Supporting information for:

Direct comparison of safer or sustainable alternative dipolar aprotic solvents for use in carbon-carbon bond formation

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Table S1. Physical properties of the selected aprotic solvents.

Solvent	MP /°C	BP /°C	FP /°C	α	β	π*	δ_D /MPa^{½}	δ_P /MPa^{½}	δ_H /MPa^{½}
1. Limonene	-74.0	175.0	49	0.00	0.00	0.24	17.2	1.8	4.3
2. p-Cymene	-68.0	177.0	27	0.00	0.13	0.39	17.3	2.3	2.4
3. CPME	-140.0	106.0	-1	0.00	0.53	0.42	16.7	4.3	4.3
4. Toluene	-93.0	110.6	4	0.00	0.12	0.50	18.0	1.4	2.0
5. NBP	<-75.0	241.0	108	0.00	0.92	0.77	17.5	9.9	5.8
6. MeCN	-46.0	81.2	2	0.35	0.37	0.80	15.3	18.0	6.1
7. GVL	-31.0	207.0	100	0.00	0.60	0.83	16.8	11.4	6.7
8. DMAc	-20.1	166.0	70	0.00	0.73	0.85	16.8	11.5	9.4
9. DMF	-60.4	153.0	58	0.00	0.71	0.88	17.4	13.7	11.3
10. NMP	-24.4	202.0	96	0.00	0.75	0.90	18.0	12.3	7.2
11. PC	-55.0	242.0	132	0.00	0.38	0.90	20.0	18.0	4.1
12. Cyrene	<-18.0	203.0	61	0.00	0.61	0.93	18.7	11.9	6.6
13. Sulfolane	28.4	287.0	177	0.00	0.30	0.96	17.8	17.4	8.7
14. DMSO	18.6	189.0	95	0.00	0.74	1.00	18.4	16.4	10.2

Key: MP, melting point; BP, boiling point; FP, flash point; α, hydrogen bond donating ability; β, hydrogen bond accepting ability; π*, dipolarity; δ_D, Hansen dispersion force solubility parameter; δ_P, Hansen dipolarity solubility parameter; δ_H, Hansen hydrogen bonding solubility parameter.

Table S2. Initial rate values of Heck and Baylis-Hillman reactions used to construct the linear solvation energy relationships.

Solvent	Initial rate (mol/L min.)		
	Heck reaction		Baylis-Hillman reaction
	Methyl acrylate	Styrene	Methyl acrylate
1. Limonene	1.93x10^{-5}	4.41x10^{-5}	-
2. p-Cymene	1.89x10^{-5}	5.08x10^{-5}	2.58x10^{-5}
3. CPME	2.36x10^{-5}	6.06x10^{-5}	2.32x10^{-5}
4. Toluene	2.92x10^{-5}	6.11x10^{-5}	-
5. NBP	8.87x10^{-4}	1.97x10^{-4}	7.98x10^{-5}
6. MeCN	1.31x10^{-4}	1.39x10^{-4}	7.83x10^{-5}
7. GVL	7.96x10^{-4}	2.80x10^{-4}	8.00x10^{-5}
8. DMAc	5.03x10^{-4}	3.06x10^{-4}	8.07x10^{-5}
9. DMF	5.45x10^{-5}	2.09x10^{-4}	1.11x10^{-4}
10. NMP	5.46x10^{-4}	6.19x10^{-4}	7.72x10^{-5}
11. PC	5.65x10^{-4}	2.67x10^{-4}	2.47x10^{-4}
12. Cyrene	2.74x10^{-4}	3.83x10^{-4}	1.65x10^{-4}
13. Sulfolane	9.29x10^{-4}	3.01x10^{-4}	1.46x10^{-4}
14. DMSO	6.41x10^{-5}	2.23x10^{-4}	2.10x10^{-4}

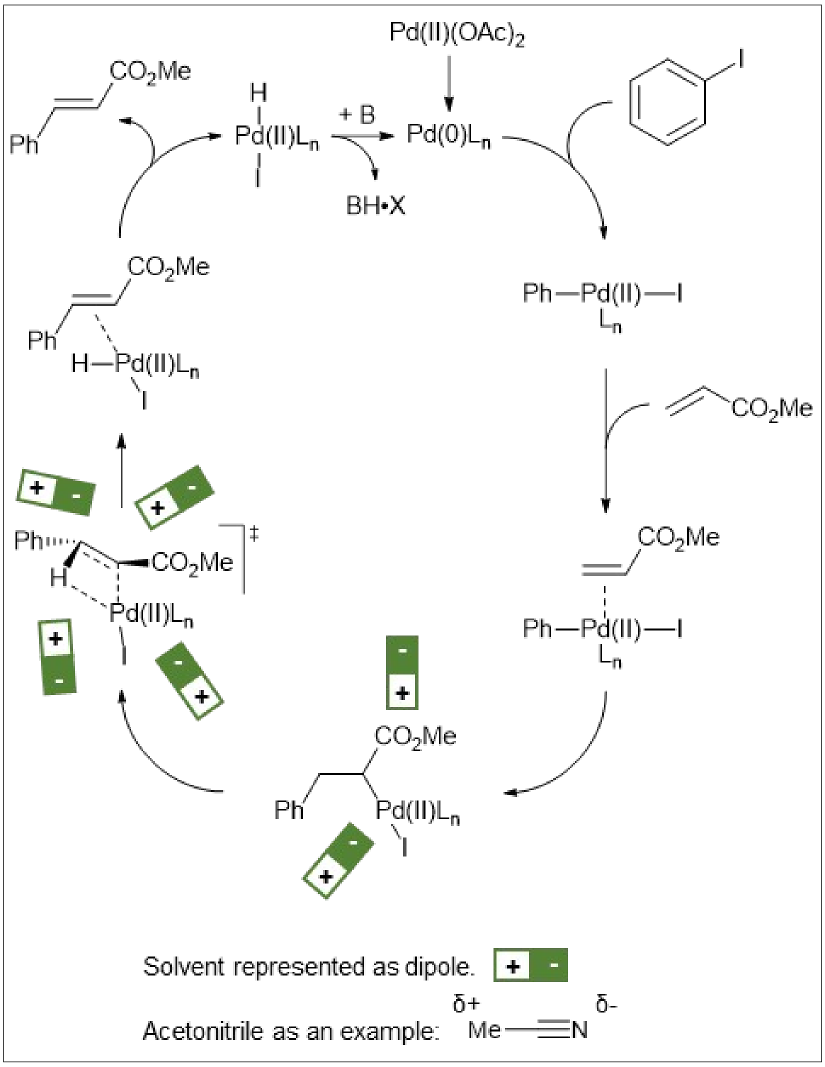

Figure S1. Representative Heck reaction mechanism indicating β-hydride elimination as the rate determining step and solvent organisation in the cybotactic region. L refers to ligands, which could be acetate, solvent, or auxiliary ligands (e.g. phosphines) if present.

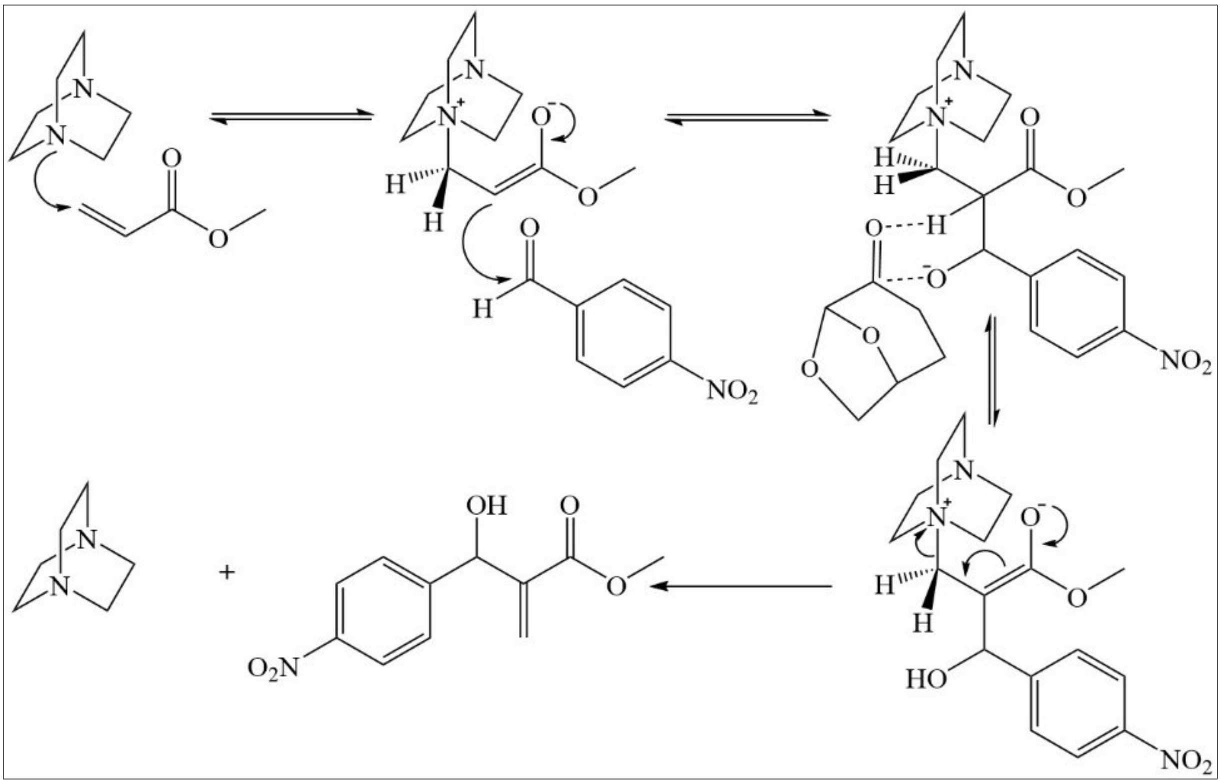

Figure S2. Schematic of Baylis-Hillman reaction mechanism with stabilisation of zwitterionic intermediate form of Cyrene.

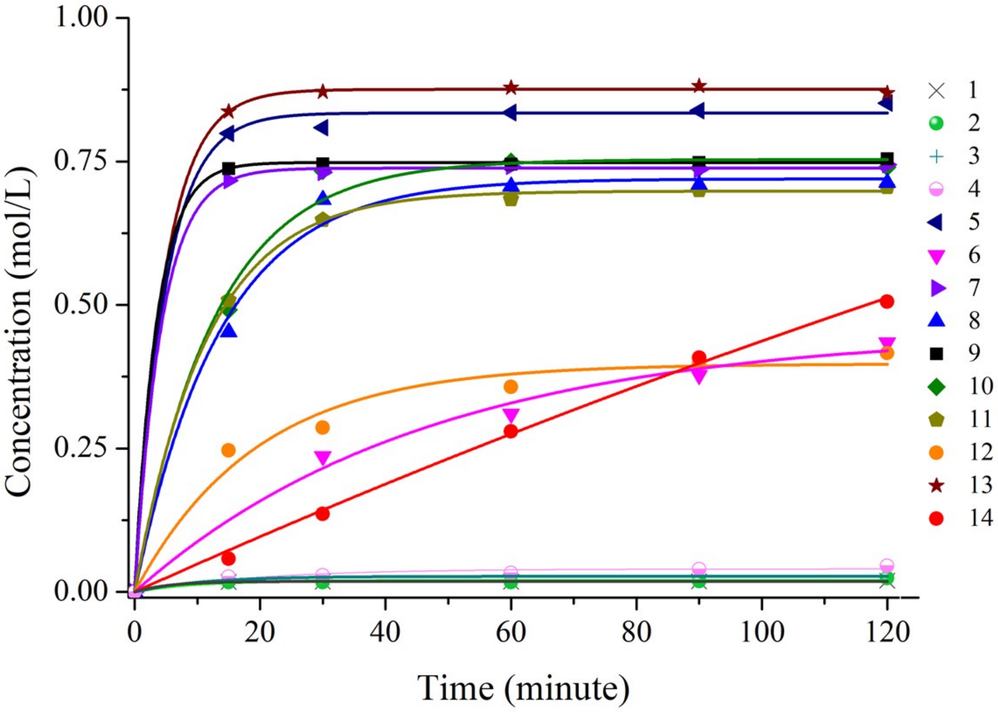

Figure S3. Time (minute) dependence of the product concentration (mol/L) of a Heck reaction of methyl acrylate.

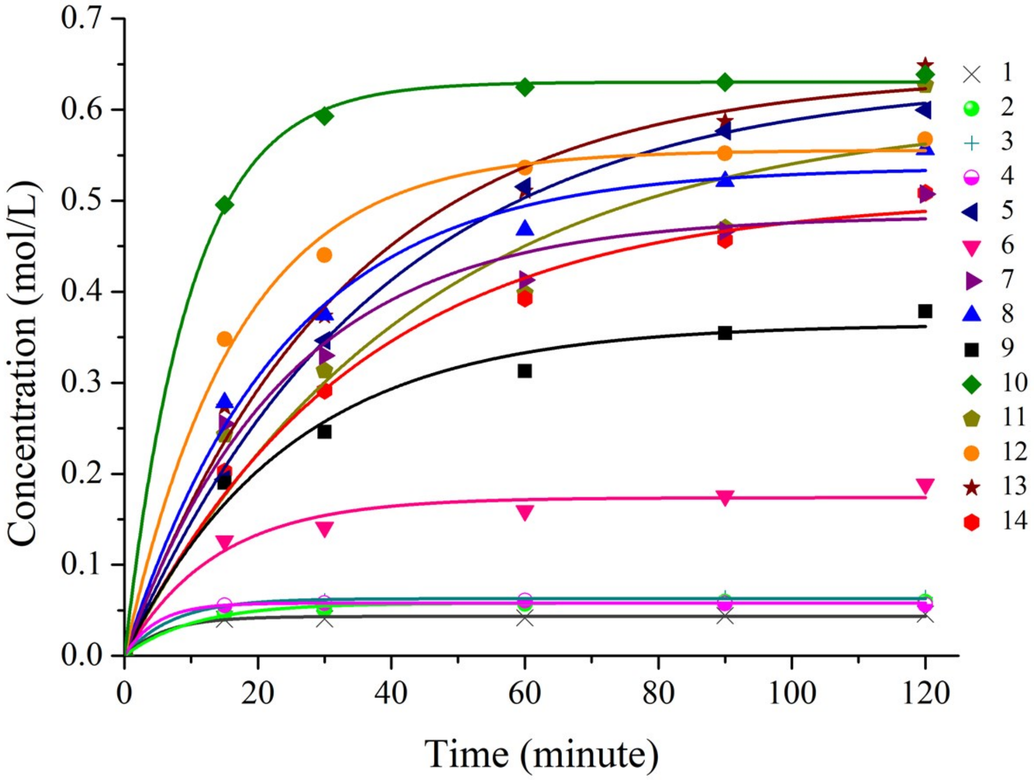

Figure S4. Time (minute) dependence of the product concentration (mol/L) of a Heck reaction of styrene.

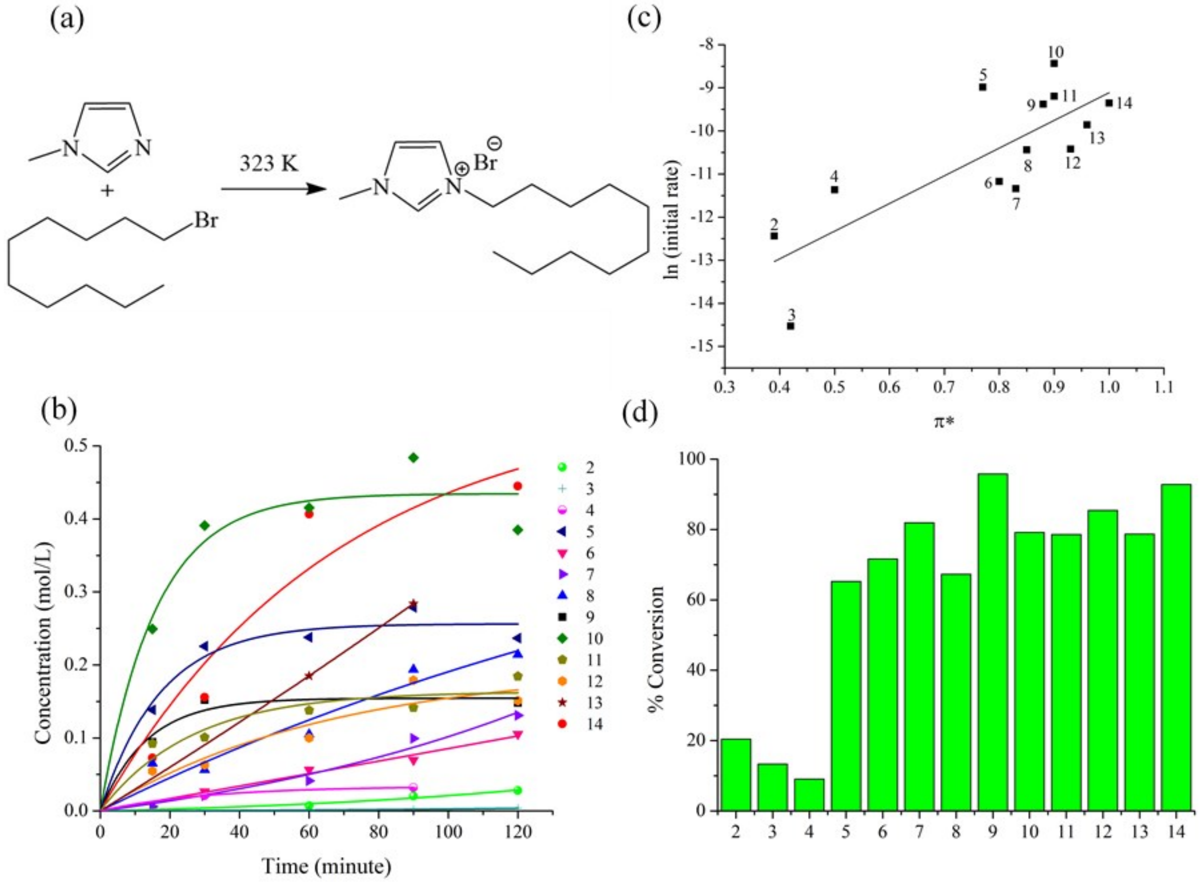

Figure S5. (a) scheme of Menshutkin reaction, (b) time (minute) dependence of the product concentration (mol/L), (c) linear solvation energy relationship and (d) conversion (%) of the Menshutkin.

Menshutkin reaction

To a solution of 1-methylimidazole (4 mmol) heated to 50 °C in the chosen solvent (4 mL) was added 1-bromodecane (4 mmol). The progression of the reaction as 1-decyl-3-methylimidazolium bromide was formed was monitored by ^{1}H-NMR spectroscopy (Figure S5). The correlation between natural logarithm of initial concentration and dipolarity (π*) was obtained as in previous reports.[1] NBP and PC exhibited higher initial rates of the reaction than that of the conventional solvents (DMF and DMSO) but were found to be inferior to NMP. In case of conversion, the reaction performed in GVL, PC and Cyrene provided a comparable conversion to NMP, but it was lower than in DMF, and DMSO. The reaction did not occur in limonene, due to its low dipolarity resulting in poor stabilisation of the transition state.[2]

References

1 J. Sherwood, H. L. Parker, K. Moonen, T. J. Farmer and A. J. Hunt, *Green Chem.*, 2016, **18**, 3990–3996.

2 F. P. Byrne, B. Forier, G. Bossaert, C. Hoebers, T. J. Farmer and A. J. Hunt, *Green Chem.*, 2018, **20**, 4003–4011.