Electronic supplementary information

The Reaction of Primary Aromatic Amines with Alkylene Carbonates for the Selective Synthesis of bis-*N*-(2-Hydroxy)alkylanilines: the Catalytic Effect of Phosphonium-based Ionic Liquids

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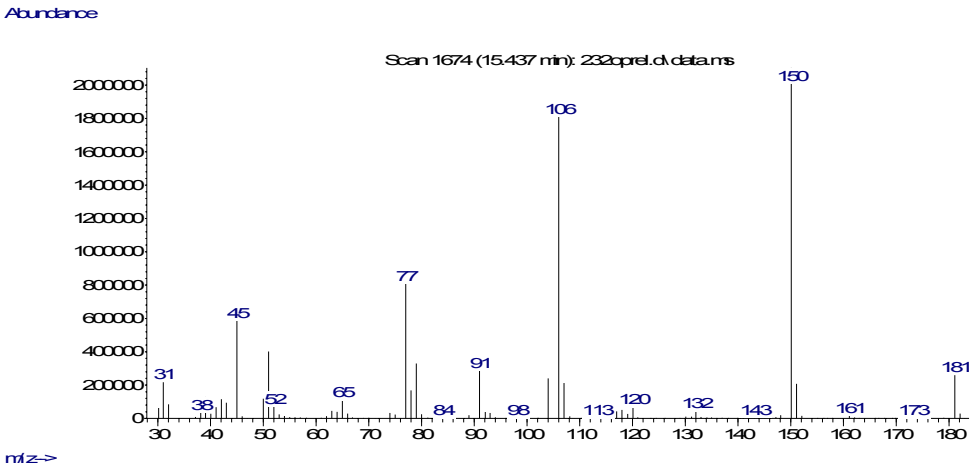
Synoptic table of major MS signals of reaction products **2a-d**, **3a-d**, **4a-d**, **5a-d**, **6a-b**, **7a-b**, **8a-b** and **9a-b**

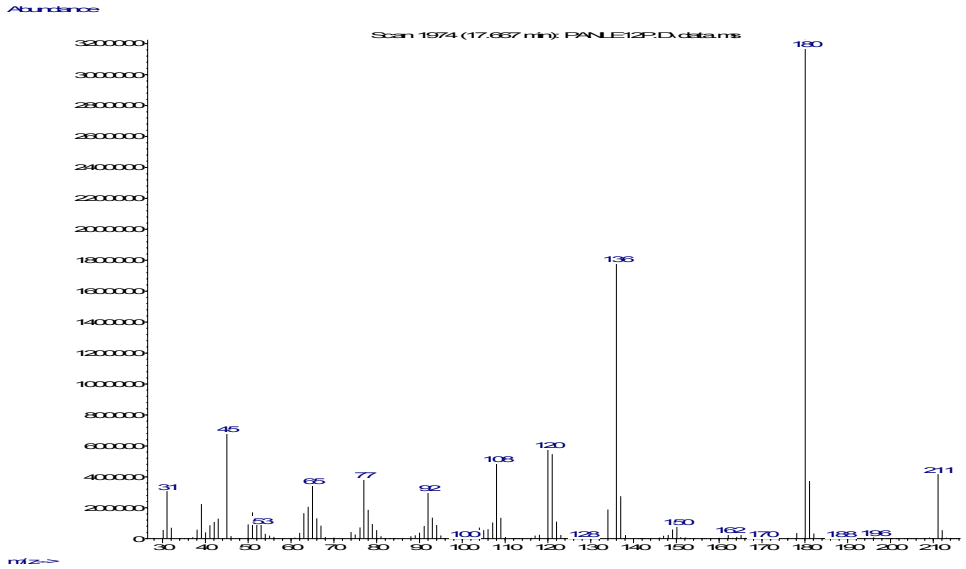
Compound	GC/MS (EI, 70 eV)
N-(2-hydroxy)ethyl aniline (**2a**)	m/z: 137 ([M]$^+$, 18%), 106 [M-CH_2OH]$^+$, 100), 79 (16), 77 (34), 54 (18), 32 (16)
Bis-N-(2-hydroxy)ethyl aniline (**3a**)	m/z: 181 ([M]$^+$, 12%), 151 (10), 150 ([M-CH_2OH]$^+$, 100), 107 (10), 106 ([M-(CH_2OH)-(CH_2CH_2O)]$^+$, 86), 104 (11), 91 ([M-(CH_2CH_2OH)$_2$]$^+$, 14), 79 (16), 77 (38), 51 (19), 45 (28), 31 ([CH_2OH]$^+$, 10)
N-phenylmorpholine (**4a**)	m/z: 163 ([M]$^+$, 38%), 106 (13), 105 ([C6H5N=CH_2]$^{+\cdot}$, 100), 104 (53), 77 (40), 51 (23), 32 (26)
3-phenyloxazolidin-2-one (**5a**)	m/z: 163 ([M]$^+$, 50%), 118 ([M-CO_2-H]$^+$, 16), 104 [M-CO_2-H-CH_2]$^+$, 81), 91 (16), 77 (100), 52 (15), 51 (27), 50 (10), 29 (10)
N-(2-hydroxy)ethyl *p*-anisidine (**2b**)	m/z: 167 ([M]$^+$, 20%), 136 ([M-CH_2OH]$^+$, 100), 121 (13), 108 (13), 32 (14)
Bis-N-(2-hydroxy)ethyl *p*-anisidine (**3b**)	m/z: 211 ([M]$^+$, 13%), 181 (12), 180 ([M-CH_2OH]$^+$, 100), 136 ([M-CH_2OH-$CHCH_2OH$]$^+$, 55), 121 ([M-(CH_2CH_2OH)$_2$]$^+$, 17), 120 (18), 108 (15), 77 (12), 65 (11), 45 (28), 31 ([CH_2OH]$^+$, 10)
4-(4-methoxyphenyl) morpholine (**4b**)	m/z: 193 ([M]$^+$, 61%), 178 (23), 136 (10), 135 ([M-CH_2OH]$^+$, 100), 121 (10), 120 (66), 92 (13), 77 (15), 65 (17), 64 (10), 39 (11)
3-(4-methoxyphenyl) oxazolidin-2-one (**5b**)	m/z: 193 ([M]$^+$, 60%), 148 ([M-CO_2-H]$^+$, 10), 135 (11), 134 ([M-CO_2-H-CH_2]$^+$, 100), 121 (17), 107 (15), 91 (12), 80 (10), 79 (10), 78 (11), 77 (25), 65 (11), 64 (16), 63 (13), 52 (13), 51 (12), 39 (12), 32 (12)
N-(2-hydroxy)ethyl *p*-toluidine (**2c**)	m/z: 151 ([M]$^+$, 18%), 121 (10), 120 ([M-CH_2OH]$^+$, 100), 91 (27), 77 (11), 65 (16)
Bis-N-(2-hydroxy)ethyl *p*-toluidine (**3c**)	m/z: 195 ([M]$^+$, 12%), 165 (11), 164 ([M-CH_2OH]$^+$, 100), 121 (10), 120 ([M-CH_2OH-$CHCH_2OH$)]$^+$, 71), 118 (12), 105 ([M-(CH_2CH_2OH)$_2$]$^+$, 10), 91 (33), 65 (18), 45 (28), 31 ([CH_2OH]$^+$, 10)
4-p-tolylmorpholine (**4c**)	m/z: 177 ([M]$^+$, 36%), 120 (18), 119 ([M-CH_2OH]$^+$, 100), 118 (31), 91 (45), 65 (22), 39 (12), 32 (36)

3-p-tolyloxazolidin-2-one (**5c**)	m/z: 177 ($[M]^+$, 54%), 132 ($[M\text{-}CO_2\text{-}H]^+$, 18), 118 ($[M\text{-}CO_2\text{-}H\text{-}CH_2]^+$, 79), 105 (20), 91 (100), 89 (10), 77 (13), 65 (36), 63 (13), 52 (10), 51 (17), 39 (21), 32 (10)
N-(2-hydroxy)ethyl *p*-chloroaniline (**2d**)	m/z: 171 ($[M]^+$, 15%), 142 (33), 141 (10), 140 ($[M\text{-}CH_2OH]^+$, 100), 111 (11), 105 (12), 77 (19), 75 (16)
Bis-N-(2-hydroxy)ethyl *p*-chloroaniline (**3d**)	m/z: 215 ($[M]^+$, 14%), 186 (35), 185 (13), 184 ($[M\text{-}CH_2OH]^+$, 100), 142 (24), 141 (12), 140 ($[M\text{-}CH_2OH\text{-}CHCH_2OH]^+$, 76), 138 (13), 125 ($[M\text{-}(CH_2CH_2OH)_2]^+$, 10), 111 (20), 105 (10), 77 (19), 75 (19), 51 (11), 45 (28), 31 ($[CH_2OH]^+$, 10)
4-(4-chlorophenyl)morpholine (**4d**)	m/z: 197 ($[M]^+$, 42%), 141 (33), 140 (22), 139 ($[M\text{-}CH_2OH]^+$, 100), 138 (40), 111 (20), 75 (16)
3-(4-chlorophenyl) oxazolidin-2-one (**5d**)	m/z: 197 ($[M]^+$, 44%), 152 ($[M\text{-}CO_2\text{-}H]^+$, 15), 140 (33), 139 (12), 138 ($[M\text{-}CO_2\text{-}H\text{-}CH_2]^+$, 100), 125 (13), 113 (26), 111 (79), 90 (10), 76 (16), 75 (36), 74 (10), 69 (14), 63 (19), 51 (14), 50 (19), 39 (10), 38 (10), 32 (93)
1-(phenylamino)propan-2-ol 2-(phenylamino)propan-1-ol (**6a**)	m/z: 151 ($[M]^+$, 11%), 106 ($[M\text{-}CH(CH_3)OH]^+$, 100), 79 (11), 77 (23), 51 (12)
Bis-N-(2-hydroxy)propyl aniline 2-(N-(2-hydroxypropyl)-N-phenylamino)propan-1-ol (**7a**)	m/z: 209 ($[M]^+$, 11%), 165 (11), 164 ($[M\text{-}CH(CH_3)OH]^+$, 100), 107 (13), 106 ($[M\text{-}CH(CH_3)OH\text{-}CH_2CH(CH_3)O]^+$, 84) 104 (10), 91 (10) 77 (25), 59 ($[CH_2CH(CH_3)OH]^+$, 28), 31 ($[CH_2OH]^+$, 12)
2,6-dimethyl-4-phenyl morpholine 2,5-dimethyl-4-phenyl morpholine (**8a**)	m/z: 191 ($[M]^+$, 24%), 106 (10), 105 ($[C_6H_5N{=}CH_2]^{+\cdot}$, 100), 104 (29), 77 (21)
5-methyl-3-phenyl oxazolidin-2-one 4-methyl-3-phenyl oxazolidin-2-one (**9a**)	m/z: 177 ($[M]^+$, 24%), 163 (10), 162 ($[M\text{-}CH_3]^+$, 100), 134 ($[M\text{-}CH_3\text{-}CO]^+$, 36), 118 ($[M\text{-}CH_3\text{-}CO_2]^+$, 32], 117 (11), 105 ($[M\text{-}CO_2CHCH_3]^+$, 15), 104 (23), 91 (22), 77 (69), 51 (28), 43 (14)
1-(4-methoxyphenylamino) propan-2-ol 2-(4-methoxyphenylamino) propan-1-ol (**6b**)	m/z: 181 ($[M]^+$, 14%), 136 ($[M\text{-}CH(CH_3)OH]^+$, 100), 121 (11), 108 (11), 77 (6)
Bis-N-(2-hydroxy)propyl *p*-anisidine 2-(N-(2-hydroxypropyl)-N-(4-methoxyphenyl)amino)propan-1-ol (**7b**)	m/z: 239 ($[M]^+$, 11%), 195 (12), 194 ($[M\text{-}CH(CH_3)OH]^+$, 100), 137 (17), 136 ($[M\text{-}(CH(CH_3)OH)\text{-}(CH_2CH(CH_3)O)]^+$, 76), 121 ($[M\text{-}(CH_2CH(CH_3)OH)_2]^+$, 15), 120 (13), 77 (10), 59 ($[CH_2CH(CH_3)OH]^+$, 14), 31 ($[CH_2OH]^+$, 14)
4-(4-methoxyphenyl)-2,6-dimethylmorpholine 4-(4-methoxyphenyl)-2,5-dimethylmorpholine (**8b**)	m/z: 221 ($[M]^+$, 39%), 136 (17), 135 ($[CH_3OC_6H_4N{=}CH_2]^{+\cdot}$, 100), 134 (11), 120 (39), 92 (9), 77 87)
3-(4-methoxyphenyl)-5-methyloxazolidin-2-one 3-(4-methoxyphenyl)-4-methyloxazolidin-2-one (**9b**)	m/z: 207 ($[M]^+$, 44%), 193 (13), 192 ($[M\text{-}CH_3]^+$, 100], 164 ($[M\text{-}CH_3\text{-}CO]^+$, 48), 162 (12), 150 (10), 148 ($[M\text{-}CO_2\text{-}CH_3]^+$, 26), 136 (11), 135 ($[M\text{-}CO_2CHCH_3]^+$, 14), 134 (76), 122 (14), 121 (35), 120 (11), 109 (11), 108 (14), 107 (20), 92 (18), 79 (10), 77 (17), 65 (13), 64 (11), 63 (13), 51 (10), 43 (13), 41 (23)

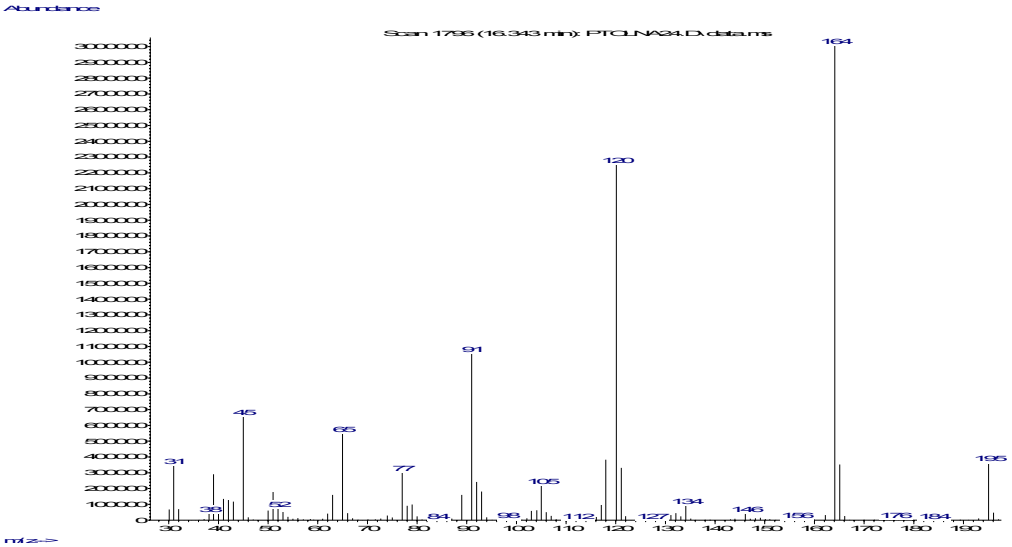
MS spectra of products **3a-d**



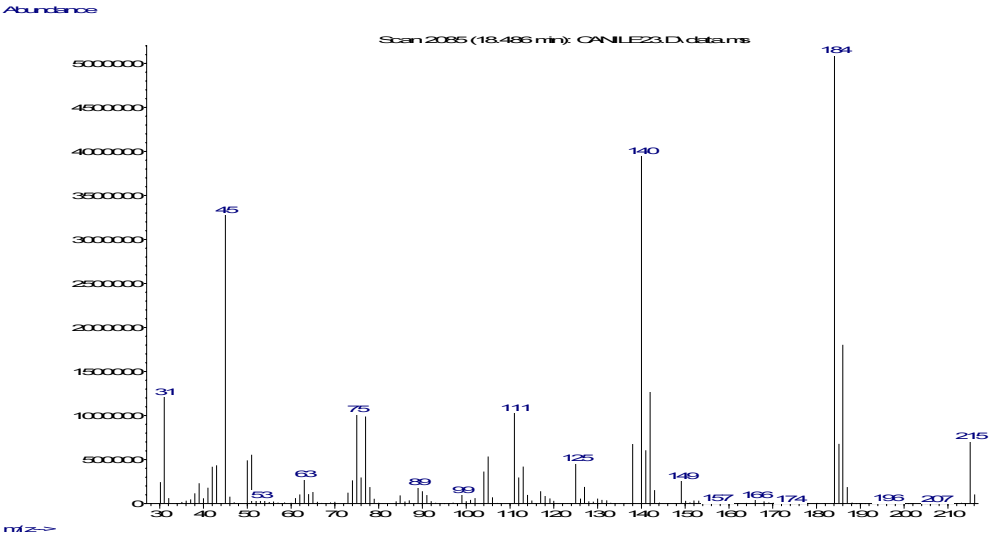
Bis-*N*-(2-hydroxy)ethyl aniline, **3a.**



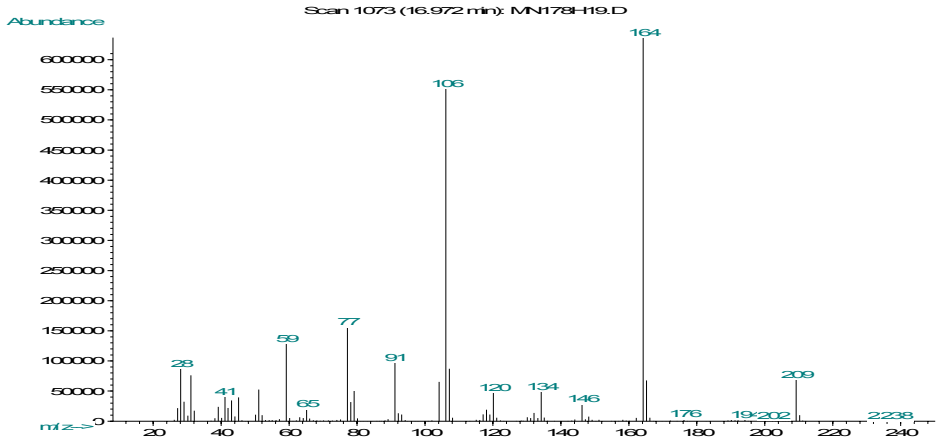
Bis-*N*-(2-hydroxy)ethyl *p*-anisidine, **3b.**



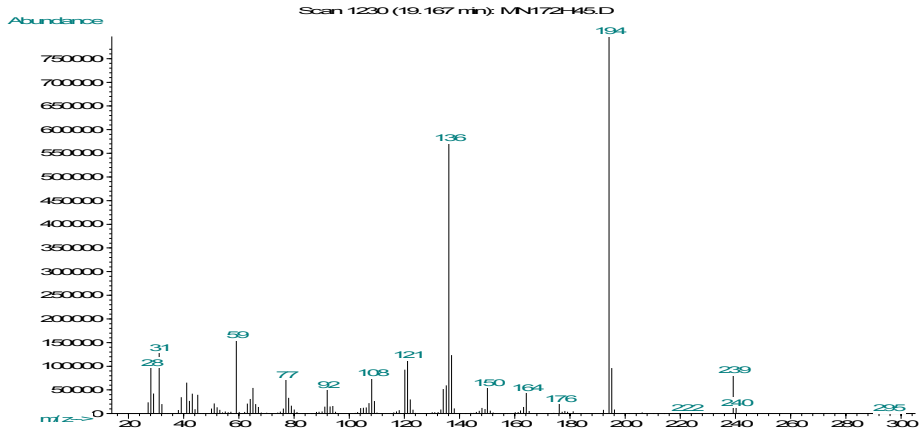
Bis-*N*-(2-hydroxy)ethyl *p*-toluidine, **3c.**



Bis-*N*-(2-hydroxy)ethyl *p*-chloroaniline, **3d.**



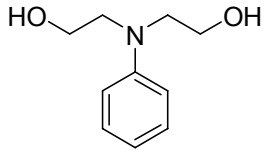
Bis-*N*-(2-hydroxy)propyl aniline, **7a.**

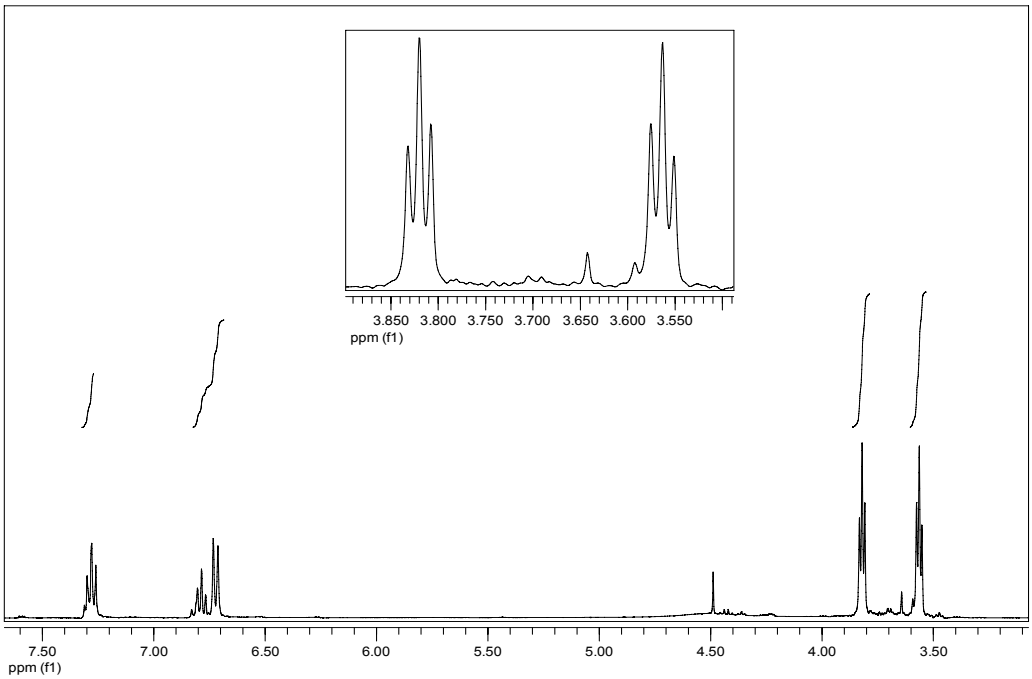


Bis-*N*-(2-hydroxy)propyl anisidine, **7b.**

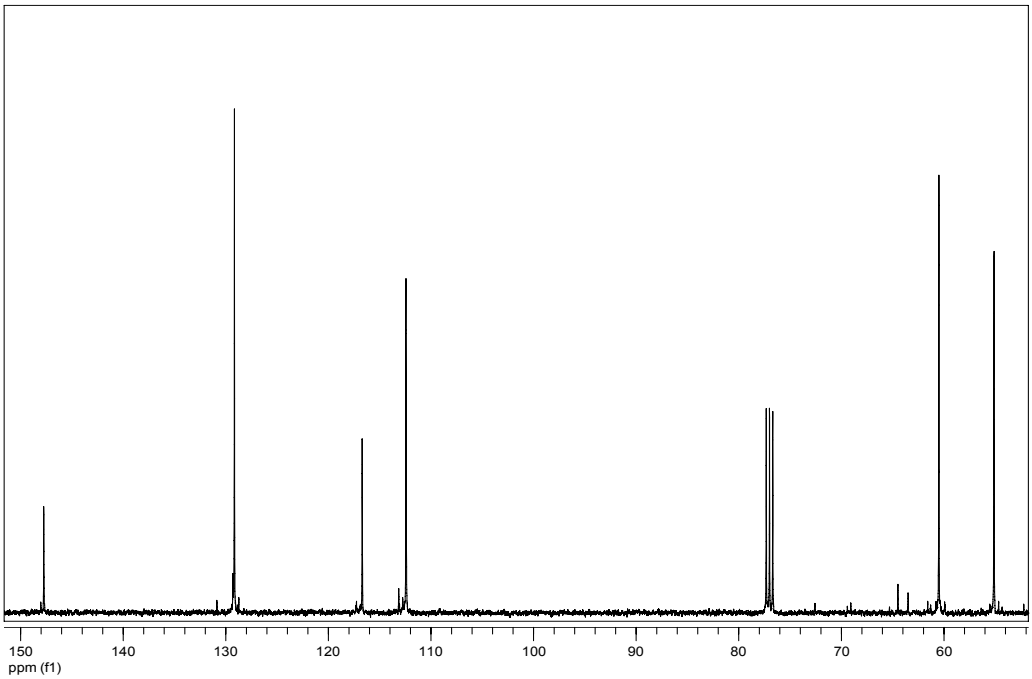
^{1}H and ^{13}C NMR spectra of products **3a-d**, **7a-b**, **PIL2-7** and **PIL9-13**.

Bis-*N*-(2-hydroxy)ethyl aniline, **3a.** The spectroscopic data were consistent with those reported in the literature.[1]



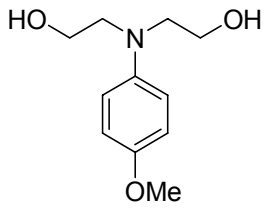


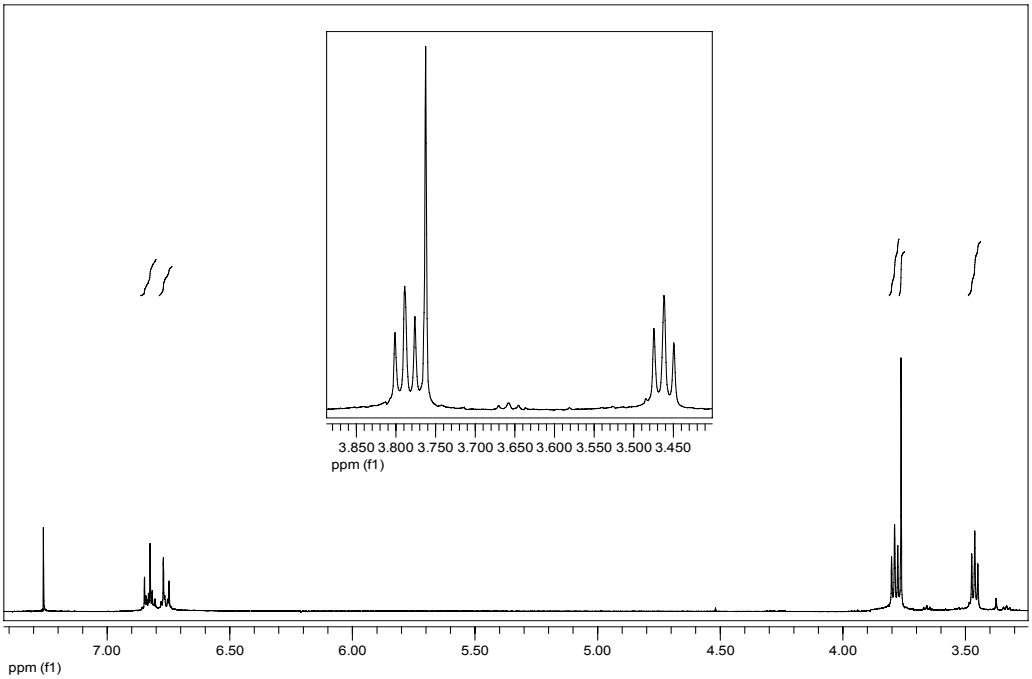
^{1}H NMR



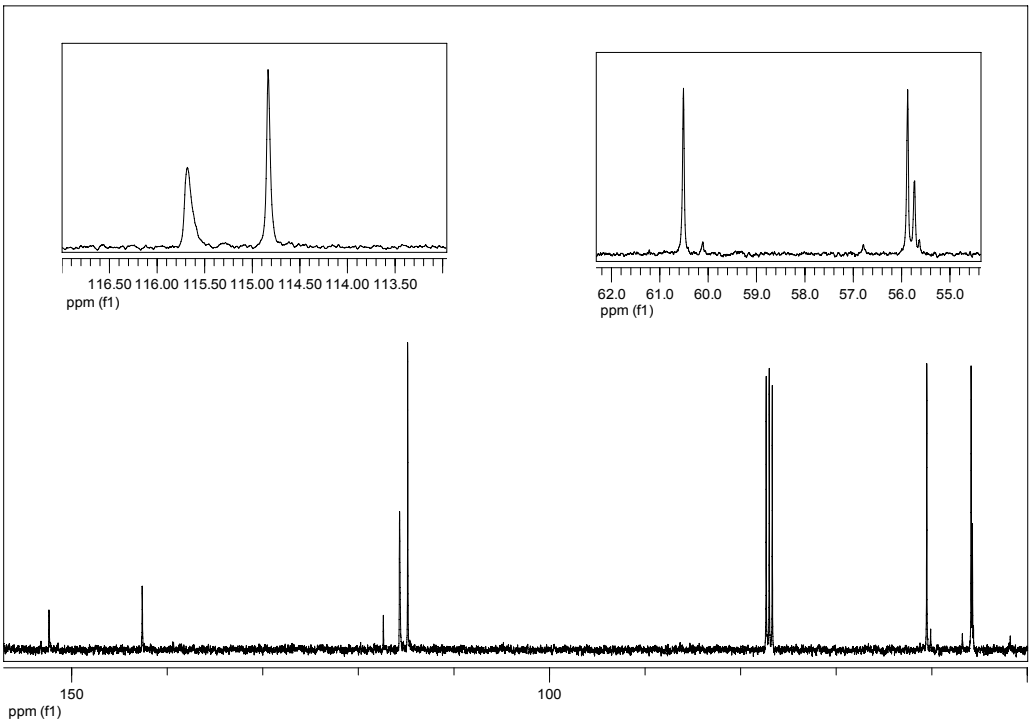
^{13}C NMR

Bis-*N*-(2-hydroxy)ethyl *p*-anisidine, **3b.** The spectroscopic data were consistent with those reported in the literature.[1]



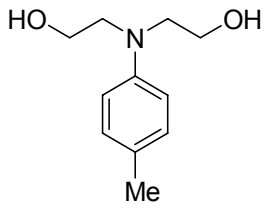


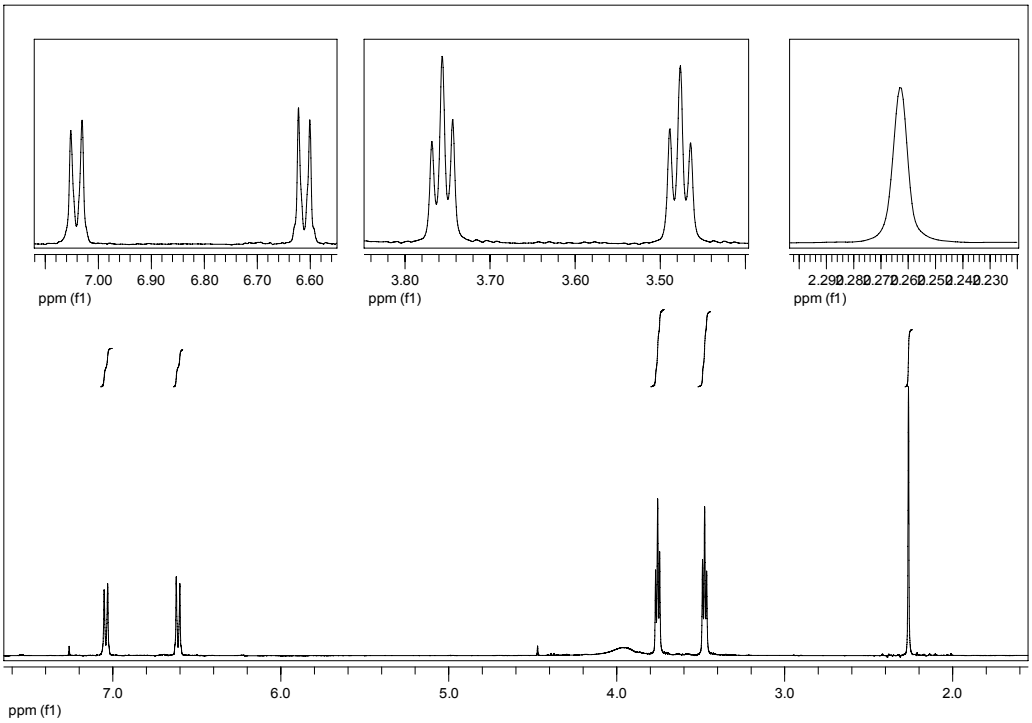
^{1}H NMR



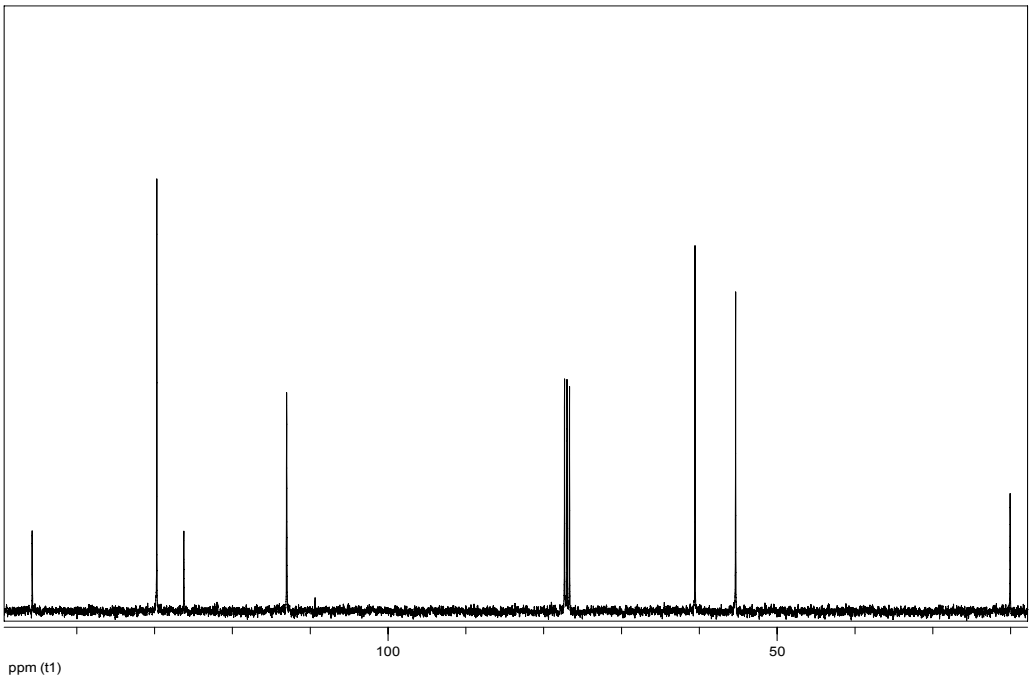
^{13}C NMR

Bis-*N*-(2-hydroxy)ethyl *p*-toluidine, **3c.**



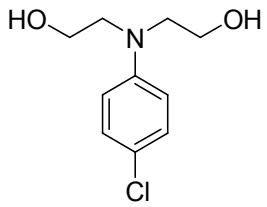


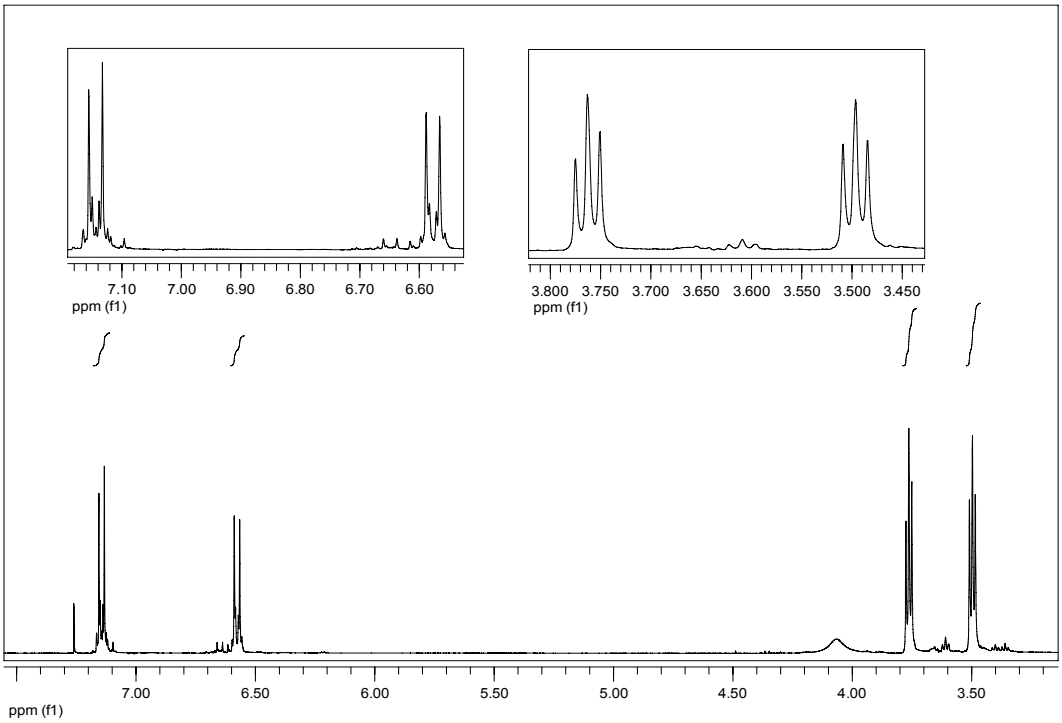
^{1}H NMR



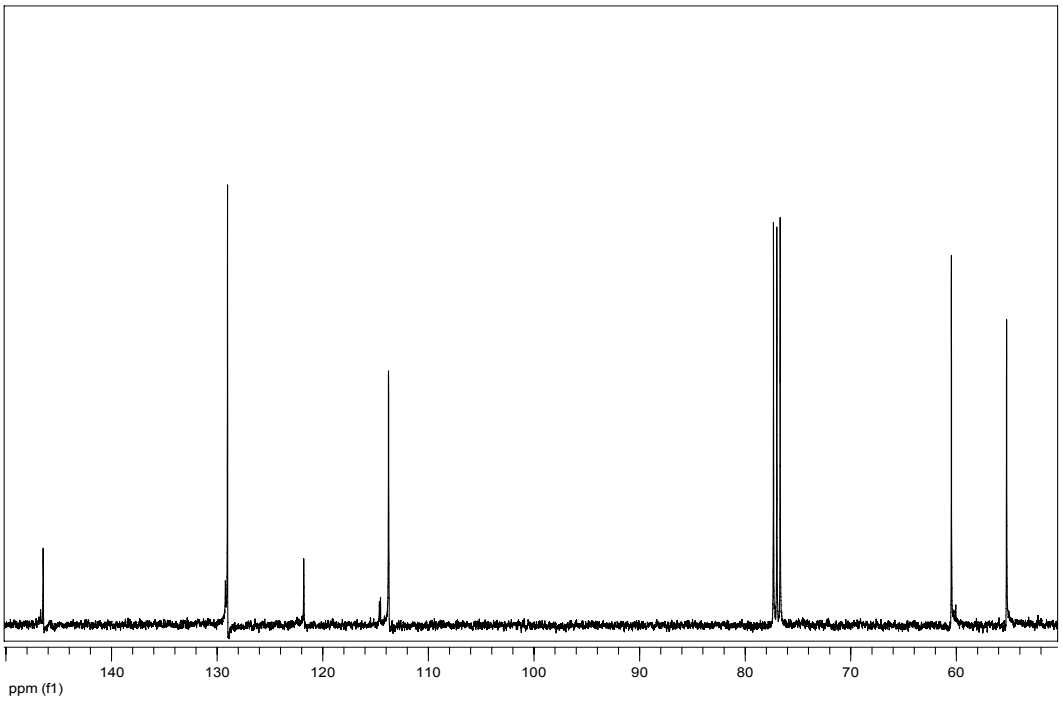
^{13}C NMR

Bis-*N*-(2-hydroxy)ethyl *p*-chloroaniline, **3d.**



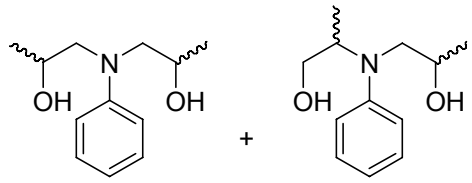


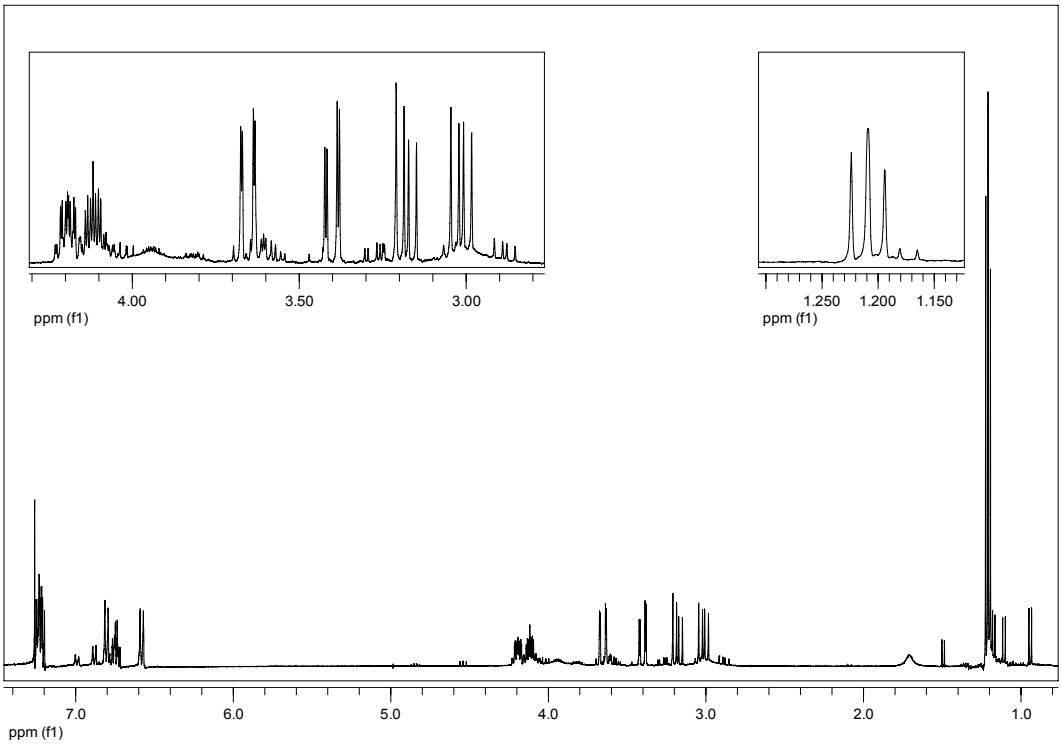
^{1}H NMR



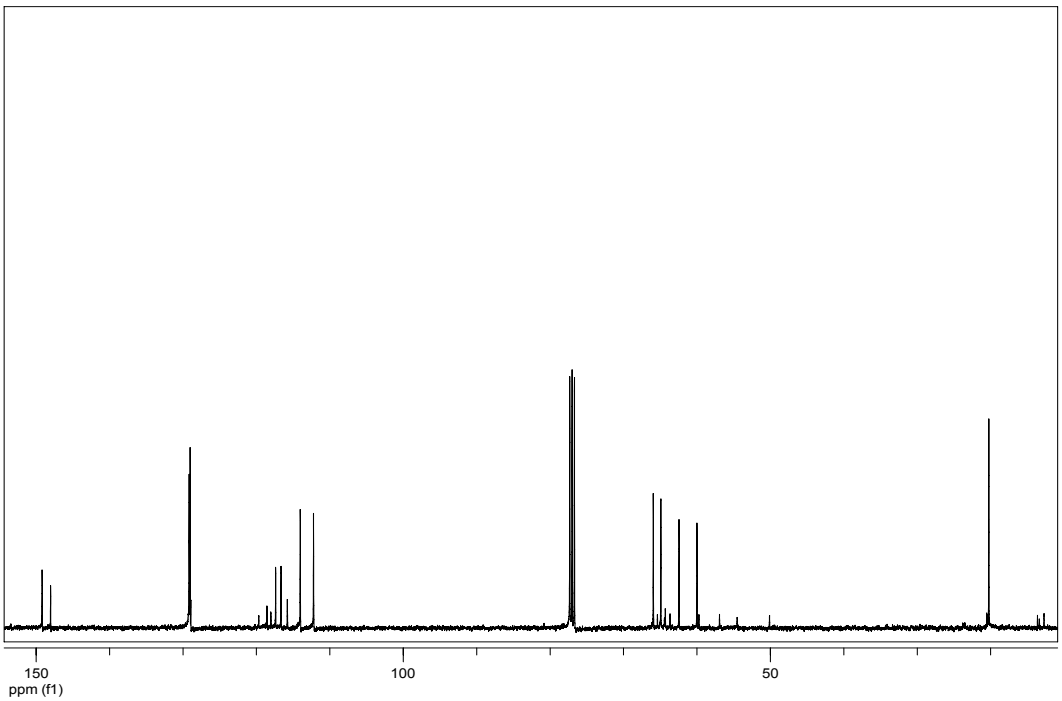
^{13}C NMR

Bis-*N*-(2-hydroxy)propyl aniline, **7a.**



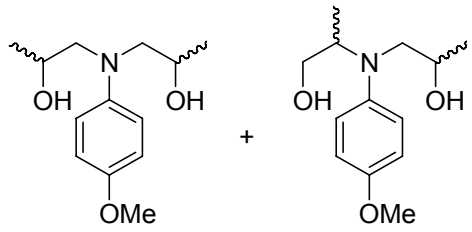


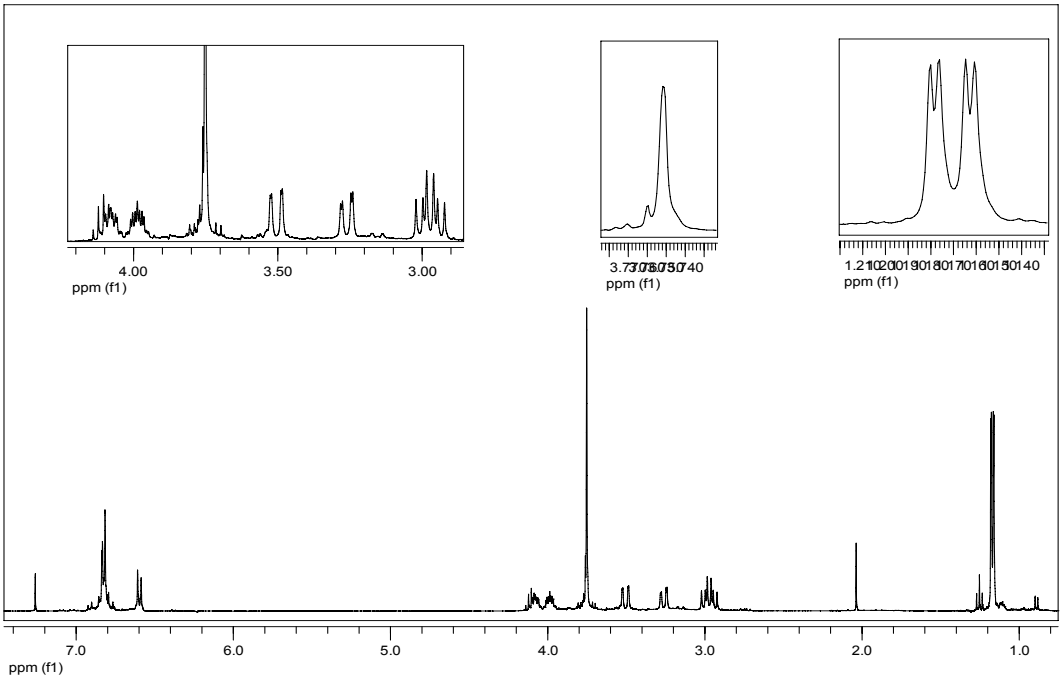
^{1}H NMR



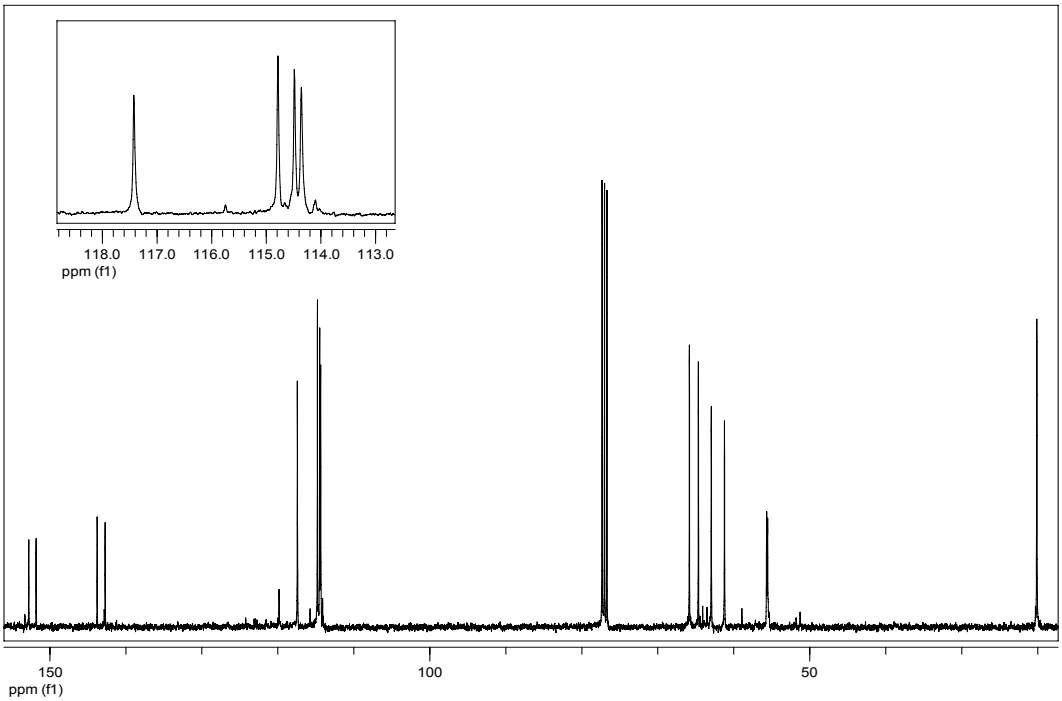
^{13}C NMR

Bis-*N*-(2-hydroxy)propyl anisidine, **7b.**



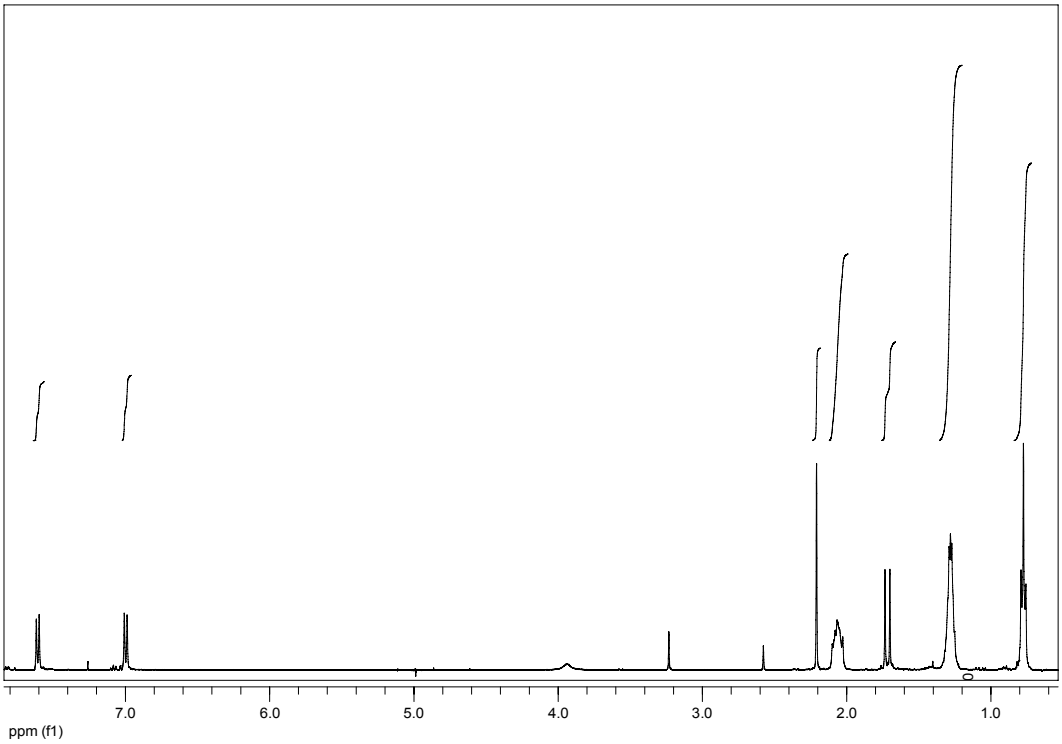


^{1}H NMR

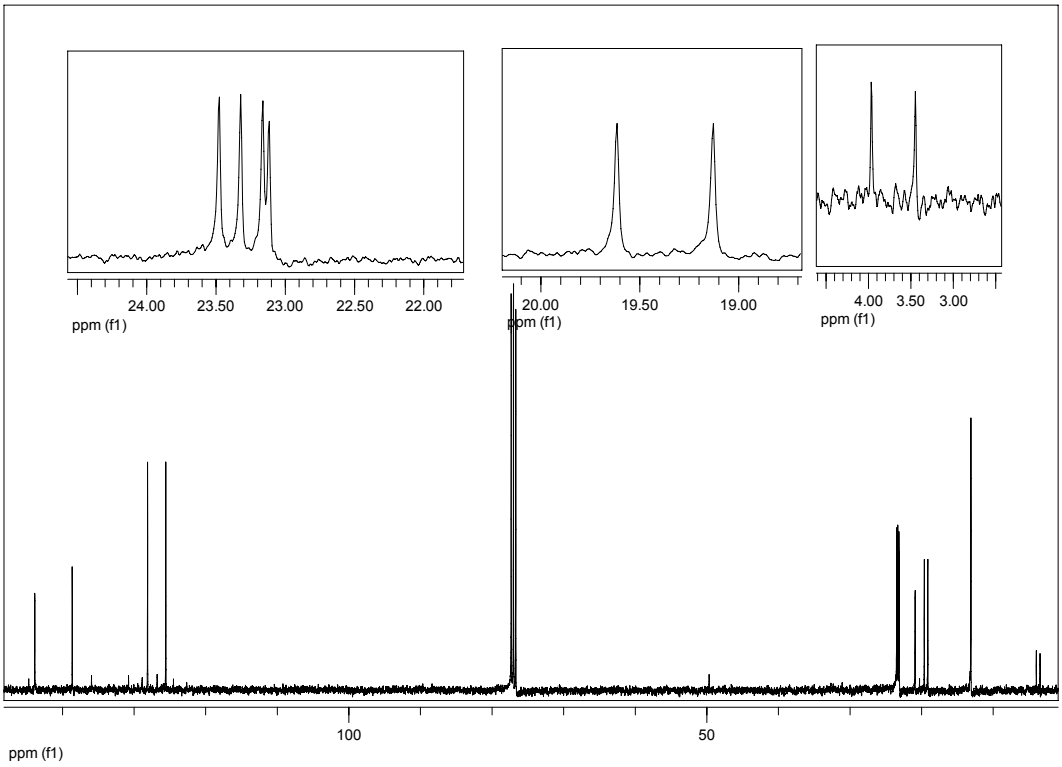


^{13}C NMR

[(*n*-Bu)$_3$MeP][TosO], **PIL2**.

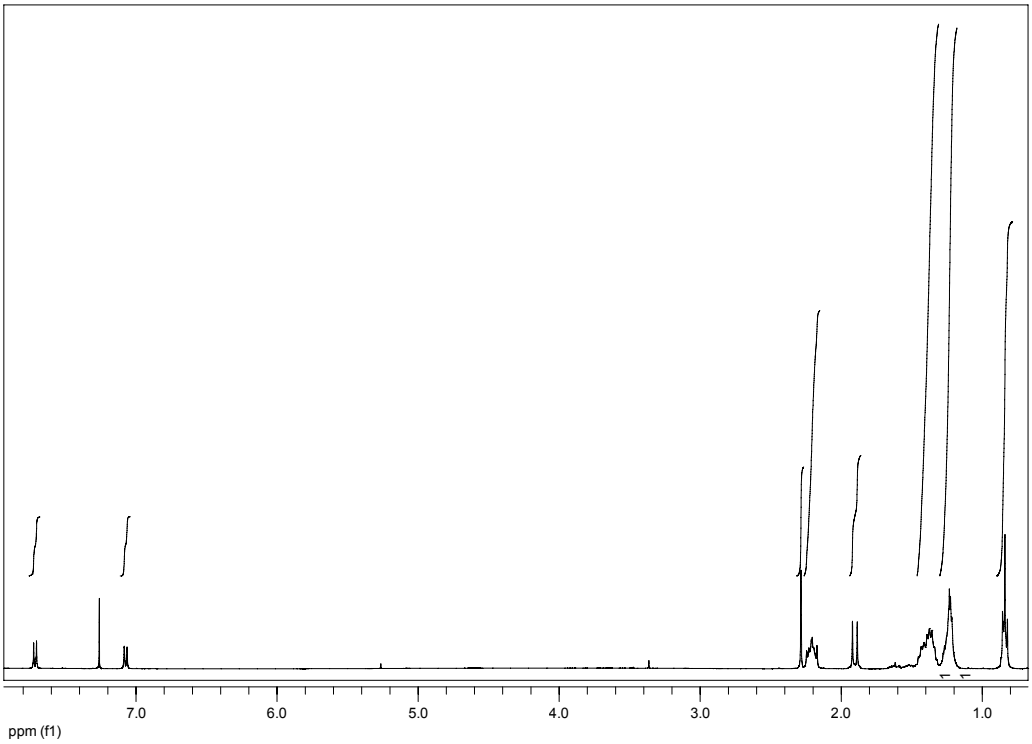


^{1}H NMR

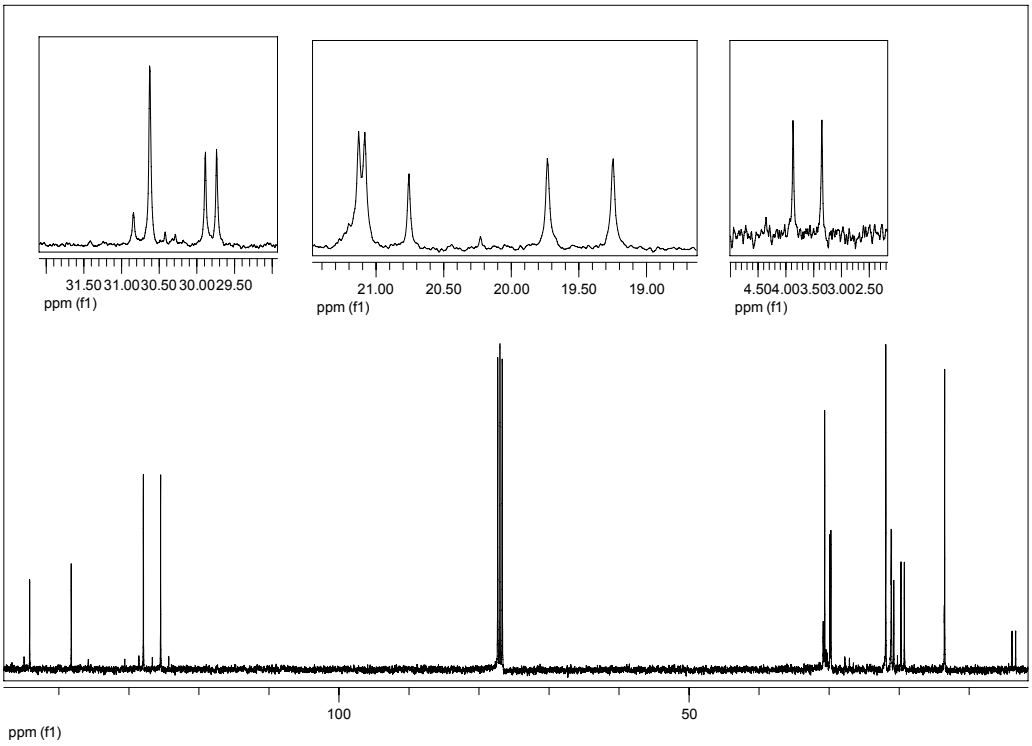


^{13}C NMR

[(*n*-Hex)$_3$MeP][TosO], **PIL3**.

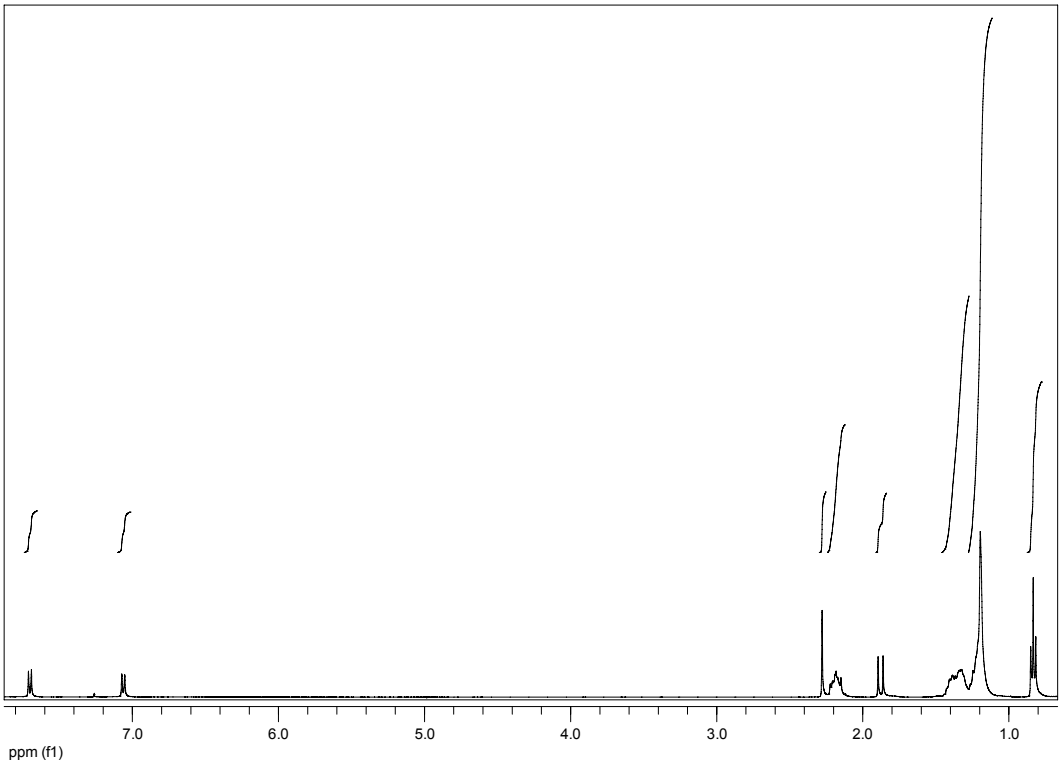


^{1}H NMR

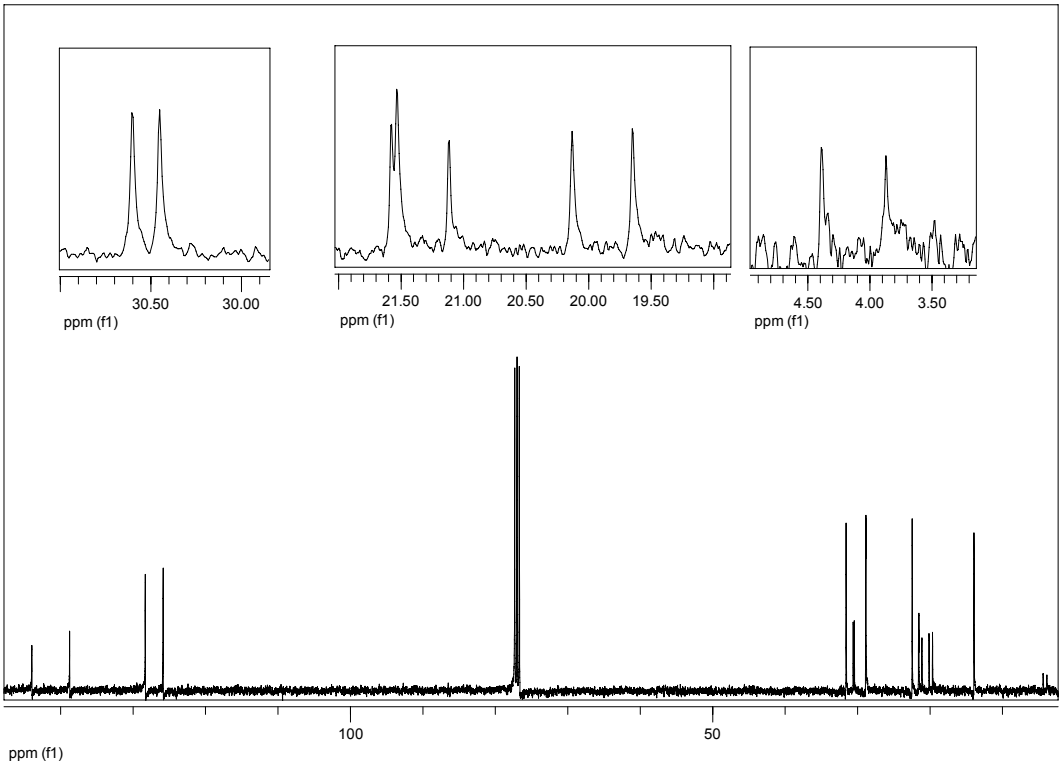


^{13}C NMR

[(*n*-Oct)$_3$MeP][TosO], **PIL4**.

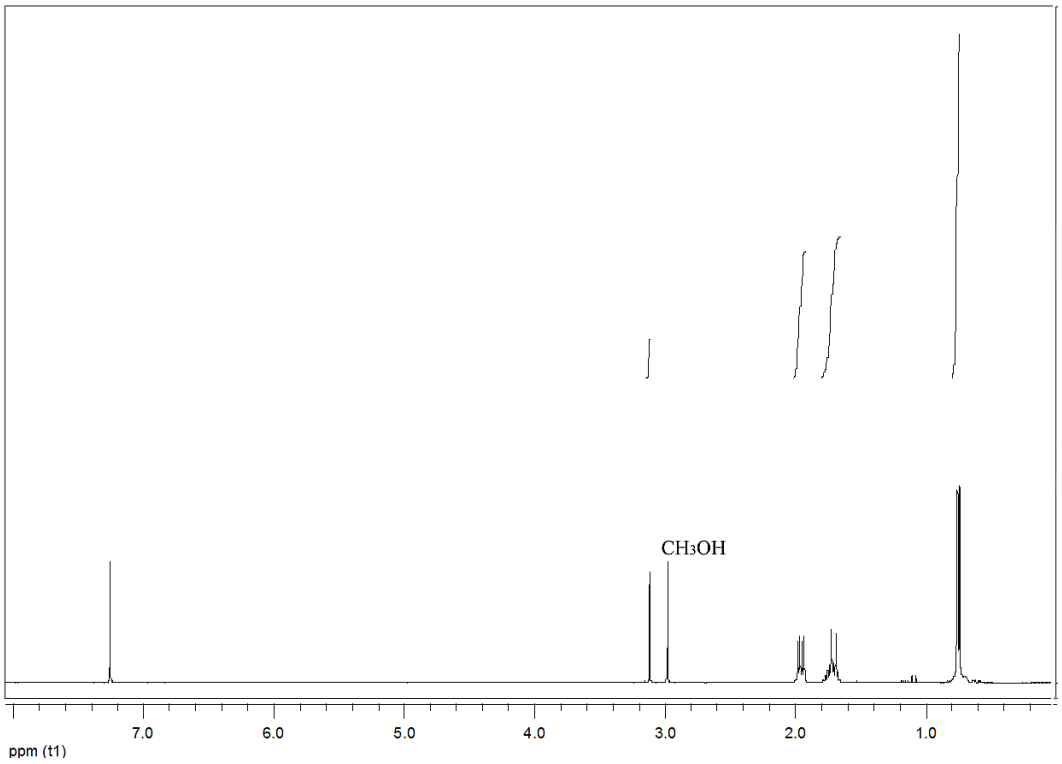


^{1}H NMR

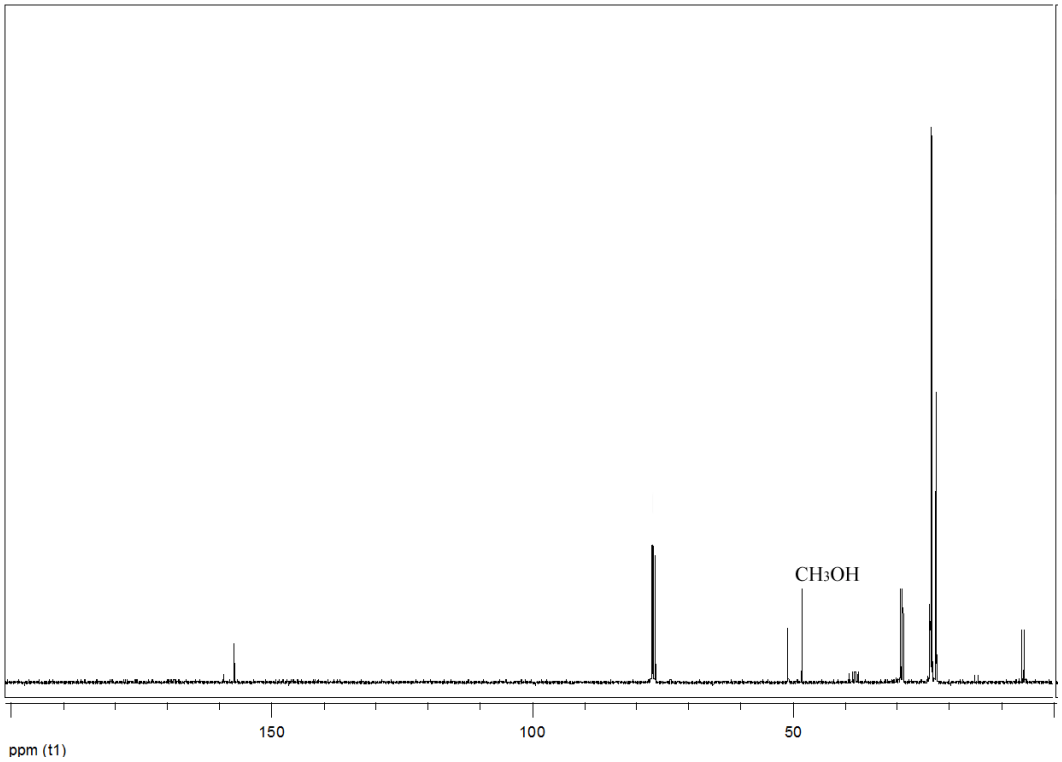


^{13}C NMR

[(*i*-Bu)$_3$MeP][OCO$_2$CH$_3$], **PIL5**.

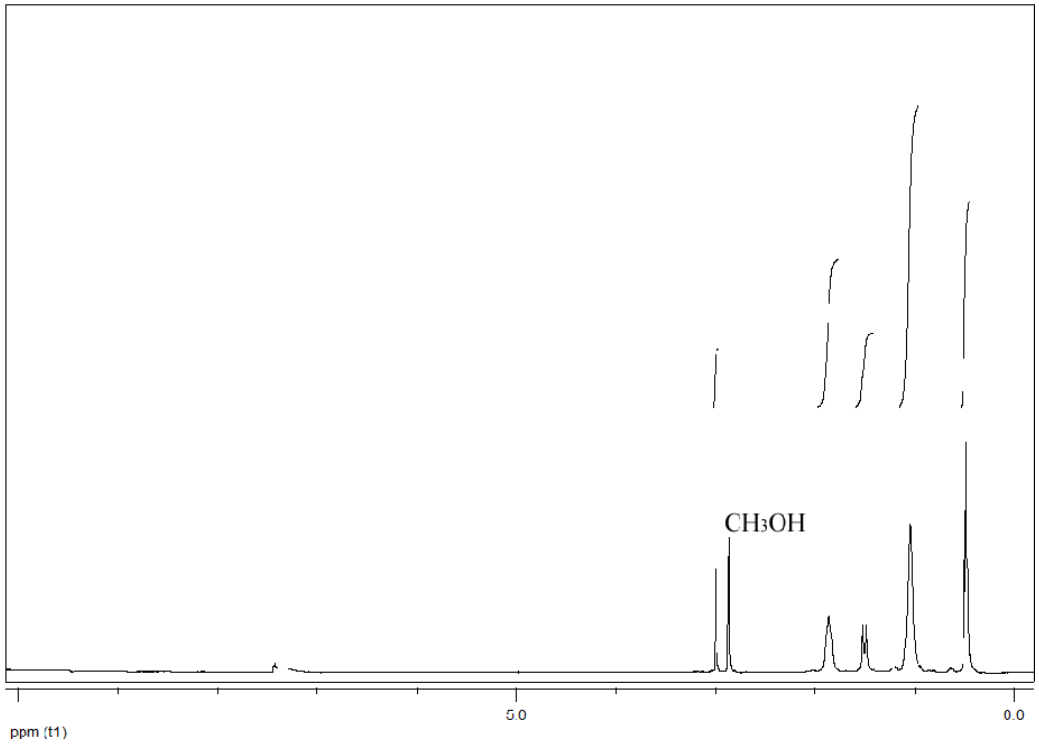


^{1}H NMR

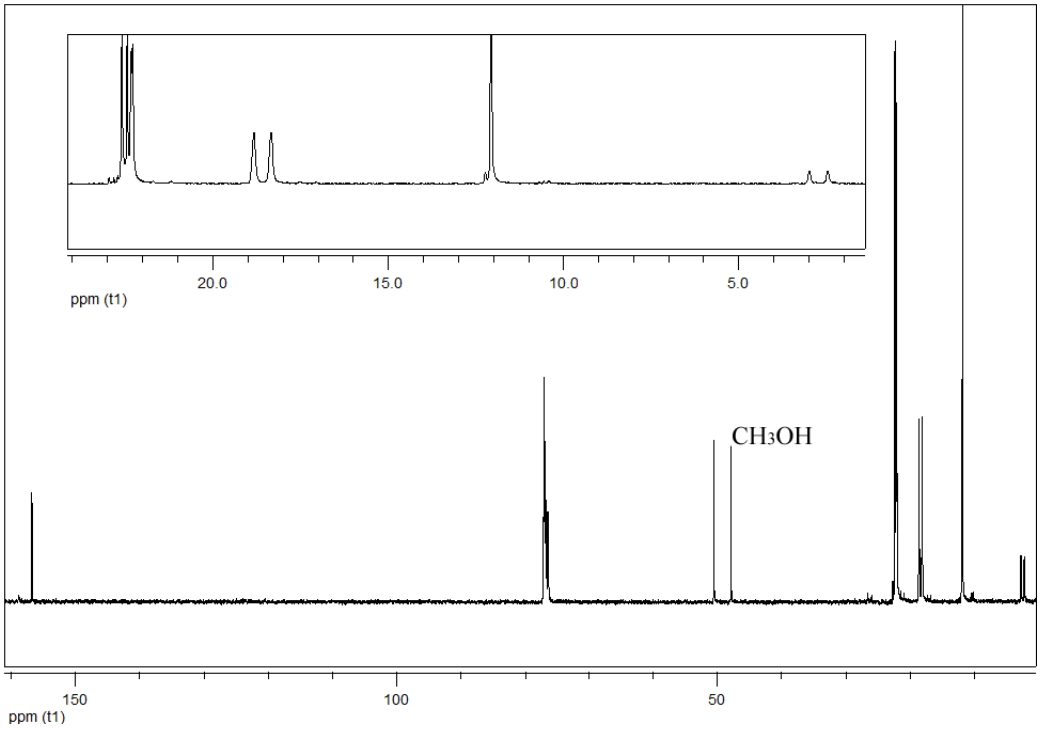


^{13}C NMR

[(*n*-Bu)$_3$MeP][OCO$_2$CH$_3$], **PIL6**.

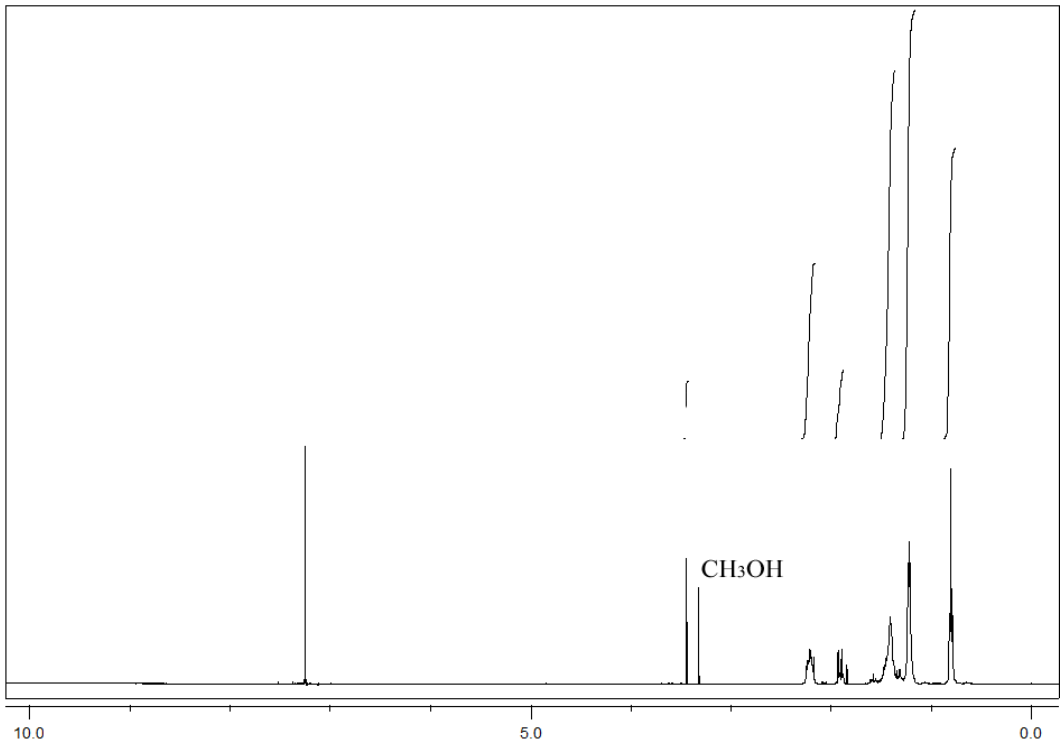


^{1}H NMR

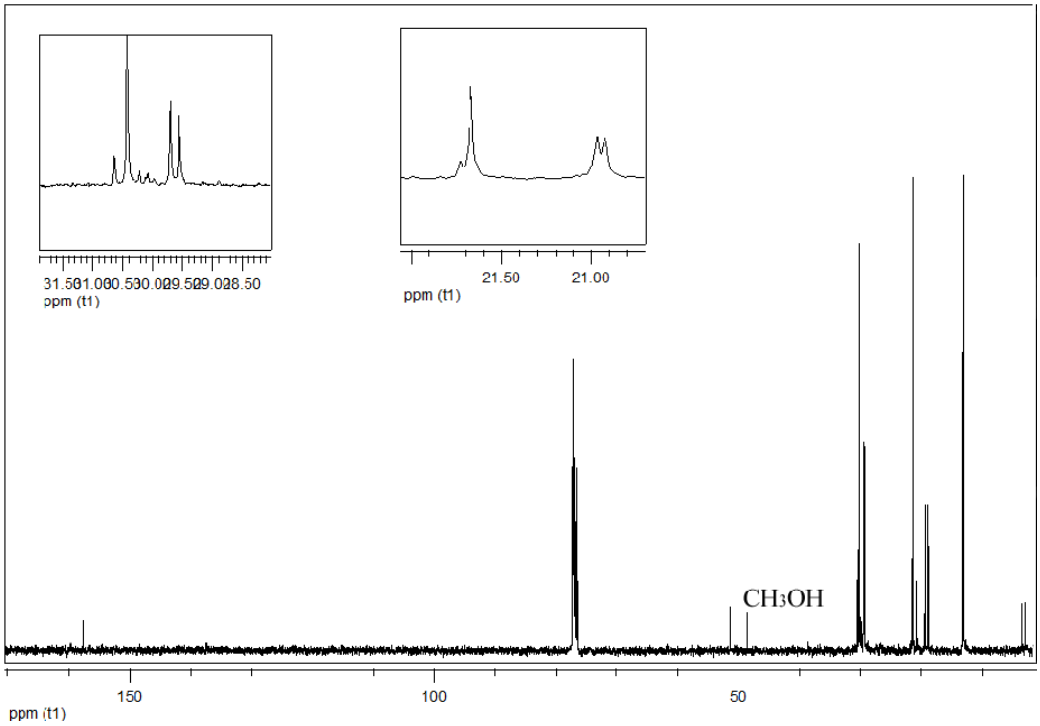


^{13}C NMR

[(*n*-Hex)$_3$MeP][OCO$_2$CH$_3$], **PIL7**.

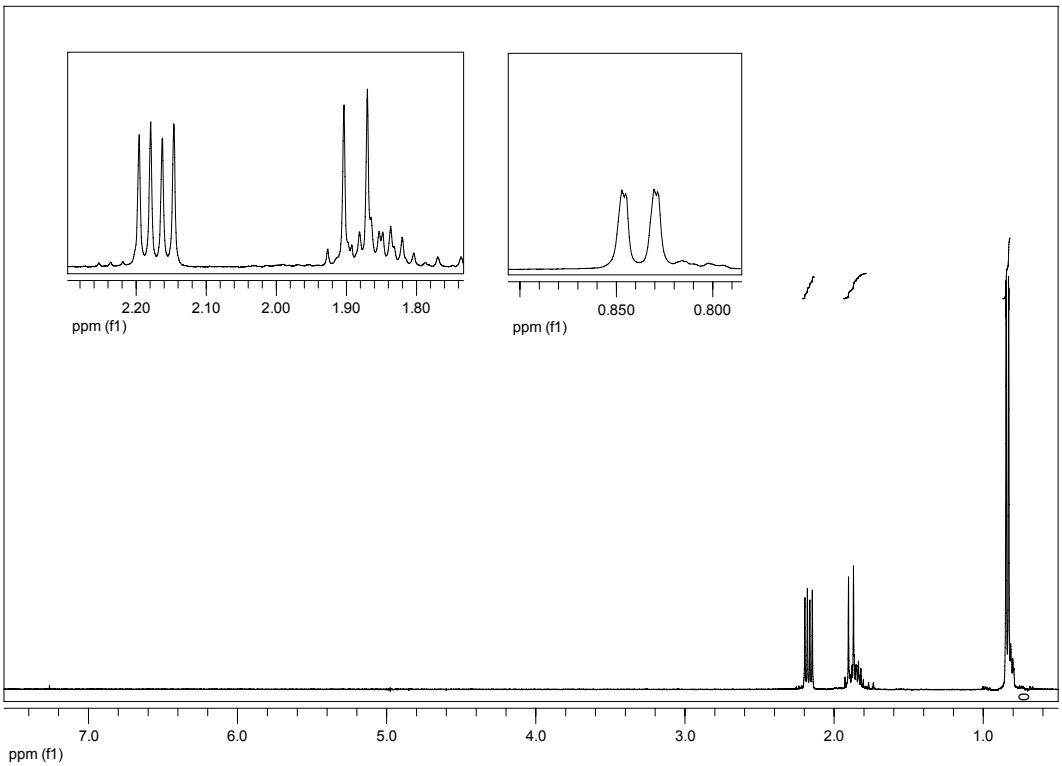


^{1}H NMR

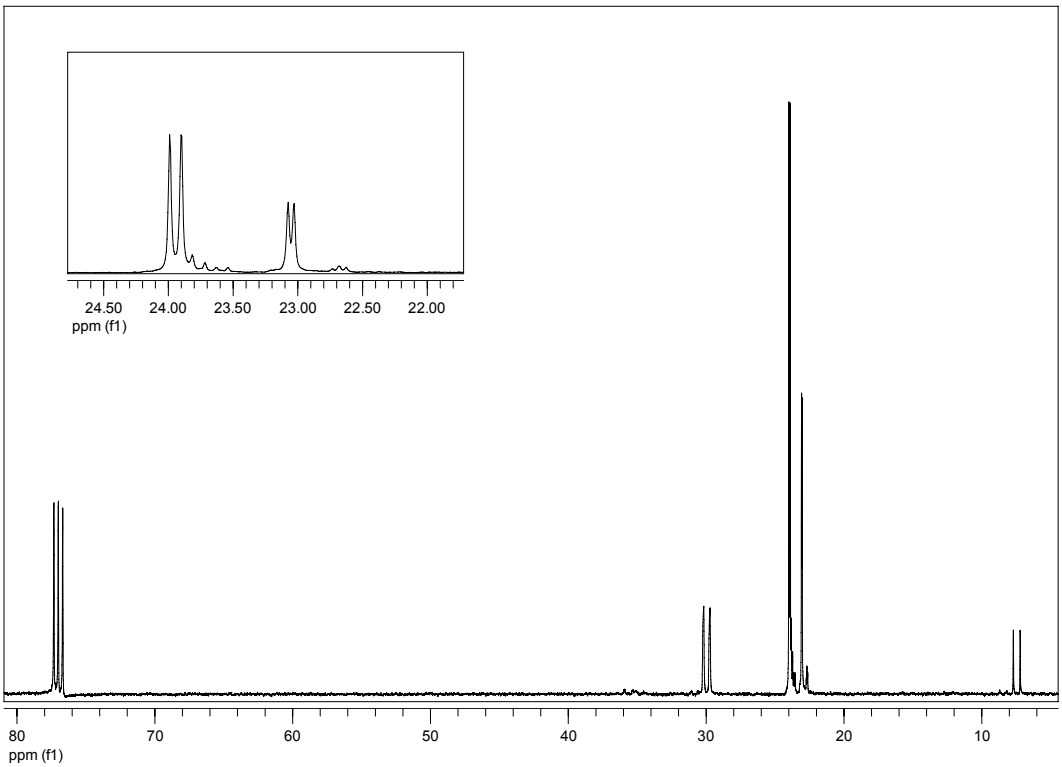


^{13}C NMR

[(*i*-Bu)$_3$MeP][Br], **PIL9**.

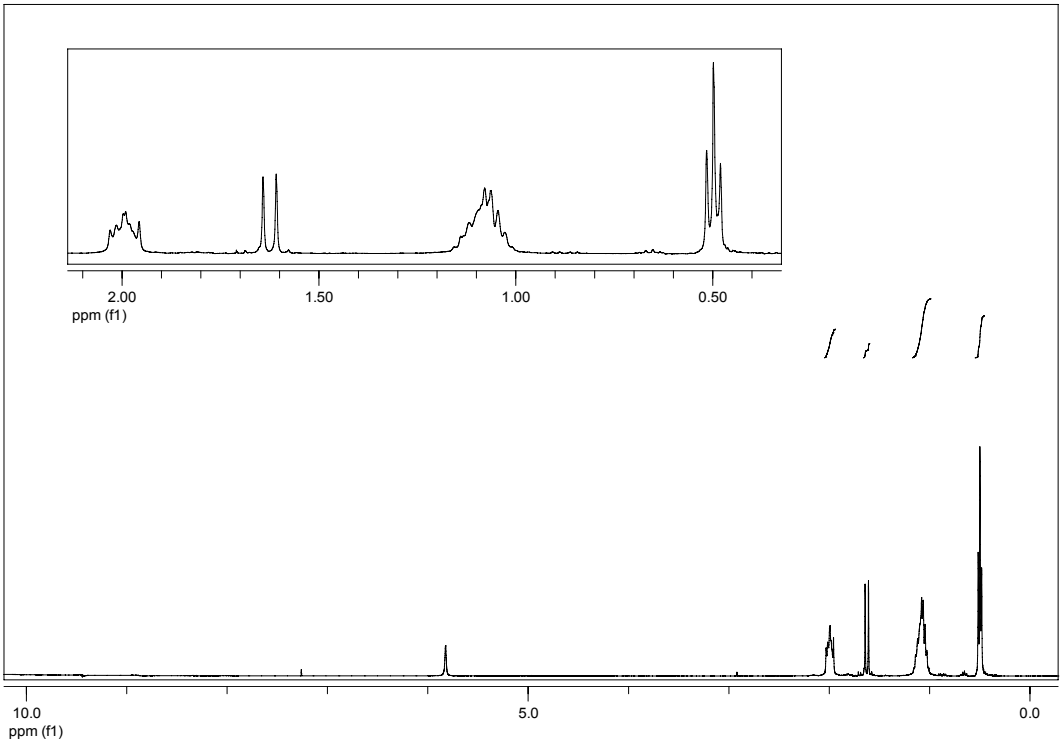


^{1}H NMR

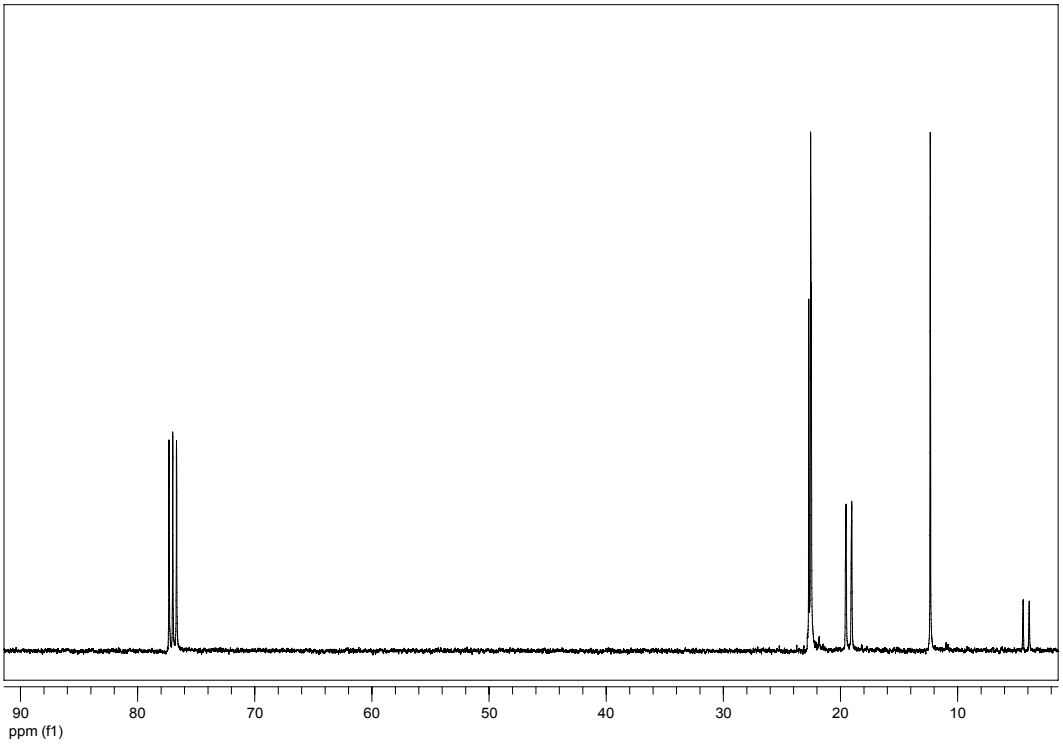


^{13}C NMR

[(*n*-Bu)$_3$MeP][Br], **PIL10**.

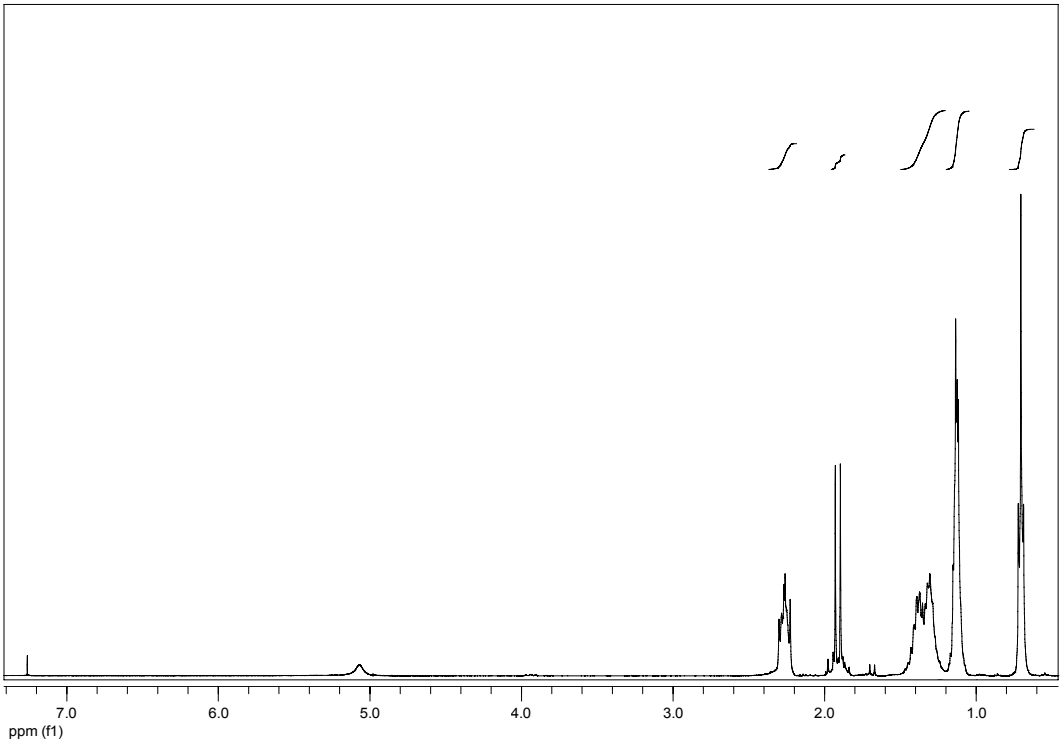


^{1}H NMR

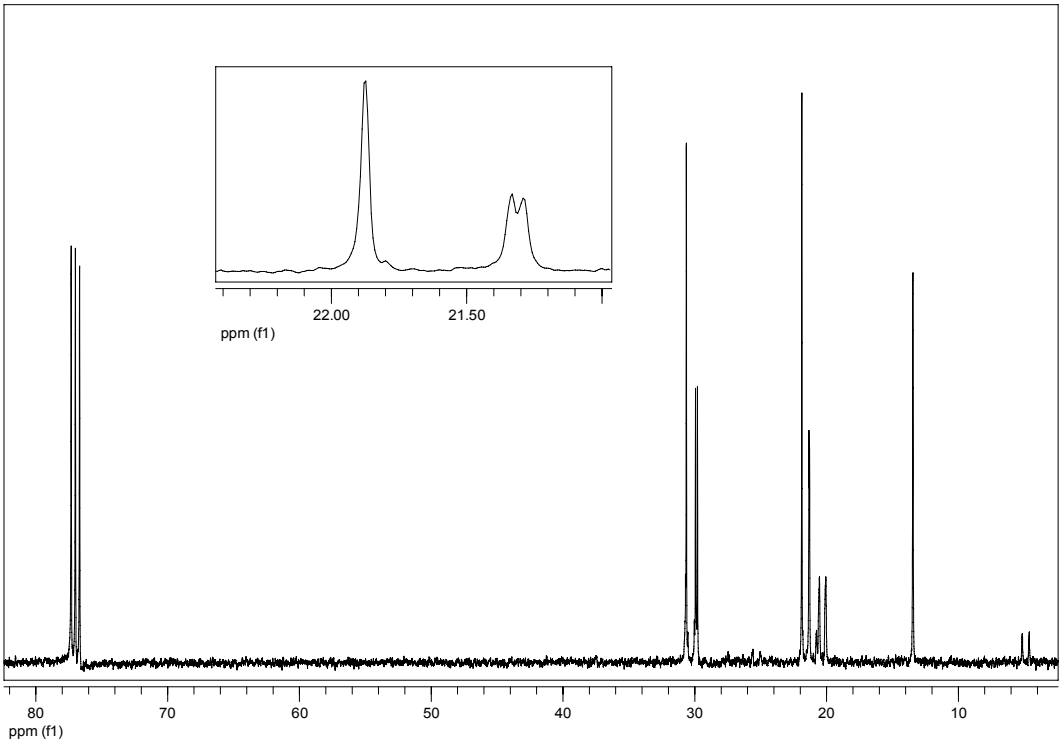


^{13}C NMR

[(*n*-Hex)$_3$MeP][Br], **PIL11**.

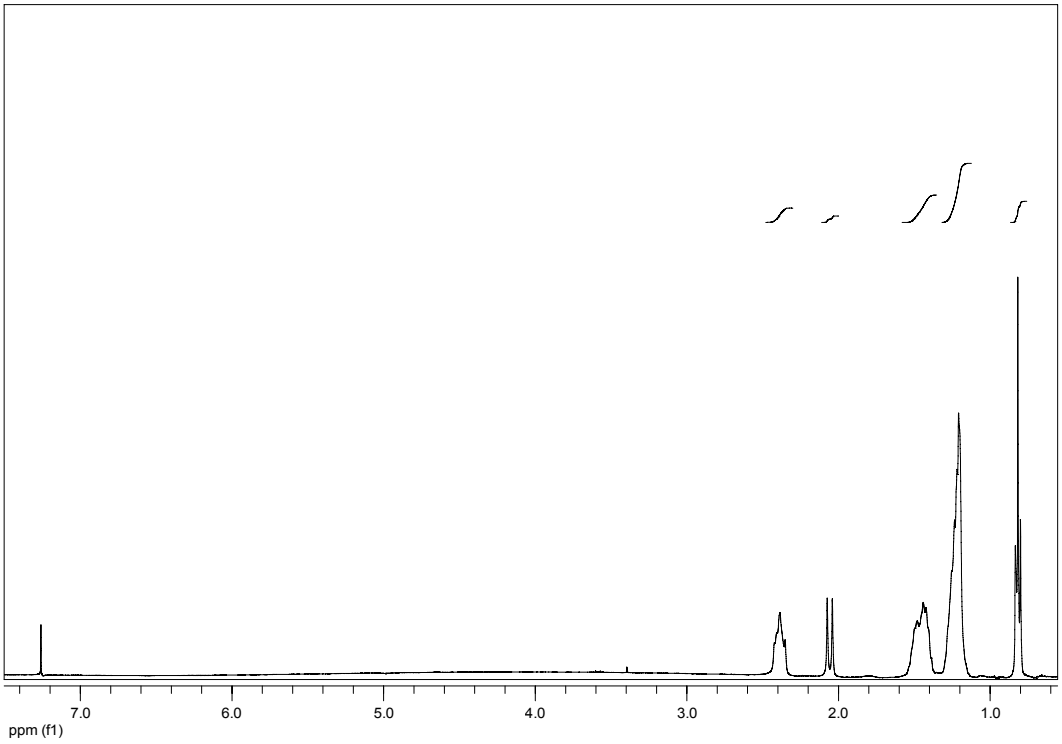


^{1}H NMR

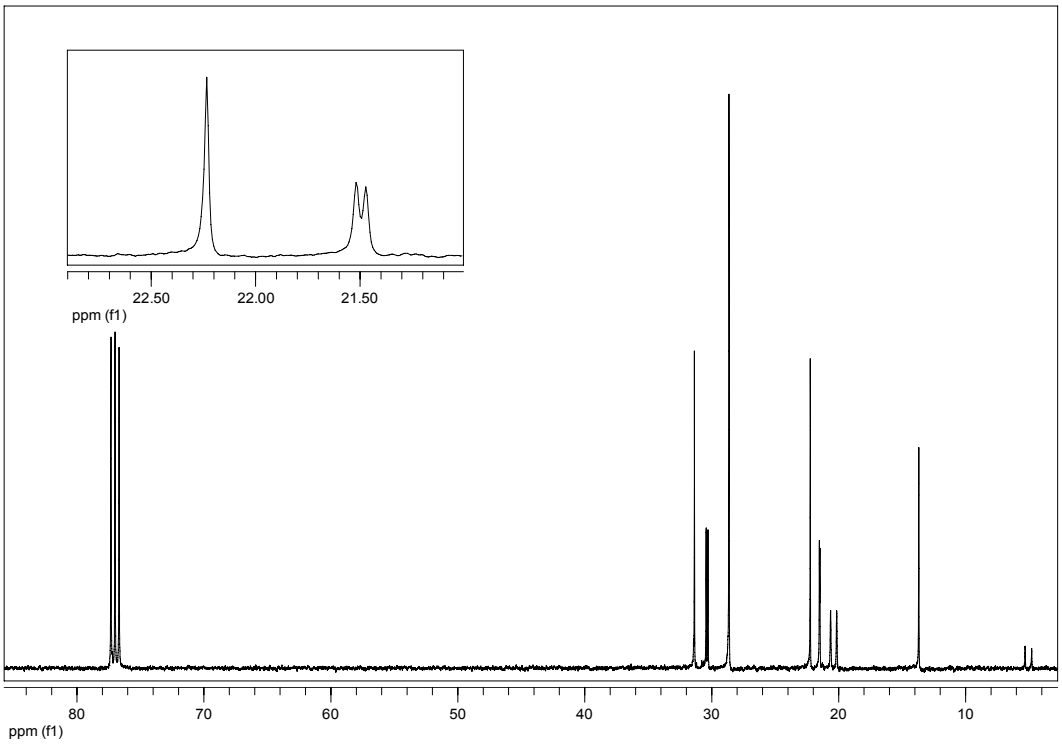


^{13}C NMR

[(*n*-Oct)$_3$MeP][Br], **PIL12**.

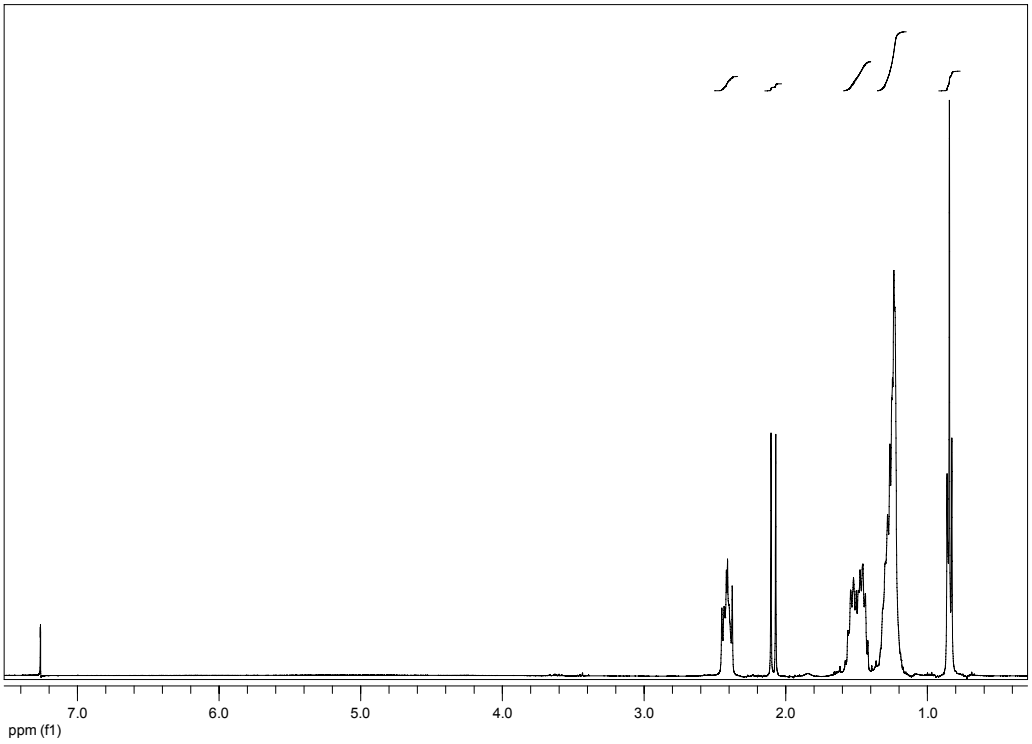


^{1}H NMR

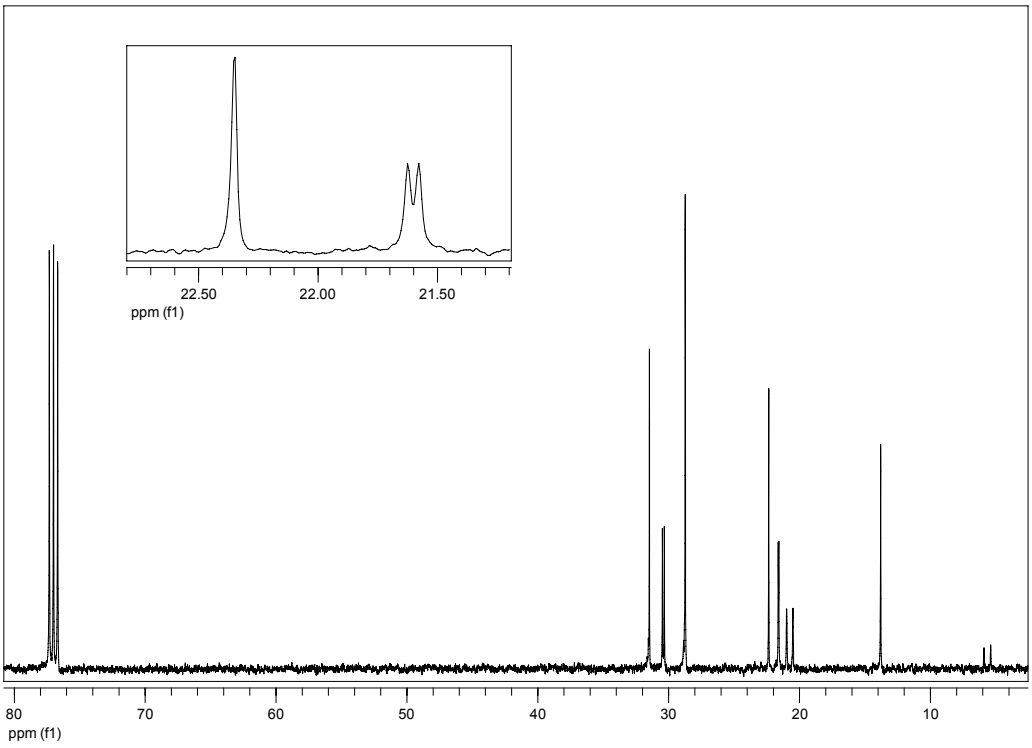


^{13}C NMR

[(*n*-Oct)$_3$MeP][I], **PIL13**.



^{1}H NMR



^{13}C NMR

References

[1] A. Clerici, A. Ghilardi, N. Pastori, C. Punta, O. Porta *Org. Lett.* 2008, **10(21)**, 5063-5066.