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Olefin Metathesis, *p*-Cresol, and the Second Generation Grubbs Catalyst: Fitting the Pieces

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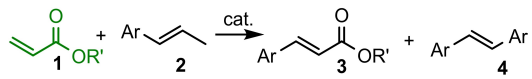
p-Cresol as additive to the Grubbs second generation catalyst (**GII**) allows the cross-metathesis of acrylates with prop-1-en-1-ylbenzenes under conditions that only give the prop-1-en-1-ylbenzene self-metathesis product in the absence of cresol. NMR and IR spectroscopy, MALDI-TOF MS and XPS supported the formation of a ruthenium benzylidene with hydrogen bonds between *p*-cresol and the chloride ligands of **GII**. XPS furthermore confirmed *p*-cresol to increase the binding energies of the **GII** Ru $3d_{5/2}$, $3d_{3/2}$, $3p_{3/2}$ and $3p_{1/2}$ photoelectron lines, whereas ^{1}H NMR spectroscopy indicated the carbene carbon and hydrogen to be shielded. It is thus postulated that *p*-cresol allows for more facile interaction between electron-deficient compounds and the ruthenium benzylidene by decreasing the electron density on the metal center and increasing the electron density on the carbene.

Introduction

The cross-metathesis (CM) of acrylates (**1**) with alkenes such as prop-1-en-1-ylbenzenes (**2**) have the potential to give access to functionalized value-added products (Scheme 1). This includes the active sunscreen ingredient 2-ethylhexyl 4-methoxycinnamate (known as octyl methoxycinnamate or OMC in the cosmetic industry) (**3 a**) (Scheme 2).[1,2] Electron deficient α,β-unsaturated carbonyl compounds such as acrylates (**1**) are poor metathesis substrates, though, and this transformation is not industrially viable yet.

In 2005, Forman and Tooze reported on the beneficial effect of phenols on olefin metathesis catalyzed by the Grubbs first (**GI**) and second generation (**GII**) catalysts (Figure 1a).[3,4] Based on NMR and UV-Vis spectroscopy, GC and DFT calculations, Forman et al.[3,4] postulated that phenols are involved in hydrogen bonds with the chloride ligands of the catalyst (**5**), thus increasing the Ru-PR_3 dissociation energies and slowing down initiation (Figure 1b). It was also proposed that the PCy_3, once dissociated from the catalyst, is captured by phenol to form a species of the type $(PhOH)_nPCy_3$ (**7**). This was postulated to result in an increase in the concentration of the 14-electron intermediate (**6**) and consequently enhanced reaction rates with the olefin substrate. Hydrogen bonds with the chloride ligands were also proposed to increase the electrophilicity of the carbene carbon, thus activating it for reaction with an olefin, whereas a hemi-labile phenol-ruthenium interaction (**8**/**9**) would stabilize the 14-electron mediate (**6**) and increase the catalyst lifetime.



Scheme 1. The cross-metathesis of acrylates (**1**) and prop-1-en-1-ylbenzenes (**2**).

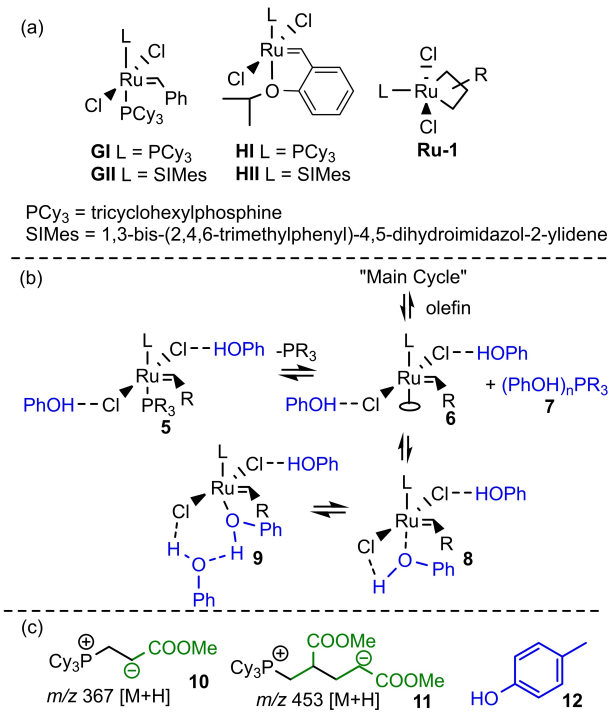


Figure 1. (a) Grubbs and Hoveyda metathesis catalysts, an intermediate ruthenacyclobutane (**Ru-1**). Proposals by Forman et al. [3,4] and Fogg et al. [5,6] for the formation of (b) hydrogen bonds between phenols and the chloride ligands of the catalyst and (c) 1,4-addition of PCy_3 to acrylates to form enolates such as **10** and **11** which may be protonated by phenols.

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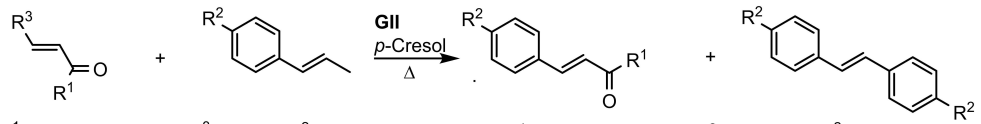
Motivated by the popularity and affordability of Grubbs II catalyst (**GII**), the Fogg group[5,6] revisited the beneficial effect of *p*-cresol (**12**) on **GII** catalyzed cross-metathesis. Fogg and co-workers[5,6] demonstrated that the phosphine, once dissociated from **GII**, is prone to 1,4-addition to acrylates (**1**), thus generating enolates such as **10** and **11** (Figure 1c). These zwitterions were postulated to deprotonate the intermediate ruthenacyclobutane (**Ru-1**) and the beneficial effect of *p*-cresol (**12**) was ascribed to the phenol protonating the enolates (e.g. **10** and **11**), thereby protecting the ruthenacyclobutane (**Ru-1**) (Figure 1a) against decomposition.

The Forman group[3,4] reported pronounced effects of *p*-cresol (**12**) on the cross-metathesis of terminal olefins and acrylates (**1**) (2 eq.) at low **GII** load (0.00625–0.10 mol%) and 50 °C. Using an excess of methyl acrylate (**1 b**) (6 eq.) and 0.5 to 2 mol% of **HII** catalyst (Figure 1a), the Fogg group[7] was able to obtain excellent selectivity towards the cross-metathesis of acrylates (**1**) and phenylpropenoids in dichloroethane at 70 °C. Fogg and co-workers[6] also prepared the cross-metathesis product of anethole (**2 a**) and 2-ethylhexyl acrylate (**1 a**) (4 eq.), 2-ethylhexyl 4-methoxycinnamate (**3 a**), in good yield in a reaction catalyzed by **GII** (1 mol%) in 1,2-dichloroethane at 70 °C, and furthermore recorded an increase in the cross-metathesis yield (**3 a**) (96% vs. 85%) and decrease in the formation of 4,4′-dimethoxystilbene (**4 a**), originating from self-metathesis (SM) of the anethole (**2 a**) (*structures in* Table 1) (2% vs. 11%), when *p*-cresol (**12**) or phenol-functionalized resin was added.

In the current project, it was noticed that (*E*)-stilbene (**4 b**), formed in quantitative yield when (*E*)-prop-1-en-1-ylbenzene (**2 b**) (1 eq.) and methyl acrylate (**1 b**) (2 eq.) were refluxed in dichloromethane (ca. 40 °C) in the presence of **GII** (0.5 mol%) (Scheme 2, Table 1, entry 1). When *p*-cresol (**12**) (0.25 eq. relative to **2 b** and 100 eq. relative to **GII**) was added to the reaction mixture, the cross-metathesis product, methyl cinnamate (**3 b**), was obtained in 38% yield together with (*E*)-stilbene (**4 b**) (36% yield) (Table 1, entry 3). The objective of this study was thus to find an explanation for how the **GII**-catalyzed *cross-metathesis* of alkenes with α,β-unsaturated carbonyl compounds (**1**) is promoted by *p*-cresol (**12**). As the purpose of this



1a R^1 = O-(2-ethylhexyl), R^3 = H
1b R^1 = OMe, R^3 = H
1c R^1 = OBu, R^3 = H
1d R^1 = Me, R^3 = H
1e R^1 = H, R^3 = H
1f R^1 = OMe, R^3 = CH_3

2a R^2 = OMe
2b R^2 = H
2c R^2 = OTf
2d R^2 = NO_2

3a R^1 = O-(2-ethylhexyl), R^2 = OMe
3b R^1 = OMe, R^2 = H,
3c R^1 = OMe, R^2 = OMe
3d R^1 = OMe, R^2 = OTf
3e R^1 = OBu, R^2 = H
3f R^1 = OBu, R^2 = OMe
3g R^1 = Me, R^2 = H
3h R^1= Me, R^2 = OMe
3i R^1 = H, R^2 = H
3j R^1 = H, R^2 = OMe
3k R^1 = O-(2-ethylhexyl), R^2 = H
3l R^1 = OMe, R^2 = NO_2

4a R^2 = OMe
4b R^2 = H
4c R^2 = OTf

Scheme 2. GII-catalyzed metathesis of α,β-unsaturated carbonyl compounds (**1**) and prop-1-en-1-ylbenzenes (**2**).

Table 1. GII-catalyzed metathesis of prop-1-en-1-ylbenzenes (**2**) and α,β-unsaturated carbonyl compounds (**1**).[a]

Entry	Reactants		Substituents		Cross-metathesis		Self-metathesis		Ratio
			R^1	R^2	Products	Yield [%]	Products	Yield [%]	CM:SM
1[b]	**1 b**	**2 b**	OMe	H	–	–	**4 b**[8]	>99	0:1
2[b]	**1 b**	**2 a**	OMe	OMe	–	–	**4 a**[9]	>99	0:1
3	**1 b**	**2 b**	OMe	H	**3 b**[10]	38	**4 b**[8]	36	1:1
4	**1 b**	**2 a**	OMe	OMe	**3 c**[11]	36	**4 a**[9]	61	0.6 :1
5	**1 b**	**2 c**	OMe	OTf	**3 d**[12]	43	**4 c**	7	6:1
6	**1 c**	**2 b**	OBu	H	**3 e**[13]	55	**4 b**[8]	18	3:1
7	**1 c**	**2 a**	OBu	OMe	**3 f**[14]	41	**4 a**[9]	57	0.7:1
8	**1 d**	**2 b**	Me	H	**3 g**[15]	34	**4 b**[8]	52	0.7:1
9	**1 d**	**2 a**	Me	OMe	**3 h**[15]	32	**4 a**[9]	47	0.7:1
10	**1 e**	**2 b**	H	H	**3 i**[16]	Trace	**4 b**[8]	76	0:1
11	**1 e**	**2 a**	H	OMe	**3 j**[17]	Trace	**4 a**[9]	94	0:1
12	**1 a**	**2 b**	O-(2-ethylhexyl)	H	**3 k**[18]	64	**4 b**[8]	12	5:1
13	**1 a**	**2 a**	O-(2-ethylhexyl)	OMe	**3 a**[19]	47	**4 a**[9]	53	0.9:1
14	**1 f**	**2 b**	OMe	H	**3 b**[10]	3.8	**4 b**[8]	54	0.1:1
15	**1 b**	**2 d**	OMe	NO_2	**3 l**[20]	56	–	–	1 : 0

[a] Reaction conditions: **2** (1.5 mmol) and **1** (2 eq.) were refluxed for 2 hours in dry dichloromethane (10 mL) with **GII** (0.5 mol%) and *p*-cresol (0.25 eq.) in a set-up with a dry ice condenser (-20 °C) while purging with Ar to remove gaseous products. [b] No cresol added.

investigation was to study subtle differences, the reactions were performed under conditions that precluded full conversion.

Results and Discussion

As baseline study, unsubstituted (*E*)-prop-1-en-1-ylbenzene (**2b**) (1 eq.) and methyl acrylate (**1b**) (2 eq.) were refluxed in dichloromethane in the presence of **GII** (0.5 mol%). The undesired self-metathesis (SM) product of the prop-1-en-1-ylbenzene (**2b**), (*E*)-stilbene (**4b**), formed in quantitative yield (Scheme 2, Table 1, entry 1). Decreasing the reaction temperature to 25 °C and 10 °C, respectively, had no effect on the selectivity or yield, with stilbene (**4b**) formation being observed right from the onset of the reaction. Changing the solvent from dichloromethane to THF, toluene and neat conditions (40 °C), respectively, also had no effect on the outcome of the reaction. Reactions at *ca.* 40 °C with 0.2, 1, 2 and 5 eq. of methyl acrylate (**1b**) all gave the stilbene (**4b**) in quantitative yield.

To investigate the influence of the electronic properties of the prop-1-en-1-ylbenzene (**2**) on the reaction, (*E*)-prop-1-en-1-ylbenzene (**2b**) was replaced by the analogue with an electron donating *p*-OMe group, (*E*)-anethole (**2a**). Self-metathesis once again prevailed, with (*E*)-4,4′-dimethoxystilbene (**4a**) being formed in > 99% yield (Table 1, entry 2).

When *p*-cresol (**12**) (0.25 eq. relative to **2b** and 100 eq. relative to **GII**) was added to the (*E*)-prop-1-en-1-ylbenzene (**2b**) - methyl acrylate (**1b**) (1 : 2 equivalents) reaction mixture, the desired cross-metathesis product, methyl cinnamate (**3b**), was obtained in 38% yield together with (*E*)-stilbene (**4b**) (36% yield) (Table 1, entry 3). The more nucleophilic (*E*)-anethole (**2a**) gave methyl (*E*)-*p*-methoxycinnamate (**3c**) in 36% yield and (*E*)-4,4′-dimethoxystilbene (**4a**) in 61% yield under these conditions (Table 1, entry 4), whereas the analogous prop-1-en-1-ylbenzenes with an electron withdrawing *p*-OTf group (**2c**), gave methyl (*E*)-3-(4-(trifluoromethylsulfonyloxy)phenyl)acrylate (**3d**) in 43% yield and the corresponding stilbene (**4c**) in 7% yield (Table 1, entry 5). Analysis of these results suggested an increase in the cross-metathesis yield and the cross-metathesis: self-metathesis product ratio with a decrease in the electron density of the prop-1-en-1-ylbenzene (**2**) double bond (Table 1, entries 4, 3 and 5 with **1b**; 7 and 6 with **1c**; 13 and 12 with **1a**). This notion was confirmed by the formation of methyl (*E*)-3-(4-nitrophenyl)acrylate (**3d**) in 56% yield from methyl acrylate (**1b**) and 1-(4-nitrophenyl)prop-1-ene (**2d**) (Table 1, entry 15).

The attention was subsequently shifted to the α,β-unsaturated carbonyl partner. Increasing the steric bulk of the alkoxy group of the acrylate by exchanging the methoxy for an *n*-butyl (**1c**) or 2-ethylhexyl group (**1a**), resulted in an increase in the cross-metathesis yield and CM : SM product ratio [Table 1, entries 3, 6 and 12 with (*E*)-prop-1-en-1-ylbenzene (**2b**); entries 4, 7 and 13 with (*E*)-anethole (**2a**)]. Rather than being a steric effect, this phenomenon may probably also be ascribed to a decrease in the electrophilicity of the acrylate (**1**) with increasing chain length and/or branching of the alkoxy group [electrophilicity index (ω) of methyl acrylate (**1b**), *n*-butyl acrylate (**1c**) and *tert*-butyl acrylate reported as 1.1018, 0.990 and 0.965 eV, respectively].[21] Increasing the electrophilicity of the α,β-unsaturated moiety by exchanging the ester (**1b**) for a ketone (**1d**) and ultimately an aldehyde (**1e**) [ω of methyl acrylate (**1b**), methyl vinyl ketone (**1d**) and acrolein (**1e**) reported as 2.76, 3.00 and 3.57 eV, respectively, in another study],[22] resulted in a progressive decrease in cross-metathesis yield (Table 1, entries 3, 8 and 10 with **2b**; entries 4, 9 and 11 with **2a**;). As expected, steric bulk on the β-carbon of the acrylate (**1f**) inhibited cross-metathesis and enhanced self-metathesis of (*E*)-prop-1-en-1-ylbenzene (**2b**) when compared to the reaction of unsubstituted methyl acrylate (**1b**) with (*E*)-prop-1-en-1-ylbenzene (**2b**) (Table 1, entries 14 and 3), even though methyl crotonate (**1f**) is less electrophilic than methyl acrylate (**1b**) [ω of methyl acrylate (**1b**) and methyl crotonate (**1f**) reported as 1.1018 and 0.847 eV, respectively].[21]

No trace of the self-metathesis product of the α,β-unsaturated carbonyl moiety (**1**) was observed, as was also encountered by Fogg and co-workers[6] at even harsher reaction conditions. The homodimer of (*E*)-prop-1-en-1-ylbenzene (**2b**), i.e. stilbene (**4b**), proved to be not consumable under the current reaction conditions since no indication of cross-metathesis product **3b** was found during the reaction of (*Z*)-stilbene ((*Z*)-**4b**) with methyl acrylate (**1b**). A computational study by Paredes-Gil et al.[23] furthermore indicated that reactions of stilbene (**4b**) with ruthenium methylidene and substituted carbenes would require high activation energies, whereas Fogg and co-workers[6] reported the metathesis reaction of 4,4′-dimethoxystilbene (**4a**) and 2-ethylhexyl acrylate (**1a**) (4 eq.) to be slow at 70 °C. Secondary metathesis involving stilbene (**4**) can therefore be considered negligible at the mild conditions (*ca.* 40 °C and 2 eq. of **1**) used in this study.

As the addition of *p*-cresol (**12**) to the reaction mixture enhanced cross-metathesis (Table 1, entries 1 and 3; 2 and 4) under reaction conditions that otherwise remained unchanged (CH_2Cl_2, 40 °C, 2 h), it was concluded that the cresol (**12**) must have modified the **GII** catalyst or catalytic cycle in some way.

Based on the common assumption that **GII** activation requires the reversible dissociation of tricyclohexylphosphine from the metal prior to alkene coordination and, secondly, the proposed capturing of the liberated PCy_3 by acrylates through phosphonium salt formation[5,6] (Figure 1), ^{13}P NMR spectra ($CDCl_3$) of **GII** (δ_P 28.9), **GII**-*p*-cresol (δ_P 28.9) and PCy_3-*p*-cresol (**12**) (1 and 2 eq.) (δ_P 33.2)[24] were acquired. As indicated in Figure 2, the resonance of the **GII** PCy_3 ligand appeared at δ_P 28.9 and the addition of cresol (**12**) had virtually no effect on the chemical shift thereof (Figure 2, part-1 and part-2) (as was also observed by Forman et al.[3]). Although no free PCy_3 (δ_P 11.2[26,27]), nor the cresol - PCy_3 complex (**7**) (δ_P 33.2) postulated by Forman et al.,[3] could be detected in the **GII**-*p*-cresol mixture, the possibility of these species being formed during the metathesis reaction was subsequently investigated.

The ^{31}P NMR spectra of the system following the addition of *p*-cresol (**12**), (*E*)-prop-1-en-1-ylbenzene (**2b**), methyl acrylate (**1b**), and combinations thereof, to **GII** were thus acquired (Figure 2). In order to have the important species in concentrations observable by NMR spectroscopy, more concentrated solutions and a smaller **GII**-*p*-cresol (**12**) ratio had to be used in

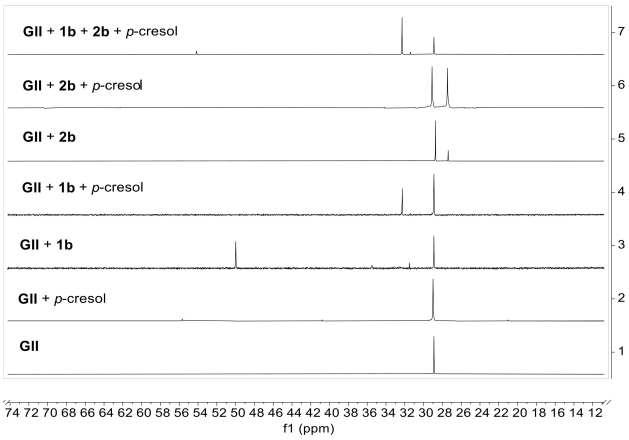


Figure 2. ^{31}P NMR of Grubbs II catalyst with different reagent combinations: **GII** (0.024 mmol) in dry DCM (5 mL) with *p*-cresol (0.094 mmol, 4 eq.), methyl acrylate (**1b**) (0.047 mmol, 2 eq.) and (*E*)-prop-1-en-1-ylbenzene (**2b**) (0.047 mmol, 2 eq.) in the combinations indicated after being refluxed (ca. 40 °C) for 1 hour. The reaction mixture was concentrated in vacuo and dissolved in $CDCl_3$ (0.6 mL) for NMR analysis at rt.

the NMR study compared to the electronic/steric study (1:4 vs. 1:100) (Table 1 vs. Figure 2 and Figure 4).

When **GII** was exposed to (*E*)-prop-1-en-1-ylbenzene (**2b**) (2 eq. relative to **GII**) for 1 hour at 40 °C, another resonance appeared at δ_P 27.4 (Figure 2, part-5) indicating some change to the ligand environment in the catalyst complex. Since the carbene proton (δ_H 18.54, q, $J = 5.3$ Hz) in this instance correlated with the phosphorous at δ_P 27.4 in an ^{1}H-^{31}P HMBC experiment, this phosphorous resonance could be allocated to the propagating ethylidene (**14**-PCy_3) (Figure 3). ^{13}C NMR confirmed the formation of a new carbene, which resonated as a singlet at δ_C 315.2 (*versus* δ_H 19.13 and δ_C 294.3 for the similar entity in **GII**). These resonances were also observed when *p*-cresol (**12**) (4 eq. relative to **GII**) was added to the **GII**-(*E*)-prop-1-en-1-ylbenzene (**2b**) reaction mixture.

A mixture of **GII** and methyl acrylate (**1b**) in $CDCl_3$ at 40 °C formed a species with a resonance corresponding to that of tricyclohexylphosphine oxide (δ_P 51.1) and a species resonating at δ_P 31.5 within 1 hour (Figure 2, part-3). Since Fogg and co-workers[5,6] reported some 'liberated' tricyclohexylphosphine to react with acrylate in a Michael addition fashion (Figure 1c), the new resonance may probably be assigned to a phosphonium

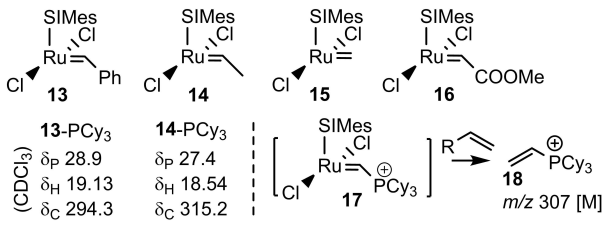


Figure 3. Ruthenium benzylidene (**13**), ethylidene (**14**), methylidene (**15**) and methyl ester substituted methylidene (**16**) derived from **GII**, NMR data for **13**-PCy_3 and **14**-PCy_3, MALDI-TOF MS (+ve) data for the tricyclohexyl-(vinyl) phosphonium ion (**18**).

zwitterion like **10** or **11**. This signal was absent in the presence of cresol (**12**) (4 eq. relative to **GII**), though another resonance appeared at δ_P 32.3 (Figure 2, part-4). The latter is probably explicable by assuming protonation of the zwitterion (**10** or **11**) by the acidic cresol moiety.

The observation of a cation with *m/z* 453, [**11**+H], by MALDI-TOF MS corroborated this postulate (Figure 1c). Similar ^{31}P NMR resonances were observed when PCy_3 was exposed to methyl acrylate (**3b**) and LiCl in CH_2Cl_2 for 4 hours.

^{31}P NMR analysis of a β-methylstyrene (**2b**) - methyl acrylate (**1b**) (1:1) reaction mixture after being heated for 1 hour at 40 °C in the presence of **GII** and *p*-cresol (**12**) (4 eq. relative to **GII**), revealed the presence of zwitterion **11** at δ_P 31.5, protonated **11** at δ_P 32.3 (Figure 1c) and a ruthenium benzylidene (**13**) complex with PCy_3 (δ_P 28.9) (Figure 2, part-7, Figure 3).

MALDI-TOF MS of the **GII**-β-methylstyrene (**4b**) - methyl acrylate (**1b**) reaction mixture confirmed the presence of protonated **10** (*m/z* 367, [M+H]) and **11** (*m/z* 453, [M+H]), whereas another prominent peak, which may be ascribed to the tricyclohexyl(vinyl)-phosphonium ion, $[CH_2CHPCy_3]^+$ (**18**),[28] was observed at *m/z* 307 (Supplementary Information). The latter indirectly confirmed the formation of the ruthenium methylidene (**15**) (Figure 3). The *m/z* 307:367 peak ratio with added cresol was 1:4 compared to 1:2.8 in the absence of cresol (**12**), which may indicate that *p*-cresol (**12**) inhibited the attack of PCy_3 on the ruthenium methylidene (**15**)[29] and/or sequestered **10** effectively to restrain the 1,4-addition cascade.[5,6]

As ester alkylidenes such as **16** are typically very unstable,[30] cross-metathesis of prop-1-en-1-ylbenzenes (**2**) and acrylates (**1**) most probably predominantly relies on benzylidene **13** (Figure 3) to react with the acrylate.[7]

Since no indication of a new cresol-modified catalyst complex or intermediate could be detected by ^{13}P NMR or MALDI-TOF MS, the investigation was subsequently turned towards an in-depth proton NMR spectroscopic analysis.

When *p*-cresol (**12**) (2 eq.) was added to **GII**, ^{1}H NMR spectroscopy indicated the 2,6-resonance of the cresol moiety to have moved downfield from δ_H 6.73 to 6.79 when compared to free cresol at the same temperature and concentration, whereas the H-3,5 resonance moved in the opposite direction, i.e. from δ_H 7.03 to 7.02, thus confirming some interaction between the cresol and the catalyst complex (Figure 4.1 and Figure 4.2). The addition of prop-1-en-1-ylbenzene (**2b**) to *p*-cresol (**12**) virtually had no effect on the ^{1}H NMR chemical shifts of the aromatic protons of *p*-cresol (**12**) (Figure 4.1 and Figure 4.3), while the spectrum of a combination of acrylate (**1b**) and *p*-cresol (**12**) resulted in a slight downfield shift of the 2,6-resonance (from δ_H 6.73 to 6.74), thus indicating some proton donating interaction between cresol and the acrylate.

While the ^{1}H NMR chemical shifts of the cresol (**12**) resonances when in combination with **GII** indicated some association with the catalyst, the changes were very small. The possibility of some complex formation between the **GII** catalyst and the cresol (**12**) was thus investigated further by 2D NMR analysis in DCM-d_2 at −40 °C. In order to be able to observe through space association between hydrogens and thus obtain

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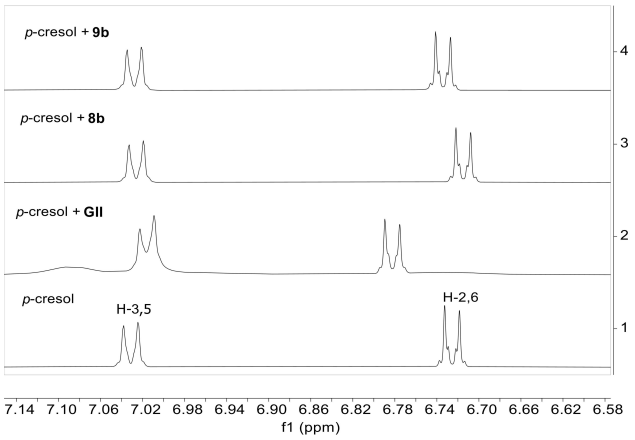


Figure 4. ^{1}H NMR of *p*-cresol with different reagents: *p*-cresol (0.094 mmol), **GII** (0.024 mmol, 0.25 eq.), (*E*)-prop-1-en-1-ylbenzene (**4b**) (0.047 mmol, 0.5 eq.) and methyl acrylate (**9b**) (0.047 mmol, 0.5 eq.) in dry DCM (5 mL) in the combinations indicated after being refluxed (ca. 40 °C) for 1 hour. The reaction mixture was concentrated in vacuo and dissolved in $CDCl_3$ (0.6 mL) for NMR spectroscopic analysis at rt.

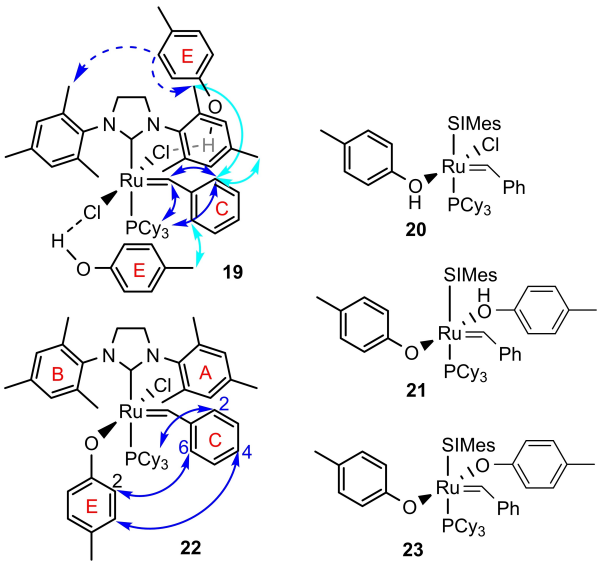


Figure 6. Possible modifications of **GII** by *p*-cresol (**12**) with supporting NOE correlations.

structural information about the **GII**-cresol complex, all resonances in the ^{1}H NMR spectrum were assigned to protons by means of 2D NMR spectroscopy (Supplementary Information). The **GII** allocations in DCM-d_2 closely resembled those previously reported in $CDCl_3$.[31]

As indicated in Figure 5 and Figure 6, NOE cross-peaks could be detected from the cyclohexyl proton resonances (δ_H 1.45–1.11 and 0.80–1.11) to the benzylidene (δ_H 18.85) and C-ring proton-2 [H-2 (C), δ_H 8.86] resonances, indicating the PCy_3 to still be attached to the metal in the presence of added cresol (**12**). The NOESY spectrum furthermore revealed a strong correlation between H-3/H-5 of the cresol entity (δ_H 7.05) and a mesitylene methyl group in an *ortho*-position (δ_H 2.52). It could therefore be concluded that both the cresol and tricyclohexylphosphine moieties are attached to the catalyst complex at

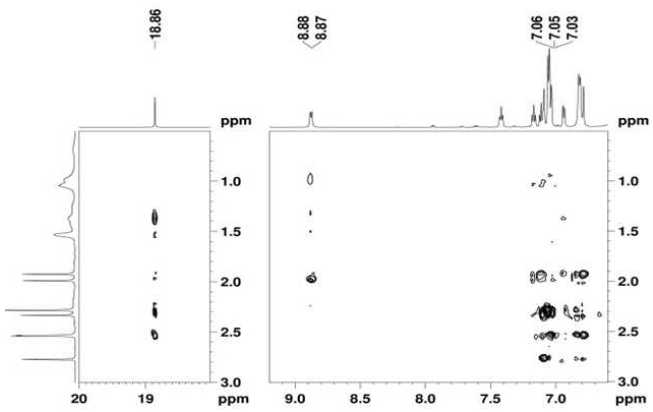


Figure 5. GII-*p*-cresol adduct: NOE association of tricyclohexyl phosphine protons with benzylidene H-1'and H-2 (C) and of *p*-cresol H-3/H-5 with a mesityl 4-CH_3.

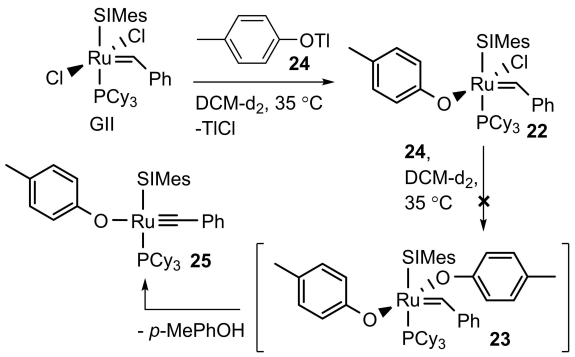
−40 °C in DCM-d_2 (a similar NOESY investigation at 35 °C in DCM-d_2 proved to be inconclusive due to signal broadening).

The interaction between **GII** and *p*-cresol (**12**) may involve hydrogen bonding interactions between the cresol and **GII** chloride ligands[32] as proposed by Forman et al.,[4] thus leading to complex structures like **19** with one or more chloride-*p*-cresol hydrogen bonds. As Fogg et al.[5,6] demonstrated the *p*-cresol to act as a proton donor, complex formation with **GII** may, however, also be ascribed to the exchange of one or both chloride ligands with *p*-cresol (**12**) or *p*-cresolate, thus leading to complexes like **20–23** (Figure 6).[33]

As far as we know, only two ruthenium benzylidenes with σ-bonded monodentate aryloxy ligands have been reported. $RuCl(OPh)(PCy_3)_2(CHPh)$ and $Ru(OPh)_2(PCy_3)_2(CHPh)$, are short-lived and were only observed in situ.[33]

Still, since complexes such as **22** and/or **23** may be involved in the metathesis reactions, the preparation thereof from **GII** and thallium *p*-cresolate (**24**) was attempted.[34]

The thallium cation is highly electrophilic and thallium salts are therefore ideally suited for the substitution of halogens from Grubbs catalysts.[35–37] Furthermore, since it is known for Grubbs 1st generation catalyst (**GI**) that a species like **23** may decompose to the carbyne analogue (**25**) and phenol,[33] it was decided to investigate the effect of 1 and 2 eq. of thallium *p*-cresolate (**24**) on **GII**. Thallium *p*-cresolate (**24**) was thus prepared from *p*-cresol (**12**) and thallium ethoxide in 76% yield, followed by complex formation thereof with **GII** in dry benzene (room temperature, 48 hours) (Scheme 3). Treatment of **GII** with 1 and 2 eq. of thallium *p*-cresolate (**24**) led to the formation of the same Ru–O coordination compound, with X-ray Photoelectron Spectroscopic (XPS) and NMR spectroscopic data strongly supporting structure **22** (Scheme 3) for this compound.[34]



Scheme 3. The preparation of ruthenium cresolate(s) from **GII**.

The *p*-cresolate-**GII** derivate (**22**), like the *p*-cresol-**GII** adduct (**19**), was isolated from the reaction mixture and analyzed without further purification as all attempts to purify it resulted in decomposition. This instability finds a precedent in the transient nature of $RuCl(OPh)(PCy_3)_2(CHPh)$ and $Ru(OPh)_2(PCy_3)_2(CHPh)$ (vide supra).[33]

As the metathesis reactions were conducted in refluxing dichloromethane, it was subsequently decided to follow the complexation of thallium *p*-cresolate (**24**) with **GII** at the reaction temperature by NMR spectroscopy in CD_2Cl_2 over time (Figure 7).

Based on the ^{1}H NMR spectrum of **GII** (Figure 7.3) and the spectrum of **GII** with 2 eq. of thallium *p*-cresolate (**24**) at time zero (Figure 7.4), the pseudo triplet at δ_H 7.28 ppm could be ascribed to H-4 of the benzylidene ring C (Figure 6), whereas the broad multiplet between δ_H 7.05 and 6.99 ppm and integrating for three protons relative to H-4 (C), could be ascribed to H-3, H-5 and H-6 of the benzylidene ring. The thallium cresolate (**24**), protons on positions 3,5 and 2,6 resonated as AA′BB′ pseudodoublets (further on referred to as doublets, $J = 7.9$ Hz) at δ_H 6.96 and 6.65 ppm, respectively

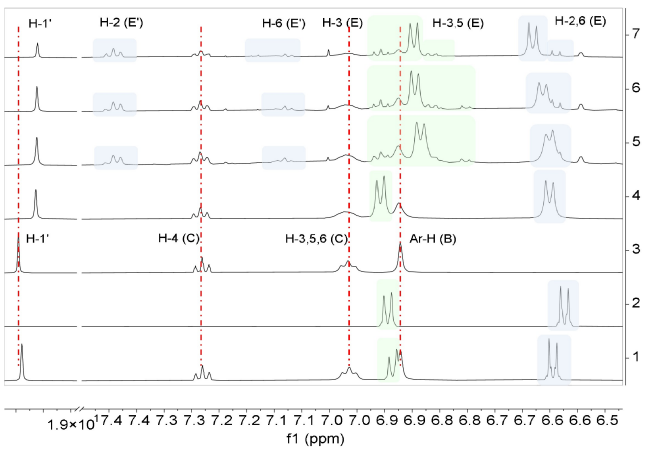


Figure 7. ^{1}H NMR spectrum (CD_2Cl_2, 35–40 °C, referenced to TMS) of **GII**-*p*-cresol (1), *p*-cresol (2), **GII** (3), **GII**/thallium *p*-cresolate at 0 min. (4), 10 min. (5), 60 min. (6) and 1800 min. (7).

(Figure 7.4). After 10 minutes in the presence of **GII**, each cresolate doublet had divided into a set of a major doublet and various smaller doublets (Figure 7.4 to Figure 7.7). The major cresolate H-3/H-5 protons [δ 6.89 (10 min.), 6.90 (1800 min.) vs. 6.96 ppm (0 min.)] were shielded and the H-2/H-6 protons [δ_H 6.65 (10 min.), 6.68 (1800 min.) vs. 6.65 (0 min.)] deshielded in the intermediates/product relative to those of thallium *p*-cresolate (**24**) (Figure 7.4 at time zero).

In analogy to phenoxide complexes of palladium, two overlapping doublets at lower field (δ_H 7.45 and 7.43 ppm) could be ascribed to H-2 of the ruthenium cresolate moiety[34] in conformations where this proton spends some time below the plane of the square pyramid and thus is deshielded by the anisotropic effect of the metal.[38] A change in the chemical shift of the carbene proton (H-1′) (δ 19.01, **GII**, Figure 7.3 vs δ 18.96, **GII**-*p*-cresolate, Figure 7.7), the formation of additional resonances in the carbene region[39,40] (δ 21.17, 19.35, 17.66; Figure 7) and a relative decrease in or broadening of the benzylidene H-4 resonance (δ_H 7.28 ppm, pseudo triplet), provided additional evidence for chloride-cresolate ligand exchange and the presence of several conformers due to restricted rotation.[41] Similar results were encountered when the NMR spectroscopic analyses were performed at room temperature in $CDCl_3$.[31,34]

The formation of carbyne complex (**25**) was, however, not observed (no resonance in the vicinity of a carbon triple bonded to ruthenium; δ_C 248 for **GI**),[33] although trace amounts of a new type of benzylidene carbon was detected at δ_c 287.6 (*vs* δ_c 293.7 for the benzylidene carbon of **GII** under the same conditions). It could therefore be concluded that the bis (cresolate) complex **23**, if formed, did not decompose to carbyne entity **25** under the prevailing conditions.

XPS strongly supported the formation of monochloride complex **22** and thallium chloride ($Ru:P:Cl_{covalent}:Cl_{ionic}:N:Tl$ 1:1:1:1:2:1) despite the presence of 2 eq. of the thallium salt.[34] XPS and NMR furthermore confirmed that the **GII**-*p*-cresolate derivative (**22**) did not correspond to the *p*-cresol-**GII** adduct (**19**) (vide infra) (Figure 7.7 vs. Figure 7.1).

With the likelihood of complexes such as **22** and **23** being formed ruled out, attention was subsequently returned towards *p*-cresol-treated **GII**. IR spectroscopic analysis of the red-brown oil formed during addition of *p*-cresol (**12**) to **GII** confirmed the presence of hydrogen-bonded O–H groups ($\nu_{O\text{-}H}$ 3280 cm^{-1})[34] in the complex, while XPS analysis of the catalyst species (Ru:P:Cl:N 1:1:2:2) in this instance confirmed the presence of two chloride ligands with identical environments to each other and one phosphorous with an environment very similar to that of the PCy_3 ligand of **GII**.[34] XPS furthermore indicated an increase in the binding energies of the Ru $3d_{5/2}$, $3d_{3/2}$, $3p_{3/2}$ and $3p_{1/2}$ photoelectrons in the presence of *p*-cresol (**12**) and thus a decrease in the electron density on the ruthenium center.[34] These results are in agreement with PhOH–Cl coordination and find a precedent in the **GI** PMe_3 *methylidene* model of Forman et al.[3] which predicted an increased positive Hirshfeld charge on Ru due to chloride-hydrogen bonding. For the same model, a decrease in the electron density of the carbene carbon was predicted due to the inductive effect of the phenol.[3] ^{1}H and ^{13}C NMR spectroscopy in the current study, however, unexpectedly

indicated the carbene hydrogen and carbon of the **GII** *benzylidene* to be slightly shielded in the presence of *p*-cresol (**12**) (δ_H 19.04 vs 19.05 ppm, CD_2Cl_2, 35 °C, Figure 7.1 vs Figure 7.3; δ_H 19.06 vs 19.14 ppm, δ_C 294.3 vs 294.4 ppm, $CDCl_3$, rt.[34] According to Cavallo and co-workers,[42] the deshielding of the carbene carbon of Ru=ylidenes in ^{13}C NMR spectroscopy can mainly be ascribed to the transition between the occupied $\sigma_{Ru=C}$ and empty $\pi^*_{Ru=C}$ orbitals. The smaller the energy gap between these orbitals, the stronger the paramagnetic coupling and the larger the deshielding (and vice versa). A larger deshielding is correlated with a stronger Ru=ylidene bond in terms of both binding energy and bond length.[42–45] As the benzylidene carbene carbon of **GII** is *less deshielded* in the presence of *p*-cresol (**12**), it can be deduced that the energy gap between the $\sigma_{Ru=C}$ and $\pi^*_{Ru=C}$ orbitals is larger and that the Ru=ylidene bond is weakened. The larger energy requirement for electronic transition in the presence of *p*-cresol (**12**) is corroborated by blue shifts in the UV-Vis absorbances of **GII** (334 vs 336 nm and 501 vs 502 nm).[34]

If this is also true for the active catalytic species (e.g. analogues of **6**), the increased electrophilicity of the ruthenium center and the decreased electrophilicity of the carbene carbon may have an influence on the coordination of the alkene as well as the formation of the ruthenacyclobutane (**Ru-1**), thus activating the catalyst for reaction with α,β-unsaturated carbonyl compounds (**1**) in addition to prop-1-en-1-ylbenzenes (**2**). This deduction is corroborated by an increase in cross-metathesis yields with a decrease in the electrophilicity of the α,β-unsaturated carbonyl compound (**1**) and a decrease in the electron density on the prop-1-en-1-ylbenzene (**2**) in reactions catalyzed by the **GII**-*p*-cresol adduct (vide supra).

Given the NOE correlation between *p*-cresol (**12**) and the benzylidene ring, steric effects and a preference for the terminal alkene (**1**) over the internal alkene (**2**) may be another contributing factor.

Conclusion

The addition of *p*-cresol (**12**) to **GII** allowed the cross-metathesis of prop-1-en-1-ylbenzenes (**2**) and electron-poor α,β-unsaturated carbonyl compounds (**1**) under conditions that only gave the prop-1-en-1-ylbenzene (**2**) self-metathesis products in the absence of *p*-cresol (**12**).

In a systematic NMR and IR spectroscopic, MALDI-TOF MS and XPS study, evidence to support a ruthenium benzylidene-*p*-cresol adduct like **19** with hydrogen bonds between the cresol and chloride ligands, as proposed by Forman et al.,[3] was observed. The exact amount of cresol moieties involved could not be determined, though. The interaction of *p*-cresol (**12**) with **GII** furthermore shielded the carbene carbon and hydrogen in ^{13}C and ^{1}H NMR spectroscopic experiments, whereas XPS indicated a decrease in electron density on the metal center. In the presence of *p*-cresol (**12**), the benzylidene carbene carbon of **GII** is *less deshielded* and the energy gap between the $\sigma_{Ru=C}$ and $\pi^*_{Ru=C}$ orbitals is thus larger,[42–45] as was also corroborated by blue shifts in the UV-Vis absorbances of **GII** (334 vs 336 nm and 501 vs 502 nm).[34]

The activity of **GII** in the presence of *p*-cresol (**12**) can thus most probably be ascribed to the increased electrophilicity of the ruthenium and the decreased electrophilicity of the C_{ene}, thus activating the catalyst for coordination and ruthenacyclobutane (**Ru-1**) formation with less electron-rich alkenes. This conclusion is substantiated by an increase in cross-metathesis yields with a decrease in the electrophilicity of the α,β-unsaturated carbonyl compound (**1**) and a decrease in the electron density on the prop-1-en-1-ylbenzene (**2**) in reactions catalyzed by the **GII**-*p*-cresol adduct. Based on the NOE correlation between *p*-cresol (**12**) and the benzylidene ring, increased steric hindrance may be another contributing factor and may favor the terminal alkene over the internal alkene, i.e. the acrylate (**1**) over the prop-1-en-1-ylbenzene (**2**).

Experimental Section

General Experimental Methods. Reagents obtained commercially were used as received. Solvents were dehydrated by filtering through a small column of activated neutral alumina (10% v/v) prior to use. Qualitative Thin-Layer Chromatography (TLC), was conducted on Merck TLC-aluminium plates: Silica Gel F_{254} (0.2 mm layer), Preparative Thin-Layer Chromatography (PLC) on glass plates (20 cm×20 cm) coated with a layer (1 mm) of Merck Kieselgel 60 PF_{254} that had been air-dried overnight at room temperature and Flash Column Chromatography in a glass column charged with 100 g of silica gel (Machery - Nagel silica gel 60, 0.063–0.2 mm/70–230 mesh ASTM) for every 1 g of crude product. The crude product was dissolved in the minimum amount of appropriate solvent, loaded onto the column and the purified products recovered by elution with the appropriate solvent system under N_2-pressure. Melting points were determined with a Barloworld Scientific Stuart Melting Point (SMP3) apparatus. IR analysis was performed on a Bruker Tensor 27 infrared spectrometer and NMR-spectroscopy on a Bruker AVANCE II 600 FT spectrometer at 25 °C in $CDCl_3$ (^{1}H and ^{13}C NMR) or 400 MHz AVANCE III spectrometer (^{31}P NMR) unless specified differently. Unless specified differently, chemical shifts are reported in parts per million (ppm) with the $CDCl_3$ solvent peak calibrated at δ7.26 ppm in the proton spectra and δ77.16 ppm in the carbon spectra, respectively, whereas coupling constants are given in Hz. ^{19}F NMR-spectra were referenced to hexafluorobenzene (δ-164.9 ppm) and ^{31}P NMR-spectra to phosphoric acid (in a glass capillary; δ0 ppm). Mass spectrometry was performed by means of electron impact (EI) ionization on a Shimadzu GC-MS QP-2010 fitted with a J & W Scientific DB-5 ms capillary column (0.25 μm film thickness, 0.32 mm ID, 30 m), helium as carrier gas at a linear velocity of 27.5 cm/s and an injector temperature of 250 °C. Injections were made in the split mode. The initial column temperature of 50 °C was kept for 3 min, where after it was increased to 250 °C at 10 °C/min and kept at this temperature for the rest of the analysis. Alternatively, MS was performed by means of Matrix Assisted Laser Desorption Ionization Time-Of-Flight (MALDI-TOF) on a Bruker Microflex LRF20 in the positive mode with 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as matrix and the minimum laser power (337 nm) required to observe signals. Spectra obtained were compared to simulated spectra generated by Bruker Daltonics Molecular Formula Generator 1.0. HRMS spectra were conducted at the University of KwaZulu-Natal, Pietermaritzburg, South Africa. A Phi 5000 Versaprobe system equipped with a monochromatic Al Ka X-ray source, was used for X-ray photoelectron spectroscopic (XPS)

analysis. HRMS of certain trifluoromethanesulfonate derivatives, the **GII**-*p*-cresol adduct (**19**) and **GII**-*p*-cresolate derivative (**22**) could not be obtained due to decomposition. *Caution*: Thallium compounds are extremely toxic and should be handled with care.

Procedures

Synthesis of (E)-4-(prop-1-en-1-yl)phenyl trifluoromethanesulfonate (2 c)

4-Propionylphenyl trifluoromethanesulfonate (**26**). Triflic anhydride (1.1 eq.) in dry DCM (25 mL) at −20 °C was added dropwise to a solution of 4′-hydroxypropiophenone (**27**) (2.00 g, 13.3 mmol) and DMAP (1.79 g, 14.7 mmol) in DCM (50 mL), also at −20 °C, under Ar. The reaction mixture was allowed to warm to rt. and stirred overnight, after which the solvent was distilled off and EtOAc (*ca.* 50 mL) and water (*ca.* 50 mL) added to the reaction mixture. The water layer was extracted into EtOAc (3×50 mL), after which the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. flash column chromatography (DCM) gave 4-propionylphenyl trifluoromethanesulfonate[46] (**26**) (3.4 g, 90 %) as a light yellow oil: R_f 0.86 (DCM); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.9 Hz, 2H, H-3′,5′), 7.33 (d, *J* = 8.9 Hz, 2H, H-2′,6 ′), 2.97 (q, *J* = 7.2 Hz, 2H, H-2), 1.18 (t, *J* = 7.2 Hz, 3H, H-3); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9 (C-1), 152.4 (C-1′), 136.8 (C-4 ′), 130.3 (C-3′,5′), 121.6 (C-2′,6′), 118.7 (q, *J* = 320.7 Hz, CF_3), 32.0 (C-2), 7.9 (C-3); ^{19}F NMR (565 MHz, $CDCl_3$): δ = −75.83 (CF_3); IR (neat) 1693 cm^{-1} (CO).

4-(1-Hydroxypropyl)phenyl trifluoromethanesulfonate (**28**). 4-Propionylphenyl trifluoromethanesulfonate (**26**) (2.5 g, 8.9 mmol) was added to a solution of $NaBH_4$ (0.503 g, 13.3 mmol, 1.5 eq.) in THF/EtOH (1 : 1, v/v; 50 mL) and stirred until the reaction was deemed to be complete by TLC. After completion of the reaction (TLC), the reaction mixture was concentrated *in vacuo*, washed with acetone (3×20 mL) and concentrated again. EtOAc (*ca.* 50 mL) and water (*ca.* 50 mL) were thus added to the reaction mixture. The water layer was extracted into EtOAc (3×50 mL), after which the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. flash column chromatography (H : A 8 : 2) gave 4-(1-hydroxypropyl)phenyl trifluoromethanesulfonate (**28**) (1.97 g, 78 %) as a *light yellow oil*: R_f 0.47 (H/A 8 : 2); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.7 Hz, 2H, H-2′,6′), 7.24 (d, *J* = 8.7 Hz, 2H, H-3′,5′), 4.63 (t, *J* = 6.5 Hz, 1H, H-1), 1.81-1.69 (m, 2H, H-2), 1.16 (d, *J* = 6.2 Hz, 1H, -OH), 0.91 (t, *J* = 7.4 Hz, 3H, H-3); ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.8(C-4′), 145.3 (C-1′), 127.9 (C-2′,6′), 121.3 (C-3′,5′), 118.9 (q, J = 320.8 Hz, CF_3), 75.0 (C-1), 32.2 (C-2), 10.1 (C-3); ^{19}F NMR (565 MHz, $CDCl_3$) δ −75.95 (CF_3).

(*E*)-4-(prop-1-en-1-yl)phenyl trifluoromethanesulfonate (**2 c**). Anhydrous $CuSO_4$ (10.84 g, 5.3 mmol) was added to a solution of 4-(1-hydroxypropyl)phenyl trifluoromethanesulfonate (**28**) (1.0 g, 3.5 mmol) in dry hexane (40 mL), after which the reaction mixture was refluxed and stirred under Ar for 4 days. The solvent was then removed *in vacuo*, and hexane (*ca.* 50 mL) added to the reaction mixture. H_2O (*ca.* 50 mL) was added to this reaction mixture and the aqueous (*aq.*) phase extracted into hexane (3×50 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent removed *in vacuo* at *ca.* 40 °C. flash column chromatography (H : A 8 : 2) gave (*E*)-4-(prop-1-en-1-yl)phenyl trifluoromethanesulfonate (**2 c**) (0.56 g, 60 %) as a *light yellow oil*: R_f 0.76 (H/A 8 : 2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.6 Hz, 2H, H-2′,6′), 7.18 (d, *J* = 8.6 Hz, 2H, H-3′,5′), 6.39 (br d, *J* = 15.8 Hz, 1H, H-1), 6.29-6.23 (m, 1H, H-2), 1.90 (m, 3H, H-3); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.3 (C-4′), 138.5 (C-1′), 129.4 (C-1), 128.3 (C-2), 127.5 (C-2′,6′), 121.5 (C-3′,5′), 118.9 (q, *J* = 320.8 Hz, CF_3), 18.6 (C-3); ^{19}F NMR (565 MHz, $CDCl_3$) δ = -75.85 (CF_3); MS (EI, 70 eV): *m/z* (%) = 266 (19) $[M]^+$.

Electronic and steric influence study

Representative Example of Metathesis with GII

(*E*)-prop-1-en-1-ylbenzene (**2 b**) (0.20 mL, 1.5 mmol, 1 eq.), methyl acrylate (**1 b**) (0.28 mL, 3.1 mmol, 2 eq.) and **GII** (6.5 mg, 0.0077 mmol, 0.5 mol%) were refluxed in dry DCM (10 mL) for 2 h hours (until completion of the reaction, TLC). The reaction mixture was then filtered and the precipitate washed with cold DCM (3× 30 mL) to yield (*E*)-stilbene[8] (**4 b**) as colorless platelets (0.27 g, 99 %): R_f 0.87 (H/A 8 : 2); Mp 123.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.55 (br d, *J* = 8.2 Hz, 4H, H-2,6), 7.39 (t, *J* = 7.7 Hz, 4H, H-3,5), 7.29 (m, 2H, H-4), 7.14 (s, 2H, CH=CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 137.5 (C-1), 128.8 (C-3,5 and CH=CH), 127.8 (C-4), 126.7 (C-2,6); MS (EI, 70 eV): *m/z* (%) = 180 (100) $[M]^+$.

Changing the temperature to 10 and 25 °C, the solvent to THF, toluene or neat conditions, and the **2 b** : **1 b** ratio (0.2 mL, 1.5 mmol, 1 eq. : 0.69 mL, 7.7 mmol, 5 eq.; 0.2 mL, 1.5 mmol, 1 eq. : 0.13 mL, 1.5 mmol, 1 eq.; 1.0 mL, 7.5 mmol, 5 eq.: 0.13 mL, 1.5 mmol, 1 eq., **2 b** : **1 b**, respectively) all gave (*E*)-stilbene (**4 b**) in quantitative yield.

Representative Example of Metathesis with GII-p-cresol

GII (2.4 mg, 0.0030 mmol, 0.5 mol%) and *p*-cresol (0.031 g, 0.30 mmol, 0.25 eq.) were heated to reflux in dry DCM (10 mL) while being stirred. A steady stream of argon was bubbled through the mixture and the vapours condensed at −20 °C. (*E*)-4-(Prop-1-en-1-yl)phenyl trifluoromethane-sulfonate (**2 c**) (0.15 g, 0.60 mmol, 1 eq.) and methyl acrylate (**1 b**) (0.10 mL, 1.1 mmol, 2 eq.) were then added to the mixture. After 2 hours at reflux (completion, TLC), the solvent was distilled off and EtOAc (50 mL) and water (50 mL) added to the reaction mixture. The water layer was extracted into EtOAc (3×50 mL), after which the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. PLC (H/A 8 : 2) gave methyl *(E)*-3-[4-(trifluoromethylsulfonyloxy)phenyl]-acrylate[12] (**3 d**) as a light yellow oil (74.5 mg, 43 %) and *(E)*-4,4′-bis (trifluoromethanesulfonyloxy)stilbene (**4 c**) (9.4 mg, 7 %), also as a *light yellow oil*:

Methyl (*E*)-3-[4-(trifluoromethylsulfonyloxy)phenyl]acrylate[12] (**3 d**): R_f 0.49 (H/A 8 : 2); ^{1}H NMR (600 MHz, $CDCl_3$,) δ = 7.66 (d, *J* = 16.0 Hz, 1H, H-3), 7.59 (d, *J* = 8.7 Hz, 2H, H-2′,6′), 7.29 (d, *J* = 8.7 Hz, 2H, H-3′,5′), 6.44 (d, *J* = 16.0 Hz, 1H, H-2), 3.81 (s, 3H, H-1′′); ^{13}C NMR (151 MHz, $CDCl_3$,) δ = 166.9 (C-1), 150.5 (C-4′), 142.5 (C-3), 134.9 (C-1′), 129.9 (C-2′,6′), 122.1(C-3′,5′), 120.0 (C-2), 118.8 (q, J = 320.9 Hz, CF_3), 52.0 (C-1′′); ^{19}F NMR (565 MHz, $CDCl_3$) δ = −75.87 (CF_3); IR (neat, cm^{-1}) 1718 (C=O); MS (EI, 70 eV): *m/z* (%) = 310 (43) $[M^+]$.

(*E*)-4,4′-bis(trifluoromethanesulfonyloxy)stilbene (**4 c**): R_f 0.58 (H/A 8 : 2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.8 Hz, 4H, H-2,6), 7.29 (d, *J* = 8.8 Hz, 4H, H-3,5), 7.09 (s, 2H, CH=CH); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.1 (C-4), 137.2 (C-1), 128.8 (CH=CH), 128.1 (C-2,6), 121.9 (C-3,5), 118.9 (q, *J* = 320.8 Hz, CF_3); ^{19}F NMR (565 MHz, $CDCl_3$) δ = −75.91 (CF_3); MS (EI, 70 eV): *m/z* (%) = 477 (6) $[M^+]$.

NMR investigation

Procedure A: The relevant reagents were dissolved in $CDCl_3$ (0.6 mL), stirred at 40 °C for 1 hour (unless specified otherwise) and analyzed by NMR. Diagnostic resonances are indicated.

Tricyclohexylphosphine + *p*-cresol

Tricyclohexylphosphine (20 mg, 0.071 mmol) and *p*-cresol (8 mg, 0.071 mmol, 1 eq.) according to procedure A: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (s, cresol: OH), 6.95 (d, *J* = 8.3 Hz, cresol:H-3,5), 6.81 (d, *J* = 8.3 Hz, cresol:H-2,6), 2.35–2.27 (m, 1H), 2.23 (s, cresol:Me), 2.02–1.62 and 1.52–1.11 (m, PCy_3:H-1-6); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 59.1, 58.8, 52.9, 50.7, 40.1, 33.2, 12.1.

Tricyclohexylphosphine (20 mg, 0.071 mmol) and *p*-cresol (15 mg, 0.143 mmol, 2 eq.) according to procedure A: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27 (s, cresol: OH), 7.01 (d, *J* = 8.3 Hz, cresol:H-3,5), 6.85 (d, *J* = 8.3 Hz, cresol:H-2,6), 2.28 (s, cresol: Me), 2.05–1.68 and 1.54–1.17 (m, PCy_3:H-1-6); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 59.8, 59.7, 54.3, 51.9, 33.2, 12.3.

Tricyclohexylphosphine + trifluoromethanesulfonic acid

Tricyclohexylphosphine (30 mg, 0.11 mmol) and trifluoromethanesulfonic acid (0.02 mL, 0.21 mmol, 2 eq.) according to procedure A:[24] ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.53–11.04 (m), 2.69–0.71 (m, $POCy_3$:H-1-6); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 86.4, 83.5, 33.6.

Tricyclohexylphosphine oxide

Tricyclohexylphosphine oxide was prepared by bubbling medical air through a solution of tricyclohexylphosphine (0.5 g, 1.78 mmol) in DCM (10 mL). The mixture was then concentrated and dried *in vacuo* according to Procedure A: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.46–4.30 (s), 2.01–1.15 (m, $POCy_3$:H-1-6); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 57.8, 51.1 ($POCy_3$), 49.7, 39.9, 31.0, 4.5, −3.1.

Tricyclohexylphosphine oxide + *p*-cresol

Tricyclohexylphosphine oxide (20 mg, 0.068 mmol) and *p*-cresol (7 mg, 0.068 mmol, 1 eq.) according to procedure A: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (s, cresol: OH), 7.00 (d, *J* = 8.3 Hz, cresol: H-3,5), 6.83 (d, *J* = 8.3 Hz, cresol:H-2,6), 2.27 (s, cresol:Me), 2.09–1.15 (m, $POCy_3$:H-1-6); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 59.1, 53.5, 51.0, 40.4, 31.1, 4.4, −3.4.

Tricyclohexylphosphine oxide (20 mg, 0.068 mmol) and *p*-cresol (15 mg, 0.135 mmol, 2 eq.) according to procedure A: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (s), 7.00 (d, *J* = 8.3 Hz, cresol:H-3,5), 6.84 (d, *J* = 8.3 Hz, cresol:H-2,6), 2.27 (s, cresol:Me), 2.01–1.17 (m, $POCy_3$: H-1-6); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 59.5, 54.1, 51.6, 40.6, 31.2, 4.4, −3.5.

Tricyclohexylphosphine oxide + trifluoromethanesulfonic acid

Tricyclohexylphosphine oxide (20 mg, 0.07 mmol) and trifluoromethanesulfonic acid (0.01 mL, 0.14 mmol, 2 eq.) according to procedure A: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.69 (s), 2.49–0.77 (m, $POCy_3$: H-1-6); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 86.0, 86.0, 83.1.

Tricyclohexylphosphine + methyl acrylate (1 b) + lithium chloride

Tricyclohexylphosphine (0.2 g, 0.7 mmol), methyl acrylate (**1 b**) (0.06 mL, 0.7 mmol) and lithium chloride (0.03 g, 0.7 mmol) were stirred in DCM (5 mL) for 4 hours, following procedure B: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.00 (s), 5.42 (s), 5.16 (s), 4.30 (s), 3.57 (s), 3.48 (s), 2.39 (dd, *J* = 58.4, 6.9 Hz), 2.19–0.96 (m); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 57.8, 51.2, 33.4, 32.6, 32.5, 32.3, 31.9, 31.3, 30.7.

Tricyclohexylphosphine + methyl acrylate (1 b) + lithium chloride + *p*-cresol

Tricyclohexylphosphine (0.2 g, 0.7 mmol), methyl acrylate (**1 b**) (0.06 mL, 0.7 mmol), lithium chloride (0.03 g, 0.7 mmol) and *p*-cresol (0.077 g, 0.7 mmol) were stirred in DCM (5 mL) for 4 hours, following procedure B: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (s), 7.11–7.01 (m), 6.93 (d, *J* = 8.5 Hz, cresol: H–Ar), 6.87 (d, *J* = 8.5 Hz, cresol: H–Ar), 6.84 – 6.78 (m), 6.43 (dt, *J* = 18.2, 9.1 Hz), 6.23 (s), 6.20–6.09 (m), 5.86 (dd, *J* = 10.5, 1.3 Hz), 5.63 (d, *J* = 1.2 Hz), 5.27 (s), 4.23 (t, *J* = 6.4 Hz), 3.79–3.76 (m), 3.74 (s), 3.71–3.68 (m), 3.67–3.62 (m), 3.42 (s), 2.83–2.63 (m), 2.59–2.28 (m), 2.23 (s, cresol:H–Me), 2.12 (s), 2.04–1.88 (m), 1.86–1.77 (m), 1.73–1.42 (m), 1.40–0.97 (m); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 60.0, 55.3, 32.1, 31.9, 31.4.

Procedure B: **GII** (20 mg, 0.024 mmol), *p*-cresol (10.2 mg, 0.094 mmol, 4 eq.), (*E*)-prop-1-en-1-ylbenzene (**2 b**) (0.005 mL, 0.047 mmol, 2 eq.) and methyl acrylate (**1 b**) (0.004 mL, 0.047 mmol, 2 eq) were refluxed in dry DCM (5 mL) for 1 h (unless specified otherwise) in the combinations indicated, where after the solution was concentrated *in vacuo*, The residue was dissolved in $CDCl_3$ (0.6 mL) and the reaction mixture analyzed by NMR. Diagnostic resonances are indicated.

GII + *p*-cresol [3]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, GII:H-1′), 7.07 (d, *J* = 8.3 Hz, cresol: H-3,5), 6.87 (d, *J* = 8.3 Hz, cresol:H2,6); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 294.3 (GII:C-1′); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 55.6, 40.7, 28.9 (**GII**).

GII + methyl acrylate (1 b)

After 1 h: ^{1}H NMR (600 MHz, $CDCl_3$): δ 19.13 (s, **GII**: H-1′).

After 2.5 h: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**: H-1′), 17.77; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 50.0, 35.5, 32.5, 32.4, 32.3, 31.5, 28.9 (**GII**); MS (MALDI-TOF, + ve): *m/z* = 453 [(**11**)].

GII + methyl acrylate (1 b) + *p*-cresol

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**: H-1′), 17.79 (s), 17.58 (s); Int. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 294.1; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 32.3, 28.9 (**GII**); MS (MALDI-TOF, + ve): *m/z* = 367 [(**10**)].

GII + (*E*)-prop-1-en-1-ylbenzene (2 b)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**:H-1′), 18.54 (q, *J* = 5.3 Hz); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 315.2, 294.3 (**GII**:C-1′); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 49.9, 28.9 (**GII**), 27.4.

GII + (*E*)-prop-1-en-1-ylbenzene (2 b) + *p*-cresol

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**: H-1′), 18.59 (q, *J* = 5.5 Hz), 17.85; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 315.4, 294.4 (**GII**: C-1′); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 28.9 (**GII**), 27.3.

GII + methyl acrylate (1 b) + (*E*)-prop-1-en-1-ylbenzene (2 b)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**:H-1′), 18.54 (q, *J* = 5.3 Hz), 17.79 (s); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 50.0, 32.5, 31.5, 28.9 (**GII**), 27.4; MS (MALDI-TOF, + ve): *m/z* = 180.1 [(**4 b**)]$^{+}$, 307.3 [CH_2CHPCy_3]$^{+}$, 367.4 [(**10**)], 453.4 [(**11**)].

GII + methyl acrylate (1 b) + (*E*)-prop-1-en-1-ylbenzene (2 b) + *p*-cresol

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**:H-1′), 18.55 (q, *J* = 5.6 Hz), 17.79 (s); ^{31}P NMR (243 MHz, $CDCl_3$): δ = 52.9, 32.3, 31.5, 28.9 (**GII**), 27.4, 25.6, 16.1; MS (MALDI-TOF, + ve): *m/z* = 307.3 $[CH_2CHPCy_3]^+$, 367.4 [(**10**)], 453.4 [(**11**)].

Procedure C: **GII** (0.02 g, 0.024 mmol), (*Z*)-stilbene ((***Z*)-4 b**) (8 mL, 0.047 mmol, 2 eq.), methyl acrylate (**1 b**) (0.004 mL, 0.047 mmol, 2 eq.) and *p*-cresol (0.01 g, 0.094 mmol, 4 eq.) were refluxed in DCM (5 mL) in the combinations indicated for 2 hours, where after the solution was concentrated *in vacuo*, The residue was dissolved in $CDCl_3$ (0.6 mL) and the reaction mixture analyzed by NMR. Diagnostic resonances are indicated.

GII + (*Z*)-stilbene ((*Z*)-4 b) + methyl acrylate (1 b)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**: H-1′), 17.80; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 49.9, 31.5, 28.9 (**GII**).

GII + (*Z*)-stilbene ((*Z*)-4 b) + methyl acrylate (1 b) + *p*-cresol

^{1}H NMR (600 MHz, $CDCl_3$): δ = 19.13 (s, **GII**: H-1′), 17.79; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 53.1, 34.2, 32.5, 31.5, 28.9 (**GII**), 21.0.

Preparation of GII derivativesGII-*p*-cresol adduct (19)

Method A: **GII** (100 mg, 0.12 mmol) and *p*-cresol (13 mg, 0.12 mmol, 1 eq. or 26 mg, 0.24 mmol, 2 eq.) were refluxed in dry DCM (10 mL) for 1 hour in a glovebox, whereafter the solvent was removed *in vacuo*. Attempted recrystallization from toluene gave a red oil: IR (neat) $\bar{\nu}_{max}$: 3280 cm^{-1} (OH). XPS results have been reported elsewhere.[34]

Method B: **GII** (20 mg, 0.024 mmol) and *p*-cresol (5.1 mg, 0.047 mmol, 2 eq.) were dissolved in DCM (0.6 mL) and stirred for 1 hour at 30 °C in a glovebox: ^{1}H NMR (600 MHz, CD_2Cl_2) and ^{13}C NMR (151 MHz, CD_2Cl_2, −40 °C): Table S1; NOESY: Figure 5; ^{31}P NMR [161.97 MHz, $CDCl_3$]: δ_P = 30.5.

GII-*p*-cresolate derivative (22). Based on a method by Grubbs et al.,[34] a solution of thallium ethoxide (0.705 g, 2.8 mmol, 1.2 eq.) in dry THF (5 mL) was filtered through glass wool and added dropwise to a solution of *p*-cresol (0.2554 g, 2.4 mmol) in dry THF (10 mL) in a glovebox. The mixture was stirred for 24 hours at room temperature, where after it was centrifuged and the supernatant concentrated in vacuo under argon to give thallium *p*-cresolate (**24**) as an off-white solid (0.447 g, 76%): ^{1}H NMR [600 MHz, C_6D_6]: δ = 7.15 (d, J = 8.2 Hz, 2H, H-3,5), 6.69 (d, J = 8.2 Hz, 2H, H-2,6), 2.29 (s, 3H, CH_3); ^{13}C NMR [151 MHz, C_6D_6]: δ = 162.0 (C-1), 130.7 (C-3,5), 125.7 (C-4), 117.5 (C-2,6), 20.8 (CH_3).

Method A: Taking precautions to protect it from light, thallium *p*-cresolate (**24**) (36 mg, 0.12 mmol, 1 eq. or 72 mg, 0.24 mmol, 2 eq.) and **GII** (100 mg, 0.118 mmol) were stirred for 48 h in dry benzene (1 mL) in a glovebox at room temperature. The reaction mixture was thus centrifuged (9000 rpm, 16 °C, 1 hour) and the supernatant concentrated in vacuo to give **22**. NMR and XPS results has been reported elsewhere.[34]

Method B: Taking precautions to protect it from light, thallium thallium *p*-cresolate (**24**) (15 mg, 0.047 mmol, 2 eq.) and **GII** (20 mg, 0.024 mmol) were combined in dry DCM (0.6 mL) and the reaction monitored by ^{1}H NMR spectroscopy at 40 °C over a period of 30 hours (Figure 7). Selected NMR data:

At t0: 1H NMR (600 MHz, CD2Cl2, 40 °C) δH = 19.01 (s, H-1′), 7.28 (pseudo t, H-4 C), 7.05–6.99 (m, H-3 C, H-5 C), 6.96 (d, J = 7.9 Hz, H-3E, H-5E), 6.65 (d, J = 7.9 Hz, H-2E, H-6E).

After 10 min.: ^{1}H NMR (600 MHz, CD_2Cl_2, 40 °C) δ_H = 20.67 (s, H-1′), 19.01 (s, H-1′), 7.45 (d, J = 8.0 Hz, H-2E), 7.43 (d, J = 8.0 Hz, H-2E), 6.89 (d, J = 7.9 Hz, H-3E, H-5E), 6.65 (d, J = 7.9 Hz, H-2E, H-6E).

After 30 h: ^{1}H NMR (600 MHz, CD_2Cl_2, 40 °C) δ_H = 21.07 (s, H-1′), 19.27 (s, H-1′), 18.96 (s, H-1′), 17.66 (s, H-1′), 7.45 (d, J = 8.0 Hz, H-2E), 7.43 (d, J = 8.0 Hz, H-2E), 6.90 (d, J = 8.0 Hz, H-2E, H-6E), 6.68 (d, J = 8.0 Hz, H-2E, H-6E), 6.64 (d, J = 8.5 Hz, H-2E, H-6E); ^{13}C NMR (151 MHz, CD_2Cl_2, 40 °C) δ_C = 293.7, 287.7.

The number of protons are not reported as various resonances are multiplied or broadened due to restricted rotation[40] and chemical exchange.

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Conflict of Interest

The authors declare no conflict of interest.

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