Supplementary Information

Light-induced synthesis of unsymmetrical organic carbonates from alcohols, methanol and CO_2 under ambient conditions

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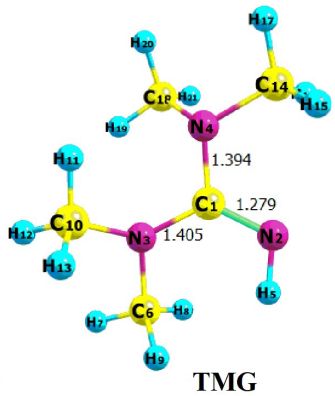
1.0 Experimental Procedure for the synthesis of methyl carbonates from CO_2

In a typical experiment, TMG (25 mol%) in DMSO (20 ml) was taken in a 60 ml vessel followed by the addition of phenol (10 mmol) and methanol (3 ml). The mixture was flushed with nitrogen to evacuate trapped air and other gases from the reaction mixture. After that the reaction mixture was saturated with CO_2 by purging and the reaction vessel was sealed, equipped with CO_2 filled balloon. The reaction vessel was irradiated with 20 W LED light for 2h. The intensity of the LED light at the reaction flask was measured to be 86 W/m^2 by intensity meter. The reaction was continued initially for 12 h followed by monitoring the progress of the reaction by thin layer chromatography using silica gel. After completion of the reaction, the solvent was evaporated under reduced pressure and the concentrated residue was subjected to column chromatography on a silica gel (100-200 mesh) column using 9:1 hexane-ethyl acetate solvent mixture as eluent to afford the methyl phenyl carbonate in 78% isolated yield.

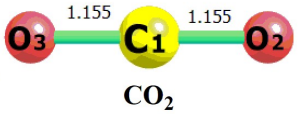
2.0 Computational Details:

Structures of all reaction species were optimized using hybrid meta-M06-2X exchange-correlation functional [1] along with 6-311++G(d,p) basis sets. Frequency calculations of all optimized species were further performed at the same level of theory. We have obtained real and positive frequency of all reaction species, except the transition state (TS). We have found only one negative frequency during the frequency calculation of TS. To validate the smooth connection of transition state with reactants and products, intrinsic reaction coordinate (IRC) calculations [2] are also performed for TSs at the same level of theory. All the DFT calculations were performed using GAUSSIAN 09 program package [3].

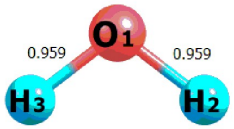
Figure S1: Optimized geometries along with some important bond lengths of all species at M06- 2X/6-311++G(d,p) level of theory.



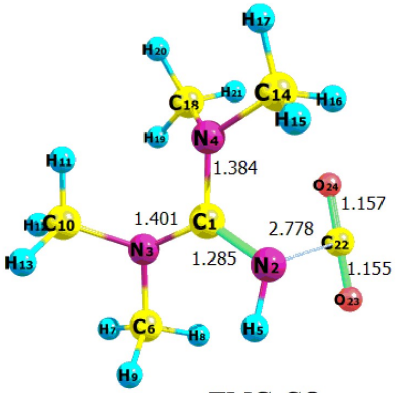
TMG



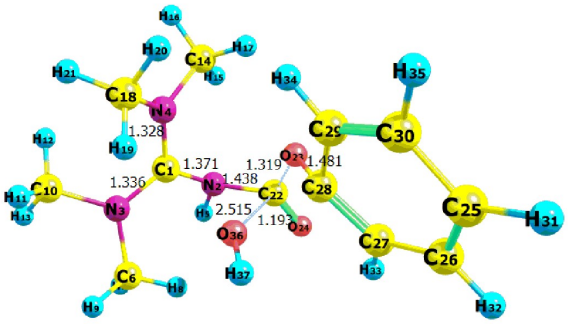
CO_2



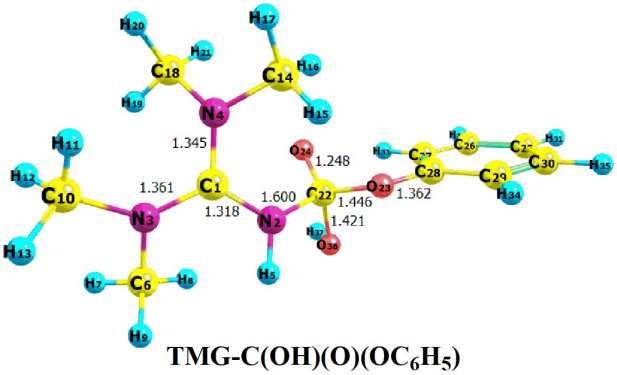
H_2O



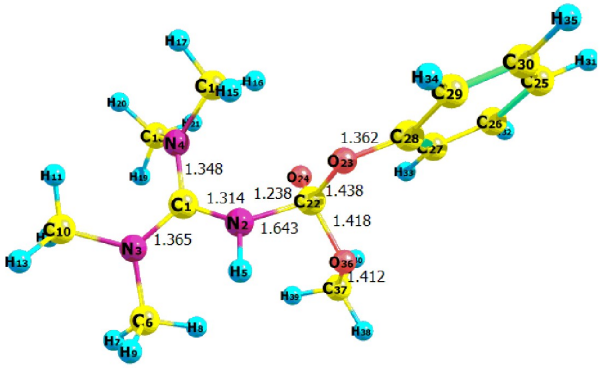
TMG-CO_2



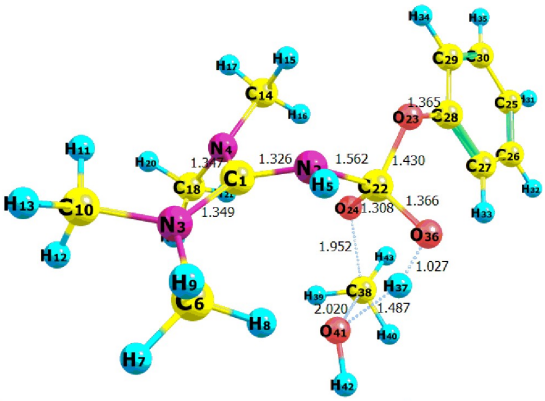
TS1(344.36*i* cm^{-1})



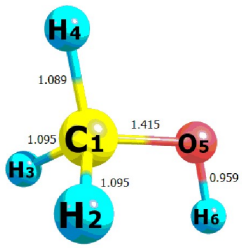
TMG-C(OH)(O)(OC_6H_5)



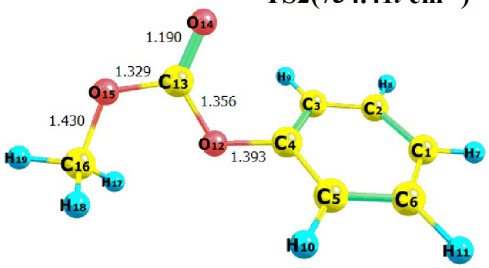
TMG-C(O)(OCH_3)(OC_6H_5)



TS2(734.41*i* cm^{-1})



CH_3OH



$C_6H_5O(CO)OCH_3$

Table S1: Enthalpy and Gibbs Free energy changes (in kcal mol^{-1}) of reaction at M06-2X/6-311++G (d,p) level of theory.

Reaction Channels	$\Delta_r H^0$	$\Delta_r G^0$
TMG + CO_2 →TMG-CO_2	-62.42	-54.68
TMG-CO_2+ C_6H_5OH →TMG-C(OH)(O)(OC_6H_5)	-43.35	-20.64
TMG-C(OH)(O)(OC_6H_5) →TMG-C(O)(OCH_3)(OC_6H_5) + H_2O	-46.30	-21.80
TMG-C(O)(OCH_3)(OC_6H_5)→TMG + $C_6H_5O(CO)OCH_3$	-53.21	-41.62

3.0 Characterization of the products

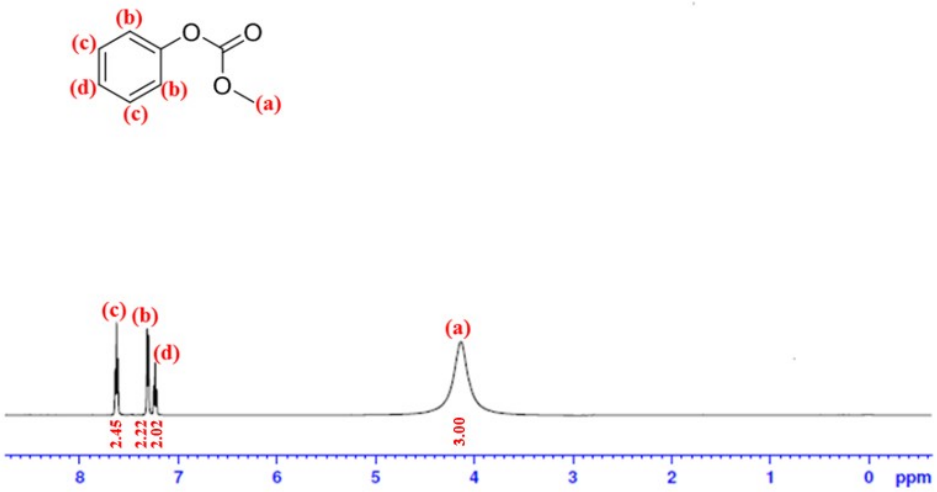


Figure S1. ^{1}H NMR spectrum of methyl phenyl carbonate

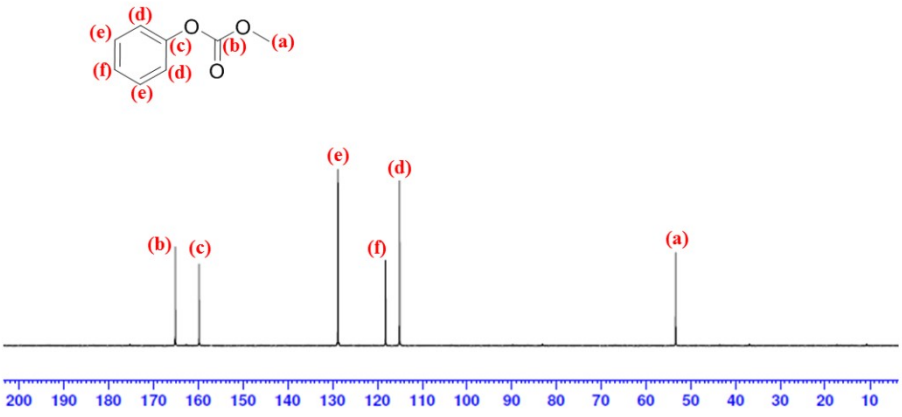


Figure S2. ^{13}C NMR spectrum of methyl phenyl carbonate

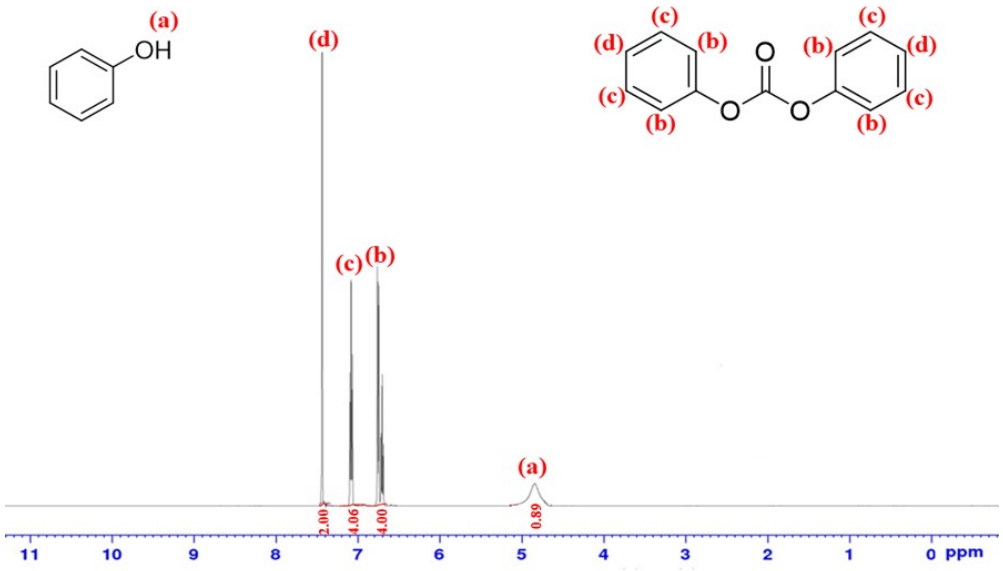


Figure S3. ^{1}H NMR spectra of diphenyl carbonate

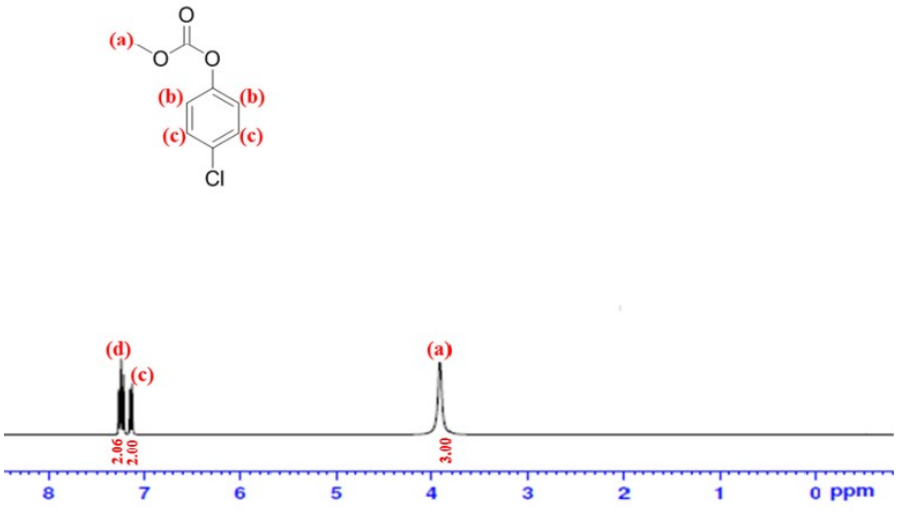


Figure S4. ^{1}H NMR spectra of 4-chlorophenyl methyl carbonate

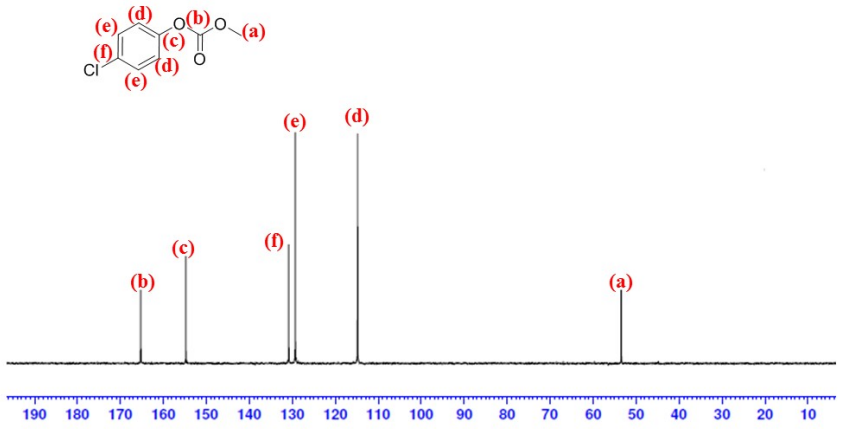


Figure S5. ^{13}C NMR spectra of 4-chlorophenyl methyl carbonate

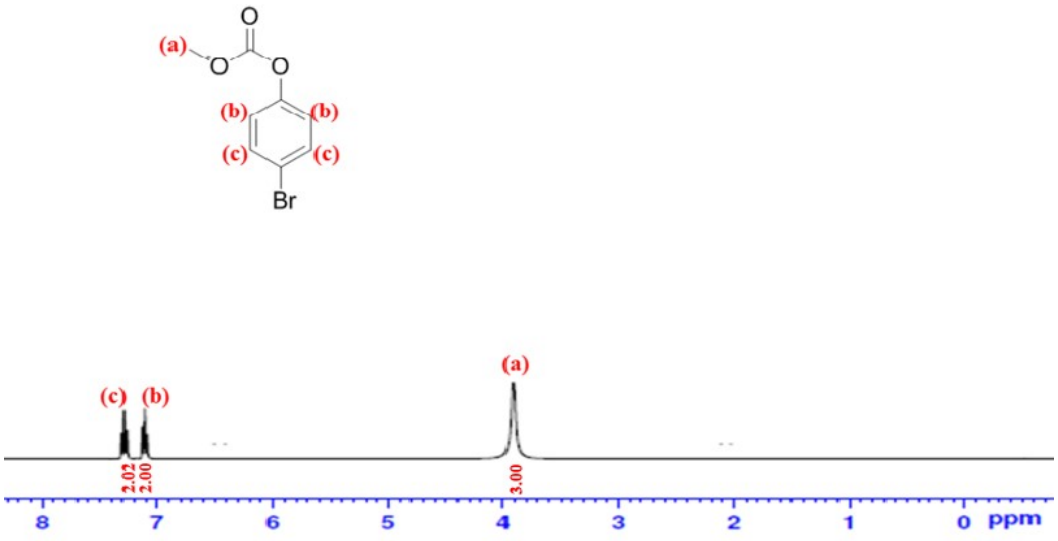


Figure S6. ^{1}H NMR spectra of 4-bromophenyl methyl carbonate

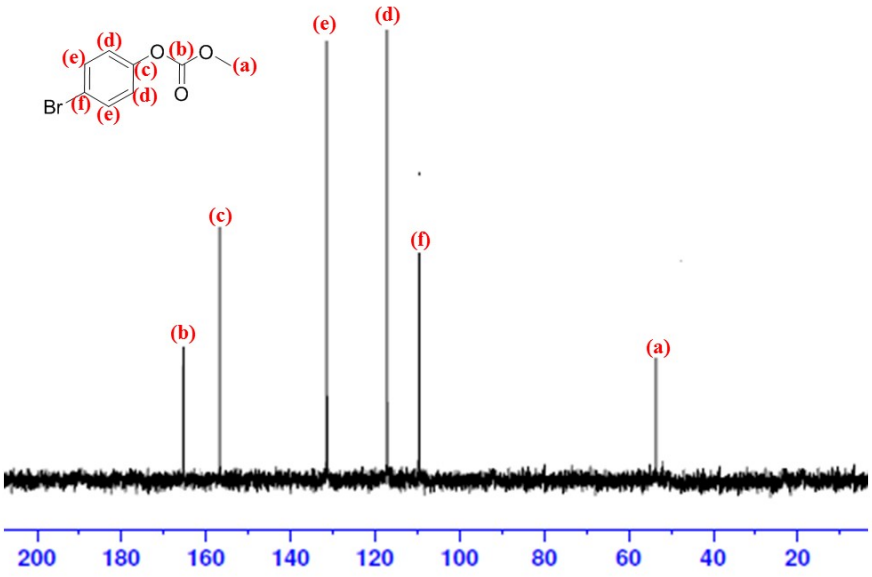


Figure S7. ^{13}C NMR spectra of 4-bromophenyl methyl carbonate

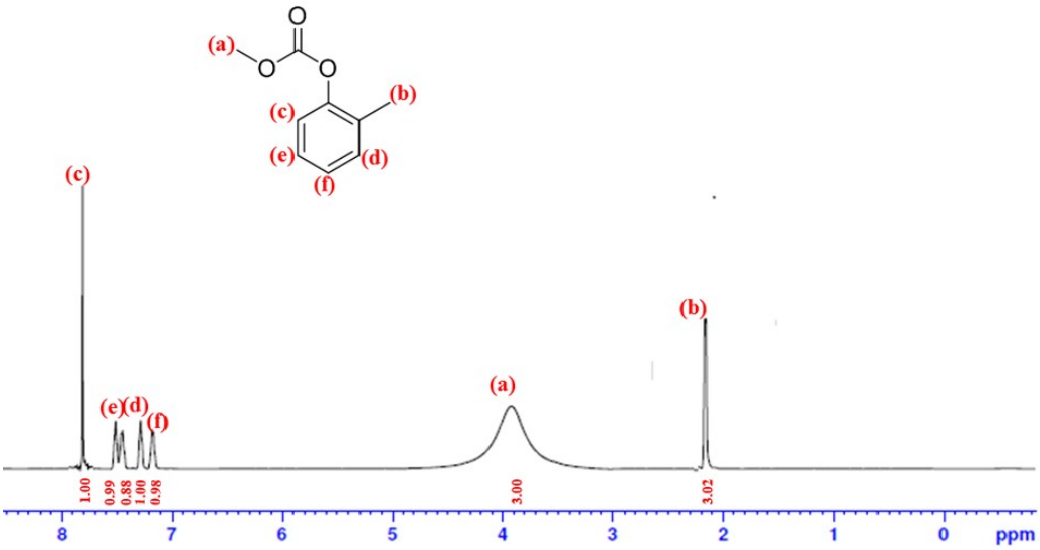


Figure S8. ^{1}H NMR spectra of methyl o-tolyl carbonate

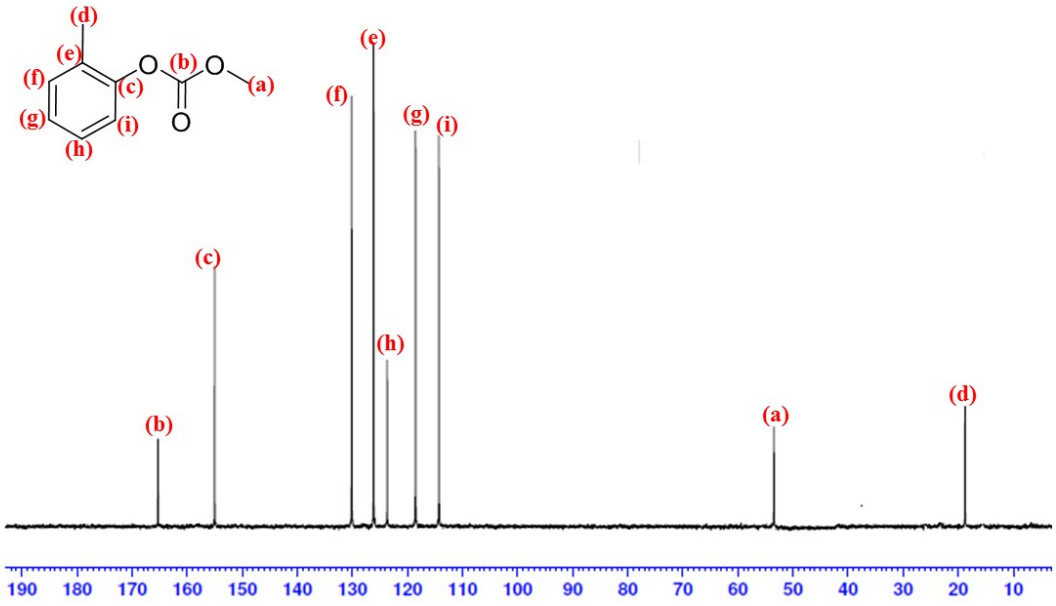


Figure S9. ^{13}C NMR spectra of methyl o-tolyl carbonate

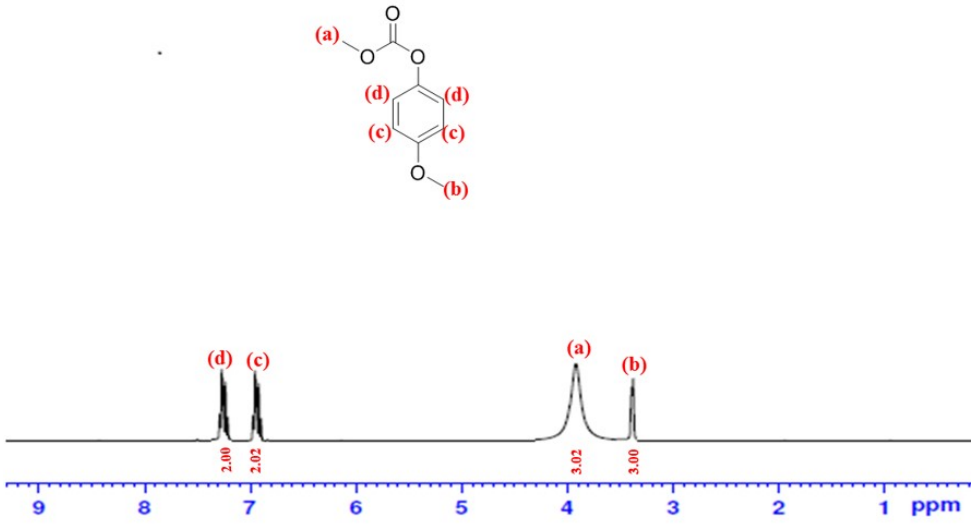


Figure S10. ^{1}H NMR spectra of 4-methoxyphenyl-methyl carbonate

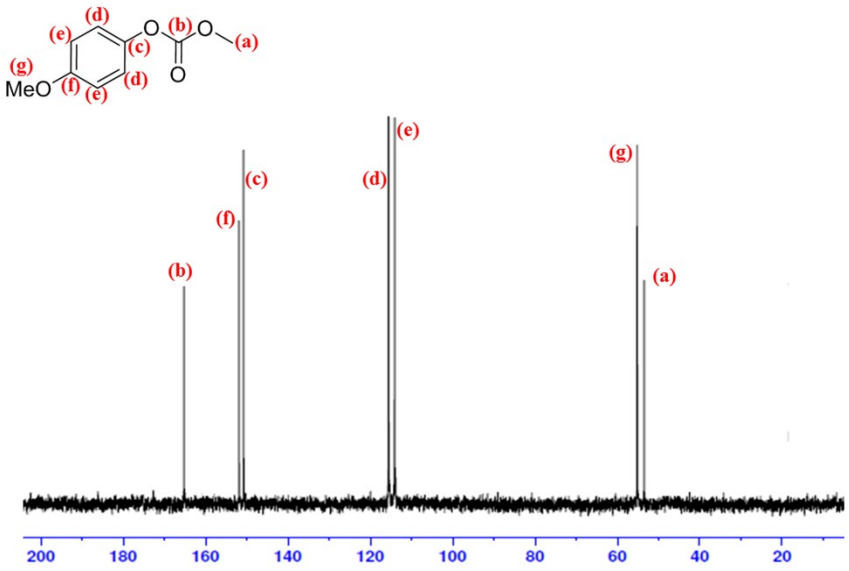


Figure S11. ^{13}C NMR spectra of 4-methoxyphenyl-methyl carbonate

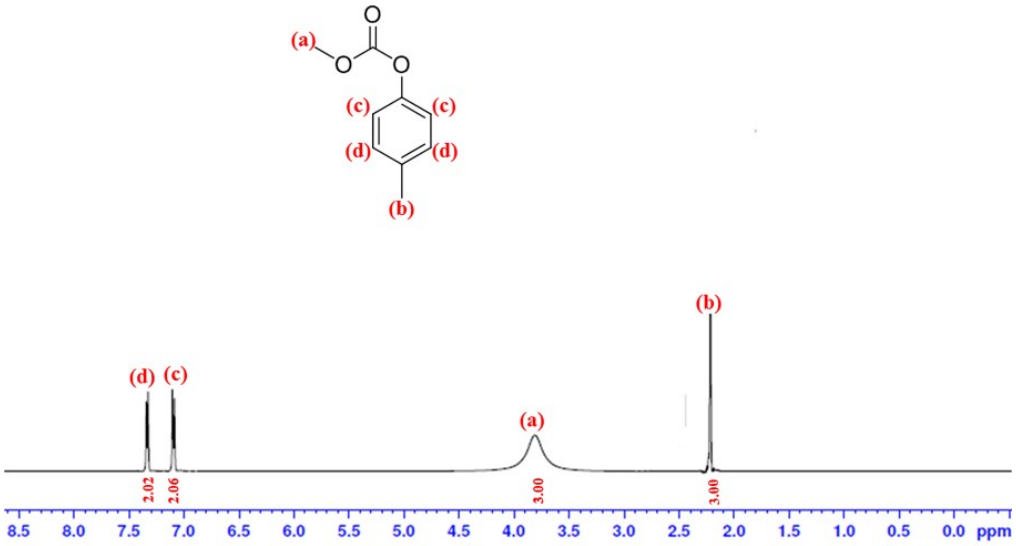


Figure S12. ^{1}H NMR spectra of methyl p-tolyl carbonate

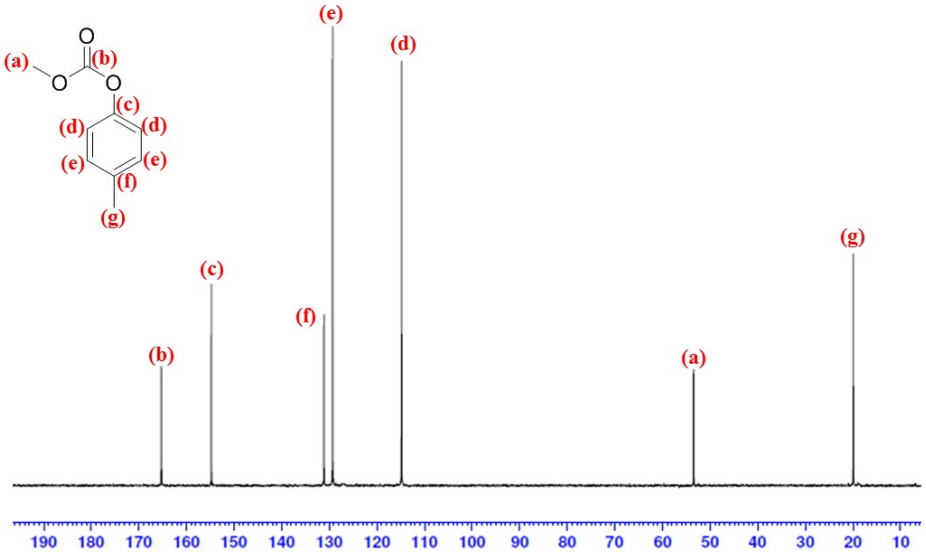


Figure S13. ^{13}C NMR spectra of methyl p-tolyl carbonate

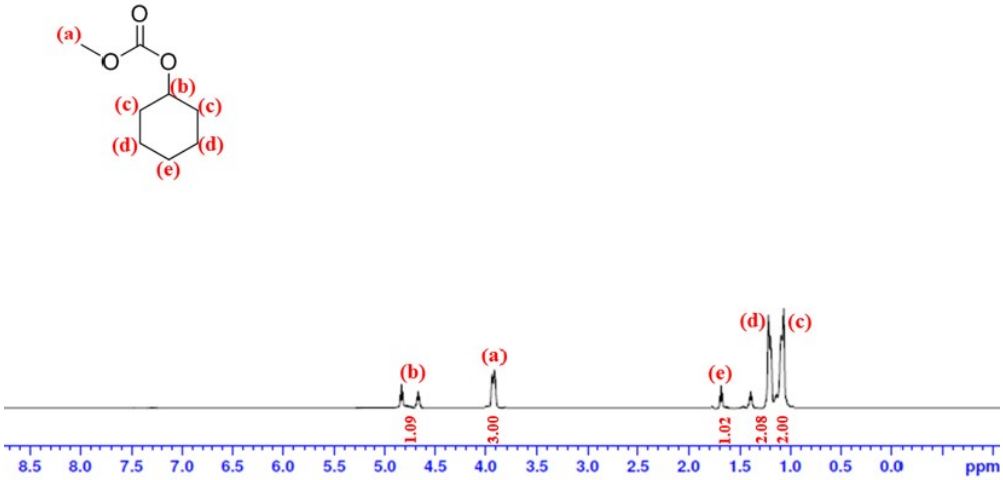


Figure S14. ^{1}H NMR spectra of cyclohexyl methyl carbonate

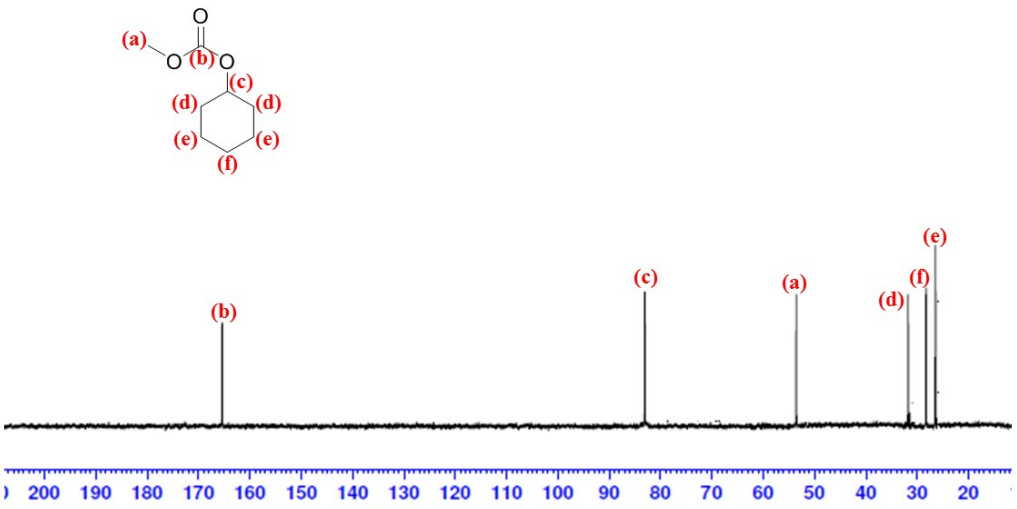


Figure S15. ^{13}C NMR spectra of cyclohexyl methyl carbonate

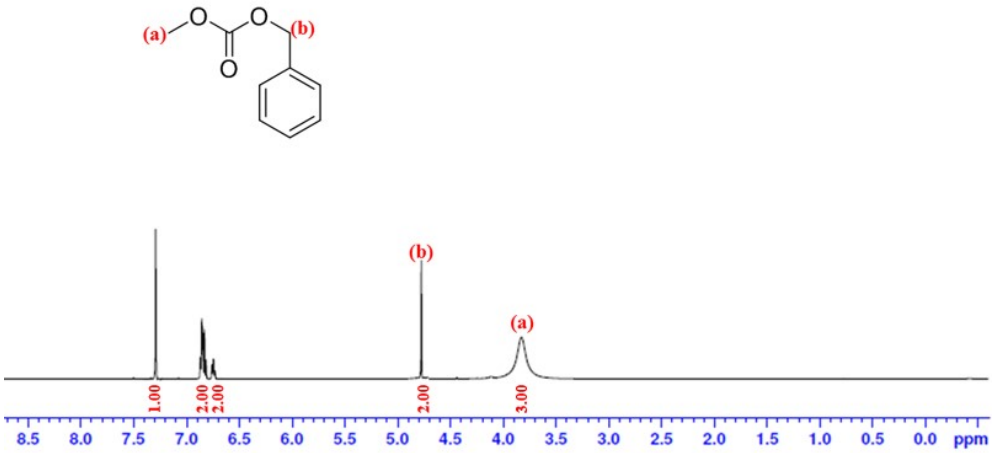


Figure S16. ^{1}H NMR spectra of benzyl methyl carbonate

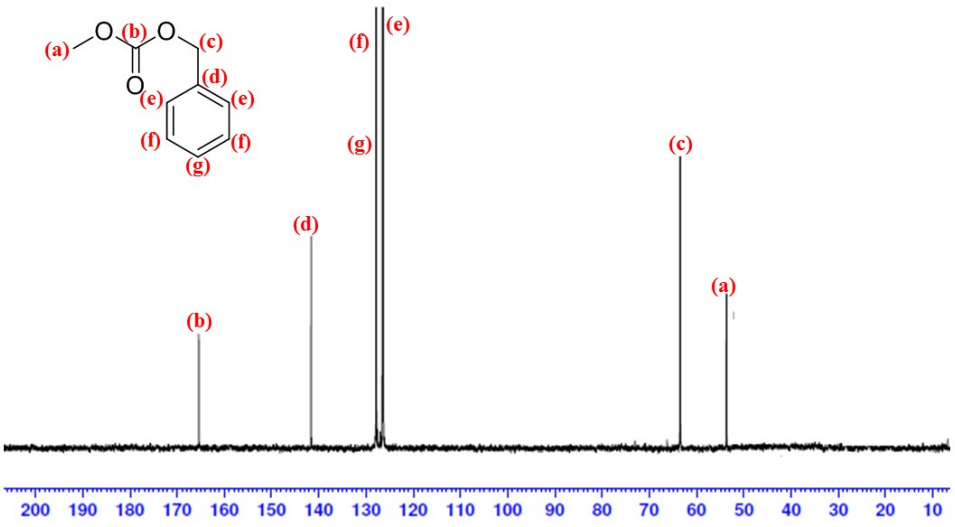


Figure S17. ^{13}C NMR spectra of benzyl methyl carbonate

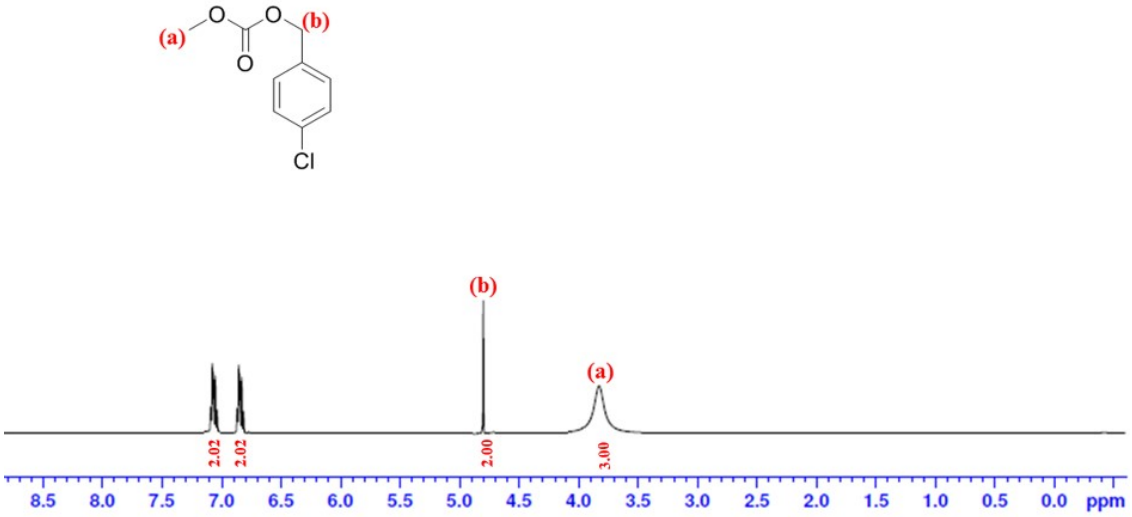


Figure S18. ^{1}H NMR spectra of 4-chlorobenzyl methyl carbonate

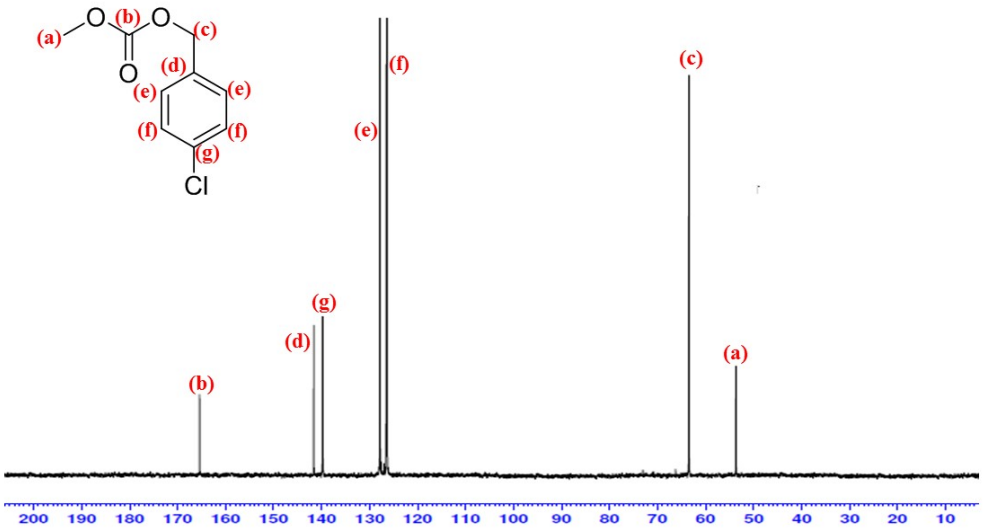


Figure S19. ^{13}C NMR spectra of 4-chlorobenzyl methyl carbonate

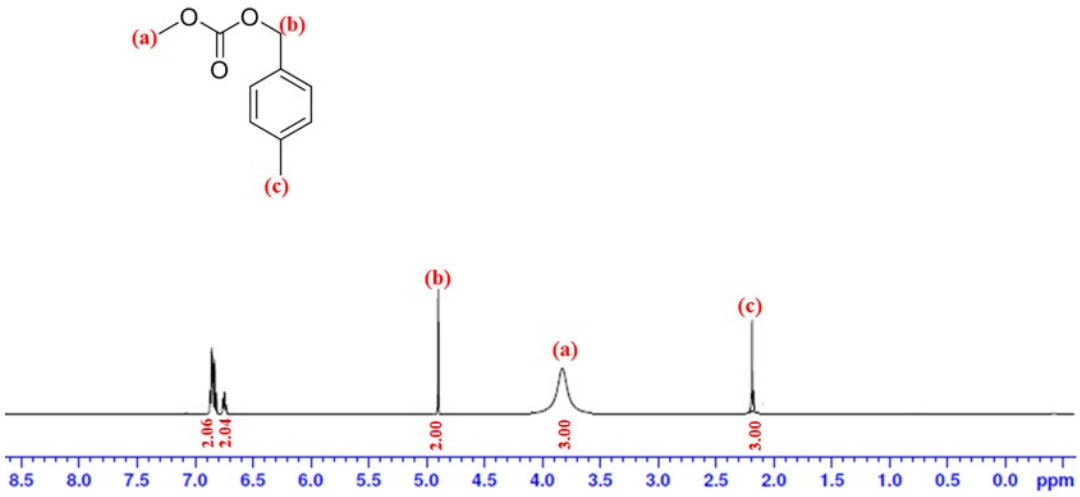


Figure S20. ^{1}H NMR spectra of methyl(4-methylbenzyl) carbonate

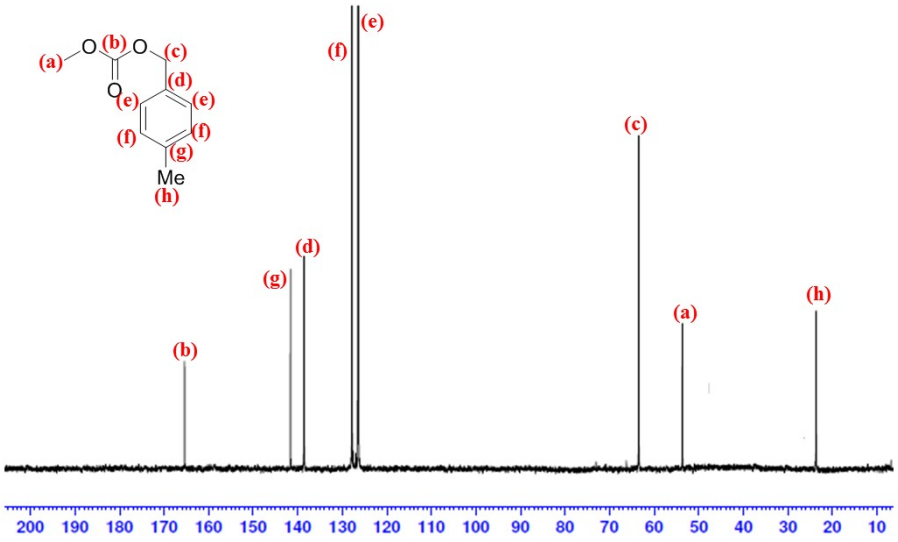


Figure S21. ^{13}C NMR spectra of methyl(4-methylbenzyl) carbonate

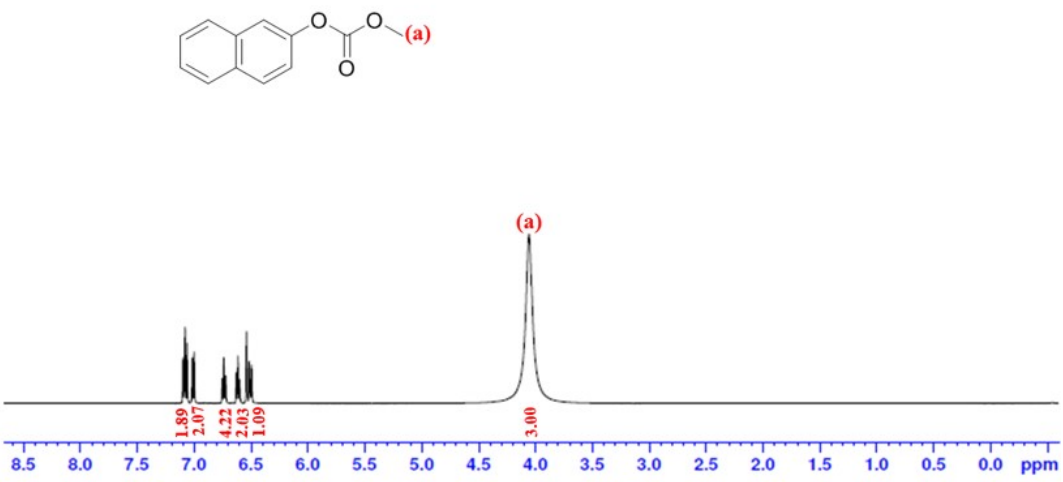


Figure S22. ^{1}H NMR spectra of methyl naphthalen-2-yl carbonate

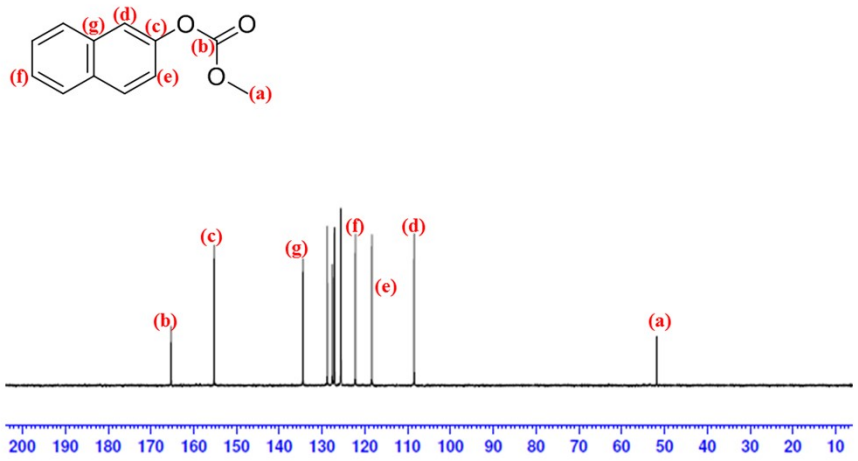


Figure S23. ^{13}C NMR spectra of methyl naphthalen-2-yl carbonate

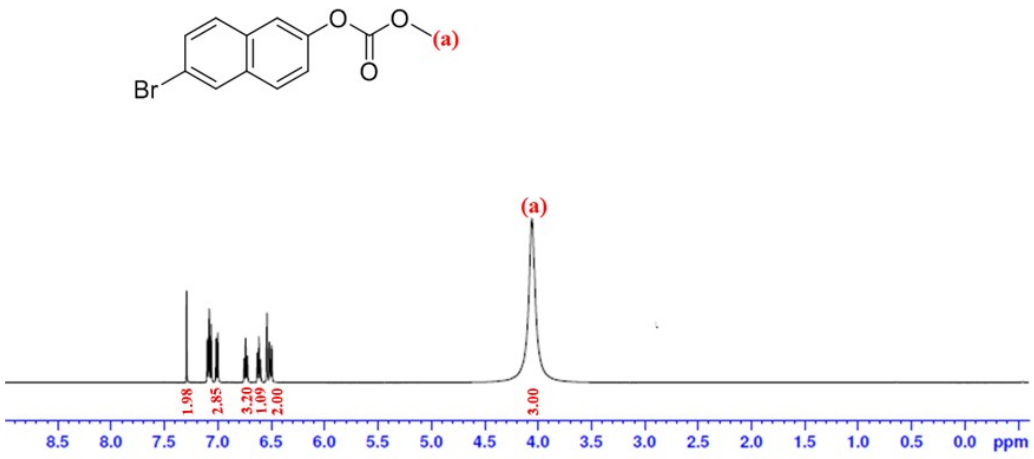


Figure S24. ^{1}H NMR spectra of 6-bromonaphthalen-2-yl-methyl carbonate

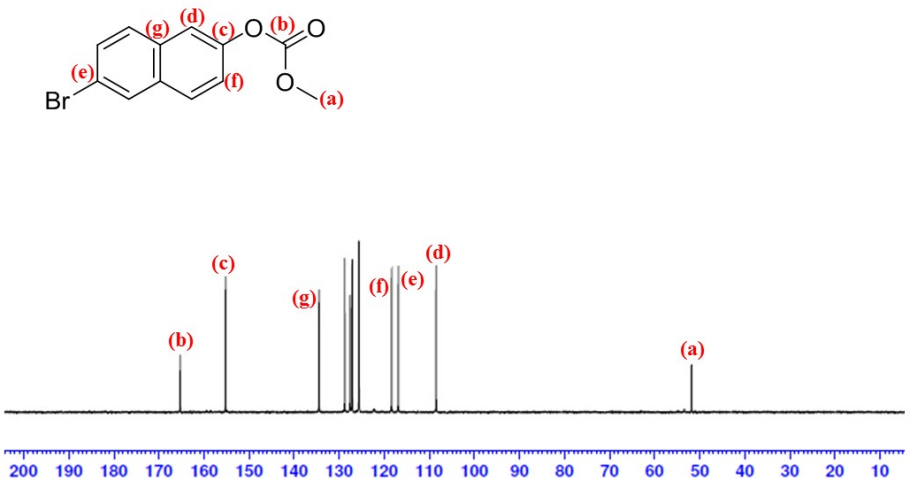


Figure S25. ^{13}C NMR spectra of 6-bromonaphthalen-2-yl-methyl carbonate

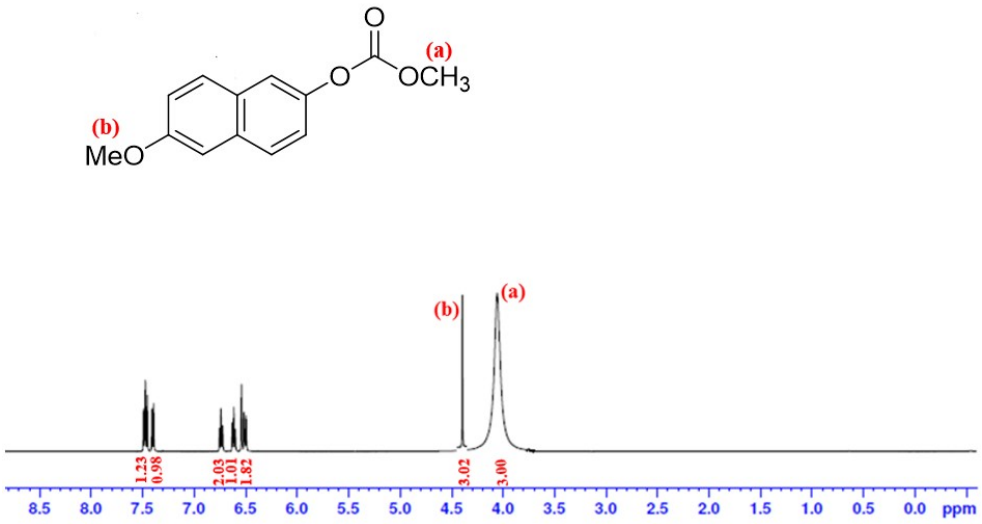


Figure S26. ^{1}H NMR spectra of 6-methoxynaphthalen-2-yl methyl carbonate

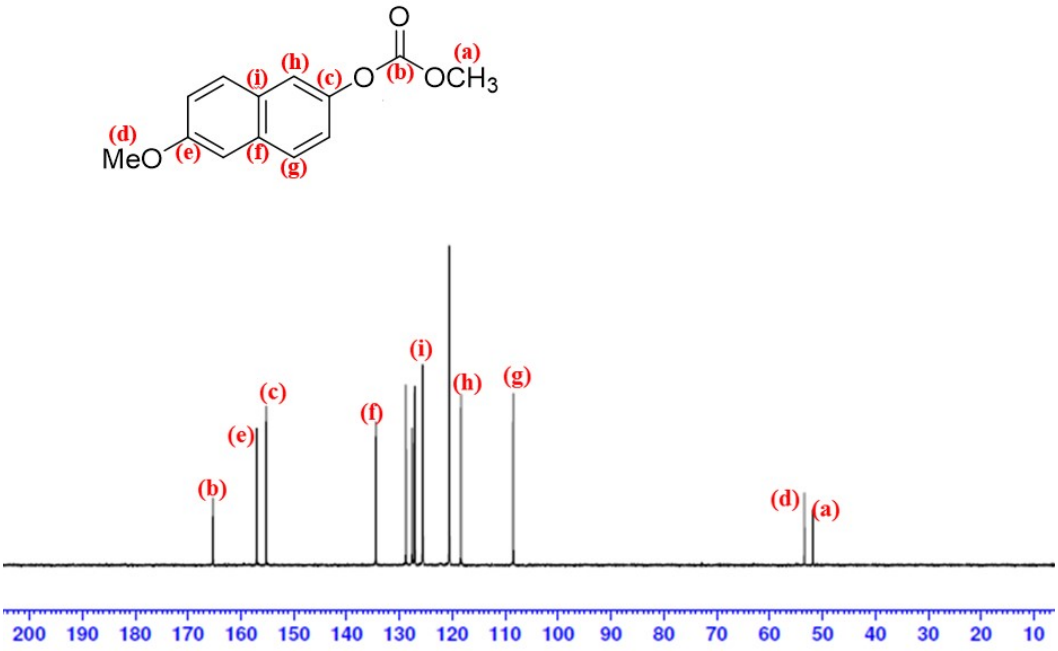


Figure S27. ^{13}C NMR spectra of 6-methoxynaphthalen-2-yl methyl

References:

1. Y. Zhao, D.G. Truhlar, Theor. *Chem. Acc*. 120 (2008) 215.
2. Gonzalez C, Schlegel HB An improved algorithm for reaction path following. *The Journal of Chemical Physics* 90 (1989) 2154-2161.
3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian09, Revision D.01, *Gaussian*, Inc.: Wallingford, CT, 2009.