

Nickel-catalyzed Tishchenko Reaction via Hetero-nickelacycles by Oxidative Cyclization of Aldehydes with Nickel(0) Complex

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Supporting Information

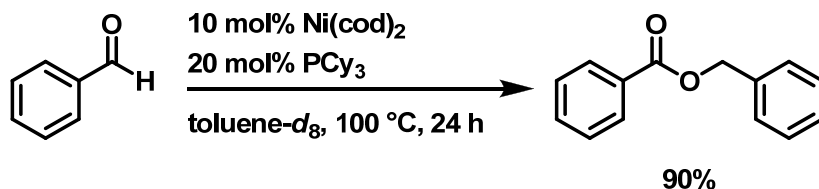
[General]

All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry box techniques. ^1H , ^{31}P , and ^{13}C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S, JEOL AL-400, Bruker DPX 400, Bruker AVANCE 400 and Varian UNITY INOVA 600 spectrometers at 25 °C unless otherwise stated. The chemical shifts in ^1H nuclear magnetic resonance spectra were recorded relative to Me_4Si or residual protiated solvent ($\text{C}_6\text{D}_5\text{H}$ (δ 7.16) or $\text{C}_7\text{D}_7\text{H}$ (δ 7.02 or 7.13)). The chemical shifts in the ^{13}C spectra were recorded relative to Me_4Si . Assignment of the resonances in ^1H and ^{13}C NMR spectra was based on ^1H - ^1H COSY, HMQC, and HMBC experiments. High resolution mass spectrometer (HRMS) and elemental analyses were performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

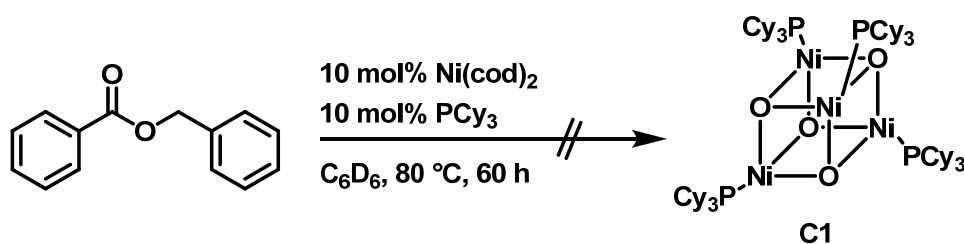
[Materials]

Toluene, C_6D_6 , and toluene- d_8 were distilled from sodium benzophenone ketyl. All commercially available reagents were distilled and degassed prior to use. IPr (1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene), IPrCl (1,3-bis-(2,6-diisopropylphenyl)-4,5-dichloroimidazol-2-ylidene) and 2-naphthaldehyde- d_1 were furnished by known procedures.^{1,2}

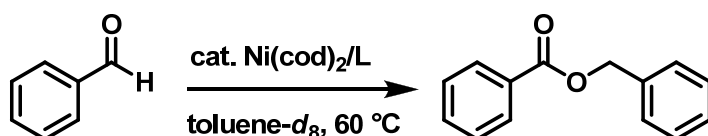
[NMR-scale experiments (Table 1)]



To a solution of Ni(cod)₂ (5.5 mg, 0.020 mmol) and PCy₃ (11.2 mg, 0.040 mmol) in 0.50 mL of toluene-*d*₈ was added benzaldehyde (20.4 mg, 0.20 mmol) at 23 °C. The reaction mixture was heated at 100 °C for 24 h. The solution changed from red to orange. The reaction was monitored by ¹H and ³¹P NMR. Benzyl benzoate and **C1** (³¹P NMR: δ 41.7) were generated as red crystals (100% conversion vs Ni). Anal Calcd for C₇₂H₁₃₂NiOP (**C1**): C, 60.88; H, 9.38. Found: C, 61.34; H, 8.66.



To a solution of Ni(cod)₂ (5.5 mg, 0.020 mmol) and PCy₃ (5.6 mg, 0.020 mmol) in 0.50 mL of C₆D₆ was added benzyl benzoate (42.4 mg, 0.20 mmol) at 23 °C. The reaction mixture was heated at 80 °C for 60 h. The reaction was monitored by ¹H and ³¹P NMR. **C1** (³¹P NMR: δ 41.7) was not formed at all, but unidentified new peaks were observed in ¹H and ³¹P NMR spectra of the crude reaction mixture



L	cat. (mol%)	Time (h)	Yield
IPr	2	6	>99
IPrCl	2	1.5	>99
.	1	3	>99

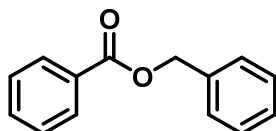
To a solution of Ni(cod)₂ (11.0 mg, 0.040 mmol) and Ligand (0.040 mmol; IPr 15.5 mg or IPrCl 18.3 mg) in 0.50 mL of toluene-*d*₈ was added benzaldehyde (212.4 mg, 2.0 mmol or 414.8 mg, 4.0 mmol) at 23 °C. The reaction mixture was heated at 60 °C. The reaction was monitored by ¹H NMR. Benzyl benzoate was obtained quantitatively.

[General experimental procedures of Ni(0)/IPrCl-catalyzed Tishchenko reaction (Table 2)]

To a solution of Ni(cod)₂ (11.0 mg, 0.040 mmol) and IPrCl (18.3 mg, 0.040 mmol) in 2 mL of toluene was added the aldehyde under inert atmosphere at 23 °C. The reaction mixture was heated at 60 °C or 80 °C for 1–24 h. The reaction was monitored by GC analysis. GC yields were determined using pentadecane as an internal standard. The product was isolated by a silica gel chromatography (eluted with EtOAc, unless otherwise noted). Spectroscopic data of the products (1, 6, 7, 8, 9, 10, 12, 13 and 14) were identical to that previously reported.³

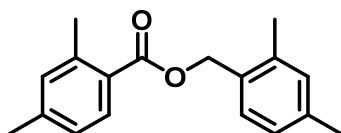
[Spectroscopic data for prepared esters]

Benzyl benzoate (1):



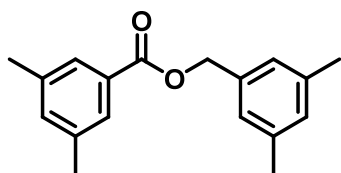
The general procedure was followed with benzaldehyde (429.0 mg, 4.04 mmol) and reaction mixture was stirred at 60 °C for 3 h. Purification by column chromatography gave **1** (429.5 mg, 2.02 mmol, > 99%) as pale yellow oil.

2,4-Dimethylbenzyl 2,4-dimethylbenzoate (2):



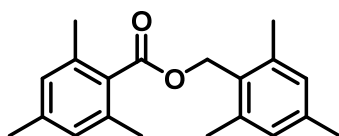
The general procedure was followed with 2,4-dimethylbenzaldehyde (536.4 mg, 4.00 mmol) and reaction mixture was stirred at 60 °C for 3 h. Purification by column chromatography gave **2** (532.8 mg, 1.99 mmol, > 99%) as colorless oil. **¹H NMR** (400 MHz, CDCl₃): δ 7.85 (d, J = 8.0 Hz, 1H, ArH), 7.31 (d, J = 8.0 Hz, 1H, ArH), 7.04 (m, 4H, ArH), 5.31 (s, 2H, OCH₂Ar), 2.59 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 2.35 (s, 3H, CH₃), 2.34 (s, 3H, CH₃). **¹³C NMR** (100 MHz, CDCl₃): δ 167.5, 142.7, 140.7, 138.4, 137.1, 132.7, 131.4, 131.3, 131.1, 129.7, 126.8, 126.7, 126.6, 64.8, 22.0, 21.5, 21.2, 19.1. **HRMS**: Calcd. for C₁₈H₂₀O₂ 268.1463, Found 268.1465.

3,5-Dimethylbenzyl 3,5-dimethylbenzoate (3):



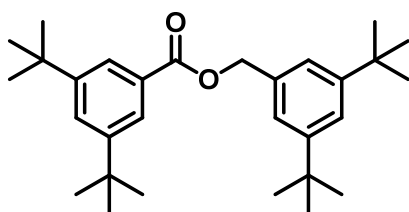
The general procedure was followed with 3,5-dimethylbenzaldehyde (542.8 mg, 4.05 mmol) and reaction mixture was stirred at 60 °C for 3 h. Purification by column chromatography gave **3** (531.5 mg, 1.98 mmol, > 99%) as colorless oil. **¹H NMR** (400 MHz, CDCl₃): δ 7.75 (s, 2H, ArH), 7.22 (s, 1H, ArH), 7.11 (s, 2H, ArH), 7.02 (s, 1H, ArH), 5.33 (s, 2H, OCH₂Ar), 2.39 (s, 6H, CH₃), 2.38 (s, 6H, CH₃). **¹³C NMR** (100 MHz, CDCl₃): δ 166.9, 138.2, 138.0, 136.1, 134.7, 130.2, 130.0, 127.5, 126.2, 66.8, 21.3, 21.2. **HRMS**: Calcd. for C₁₈H₂₀O₂ 268.1463, Found 268.1458.

2,4,6-Trimethylbenzyl 2,4,6-trimethylbenzoate (**4**):



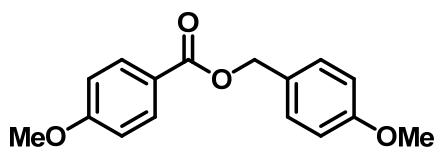
The general procedure was followed with 2,4,6-trimethylbenzaldehyde (202.1 mg, 1.36 mmol) and reaction mixture was stirred at 60 °C for 24 h. Purification by column chromatography gave **4** (170.3 mg, 0.57 mmol, 84%) as yellow oil. **¹H NMR** (400 MHz, CDCl₃): δ 6.88 (s, 2H, ArH), 6.82 (s, 2H, ArH), 5.40 (s, 2H, OCH₂Ar), 2.40 (s, 6H, CH₃), 2.27 (s, 6H, CH₃), 2.26 (s, 6H, CH₃). **¹³C NMR** (100 MHz, CDCl₃): δ 170.4, 139.1, 138.5, 138.2, 134.9, 131.3, 129.1, 128.8, 128.3, 61.4, 21.1, 21.0, 19.7, 19.6. **HRMS**: Calcd. for C₂₀H₂₄O₂ 296.1776, Found 296.1774.

3,5-Di-tert-butylbenzyl 3,5-di-tert-butylbenzoate (**5**):



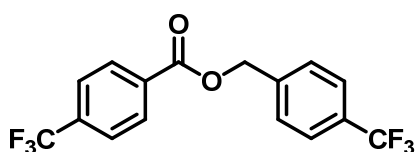
The general procedure was followed with 3,5-di-tert-butylbenzaldehyde (439.1 mg, 2.01 mmol) and reaction mixture was stirred at 80 °C for 2 h. Purification by column chromatography gave **5** (441.2 mg, 2.01 mmol, > 99%) as yellow oil. **¹H NMR** (400 MHz, CDCl₃): δ 8.22 (s, 2H, ArH), 7.85 (s, 1H, ArH), 7.62 (s, 1H, ArH), 7.55 (s, 2H, ArH), 5.63 (s, 2H, OCH₂Ar), 1.55 (s, 36H, CH₃). **¹³C NMR** (100 MHz, CDCl₃): δ 167.0, 151.0, 150.9, 135.7, 129.9, 127.1, 124.0, 122.0, 121.9, 67.0, 34.9, 34.8, 31.6, 31.5. **HRMS**: Calcd. for C₃₀H₄₄O₂ 436.3341, Found 436.3344.

4-Methoxybenzyl 4-methoxybenzoate (**6**):



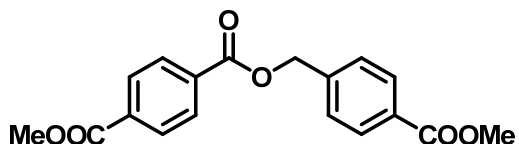
The general procedure was followed with 4-methoxybenzaldehyde (274.3 mg, 2.01 mmol) and reaction mixture was stirred at 60 °C for 2 h. Purification by column chromatography gave **6** (260.8 mg, 1.92 mmol, 95%) as yellow oil.

4-(Trifluoromethyl)benzyl 4-(trifluoromethyl)benzoate (**7**):



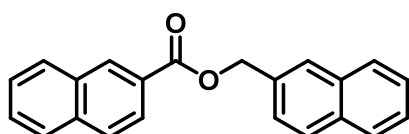
The general procedure was followed with 4-trifluoromethylbenzaldehyde (69.8 mg, 0.40 mmol) and reaction mixture was stirred at 60 °C for 4 h. Purification by column chromatography gave **7** (61.4 mg, 0.18 mmol, 88% as crude yield). Further purification by recrystallization gave **7** (57.2 mg, 0.17 mmol, 82%) as colorless solid.

4-(Methoxycarbonyl)benzyl methyl terephthalate (**8**):



The general procedure was followed with 4-methoxycarbonylbenzaldehyde (329.6 mg, 2.01 mmol) and reaction mixture was stirred at 80 °C for 4 h. Purification by column chromatography gave **8** (324.7 mg, 0.99 mmol, 99%). Further purification by recrystallization gave **8** as colorless solid.

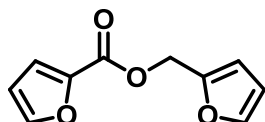
Naphthalen-2-ylmethyl 2-naphthoate (**9**):



The general procedure was followed with 2-naphthadehyde (208.6 mg, 1.34 mmol) and reaction mixture was stirred at 60 °C for 3 h. Purification by column chromatography gave **9** (195.8 mg, 0.63

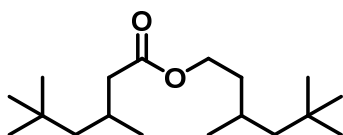
mmol, 94% as crude yield). Further purification by recrystallization gave **8** (170.8 mg, 0.55 mmol, 82%) as colorless solid. NMR scale experiment was conducted followed by procedure noted in p S12.

Furfuryl furoate (10):



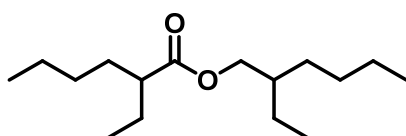
The general procedure was followed with furfural (192.2 mg, 2.00 mmol) and reaction mixture was stirred at 60 °C for 3 h. Purification by column chromatography gave **10** (118.6 mg, 0.62 mmol, 62%) as yellow oil. The yellow solid was produced as unidentified byproduct.

3,5,5-Trimethylhexyl 3,5,5-trimethylhexanoate (11):



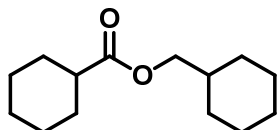
The general procedure was followed with 3,5,5-trimethylhexanal (569.9 mg, 4.01 mmol) and reaction mixture was stirred at 60 °C for 1 h. Purification by column chromatography gave **11** (543.3 mg, 1.91 mmol, 96%) as colorless oil. This product was obtained as a diastereomer mixture **11/11'** (60/40, estimated by $^1\text{H NMR}$). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 4.09–4.05 (m, 2H of **11** and **11'**, OCH_2CH_2), 2.31–2.29 (m, 1H of **11'**, $^t\text{BuCH}_2\text{CH}(\text{Me})\text{CH}_2$), 2.28–2.26 (m, 1H of **11**, $^t\text{BuCH}_2\text{CH}(\text{Me})\text{CH}_2$), 2.13–2.03 (m, 2H), 1.63–1.59 (m, 2H), 1.44–1.42 (m, 1H), 1.25 (t, $J = 4.0$ Hz, 2H of **11'**, $^t\text{BuCH}_2\text{CH}(\text{Me})\text{CH}_2$), 1.21 (t, $J = 4$ Hz, 2H of **11**, $^t\text{BuCH}_2\text{CH}(\text{Me})\text{CH}_2$), 1.13–1.01 (ddd, 2H), 0.97 (d, $J = 4.0$ Hz, 3H of **11'**, Me- H), 0.95 (d, $J = 4.0$ Hz, 3H of **11'**, Me- H), 0.89 (s, 9H of **11** and **11'**, $^t\text{Bu-H}$), 0.87 (s, 9H of **11** and **11'**, $^t\text{Bu-H}$). $^{13}\text{C NMR}$ (CDCl_3 , 67 MHz): δ 173.4, 62.8, 51.1 (**11'**), 51.1 (**11**), 50.7, 44.3, 38.0, 31.2, 30.2 (**11'**), 30.1 (**11**), 27.1 (**11**), 26.9 (**11'**), 26.3, 22.8 (**11'**), 22.8 (**11**), 22.7 (**11**), 22.6 (**11'**). **HRMS**: Calcd. for $\text{C}_{18}\text{H}_{36}\text{O}_2$ 284.2715, Found 284.2713.

2-Ethylhexyl 2-ethylhexanoate (12):



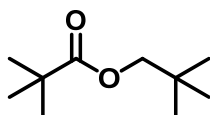
The general procedure was followed with 2-ethylhexanal (519.3 mg, 4.05 mmol) and reaction mixture was stirred at 60 °C for 1 h. Purification by column chromatography gave **12** (483.3 mg, 1.88 mmol, 94%) as colorless oil.

Cyclohexylmethyl cyclohexanecarboxylate (13):



The general procedure was followed with cyclohexanecarbaldehyde (450.2 mg, 4.01 mmol) and reaction mixture was stirred at 60 °C for 1 h. Purification by column chromatography gave **13** (451.5 mg, 2.01 mmol, 99%) as colorless oil.

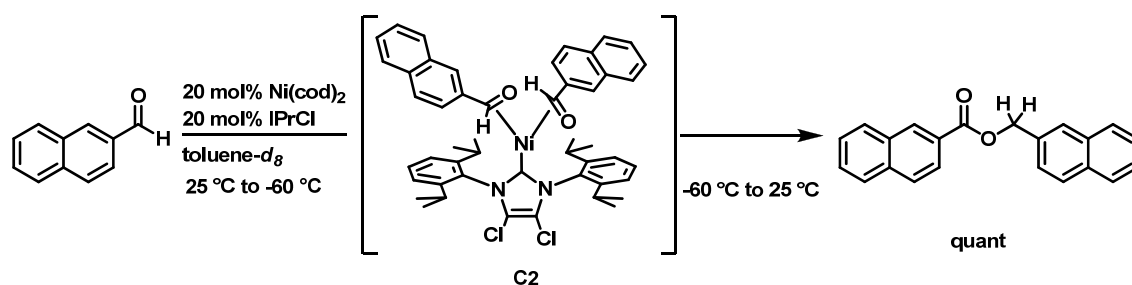
Neopentyl pivalate (Scheme 2, Entry 14):



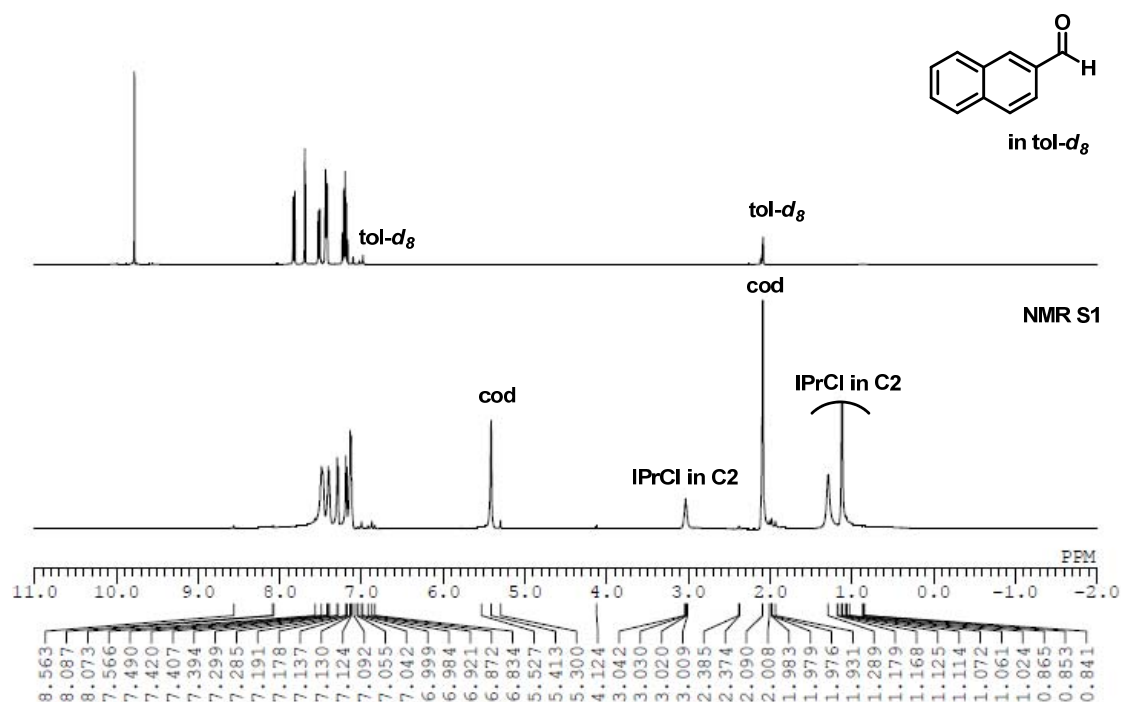
The general procedure was followed with pivalaldehyde (442 uL, 344.8 mg, 4.00 mmol) and reaction mixture was stirred at 60 °C for 1 h. Neopentyl pivalate (**14**) is difficult to isolate because of its low boiling point. Therefore, product yield was determined by GC.

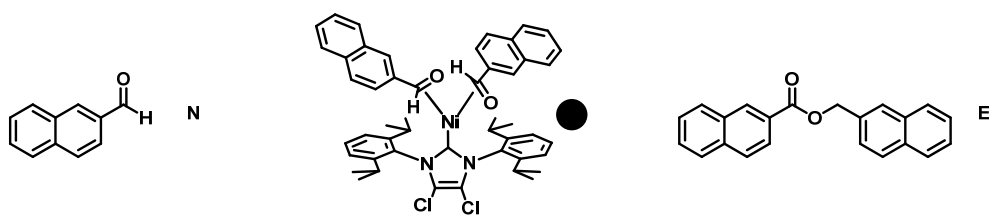
[Mechanistic investigations]

NMR Monitoring of the Tishchenko reaction of 2-naphthaldehyde:

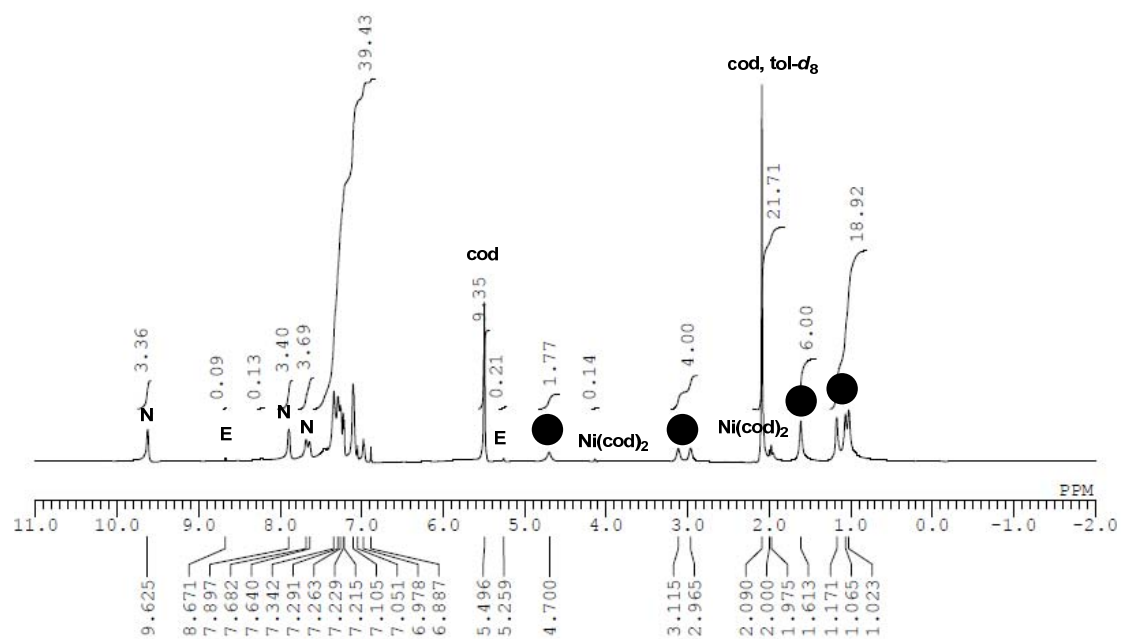


To a solution of Ni(cod)₂ (110.0 mg, 0.40 mmol) and IPrCl (183.2 mg, 0.40 mmol) in 2 mL of toluene-*d*₈ was added 2-naphthaldehyde (312.4 mg, 2.00 mmol) at 23 °C and the sample was transferred to an NMR tube equipped with a sealable teflon cap. The tube was sealed and inserted in a NMR spectrometer. The ¹H NMR analysis was conducted at 25 °C (NMR S1) and then the sample was cooled to -60 °C. After the measurement of ¹H NMR (NMR S2), ¹³C NMR (NMR S3) and HMBC (NMR S4) at -60 °C, the sample was allowed to warm to 25 °C. Then, ¹H NMR analysis was conducted at 25 °C again to verify that the reaction is not proceeded from when the first ¹H NMR analysis had been conducted at 25 °C. The reaction at room temperature was monitored by ¹H NMR for 1 d and the 2-naphthaldehyde was consumed to give corresponding ester quantitatively. Spectral data for **C2**: **¹H NMR** (600 MHz, toluene-*d*₈, -60 °C): δ 4.70 (brs, 2H, ArCHO), 3.12 (br, 2H, ^{*i*}Pr-H), 2.97 (br, 2H, ^{*i*}Pr-H), 1.61 (br, 6H, ^{*i*}Pr-H), 1.17 (br, 6H, ^{*i*}Pr-H), 1.07 (br, 6H, ^{*i*}Pr-H), 1.02 (br, 6H, ^{*i*}Pr-H). **¹³C NMR** (150 MHz, toluene-*d*₈): δ 196.0, 109.3, 29.6, 28.8, 24.8, 24.3, 24.0, 23.6..

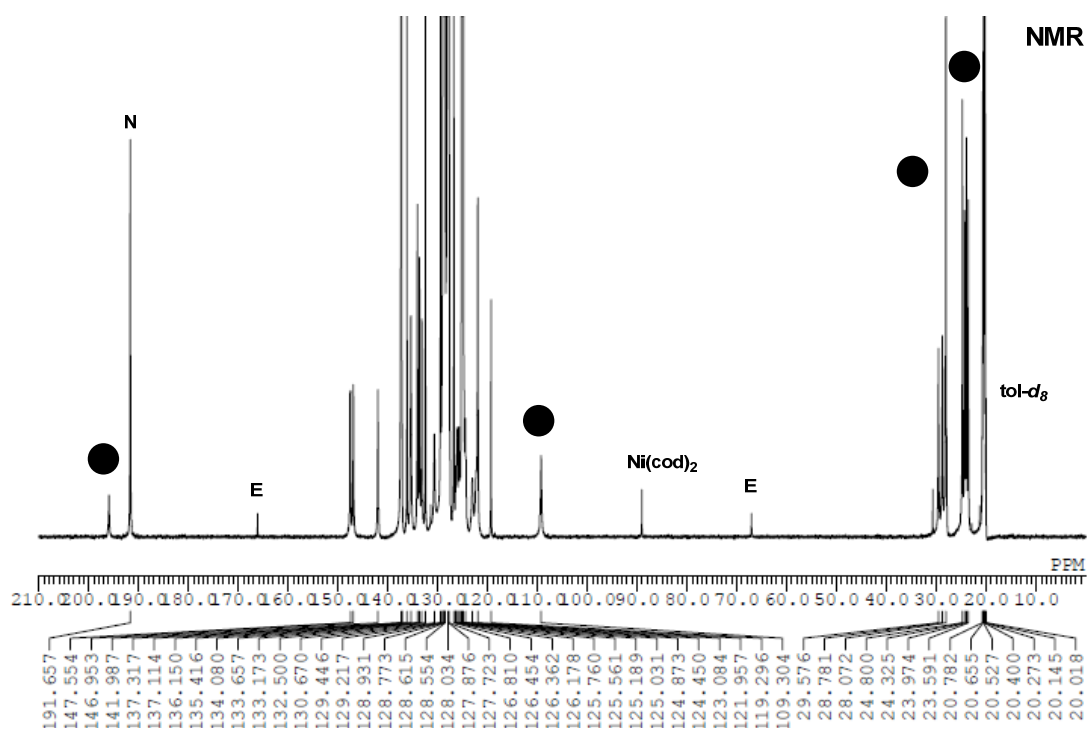


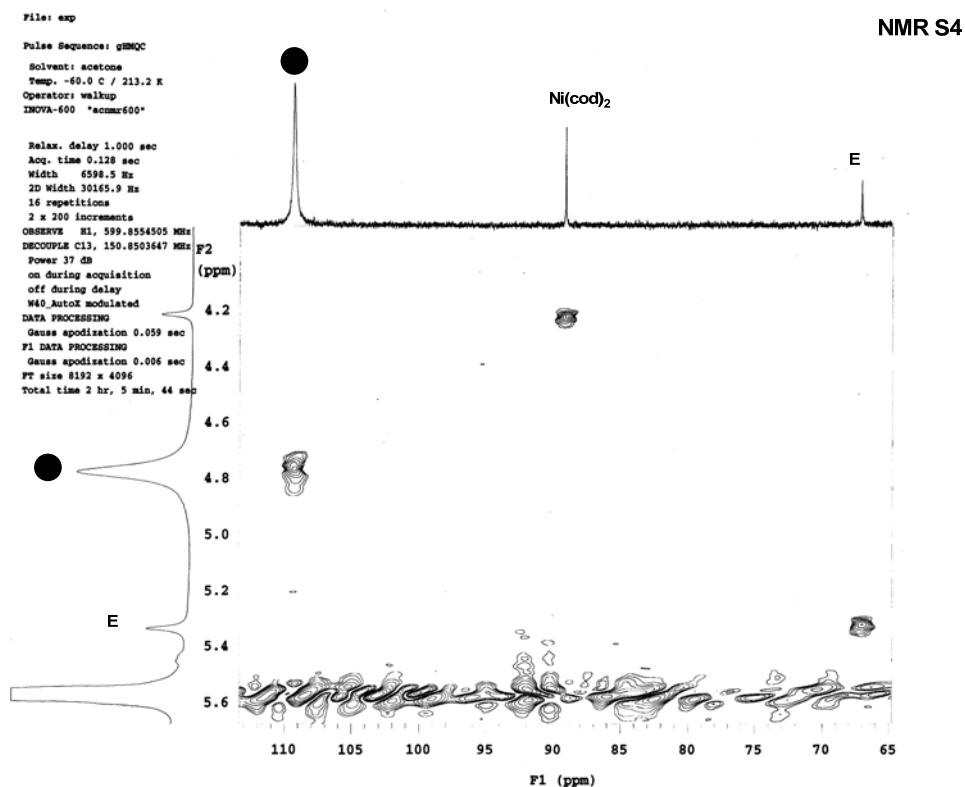


NMR S2

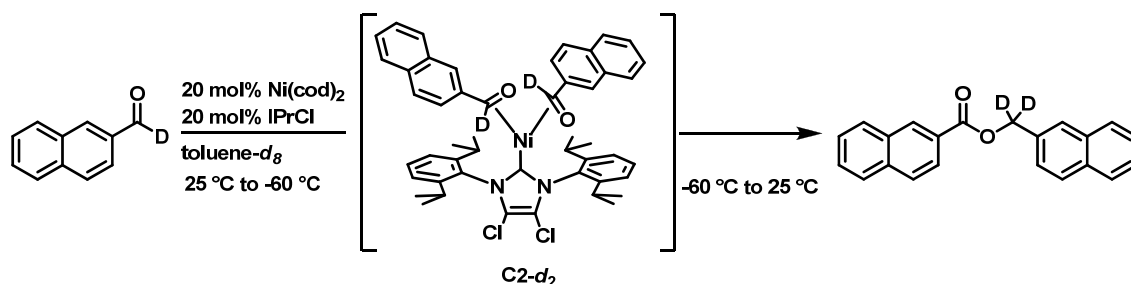


NMR S3

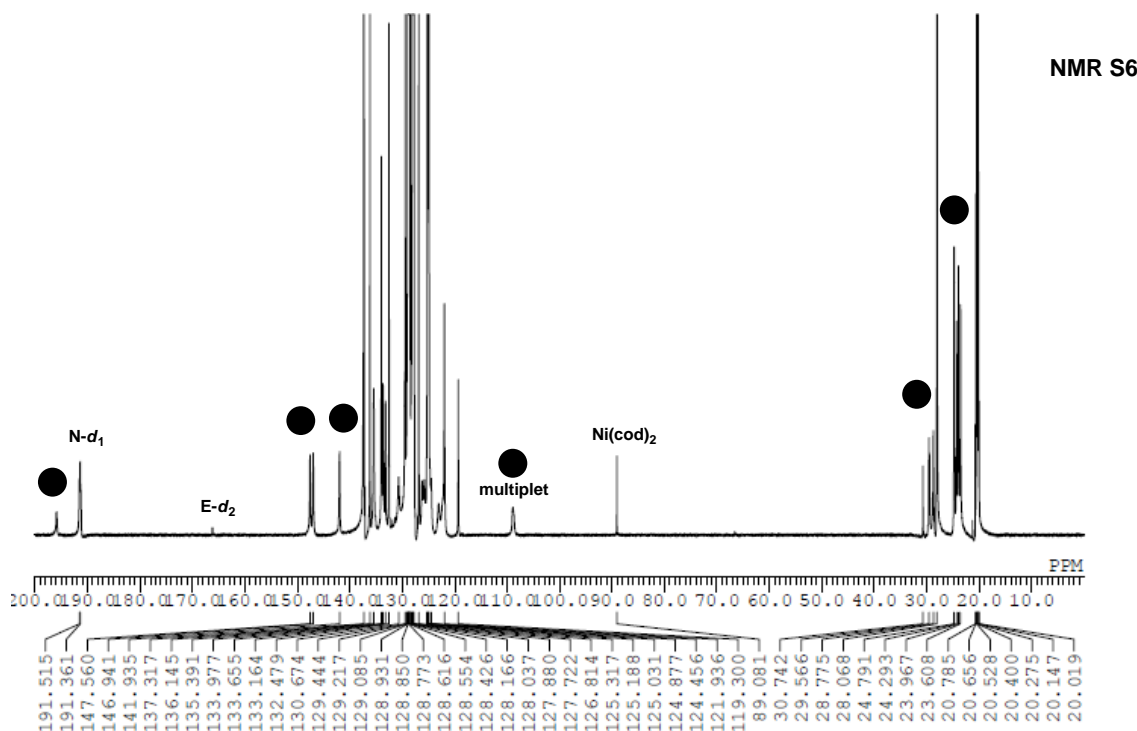
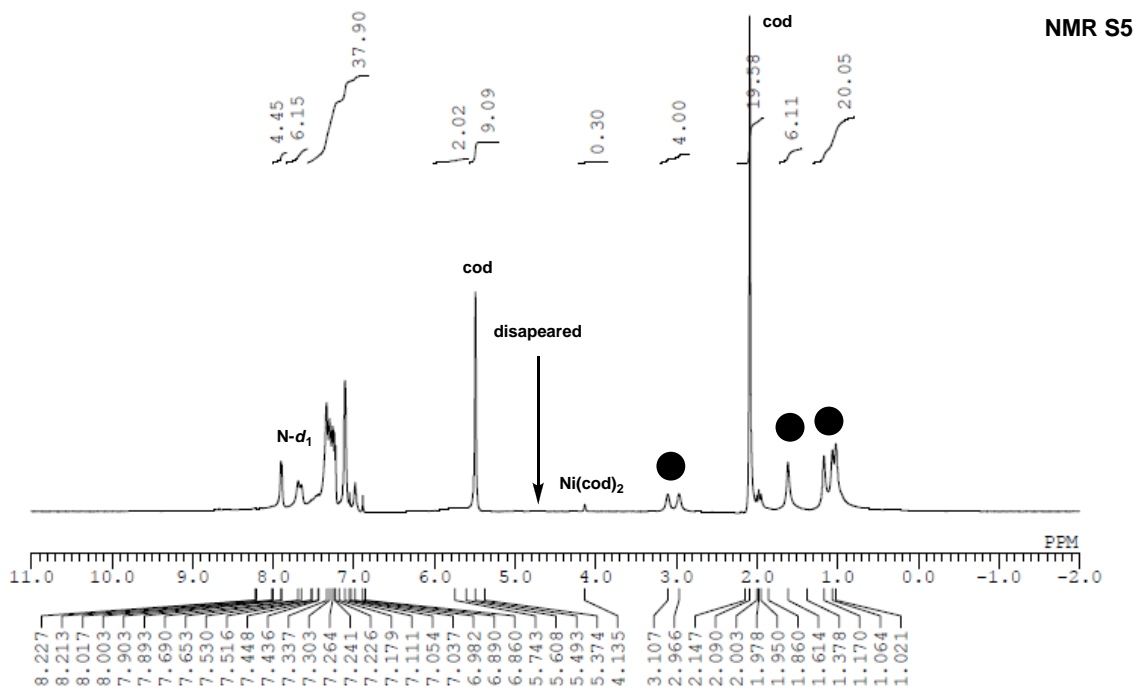
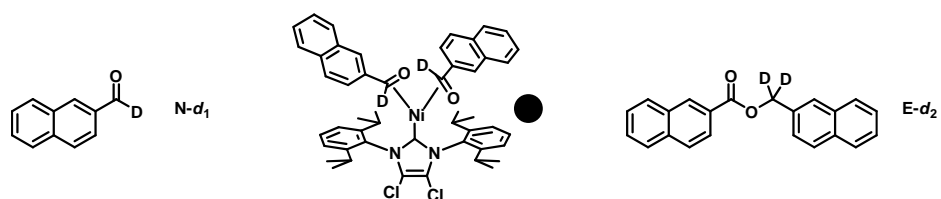




NMR Monitoring of the Tishchenko reaction of 2-naphthaldehyde- d_1 :



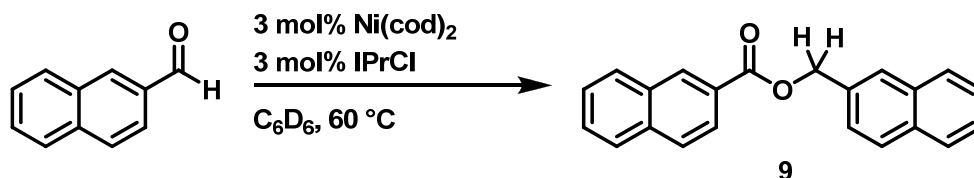
To a solution of Ni(cod)₂ (110.0 mg, 0.40 mmol) and IPrCl (183.2 mg, 0.40 mmol) in 2 mL of toluene-*d*₈ was added 2-naphthaldehyde-*d*₁ (314.4 mg, 2.00 mmol) at 23 °C and the sample was transferred to an NMR tube equipped with a sealable teflon cap. The tube was sealed and inserted in a NMR spectrometer. The ¹H NMR analysis was conducted at 25 °C and then the sample was cooled to -60 °C. After the measurement of ¹H NMR (NMR S5) and ¹³C NMR (NMR S6) at -60 °C, the sample was allowed to warm to 25 °C. Then, ¹H NMR analysis was conducted at 25 °C again to verify that the reaction is not proceeded from when the first ¹H NMR analysis had been conducted at 25 °C.



[Determination of reaction rate constant and KIE]

For all kinetic analyses, each measurement was repeated at least twice.

Reaction rate constant of the Tishchenko reaction of 2-naphthaldehyde, k_H :



94% NMR yield, $d[C_{10}H_7CHO]/dt = k_H = 3.55(3) \times 10^{-4} [\text{mol} \cdot \text{m}^{-3} \cdot \text{sec}^{-1}]$

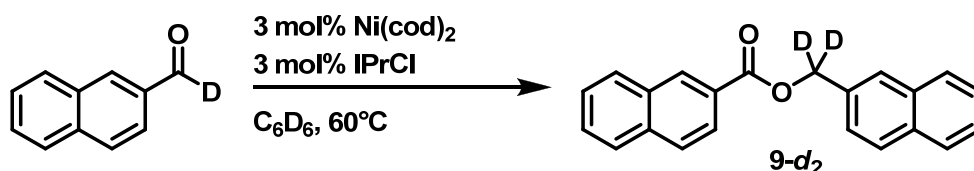
To a solution of $\text{Ni}(\text{cod})_2$ (11.0 mg, 0.040 mmol) and IPrCl (18.3 mg, 0.040 mmol) in 0.5 mL of C_6D_6 was added 2-naphthaldehyde (206.2 mg, 1.32 mmol) and 1,4-dioxane (39.5 mg, 0.45 mmol) as an internal standard at 25 °C. The reaction mixture was thermostated at 60 °C, and then the integral values at δ_H 8.12 ppm and 3.32 ppm, the resonances attributable to the aromatic proton in **9** and to 1,4-dioxane, respectively, were monitored periodically (every 5 minutes) by means of ^1H NMR spectroscopy (Table S1). The rate constant of disappearance of $\text{C}_{10}\text{H}_7\text{CHO}$ (k_H) was evaluated by least-squares fitting of the conversion-time profiles to a zero-order rate equation (eq. S1).

$$-d[C_{10}H_7CHO]/dt = k_H \quad (\text{S1})$$

where $[C_{10}H_7CHO] = [C_{10}H_7CHO]_0 - 2[\mathbf{9}]$, $[C_{10}H_7CHO]_0 = 1.169(5) [\text{mol m}^{-3}]$

($[C_{10}H_7CHO]_0$ means the concentration of $[C_{10}H_7CHO]$ at $t = 0$.)

Reaction rate constant of the Tishchenko reaction of 2-naphthaldehyde- d_1 , k_D :



95% NMR yield, $d[C_{10}H_7CDO]/dt = k_D = 1.87(1) \times 10^{-4} [\text{mol} \cdot \text{m}^{-3} \cdot \text{sec}^{-1}]$

To a solution of $\text{Ni}(\text{cod})_2$ (11.0 mg, 0.040 mmol) and IPrCl (18.3 mg, 0.040 mmol) in 0.5 mL of C_6D_6 was added 2-naphthaldehyde- d_1 (207.5 mg, 1.32 mmol) and 1,4-dioxane (40.5 mg, 0.46 mmol) as an internal standard at 25 °C. The reaction mixture was thermostated at 60 °C, and then the integral values at δ_H 8.12 ppm and 3.32 ppm, the resonances attributable to the aromatic proton in **9-d₂** and to 1,4-dioxane, respectively, were monitored periodically (every 5 minutes) by means of ^1H NMR spectroscopy (Table S2). The rate constant of disappearance of $\text{C}_{10}\text{H}_7\text{CDO}$ (k_D) was evaluated by least-squares fitting of the conversion-time profiles to a zero-order rate equation (eq. S2).

$$-d[C_{10}H_7CDO]/dt = k_D \quad (\text{S2})$$

where $[C_{10}H_7CDO] = [C_{10}H_7CDO]_0 - 2[9-d_2]$, $[C_{10}H_7CDO]_0 = 1.180(4)$ $[mol\ m^{-3}]$
($[C_{10}H_7CDO]_0$ means the concentration of $[C_{10}H_7CDO]$ at $t = 0$.)

These two experiments show a KIE value of reaction rate ($k_H/k_D = 3.55 \times 10^{-4}/1.87 \times 10^{-4} = 1.9$).

Table S1

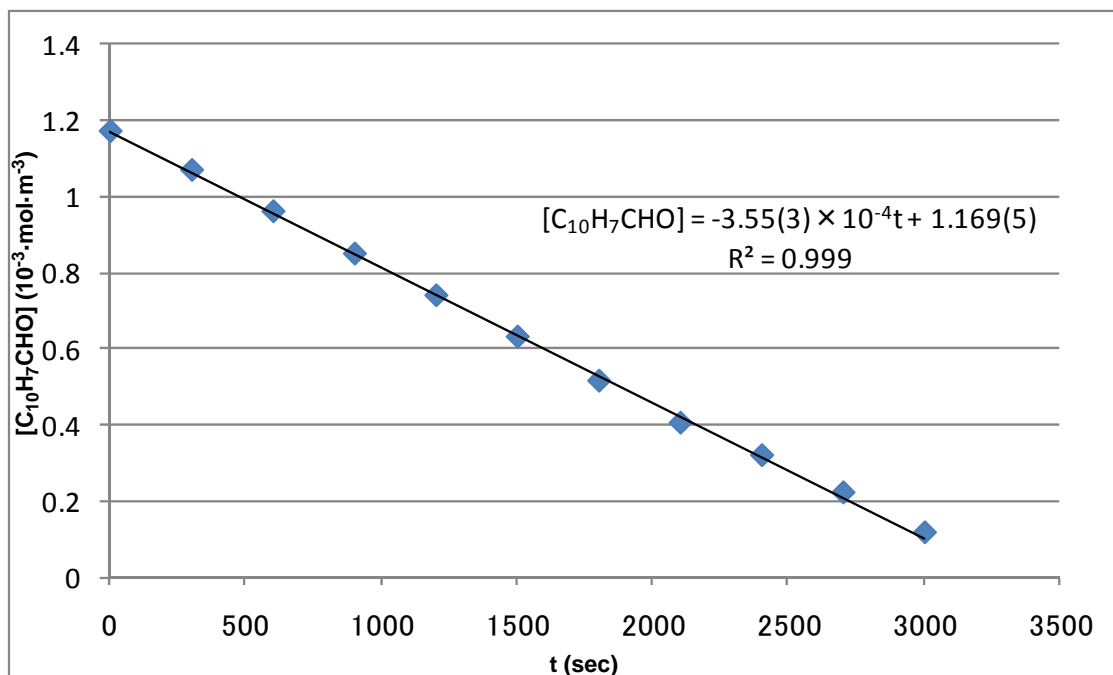
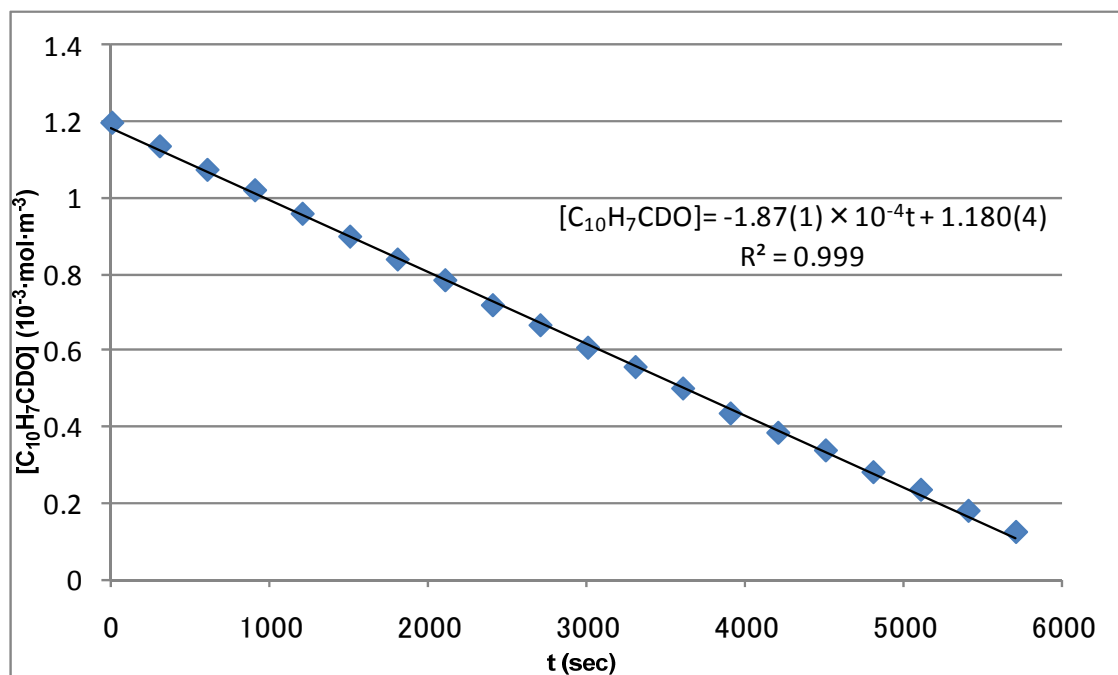


Table S2



References

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2. V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.*, 1981, **103**, 5503.
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[NMR spectra of new esters]

Supplementary Material (ESI) for Chemical Communications
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Current Data Parameters
 NAME hoshimoto
 EXPNO 77
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20090529
 Time_ 14.03
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 143.7
 DW 60.400 usec
 DE 6.00 usec
 TE 298.2 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 DELTA 0.89999998 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 2.60 dB
 SFO1 400.1324710 MHz

==== CHANNEL f2 =====
 CPDPRG2
 NUC2 off
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 120.00 dB
 PL13 120.00 dB
 SFO2 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300106 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

2.587
 2.386
 2.346
 2.339

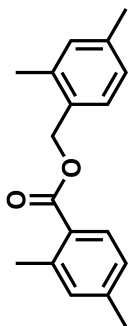
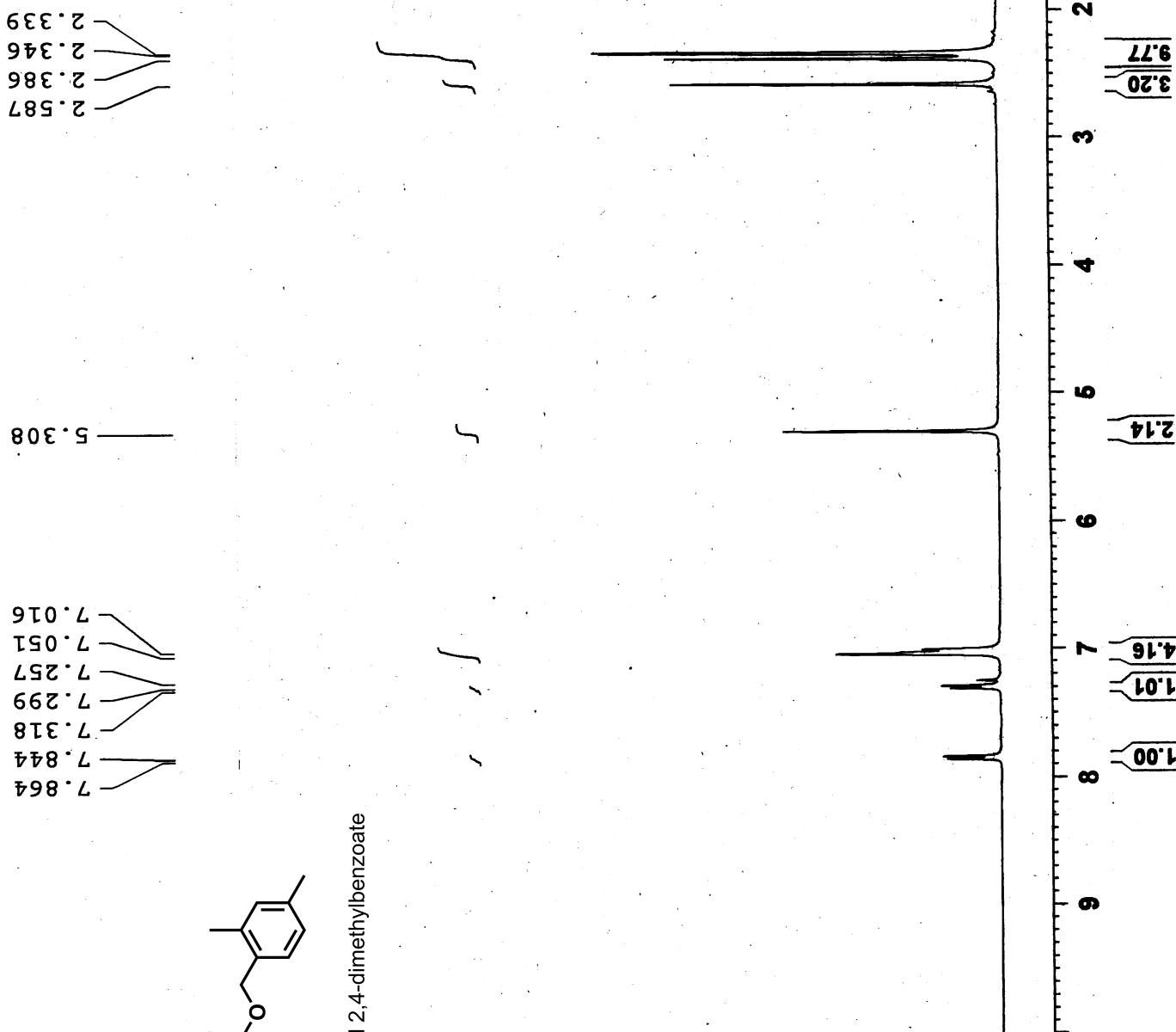
5.308

7.864
 7.844
 7.318
 7.299
 7.257
 7.051
 7.016

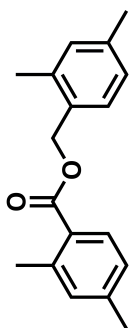
3.20
 9.77

2.14

1.00
 1.01
 4.16



2,4-dimethylbenzyl 2,4-dimethylbenzoate



2,4-dimethylbenzyl 2,4-dimethylbenzoate

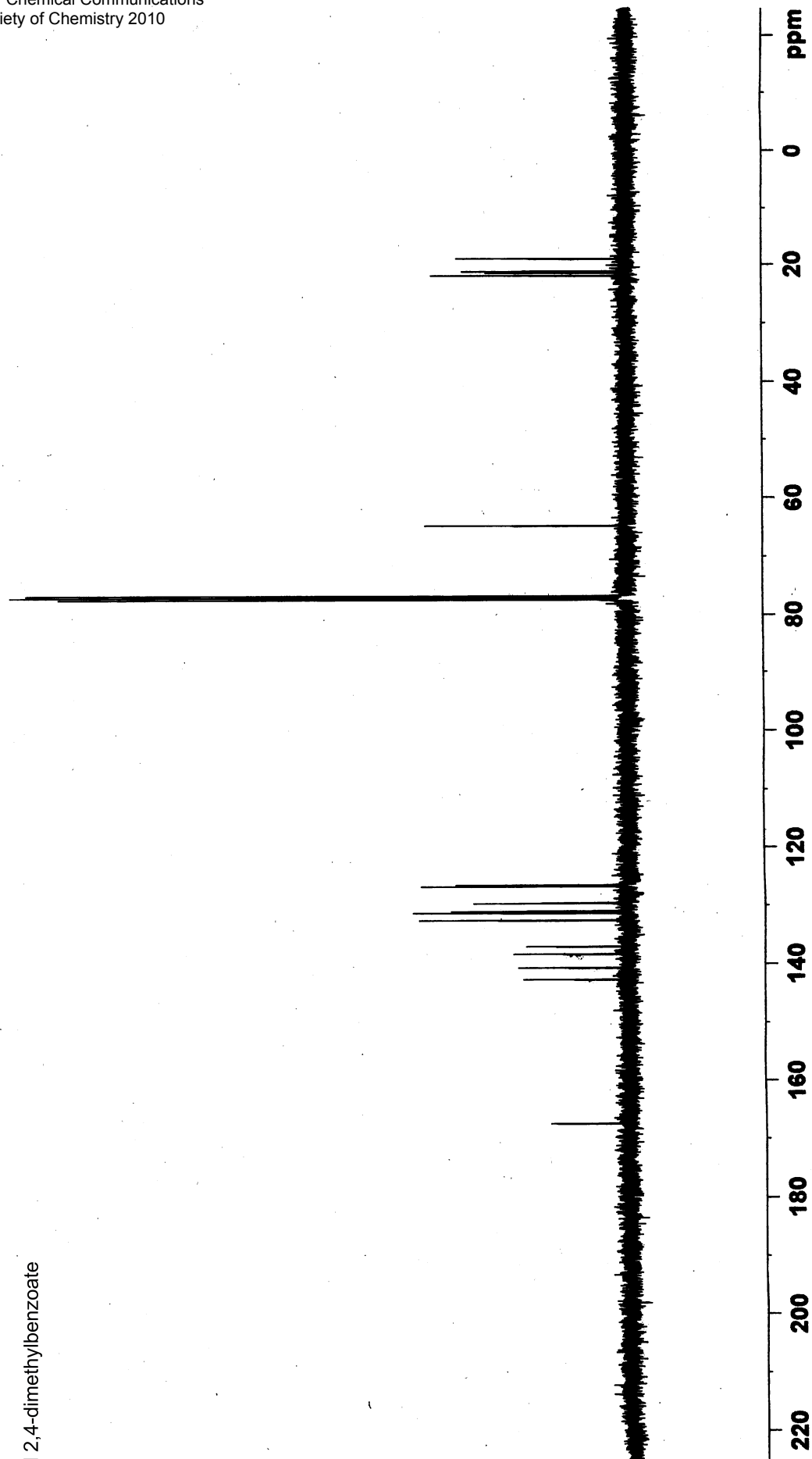
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21.50
21.24
19.07

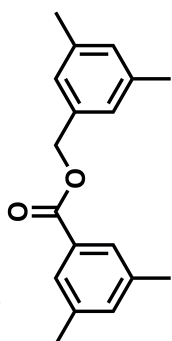
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76.85
77.16
77.48

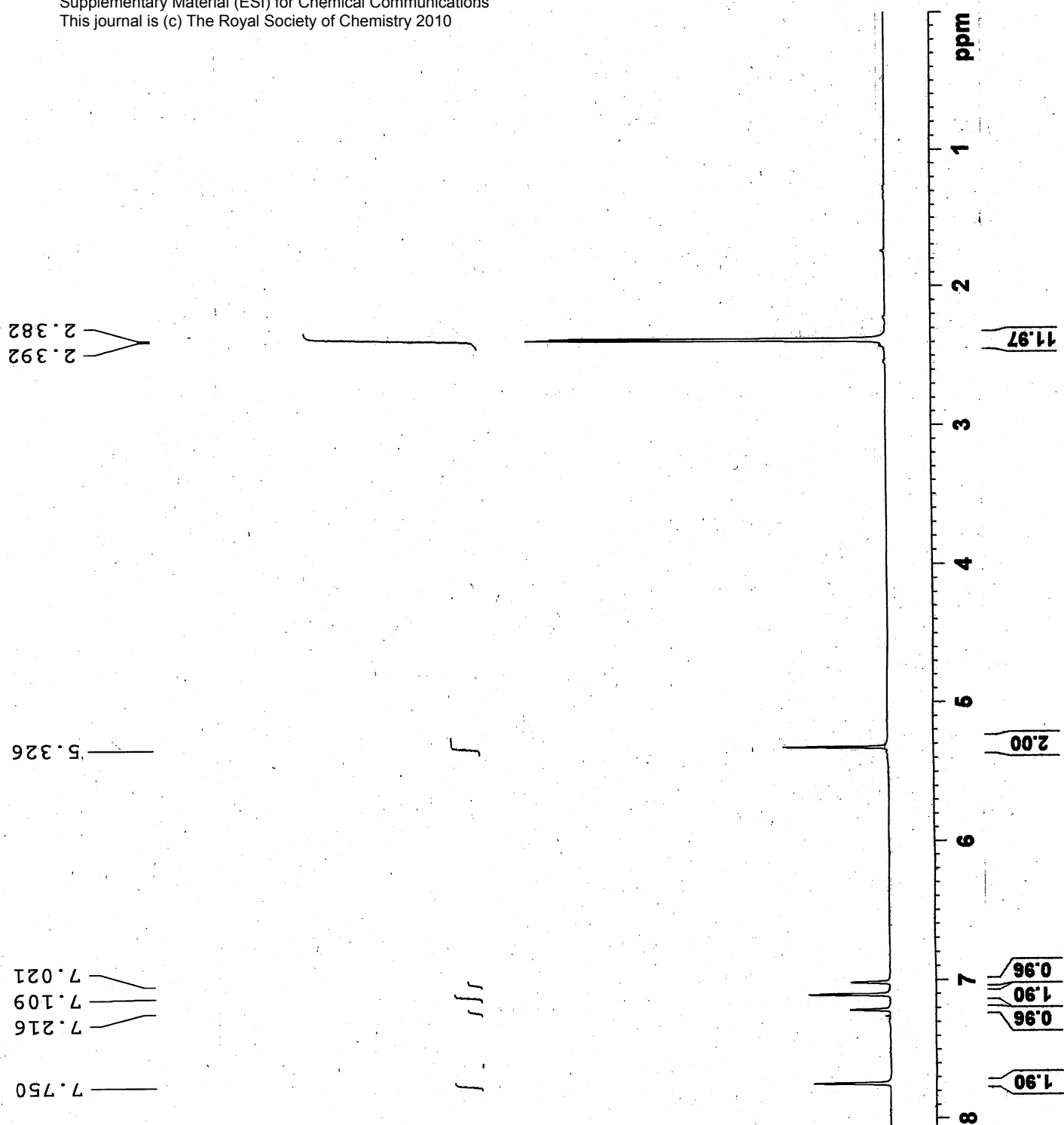
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140.68
138.39
137.12
132.65
131.37
131.34
131.06
129.69
126.76
126.69
126.55

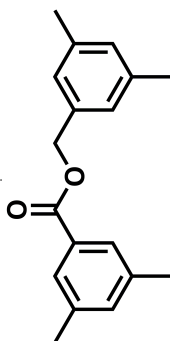
167.46





3,5-dimethylbenzyl 3,5-dimethylbenzoate





3,5-dimethylbenzyl 3,5-dimethylbenzoate

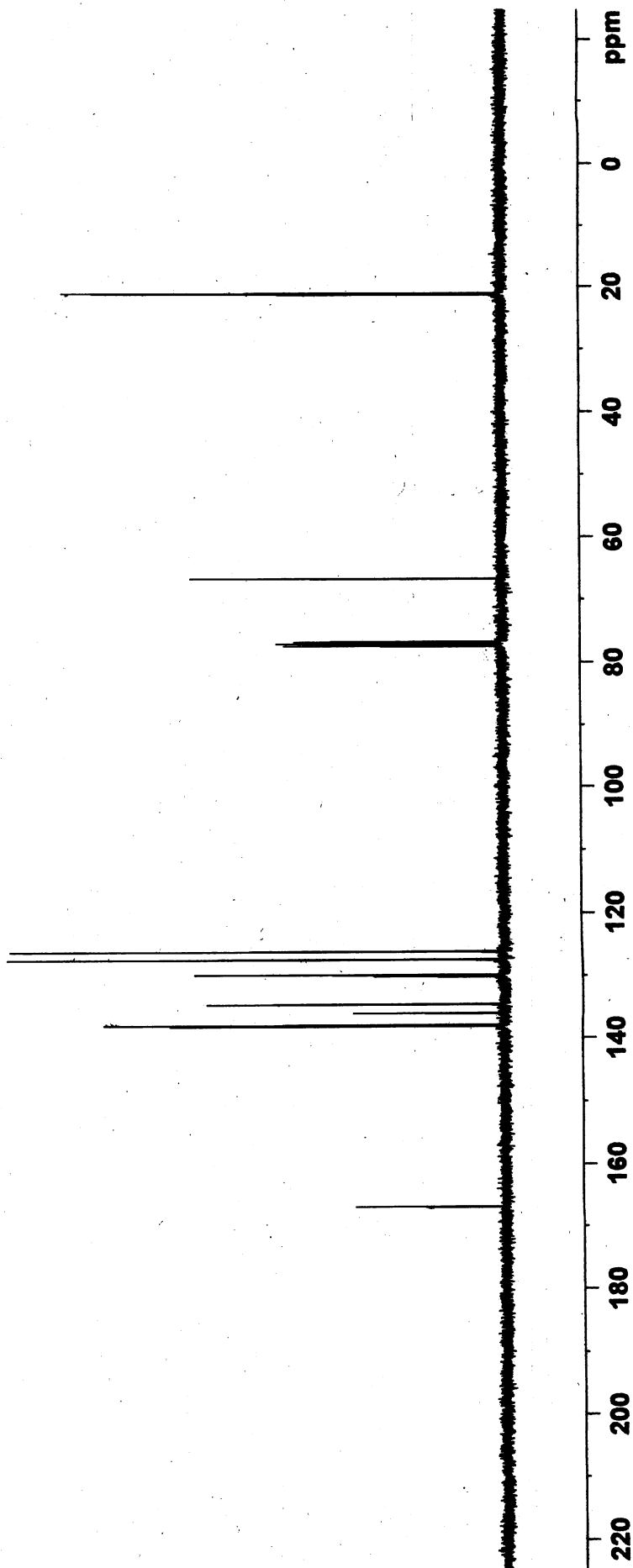
21.32
21.19

66.77

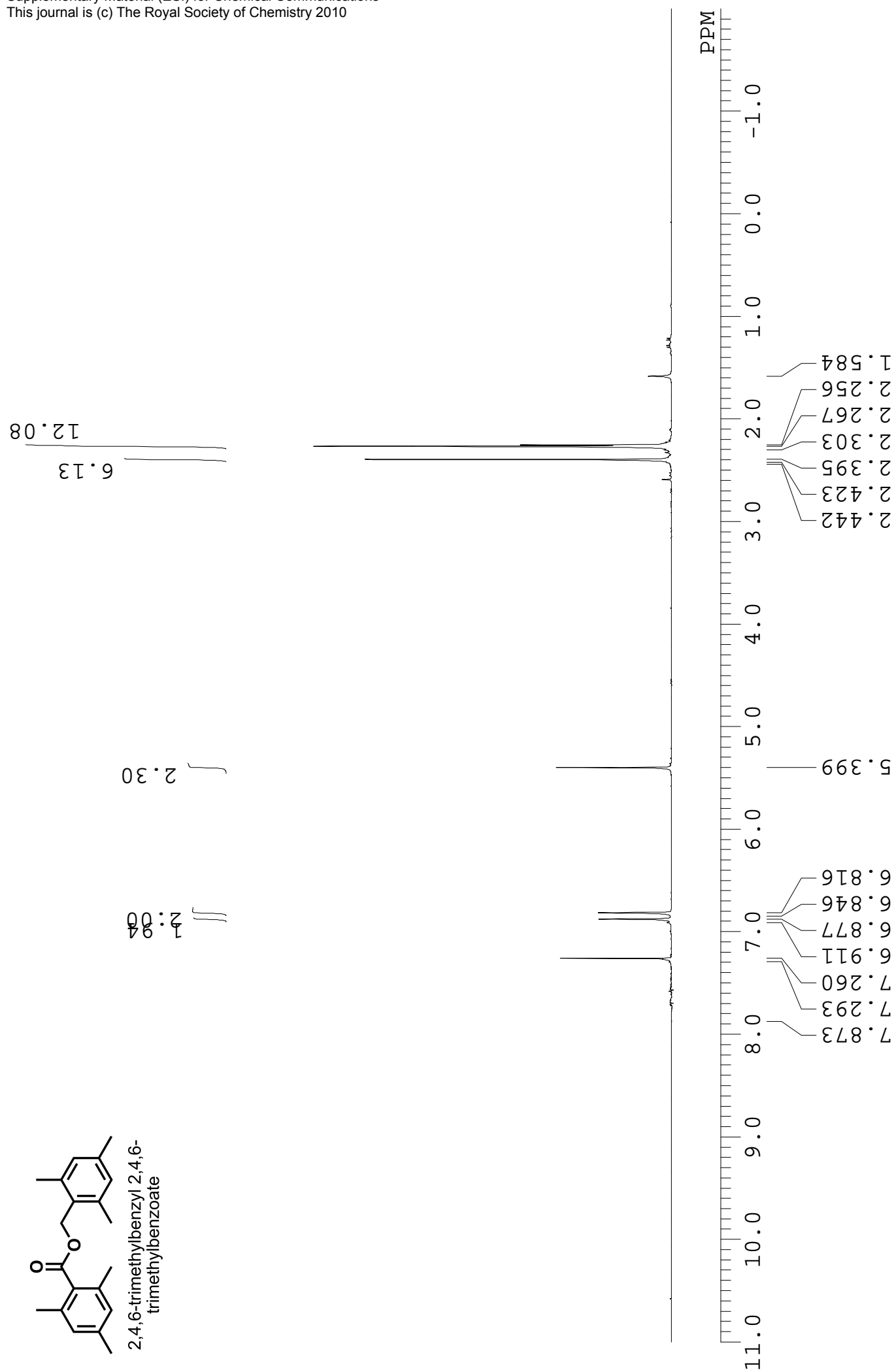
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77.14
77.46

126.23
127.50
129.95
130.17
134.69
136.10
138.04
138.22

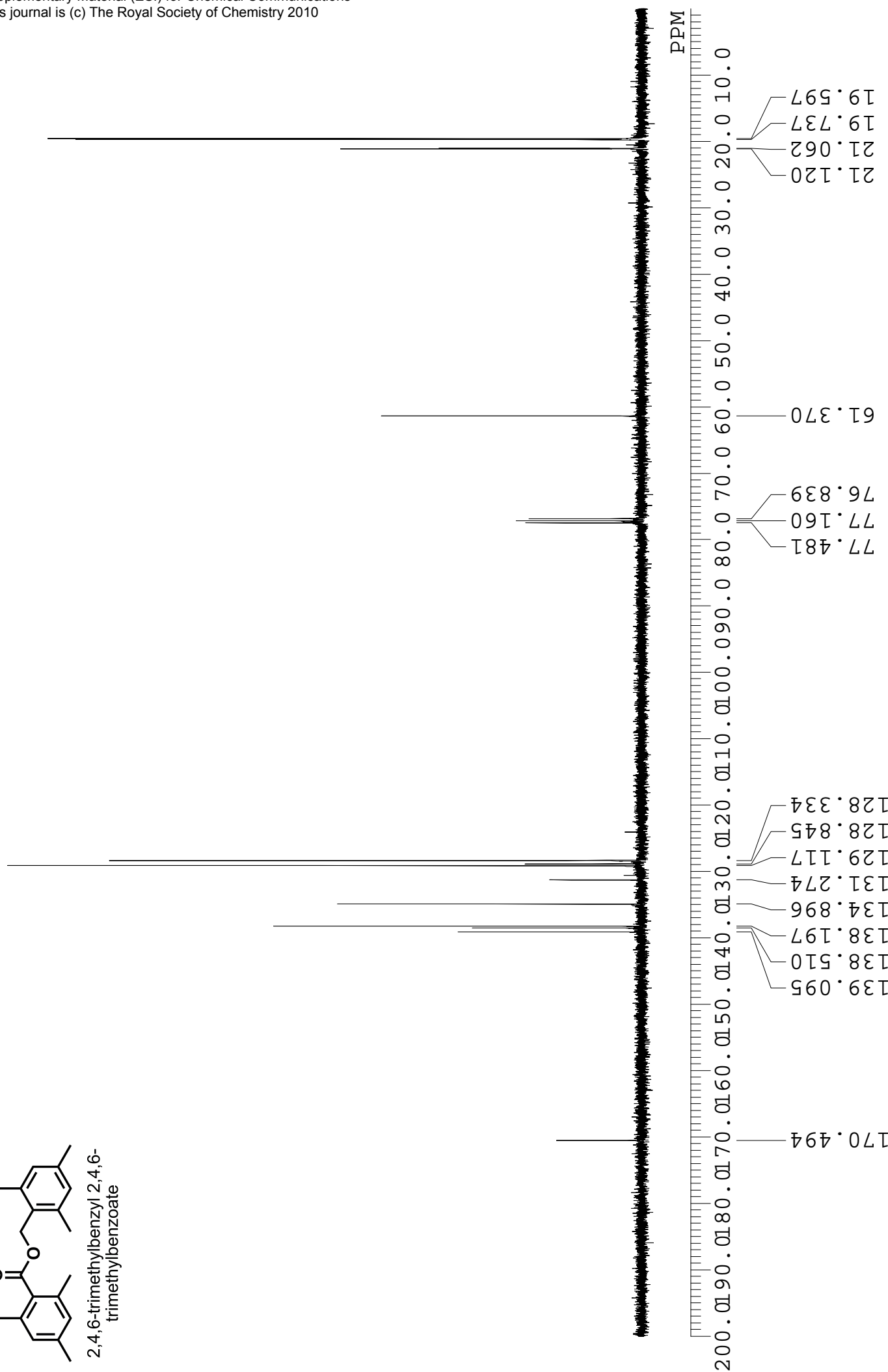
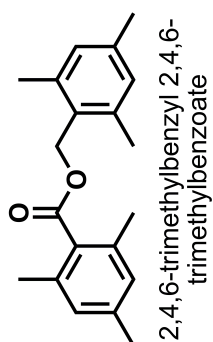
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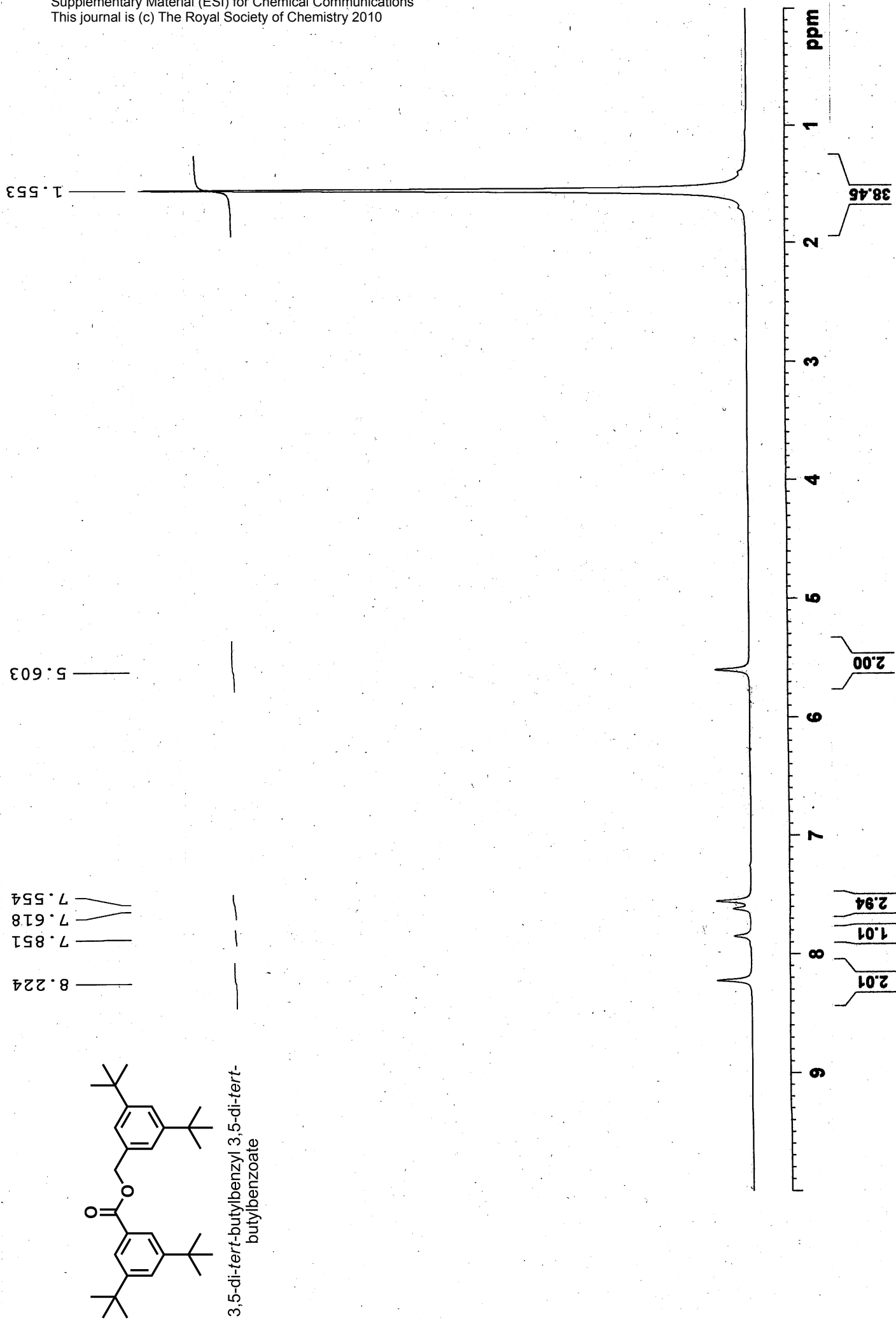


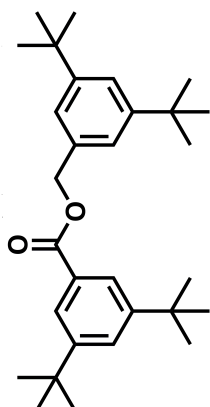
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\\HD300G\share\hoshimoto\H-NMR after\R.600-R.699\R.611\13CNMR CD3CL.als







3,5-di-*tert*-butylbenzyl 3,5-di-*tert*-butylbenzoate

34.94
34.87
31.55
31.45

66.95

77.47
77.15
76.83

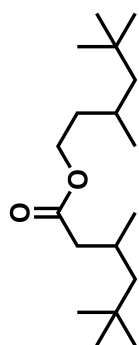
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121.97
123.99
127.06
129.89

135.65

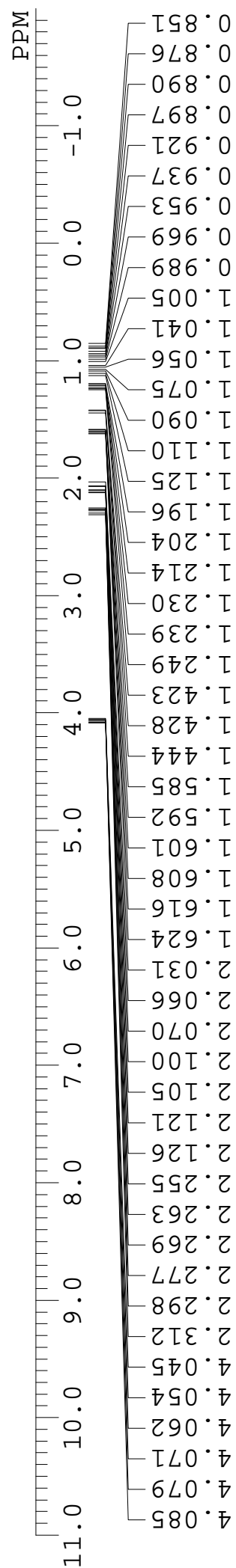
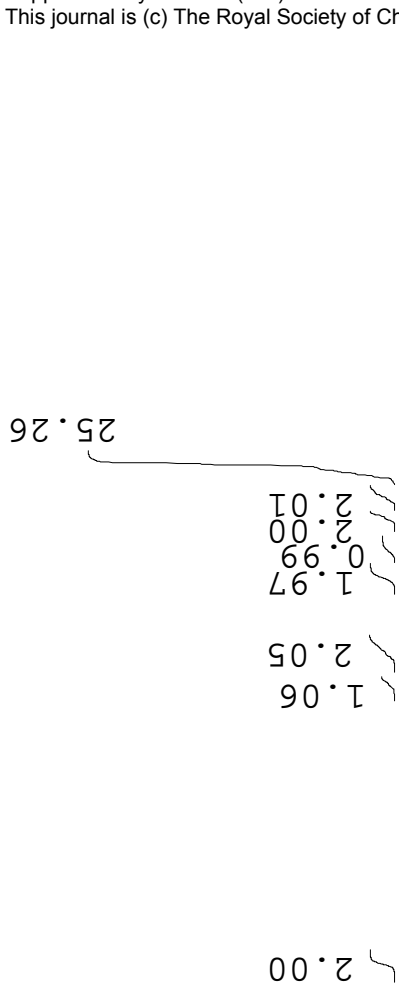
150.98
151.00

167.04

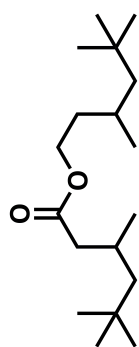
ppm
0
20
40
60
80
100
120
140
160
180
200
220



3,5,5-trimethylhexyl 3,5,5-trimethylhexanoate



\\HD300G\share\hoshimoto\H-NMR after\R.500-R.599\R.512\R.512 CNMR used sample CDCl3.als



3,5,5-trimethylhexyl 3,5,5-trimethylhexanoate

