

Supplementary Material

Expedient method for acylation of amines, alcohols and thiol using Trimethylsilyl acetate

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1) General methods.

Unless otherwise noted all reactions were carried out under inert atmosphere. Solvents and reagents were purchased at the highest commercial quality and used without further drying and purification respectively. Reactions were monitored by thin-layer chromatography (TLC) analysis using TLC aluminum sheets silica gel 60 F₂₅₄.

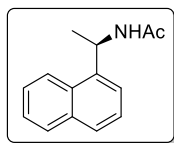
The ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ and DMSO-d₆ at 400 to 600 MHz. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ¹H NMR and ¹³C NMR. Flash chromatography was carried out on silica gel (100-200 mesh) using column of the appropriate diameter and length.

2) General procedure for acetylation:

In a typical experimental procedure; to a mixture of amines/alcohol/phenol/thiols (1.0 mmol) and trimethylsilyl acetate (2.0 mmol) in dichloromethane solvent (10 mL), trimethylsilyl trifluoromethanesulfonate (1.0 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 24 hrs. Completion of reaction was monitored by TLC after quenching with water, separated the bottom dichloromethane layer and further extracted product into dichloromethane (1 X 10 mL). The combined organic layer was washed with saturated NaHCO₃ solution, brine solution dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. All products were characterized by means of orthogonal spectroscopic techniques.

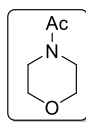
All the products were characterized by NMR and Mass spectroscopy. All the new compounds gave satisfactory spectroscopic data in accordance with their structure.

3) Characterization of N-acetyl naphthylethylamine (3a*)



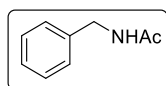
Nature:	Solid
$^1\text{H NMR}$ (400 MHz, CDCl_3):	δ 8.10 (1H, d), 7.87-7.78 (2H, br), 7.54-7.42 (4H, m), 5.93 (1H, m), 1.95 (3H, s), 1.66 (3H, d).
$^{13}\text{C NMR}$ (400 MHz, CDCl_3):	168.9, 138.2, 133.9, 131.1, 128.8, 128.4, 126.6, 125.9, 125.2, 123.5, 122.6, 44.6, 23.4, 20.6.

Characterization of N-acetyl morpholine (3b*):



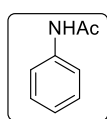
Nature	: Liquid
$^1\text{H NMR}$ (400 MHz, CDCl_3)	: δ 3.78-3.44 (8H, m), 2.09 (3H, s).
$^{13}\text{C NMR}$ (400 MHz, CDCl_3)	: 169.2, 66.9, 66.6, 66.3, 46.7, 41.8, 21.1.

Characterization of Benzyl acetamide (3c*):



Nature:	Solid
$^1\text{H NMR}$ (400 MHz, CDCl_3):	δ 7.38-7.21 (5H, m), 5.88 (1H, br), 4.43 (2H, br), 2.01 (3H, s).
$^{13}\text{C NMR}$ (400 MHz, CDCl_3):	170.0, 138.2, 128.7, 127.9, 127.5, 43.8, 23.2.

Characterization of Acetanilide (3d*):

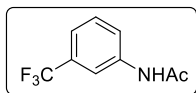


Nature	: Solid
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¹H NMR (400 MHz, CDCl₃): δ 7.49-7.38 (2H, br), 7.29-7.18 (2H, m), 7.01-6.98 (1H, br), 2.15 (3H, s).

¹³C NMR (400 MHz, CDCl₃): 168.7,137.8,129.0,124.4,120.1,24.5.

Characterization of Benzyl acetamide (3e*):

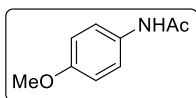


Nature: Solid

¹H NMR (400 MHz, CDCl₃): δ 7.74-7.70 (2H, br), 7.61 (1H, br), 7.36-7.28 (2H, m), 2.24 (3H, s).

¹³C NMR (400 MHz, CDCl₃): 169.0,138.4,131.5,131.1,129.5,125.2,123.0, 122.5,120.9,116.7,116.6,24.4.

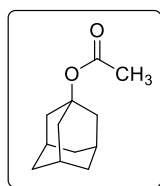
Characterization of N-(4-methoxyphenyl)acetamide (3f*):



Nature: Solid

¹H NMR (400 MHz, CDCl₃): δ 7.41-7.38 (2H, br), 6.96-6.80 (2H, br), 3.78 (3H, s), 2.26 (3H, s).

Characterization of (3s,5s,7s)-adamantan-1-yl acetate (3g*):

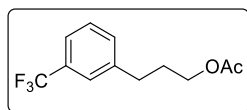


Nature: Solid

¹H NMR (400 MHz, CDCl₃): δ 2.08 (3H, s), 2.03 (6H, s), 1.89 (3H, s), 1.59 (6H, s).

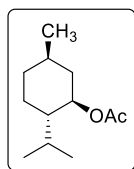
¹³C NMR (400 MHz, CDCl₃): δ 169.3, 79.3, 40.3, 35.2, 29.8, 21.7.

Characterization of O-acetyltrifluoromethylphenylpropanol (3h*):



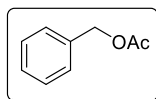
Nature:	Crude Oil
¹H NMR (400 MHz, CDCl₃):	δ 7.38-7.29 (4H, m), 4.02 (2H, q), 2.69 (2H, q), 1.98-1.81 (5H, m).
¹³C NMR (400 MHz, CDCl₃):	171.1, 142.2, 131.8, 131.2, 130.9, 130.2, 128.9, 128.3, , 125.6, 125.0, 123.0, 122.9, 120.2, 63.5, 32.0, 30.0, 20.8.

Characterization of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl acetate (3i*):



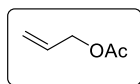
Nature:	Crude Oil
¹H NMR (400 MHz, CDCl₃):	δ 4.63-4.57 (1H, td, <i>J</i> = 4.4 Hz), 1.95 (3H, s), 1.93-1.90 (1H, m), 1.83-1.75 (1H, m), 1.62-1.57 (2H, m), 1.45-1.37 (1H, m), 1.32-1.18 (1H, m), 1.03-0.87 (2H, m), 0.83-0.82 (6H, d, <i>J</i> = 6.52 Hz), 0.70-0.68 (3H, d, <i>J</i> = 6.96 Hz).
¹³C NMR (400 MHz, CDCl₃):	170.6, 74.1, 47.0, 40.9, 34.2, 31.3, 26.3, 23.5, 22.0, 21.3, 20.7, 16.4.
[α]_D²⁵:	+ 77 (<i>c</i> 1.0, CHCl ₃)

Characterization of Benzyl acetate (3j*):



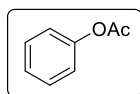
Nature:	Crude Oil
¹H NMR (400 MHz, CDCl₃):	δ 7.35-7.29 (5H, m), 5.08 (2H, s), 2.06 (3H, s).
¹³C NMR (400 MHz, CDCl₃):	170.8, 136.0, 128.6, 128.3, 66.3, 21.0.
EI-Mass:	<i>m/z</i> 151 [M+H] ⁺ .

Characterization of Allyl acetate (3k*):



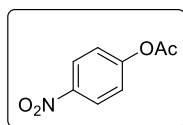
- Nature:** Crude oil.
- ¹H NMR (400 MHz, CDCl₃):** δ 5.95-5.87 (1H, m), 5.34-5.21 (2H, dd, *J* = 17.2, 17.6 Hz), 4.58-4.56 (2H, m), 2.08 (3H, s).
- ¹³C NMR (400 MHz, CDCl₃):** δ 170.6, 132.2, 118.1, 65.1, 20.8.

Characterization of Phenyl acetate (3l*):



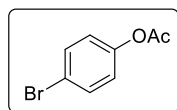
- Nature:** Crude Oil.
- ¹H NMR (400 MHz, CDCl₃):** δ 7.36-7.32 (2H, t, *J* = 7.40 Hz), 7.20-7.16 (1H, t, *J* = 7.44 Hz), 7.07-7.05 (2H, d, *J* = 8.56 Hz), 2.23 (3H, s).
- ¹³C NMR (400 MHz, CDCl₃):** 169.5, 150.8, 129.5, 125.8, 121.6, 21.1.
- EI-Mass:** *m/z* 137 [M+H]⁺.

Characterization of 4-Nitrophenyl acetate (3m*):



- Nature:** Solid
- ¹H NMR (400 MHz, CDCl₃):** δ 8.20-8.17 (2H, d, *J* = 9.12 Hz), 7.22-7.19 (2H, d, *J* = 9.12 Hz), 2.27 (3H, s).
- ¹³C NMR (400 MHz, CDCl₃):** 168.4, 155.4, 155.3, 125.2, 122.4, 21.1.
- EI-Mass:** *m/z* 182 [M+H]⁺

Characterization of 4-Bromophenyl acetate (3n*):



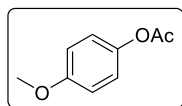
- Nature:** Crude Oil

¹H NMR (400 MHz, CDCl₃): δ 7.48-7.46 (2H, d, *J* = 8.8 Hz), 6.98-6.96 (2H, d, *J* = 8.88 Hz), 2.27 (3H, s)

¹³C NMR (400 MHz, CDCl₃): 169.1, 149.7, 132.5, 123.4, 118.9, 21.1.

EI-Mass: *m/z* 215 [M+H]⁺

Characterization of 4-Methoxyphenyl acetate (3o*):



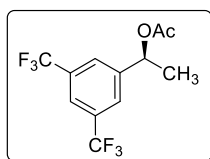
Nature: Crude Oil;

¹H NMR (400 MHz, CDCl₃): δ 6.99-6.97 (2H, d, *J* = 9.16 Hz), 6.87-6.85 (2H, d, *J* = 9.16 Hz), 3.75 (3H, s), 2.24 (3H, s).

¹³C NMR (400 MHz, CDCl₃): 169.9, 157.3, 144.2, 122.3, 114.4, 55.5, 21.0.

EI-Mass: *m/z* 167 [M+H]⁺

Characterization of (S)-1-(3,5-bis(trifluoromethyl)phenyl)ethyl acetate (3p*):



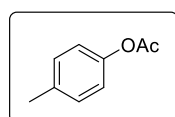
Nature: Crude Oil

¹H NMR (400 MHz, CDCl₃): δ 7.81 (3H, s), 5.98-5.93 (1H, q, *J* = 6.68, 6.64 Hz), 2.12 (3H, s), 1.58-1.57 (3H, d, *J* = 6.64 Hz).

¹³C NMR (400 MHz, CDCl₃): 170.0, 144.4, 132.4, 126.3, 124.5, 121.9, 7.9, 22.2, 21.0.

EI-Mass: *m/z* 301 [M+H]⁺

Characterization of p-tolyl acetate (3q*):

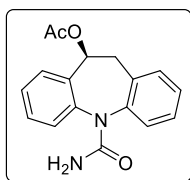


¹H NMR (400 MHz, CDCl₃): δ 7.19-7.10 (2H, br), 6.98-6.90 (2H, br), 2.39 (3H, s), 2.26 (3H, s)

^{13}C NMR (400 MHz, CDCl_3): 169.7, 148.5, 135.5, 129.9, 121.2, 21.1, 20.9.

EI-Mass: m/z 152 $[\text{M}+\text{H}]^+$.

Characterization of (*S*)-5-carbamoyl-10,11-dihydro-5H-dibenzo[*b,f*]azepin-10-yl acetate (3r***):**



Nature: Solid;

^1H NMR (400 MHz, CDCl_3): δ 7.47-7.42 (2H, m), 7.32-7.23 (6H, m), 6.40-5.99 (1H, b), 5.03 (2H, br), 3.61-3.58 (1H, d, $J = 13.48$ Hz), 3.19-3.05 (1H, dd, $J = 13.48, 4.09$ Hz), 2.09 (3H, s);

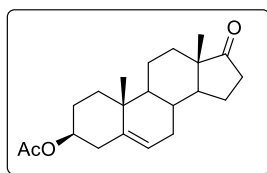
^{13}C NMR (400 MHz, CDCl_3): δ 170.7, 170.2, 157.0, 156.7, 141.3, 140.6, 139.1, 134.4, 133.5, 131.0, 129.3, 128.9, 128.3, 128.1, 128.0, 127.8, 72.3, 70.1, 36.0, 35.8, 21.1.

HRMS calc for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$: 297.1239, found: 297.124;

IR (KBr): 3476, 3361, 2934, 1726, 1653, 1411, 1254 cm^{-1} .

$[\alpha]_{\text{D}}^{25}$: 21.0 ($c = 1$, pyridine).

Characterization of (*3S,10R,13S*)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl acetate (3s***):**



Nature: Solid

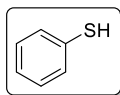
^1H NMR (400 MHz, CDCl_3): δ 5.34-5.33 (1H, d, $J = 5.12$ Hz), 4.56-4.49 (1H, m), 2.42-2.35 (1H, dd $J = 8.4$ Hz), 2.28-2.24 (2H, m), 2.06-1.97 (2H, m), 1.96 (3H, s), 1.91-1.85 (3H, m), 1.63-1.39 (6H, m), 1.26-1.18 (2H, m), 1.11-1.05 (1H, m), 0.98-0.93 (4H, m), 0.81 (3H, s).

^{13}C NMR (400 MHz, CDCl_3): δ 221.0, 170.5, 139.9, 121.9, 73.7, 51.7, 50.1, 47.5, 38.1, 36.9, 36.7, 35.8, 31.5, 31.4, 30.8, 27.7, 21.9, 21.4, 20.3, 19.3, 13.5

IR (KBr): 1240.0, 1734.6, 1460.7, 1434.4, 1369.7, 2949.3, 1023.7 cm^{-1}

EI-Mass: m/z 348.4 $[\text{M}+\text{NH}_4]^+$.

Characterization of *S*-phenyl ethanethioate (3t*):



Nature : Crude Oil

^1H NMR (400 MHz, CDCl_3) : δ 7.41-7.7.37 (5H, m), 2.38 (3H, s)

^{13}C NMR (400 MHz, CDCl_3) : 194.0, 134.5, 129.5, 129.2, 128.0, 30.2

EI-Mass : m/z 152 $[\text{M}+\text{H}]^+$.

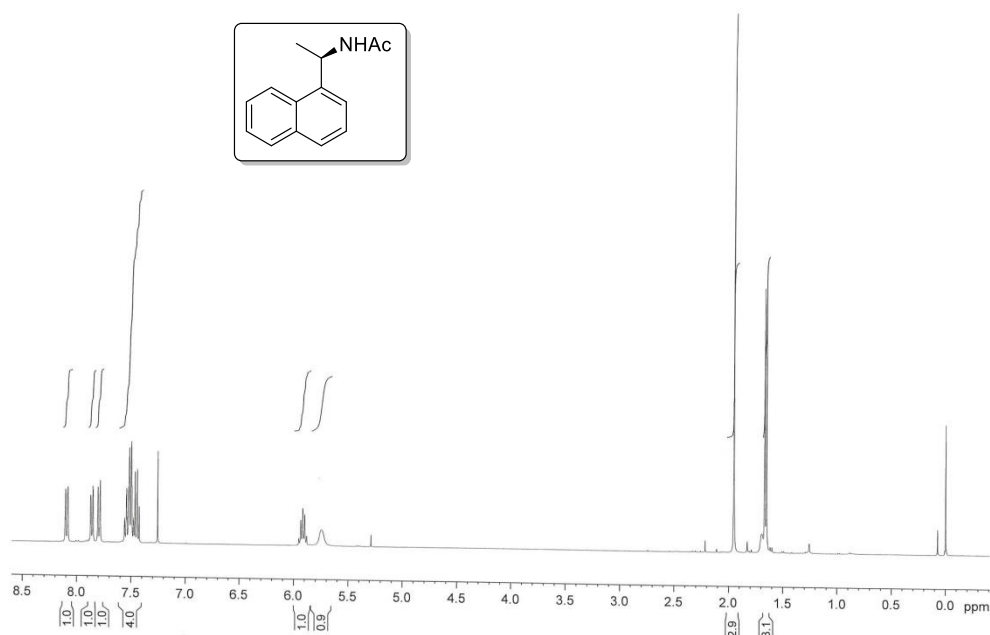


Figure 1: ¹H NMR spectrum of compound 3a* in CDCl₃

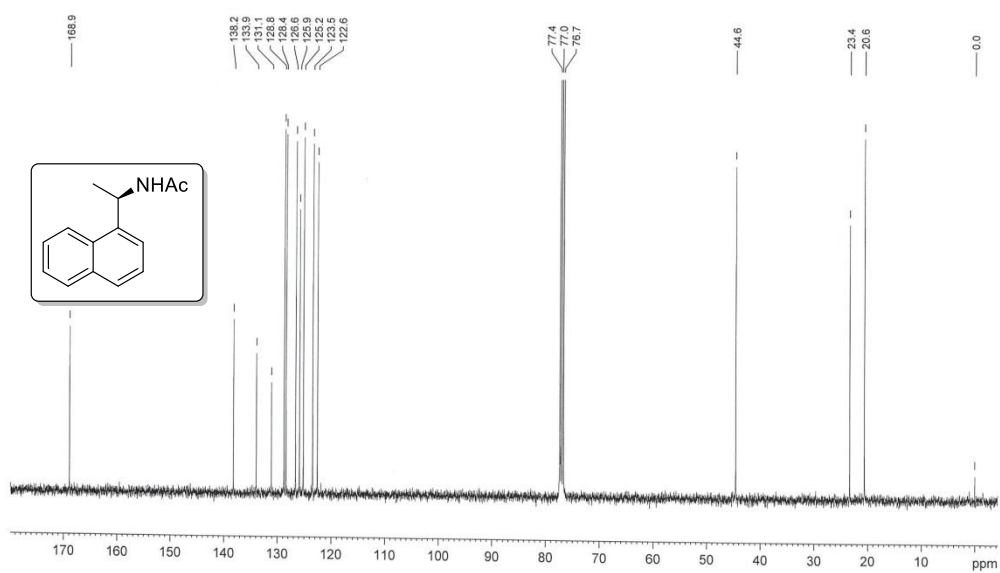


Figure 2: ¹³C NMR spectrum of compound 3a* in CDCl₃

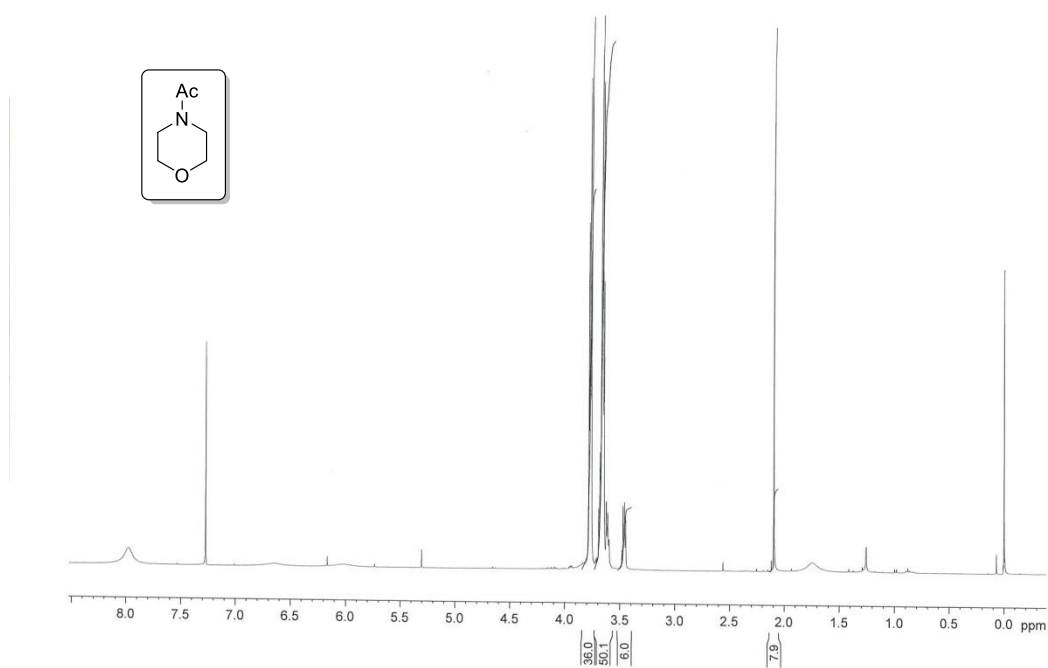


Figure 3: ¹H NMR spectrum of compound 3b* in CDCl₃

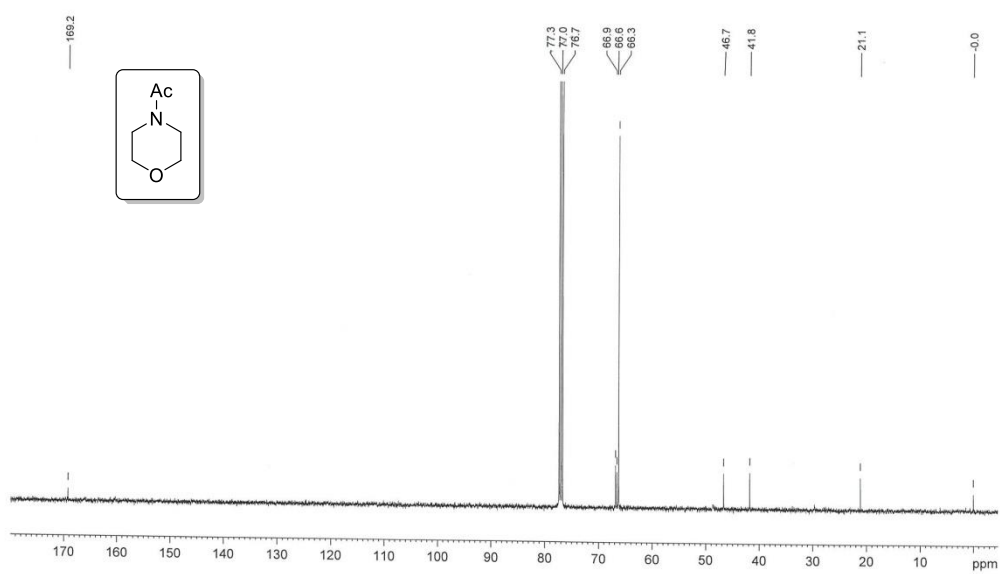


Figure 4: ¹³C NMR spectrum of compound 3b* in CDCl₃

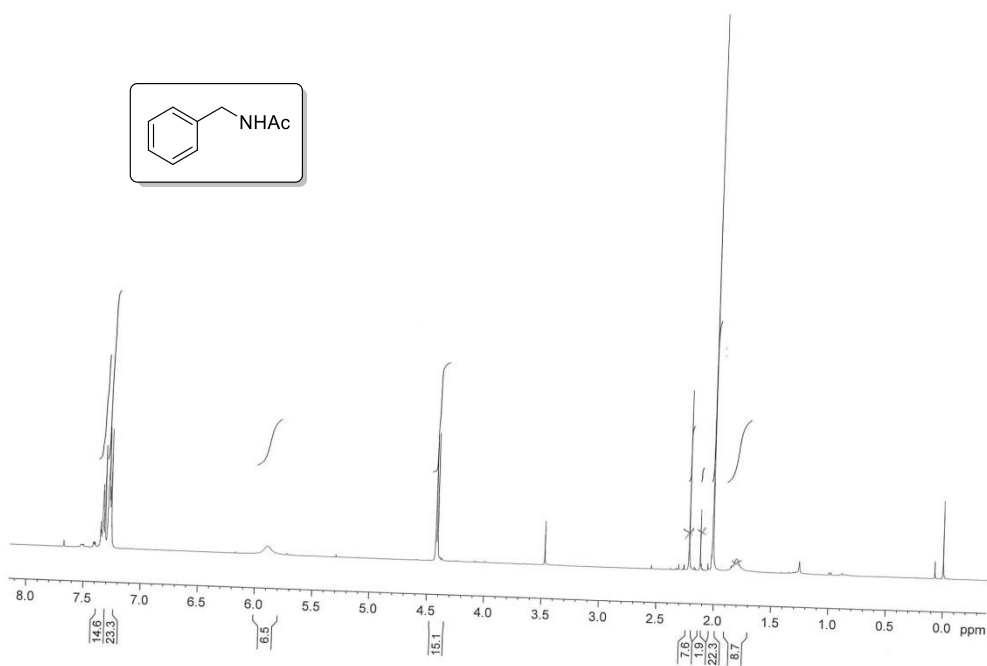


Figure 5: ^1H NMR spectrum of compound 3c* in CDCl₃

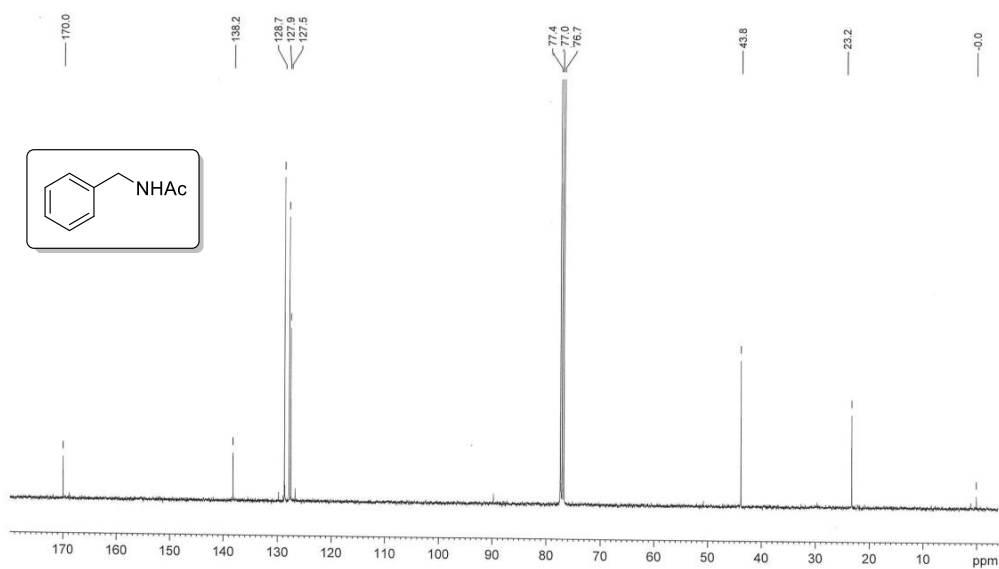


Figure 6: ^{13}C NMR spectrum of compound 3c* in CDCl₃

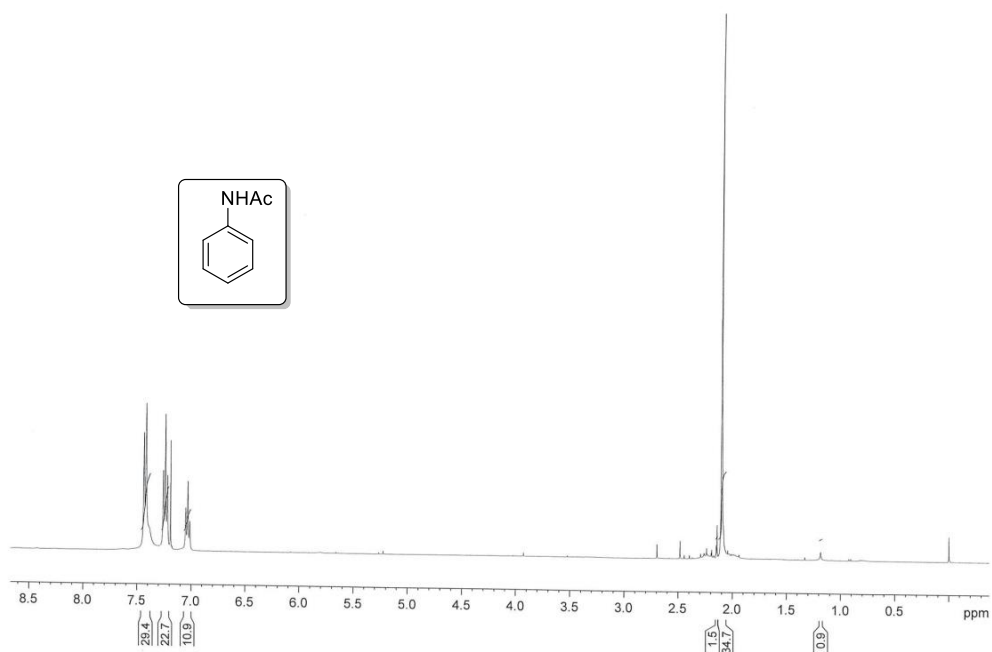


Figure 7: ^1H NMR spectrum of compound 3d* in CDCl_3

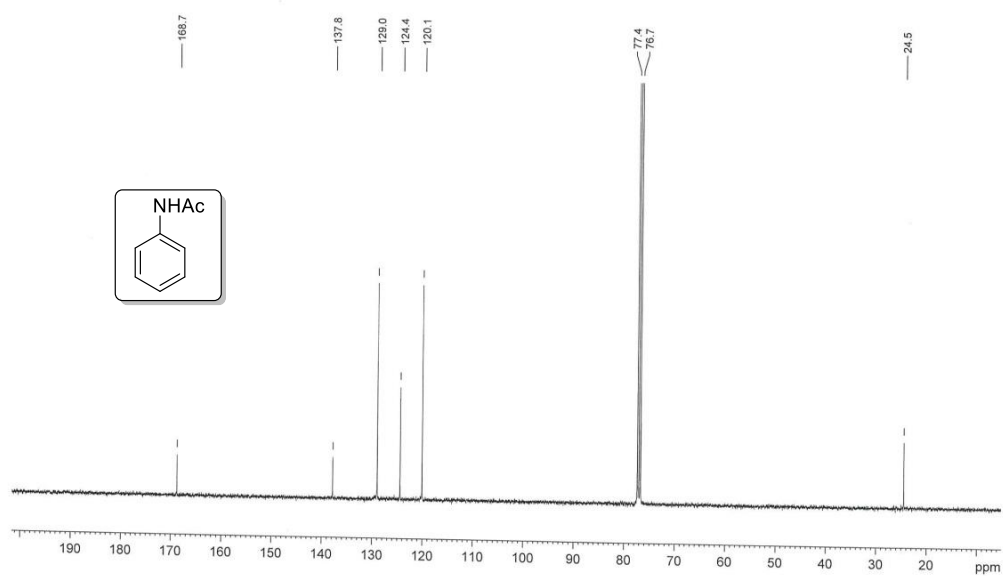


Figure 8: ^{13}C NMR spectrum of compound 3d* in CDCl_3

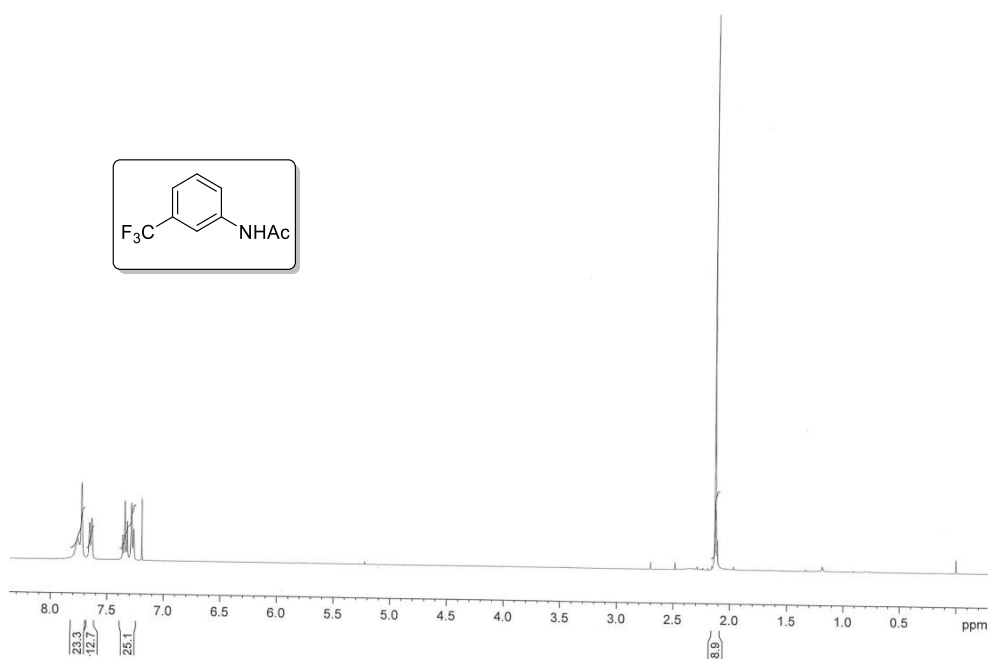


Figure 9: ¹H NMR spectrum of compound 3e* in CDCl₃

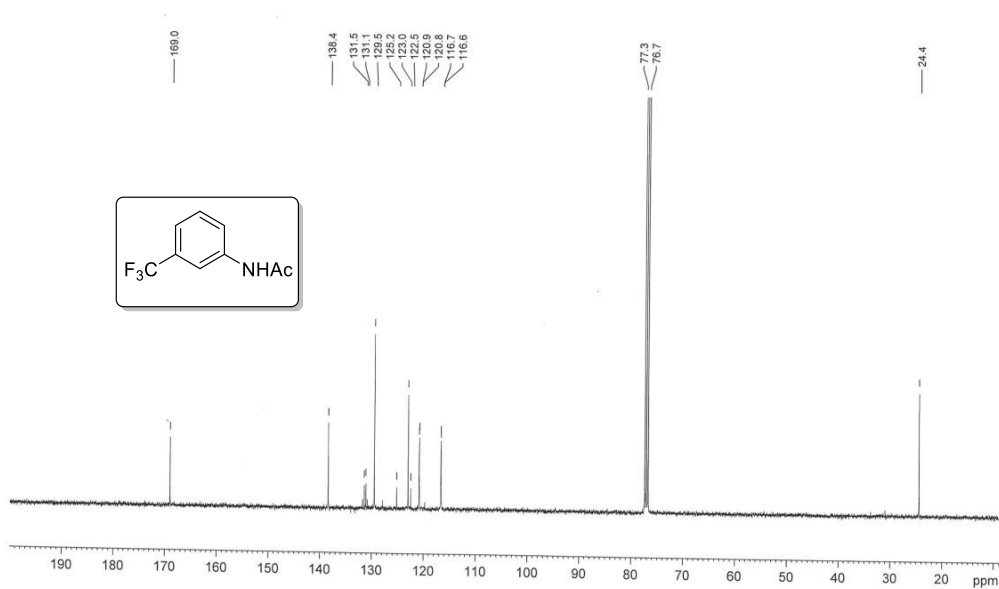


Figure 10: ¹³C NMR spectrum of compound 3e* in CDCl₃

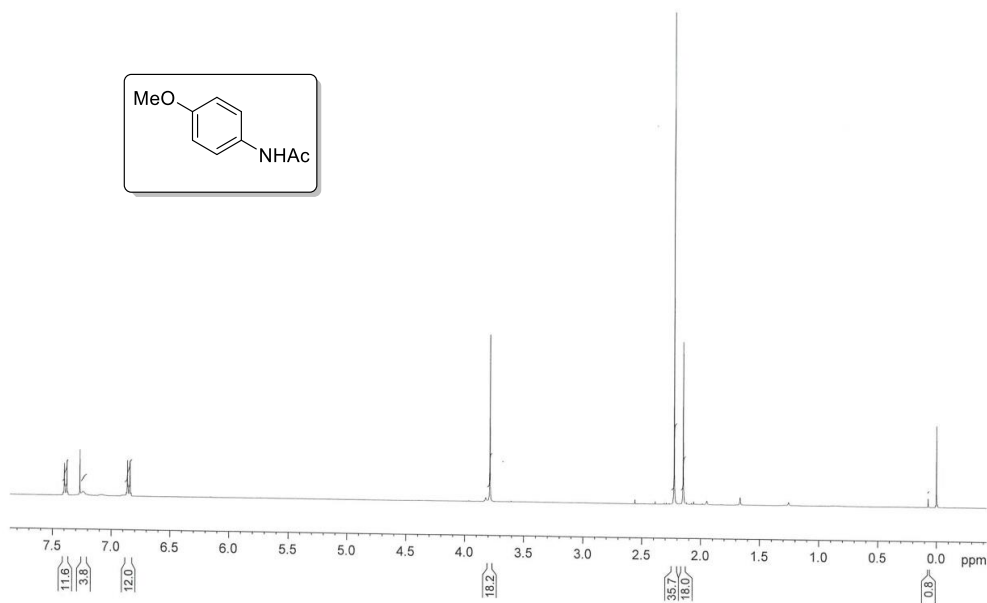


Figure 11: ^1H NMR spectrum of compound 3f* in CDCl_3

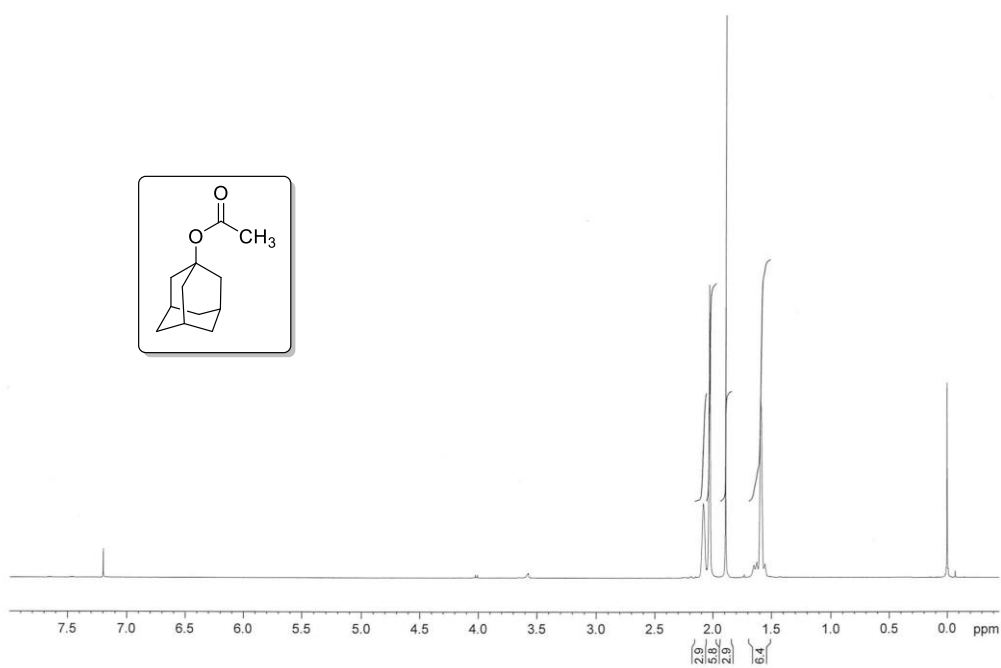


Figure 12: ^1H NMR spectrum of compound 3g* in CDCl_3

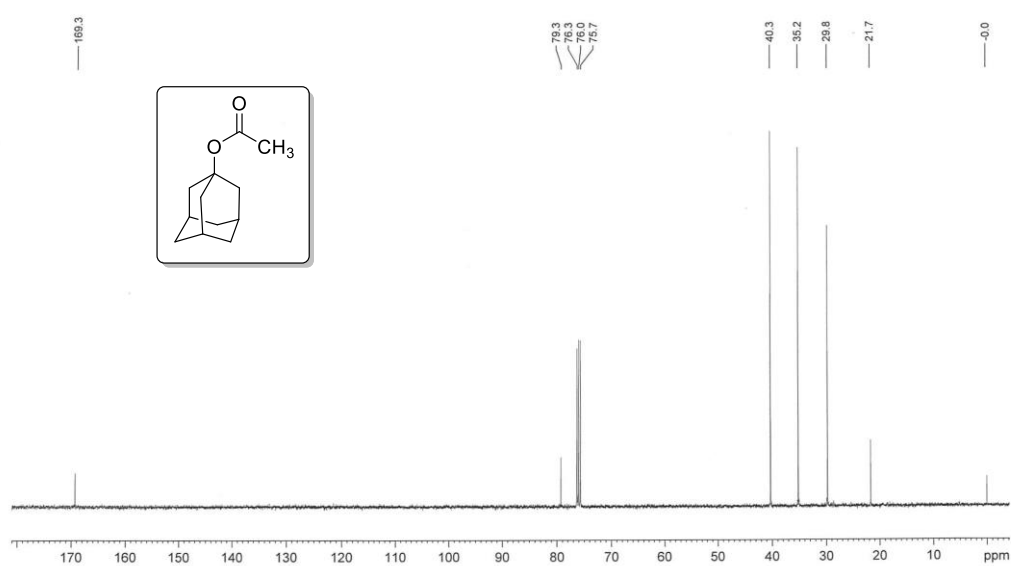


Figure 13: ^{13}C NMR spectrum of compound 3g* in CDCl_3

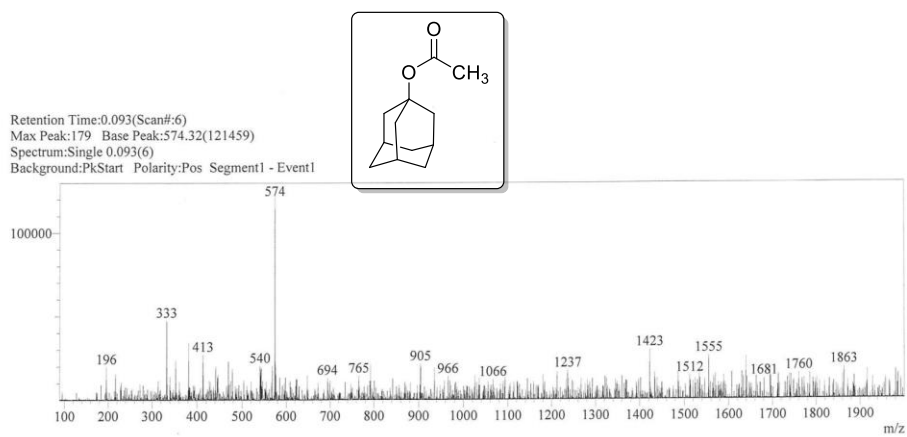


Figure 14: ESI(+ve) mass spectrum of compound 3g*

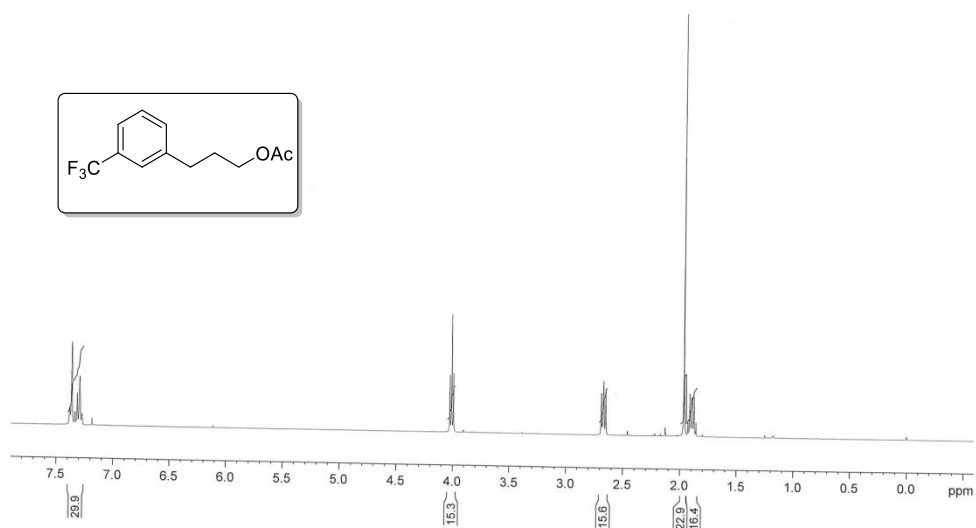


Figure 15: ^1H NMR spectrum of compound 3h* in CDCl₃

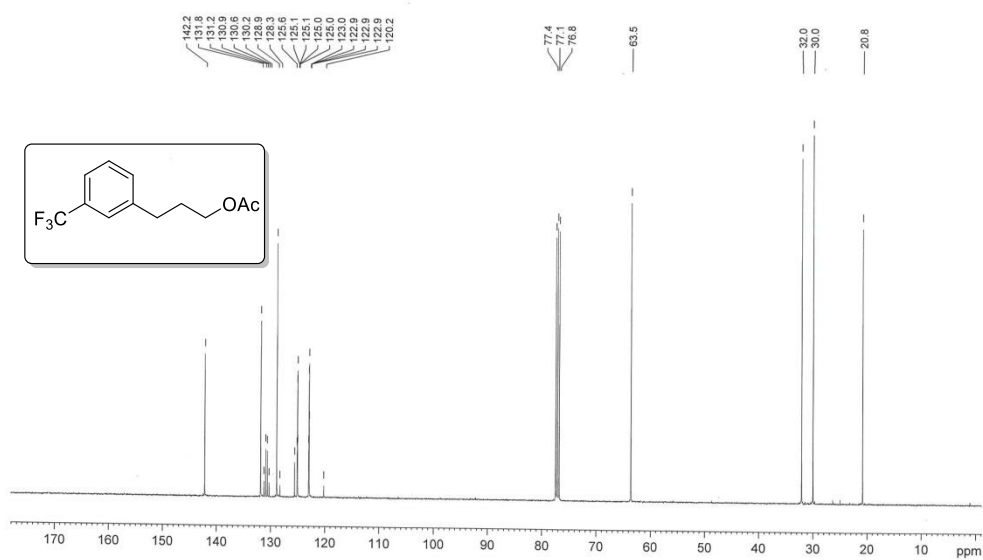


Figure 16: ^{13}C NMR spectrum of compound 3h* in CDCl₃

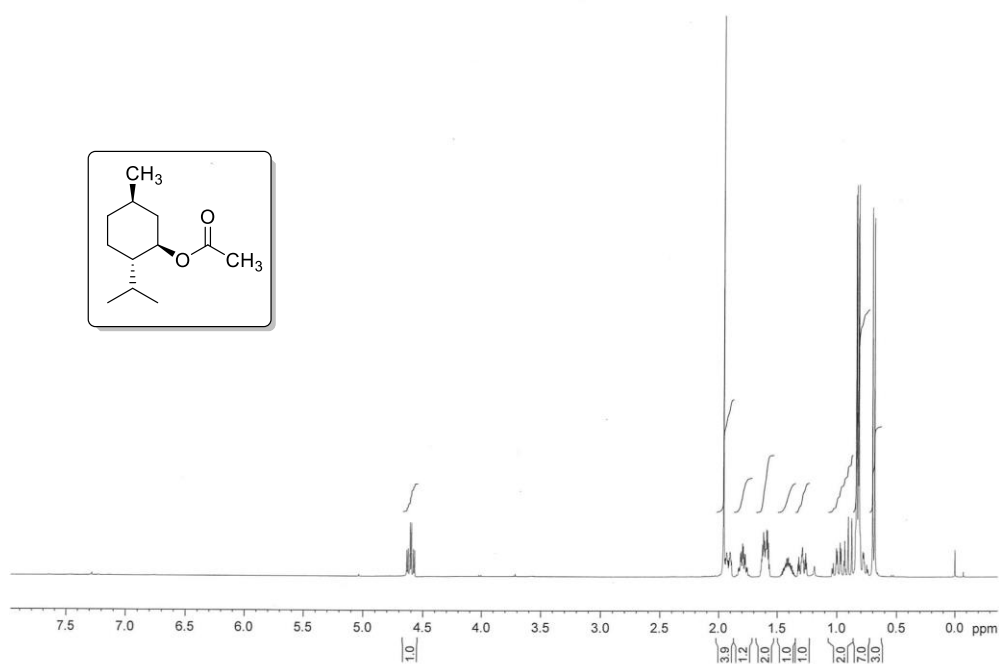


Figure 17: ^1H NMR spectrum of compound **3i*** in CDCl_3

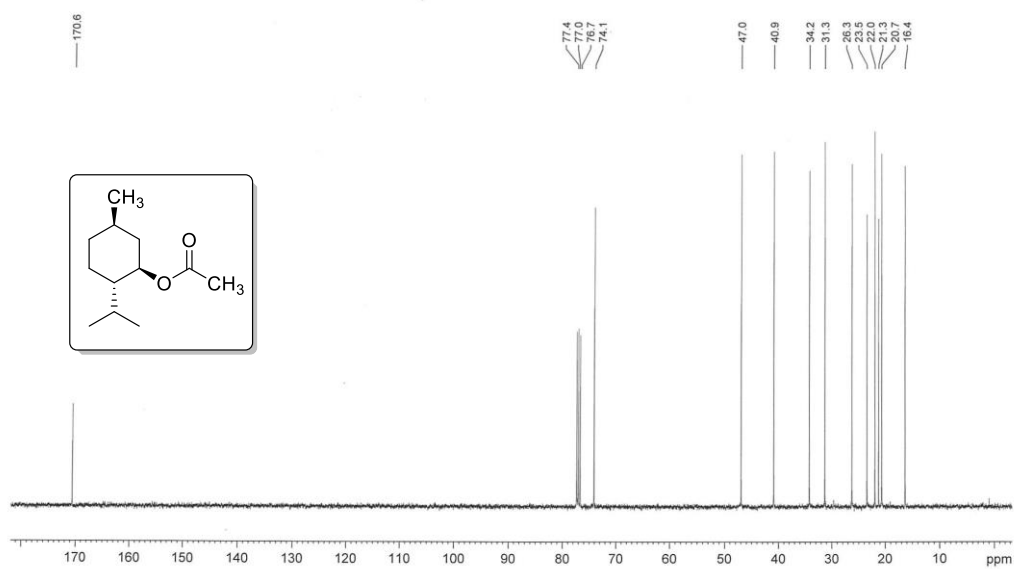


Figure 18: ^{13}C NMR spectrum of compound **3i*** in CDCl_3

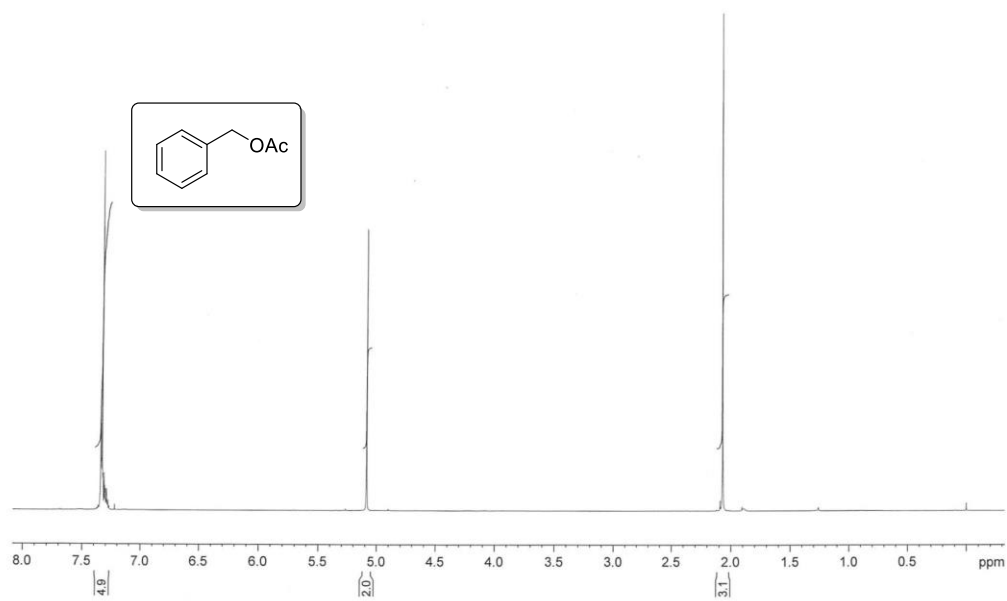


Figure 19: ^1H NMR spectrum of compound 3j* in CDCl_3

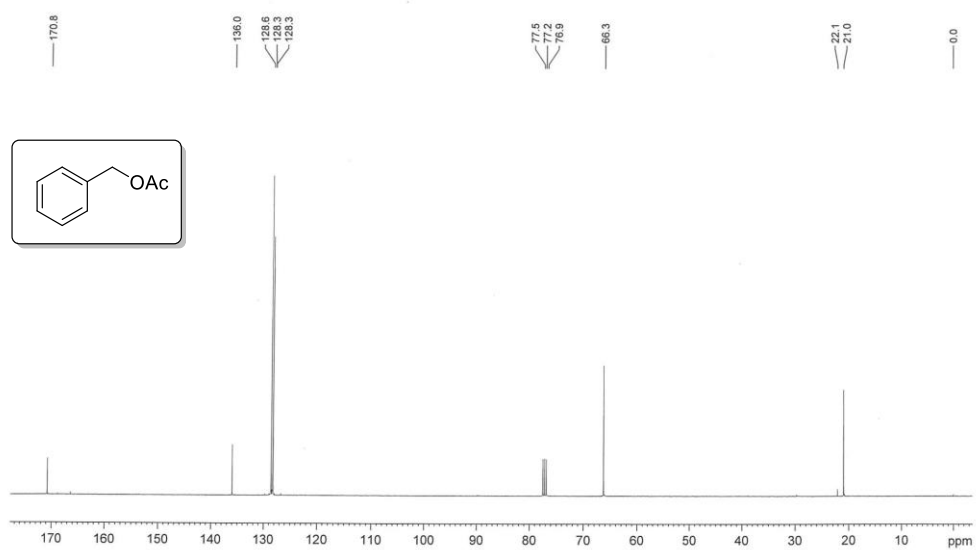


Figure 20: ^{13}C NMR spectrum of compound 3j* in CDCl_3

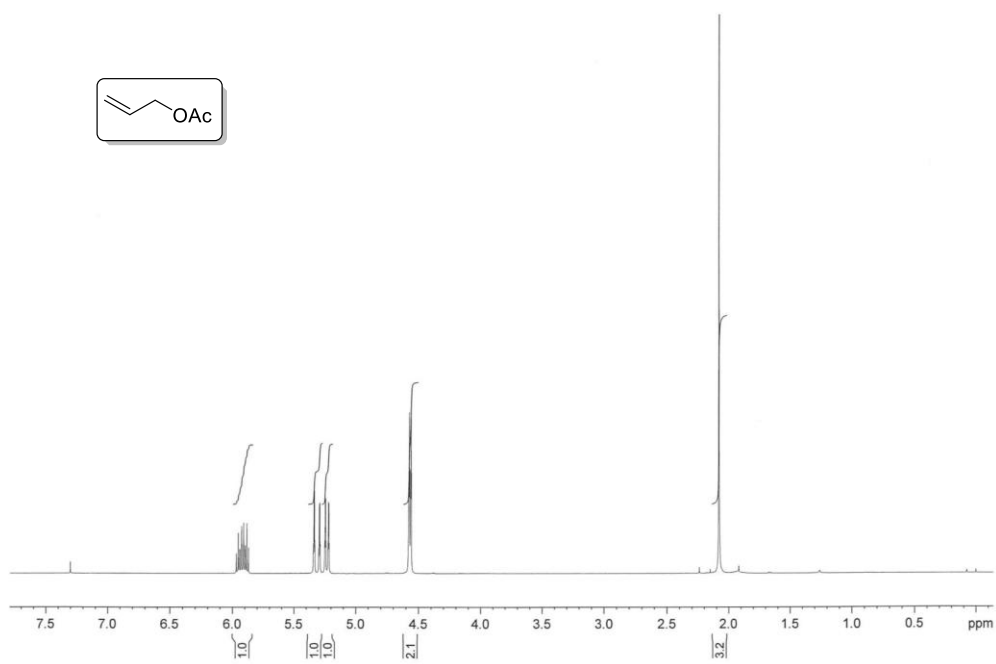


Figure 21: ¹H NMR spectrum of compound 3k* in CDCl₃

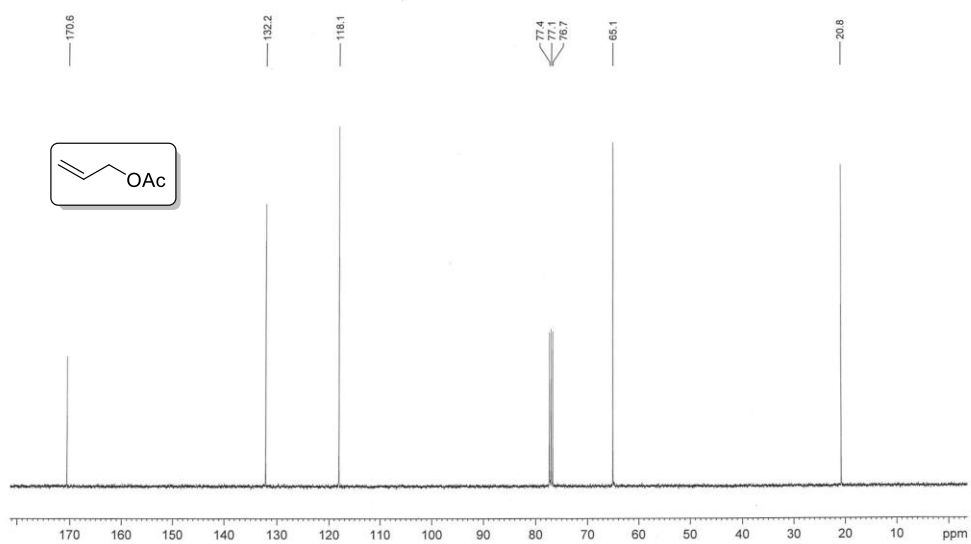


Figure 22: ¹³C NMR spectrum of compound 3k* in CDCl₃

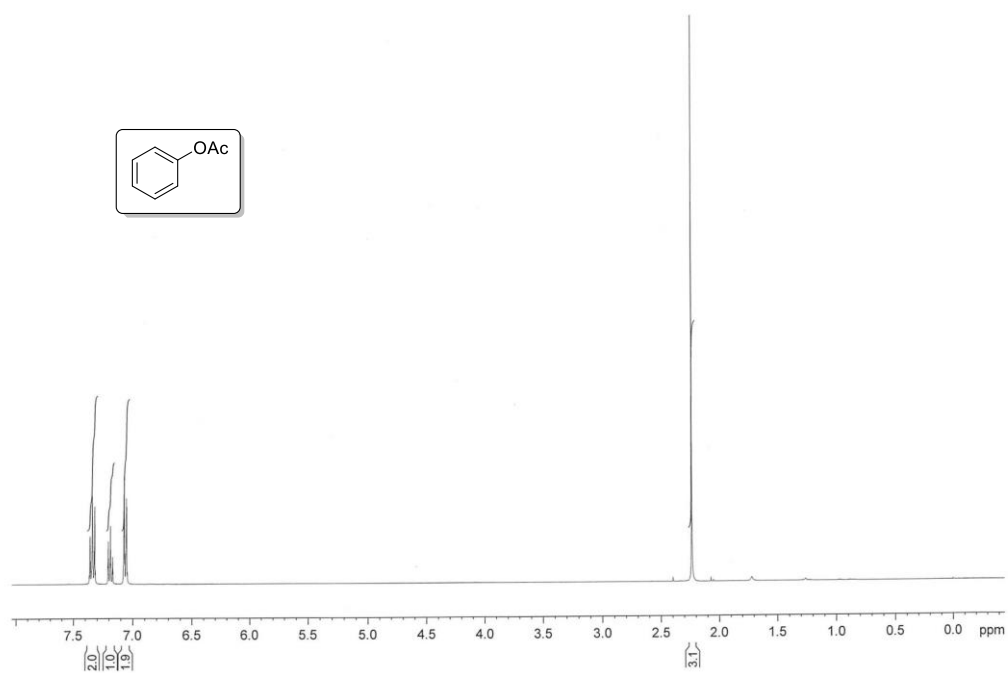


Figure 23: ¹H NMR spectrum of compound 3l* in CDCl₃

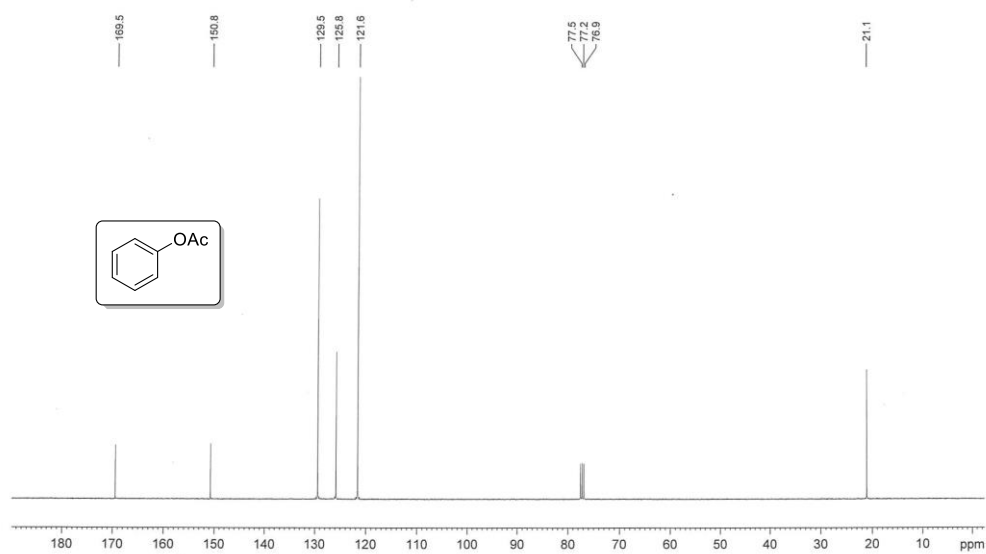


Figure 24: ¹³C NMR spectrum of compound 3l* in CDCl₃

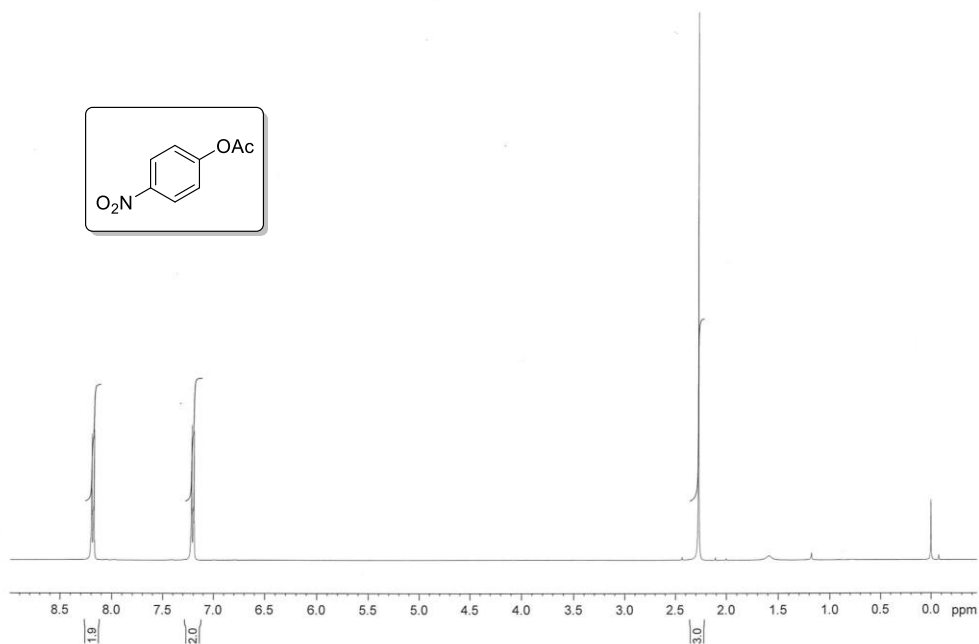


Figure 25: ¹H NMR spectrum of compound 3m* in CDCl₃

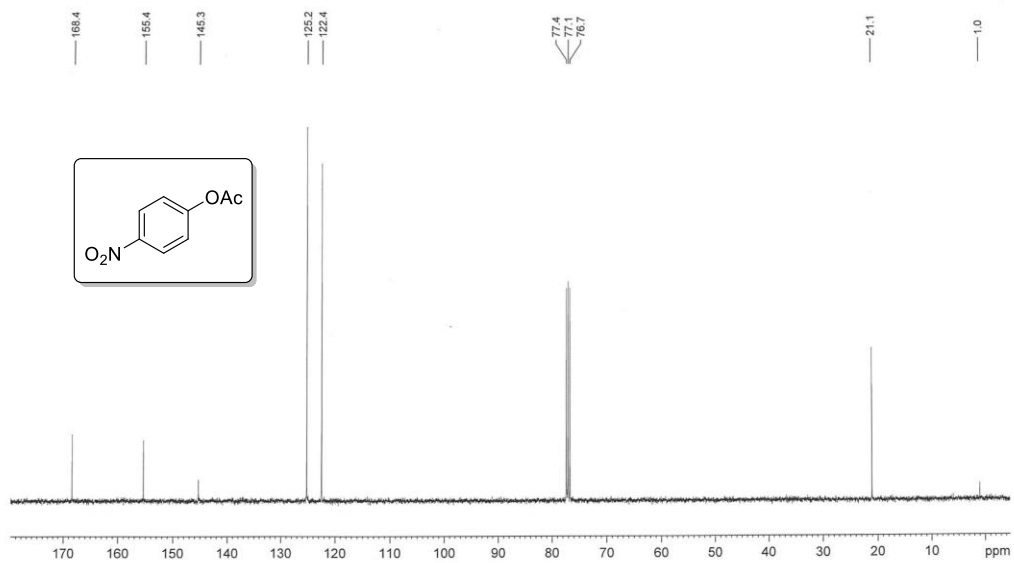


Figure 26: ¹³C NMR spectrum of compound 3m* in CDCl₃

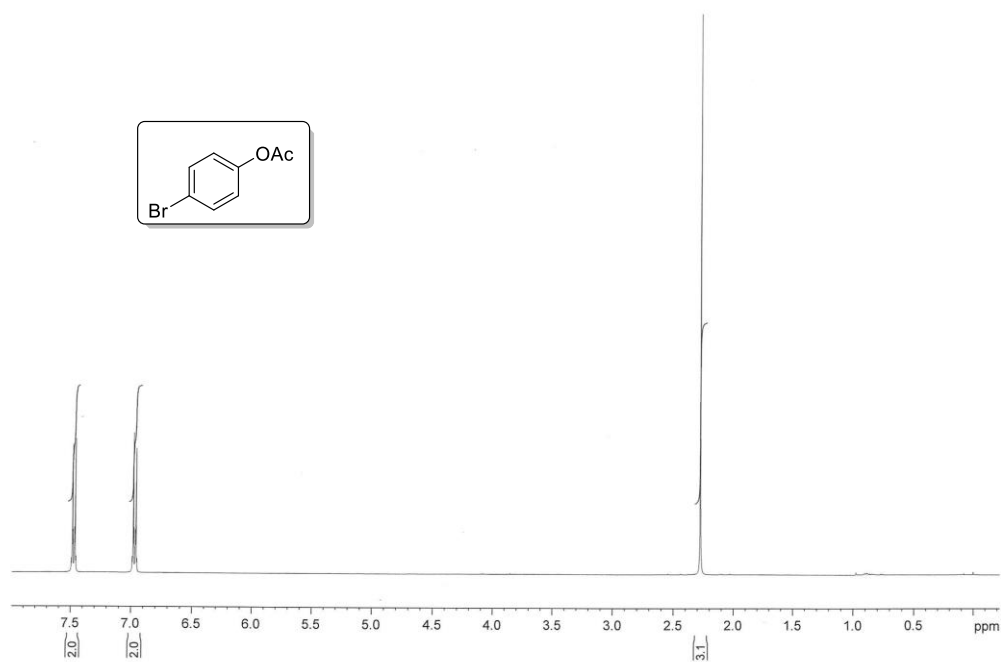


Figure 27: ¹H NMR spectrum of compound 3n* in CDCl₃

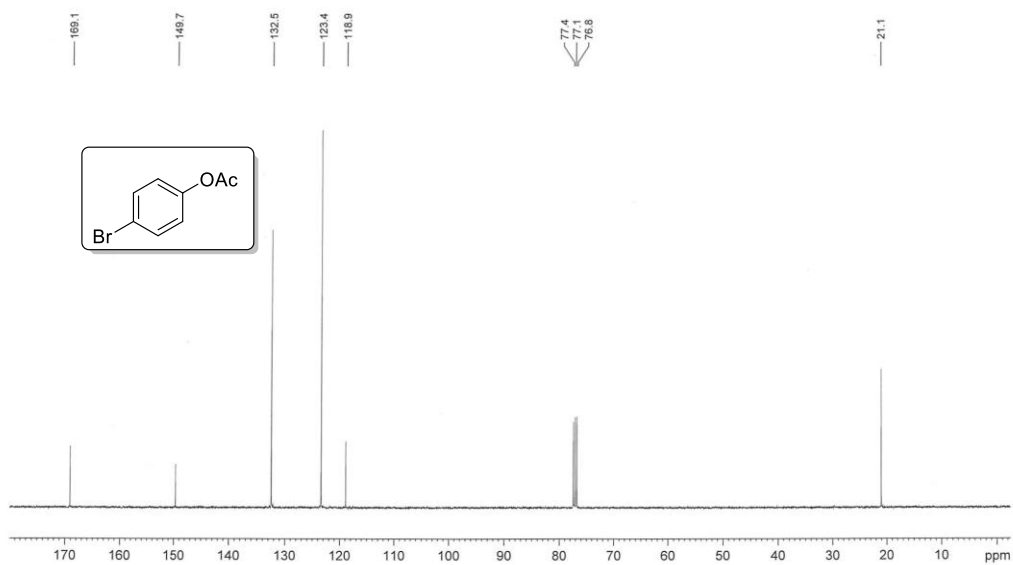


Figure 28: ¹³C NMR spectrum of compound 3n* in CDCl₃

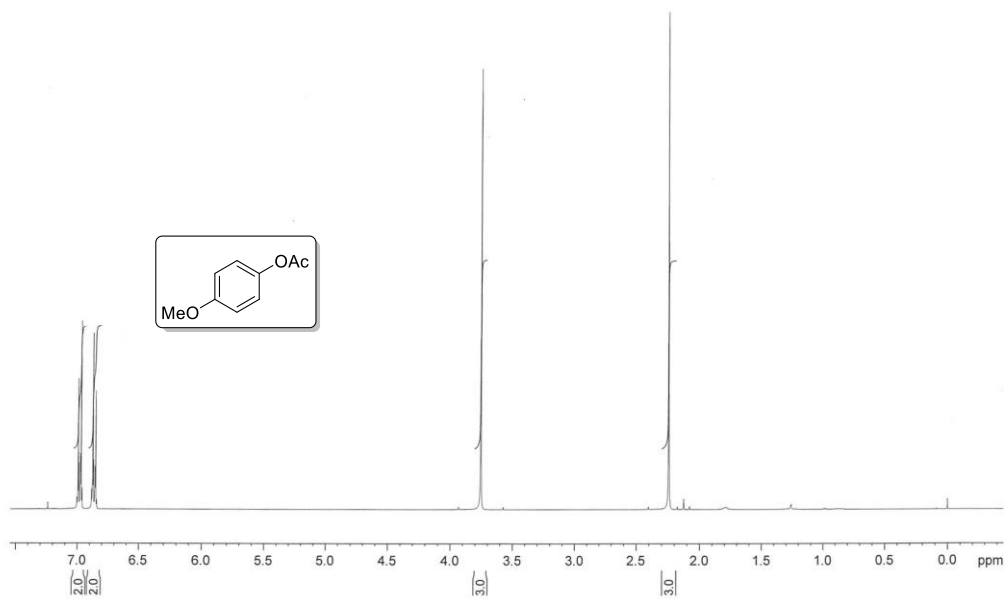


Figure 29: ¹H NMR spectrum of compound 3o* in CDCl₃

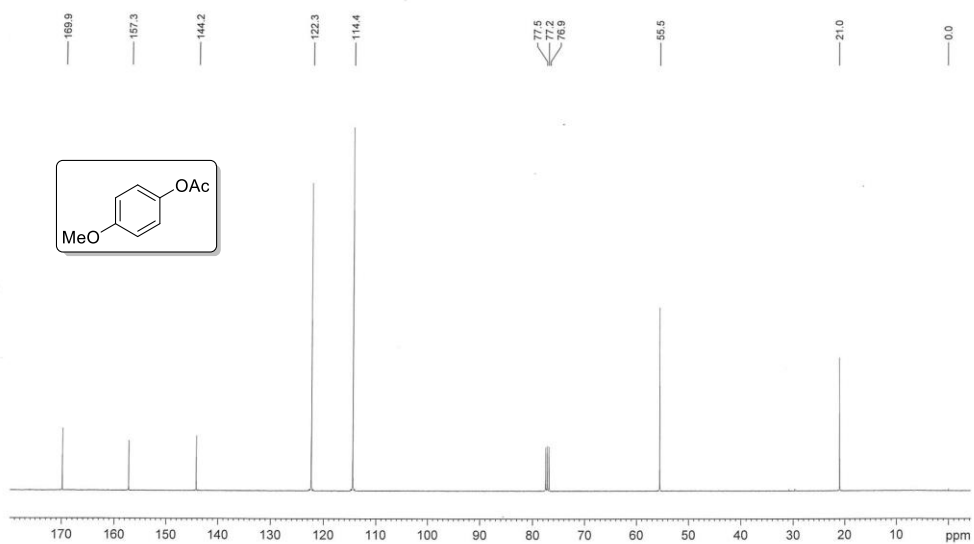


Figure 30: ¹³C NMR spectrum of compound 3o* in CDCl₃

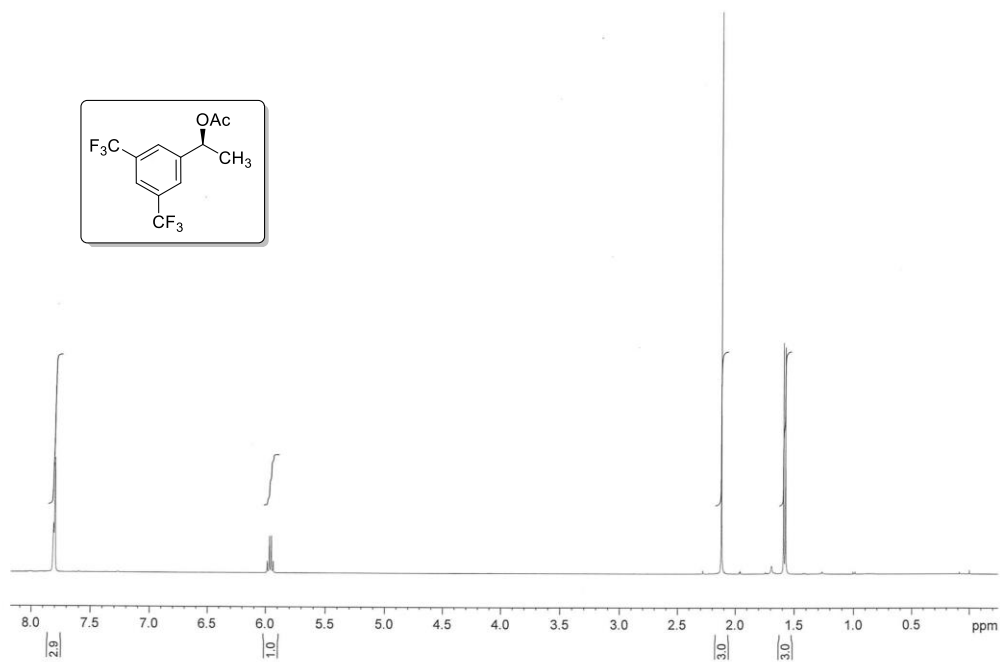


Figure 31: ¹H NMR spectrum of compound 3p* in CDCl₃

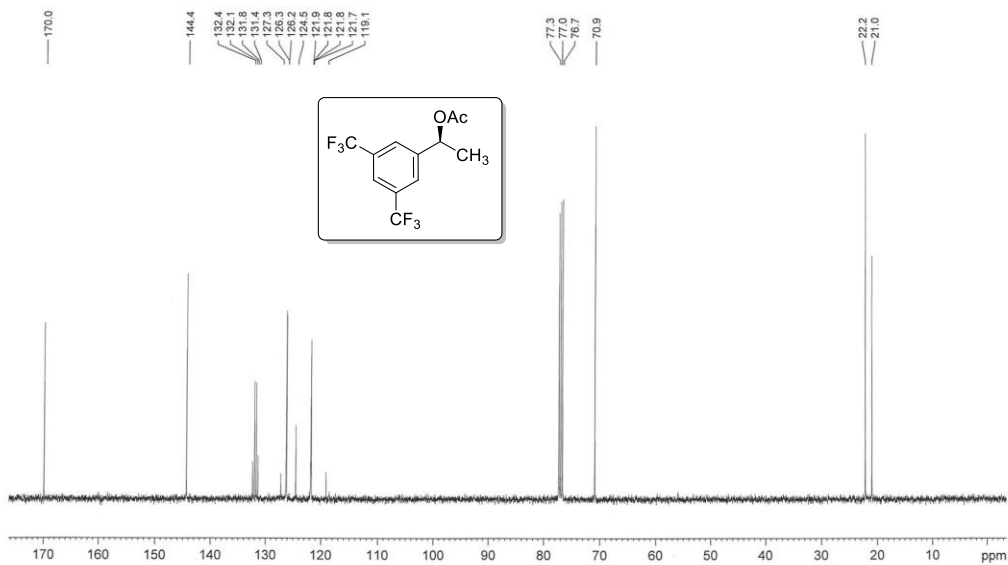


Figure 32: ¹³C NMR spectrum of compound 3p* in CDCl₃

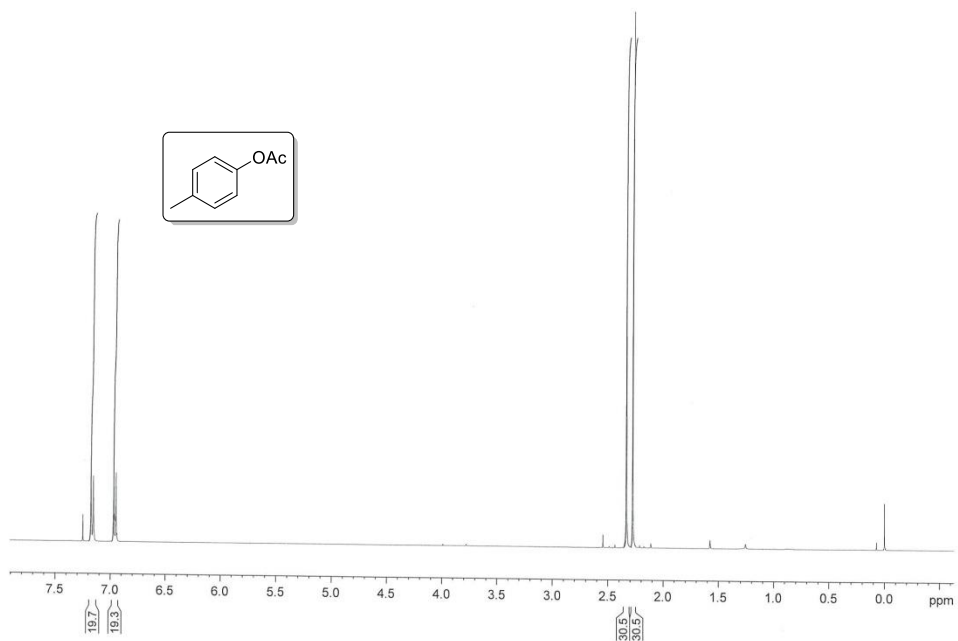


Figure 33: ^1H NMR spectrum of compound 3q* in CDCl_3

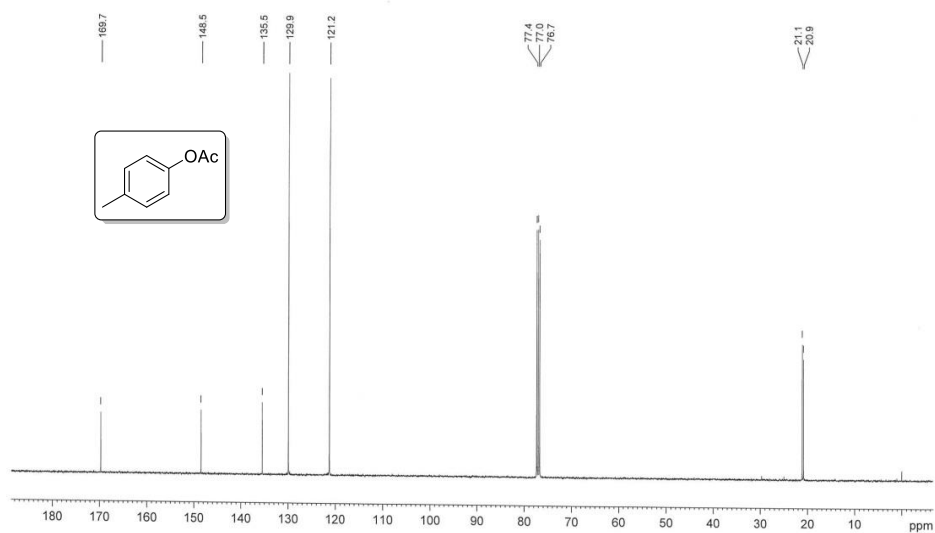


Figure 34: ^{13}C NMR spectrum of compound 3q* in CDCl_3

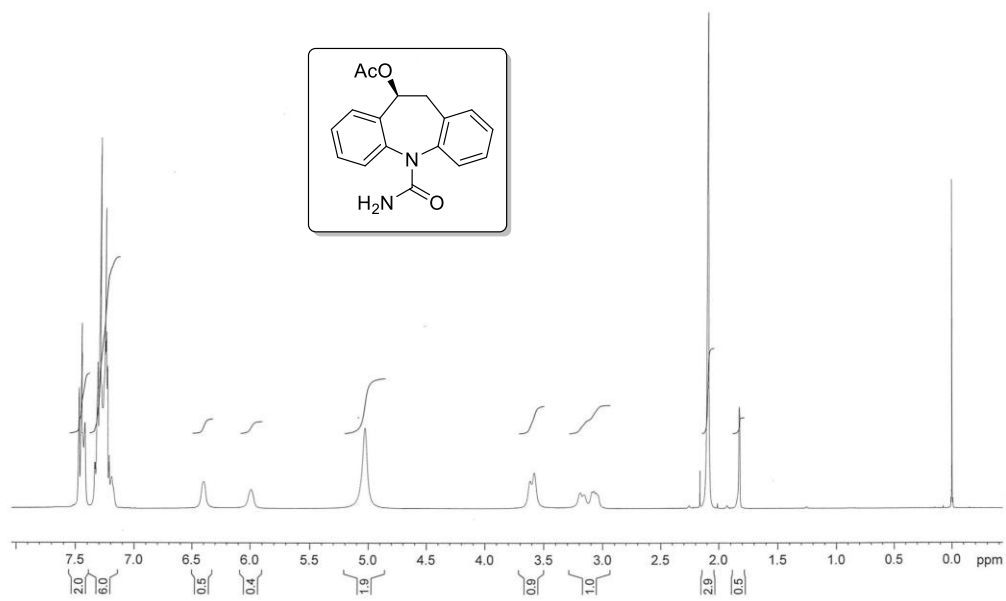


Figure 35: ¹H NMR spectrum of compound 3r* in CDCl₃

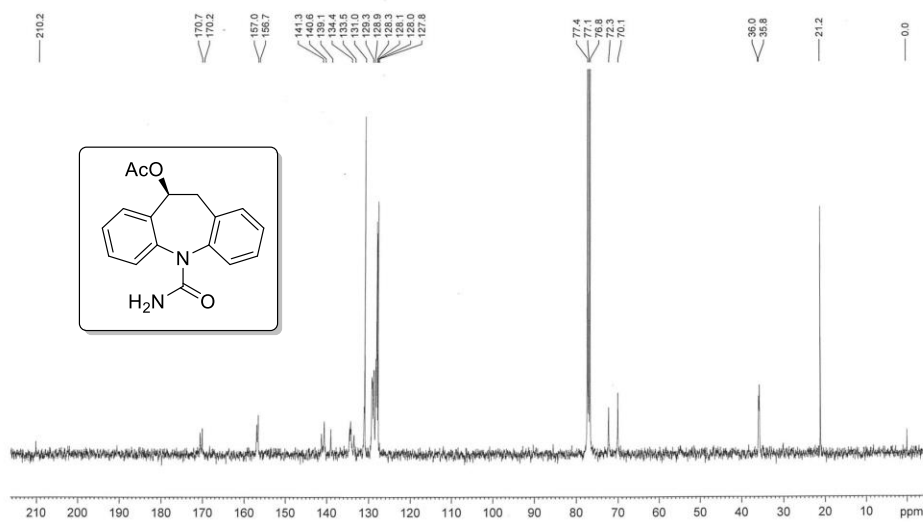


Figure 36: ¹³C NMR spectrum of compound 3r* in CDCl₃

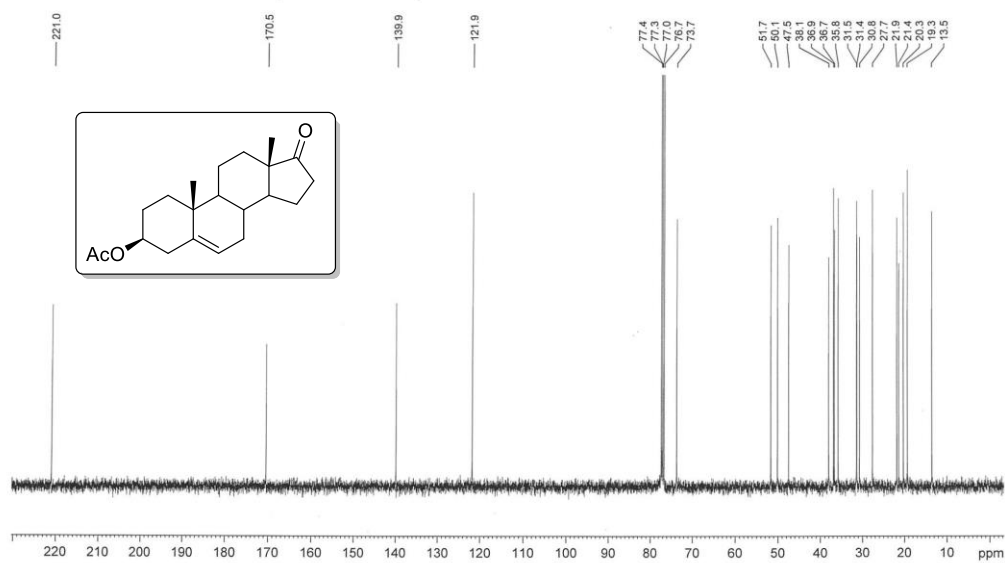


Figure 39: ^{13}C NMR spectrum of compound 3s* in CDCl_3

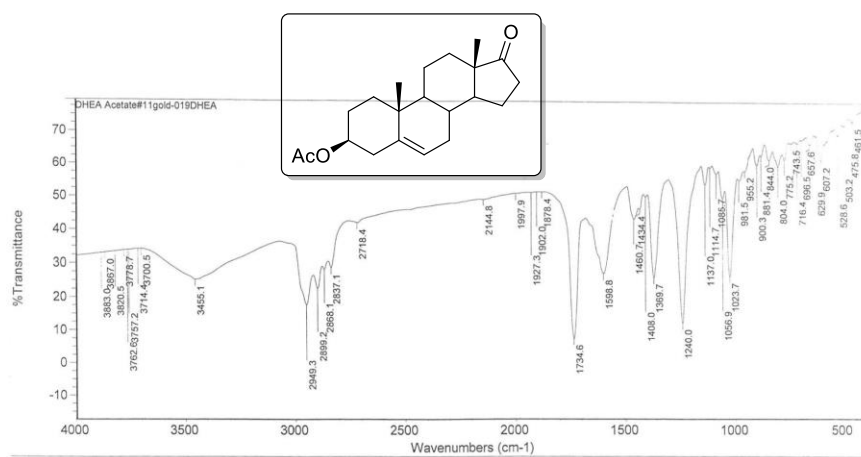


Figure 40: FT-IR spectrum of compound 3s*

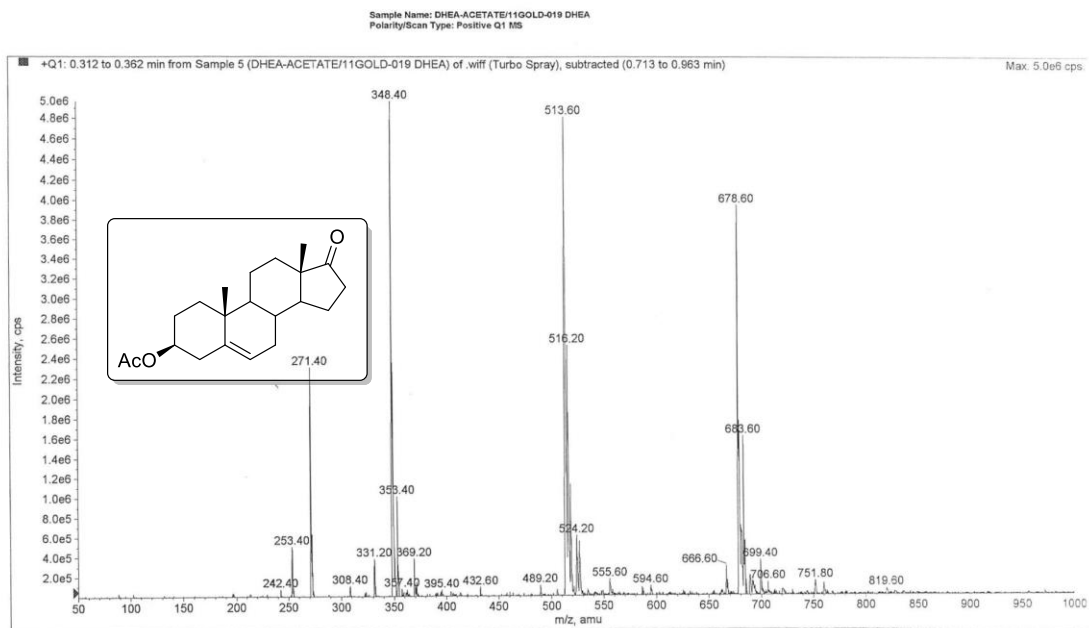


Figure 41: ES-MS/MS spectrum of compound 3s*

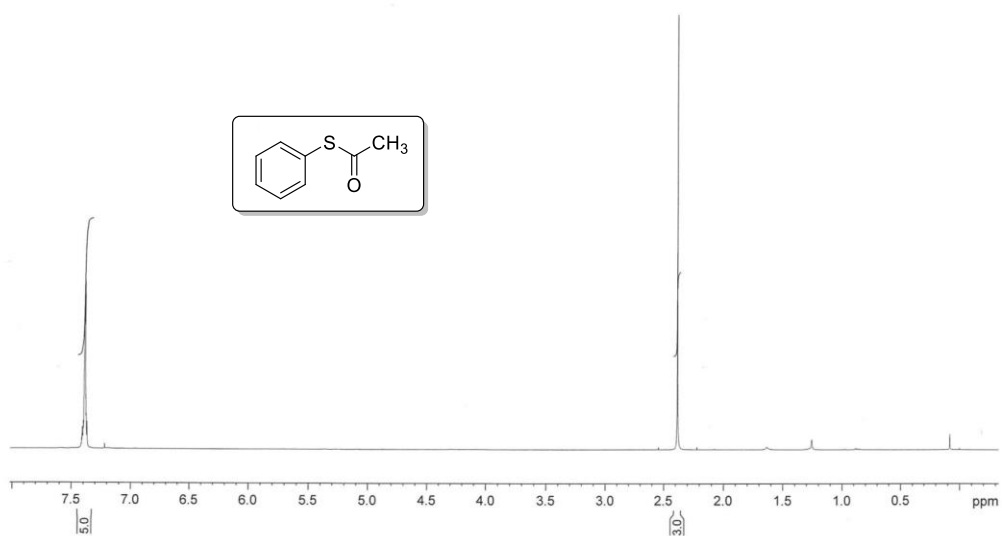


Figure 42: ^1H NMR spectrum of compound 3t* in CDCl_3

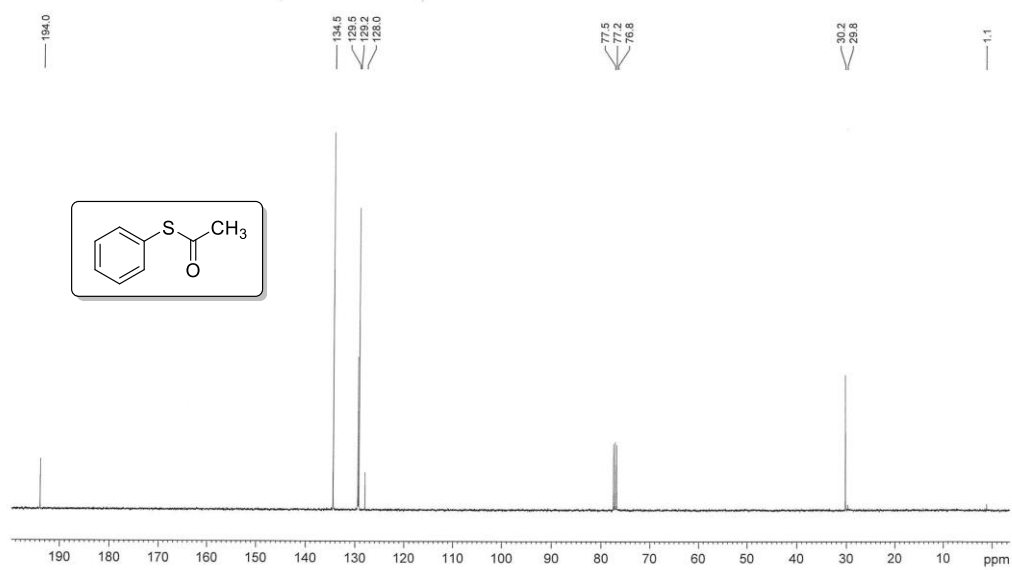


Figure 43: ^{13}C NMR spectrum of compound 3t* in CDCl_3