catalysts

Supplementary Materials: Stereoselective Enzymatic Reduction of 1,4-Diaryl-1,4-Diones to the Corresponding Diols Employing Alcohol Dehydrogenases

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1. Substrates and products studied in this contribution

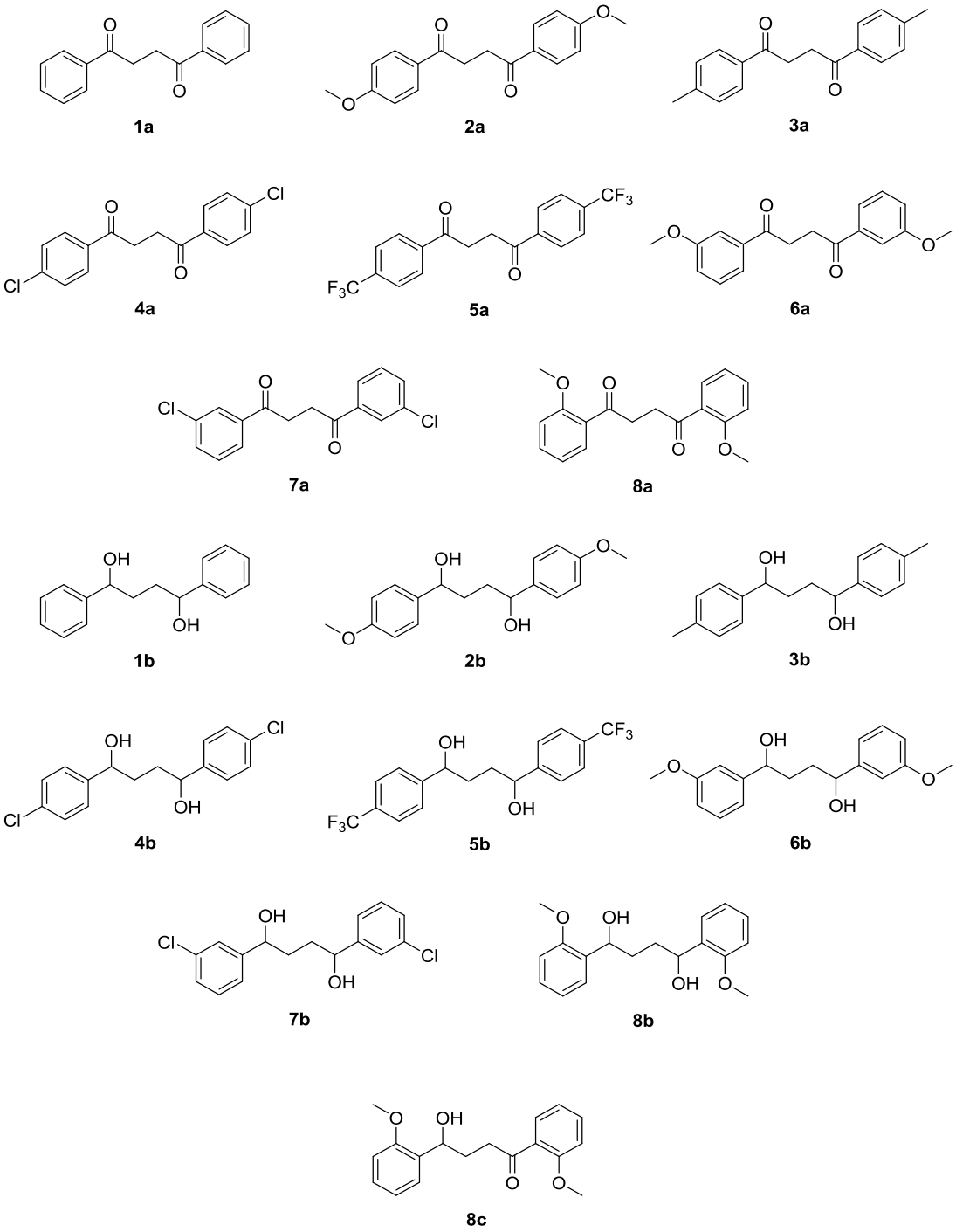


Figure S1. (**a**) 1,4-Diaryl-1,4-diketones **1-8a** (**b**) 1,4-Diaryl-1,4-diols **1-8b** (**c**) 1,4-Diaryl-4-hydroxy ketone **8c.**

2. HPLC separations

For the determination of bioreduction conversions, and the diastereomeric and enantiomeric excesses of compounds **1**-**8b** (Table S1), the following columns were employed: Chiralpak AD-H (25 cm × 4.6 mm) and Chiralpak IA (25 cm × 4.6 mm), both from Daicel.

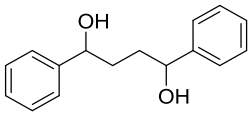
Table S1. Analytical separation of diketones **1-8a** and diols **1-8b.**

Compound	Column	Eluent[a]	Temperature (°C)	Flow (mL/min)	Time (min)
1a	IA	85:15	30	1.0	10.1
2a	IA	90:10	30	1.0	48.5
3a	IA	90:10	30	1.0	19.0
4a	AD-H	90:10	30	0.8	25.9
5a	IA	95:5	30	0.8	19.9
6a	IA	90:10	30	1.0	22.7
7a	AD-H	90:10	40	0.8	15.9
8a	AD-H	90:10	30	1.0	15.8
(±)-**1b**	IA	85:15	30	1.0	9.6, 11.2, 11.7
(±)-**2b**	IA	90:10	30	1.0	29.6, 37.4, 38.3
(±)-**3b**	IA	90:10	30	1.0	21.8, 25.3, 27.5
(±)-**4b**	AD-H	90:10	30	0.8	21.1, 24.3, 25.4
(±)-**5b**	IA	95:5	30	0.8	27.5, 30.5, 31.7
(±)-**6b**	IA	90:10	30	1.0	30.7, 42.7
(±)-**7b**	AD-H	90:10	40	0.8	17.8, 24.8, 27.1
(±)-**8b**	AD-H	90:10	30	1.0	38.1, 51.1, 57.6
(±)-**8c**	AD-H	90:10	30	1.0	25.0, 29.6

[a] Measurements were performed in mixtures of *n*-hexane/2-propanol, and 30 ºC for the column temperature was set up in all cases. All measurements were carried out with an isocratic eluent.

3. HPLC chromatograms of optically active 1,4-diaryl-1,4-diols

1,4-Diphenylbutane-1,4-diol (1b)



Analytical data for 1,4-diol 1b

Column: Chiralpak IA Eluent: *n*-hexane/2-propanol 85:15

Flow: 1.0 mL/min Temperature: 30 °C

Retention times: t_R (*S*,*S*) = 9.6 min, t_R (*R*,*S*) = 11.2 min and t_R (*R*,*R*) = 11.7 min

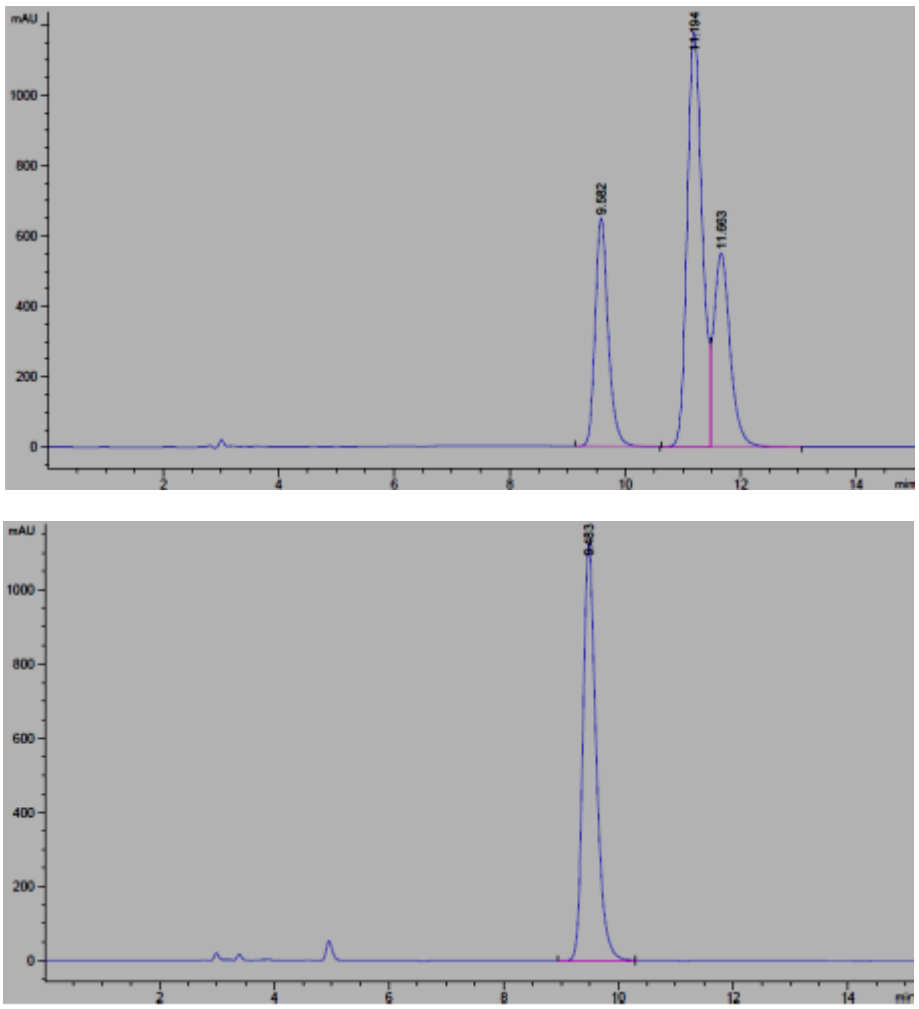
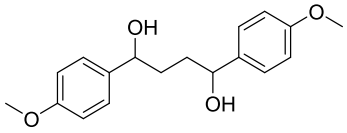


Figure S2. (top) HPLC separation for (±)-1b (down) (–)-(1*S*,4*S*)-1b in >99% *de* and >99% *ee*.

1,4-Bis(4-methoxyphenyl)butane-1,4-diol (2b)



Analytical data for 1,4-diol 2b

Column: Chiralpak IA Eluent: *n*-hexane/2-propanol 90:10

Flow: 1.0 mL/min Temperature: 30 °C

Retention times: t_R (*S*,*S*) = 29.6 min, t_R (*R*,*S*) = 37.4 min and t_R (*R*,*R*) = 38.3 min

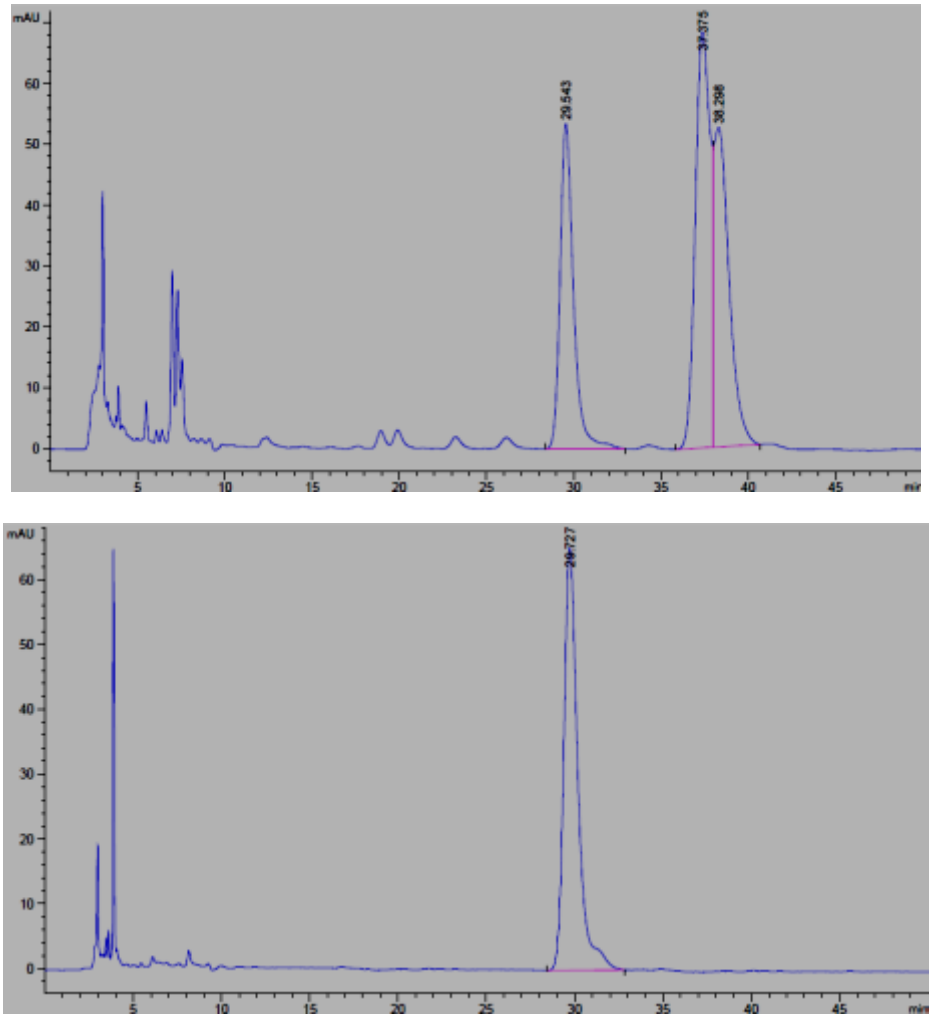
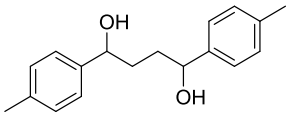


Figure S3. (top) HPLC separation for (±)-2b (down) (–)-(1*S*,4*S*)-2b in >99% *de* and >99% *ee*.

1,4-Bis(4-methylphenyl)butane-1,4-diol (3b)



Analytical data for 1,4-diol 3b

Column: Chiralpak IA Eluent: *n*-hexane/2-propanol 90:10

Flow: 1.0 mL/min Temperature: 30 °C

Retention times: t_R (*S*,*S*) = 21.8 min, t_R (*R*,*R*) = 25.3 min and t_R (*R*,*S*) = 27.5 min

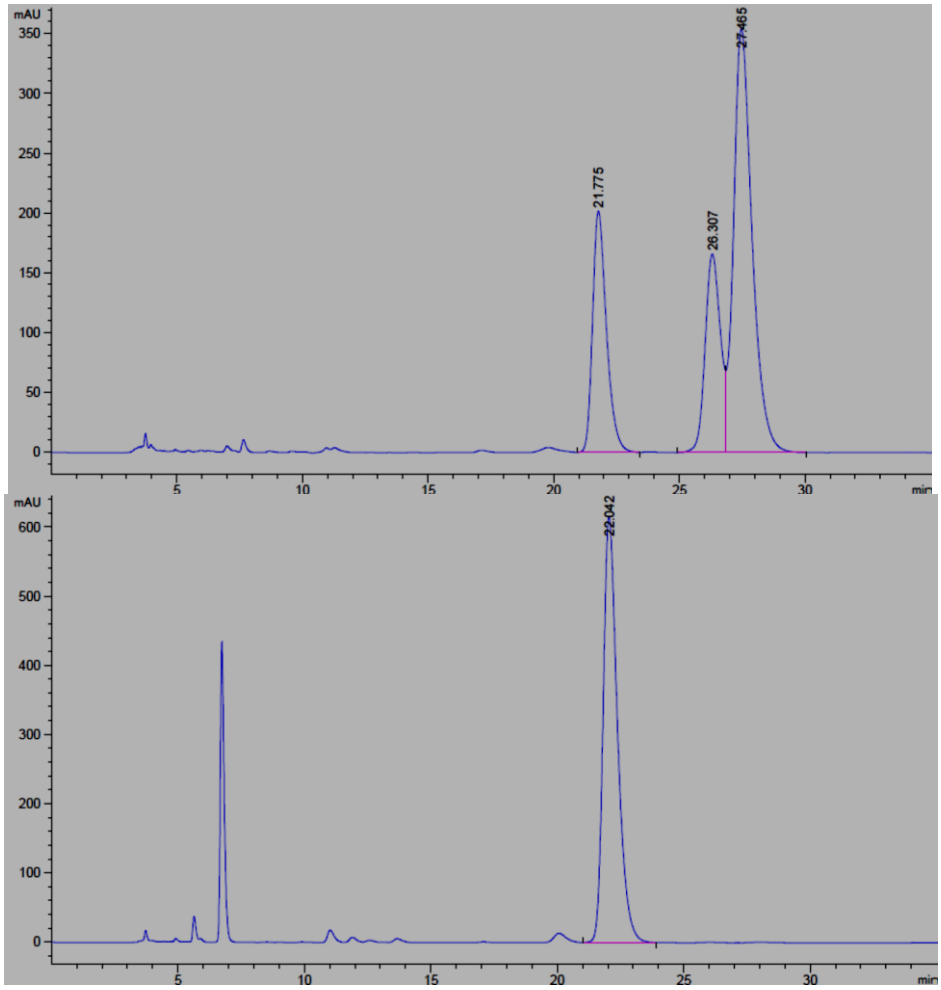
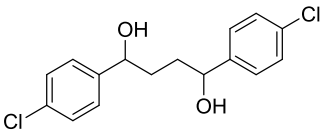


Figure S4. (top) HPLC separation for (±)-3b (down) (–)-(1*S*,4*S*)-3b in >99% *de* and >99% *ee*.

1,4-Bis(4-chlorophenyl)butane-1,4-diol (4b)



Analytical data for 1,4-diol 4b

Column: Chiralpak AD-H Eluent: *n*-hexane/2-propanol 90:10

Flow: 0.8 mL/min Temperature: 30 °C

Retention times: t_R (*S*,*S*) = 21.1 min, t_R (*R*,*S*) = 24.3 min and t_R (*R*,*R*) = 25.4 min

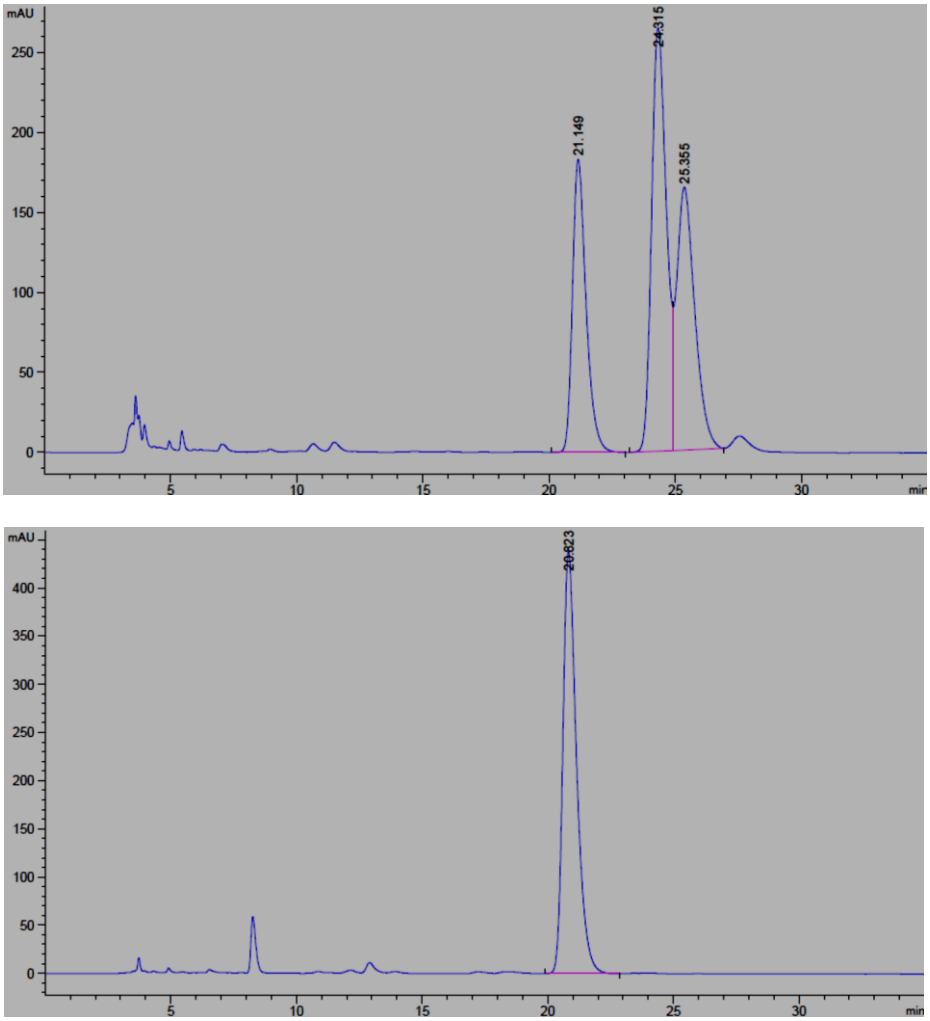
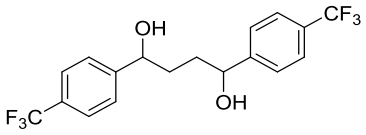


Figure S5. (top) HPLC separation for (±)-4b (down) (–)-(1*S*,4*S*)-4b in >99% *de* and >99% *ee*.

1,4-Bis[4-(trifluoromethyl)phenyl]butane-1,4-diol (5b)



Analytical data for 1,4-diol 5b

Column: Chiralpak IA Eluent: *n*-hexane/2-propanol 95:5

Flow: 0.8 mL/min Temperature: 30 °C

Retention times: t_R (*S*,*S*) = 27.5 min, t_R (*R*,*R*) = 30.5 min and t_R (*R*,*S*) = 31.7 min

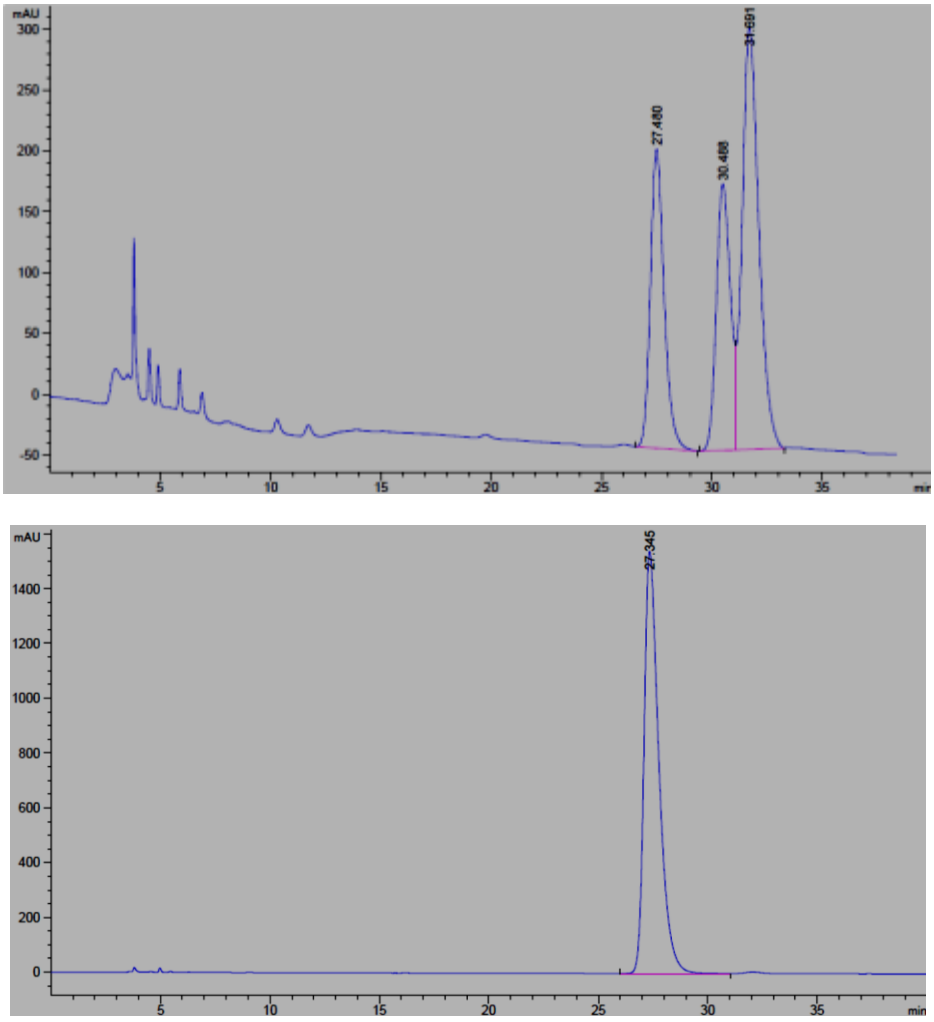
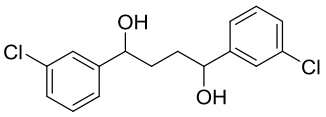


Figure S6. (top) **HPLC separation for (±)-5b** (down) **(–)-(1*S*,4*S*)-5b in >99% *de* and >99% *ee*.**

1,4-Bis(3-chlorophenyl)butane-1,4-diol (7b)



Analytical data for 1,4-diol 7b

Column: Chiralpak AD-H Eluent: *n*-hexane/2-propanol 90:10

Flow: 0.8 mL/min Temperature: 40 °C

Retention times: t_R (*S*,*S*) = 17.8 min, t_R (*R*,*S*) = 24.8 min and t_R (*R*,*R*) = 27.1 min

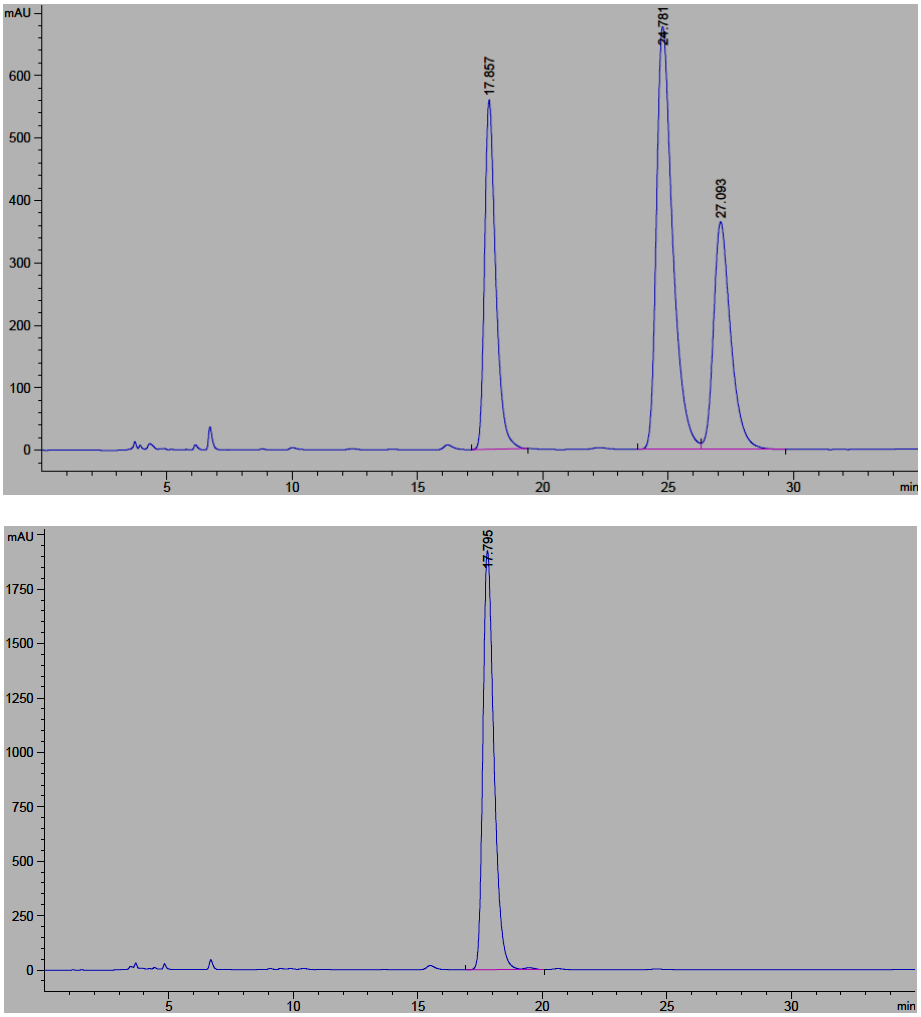
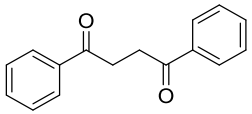


Figure S7. (top) HPLC separation for (±)-7b (down) (–)-(1*S*,4*S*)-7b in >99% *de* and >99% *ee*.

4. NMR spectra



1a

^{1}H-NMR

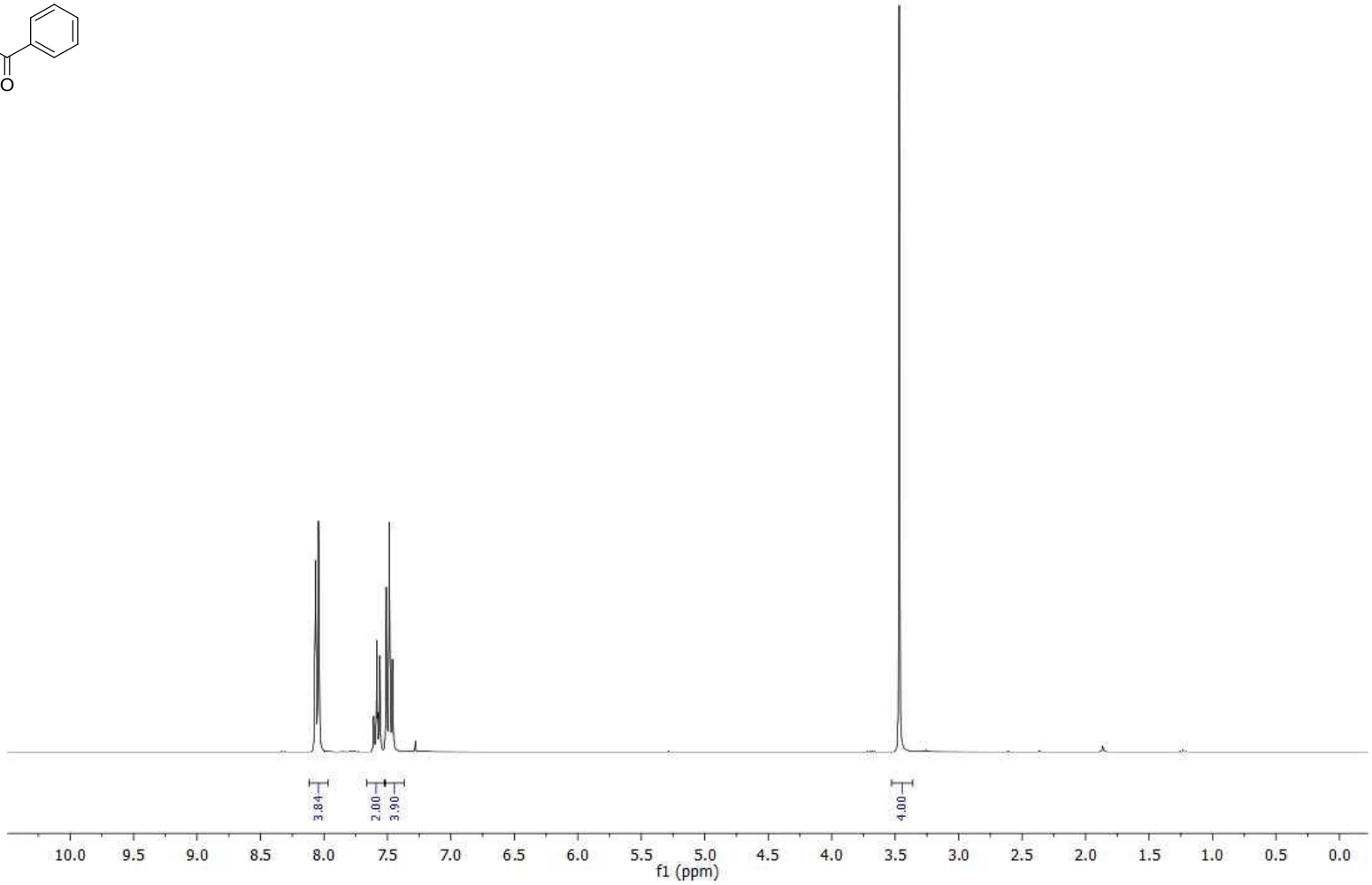
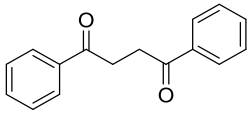


Figure S8. ^{1}H-NMR of **1a.**



1a

^{13}C-NMR

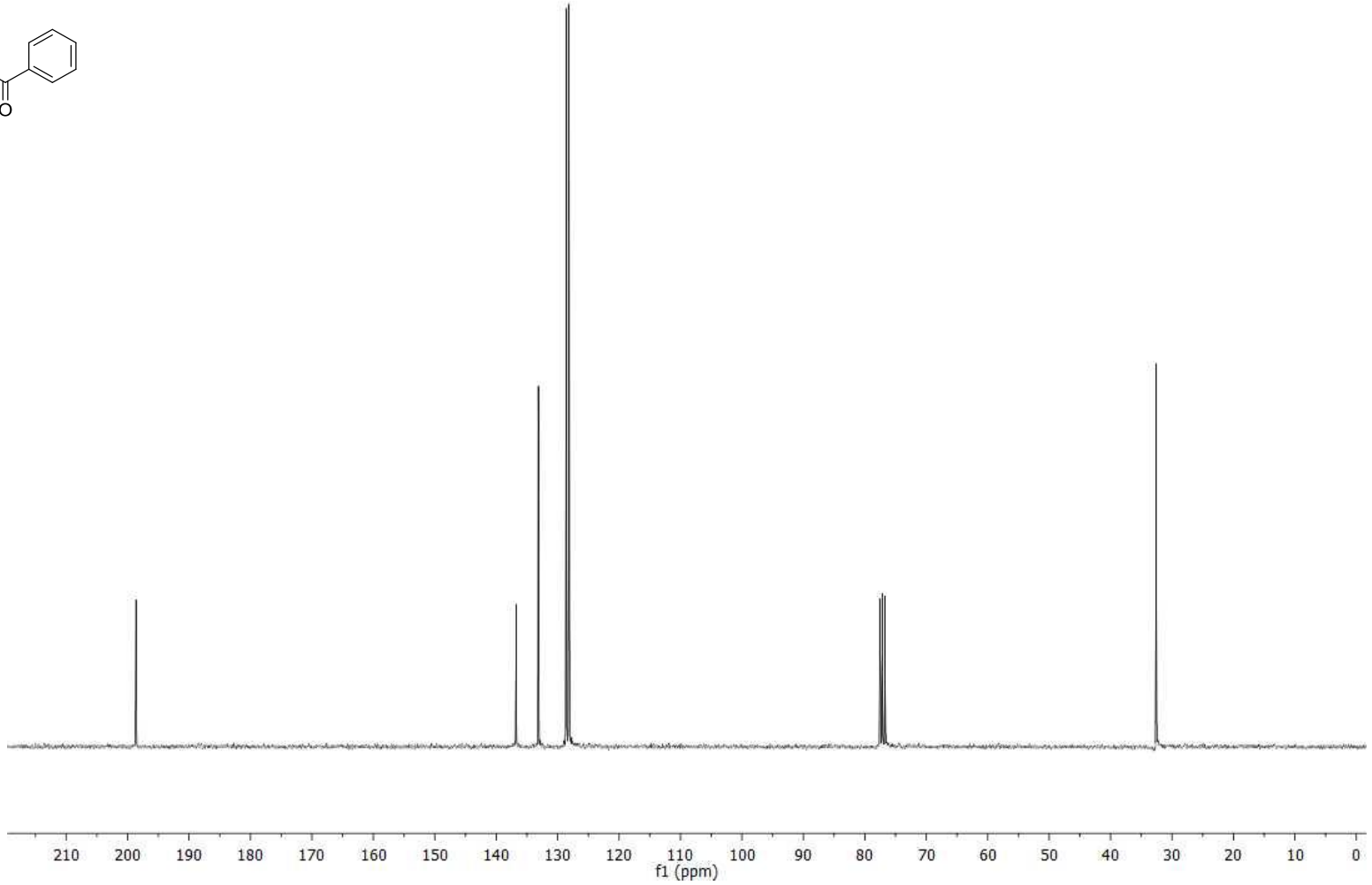
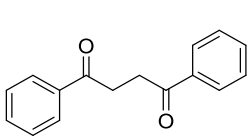


Figure S9. ^{13}C-NMR of **1a.**



1a

DEPT

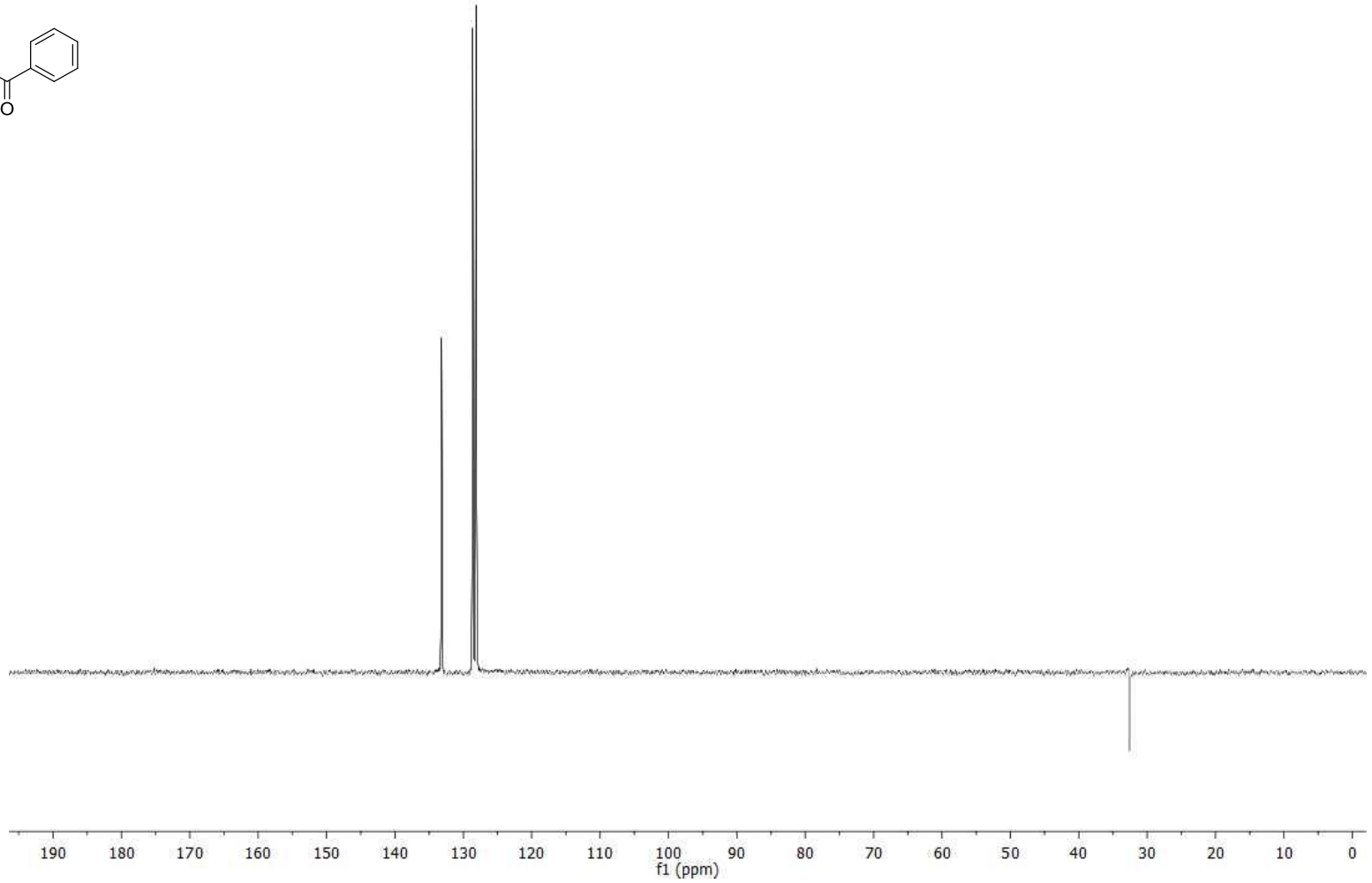
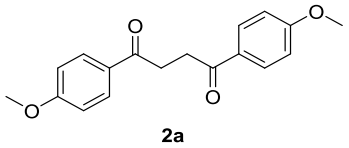


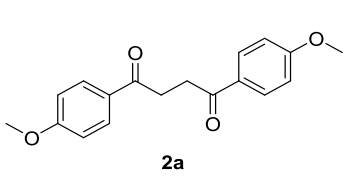
Figure S10. DEPT of **1a.**



2a

^{1}H-NMR

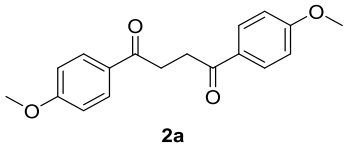
Figure S11. ^{1}H-NMR of **2a.**



2a

^{13}C-NMR

Figure S12. ^{13}C-NMR of **2a.**



2a

DEPT

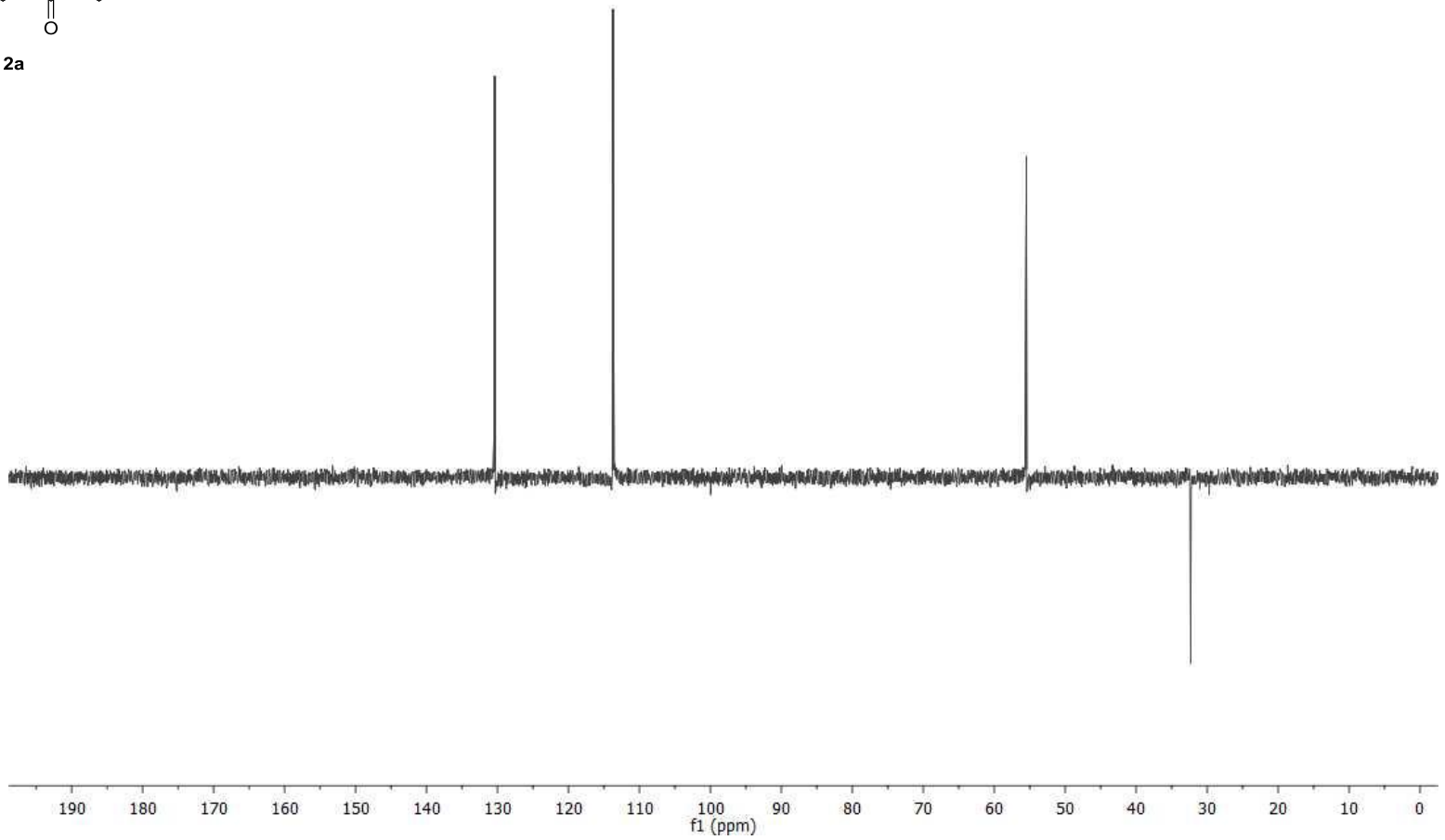
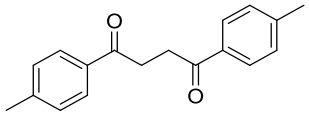


Figure S13. DEPT of **2a.**



3a

^{1}H-NMR

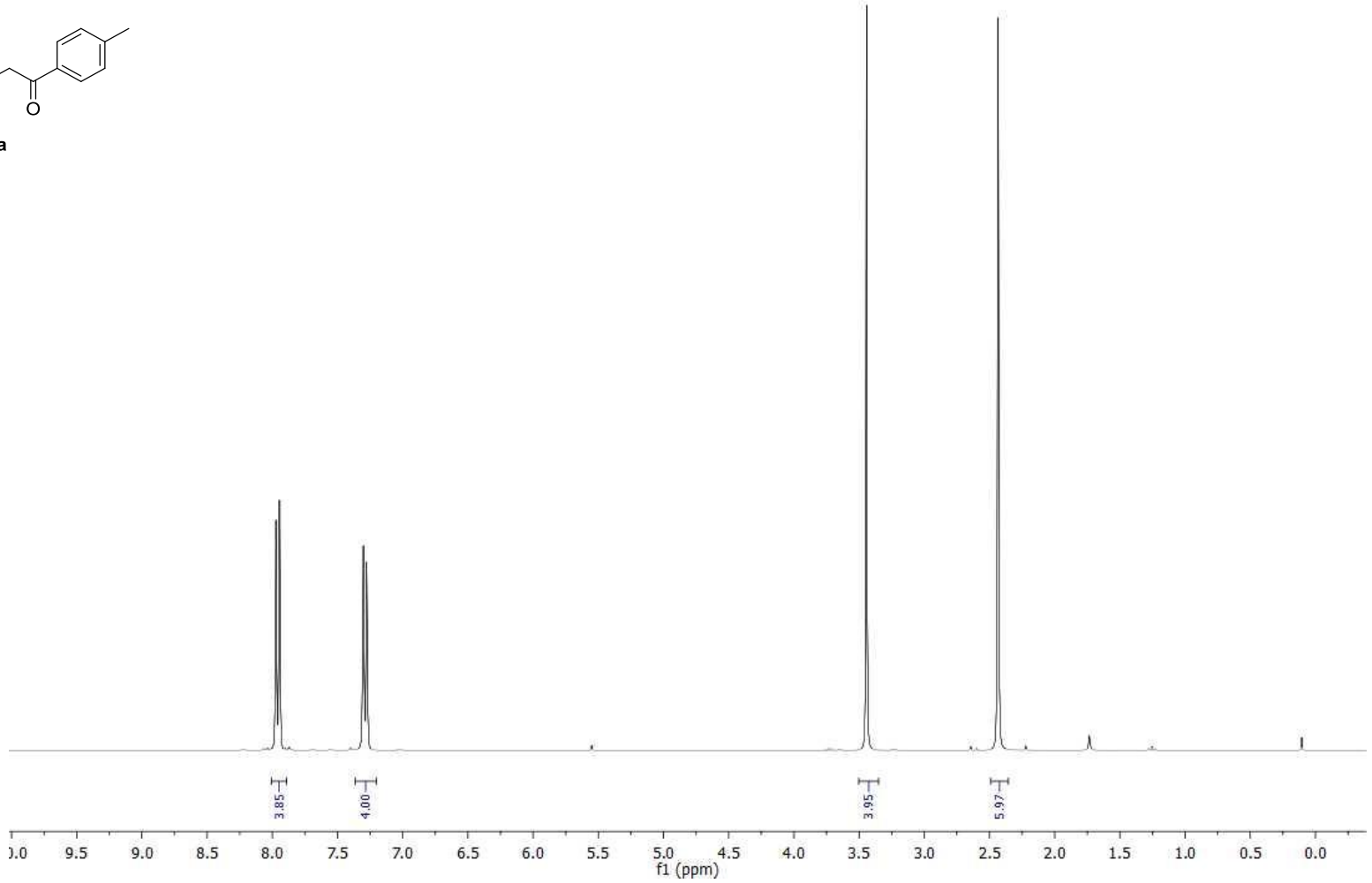
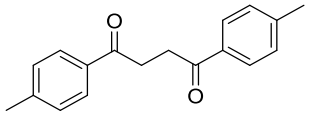


Figure S14. ^{1}H-NMR of **3a.**



3a

^{13}C-NMR

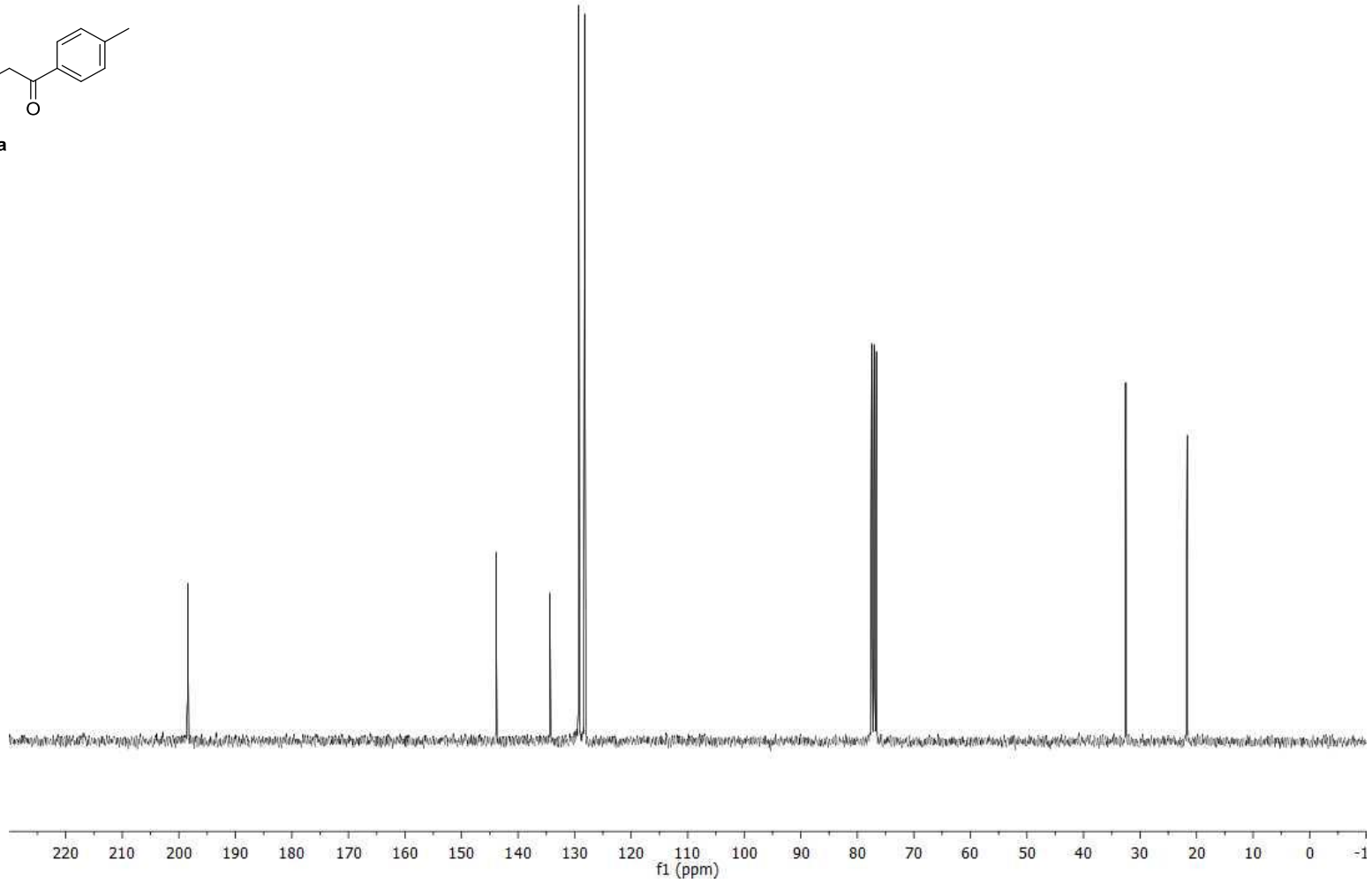
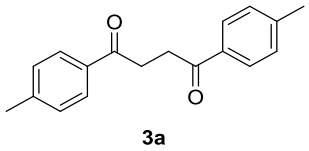


Figure S15. ^{13}C-NMR of **3a.**



3a

DEPT

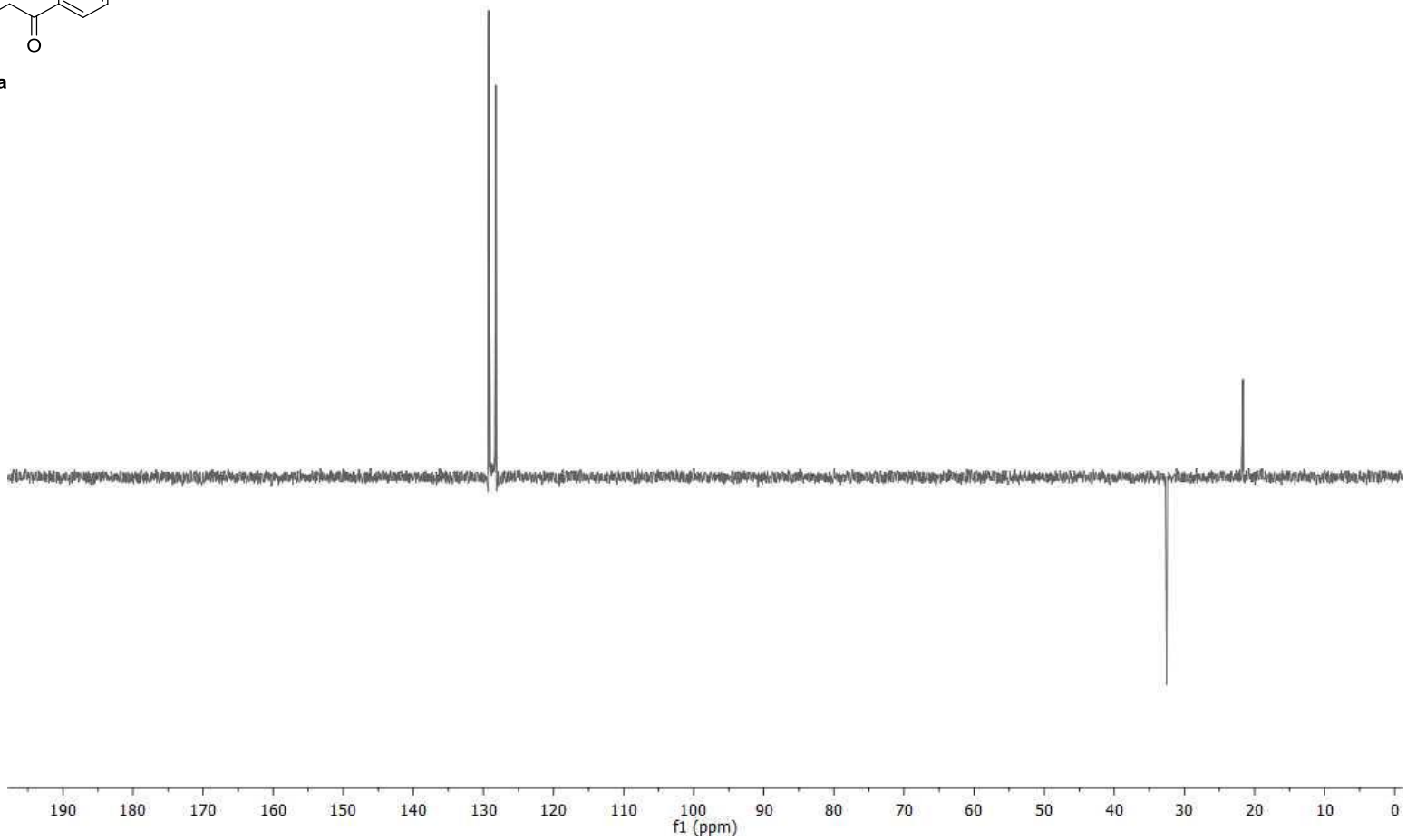
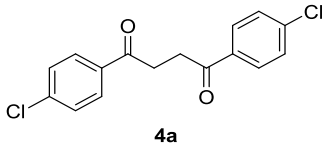


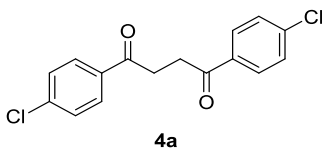
Figure S16. DEPT of **3a.**



4a

^{1}H-NMR

Figure S17. ^{1}H-NMR of **4a.**



4a

^{13}C-NMR

Figure S18. ^{13}C-NMR of **4a.**

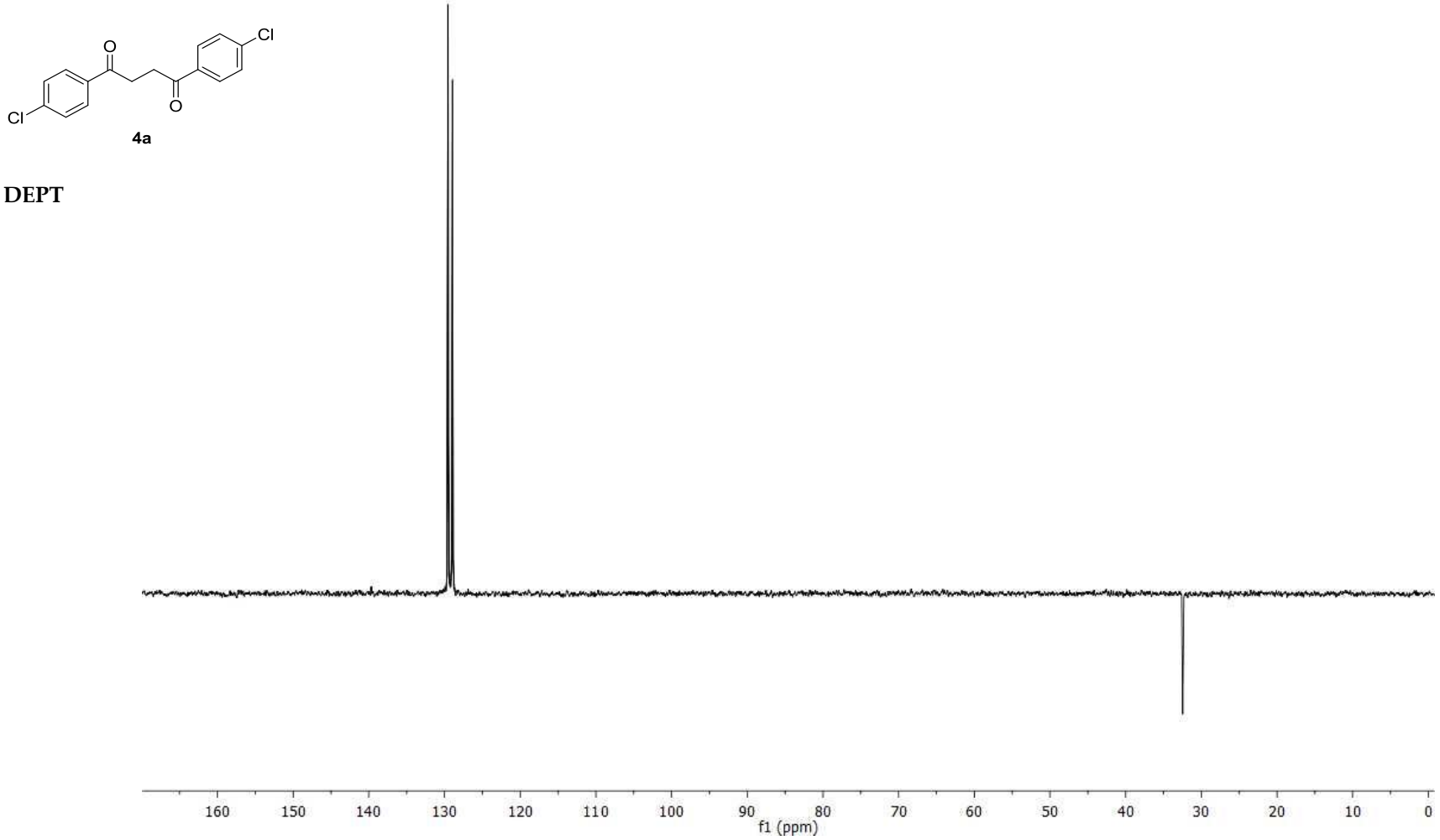
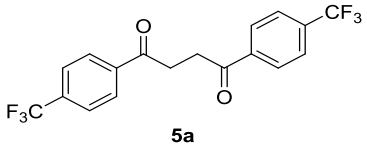


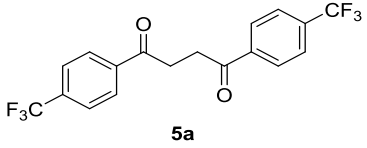
Figure S19. DEPT of **4a.**



5a

^{1}H-NMR

Figure S20. ^{1}H-NMR of **5a.**



5a

^{13}C-NMR

Figure S21. ^{13}C-NMR of **5a.**

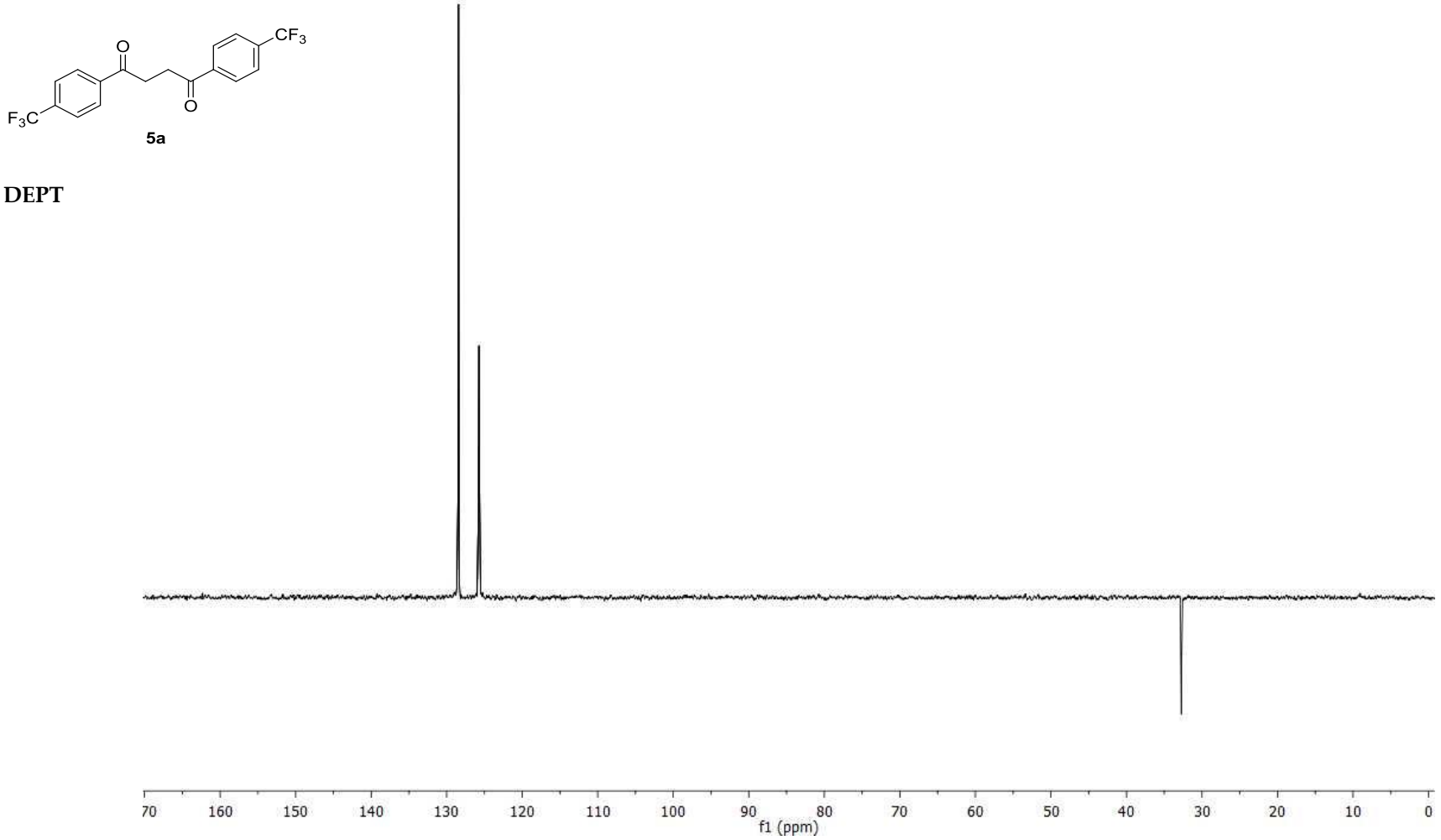
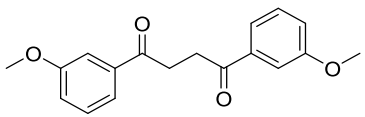


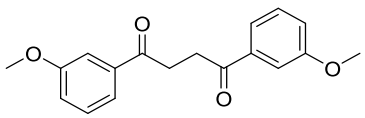
Figure S22. DEPT of **5a.**



6a

^{1}H-NMR

Figure S23. ^{1}H-NMR of **6a.**



6a

^{13}C-NMR

Figure S24. ^{13}C-NMR of **6a.**

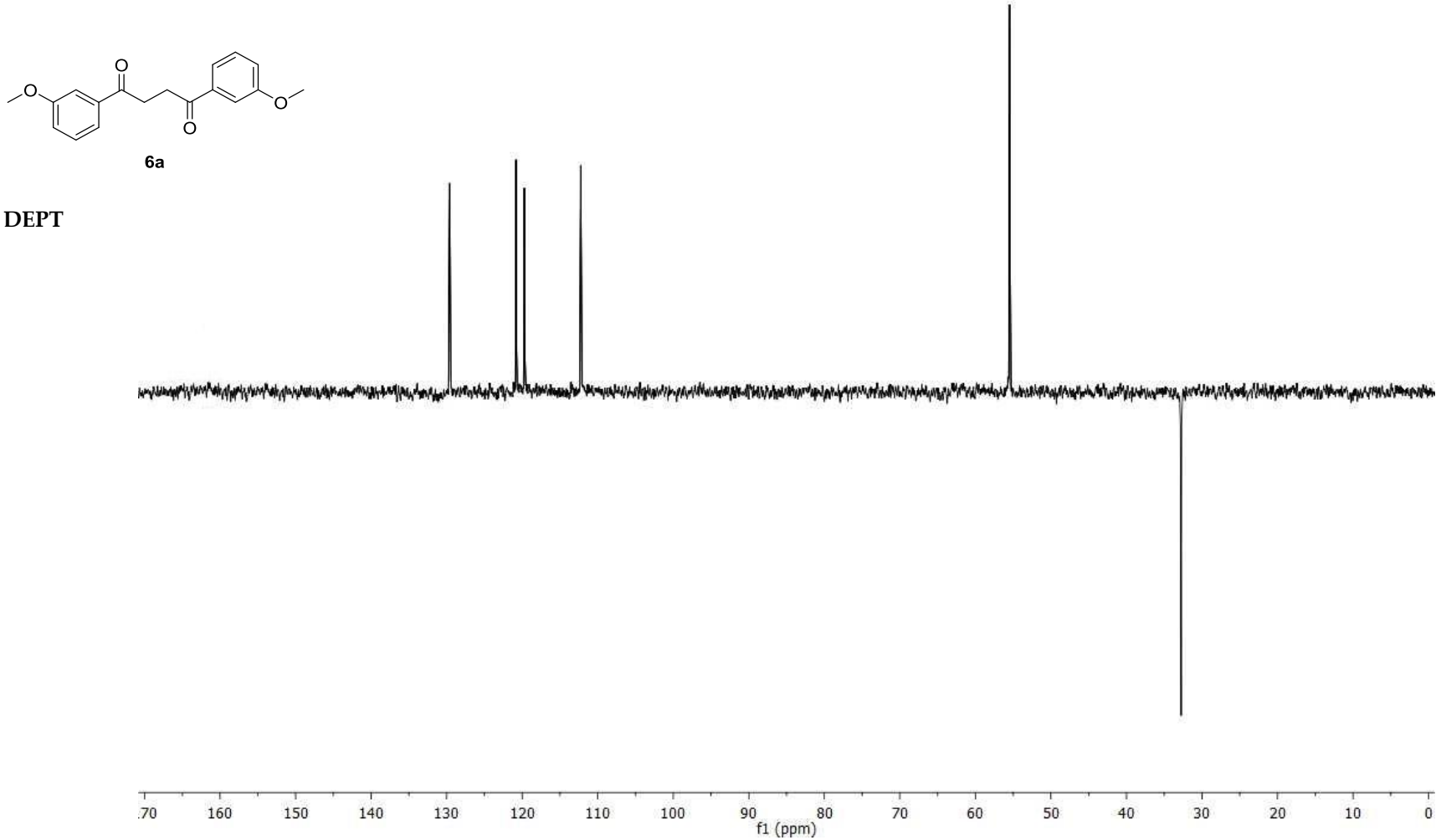
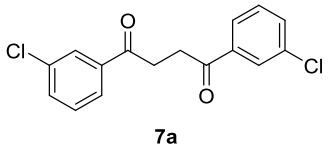


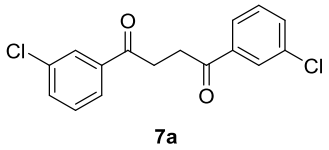
Figure S25. DEPT of **6a.**



7a

^{1}H-NMR

Figure S26. ^{1}H-NMR of **7a.**



7a

^{13}C-NMR

Figure S27. ^{13}C-NMR of **7a.**

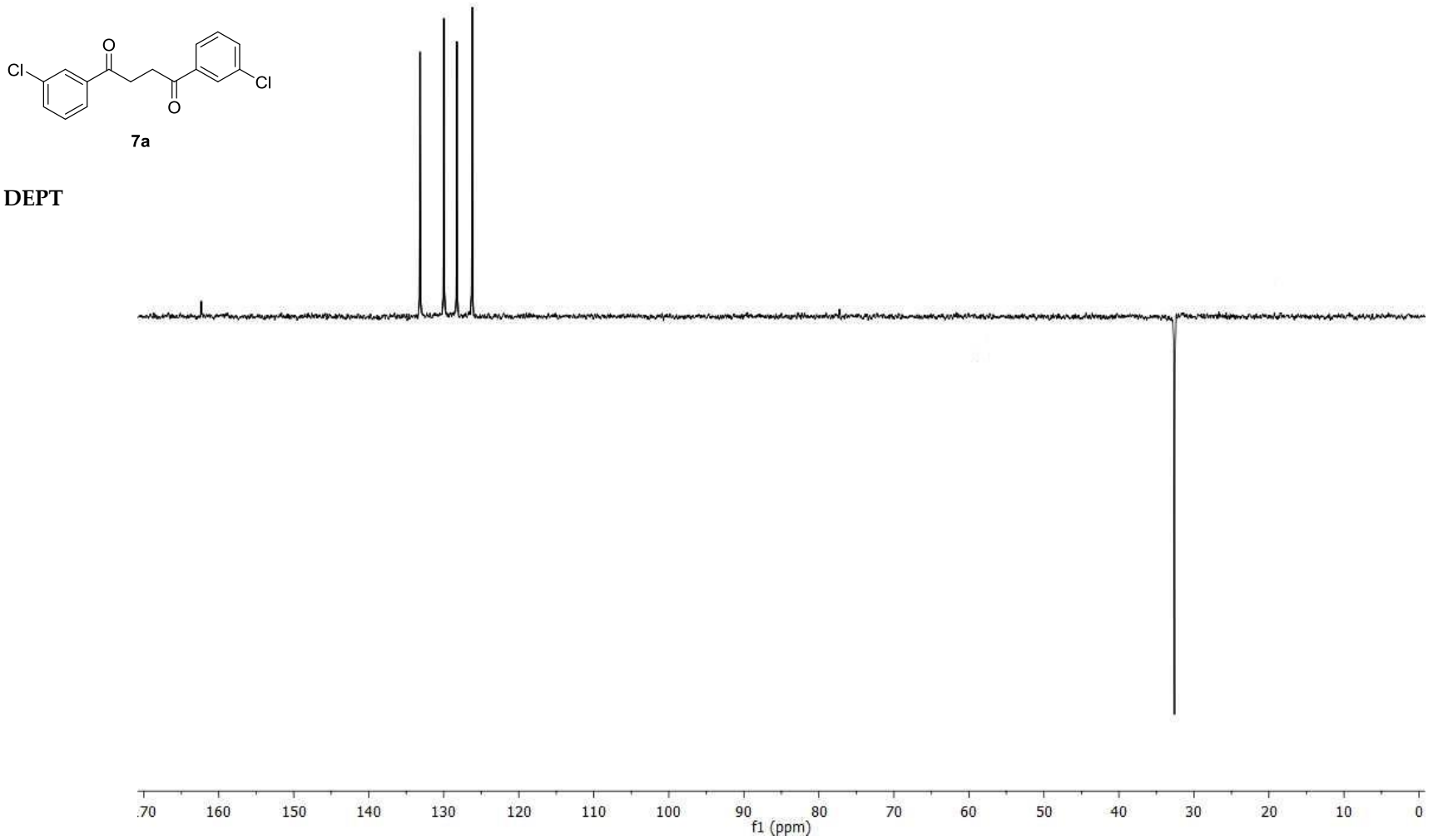
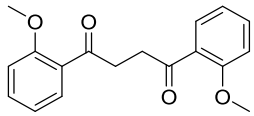


Figure S28. DEPT of **7a.**



8a

^{1}H-NMR

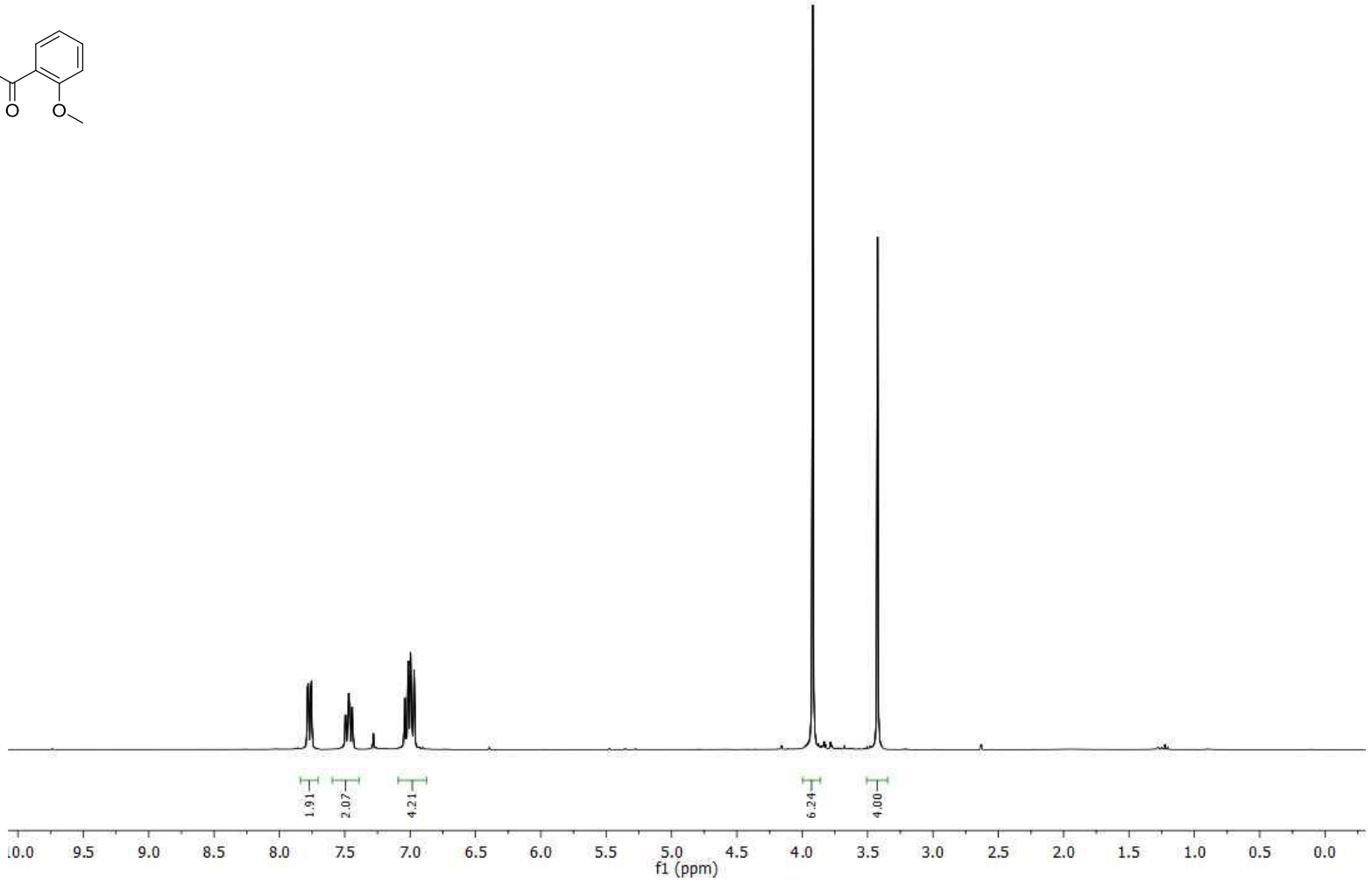
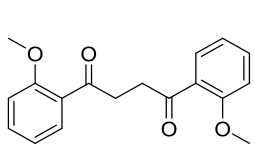


Figure S29. ^{1}H-NMR of **8a.**



8a

^{13}C-NMR

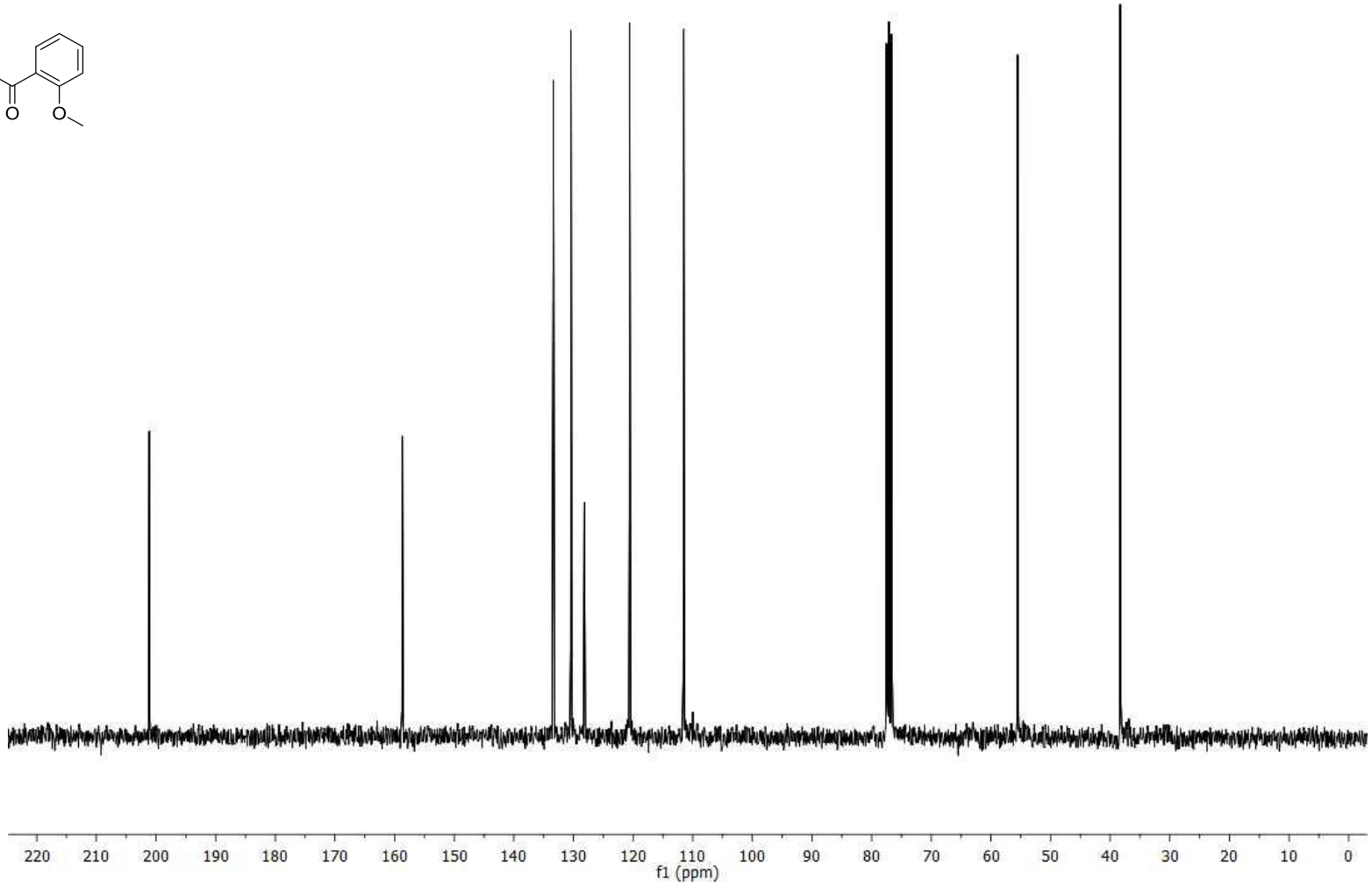


Figure S30. ^{13}C-NMR of **8a.**

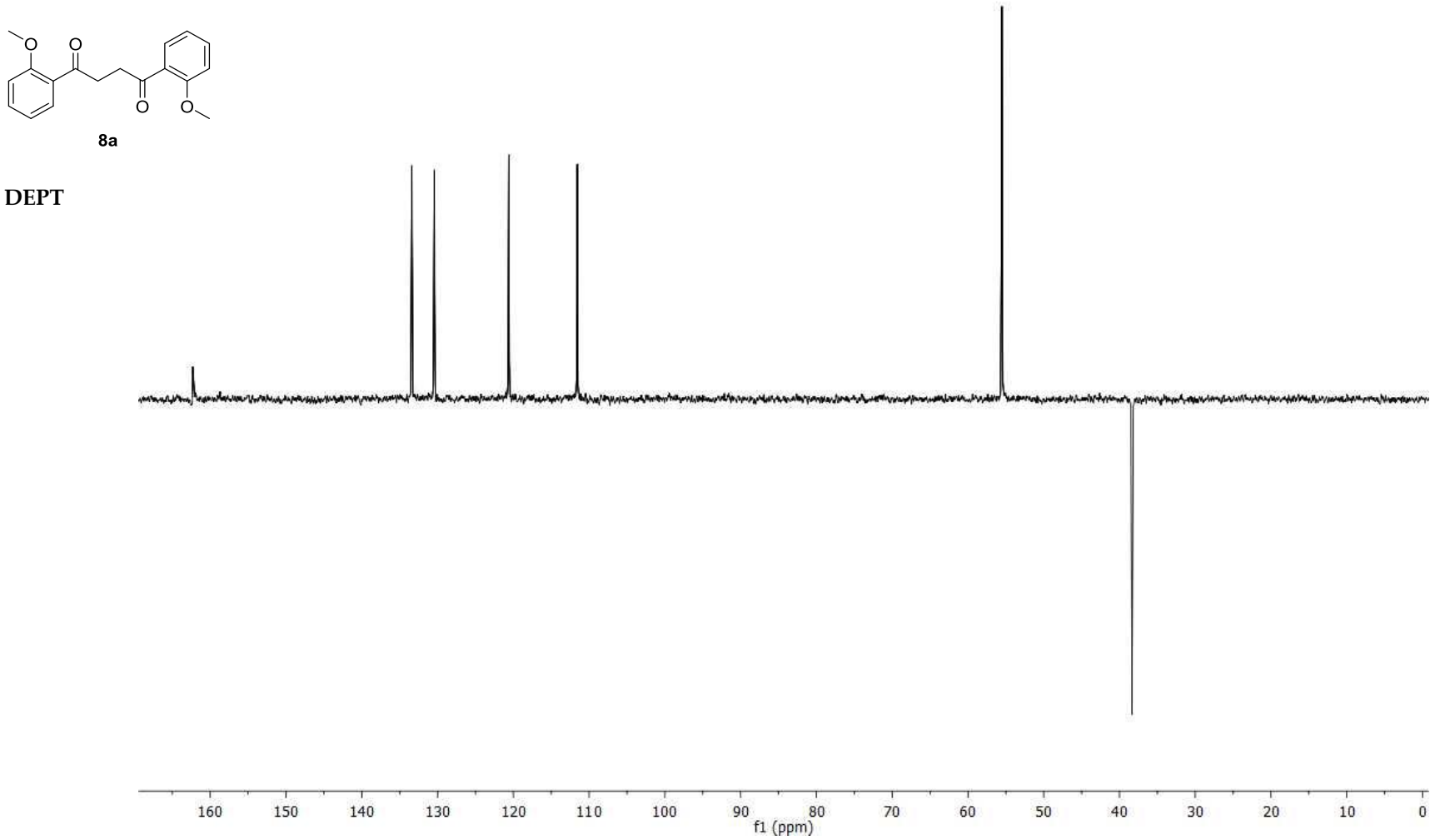
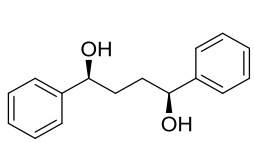


Figure S31. DEPT of **8a.**



(-)-(1*S*,4*S*)-**1b**

^{1}H-NMR

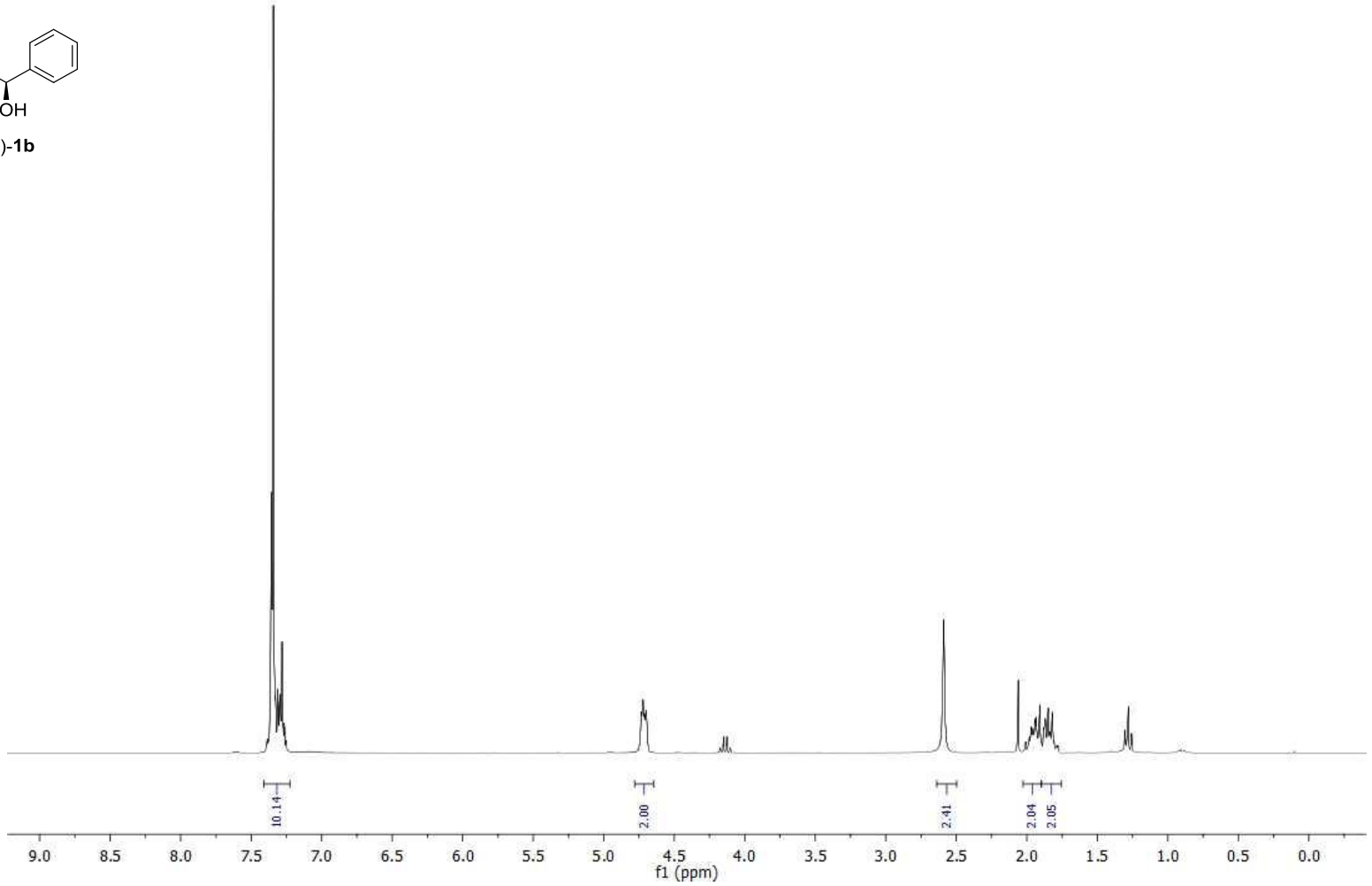
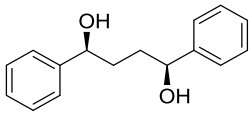


Figure S32. ^{1}H-NMR of (–)-(1S,4S)-**1b.**



(-)-(1*S*,4*S*)-**1b**

^{13}C-NMR

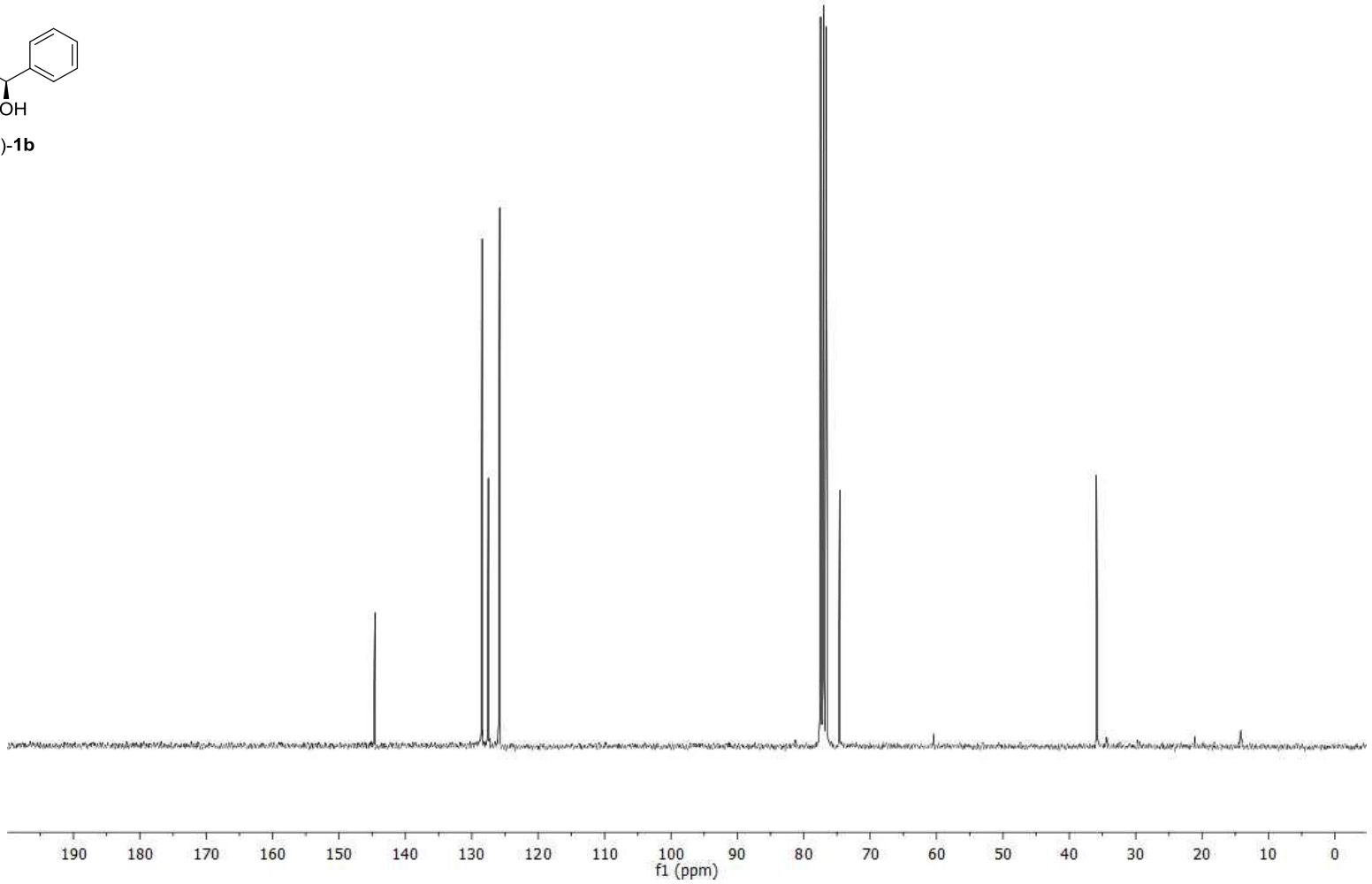
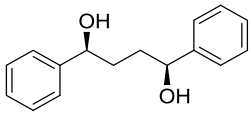


Figure S33. ^{13}C-NMR of (–)-(1S,4S)-**1b.**



(-)-(1*S*,4*S*)-**1b**

DEPT

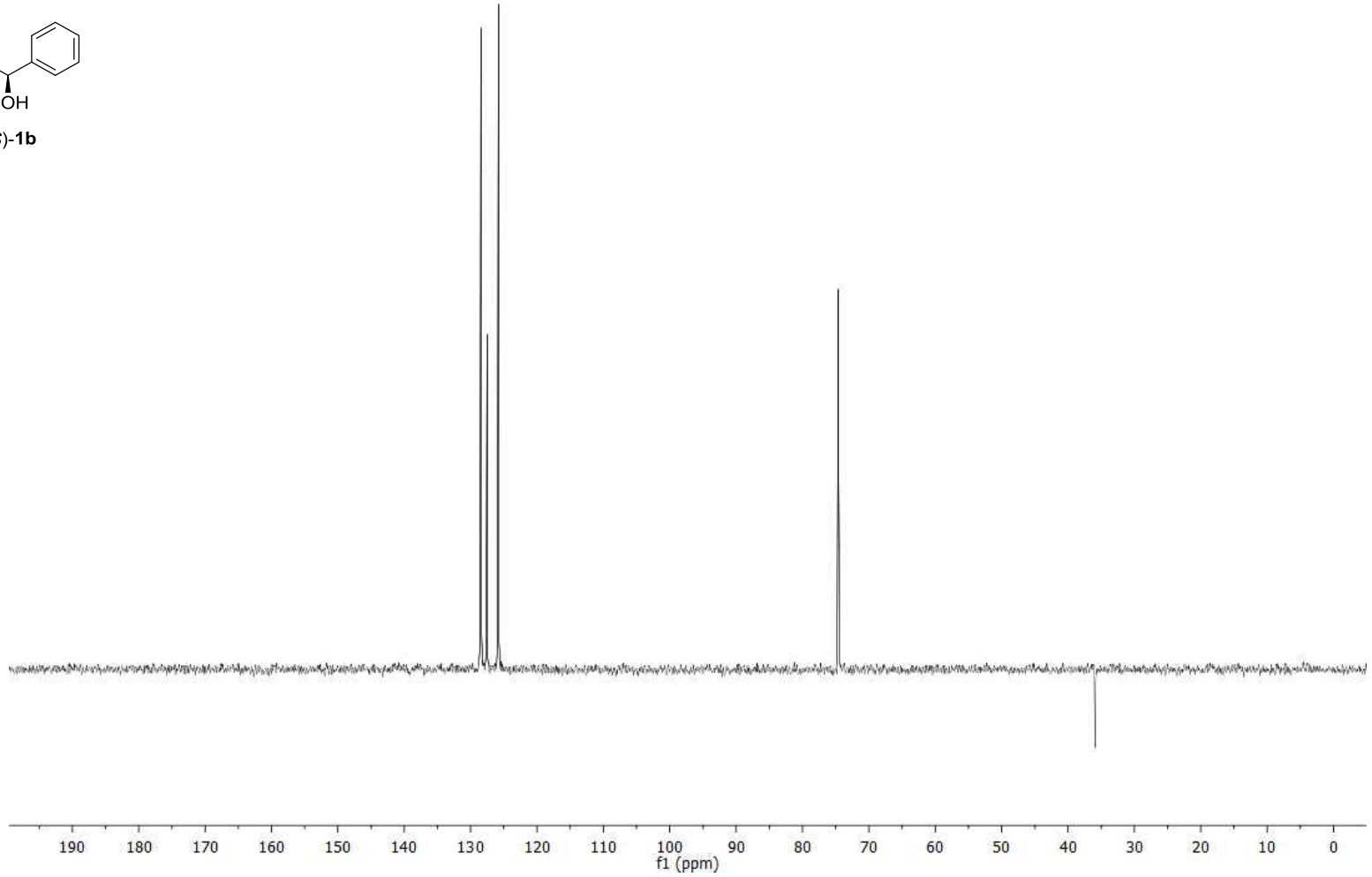
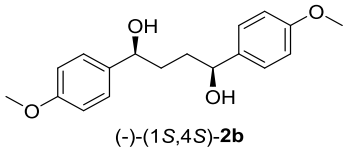


Figure S34. DEPT of (–)-(1S,4S)-**1b.**



(-)-(1*S*,4*S*)-**2b**

^{1}H-NMR

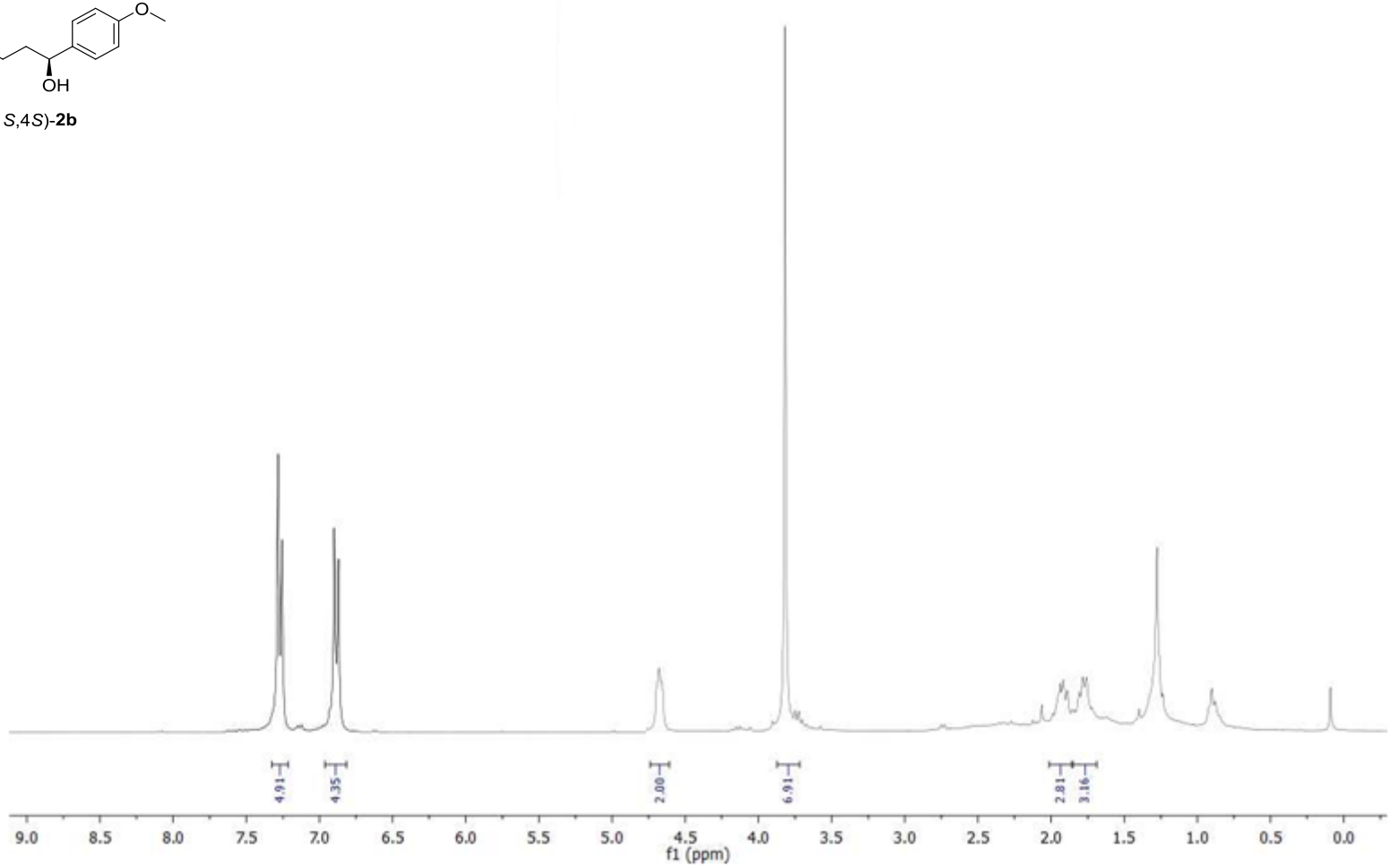
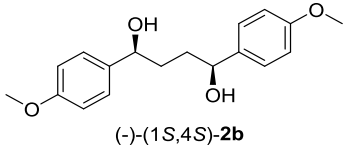


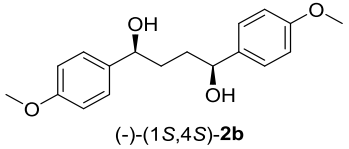
Figure S35. ^{1}H-NMR of (–)-(1S,4S)-**2b.**



(-)-(1*S*,4*S*)-**2b**

^{13}C-NMR

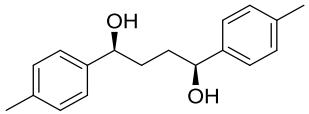
Figure S36. ^{13}C-NMR of (–)-(1S,4S)-**2b.**



(-)-(1*S*,4*S*)-**2b**

DEPT

Figure S37. DEPT of (–)-(1S,4S)-**2b.**



(-)-(1*S*,4*S*)-**3b**

^{1}H-NMR

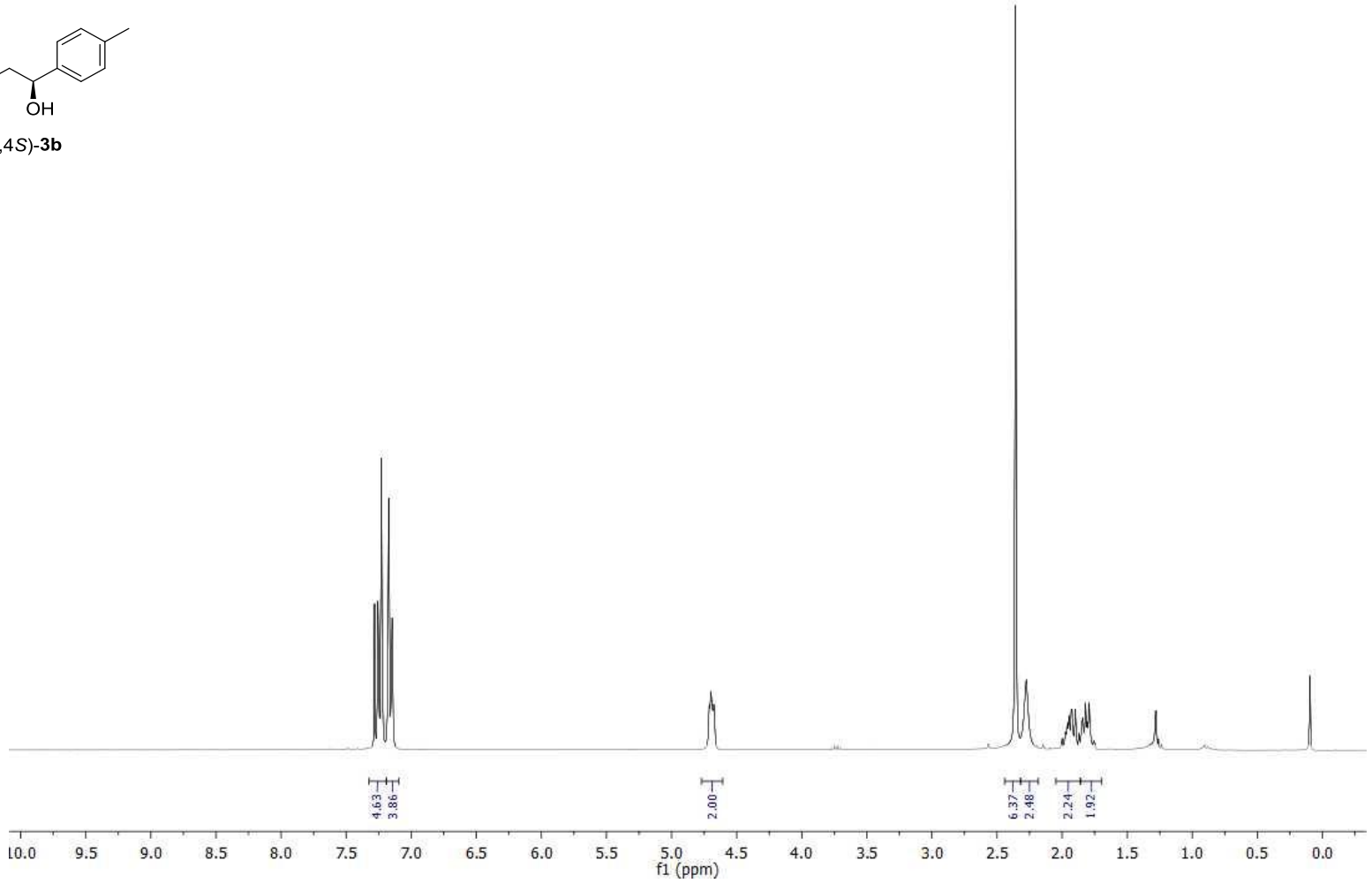
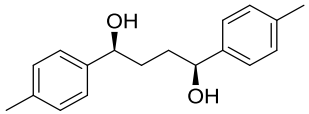


Figure S38. ^{1}H-NMR of (–)-(1S,4S)-**3b.**



(-)-(1*S*,4*S*)-**3b**

^{13}C-NMR

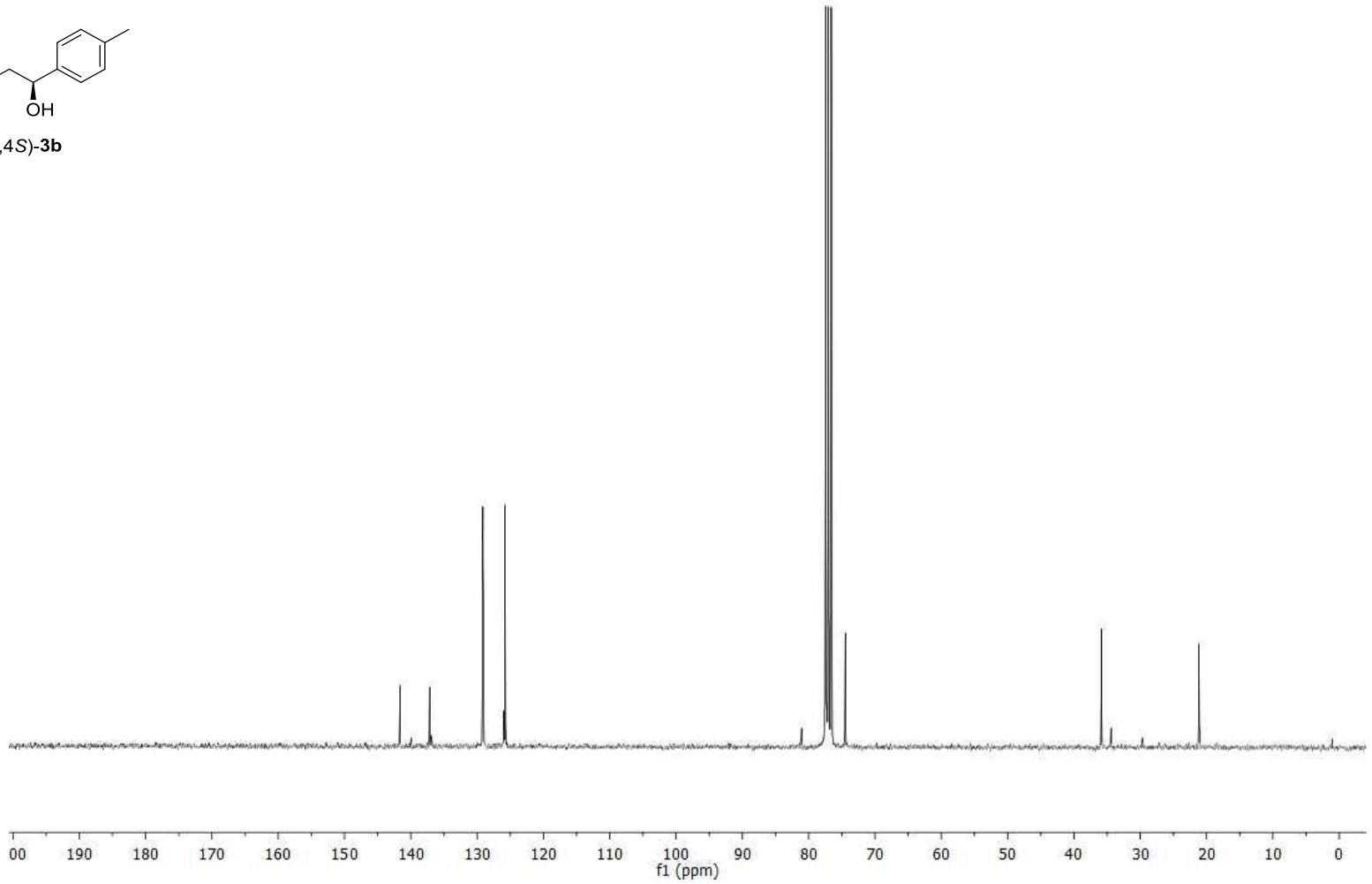
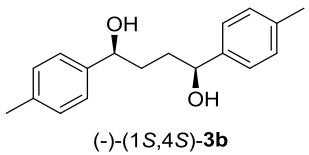


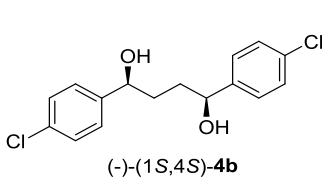
Figure S39. ^{13}C-NMR of (–)-(1S,4S)-**3b.**



(-)-(1*S*,4*S*)-**3b**

DEPT

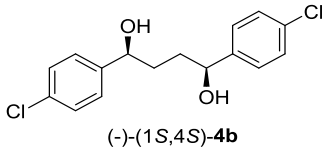
Figure S40. DEPT of (–)-(1S,4S)-**3b.**



(-)-(1*S*,4*S*)-**4b**

^{1}H-NMR

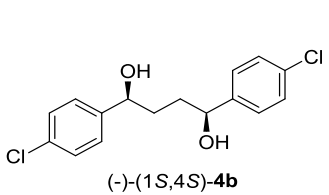
Figure S41. ^{1}H-NMR of (–)-(1S,4S)-**4b.**



(-)-(1*S*,4*S*)-**4b**

^{13}C-NMR

Figure S42. ^{13}C-NMR of (–)-(1S,4S)-**4b.**



(-)-(1*S*,4*S*)-**4b**

DEPT

Figure S43. DEPT of (–)-(1S,4S)-**4b.**

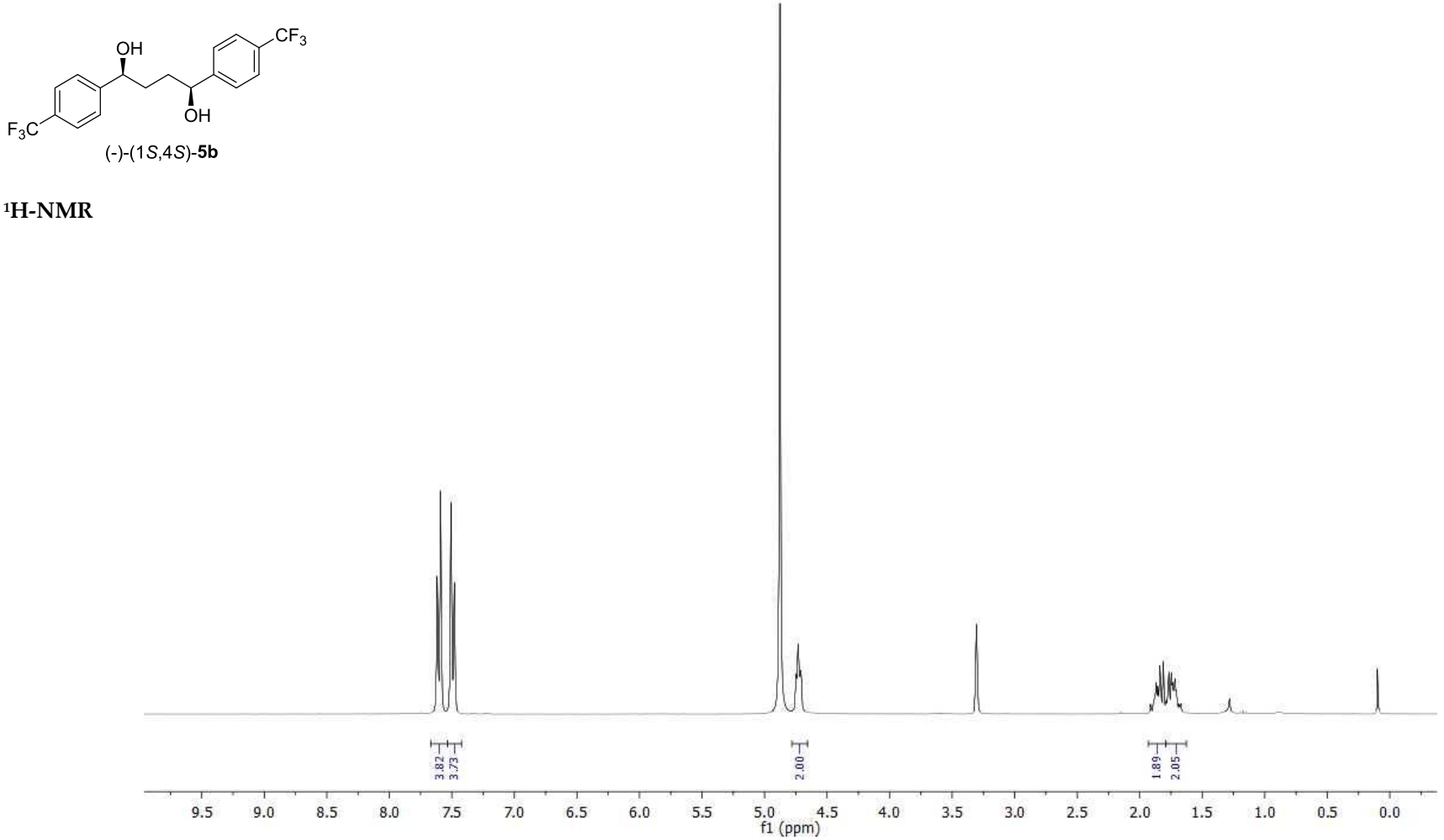
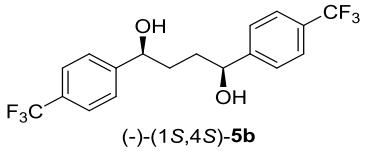


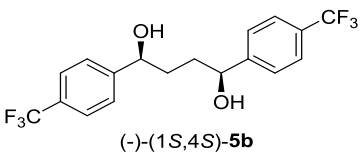
Figure S44. ^{1}H-NMR of (–)-(1S,4S)-**5b.**



(-)-(1*S*,4*S*)-**5b**

^{13}C-NMR

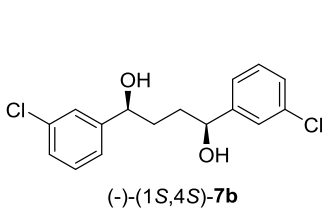
Figure S45. ^{13}C-NMR of (–)-(1S,4S)-**5b.**



(-)-(1*S*,4*S*)-**5b**

DEPT

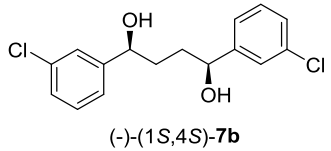
Figure S46. DEPT of (–)-(1S,4S)-**5b.**



(-)-(1*S*,4*S*)-**7b**

^{1}H-NMR

Figure S47. ^{1}H-NMR of (–)-(1S,4S)-**7b.**



(-)-(1*S*,4*S*)-**7b**

^{13}C-NMR

Figure S48. ^{13}C-NMR of (–)-(1S,4S)-**7b.**

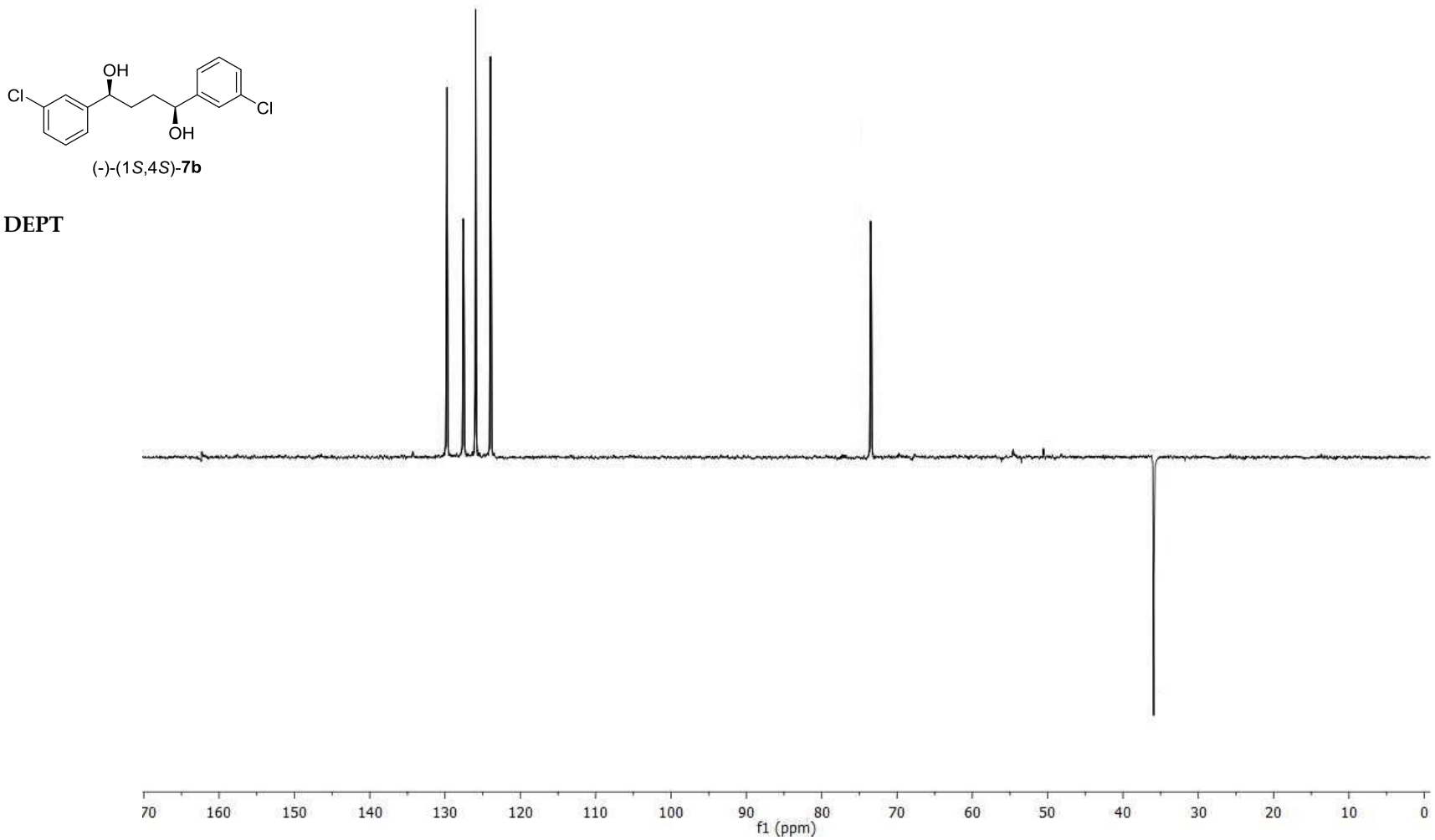
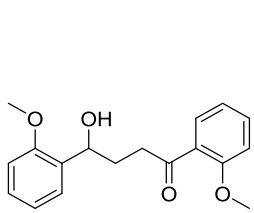


Figure S49. ^{1}H-NMR of (–)-(1S,4S)-**7b.**



8c

^{1}H-NMR

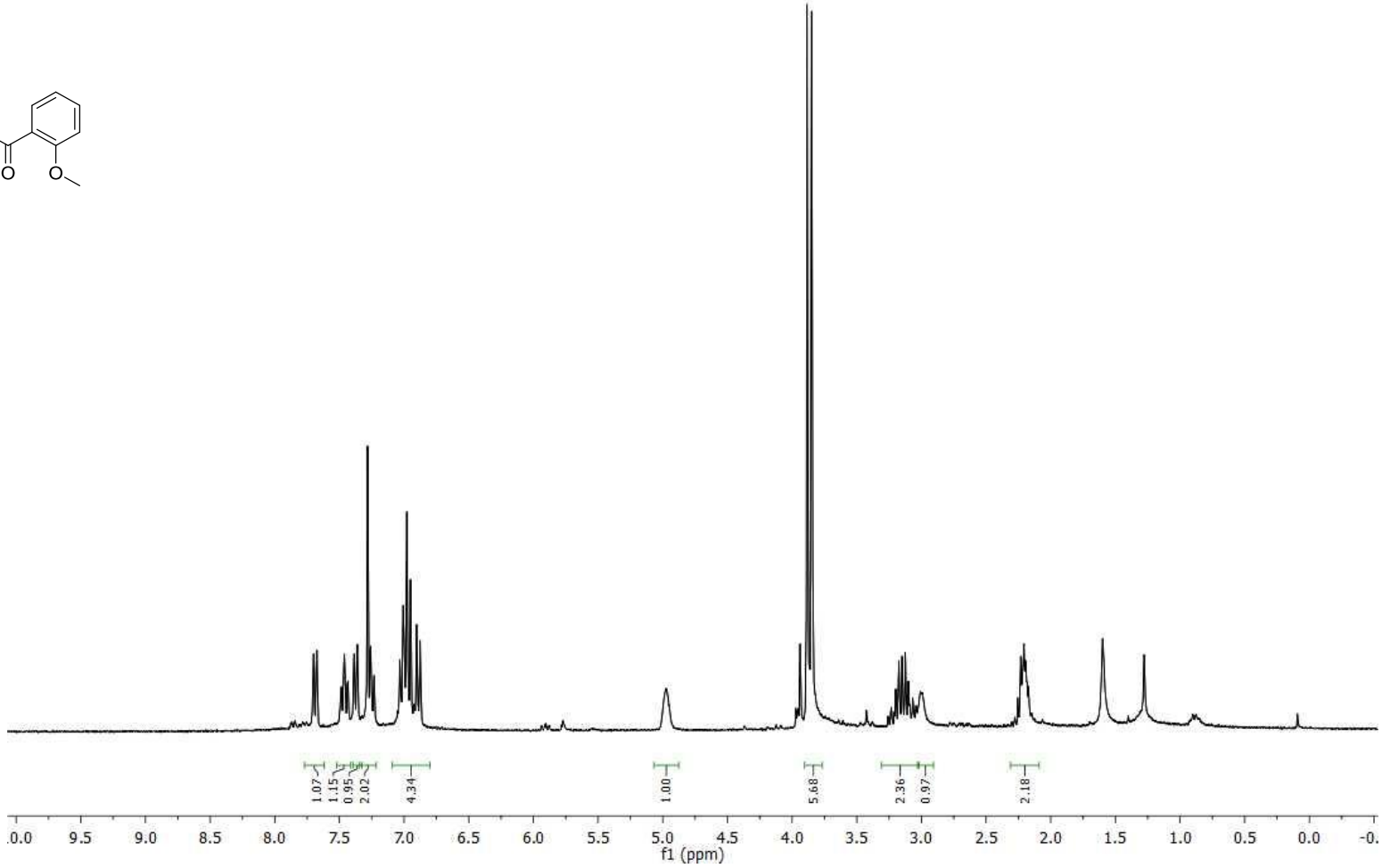


Figure S50. DEPT of (–)-(1S,4S)-**8c.**