

Supporting Information for:

**An Efficient Protocol for Alcohols Protection under Solvent
and Catalyst Free Conditions**

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General Information:

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp or I₂ stain. All products were characterized by their NMR and MS spectra. ¹H and ¹³C NMR was recorded on 200 and 300 MHz, in CDCl₃ using TMS as the internal standard, Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane.

General Experimental Procedure:

The pivoylation of alcohols carried out by simple addition of Piv-Cl (1.1 mmol) to hydroxy compound (1.0 mmol) in a 5 ml round bottom flask without using catalyst and solvent in closed vessel condition. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was dissolved in 5.0 mL of DCM and washed with distilled water then the organic layer was dried with Na₂SO₄ and solvent was evaporated under vacuum to yield the corresponding product (column chromatography was performed whenever it requires).

Spectral data of Compounds:

2-Pheny-ethyl pivalate (Table 2 entry 1) ^a

¹H NMR (300 MHz, CDCl₃): δ 7.28-7.14 (m, 5H), 4.24 (t, 2H, *J* = 6.9 Hz), 2.91 (t, 2H, *J* = 6.9 Hz), 1.14 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.0, 138.1, 129.0 (2C), 128.0 (2C), 126.5, 65.0, 38.5, 35.0, 27.0 (3C).

IR (ν_{max}): 1728 cm⁻¹. Mass (ESI): *m/z* = 229.3 (M+23).

Benzyl pivalate (Table 2 entry 2) ^a

¹H NMR (300 MHz, CDCl₃): δ 7.36-7.23 (m, 5H), 5.08 (s, 2H), 1.24 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.2, 136.3, 128.3 (2C), 127.8, 127.5 (2C), 65.9, 38.6, 27.0 (3C).

IR (ν_{max}): 1730 cm⁻¹. Mass (ESI): *m/z* = 215.1 (M+23)

2,3-Di hydro-1H-inden-2-yl pivalate (Table 2 entry 3)

¹H NMR (300 MHz, CDCl₃): δ 7.24-7.13 (m, 4H), 5.48-5.46 (m, 1H), 3.30 (d d, 2H, *J* = 6.9Hz, 16.6 Hz), 2.96 (d d, 2H, *J* = 3.0Hz, 17.3 Hz), 1.15 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.4, 140.4 (2C), 126.6 (2C), 124.5 (2C), 74.7, 39.5 (2C), 38.5, 27.0 (3C).

IR (ν_{max}): 1715 cm⁻¹. Mass (ESI): *m/z* = 219 .3 (M+1)

Anal calcd for: C₁₄H₁₈O₂ (218) C: 77.03, H: 8.31

Found: C: 76.90, H: 8.27

cyclopentylmethyl pivalate (Table 2 entry 4) ^a

¹H NMR (300 MHz, CDCl₃): δ 3.91 (d, 2H, *J* = 7.5 Hz), 2.28-2.11 (m, 1H), 1.82-1.67 (m, 2H), 1.66-1.50 (m, 4H), 1.33-1.21 (m, 2H), 1.19 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.6, 68.4, 39.0, 38.9, 29.5 (2C), 27.5 (3C), 25.6 (2C).

IR (ν_{max}): 1723 cm⁻¹. Mass (ESI): *m/z* = 181.1 (M+1)

Cyclohexyl pivalate (Table 2 entry 5)

¹H NMR (300 MHz, CDCl₃): δ 4.72-4.70 (m, 1H), 1.76-1.70 (m, 5H), 1.53-1.53 (m, 5H), 1.18 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.0, 72.0, 39.0, 31.3 (2C), 27.4 (3C), 26.0, 23.8 (2C).

IR (ν_{max}): 1703 cm⁻¹, **Mass** (ESI): *m/z* = 207.2 (M+23).

Anal calcd for: C₁₁H₂₀O₂ (184) C: 71.70, H: 10.94

Found: C: 71.66, H: 10.89

(1R, 2S, 5R)-2-isopropyl-5-methylcyclohexyl pivalate (Table 2 entry 6)

¹H NMR (300 MHz, CDCl₃): δ 4.57 (t d, 1H), 1.99-1.79 (m, 2H), 1.74-1.64 (m, 2H), 1.57- 1.32 (m, 2H), 1.18 (s, 9H), 1.12-0.95 (m, 2H), 0.92-0.85 (m, 6H), 0.75 (d, 3H, *J* = 6.78 Hz).

¹³C NMR (75 MHz, CDCl₃): δ 177.7, 73.6, 47.1, 40.7, 38.7, 34.4, 31.3, 27.0 (3C), 26.1, 23.3, 22.0, 20.8, 16.1.

IR (ν_{max}): 1725 cm⁻¹, **Mass** (ESI): *m/z* = 263.3 (M+23)

Anal calcd for: C₁₅H₂₈O₂ (240) C: 74.95, H: 11.74

Found: C: 74.90, H: 11.68

4-methoxybenzyl pivalate (Table 2 entry 7) ^a

¹H NMR (200 MHz, CDCl₃): δ 7.21 (d, 2H, *J* = 8.5Hz), 6.81 (d, 2H, *J* = 8.5Hz), 5.0 (s, 2H), 3.78 (s, 2H), 1.19 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 177.8, 136.4, 128.4 (2C), 127.9, 127.7 (2C), 65.9, 38.7, 27.2 (3C).

IR: 1701 cm⁻¹. **Mass** (ESI): *m/z* = 223.4 (M+1)

(Naphthalen-6-yl) Methyl pivalate (Table 2 entry 8)

¹H NMR (300 MHz, CDCl₃): δ 7.80-7.76 (m, 4H), 7.47-7.37 (m, 3H), 5.23 (s, 2H), 1.23 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.3, 133.8, 133.1, 133.0, 128.2, 127.9, 127.6, 126.8, 126.2, 126.1, 125.5, 66.2, 38.8, 27.1 (3C).

IR (ν_{max}): 1729 cm⁻¹, **Mass** (ESI): *m/z* = 243.6 (M+1).

Anal calcd for: C₁₆H₁₈O₂ (242) C: 79.31, H: 7.49

Found: C: 79.28, H: 7.45

1,2-Diphenylethane-1, 2-Di pivalate (Table 2 entry 9)

¹H NMR (300 MHz, CDCl₃): δ 7.27-7.23 (m, 6H), 7.20-7.14 (m, 4H), 6.01 (s, 2H), 1.09 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 176.7 (2C), 136.5 (2C), 128.2 (2C), 128.0 (4C), 127.4 (4C), 38.7 (2C), 26.9 (6C).

IR (ν_{max}): 1721 cm⁻¹. **Mass** (ESI): *m/z* = 405.1 (M+23).

Anal calcd for: C₂₄H₃₀O₄ (382) C: 75.36, H: 7.91

Found: C: 75.33, H: 7.85

Decyl pivalate (Table 2 entry 10) ^a

¹H NMR (300 MHz, CDCl₃): δ 4.02 (t, 2H, *J* = 6.79 Hz), 1.65-1.51 (m, 2H), 1.39-1.26 (m, 14H), 0.88 (t, 3H, *J* = 6.03 Hz), 1.18 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.9, 64.9, 39.0, 32.0, 29.8 (2C), 29.5 (2C), 28.9, 27.0 (3C), 26.0, 23.0, 14.3.

IR (ν_{max}): 1731 cm⁻¹. **Mass** (ESI): *m/z* = 243.1 (M+1).

Isobutyl pivalate (Table 2 entry 11)

¹H NMR (300 MHz, CDCl₃): δ 3.83 (d, 2H, *J* = 6.5 Hz), 2.00-1.85 (m, 1H), 1.2 (s, 9H), 0.93 (d, 6H, *J* = 6.5 Hz).

IR (ν_{max}): 1730 cm⁻¹. **Mass** (ESI): *m/z* = 181.2 (M+23)

Anal calcd for: C₉H₁₈O₂ (158) C: 68.31, H: 11.47

Found: C: 68.28, H: 11.42

Prop-2-ynyl pivalate (Table 2 entry 12)^a

¹H NMR (300 MHz, CDCl₃): δ 4.62 (d, 2H, *J* = 3.0 Hz), 2.38 (t, 1H, *J* = 3.0 Hz,), 1.22 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 185.6, 111.9, 107.4, 46.7, 38.6, 26.9 (3C)

IR (ν_{max}): 1727 cm⁻¹, 2364 cm⁻¹. **Mass** (ESI): *m/z* = 141.3 (M+1)

Butane-1, 4-Dipivalate (Table 2 entry 13) ^a

¹H NMR (300 MHz, CDCl₃): δ 4.08 (t, 4H, *J* = 6.04 Hz), 1.73-1.68 (m, 4H), 1.20 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 178.0 (2C), 64.2 (2C), 39.0 (2C), 27.5 (6C), 25.8 (2C).

IR(ν_{max}): 1730 cm⁻¹ , **Mass** (ESI): *m/z* = 259.2 (M+1).

(E)-hex-2-enyl pivalate (Table 2 entry 14)

¹H NMR (300 MHz, CDCl₃): δ 5.76-5.67 (m, 1H), 5.56-5.47 (m, 1H), 4.47 (d, 2H, *J* = 6.5 Hz), 2.02 (q, 2H, *J* = 6.5 Hz), 1.48-1.34 (m, 2H), 1.19 (s, 9H), 0.91 (t, 3H, *J* = 7.0 Hz),

IR (ν_{max}): 1731 cm⁻¹. **Mass** (ESI): *m/z* = 185.1 (M+1)

Anal calcd for: C₁₁H₂₀O₂ (184) C: 71.70, H: 10.94

Found: C: 71.67, H: 10.90

2-methoxyethyl pivalate (Table 2 entry 15)

¹H NMR (300 MHz, CDCl₃): δ 4.17 (t, 2H, *J* = 4.53 Hz), 3.55 (t, 2H, *J* = 4.53 Hz), 3.36 (s, 3H), 3.36 (s, 9H).

IR (ν_{max}): 1728 cm⁻¹. **Mass** (ESI): *m/z* = 161.4 (M+1)

Anal calcd for: C₈H₁₆O₃ (160) C: 59.97, H: 10.07

Found: C: 59.92, H: 10.10

Naphthalen-8-yl pivalate (Table 3 entry 3)

¹H NMR (300 MHz, CDCl₃): δ 7.81 (q, 2H, *J* = 3.0 Hz), 7.70 (d, 1H, *J* = 8.3 Hz), 7.48- 7.406 (m, 3H), 7.18 (d, 1H, *J* = 6.8 Hz), 1.49 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 176.9, 147.1, 134.9, 128.3, 127.3, 126.5 (2C), 125.9, 125.6, 121.2, 118.1, 39.7, 27.6 (3C).

IR (ν_{max}): 1732 cm⁻¹. **Mass** (ESI): *m/z* = 229.4 (M+1)

Anal calcd for: C₁₅H₁₆O₂ (228) C: 78.92, H: 7.06

Found C: 78.87, H: 7.02

Naphthalen-7-yl pivalate (Table 3 entry 4)

¹H NMR (300 MHz, CDCl₃): δ 7.91-7.76 (m, 3H), 7.57-7.43 (m, 3H), 7.19 (d d, 1H, *J* = 2.2 Hz, 8.8 Hz), 1.41 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 177.2, 148.7, 133.7, 131.3, 129.2, 127.7, 127.5, 126.4, 125.5, 121.1, 118.3, 39.1, 27.1 (3C).

IR (ν_{max}): 1725 cm⁻¹. **Mass** (ESI): *m/z* = 229.4 (M+1)

Anal calcd for: C₁₅H₁₆O₂ (228) C: 78.92, H: 7.06

found C: 78.83, H: 7.01

Naphthalene-2, 3-Di-pivalate (Table 3 entry 5)

¹H NMR (300 MHz, CDCl₃): δ 7.77-7.72 (m, 2H), 7.56 (s, 2H), 7.44-7.38 (m, 2H), 1.38 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 176.4 (2C), 141.8 (2C), 131.7 (2C), 127.5 (2C), 126.3 (2C), 120.9 (2C), 39.4 (2C), 27.5 (6C).

IR (ν_{max}): 1758 cm⁻¹. **Mass** (ESI): *m/z* = 351.1 (M+23)

Anal calcd for: C₂₀H₂O₄ (328) C: 73.15, H: 7.37

Found: C: 73.11, H: 8.31

3-(benzyloxy)-2-Hydroxyhex-5-enyl pivalate (Scheme 2. 2b)

¹H NMR (300 MHz, CDCl₃): δ 7.29-7.29 (m, 5H), 6.00-5.69 (m, 1H), 5.312-5.07 (m, 2H), 4.65 (d d, 1H, *J* = 9.8, 11.7 Hz), 4.50 (d d, 1H, *J* = 3.9 Hz, 11.7 Hz), 4.32-4.09 (m, 2H), 3.83-3.74 (m, 1H), 3.55-3.40 (m, 1H), 2.59-2.34 (m, 2H), 2.37 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 179.1, 138.0, 134.2, 128.4 (2C), 127.8 (3C), 117.7, 79.1, 72.2, 71.1, 65.7, 34.4, 31.6, 27.2 (3C).

IR (ν_{max}): 1727 cm⁻¹, (Broad Peak) 3469.2 cm⁻¹. **Mass** (ESI): *m/z* = 329.9 (M+23)

Anal calcd for: C₁₈H₂₆O₄ (306) C: 70.56, H: 8.55

Found: C: 70.51, H: 8.49

3-(benzyloxy)-1-tert-butyldimethylsilane - hex-5-enyl-2-pivalate (Scheme 2. 1b)

¹H NMR (200 MHz, CDCl₃): δ 7.27-7.18 (m, 5H), 5.89-5.71 (m, 1H), 5.10-4.98 (m, 2H), 4.93-4.87 (m, 1H), 4.60-4.46 (m, 2H), 3.81-3.57 (m, 3H), 2.40-2.18 (m, 2H), 1.20 (s, 9H), 0.88 (s, 9H), 0.03 (s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 177.3, 138.4, 134.5, 128.2(2C), 127.7 (2C), 127.5, 117.3, 77.2, 74.4, 72.3, 61.2, 38.8, 35.2, 27.3 (3C), 25.9 (3C), 18.2, - 5.3 (2C).

IR (ν_{max}): 1730 cm⁻¹. **Mass** (ESI): *m/z* = 421.9 (M+1)

Anal calcd for: C₂₄H₄₀O₄ (420) C: 68.53, H: 9.58

Found: C: 68.48, H: 9.52

3-(benzyloxy)-1-Hydroxyhex-5-en-2-yl pivalate (Scheme 2. 1c)

¹H NMR (300 MHz, CDCl₃): δ 7.42- 7.20 (m, 5H), 5.98-5.64 (m, 1H), 5.22- 4.87 (m, 3H), 4.54 (s, 2H), 4.38-4.12 (m, 1H), 4.00-3.83 (m, 1H), 3.58-3.36 (m, 1H), 2.59- 2.29 (m, 2H), 1.30-1.12 (m, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 179.0, 137.8, 134.0, 128.2 (2C), 127.8 (3C), 117.6, 78.9, 72.1, 71.1, 65.8, 34.3, 31.7, 27.1 (3C).

IR (ν_{max}): 1727 cm⁻¹, (Broad Peak) 3481.5 cm⁻¹. **Mass** (ESI): *m/z* = 329.9 (M+23)

Anal calcd for: C₁₈H₂₆O₄ (306) C: 70.56, H: 8.55

Found: C: 70.51, H: 8.48

3-(benzyloxy)-Hex-5-enyl-1,2-Di-pivalate (Scheme 2. 1d).

¹H NMR (300 MHz, CDCl₃): δ 7.29-7.25 (m, 5H), 5.90-5.74 (m, 1H), 5.20-5.05 (m, 3H), 4.57 (s, 2H), 4.43 (d, 1H, *J* = 11.1 Hz), 4.19-4.09 (m, 1H), 3.65-3.59 (m, 1H), 2.48-2.30 (m, 2H), 1.17 (d, 18H).

¹³C NMR (75 MHz, CDCl₃): δ 177.5, 176.8, 137.9, 133.6, 128.3 (2C), 127.7 (3C), 118.0, 77.5, 72.3, 72.1, 62.4, 38.7 (2C), 35.3, 27.2 (6C).

IR (ν_{max}): 1732 cm⁻¹. **Mass** (ESI): *m/z* = 391.7 (M+1)

Anal calcd for: C₂₃H₃₄O₅ (390) C: 70.74, H: 8.78

Found: C: 70.68, H: 8.74

^aP. Prabhakar, N. Suryakiran, Y. Venkateswarlu, *Chemistry Lett.*,2007, **36**, 732.

On suggestion of reviewers

We have tried for acetylation on substrate **1a** (scheme-2) and results are summarized here.

Acetylation products of **1a** (scheme-2), using Acetyl Chloride under catalyst and solvent free closed vessel conditions at room temperature leads to give TBS deprotected secondary mono-acetylated primary alcohol (NMR-P.no-S33) in less yields about 17% only and predominantly gives Di-acetylated product (NMR-P.no-S33) in 61% yields. The products are characterized by Mass & NMR Spectra. The signal at 2.04 (s, 3H) in NMR spectrum of minor product indicates Mono-Acetylation and the signal at 2.15-2.196 (d, 6H) in major product indicating the Di-Acetylation. The Mass spectral values 287 & 329 also conforming the products.

Mass & NMR Spectral data

Acetylated Product of **1a** (17% Yields^b)

¹H NMR (300 MHz, CDCl₃): δ 7.33 (m, 5H), 5.93-5.77 (m, 1H), 5.16-5.09 (m, 2H), 4.56 (s, 2H), 3.78-3.55 (m, 4H), 2.67-2.49 (b s, 1H), 2.31 (t, 2H *J* = 6.79 Hz), 2.04 (s, 3H).

Mass (ESI): *m/z* = 287 (M+23).

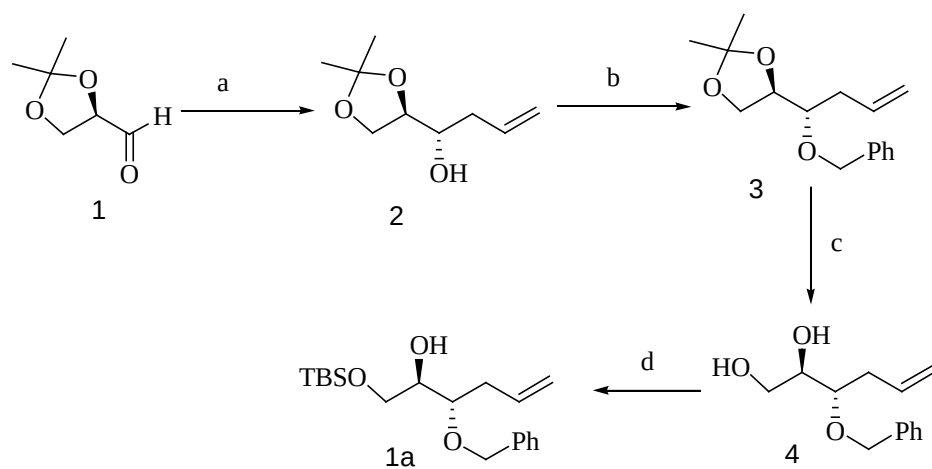
Acetylated Product of **1a(a)**(61% Yields^b)

¹H NMR (300 MHz, CDCl₃): δ 7.31 (m, 5H), 5.93-5.74 (m, 1H), 5.23-5.02 (m, 2H), 4.58 (d, 2H, *J* = 3.58 Hz), 4.57-4.39 (m, 1H), 4.23-4.16 (m, 1H), 3.74-3.61 (m, 1H), 3.58-3.48 (m, 1H), 2.38 (t, 2H, *J* = 6.79 Hz), 2.15-1.96 (d, 6H).

Mass (ESI): *m/z* = 329 (M+23).

^bYields of isolated products.

Preparation of **1a** (scheme-2)



Reagents and conditions : a) ref: S. P. Kumar et al, *Tetrahedron Lett* **2006**, 47, 7149–7; b) ref: S. Czernecki, C. Georgoulis, C. Provelenghiou, *Tetrahedron Lett.*, **1976**, 17, 3535-3536 ;c) ref: S. Malla Reddy, Y. Venkat Reddy, Y. Venkateswarlu, *Tetrahedron Lett* 2005, 46, 7439–7441; d) A. Bartoszewicz, M. Kalek, J. Nilsson, R. Hiresova, J. Stawinski, *Synlett*, **2008**, 37-40.

^1H and ^{13}C NMR Spectra of Compounds

Table-2, Entry-1

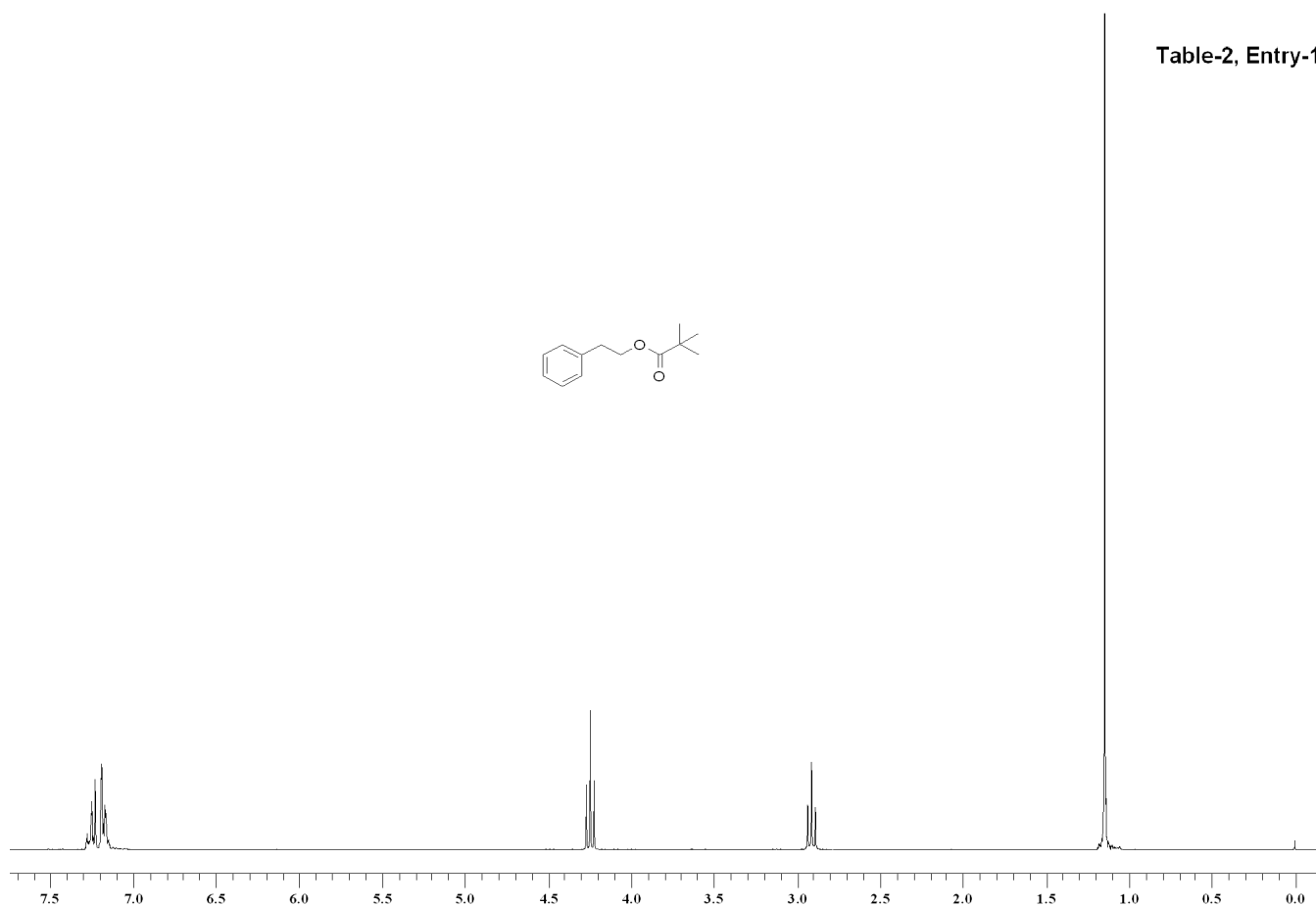


Table-2, Entry-1

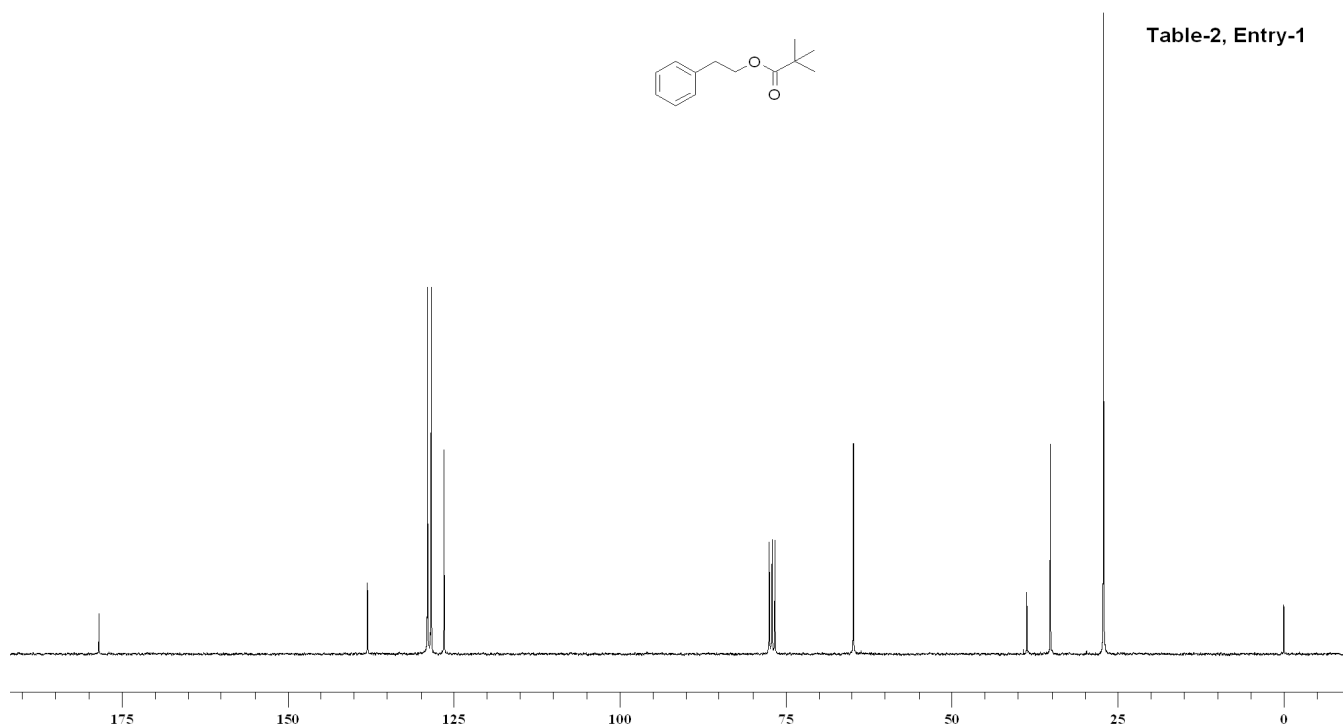


Table-2, Entry-2

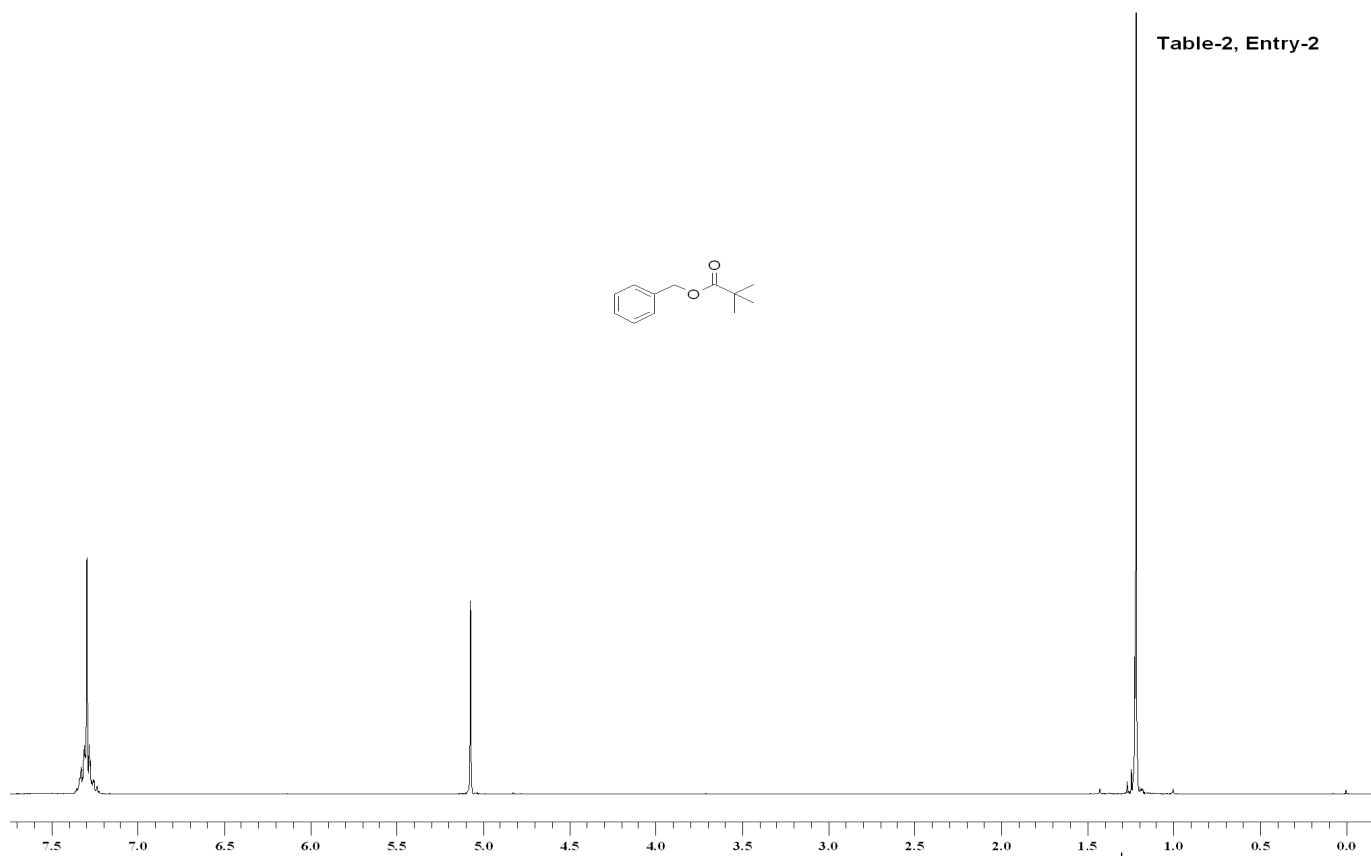
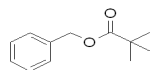


Table-2, Entry-2

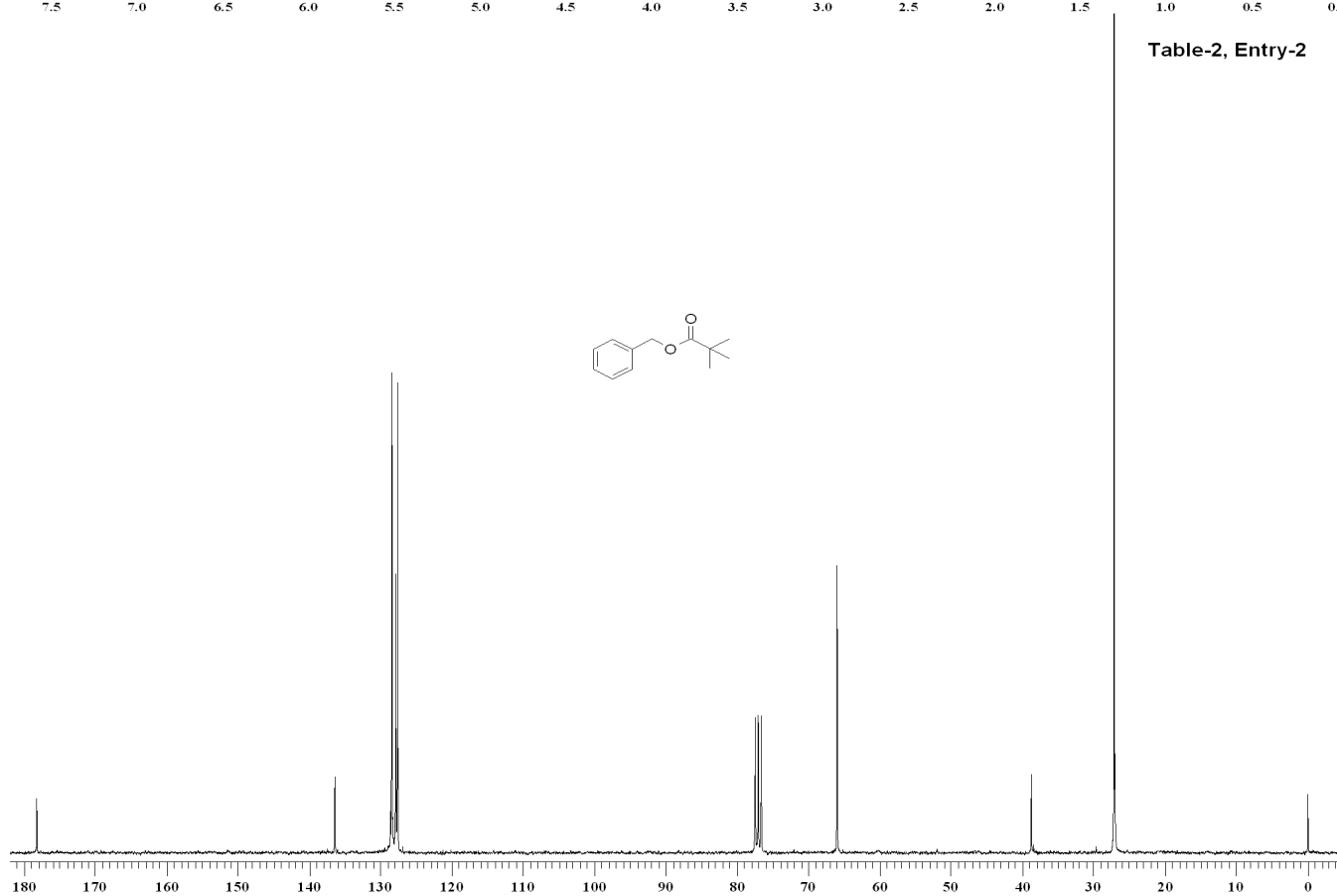
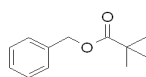


Table-2, Entry-3

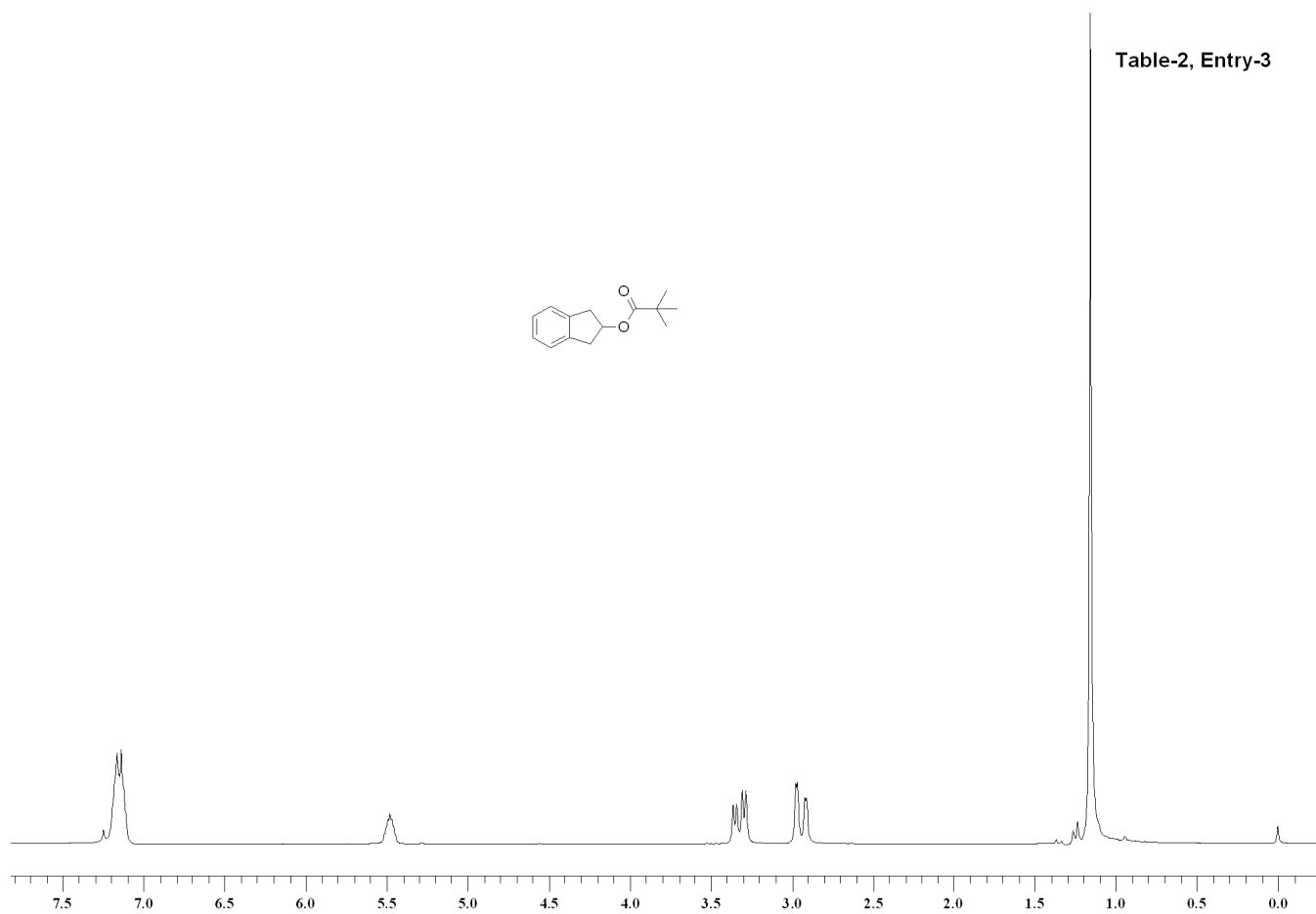


Table-2, Entry-3

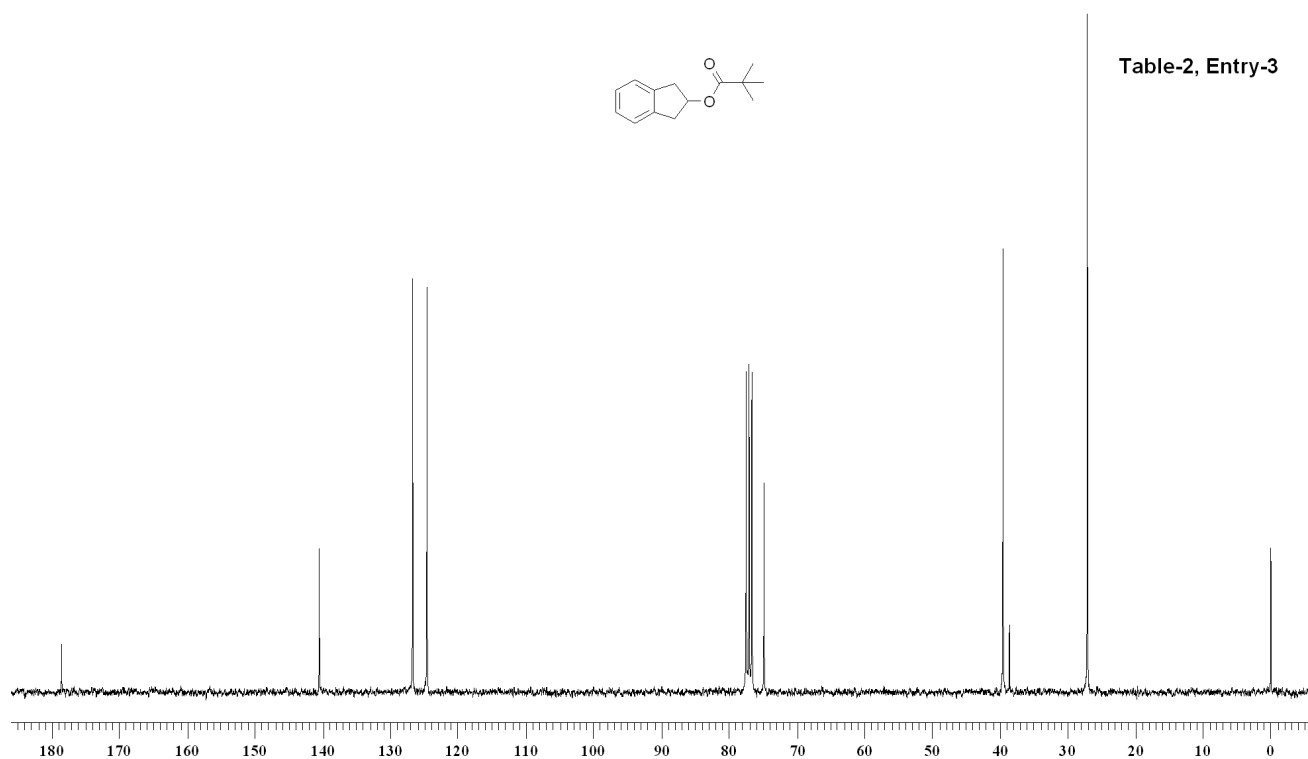


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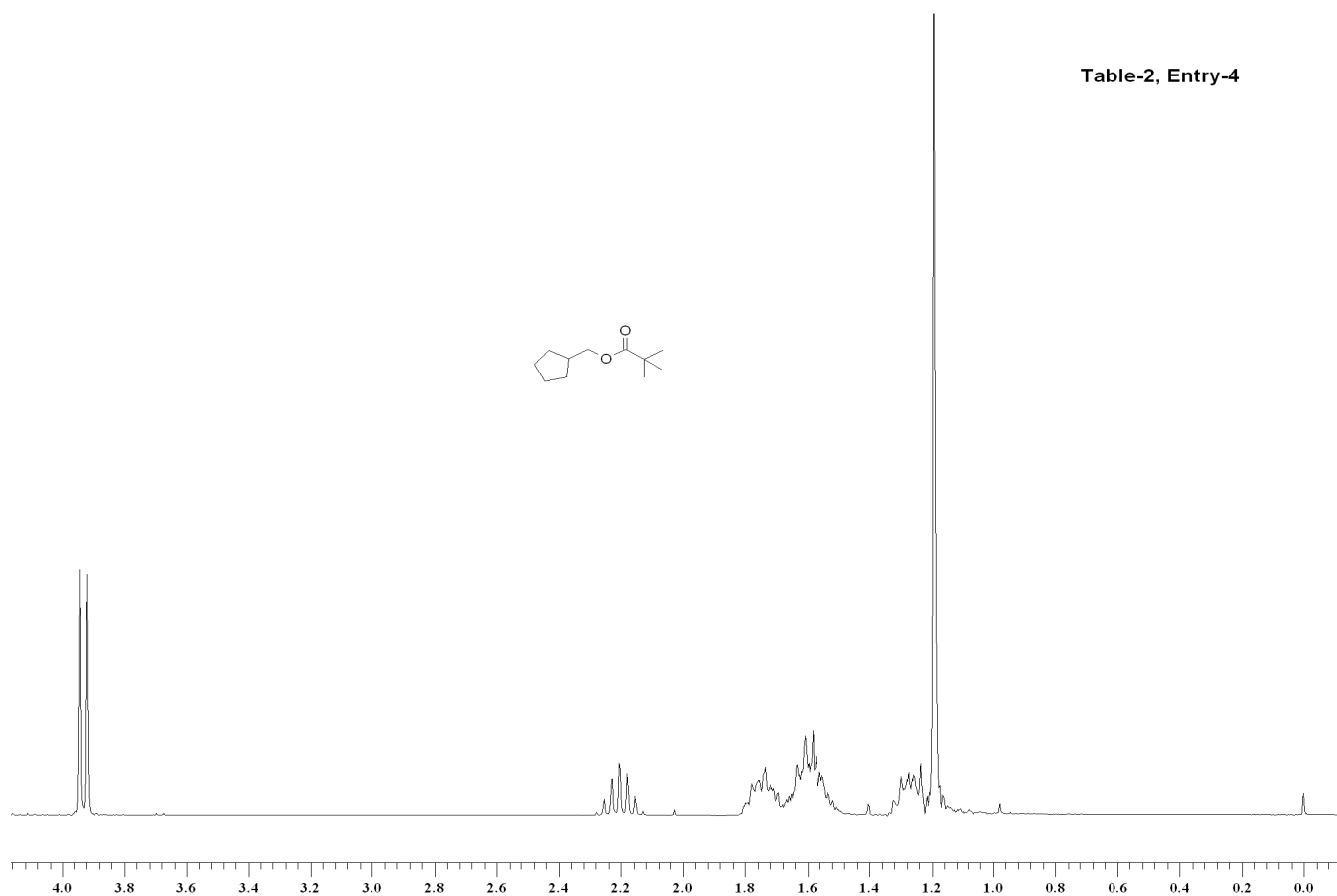


Table-2, Entry-4

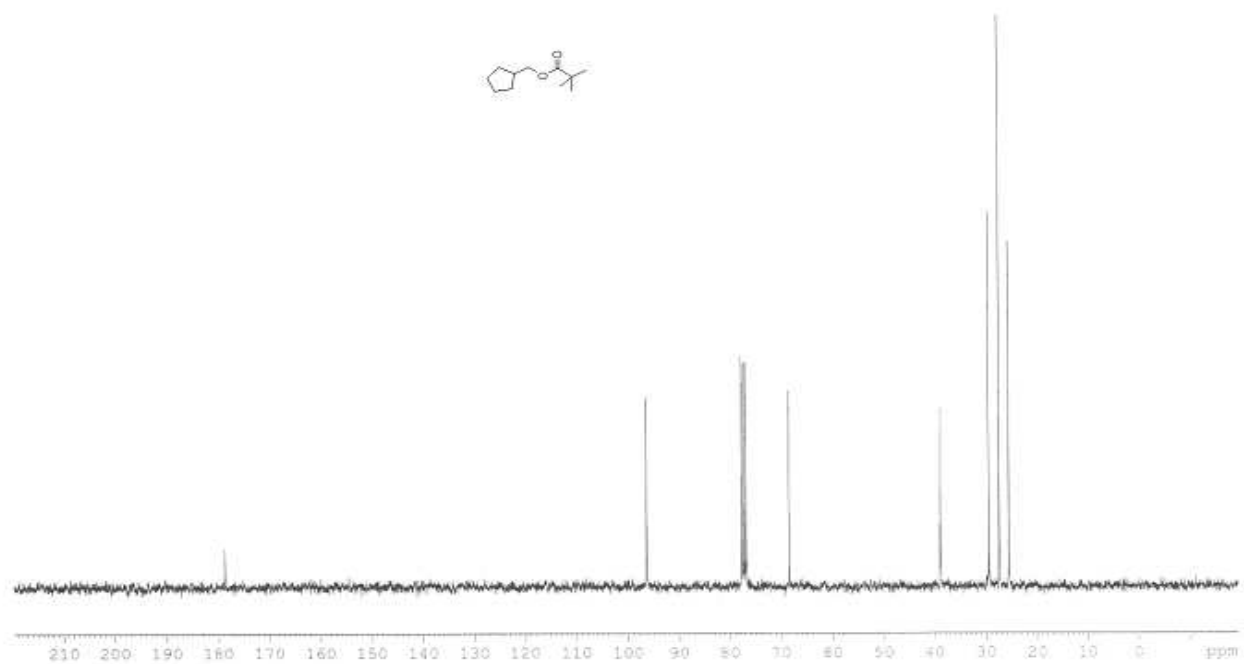


Table-2, Entry-5

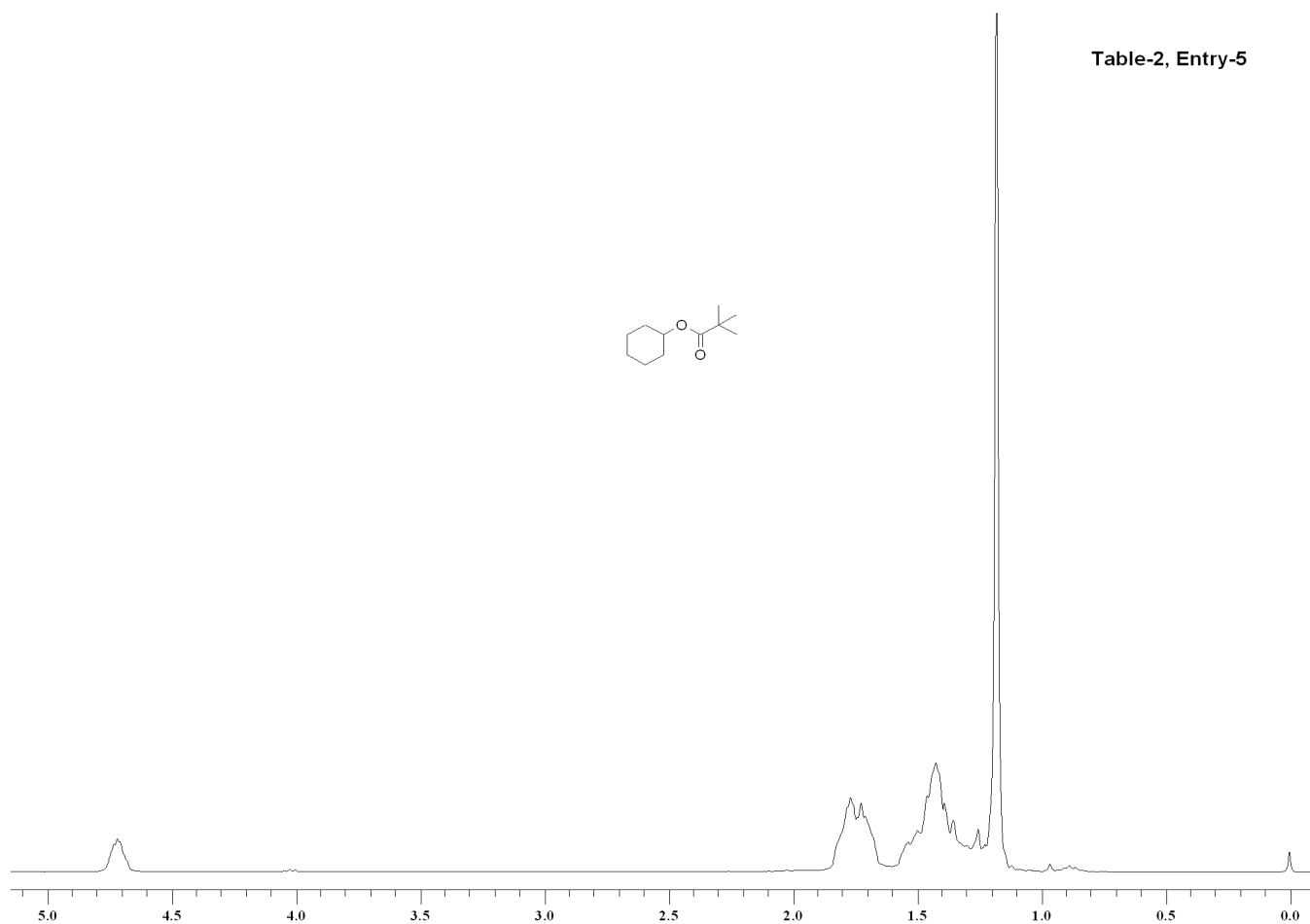
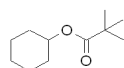


Table-2, Entry-5

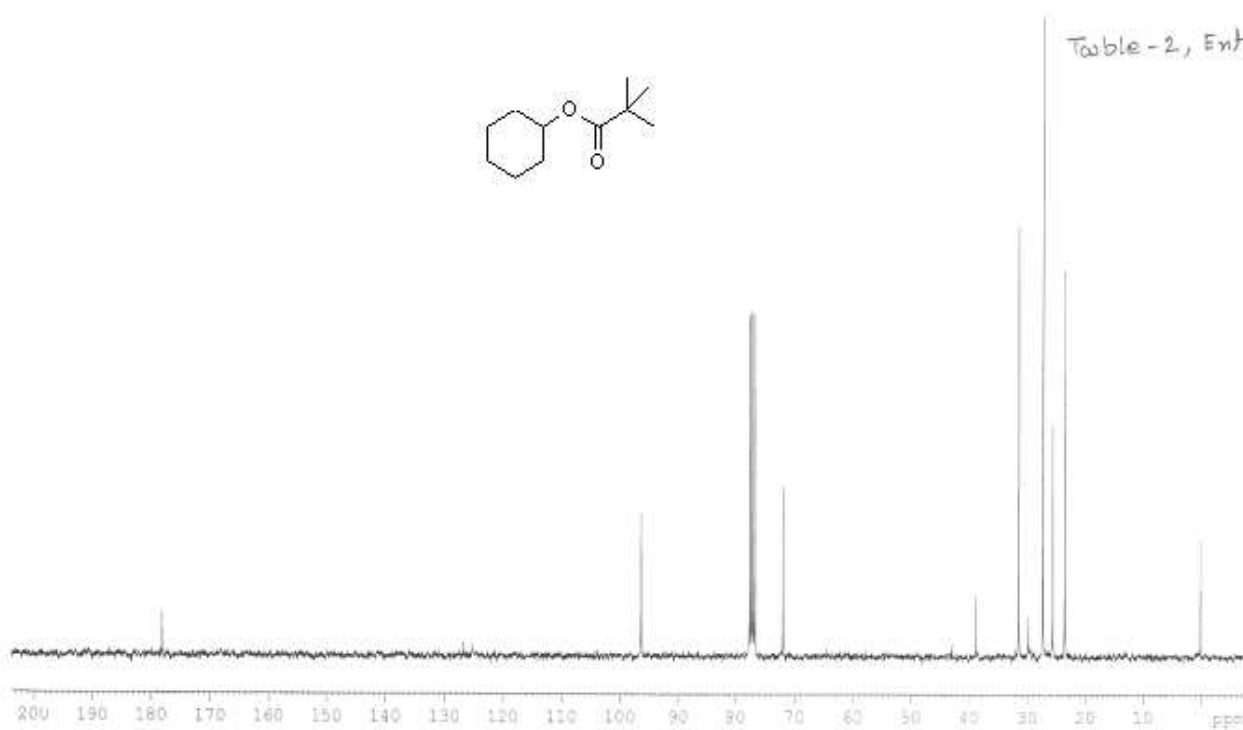
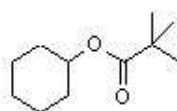


Table-2, Entry-6

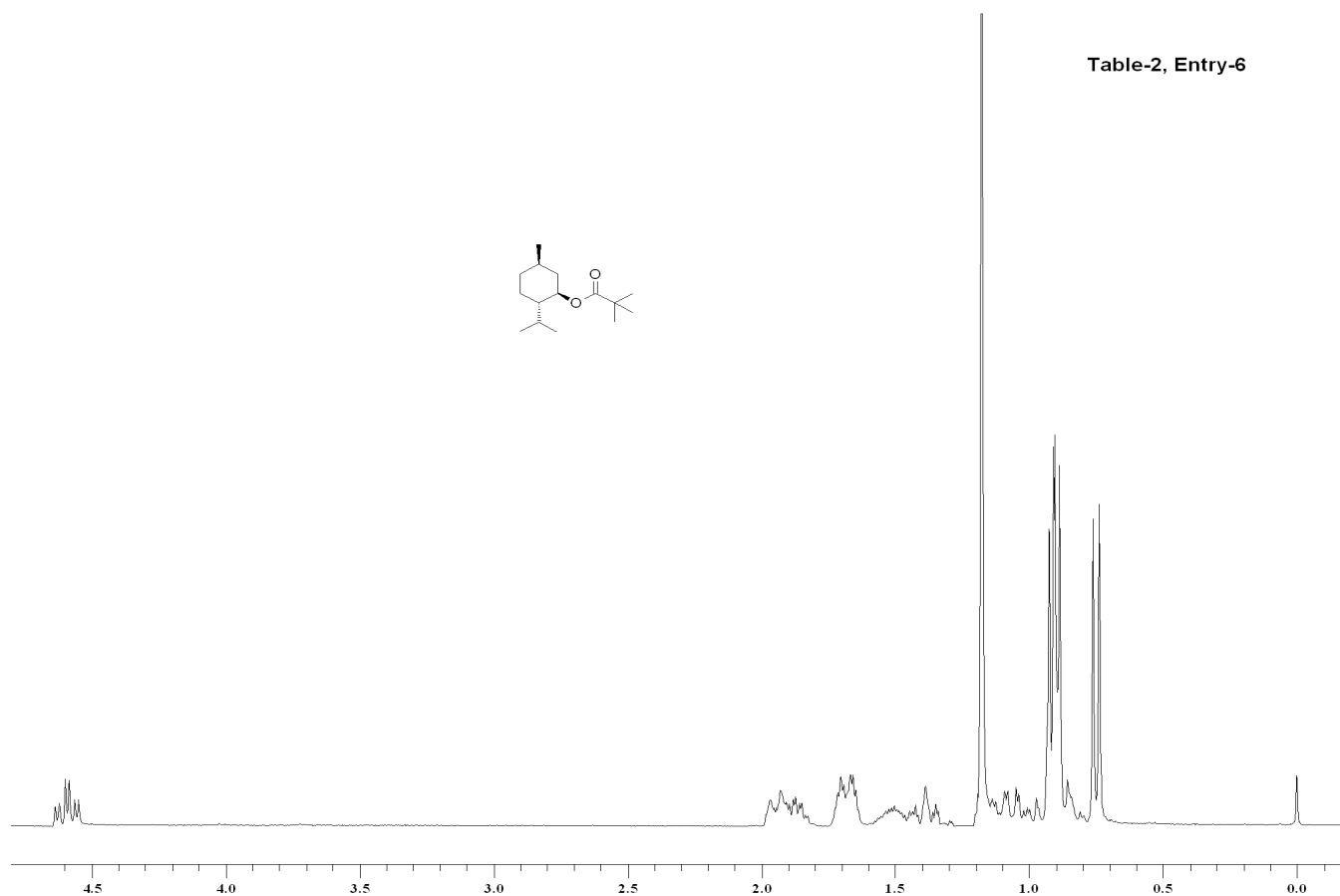
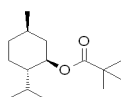


Table-2 Entry-6

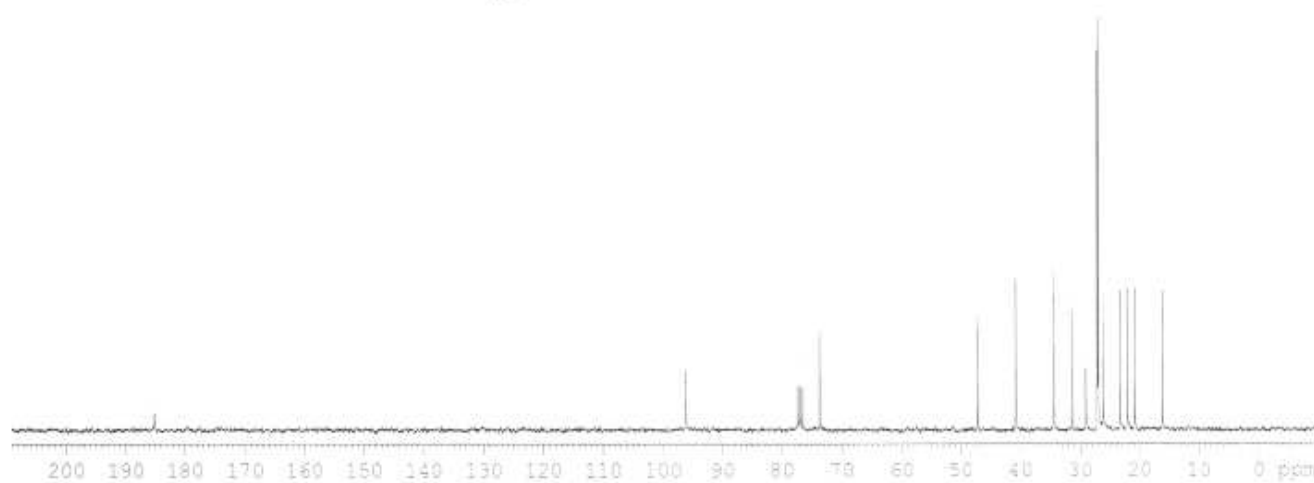


Table-2, Entry-7

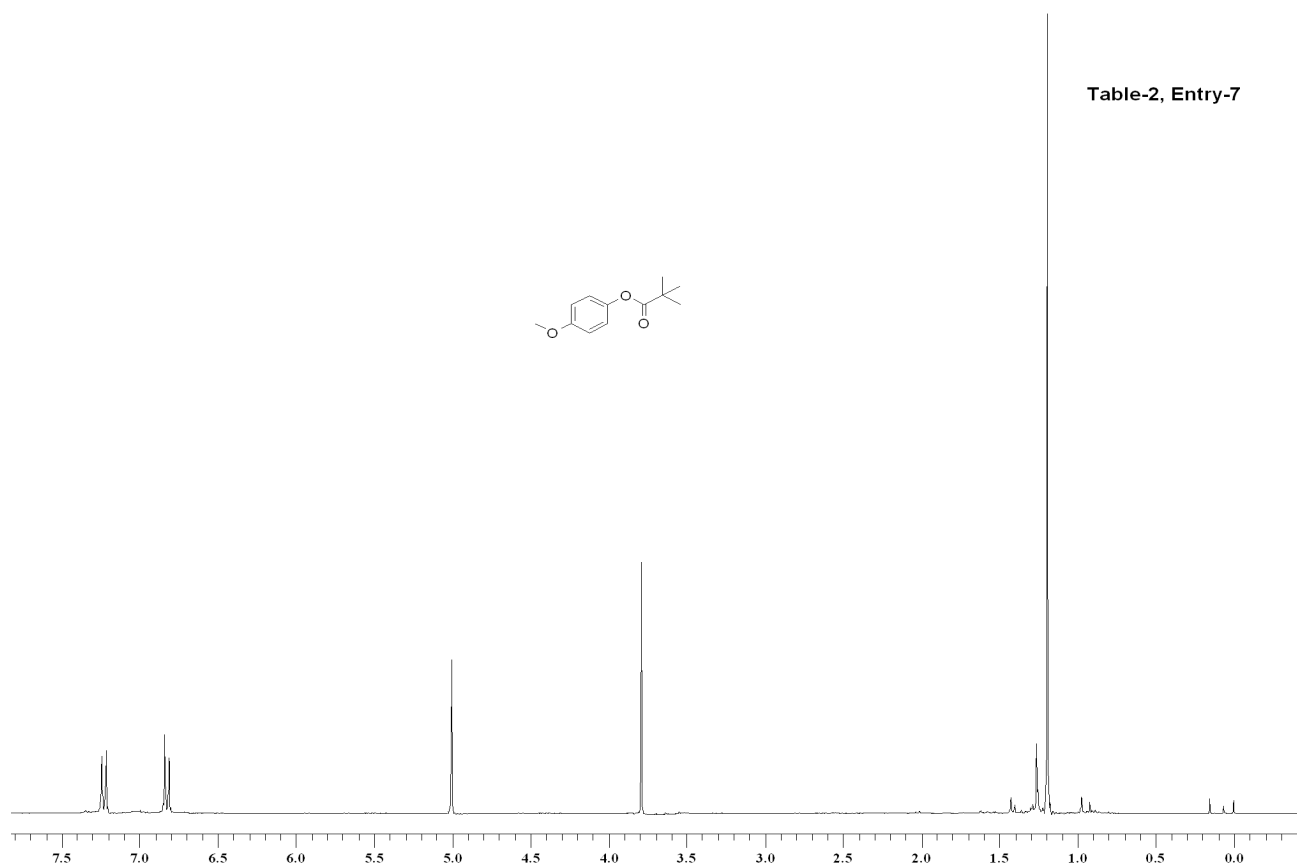


Table-2, Entry-7

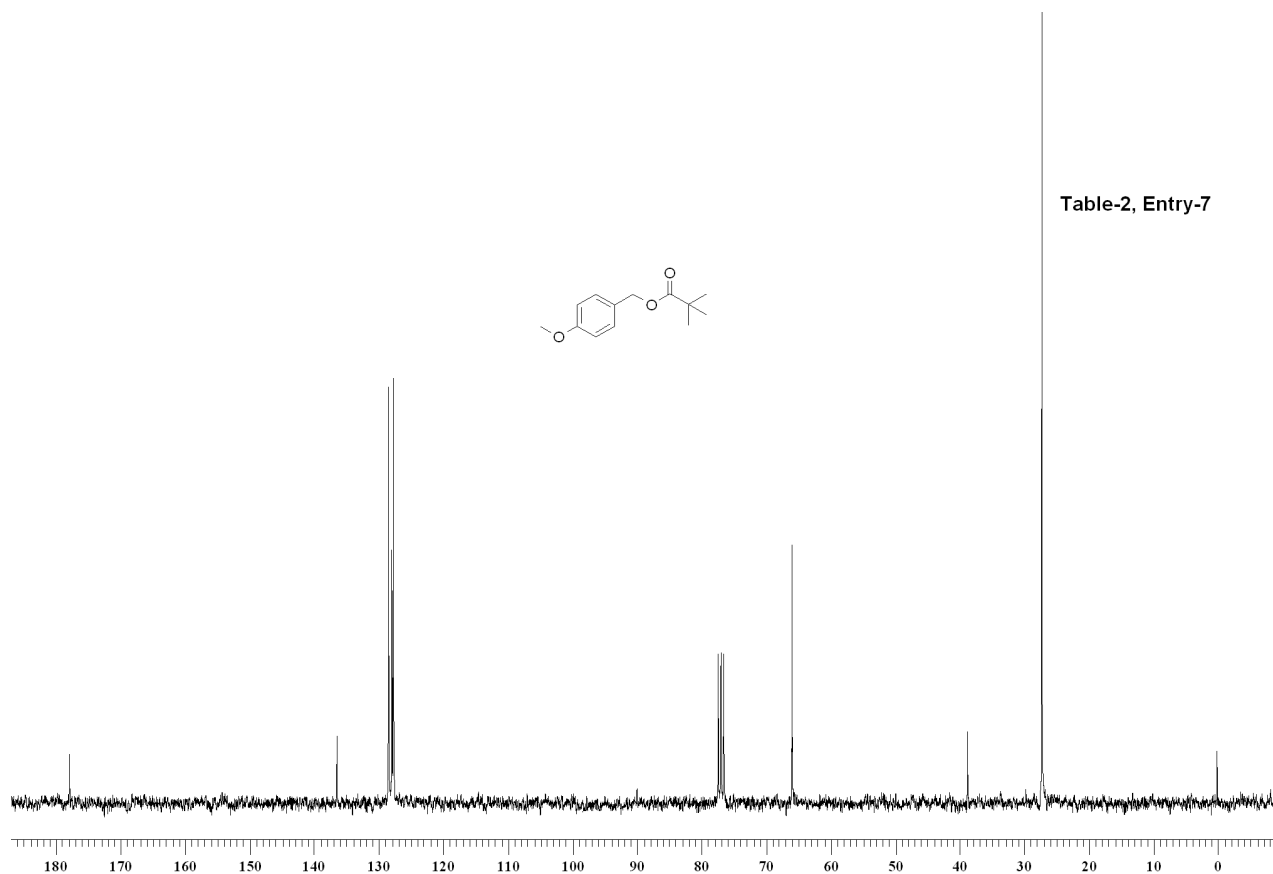


Table-2, Entry-8

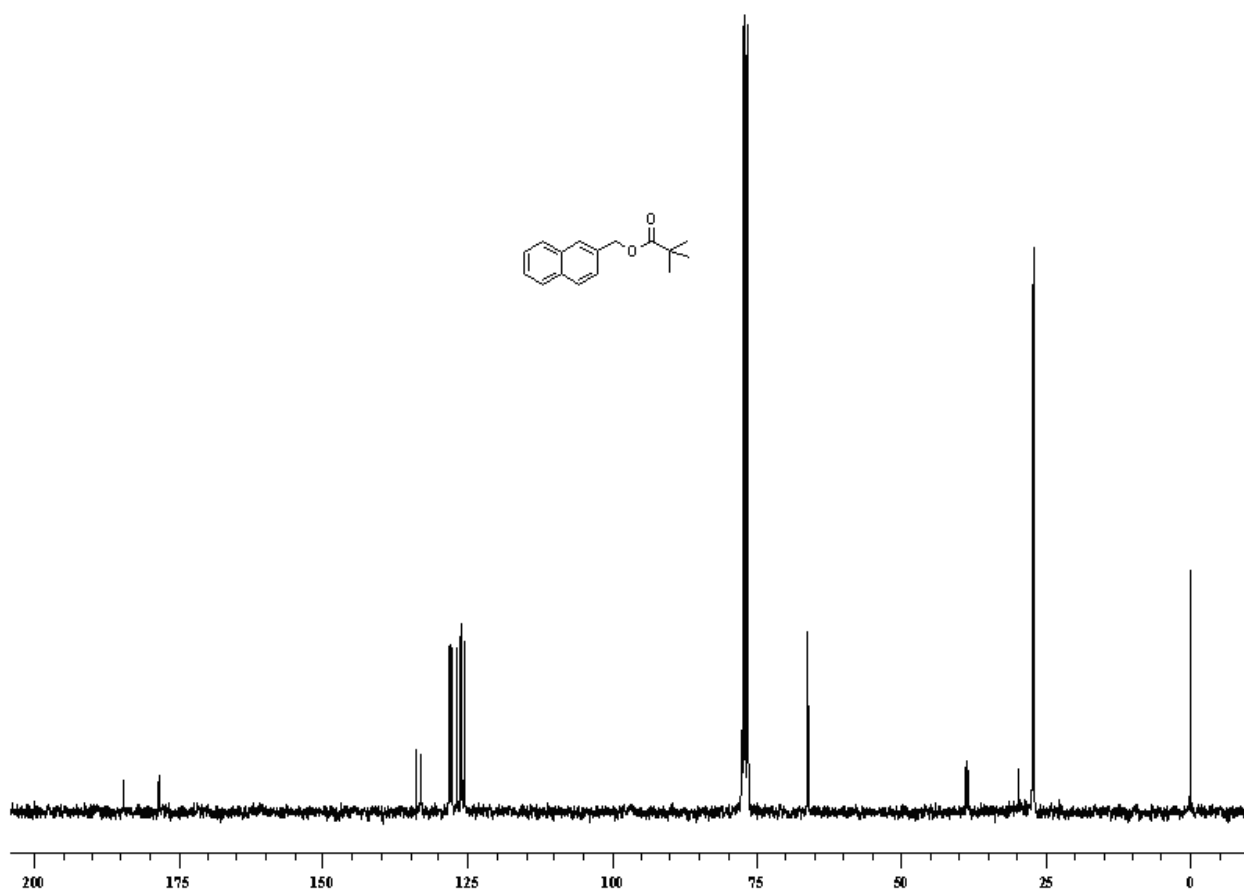
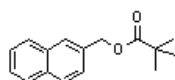
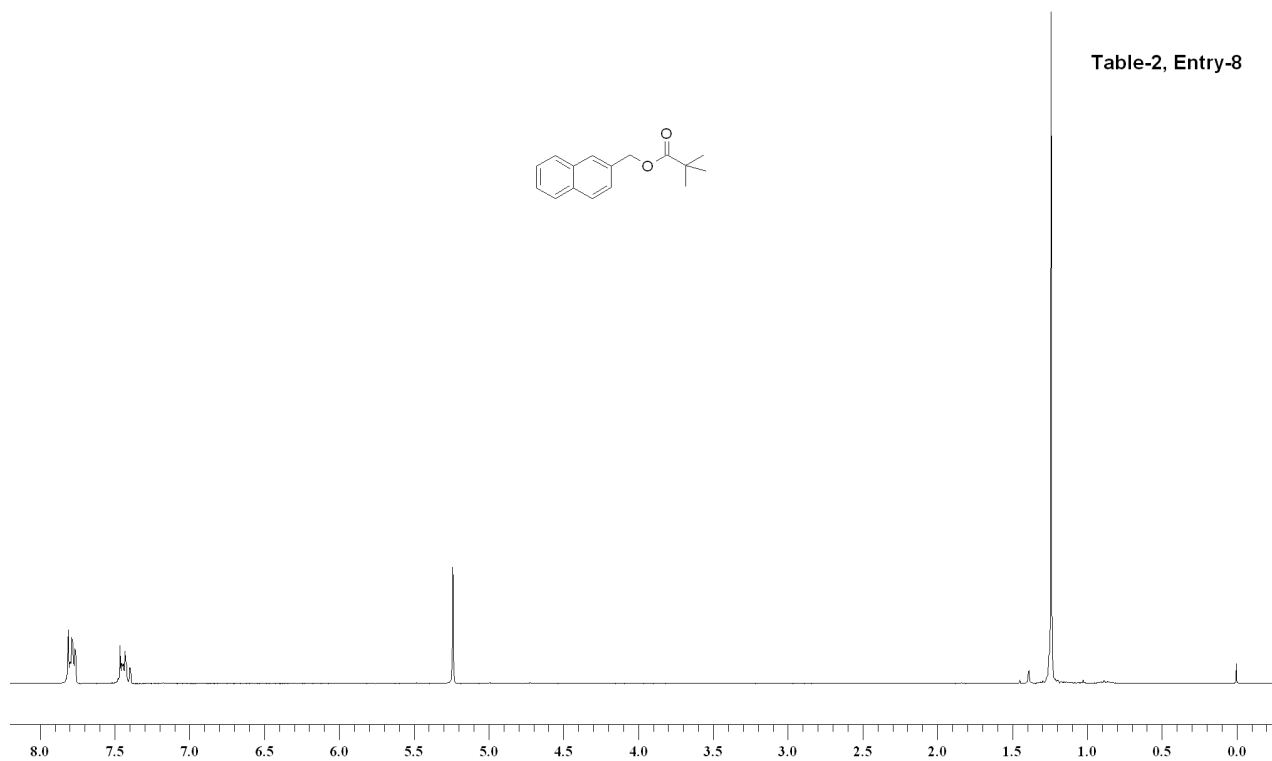
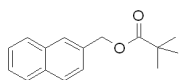


Table-2, Entry-9

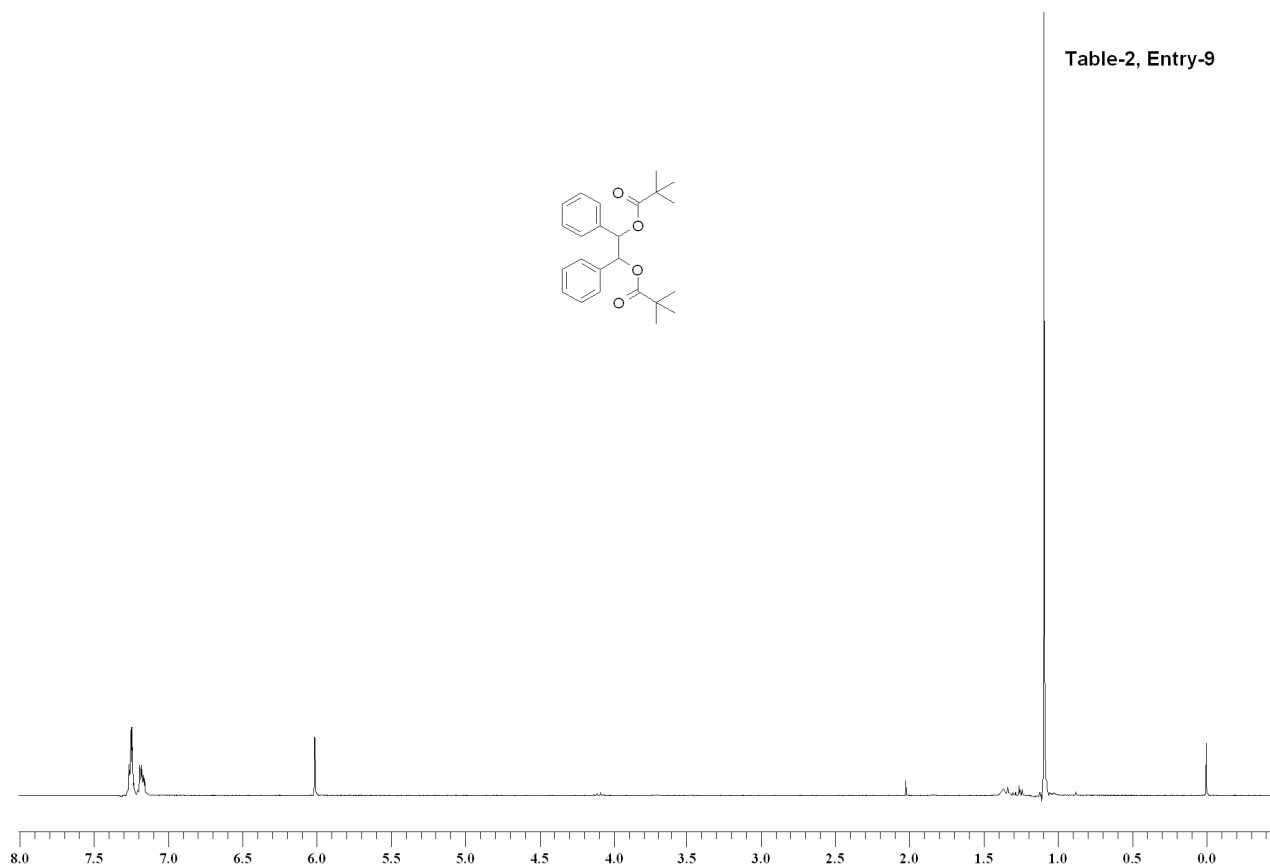
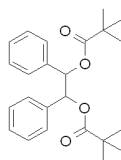


Table-2, Entry-9

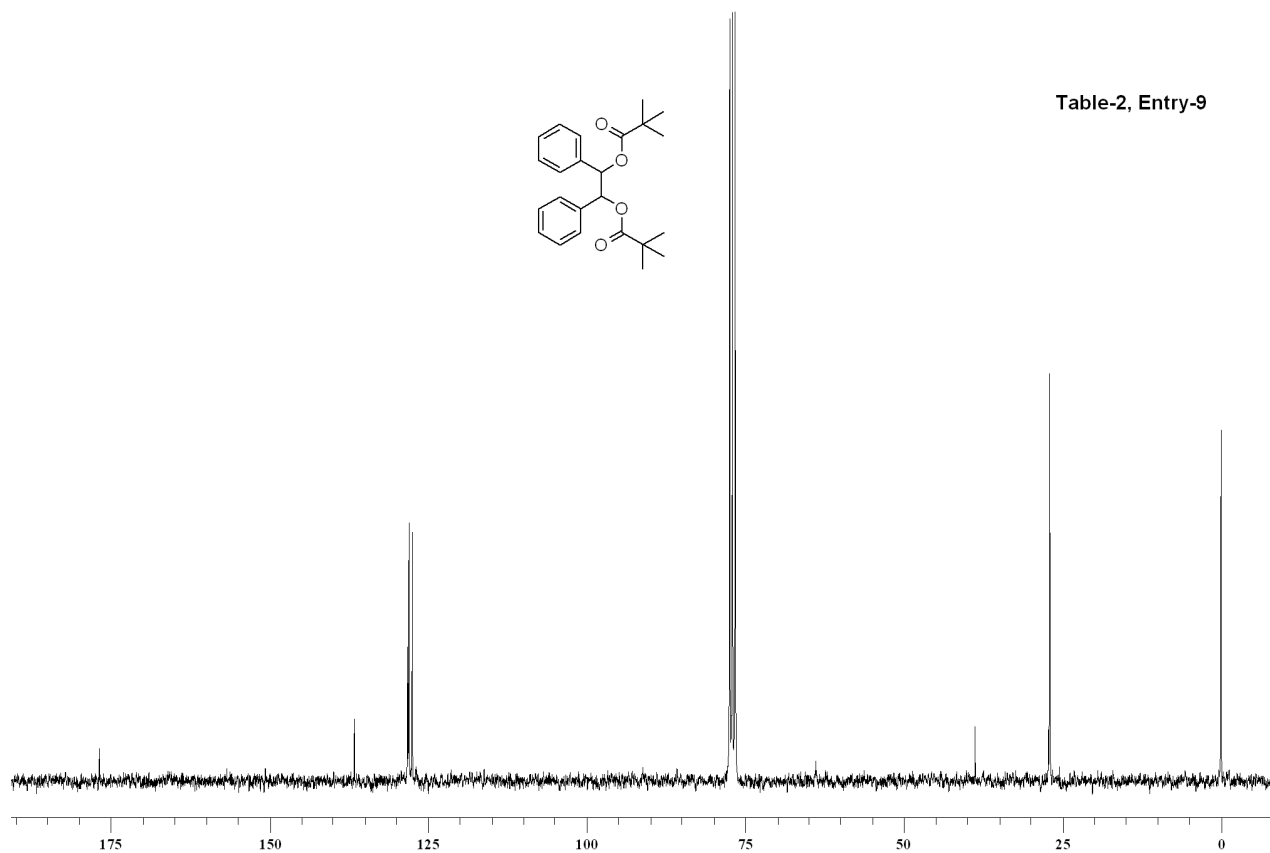
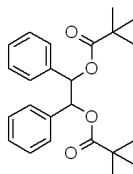


Table-2, Entry-10

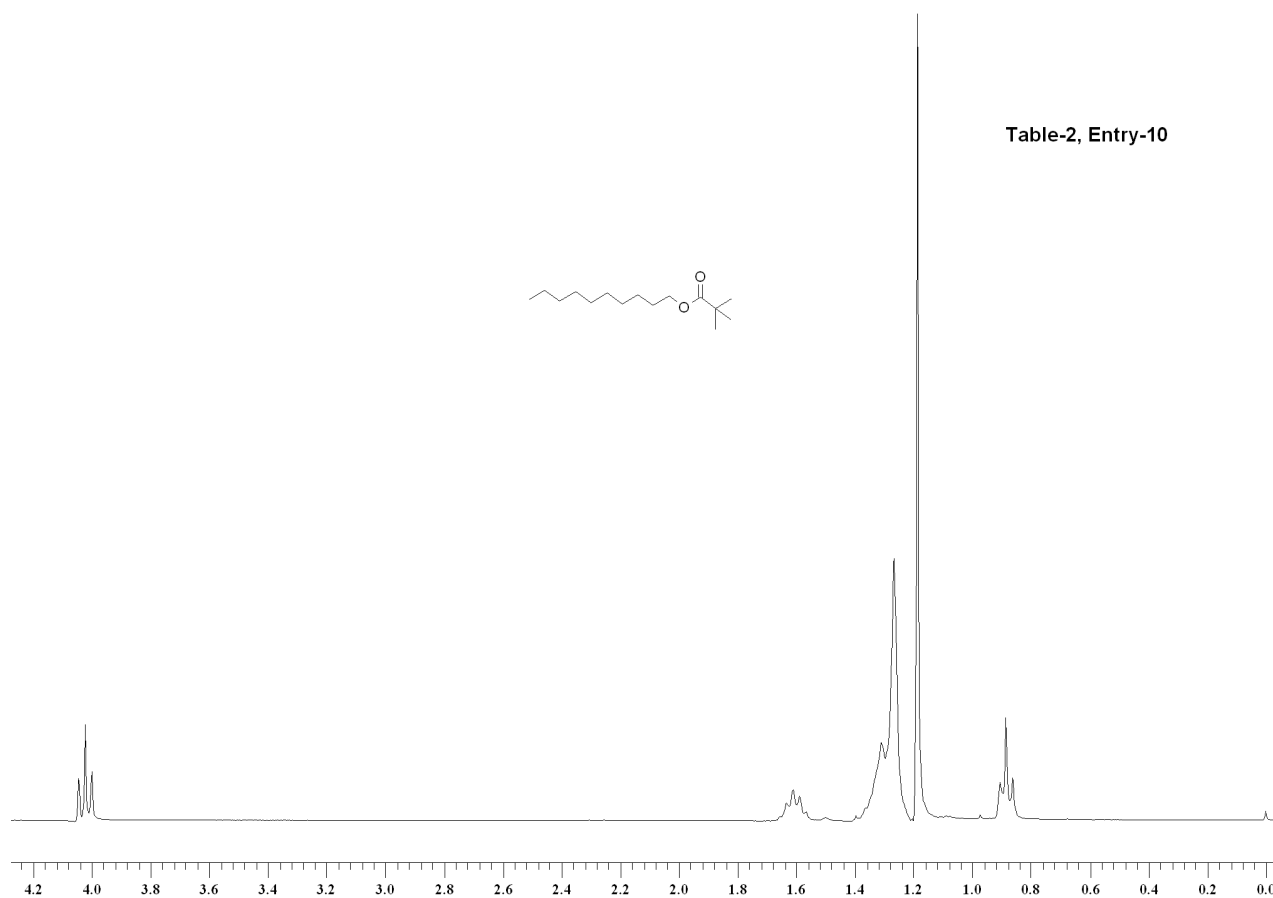
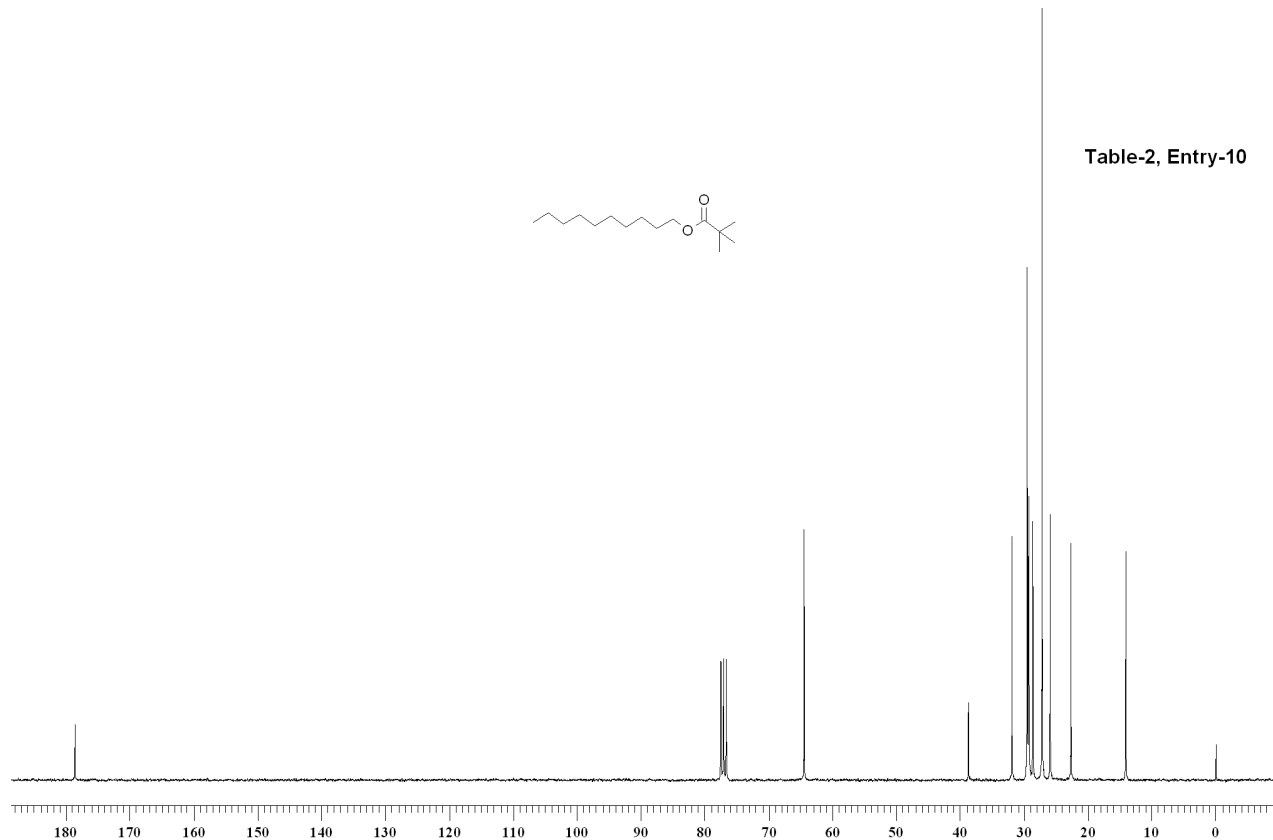
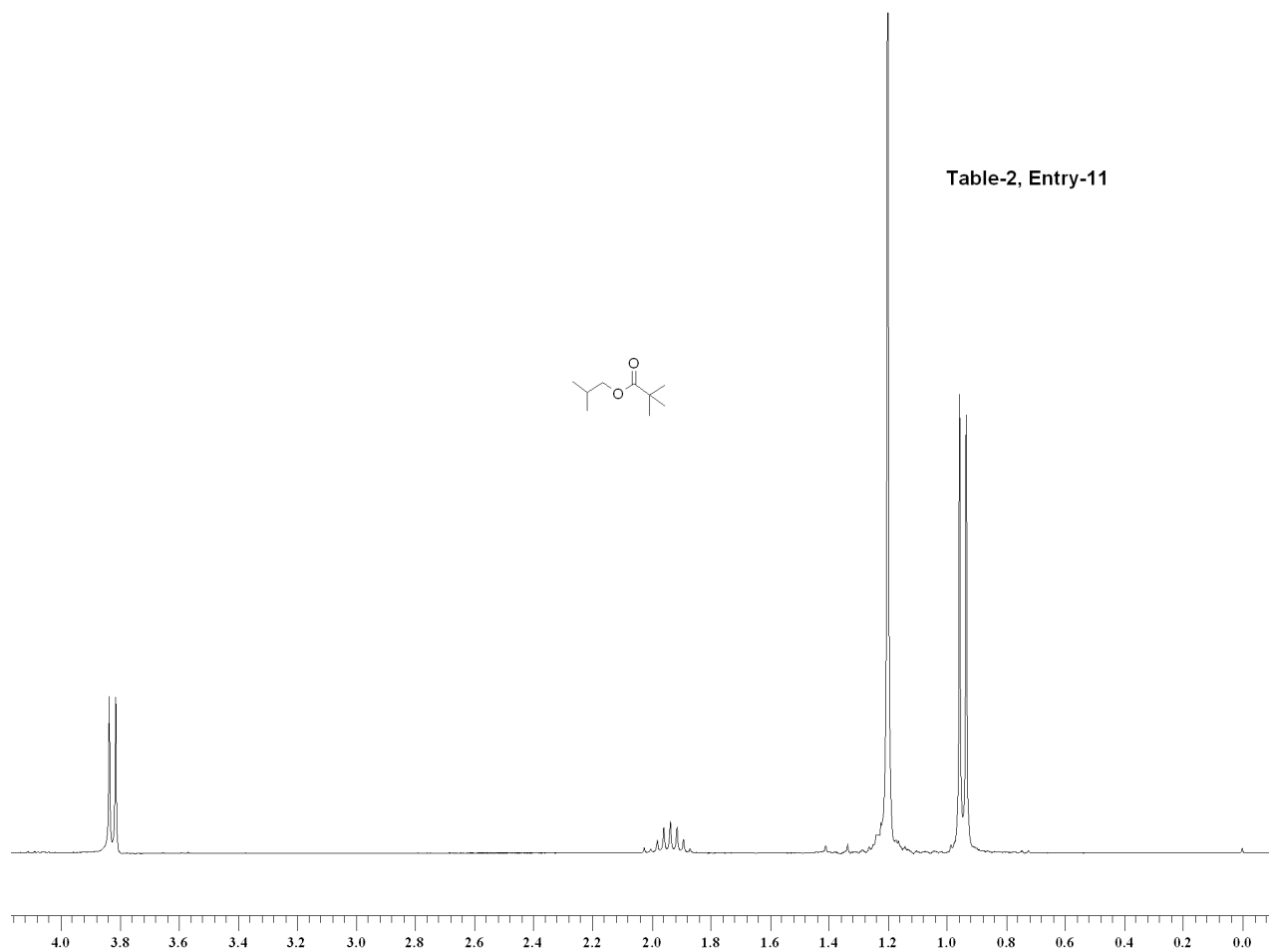


Table-2, Entry-10





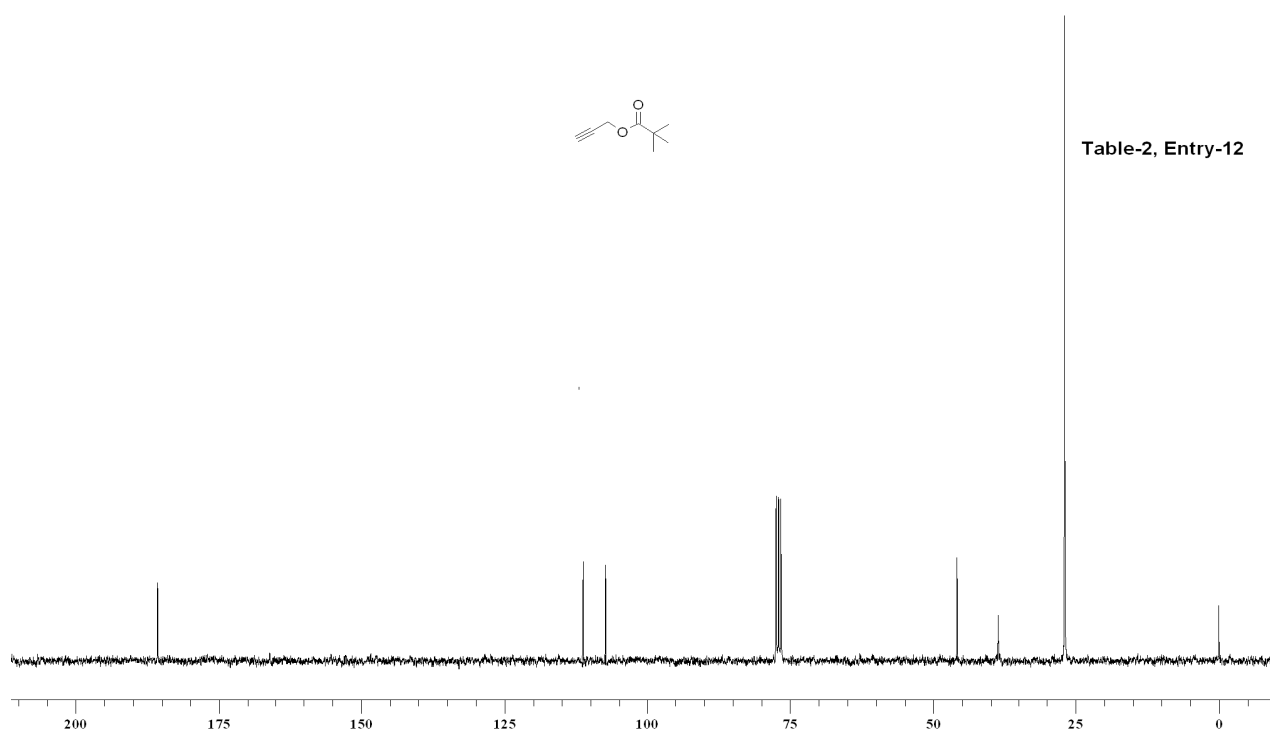
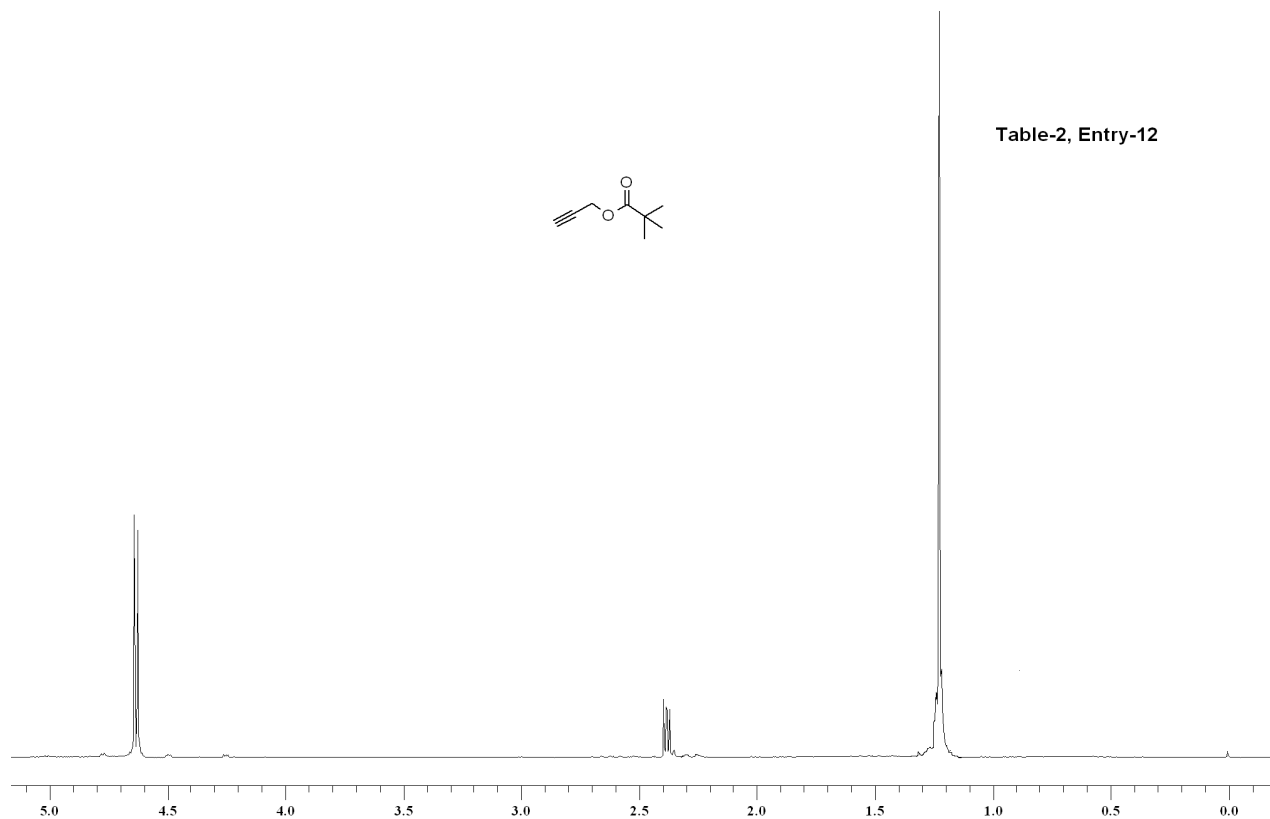


Table-2, Entry-13

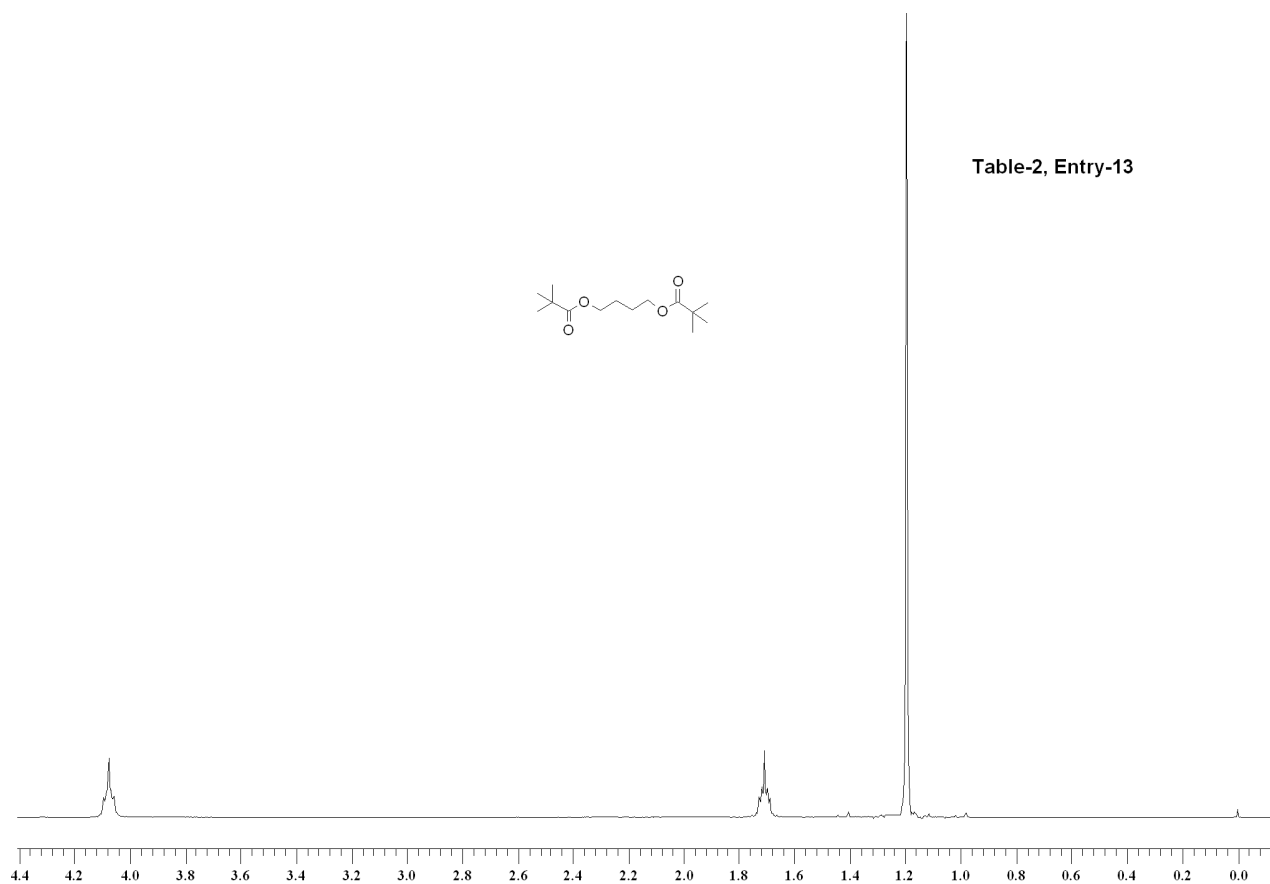
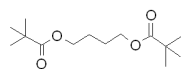
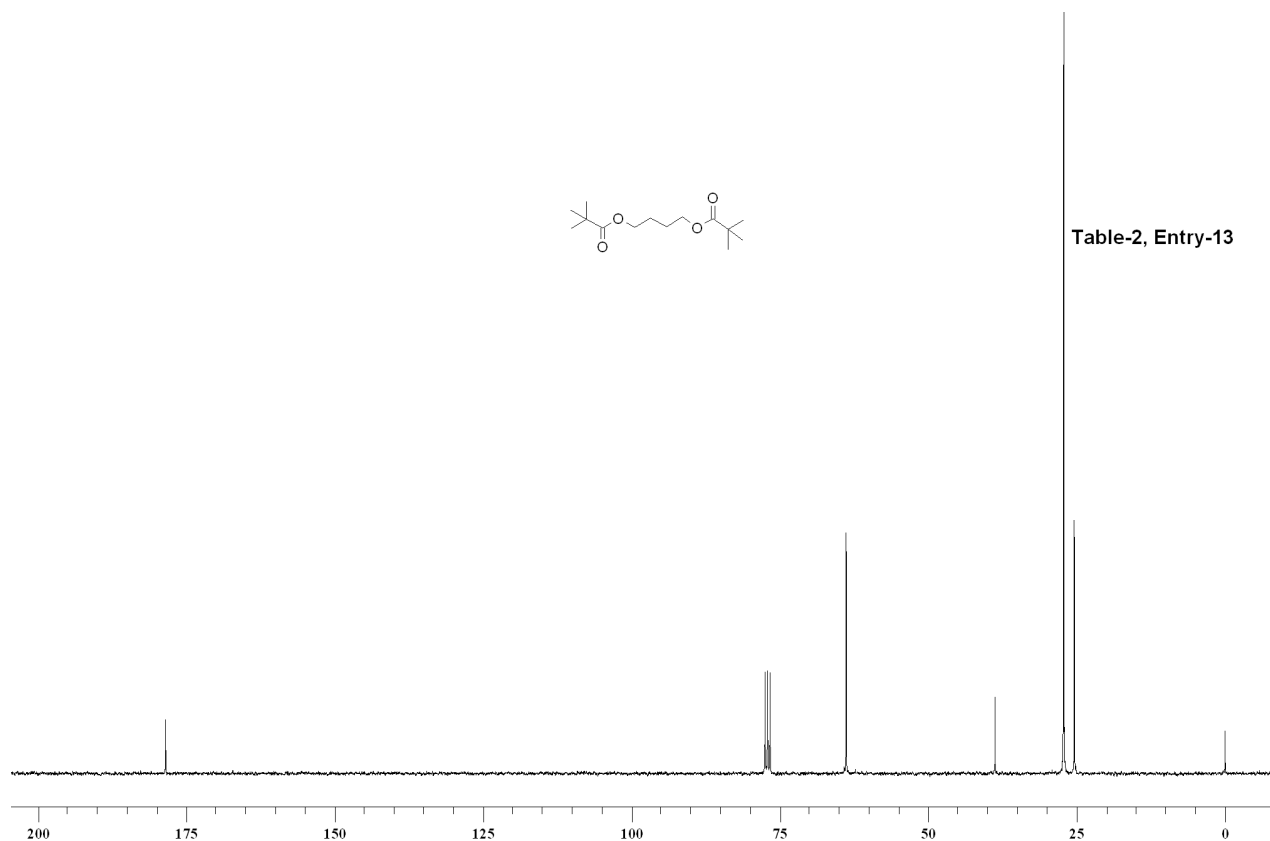
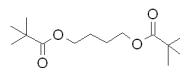
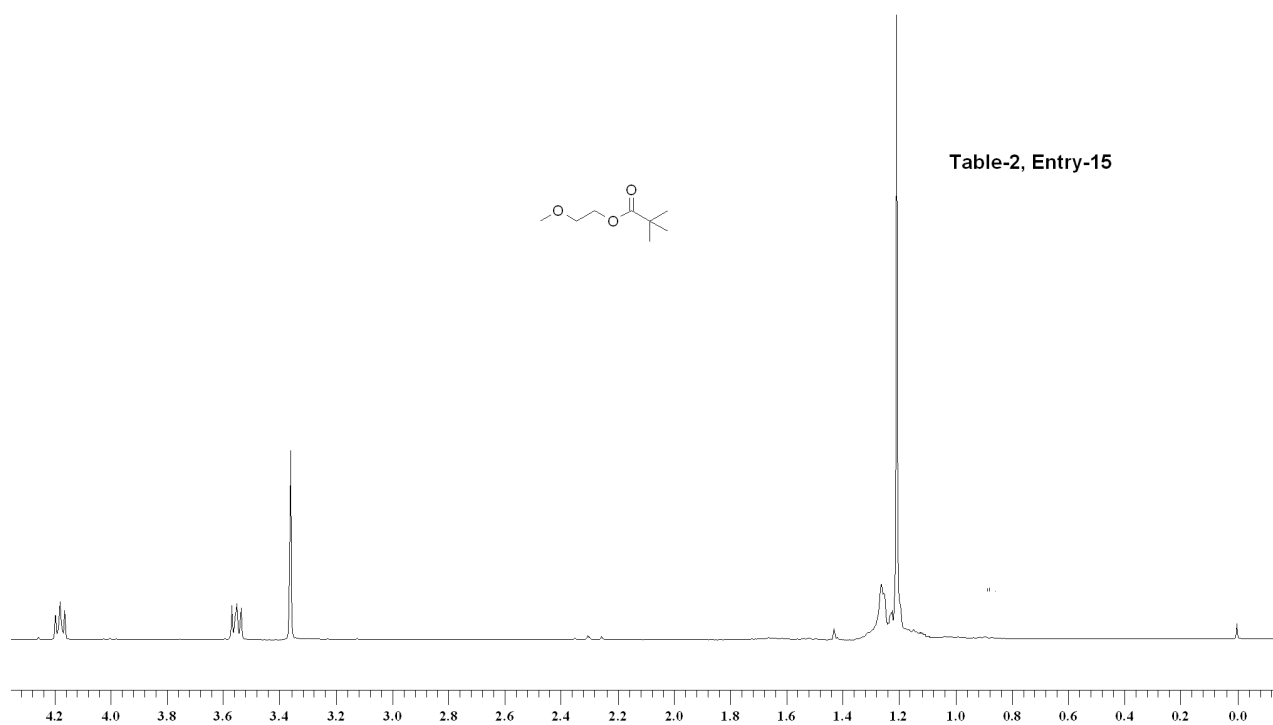
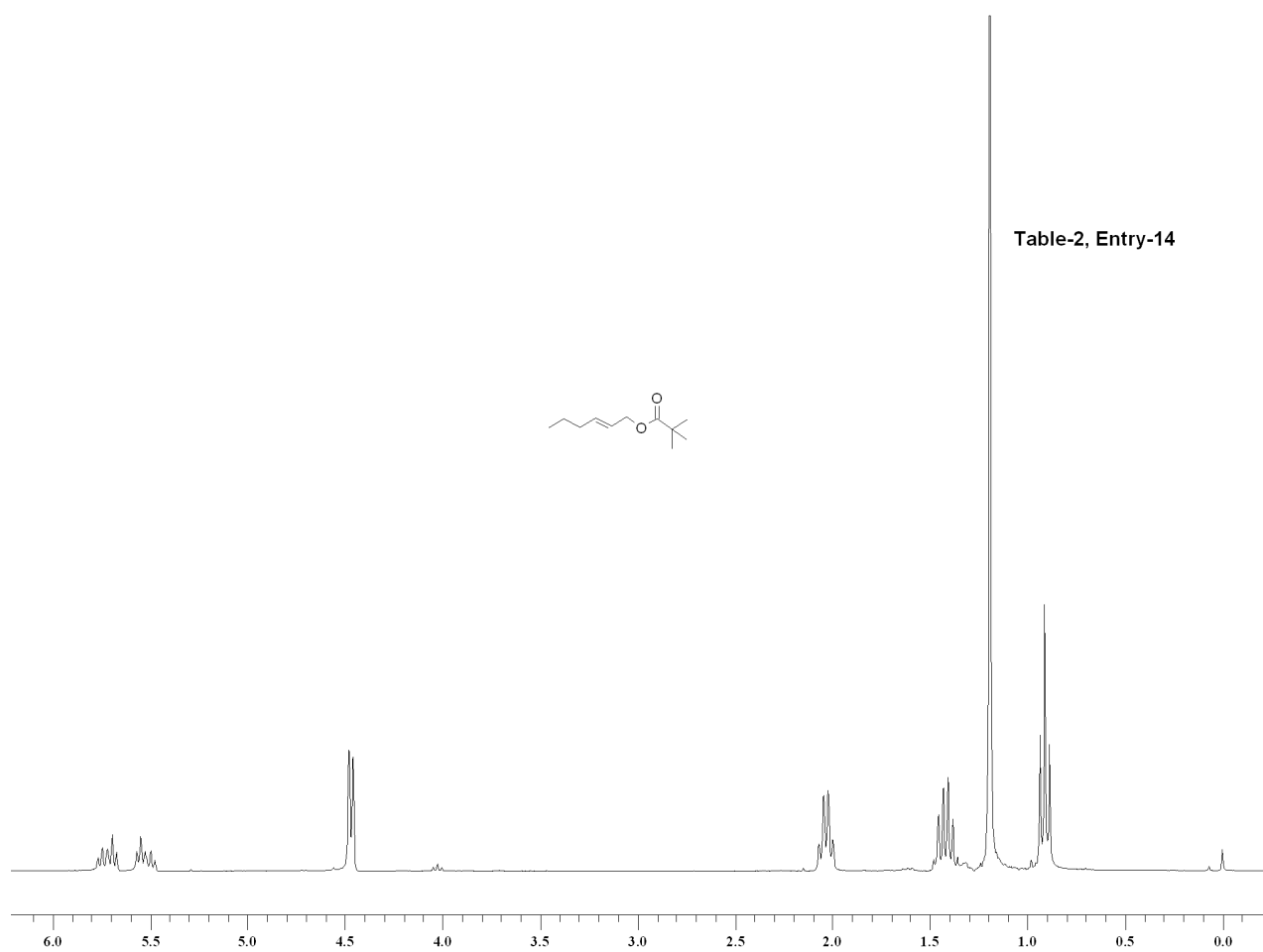
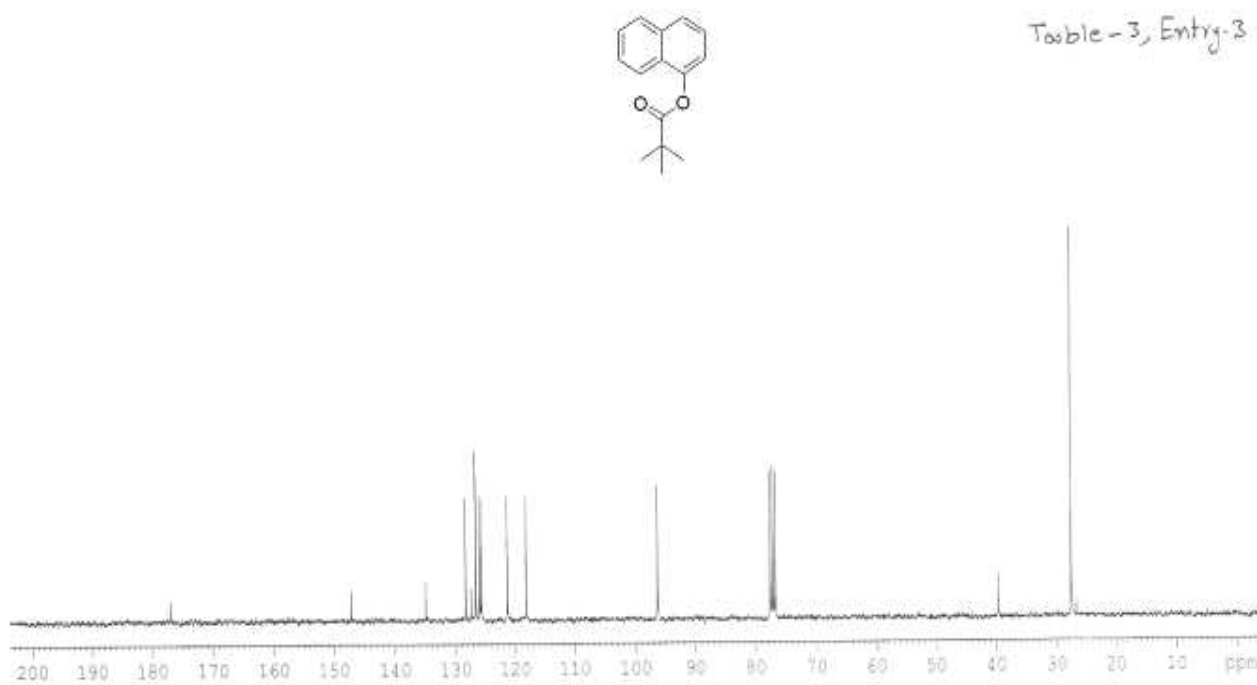
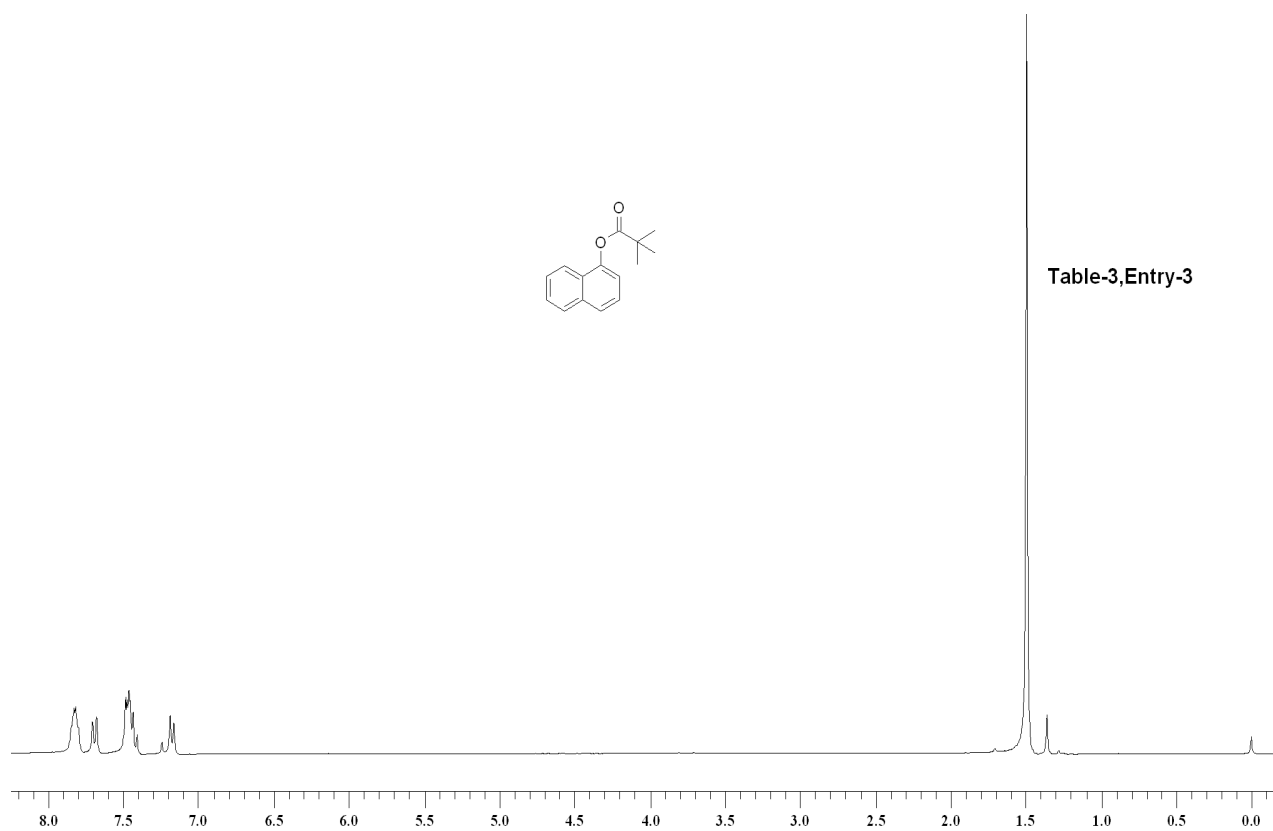


Table-2, Entry-13







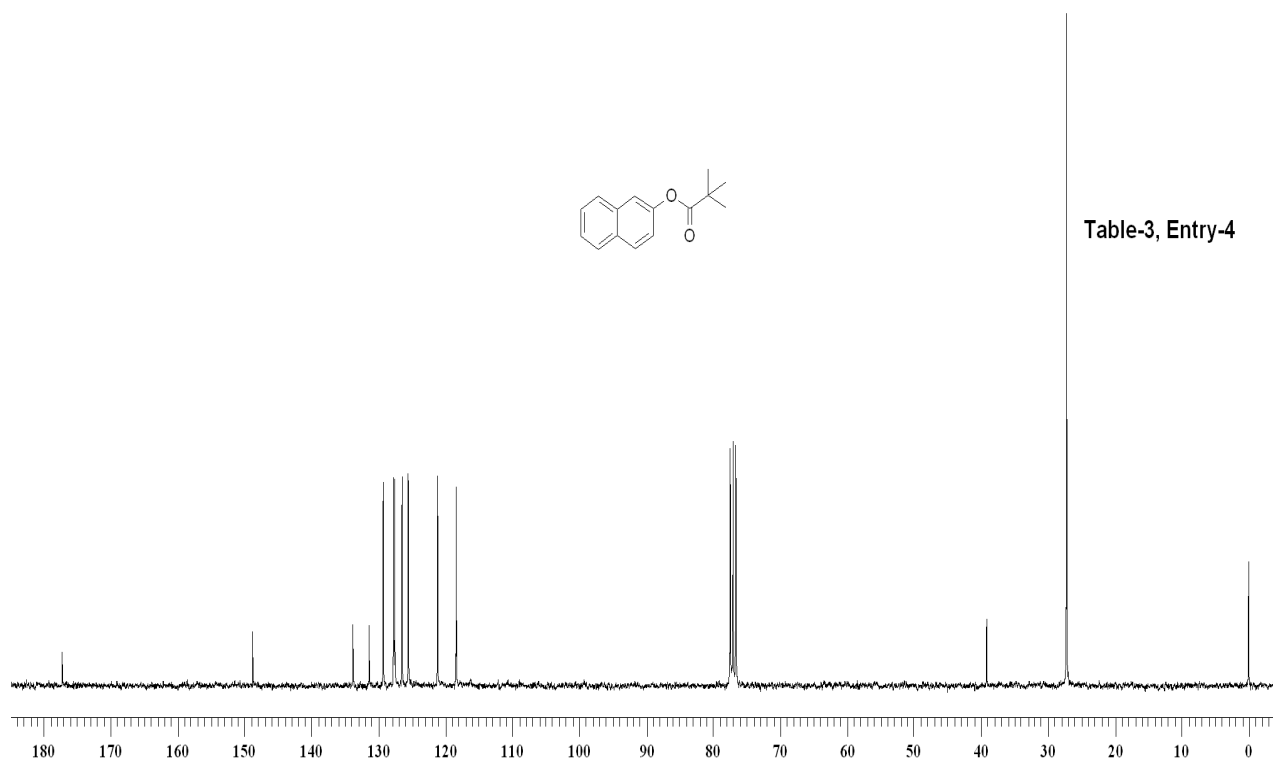
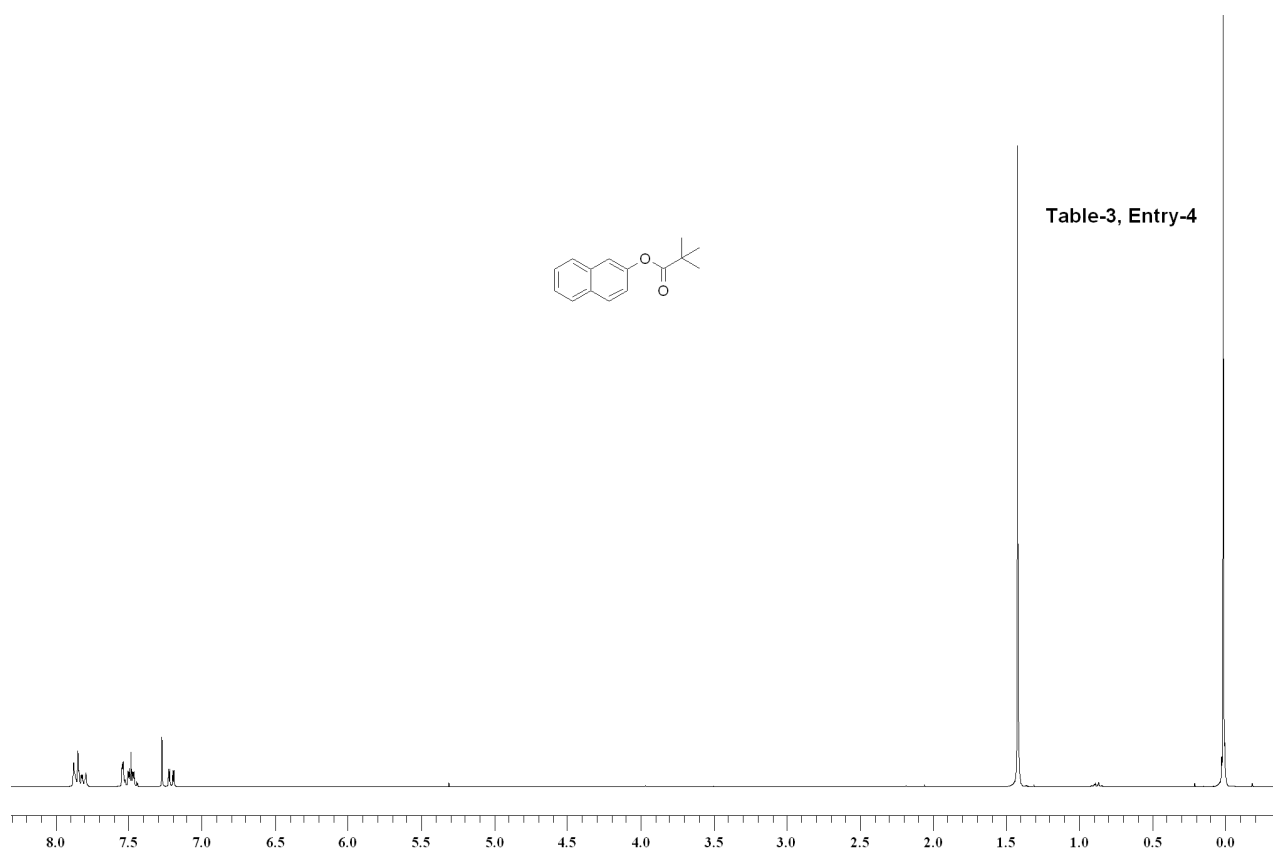


Table-2, Entry-5

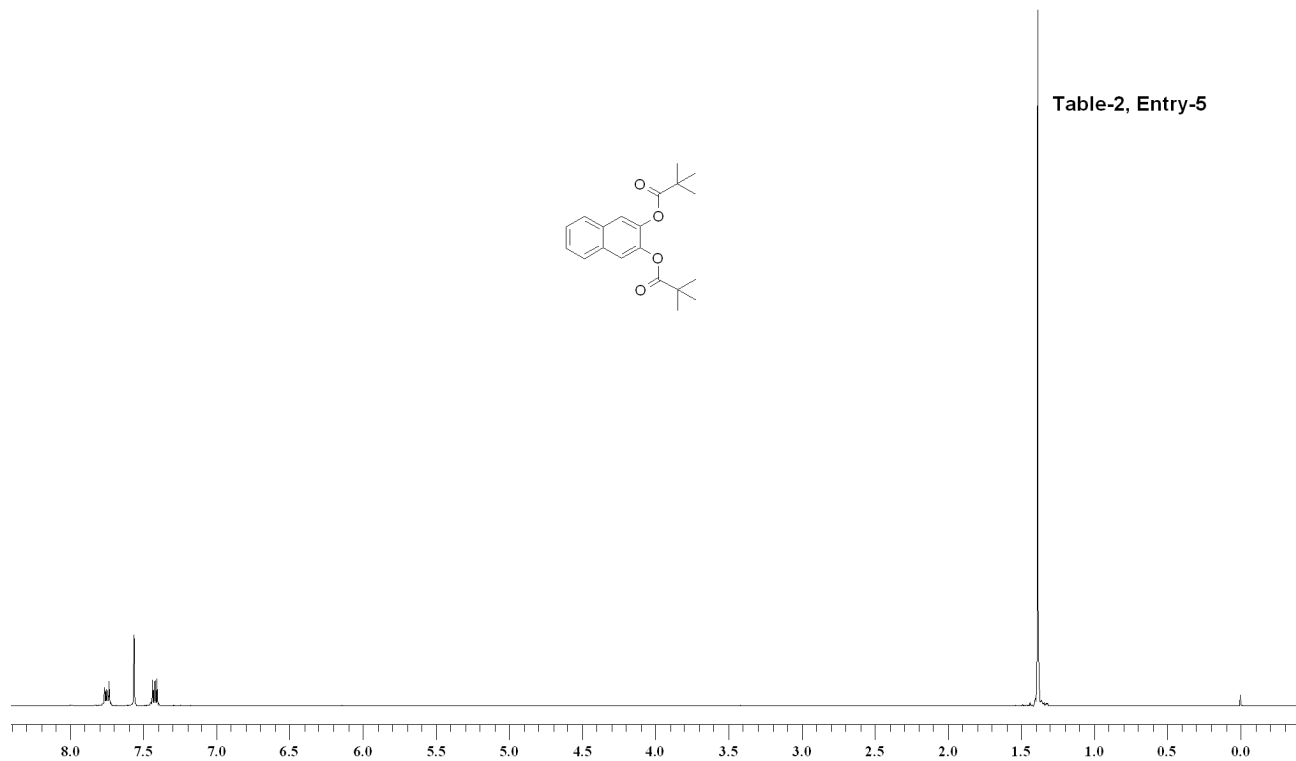
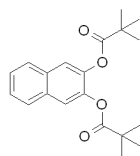
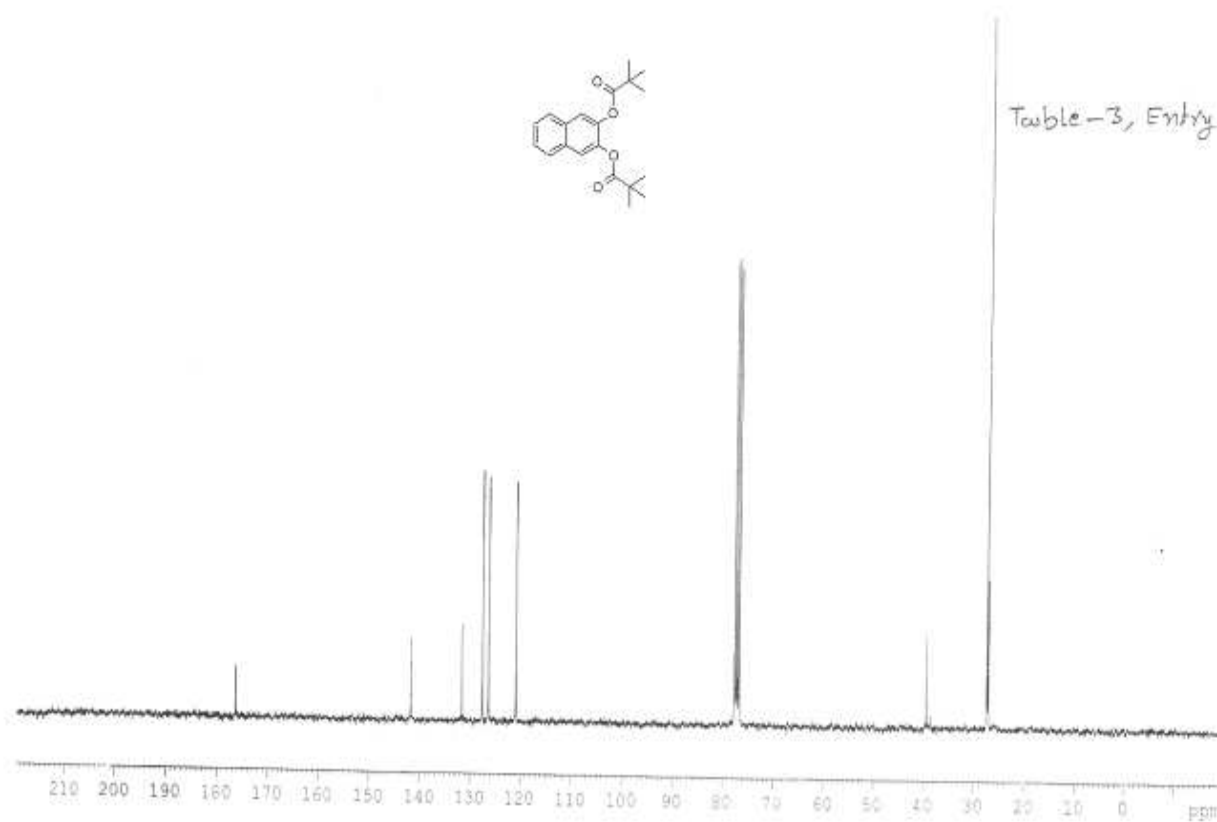
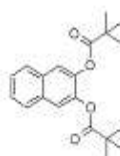
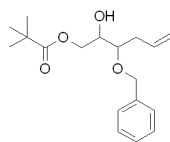
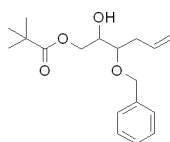
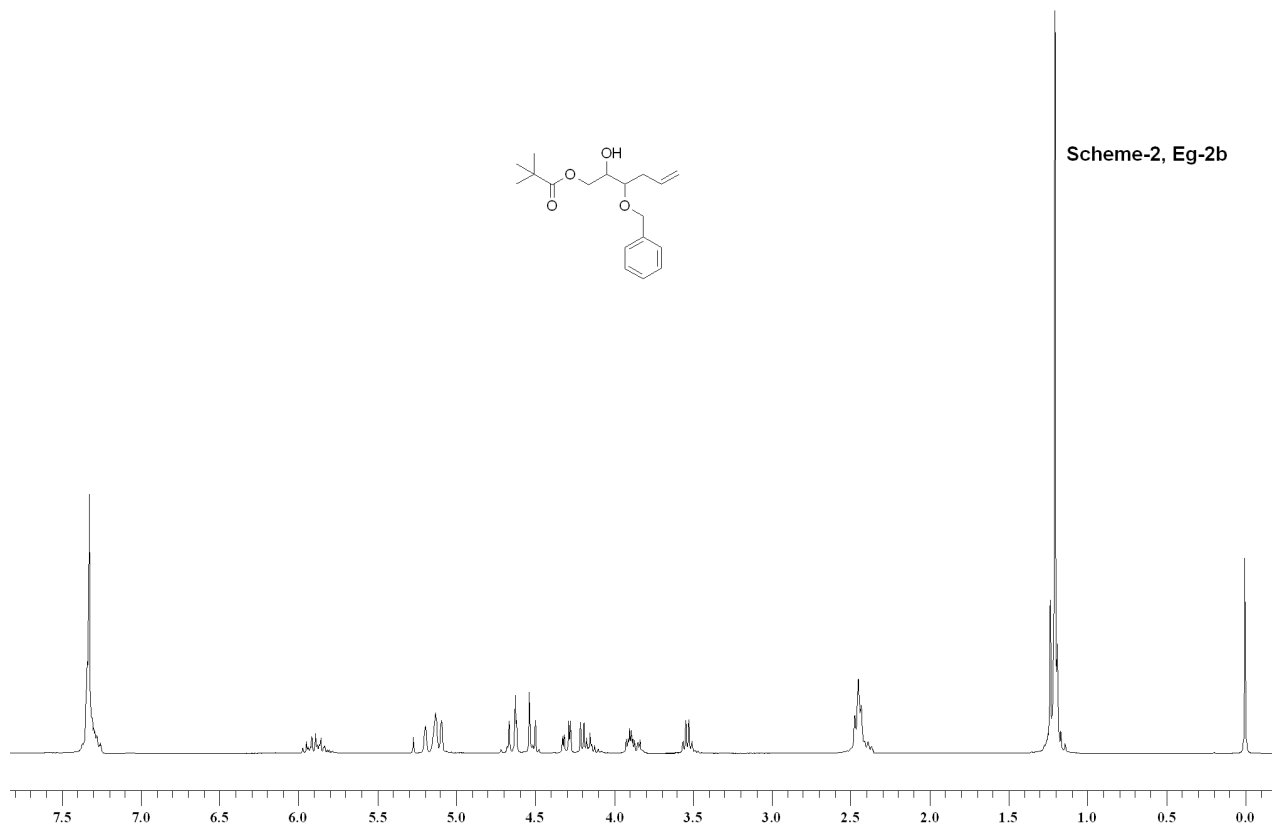


Table-3, Entry-5

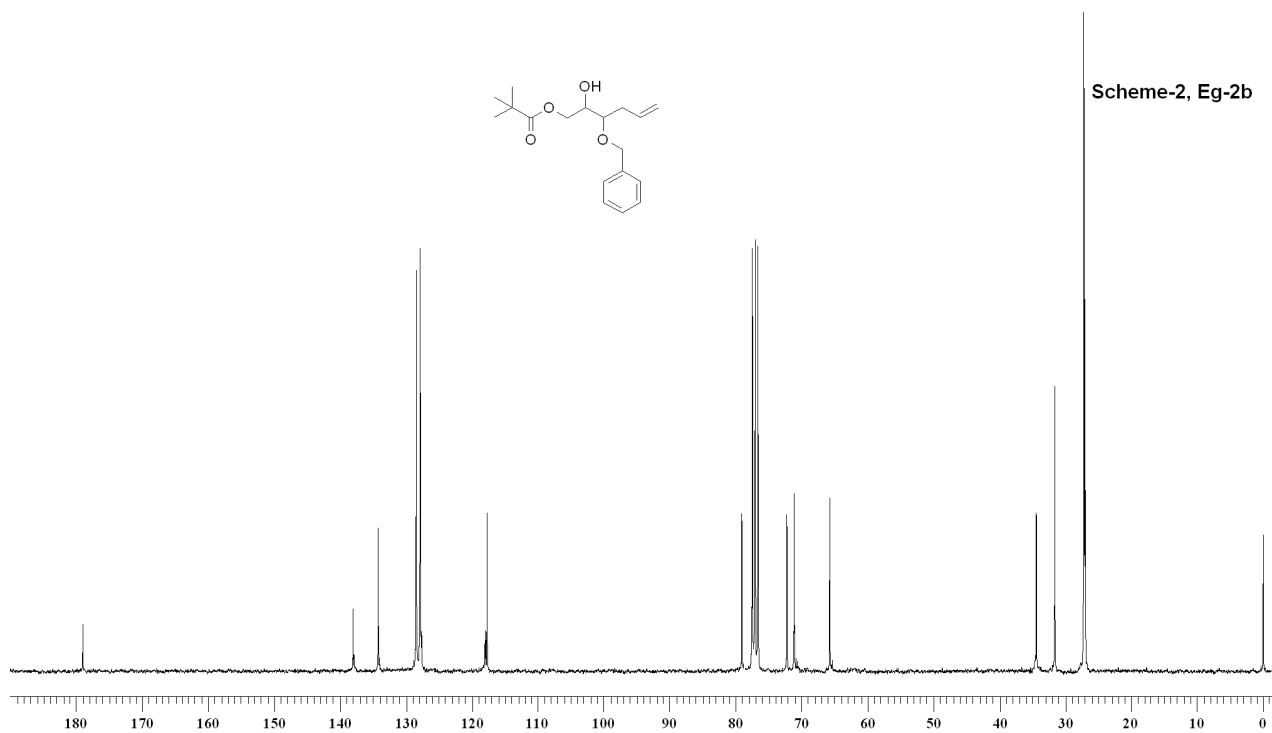


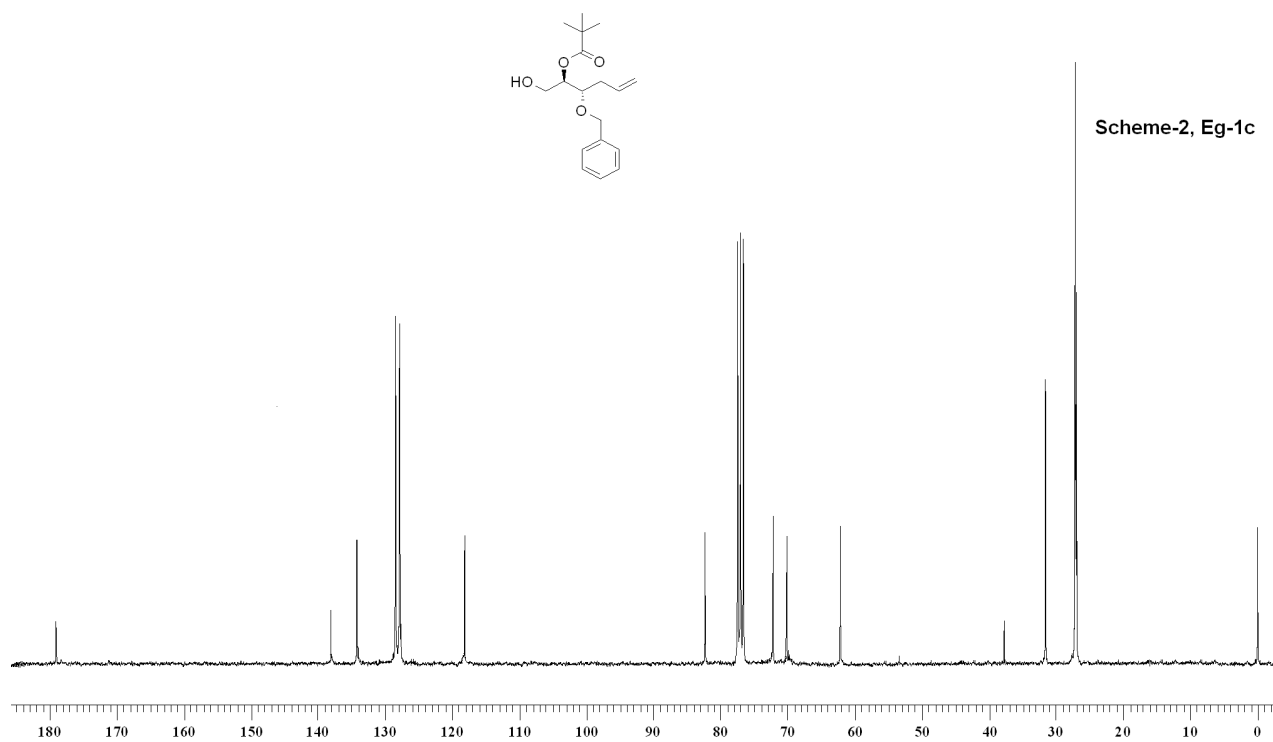
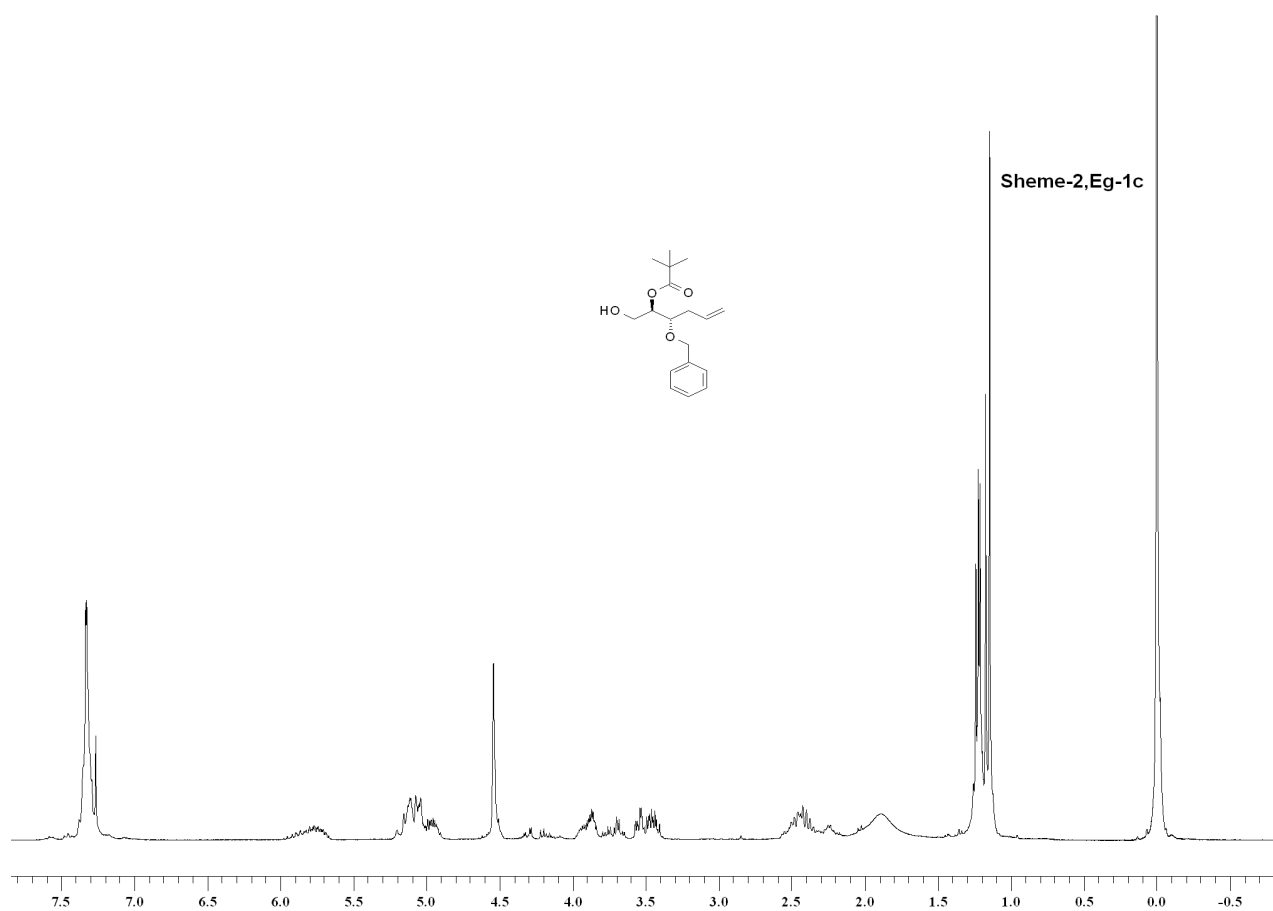


Scheme-2, Eg-2b

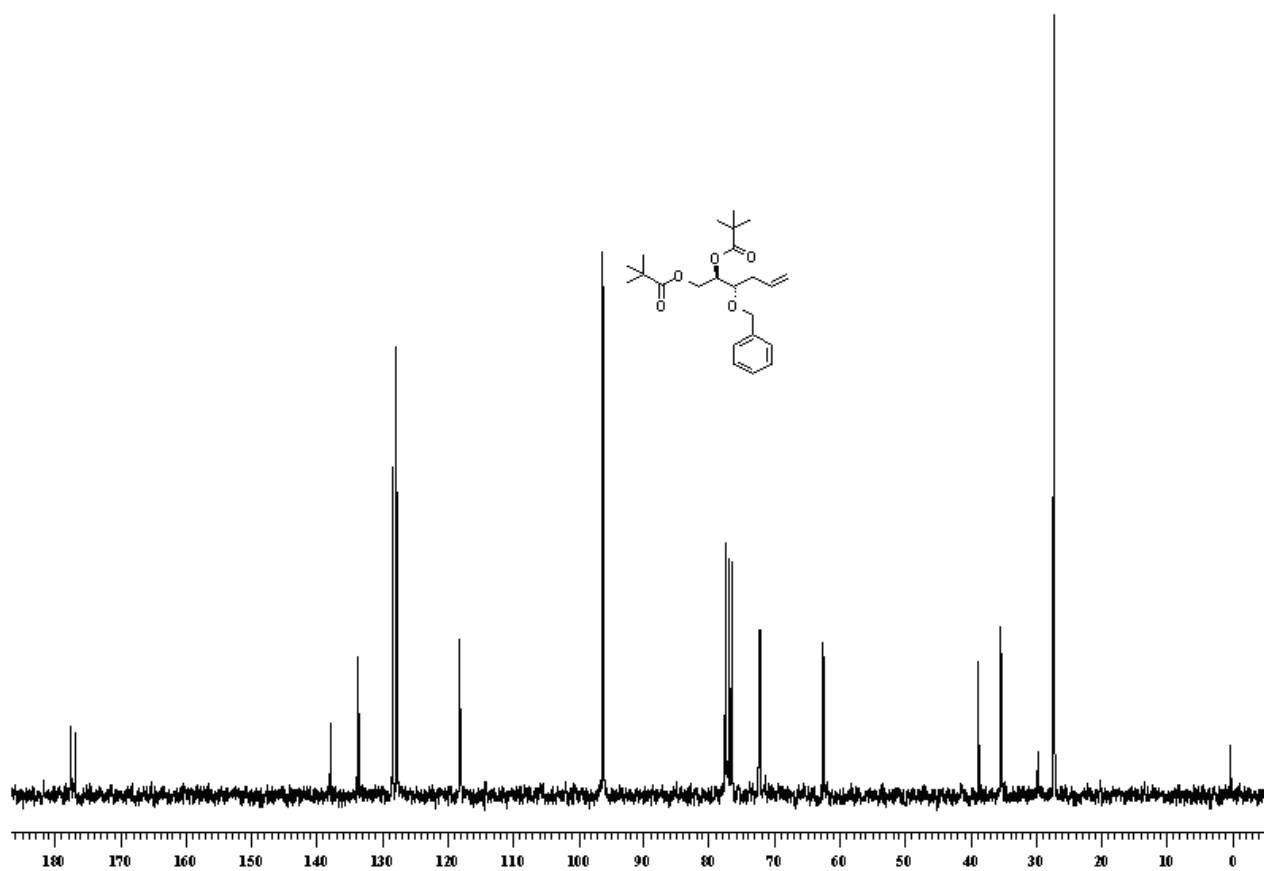
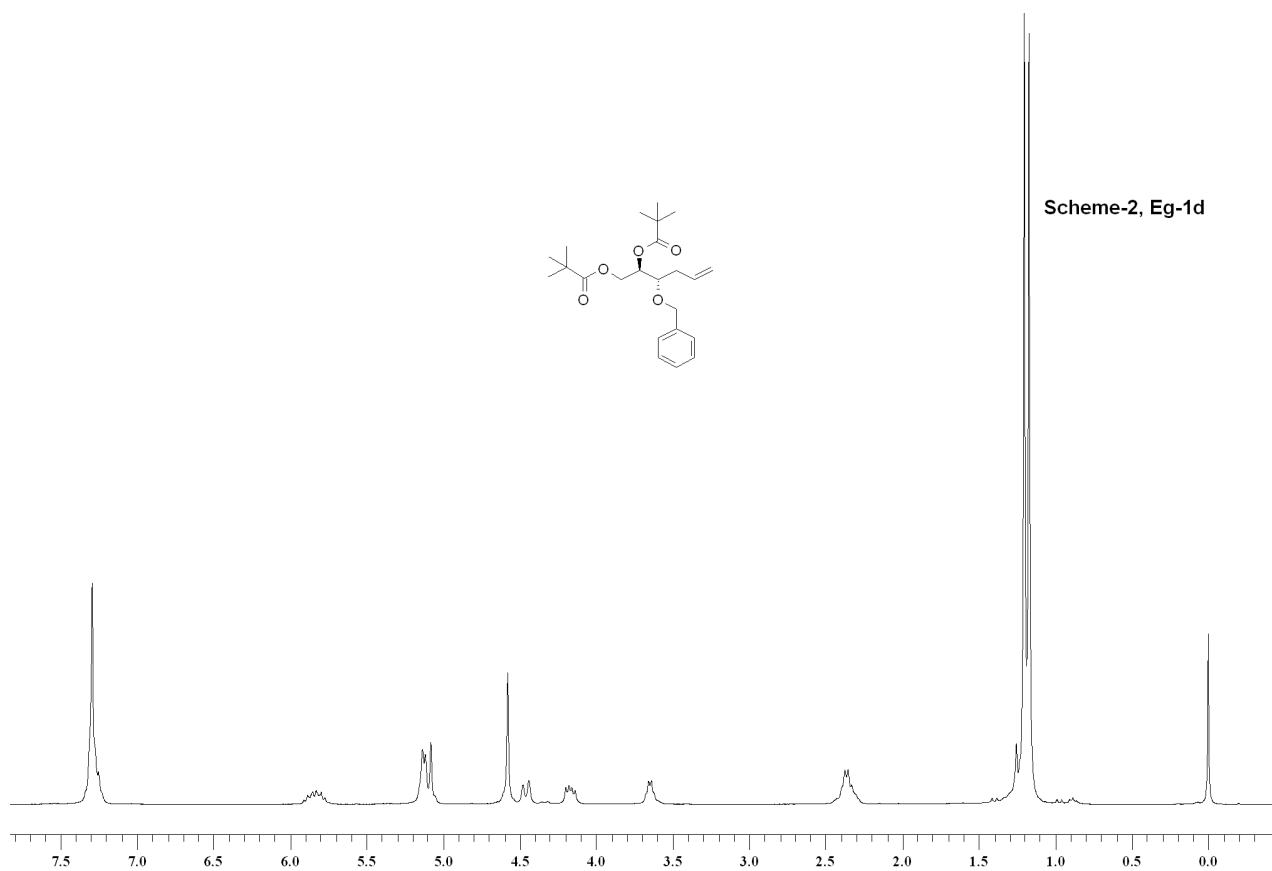
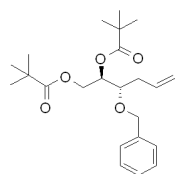


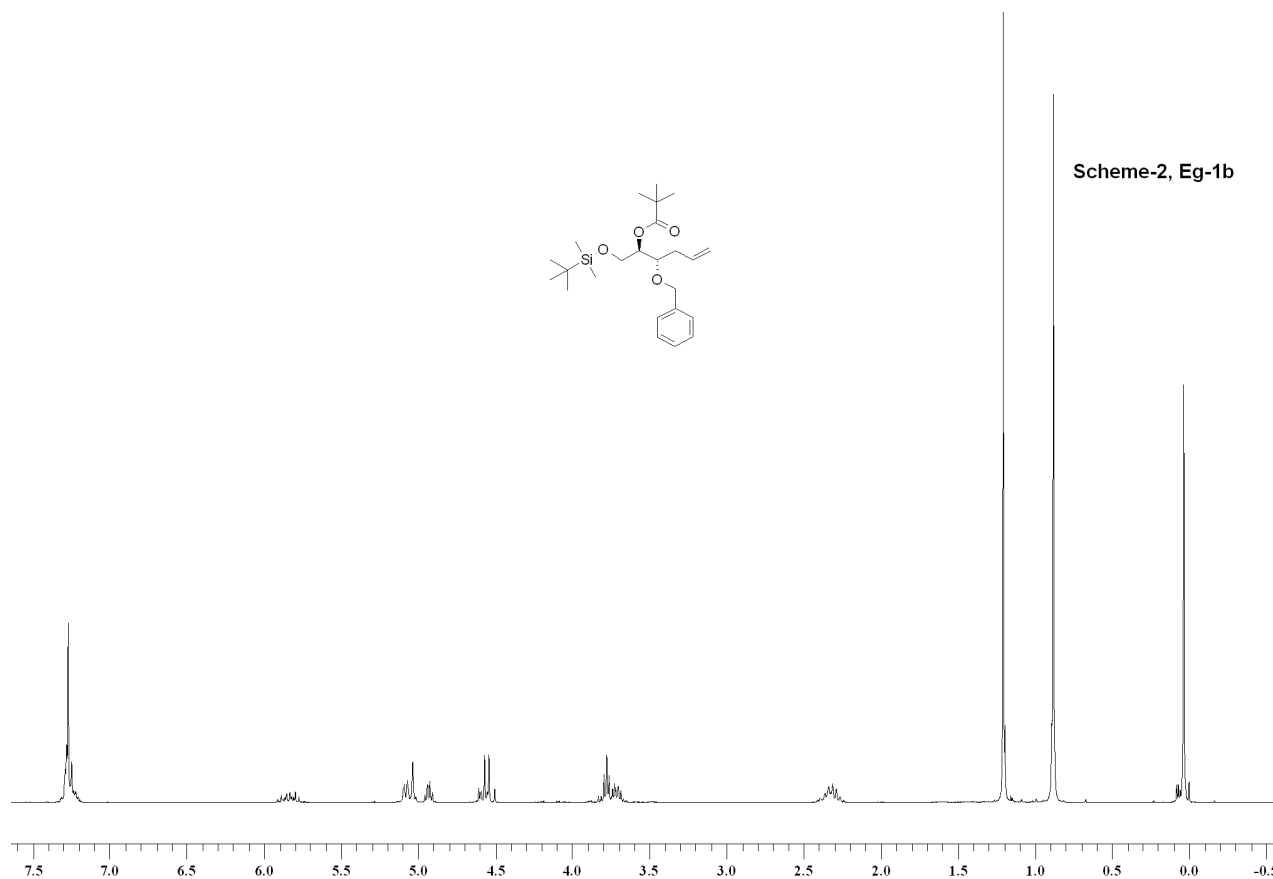
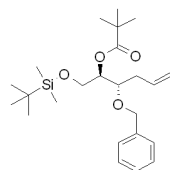
Scheme-2, Eg-2b



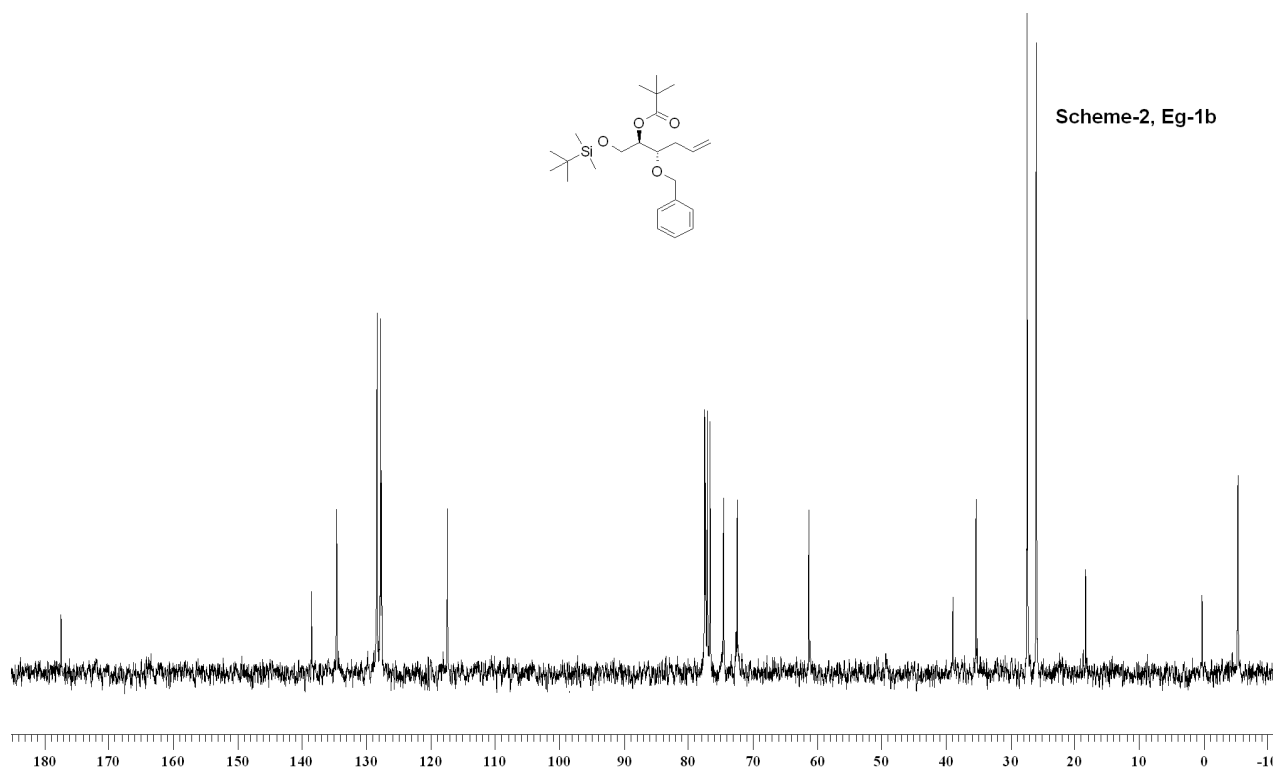
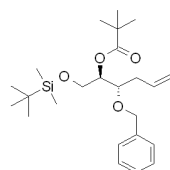


Scheme-2, Eg-1d



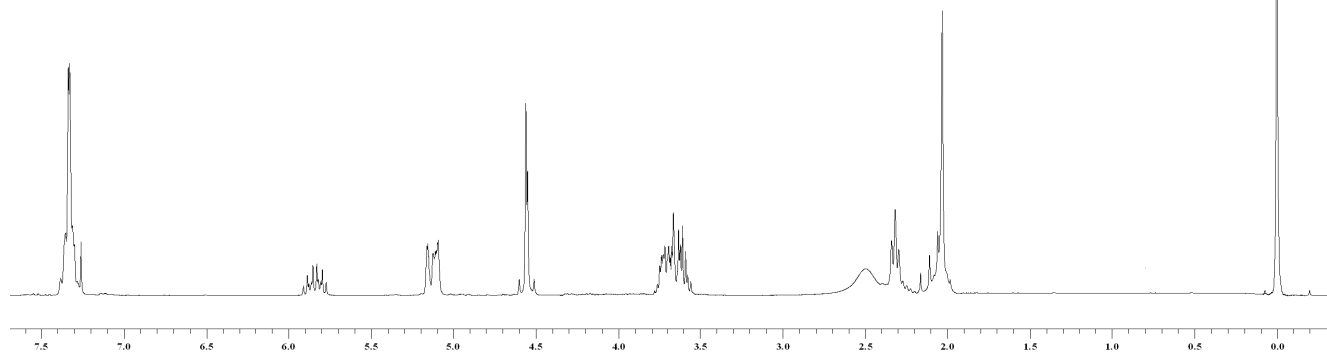
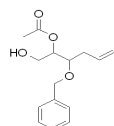


Scheme-2, Eg-1b



Scheme-2, Eg-1b

Acetylation product of 1a



Acetylation product of 1a(a)

