Electronic Supplementary Material (ESI) for Catalysis Science .

Supporting information:

A Simple and Readily Accessible Ferrocene-Based Bifunc-tional Amine-Thiourea as an Organocatalyst for Highly Enantioselective Nitro-Michael Addition

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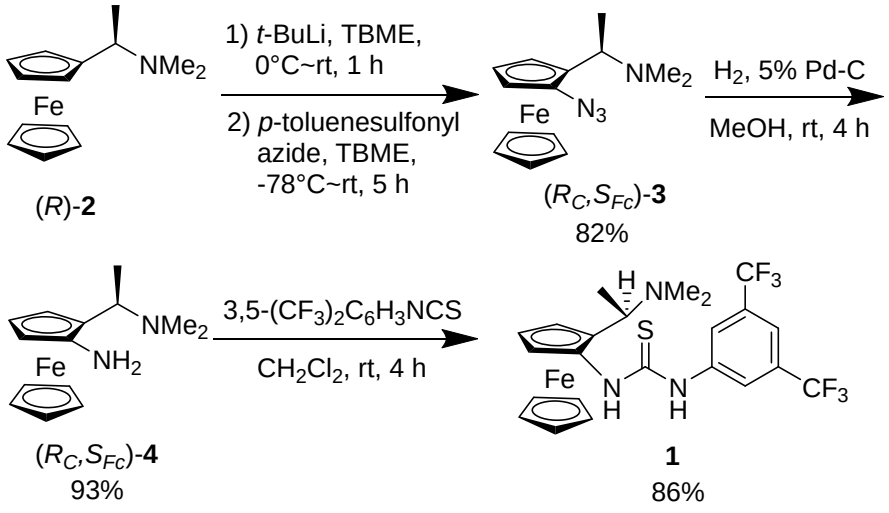
CONTENTS:

General information

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer using TMS as an internal reference. Coupling constant (*J*) values were given in Hz. HRMS were recorded on ZAB-HS spectrometer with ES ionization (ESI). All commercially available reagents were used as received. Solvents and reagents were purified and dried by standard methods prior to use. Products were purified by flash column chromatography on silica gel purchased from Qingdao Haiyang Chemical Co., Ltd. All reactions involving air or moisture sensitive species were performed under inert atmosphere in oven-dried glassware. Enantiomeric excesses (*ee*) were determined by HPLC analysis using an Agilent 1100 Series instrumentwith Daicel Chiralpak AD-H column, as indicated. Optical rotation data were measured on a Jasco DIP-1000Digital Polarimeter at the indicated concentration with unit g/100mL.

I. Preparation of ferrocene-based bifunctional amine-thiourea(R_C,S_{Fc})-1:



To a degassed solution of (*R*)-(+)-N,N-dimethyl-1-ferrocenylethylamine (*R*)-**2** (Ugi's amine, >99% *ee*, 6.0 g, 23.3 mmol) in TBME (15 mL) was added dropwise at 0°C a solution of *t*-BuLi in pentane (1.7M, 16.47 mL, 28.0 mmol). After stirring for 1 h at ambient temperature, the mixture was cooled to -78°C. A solution of *p*-tosylazide (5.52 g, 28.0 mmol, 1.2 equiv) in TBME (15 mL) was added dropwise. The mixture was stirred at –78°C for 5 h, warmed to 0°C, stirred for 10 min, and then $Na_4P_2O_7.10H_2O$ (11.60 g, 26 mmol, 1.1 equiv) in H_2O (250 mL) was added. After stirring overnight at room temperature, the mixture was extracted with CH_2Cl_2 (3×50 mL). The combined organic solutions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography to afford a red brown oil (R_C,S_{Fc})-**3** (5.7 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.44 – 4.37 (m, 1H), 4.24 (s, 5H), 4.09 – 4.01 (m, 2H), 3.81 (q, *J* = 6.9 Hz, 1H), 2.13 (s, 6H), 1.49 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 97.95, 80.82, 69.72 , 65.14 , 63.35 , 59.41 , 55.42 , 40.55 , 15.21.

(R_C,S_{Fc})-**3** (2.76 g, 9.3 mmol) was dissolved in MeOH (60 mL). The solution was degassed by passing nitrogen for 5 min. Then 5% Pd/C (0.36 g) was added and the mixture was stirred for 4 h at a H_2 pressure of 1bar. The mixture was filtered through Celite and the Celite washed with a small amount of CH_2Cl_2. The solvent was removed and resulting yellow oil was kept under nitrogen, to furnish (R_C,S_{Fc})-**4**（2.39 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 – 4.10 (m,

2H), 4.04 (s, 5H), 3.86 (d, J = 22.9 Hz, 2H), 2.24 (s, 6H), 1.43 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 105.81, 70.00, 69.54, 62.70, 60.91, 58.23, 57.39, 39.85, 10.56.

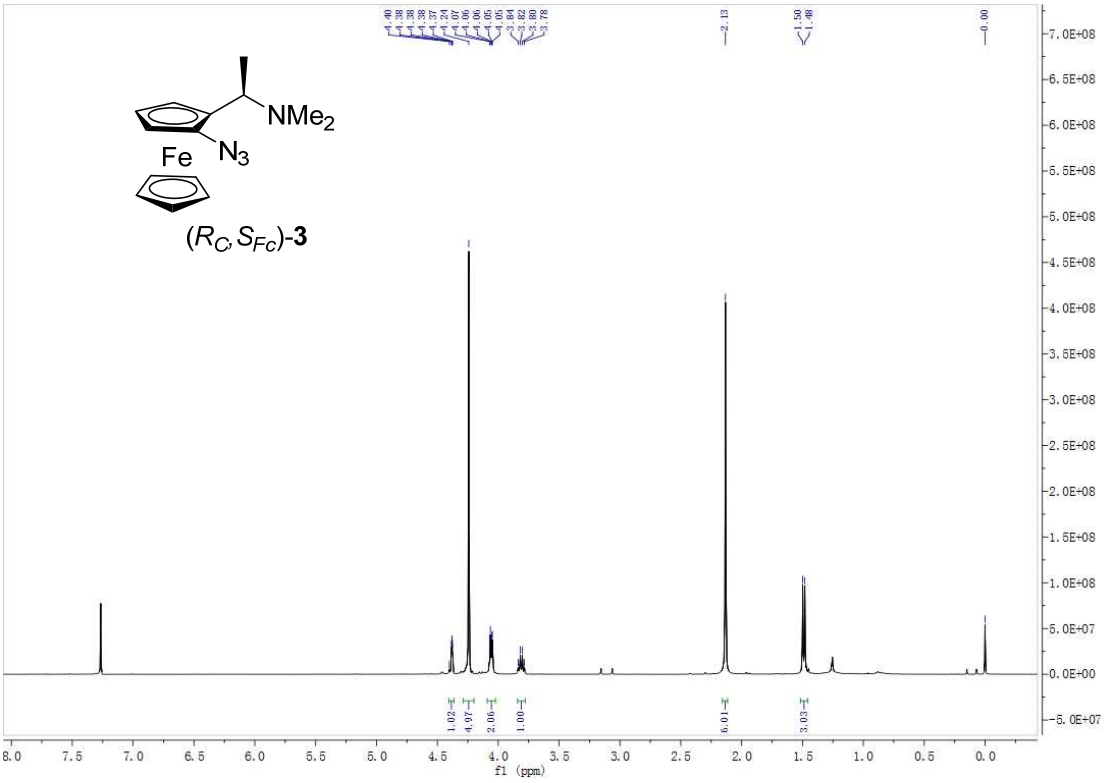
To a solution of (R_C,S_{Fc})-**4** (1.36 g, 5 mmol) in DCM (30 mL) was added to a solution of 3,5-Difluorophenyl isothiocyanate (2.66 g, 5.5 mmol) in DCM (30 mL) slowly. The mixture was stirred at room temperature for 4 h and then purified by column chromatography to afford (R_C,S_{Fc})-**1** (2.34 g, 86%) as yellow crystals. mp: 196.1 – 198.0ºC; $[\alpha]_D^{25}$ = −82.1 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 2H), 7.59 (s, 1H), 4.38 (s, 1H), 4.23 (s, 5H), 4.19 (s, 1H), 4.14 – 4.17 (m, 1H), 4.02 (d, J = 6.4 Hz, 1H), 2.21 (s, 6H), 1.40 (d, J = 6.8 Hz, 3H); ^{13}C NMR(101 MHz, $CDCl_3$): δ 184.50, 141.97, 131.72 (q, J = 33 Hz), 123.19, 123.15 (d, J = 271 Hz), 117.94, 92.09, 88.75, 70.31, 64.95, 64.20, 55.81, 39.18, 7.99; HRMS (ESI) Calcd for $C_{23}H_{23}F_6FeN_3S$+H $(M+H)^+$:544.0944, Found: 544.0951.

II. General procedure for Michael addition.

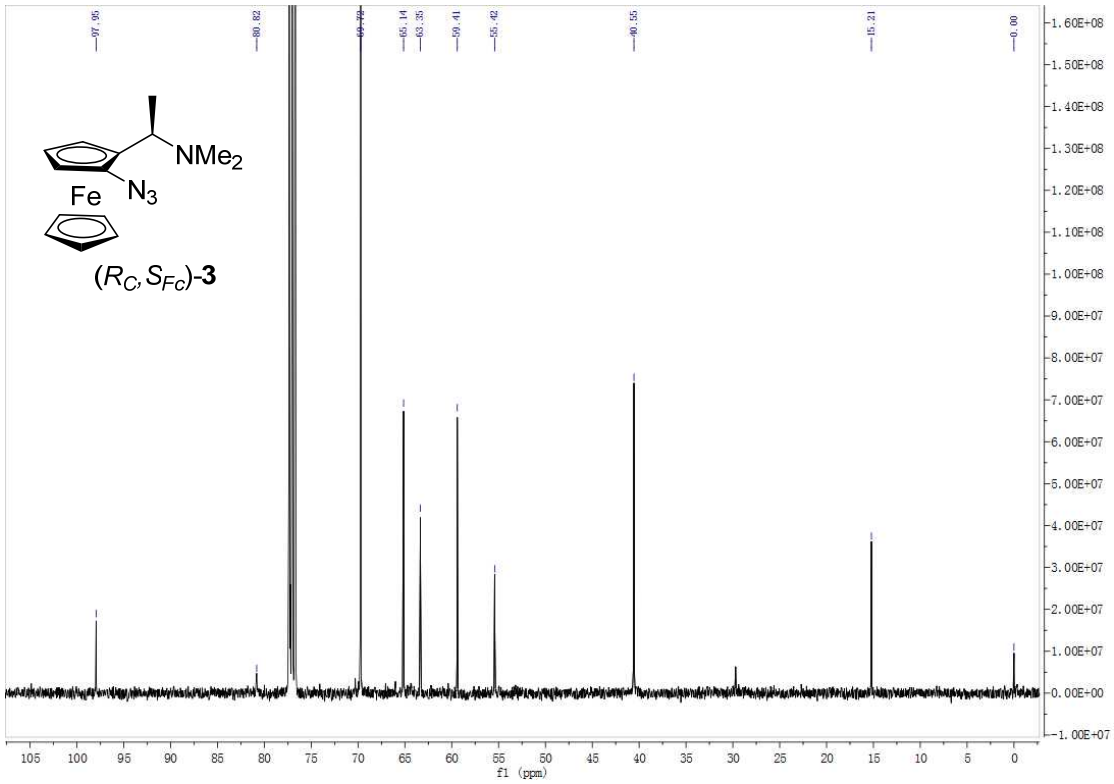
The catalyst (R_C,S_{Fc})-**1** (10.8 mg, 0.02 mmol) was added to a vial containing 2,4-pentanedione (0.04 g, 0.4 mmol) and nitroolefin (0.2 mmol) in 1 mL of dried toluene. After 60 hours of stirring at room temperature, TLC analysis indicated completion of the reaction. The reaction mixture was concentrated and purified by column chromatography to afford the Michael addition product. Spectral data match those previously reported.[1-5]

III. ^{1}H and^{13}C NMR Spectra

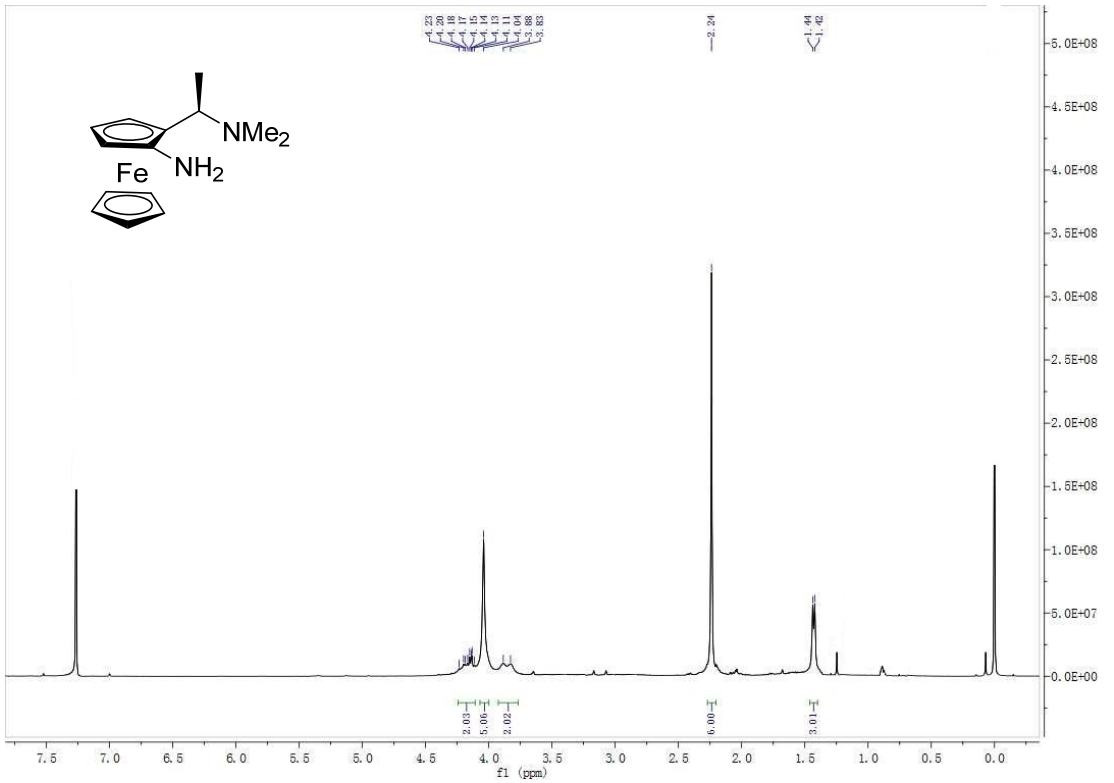
^{1}H NMR of (R_C,S_{Fc})-**3**



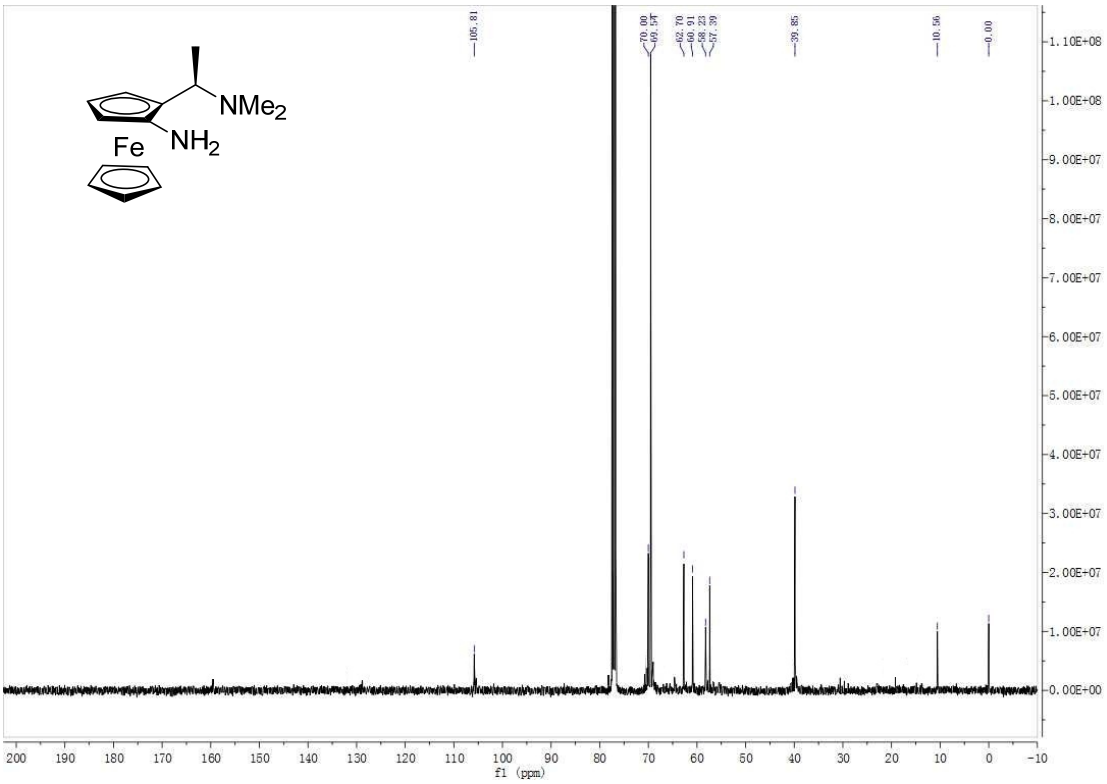
^{13}C NMR of (R_C,S_{Fc})-**3**



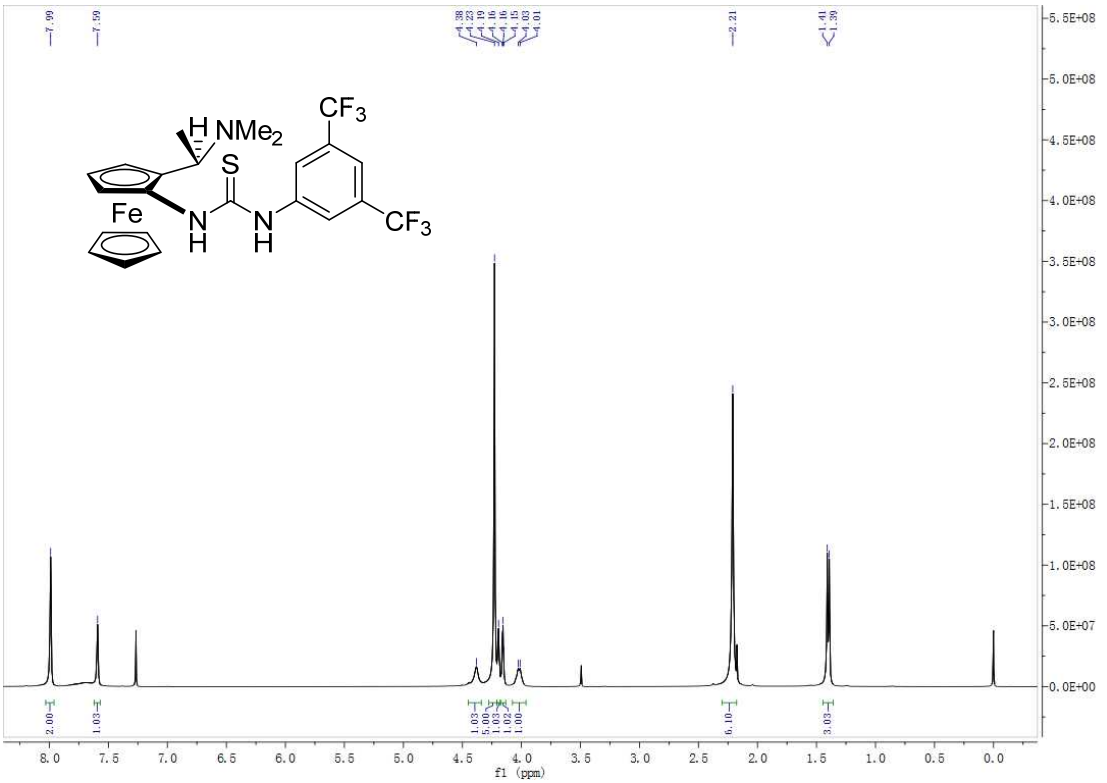
^{1}H NMR of (R_C,S_{Fc})-**4**



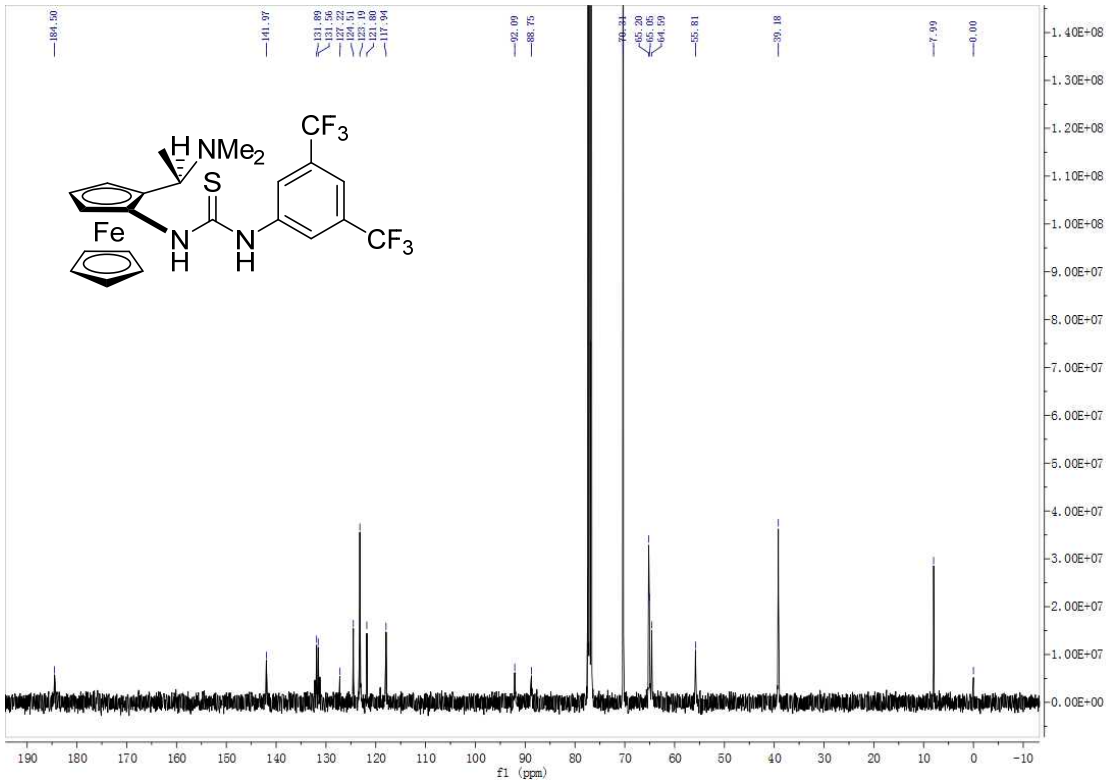
^{13}C NMR of (R_C,S_{Fc})-**4**



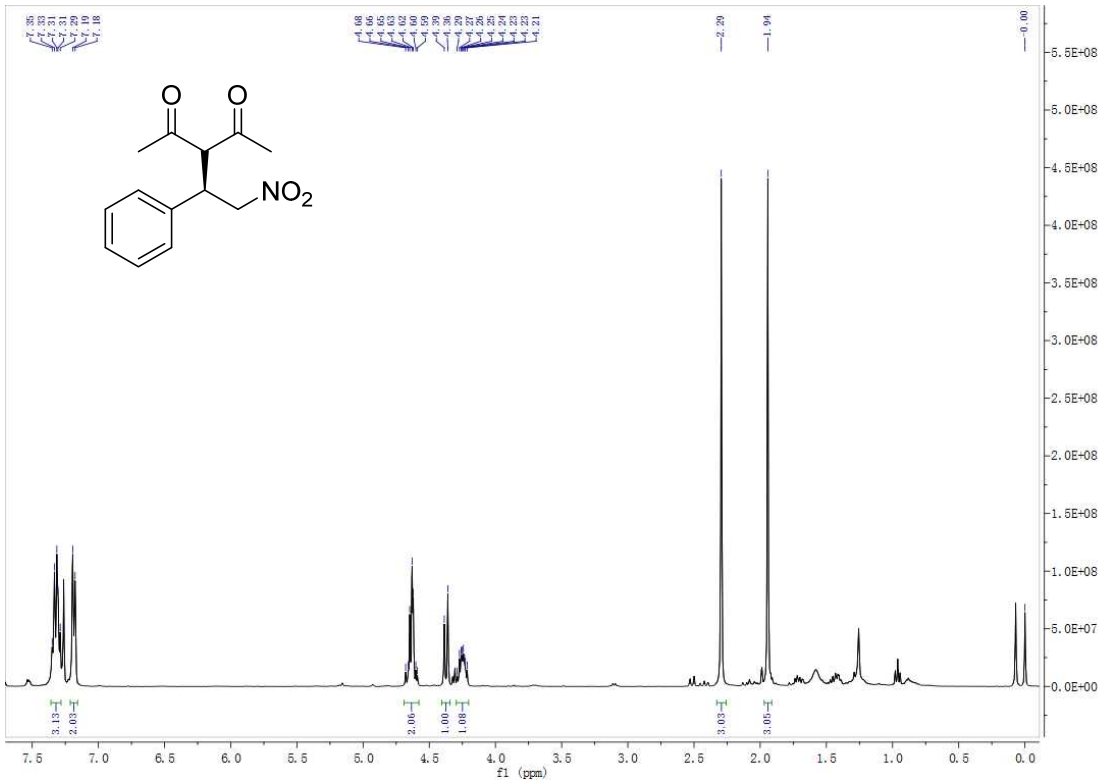
^{1}H NMR of (R_C,S_{Fc})-**1**



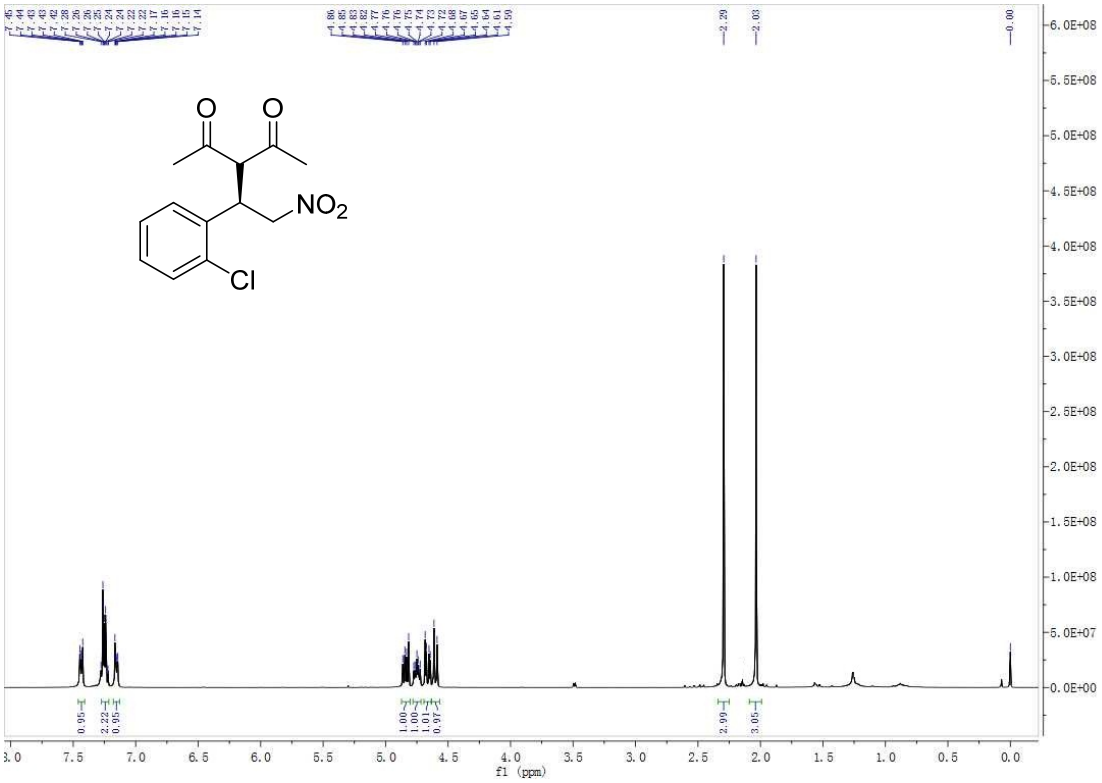
^{13}C NMR of (R_C,S_{Fc})-**1**



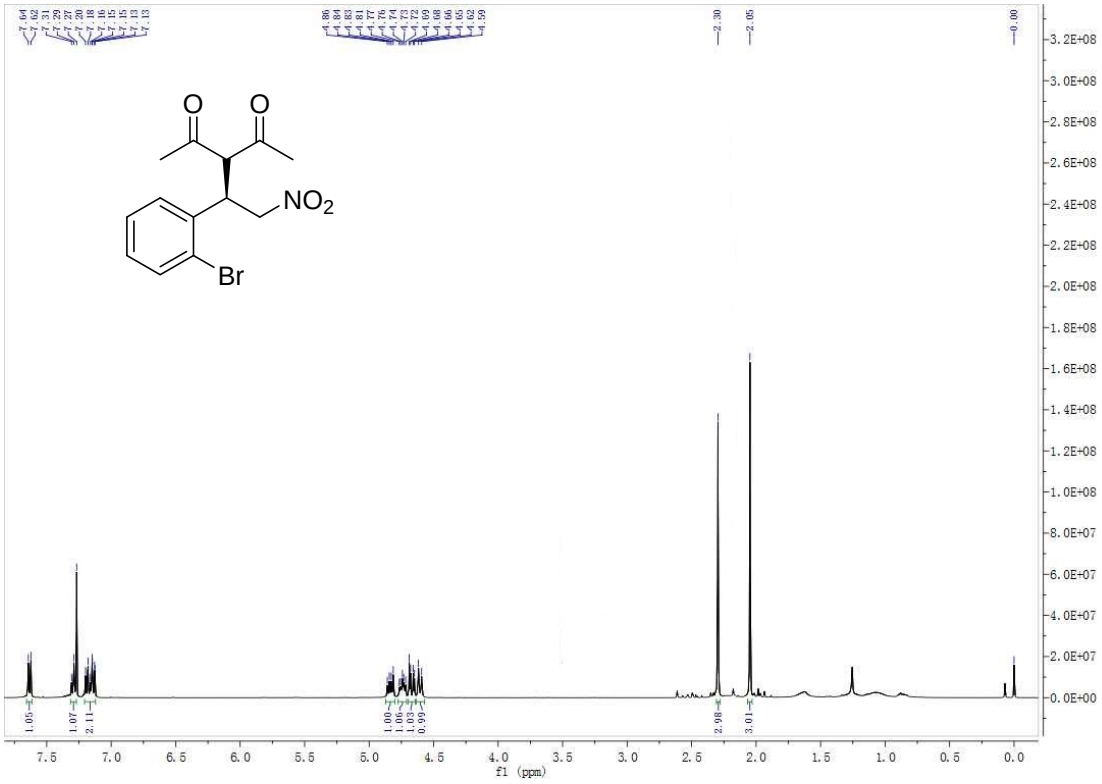
^{1}H NMR of **7a**



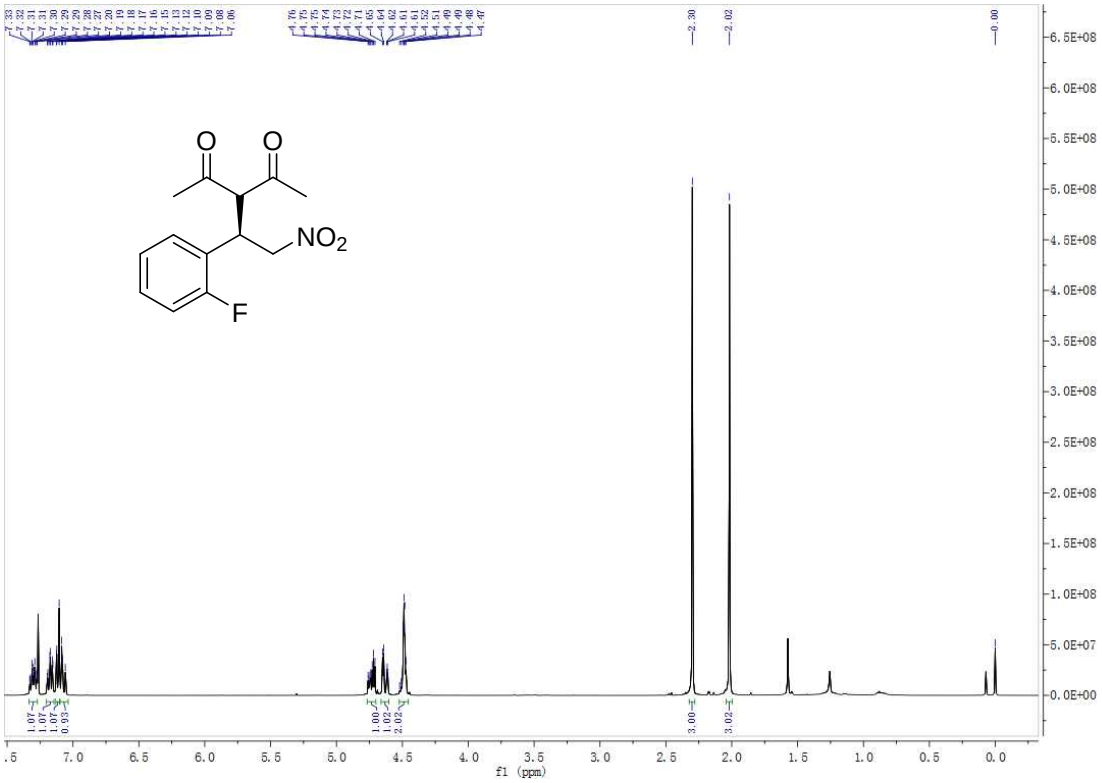
^{1}H NMR of **7b**



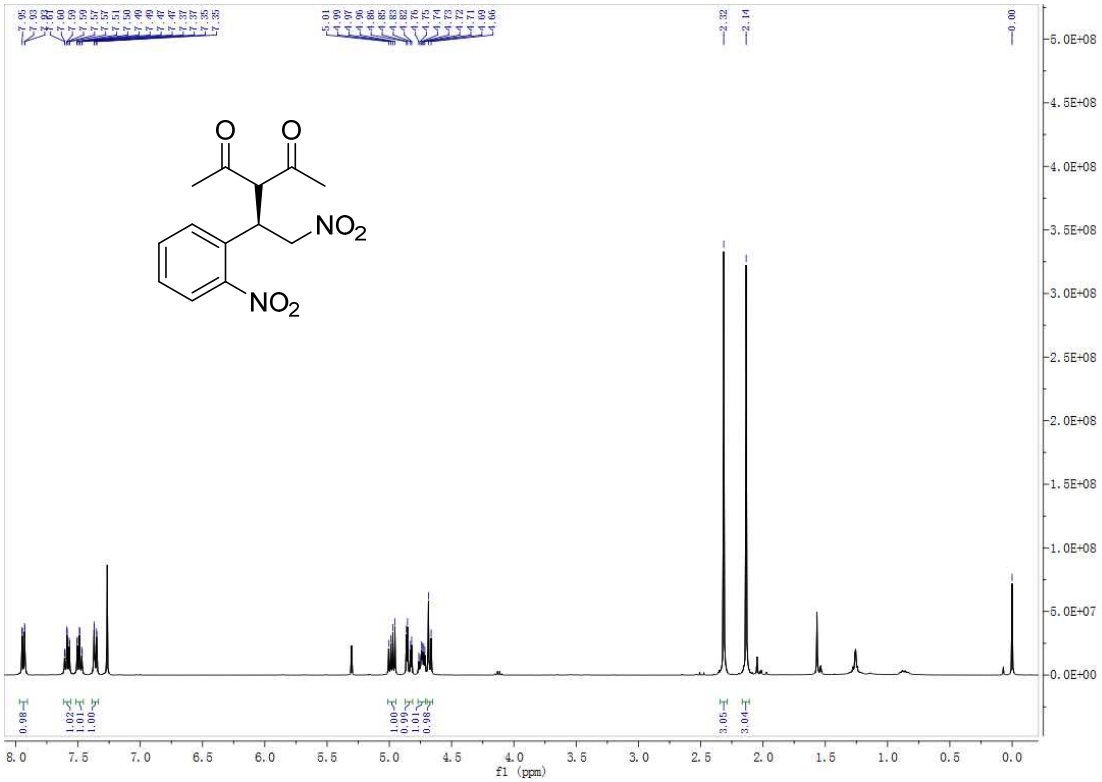
^{1}H NMR of **7c**



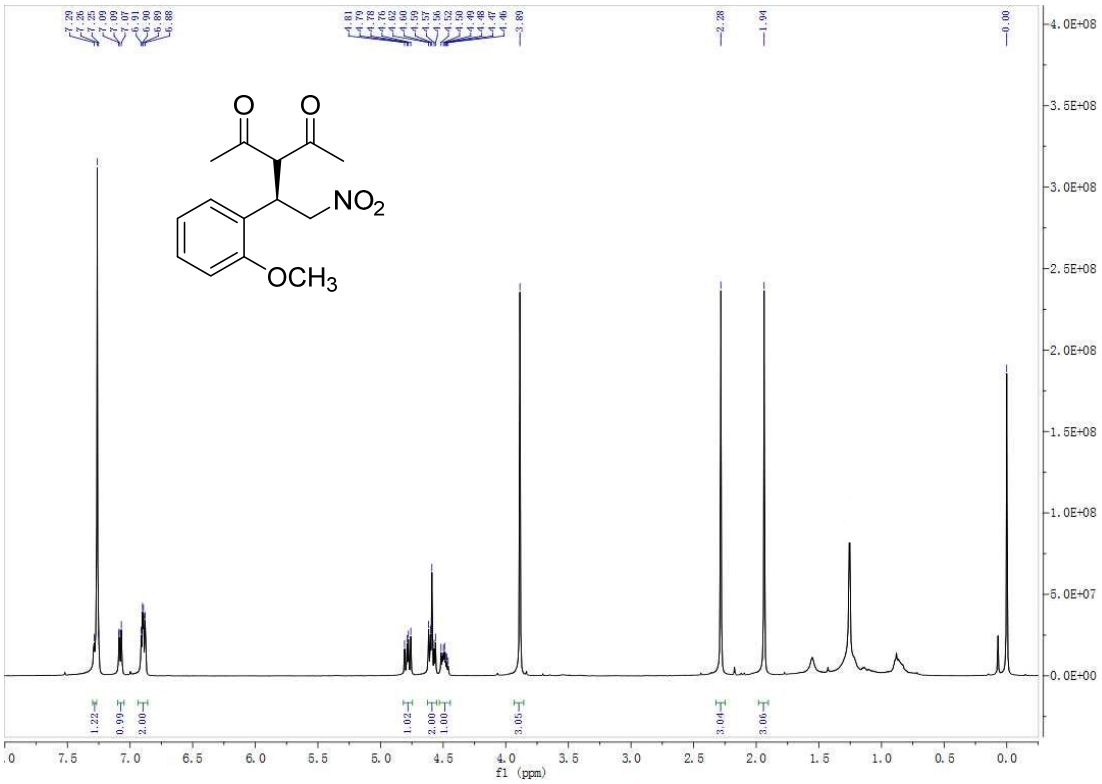
^{1}H NMR of **7d**



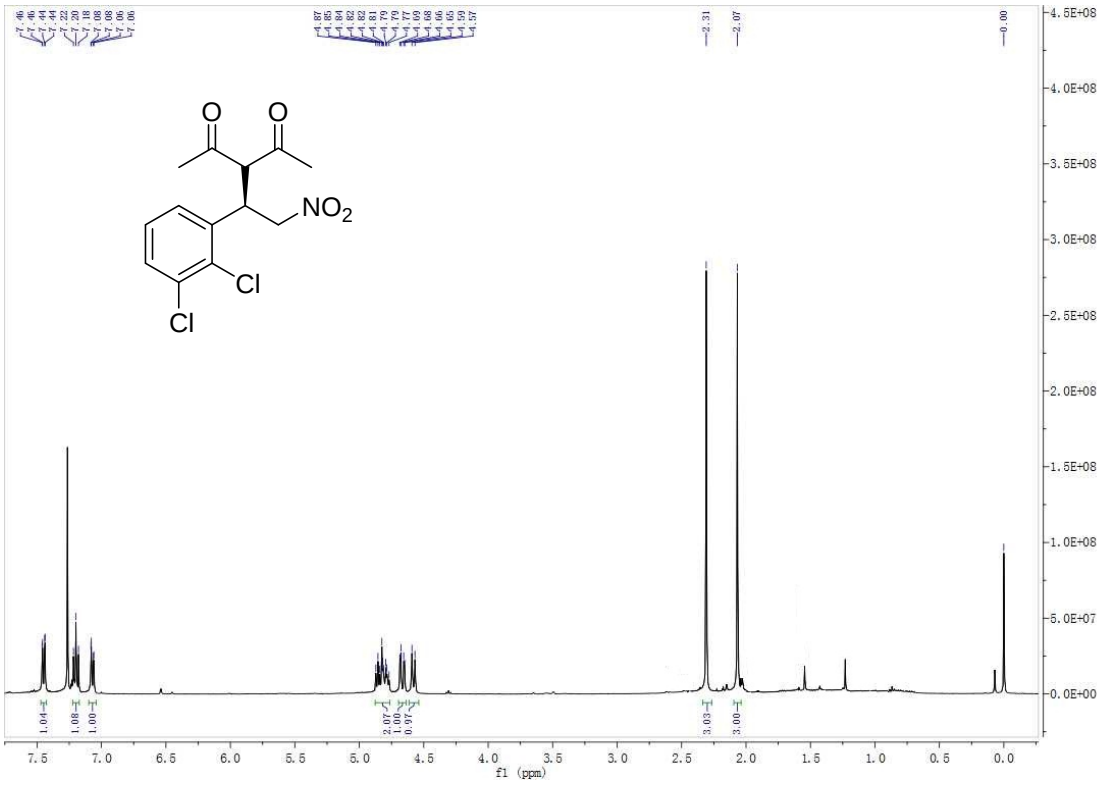
^{1}H NMR of **7e**



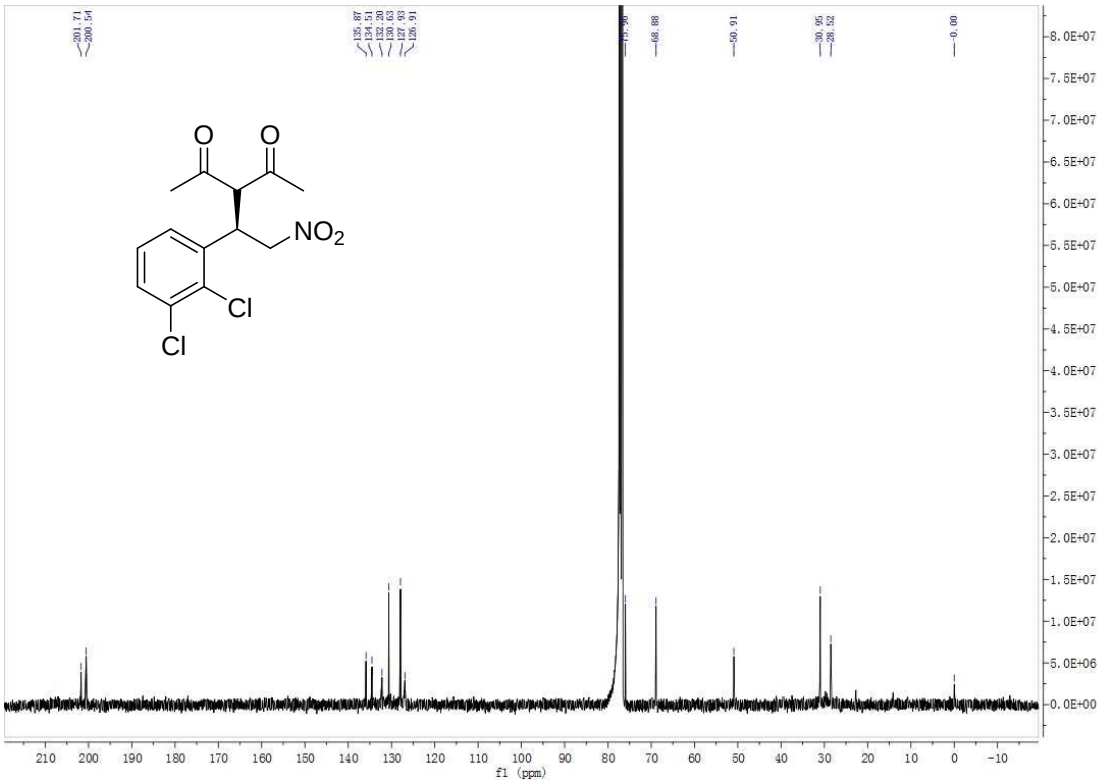
^{1}H NMR of **7f**



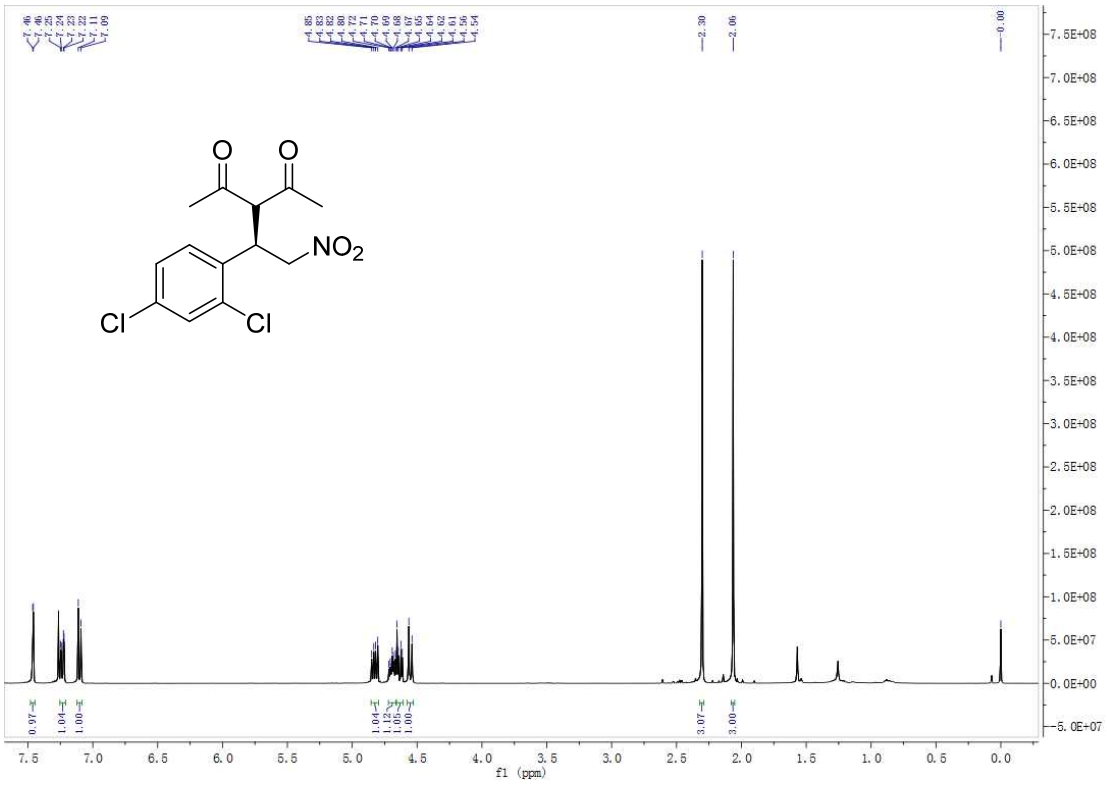
^{1}H NMR of **7g**



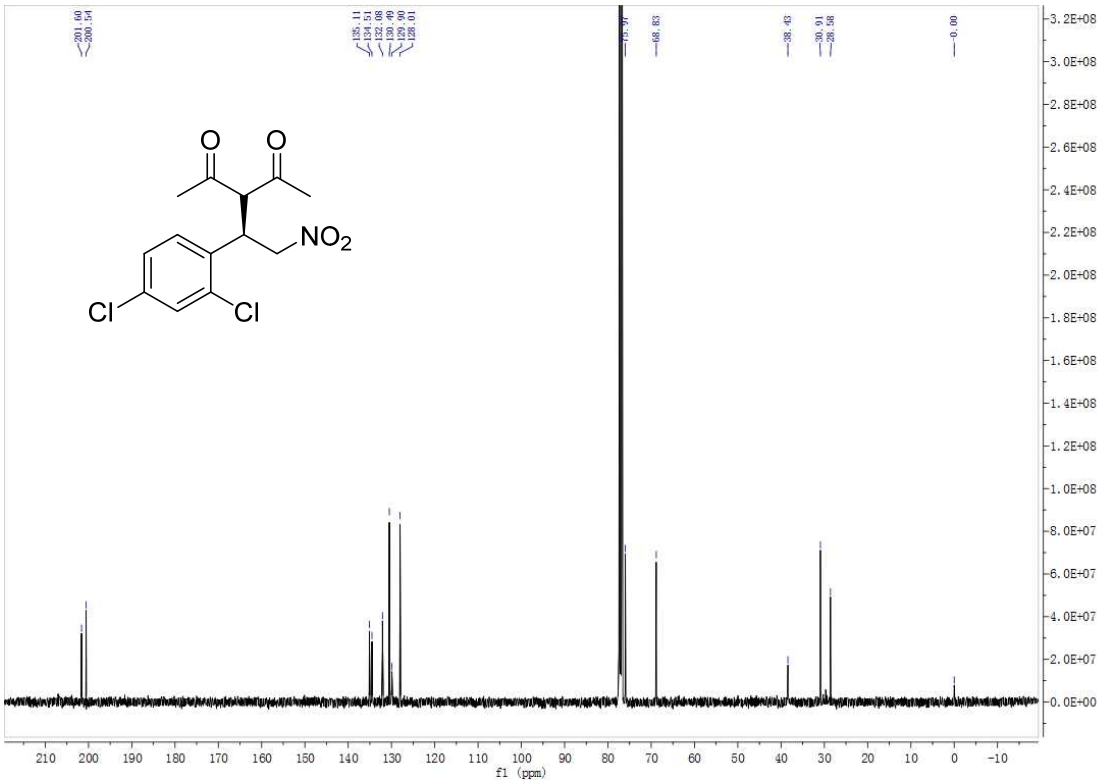
^{13} C NMR of **7g**



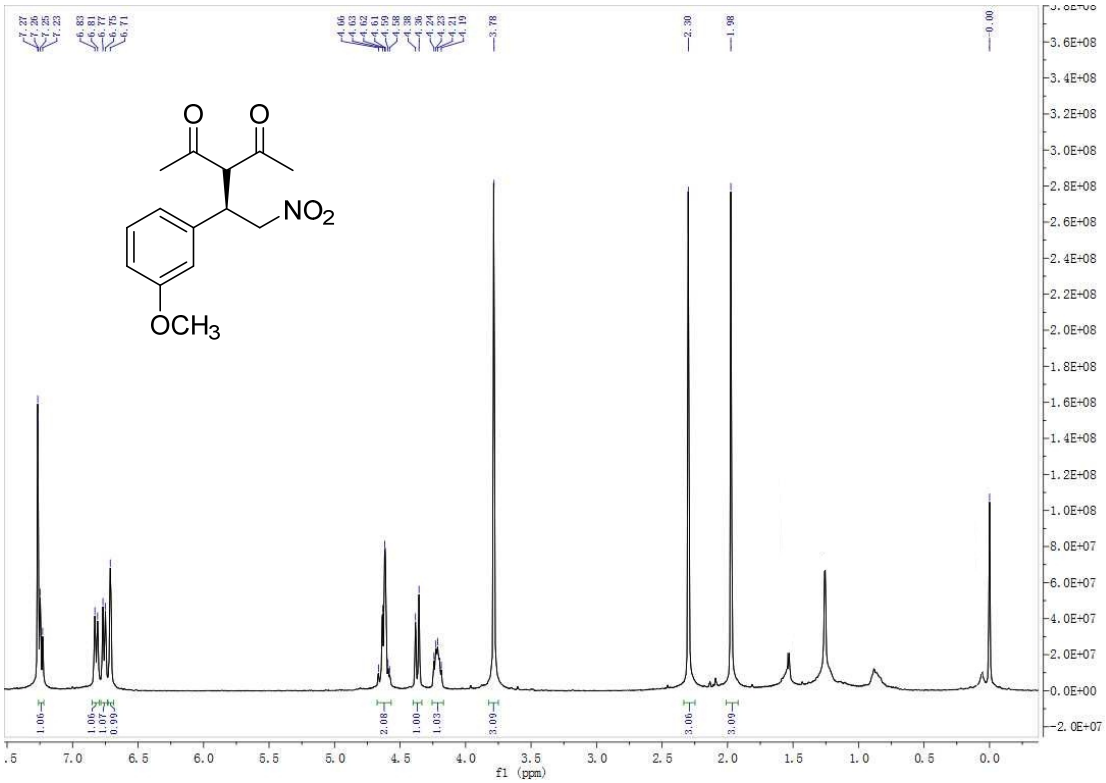
^{1}H NMR of **7h**



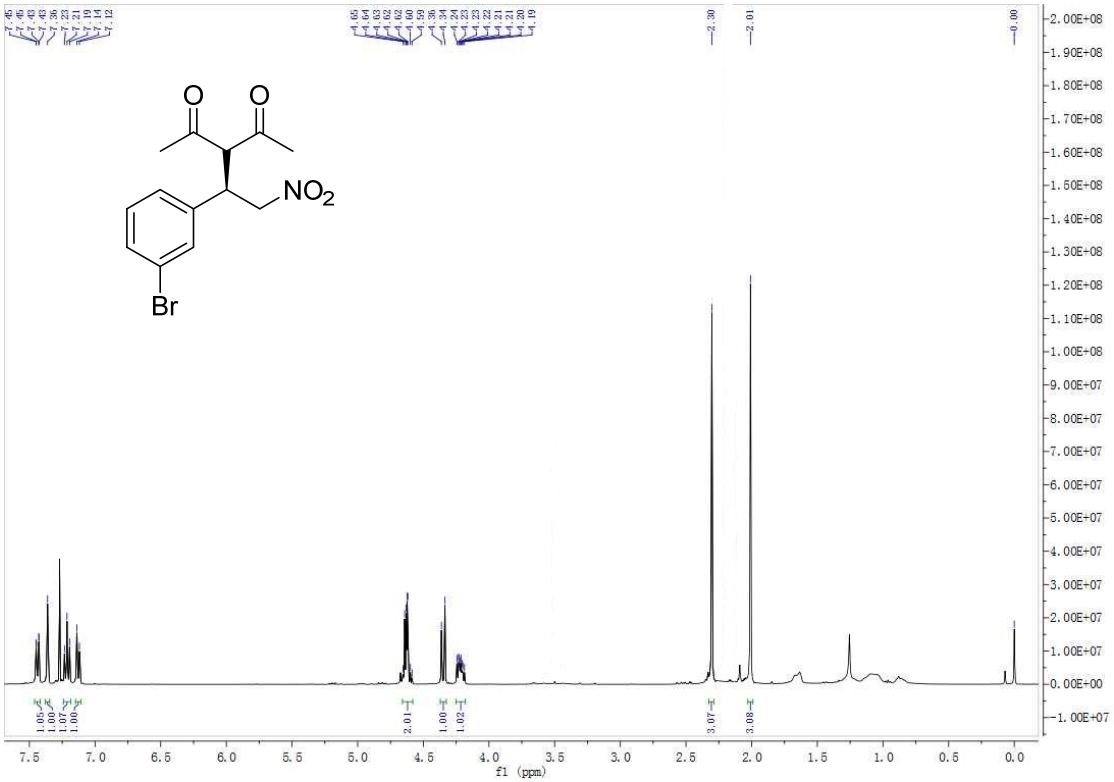
^{13} C NMR of **7h**



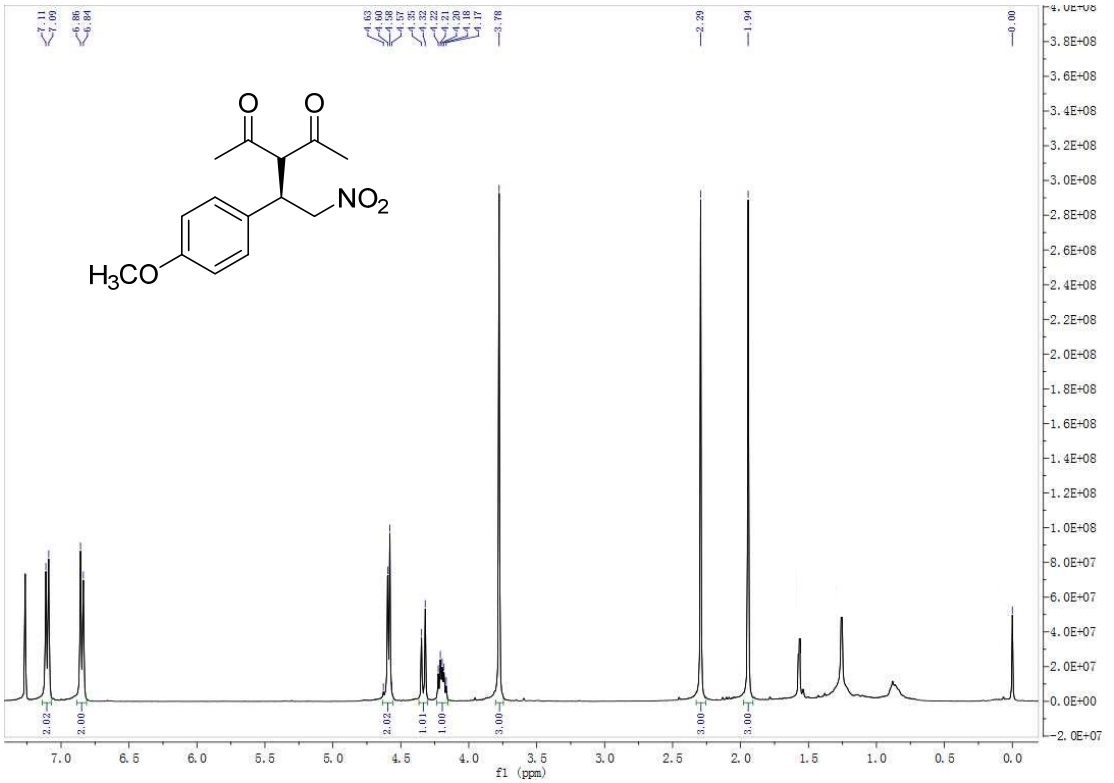
^{1}H NMR of **7i**



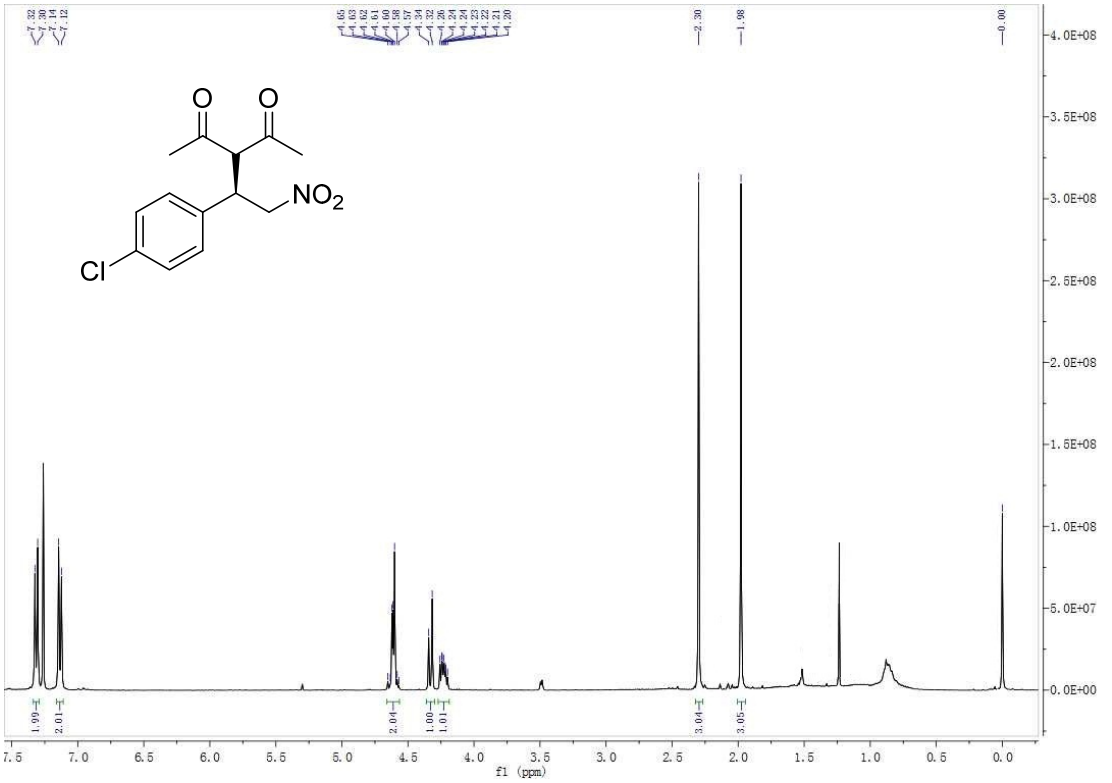
^{1}H NMR of **7j**



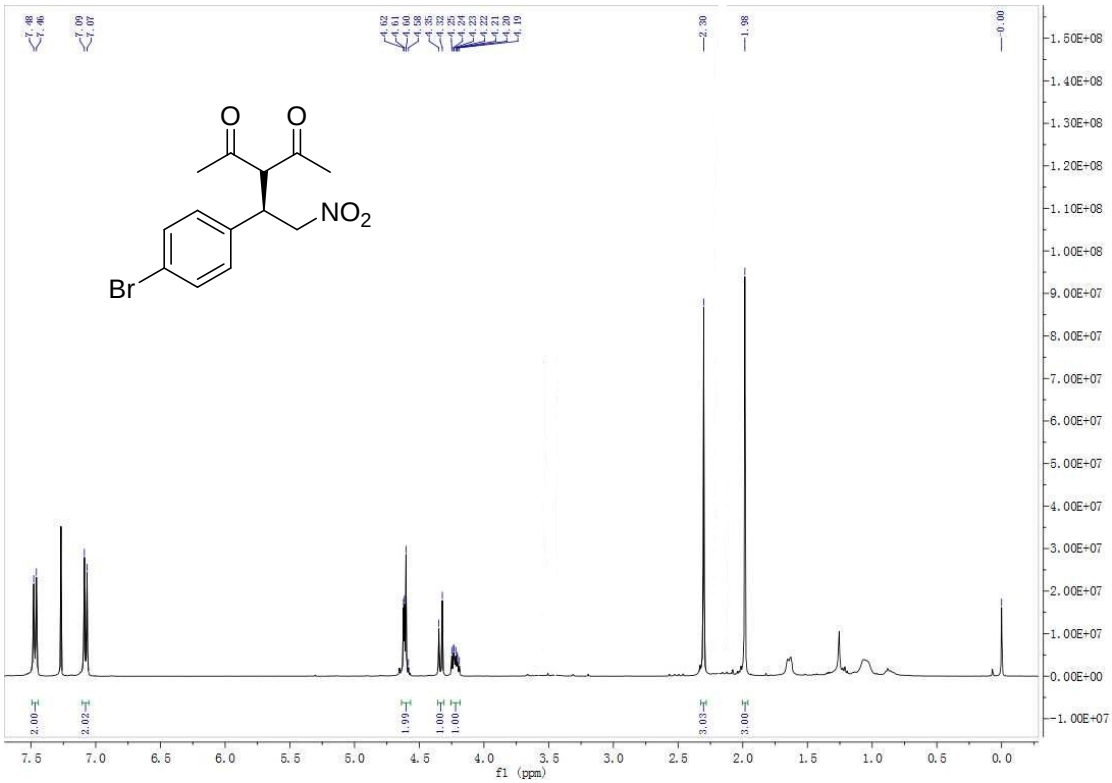
^{1}H NMR of **7k**



^{1}H NMR of **7l**

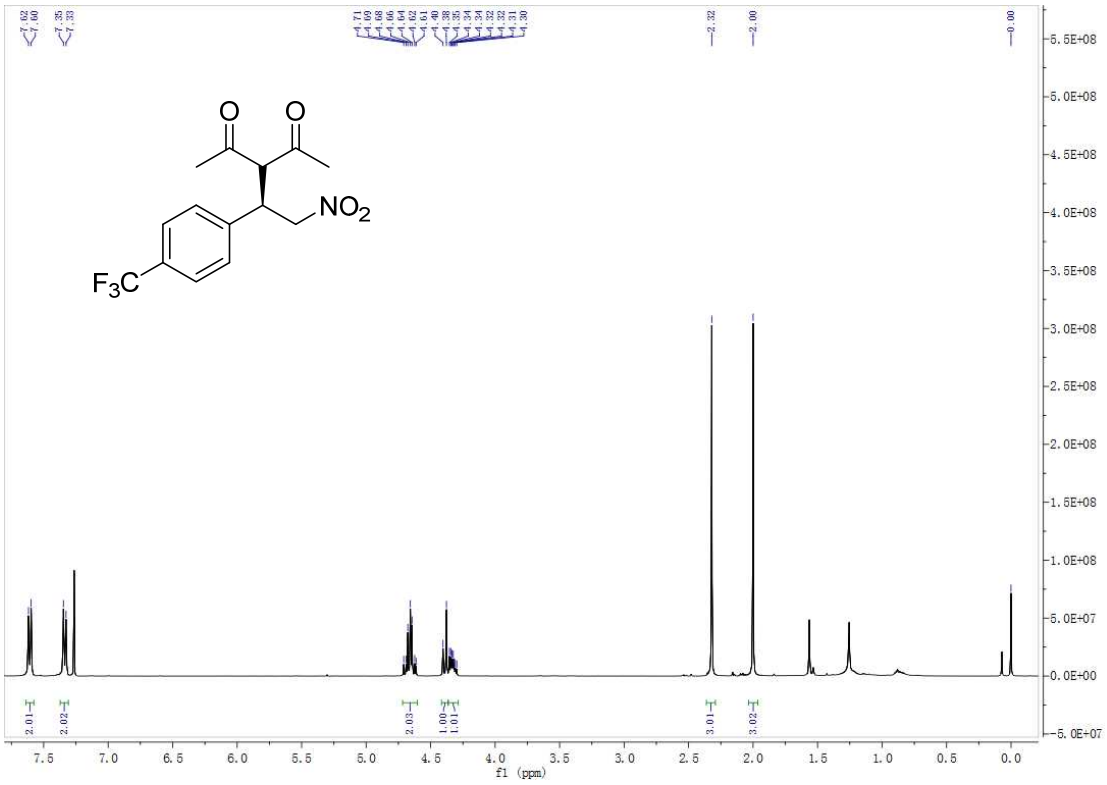


^{1}H NMR of **7m**

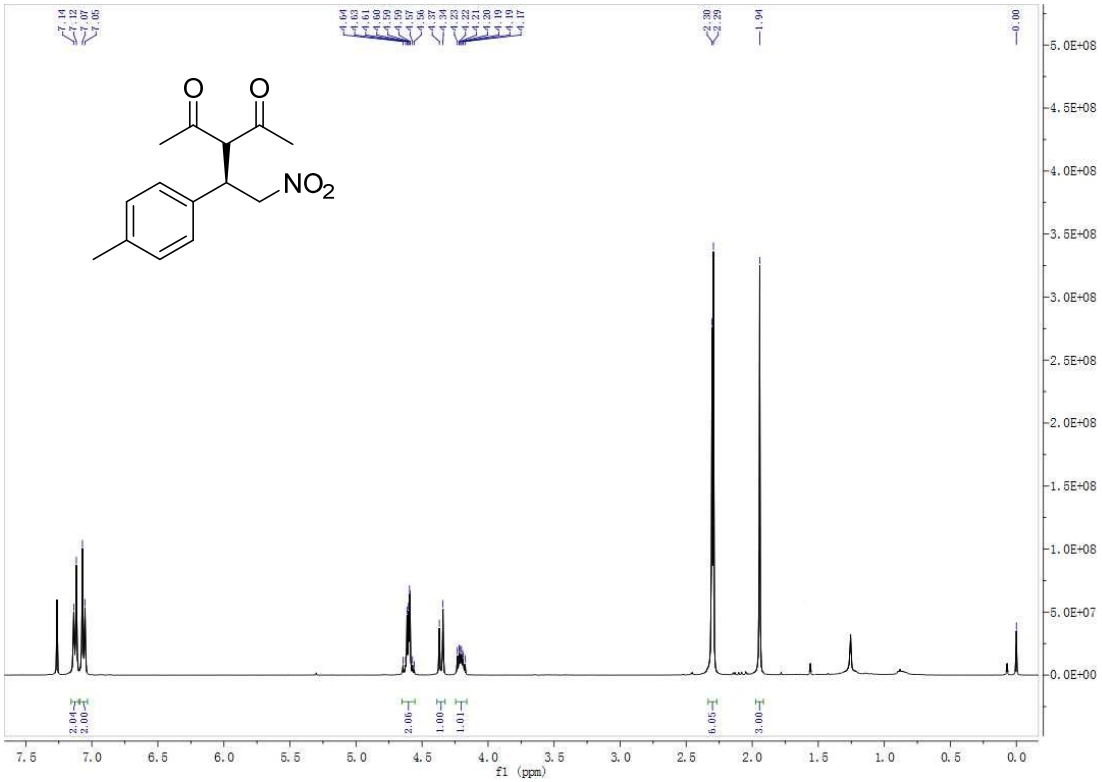


^{1}H NMR of **7n**

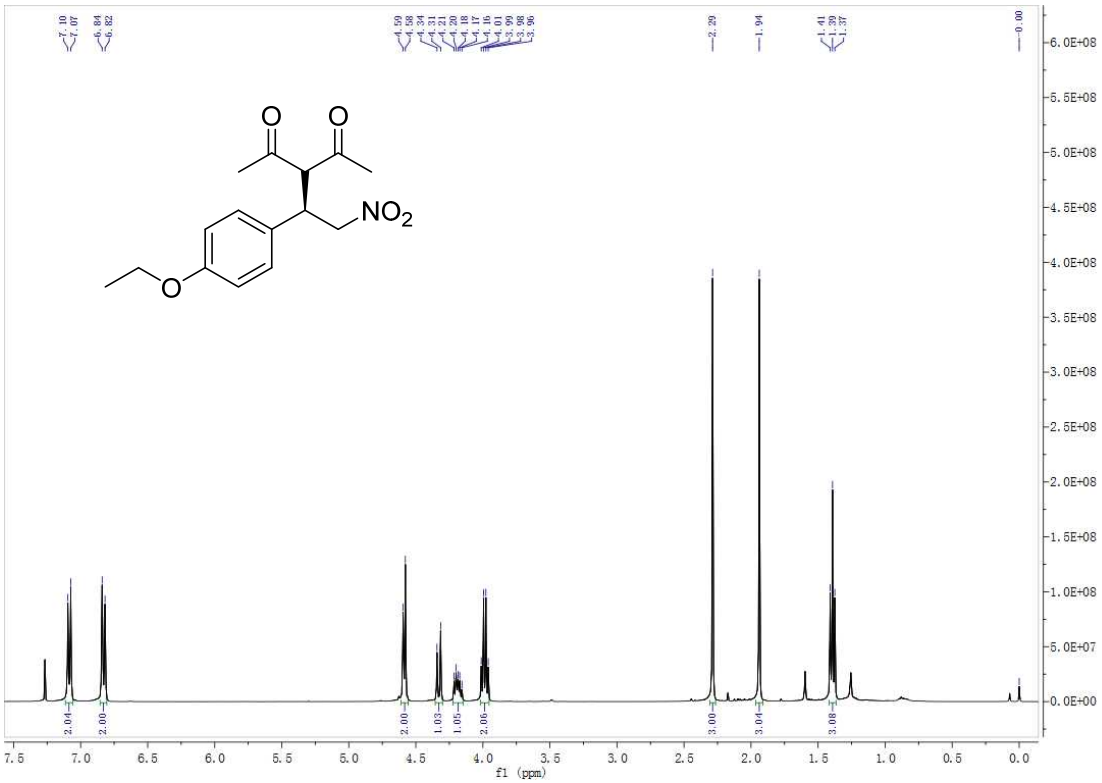
^{1}H NMR of **7o**



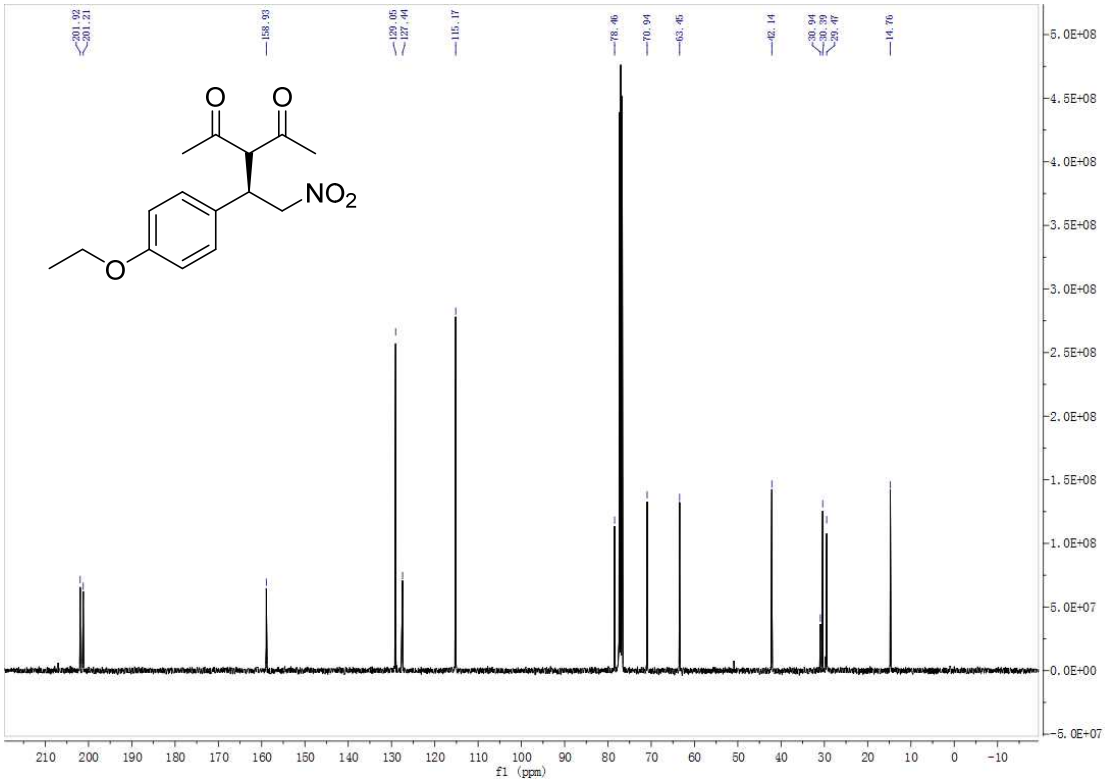
^{1}H NMR of **7p**



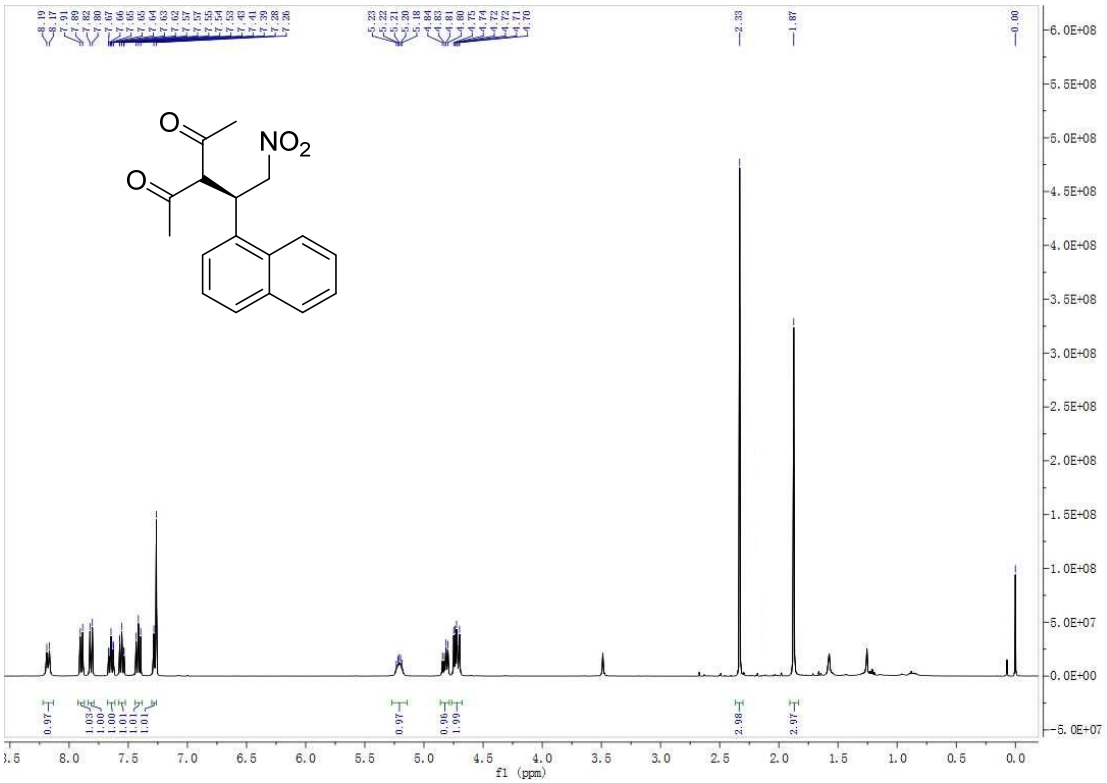
^{1}H NMR of **7q**



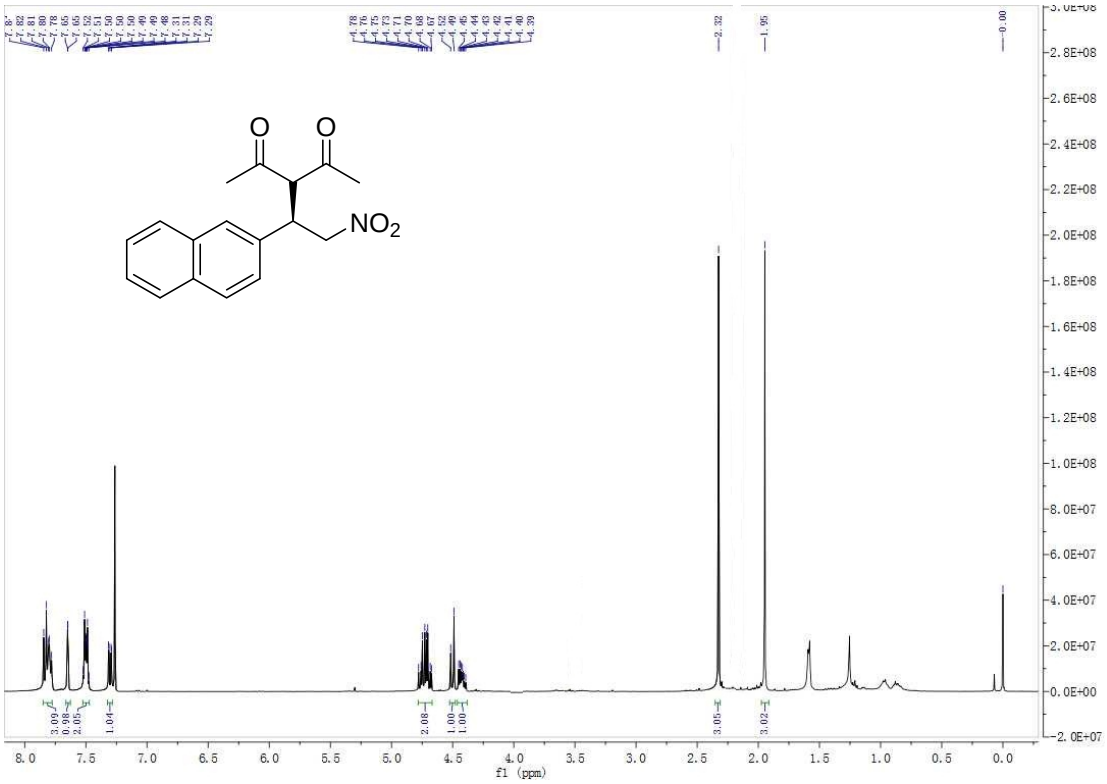
13 C NMR of **7q**



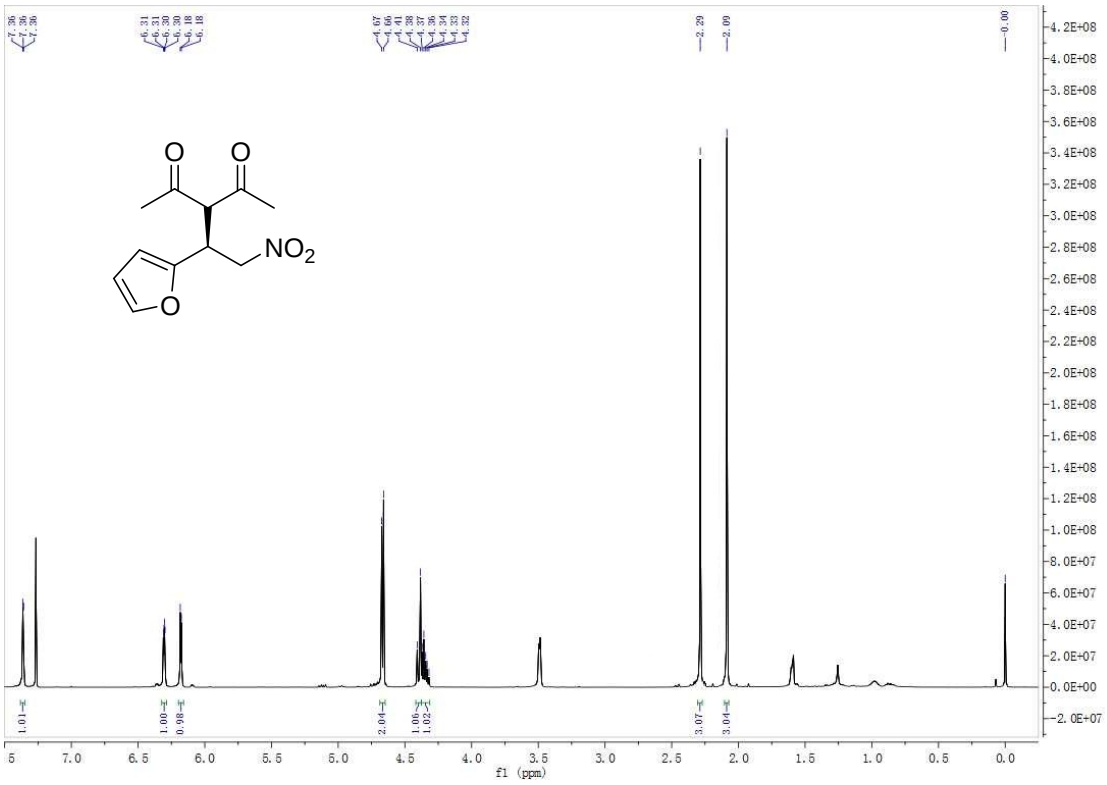
^{1}H NMR of **7r**



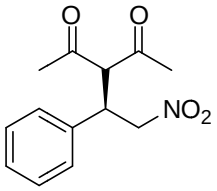
^{1}H NMR of **7s**



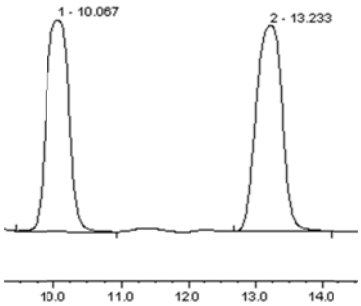
^{1}H NMR of **7t**



IV. HPLC Charts of Michael addition products

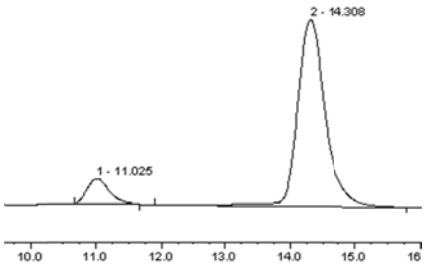


(*R*)-3-(2-Nitro-1-phenyl-ethyl)-pentane-2,4-dione (7a)[1]**,** White solid, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.28 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 2H), 4.69 – 4.58 (m, 2H), 4.37 (d, *J* = 10.8 Hz, 1H), 4.20 – 4.30 (m, 1H), 2.29 (s, 3H), 1.94 (s, 3H); HPLC (Chiralpak AD-H, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm): t_r = 11.0 min [minor (*S*)-enantiomer], t_r = 14.3 min [major (*R*)-enantiomer], 81% *ee*; $[\alpha]_D^{25}$ = −125.5 (*c* = 0.4 in $CHCl_3$).

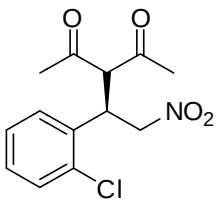


Racemate

		min	mAU*min			mAU	%	
1	n.a.	10.067	405.0265	n.a.	BMB*	1032.375	47.54	4.64
2	n.a.	13.233	446.9229	n.a.	BMB*	1007.128	52.46	n.a.
Total:			851.9494	0.0000		2039.503	100.00	

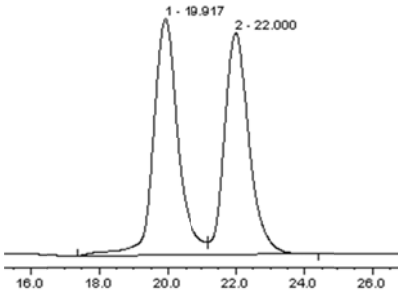


		min	mAU*min			mAU	%	
1	n.a.	11.025	66.2914	n.a.	BMB*	171.125	9.52	4.91
2	n.a.	14.308	629.7024	n.a.	BMB	1269.535	90.48	n.a.
Total:			695.9938	0.0000		1440.660	100.00	



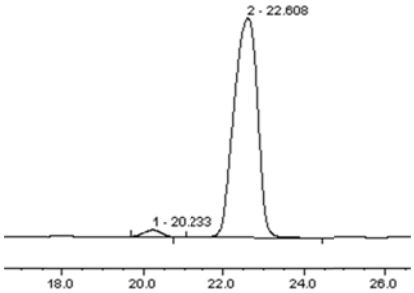
(*R*)-3-[1-(2-Chloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7b)[5], White

solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.41 (m, 1H), 7.27–7.21 (m, 2H), 7.18 – 7.13 (m, 1H), 4.84 (dd, *J* = 12.2, 6.7 Hz, 1H), 4.78 – 4.71 (m, 1H), 4.66 (dd, *J* = 12.2, 3.9 Hz, 1H), 4.60 (d, *J* = 9.9 Hz, 1H), 2.29 (s, 3H), 2.03 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 98 : 2, 1 mL/min, wavelength = 210 nm): t_r = 20.2 min [minor (*S*)-enantiomer], t_r = 22.6 min [major (*R*)-enantiomer], 96% *ee*; $[\alpha]_D^{25}$ = −136.3 (*c* = 0.9 in $CHCl_3$).

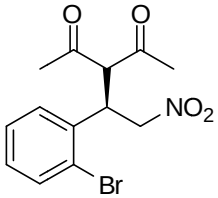


Racemate

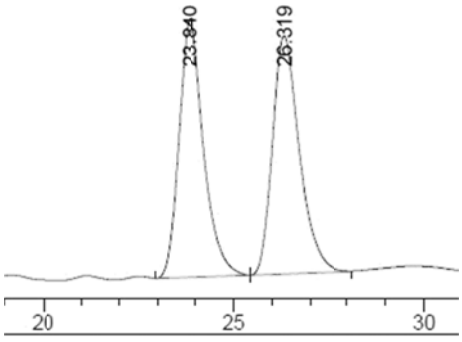
		min	mAU*min			mAU	%	
1	n.a.	19.917	340.2315	n.a.	BM	408.117	51.88	1.70
2	n.a.	22.000	315.6140	n.a.	MB*	382.687	48.12	n.a.
Total:			655.8455	0.0000		790.804	100.00	



		min	mAU*min			mAU	%	
1	n.a.	20.233	14.9141	n.a.	BMB*	30.556	2.19	2.47
2	n.a.	22.608	665.4245	n.a.	BMB*	991.123	97.81	n.a.
Total:			680.3385	0.0000		1021.679	100.00	

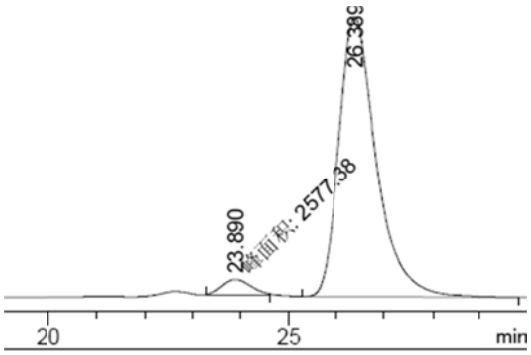


(*R*)-3-[1-(2-Bromo-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7c)[1]**,** white solid, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.21 – 7.12 (m, 2H), 4.84 (dd, *J* = 12.1, 6.3 Hz, 1H), 4.77 – 4.71 (m, 1H), 4.67 (dd, *J* = 12.2, 3.9 Hz, 1H), 4.61 (d, *J* = 9.7 Hz, 1H), 2.30 (s, 3H), 2.05 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 98 : 2, 1 mL/min, wavelength = 210 nm.): t_r = 23.9 min [minor (*S*)-enantiomer], t_r = 26.4 min [major (*R*)-enantiomer], 92% *ee*; $[\alpha]_D^{25}$ = −174.6 (*c* = 0.65 in $CHCl_3$).

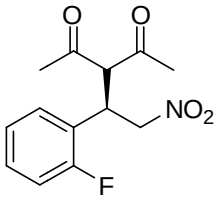


Racemate

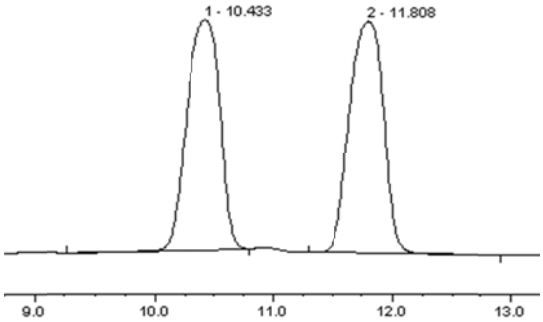
	min		mAU*s	mAU	%
1	23.840	VB	19287.71	416.424	50.82
2	26.319	BB	18663.32	382.567	49.18
Total:			37951.03	798.991	100.00



	min		mAU*s	mAU	%
1	23.890	MM	2577.38	61.8862	4.14
2	26.389	BBA	59712.22	1103.4598	95.86
Total:			62289.60	1165.3460	100.00

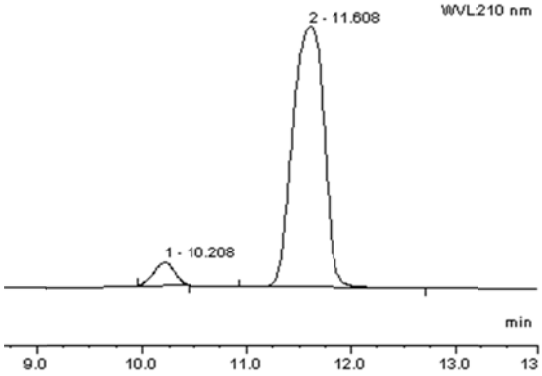


(*R*)-3-[1-(2-Fluoro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7d)[1]**,** white solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 1H), 7.17 (td, *J* = 7.7, 1.8 Hz, 1H), 7.13 – 7.10 (m, 1H), 7.10 – 7.04 (m, 1H), 4.77 – 4.70 (m, 1H), 4.66 – 4.60 (m, 1H), 4.52 – 4.46 (m, 2H), 2.30 (s, 3H), 2.02 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r = 10.2 min [minor (*S*)-enantiomer], t_r = 11.6 min [major (*R*)-enantiomer], 89% *ee*; $[\alpha]_D^{25}$ = −186.8 (***c*** = 0.4 in $CHCl_3$).

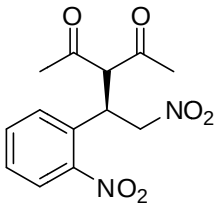


Racemate

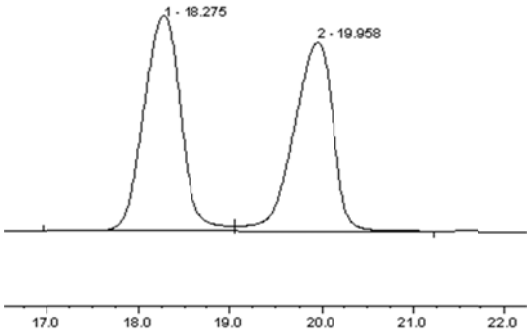
		min	mAU*min			mAU	%	
1	n.a.	10.433	346.3500	n.a.	BMB*	1058.228	49.75	2.51
2	n.a.	11.808	349.7761	n.a.	BMB*	1066.753	50.25	n.a.
Total:			696.1261	0.0000		2124.981	100.00	



		min	mAU*min			mAU	%	
1	n.a.	10.208	21.8837	n.a.	BMB*	95.997	5.52	2.95
2	n.a.	11.608	374.6195	n.a.	BMB*	1075.866	94.48	n.a.
Total:			396.5032	0.0000		1171.863	100.00	

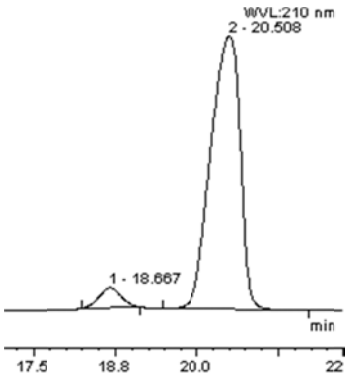


(*R*)-3-[2-Nitro-1-(2-nitro-phenyl)-ethyl]-pentane-2,4-dione (7e)[1]**,** white solid, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.59 (td, *J* = 7.7, 1.2 Hz, 1H), 7.49 (td, *J* = 8.1, 1.3 Hz, 1H), 7.36 (dd, *J* = 7.8, 1.1 Hz, 1H), 4.98 (dd, *J* = 13.3, 7.0 Hz, 1H), 4.84 (dd, *J* = 13.3, 3.6 Hz, 1H), 4.77 – 4.71 (m, 1H), 4.68 (d, *J* = 8.8 Hz, 1H), 2.32 (s, 3H), 2.14 (s, 3H); HPLC (Chiralpak AD-**H** column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r =18.7 min [minor (*S*)-enantiomer], t_r = 20.5 min [major (*R*)-enantiomer], 90% *ee*; $[\alpha]_D^{25}$ = −106.4 (*c* = 0.25 in $CHCl_3$).

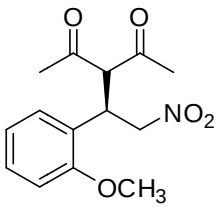


Racemate

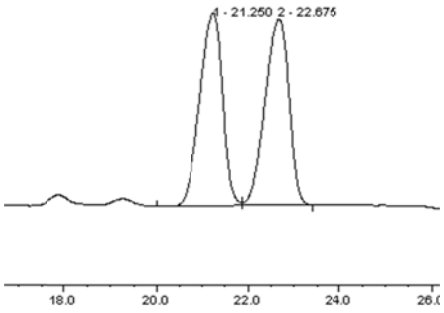
		min	mAU*min			mAU	%	
1	n.a.	18.275	360.1002	n.a.	BM	772.549	51.54	2.20
2	n.a.	19.958	338.6483	n.a.	MB	676.659	48.46	n.a.
Total:			698.7485	0.0000		1449.208	100.00	



		min	mAU*min			mAU	%	
1	n.a.	18.667	27.3436	n.a.	BMB*	70.010	5.17	2.46
2	n.a.	20.508	501.3112	n.a.	BMB*	959.152	94.83	n.a.
Total:			528.6547	0.0000		1029.162	100.00	

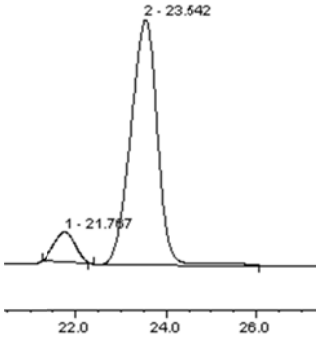


(*R*)-3-(1-(2-methoxyphenyl)-2-nitroethyl)-pentane-2,4-dione (7f)[2]**,** white solid, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 1H), 7.10 – 7.05 (m, 1H), 6.90 (dd, *J* = 7.8, 4.6 Hz, 2H), 4.78 (dd, *J* = 12.1, 7.8 Hz, 1H), 4.63 – 4.55 (m, 2H), 4.53 – 4.44 (m, 1H), 3.89 (s, 3H), 2.28 (s, 3H), 1.94 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 98 : 2, 1 mL/min, wavelength = 210 nm.): t_r = 21.8 min [minor (*S*)-enantiomer], t_r = 23.5 min [major (*R*)-enantiomer], 83% *ee*; $[\alpha]_D^{25}$ = −123.0 (***c*** = 0.5 in $CHCl_3$).

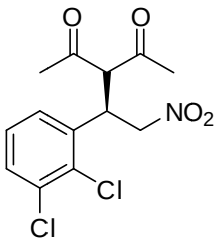


Racemate

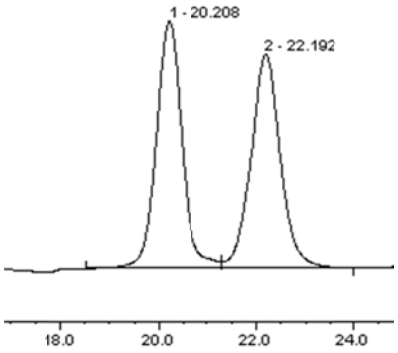
		min	mAU*min			mAU	%	
1	n.a.	21.250	404.4251	n.a.	BM	692.915	50.08	1.48
2	n.a.	22.675	403.0943	n.a.	MB*	669.369	49.92	n.a.
Total:			807.5193	0.0000		1362.284	100.00	



		min	mAU*min			mAU	%	
1	n.a.	21.767	22.1890	n.a.	BMB*	41.174	8.73	1.81
2	n.a.	23.542	231.9002	n.a.	BMB*	343.937	91.27	n.a.
Total:			254.0892	0.0000		385.111	100.00	

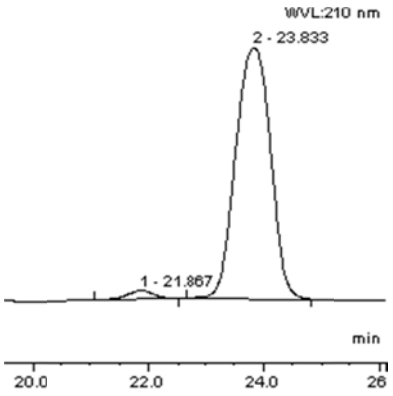


(*R*)-3-[1-(2,3-Dichloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7g), colorless oil, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.88 – 4.76 (m, 2H), 4.67 (dd, *J* = 12.1, 3.5 Hz, 1H), 4.58 (d, *J* = 9.5 Hz, 1H), 2.31 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ = 201.71, 200.54, 135.87, 134.51, 132.20, 130.63, 127.93, 126.91, 75.96, 68.88, 50.91, 30.95, 28.52; HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 98 : 2, 1 mL/min, wavelength = 210 nm.): t_r = 21.9 min [minor (*S*)-enantiomer], t_r = 23.8 min [major (*R*)-enantiomer], 95% *ee*; $[\alpha]_D^{25}$ = −57.8 (*c* = 1.25 in $CHCl_3$).

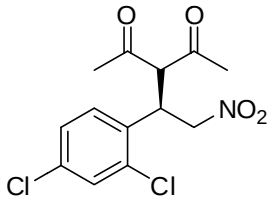


Racemate

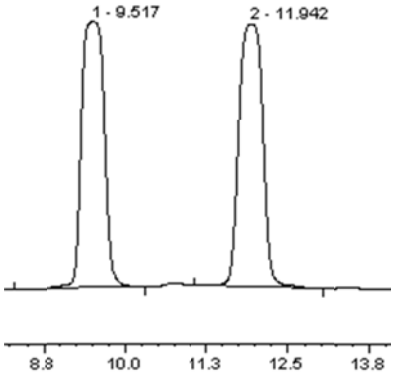
		min	mAU*min			mAU	%	
1	n.a.	20.208	197.2988	n.a.	M *	325.305	50.36	2.03
2	n.a.	22.192	194.4671	n.a.	MB*	282.015	49.64	n.a.
Total:			391.7659	0.0000		607.320	100.00	



		min	mAU*min			mAU	%	
1	n.a.	21.867	16.6715	n.a.	BMB*	32.836	2.36	2.02
2	n.a.	23.833	688.6620	n.a.	BMB*	990.816	97.64	n.a.
Total:			705.3335	0.0000		1023.653	100.00	

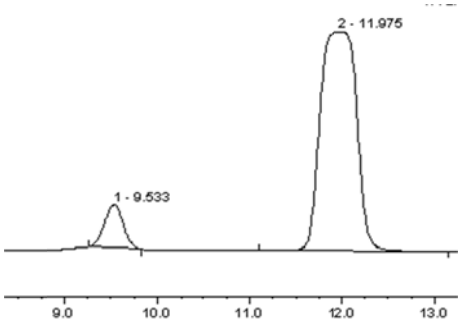


(*R*)-3-[1-(2,4-Dichloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7h)[1]**,** colorless oil, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 2.1 **H**z, 1H), 7.23 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.83 (dd, *J* = 12.3, 6.5 Hz, 1H), 4.72 – 4.66 (m, 1H), 4.63 (dd, *J* = 12.3, 4.0 Hz, 1H), 4.55 (d, *J* = 9.8 Hz, 1H), 2.30 (s, 3H), 2.06 (s, 3H); ^{13}C NMR(101MHz, $CDCl_3$): δ 201.60, 200.54, 135.11, 134.51, 132.08, 130.49, 129.90, 128.01, 75.97, 68.83, 38.43, 30.91, 28.58; HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r = 9.5 min [mino**r** (*S*)-enantiomer], t_r = 12.0 min [majo**r** (*R*)-enantiomer], 83% *ee*; $[\alpha]_D^{25}$ = −59.1 (*c* = 2.25 in $CHCl_3$).

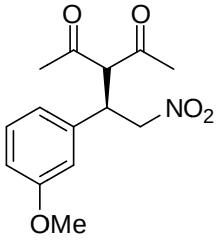


Racemate

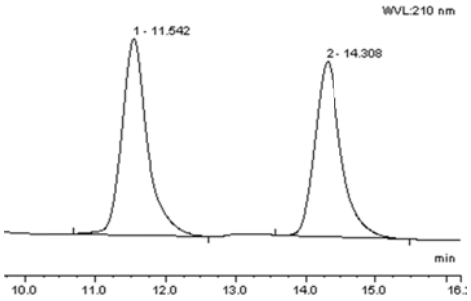
		min	mAU*min		mAU	%	
1	n.a.	9.517	459.7149	n.a. BMB*	1157.785	48.74	3.62
2	n.a.	11.942	483.4493	n.a. BMB*	1146.533	51.26	n.a.
Total:			943.1642	0.0000	2304.319	100.00	



		min	mAU*min		mAU	%	
1	n.a.	9.533	52.5547	n.a. BMB*	226.477	8.88	4.29
2	n.a.	11.975	538.9632	n.a. BMB*	1161.864	91.12	n.a.
Total:			591.5179	0.0000	1388.342	100.00	

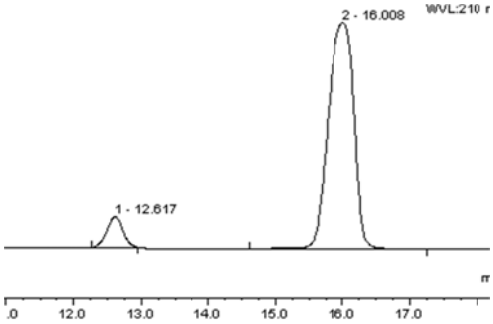


(*R*)-3-[1-(3-Methoxy-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7i)[4], yellow oil, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 4.68 – 4.57 (m, 2H), 4.37 (d, *J* = 10.9 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.78 (s, 3H), 2.30 (s, 3H), 1.98 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r = 12.6 min [minor (*S*)-enantiomer], t_r = 16.0 min [major (*R*)-enantiomer], 85% *ee*; $[\alpha]_D^{25}$ = −207.3 (*c* = 0.25 in $CHCl_3$).

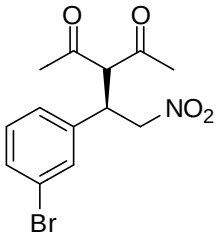


Racemate

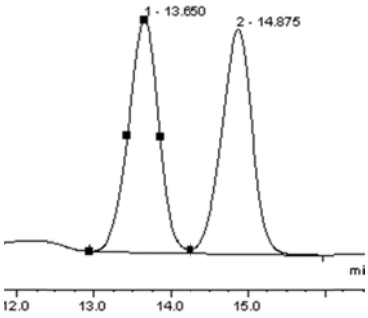
		min	mAU*min			mAU	%	
1	n.a.	11.542	545.0300	n.a.	BMB*	1316.177	51.21	4.42
2	n.a.	14.308	519.2414	n.a.	BMB*	1174.382	48.79	n.a.
Total:			1064.2714	0.0000		2490.559	100.00	



		min	mAU*min			mAU	%	
1	n.a.	12.617	39.0304	n.a.	BMB*	145.348	7.45	5.84
2	n.a.	16.008	484.5420	n.a.	BMB	1077.328	92.55	n.a.
Total:			523.5724	0.0000		1222.676	100.00	

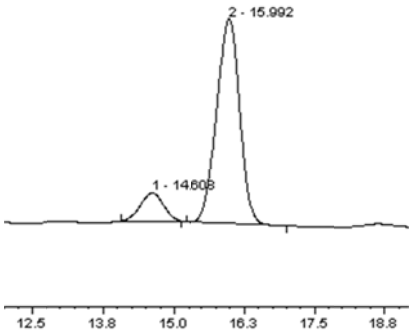


(*R*)-3-[1-(3-Bromo-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7j)[1]**,** white solid, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.36 (s, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 4.66 – 4.58 (m, 2H), 4.35 (d, *J* = 10.6 Hz, 1H), 4.22 (ddd, *J* = 10.8, 7.6, 5.0 Hz, 1H), 2.30 (s, 3H), 2.01 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 93 : 7, 1 mL/min, wavelength = 210 nm.); t_r =14.6 min [minor (*S*)-enantiomer], t_r = 16.0 min [major (*R*)-enantiomer], 77% *ee.*

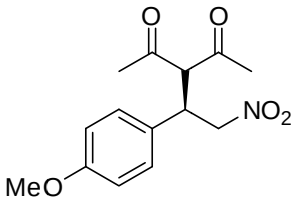


Racemate

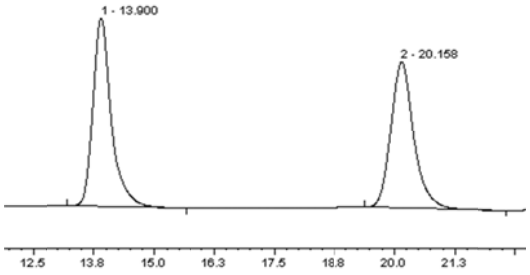
		min	mAU*min			mAU	%	
1	n.a.	13.650	192.0738	n.a.	BM *	425.504	50.66	1.71
2	n.a.	14.875	187.0733	n.a.	MB*	410.613	49.34	n.a.
Total:			379.1471	0.0000		836.117	100.00	



		min	mAU*min			mAU	%	
1	n.a.	14.608	29.0940	n.a.	BMB*	62.443	11.79	1.84
2	n.a.	15.992	217.7254	n.a.	BMB*	461.407	88.21	n.a.
Total:			246.8193	0.0000		523.850	100.00	

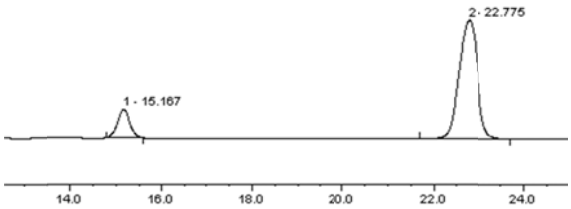


(*R*)-3-[1-(4-Methoxy-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7k)[4]**,** white solid, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.64 – 4.56 (m, 2H), 4.33 (d, *J* = 10.9 Hz, 1H), 4.24 – 4.15 (m, 1H), 3.78 (s, 3H), 2.29 (s, 3H), 1.94 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r = 15.2 min [minor (*S*)-enantiomer], t_r = 22.8 min [major (*R*)-enantiomer], 74% *ee*; $[\alpha]_D^{25}$ = −81.8 (*c* = 0.4 in $CHCl_3$).

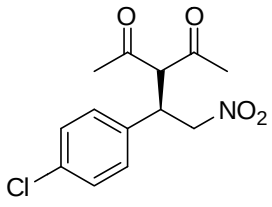


Racemate

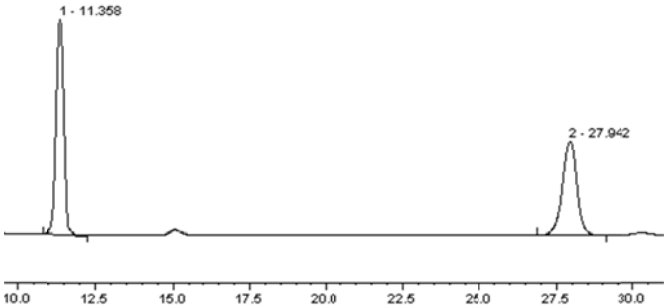
		min	mAU*min			mAU	%	
1	n.a.	13.900	487.6282	n.a.	BMB*	1126.498	51.00	8.69
2	n.a.	20.158	468.5038	n.a.	BMB*	874.850	49.00	n.a.
Total:			956.1320	0.0000		2001.348	100.00	



		min	mAU*min			mAU	%	
1	n.a.	15.167	44.0571	n.a.	BMB*	144.638	13.06	12.13
2	n.a.	22.775	293.3499	n.a.	BMB	607.851	86.94	n.a.
Total:			337.4070	0.0000		752.489	100.00	

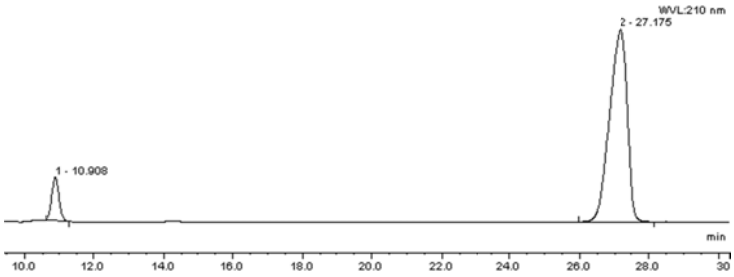


(*R*)-3-[1-(4-Chloro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7l)[2], white solid, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.66 – 4.56 (m, 2H), 4.33 (d, *J* = 10.7 Hz, 1H), 4.27 – 4.19 (m, 1H), 2.30 (s, 3H), 1.98 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 85 : 15, 1 mL/min, wavelength = 210 nm.): t_r =10.9 min [minor (*S*)-enantiomer], t_r = 27.2 min [major (*R*)-enantiomer], 84% *ee*; $[\alpha]_D^{25}$ = −86.3 (*c* = 0.4 in $CHCl_3$).

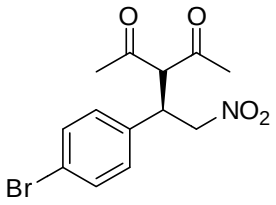


Racemate

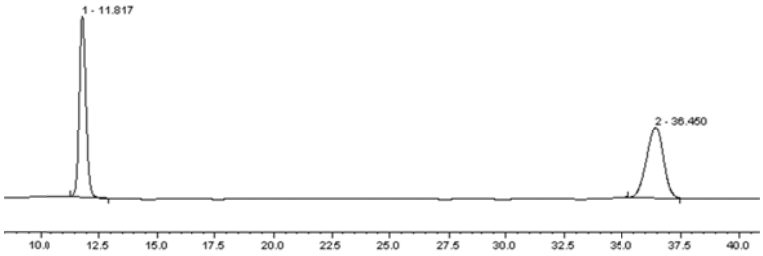
		min	mAU*min			mAU	%	
1	n.a.	11.358	137.7452	n.a.	BMB*	501.567	53.89	26.04
2	n.a.	27.942	117.8650	n.a.	BMB	223.442	46.11	n.a.
Total:			255.6102	0.0000		725.010	100.00	



		min	mAU*min			mAU	%	
1	n.a.	10.908	42.2391	n.a.	BMB*	174.102	7.96	23.08
2	n.a.	27.175	488.1065	n.a.	BMB	780.987	92.04	n.a.
Total:			530.3456	0.0000		955.089	100.00	

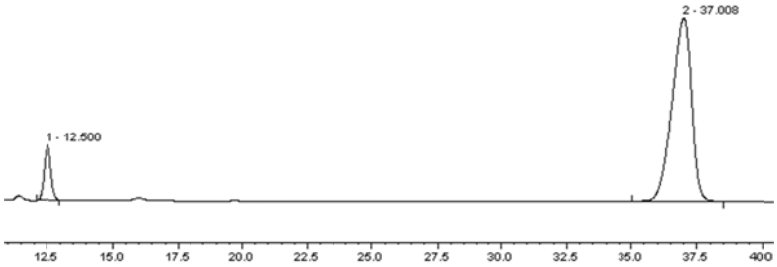


(*R*)-3-[1-(4-Bromo-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7m)[1], white solid, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.64 – 4.57 (m, 2H), 4.33 (d, *J* = 10.7 Hz, 1H), 4.26 – 4.18 (m, 1H), 2.30 (s, 3H), 1.98 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 85 : 15, 1 mL/min, wavelength = 210 nm.): t_r =12.5 min [minor (*S*)-enantiomer], t_r = 37.0 min [major (*R*)-enantiomer], 80% *ee*; $[\alpha]_D^{25}$ = −87.0 (*c* = 0.6 in $CHCl_3$).

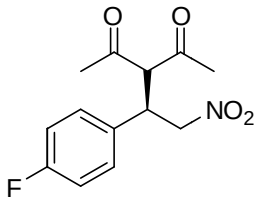


Racemate

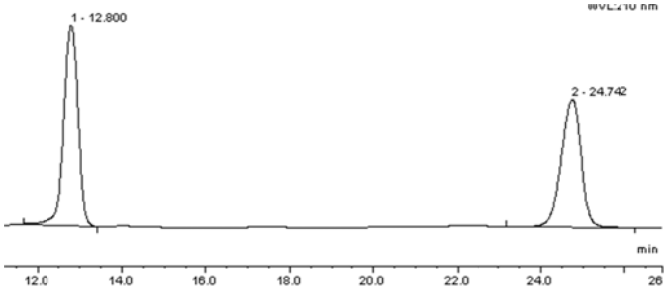
		min	mAU*min			mAU	%	
1	n.a.	11.817	219.6037	n.a.	BMB*	672.979	50.36	26.77
2	n.a.	36.450	216.4762	n.a.	BMB*	260.937	49.64	n.a.
Total:			436.0799	0.0000		933.916	100.00	



		min	mAU*min			mAU	%	
1	n.a.	12.500	66.4695	n.a.	BMB*	210.268	9.99	26.39
2	n.a.	37.008	599.1390	n.a.	BMB	700.216	90.01	n.a.
Total:			665.6085	0.0000		910.484	100.00	

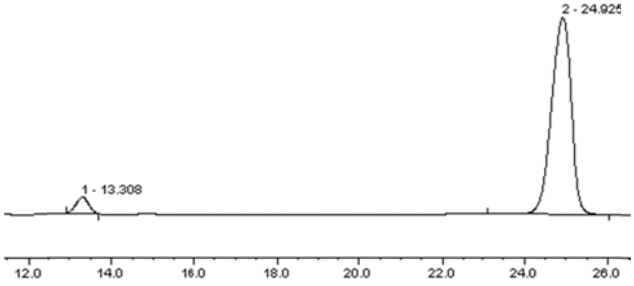


(*R*)-3-[1-(4-Fluoro-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7n)[4], white solid, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 – 7.15 (m, 2H), 7.06 – 7.00 (m, 2H), 4.64 – 4.57 (m, 2H), 4.33 (d, *J* = 10.8 Hz, 1H), 4.28 – 4.20 (m, 1H), 2.30 (s, 3H), 1.97 (s, 3H); HPLC (Chiralpak AD-H column, Hex : ***i***-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r =13.3 min [minor (*S*)-enantiomer], t_r = 24.9 min [major (*R*)-enantiomer], 90% *ee*; $[\alpha]_D^{25}$ = −226.5 (*c* = 0.2 in $CHCl_3$).

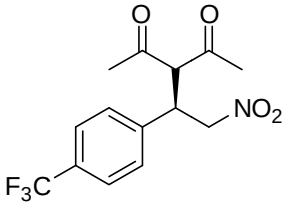


Racemate

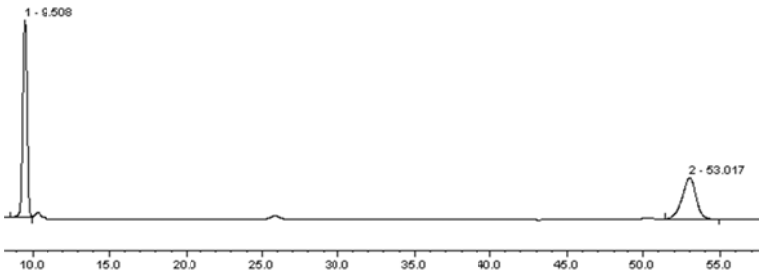
		min	mAU*min			mAU	%	
1	n.a.	12.800	236.2425	n.a.	BMB*	603.825	53.14	16.24
2	n.a.	24.742	208.3518	n.a.	BMB*	385.738	46.86	n.a.
Total:			444.5942	0.0000		989.564	100.00	



		min	mAU*min			mAU	%	
1	n.a.	13.308	15.5255	n.a.	BMB*	44.861	4.95	16.10
2	n.a.	24.925	297.9256	n.a.	BMB	548.572	95.05	n.a.
Total:			313.4511	0.0000		593.434	100.00	

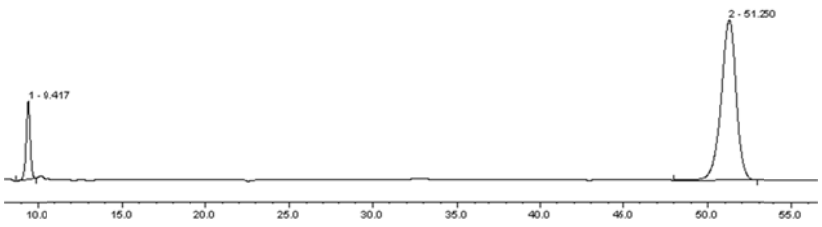


(*R*)-3-[2-Nitro-1-(4-trifluoromethyl-phenyl)-ethyl]-pentane-2,4-dione (7o)[5]**,** white solid, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.72 – 4.60 (m, 2H), 4.39 **(**d, *J* = 10.6 Hz, 1H), 4.36 – 4.29 (m, 1H), 2.32 (s, 3H), 2.00 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 85 : 15, 1 mL/min, wavelength = 210 nm.): t_r = 9.4 min [minor (*S*)-enantiomer], t_r = 51.3 min [major (*R*)-enantiomer**]**, 78% *ee*; $[\alpha]_D^{25}$ = −66.6 (*c* = 0.5 in $CHCl_3$).

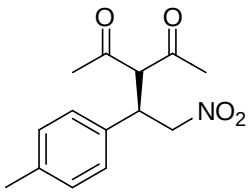


Racemate

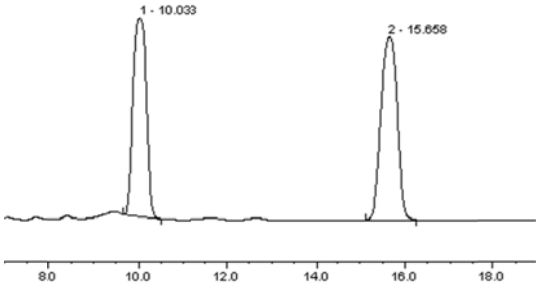
		min	mAU*min			mAU	%	
1	n.a.	9.508	235.0041	n.a.	BMB*	749.811	59.67	41.71
2	n.a.	53.017	158.8544	n.a.	BMB	153.409	40.33	n.a.
Total:			393.8585	0.0000		903.220	100.00	



		min	mAU*min			mAU	%	
1	n.a.	9.417	23.8663	n.a.	BMB*	90.105	11.09	42.92
2	n.a.	51.250	191.2741	n.a.	BMB	186.636	88.91	n.a.
Total:			215.1404	0.0000		276.741	100.00	

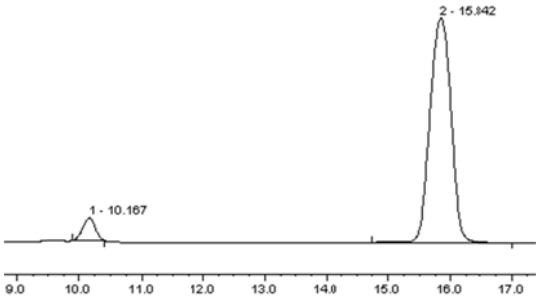


(*R*)-3-(2-Nitro-1-p-tolyl-ethyl)-pentane-2,4-dione (7p)[1]**,** white solid, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.65 – 4.55 (m, 2H), 4.36 (d, *J* = 10.9 Hz, 1H), 4.25 – 4.16 (m, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 1.94 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r =10.1 min [minor (*S*)-enantiomer], t_r = 15.8 min [major (*R*)-enantiomer], 89% *ee*; $[\alpha]_D^{25}$ = −62.5 (*c* = 0.75 in $CHCl_3$).

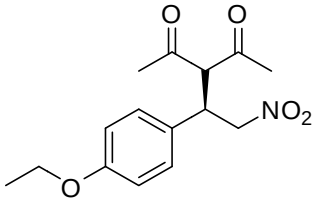


Racemate

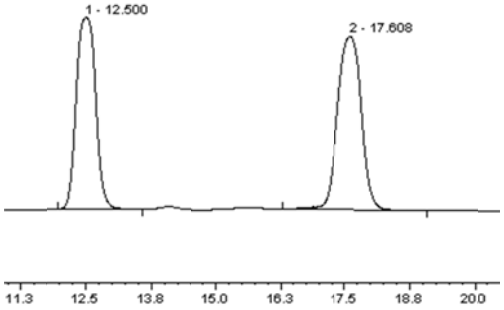
		min	mAU*min			mAU	%	
1	n.a.	10.033	393.8666	n.a.	BMB*	1156.218	47.05	8.91
2	n.a.	15.658	443.1923	n.a.	BMB*	1066.319	52.95	n.a.
Total:			837.0589	0.0000		2222.537	100.00	



		min	mAU*min			mAU	%	
1	n.a.	10.167	20.4468	n.a.	BMB*	90.152	5.56	11.33
2	n.a.	15.842	347.5635	n.a.	BMB	897.981	94.44	n.a.
Total:			368.0103	0.0000		988.133	100.00	

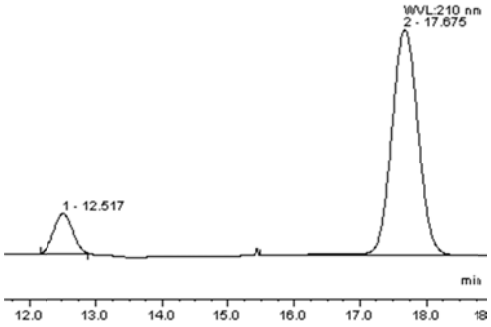


(*R*)-3-[1-(4-Ethoxy-phenyl)-2-nitro-ethyl]-pentane-2,4-dione (7q), white solid, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.63 – 4.56 (m, 2H), 4.33 (d, *J* = 10.9 Hz, 1H), 4.22 – 4.15 (m, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 1.94 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR(101MHz, $CDCl_3$): δ 201.92, 201.21, 158.93, 129.05, 127.44, 115.17, 78.46, 70.94, 63.45, 42.14, 30.94, 30.39, 29.47, 14.76; HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r = 12.5 min [minor (*S*)-enantiomer], t_r = 17.7 min [major (*R*)-enantiomer], 78% *ee*; HRMS (ESI) calcd for $C_{15}H_{19}NO_5Na^+$ $(M+Na)^+$: 316.1161, Found: 316.1150.

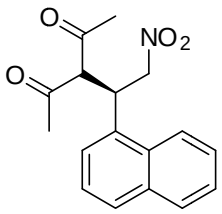


Racemate

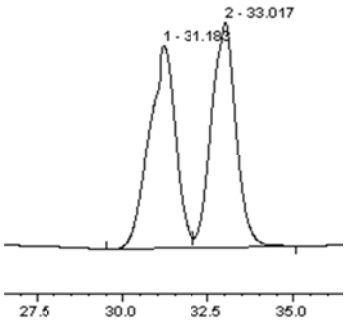
		min	mAU*min			mAU	%	
1	n.a.	12.500	486.1065	n.a.	BMB	1147.324	46.77	6.62
2	n.a.	17.608	553.3369	n.a.	BMB*	1038.320	53.23	n.a.
Total:			1039.4434	0.0000		2185.643	100.00	



		min	mAU*min			mAU	%	
1	n.a.	12.517	35.2613	n.a.	BMB*	107.428	11.13	8.22
2	n.a.	17.675	281.5996	n.a.	BMB*	613.186	88.87	n.a.
Total:			316.8610	0.0000		720.613	100.00	

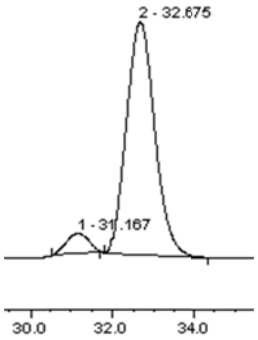


(*R*)-3-(1-Naphthalen-1-yl-2-nitro-ethyl)-pentane-2,4-dione (7r)[4]**,** yellow solid, 72% yield; ^{1}H NMR (400 MHz, CD**C**l$_3$): δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.90 (**d**, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.44 – 7.38 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 5.27 – 5.14 (m, 1H), 4.82 (dd, *J* = 12.2, 6.5 Hz, 1H), 4.77 – 4.68 (m, 2H), 2.33 (s, 3H), 1.87 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 98 : 2, 1 mL/min, wavelength = 210 nm.): t_r = 31.2 min [minor (*S*)-enantiomer], t_r = 32.3 min [major (*R*)-enantiomer], 88% *ee*; $[\alpha]_D^{25}$ = −81.5 (*c* = 0.4 in CHCl$_3$).

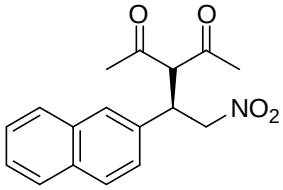


Racemate

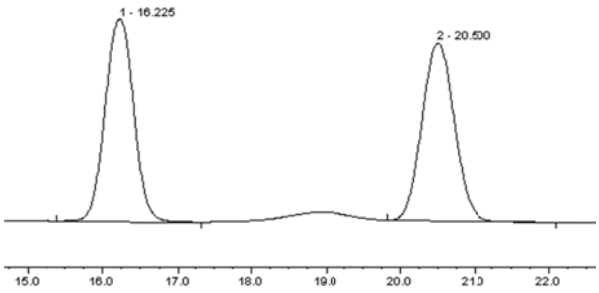
		min	mAU*min		mAU	%	
1	n.a.	31.183	442.9658	n.a. BM	495.391	49.32	1.32
2	n.a.	33.017	455.1930	n.a. MB	549.433	50.68	n.a.
Total:			898.1588	0.0000	1044.823	100.00	



		min	mAU*min		mAU	%	
1	n.a.	31.167	14.1294	n.a. BMB*	22.613	6.21	1.30
2	n.a.	32.675	213.3328	n.a. BMB*	268.625	93.79	n.a.
Total:			227.4623	0.0000	291.237	100.00	

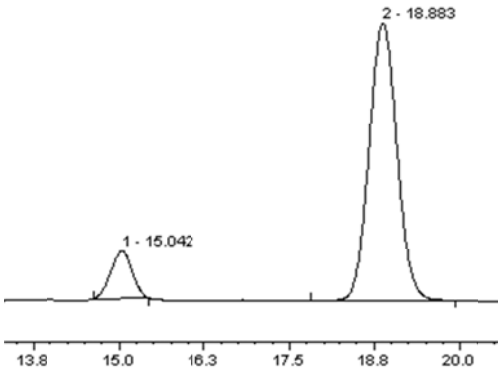


(*R*)-3-(1-Naphthalen-2-yl-2-nitro-ethyl)-pentane-2,4-dione (7s)[4]**,** light yellow solid, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.78 (m, 3H), 7.65 (d, *J* = 1.1 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.30 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.72 (qd, *J* = 12.4, 6.2 Hz, 2H), 4.50 (d, *J* = 10.8 Hz, 1H), 4.46 – 4.38 (m, 1H), 2.32 (s, 3H), 1.95 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r = 15.0 min [minor (*S*)-enantiomer], t_r = 18.9 min [major (*R*)-enantiomer], 77% *ee*; $[\alpha]_D^{25}$ = −72.6 (*c* = 0.5 in $CHCl_3$).

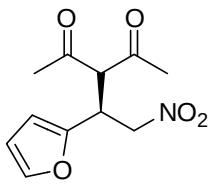


Racemate

		min	mAU*min		mAU	%	
1	n.a.	16.225	931.5814	n.a. BMB*	2131.686	49.87	5.71
2	n.a.	20.500	936.3895	n.a. BMB*	1873.827	50.13	n.a.
Total:			1867.9709	0.0000	4005.512	100.00	

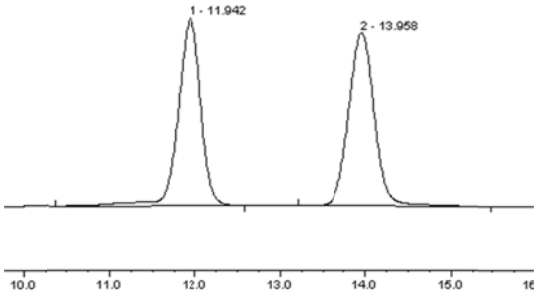


		min	mAU*min		mAU	%	
1	n.a.	15.042	27.5491	n.a. BMB*	76.772	11.66	5.82
2	n.a.	18.883	208.7117	n.a. BMB	447.894	88.34	n.a.
Total:			236.2607	0.0000	524.666	100.00	



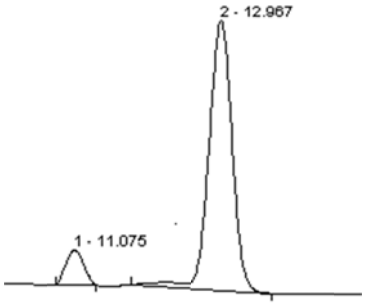
(*S*)-3-(1-Furan-2-yl-2-nitro-ethyl)-pentane-2,4-dione (7t)[1]**,** colorless oil,

80% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.35 (m, 1H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.18 (d, *J* = 3.3 Hz, 1H), 4.67 (d, *J* = 5.4 Hz, 2H), 4.40 (d, *J* = 9.8 Hz, 1H), 4.38 – 4.31 (m, 1H), 2.29 (s, 3H), 2.09 (s, 3H); HPLC (Chiralpak AD-H column, Hex : *i*-Pro = 90 : 10, 1 mL/min, wavelength = 210 nm.): t_r = 11.1 min [minor(*R*)-enantiomer], t_r = 13.0 min [major (*S*)-enantiomer], 81% *ee*; $[\alpha]_D^{25}$ = −112.8 (*c* = 0.5 in $CHCl_3$).



Racemate

		min	mAU*min			mAU	%	
1	n.a.	11.942	445.7830	n.a.	BMB*	1397.902	49.94	3.94
2	n.a.	13.958	446.9043	n.a.	BMB	1287.806	50.06	n.a.
Total:			892.6873	0.0000		2685.708	100.00	



		min	mAU*min			mAU	%	
1	n.a.	11.075	12.8866	n.a.	BMB*	45.363	9.56	3.30
2	n.a.	12.967	121.9774	n.a.	BMB*	353.383	90.44	n.a.
Total:			134.8639	0.0000		398.746	100.00	

Reference:

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