Electronic supplementary information

Carbonate, Acetate and Phenate Exchanged Phosphonium Salts as Catalysts in Transesterification Reactions for the Synthesis of Non Symmetric Dialkyl Carbonates

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Synoptic table of major MS signals of reaction products.

Compound	GC/MS (EI, 70 eV)
Cyclohexyl methyl carbonate	m/z: 99 ($M-CH_3-CO_2]^+$, 32%), 83 ($M-CH_3OCO_2]^+$, 52), 82 ($M-CH_3OCO_2-H]^+$, 98), 81 (21), 77 (63), 71 (42), 67 (100), 59 (27), 55 (47), 54 (31).
Cyclohexyl ethyl carbonate	m/z: 99 ($M-CH_2CH_3-CO_2]^+$, 57%), 91 (100), 83 ($M-CH_3CH_2OCO_2]^+$, 63), 82 ($M-CH_3CH_2OCO_2-H]^+$, 67), 81 (22), 67 (74), 63 (35), 57 (51), 55 (44).
Cyclopentyl methyl carbonate	m/z: 85 ($M-CH_3-CO_2]^+$, 92%), 77 (39), 71 ($[CH_3(CH_2)_3CH_2]^+$, 100), 69 ($M-CH_3OCO_2]^+$, 61), 68 ($M-CH_3OCO_2-H]^+$, 70), 67 (34), 59 (34), 57 (14).
Cyclopentyl ethyl carbonate	m/z: 91 (25%), 85 ($M-CH_3CH_2-CO_2]^+$, 80), 69 ($M-CH_3CH_2OCO_2]^+$, 53), 68 ($M-CH_3OCO_2-H]^+$, 28), 67 (22), 63 (12), 58 (11), 57 (100).
Benzyl methyl carbonate	m/z: 166 $(M]^+$, 67%), 122 $(M-CO_2]^+$, 14), 121 ($[M-CO_2-H]^+$, 20), 107 ($[M-CO_2\ CH_3]^+$, 51) 91 ($[C_7H_7]^+$, 100), 90 (41), 79 (30), 77 (25), 65 (15).
Menthyl methyl carbonate	m/z: 139 ($M-CH_3OCO_2]^+$, 12%), 138 ($[M-CH_3OCO_2-H]^+$, 55), 123 ($[M-CH_3OCO_2-CH_4]^+$, 54) 109 ($[M-CH_3OCO_2-CH_4-CH_2]^+$, 11), 95 ($[C_7H_{11}]^+$, 100), 82 (23), 81 (61), 69 (12), 67 (20). (34), 57 (14).
Menthyl ethyl carbonate	m/z: 139 ($M-CH_3CH_2OCO_2]^+$, 15%), 138 ($[M-CH_3CH_2OCO_2-H]^+$, 65), 123 ($[M-CH_3CH_2OCO_2-CH_4]^+$, 52) 109 ($[M-CH_3CH_2OCO_2-CH_4-CH_2]^+$, 11), 95 ($[C_7H_{11}]^+$, 100), 82 (24), 81 (60), 71 (13), 69 (15), 67 (18), 57 (10), 55 (21).
Triphenylmethyl methyl ether[1]	m/z: 274 ($[M]^+$, 62%), 243 ($[Ph_3C]^+$, 75), 197 ($[M]^+$, 100), 165 (37), 105 ($[PhCO]^+$, 30), 77 (17). Match quality: 94.9% (ref. NIST)
1,1 diphenylethene	m/z: 180 ($[M]^+$, 100%), 179 ($[M-H]^+$, 74), 178 ($[M-2H]^+$, 62), 165 (83), 152 (12), 89 (12).

NMR spectra of prepared catalysts

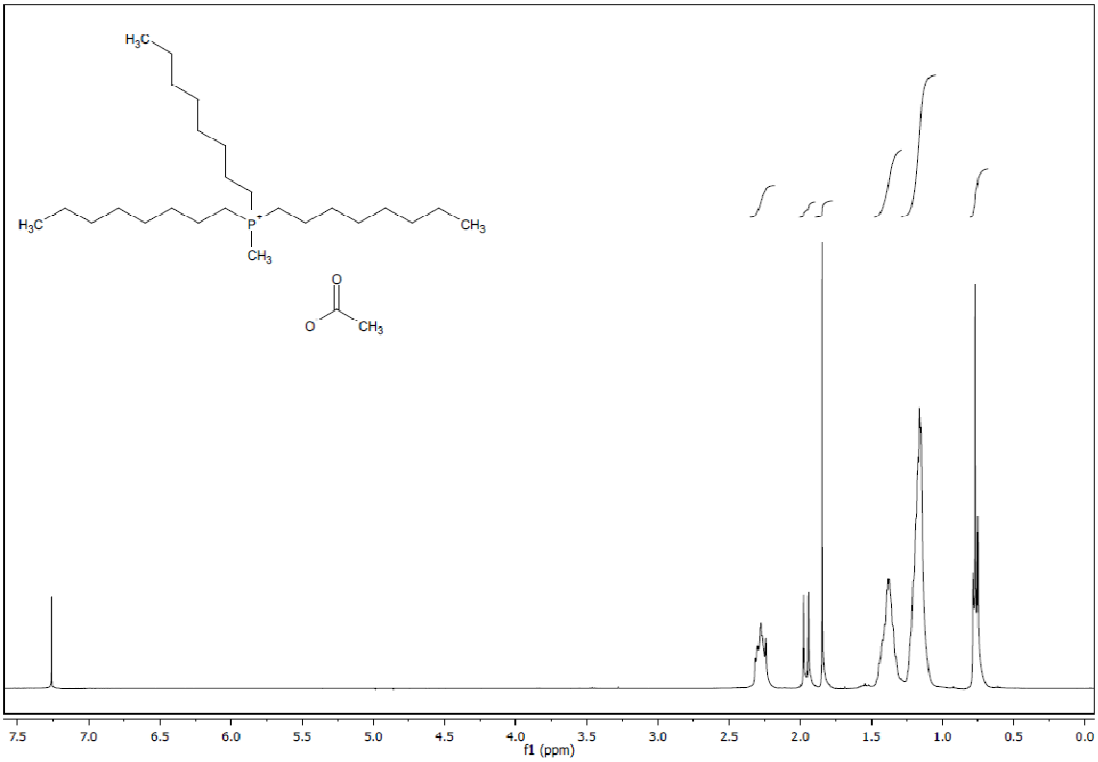

Figure S1 ^{1}H-NMR of compound **1c** in $CDCl_3$.

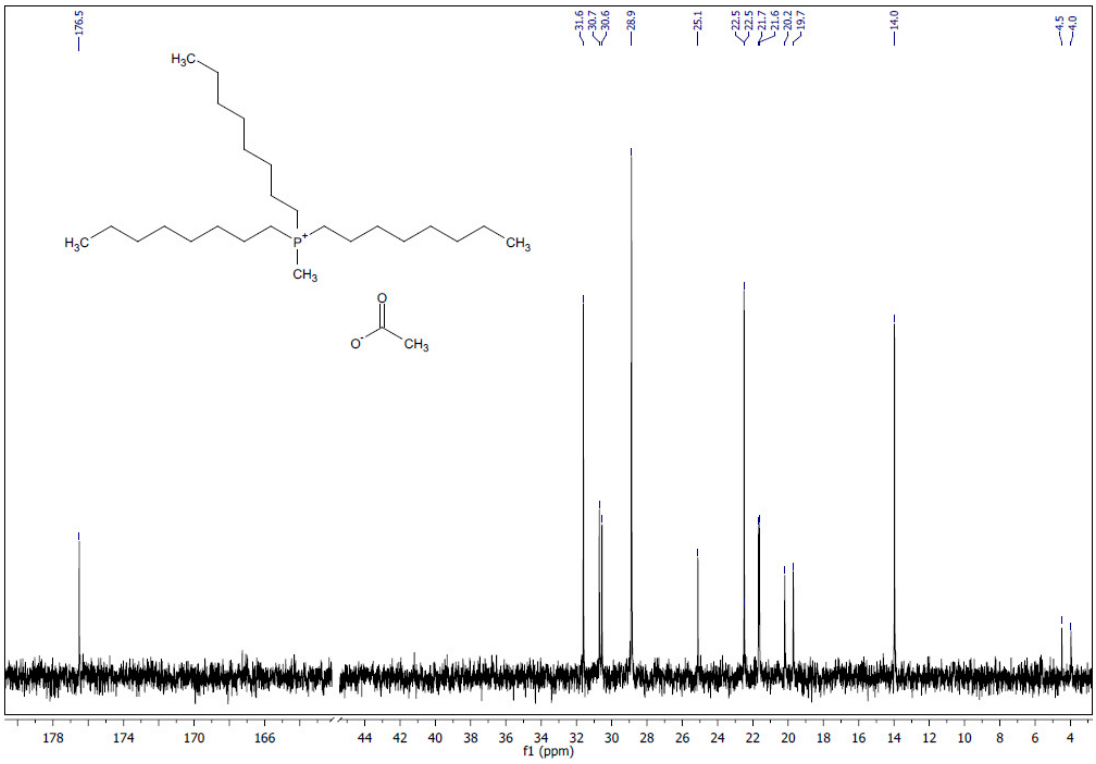

Figure S2 ^{13}C-NMR of compound **1c** in $CDCl_3$.

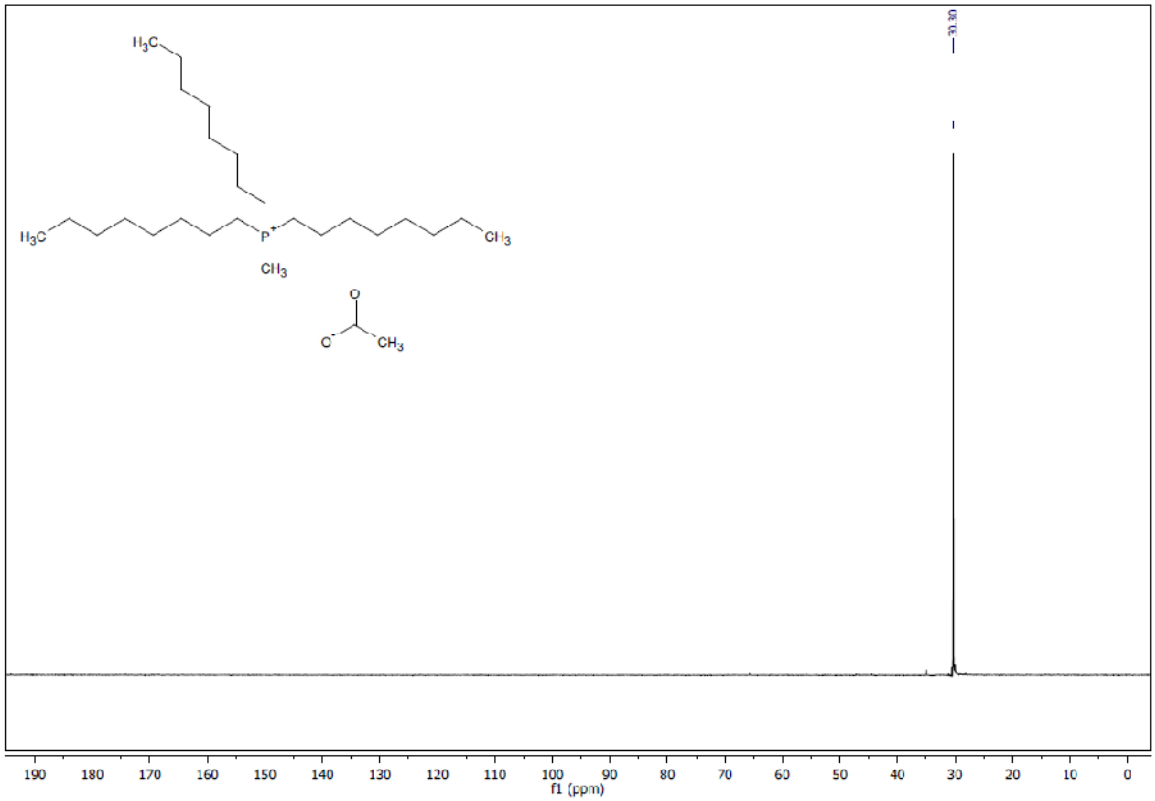

Figure S3 ^{31}P-NMR of compound **1c** in $CDCl_3$.

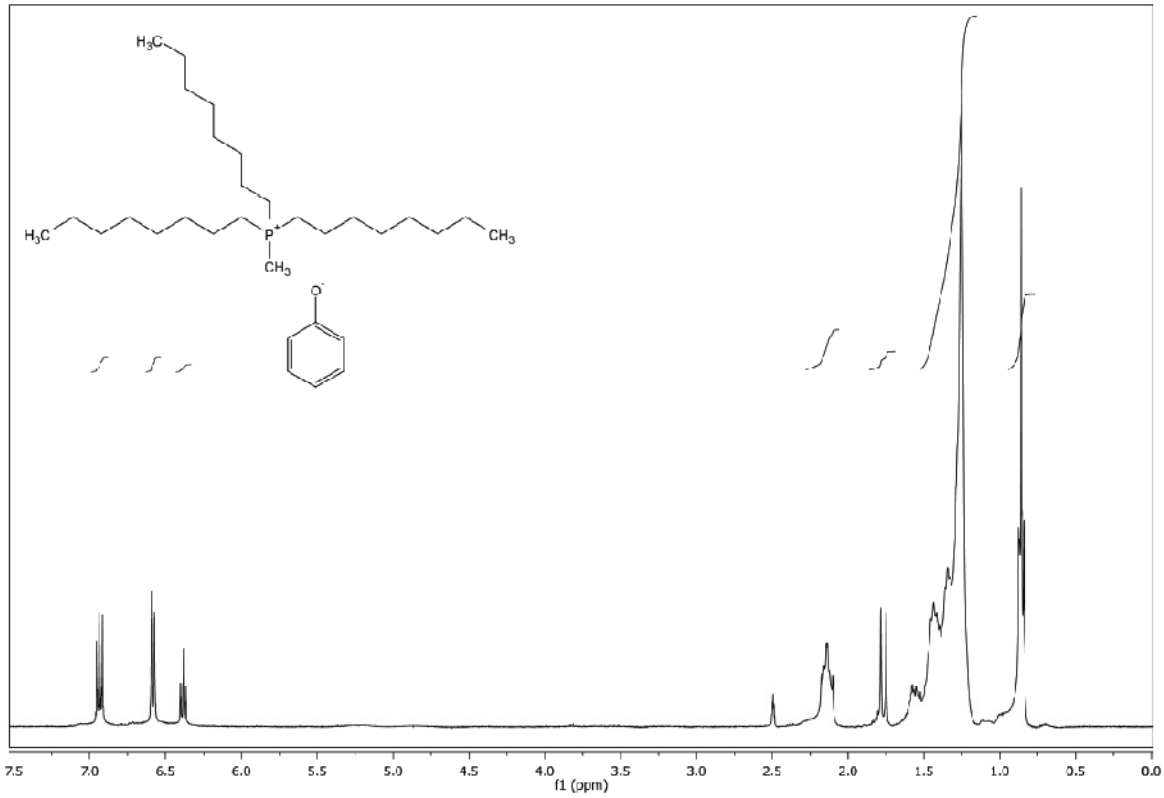

Figure S4 ^{1}H-NMR of compound **1d** in DMSO-d_6.

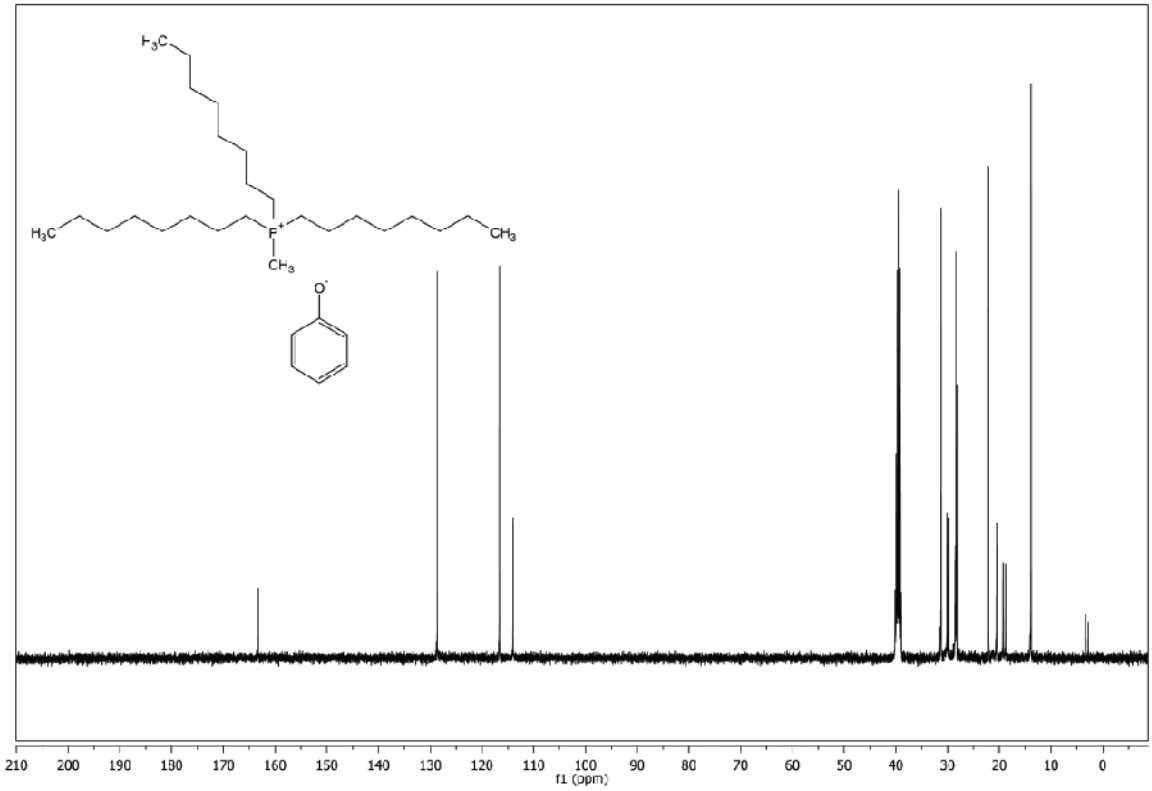

Figure S5 ^{13}C-NMR of compound **1d** in DMSO-d_6.

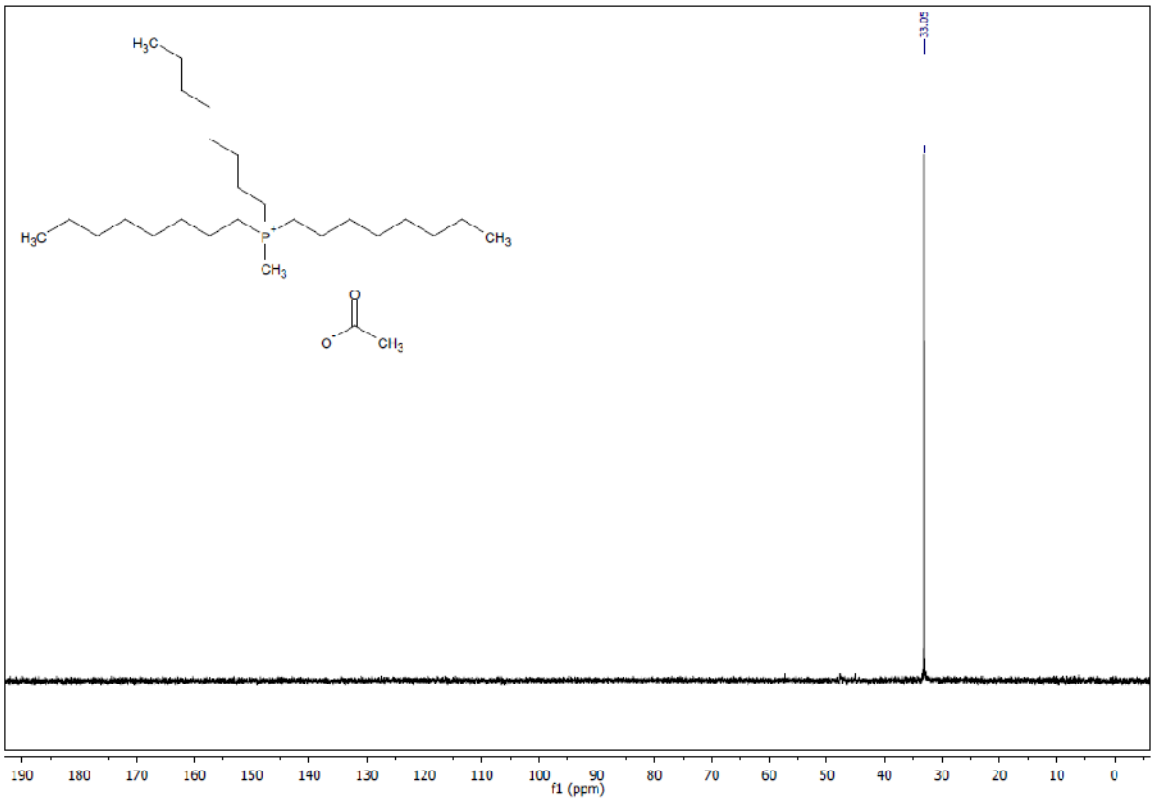

Figure S6 ^{31}P-NMR of compound **1d** in DMSO-d_6.

ESI-MS spectra of prepared catalysts

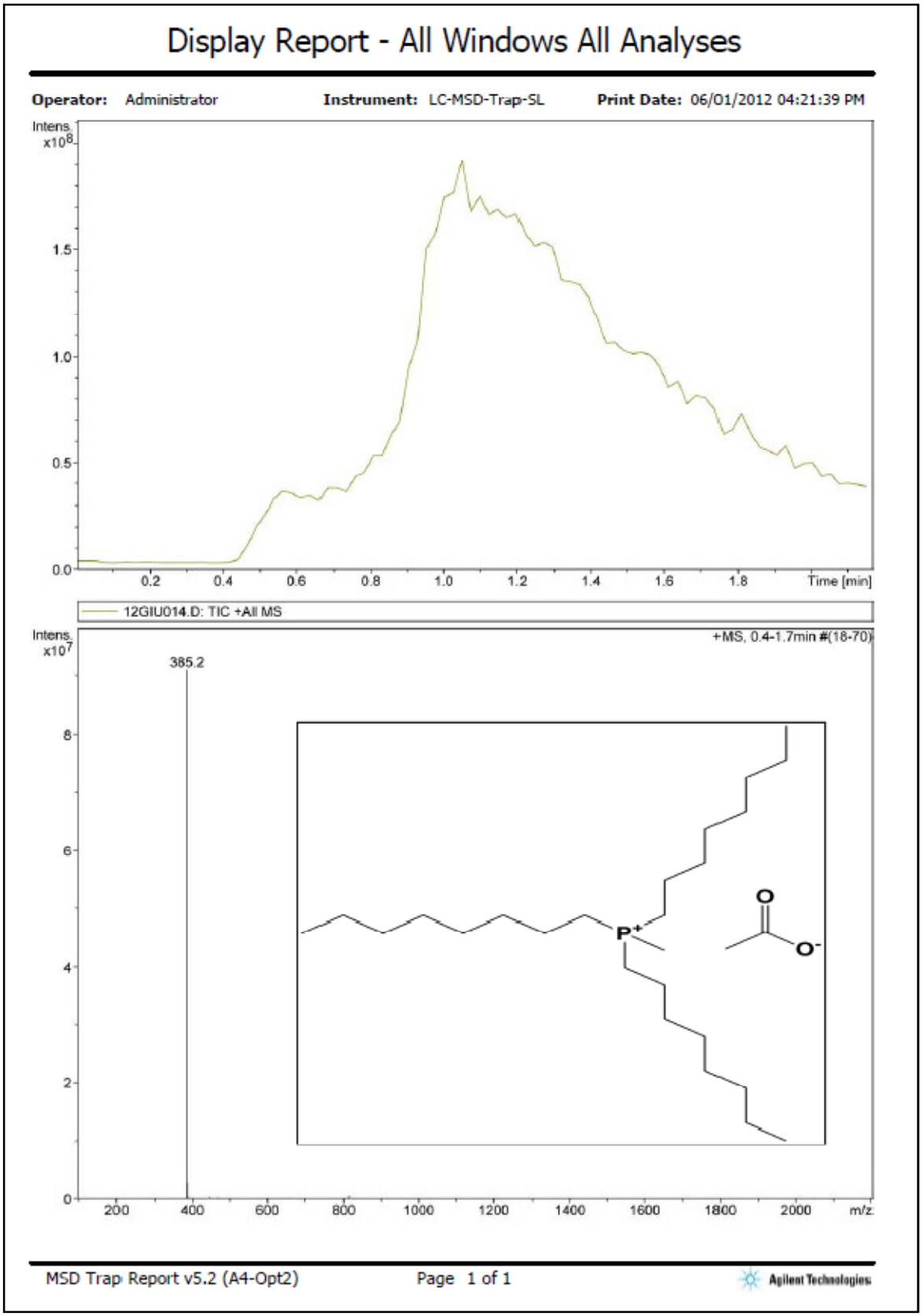

Figure S7 ESI-MS of compound **1c** in acetonitrile. The spectrum shows a strong positive ion at m/z 385 corresponding to the P_{8881} cation (the anion mass was too low to be detected by ESI-MS).

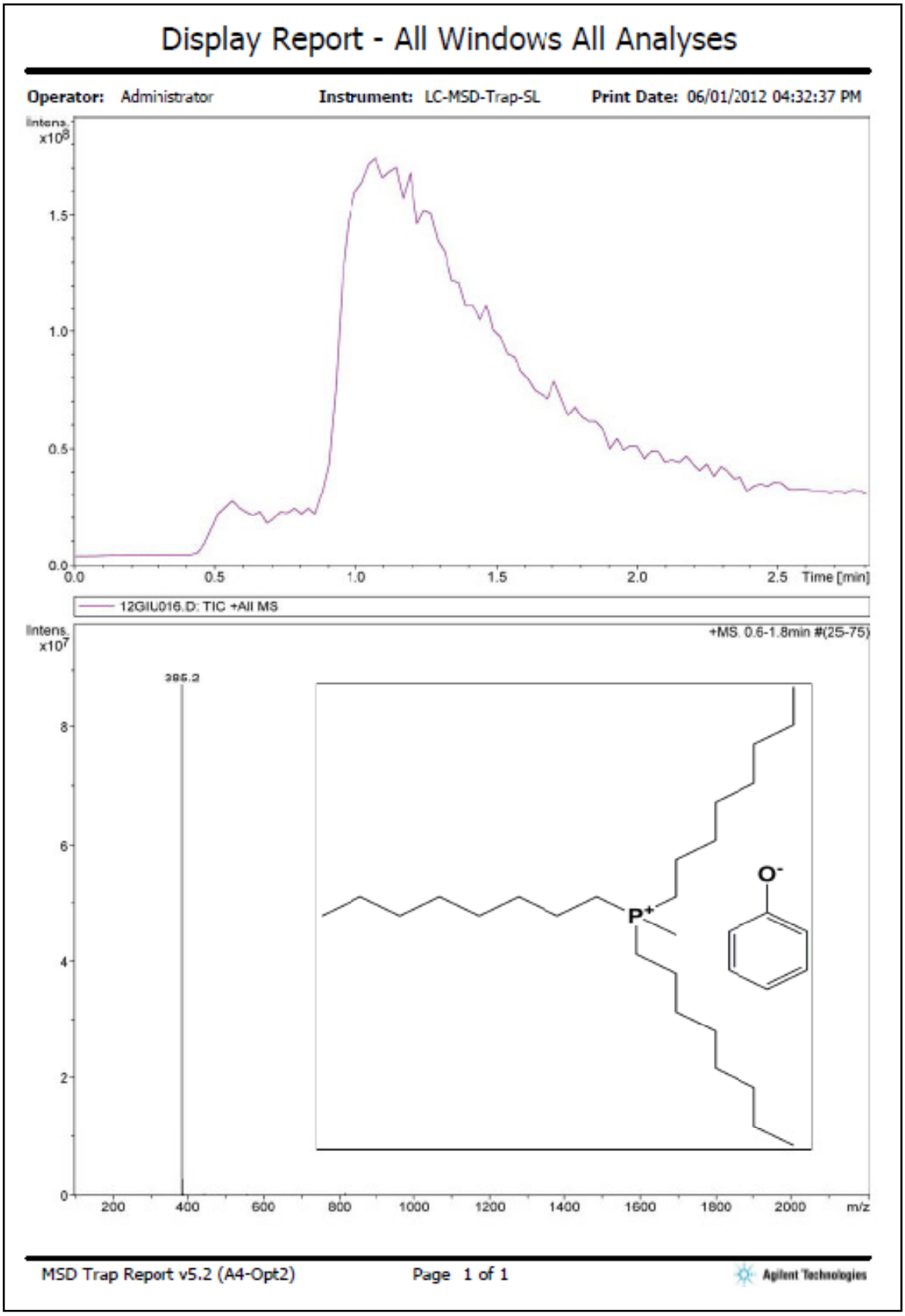

Figure S8 ESI-MS of compound **1d** in acetonitrile. The spectrum shows a strong positive ion at m/z 385 corresponding to the P_{8881} cation (the anion mass was too low to be detected by ESI-MS).

NMR spectra of the isolated products

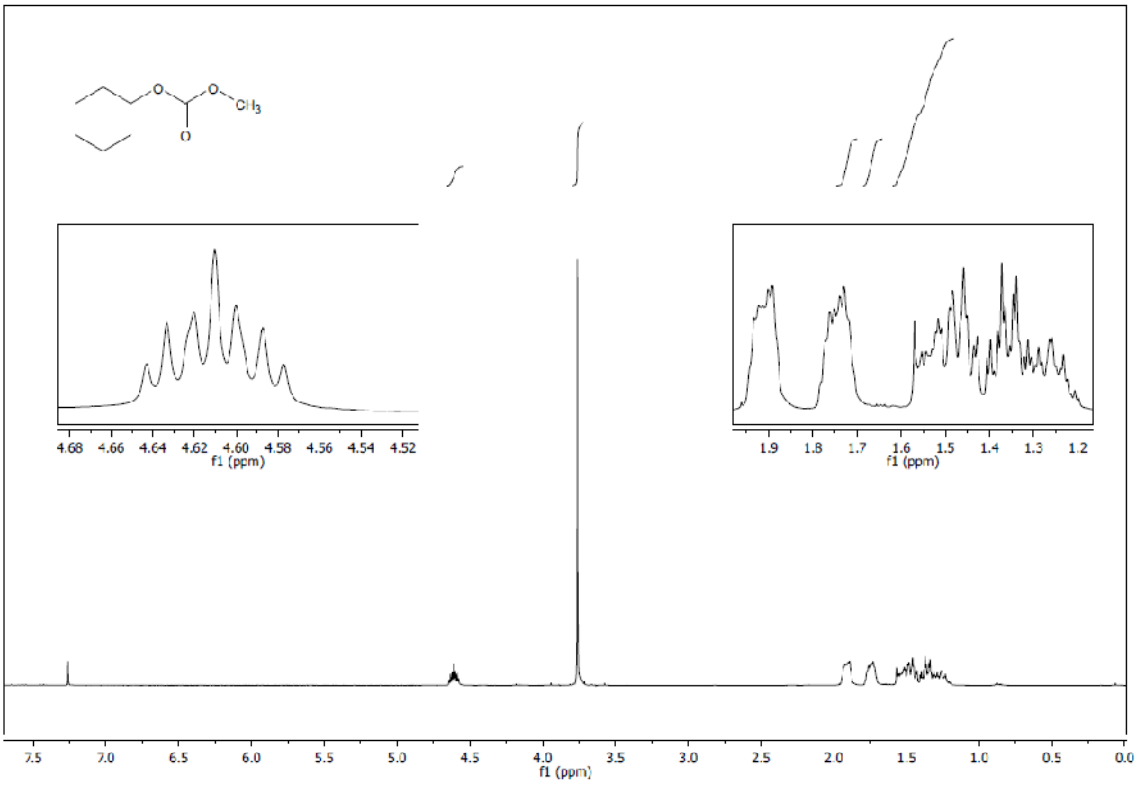

Figure S9 ^{1}H-NMR of cyclohexyl methyl carbonate in $CDCl_3$.

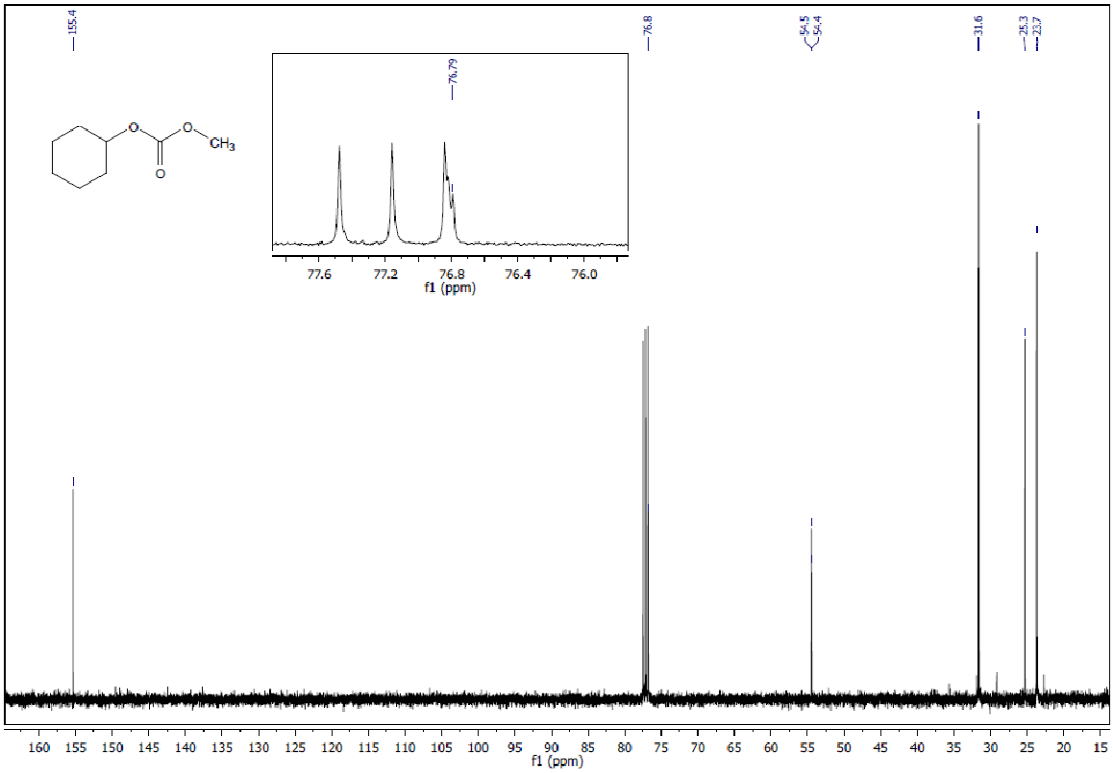

Figure S10 ^{13}C-NMR of cyclohexyl methyl carbonate in $CDCl_3$.

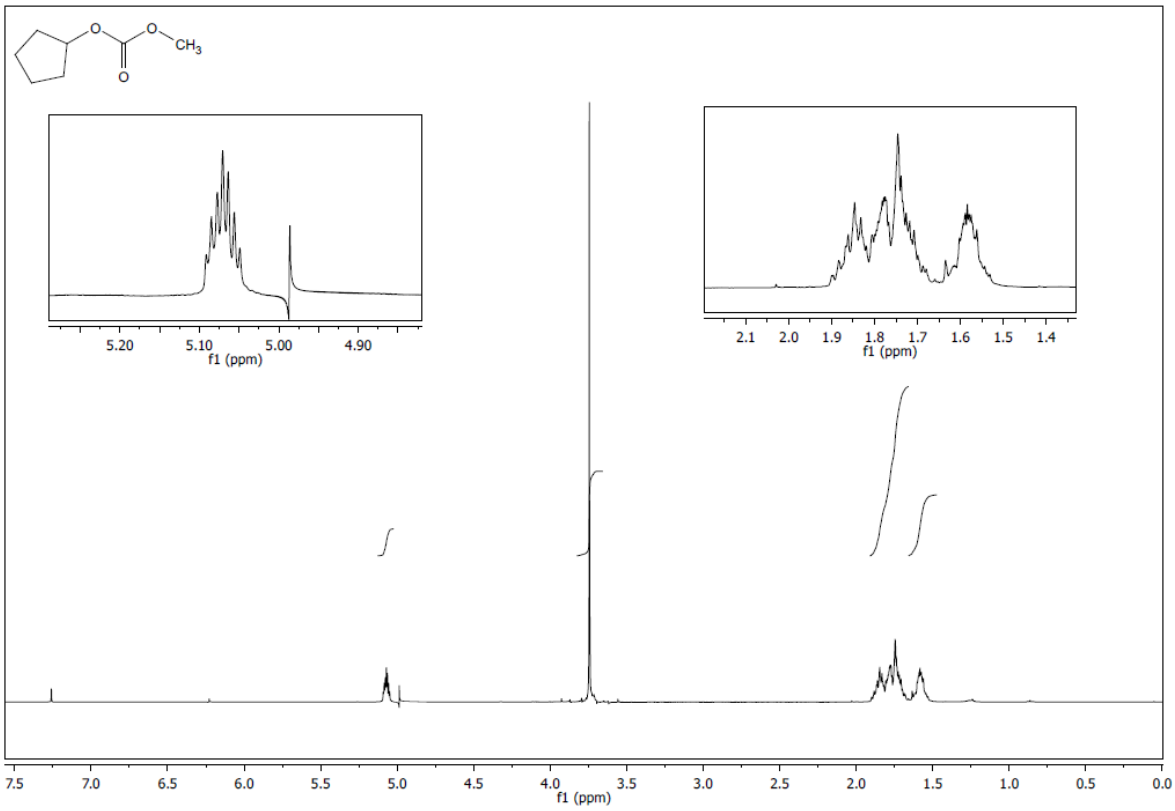

Figure S11 ^{1}H-NMR of cyclopentyl methyl carbonate in $CDCl_3$.

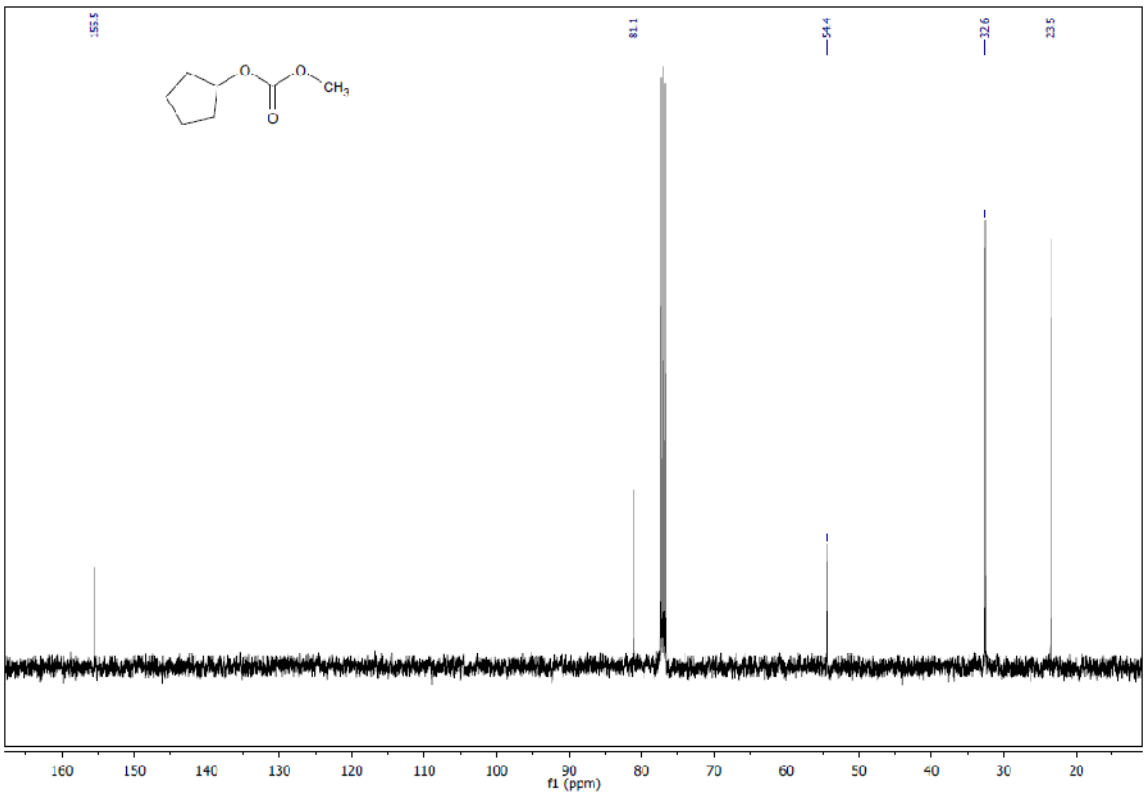

Figure S12 ^{13}C-NMR of cyclopentyl methyl carbonate in $CDCl_3$.

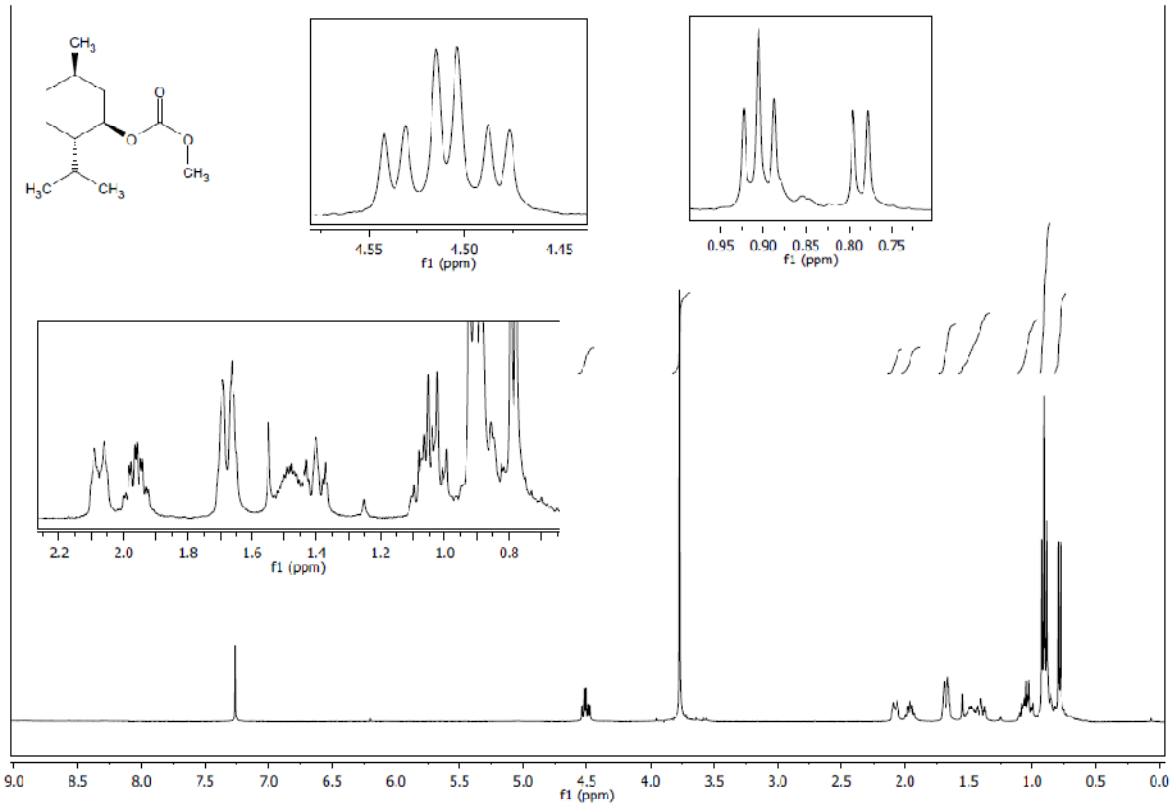

Figure S13 ^{1}H-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl methyl carbonate (menthyl methyl carbonate) in $CDCl_3$.

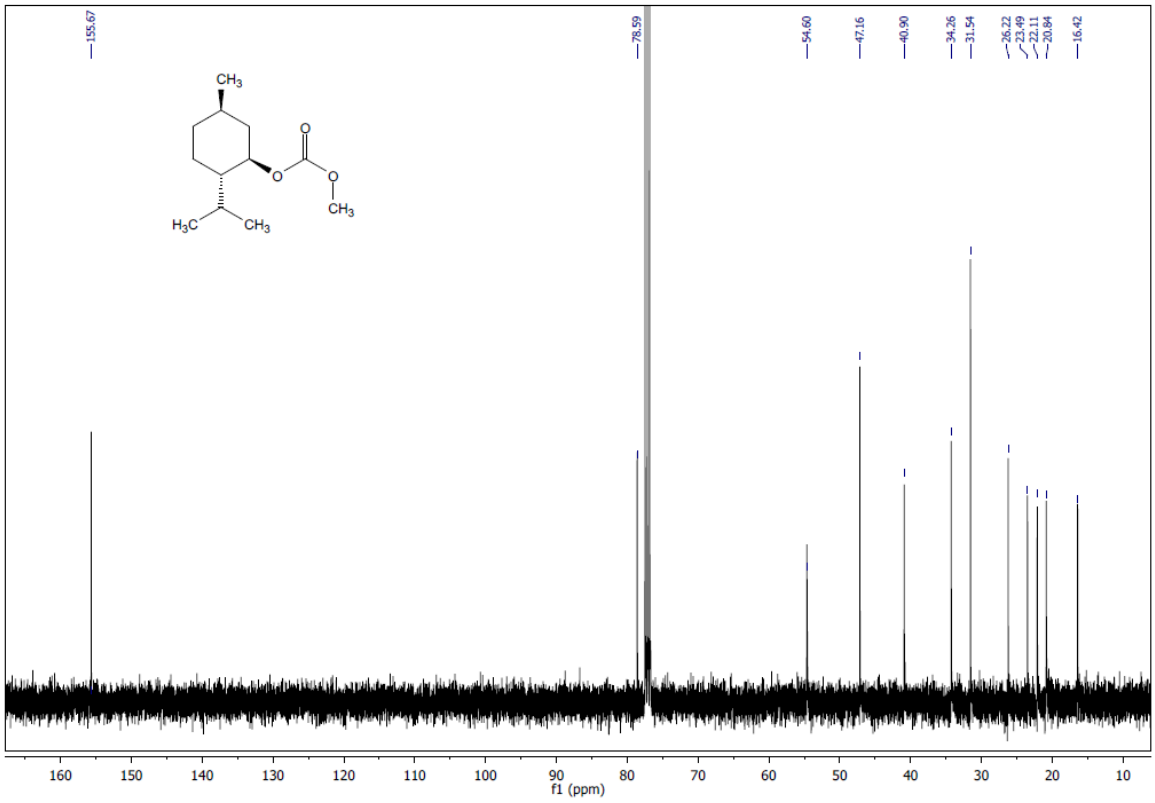

Figure S14 ^{13}C-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl methyl carbonate (menthyl methyl carbonate) in $CDCl_3$.

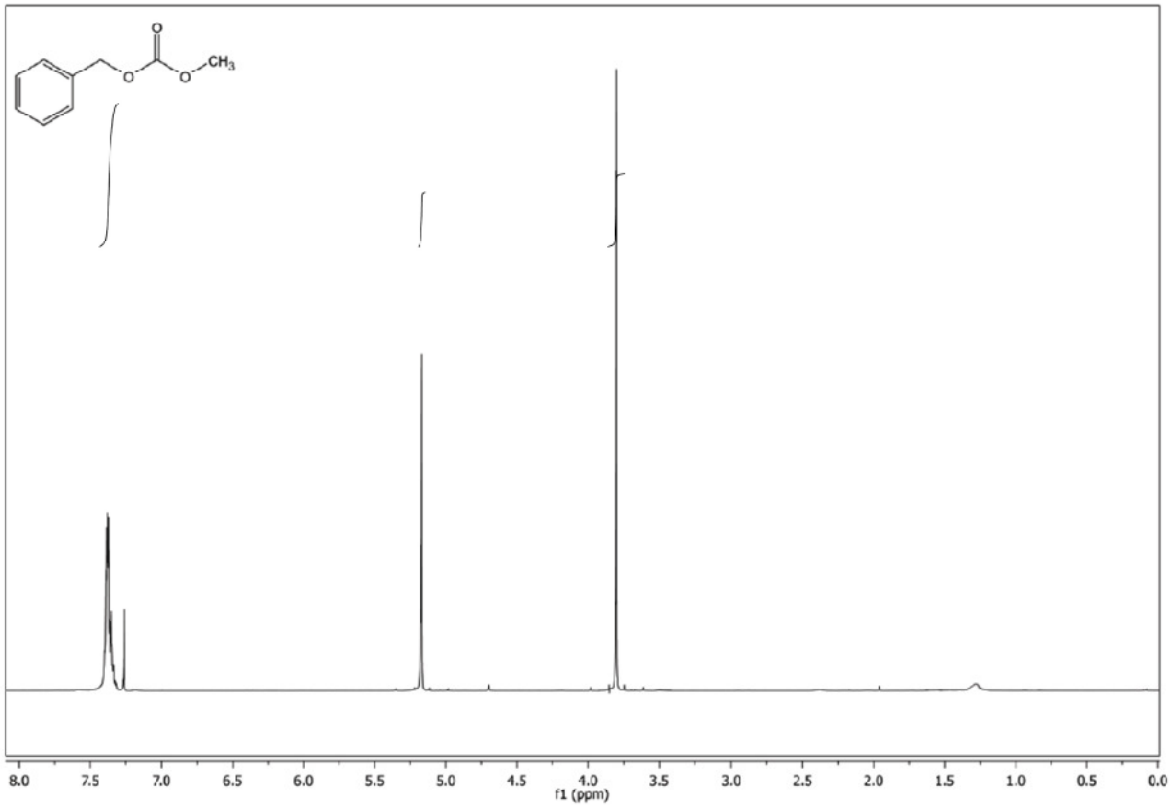

Figure S15 ^{1}H-NMR of benzyl methyl carbonate in $CDCl_3$.

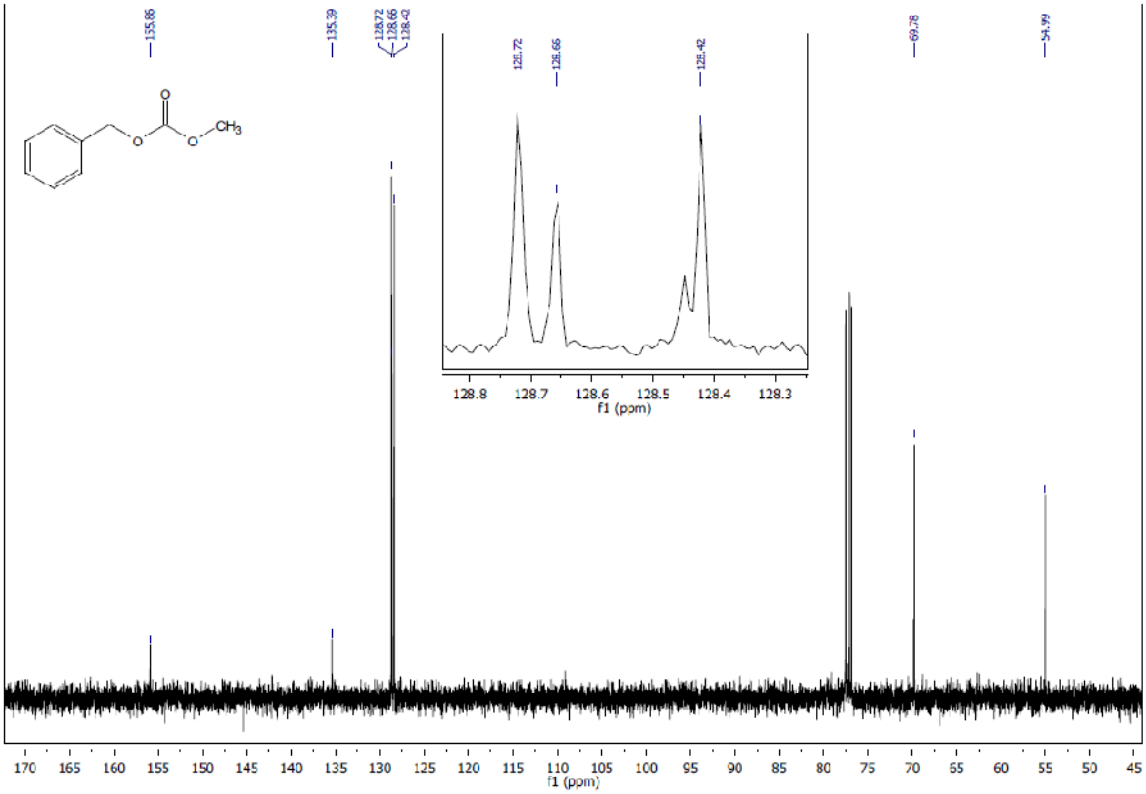

Figure S16 ^{13}C-NMR of benzyl methyl carbonate in $CDCl_3$.

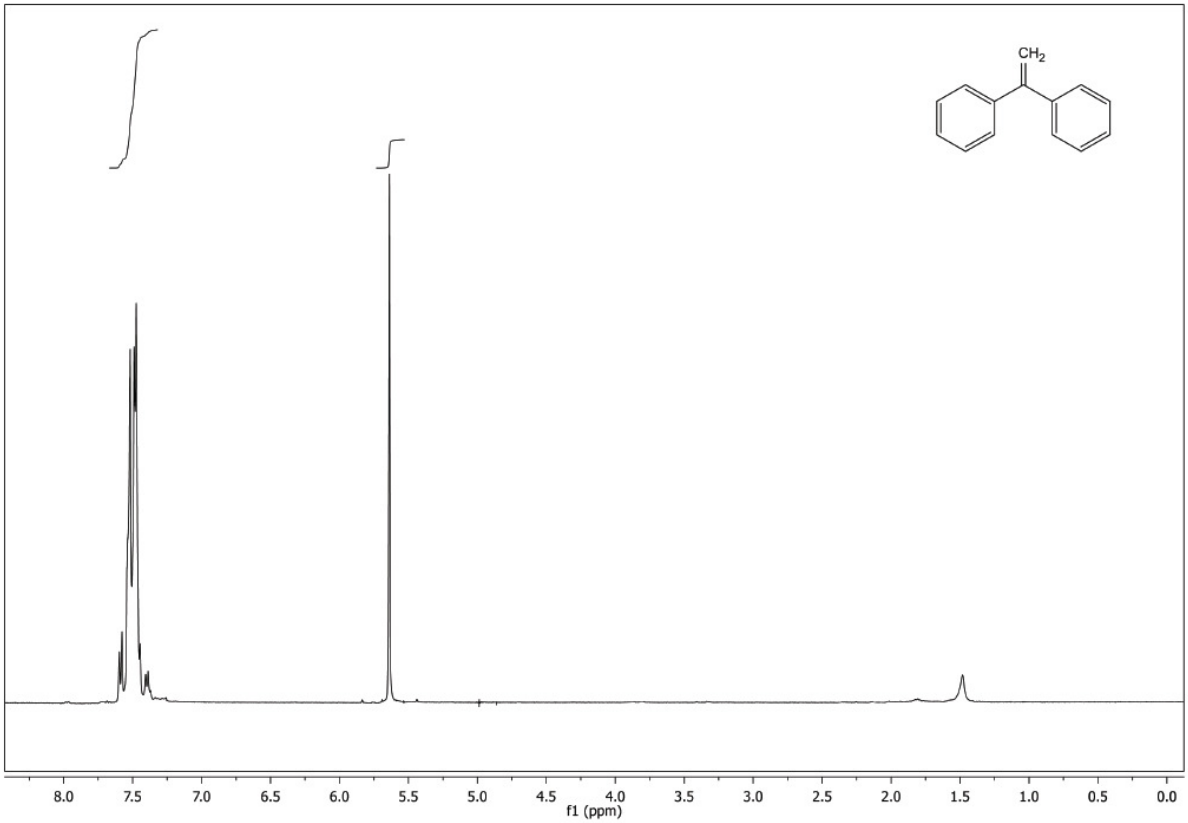

Figure S17 ^{1}H-NMR of 1,1-diphenylethene in $CDCl_3$.

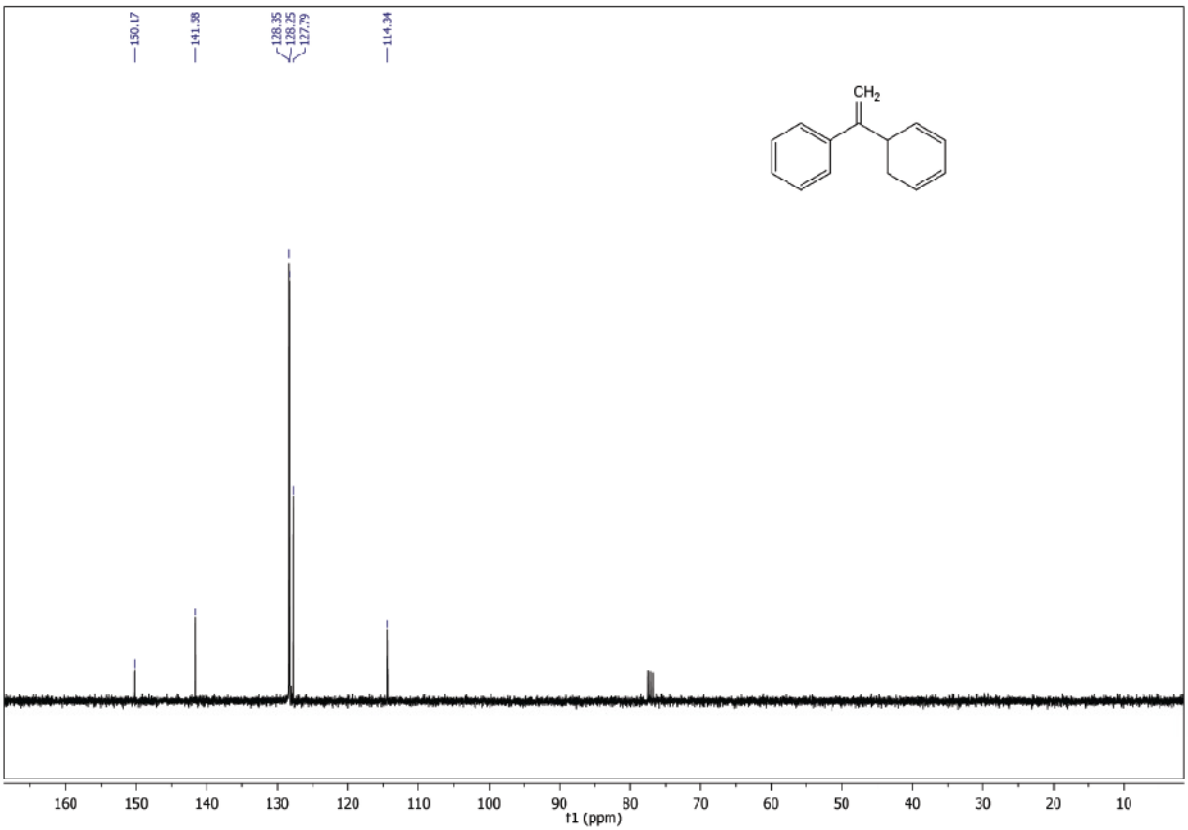

Figure S18 ^{13}C-NMR of 1,1-diphenylethene in $CDCl_3$.

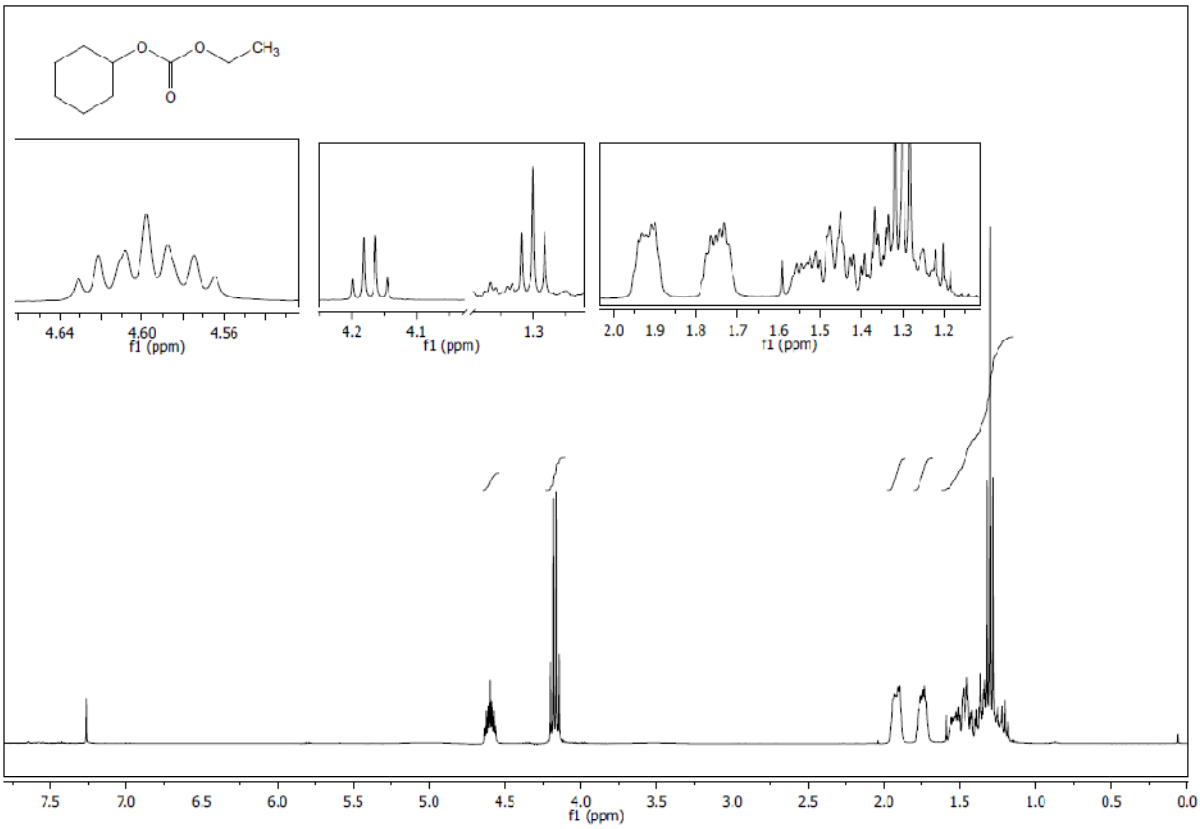

Figure S19 ^{1}H-NMR of cyclohexyl ethyl carbonate in $CDCl_3$.

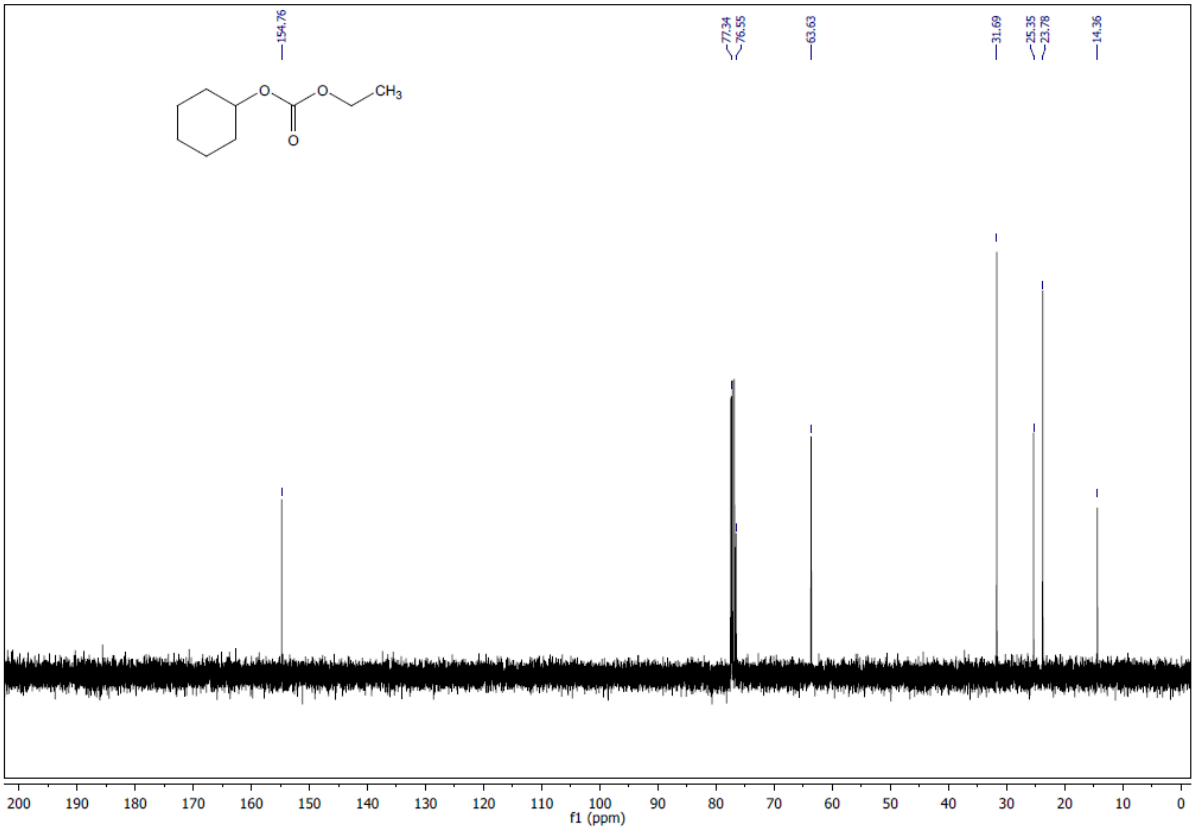

Figure S20 ^{13}C-NMR of cyclohexyl ethyl carbonate in $CDCl_3$.

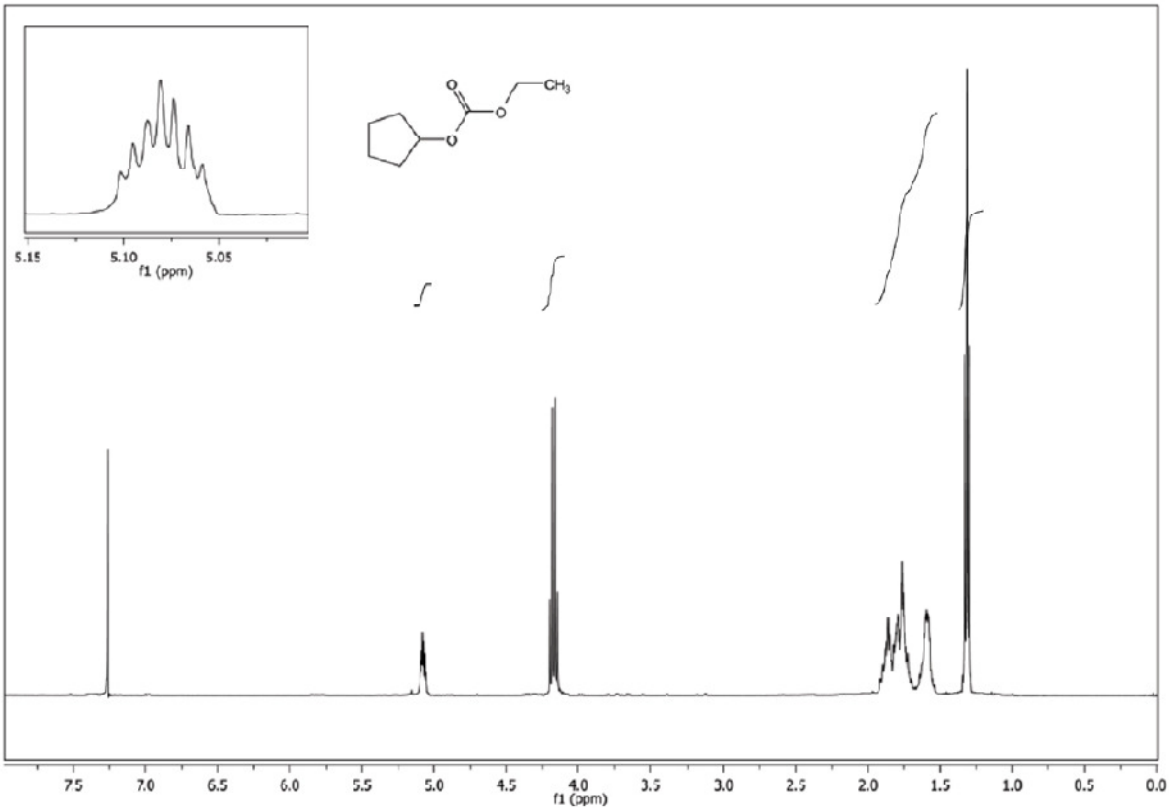

Figure S21 ^{1}H-NMR of cyclopentyl ethyl carbonate in $CDCl_3$.

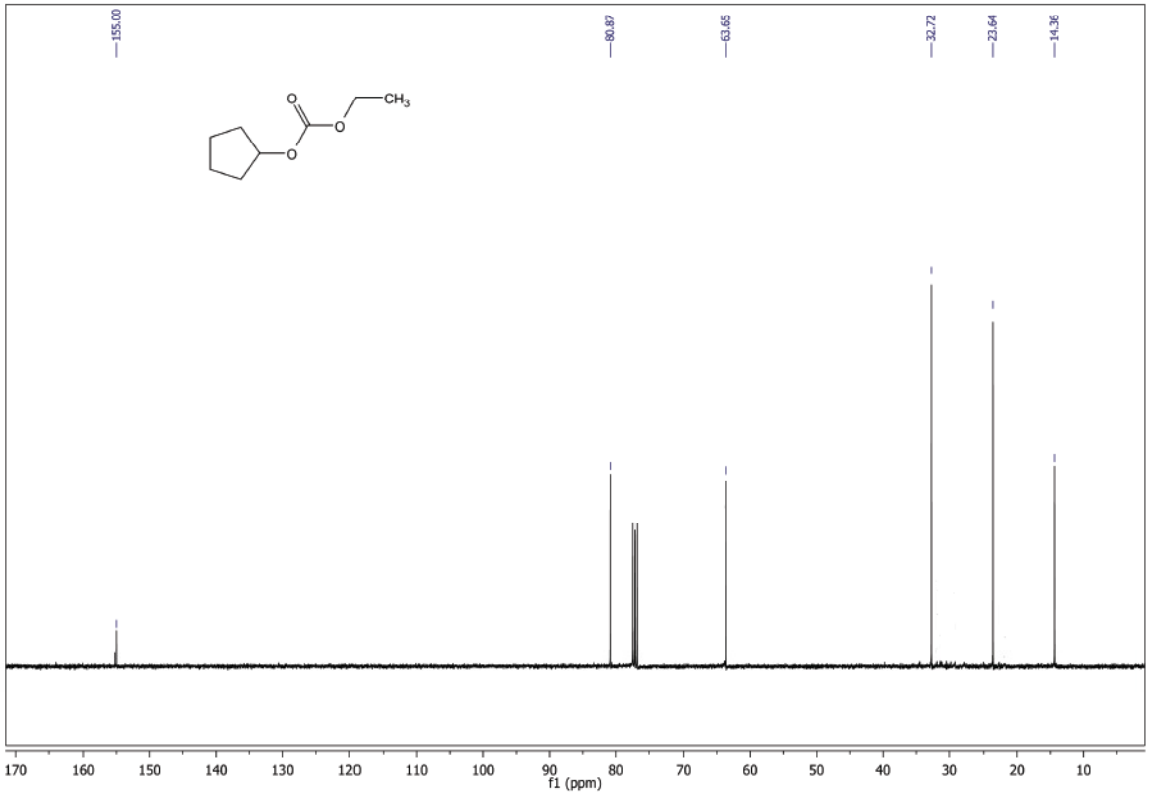

Figure S22 ^{1}H-NMR of cyclopentyl ethyl carbonate in $CDCl_3$.

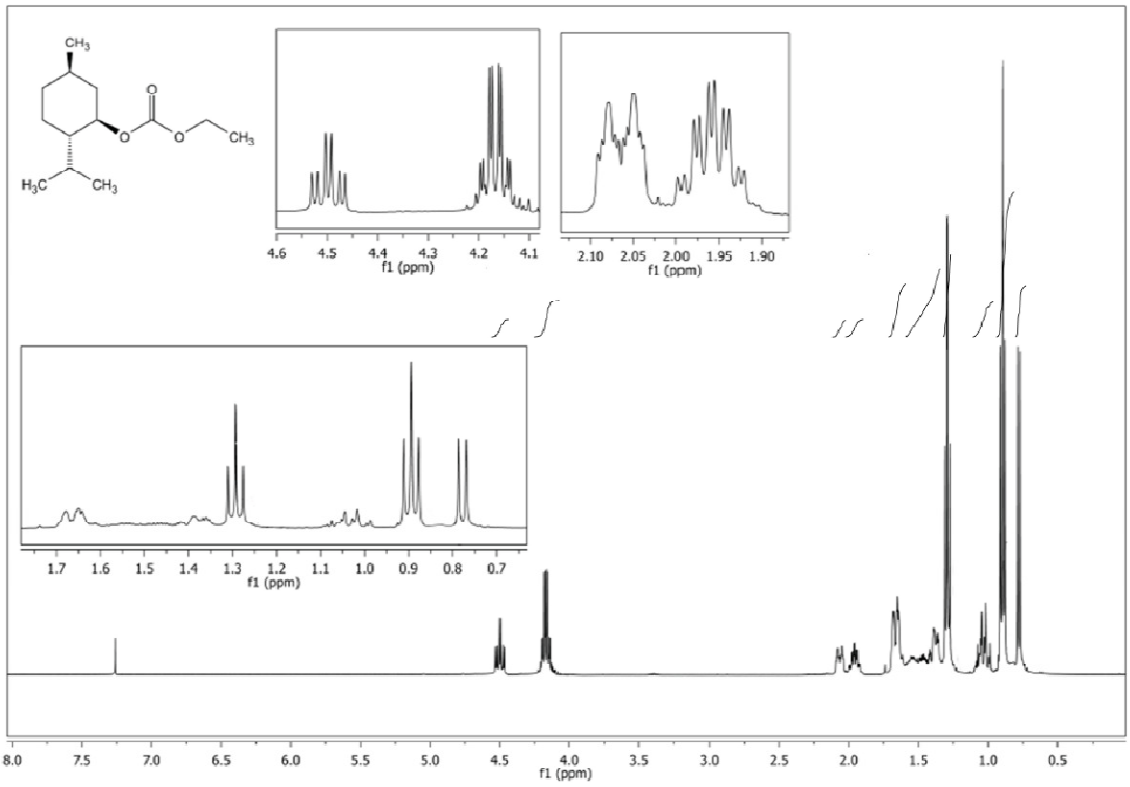

Figure S23 ^{1}H-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl ethyl carbonate (menthyl ethyl carbonate) in $CDCl_3$.

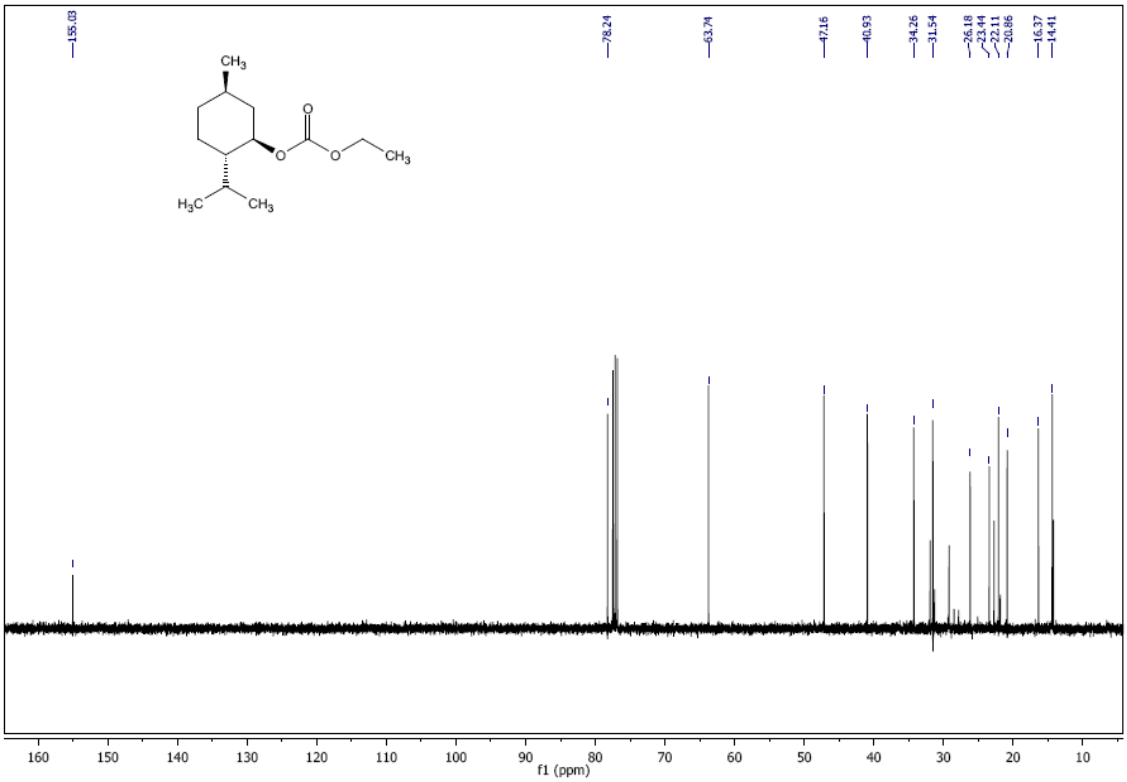

Figure S24 ^{1}H-NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl ethyl carbonate (menthyl ethyl carbonate) in $CDCl_3$.

IR spectra of new products

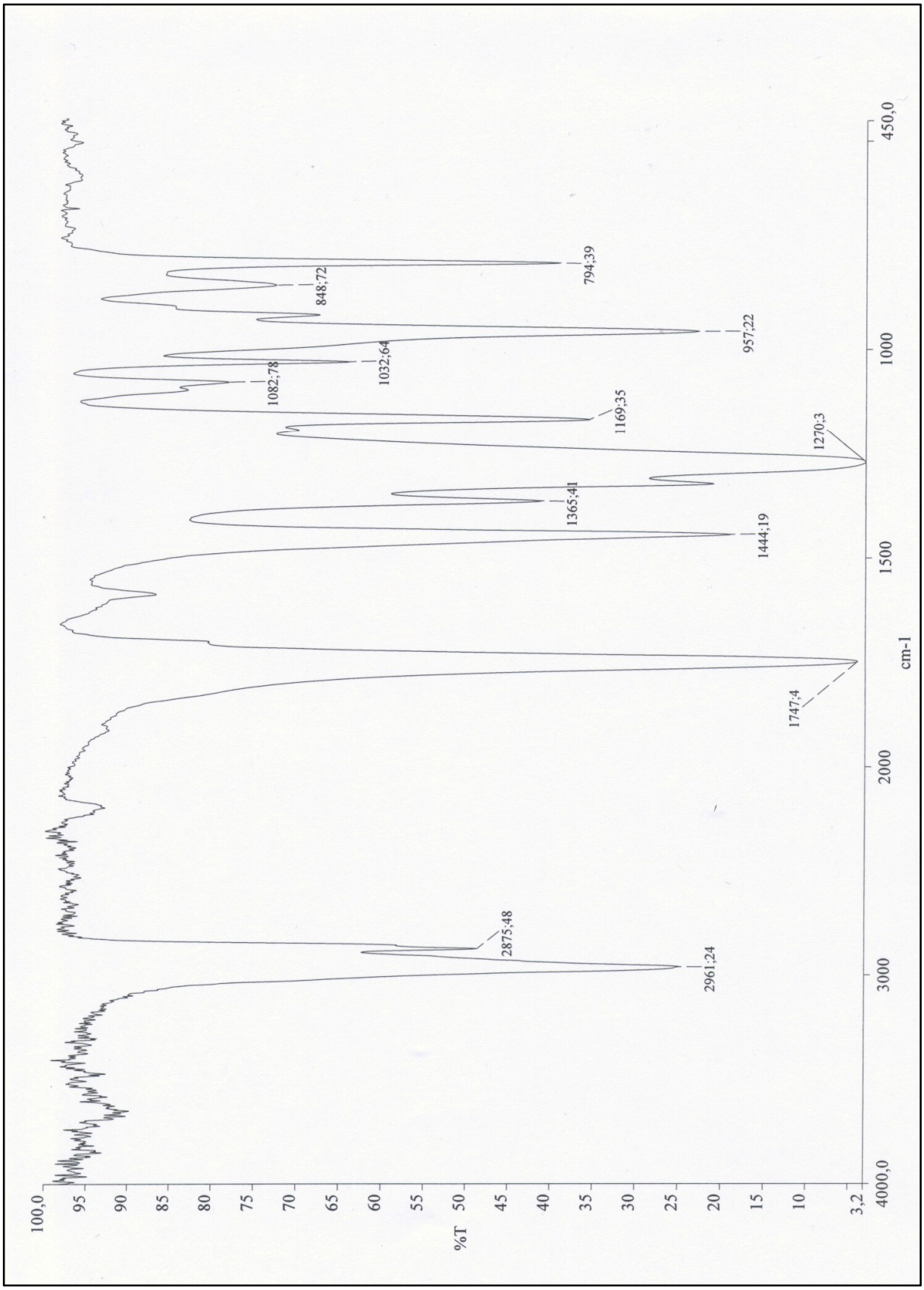

Figure S25 IR spectrum of cyclopentyl methyl carbonate.

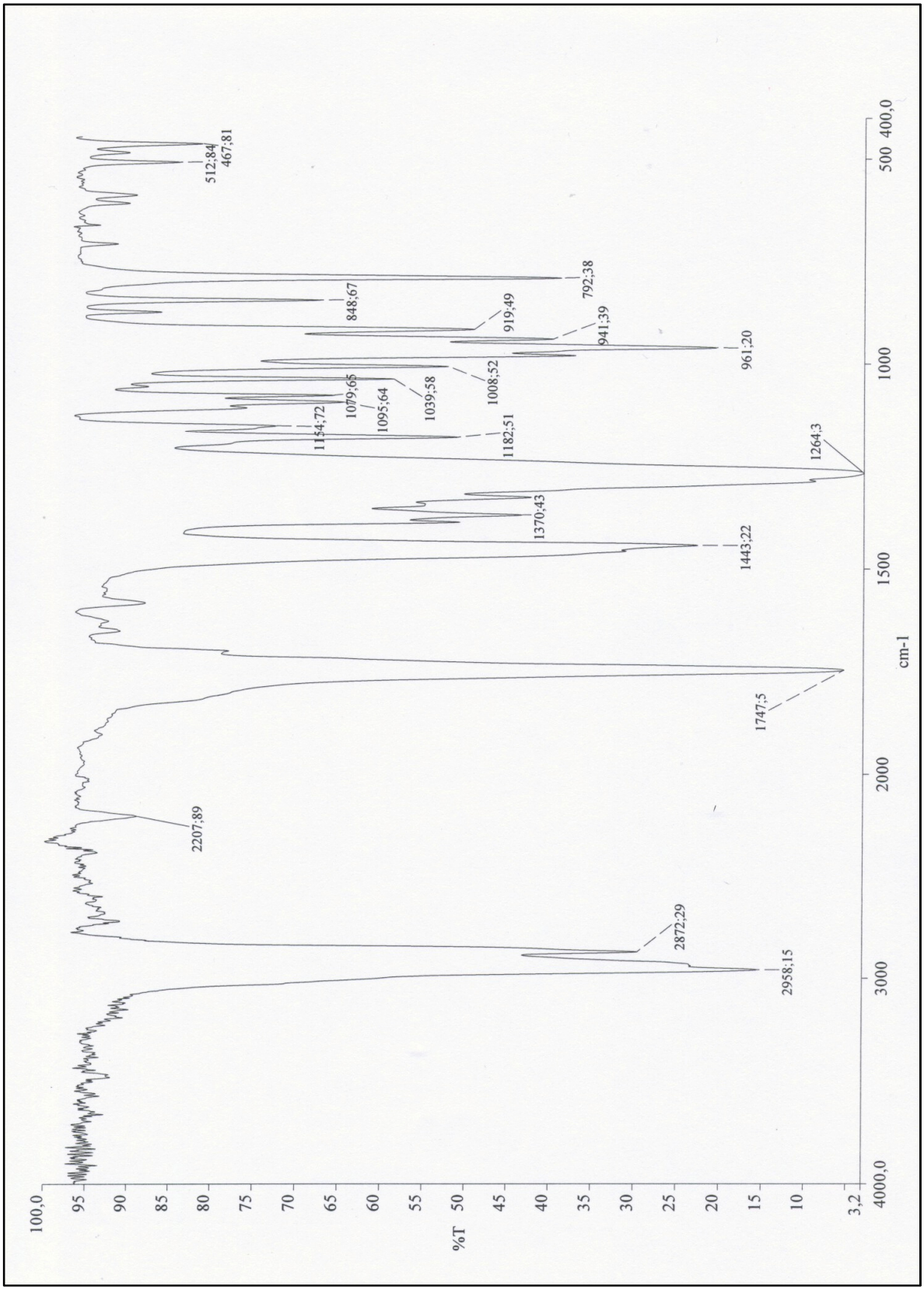

Figure S26 IR spectrum of menthyl methyl carbonate.

References

[1] M. Selva, E. Militello and M. Fabris, *Green Chem.*, 2008, **10**, 73–79.