745872	-2.684825	1.168661
8	7	0	0.614393	-4.067866	0.256475
9	1	0	0.348255	-5.046438	0.204585
10	7	0	-3.316347	3.293500	0.184806
11	1	0	-3.536813	4.027620	0.850487
12	6	0	-2.691521	2.190045	0.619477
13	6	0	-2.327217	2.217543	2.089817
14	1	0	-3.147952	2.691261	2.652754

15	6	0	-1.010774	2.922778	2.393391
16	1	0	-1.110601	4.008323	2.275233
17	1	0	-0.240315	2.565331	1.694650
18	6	0	-0.712378	2.487072	3.834211
19	1	0	-0.953960	3.297936	4.536108
20	6	0	-1.649570	1.294624	4.138114
21	1	0	-2.563345	1.600256	4.665607
22	6	0	-3.410973	0.065029	2.725413
23	1	0	-3.737201	0.034735	1.681794
24	1	0	-4.134238	0.640927	3.318824
25	6	0	-3.310094	-1.348211	3.281700
26	1	0	-4.339112	-1.734853	3.311501
27	1	0	-2.990677	-1.312199	4.333265
28	6	0	-2.397536	-2.360271	2.600934
29	1	0	-1.368606	-1.990118	2.584207
30	1	0	-2.436973	-3.309333	3.152731
31	6	0	-4.049829	-3.506313	1.011182
32	6	0	-3.880615	-4.194152	-0.363417
33	6	0	-2.397427	-4.070419	-0.732961
34	1	0	-1.964284	-4.999382	-1.124495
35	1	0	-2.234472	-3.272162	-1.470350
36	6	0	-1.744798	-3.674732	0.585837
37	1	0	-1.736575	-4.535140	1.274998
38	6	0	-0.335729	-3.141349	0.448863
39	6	0	1.967077	-3.692794	-0.076640
40	6	0	2.365548	-3.819400	-1.418285
41	6	0	3.680757	-3.484675	-1.736952
42	1	0	4.031505	-3.579397	-2.762660
43	6	0	4.551037	-3.017465	-0.760747
44	6	0	4.115758	-2.860925	0.546978
45	1	0	4.808332	-2.469151	1.292316
46	6	0	2.810964	-3.187017	0.921922
47	6	0	-3.629801	3.491955	-1.208480
48	6	0	-2.805624	4.354342	-1.948768
49	6	0	-3.101902	4.524777	-3.299017
50	1	0	-2.493169	5.191158	-3.906909
51	6	0	-4.168809	3.851508	-3.883679
52	6	0	-4.960583	3.000723	-3.127380
53	1	0	-5.793686	2.483317	-3.601624
54	6	0	-4.713298	2.802519	-1.767289
55	1	0	-4.158413	-5.251861	-0.250979
56	1	0	-4.030902	-4.222896	1.843371
57	6	0	2.357838	-2.938576	2.344991
58	1	0	1.350787	-3.367329	2.467108

59	6	0	1.403231	-4.325561	-2.472924
60	1	0	0.394863	-3.954238	-2.209946
61	6	0	2.257061	-1.434405	2.622954
62	1	0	1.620094	-0.925632	1.884361
63	1	0	1.837331	-1.261631	3.625846
64	1	0	3.254652	-0.967220	2.606084
65	6	0	3.262745	-3.621427	3.368151
66	1	0	2.861870	-3.488494	4.381510
67	1	0	3.353166	-4.697674	3.176641
68	1	0	4.275687	-3.197133	3.362593
69	6	0	1.361030	-5.855362	-2.472535
70	1	0	0.637185	-6.233715	-3.206194
71	1	0	2.348440	-6.259667	-2.734570
72	1	0	1.097738	-6.275416	-1.491134
73	6	0	1.718943	-3.816506	-3.874237
74	1	0	0.914872	-4.096767	-4.567324
75	1	0	1.832622	-2.723239	-3.892934
76	1	0	2.642291	-4.259505	-4.270897
77	6	0	-5.594020	1.862946	-0.971328
78	1	0	-5.322230	1.953949	0.093177
79	6	0	-1.601630	5.019252	-1.313685
80	1	0	-1.835457	5.210742	-0.253192
81	6	0	-1.240115	6.360805	-1.940223
82	1	0	-0.841929	6.241851	-2.957092
83	1	0	-2.104004	7.034412	-1.992613
84	1	0	-0.459976	6.855563	-1.348209
85	6	0	-0.395719	4.073844	-1.354518
86	1	0	0.467787	4.534158	-0.851563
87	1	0	-0.595811	3.101207	-0.880453
88	1	0	-0.114130	3.875965	-2.400314
89	6	0	-7.072300	2.227933	-1.095615
90	1	0	-7.442188	2.070981	-2.117399
91	1	0	-7.679538	1.597896	-0.432857
92	1	0	-7.257541	3.276778	-0.833283
93	6	0	-5.358983	0.408450	-1.385397
94	1	0	-4.314254	0.101544	-1.234288
95	1	0	-6.006506	-0.258167	-0.795639
96	1	0	-5.612734	0.256372	-2.444185
97	1	0	5.574968	-2.755502	-1.024776
98	1	0	-4.386347	3.998174	-4.939980
99	6	0	-5.336121	-2.688656	0.949601
100	1	0	-5.944162	-2.788798	1.856406
101	1	0	-5.075085	-1.632087	0.811628
102	6	0	-4.895273	-3.496035	-1.268186

103	1	0	-4.461516	-2.555638	-1.641325
104	1	0	-5.190217	-4.105743	-2.129803
105	6	0	-0.828984	0.260489	4.905306
106	1	0	-1.372344	-0.153811	5.762625
107	1	0	-0.562662	-0.559540	4.227446
108	6	0	0.688533	1.957571	4.137627
109	1	0	1.054040	1.390757	3.266197
110	1	0	1.405352	2.757301	4.360630
111	6	0	0.448542	1.011167	5.308692
112	1	0	1.287148	0.331657	5.502494
113	6	0	-6.046054	-3.195455	-0.313975
114	1	0	-6.608349	-4.114874	-0.094903
115	1	0	-6.763207	-2.467392	-0.711474
116	28	0	-1.241261	-0.337961	0.213867
117	6	0	5.058964	3.511402	0.064395
118	6	0	3.983170	2.843717	0.668265
119	6	0	4.041443	2.554537	2.030098
120	6	0	5.168041	2.949304	2.741594
121	6	0	6.229384	3.615964	2.112539
122	6	0	6.194786	3.910488	0.755887
123	6	0	3.553367	3.105588	-1.551917
124	6	0	3.039498	2.490481	-0.386145
125	1	0	3.225811	2.019829	2.518005
126	1	0	5.233204	2.739918	3.807276
127	1	0	7.096852	3.910305	2.698879
128	1	0	7.019298	4.423536	0.265362
129	1	0	3.144984	3.084049	-2.557360
130	1	0	1.970612	2.350486	-0.213908
131	7	0	4.743382	3.648580	-1.295927
132	1	0	5.361195	4.048357	-1.993525
133	6	0	0.989686	0.187901	-1.360944
134	6	0	2.314387	0.192209	-1.734351
135	6	0	3.320569	0.586501	-0.791239
136	6	0	4.751758	0.380580	-1.086299
137	8	0	-1.145241	-0.736328	-1.873543
138	1	0	2.583059	-0.115747	-2.741629
139	1	0	3.048803	0.355418	0.246610
140	6	0	5.244559	0.361760	-2.397503
141	6	0	5.654005	0.199968	-0.030617
142	6	0	7.005447	-0.010158	-0.274978
143	6	0	6.593881	0.145544	-2.645490
144	6	0	7.477889	-0.043304	-1.584318
145	1	0	4.564608	0.515378	-3.236136
146	1	0	5.286592	0.228374	0.995957

147	1	0	7.692293	-0.149772	0.557414
148	1	0	8.534922	-0.213011	-1.779513
149	1	0	6.959923	0.123214	-3.670090
150	6	0	-0.035705	-0.409481	-2.290162
151	8	0	0.523286	0.617116	-0.247042
152	8	0	0.330139	-0.553598	-3.545509
153	6	0	-0.638068	-1.136841	-4.430149
154	1	0	-0.158882	-1.173788	-5.409073
155	1	0	-0.895682	-2.145989	-4.090042
156	1	0	-1.540054	-0.518359	-4.458799

L10-COM

Zero-point correction= 1.326755 (a.u.)
Thermal correction to Gibbs Free Energy= 1.223533 (a.u.)
Sum of electronic and zero-point Energies= -3170.570749 (a.u.)
Sum of electronic and thermal Free Energies= -3170.673971 (a.u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.350693	-0.870510	7.083245
2	6	0	0.252333	1.293888	-0.514260
3	6	0	0.570570	2.662233	-0.747266
4	6	0	0.633974	3.535060	0.302235
5	6	0	1.020480	4.914676	0.274000
6	8	0	-0.055243	-0.855195	-1.518678
7	1	0	0.796844	2.962462	-1.767606
8	1	0	0.393755	3.124342	1.287647
9	6	0	1.347739	5.592636	-0.917483
10	6	0	1.122388	5.601722	1.499114
11	6	0	1.547906	6.919214	1.538160
12	6	0	1.768380	6.908353	-0.876106
13	6	0	1.871799	7.571760	0.350164
14	1	0	1.272665	5.081006	-1.875769
15	1	0	0.868824	5.078660	2.421465
16	1	0	1.627833	7.441125	2.488792
17	1	0	2.205558	8.607094	0.375558
18	1	0	2.019747	7.429588	-1.796866
19	8	0	-2.229094	-1.102865	0.615009
20	8	0	-0.192552	-1.377458	2.577878
21	8	0	-0.327190	-3.263486	0.187526
22	8	0	1.836528	-1.457208	0.497132
23	7	0	-1.257639	-1.925317	3.230709

24	7	0	0.666880	-4.101796	0.594669
25	7	0	3.715124	-2.226708	-0.499598
26	1	0	4.166442	-3.046607	-0.893795
27	7	0	-4.128547	-0.257536	1.516634
28	1	0	-4.654767	-0.160081	2.379383
29	6	0	-2.919210	-0.829560	1.607031
30	6	0	-2.490459	-1.058532	3.050953
31	1	0	-3.300760	-1.582845	3.584547
32	6	0	-2.121593	0.219980	3.797416
33	1	0	-3.017148	0.799103	4.048752
34	1	0	-1.482898	0.843184	3.158216
35	6	0	-1.360729	-0.285728	5.027021
36	1	0	-2.002466	-0.242300	5.918525
37	6	0	-1.021724	-1.767796	4.754534
38	1	0	-1.742230	-2.454634	5.218531
39	6	0	-1.535445	-3.349503	2.815513
40	1	0	-1.893454	-3.302618	1.784953
41	1	0	-2.346999	-3.705134	3.464223
42	6	0	-0.352887	-4.300412	2.928803
43	1	0	-0.751764	-5.303267	2.718959
44	1	0	-0.008025	-4.343036	3.971900
45	6	0	0.888638	-4.050901	2.085474
46	1	0	1.302344	-3.063141	2.297967
47	1	0	1.642346	-4.816561	2.312669
48	6	0	0.352935	-5.527751	0.072475
49	6	0	0.771844	-5.482734	-1.414384
50	6	0	1.596508	-4.204380	-1.593116
51	1	0	2.497617	-4.355503	-2.198325
52	1	0	1.001063	-3.405686	-2.054710
53	6	0	1.951777	-3.809098	-0.163088
54	1	0	2.701002	-4.509648	0.241945
55	6	0	2.477101	-2.388799	-0.009805
56	6	0	4.460194	-1.015703	-0.644695
57	6	0	4.217601	0.109644	0.138812
58	6	0	4.997955	1.253035	-0.049426
59	6	0	6.002153	1.220548	-1.019244
60	6	0	6.265966	0.095820	-1.806786
61	6	0	5.470845	-1.030221	-1.603136
62	6	0	-4.798858	0.248352	0.361216
63	6	0	-4.108757	0.639107	-0.782042
64	6	0	-4.814881	1.193034	-1.850419
65	6	0	-6.199390	1.331850	-1.729471
66	6	0	-6.907949	0.947602	-0.588113
67	6	0	-6.178906	0.398494	0.465159

68	1	0	1.393997	-6.365801	-1.618333
69	1	0	0.999976	-6.186634	0.667078
70	1	0	6.615567	2.109410	-1.164147
71	1	0	-6.755005	1.766140	-2.560595
72	6	0	-1.117108	-5.934692	0.112341
73	1	0	-1.334461	-6.657836	0.907261
74	1	0	-1.727456	-5.038248	0.271631
75	6	0	-0.538131	-5.598959	-2.193692
76	1	0	-1.000492	-4.605786	-2.293205
77	1	0	-0.398014	-6.009268	-3.200142
78	6	0	0.413823	-1.994106	5.220676
79	1	0	0.534704	-2.932929	5.774023
80	1	0	1.070527	-2.013795	4.343319
81	6	0	-0.013227	0.364353	5.342887
82	1	0	0.498939	0.618346	4.402382
83	1	0	-0.110900	1.278561	5.939273
84	6	0	0.737985	-0.751537	6.061003
85	1	0	1.815704	-0.573224	6.143072
86	6	0	-1.390982	-6.486323	-1.293275
87	1	0	-1.055191	-7.530946	-1.365230
88	1	0	-2.456388	-6.471775	-1.547107
89	6	0	0.240869	0.319036	-1.693739
90	8	0	-0.017935	0.782985	0.586397
91	8	0	0.562784	0.842731	-2.847319
92	6	0	0.564767	-0.038734	-3.985448
93	1	0	0.810910	0.588599	-4.841834
94	1	0	1.321416	-0.816801	-3.844567
95	1	0	-0.424087	-0.492237	-4.102981
96	1	0	-6.681560	0.081871	1.378998
97	1	0	-3.033596	0.508656	-0.826211
98	6	0	-8.419882	1.147802	-0.525563
99	6	0	-4.122309	1.656735	-3.130458
100	6	0	-4.374124	3.155331	-3.333557
101	1	0	-3.876217	3.505014	-4.248717
102	1	0	-5.442100	3.384480	-3.433969
103	1	0	-3.985404	3.738983	-2.487688
104	6	0	-4.676914	0.872289	-4.325370
105	1	0	-4.182476	1.192462	-5.253250
106	1	0	-4.509763	-0.206724	-4.201993
107	1	0	-5.754424	1.029021	-4.458301
108	6	0	-2.611663	1.434435	-3.083952
109	1	0	-2.137510	2.003011	-2.268035
110	1	0	-2.368710	0.366939	-2.960772
111	1	0	-2.162494	1.778690	-4.026176

112	6	0	-9.015655	0.643214	0.786647
113	1	0	-8.848057	-0.434165	0.927474
114	1	0	-8.609850	1.178998	1.656738
115	1	0	-10.100783	0.805350	0.784569
116	6	0	-8.732200	2.644270	-0.649096
117	1	0	-8.379532	3.065312	-1.599489
118	1	0	-9.817175	2.807491	-0.598324
119	1	0	-8.265354	3.213873	0.166276
120	6	0	-9.084533	0.384944	-1.677307
121	1	0	-8.742747	0.734046	-2.660120
122	1	0	-8.878006	-0.691989	-1.611047
123	1	0	-10.173447	0.523814	-1.640149
124	1	0	3.442243	0.079991	0.894641
125	1	0	5.632271	-1.931927	-2.193729
126	6	0	7.389756	0.130787	-2.840034
127	6	0	4.787197	2.518976	0.780896
128	6	0	4.458766	3.688553	-0.155305
129	1	0	4.289539	4.608422	0.424240
130	1	0	5.270569	3.893005	-0.864503
131	1	0	3.550310	3.479310	-0.740160
132	6	0	6.066063	2.834386	1.565688
133	1	0	5.923690	3.736313	2.177002
134	1	0	6.330749	2.006640	2.237249
135	1	0	6.922909	3.016483	0.905111
136	6	0	3.642931	2.370071	1.782628
137	1	0	2.691877	2.119706	1.287348
138	1	0	3.851598	1.592979	2.531437
139	1	0	3.502452	3.317285	2.321573
140	6	0	7.117622	1.252693	-3.849172
141	1	0	7.082812	2.241546	-3.374114
142	1	0	7.913946	1.280226	-4.605037
143	1	0	6.162708	1.093683	-4.369416
144	6	0	8.722643	0.389730	-2.127417
145	1	0	8.731870	1.350728	-1.597293
146	1	0	8.939593	-0.400578	-1.396024
147	1	0	9.542384	0.409035	-2.858233
148	6	0	7.509182	-1.182497	-3.609889
149	1	0	7.747618	-2.027892	-2.949096
150	1	0	6.591456	-1.418989	-4.167512
151	1	0	8.322385	-1.105873	-4.342501
152	28	0	-0.204733	-1.320592	0.591014

L10-*Re*-TS1

Zero-point correction= 1.457822 (a.u.)
Thermal correction to Gibbs Free Energy= 1.347109 (a.u.)
Sum of electronic and zero-point Energies= -3533.967988 (a.u.)
Sum of electronic and thermal Free Energies= -3534.078701 (a.u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.858032	-0.047447	6.158293
2	8	0	-2.113464	-1.366979	0.562662
3	8	0	0.406236	-1.309061	1.984227
4	8	0	-0.217025	-3.481684	0.067252
5	8	0	1.879899	-1.612770	-0.507176
6	7	0	-0.464954	-1.716784	2.950245
7	7	0	0.861339	-4.258111	0.341263
8	7	0	3.902337	-2.605307	-0.728315
9	1	0	4.380875	-3.482119	-0.904057
10	7	0	-3.818866	-0.551066	1.822870
11	1	0	-4.099826	-0.331760	2.773151
12	6	0	-2.554514	-0.970897	1.646895
13	6	0	-1.733769	-0.878080	2.924404
14	1	0	-2.345190	-1.257168	3.760326
15	6	0	-1.214345	0.510042	3.269532
16	1	0	-2.033750	1.176995	3.560756
17	1	0	-0.713645	0.932573	2.386940
18	6	0	-0.225966	0.222504	4.404904
19	1	0	-0.700810	0.416877	5.377612
20	6	0	0.103309	-1.289249	4.325559
21	1	0	-0.463296	-1.877236	5.059990
22	6	0	-0.813772	-3.184559	2.865240
23	1	0	-1.403965	-3.302202	1.954583
24	1	0	-1.444803	-3.399497	3.738139
25	6	0	0.361057	-4.150216	2.850763
26	1	0	-0.079362	-5.158351	2.861336
27	1	0	0.923626	-4.073300	3.792778
28	6	0	1.389922	-4.047526	1.736940
29	1	0	1.839093	-3.050212	1.740456
30	1	0	2.173961	-4.801241	1.891284
31	6	0	0.484891	-5.718396	-0.003386
32	6	0	0.553756	-5.739698	-1.550231
33	6	0	1.321199	-4.476878	-1.974049
34	1	0	2.074905	-4.663594	-2.747289
35	1	0	0.641948	-3.690501	-2.326141
36	6	0	1.976375	-4.036586	-0.676253

37	1	0	2.758776	-4.759695	-0.396021
38	6	0	2.560920	-2.636643	-0.628513
39	6	0	4.743654	-1.452507	-0.652072
40	6	0	4.469714	-0.437758	0.258530
41	6	0	5.362538	0.626419	0.387448
42	6	0	6.499353	0.634489	-0.425382
43	6	0	6.791042	-0.377916	-1.344413
44	6	0	5.885513	-1.434589	-1.444767
45	6	0	-4.862760	-0.414811	0.859174
46	6	0	-4.599443	-0.244608	-0.495425
47	6	0	-5.663923	-0.079241	-1.382692
48	6	0	-6.962485	-0.087512	-0.868684
49	6	0	-7.244733	-0.253102	0.490322
50	6	0	-6.163879	-0.417320	1.354162
51	1	0	1.107395	-6.640057	-1.853103
52	1	0	1.266553	-6.332537	0.464422
53	1	0	7.202121	1.462467	-0.329402
54	1	0	-7.796344	0.041970	-1.558481
55	6	0	-0.928530	-6.134437	0.391614
56	1	0	-0.940804	-6.836492	1.233759
57	1	0	-1.494930	-5.238132	0.669141
58	6	0	-0.903040	-5.864844	-1.996845
59	1	0	-1.368267	-4.867736	-2.008472
60	1	0	-1.005035	-6.303570	-2.996084
61	6	0	1.612766	-1.428388	4.491388
62	1	0	1.896615	-2.282625	5.117241
63	1	0	2.065112	-1.549087	3.499127
64	6	0	1.136042	0.911076	4.354403
65	1	0	1.451676	0.999465	3.303210
66	1	0	1.132891	1.913767	4.801104
67	6	0	2.045880	-0.077371	5.075064
68	1	0	3.113752	0.121876	4.926393
69	6	0	-1.523463	-6.720802	-0.896633
70	1	0	-1.215372	-7.769755	-1.015630
71	1	0	-2.618740	-6.704437	-0.895115
72	1	0	-6.323298	-0.556122	2.423122
73	1	0	-3.571594	-0.247137	-0.838399
74	6	0	-8.693117	-0.256146	0.974118
75	6	0	-5.447096	0.105141	-2.883068
76	6	0	-6.041890	1.445958	-3.328202
77	1	0	-5.885007	1.590646	-4.406311
78	1	0	-7.121844	1.502511	-3.144065
79	1	0	-5.566713	2.283247	-2.798707
80	6	0	-6.132178	-1.040460	-3.637451

81	1	0	-5.976423	-0.930527	-4.719787
82	1	0	-5.725160	-2.013745	-3.329576
83	1	0	-7.215197	-1.061609	-3.462312
84	6	0	-3.965961	0.100526	-3.254153
85	1	0	-3.417935	0.920829	-2.766618
86	1	0	-3.484785	-0.851830	-2.979676
87	1	0	-3.858594	0.232819	-4.339914
88	6	0	-8.799531	-0.443153	2.486017
89	1	0	-8.377483	-1.403920	2.813809
90	1	0	-8.299633	0.366635	3.036658
91	1	0	-9.855732	-0.433997	2.783712
92	6	0	-9.353903	1.079428	0.612348
93	1	0	-9.365363	1.259940	-0.470066
94	1	0	-10.396683	1.087767	0.957705
95	1	0	-8.832688	1.920821	1.089288
96	6	0	-9.447843	-1.405421	0.295654
97	1	0	-9.460530	-1.305703	-0.797289
98	1	0	-8.993007	-2.375200	0.540058
99	1	0	-10.491772	-1.424657	0.637042
100	1	0	3.571161	-0.499131	0.865789
101	1	0	6.058831	-2.255132	-2.139968
102	6	0	8.065187	-0.307212	-2.182895
103	6	0	5.141771	1.748766	1.398962
104	6	0	5.015482	3.085524	0.660190
105	1	0	4.813058	3.899442	1.372600
106	1	0	5.931600	3.340808	0.112369
107	1	0	4.188370	3.048522	-0.065010
108	6	0	6.328192	1.807697	2.368452
109	1	0	6.174230	2.602838	3.111268
110	1	0	6.443983	0.856991	2.906508
111	1	0	7.274814	2.016559	1.854937
112	6	0	3.873874	1.533047	2.223038
113	1	0	2.967829	1.513133	1.596632
114	1	0	3.916587	0.590219	2.789701
115	1	0	3.757872	2.350763	2.949070
116	6	0	8.040586	0.964155	-3.039286
117	1	0	8.000529	1.875537	-2.428582
118	1	0	8.948631	1.020584	-3.654835
119	1	0	7.173709	0.968979	-3.714581
120	6	0	9.283904	-0.277733	-1.252357
121	1	0	9.282334	0.597692	-0.590392
122	1	0	9.321337	-1.176555	-0.621951
123	1	0	10.208433	-0.241062	-1.844368
124	6	0	8.208739	-1.507603	-3.116066

125	1	0	8.268814	-2.454717	-2.561397
126	1	0	7.378141	-1.573544	-3.833169
127	1	0	9.134662	-1.413606	-3.697321
128	28	0	-0.114168	-1.486052	0.044306
129	6	0	2.083660	5.326737	0.118235
130	6	0	1.563938	4.117901	0.601499
131	6	0	1.230315	4.007090	1.948822
132	6	0	1.441838	5.105692	2.772528
133	6	0	1.964937	6.304210	2.264611
134	6	0	2.294872	6.438887	0.921901
135	6	0	2.001491	3.905549	-1.619717
136	6	0	1.417278	3.213286	-0.531303
137	1	0	0.818346	3.074782	2.338978
138	1	0	1.199005	5.042298	3.831572
139	1	0	2.116258	7.146097	2.936225
140	1	0	2.696125	7.370113	0.527788
141	1	0	2.096447	3.579991	-2.650561
142	1	0	1.459883	2.128240	-0.418333
143	7	0	2.330110	5.143910	-1.250871
144	1	0	2.655646	5.867964	-1.881800
145	6	0	-0.472975	0.843098	-1.502283
146	6	0	-0.636895	2.131462	-1.959927
147	6	0	-0.475003	3.217985	-1.037930
148	6	0	-0.868878	4.596438	-1.384332
149	8	0	-0.617244	-1.473515	-2.020912
150	1	0	-0.848045	2.303829	-3.011653
151	1	0	-0.731188	2.941525	-0.008709
152	6	0	-0.869359	5.065074	-2.705142
153	6	0	-1.234705	5.477281	-0.359426
154	6	0	-1.600194	6.787451	-0.643976
155	6	0	-1.237098	6.372314	-2.991300
156	6	0	-1.603234	7.237007	-1.960468
157	1	0	-0.581403	4.400718	-3.520775
158	1	0	-1.230029	5.127072	0.673685
159	1	0	-1.888749	7.457037	0.163559
160	1	0	-1.893385	8.260965	-2.187157
161	1	0	-1.244351	6.719710	-4.022504
162	6	0	-0.642356	-0.319524	-2.443946
163	8	0	-0.147929	0.524026	-0.303725
164	8	0	-0.791463	-0.020162	-3.714439
165	6	0	-0.930658	-1.121417	-4.624003
166	1	0	-1.072971	-0.673704	-5.608004
167	1	0	-0.024477	-1.735618	-4.606656
168	1	0	-1.795803	-1.732354	-4.347749

L10-*Si*-TS1

Zero-point correction= 1.461530 (a.u.)
Thermal correction to Gibbs Free Energy= 1.356548 (a.u.)
Sum of electronic and zero-point Energies= -3533.974811 (a.u.)
Sum of electronic and thermal Free Energies= -3534.079793 (a.u.)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.050501	0.255412	7.405135
2	8	0	-1.959624	-1.367342	0.870497
3	8	0	-0.190016	-1.359546	3.136246
4	8	0	-0.447968	-3.787087	1.254540
5	8	0	2.009731	-2.393061	1.613521
6	7	0	-1.404285	-1.522218	3.723868
7	7	0	0.312884	-4.631441	2.008444
8	7	0	3.350964	-3.518479	0.173082
9	1	0	3.566178	-4.436679	-0.200927
10	7	0	-3.559410	0.210414	1.191668
11	1	0	-4.075082	0.713502	1.906699
12	6	0	-2.602692	-0.634247	1.626452
13	6	0	-2.400525	-0.538794	3.135071
14	1	0	-3.361339	-0.741425	3.637894
15	6	0	-1.839962	0.807282	3.588300
16	1	0	-2.595411	1.599584	3.524678
17	1	0	-0.997087	1.076928	2.934432
18	6	0	-1.360935	0.539890	5.016189
19	1	0	-2.081384	0.938402	5.744780
20	6	0	-1.310447	-0.995105	5.178654
21	1	0	-2.203306	-1.393461	5.679128
22	6	0	-1.900063	-2.944375	3.636427
23	1	0	-2.130992	-3.122420	2.583596
24	1	0	-2.825616	-2.987201	4.226567
25	6	0	-0.920779	-3.990694	4.153539
26	1	0	-1.476432	-4.939011	4.170333
27	1	0	-0.680318	-3.786942	5.206610
28	6	0	0.417054	-4.183758	3.449179
29	1	0	0.994942	-3.258431	3.441676
30	1	0	0.987956	-4.962283	3.972696
31	6	0	-0.250105	-6.071027	1.901413
32	6	0	0.300137	-6.611835	0.566671
33	6	0	1.378987	-5.627787	0.117059

34	1	0	2.275498	-6.140331	-0.251985
35	1	0	1.006142	-4.966668	-0.676650
36	6	0	1.683324	-4.791643	1.356878
37	1	0	2.301982	-5.362158	2.069901
38	6	0	2.356054	-3.450359	1.067223
39	6	0	4.068514	-2.458826	-0.453459
40	6	0	4.015264	-1.133475	-0.023671
41	6	0	4.735983	-0.160977	-0.724722
42	6	0	5.465711	-0.552400	-1.848832
43	6	0	5.534682	-1.876525	-2.290983
44	6	0	4.827742	-2.831032	-1.563981
45	6	0	-3.928515	0.565069	-0.135833
46	6	0	-3.271479	0.082029	-1.270463
47	6	0	-3.674411	0.522350	-2.531288
48	6	0	-4.734378	1.437052	-2.621119
49	6	0	-5.401119	1.928396	-1.499712
50	6	0	-4.967411	1.482495	-0.248044
51	1	0	0.739695	-7.601694	0.753912
52	1	0	0.181268	-6.597163	2.763115
53	1	0	6.021751	0.206163	-2.398501
54	1	0	-5.058706	1.759769	-3.608149
55	6	0	-1.771327	-6.180701	1.833008
56	1	0	-2.216308	-6.526488	2.773561
57	1	0	-2.181419	-5.194169	1.586689
58	6	0	-0.927961	-6.767333	-0.331084
59	1	0	-1.160679	-5.802432	-0.806257
60	1	0	-0.785464	-7.510564	-1.123644
61	6	0	-0.008894	-1.323726	5.906346
62	1	0	-0.139241	-2.087573	6.682007
63	1	0	0.721879	-1.683229	5.172262
64	6	0	0.046391	1.013719	5.379234
65	1	0	0.702540	0.906322	4.501728
66	1	0	0.072545	2.059686	5.708248
67	6	0	0.466218	0.025454	6.461987
68	1	0	1.541372	0.034630	6.671069
69	6	0	-2.025793	-7.135724	0.660279
70	1	0	-1.909611	-8.180337	0.983711
71	1	0	-3.036929	-7.034284	0.251060
72	1	0	-5.453116	1.850658	0.657389
73	1	0	-2.464680	-0.631811	-1.155843
74	6	0	-6.531229	2.952340	-1.594027
75	6	0	-3.010208	0.025358	-3.814312
76	6	0	-2.497596	1.220431	-4.627050
77	1	0	-2.027641	0.872538	-5.556962

78	1	0	-3.298260	1.915617	-4.907680
79	1	0	-1.737883	1.784602	-4.062424
80	6	0	-4.038547	-0.757745	-4.639517
81	1	0	-3.579782	-1.127351	-5.566860
82	1	0	-4.413843	-1.623517	-4.077483
83	1	0	-4.901561	-0.141375	-4.921486
84	6	0	-1.818000	-0.886665	-3.536333
85	1	0	-1.035023	-0.352955	-2.977112
86	1	0	-2.099830	-1.789374	-2.975425
87	1	0	-1.379043	-1.212956	-4.489202
88	6	0	-7.694494	2.556977	-0.678379
89	1	0	-8.085983	1.565363	-0.941133
90	1	0	-7.414984	2.542865	0.383184
91	1	0	-8.513218	3.280685	-0.783709
92	6	0	-5.984062	4.317980	-1.159143
93	1	0	-5.177905	4.640835	-1.837043
94	1	0	-6.774986	5.079215	-1.200640
95	1	0	-5.591411	4.296640	-0.132074
96	6	0	-7.076794	3.082823	-3.015490
97	1	0	-6.328986	3.474163	-3.718434
98	1	0	-7.446048	2.122587	-3.400411
99	1	0	-7.918832	3.786479	-3.021928
100	1	0	3.426717	-0.877385	0.849653
101	1	0	4.853742	-3.879692	-1.861375
102	6	0	6.360062	-2.227482	-3.525602
103	6	0	4.767365	1.302220	-0.284635
104	6	0	4.229127	2.189163	-1.413622
105	1	0	4.231998	3.243706	-1.101805
106	1	0	4.834527	2.115205	-2.326040
107	1	0	3.195676	1.912491	-1.668293
108	6	0	6.214227	1.700481	0.033715
109	1	0	6.250577	2.744483	0.374573
110	1	0	6.632081	1.068902	0.829316
111	1	0	6.871749	1.617016	-0.840902
112	6	0	3.927125	1.550372	0.967536
113	1	0	2.872085	1.276219	0.823052
114	1	0	4.307969	0.991153	1.833678
115	1	0	3.967606	2.618182	1.224974
116	6	0	5.830369	-1.438285	-4.728919
117	1	0	5.898246	-0.352951	-4.580921
118	1	0	6.411885	-1.685559	-5.627371
119	1	0	4.778154	-1.687057	-4.931124
120	6	0	7.827917	-1.861858	-3.274648
121	1	0	7.962908	-0.789632	-3.083153

122	1	0	8.229374	-2.410915	-2.412330
123	1	0	8.435508	-2.119160	-4.152851
124	6	0	6.290380	-3.714114	-3.868422
125	1	0	6.691180	-4.343940	-3.061882
126	1	0	5.262751	-4.038647	-4.090821
127	1	0	6.892988	-3.914323	-4.763392
128	28	0	0.042389	-1.828385	1.213997
129	6	0	-1.943329	5.018055	0.697235
130	6	0	-1.321910	3.950030	1.364382
131	6	0	-0.767540	4.169023	2.625226
132	6	0	-0.861911	5.440912	3.177919
133	6	0	-1.488011	6.488929	2.489336
134	6	0	-2.040795	6.296060	1.229695
135	6	0	-2.074811	3.235675	-0.665326
136	6	0	-1.310926	2.816366	0.447335
137	1	0	-0.261777	3.362747	3.159808
138	1	0	-0.440930	5.631552	4.162966
139	1	0	-1.543060	7.472692	2.949768
140	1	0	-2.521591	7.110197	0.691424
141	1	0	-2.330612	2.667937	-1.557911
142	1	0	-1.265756	1.773018	0.762327
143	7	0	-2.387851	4.525943	-0.537971
144	1	0	-2.857304	5.078320	-1.246493
145	6	0	0.643384	0.343362	-0.477345
146	6	0	0.659341	1.579342	-1.085029
147	6	0	0.542623	2.763949	-0.289785
148	6	0	0.854253	4.087208	-0.849929
149	8	0	0.595046	-2.005738	-0.842107
150	1	0	0.800350	1.641504	-2.161448
151	1	0	0.905124	2.627730	0.735807
152	6	0	0.580338	4.413728	-2.185293
153	6	0	1.445640	5.055304	-0.028168
154	6	0	1.761017	6.313115	-0.526717
155	6	0	0.895305	5.669557	-2.684331
156	6	0	1.485541	6.622573	-1.855315
157	1	0	0.113659	3.678239	-2.842783
158	1	0	1.666084	4.811259	1.011464
159	1	0	2.226781	7.051864	0.122029
160	1	0	1.733797	7.606168	-2.248908
161	1	0	0.684836	5.908394	-3.725025
162	6	0	0.877769	-0.896937	-1.296939
163	8	0	0.420409	0.129543	0.766196
164	8	0	1.393114	-0.702600	-2.487051
165	6	0	1.684482	-1.865366	-3.275270

166	1	0	1.943358	-1.490245	-4.266087
167	1	0	2.538991	-2.394416	-2.831991
168	1	0	0.807256	-2.518950	-3.322014

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