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Electronic Supporting Information for

Ether formation through reductive coupling of ketones or aldehydes catalyzed by a mesoionic carbene iridium complex

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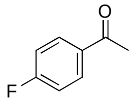
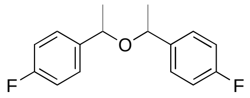
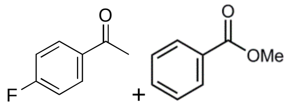
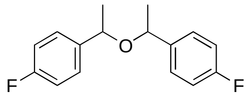
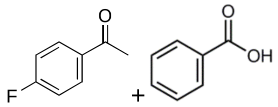
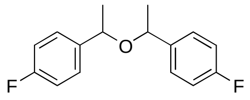
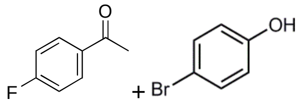
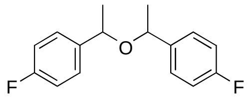
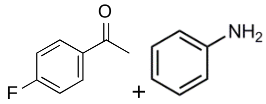
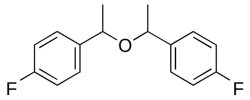
Content

Table S1. Functional group tolerance exploited by converting fluoroacetophenone in the presence of various functional groups a)

entry	substrate	conversion	Ether	yield
1		>99%		90%
2		>99%		90%
3		20%		0%
4		80% (100%) b)		28% (39%) b)
5		0%		0%

a) Conditions identical to those described in Table 2; the second substrate was added in stoichiometric quantity with respect to fluoroacetophenone; conversions and ^{1}H NMR spectroscopic yields determined after 5 min using anisole as an internal standard; b) after 15 min.

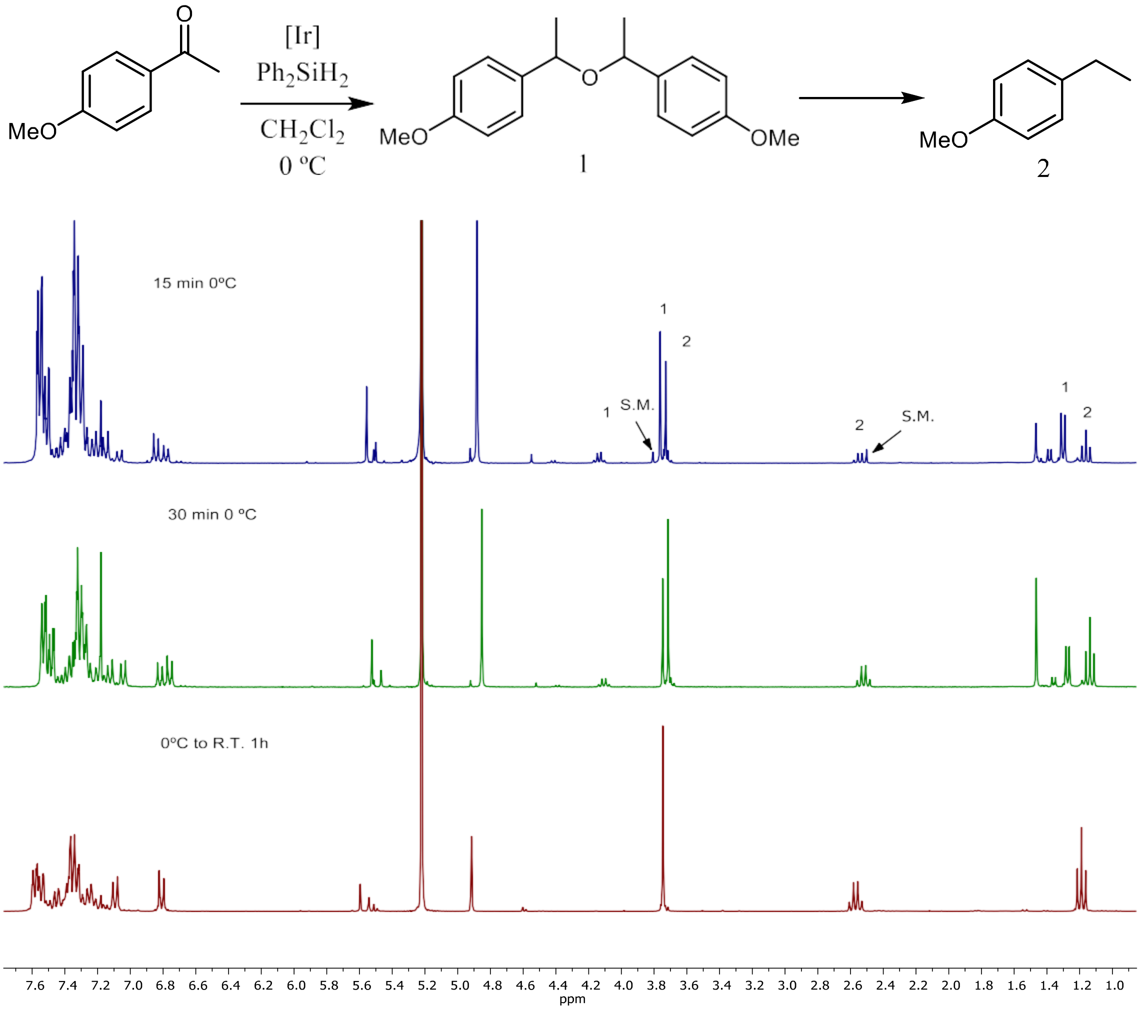
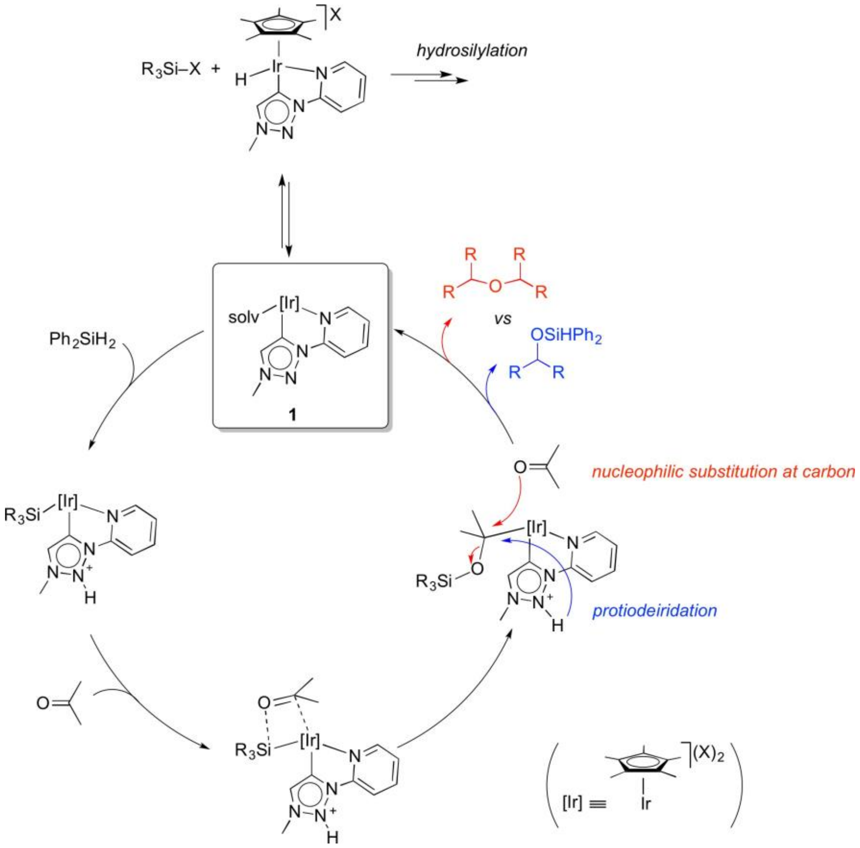


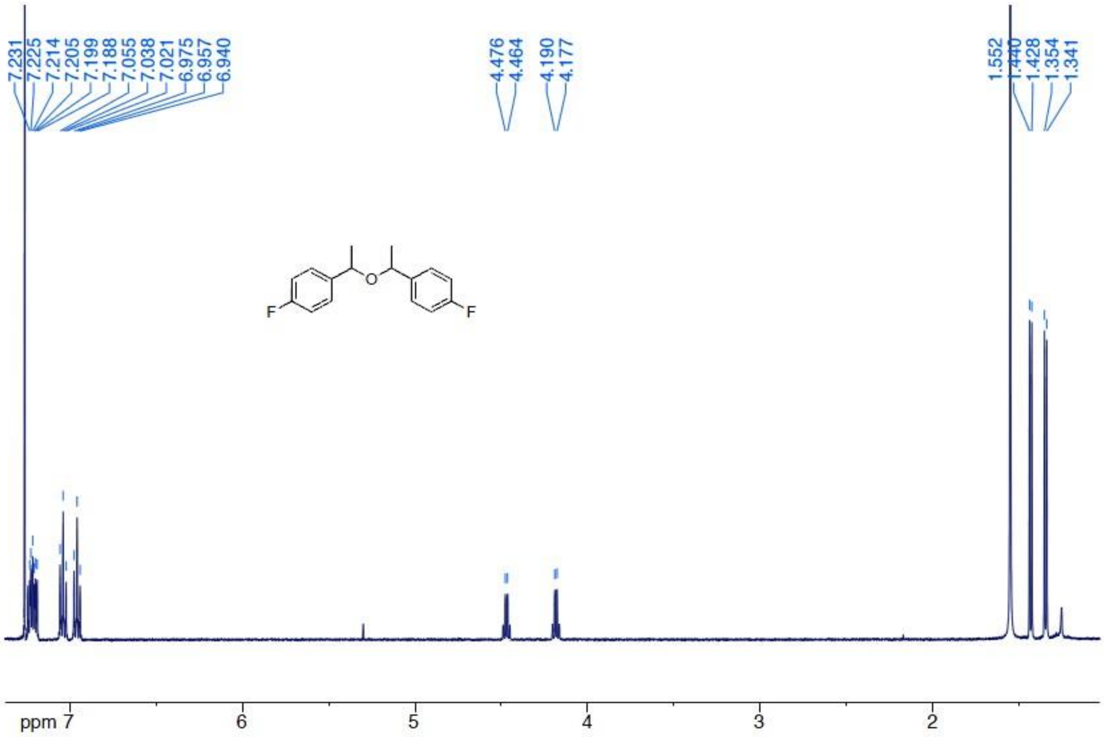
Fig. S1. Monitoring of the low temperature stepwise conversion of 4-MeO-acetophenone to ether and subsequently to dehydrated ethyl anisole. Reaction performed at 0 ºC and ^{1}H NMR spectra recorded after 15 (blue), 30 (green), and 60 min (red). At room temperature, the reaction is complete within 5 min and yields ethyl anisole as the exclusive product.

Scheme S1. Tentative proposal of a catalytic cycle. Note that protonation may occur on the triazole N2 or on C4 (with concomitant dearomatization). The hydride may be outside the catalytic cycle (as suggested here) or part of the catalytic cycle, in any case, combination of the hydride species and the N2-protonated species is a plausible mechanism for the formation of H2 as observed in all reactions.

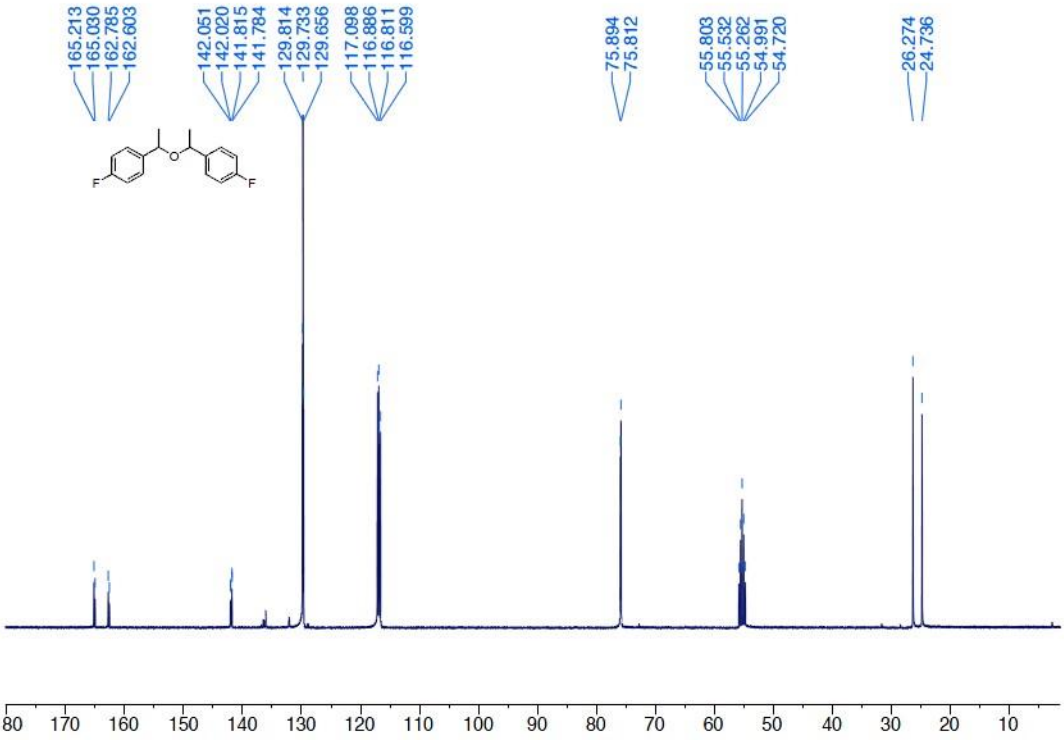


NMR spectra of reported products

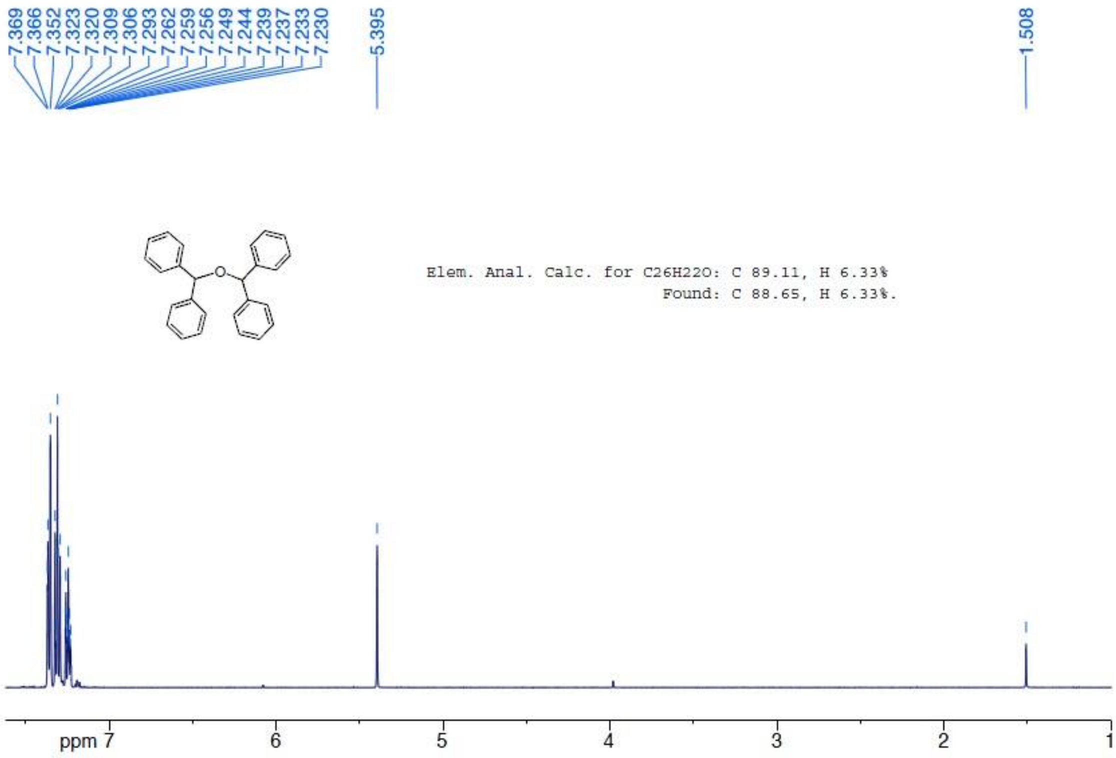
Bis(4-fluoro-α-methyl-benzyl)ether: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.22-7.17 (m, 4H, H$_{Ar}$), 7.04 -7.02(m, 2H, H$_{Ar}$), 6.91-6.80 (d, 2H, H$_{Ar}$), 4.47 (q, 1H, $^{3}J_{HH}$ = 6.5 Hz, H$_{benz}$), 4.18 (q, 1H, ^{3}J$_{HH}$ = 6.5 Hz, H$_{benz}$), 1.43 (d, 3H, $^{3}J_{HH}$ = 6.5 Hz, Me), 1.34 (d, 3H, $^{3}J_{HH}$ = 6.5 Hz, Me) ppm.



^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$): δ 165.2, 165.0, 162.8, 162.6 (2 CF), 142.0, 141.8 (C$_{Ar}$), 129.8, 129.7 (4 CH$_{Ar}$), 117.1, 116.9, 116.8, 116.6 (4 CH$_{Ar}$), 75.9, 75.8 (2 CH$_{benz}$), 26.3, 24.7 ppm (2 CH$_3$).

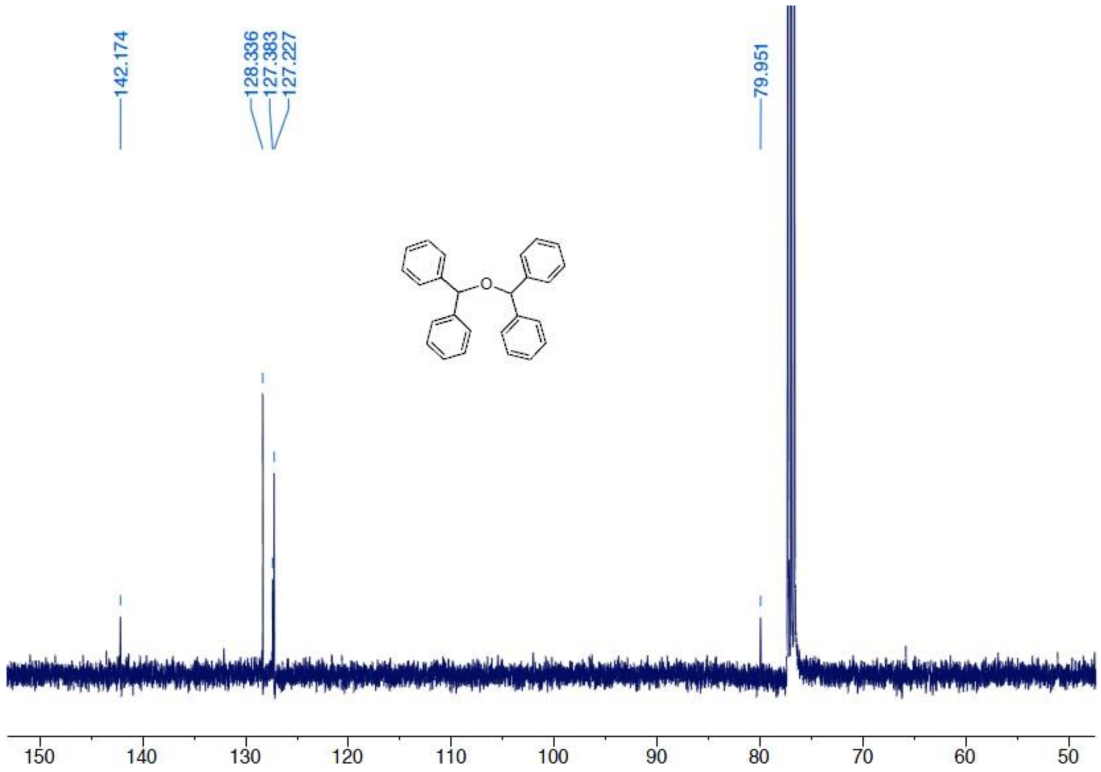


Bis(diphenylmethyl)ether:[S1] ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.38-7.23 (m, 20H, H$_{Ar}$), 5.40 (s, 2H, H$_{Benz.}$) ppm.

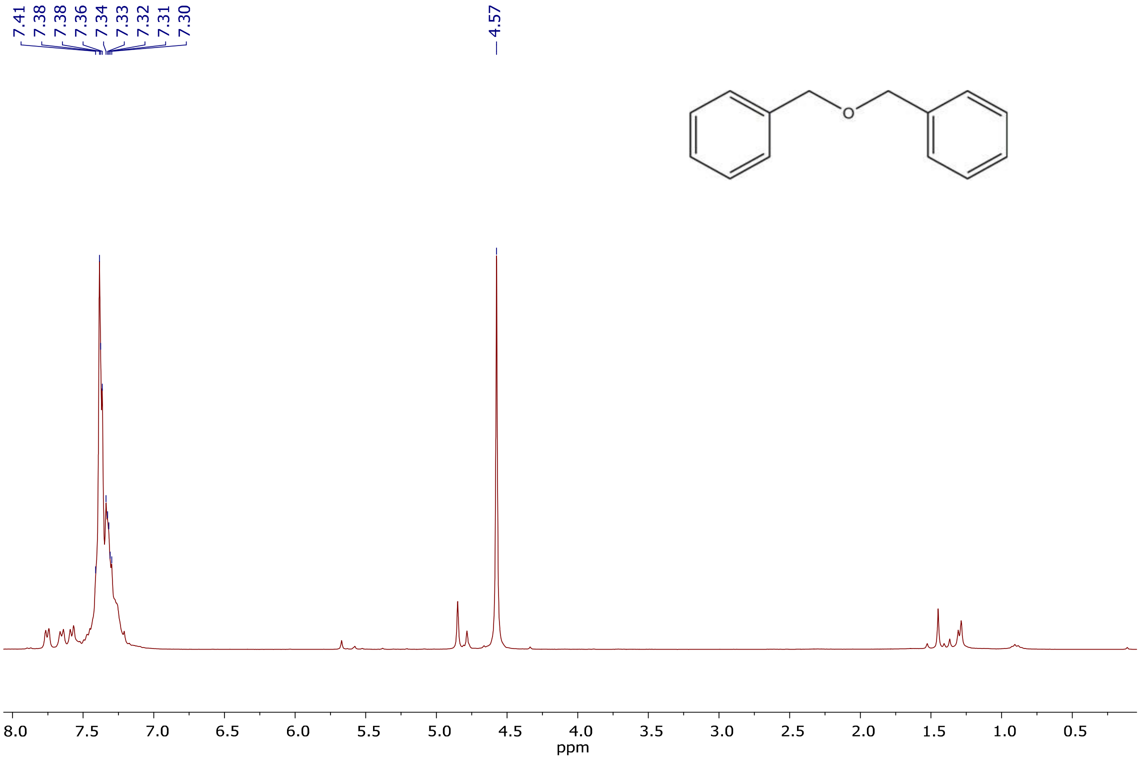


Elem. Anal. Calc. for $C_{26}H_{22}O$: C 89.11, H 6.33%
Found: C 88.65, H 6.33%.

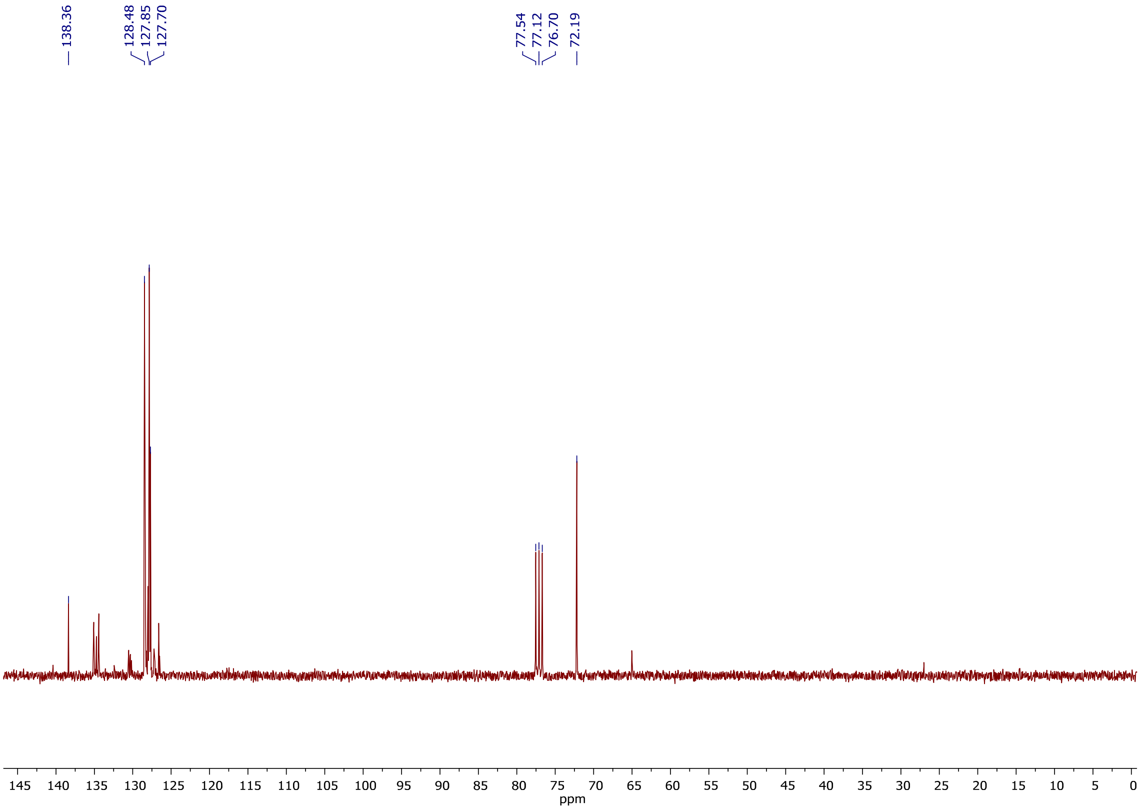
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 142.2 (C$_{Ar}$), 128.3, 127.4, 127.2 (CH$_{Ar}$), 79.9 (CH$_{Benz}$).



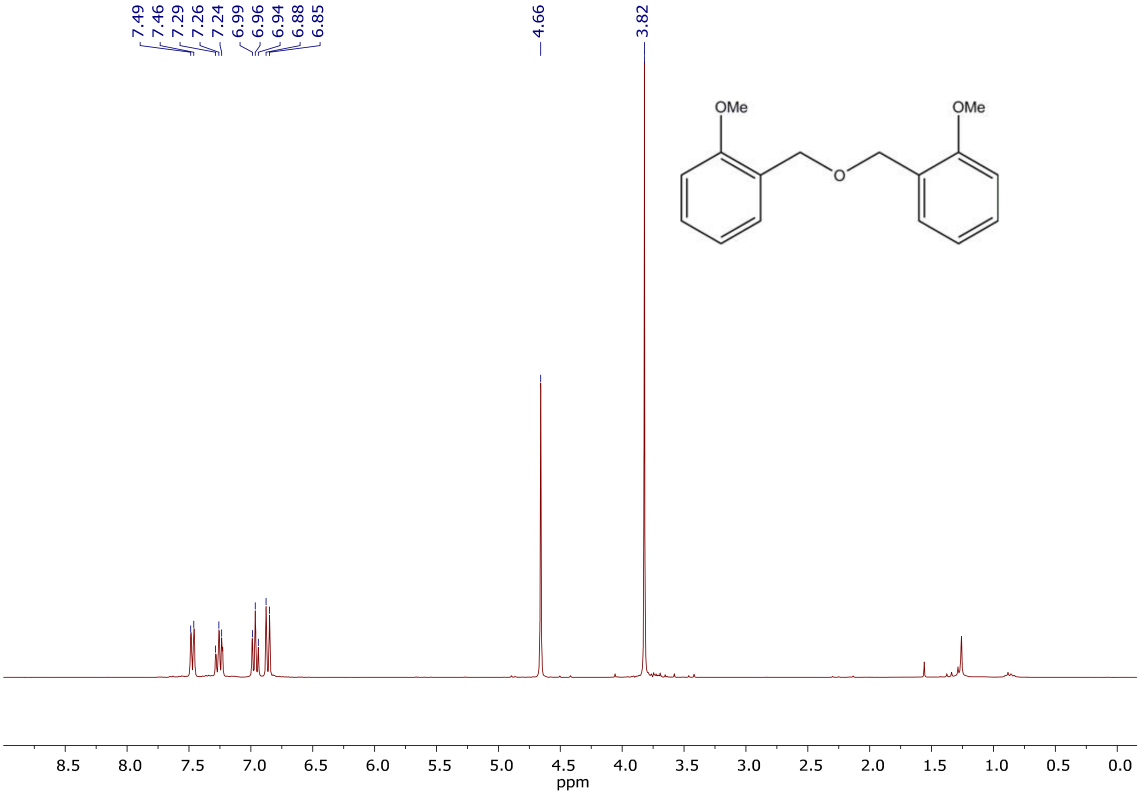
Dibenzyl ether:[S2] ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41-7.30 (m, 10H, H$_{\mathrm{Ar}}$), 4.57 (s, 4H, H$_{\mathrm{benz}}$) ppm.



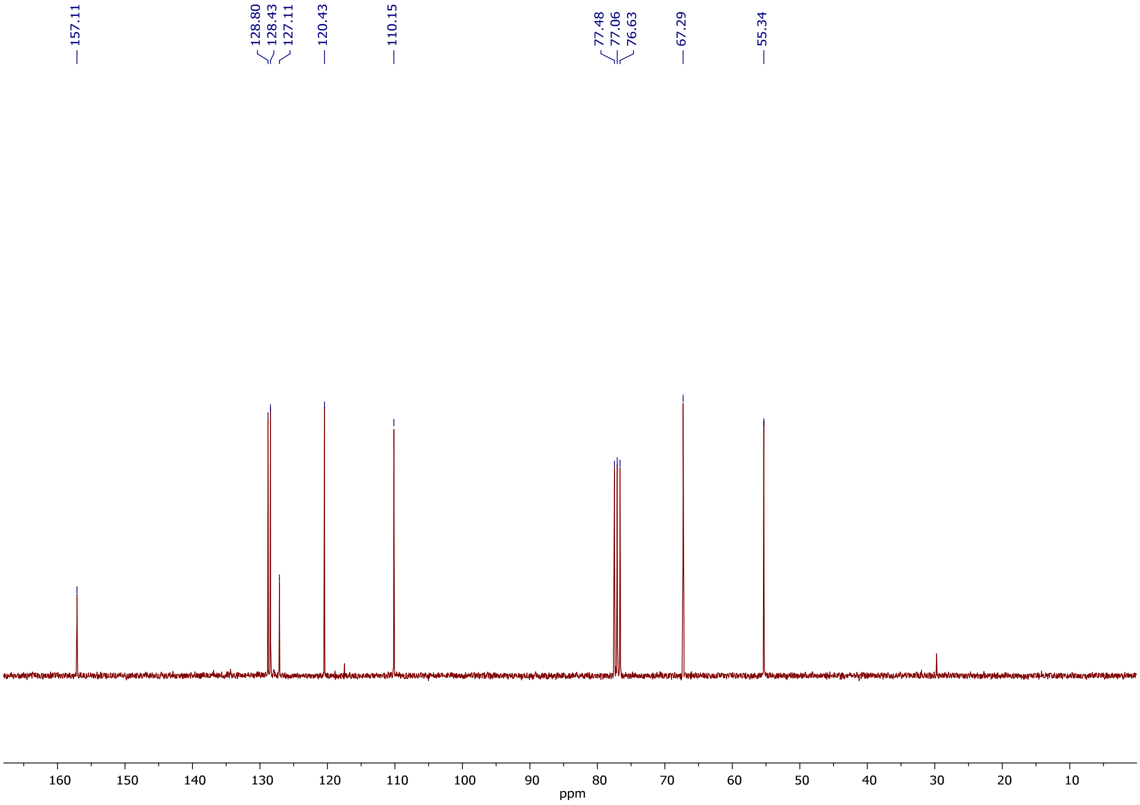
^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 138.4 (C$_{\mathrm{Ar}}$), 128.5, 127.9, 127.7 (CH$_{\mathrm{Ar}}$), 72.2 (CH$_{\mathrm{Benz}}$) ppm.



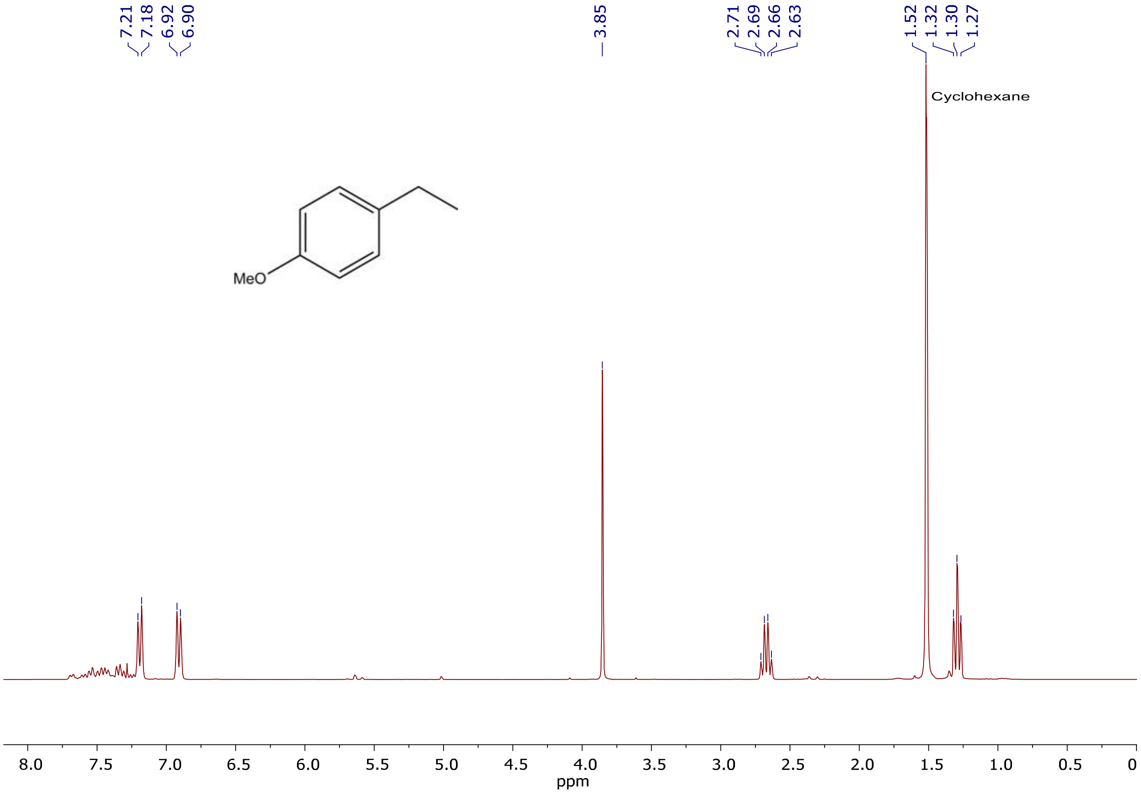
Bis(2-methoxy benzyl) ether: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.47 (d, 2H, H$_{Ar}$), 7.26 (t, 2H, HAr), 6.96 (t, 2H, HAr), 6.87 (d, 2H, HAr), 4.66 (s, 4H, H$_{benz}$), 3.82 (s, 6H, OMe) ppm.



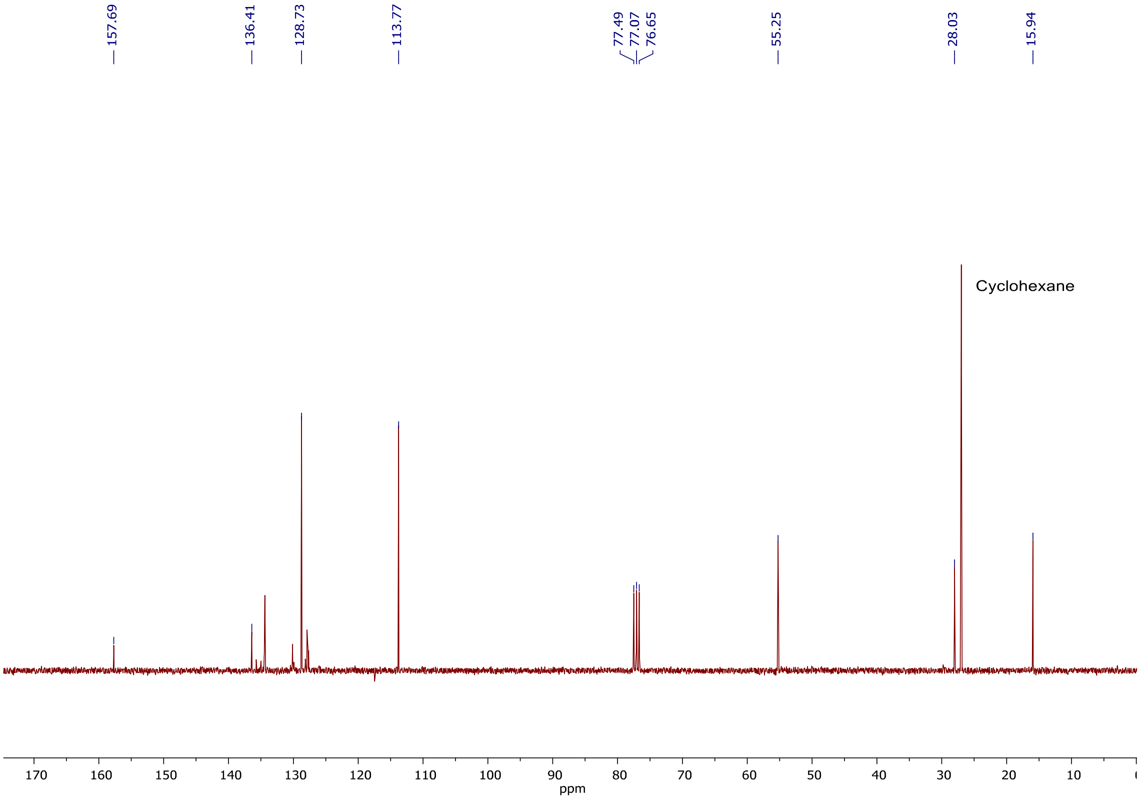
^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 157.1 (C$_{OMe}$), 128.8, 128.4, 120.4, 110.2 (CH$_{Ar}$), 127.1 (C$_{Ar}$), 67.3 (CH$_{Benz}$), 55.3 (OMe) ppm.



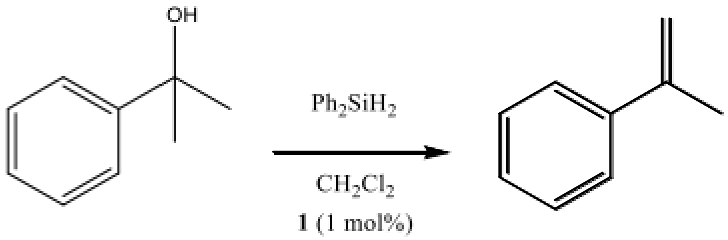
***p*-ethyl anisole**:[S3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H_{Ar}), 6.91 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H_{Ar}), 3.85 (s, 3H), 2.67 (q, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2CH_3), 1.30 (t, J = 7.3 Hz, 3H) ppm.

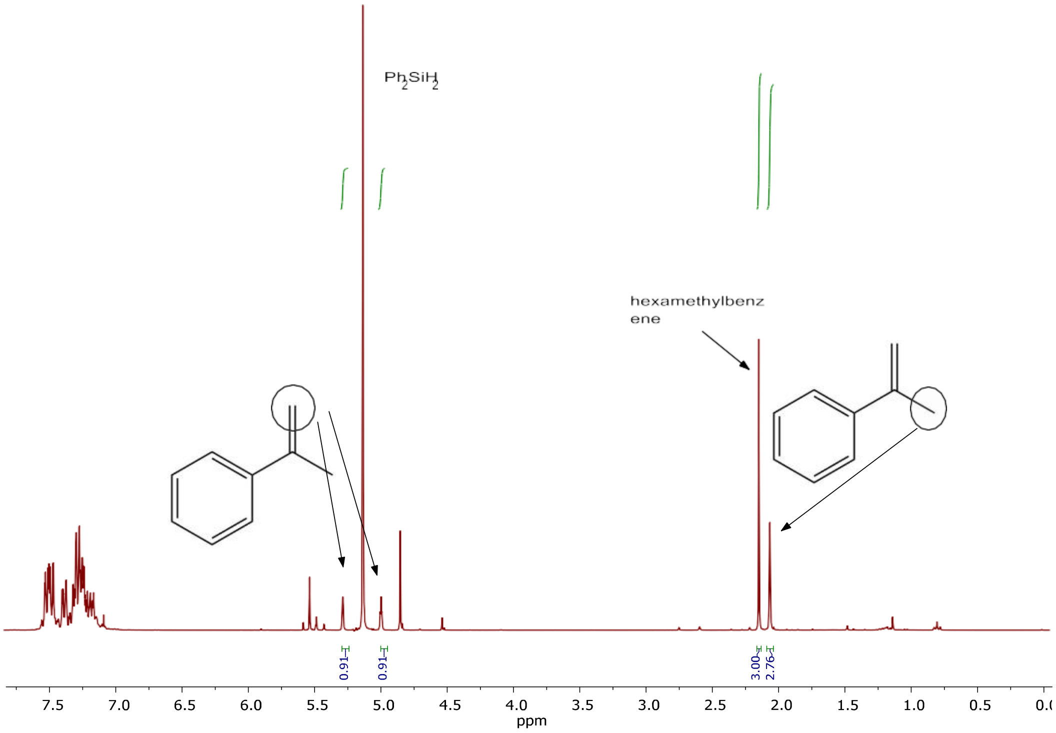


^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7 (C_{OMe}), 136.4 (C_{Ar}), 128.7, 113.8 (CH_{Ar}), 55.3 (OMe), 28.0 (CH_2CH_3), 15.9 (CH_2CH_3) ppm.



^{1}H NMR (300 MHz, $CDCl_3$) of the reaction crude. We were not able to isolate the formed α-methyl styrene. 100% conversion, 92% yield. Hexamethylbenzene as an internal standard.





References

S1. M. Barbero, S. Bazzi, S. Cadamuro and S. Dughera, *Eur. J. Org. Chem.* 2009, 430.

S2. G. Molander and B. Canturk, *Org. Lett.* 2008, **10**, 2135.

S3. *Commercially available from Aldrich.*