Supporting Information for

Highly Efficient Enantioselective Direct Aldol Reaction of α-Keto Esters Catalyzed by (S_a)-Binam-D-prolinamide under *quasi* Solvent-free Conditions.

Santiago F. Viózquez,[a] *Abraham Bañón-Caballero,*[a] *Gabriela Guillena,**[a] *Carmen Nájera,**[a] *Enrique Gómez-Bengoa, **[b]

[a]. *Dpto. Química Orgánica and Instituto de Síntesis Orgánica, Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain.* [b]. *Departamento de Química Orgánica I, Universidad del País Vasco, Apdo.1072, 20080 San Sebastián, Spain.*

gabriela.guillena@ua.es, cnajera@ua.es, enrique.gomez@ehu.es

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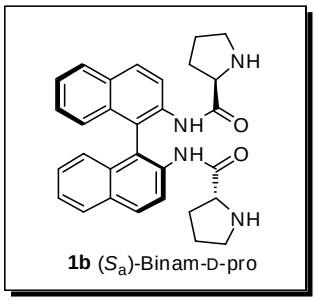
General Information: Catalysts **1a-c** were prepared following the described procedures.[1a,b] Dry DMF, dry toluene, dry CH_2Cl_2, piperidine and triethylamine and all others reagents were commercially available and used without further purification. Only the structural most important peaks of the IR spectra (recorded on a Nicolet Impact 400D) are listed. ^{1}H NMR (300 MHz, 400 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a Bruker AC-300 using $CDCl_3$ as solvent and TMS as internal standard, unless otherwise stated. Optical rotations were measured on a Perkin Elmer 341 polarimeter. HPLC analyses were performed on a Agilent 1100 series equipped with a chiral column (detailed for each compound below), using mixtures of n-hexane/isopropyl alcohol (IPA) as mobile phase, at 25 ºC. GC analyses were performed on a Agilent 7802A series equipped with a chiral column (detailed for each compound below). Analytical TLC was performed on Schleicher & Schuell F1400/LS silica gel plates and the spots were visualised under UV light (λ=254 nm). For flash chromatography we employed Merck silica gel 60 (0.063-0.2 mm). Elemental analysis was carried out in the Research Technical Services of the University of Alicante.

Description of catalyst:

(S_a)-BINAM-D-Pro (1b):



1b (S_a)-Binam-D-pro

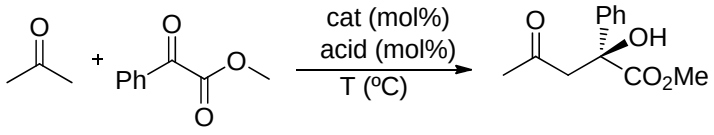
Pale yellow solid; $[\alpha]^{29}_D$ = +60.7 (c 1, MeOH); Mp 120 ºC ($CHCl_3$, Et_2O); R_f= 0.21 (EtOAc/MeOH 1:1); IR (KBr): ν 3466, 3345, 3203, 3055, 2970, 1668, 1591 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19-1.38 (m, 2H), 1.42-1.56 (m, 2H), 1.66-1.80 (m, 2H), 1.86-1.99 (m, 2H), 2.48-2.66 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 7.12-7.45 (m, 6H,), 7.71 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 9.1, 1H), 7.99 (d, 1H, J = 9.0 Hz), 8.82 (d, 1H, J = 8.9 Hz), 9.73 (broad s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.2, 25.2, 30.7, 46.2, 60.7, 111.4, 118.1, 119.9, 120.2, 122.5, 123.6, 124.8 , 125.1, 126.8, 126.9, 128.0, 128.3, 129.2, 129.9, 131.0, 132.3, 133.6, 135.2, 142.6, 173.9; HRMS (*m/z*): Cald for $C_{30}H_{30}N_4O_2$: 478,2525; found: 478,2501.

General procedure for the aldol reaction:

To a mixture of the corresponding α-ketoester **2** (0.25 mmol), catalyst (0.2 equiv.) and acid at the indicated temperature was added the corresponding ketone **3** (1.25 mmol, 5 equiv.). The reaction was stirred until the α-ketoester was consumed (monitored by TLC). Then, CH_2Cl_2 (0.5 mL) was added to the mixture and was purified by flash chromatography (hexanes/AcOEt) to yield the pure product **4**.

Optimization of the reaction conditions

TABLE 1. Optimization of the reaction conditions between acetone (2a) and 2-phenyl-2-oxoacetate (3a).[a]



2a **3a** **4aa**

Entry	Cat.	Acid (mol%)	Solvent (mL)	T (ºC)	t (h)	Yield (%)[b]	ee (%)[c]
1	**1a**	AcOH (150)	Acetone (0.5)	25	17	90	16 (*R*)
2	**1a**	AcOH (150)	-	25	17	90	15 (*R*)
3	**1a**	AcOH (20)	-	25	17	93	4 (*R*)
4	**1a**	AcOH (150)	-	0	24	95	32 (*R*)
5	***ent*-1a**	AcOH (150)	-	0	24	98	36 (*S*)
6	**1b**	AcOH (150)	-	0	48	96	56 (*S*)
7	**1c**	AcOH (150)	-	0	48	75	0
8	**1b**	AcOH (150)	-	-20	48	95	56 (*S*)
9	**1b**	AcOH (100)	-	0	48	90	60 (*S*)
10	**1b**	AcOH (300)	-	0	48	90	60 (*S*)
11	**1b**	AcOH (100)	H_2O (0.125)	0	96	50	42 (*S*)
12	**1b**	AcOH (100)	Hexane (0.125)	0	48	50	64 (*S*)
13	**1b**	AcOH (100)	CH_2Cl_2 (0.125)	0	96	80	62 (*S*)
14	**1b**	AcOH (100)	THF (0.125)	0	96	75	32 (*S*)
15	**1b**	AcOH (100)	MeOH (0.125)	0	96	40	20 (*S*)
16	**1b**	AcOH (100)	-	25	30	84	16 (*S*)
17	**1b**	Me_3CCO_2H (100)	-	25	30	95	0
18	**1b**	ICH_2CO_2H (100)	-	25	30	97	60 (*S*)
19	**1b**	$ClCH_2CO_2H$ (100)	-	25	30	95	62 (*S*)
20	**1b**	$BrCH_2CO_2H$ (100)	-	25	30	98	50 (*S*)
21	**1b**	Cl_2CHCO_2H (100)	-	25	30	40	30 (*S*)
22	**1b**	CF_3CO_2H (100)	-	25	30	40	16 (*S*)
23	**1b**	Cl_2CHCO_2H (100)	-	0	72	82	70 (*S*)

[a] The reaction was carried out using 5 equiv of acetone (otherwise stated), 20 mol% of catalyst, the indicated amount of acid as co-catalysts at the indicated temperature. [b] Isolated yield after column chromatography. [c] Determined by HPLC

General procedure for the solvent-free aldol reaction catalysed by 1b:

To a mixture of the corresponding α-ketoester **3** (0.25 mmol), catalyst **1b** (0.024 g, 0.05 mmol, 0.2

equiv.) and chloroacetic acid (0.024 g, 0.25 mmol, 1 equiv.) at 0 ºC was added the corresponding ketone **2** (1.25 mmol, 5 equiv.). The reaction was stirred until the α-ketoester was consumed (monitored by TLC). Then, CH_2Cl_2 (0.5 mL) was added to the mixture and was purified by flash chromatography (hexanes/AcOEt) to yield the pure product **4**.

Spectra and HPLC data of aldol products:

(*S*)-Methyl 2-hydroxy-4-oxo-2-phenylpentanoate (6aa).[2]

White solid; Mp = 56 ºC (EtOAc); R_f = 0.35 (hexanes/EtOAC 7:3); δ_H (300 MHz; $CDCl_3$, Me_4Si) 2.21 (s, 3H, CH_3C=O), 3.01 (d, *J* = 17.6 Hz, 1H, CH_2), 3.56 (d, *J* = 17.6 Hz, 1H, CH2), 3.76 (s, 3H, CO_2CH_3), 4.43 (s, 1H, OH), 7.28-7.43 (m, 3H), 7.56 (d, *J* = 8.9 Hz, 2H, ArH); δ_c (75 MHz; $CDCl_3$, Me_4Si) 30.6 (CH_3C=O), 52.9 (CH_2), 53.1 (CO_2CH_3), 76.3 (C-OH), 124.8 (ArCH), 128.0 (ArCH), 128.4 (ArCH), 140.1 (ArC), 174.3 ($CO_2CH_2CH_3$), 207.8 (C=O); HPLC (Chiralpak AD, n-hexane/i-PrOH: 80/20, 0.8 mL/min), t_R 9.508 (minor), t_R 11.189 (major).

(*S*)-Ethyl 2-hydroxy-4-oxo-2-phenylpentanoate (6ab).[2]

White solid; Mp = 60 ºC (EtOAc);R_f = 0.33 (hexanes/EtOAC 7:3); δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.25 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 2.20 (s, 3H, $COCH_3$), 3.02 (d, *J* = 17.6 Hz, 1H, CH_2), 3.55 (d, *J* = 17.6 Hz, 1H, CH_2), 4.22 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 4.39 (s, 1H, OH), 7.27-7.41 (m, 3H), 7.51-7.65 (m, 2H, ArH); δ_c (75 MHz; $CDCl_3$, Me_4Si) 13.9 (OCH_2CH_3), 30.6 (CH_3C=O), 53.0 (CH_2), 62.2 (OCH_2CH_3), 76.5 (C-OH), 124.8 (ArCH), 128.0 (ArCH), 128.4 (ArC), 140.3 (ArC), 173.8 ($CO_2CH_2CH_3$), 207.6 (C=O); HPLC (Chiralcel ODH, n-hexane/i-PrOH: 90/10, 0.8 mL/min), t_R 21.090 (minor), t_R 26.470 (major).

(S)-Ethyl 2-hydroxy-2-methyl-4-oxopentanoate (6ac).[3]

Colorless oil; R_f = 0.29 (hexanes/EtOAC 7:3); δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.28 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.39 (s, 3H, CH_3C=O), 2.17 (s, 3H, CH_3COH), 2.81 (d, *J* = 17.6 Hz, 1H, CH_2), 3.13 (d, *J* = 17.6 Hz, 1H, CH_2), 3.82 (s, 1H, OH), 4.23 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3); δ_c (75 MHz; $CDCl_3$, Me_4Si) 14.0 (OCH_2CH_3), 26.1 (CH_3COH), 30.5 (CH_3C=O), 52.2 (CH_2), 61.7 (OCH_2CH_3), 72.4 (COH), 175.7 ($CO_2CH_2CH_3$), 207.7 (C=O); GC (Lipodex E,50 m, 0.25 mm, T = 100 ºC, P = 14.3 psi), t_R 70.6 (minor), t_R 84.3 (major).

(*S*)-Ethyl 2-hydroxy-2-(4-nitrophenyl)-4-oxopentanoate (6ad).[2]

White solid; Mp = 67 ºC (EtOAc); R_f = 0.35 (hexanes/EtOAC 7:3); δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.27 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 2.24 (s, 3H, CH_3C=O), 3.01 (d, *J* = 17.6 Hz, 1H, CH2), 3.57 (d, *J* = 17.6 Hz, 1H, CH_2), 4.25 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 4.53 (s, 1H, OH), 7.80 (d, *J* = 8.9 Hz, 2H, ArH), 8.22 (d, *J* = 8.9 Hz, 2H, ArH); δ_c (75 MHz; $CDCl_3$, Me_4Si) 13.8 (OCH_2CH_3), 30.5 (CH_3C=O), 52.8 (CH_2), 62.8 (OCH_2CH_3), 76.1 (COH), 123.5 (ArCH), 126.0 (ArCH), 147.2 (Ar), 147.6 (ArC), 172.7 (CO_2), 206.8 (C=O); HPLC (Chiralpak AD, n-hexane/i-PrOH: 90/10, 0.6 mL/min), t_R 21.427 (minor), t_R 23.833 (major).

(*R*)-Ethyl 2-hydroxy-4-oxo-2-(thiophen-2-yl)pentanoate (6ae).[4]

Colorless oil; R_f = 0.33 (hexanes/EtOAC 7:3); δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.28 (t, *J* = 7.1 Hz, 3H,

OCH_2CH_3), 2.20 (s, 3H, CH_3CO), 3.20 (d, J = 17.6 Hz, 1H, CH_2), 3.51 (d, J = 17.6 Hz, 1H, CH_2), 4.26 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 4.45 (s, 1H, OH), 6.97 (dd, J = 3.6, 5.1 Hz, 1H, ArH), 7.06 (dd, J = 1.3, 3.6 Hz, 1H, ArH), 7.36–7.22 (m, 1H, ArH).; δ_c (75 MHz; $CDCl_3$, Me_4Si) 13.9 (OCH_2CH_3), 30.5 (CH_3C=O), 53.6 (CH_2), 62.6 (OCH_2CH_3), 74.8 (COH), 123.7 (ArCH), 125.3 (ArCH), 127.0 (ArCH), 145.1 (ArC), 172.8 (CO_2), 206.2 (C=O); HPLC (Chiralpak AD, n-hexane/i-PrOH: 90/10, 0.6 mL/min), t_R 21.218 (major), t_R 26.330 (minor).

(*S*)-Ethyl 2-hydroxy-2-(4-nitrophenyl)-4-oxohexanoate (6bd).

Yellow solid; Mp = 55 ºC (EtOAc); $[\alpha]^{25}_D$ = 47 (c 1.3, $CHCl_3$);R_f = 0.29 (hexanes/EtOAC 7:3); IR ν_{max}/cm^1 (KBr) 3485, 3112, 2981, 1730, 1605, 1593, 1516, 1403, 1341, 1268, 1109, 855 cm^{-1}; δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.09 (t, J = 7.3 Hz, 3H, $OCCH_2CH_3$), 1.27 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.40-2.66 (m, 2H, $OCCH_2CH_3$), 2.99 (d, J = 17.4 Hz, 1H, CH_2), 3.54 (d, J = 17.4 Hz, 1H, CH_2), 4.26 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 4.60 (s, 1H, OH), 7.81 (d, J = 8.8 Hz, 2H, ArCH), 8.21 (d, J = 8.8 Hz, 2H, ArCH); δ_c (75 MHz; $CDCl_3$, Me_4Si) 7.2 ($O=CCH_2CH_3$), 13.8 (OCH_2CH_3), 36.5 (CH_2), 51.6 (CH_2), 63.3 (OCH_2CH_3), 76.2 (C-OH), 123.7 (ArH), 126.3 (ArH), 147.0 (Ar), 147.8 (Ar), 172.4 ($CO_2CH_2CH_3$), 200.3 (C=O) HRMS-DIP (m/z): [M$^+$-CO_2Et] calcd for $C_{13}H_{12}NO_4$ 222.0766; found: 222.0765. HPLC (Chiralcel ODH, n-hexane/i-PrOH: 90/10, 0.5 mL/min), t_R 22.902 (minor), t_R 31.025 (major).

(*R*)-ethyl 2-hydroxy-3-methoxy-2-(4-nitrophenyl)-4-oxopentanoate (7cd).

Brown oil; $[\alpha]^{25}_D$ = −124 (c 1.17, $CHCl_3$); R_f = 0.30 (hexanes/EtOAC 7:3); IR ν_{max}/cm^1 (film) 3335, 3192, 2964, 2869, 1676, 1592; δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.34 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 2.15 (s, 3H, $O=CCH_3$), 3.46 (s, 3H, OCH_3), 4.20 (s, 1H, OH), 4.26 (s, 1H, $CHOCH_3$), 4.35 (m, 2H, OCH_2CH_3), 7.88 (d, J = 9.0 Hz, 2H, ArCH), 8.21 (d, J = 9.0 Hz, 2H, ArCH); δ_c (75 MHz; $CDCl_3$, Me_4Si) 14.1 (OCH_2CH_3), 27.7 ($O=CCH_3$), 59.5 (OCH_3), 63.6 (OCH_2CH_3), 80.0 (C-OH), 90.3 ($HCOCH_3$), 123.2 (ArCH), 127.7 (ArCH), 143.1 (ArC), 147.8 (ArC), 171.1 ($CO_2CH_2CH_3$), 207.7 (C=O); HRMS-DIP (m/z): [M$^+$-COMe] calcd for $C_{12}H_{14}NO_6$ 268.0821; found: 268.0828. HPLC (Chiralpak AD, n-hexane/i-PrOH: 90/10, 0.5 mL/min), t_R 59.164 (minor), t_R 31.471 (major).

(*S*)-ethyl 5-chloro-2-hydroxy-2-(4-nitrophenyl)-4-oxopentanoate (6dd).

Colorless solid; Mp = 95 ºC (EtOAc); $[\alpha]^{25}_D$ = −185 (c 1, $CHCl_3$); R_f= 0.29 (hexanes/EtOAC 7:3 IR ν_{max}/cm^1 (film) 3475, 3108, 3077, 3000, 2939, 1734, 1722, 1686, 1593, 1516, 1403, 1341, 1268, 1101, 859; δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.29 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.22 (d, J = 17.4 Hz, 1H, CH_2), 3.63 (d, J = 17.4 Hz, 1H, CH_2), 4.14 (s, 2H, $ClCH_2CO$), 4.29 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.33 (s, 1H, OH), 7.81 (d, J = 9.0 Hz, 2H, ArH), 8.24 (d, J = 9.0 Hz, 2H, ArH); δ_c (75 MHz; $CDCl_3$, Me_4Si) 13.9 (CH_3), 48.3 (CH_2), 49.3 ($ClCH_2$), 63.3 (OCH_2CH_3), 76.0 (C-OH), 123.4 (ArCH), 126.1 (ArCH), 147.0 (ArC), 147.8 (ArC), 172.7 ($CO_2CH_2CH_3$), 200.3 (CO); HRMS-DIP (m/z): [M$^+$-CO_2Et] calcd for $C_{10}H_9ClNO_4$ 243.0220; found 243.10218; HPLC (Chiralpak AD, n-hexane/i-PrOH: 90/10, 1.0 mL/min), t_R 21.344 (minor), t_R 31.130 (mayor).

(*S*)-ethyl 5-(benzyloxy)-2-hydroxy-2-(4-nitrophenyl)-4-oxopentanoate (6ed).

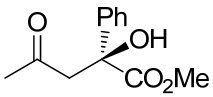
Brown oil; R_f = 0.29 (hexanes/EtOAC 7:3); 3 IR ν_{max}/cm^1 (film) 3493, 2977, 2921, 2864, 1732, 1603, 1521, 1348, 1258, 1211, 1106; cm^{-1}; δ_H (300 MHz; $CDCl_3$, Me_4Si) 1.27 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 3.12 (d, J = 17.7 Hz, 1H, CH_2), 3.54 (d, J = 17.7 Hz, 1H, CH_2), 4.09 (s, 2H, $O=CCH_2OBn$), 4.26 (q, J =

7.1 Hz, 2H, OCH_2CH$_3$), 4.40 (s, 1H, OH), 4.59 (s, 2H, OCH$_2$Ph), 7.29 – 7.41 (m, 5H, ArH),7.82 (d, J = 9.0 Hz, 2H, ArH), 8.22 (d, J = 9.0 Hz, 2H, ArH); δ_c (75 MHz; CDCl$_3$, Me$_4$Si) 13.9 (CH$_3$), 48.8 (O=CCH$_2$COH), 63.0(OCH$_2$), 73.6(CH2Ar), 75.2(O=CCH$_2$OBn), 76.0(HOCAr), 123.6(ArC), 126.3(ArC), 128.0(ArC), 128.2(ArC), 128.6(ArC), 136.7(ArC), 147.4(ArC), 147.7(ArC), 172.7(CO$_2$CH$_2$CH$_3$), 206.9(CO); HRMS-DIP (m/z): [M$^+$-CO$_2$Et] calcd for C$_{17}$H$_{17}$NO$_5$ 314.1000; found 314.1034; HPLC (Chiralpak AD, n-hexane/i-PrOH: 90/10, 1.0 mL/min), t_R 32.022 (minor), t_R 46.248 (major).

(S)-ethyl 2-hydroxy-5-(methylthio)-2-(4-nitrophenyl)-4-oxopentanoate (6fd).

Brown oil; $[\alpha]^{25}_D$ = −65 (c 1, CHCl$_3$); R_f= 0.35 (hexanes/EtOAC 7:3); IR ν_{max}/cm^{-1} (film) 3485, 3192, 2981, 2920, 1735, 1605, 1522, 1348, 1105, 856; δ_H (300 MHz; CDCl$_3$, Me$_4$Si) 1.28 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), 2.07 (s, 3H, SCH$_3$), 3.22 (s, 2H, SCH$_3$CH_2CO), 3.30 (d, J = 17.5 Hz, 1H, CH$_2$), 3.72 (d, J = 17.5 Hz, 1H, CH$_2$), 4.27 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 4.49 (s, 1H, OH), 7.82 (d, J = 9.0 Hz, 2H, ArH), 8.22 (d, J = 9.0 Hz, 2H, ArH); δ_c (75 MHz; CDCl$_3$, Me$_4$Si) 13.9 (CH$_3$), 15.4 (SCH$_3$), 43.2 (CH$_2$), 49.3 (CH$_2$), 62.9 (OCH$_2$CH$_3$), 76.1 (C-OH), 123.5 (ArH), 126.3 (ArH), 147.3 (Ar), 147.6 (Ar), 172.7 (CO$_2$CH$_2$CH$_3$), 203.2 (C=O); HRMS-DIP (m/z): [M$^+$] calcd for C$_{13}$H$_{17}$NO$_7$ 327.0777; found 327.0791; HPLC (Chiralpak AD, n-hexane/i-PrOH: 90/10, 0.9 mL/min), t_R 38.943 (minor), t_R 59.684 (major).

NMR spectra for aldol products



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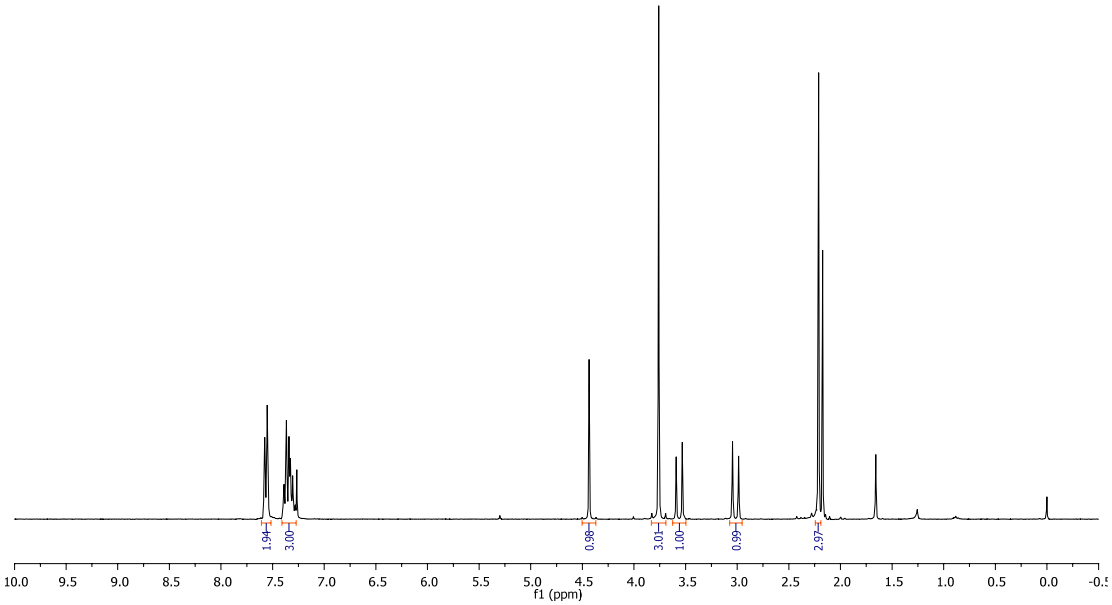

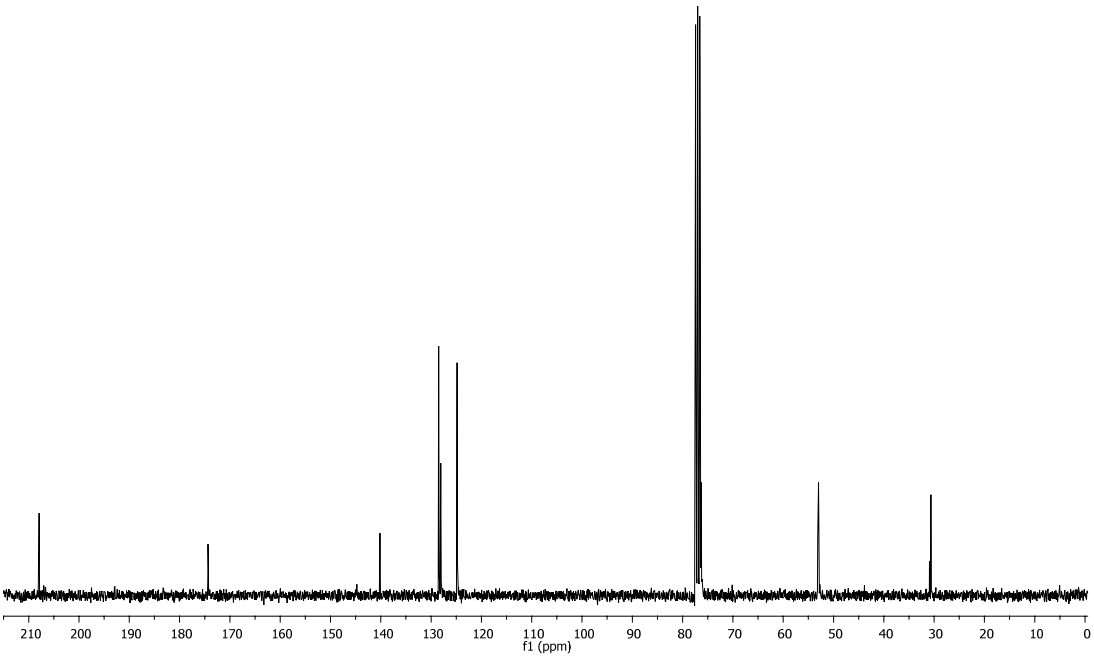

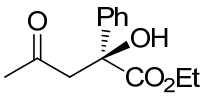

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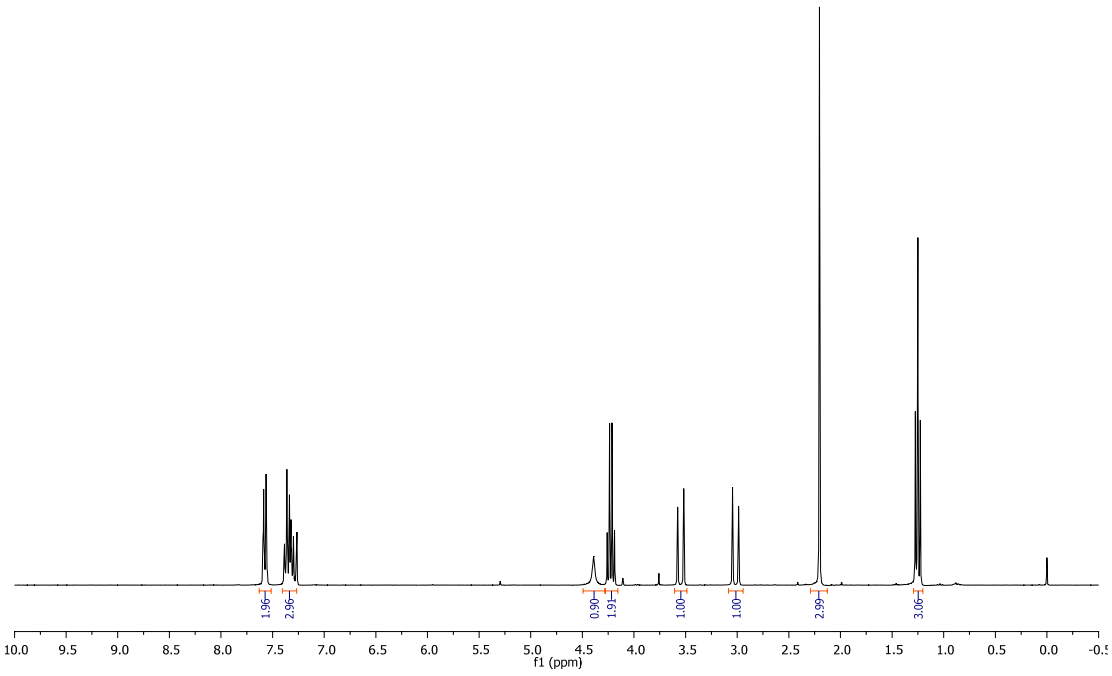

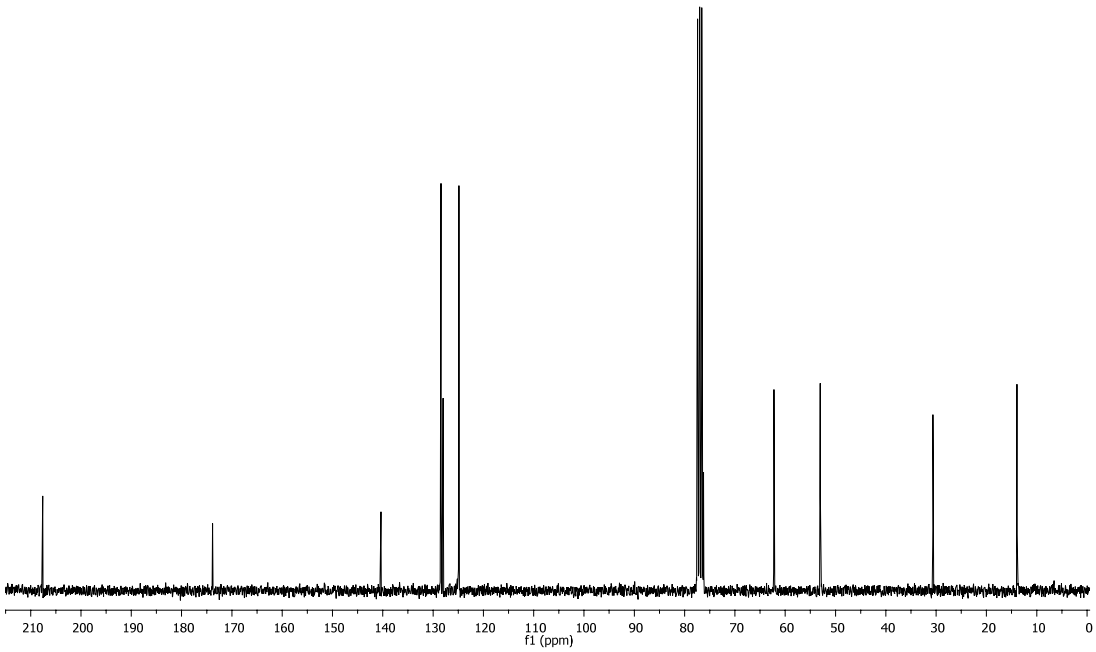

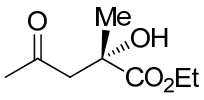

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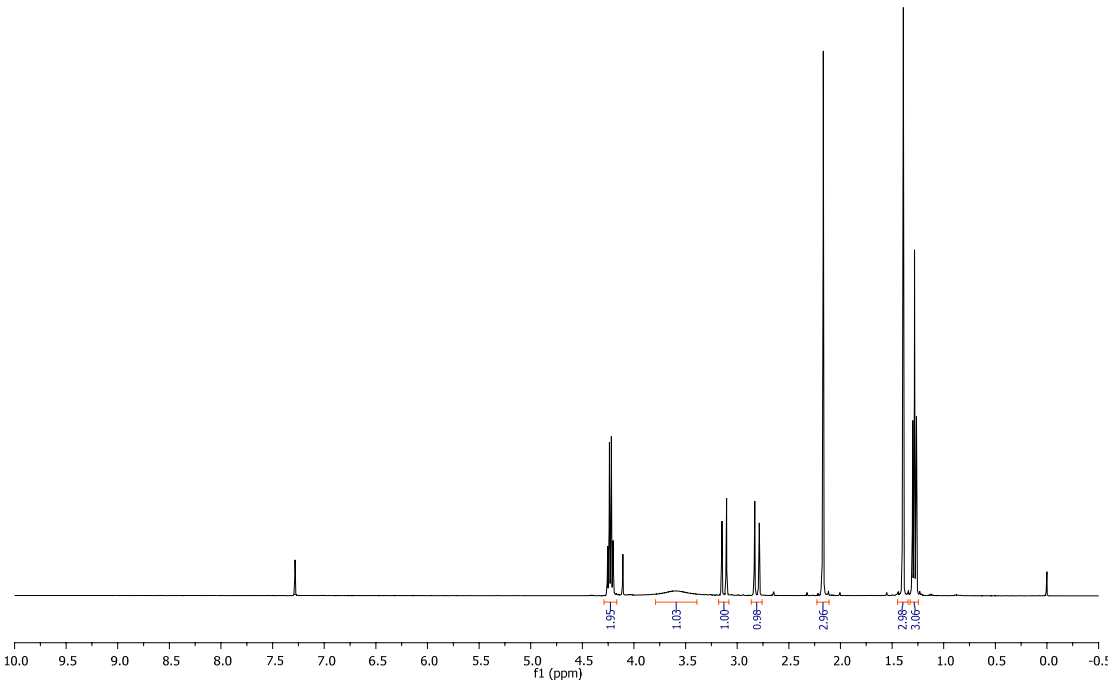

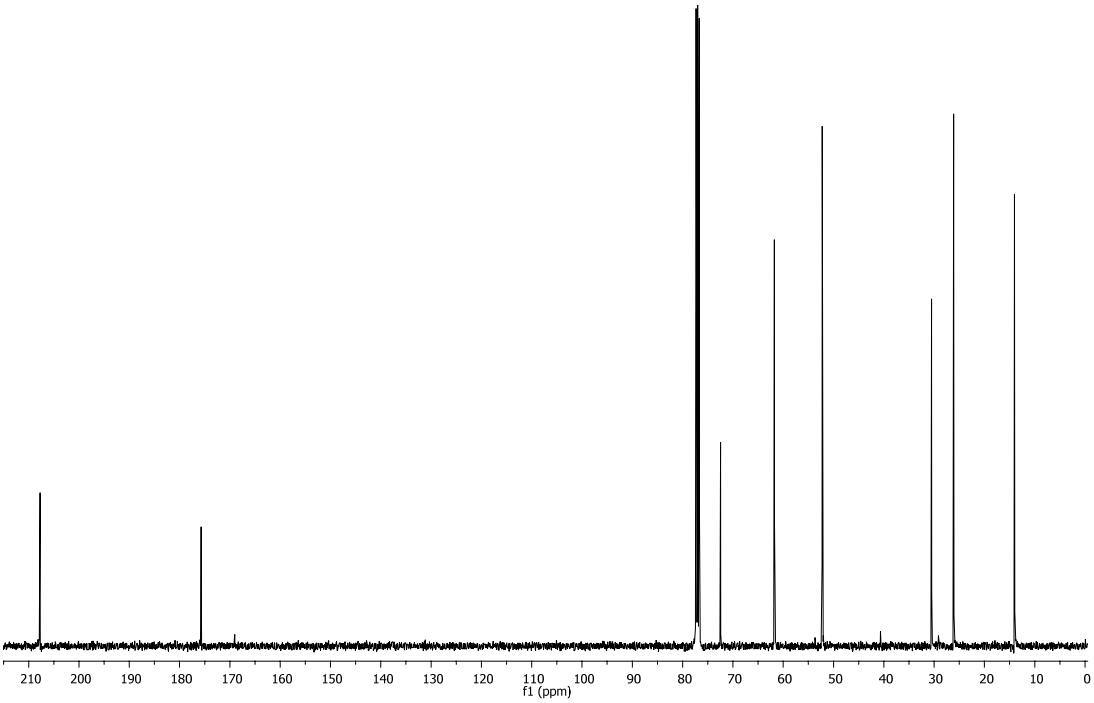
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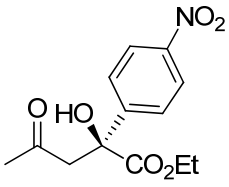
f1 (ppm)


NO2
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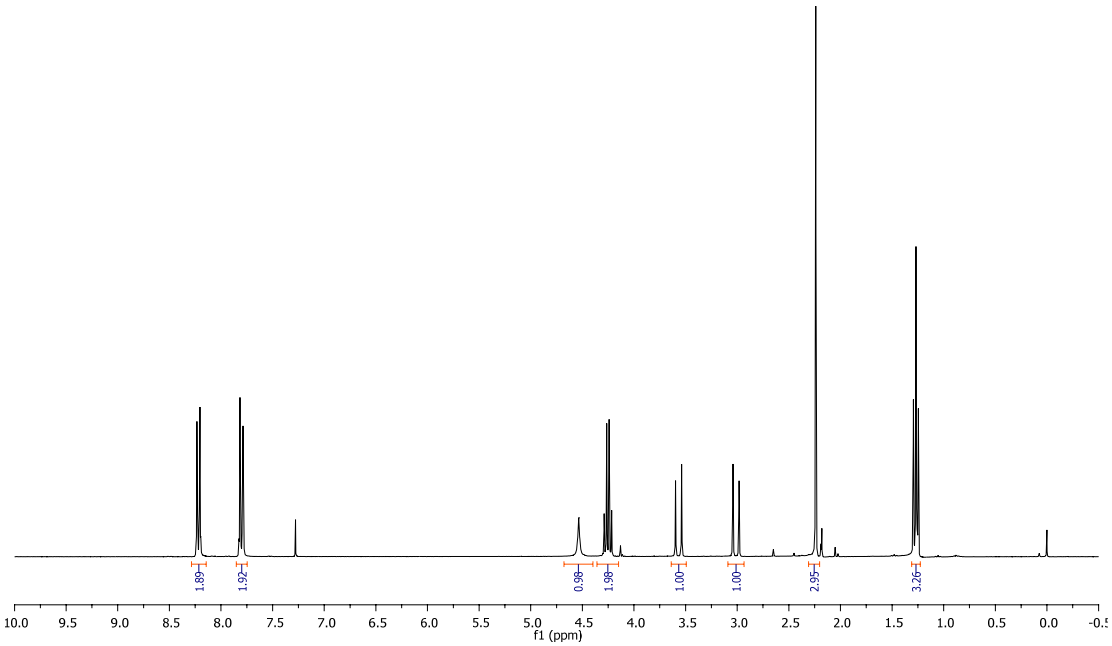
HO
CO2Et

6ad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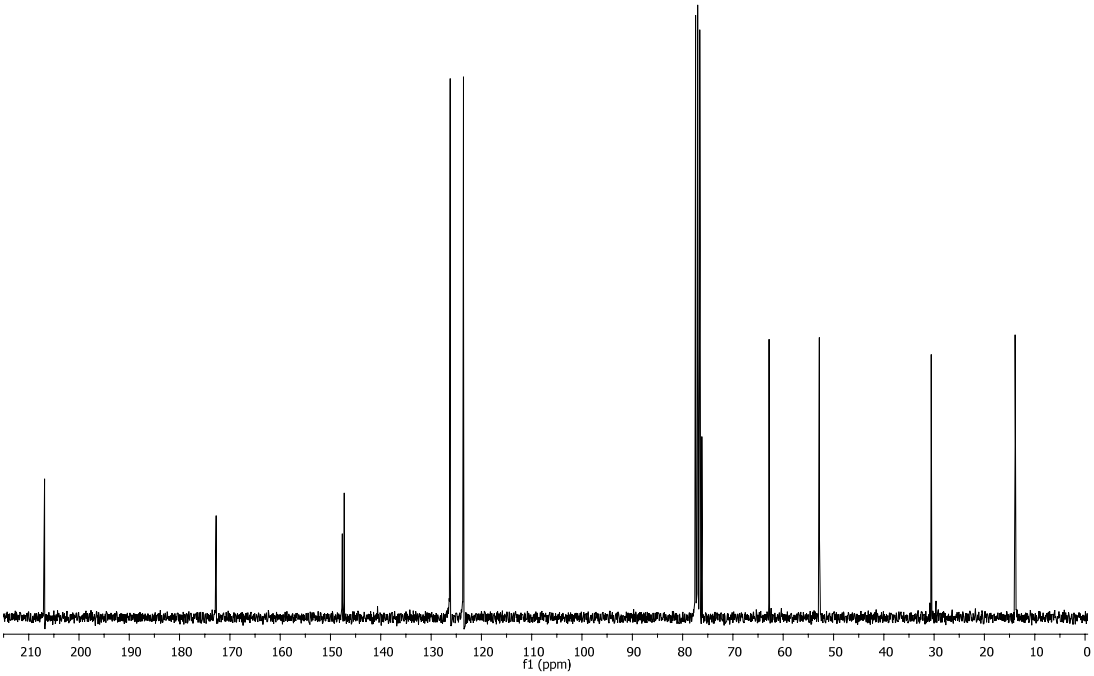
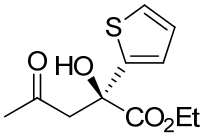
f1 (ppm)





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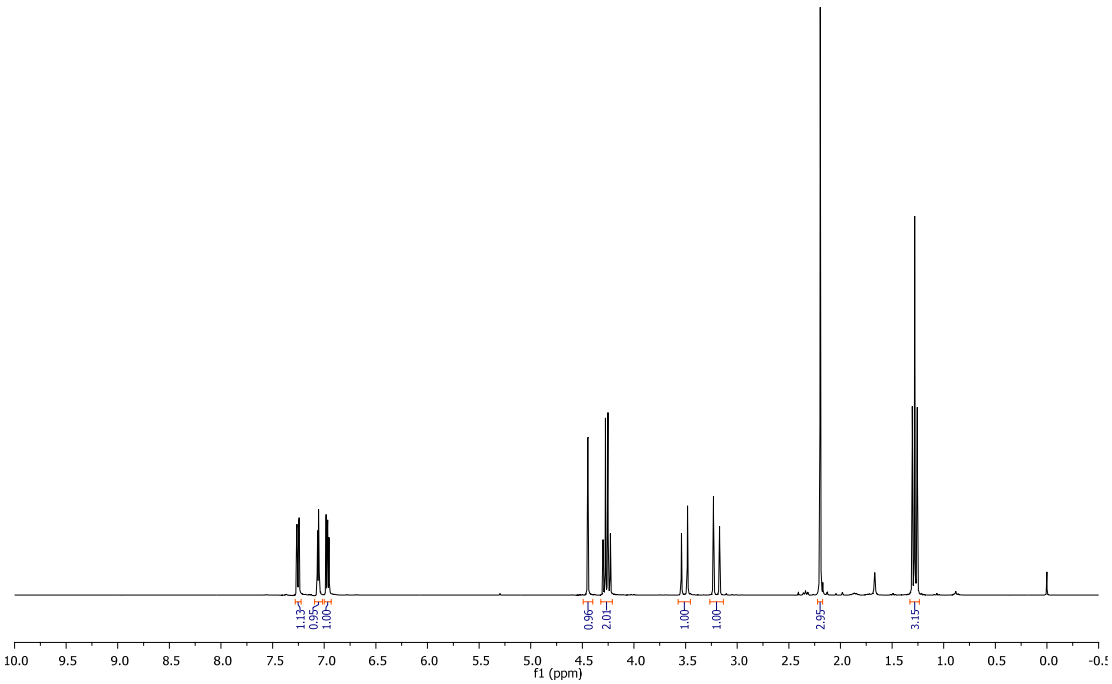

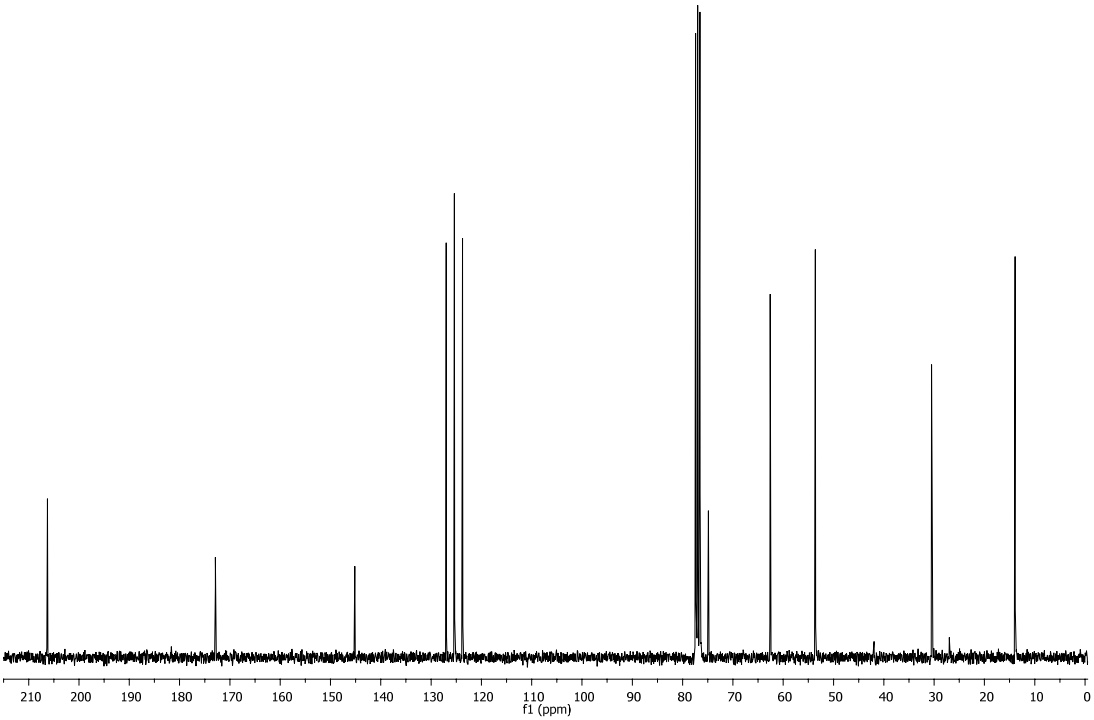

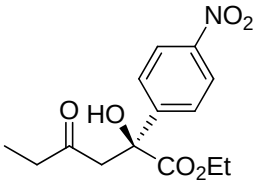

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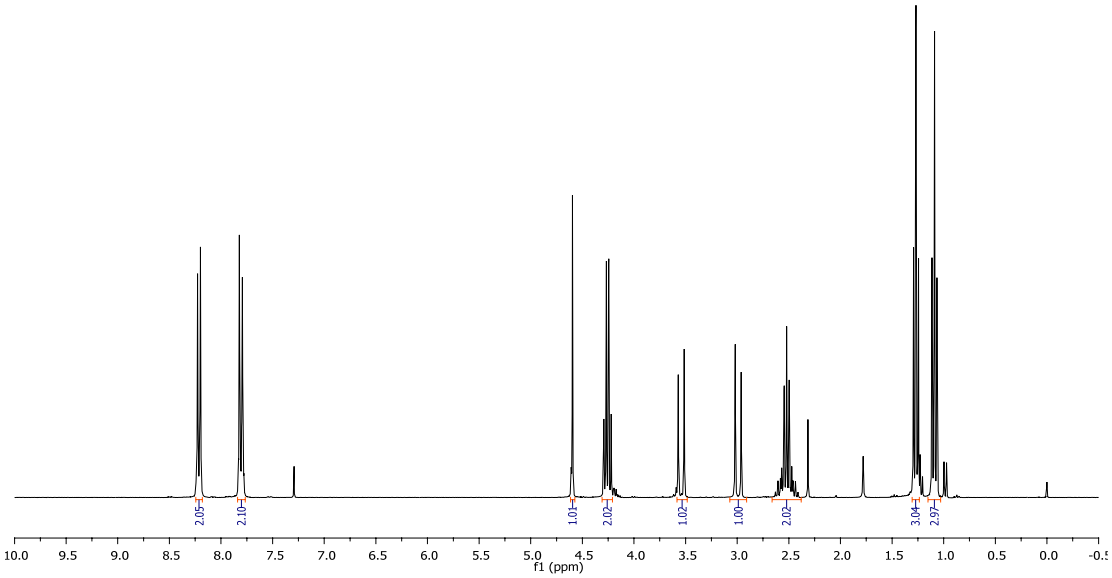

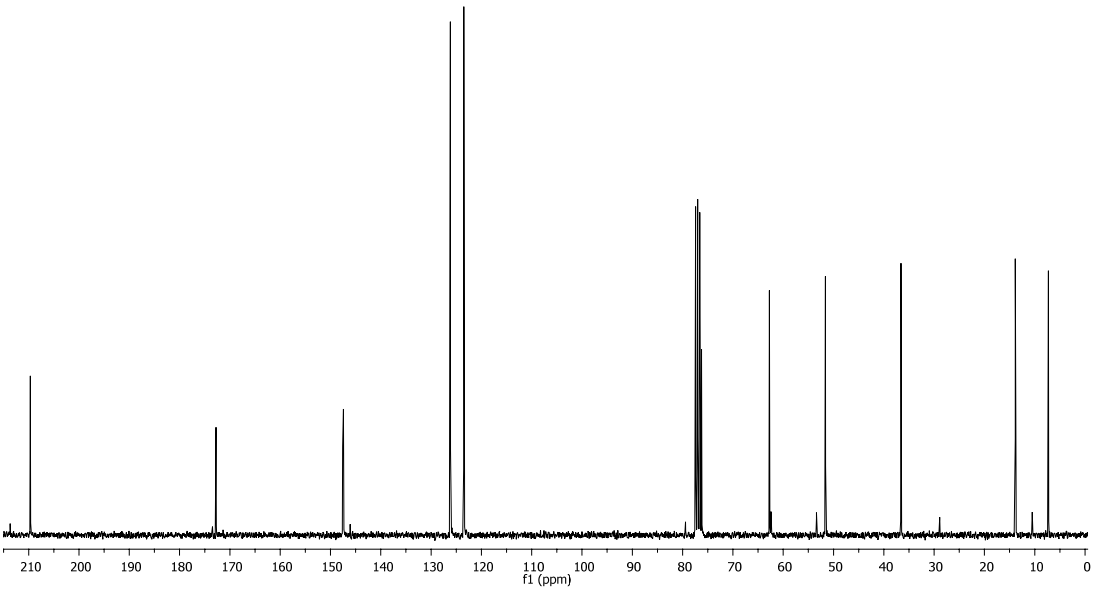

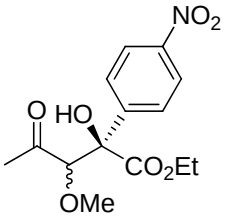

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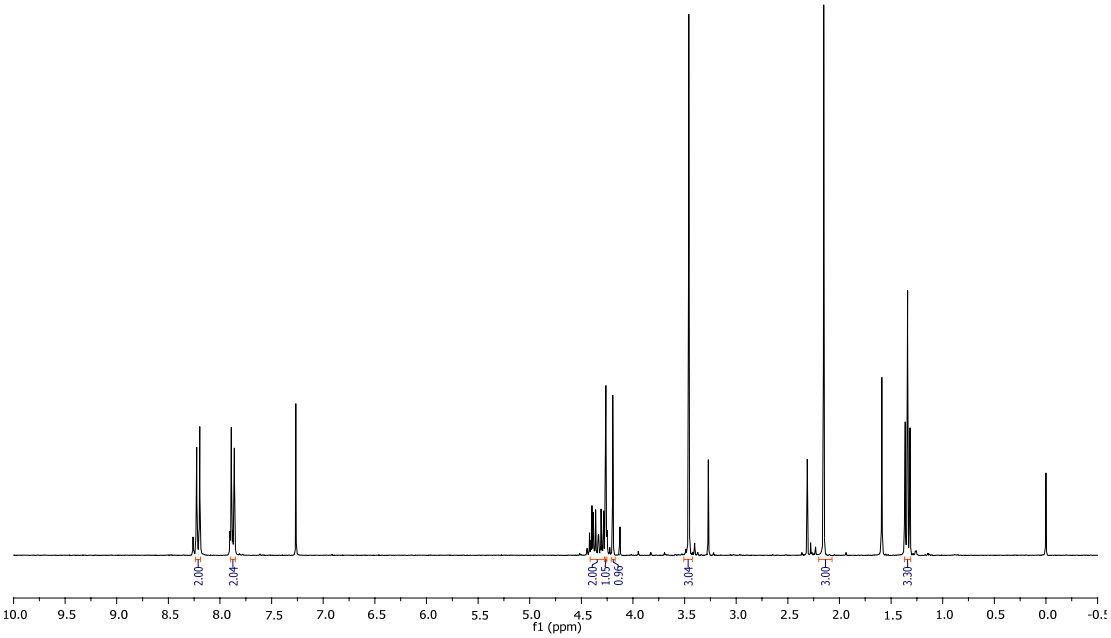

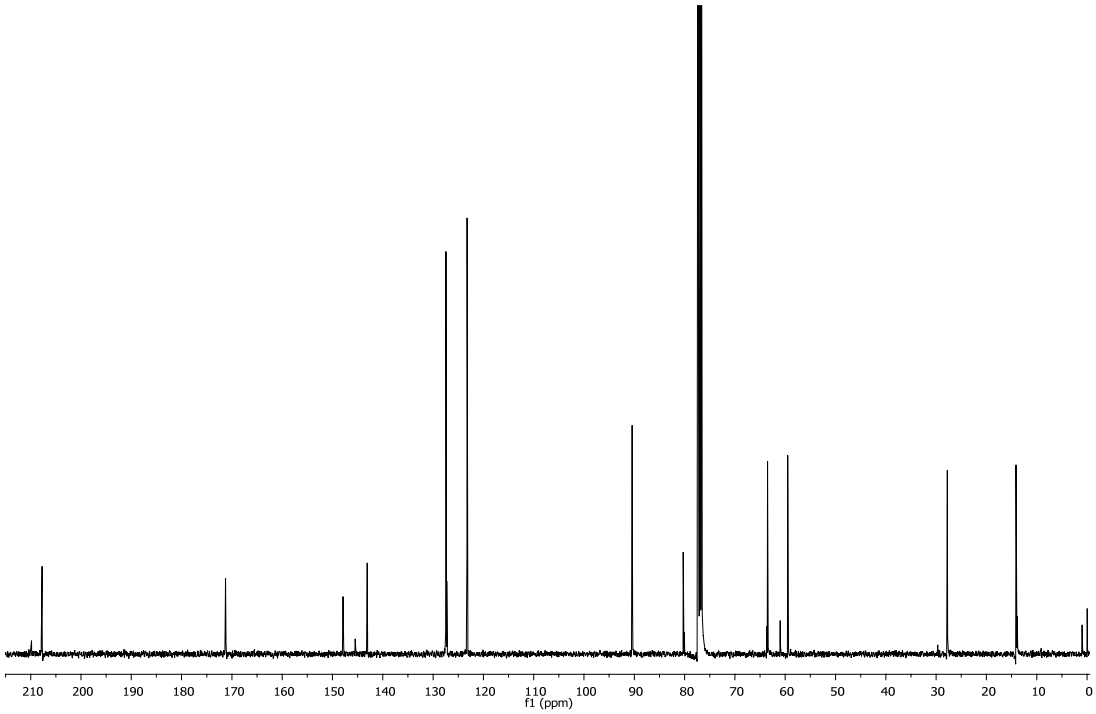

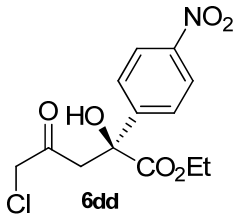

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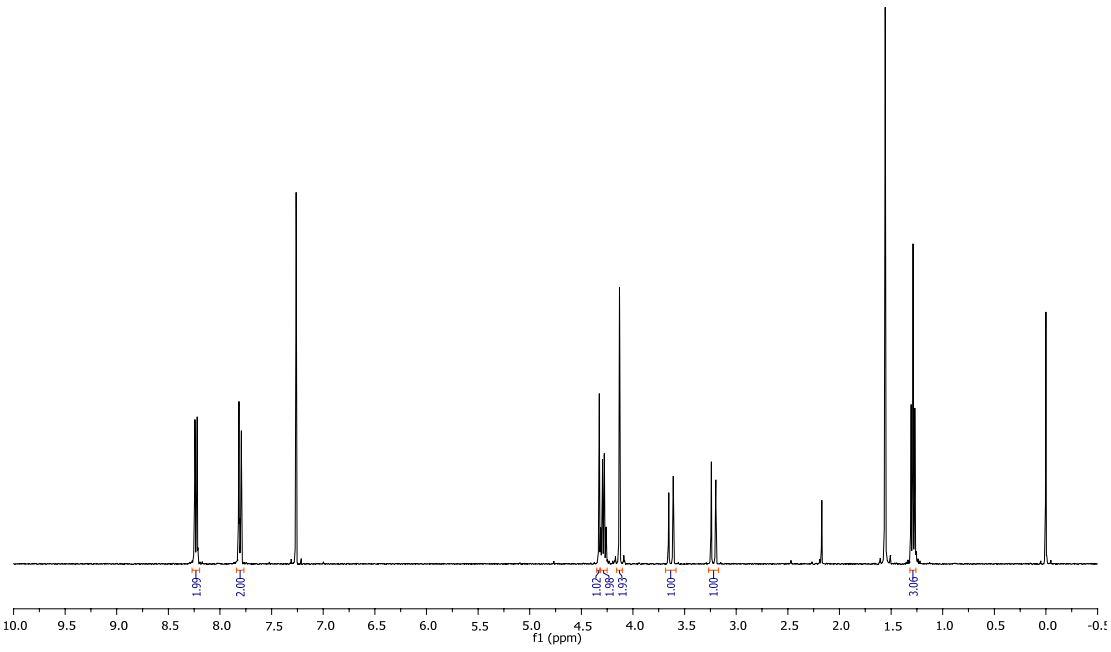

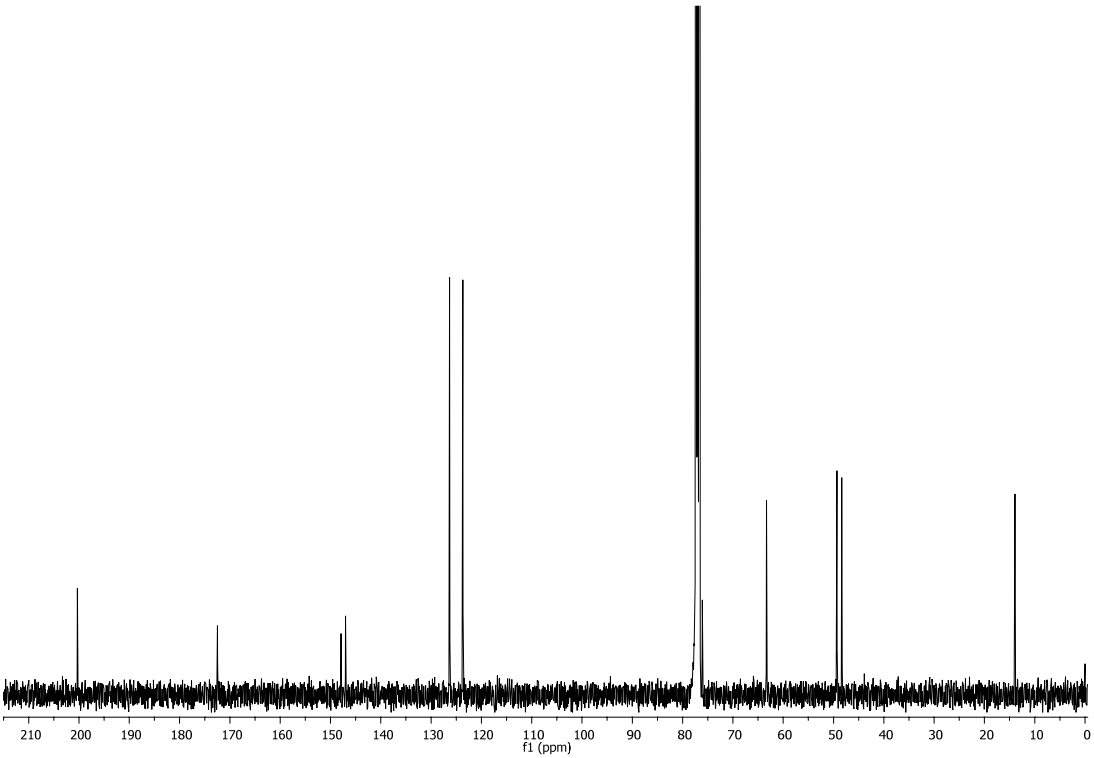
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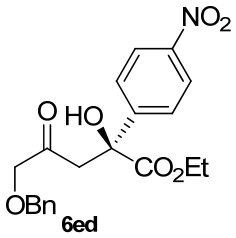
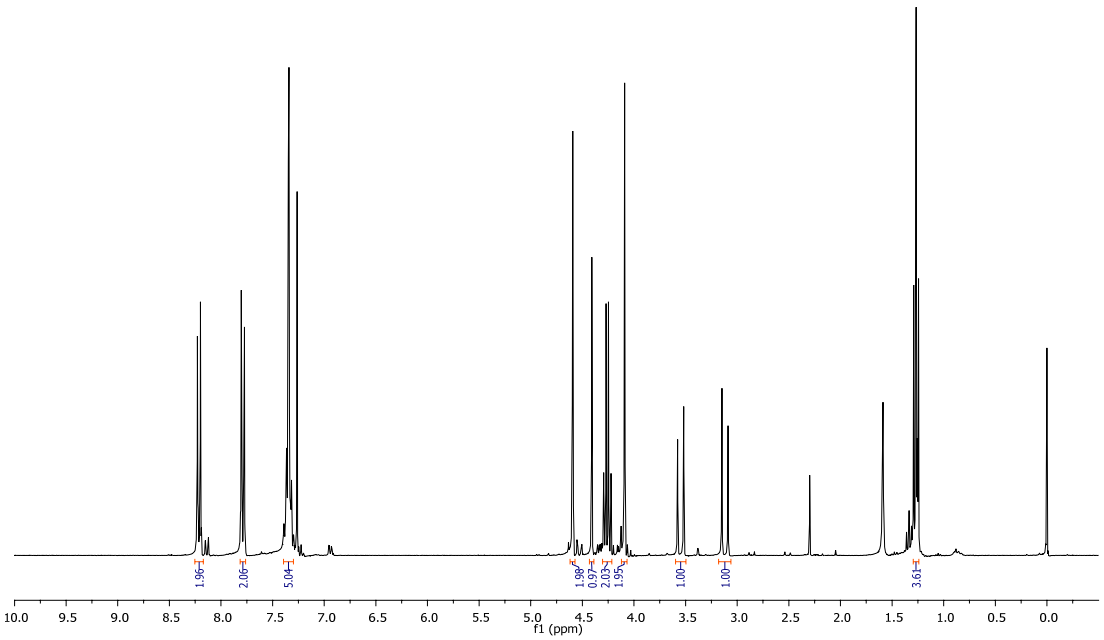
f1 (ppm)


NO2
O
HO
CO2Et
OBn

6ed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1.00
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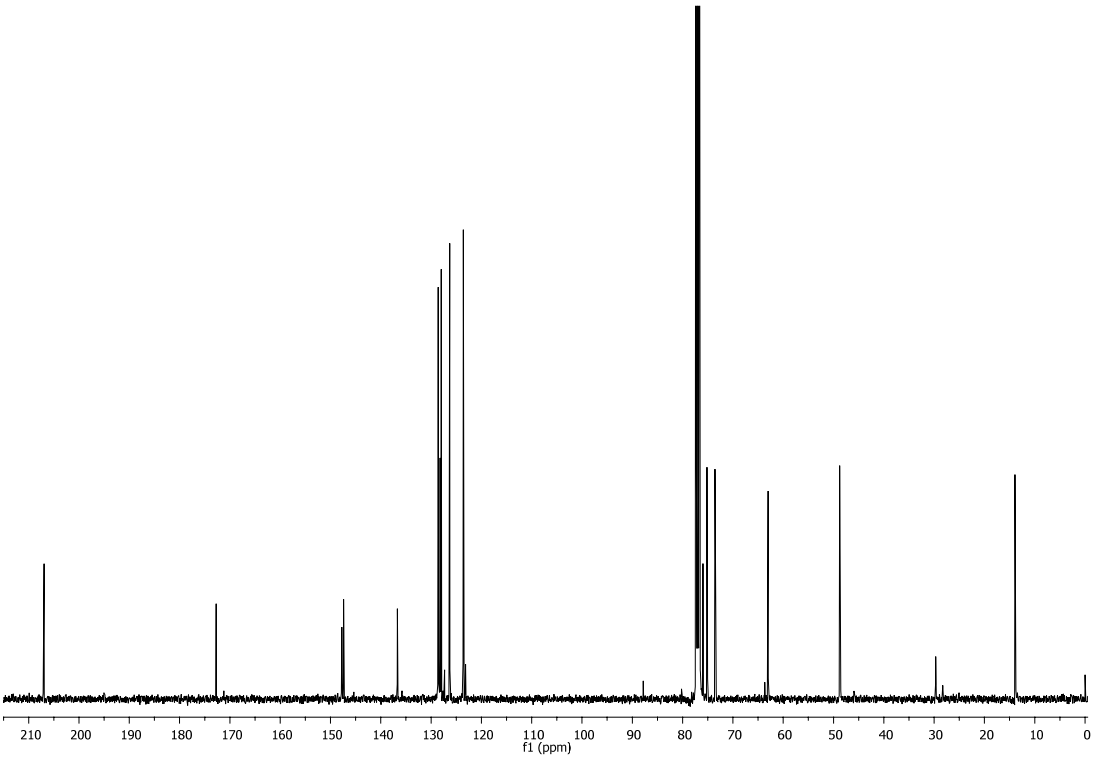
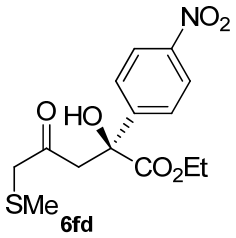
3.61
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)





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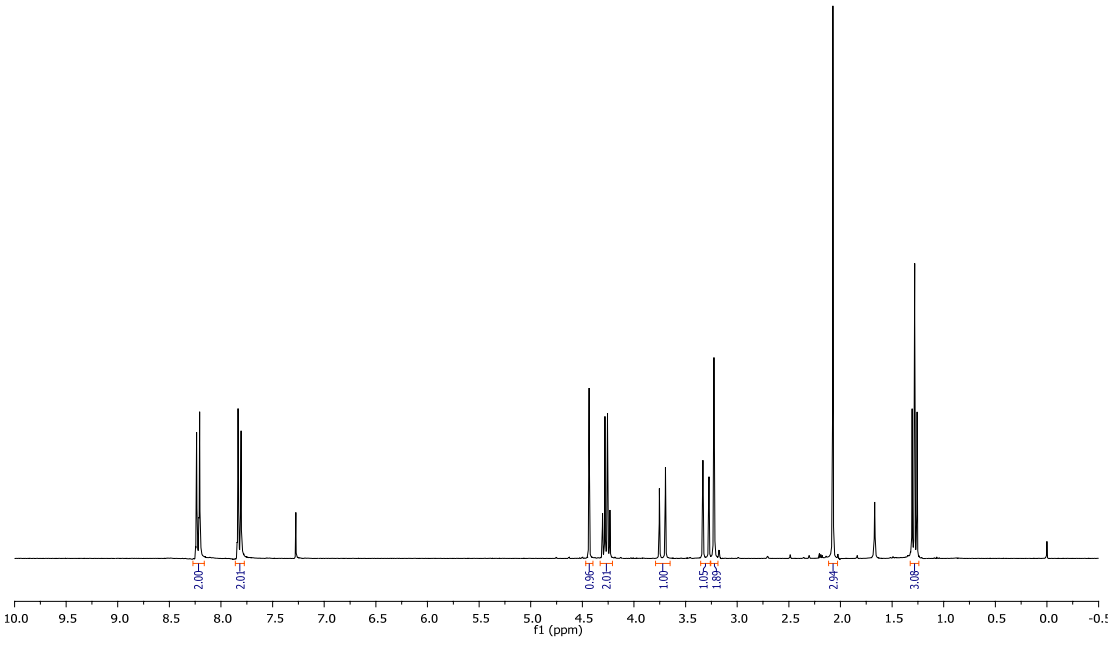
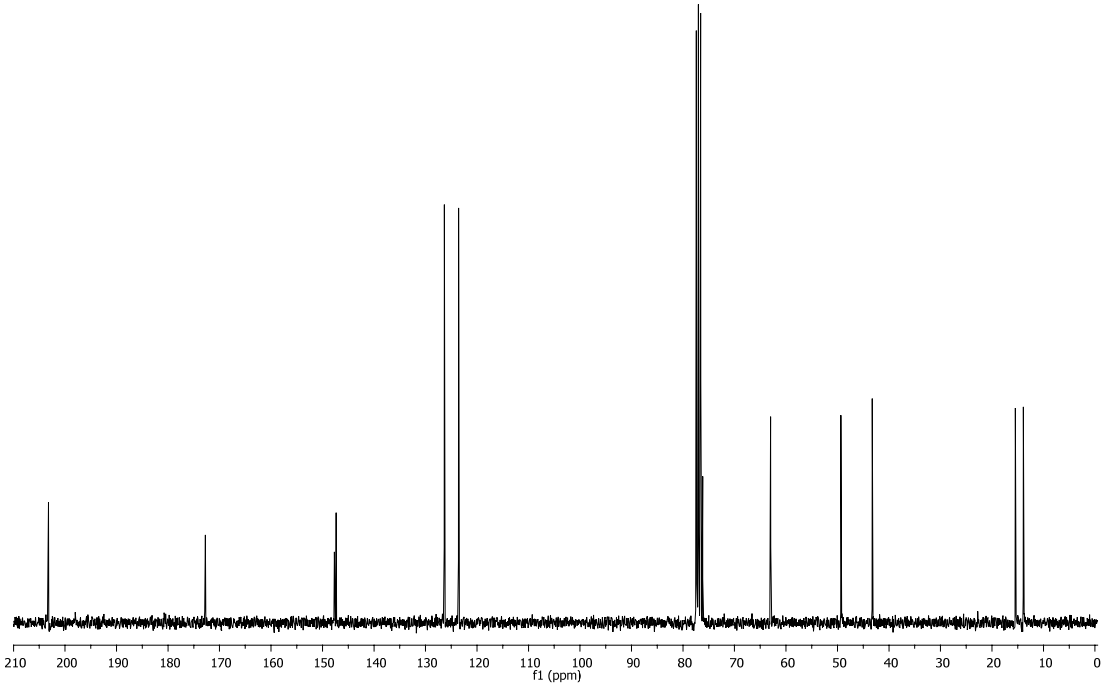
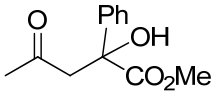
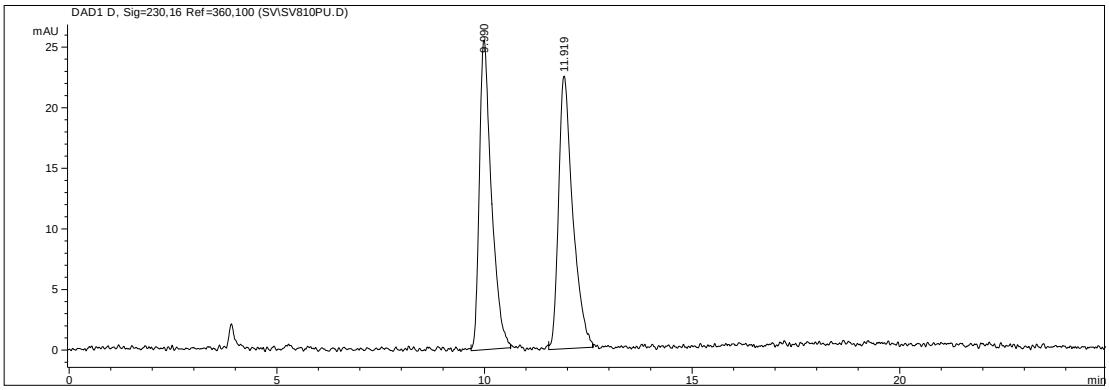




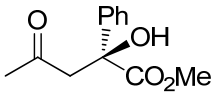
HPLC chromatograms for aldol products



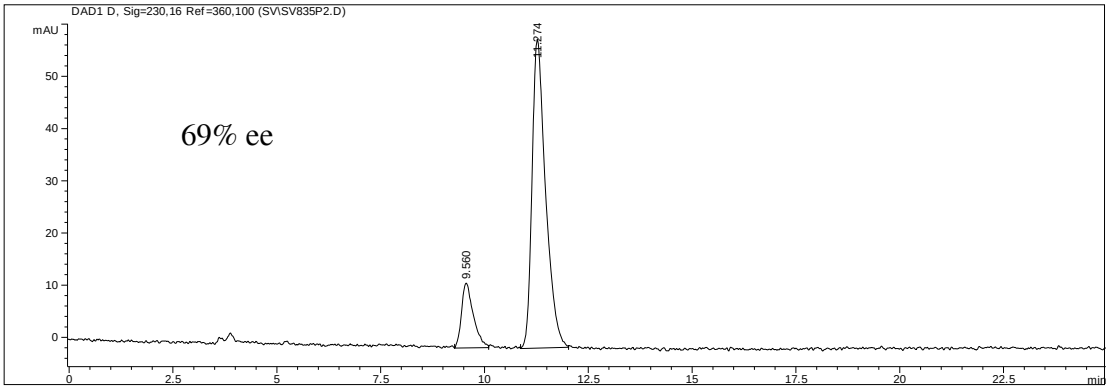
rac-**6aa**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.990	BB	0.2914	515.65900	25.55392	49.1322
2	11.919	BB	0.3308	533.87573	22.50472	50.8678



6aa



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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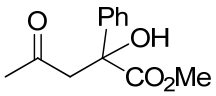
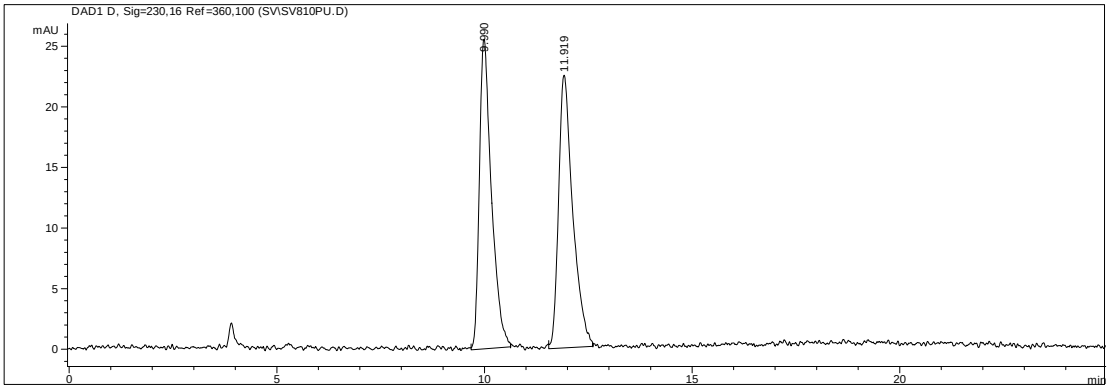
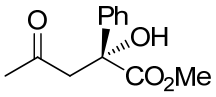
2	11.274	VB	0.3287	1342.36902	59.16234	84.5570



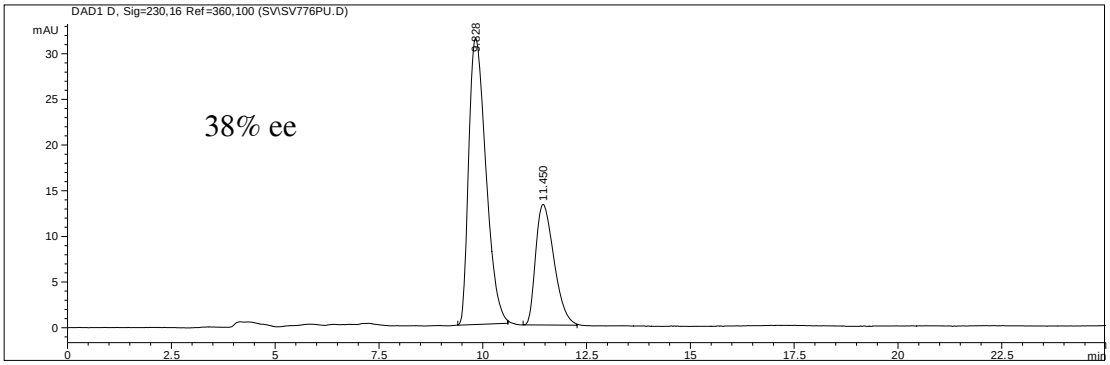
rac-**6aa**



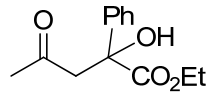
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.990	BB	0.2914	515.65900	25.55392	49.1322
2	11.919	BB	0.3308	533.87573	22.50472	50.8678



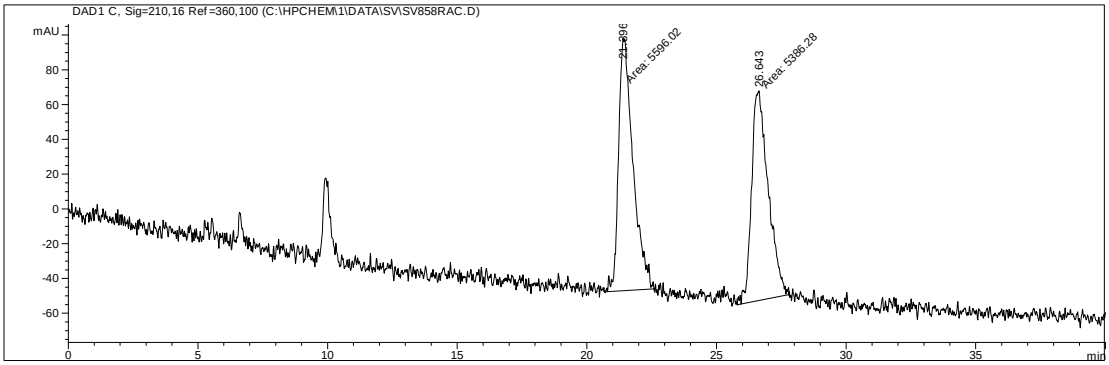
ent-**6aa**



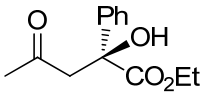
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.828	BB	0.4476	901.59406	31.34191	68.9937
2	11.450	PB	0.4782	405.18329	13.19829	31.0063



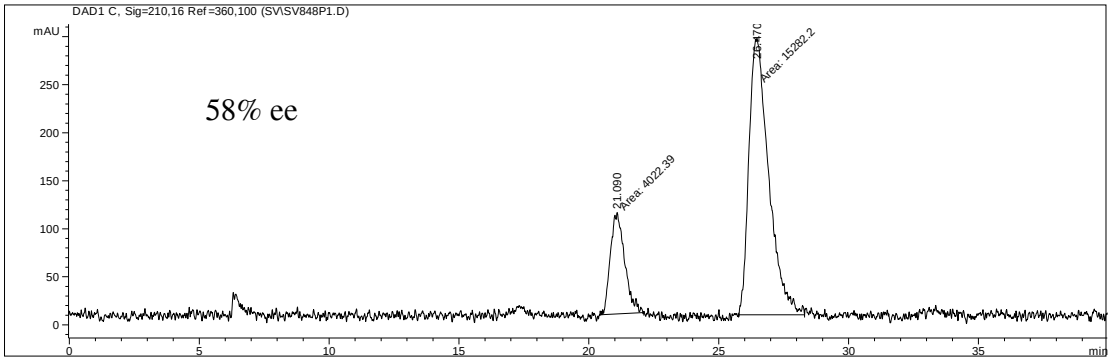
rac-**6ab**



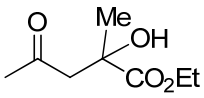
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.396	MM T	0.6433	5596.01514	144.97832	50.9549
2	26.643	MM T	0.7816	5386.27539	120.47549	49.0451



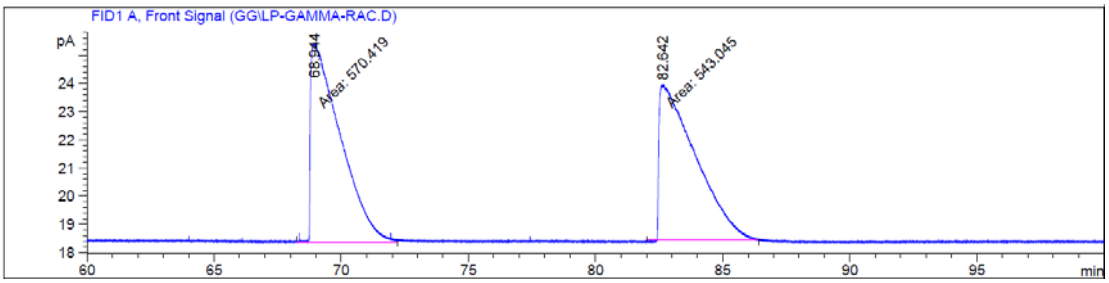
6ab



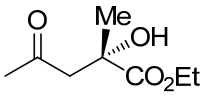
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.090	MM T	0.6357	4022.39331	105.46560	20.8365
2	26.470	MM T	0.8850	1.52822e4	287.78452	79.1635



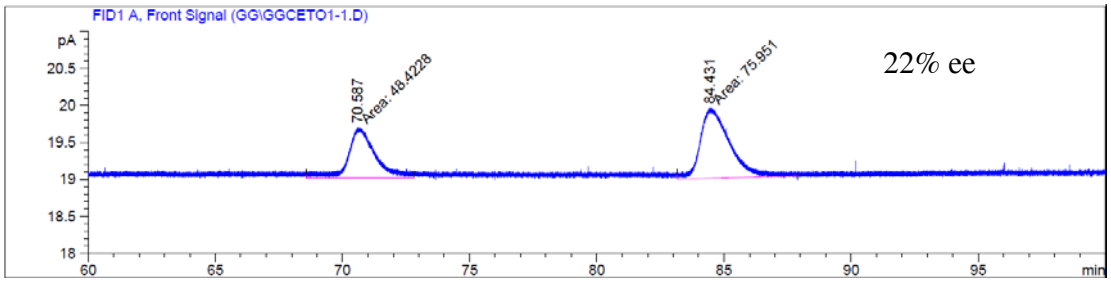
rac-**6ac**



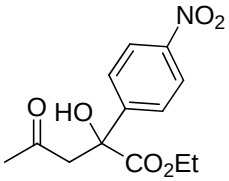
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	68.944	MM T	1.3401	570.41864	7.09408	51.22921
2	82.642	MM T	1.6421	543.04492	5.51167	48.77079



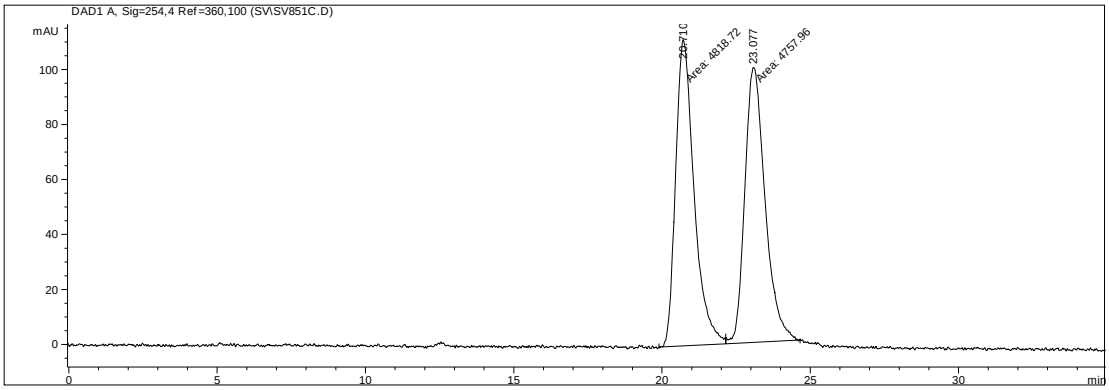
6ac



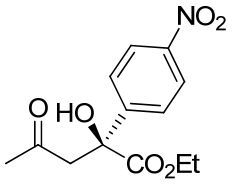
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	70.587	MM	1.1905	48.42283	6.77880e-1	38.93331
2	84.431	MM	1.3233	75.95096	9.56608e-1	61.06669



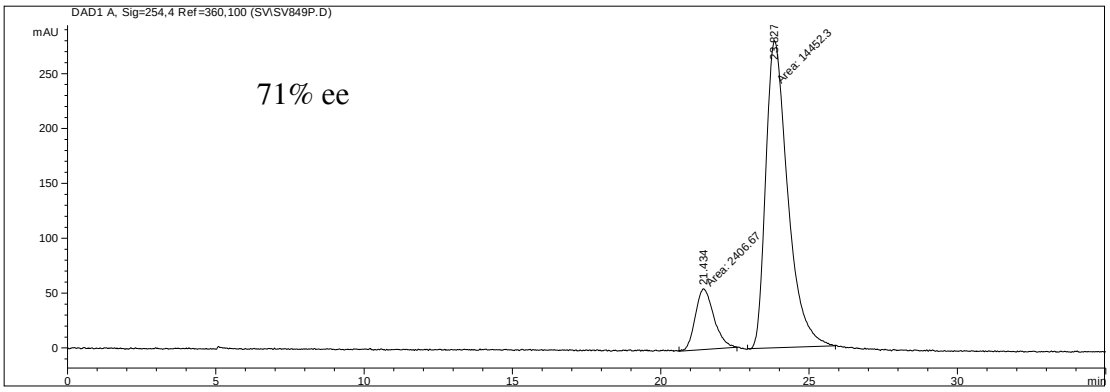
rac-**6ad**



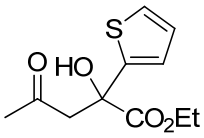
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.710	MF T	0.7215	4818.72217	111.31969	50.3172
2	23.077	FM T	0.8333	4757.96289	99.91671	49.6828



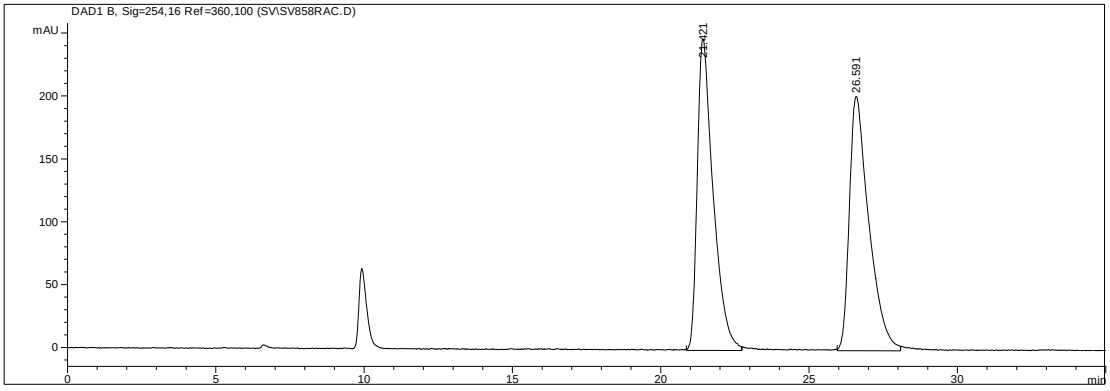
6ad



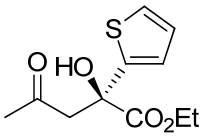
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.434	MM T	0.7246	2406.66821	55.35408	14.2753
2	23.827	MM T	0.8610	1.44523e4	279.74390	85.7247



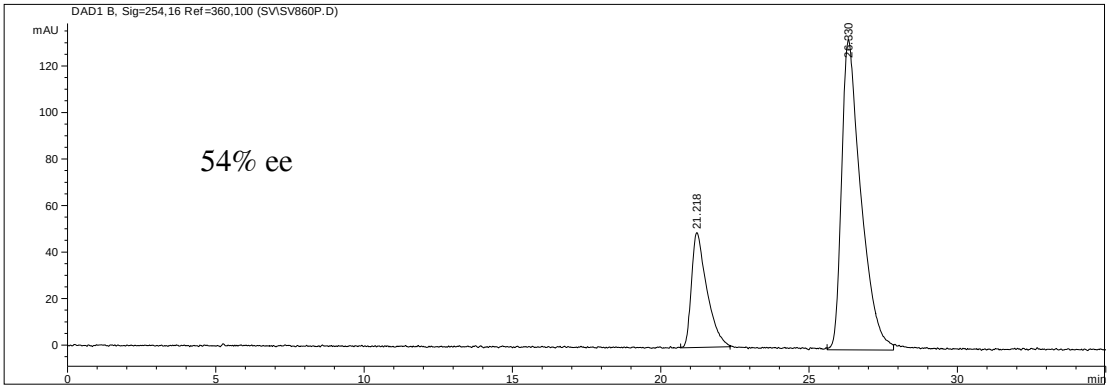
rac-**6ae**



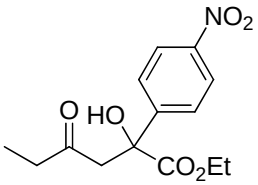
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.421	VV	0.5157	9253.93164	247.79085	50.0575
2	26.591	VV	0.6307	9232.67383	202.20561	49.9425



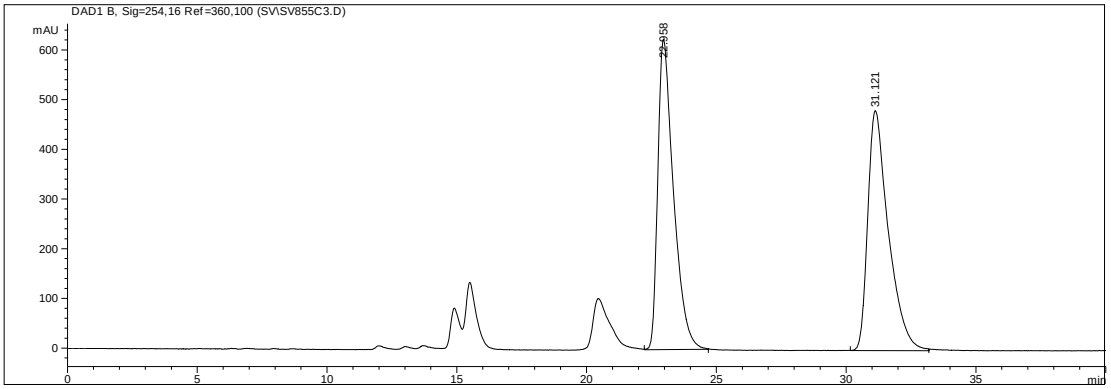
6ae



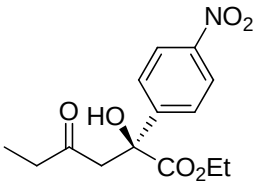
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.218	VB	0.4577	1786.98254	49.44181	22.8817
2	26.330	VV	0.5895	6022.67578	133.69775	77.1183



rac-**6bd**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.958	VB	0.5798	2.62197e4	624.54053	49.5557
2	31.121	VB	0.7563	2.66898e4	483.26413	50.4443



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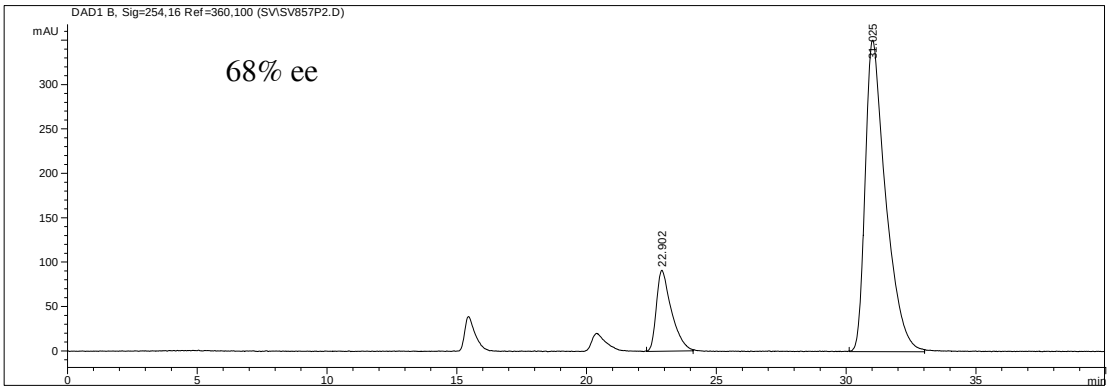
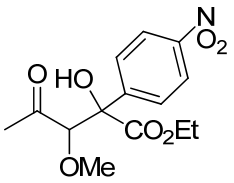
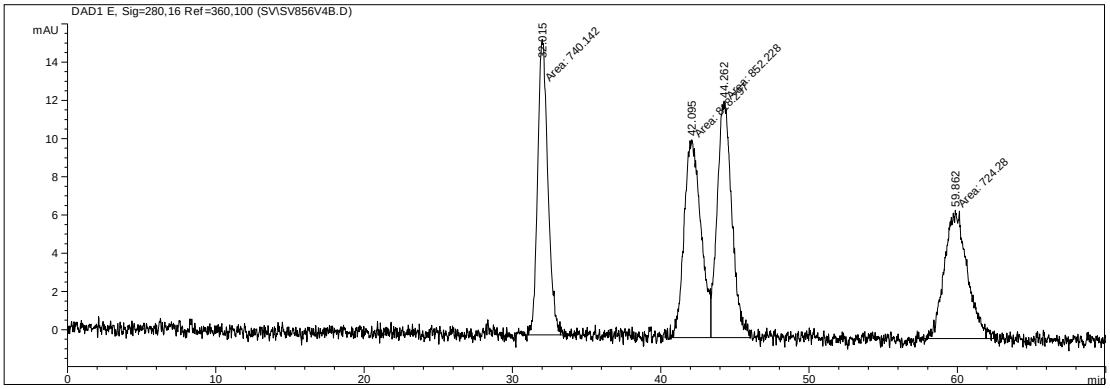


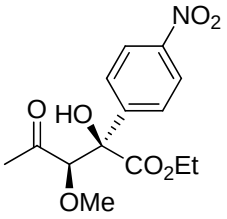
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.902	VV	0.5428	3665.29224	91.21157	16.0235
2	31.025	VB	0.7286	1.92092e4	350.96045	83.9765



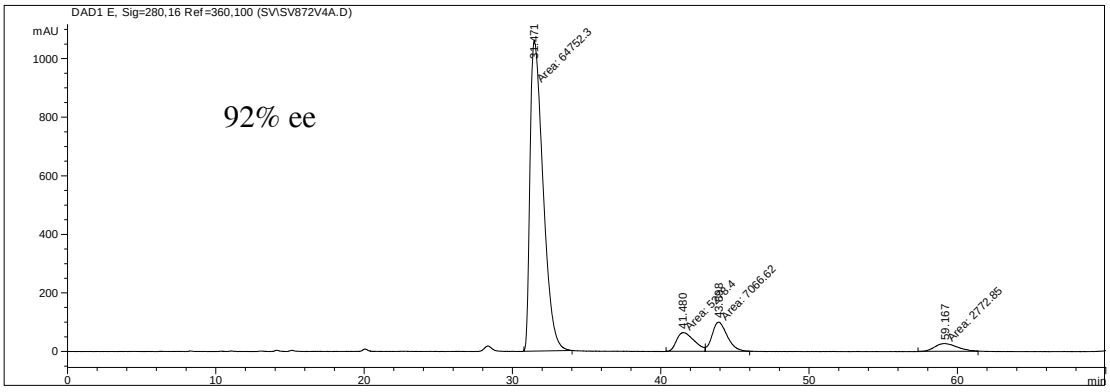
rac-**7cd**



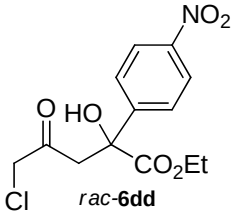
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.015	MM T	0.7976	740.14203	15.46687	23.6094
2	42.095	MF T	1.3163	818.29742	10.36124	26.1024
3	44.262	FM T	1.1484	852.22754	12.36825	27.1847
4	59.862	MM T	1.7958	724.28033	6.72205	23.1034



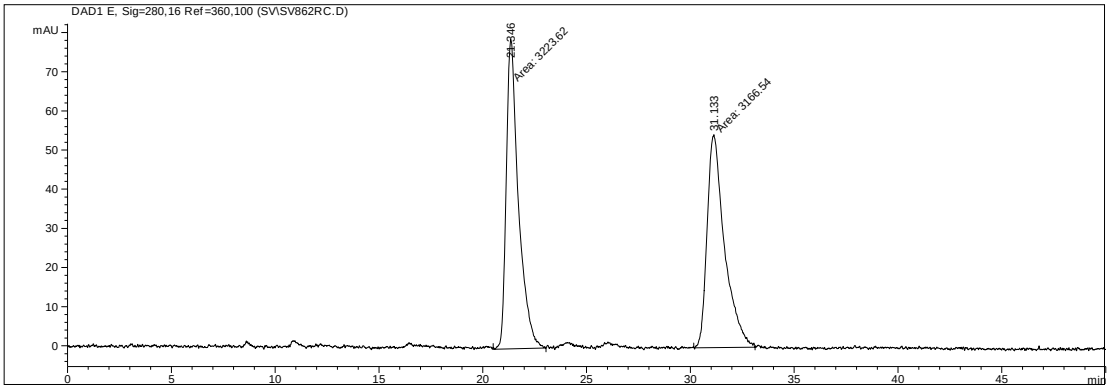
7cd



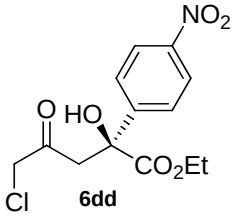
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.471	MM T	1.0154	6.47523e4	1062.88794	81.0720
2	41.480	MF T	1.3689	5278.40283	64.26523	6.6087
3	43.898	FM T	1.1787	7066.62012	99.92454	8.8476
4	59.167	MM T	1.7235	2772.84619	26.81349	3.4717



rac-**6dd**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.346	MM T	0.6796	3223.62183	79.05855	50.4467
2	31.133	MM T	0.9704	3166.53564	54.38551	49.5533



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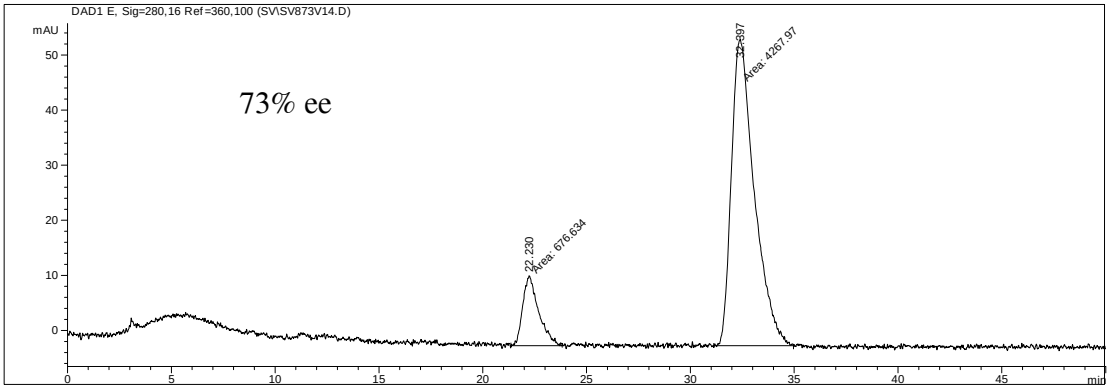
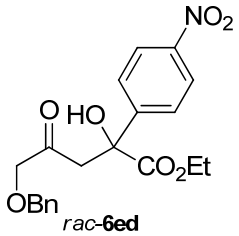
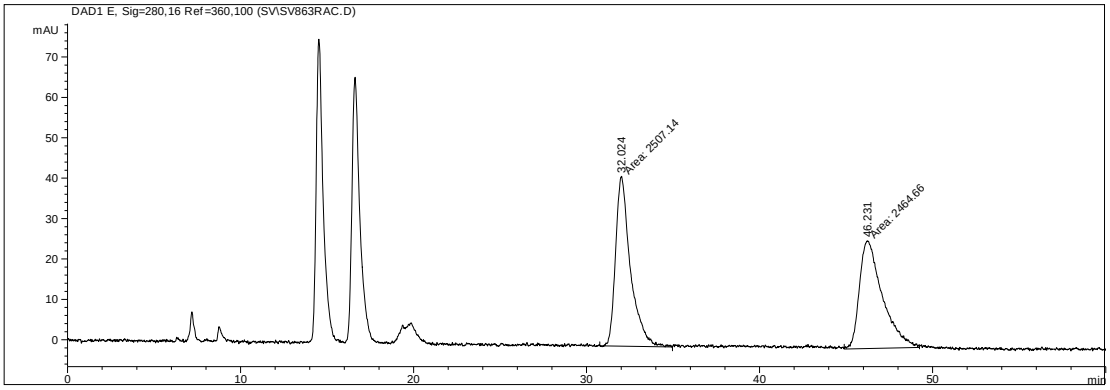


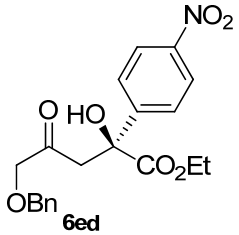
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.230	MM T	0.8874	676.63385	12.70885	13.6843
2	32.397	MM T	1.2777	4267.97266	55.67236	86.3157



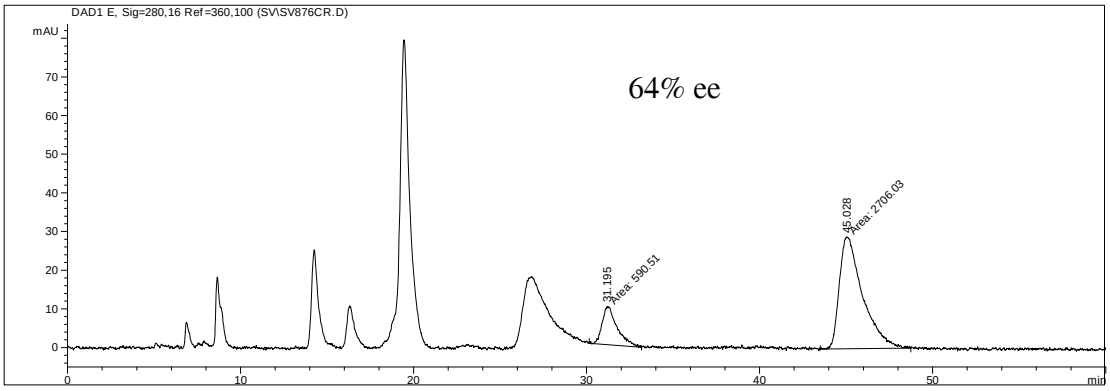
rac-**6ed**



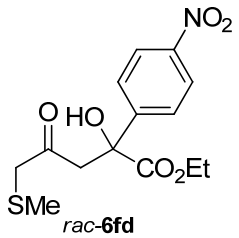
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.024	MM T	1.0769	2507.14087	42.03511	50.4273
2	46.231	MM T	1.5428	2464.65576	26.62500	49.5727



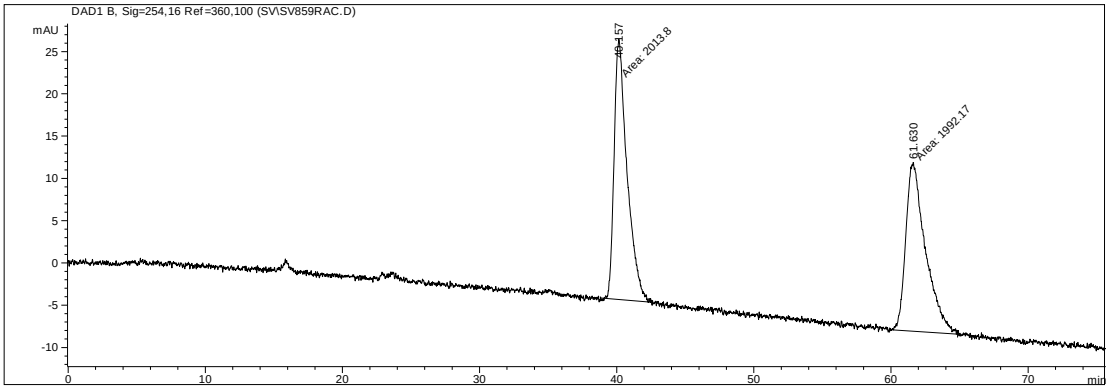
6ed



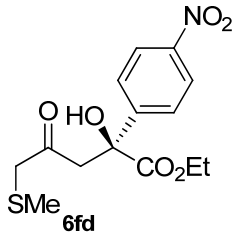
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.195	MM T	0.9908	590.50989	9.93366	17.9130
2	45.028	MM T	1.5558	2706.02930	28.98879	82.0870



rac-**6fd**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.157	MM T	1.0902	2013.80115	30.78527	50.2700
2	61.630	MM T	1.6626	1992.17163	19.97056	49.7300



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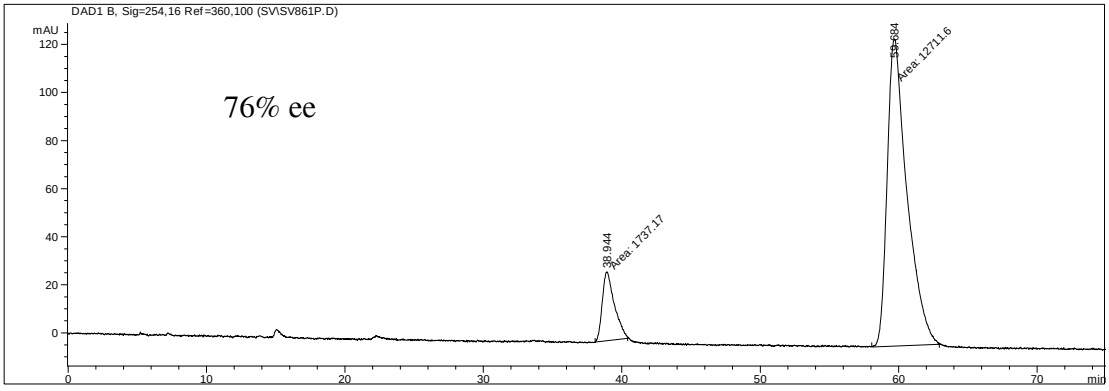

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.944	MM T	1.0130	1737.17407	28.58001	12.0230
2	59.684	MM T	1.6577	1.27116e4	127.80547	87.9770

Computational Methods:

All structures were optimized using the functional B3LYP[5] and the 6-311+G** basis set as implemented in Gaussian 09,[6] including polarization functions for the better description of hydrogen bonds involved in the reaction. The solvation factors were introduced with the IEF-PCM method.[7] As the reactions are run in solvent free conditions, we chose acetone as the model solvent, since it is the major substrate in the reaction mixture, sometimes used in a 5:1 relation to the electrophile.

The stationary points were characterized by frequency calculations in order to verify that they have the right number of imaginary frequencies.

The intrinsic reaction coordinates (IRC)[8] were followed to verify the energy profiles connecting each TS to the correct associated local minima.

It was assumed that the reaction is initiated with the formation of an enamine between catalyst **1a** (or **1b**) and acetone, and subsequent protonation of one of the pyrrolidine rings with the acetic acid additive (Figure S1). Next, the nucleophilic attack of the enamine (**8a** or **8b**) to the ketoester **5a** should lead to the C-C bond formation. We computed the transition states for that transformation. The activation energies were measured relative to the sum of the enamines **8a** or **8b** and ketoester **5a**, which was taken as G=0.

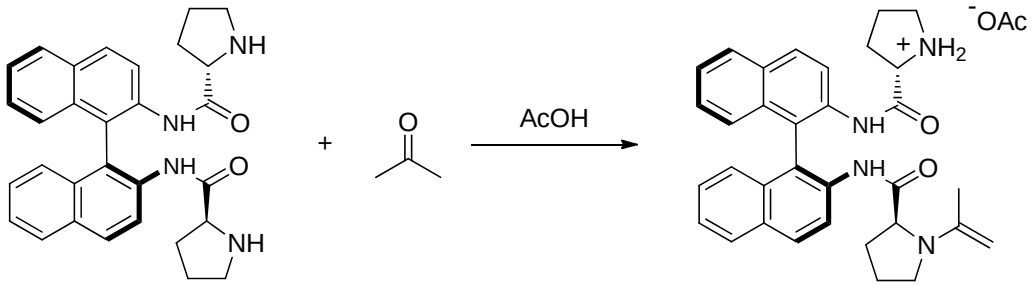

Figure S1. Formation of the reactive enamine **8a** (or **8b**) by reaction of the catalyst **1a** (or **1b**) with acetone and subsequent protonation with acetic acid.

We computed four families of transition states, corresponding to the diastereoisomeric transition states of enamines **8a** and **8b** through the *Re* and *Si* faces of the ketoester **5a**. In each family, several H-bonding patterns between the 4 NH groups of the catalyst and the two carbonyl oxygens in **5a** were screened and evaluated. In the following description and in the Main Text, only the most stable complexes and transition states of each set of conformational structures are shown. Other higher-lying conformational structures were computed in each case.

We found that the activation energy is related to the disposition of the phenyl group during the transition state. When it adopts an inward position with respect to the bulky substituents of the catalyst

(**TS-1a-*S*** and **TS-1b-*R***) the energy was always higher than the cases where the phenyl is positioned in the more free outward area (**TS-1a-*R*** and **TS-1b-*S***).

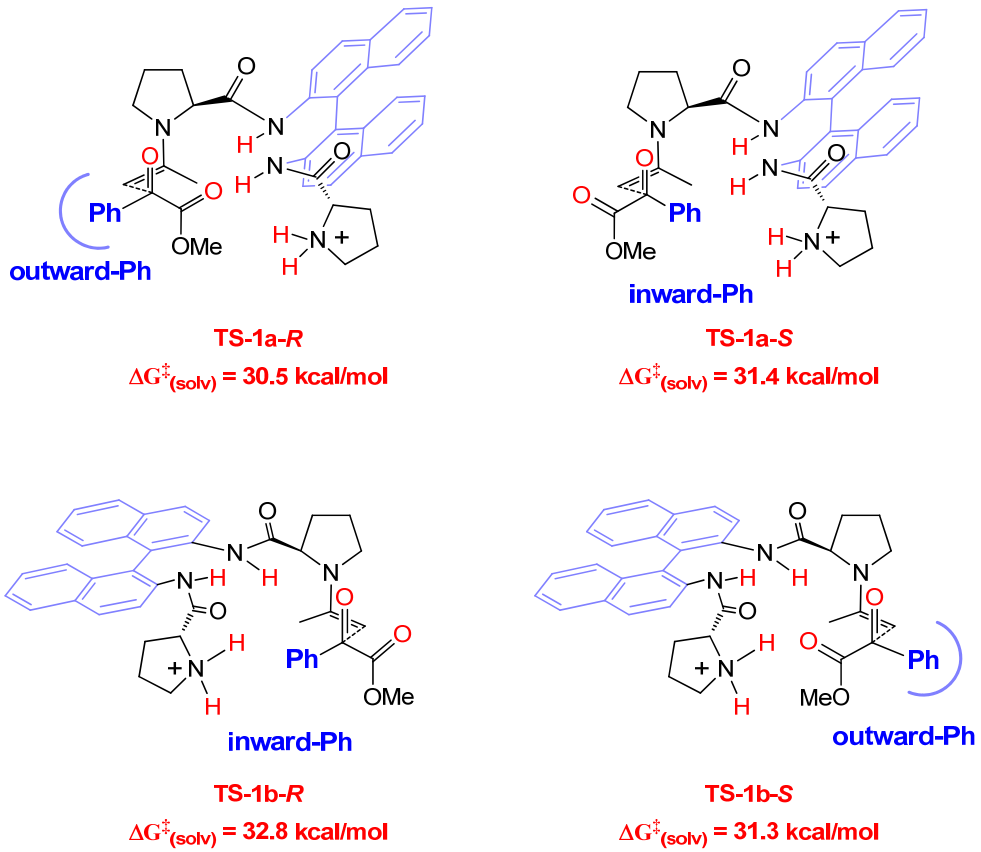

Figure S2. Four families of transition structures computed for the reaction of enamines **8a** and **8b** with ketoester **5a**

Table S1. Energies of the structures involved in the computational study

	G (B3LYP/6-311+G**, IEF-PCM, Acetone)	relative **G**	Frequency
Enamine **8a**	-1647.831185		
Enamine **8b**	-1647.827526		
Ketoester **5a**	-573.498167		
8a + **5a**	-2221.329352	0	
8b + **5a**	-2221.325693	0	

TS-1a-*R*	-2221.280690	30.54	-162.0
TS-1a-*S*	-2221.279246	31.44	-170.7
TS-1b-*R*	-2221.273374	32.83	-202.1
TS-1b-*S*	-2221.275823	31.29	-218.4

Cartesian Coordinates of the structures involved in the computational study

Enamine 8a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.584429	1.598048	2.692892
2	1	0	-0.799221	-1.877205	-4.281317
3	1	0	1.799521	0.913419	-0.435348
4	1	0	0.421142	0.627721	3.543063
5	1	0	2.746237	0.012322	4.115307
6	1	0	-1.542438	-5.976713	-1.958321
7	1	0	-5.440554	-0.356447	1.766505
8	1	0	-1.446564	-4.169098	-3.644505
9	1	0	-3.000233	-0.283388	3.619905
10	1	0	5.308017	-2.991774	-0.304871
11	1	0	-4.661319	0.185416	3.998061
12	1	0	0.416220	-3.453030	0.916101
13	1	0	-2.920389	2.179985	3.335306
14	1	0	-0.609746	-5.606999	0.319703
15	1	0	-4.509241	2.168300	2.558715
16	1	0	3.003060	-2.382965	-0.903035
17	1	0	-3.171369	2.155075	0.621935

18	1	0	4.868526	-1.090831	3.525929
19	1	0	6.251604	-2.355257	1.909751
20	1	0	-3.561433	0.319549	-2.516879
21	1	0	-2.212953	0.674661	-1.433301
22	1	0	-5.127848	-1.248338	-1.848598
23	1	0	-5.390680	-1.715542	-0.085037
24	1	0	-4.220728	-1.617832	1.993287
25	1	0	-1.522342	-0.697706	1.010636
26	1	0	3.102770	3.052409	-1.292987
27	1	0	1.811146	6.285546	-0.985250
28	1	0	0.304115	6.056385	-1.906429
29	1	0	-0.446593	4.293777	-0.338623
30	1	0	0.329582	5.424982	0.766738
31	1	0	1.181555	2.898486	0.769317
32	1	0	2.434206	4.158495	0.709265
33	1	0	-3.623855	1.739607	-1.474027
34	1	0	1.102478	4.059696	-2.838463
35	1	0	2.577616	4.849060	-2.594548
36	6	0	-3.304327	0.691727	-1.524444
37	6	0	-1.424213	1.268177	1.426720
38	1	0	0.201198	0.302791	-3.711608
39	6	0	-4.370363	-0.533982	1.949879
40	6	0	-3.974835	-0.155411	-0.469373
41	6	0	-4.883693	-1.088012	-0.806197
42	6	0	-3.900806	0.190151	3.213832
43	6	0	-2.958303	1.326695	1.301919
44	6	0	-0.459674	-2.758902	-2.335789
45	6	0	0.479720	-0.293367	1.587914
46	6	0	3.131723	-1.001214	2.241424
47	6	0	1.036000	0.077236	2.840973
48	6	0	1.233088	-0.991755	0.649346
49	6	0	2.327180	-0.266053	3.152479
50	6	0	0.660795	-1.275585	-0.706541
51	6	0	-0.395780	-1.708761	-3.287141
52	6	0	2.582155	-1.371709	0.969210
53	6	0	0.079121	-2.542425	-1.024313
54	6	0	0.688024	-0.280000	-1.680673
55	6	0	0.163842	-0.492415	-2.980412

56	6	0	-1.042096	-4.015392	-2.648127
57	6	0	-1.095136	-5.019700	-1.709487
58	6	0	0.007552	-3.602428	-0.077612
59	6	0	-0.565158	-4.808235	-0.414129
60	6	0	3.406322	-2.092649	0.060910
61	6	0	4.465837	-1.371262	2.556637
62	6	0	5.234311	-2.073757	1.656943
63	6	0	4.697222	-2.434558	0.398759
64	6	0	1.212023	2.154732	-1.906472
65	6	0	2.037982	3.290952	-1.235545
66	6	0	1.051724	5.560749	-1.285806
67	6	0	0.503044	4.777966	-0.094666
68	6	0	1.585316	3.721075	0.174164
69	7	0	1.304418	0.955569	-1.320337
70	7	0	-0.879205	0.024263	1.323895
71	7	0	1.747109	4.494586	-2.119736
72	7	0	-3.567811	0.061216	0.863809
73	8	0	-0.771742	2.291462	1.642071
74	8	0	0.568233	2.438088	-2.927502

Enamine 8b

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.535229	3.751368	0.162759
2	1	0	1.879176	3.512741	-1.396169
3	1	0	-4.100731	0.777385	-2.230021
4	1	0	5.136208	2.811189	0.607104
5	1	0	5.101837	1.962231	-0.944412
6	1	0	5.462320	4.713941	-0.853875
7	1	0	4.488336	3.991206	-2.139984
8	1	0	2.884341	5.561770	-1.104378
9	1	0	3.445128	5.113216	0.527986

10	1	0	2.941214	2.134970	0.938845
11	1	0	-1.377502	1.302852	0.768547
12	1	0	-3.125945	3.574902	1.592982
13	1	0	-3.543381	4.482987	-0.587534
14	1	0	-3.287908	4.011307	-2.340561
15	1	0	-2.403262	0.602319	-1.770072
16	1	0	-2.877517	1.801895	-2.990049
17	1	0	4.818603	-3.511194	2.820172
18	1	0	3.313311	-2.192824	4.276409
19	1	0	-4.327098	0.019732	-0.152235
20	1	0	2.416156	-2.539719	-0.605136
21	1	0	-5.888620	0.889964	1.442131
22	1	0	-2.012998	-5.190599	-0.357896
23	1	0	-4.886465	-0.145180	2.478717
24	1	0	-0.868591	-3.250258	0.626505
25	1	0	-5.134141	2.489510	3.163565
26	1	0	4.359795	-3.671978	0.376050
27	1	0	-3.511794	1.787169	3.167756
28	1	0	-1.429069	-3.593523	-4.309037
29	1	0	-4.802891	3.534335	1.018949
30	1	0	-2.294379	-5.374985	-2.825908
31	1	0	1.321926	-0.777420	4.562945
32	1	0	-0.660133	0.353249	3.590836
33	1	0	0.700975	1.720111	-0.692923
34	1	0	-0.266226	-1.446741	-4.609580
35	1	0	0.884782	0.531021	-3.628358
36	8	0	3.491450	0.312221	-1.340178
37	8	0	-2.858069	-1.396415	1.545384
38	7	0	-3.596595	1.967464	0.279298
39	7	0	2.340180	3.606548	-0.463372
40	7	0	-1.440233	0.338117	1.078928
41	7	0	1.322232	0.996330	-1.056348
42	6	0	4.613343	2.737519	-0.351104
43	6	0	4.574892	4.109384	-1.053333
44	6	0	3.310009	4.760804	-0.497895
45	6	0	3.139074	2.347147	-0.114574
46	6	0	2.670511	1.113827	-0.928277
47	6	0	3.690625	-3.099311	1.012782

48	6	0	3.954184	-3.005652	2.399806
49	6	0	3.118693	-2.272531	3.209968
50	6	0	2.596807	-2.470667	0.460692
51	6	0	-1.616846	-4.412187	-1.003682
52	6	0	-0.966377	-3.332333	-0.450123
53	6	0	-1.782401	-4.513727	-2.405162
54	6	0	-1.301627	-3.524003	-3.231481
55	6	0	0.503040	-0.266898	-2.997930
56	6	0	0.689105	-0.174222	-1.598114
57	6	0	-0.446909	-2.296869	-1.274532
58	6	0	1.703883	-1.715927	1.270507
59	6	0	-0.133681	-1.359616	-3.533448
60	6	0	0.247332	-1.164055	-0.735190
61	6	0	1.111893	-0.848093	3.498175
62	6	0	0.545344	-1.059439	0.730281
63	6	0	0.016254	-0.218510	2.963108
64	6	0	1.980790	-1.611410	2.675278
65	6	0	-0.267877	-0.324962	1.578760
66	6	0	-0.628491	-2.393616	-2.695967
67	6	0	-3.883486	0.573095	0.677748
68	6	0	-4.377591	2.014406	2.534911
69	6	0	-3.236541	3.728738	-1.300006
70	6	0	-3.365170	2.381692	-0.985981
71	6	0	-3.965137	2.914076	1.362314
72	6	0	-4.878713	0.740497	1.840796
73	6	0	-2.666357	-0.259579	1.143029
74	6	0	-3.171377	1.331986	-2.050578

5a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	1	0	3.753128	-1.500792	-0.782212
2	1	0	4.325710	-0.531495	0.594907
3	1	0	4.664520	0.018345	-1.079339
4	1	0	-4.526954	-0.959296	-0.285709
5	1	0	-2.668210	-2.604375	-0.239892
6	1	0	-4.039661	1.471589	-0.113878
7	1	0	-1.675458	2.244778	0.097382
8	1	0	-0.329177	-1.831013	-0.009126
9	8	0	2.750961	0.311134	-0.488189
10	8	0	1.730679	-1.186491	0.865133
11	8	0	0.756459	2.008901	0.214806
12	6	0	3.950287	-0.484973	-0.429699
13	6	0	1.717072	-0.160746	0.216969
14	6	0	-2.456289	-1.542358	-0.167889
15	6	0	-3.227726	0.751748	-0.094594
16	6	0	-1.914084	1.189565	0.024131
17	6	0	-1.136471	-1.110155	-0.045246
18	6	0	-3.500619	-0.616655	-0.192047
19	6	0	-0.855904	0.263419	0.051605
20	6	0	0.522286	0.814140	0.150748

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Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.663016	-1.950577	-3.139300
2	6	0	-0.702237	-2.120912	-2.103506
3	6	0	-0.238207	-4.419307	-1.135396
4	6	0	1.504137	-3.441294	0.213321
5	6	0	2.667756	-2.323904	-1.678604
6	6	0	3.764425	-2.009081	-0.874908
7	6	0	0.104085	-4.059461	0.317463
8	6	0	0.351573	-3.241298	-1.936418
9	6	0	-3.410484	-2.298707	2.049844

10	6	0	-1.399082	0.134823	-1.495079
11	6	0	-3.155754	2.328954	-1.738080
12	6	0	-1.404724	0.929881	-2.672570
13	6	0	-2.266306	0.405215	-0.442133
14	6	0	-2.265664	1.993494	-2.793457
15	6	0	-2.322615	-0.481418	0.767865
16	6	0	-2.494488	-2.064219	3.108863
17	6	0	-3.155510	1.533109	-0.542471
18	6	0	-3.324436	-1.505006	0.856516
19	6	0	-1.440992	-0.308237	1.825666
20	6	0	-1.525126	-1.097227	2.997460
21	6	0	-4.409134	-3.305045	2.142928
22	6	0	-5.280817	-3.531139	1.102997
23	6	0	-4.233763	-1.775104	-0.204145
24	6	0	-5.185099	-2.763044	-0.081964
25	6	0	-4.047790	1.891231	0.506467
26	6	0	-4.045693	3.432141	-1.840470
27	6	0	-4.901419	3.743383	-0.808976
28	6	0	-4.897349	2.966605	0.374121
29	6	0	-0.531125	1.984883	1.938641
30	6	0	0.633723	2.819314	1.346646
31	6	0	0.337388	4.107474	-0.744966
32	6	0	-0.245902	4.888321	0.430632
33	6	0	0.514430	4.319194	1.640129
34	1	0	-0.822331	-0.910956	3.803530
35	1	0	-2.571238	-2.661879	4.013365
36	1	0	0.504064	0.326639	1.310338
37	1	0	-0.730155	0.663474	-3.479955
38	1	0	-2.283452	2.583688	-3.706367
39	1	0	-6.041269	-4.302246	1.185631
40	1	0	2.292744	-4.199095	0.305874
41	1	0	-4.471076	-3.894374	3.054271
42	1	0	-0.609252	-3.327616	0.709283
43	1	0	-5.569302	3.223876	1.187431
44	1	0	0.094411	-4.925349	0.984230
45	1	0	-4.159943	-1.207829	-1.125058
46	1	0	-1.306936	-4.529100	-1.327114
47	1	0	-5.867226	-2.957327	-0.904436

48	1	0	0.262848	-5.347242	-1.432471
49	1	0	-4.040526	1.316775	1.424890
50	1	0	0.625079	-3.547737	-2.948196
51	1	0	-4.043903	4.020624	-2.754654
52	1	0	-5.582205	4.584851	-0.899477
53	1	0	3.583892	-1.425159	-3.395188
54	1	0	1.810058	-1.310898	-3.392676
55	1	0	4.693702	-1.755577	-1.367336
56	1	0	3.861878	-2.468964	0.099839
57	1	0	1.687255	-2.659029	0.950952
58	1	0	0.383199	-0.837845	-0.890260
59	1	0	1.597907	2.390619	1.628302
60	1	0	1.326616	4.471297	-1.033349
61	1	0	-0.298429	4.044060	-1.628939
62	1	0	-1.317157	4.686267	0.530932
63	1	0	-0.108666	5.965401	0.306957
64	1	0	-0.023073	4.474287	2.576919
65	1	0	1.509369	4.768994	1.721495
66	1	0	2.599700	-2.844459	-3.771572
67	1	0	-0.266524	2.111289	-0.442475
68	1	0	1.369966	2.247257	-0.604184
69	7	0	-0.379022	0.651575	1.711686
70	7	0	-0.478881	-0.959495	-1.422280
71	7	0	0.530133	2.710395	-0.188885
72	7	0	1.555025	-2.873170	-1.160808
73	8	0	-1.679547	-2.334859	-2.803436
74	8	0	-1.492668	2.517314	2.467110
75	6	0	3.153553	-0.035501	-0.037771
76	8	0	1.902579	-0.088293	0.164319
77	6	0	4.104282	-0.054426	1.132790
78	6	0	5.745898	-0.050980	3.417157
79	6	0	5.490210	0.151262	1.017522
80	6	0	3.557160	-0.259145	2.411326
81	6	0	4.370071	-0.257162	3.542254
82	6	0	6.300063	0.152605	2.152014
83	1	0	5.941462	0.300286	0.044071
84	1	0	2.488481	-0.415518	2.509790
85	1	0	3.929600	-0.414699	4.522719

86	1	0	7.369244	0.311591	2.045567
87	1	0	6.380820	-0.050077	4.298265
88	6	0	3.538204	0.879544	-1.227591
89	8	0	2.819434	1.822546	-1.537590
90	8	0	4.678831	0.622392	-1.861134
91	6	0	5.063908	1.554194	-2.904919
92	1	0	6.011867	1.177487	-3.285603
93	1	0	5.181855	2.555727	-2.486788
94	1	0	4.305829	1.569960	-3.690080

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Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.323083	-1.503543	-3.137400
2	6	0	-0.926713	-1.325784	-1.839945
3	6	0	-0.740824	-3.770930	-1.157606
4	6	0	1.235627	-3.235392	0.123641
5	6	0	2.392593	-2.080524	-1.748088
6	6	0	3.608525	-2.085608	-1.052325
7	6	0	-0.222311	-3.681390	0.284558
8	6	0	-0.042120	-2.592322	-1.867807
9	6	0	-4.672400	-2.071854	0.601021
10	6	0	-1.280939	0.930962	-0.966789
11	6	0	-2.620652	3.412863	-0.863538
12	6	0	-0.731957	2.077666	-1.594956
13	6	0	-2.501296	0.995424	-0.301239
14	6	0	-1.381689	3.286879	-1.541564
15	6	0	-3.064223	-0.202892	0.403018
16	6	0	-4.067173	-2.425212	1.835921
17	6	0	-3.192385	2.255335	-0.235617
18	6	0	-4.164960	-0.948284	-0.133279
19	6	0	-2.527673	-0.584913	1.625416

20	6	0	-3.019578	-1.700239	2.347035
21	6	0	-5.770607	-2.805549	0.078093
22	6	0	-6.346709	-2.451309	-1.119758
23	6	0	-4.774537	-0.620414	-1.375195
24	6	0	-5.838578	-1.351576	-1.851855
25	6	0	-4.426734	2.409787	0.457880
26	6	0	-3.303107	4.656728	-0.788544
27	6	0	-4.497294	4.767070	-0.115068
28	6	0	-5.059444	3.631613	0.515617
29	6	0	-0.343380	-0.234764	2.745859
30	6	0	0.598455	0.851724	3.281161
31	6	0	2.865239	1.514473	3.536051
32	6	0	2.150564	2.710295	2.871547
33	6	0	0.686097	2.238613	2.617473
34	1	0	-2.566041	-1.963942	3.294887
35	1	0	-4.457176	-3.277028	2.386880
36	1	0	-1.553602	1.209264	1.990439
37	1	0	0.200960	1.972773	-2.139836
38	1	0	-0.958922	4.159392	-2.033146
39	1	0	-7.188009	-3.016681	-1.510025
40	1	0	1.918804	-4.090680	0.044183
41	1	0	-6.148963	-3.652020	0.645677
42	1	0	-0.779747	-2.938980	0.860280
43	1	0	-6.002638	3.724471	1.046307
44	1	0	-0.291520	-4.633157	0.817696
45	1	0	-4.375241	0.200952	-1.957990
46	1	0	-1.826084	-3.696283	-1.245772
47	1	0	-6.288641	-1.087666	-2.804450
48	1	0	-0.423524	-4.709214	-1.626232
49	1	0	-4.874342	1.547212	0.938922
50	1	0	0.110920	-2.809879	-2.926653
51	1	0	-2.862097	5.522249	-1.276676
52	1	0	-5.011816	5.722247	-0.066080
53	1	0	3.277778	-1.051834	-3.407545
54	1	0	1.544463	-0.738151	-3.220593
55	1	0	4.509729	-1.962324	-1.638231
56	1	0	3.706523	-2.724620	-0.181431
57	1	0	1.574814	-2.586136	0.931493

58	1	0	0.395331	-0.307757	-0.616656
59	1	0	0.398580	0.961193	4.354366
60	1	0	2.867275	1.588968	4.626609
61	1	0	3.878791	1.326700	3.187302
62	1	0	2.633886	2.971095	1.927095
63	1	0	2.194806	3.589242	3.518397
64	1	0	0.496986	2.157351	1.542936
65	1	0	-0.050633	2.924977	3.041854
66	1	0	2.095998	-2.286583	-3.871724
67	1	0	2.208199	0.063483	2.154459
68	1	0	2.163136	-0.498207	3.719282
69	7	0	-1.491133	0.218864	2.191167
70	7	0	-0.533417	-0.289402	-1.036806
71	7	0	2.004429	0.344672	3.161937
72	7	0	1.258816	-2.500488	-1.172061
73	8	0	-1.942482	-1.325233	-2.515437
74	8	0	-0.023640	-1.411352	2.897601
75	6	0	3.508882	-0.141031	-0.046160
76	8	0	2.347168	-0.006375	0.464258
77	6	0	4.572837	-0.647831	0.954771
78	8	0	4.287269	-0.880562	2.117834
79	8	0	5.803049	-0.800125	0.461159
80	6	0	6.809311	-1.272554	1.386192
81	1	0	7.726139	-1.340307	0.802356
82	1	0	6.527601	-2.250070	1.783555
83	1	0	6.927170	-0.564777	2.209535
84	6	0	3.926021	0.821029	-1.136624
85	6	0	4.550232	2.767526	-3.080174
86	6	0	3.071689	1.911443	-1.370699
87	6	0	5.106730	0.726834	-1.895786
88	6	0	5.410302	1.689504	-2.856985
89	6	0	3.379522	2.875930	-2.329740
90	1	0	2.166400	1.996759	-0.781412
91	1	0	5.795207	-0.092507	-1.735386
92	1	0	6.326008	1.596593	-3.433966
93	1	0	2.707180	3.715255	-2.485853
94	1	0	4.793989	3.515580	-3.828939

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Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.451093	-2.393678	-0.473640
2	1	0	-2.638993	-3.378085	0.665316
3	1	0	-1.353547	4.114659	2.350413
4	1	0	-1.214660	-3.702948	-2.845786
5	1	0	0.039157	-4.241763	-1.723530
6	1	0	-2.073171	-5.897973	-2.181815
7	1	0	-1.546313	-5.663870	-0.506357
8	1	0	-3.923904	-5.001724	-0.390211
9	1	0	-3.800190	-4.135758	-1.942333
10	1	0	-1.488655	-1.861871	-1.363377
11	1	0	-0.056671	1.354632	-0.615379
12	1	0	-1.999954	2.725857	-2.247985
13	1	0	-3.847919	2.806848	-0.588888
14	1	0	-4.045038	2.487653	1.197452
15	1	0	-0.614043	2.526668	2.100467
16	1	0	-2.272749	2.644993	2.710423
17	1	0	5.963190	-3.274571	-3.433643
18	1	0	4.707003	-1.478555	-4.586598
19	1	0	0.247026	4.353183	0.780174
20	1	0	4.069557	-2.256193	0.284834
21	1	0	-0.410396	5.986718	-0.882357
22	1	0	5.628577	2.577398	2.024442
23	1	0	1.136952	5.389296	-1.524994
24	1	0	4.183064	1.528318	0.341010
25	1	0	-1.076119	5.239312	-3.132551
26	1	0	5.634628	-3.648208	-0.991887
27	1	0	-0.013499	3.834212	-3.034038
28	1	0	3.890894	0.142504	5.115637
29	1	0	-2.710710	4.254747	-1.698225

30	1	0	5.495690	1.894173	4.416783
31	1	0	3.088272	0.371584	-4.522178
32	1	0	1.512881	1.788873	-3.250056
33	1	0	0.663147	-1.503891	-0.664788
34	1	0	2.150097	-1.503573	4.544596
35	1	0	0.664981	-2.567441	2.880242
36	8	0	-0.898757	-3.291069	1.431232
37	8	0	2.365213	3.430864	-0.671067
38	7	0	-1.282533	3.443238	-0.380779
39	7	0	-2.792647	-3.194273	-0.346612
40	7	0	0.914825	1.665119	-0.712081
41	7	0	0.558966	-1.946078	0.242799
42	6	0	-1.021875	-3.993521	-1.807882
43	6	0	-1.942664	-5.154896	-1.391427
44	6	0	-3.253092	-4.447676	-1.049218
45	6	0	-1.414670	-2.829392	-0.862773
46	6	0	-0.536273	-2.713089	0.402969
47	6	0	5.074842	-2.865783	-1.496392
48	6	0	5.263539	-2.653557	-2.881844
49	6	0	4.565657	-1.656232	-3.523478
50	6	0	4.194414	-2.085841	-0.778645
51	6	0	4.931067	1.800207	2.323100
52	6	0	4.130600	1.204125	1.374224
53	6	0	4.852792	1.416163	3.683319
54	6	0	3.961390	0.443171	4.073224
55	6	0	1.365346	-1.798701	2.585163
56	6	0	1.439539	-1.407934	1.222530
57	6	0	3.201176	0.191535	1.743064
58	6	0	3.455131	-1.046419	-1.408839
59	6	0	2.194680	-1.199076	3.501989
60	6	0	2.356285	-0.454139	0.786071
61	6	0	2.933804	0.205728	-3.459124
62	6	0	2.534507	-0.205943	-0.682389
63	6	0	2.058900	0.991574	-2.756007
64	6	0	3.653863	-0.832322	-2.812132
65	6	0	1.850678	0.790816	-1.364263
66	6	0	3.116101	-0.189131	3.123656
67	6	0	0.086402	3.979990	-0.232189

68	6	0	-0.666745	4.490735	-2.449596
69	6	0	-3.372696	2.556337	0.349858
70	6	0	-2.092228	3.072571	0.617044
71	6	0	-1.780501	3.679711	-1.764540
72	6	0	0.112711	5.109034	-1.278022
73	6	0	1.234350	2.981121	-0.549574
74	6	0	-1.552325	3.086588	2.022119
75	8	0	-1.744570	0.485532	-0.607962
76	6	0	-2.897250	0.553189	-0.065581
77	6	0	-3.972582	0.150672	-1.106941
78	8	0	-4.304261	-1.026536	-1.240742
79	8	0	-4.368864	1.094776	-1.950355
80	6	0	-5.198912	0.668375	-3.058448
81	1	0	-4.649461	-0.034797	-3.687924
82	1	0	-5.432186	1.579521	-3.607199
83	1	0	-6.109172	0.194930	-2.685923
84	6	0	-3.147878	-0.007694	1.317710
85	6	0	-3.548562	-0.997950	3.915860
86	6	0	-2.057207	-0.281390	2.150426
87	6	0	-4.446537	-0.240748	1.800471
88	6	0	-4.644852	-0.733659	3.088609
89	6	0	-2.255778	-0.771267	3.442193
90	1	0	-1.053905	-0.107565	1.777671
91	1	0	-5.308979	-0.032359	1.171948
92	1	0	-5.654638	-0.908587	3.449236
93	1	0	-1.396259	-0.980018	4.072043
94	1	0	-3.704137	-1.378905	4.921061

TS-1b-*S*

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.216243	2.914584	0.942763
2	1	0	2.054495	3.842144	1.671654

3	1	0	0.428380	-4.001599	2.317407
4	1	0	1.269044	3.772825	-2.047984
5	1	0	-0.168712	4.171994	-1.104784
6	1	0	1.793698	6.061271	-1.418575
7	1	0	1.017894	5.882858	0.160914
8	1	0	3.396483	5.548630	0.727537
9	1	0	3.651515	4.567259	-0.737836
10	1	0	1.700964	2.068081	-0.480041
11	1	0	0.120185	-1.283892	-0.626775
12	1	0	2.487561	-2.632205	-1.796400
13	1	0	3.758702	-2.776729	0.277842
14	1	0	3.444376	-2.399683	2.027683
15	1	0	-0.056729	-2.338855	1.945938
16	1	0	1.330809	-2.639254	3.003909
17	1	0	-5.418272	3.813823	-3.575009
18	1	0	-3.971679	2.218870	-4.797478
19	1	0	-0.516686	-4.374012	0.424607
20	1	0	-4.132622	2.156668	0.174241
21	1	0	0.512895	-5.893031	-1.142701
22	1	0	-5.894470	-2.878298	0.795746
23	1	0	-0.806164	-5.199750	-2.111994
24	1	0	-4.216371	-1.574923	-0.433819
25	1	0	1.744933	-5.000459	-3.084583
26	1	0	-5.489621	3.768515	-1.084604
27	1	0	0.719143	-3.563624	-3.131687
28	1	0	-4.665535	-1.070052	4.500308
29	1	0	2.947987	-4.223578	-1.162874
30	1	0	-6.132908	-2.634966	3.263820
31	1	0	-2.361888	0.361023	-4.788538
32	1	0	-0.988274	-1.274144	-3.536505
33	1	0	-0.523031	1.421046	-0.300491
34	1	0	-2.865944	0.611004	4.505110
35	1	0	-1.156254	1.927004	3.303513
36	8	0	0.398011	3.153265	2.183740
37	8	0	-2.237118	-3.304516	-1.377568
38	7	0	1.242329	-3.389662	-0.245972
39	7	0	2.486289	3.623002	0.746582
40	7	0	-0.811759	-1.571482	-0.939612

41	7	0	-0.641938	1.777005	0.642559
42	6	0	0.917970	4.067622	-1.054329
43	6	0	1.616337	5.364292	-0.596276
44	6	0	2.923034	4.864629	0.020806
45	6	0	1.344107	2.992114	-0.017993
46	6	0	0.292322	2.644480	1.059970
47	6	0	-4.846627	3.073305	-1.616906
48	6	0	-4.808156	3.098973	-3.030546
49	6	0	-4.004230	2.213276	-3.710883
50	6	0	-4.083570	2.170343	-0.908987
51	6	0	-5.256411	-2.181031	1.330861
52	6	0	-4.325079	-1.441508	0.636447
53	6	0	-5.388912	-2.047324	2.733806
54	6	0	-4.574016	-1.178243	3.422381
55	6	0	-1.792931	1.233441	2.772012
56	6	0	-1.658410	1.095607	1.366403
57	6	0	-3.469736	-0.530538	1.317223
58	6	0	-3.240727	1.240590	-1.578882
59	6	0	-2.750102	0.500270	3.429935
60	6	0	-2.494208	0.259267	0.630553
61	6	0	-2.379863	0.343393	-3.701912
62	6	0	-2.438521	0.276516	-0.868772
63	6	0	-1.617062	-0.562150	-3.011461
64	6	0	-3.207805	1.267827	-3.012005
65	6	0	-1.639347	-0.597534	-1.591631
66	6	0	-3.597844	-0.404641	2.740755
67	6	0	-0.114708	-3.925001	-0.485140
68	6	0	1.187448	-4.294761	-2.463824
69	6	0	3.038031	-2.466318	1.024426
70	6	0	1.730895	-2.991629	0.931374
71	6	0	2.099717	-3.590444	-1.448038
72	6	0	0.122418	-4.971271	-1.588048
73	6	0	-1.159891	-2.887653	-0.974973
74	6	0	0.806462	-2.991975	2.118611
75	8	0	1.709428	-0.306614	-0.184710
76	6	0	2.824691	-0.489448	0.413402
77	6	0	2.880837	0.244253	1.776877
78	8	0	3.410052	1.346148	1.889911

79	8	0	2.195669	-0.316023	2.766097
80	6	0	2.064422	0.460882	3.983151
81	1	0	3.050361	0.657281	4.409437
82	1	0	1.469946	-0.159063	4.652901
83	1	0	1.555236	1.402496	3.770669
84	6	0	4.107322	-0.345385	-0.387333
85	6	0	6.418914	-0.064361	-1.956190
86	6	0	5.378502	-0.406238	0.201613
87	6	0	4.008440	-0.135929	-1.768056
88	6	0	5.157047	0.002168	-2.549325
89	6	0	6.525774	-0.267061	-0.576939
90	1	0	5.476717	-0.561486	1.273210
91	1	0	3.019559	-0.080222	-2.212996
92	1	0	5.066949	0.162255	-3.620527
93	1	0	7.504700	-0.317235	-0.108509
94	1	0	7.314393	0.040490	-2.562083

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